

RECENT ADVANCES IN THE SPECTROSCOPY OF SPONTANEOUS RAMAN SCATTERING

Ya. S. BOBOVICH

Usp. Fiz. Nauk 97, 37-76 (January, 1969)

I. INTRODUCTION

RAMAN scattering has played an important role in the development of our concepts of the interaction of light with matter. Shortly after this remarkable phenomenon had been discovered (about forty years ago), a number of fundamental studies of experimental and theoretical nature ensued. They made it possible to interpret it correctly and to mark the course of further studies. Simultaneously, the technical means were perfected, and new experimental procedures and methods were sought out. Without question, the development of the photoelectric method of recording spectra, which began in the postwar years, occupies a very important place here. It culminated in the invention of apparatus that radically simplified and accelerated quantitative measurements of spectra. Studies of the electrooptic properties of molecules were consequently greatly intensified. Invention of new sources for exciting spectra, especially powerful low-pressure mercury lamps, had a no less substantial influence on broadening the front of the studies and on determining their very nature. When combined with double monochromators, they permitted one to get Raman spectra easily from powdered substances. Raman spectroscopy of gases and vapors was also put on a different basis. Thus the field of accessible objects and problems was considerably broadened. The monograph^[1] and a number of reviews (see, e.g.,^[2-4]) have been devoted to systematic presentation of all the pertinent problems.

A powerful new stimulus to development of studies in the field of Raman scattering has been the invention of continuous and pulsed lasers in the early sixties. Of course, a most interesting topic here is stimulated Raman scattering (SRS), which was discovered in 1962. It is a non-linear process that arises at huge radiation densities that were formerly unattainable. Suitable conditions are realized in pulsed lasers operating in a Q-switching mode ("giant pulses"). When the material is simultaneously illuminated with monochromatic and continuous radiation, two other new phenomena could be observed: inverse spontaneous scattering and stimulated Raman scattering, which are manifested in the form of absorption lines. The "old" problem has been solved: to excite electronic Raman spectra in free atoms and ions. It has recently proved possible to detect both spontaneous and stimulated processes of this type. It has become possible to study substances like semiconductors that are slightly transparent or completely opaque (in the visible). Favorable conditions have been created for systematic study of resonance spectra. Broad perspectives have been opened up in spontaneous Raman spectroscopy of fast processes. The very technique of exciting spectra has been changed radically, and thus the requirements of the amount of material to be studied have been reduced considerably. This fact is very important in structural applications of

the spontaneous Raman scattering method. Polarization measurements have been simplified and their accuracy improved considerably. Consequently, the limits of applicability of spontaneous Raman scattering spectroscopy have been greatly extended toward the solution of various problems of physics and chemistry. The spontaneous Raman scattering method has become comparable in its potentialities in molecular analysis with the method of infrared absorption spectra, and has considerably surpassed the latter in the volume of information contained therein on spectral and other properties of matter.

In writing this review, I have adopted the aim of casting light on the present state and trends of development of experimental technique, and of showing new potentialities in spontaneous Raman scattering spectroscopy, using typical examples of research. I have chosen among these only problems that have recently appeared, as well as some problems that have long attracted the attention of spectroscopists, but which stand a good chance of complete solution, precisely because of considerable progress in inventing new means and methods of experiment. Further information on various allied problems can be found in^[5,6].

II. LASERS AS SOURCES FOR EXCITING SPECTRA

The blue line of the high-pressure mercury lamp ($\lambda = 4358 \text{ \AA}$) has been the main source used for exciting spontaneous Raman spectra for almost 20 years. This has restricted the possibilities of studying colored and photochemically unstable substances. An essential difficulty has also been the background intrinsic to these lamps, and in some cases, the excessive line width. A substantial advance was the development of powerful low-pressure mercury lamps, which are distinguished by more favorable composition of radiation. At the same time, other sources have come into use: gas discharge lamps filled with helium or the vapors of different metals: potassium, sodium, rubidium, cesium, cadmium, and thallium. However, all of them have been considerably inferior to low-pressure mercury lamps in background level and line width. It is only with the appearance of lasers that the experimenter has had access to a perfect monochromatic source for exciting spectra. The concentration of the laser radiation into a narrowly collimated beam has extremely simplified the geometry of illumination of the specimen, and thereby has simplified experimentation as well. The assortment of lines suitable for excitation has been extended, and as is most important, especially in the red and near infrared. Not nearly all types of existing lasers have been tested and applied for spontaneous Raman scattering. However, this line of technology is being developed very rapidly. In such a situation, we can suppose that the ordinary gas-discharge lamps will be completely supplanted in use as sources for exciting spontaneous Raman spectra.

1. Continuous Gas Lasers Based on He-Ne Mixtures and on Ionized Ar

Laser action in a helium-neon mixture at the line $\lambda = 11,500 \text{ \AA}$ was first achieved by Javan, Bennett, and Herriott.^[7] A year later, Rigrod and his associates^[8] developed a laser suitable for practice, with two spherical exit mirrors. These same authors are responsible for the idea of equipping the gas-discharge tube with windows cemented to the ends at the Brewster angle, which leads to minimum loss of light polarized in the plane of incidence. The standard length of the gas-discharge tube of the lasers in application is 120 mm, and the diameter is 7 mm. The mirrors are usually confocal, and have a dielectric coating. The spectra of some substances can be excited even with a laser of only one milliwatt power.^[9] The power of contemporary lasers is as much as 150 milliwatts.^[10] The 6328- \AA line has been used for excitation in all the studies conducted up to now. In multimode operation, its width is 0.05 cm^{-1} .^[11]

An ionized-argon laser generates seven major lines with varying intensities. Their wavelengths lie in the blue-green. This latter fact entails a well-known advantage: the high efficiency of these lines for exciting spontaneous Raman scattering (the law is $I \sim 1/\lambda^4$). On the other hand, their location in the spectrum restricts the set of substances amenable to study. More justly, we can consider that the two discussed lasers supplement each other. The power of a modern ionized-argon laser manufactured by the firm Spectra Physics amounts to 900, 60, 25, and 15 milliwatts, respectively, for the lines at 4880 and 5145, 4965 and 4765, 4579 and 4727, and 4658 \AA .^[12] Hence its operation requires vigorous water cooling. A laser developed by Rigden^[13] has worked out well for studying gases. In this instrument the plasma tube is constructed of 14 assembled aluminum disks having 3 mm apertures. This ensures reliable operation. With one-time argon filling of the tube, the continuous-operation life of the laser is 20 hours. The output power of this laser is as much as 800 milliwatts, with a current of 30 A. The line width of an ionized-argon laser is about three times as large as for helium-neon lasers.^[11]

2. The Solid-state Continuous Laser Based on a Neodymium-activated Yttrium Aluminum Garnet Crystal

Some substances are not transparent in the visible. For example, these include semiconductor crystals formed from elements of groups III and V (GaAs, InP, and AlSb). One can excite spontaneous Raman scattering in these substances only by using the near infrared. Mooradian and Wright^[14] used for this purpose the line $\lambda = 10,648 \text{ \AA}$ of the laser mentioned in the title. The power in this line amounted to one watt. The article contains no other information on the laser.

3. The Continuous Ruby Laser

Such instruments have been built by a number of authors.^[15-18] One of them is most fully described in^[18]. The basis of their laser was a high-quality ruby crystal 3 mm in diameter and 75 mm long, activated with 0.03% chromium. The pumping source was a mercury

capillary lamp of the type A 2359 PEK having 4 kW power. According to the data of^[18], the chosen crystal diameter is an optimum, but its length can be increased, and is thus far limited by the dimensions of the existing pumping lamps. The single-lamp illuminator is elliptical, and consists of two dismountable halves. The reflecting surface proper is formed by a thin-wall silvered metallic tube held between the halves of the illuminator, thus acquiring the form of an elliptic cylinder. The resonator is made of spherical mirrors. Under these conditions, the threshold for continuous laser action is 2.2 kW. The power in the ruby line ($\lambda = 6943 \text{ \AA}$) can be as much as 1.6 W. Ways of further increasing the power of the instrument were pointed out: to lengthen the crystal and correspondingly lengthen the lamps themselves, to improve the distribution of illumination energy of the lamps by adding other elements to the mercury, and finally, to use an illuminator having several elliptic cylinders and one common focus on the crystal. The authors^[18] quite reasonably point out the great promise of using such lasers in spontaneous Raman spectroscopy. However, there are no studies of this type in the literature up to now.

4. The Low-power Pulsed Ruby Laser

Porto and Wood^[19] demonstrated in 1962 the possibility of using such lasers in a free-generation mode to excite spontaneous Raman spectra. The crystal used in the apparatus that they described contained 0.05% chromium. The end surfaces were polished to the required accuracy and were silvered. The end facing the specimen had a reflection coefficient of 25%. The crystal was cooled with nitrogen vapor. They studied benzene and carbon tetrachloride by the photographic method. In order to diminish greatly the effects of stray light from the xenon lamp used for pumping and of the luminescence of the crystal itself, the latter moved 1.5 meters away from the cuvette containing the liquid. An accumulation of 50 flashes was needed to obtain the fundamental lines in the spectra. Stoicheff^[20] reported analogous results a year later. A study by Porto, Cheesman, and de Siqueira was concerned with perfecting the cuvettes containing the liquid. Danil'tseva, Zubov, Sushchinskiĭ, and Shuvalov have concentrated their attention on studying powders.^[21] They were the first to get the spectra of some highly-absorbing substances. It took no less than 30 laser flashes to reveal the fundamental lines. They used a very high-aperture spectrograph to record the spectra. Schrader and Stockburger^[22] later described a method of studying powdered specimens. The latter studies contain a number of interesting details.

The laser in^[22] was based on a ruby crystal 6 mm in diameter and 51 mm long. One of its ends was shaped into a prism and the other end was flat. This eliminated the dead-end mirror from the apparatus. The flash energy was 0.5 J. The distance between the ruby and the sample was one meter. The reduction in stray light thus attained was so great that it became noticeable only with 1000 flashes. The spectra could be excited by a pulse sequence at a repetition frequency of 5-10 flashes per minute, owing to efficient cooling of the crystal by nitrogen vapor. They studied with this apparatus a number of powders, both colorless and col-

ored. For example, they could obtain an intense spectrum of *p*-nitroaniline even with 5–10 flashes. The technique of recording the spectra was photographic. They used a Steinheil spectrograph with a camera having $f = 240$ mm (relative aperture $f/4$). As in^[21], the method of excitation was "by transmission." The powders were pressed into tablets in individual cases. In some studies, in particular^[22], such a tablet was put at the center of two hemispherical mirrors having small holes for the illuminating and scattered beams. According to the data of^[22], this enhanced the spectra eightfold. Apparently, use of an Ulbricht sphere for the same purpose also promises great advantages, similarly to what was done in^[23]. The authors of^[22] put in the scattered beam a narrow-band interference filter from which the beam was reflected twice. Its purpose was to attenuate the ruby line in the scattered radiation, since it gave rise

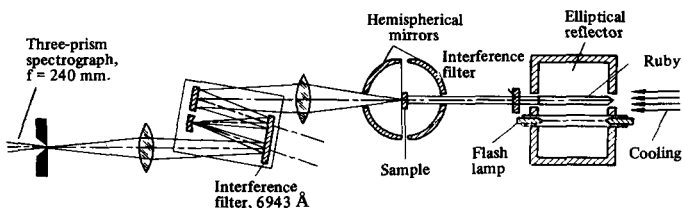


FIG. 1. Diagram of the apparatus of Schrader and Stockburger^[22] for excitation of spontaneous Raman spectra from powdered samples.

to a parasitic background in the spectroscopic instrument. As was shown in^[24], such a filter acts more efficiently than an absorption filter. Fig. 1 shows a diagram of the apparatus. It has the same essential features also when the spectra are excited by other lasers.

One of the studies of^[22] describes also the results of some interesting experiments on photoelectric recording of spectra excited by identical sequences of pulses while the diffraction grating of the monochromator is rotated. The spectrum acquires a characteristic appearance: it is made of a number of vertical lines (spaced 1 cm^{-1} apart) whose envelope gives the intensity distribution. The authors propose that if one has recorded a spectrum in this way for orientation, one can then set the monochromator on some particular line and (now keeping the grating stationary) photoelectrically measure the integral intensity of this line. They consider this method especially promising since the industry now produces lasers having a repetition frequency of pulses of 10 Hz. One can easily record an entire spontaneous Raman spectrum in seven minutes using such sources.

Delhaye and Migeon have taken up the problem of obtaining single-flash spectra. This is important in studying fast processes. The maximum rates of such processes are limited by the flash duration of ruby in free generation, which is 10^{-3} sec. Such an apparatus has been described in^[25,26]. Its essential feature consists in the method of recording spectra, which is based on using an image converter. This problem will be discussed below. However, it is appropriate to characterize here the optical part of the apparatus. The spectra were excited with a CSF-LA 610 laser containing a ruby of small dimensions ($4 \times 40 \text{ mm}^2$). A xenon lamp was

used for pumping as usual. The lamp was helical in shape. The power contained in the ruby line was 0.1 J in all. The cuvette was cylindrical with sealed-on flat windows ($4 \times 20 \text{ mm}^2$). A system of diaphragms was installed to eliminate the direct light of the lamps from the laser beam. Observation was made from the side. They used a Bausch and Lomb spectrograph having a $102 \times 102 \text{ mm}^2$ diffraction grating with 1200 lines/mm and a set of cameras, in particular, one having a relative aperture of $f/0.75$. They studied the spectra (including polarization measurements) of phosphorus tribromide, benzene, carbon tetrachloride, and chloroform. In^[25], one of the authors obtained single-flash spectra of other more poorly-scattering substances with the same apparatus, but with a considerably more powerful laser (35 J).

5. The Pulsed Semiconductor Laser Based on a Gallium Arsenide Crystal

There is only one study where they used the $8400\text{-}\text{\AA}$ line of this laser to excite spontaneous Raman scattering.^[27] In particular, the authors^[27] used this technique to get the spectrum of a cyanine dye in highly dilute solution. They note the convenience of using the gallium arsenide crystal as a light filter to absorb the exciting line in the scattered light beam before it enters the spectroscopic apparatus. A fault of this laser as compared with others, and particularly gas lasers, consists in the large line width ($1\text{--}10 \text{ \AA}$). The methods of recording and obtaining spectra will be discussed below.

6. Features of Specimen Illumination

One can excite spontaneous Raman spectra (just as with stimulated Raman spectra) with lasers in two ways. In one of them, the substance is illuminated by the laser beam transmitted by the semitransparent mirror of the resonator. In the other, the cuvette containing the liquid is put inside the resonator.

In exciting spontaneous Raman scattering by gas lasers, the latter method was the first one applied.^[28] The cuvette was 10 mm thick, and was fitted with windows of high optical finish cemented on at the Brewster angle. The latter was necessary to prevent large losses that would stop laser action. Two standard He-Ne lasers were used for illumination in order to intensify the scattering. The centers of curvature of the two dead-end spherical mirrors of the resonator coincided, and lay within the cuvette. Observation was made from the side, and recording was photographic. Leite and Porto^[29] later adapted the same apparatus to photoelectric recording. They used a.c. amplification; the monochromator was a Perkin-Elmer Model 210 having a diffraction grating with 600 lines/mm; the detector was a dry-ice-cooled EMI 9558 B photomultiplier with a S-20 photocathode. The dark current was 2×10^{-11} A under these conditions. Using an 18-mW laser as the excitation source, the authors of^[29] were able to record the spontaneous Raman spectra of carbon tetrachloride, benzene, and carbon disulfide at a slit width of 12 cm^{-1} and a time constant of 3 sec in the detecting and amplifying apparatus. They note the abundance of stray light, which limits the sensitivity of the apparatus. The method of illuminating the specimen within the resonator proved

to be efficient enough also in studying gases.

Setting the cuvette outside the resonator simplifies experimentation substantially. At the same time, the efficiency of this method can be increased greatly by passing the beam repeatedly through the cuvette containing the liquid or gas and focusing it sharply. This has been shown in a number of studies, and is now used in contemporary instruments. Besides, this is the only method for studying powders and colored solutions. In view of the mentioned arguments, it is currently being granted preference.

Delhay and Migeon^[30] have discussed the role of focusing of the laser beam in exciting spontaneous Raman scattering. We shall present their fundamental results.

The light flux passing through a unit area of the effective cross-section of the spectroscopic apparatus can be written as follows:

$$d\Phi \sim \frac{lh}{f^2} d\sigma, \quad (1)$$

Here l and h are the width and length of the spectroscopic slit, respectively, f is the focal length of the collimator, and $d\sigma$ is an element of area on the surface of the collimator objective. In order to take into account the properties of the volume source of radiation, one usually considers the images of all diaphragms in the system (the slit, the collimator objective, and the illuminating optics), as obtained by tracing back the rays into the volume source. All rays that simultaneously pass through these images enter the apparatus (see, e.g.,^[31]). The authors of^[30] have used this method in analyzing the problem theoretically. Here they transformed Eq. (1) into

$$d\Phi = k \frac{l'h'}{f'^2} d\sigma; \quad (2)$$

Here the quantities l' , h' , and f' refer to the image within the source, and k is a coefficient characterizing the brilliance of the scattered radiation.

The authors of^[30] integrated (2) over the volume of the substance and the aperture of the apparatus in the two cases in which the diameter of the laser beam is large or similar in comparison with the slit width of the inverse image. Thus they derived two formulas for the light flux reaching the receiver:

$$\Phi = \frac{k}{N^2} \cdot \frac{4}{\pi} \frac{lh}{D} \frac{1}{f^2} S_{sp}, \quad (3)$$

$$\Phi = \frac{k}{N^2} \frac{W}{D} \frac{lh}{f^2} S_{sp}, \quad (4)$$

Here N is the intensity coefficient of the scattered light, W is the power of the exciting beam, D is its diameter, and S_{sp} is the area of the effective aperture of the spectroscopic instrument. The other symbols are previously defined.

We see directly from Eqs. (3) and (4) that the light flux Φ received by the spectroscopic instrument is inversely proportional to the diameter D of the laser beam. The latter quantity has just as much effect in exciting spontaneous Raman spectra as does the laser power itself. On the basis of the formulas given above, it made sense to consider individually the two cases of recording spectra.

a) Photoelectric recording. Here, as we know, the intensity of the spontaneous Raman lines is proportional

to the light flux Φ . Let us undertake a definite solution. This implies fixing the slit width l . Let it be small and equal to l' . Correspondingly, the light flux Φ also decreases. However, the losses can be compensated by further narrowing of the laser beam (the quantity D). Thus, one can increase the resolution under these conditions without losing intensity. Diffraction imposes the limit. Besides, polarization measurements become less accurate when the beam is narrowed too much.

b) Photographic recording. Here the essential feature is the illumination in the focal plane of the objective. If for simplicity we take the mean illumination, we have

$$\bar{E} = \frac{\Phi}{F'} = k \frac{W}{D} \frac{S_{sp}}{f_{cam}^2}, \quad (5)$$

where $F' = F(f_{cam}^2/f_{col}^2)$, F' is the area of the slit image, and f_{cam} and f_{col} are respectively the focal lengths of the camera objective and the collimator. Here it is again very interesting that, if we simultaneously decrease the slit width and the diameter of the laser beam, and hence decrease the volume of material itself, we increase the resolution in the spectrum and the illumination in the focal plane of the instrument. The characteristics of the emulsion in the photographic film and the optics of the instrument will determine the limiting resolution.

The conclusions drawn here have been tested experimentally in^[30]. At first they used a low-power (1 mW) helium-neon laser, but a very wide-aperture spectrograph (having a relative camera aperture of $f/0.75$). Without focusing, they obtained the spectrum of PBr_3 molecules in 4 min. When the beam was narrowed to a diameter of 0.3–0.4 mm, other conditions remaining identical, an exposure of only 15 sec was needed.

Using an apparatus equipped with an $f/4.5$ camera, with a concentrated light beam from a powerful helium-neon laser (50 mW), they could record the spectrum of the same substance in 15 sec. The spectrum was easily visible to the eye. The technique of focusing the beam on the material permitted the authors also to obtain single-flash spectra, using a low-power pulsed ruby laser for excitation.

III. PHOTOGRAPHIC AND PHOTOELECTRIC METHODS OF RECORDING

The idea that the photographic method is more sensitive has taken root. However, this is apparently not true, as one can judge from Figs. 2 and 3, which are taken from^[32]. We see that photographic emulsions are evidently inferior to photocathodes in their sensitivity, as determined by the quantum yield. Photoelectric detectors are preferable also from the purely technical standpoint (their output signals are linear; measurements can be made much more rapidly and accurately with them; they make it possible to use double monochromatization of the light, which is especially important in studying inhomogeneous materials; and the noise level is relatively low). The set of circumstances noted above makes understandable the quite distinct tendency to replace photographic techniques completely by photoelectric, even when one requires high resolution in the spectra (e.g., in studying gases; see below). A number of photoelectric instruments have recently been des-

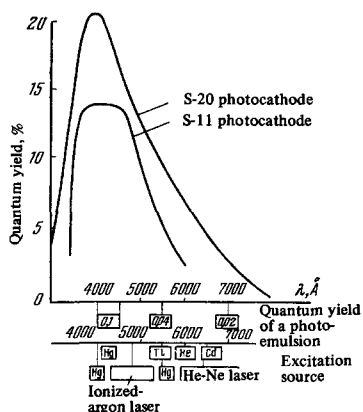


FIG. 2. Comparison of the sensitivities of S-20 and S-11 photocathodes and photoemulsions.

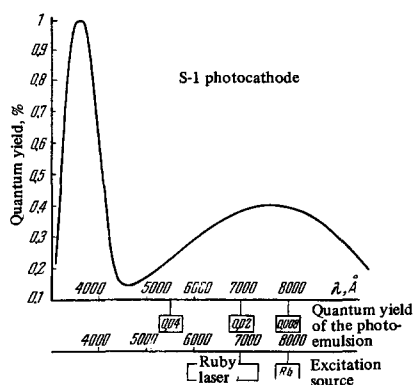


FIG. 3. Comparison of the sensitivities of an S-1 photocathode and a photoemulsion.

cribed that are designed for obtaining spontaneous Raman spectra using gas lasers. Some of them are being produced commercially. Their characteristics will be given in another chapter of this review.

The photoelectric circuits of most of the instruments are similar in principle to those used earlier. There are just two problems along this line that are worthy of special note.

As we know, even when the light flux is completely stable, the photocurrent at the output of the detector fluctuates in time. The reason for this lies in the statistical nature of the process of emitting electrons. Hence, we can treat the output signal as consisting of a constant and a variable component. Usually one measures the former. However, at low enough light fluxes a considerable fraction of the power occurs in the variable component (shot noise). Here the fluctuations prove to be proportional to the light flux. Here it is reasonable to measure the incident light signal indirectly, i.e., not from its weak constant component, but from the amount of shot noise. This problem has been the subject of a note by Pao, Zitter, and Griffiths,^[33] as well as two subsequent thorough articles by Pao and Griffiths^[34] and Griffiths and Pao.^[35] The authors illustrate the potentialities of the method with a multitude of examples, and in particular, that of recording a very weak spontaneous Raman spectrum. In their opinion, the results show considerable advantages of the method that they have developed over the ordinary method, in which the signal is modulated, applied to a photomultiplier, and then subjected to synchronous amplification.

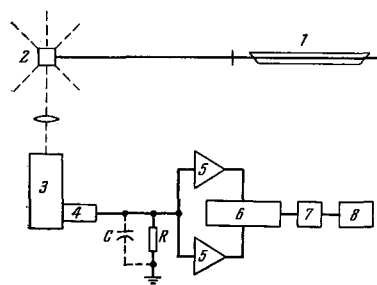


FIG. 4. System for exciting and recording spontaneous Raman spectra in the study of Pao et al. [33]

Figure 4 shows the described system. It contains two completely identical wide-band amplification channels operating in parallel. The variable component of the signal, i.e., the fluctuating photocurrent Δi , is applied to their inputs from the photomultiplier. This photocurrent, as amplified in each of these channels, is in turn applied to a multiplying circuit, which produces the signal $(\Delta i)^2$. Further on, an RC filter is used to extract from the latter the d.c. component, which is measured by a recorder. It is proportional to the shot noise at the output of the photomultiplier. Hence, considering what I have said above, it is also proportional to the weak light flux incident on the photocathode. Since the noises arising in the amplifiers are random, they are considerably attenuated in this system. On the contrary, the fluctuations in photocurrent that arise from the same source, the photomultiplier, are therefore mutually correlated. Thus they pass through the system without hindrance. Unfortunately, for the same reason, the thermal Johnson noises of the input resistance are also not attenuated.

In order to demonstrate the efficiency of the new method of amplifying weak signals, the authors of^[33] have recorded the isotope structure of the 459-cm^{-1} spontaneous Raman line of carbon tetrachloride. The spectrum was excited with a helium-neon laser. The spectral slit width was 0.8 cm^{-1} . The time constant was 3 sec. Figure 5 shows the recording. The signal-noise ratio proved to be about 70 on the average. The same diagram shows a recording of the 459-cm^{-1} line obtained with an ordinary system, other conditions being the same. Much more noise can be seen. As estimated, this variant method of amplification gives a signal-noise ratio no better than 15.

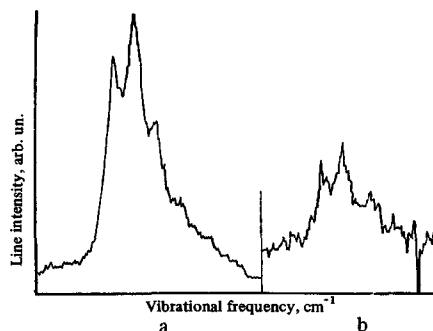


FIG. 5. Samples of recordings of the isotope structure of the 459-cm^{-1} line in the spontaneous Raman spectrum of carbon tetrachloride, as made with the apparatus developed in [93] (a) and with ordinary apparatus (b).

Kozlov^[36] has criticized the theoretical bases of the new method. He discussed the counting statistics of photoelectrons, and showed that this method is equivalent in accuracy to the ordinary method only in the limiting case, but in general is inferior. Hence, we should rather ascribe the difference in experimental results found in^[33-35] to technical imperfection in the system used to carry out the ordinary method of rate measurement. On the other hand, they effected the method proposed in^[33] so well that it permitted them to attain the theoretical limit of accuracy. The latter fact also reveals the error in the statement of the authors of^[33] that further widening of the transmission bands of the amplification channels should increase the signal-noise ratio even further, i.e., increase the efficiency of amplification of weak signals. We note that two of the authors of^[33] came essentially to the same conclusion in a more detailed analysis of the problem in^[34]. The reasons for the imperfection of the ordinary systems are thus far not clear.

Even if the amplification system is technically irreproachable, one still must always consider one serious factor limiting the possibilities of measurement. This is the dark current of the photomultiplier, or more precisely, its fluctuations. The main reason that the dark current exists is the thermal emission of electrons from the photocathode. In fact, this decreases its sensitivity at the same time. Another method consists in reducing the dimensions of the receiving area. For example, this is realized in the FÉU-79 developed in our country, which has a multialkali photocathode. Let us give the characteristics of a typical sample of this photomultiplier:

integral sensitivity of the cathode—120 $\mu\text{A/lumen}$,
 integral anode sensitivity—100 A/lumen ,
 supply voltage—1620 V,
 dark current— 4.2×10^{-10} A,
 diameter of the receiving area—6 mm,
 region of spectral sensitivity—300–830 nm.

When the experimenter has no such photomultiplier at his disposal, he can achieve a substantial effect as follows. A very small image of the source is projected on the photocathode, and the trajectory of the electrons emitted from the unilluminated part of the photocathode is altered by a magnetic or electric field applied to the photomultiplier. Then the electrons cannot strike the first dynode, i.e., "they are out of the game." The authors of^[37,38] have used this method of reducing the dark current.

Along with an improved photomultiplier, the amplification system described above has been used successfully to record electronic Raman spectra.^[39]

IV. A COMPARISON OF THE EFFICIENCY OF EXCITATION OF LOW-PRESSURE MERCURY LAMPS AND LASERS

Rigorous estimates of this type are difficult. To do this, we would have to deal with the values of the quantum yields of Raman scattering, which are not available to us. Consequently, we have to restrict ourselves to comparing some experimental data obtained under typical conditions.

Evans, Hard, and Murphy^[40] have taken up this problem. They studied liquid carbon tetrachloride by photo-

graphic and photoelectric methods. They used a large-aperture apparatus having a diffraction grating operating in different orders of the spectrum, depending on the exciting line. The reflective characteristics of the grating were taken into account. They chose as sources two straight low-pressure mercury lamps drawing 20 A current (4358 and 5461 Å lines) and a helium-neon laser of 30 mW power. With the first source, they used an elliptical illuminator designed for two lamps, and a cuvette 10 mm in diameter and 110 mm long. When they excited the spectrum with the gas laser, they used a reflective multipass cuvette having ten passages of the beam. It was equipped with a spherical mirror, which increased the intensity of the scattered light by about 70%. They photographed the spectral region arising from excitation by the 4358-Å line on Eastman 103-aJ plates, and they used Eastman 103-aF plates for the green-red region. In the photoelectric variant of recording, the detector was a photomultiplier having an S-20 cathode. They used an a.c. amplifier. The time constant was 4 sec. The spectral slit width was 10 cm^{-1} when the spectrum was excited with the mercury lamp, and 5 cm^{-1} with the laser.

Under these conditions, it turned out that excitation of the spectrum by all three lines in the vibrational-frequency region up to 1000 cm^{-1} was about equally effective in the photoelectric variant. Outside this region, the decline in sensitivity of the photomultiplier begins to have an effect, and the circumstances add up to favor the blue line of mercury. With photographic recording, all three exciting lines are of equal merit throughout the frequency range.

Brandmüller, Hacker, and Schrötter have compared spectra excited by the ordinary technique ($\lambda = 4358$ Å) and by a 60 mW helium-neon laser put out by the firm Spectra Physics (Model 125), used with a multipass cuvette having ten passages of the light beam. They took into account the polarization of the radiation from the latter source. Here they showed that the laser is twice as efficient as the mercury lamp.^[41] However, Koningstein and Smith had arrived at contrary results in an earlier study.^[42] However, this contradiction seems to be illusory. It is explained by the fact that the above-cited authors, in distinction from those of^[41], used a simple rather than a multipass cuvette in their studies, and indeed, one having silvered walls that somewhat intensified the scattered light. Furthermore, they did not refer the results to the same polarization state of the incident radiation.

Thus, direct measurements show that continuous helium-neon lasers (the least powerful of this type of source) under suitable experimental conditions at least are not inferior in efficiency of exciting spontaneous Raman scattering to the most highly perfected lamps of the ordinary kind.

It is not hard to define the status of pulsed lasers as sources for exciting spontaneous Raman scattering, as compared with gas lasers. Naturally, we first consider pulsed ruby lasers. We have seen above that an experiment has been performed using these lasers with energies up to 35 J, operating in a free-generation mode.^[25] This means that the stated energy is emitted in a time interval of 10^{-3} sec, i.e., in one ruby pulse, which corresponds to a power of 35 kW. As I have stated, the power of current helium-neon lasers is as much as 150 mW.

Hence, the ruby laser has a power advantage of almost 10^6 . The action time of a single ruby pulse is about 10^4 times shorter than the acceptable exposure when one photographs a spontaneous Raman spectrum of a substance that scatters well. This implies that the pulsed ruby laser should be much more efficient. In fact, this is not so. The relatively low sensitivity of the photographic material probably introduces considerable correction factors. A certain correction is also demanded by virtue of the law $I \sim 1/\lambda^4$. However, it would be correct to say that the potentialities of each of the sources are comparable. It would hardly be expedient to increase the power of the ruby laser substantially, or a fortiori to adopt the giant-pulse mode, since this would entail the risk of entering the region of radiation densities above the threshold for generating stimulated Raman scattering.

V. USE OF IMAGE CONVERTERS TO RECORD SPECTRA

A substantial advantage of the photographic over the photoelectric method consists in the simultaneous recording of the entire working range of frequencies in the spectrum. This fact plays a large role in studying unstable compounds or fast processes. On the other hand, as we have seen, the photographic emulsion is more or less inferior in sensitivity to the layer forming the photocathode of the photomultiplier. A compromise solution of the problem of recording spectra consists in using the so-called electro-optic image converters. As for spontaneous Raman spectra, this problem was first taken up and solved successfully in the studies of some French authors.^[43,25,28,32]

The image converter was invented at the beginning of the forties. However, their use in scientific studies, and especially in astronomy, dates to 1948 and later. People generally consider that the field where they can be used most expediently is in recording weak light fluxes, especially in the long-wavelength region of the spectrum. The latter condition precisely fits spontaneous Raman spectra, as excited, e.g., by the ruby red line. The pulsed nature of the radiation of these lasers also favors greatly the use of image converters.

An image converter is a variety of vacuum photoelement designed to convert and amplify optical images. The simplest device in this class consists of a cylindrical, evacuated tube, one end of which is coated on the inside with a semitransparent photosensitive layer (the photocathode), and the other with a layer of fluorescent material (the screen). The image of the object to be observed, a spectrum in our case, is projected on the photocathode by ordinary optics. Electron-optical electrodes are mounted within the tube. An accelerating potential is applied between the cathode and the screen. The purpose of the electron optics is to form an electron image on the screen. The image can easily be photographed from the screen with a camera. Here one gets a more or less substantial gain in sensitivity, as compared with directly photographing the spectrum. The spectral sensitivity of an image converter is entirely determined by its photocathode. Of importance in practice are multialkali and cesium oxide layers. As is usual, the latter can be refrigerated to advantage.

The scale of the electron image on the screen with respect to the photocathode can be greater or less than unity. Correspondingly, the energy density in the image is decreased or increased. Of course, the resolution varies simultaneously. One can expediently use an image converter having a magnification greater than unity in order to increase the resolving power when the image has plenty of intensity. One must necessarily take both of the above-mentioned features of an image converter into account in estimating its efficiency.

The fundamental problem in the development of the image converter is to increase sharply its amplification coefficient without appreciably lowering its resolving power. This is achieved by multistage amplification, in which the image on the screen is transferred to the next photocathode, etc. Contact image transfer is widely used. However, here we must not lose sight of the relatively low sensitivity of the emulsion. Thus we must adopt an amplification coefficient that will not limit the amount of required information about the object.^[44]

In addition to converters having a fluorescent screen, one can also use a device in which the electron image is directly recorded on a special emulsion, in order to increase the resolving power. This is the so-called Lallemand-Duchesne camera. This camera consists of a glass housing in which are mounted the photocathode, the electron optics, and a cassette containing a set of photo plates. Now, when one uses photo plates, one has to break the vacuum to take them out of the vacuum system, and the photocathode is consequently destroyed. Thus, a measure has been provided for replacing it quickly: a new photocathode prepared outside the electron camera is introduced in an ampule made of thin glass. After the system has been pumped out, the ampule is broken, and the photocathode is adjusted with a magnetic device. The electron-optic system of the camera consists of three electrodes, and is purely electrostatic. The accelerating potential is high (25–30 kV). The photocathode and the cassette containing the plates are refrigerated with liquid nitrogen. This prevents outgassing of the emulsion, with resultant poisoning of the photocathode. The exposures can amount to several tens of minutes. The plates are changed with an electromagnet. It takes about eight hours to prepare the camera for use.^[44]

What I have said above shows that Lallemand-Duchesne cameras are rather complex, and they take much time for performing experiments. However, these defects are more than offset by the extremely small background density on the photographs, and hence, by their high contrast and large gain in sensitivity (which is limited by the quantum nature of light). This is the very reason why the camera has been applied in astronomical studies.^[44] It has also been tested in spontaneous Raman spectroscopy.

Bridoux^[45] has obtained the first results from recording spontaneous Raman spectra with a very simple image converter. The author used the tube produced by the French company C.F.T.H., No. 9450 A, as described in^[45]. The sensitivity peak of the photocathode is at about 4400 Å. The electron optics reduced the image sevenfold. This achieved a considerable brilliance in the image. The spectrum was photographed from the tube screen by a high-aperture camera. The excitation

source of the spectrum was powerful (1.8–2 kW) mercury lamps ($\lambda = 4358 \text{ \AA}$). Thus the conditions of application of the image converter were least favorable (in the visible region of the spectrum). In one setup, the spectroscopic apparatus was a Huet spectrograph (two prisms, a long focal-length camera, and a reciprocal dispersion in the 4358- \AA region of $30 \text{ cm}^{-1}/\text{mm}$). In the other setup, it was a spectrograph having a flat diffraction grating (mirror-and-lens optics, and a reciprocal dispersion in the same region of the spectrum of $23 \text{ cm}^{-1}/\text{mm}$). The resolution on the screen was about twice as poor as on the photocathode.

They were able to photograph the spectrum of PBr_3 molecules with the described apparatus. It took an exposure of 0.2 sec. The spectrum of the same substance under identical conditions was obtained in 100 sec with direct photography. As the author notes,^[43] this gain is apparently illusory. In the treatment, one must necessarily include the factor of the resolution for a correct estimate. We have taken up this point earlier. Appropriate experiments were carried out in^[43], in which the coarsening of the resolution in direct photography was attained by using in the spectrograph a camera having a considerably shorter focal length, but about seven times more relative aperture. It turned out that an equally intense PBr_3 spectrum was obtained in 2 sec. This means that the actual gain (referred to the same relative aperture) is no greater than a factor of ten.

The next important step along the path of perfecting the method was taken by Delhaye and Bridoux,^[32] who used an image converter with multistage amplification. The fundamental data on the image converter are given in^[32]: the electronic magnification is unity, the amplification is 45,000, and the sensitivity of the S-11 photocathode is 47 mA/lumen. More detailed information on the image converter is found in^[46]. As before, the spectra were excited by the 4358- \AA line of a powerful (2 kW) electrodeless mercury lamp. Using Kodak Tri-X film and spectrographs having reciprocal dispersions of 25 and $30 \text{ cm}^{-1}/\text{mm}$, they could obtain the spectra of CCl_4 and $\text{PSCl}_3 + \text{PCl}_3$ and $\text{PBr}_2 + \text{PFCl}_2$ mixtures with exposures of 0.04, 0.02, and 0.1 sec, respectively. The authors of^[32] report that they have adapted an image converter having an S-20 photocathode in order to extend the method into the long-wavelength region. The literature thus far gives no information on the results of these experiments.

Up to now, the image converter has been applied with apparatus in which the spectra were excited by a continuously-acting source: a mercury lamp. However, pulsed excitation of spectra is much more advantageous. With appropriate measures taken, it permits one to increase sharply the signal-noise ratio, i.e., the quantity determining the sensitivity threshold of the method. On the other hand, as we have noted, the image converter can be used most effectively in the near infrared. The pulsed ruby laser realizes both advantages. Furthermore, under these conditions we can expect to shorten the exposures by another order of magnitude. This is quite essential in the spectroscopy of fast processes. Therefore, a pioneering study by Delhaye and Migeon on this topic is of great interest.^[26]

The experimental details of excitation of spectra have been described in another chapter of this review.

The spectrum was incident on the photocathode of an RCA S-1 image converter having one amplification stage. Further on, its image was transferred by the electron optics to the fluorescent screen, from which it was photographed on Kodak 135 Tri-X film. The relative aperture of the camera objective was $f/0.95$. The electronic magnification was unity. The flashes were synchronized with the shutter by an intermediate thyatron. Hence the photographic emulsion saw the screen only during the flashes, and thus the best signal-noise ratio was attained. In^[26], they were able to observe single-flash spectra of various compounds with this apparatus. In the opinion of the authors of^[26], their encouraging results could be further improved by using an image converter having several amplification stages.

Difficulties involving the resolution owing to scattering of light by the grains of the film can be eliminated by using special emulsions. This circumstance was discussed above. The Lallemand-Duchesne electronic camera serves for this purpose. Berger and Kara^[47] have described the only experiment using it in spontaneous Raman spectroscopy. The fundamental characteristics of this camera are: cesium-antimonide photocathode, electronic magnification = 0.8, resolving power = 50 double lines/mm, 12-plate cassette, pumping time 3 hours at 300°C , photocathode and cassette cooled with liquid nitrogen, accelerating potential = 30 kV. The spectrum was obtained with a double-prism instrument with an $f/4.5$ camera objective. The spectrum was excited with a Toronto-type helical mercury lamp. They showed by using carbon tetrachloride that they gained by a factor of 25 in exposure while maintaining the same resolution. While the obtained results hardly prove that this camera has decisive advantages over the image converter, its inconveniences of operation are obvious. Nevertheless, we can count on further refinements of this method as well.

Our industry produces image converters of the types PIO-1, PIM-3, and PIM-4. However, the brightness coefficient, i.e., the ratio of the brightness of the screen (in apostilbs) to the illumination of the photocathode (in luxes) is small in these devices, being 16 at most.^[48] Hence, using them in spontaneous Raman spectroscopy cannot give appreciable results. Image converters having a high coefficient of brightness amplification that are suitable for multiframe recording of weak pulsed spectra, at least when one doesn't need too high resolution, have been developed, e.g., by Zavoiskiĭ and his associates (see^[48]).

The converter consists of a PIM-4 input camera and several amplifying stages linked by optical contact through a thin transparent film. A luminescent composition is coated on one side of the film, and a sensitive layer forming a photocathode on the other. The electrons are focused by the homogeneous magnetic field of a solenoid. An electrostatic field is used for focusing in the input camera. The instrument has an electron amplification coefficient greater than in modern photomultipliers and a resolving power of about 10 lines/mm.

VI. AN EXPERIMENT USING A FOURIER SPECTROMETER

Fourier spectrometers show the greatest effect with thermal detectors, whose noises do not depend on the

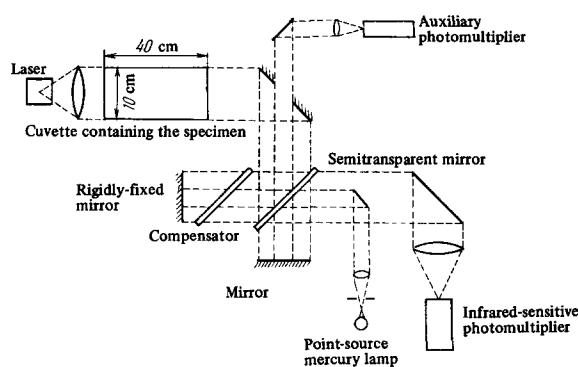


FIG. 6. Diagram of an apparatus for exciting and recording spontaneous Raman spectra, based on using a Fourier spectrometer (the lower mirror in the diagram is movable).

intensity of the incident radiation (in contrast to photomultipliers). Correspondingly, the most favorable objects of study are continuous spectra or those rich in lines (or bands). Raman scattering does not stand well in this regard. This fact did not hinder Chantry, Gebbie, and Hilsum from trying to use such a spectrometer for recording spontaneous Raman spectra.^[27]

Figure 6 shows a diagram of the apparatus. The spectra were excited with the 8400-Å line of a semiconductor laser based on a gallium arsenide crystal. The cuvette for the liquid sample was 100 mm in diameter and 400 mm long, and was fitted with precisely-worked flat windows. Because of this, it was set directly inside the interferometer. The laser pulses were synchronized with the voltage pulses supplied to the photomultiplier. This reduced the noise level. A digital computer was connected to the output of the spectrometer, and it operated concurrently with discrete displacements of the mirror corresponding to the wavelength of the violet line of mercury.

Using this apparatus, they obtained both the Stokes and anti-Stokes regions of the spectrum of iodine dissolved in carbon tetrachloride and the spectrum of 1,1'-diethylthiatricarbocyanine iodide dissolved in methanol. The authors of^[27] conclude that the spectra of both substances are to be ascribed to stimulated scattering, although this probably contradicts the power of the laser used, which was too low.

VII. ROTATIONAL AND ROTATIONAL-VIBRATIONAL SPECTRA OF GASES

There are only three known publications^[11,49,50] on this problem as applied to lasers. However, the obtained results are so good that we can be sure of an extremely rapid development of this interesting line of research.

We must bear in mind two questions in evaluating the potentialities of spontaneous Raman spectroscopy of gaseous substances: what is the width of the exciting line, and is it generally powerful enough to excite very weak lines in the spectrum? As for the first question, the advantages of lasers over ordinary sources are obvious. In the best of these sources used in spontaneous Raman spectroscopy, which is a powerful mercury lamp having water-cooled liquid mercury electrodes, the half-width of the lines amounts to 0.20–0.25 cm^{-1} . In a helium-neon laser, even in multimode operation, the

half-width of the lines is smaller by a factor of four or five. As for the second question, we can predict nothing in advance. This requires experimentation.

Weber and Porto^[49] were the first to get spontaneous Raman spectra of gases with a laser. For excitation, they used the 6328-Å line of a helium-neon laser of 20 mW power. The cuvette had windows at the Brewster angle and a system of internal diaphragms to attenuate the stray light, and it was set inside the resonator cavity, which was formed by two spherical mirrors. Its effective volume was 0.59 cm^3 . The cross-section of the laser beam in the working region of the cuvette was 5 mm. The cuvette was equipped with a window for observation from the side. A Dove prism gave a vertical image of the horizontal cuvette. The method of recording was photographic. The spectrograph had a diffraction grating with 300 lines/mm. The working order of the spectrum was the ninth. The focal length of the camera was 2 meters. The reciprocal dispersion of the instrument was 2 cm^{-1}/mm . A short-focus cylindrical lens was set in front of the photographic plate to enhance the brilliance of the spectrum. They could get the purely-rotational spectrum of the methylacetylene molecule at a vapor pressure of 0.5 atm in 58 hours. For comparison, the authors point out that the ordinary method (four mercury lamps and a two-meter multipass cuvette) requires exposures of only 14 hours to photograph the spectrum of the same molecules, without a cylindrical lens.

However, there are many possibilities of refining the apparatus described above. These authors, together with Cheesman and Barrett^[50,11], have not failed to take advantage of this situation in subsequent studies.

First of all, the gas cuvette was redesigned. Figure 7 shows a diagram of it. As we see, the cuvette is multipass in the transverse direction (in the direction of observation). This is achieved with a system of spherical mirrors. This gives a significant gain in the intensity of scattered light. Very substantial roles are also played by the geometry of the laser beam at the site where the cuvette is placed, and by the relative positions of the cuvette, the illuminating lens, and the slit of the spectroscopic instrument. The system showed itself to best advantage when the focus of the laser beam and the image of the slit were made to coincide within the cuvette. Finally, a trivial source of increased efficiency of the apparatus is the much more powerful ionized-argon laser that they used in^[50,11], along with the helium-neon laser.

Apparatus to study gases has been built in two variants: photographic and photoelectric. The spectrograph is the same as that used in the initial study.^[49] In order to eliminate the strong background of the Rayleigh line, the authors oriented the polarization vector of the laser beam along the direction of observation. Since the Rayleigh line is almost completely polarized, while on the contrary, the rotational lines are always depolarized, this measure led to a sharp selective weakening of the Rayleigh line in particular. They recorded the spectra photoelectrically only when excited by the ionized-argon laser. Initially, they performed the experiments with a single-pass cuvette. The results proved quite satisfactory. Later on, they changed to a multipass cuvette. The cuvette was set both inside and

outside the resonator. They used two monochromators, a single and a double one. The detecting and amplifying apparatus was built out of standard components. The signal-noise ratio was 100. They studied the spectra of gaseous N_2 , O_2 , CO_2 , and methylacetylene vapor. They performed partially-polarized measurements. The effective volume of the gas was 10^{-7} – 10^{-8} l.

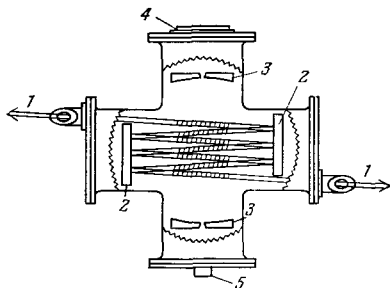


FIG. 7. Diagram of a gas cuvette: 1 – laser beam, 2 – flat mirrors, 3 – spherical mirrors, 4 – exit window, 5 – filling valve.

VIII. CHARACTERISTICS OF TYPICAL APPARATUS

Up-to-date apparatus for studying spontaneous Raman spectra is being produced commercially in a number of countries. Some original designs have been built in the form of working models. One can find them described in the periodical literature. Finally, there are instruments assembled from standard components and modules that are also of undoubted interest. The topic of this chapter consists in systematizing the most typical material on this problem.

1. The Cary 81 Spectrometer (USA)

This spectrometer is produced by the company Cary Instruments, Applied Physics Corp. It is probably the most widely used, to judge from the existing publications. For example, it has been described in some detail in^[1,4]. Hence I need not repeat this material. It seems a propos simply to consider one innovation, to give a diagram of the instrument and its overall appearance, and to summarize its measurement characteristics.

Fundamentally, the modernization of the instrument has involved the source for exciting spectra. A standard helium-neon laser has been added to the existing low-pressure mercury lamp. It is firmly mounted on the monochromator housing, along with all its attachments. A narrow-band interference filter is placed in the laser beam. The beam is sharply focused with a lens into the center of the cuvette, which is a capillary of inside diameter 0.5 mm and length 50 mm. The scattering is observed from the side. A double-slit variant of the monochromator is used when the spectrum is excited by a laser. A fraction of the light reflected from the interference filter serves to furnish the reference signals required by the double-beam system of recording when operating with a gas laser.

Figure 8 shows a fundamental diagram of the instrument. One can get an overall view of the instrument in Fig. 9. The company's brochure gives data characterizing the measurement standards of the instrument:^[5]

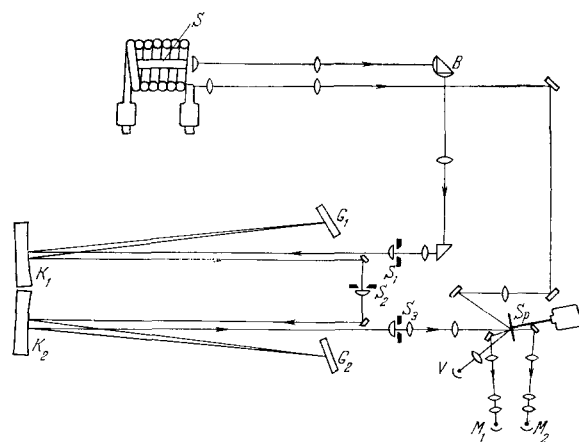


FIG. 8. Fundamental diagram of the Cary 81 spectrometer: S – cuvette containing the working substance; G_1, G_2 – flat diffraction gratings; K_1, K_2 – off-axis collimating mirrors; S_1, S_2, S_3 – double slits; B – image divider; M_1, M_2 – photomultipliers to detect the working signals; V – photomultiplier for the comparison channel, S_p – rotating sector mirror.

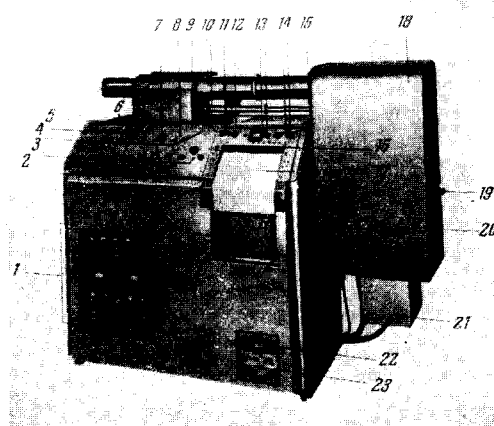


FIG. 9. Overall view of the Cary 81 instrument: 1 – control panel; 2 – rotation of the slit drum; 3 – scales for reading the absolute and relative frequencies of lines and slit widths; 4 – automatic release for strip-chart drive; 5 – switch to reverse rotation of gratings; 6 – stainless-steel container for pouring liquid samples and light filters; 7 – scanning speed selector; 8 – starter for mirror rotation and chart drive; 9 – illuminator; 10 – illuminating optics; 11 – zero-point adjustment; 12 – time-constant adjustment; 13 – adjustment of reference signal to an assigned value; 14 – sensitivity adjustment; 15 – optical regulator of the reference signal; 16 – frequency markers; 17 – recording potentiometer; 18 – image dividers and the pertaining optics; 19 – ribbon lamp for photometric measurements; 20 – device for attenuating the light beam as the Rayleigh line passes through the exit slit of the monochromator; 21 – photomultipliers; 22 – terminal board; 23 – power supply for the photomultipliers.

photometric accuracy: 0.2%,
 photometric reproducibility: 0.1%,
 accuracy of frequency measurement: 0.5 cm^{-1} ,
 accuracy of reproduction of frequencies: 0.1 cm^{-1} ,
 resolution: 1 cm^{-1} .

2. The Perkin-Elmer LR-1 Spectrometer (USA)

We have had at our disposal only sparse information on this instrument, although it is used in many foreign

laboratories to study spontaneous Raman scattering. Apparently the instrument is built around a simple monochromator put out by the same company (Model 83) that has been redesigned into a double monochromator. The instrument is designed to operate in conjunction with a gas laser, and to take both liquid and solid, powdered samples. The minimum volume of liquid is 0.2 ml. The laser beam passes repeatedly through the cuvette. The back-scattered radiation is used. Spectra of powders are observed in reflection. The powder is poured into a small hole in a stainless-steel plate. One setup can be replaced by another very quickly. The instrument is equipped with a helium-neon laser. In the best variant, this is one having 50 mW power, produced by the firm Spectra Physics (model 125).^[1,41,52,53]

3. The Steinheil Spectrometer (West Germany)

Following established traditions, this instrument uses a prism spectrograph developed by the same company some tens of years ago. The light is dispersed in it by three large prisms 70 mm high. The relative aperture of the collimator and camera is $f/10$. Instead of scanning the spectrum by rotating the dispersive element, as is usually done, on the contrary, in this instrument the exit slit is translated in the focal plane, the prisms remaining fixed. For this purpose, the photomultiplier and the slit are mounted on a special plate set in the cassette region of the camera. The defect of this variant is that it does not permit one to maintain the axes of the beams corresponding to different wavelengths in the same direction with respect to the photocathode of the photomultiplier. The remaining parts of the instrument are built in the form of individual modules. More detailed information on it can be found in^[1].

4. The RS-2 Spectrometer (East Germany)

Figure 10 shows a diagram of the optical part of this instrument. It is built on the principle of double monochromatization. This makes possible practically complete elimination of stray scattering and it doubles the angular dispersion. Instead of prisms, which were used in the prototype of this instrument (RS-1), flat diffraction gratings are used here for dispersion of the light. The dimensions of the ruled area are 70×60 mm, with 650 lines/mm, operating in the first order of the spectrum. The latter feature is very unfavorable, because the light flux transmitted by the monochromator in a given spectral interval is proportional to the angular dispersion of the monochromator, and so is the efficiency of photoelectric recording. It would be far more advantageous to use gratings designed, e.g., to concentrate the energy in the second order of the spectrum. Both gratings are rotated by an auxiliary cam device. This makes the dispersion linear (on a reciprocal-centimeter scale) in the region $25,000-15,000$ cm^{-1} . The length of the spectroscopic slits is 40 mm. The entrance slit is curved (with radius of curvature 340 mm). A glass disk, half of which is coated with a reflective layer, rotates at 11 Hz frequency, and directs the light passed by the monochromator alternately to one or the other photomultiplier. Further on, the signals are applied to two completely identical amplifying channels, and are then integrated. This improves the signal-noise

ratio. Fluctuations in the intensity of the exciting source are taken into account. The instrument is designed to operate with a Toronto-type lamp, although it can be adapted to other sources as well, lasers in particular.^[54]

5. A Laboratory-type Instrument (West Germany)

This apparatus is assembled from individual components, and has been described by Brandmüller, Burchardi, Hacker, and Schrötter.^[56] Figure 11 shows a diagram of it. The spectroscopic apparatus is a Jarrell-Ash monochromator, Model 78-467, built according to the Czerny-Turner design. A flat diffraction grating is used to disperse the light. It has 1180 lines/mm, and it directs a considerable fraction of the energy into the first order of the spectrum in the 7500-Å region. The collimators are parabolic mirrors of focal length one meter and relative aperture $f/8.6$. The slits are curved and are 20 mm long. As we see, this instrument has a moderate light efficiency (in the sense of the transmitted light flux), as the previous one does. This arises from the poor choice of a grating that doesn't concentrate the light into the higher orders of the spectrum. The apparatus is equipped with a Spectra Physics helium-neon laser (Model 125) having 50 mW power, and with accessories for studying liquids and crystals. Lateral observation is used in the first case, and observation by transmission in the latter case. Two methods of polarization measurements can be carried out. The efficiency of the liquid cuvette is considerably enhanced by multiple reflection of the light beam by two flat mirrors. In studying powders, a filter is put in front of the entrance slit to prevent the brilliant light of the

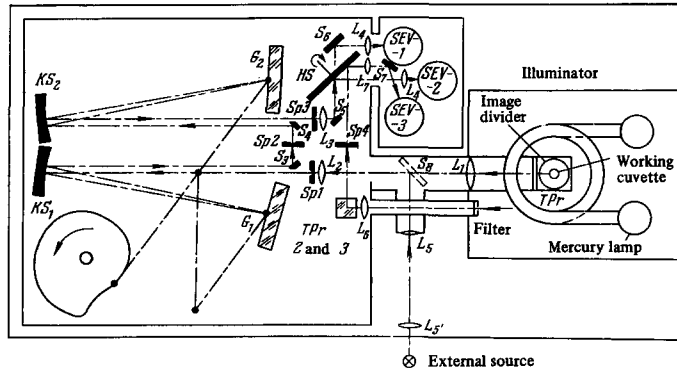


FIG. 10. Diagram of the RS-2 spectrometer: Main parts: Sp_1 , Sp_2 , and Sp_3 – entrance, intermediate, and exit slits of the monochromator, respectively; KS_1 and KS_2 – spherical mirrors; G_1 and G_2 – flat diffraction gratings; HS – rotating mirror; SEV-1, SEV-2, and SEV-3 – photomultipliers.

laser line from entering the instrument. In particular, solutions of cyanine dyes proved suitable for this purpose. However, in distinction from double monochromatization of the light, these filters more or less weaken the region of vibrational frequencies up to 500 cm^{-1} . The scattered radiation is detected by a photomultiplier cooled to -25°C . Standard Steinheil two-channel DCA amplifiers and a Speedomax Leeds and Northrup recorder are used. The time constant can be varied over the range from 0.5 to 32 sec.

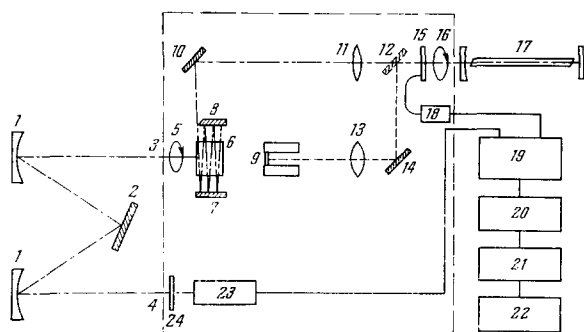


FIG. 11. Diagram of the apparatus described by Brandmüller et al. [56]: 1 – spherical mirrors; 2 – flat diffraction grating; 3, 4 – entrance and exit slits; 5, 16 – devices for rotating the plane of polarization of the light; 6 – cuvette containing the liquid; 7, 8 – coated flat mirrors; 9 – pressed-power specimen in a holder; 10, 12, 14 – rotating mirrors; 11, 13 – lenses; 15, 24 – light filters; 17 – helium-neon laser; 18 – photomultiplier with a light guide to detect the reference signals; 19 – amplifier; 20 – recorder; 21 – electronic integrator for integrating the intensities of spectral lines over their contours; 22 – recorder for recording the integral intensities of lines; 23 – photomultiplier to detect the working signals.

6. A Spectrometer with Improved Measurement Parameters (USSR)

The instrument DFS-12 has already been in production in our country for Raman scattering purposes for ten years. It includes a spectroscopic instrument and the appropriate components: a detecting and amplifying instrument, a potentiometer, an illuminator having a helical low-pressure mercury lamp, and a stabilized rectifier as power supply for the lamp. A detailed description of the entire apparatus is given in [55,41]. Double dispersion of the light and the presence of an intermediate slit in the monochromator of this instrument make it possible to record spontaneous Raman spectra of powders and other inhomogeneous substances. However, it has some intrinsic defects. The major ones involve the lack of devices that would permit one to measure more accurately the positions of spectral lines, or would compensate for fluctuations in the brightness of the excitation source. These general problems (and some others) have been the topic of special study. As a result, it has been possible to build an essentially completely new apparatus distinguished by a complex of unique measurement qualities. [57]

The basis of the apparatus is a somewhat modernized DFS-12 double monochromator. The modernization has mainly involved its spectral range, which has been extended to 10,000 Å. This permits one to use the instrument while working with lasers as sources for exciting spontaneous Raman spectra. A Fabry-Perot etalon illuminated by a source of continuous radiation is used as the frequency marker. The spacing between marks is 5 cm⁻¹. Linear interpolation is carried out inside these intervals. The error is no greater than 0.1–0.15 cm⁻¹. Here the total error of frequency measurement in the 2000 cm⁻¹ range lies within the limits of 0.25 cm⁻¹. The light signals forming the frequency take up a small part of the height of the entrance slit of

the monochromator at the top and bottom. The marks are recorded by a double-beam system. The effect of fluctuations in the brightness of the excitation source on the intensity of spectral lines is eliminated in an analogous way. A specially-designed electrometric d.c. amplifier is used in the recording system. For an input resistance of 680 megohms, the current amplification coefficient is 2.2×10^5 . The sensitivity of the amplifier is 4×10^{-12} A/division. Automatic sensitivity switching (1:1 and 1:10) has been provided to increase the accuracy of measurement of the intensities of spectral lines. The zero-point drift of the amplifier does not exceed half a division on the most sensitive scale. The recording apparatus can also be used in a single-beam system. It is equipped with a specially-designed photomultiplier having a small detecting area in order to improve greatly the signal-noise ratio, i.e., the sensitivity threshold of the instrument.

The following data give a picture of the measurement standards of the instrument:

photometric accuracy: no worse than 0.3%,
accuracy of frequency measurement: 0.25 cm⁻¹,
resolution: 0.2–0.3 cm⁻¹.

Bearing in mind also the high relative aperture of the monochromator and the purity of the spectrum that it gives, I can state that the apparatus under discussion is one of the best of those described in the literature.

In concluding this section, I have shown in Figs. 12–15 some typical spontaneous Raman spectra obtained with the described apparatus and analogous apparatus to show their potentialities.

IX. A COMPARATIVE EVALUATION OF THE POTENTIALITIES OF RAMAN SPECTROSCOPY AND INFRARED ABSORPTION

The two methods are similar in the sense that both of them give information on the vibrational and rotational levels of molecules in their electronic ground states. This is the basis of using the methods in molecular analysis. However, Raman spectra also indirectly reflect the characteristics of the excited electronic states. This feature of them is very distinctly manifested in the behavior of intense bands in spectra that are especially close to the intrinsic absorption of the molecules, i.e., under conditions of resonance excitation. In individual cases, one can directly decide from Raman spectra on the positions of electronic levels. Examples of this will be discussed below. Recent advances in experimental technique have substantially simplified the study of resonance and electronic Raman spectra, and the region of accessible objects has been extended considerably. The process of stimulated scattering provides highly interesting and unique possibilities of studying macroscopic and molecular properties of matter (see the reviews [5,58,59]). Hence I can state that currently Raman spectra incomparably surpass infrared absorption spectra in the volume of varied scientific information provided.

The two methods are also not matched from the standpoint of purely technical features of experimentation and apparatus. Thus, for example, we know that it is hard to study aqueous solutions of substances in the infrared, and the spectra themselves cannot be obtained

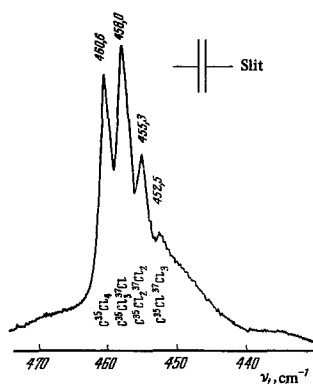


FIG. 12. Isotope structure of the 459-cm⁻¹ line in the spontaneous Raman spectrum of CCl₄. Recording made with the apparatus of [56].

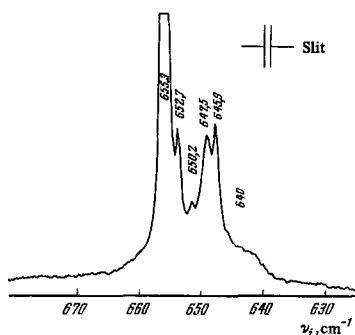


FIG. 13. Isotope structure of the 656-cm⁻¹ line in the spontaneous Raman spectrum of CS₂. Recording made with the apparatus of [56].

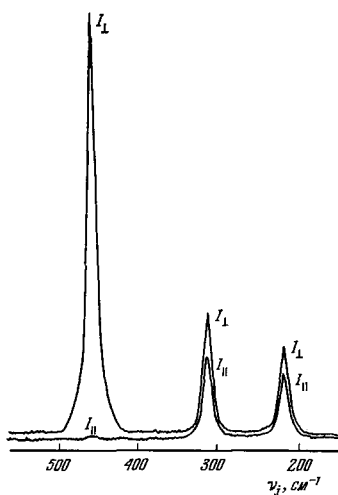


FIG. 14. Polarization spontaneous Raman spectrum of CCl₄. Recording made with the apparatus of [56].

at one time over the entire range of vibrational frequencies. On the other hand, Raman spectroscopy has been deficient in that it imposes specific requirements on the substance being studied. As a rule, it has been possible to record top-quality spectra when the substance does not luminesce nor absorb within the region of the spectral lines, and it is present in sufficient quantity.

Use of lasers as sources for exciting spontaneous Raman scattering has changed the situation. As I have noted, at present one can often do with tenths of a milli-

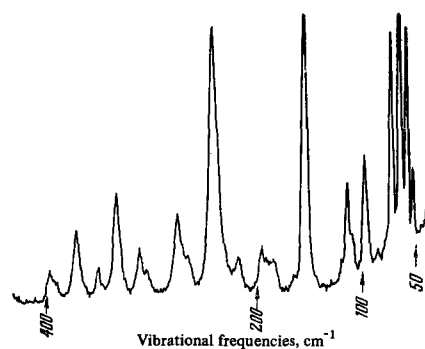


FIG. 15. Portion of the spectrum of powdered I₂O₅ recorded with the apparatus made by the French firm Coberg. [10].

meter of a liquid or several milligrams of a powder in studying spontaneous Raman scattering. The conditions of experiment are about the same in the infrared. On the other hand, availability of exciting lines of long wavelength permits one to work usually in a region where the substance is transparent, and this also rules out luminescence.

One of the most important characteristics of spectroscopic apparatus is the resolution that it provides in spectra. This is closely connected with the sensitivity threshold of the apparatus, the efficiency of excitation of spectra, the width of the exciting line, the optical quality of the spectroscopic instrument, and the conditions of photography or photoelectric recording of spectra. In turn, the sensitivity threshold depends on the amount and properties of the substance being studied. When one excites spectra by ordinary gas-discharge lamps, decrease in the amount of the substance necessarily entails weakening of the spectrum. The situation differs when one uses lasers. Here the geometry of illumination of specimens is changed, and in such a way that one can maintain a constant light flux while the volume of acting substance decreases by narrowing the light beam and the spectral slit of the instrument. Simultaneously, this increases the resolution in the spectra (Sec. 6, Chap. II). Hence, in the final analysis, the resolution for a given substance will be completely determined by other factors whose effects have been well discussed in the literature.

Let us estimate the limiting parameters of a spectroscopic instrument to make possible maximum resolution in spontaneous Raman spectra. We shall start with the idea that the half-width of the exciting line of a gas laser is several hundredths of a reciprocal centimeter.^[11] By using the known formulas

$$R = \frac{\lambda}{\Delta\lambda} \quad (6)$$

and

$$R = \frac{2a \sin \beta}{\lambda}, \quad (7)$$

where R is the resolution, λ is the wavelength, $\Delta\lambda$ is the spectral interval to be resolved by the instrument, a is the width of the grating, and β is the diffraction angle, we derive a formula permitting us to determine the width of the grating, other conditions remaining fixed:

$$a = \frac{\lambda^2}{2\Delta\lambda \cdot \sin \beta} \quad (8)$$

If we take $\lambda = 7000 \text{ \AA}$, $\Delta\lambda = 0.015 \text{ \AA}$ (0.03 cm^{-1}), and choose a grating having 600 lines/mm working in the fourth order of the spectrum, i.e., with a β of about 60° , we get $a = 200 \text{ mm}$. These dimensions are still realizable, even in high-quality gratings.

In order to resolve two lines separated by 0.03 cm^{-1} by the photographic method when the grain size of the emulsion is about 0.01 mm , the reciprocal dispersion of the spectroscopic instrument must be no poorer than 1 \AA/mm . Then we get the value 2 m for the focal length of the objective, from the formula

$$F = \frac{\lambda}{2 \text{tg} \beta \cdot D}, \quad (9)$$

where D is the reciprocal dispersion and the rest of the quantities are as defined above. In fact, the focal length must be chosen to be at least twice as large. Such a camera will correspond to an actual relative aperture of about $f/30$. The low aperture itself, not to mention the difficulties of preparing large high-quality gratings, determines the limiting potentialities. This is approximately the type of apparatus used in^[11] to record spontaneous Raman spectra of certain gases. Of course, the attainable resolution also depends on the nature of the spectral lines. Since gases and vapors are studied at relatively high temperatures and pressures, Doppler broadening of the levels takes on a substantial role. This is what limits the resolution even before the instrumental parameters do. A similar situation occurs also in the infrared. Here, however, it has been possible to resolve 0.025 cm^{-1} under the most favorable conditions (the $2-6 \mu$ region).^[60]

Thus, when using classical spectroscopic instruments, the Raman-scattering and infrared-absorption methods differ little in principle in their possible resolutions.

An important trend in the development of modern spectrometry is the invention of instruments that permit one to study fast physical, chemical, and biological processes. Such instruments have also been built for the infrared. Low-lag semiconductor detectors have recently become available, and are sensitive out to 120μ . Their use has permitted the time to record a single spectrum on such instruments to be reduced to $10^{-5}-10^{-6} \text{ sec}$.^[61]

Fast spontaneous Raman spectroscopy began to develop with especial success after pulsed lasers had appeared. The possibility of obtaining single-flash spontaneous Raman spectra using an image converter means that processes having a duration of 10^{-3} sec have become accessible to study by this method. Using an image converter with multistage amplification will probably permit a shortening of this time by another order of magnitude or two. Then spontaneous Raman spectra will not be very inferior in this regard to infrared absorption spectra.

X. EXAMPLES OF PREVIOUSLY IMPOSSIBLE STUDIES

1. Electronic Transitions in Scattering

Usually Raman scattering is associated with vibrational states (and more rarely rotational). However,

the general theory of the phenomenon also covers processes involving ions and free atoms, and the frequency difference between the exciting and the shifted lines is ascribed to change in electronic energy. The first attempt to observe electronic spontaneous Raman scattering (ESRS) in condensed systems was made by some Indian authors, and dates from as early as 1939.^[62] They selected as their object of study an aqueous solution of samarium nitrate. The spectrum showed a number of relatively narrow bands that were interpreted as ESRS bands. However, a year later Gross, Raskin, and Zaidel^[63] called attention to an error in the experiments of the authors of^[62] that had led them to erroneous conclusions. This problem was taken up again only after almost 25 years.

Observation of electronic levels from ESRS spectra has a number of advantages over the direct methods. They can be advantages in principle, or purely methodological. The former involve the differing selection rules for the line intensities: for dipole transitions, transitions are permitted between levels of differing parity. In ESRS, on the contrary, they are permitted between levels of the same parity. Circumstances can favor study by ESRS. I shall discuss below a number of such examples. As for the methodological side of the problem, one encounters this when the energy difference of the states in question lies far enough in the infrared. Then it is much simpler to detect the electronic transitions in scattering.

Most of the studies performed thus far have involved ESRS of the ions of various rare-earth elements. The choice of objects is not fortuitous. First, they are characterized by relatively narrow electronic levels, especially at low temperatures. Second, dipole transitions involving $(4f)^n$ electronic configurations, which are typical of the rare-earth elements, are forbidden, strictly speaking. They are observed only in activated crystals by virtue of breakdown of the selection rules. Hence, application of the ESRS method would be of great interest here. The authors of^[64] point out the possibility of obtaining ESRS spectra in such systems. These systems are very promising for laser action, and any new information on their properties may undoubtedly prove useful in inventing lasers.

The first study obtaining reliable results on ESRS spectra was performed by Hougen and Singh.^[65] They studied a single crystal of PrCl_3 . The exciting line was the 2537-\AA line of a mercury lamp. They made a comparison with the isomorphous crystal LaCl_3 . The spectra were photographed with a spectrometric instrument having a curved diffraction grating of 21-foot radius (reciprocal dispersion = 0.8 \AA/mm). The exciting line in the secondary beam was absorbed by mercury vapor. The exposures were 4–20 hours.

At room temperature, the spectrum of each of the crystals showed five each of Stokes and anti-Stokes lines. They were interpreted as being vibrational. The absence of electronic lines was ascribed to the considerable width of the corresponding levels under the conditions of experiment. At 77°K , the spectrum of PrCl_3 (but not LaCl_3) showed ten additional lines. They were ascribed to electronic scattering, and namely, to transitions from the lowest Stark level of the $^3\text{H}_4$ state to the remaining three Stark levels of the same state, to five

Stark levels of the 3H_5 state, and to two Stark levels of the 3F_2 state. The width of all the ESRS lines amounted to several reciprocal centimeters. Their intensities were comparable with those of the vibrational lines.

Further progress in ESRS spectroscopy is associated with the studies of Chau,^[66] Koningstein,^[39,67] and Koningstein and Mortensen,^[68] who went over to studying crystals activated with rare earths. The technically-permitted variation of the conditions (i.e., ultimately the symmetry of the field acting on the rare-earth ion) creates a variety of possibilities for the light-scattering process. At the same time, it is not hard to distinguish the electronic from the vibrational lines, and this can be done in various ways, e.g., by studying the crystals at various temperatures and with different amounts of the activating additives.

Chau^[66] studied a specimen of calcium tungstate containing 1% of cerium ions. Since the latter absorb in the ultraviolet, the blue line of mercury was used for excitation. The spectra were photographed with an instrument having a diffraction grating (of reciprocal dispersion $4 \text{ cm}^{-1}/\text{mm}$). The exposures were 1.5–3 hours. The specimen was studied at room temperature and also at 77° and 2.2°K .

In the latter case the spectrum showed four ESRS lines. The two most intense of them appeared also at 77°K . The room-temperature experiments proved to be unsuccessful. The observed lines were ascribed to $^2F_{7/2} \rightarrow ^2F_{5/2}$ transitions. According to the theory, when the symmetry is C_{4h} as in the CaWO_4 crystal, or with lower field symmetry, the $^2F_{7/2}$ level must split into four doubly-degenerate states and the $^2F_{5/2}$ level into three. The fact that only four lines actually appear possibly indicates that the excited states are insufficiently populated.

Most rare-earth ions absorb in the visible. This fact rules out studying them with ordinary excitation sources. The way out consists in using the 6328-\AA line of a helium-neon laser for excitation. This is what Koningstein did in^[39,67]. This permitted him to study ytterbium, europium, and neodymium ions in yttrium gallium garnet. At the same time, low-temperature experimentation itself was considerably simplified. Polarization measurements were made in the ESRS spectrum of yttrium vanadate activated with europium in^[69].

The crystals were cylinders 10 mm long and 3 mm in diameter. They contained 2–5% of the activating additive. The cylindrical surfaces of the specimens were blackened in order to reduce stray scattering, except for a small region for lateral observation. The specimens were attached to a massive brass plate. This facilitated study at liquid-helium temperature. At first, the ESRS spectra were recorded photoelectrically. They used for this purpose a Jarrell-Ash spectrometer equipped with a 9558 EMI photomultiplier. The electronic amplification system was that of Pao and Griffiths.^[33] An additional means of increasing the sensitivity of the apparatus was by magnetic focusing of the electrons in the photomultiplier with an external field.

They could record top-quality spectra for all three systems and identify ESRS lines in them. They were ascribed to transitions to one of the Stark levels of $^2F_{7/2}$ in Yb: YGaG , to the 7F_1 level in Eu: YGaG , and to

the first excited state in Nd: YGaG . Study of the intensities showed that the matrix elements $\langle (4f)^N | \mu | (4f)^{N-1} 5d \rangle$ contributed most to the scattering, and that the ESRS was not appreciably enhanced as the exciting line approached intrinsic absorption lines, as usually happens in vibrational transitions.

We cannot consider the absence of a resonance effect that was established in^[67] to be in any case a universal law. This is indicated by results obtained by Rokni and Yatsiv.^[69] They studied the ESRS of potassium vapor. The possibility of observing scattering from the excited level $4P_{3/2}$ was especially favorable, since here resonance conditions are realized for the ruby line. In order to populate the $4P_{3/2}$ level sufficiently, they illuminated the cuvette containing the potassium vapor with the Stokes lines of stimulated Raman scattering excited in a number of substances: nitrobenzene and bromo-, chloro-, and methylnaphthalene. The corresponding lines are absorbed to give this level.

In addition, they synchronized the pumping and excitation in this experiment. The spectra were recorded with a PbS photoresistor using a Perkin-Elmer infrared spectrometer.

When they used all four liquids, they actually observed in the near infrared an intense line at the displaced frequency 2720.6 cm^{-1} . It turned out that this line grew in intensity with rising temperature, and hence, with increasing vapor pressure of potassium. The line was not observed in the absence of the cuvettes containing the liquids. It could not be ascribed to the energy difference between any of the pairs of levels belonging to potassium atoms. On the other hand, within the limits of accuracy of measurement ($\pm 0.5 \text{ cm}^{-1}$), its frequency was the same as for electronic scattering from the $4P_{3/2}$ to the $5P_{3/2}$ level.

They performed control experiments for a final test of the validity of their conclusions on the nature of the line. In one of these, the temperature of the ruby rod was 24° while the spectrum was being recorded, and $+45.5^\circ \text{C}$ in the other experiment. Here the frequency of emission of the ruby line was shifted by 2.9 cm^{-1} . The displacement of the 2720.6 cm^{-1} line was fixed correspondingly. The established result is compatible only with ascribing the line in question to electronic scattering. The authors of^[69] ascribe it to stimulated scattering on the basis of intensity estimates.

Up to now, we have been discussing electronic scattering in pure and activated ionic crystals and also in free atoms. However, the experiments have recently been extended to semiconductor materials as well. Henry, Hopfield, and Luther have obtained ESRS spectra from a gallium phosphide crystal containing added neutral acceptors (Zn and Mg). They ascribed the observed lines to transitions between degenerate levels of the ground state, and in particular, to the valence band.^[70] Wright and Mooradian's^[71] object of study was a Si crystal activated with phosphorus (donor) and boron (acceptor).

The fundamental difficulty in such experiments involves luminescence of the crystal at low temperatures. Nevertheless, they were able in^[70] to excite spectra with a helium-neon laser. They used two of its lines: $\lambda = 6328$ and 6118 \AA . This was required in order to distinguish scattering from luminescence. The power

in these lines was 50 and 2 mW, respectively. The spectra were recorded photographically with a Bausch and Lomb spectrograph having an f/18 camera. The specimens were cooled with helium vapors to 20°K. They adopted the optimum concentration of activator. In^[71], the spectra were excited with the 10,648-Å line of neodymium in an yttrium-aluminum garnet crystal. The method of recording was photoelectric. They used a double monochromator. The radiation receiver was a photomultiplier with a refrigerated photocathode (S-1). Cooling the specimens to liquid-helium temperature completely eliminated absorption and luminescence. They began to interfere with the study as low as liquid-nitrogen temperature.

2. Inverse Raman Spectra

The transitions that occur during Raman scattering are usually observed in emission. As we know, two cases can happen here. In the former, a molecule originally occurring in a lower vibrational or rotational level absorbs a quantum $h\nu_0$ of the incident radiation and simultaneously emits a quantum $h\nu'$ of lower frequency. This is Stokes scattering. In the latter case, the transition starts from an excited level. The emitted quantum is larger than the incident one. The corresponding line in the spectrum is shifted toward the violet with respect to the exciting line. This is anti-Stokes scattering. It is generally considerably weaker than Stokes scattering because of the thermal distribution of the molecules over the vibrational (or rotational) states. Placzek^[72] has derived the following formula for the probability of transitions in Raman scattering in a given direction per unit time:

$$W_{kn} \sim \left[\rho(\nu_0) \frac{h\nu'^3}{c^3} + \rho(\nu_0) \rho(\nu') \right] |S|^2, \quad (10)$$

where ν_0 and ν' are the frequencies of the exciting and the scattered radiation, $\rho(\nu_0)$ and $\rho(\nu')$ are their densities, and S is the second-order scattering tensor. We can write it in still another way:

$$W_{kn} \sim \rho(\nu_0) [a_{kn} + b_{kn}\rho(\nu')] |S|^2, \quad (11)$$

by introducing the Einstein coefficients a_{kn} for spontaneous and b_{kn} for stimulated emission.

As we see, the formulas for the scattering probability contain two terms: the first term corresponds to spontaneous and the second to stimulated scattering. The latter arises from the quantity $\rho(\nu')$, which is due at the initial instant of time to spontaneous scattering. Under the usual conditions of experiment, the density $\rho(\nu')$ is small, and concomitantly, stimulated scattering plays a negligible role. The effect is manifested at large densities $\rho(\nu')$ of shifted scattering, which are attainable when matter is irradiated with a powerful laser pulse.

What I have presented above implies that the final result of the light-scattering event is a transition of the system from one state to another, usually with a change of unity in a quantum number. In principle, this process is realizable not only in the way mentioned above, but also in another way. Let the system be irradiated simultaneously by powerful monochromatic radiation and by continuous radiation covering the region of vibrational frequencies. Then the transitions shown in Fig.

16 can occur. As we see, they correspond to spectra inverted with respect to the ordinary spectra in two ways: they are manifested in absorption rather than emission, and besides, are far stronger in the anti-Stokes than in the Stokes region. They are the so-called inverse Raman spectra. The anti-Stokes case is simpler, and was discovered by Jones and Stoicheff in 1964.^[73] The Stokes case was discovered later by Dumartin, Oksengorn, and Vodar,^[74a] although the first experiments, which were set up by Landsberg and Baryshanskaya, date back to 1930.^[74b]

In order to make Placzek's formula describe the inverse spectra, we must interchange the symbols of the appropriate quantities in it. Then we have

$$(W_{kn})_{\text{inv}} \sim \left[\rho(\nu') \frac{h\nu_0^3}{c^3} + \rho(\nu_0) \rho(\nu') \right] |S|^2. \quad (12)$$

We can also derive from this formula the experimental conditions under which we can observe inverse spectra of either particular type. Since the first term in the brackets is responsible for this effect, evidently we must make it predominate over the second term. A sufficient condition in experiments in the anti-Stokes region is a moderately high density $\rho(\nu')$. On the contrary, to get inverse spectra in the Stokes region requires that we compensate for the low population of the initial (vibrationally-excited) level. Hence, this can be done with a more "delicate" adjustment of the determining quantities, namely, with a very powerful continuum, but not so much so as to start stimulated Raman scattering. These spectra have actually been observed near the threshold for generation of stimulated Raman scattering. They showed the properties of a stimulated process. Hence, in distinction from the Jones-Stoicheff effect, the authors^[74] called them inverse stimulated Raman spectra. A detailed theory of both effects has now been developed. I shall not treat them in this review, and shall limit myself to the graphic interpretation given above of the processes that occur.

Figure 17 shows a diagram of Jones and Stoicheff's experiment. A ruby-laser giant pulse was successively focused on cuvettes containing toluene and benzene. As had been established, the anti-Stokes stimulated Raman line of toluene in the region $\sim 1000 \text{ cm}^{-1}$ is greatly broadened under certain conditions (by as much as $\sim 100 \text{ cm}^{-1}$). This is the radiation used as the continuum within which the stimulated Raman line of benzene at 992 cm^{-1} falls. Consequently, absorption occurs at this frequency. An analogous effect was observed when the second cuvette was filled with pyridine or nitromethane instead of benzene (with lines at a 990 and 917 cm^{-1} , respectively).

Upon analyzing the experimental material, the authors^[73] drew the following important conclusions:

1. Induced absorption is not limited to threshold conditions. Hence, in principle, inverse Raman spectra can manifest all normal vibrations characteristic of the system and active in spontaneous Raman scattering.

2. Since the induced-absorption process occurs at rather large energy densities, deviations from strict selection rules can occur. This must be accompanied by excitation of new lines forbidden in spontaneous Raman scattering.

3. An inverse Raman effect is not ruled out for rotational lines.

4. Inverse Raman scattering makes it possible to study fluorescent substances.

Thus, inverse Raman scattering is a new, effective method of spectroscopic study showing great promise of further development.

3. Vibrational Spectra of Some Semiconductor Crystals. Perspectives of Studying the Glassy State of Matter

Until recently, spectroscopic studies of semiconductors were performed in the infrared. However, the information obtained was one-sided in nature. At the same time, the strong absorption characteristic of many representatives of this type of substance interfered with study of the spontaneous Raman spectra.

Hobden and Russell^[75] performed the first study in which they could get a spontaneous Raman spectrum of a semiconductor crystal formed by elements of groups III and V, namely gallium phosphide. They used the 6328-Å line of a helium-neon laser for excitation. They photographed the spectrum with a spectrograph of moderate relative aperture ($f/6$). Here the exposures proved to be quite acceptable (from 1 to 12 hours), and the spectrum itself was very intense. It contained 19 lines and bands of the first and second orders, some of them appearing even in the anti-Stokes region. The authors^[75] introduced some corrections into the existing interpretation of the vibrational bands, which were based on analyzing infrared spectra alone. However, they deferred the possibility of formulating final conclusions until the polarization relations in the spectra had been studied.

Marlow, Russell, and Sennett^[76] have taken up this latter problem. They started with the idea that one can determine the nature of the interaction of the incident radiation with the crystal structure of the substance from data on the polarization states of the lines, especially the second-order ones. According to the theory (in particular, that developed by Born and Huang), we can expect that the second-order lines will be depolarized whenever long-range action plays a substantial role. If, on the contrary, interaction of adjacent nuclei predominates, then the same lines will probably be strongly polarized. Experiment has shown that the latter case holds.

Mooradian and Wright^[14] have extended the spontaneous Raman method to study a number of new crystals formed by other combinations of elements of the same groups (GaAs, InP, and AlSb), and they also repeated the GaP experiments. The absorption edge of the first three crystals is even more strongly shifted to longer wavelengths, and they are opaque to the 6328-Å line of the gas laser. Hence, they used another source for excitation: a solid-state continuous laser based on an yttrium-aluminum garnet crystal activated with neodymium (with a line at 10,648 Å). The spectra were recorded photoelectrically, and the detector was a photomultiplier with a refrigerated S-1 cathode. The resolution in the spectra amounted to several reciprocal centimeters, while the signal-noise ratio in the most favorable case was several hundred. The spectrum of GaP proved to be about an order of magnitude weaker than those of the other crystals under identical conditions of experiment. The authors ascribed this result to a resonance effect.

The obtained spectroscopic data characterize the longitudinal and transverse vibrations near the center of the band of the crystal. The precise values of the frequency differences for the different vibrations are used to calculate the electron-phonon and polaron binding constants.

Studies by Russell,^[77] and by Parker, Feldman, and Ashkin^[78] are related to this one in essence. Here they obtained spontaneous Raman spectra from opaque substances in reflected light: silicon and germanium crystals. The scattering line in silicon at 523 cm^{-1} could be recorded for the first time in^[77]. This was in good agreement with the results of studying this substance in infrared absorption. The intensity of the line was stated to be several times as intense as its analog in diamond. It was also noted that one can get a spectrum from a metal by this method (in reflected light). In fact, there has been no information in the literature up to now on performance of such experiments. We note that the method gives a certain chance of success in studying the spontaneous Raman spectra of a substance in the superconducting state, i.e., in solving the problem posed in^[79]. In addition to the line at 520 cm^{-1} , the authors of^[78] found in the spectrum of silicon its first overtone as well, and a line near 300 cm^{-1} in the spectrum of germanium. The experimental details in^[78] are curious and worthy of special description.

The specimens had the form of well-polished plates, and were set inside the resonator of an argon laser at an angle of incidence of 82° (Fig. 18). The resonator consisted of a spherical and a flat mirror. The latter was set at a small angle to the axis of the beam, and operated in conjunction with the mirror plate of the crystal under study. The spectra were excited by one of the argon lines at 5145 and 4765 Å in the Stokes region, and by the 4880 Å line simultaneously in the Stokes and anti-Stokes regions. This made it possible unambiguously to assign the shifted lines to spontaneous Raman scattering (i.e., to distinguish scattering from luminescence). The laser power in the 4880 Å line was two watts. The polarization vector of the exciting light was in the plane of the specimen. The method of recording was photoelectric, with double monochromatization of the light.

Experiments to get spontaneous Raman spectra from semiconductor crystals were further developed by Feldman, Ashkin, and Parker.^[80] These authors studied mixed crystals of silicon and germanium, exciting the spectra as before with the 4880-Å line. They established that slightly-shifted vibrations of the Ge atoms are manifested here, together with a number of vibrations interpreted as local vibrations involving Si atoms. Thus they showed in^[80] that the spontaneous Raman method can be successfully used to study the structures of complex crystallized systems. The results obtained in^[81] lead also to analogous conclusions.

In line with the results presented above, it would be quite logical to go over to studying semiconductor glasses. Here one can count on getting very important information, not only on the structures of these substances, which are of great interest in themselves, but also on the problem of the glassy state as a whole. Nevertheless, apparently no one has undertaken such studies yet. Indeed, the methodological side of the problem has been elucidated with the example of silicate

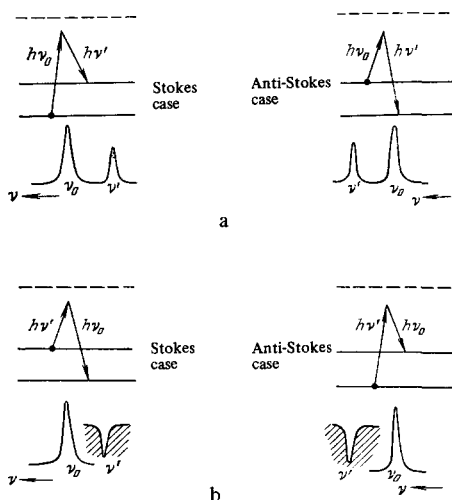


FIG. 16. Diagram of the transitions in direct (a) and inverse (b) scattering processes.

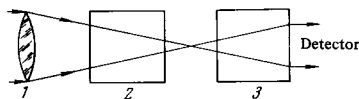


FIG. 17. Diagram of the experiment of Jones and Stoicheff. [73] 1 - focusing lens; 2, 3 - cuvettes containing the liquids.

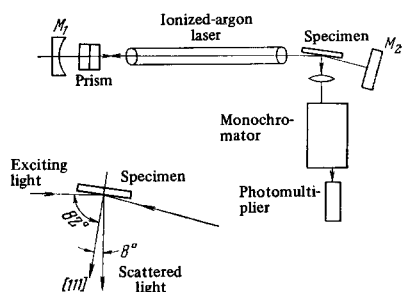


FIG. 18. Diagram of apparatus for observing spontaneous Raman spectra in reflected light. M_1 and M_2 are spherical and flat mirrors, respectively.

glasses in^[82]. They used a modified apparatus for recording spontaneous Raman spectra, using an image converter. The authors of^[82] were able to photograph on Royal X Parde 1250 ASA film a quite distinct spectrum of a particular specimen with five ruby pulses. The slit width of the spectroscopic apparatus was 30 Å. The spectra of semiconductor glasses, which are substances having covalent chemical bonds, should be considerably more intense.

Comparative studies of liquid-crystalline substances seem very promising, especially of those that become glasses while maintaining the order characteristic of their melts. These systems can be considered to be a type of model to be used in the problem of the very existence and spectroscopic manifestation of crystallites in a glass. On the other hand, the so-called nematic liquid crystals, with a suitable orientation, form a model for highly anisotropic molecules of a liquid in the field of the powerful light wave of a laser. Their vibrational

spectra in the low-frequency range may contain information of interest in the theory of crystal vibrations, and possibly may serve in identifying rocking degrees of freedom. Finally, such studies are important in developing ideas on the nature of the liquid-crystalline state itself, and in the more general sense, on intermolecular interactions in the condensed state of matter. These latter studies have acquired a new importance since the discovery by Freund and Rentzepis that liquid crystals can generate the second harmonic.^[83]

Only three studies had been published until recently^[84-86] on the application of spontaneous Raman spectra to the set of problems touched on above. However, this situation is explained by the difficulty of getting spectra using the ordinary technical means.

However, the invention of lasers has simplified experimentation considerably. This has permitted the authors of^[87] to undertake systematic studies of this type.

A complicated organic substance of the structural

formula $C_6H_5N=N-\text{C}_6\text{H}_4-\text{N}=\text{CHC}_6\text{H}_4\text{CH}_3$ was chosen as

the object of study in^[87]. It has the property that it turns into a glass upon rapid cooling from the melt, while maintaining liquid-crystalline order of the nematic type. This provided the advantage of studying each of the states of the substance at the same temperature, as is very important in interpreting the results. The spectra were excited with the 6328-Å line of a standard helium-neon LG-35 laser, and were recorded photographically. A KC-17 glass filter was placed in front of the spectroscopic slit and a narrow-band interference filter in the exciting light beam to eliminate interfering radiation. However, the region of vibrational frequencies adjoining the exciting line was unavoidably absorbed here as well, and besides, all information on the crystal-vibration spectrum was lost.

They obtained spectra that were rich in lines of various intensities. Among them were some weak lines whose frequencies were characteristic of the state of the substance. They occurred in the range above 1600 cm^{-1} . The very fact that the frequencies of these lines varied rules out the idea that they belong to traces of impurities. Hence, we must interpret them as combinations of internal or of internal and external vibrations. The latter case is especially interesting. If this in fact is what happens, it immediately means that the lines of external vibrations persist at least partially in the spectra under the ordered arrangement of molecules characteristic of nematic liquid crystals.

Another observation in^[87] was in the frequency range $1135-1182\text{ cm}^{-1}$. Here the spectrum of the crystalline substance contains a line of medium intensity that is absent in the spectrum of the liquid-crystalline analog. We can call it a "crystallinity" line. It is not ruled out that it arises from Davydov resonance splitting, and hence disappears when the crystalline order is destroyed.

Studies of organic polymers are directly related to the problem of the glassy state of matter. Even monolithic specimens, not to speak of the powdered substances, have previously been difficult objects for the spontaneous Raman method. This is because the mercury lamp concurrently excited luminescence and photolyzed

the substance itself. Schaufele^[88] has described the first experiment to apply the new technique for this purpose. The problem that he took up concerned the spontaneous Raman spectrum of isotactic polypropylene. The polymer could be obtained and was studied in the form of a powder. The spectrum was excited with the 6328-Å line of a gas laser, and was recorded by the photoelectric method with a double monochromator. He could get a good spectrum down to the low-frequency region, and thus introduce some exhaustive clarity into the discussion that has arisen in the literature on the spectroscopic features of this polymer. These results show the great potentialities of Raman spectroscopy in solving various problems of the physics and chemistry of high-polymer compounds.

4. Resonance Vibrational Spectra

As the exciting line approaches electronic absorption bands of the scattering system, a more or less sharp, selective enhancement of the spontaneous Raman lines results. This constitutes the resonance effect. It reflects various parameters of the excited electronic-vibrational states. To elucidate the interrelation between these parameters and the intensities of the spontaneous Raman lines is the central problem of studying resonance spectra.

The studies of Shorygin^[89] initiated this extremely important field of spectroscopy. He and his associates are responsible for thorough and many-sided experimental and theoretical studies of the various aspects of the problem. The following topics are of great interest. Scattering and luminescence processes occurring simultaneously were observed by Shorygin and Ivanova^[90] and established by the same authors in^[91]. Also, Ivanova, Yanovskaya, and Shorygin^[92] observed an unusually high intensity of overtones and compound vibrations in spontaneous Raman spectra of a number of substances having structured electronic absorption bands. Further, Shorygin and Krushinskiĭ^[93] have made a theoretical analysis of the problem of the criteria for scattering, luminescence, and transition processes. The resonance effect in spontaneous Raman scattering has been applied in structural chemistry. It is being intensively studied at present in our country and abroad.

In itself, the invention of new sources for exciting spontaneous Raman scattering (different types of lasers) has opened up unique possibilities of studying heretofore intractable substances. These are the colored substances, which absorb strongly in the visible, but which give resonance spectra under long-wavelength excitation. Krasser and Nürnberg^[94] who measured the intensity coefficients in the spectra of a large group of inorganic complex compounds, did not fail to take advantage of this fact. For this purpose they used a Perkin-Elmer LR-1 photoelectric apparatus equipped with a helium-neon laser. The substances were dissolved in water. In individual cases the concentrations amounted to only 10^{-5} – 10^{-6} mg/l. Upon comparing the measured quantities, they drew some conclusions on the structures of the studied substances, and also on the nature of the scattering itself. Resonance or almost-resonance spectra have in essence been observed in many other studies, although this was not especially empha-

sized. This is especially true of crystalline powders and single crystals.

Worlock and Porto^[95] have described a very interesting and new application of resonance spontaneous Raman spectroscopy. They studied the spontaneous Raman scattering of F centers in alkali-halide crystals. As we know, F centers in these crystals are responsible for intense, broad absorption and luminescence bands in the near ultraviolet, visible, and near infrared. There were grounds for thinking that strong coupling occurs between the electrons and phonons. Hence, the authors tried to gain information on it from spontaneous Raman spectra. This was facilitated by the fact that they could realize experimental conditions that were close to resonance. As expected, these conditions compensated to a certain degree for the extremely low concentration of F centers.

The crystals were studied at liquid-nitrogen temperature. Here they bore in mind two factors: to narrow the absorption bands, and to stabilize the F centers. The spectra were excited with the 6328, 5145, and 4880-Å lines of gas lasers. Recording was photoelectric. They used a spectrometer based on a Czerny-Turner double monochromator. They performed polarization measurements as well as the ordinary ones. By obtaining the spectra with different exciting lines, they could assign the emission specifically to scattering. A characteristic feature of these spectra was the great width of the bands, which showed no fine detail when spectroscopic apparatus of the best resolution was used. They gave a preliminary interpretation of the experimental material, and tried to get spectra of higher quality by cooling the specimens to liquid-helium temperature. The encouraging results of this study stimulated the development of theoretical ideas on light scattering by various color centers.^[96,97]

A very fruitful and widely-used method of studying spontaneous Raman spectra consists in measuring the line intensities as a function of the frequency of the exciting light. Experiments of this type near and within electronic absorption bands are of especial interest. However, the lack until recent years of excitation sources having a suitable spectral composition has limited the studies. This fact impelled the authors of^[98] to use an artificial method. Namely, instead of varying the exciting lines, they varied the position of the absorption band of the substance by varying the composition of the two-component solvent. As the latter, they used mixtures of carbon tetrachloride with chloroform, of o-dichlorobenzene with toluene, of toluene with chloroform, and ethyl alcohol with water. The object of study was the molecule of p-nitrosodimethylaniline. Although they specially analyzed in^[98] the problem of possible errors involving the action of the solvent on the molecules being studied, and estimated their size, still we cannot consider this method to be universal, and we can cast doubt on the adequacy of shifting the exciting line itself in other cases.

The ionized-argon lasers that have been put into use emit several rather closely-spaced lines of sufficient intensity, and have opened up new possibilities of studying resonance spectra, as carried out by Leite and Porto.^[99] The spectrum of a single crystal of CdS, which has its absorption edge at about 5200 Å, was exci-

ted at a temperature of 77°K by the lines 5145, 4965, 4880, and 4765 Å. With a suitable orientation of the optic axis of the crystal, and oblique orientation of the exciting light, they observed the fundamental vibration at 305 cm⁻¹ and also its first, second, and third overtones (at frequencies of 604, 909, and 1200 cm⁻¹). This phenomenon is fully analogous to that observed previously by Shorygin and his associates when they excited spontaneous Raman spectra in a discrete absorption band of polyenes.^[91,92] It evidently has the same nature: the overtones have a sharper frequency-dependence than the fundamental vibrations. In order to eliminate the uncertainty in the effective intensity of the exciting light caused by closeness to the absorption region of the crystal, the authors of^[99] measured the relative intensity of the fundamental vibration as compared with the first overtone. It turned out that one can describe the experimental data well by choosing as the actual transition an "effective" electronic transition corresponding to the edge of the absorption band.

An analogous conclusion has also been drawn from an indirect treatment of data on the frequency-variation of the intensity in spontaneous Raman spectra of various compounds^[100] based on using the formula proposed by the authors of^[101,102]. After subsequently testing this formula experimentally on other compounds, Buyken, Klauss, and Moser also state that it usually permits one to get reasonable values of the frequencies of the "effective" transitions.^[103] On the contrary, the formula from Shorygin's semiclassical theory invariably gives results devoid of physical meaning. Nevertheless, on the basis of performed experiments, the authors of^[103] are inclined to consider the concept of "effective" transitions to be insufficiently well-grounded in itself. In one way or another, these results of theirs cast serious doubt on the estimates of "effective" transitions in scattering that Shorygin and his associates have made repeatedly. We note in conclusion that the method of measuring the frequency-dependence of the intensities, which avoids the defects of the discussed method (the choice of some particular formula to describe the intensities of the spontaneous Raman lines), gives a value of the frequency of the actual transition that also occurs on the long-wavelength edge of the electronic absorption band.^[98] The remaining problem consists in interpreting these facts correctly.

Thus, using laser techniques for exciting spontaneous Raman spectra allows us to expect progress in the field of resonance spontaneous Raman spectroscopy as well.

Note added in proof: Since this review was written, a number of interesting studies have been carried out in this field: Feldman, Parker, and Ashkin were able to obtain spontaneous Raman spectra from Be and the alloy AuAl₂ (Phys. Rev. Lett. 21, 607 (1968)); Koningstein and Mortensen showed that the ERS tensor is antisymmetric (Nature 217, 445 (1968)); Ganguly and Birman have developed a detailed theory of the spontaneous Raman scattering of semiconductors (Phys. Rev. 162, 806 (1967)); Barrett and Adams have built an apparatus containing a laser for excitation of spontaneous Raman scattering in extremely small volumes of gases (J. Opt. Soc. Am. 58, 311 (1968)).

1962 (Russ. Transl., M., "Mir", 1964).

²B. P. Stoicheff, in *Advances in Spectroscopy*, Vol. 1, Ed. H. W. Thompson, Interscience, New York, 1959, p. 91.

³Ya. S. Bobovich and V. M. Pivovarov, *Usp. Fiz. Nauk* 60, 689 (1956).

⁴Ya. S. Bobovich, *ibid.* 84, 37 (1964) [*Sov. Phys.-Uspekhi* 7, 656 (1965)].

⁵V. A. Zuvov, M. M. Sushchinskiĭ, and I. K. Shuvalov, *ibid.* 83, 197 (1964) [*Sov.-Phys.-Uspekhi*

⁶V. A. Zubov, M. M. Sushchinskiĭ, and I. K. Shuvalov, *ibid.* 89, 49 (1966) [*Sov. Phys.-Uspekhi* 9, 346 (1966)].

⁷A. Javan, W. B. Bennett, and D. R. Herriott, *Phys. Rev. Lett.* 6, 106 (1961).

⁸W. W. Rigrod, H. Kogelnik, D. H. Brangaccio, and D. R. Herriott, *J. Appl. Phys.* 33, 743 (1962).

⁹M. Delhayé and M. Migeon, *Compt. Rend.* 262B, 1513 (1966).

¹⁰Brochure of the French firm Coderg.

¹¹A. Weber, S. P. S. Porto, L. E. Cheesman, and J. J. Barrett, *J. Opt. Soc. Am.* 57, 19 (1967).

¹²J. Brandmüller, *Naturwiss.* 54, 293 (1967).

¹³J. D. Rigden, *IEEE J. Quant. Electronics* 1, 221 (1965).

¹⁴A. Mooradian and G. B. Wright, *Solid State Commun.* 4, 431 (1965).

¹⁵V. Evtuchon and J. K. Neeland, *Appl. Phys. Lett.* 6, 75 (1965).

¹⁶D. Röss, *Microwaves* 4, 29 (1965); *IEEE J. Quant. Electronics* 2, 208 (1966).

¹⁷K. Gürs, *Phys. Lett.* 16, 125 (1965).

¹⁸K. Gürs and H. Westermeier, *Z. angew. Phys.* 21, 181 (1966).

¹⁹S. P. S. Porto and D. L. Wood, *J. Opt. Soc. Am.* 52, 251 (1962).

²⁰B. P. Stoicheff, 10th International Colloquium on Spectroscopy, Washington, 1963.

²¹G. E. Danil'tseva, V. A. Zubov, M. M. Sushchinskiĭ, and I. K. Shuvalov, *Zh. Eksp. Teor. Fiz.* 44, 2193 (1963) [*Sov. Phys.-JETP* 17, 1473 (1963)].

²²B. Schrader and M. Stockburger, *Naturwiss.* 52, 298 (1965); *Z. anal. Chem.* 216, 117 (1966).

²³G. Bergmann and G. Thimm, *Naturwiss.*, 45, 359 (1958).

²⁴W. Guber and K. H. Riggert, *Z. Naturforsch.* 6a, 464 (1951).

²⁵M. Migeon, *Bull. Soc. chim. Fr.* 1964, 2743.

²⁶M. Delhayé and M. Migeon, *Compt. Rend.* 261, 2613 (1965).

²⁷G. W. Chantry, H. A. Gebbie, and C. Hilsum, *Nature* 203, 1052 (1964).

²⁸H. Kogelnik and S. P. S. Porto, *J. Opt. Soc. Am.* 53, 1446 (1963).

²⁹R. C. C. Leite and S. P. S. Porto, *ibid.* 54, 981 (1964).

³⁰M. Delhayé and M. Migeon, *Compt. Rend.* 262B, 702, 1513 (1966).

³¹G. G. Slyusarev and V. M. Chulanovskiĭ, *Zh. Eksp. Teor. Fiz.* 18, 665 (1948).

³²M. Delhayé and M. Bridoux, *Compt. Rend.* 261, 2079 (1965).

³³Yoh-Han Pao, R. N. Zitter, and J. E. Griffiths, *J. Opt. Soc. Am.* 56, 1133 (1966).

³⁴Yoh-Han Pao and J. E. Griffiths, *J. Chem. Phys.*

¹J. Brandmüller and G. Moser, *Einführung in die Ramanspektroskopie*, D. Steinkopff Verlag, Darmstadt,

- 46, 1671 (1967).
- ³⁵J. E. Griffiths and Yoh-Han Pao, *ibid.* 46, 1679 (1967).
- ³⁶V. P. Kozlov, *Optika i Spektroskopiya*, Letter to the Editor 24, 840 (1968).
- ³⁷Z. Naray, *J. Sci. Instrum.* 33, 476 (1956).
- ³⁸G. Farkas and P. Varga, *ibid.* 41, 704 (1964).
- ³⁹J. A. Koningstein, *J. Opt. Soc. Am.* 56, 1405 (1966).
- ⁴⁰M. V. Evans, T. M. Hard, and M. F. Murphy, *ibid.* 56, 1638 (1966).
- ⁴¹J. Brandmüller, H. Hacker, and H. W. Schrötter, *Chem. Ber.* 99, 765 (1966).
- ⁴²J. A. Koningstein and R. G. Smith, *J. Opt. Soc. Am.* 54, 1061 (1964).
- ⁴³M. Bridoux, *Compt. Rend.* 258, 5620 (1964).
- ⁴⁴P. V. Shcheglov, *Elektronnaya teleskopiya (Electronic Telescope)*, M., "Nauka", 1963.
- ⁴⁵L. F. Guyot, *L'onde électrique* 41, No. 408, 220 (1951).
- ⁴⁶D. L. Emberson, A. Todkill, and W. L. Wilckock, *Adv. Electronics Electr. Phys.* 16, 127 (1962).
- ⁴⁷J. Berger and R. Kara, *Compt. rend.* 263B, 162 (1966).
- ⁴⁸M. M. Butslav, *Uspekhi nauchnoy fotografii (Advances in Scientific Photography)*, Vol. 6, AN SSSR, M.-L., 1959, p. 76.
- ⁴⁹A. Weber and S. P. S. Porto, *J. Opt. Soc. Am.* 55, 1033 (1965).
- ⁵⁰S. P. S. Porto, L. E. Cheesman, A. Weber, and J. J. Barrette, *ibid.* 56, 551A (1966).
- ⁵¹Brochure on the Model 81 Raman spectrophotometer by the Cary firm.
- ⁵²*Instrument News*, Perkin-Elmer Corp. 16, Nos. 2 and 3 (1965).
- ⁵³Brochure by the Perkin-Elmer Corp., *Analysengeräte*.
- ⁵⁴G. Geppert, *Exp. Techn. d. Phys.* 14, 341 (1966).
- ⁵⁵S. L. Berkovich, M. F. Gofren, M. V. Lobachev, T. K. Fal'k, and D. I. Sharonov, *Optika i Spektroskopiya* 6, 824 (1959).
- ⁵⁶J. Brandmüller, K. Burchardi, H. Hacker, and H. W. Schrötter, *Z. angew. Phys.* 22, 177 (1967).
- ⁵⁷A. N. Mogilevskiy, Candidate's dissertation, Commission on Spectroscopy of the Academy of Sciences of the USSR, Moscow, 1966.
- ⁵⁸A. M. Bonch-Bruevich and V. A. Khodovoï, *Usp. Fiz. Nauk* 85, 3 (1965) [*Sov. Phys.-Uspekhi* 8, 1 (1965)].
- ⁵⁹S. A. Akhmanov, A. P. Sukhorukov, and R. V. Khokhlov, *ibid.* 93, 19 (1967) [*Sov. Phys.-Uspekhi* 10, 609 (1968)].
- ⁶⁰E. K. Plyer and E. D. Tidwell, *Advances in Molecular Spectroscopy*, Pergamon Press, New York, 1962, p. 1336.
- ⁶¹O. D. Dmitrievskiy, *Opt.-mekh. prom-st'* 2, 55 (1967).
- ⁶²L. Sibaiya and H. Venkataramiah, *Phys. Rev.* 56, 381 (1939).
- ⁶³E. F. Gross, Sh. Sh. Raskin, and A. N. Zaïdel', *Acta Physicochimica URSS* 13, 591 (1940).
- ⁶⁴R. J. Elliott and R. Loudon, *Phys. Lett.* 3, 189 (1963).
- ⁶⁵J. T. Hougen and S. Singh, *Phys. Rev. Lett.* 10, 406 (1963).
- ⁶⁶J. Y. H. Chau, *J. Chem. Phys.* 44, 1708 (1966).
- ⁶⁷J. A. Koningstein, *J. Chem. Phys.* 46, 2811 (1967).
- ⁶⁸J. A. Koningstein and O. S. Mortensen, *Phys. Rev. Lett.* 18, 831 (1967).
- ⁶⁹M. Rokni and S. Yatsiv, *Phys. Lett.* 24A, 277 (1967).
- ⁷⁰C. H. Henry, J. J. Hopfield, and L. C. Luther, *Phys. Rev. Lett.* 17, 1178 (1966).
- ⁷¹G. B. Wright and A. Mooradian, *Phys. Rev. Lett.* 18, 608 (1967).
- ⁷²G. Placzek, *Handbuch der Radiologie*, Vol. 6, Part 2, Ed. E. A. Marx, Akademische Verlagsgesellschaft, Leipzig, 1934 (Engl. transl., *The Rayleigh and Raman Scattering*, Lawrence Radiation Lab., Univ. of Calif., Livermore, Calif., 1959; Russ. transl., ONTIU, Khar'kov, 1935).
- ⁷³W. J. Jones and B. P. Stoicheff, *Phys. Rev. Lett.* 13, 657 (1964).
- ^{74a}S. Dumartin, B. Oksengorn, and B. Vodar, *Compt. Rend.* 261, 3767 (1965).
- ^{74b}G. S. Landsberg and F. S. Baryshanskaya, *Naturwiss.* 8, 183 (1930).
- ⁷⁵M. B. Hobden and J. P. Russell, *Phys. Lett.* 13, 39 (1964).
- ⁷⁶P. G. Marlow, J. P. Russell, and C. T. Sennett, *Phys. Lett.* 20, 610 (1966).
- ⁷⁷J. P. Russell, *Appl. Phys. Lett.* 6, 223 (1965).
- ⁷⁸J. H. Parker, D. W. Feldman, and M. Ashkin, *Phys. Rev.* 155, 712 (1967).
- ⁷⁹M. S. Khaikin and V. P. Bykov, *Zh. Eksp. Teor. Fiz.* 30, 191 (1956) [*Sov. Phys.-JETP* 3, 119 (1956)].
- ⁸⁰D. W. Feldman, M. A. Ashkin, and J. H. Parker, *Phys. Rev. Lett.* 17, 1209 (1966).
- ⁸¹R. K. Chang, B. Lacina, and P. S. Pershan, *ibid.* 17, 755 (1966).
- ⁸²F. Teissier du Cros and J. Huriet, *J. phys. suppl.* 27, 124 (1966).
- ⁸³I. Freund and P. M. Rentzepis, *Phys. Rev. Lett.* 18, 393 (1967).
- ⁸⁴R. Freumann and R. Servant, *Ann. d. phys.* 20, 131 (1945).
- ⁸⁵M. M. Sushchinskiy and A. S. L'vova, *FIAN Preprint A-92*, 1965.
- ⁸⁶K. Koller, K. Lorenzen, and G. M. Schwab, *Z. phys. Chem. (West Germany)* 44, 101 (1965).
- ⁸⁷Ya. S. Bobovich and N. M. Belyaevskaya, *Zh. Prikl. Spekt.* 8, 1018 (1968).
- ⁸⁸R. F. Schaufele, *J. Opt. Soc. Am.* 57, 105 (1967).
- ⁸⁹P. P. Shorygin, *Pure and Appl. Chem.* 4, 87 (1962).
- ⁹⁰P. P. Shorygin and T. M. Ivanova, *Dokl. Akad. Nauk SSSR* 121, 70 (1958) [*Sov. Phys.-Doklady* 3, 764 (1958)].
- ⁹¹P. P. Shorygin and T. M. Ivanova, *ibid.* 150, 533 (1963) [*Sov. Phys.-Doklady* 8, 493 (1963)]; *Optika i Spektroskopiya* 15, 176 (1963).
- ⁹²T. M. Ivanova, L. A. Yanovskaya, and P. P. Shorygin, *Optika i Spektroskopiya* 18, 206 (1965).
- ⁹³P. P. Shorygin and L. L. Krushinskiy, *Dokl. Akad. Nauk SSSR* 154, 571 (1964) [*Sov. Phys.-Doklady* 9, 78 (1964)].
- ⁹⁴W. Krasser and H. W. Nürnberg, *Naturwiss.* 54, 134 (1967).
- ⁹⁵J. M. Worlock and S. P. S. Porto, *Phys. Rev. Lett.* 15, 697 (1965).
- ⁹⁶C. Henry, *Phys. Rev.* 152, 699 (1966).
- ⁹⁷G. Benedek and G. F. Nardelli, *Phys. Rev.* 154, 872 (1967).

⁹⁸ M. Ya. Tsenter and Ya. S. Bobovich, *Optika i Spektroskopiya* **16**, 417 (1964).

⁹⁹ R. C. C. Leite and S. P. S. Porto, *Phys. Rev. Lett.* **17**, 10 (1966).

¹⁰⁰ M. Ya. Tsenter and Ya. S. Bobovich, *Optika i Spektroskopiya* **16**, 246 (1964).

¹⁰¹ I. I. Kondilenko, P. A. Korotkov, and V. L.

Strizhevskii, *ibid.* **9**, 26 (1960).

¹⁰² I. I. Kondilenko and V. L. Strizhevskii, *ibid.* **11**, 262 (1961).

¹⁰³ H. Buyken, K. Klauss, and H. Moser, *Ber. Bunsengesellsch. Phys. Chem.* **71**, 578 (1967).

Translated by M. V. King