

LASER SPECTROSCOPY UTILIZING SPONTANEOUS RAMAN SCATTERING OF
 WEAKLY INTERACTING MOLECULES AND ITS APPLICATIONS

Ya. S. BOBOVICH

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1. INTRODUCTION

THE current theories of the spontaneous Raman scattering presuppose the absence of any interaction between particles forming the scattering medium. Consequently, only the spectra of isolated particles can be interpreted rigorously. Therefore, investigations of gases and vapors at relatively low pressures are of basic importance. Another important feature is that molecules in gases and vapors rotate practically freely. This is reflected in the rotational spectra. The interaction between rotation and vibration is manifested in the rotational-vibrational spectra. Rotation and vibration are both related to the moments of inertia of quiescent and vibrating molecules, i.e., in the final analysis they are related to the molecular configurations and symmetry. Thus, investigations of gases and vapors should not only enable us to verify the theoretical conclusions but also provide a unique source of information on the molecular structure.

The development of the spectroscopy utilizing spontaneous Raman scattering (we shall refer to it briefly as the Raman spectroscopy) of gases and vapors can be divided into three very distinct stages. The first stage covers approximately the period from 1930 to 1952. It is characterized by the use of the fairly primitive technology available at the time and, particularly, by the use of excitation sources usually in the form of low-power glow-discharge or arc mercury lamps, which give rise to considerable complications in the experimental work. The second stage is characterized by important improvements in the mercury lamps involv-

ing local cooling of liquid-mercury electrodes, which has increased considerably the electrical and optical power levels without distortion of the desirable spectral composition of the radiation. This stage has seen also the development and introduction of multipath mirror cuvettes. These improvements have altered radically the experimental capabilities with the immediate effect of rapid increase in the number of investigations. The progress made during this stage is described in several review papers.^[1-6] The beginning of the third stage can be placed in 1965, corresponding to the first paper on the laser excitation of the spontaneous Raman scattering spectra in simple gases. Investigations of this type have been found to be very profitable and they have been developed further in the theoretical and practical respects, leading to new very important applications.

The small angular divergence and the exceptionally high density of the laser radiation concentrated in a very narrow spectral range have provided the basis for further successes in the high-resolution Raman spectroscopy of gases. The most important improvement has resulted from the replacement of spectrographs and spectrometers with Fabry-Perot etalons, which has made it possible to measure with precision the rotational constants and to reveal several very fine effects such as the dependence of the Doppler broadening of spectral lines on the direction of observation. It must be stressed that the capabilities of high-resolution Raman spectroscopy of gases. The most important improvement has resulted from the replacement of spectrographs and spectrometers with Fabry-Perot etalons, which has made it possible to measure with precision

the rotational constants and to reveal several very fine effects such as the dependence of the Doppler broadening of spectral lines on the direction of observation. It must be stressed that the capabilities of high-resolution Raman spectroscopy are, to a considerable degree, governed also by the properties of the excitation source. Further improvements in the resolution will follow from the use of single-mode and single-frequency lasers, which are already developed and are based on the discrimination between transverse laser-oscillation modes or on the selection of just one longitudinal mode.

It has been difficult to study the influence of temperature on the Raman spectra with the aid of gas-discharge lamps. The geometry of the laser beams makes it possible to separate spatially the source and the sample and thus avoid all the experimental difficulties. This has made it easy to carry out measurements at low temperatures, including liquid helium temperatures. Some investigations have followed a new direction of the Raman spectroscopy of nonvolatile substances, which can now be studied in the vapor state. The numerous results obtained by this method are of great importance in the structural and physical chemistry and in the understanding of the relationship between the luminescence and the spontaneous Raman scattering processes.^[7]

When the Raman spectra of gases and vapors are excited with lamps, one needs to fill a large volume with the substance under investigation. Moreover, multipath cuvettes are usually employed in order to amplify the Raman effect. Therefore, the optical paths of the exciting and scattered radiation are very long. Thus one cannot investigate strongly absorbing gases because it is difficult to obtain the resonance spectra of such substances. For these reasons the resonance Raman spectroscopy in the "pre-laser" stages has been confined principally to liquid solutions of absorbing substances.

The relative simplicity and ease of resonance experiments carried out with the aid of laser radiation stems primarily from the small angular divergence of the angular beams. This small divergence makes it possible to concentrate easily high-power radiation in a small volume. A laser beam can be focused close to the walls of a gas cuvette and this can minimize the light losses and approach closely the fundamental absorption region of molecules in the excitation of the Raman spectra. This is the way in which the actual experiments with gases and vapors are carried out. Moreover, the capabilities of laser radiation in respect of the frequency characteristics are practically unlimited.^[8]

These circumstances have made it possible to formulate and solve certain very important problems relating to the resonance interaction between radiation and gaseous substances. Investigations have been carried out on the simplest (diatomic) molecules, which are distinguished by discrete absorption, and on more complex molecules of inorganic substances in the vapor state. Such molecules have been excited within a "fence" of absorption lines in the continuum at the dissociation edge, or in the direct vicinity of the absorption spectrum on its long-wavelength side. This has led to the discovery of two types of secondary radiation: the resonance Raman effect or the resonance luminescence,

depending on the frequency of the exciting light and the gas pressure, or a mixture of both these effects. Variation of the excitation conditions has made it possible to convert gradually one type of the secondary radiation into the other.

This has bridged two very important and basically different phenomena. The simplicity of the majority of the investigated molecules makes it possible to give a rigorous theoretical interpretation.

The special geometry of a laser beam not only radically removes the principal difficulties in the resonance experiments but, as mentioned above, allows us to study remote objects. This is known as the remote-sensing (or simply remote) Raman spectroscopy: it has been developed to an advanced stage and has found very important applications.

The most interesting results obtained using the remote Raman spectroscopy relate to the physics and the composition of the atmosphere. In these experiments a beam produced by a high-power pulsed laser is additionally collimated with a telescope and sent into the atmosphere. The backscattered signal is then measured. This type of investigation is closely related to studies of the resonance Raman effect in gases although at first sight it might seem that the latter effect is of purely academic interest.

Another example of the use of remote-sensing capabilities of the spontaneous Raman spectroscopy is the very important technical application of plasma diagnostics. Only the first steps have been made in this direction but they show a considerable promise.

We can certainly say that in the nearest future the remote Raman spectroscopy will be used in chemical industry because this method is distinguished by a high selectivity and sensitivity and it does not require (in contrast to other spectroscopic methods) any selection of the optimal thickness of the layer being investigated or the concentration of the substance under study.

We have considered so far the isolation of molecules by transforming a substance into its vapor. However, the same results can be achieved also in a different way when a very small amount of matter is introduced at a low temperature (usually 4°K) into a solid matrix, which normally consists of an inert gas. This matrix isolation method has been used very successfully in the preparation of free radicals and various unstable molecules and in the study of their infrared and ultraviolet absorption spectra. Very recently experiments have been reported in which the matrix isolation method has been applied in combination with the spontaneous Raman spectroscopy. The results are so interesting they deserve a special mention.

The Raman spectroscopy of weakly interacting molecules has become an independent subject with capabilities which have been realized only very partially. This spectroscopy is characterized by the use of special media and experimental methods, a special approach to the interpretation of the results, and a certain range of applications. All this justifies the present review and the attempt to predict the future development of this type of spectroscopy.

2. HIGH-RESOLUTION ROTATIONAL AND ROTATIONAL-VIBRATIONAL SPECTRA

The highest attainable spectral resolution is deter-

mined by the combined effect of many factors, which include the threshold sensitivity of the apparatus as a whole, the nature and the parameters of the spectroscopic instrument, the width of the exciting radiation line, the physical conditions (temperature and pressure) in the gas being investigated, and the direction of observations. The first of these factors depends on the output power of the source, the wavelength of the exciting radiation, the parameters of the radiation detector, the method of excitation of the spectra (inside or outside a resonator, with or without multipath systems), and the recording method. The threshold sensitivity of the apparatus is related to the degree to which the scattered radiation is utilized. All this makes the optimization of the experimental conditions a very difficult problem which has not yet been finally solved.

The laser Raman spectroscopy of gases and vapors starts with the paper by Weber and Porto, published in 1965.^[9] Weber and Porto used a low-power (20 mW) helium-neon laser and recorded the spectra photographically. A cuvette with windows inclined at the Brewster angle was placed inside the resonator. The observations were made at right-angles to the laser beam. Although the imperfections of the source and the recording method were quite considerable, Weber and Porto^[9] were able to obtain the spectra of some substances (the exposures had to be fairly long).

This success has stimulated further efforts. The efficiency was improved by the use of a laser with the active medium in the form of ionized argon. Lasers of this type are much more powerful than the helium-neon sources. Even the mass-produced argon lasers can have a output of at least 1 W. Moreover, they emit a group of lines in the blue-green region and this gives rise to an additional gain in the efficiency of the apparatus ($I_{\text{scatt}} \sim 1/\lambda^4$ and the sensitivity of the detector is higher in this region).^[4,8,10] The use of the argon laser made it possible to employ photoelectric recording of the spectra.^[10] This method has replaced almost completely the photographic technique.

Argon lasers are inferior to helium-neon lasers in the multimode regime because the half-width of the emission lines of the former is relatively large (0.1 cm^{-1} , compared with 0.05 cm^{-1} for He-Ne lasers). However, even this large half-width is 3–5 times smaller than the corresponding half-width of the lines emitted by high-power low-pressure mercury lamps. The subsequent work has been concerned with the matching of the sensitivity of the apparatus to the characteristics of laser sources.

First of all, quantitative comparisons were made of the two methods of excitation of the spectra inside and outside a resonator. For example, Chapput et al.^[11] used a 50-ml cuvette with windows inclined at a Brewster angle. First they placed this cuvette inside the resonator of a He-Ne laser with an output of 160 mW. They recorded the radiation scattered at 90° . Next, the same cuvette was used in conjunction with a Coderg mirror spectrometer designed for liquids. The spectrum was excited with an argon laser (700 mW). All the other conditions were kept the same and a correction was made for the different spectral sensitivities of the photomultipliers. It was found that the first method was three times as effective as the second. In other words, the density of the radiation inside the

resonator was more than an order of magnitude higher than the density outside the resonator. Similar estimates, but without any justification, are quoted by other workers. Therefore, one should clearly give preference to the first method of excitation of the Raman spectra, at least in the case of transparent and nonaggressive gases which cannot damage the windows, and, consequently, cannot affect significantly the laser emission conditions.^[12-15]

A careful analysis of the geometry and optics of the excitation problem was made by Barrett and Adams,^[12] who formulated the optimal experimental conditions. They considered the case of transverse observation of the scattered radiation excited in a gas inside a resonator with the laser beam focused sharply on the sample. They assumed that the gas was transparent, that there were no additional stimulated emission processes, and that the scattering occurred within the brightest part of the diffraction-limited beam which could be approximated by a cylinder of length $16\lambda/\pi\alpha^2$ and diameter $4\lambda/\pi\alpha$, where $\alpha \approx d/f$ (d is the beam diameter and f is the focal length of the mirror). They also considered the conditions for maximal utilization of the scattered light in the spectrometer, i.e., the problem of the fullest collection of the scattered light from the illuminated gas column. The analysis was made using the backward ray method.^[5]

The results of their analysis led Barrett and Adams^[12] to the following conclusions: 1) the lenses collecting the scattered light onto the slit of a spectroscopic instrument should magnify as much as possible (within the limits set by the slit dimensions) the working gas column; 2) there is an optimal aperture of the optical part of the apparatus that concentrates the laser radiation on the sample. For the apparatus considered this aperture was close to 6° .

These conclusions were utilized in the final assembly of the apparatus. This apparatus consisted of an argon laser with a 0.5 W output (4880 or 5145 Å), an open cuvette through which the gas investigated (O_2 , N_2 , CO_2) was passed slowly, and a Perkin-Elmer spectrometer, model E-1 (Ebert-Fastie monochromator, diffraction grating with 1440 lines/mm, reciprocal dispersion 5.3 \AA/mm , relative aperture 1:8). The spectra were recorded by photon counting. An EM-1 6256S-A photomultiplier (S-11 photocathode) cooled to about -40°C , was employed (cooling reduced the noise by a factor of

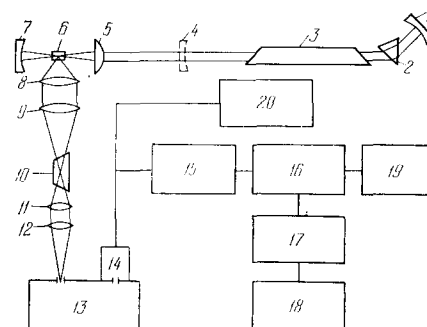


FIG. 1. Apparatus used in investigations of gases: 1, 4, 7—mirrors forming a resonator; 2—prism for selection of radiation with the necessary wavelengths; 3—argon laser; 5, 8, 9, 11, 12—lenses; 6—gas-filled cuvette; 10—rotatable Dove prism; 13—monochromator; 14—photomultiplier; 15—amplifier; 16—discriminator; 17—integrator; 18—phototimer; 19—digital counter; 20—oscillograph.

more than 200). Optimization of the excitation geometry and the slit illumination, alongside with improvements in the technique for the detection and recording of the signals, enabled Barrett and Adams to obtain well-resolved rotational-vibrational spectra of gases in a volume smaller than 10^{-7} cm³, i.e., a volume containing $\sim 10^{11}$ molecules. The apparatus used by Barrett and Adams is shown schematically in Fig. 1.

We had pointed out above that the half-width of the lines emitted by multimode gas lasers employed in Raman spectroscopy can be as large as 0.1 cm⁻¹. However, single-mode and single-frequency lasers are now available and the lines emitted by these lasers are much narrower (0.01 – 0.005 cm⁻¹) and their positions are more stable. The discrimination between transverse laser-oscillation modes or the selection of just one longitudinal mode is attained by simple means and without any significant losses: an additional planar reflector or an interferometer is introduced into the resonator.^[8] Therefore, these techniques can be used quite successfully in the Raman spectroscopy of gases. However, all the advantages can be realized only if specially developed spectroscopic instruments are used.

Cooper et al.^[16] were the first to use the Fabry-Perot etalon as the high-resolution spectroscopic instrument; they also employed the scanning method. The etalon was an integral part of the apparatus which included a helium-neon laser with an output 100 mW, a high-pressure gas cuvette, a system of interference filters, an ITT FW-130 cooled photomultiplier, and an electronic photon counter. The spectra were scanned by smooth variation of the pressure in the etalon gap. The task of this investigation was to establish, within a fairly wide range of pressures, the contribution of the impact mechanism to the broadening and narrowing of the rotational lines.

The next investigation of this type was also carried out by Cooper et al.^[17] but the apparatus was improved in two respects: 1) a laser with a higher output (150 mW) was used; 2) the scanning of the spectra was discrete (this was done by discrete changes of the pressure with a special electromechanical device). This enabled Cooper et al. to count photons more easily than in the first investigation. It also increased the sensitivity of the apparatus and reduced the distortions of the line profiles, which were inherent in the continuous scanning method. The instrumental line width was reduced to 0.03 cm⁻¹.

Butcher et al.^[15] used a helium-neon laser in conjunction with a Fabry-Perot etalon consisting of plates separated by a fixed distance. This setup was used in precision measurements of the frequencies of rotational lines in the Raman spectra, which were then employed in a determination of the rotational constants with a higher degree of precision than achieved previously. Special measures were taken to increase the efficiency of the etalon. Multilayer dielectric coatings replaced the metallized mirrors. The theoretical resolution of the etalon was 5×10^5 at 5000 Å. The etalon was crossed with a moderate-dispersion spectrograph. The excitation source was an argon laser built by the authors. The investigated substances were placed inside the resonator where the radiation density was 300 W/cm². The wavelengths of the incident radiation

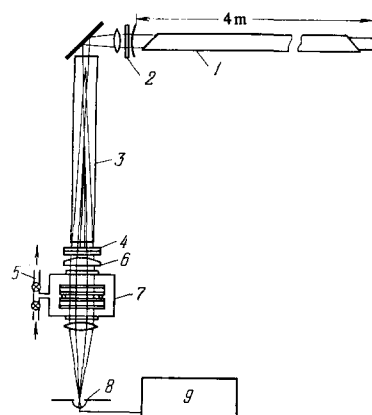


FIG. 2. Schematic diagram of the apparatus used in measurements of the Raman line profiles of gases in the forward scattering direction: 1—helium-neon laser; 2, 4—interference filters; 3—gas-filled cuvette; 5—vacuum system; 6—conical lens; 7—Fabry-Perot interferometer; 8—photomultiplier; 9—photon counting system.

were 4880 and 4765 Å. In the latter case the spectra were sharper because the intrinsic line width was smaller. The observations were made at 90° with respect to the laser beam direction. The gas pressure was 1 atm. The spectra were recorded photographically. Butcher et al. investigated purely rotational spectra of O_2 and N_2 (exposures of 2–4 h were needed). The precision of the final results could be improved, as suggested in^[15], by the use of a laser with mode selection and of lower gas pressures.

One of the physical factors that impose the limit on the resolving power of the apparatus is the Doppler broadening of the scattering lines. This broadening depends on the direction of observation and has its smallest value in the forward direction.^[18] A convincing experimental demonstration of this point was reported by Clements and Stoicheff.^[19]

The apparatus used by Clements and Stoicheff is shown in Fig. 2. The excitation source was a specially developed helium-neon laser, which was 4 m long and had an output power of 400 mW. The spectral width of the $\lambda = 6328$ Å line was 0.025 cm⁻¹. This small width was ensured by the diameter of the plasma tube (15 mm) and the small transmission coefficient of the exit mirror (2%). The laser radiation was selected by an interference filter with a band half-width of 10 Å and collected by a long-focus lens within a cuvette 1 m long. The gas pressure was up to 2 atm. The system of narrow-band interference filters, placed on the exit side of the gas cuvette, removed the exciting radiation but passed the scattered component which was then collected by a conical lens into a beam of 2° aperture on the slit of an intermediate monochromator (in the case of purely rotational lines with small frequency displacements) or was directed immediately to a Fabry-Perot etalon in which the optical path was varied by altering the pressure in the chamber.

This apparatus was used first of all to measure the width of the S(1) rotational line of hydrogen in the forward direction (in accordance with the arrangement shown in Fig. 2) and at an angle of 90° . The effective resolution of the apparatus was about 0.02 cm⁻¹. In the first case the line width was 0.04 cm⁻¹ and in the second it was 0.15 cm⁻¹. However, the value 0.04 cm⁻¹ was

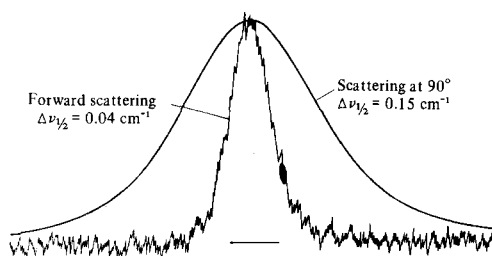


FIG. 3. Profiles of the S(1) rotational line of gaseous hydrogen (2 atm) obtained using different directions of observation.

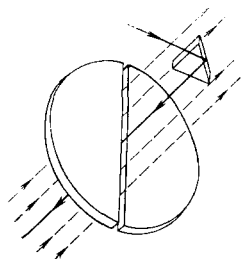


FIG. 4. Schematic representation of the paths of rays in a gas cuvette fitted with mirrors and used in laser excitation of Raman spectrum.

not the intrinsic width but it included the distortions introduced by the apparatus. Under the experimental conditions employed by Clements and Stoicheff^[19] the line profile should be governed entirely by the impact broadening, which is an order of magnitude smaller. The profiles obtained in the forward and the 90° directions are plotted in Fig. 3.

In other experiments Clements and Stoicheff investigated the Q branch of the fully symmetric band of gaseous CH₄ (this branch was 0.3 cm⁻¹ wide and the pressure of 2 atm). The distortions introduced by the apparatus amounted to about 0.07 cm⁻¹. The fine structure of the band was revealed and this structure was interpreted making allowance for small differences between the rotational constants of the different levels.

We shall complete this section of our review by discussing the work of Rich and Welsh,^[20] who used a multipath cuvette to study gases excited by a laser. The cuvette is shown schematically in Fig. 4. Its diameter was 4 cm and it was 1 m long. Two halves of a spherical mirror placed at the exit to the cuvette formed a slit which was used to illuminate the gas with the laser beam and to extract the backscattered radiation. The rear mirror also consisted of two halves. The laser beam was focused by a lens and a small prism in the plane of a slit in such a way as to fill completely the aperture of the cuvette. A suitable adjustment of the rear mirror produced about 50 images at the front mirror. This ensured the multiple passage of the exciting radiation through the working gas. The scattered light was collected in a very efficient manner. The efficiency was achieved by the use of mirrors which were characterized by high reflection coefficients over a wide range of wavelengths. Rich and Welsh used aluminized mirrors with multiple coatings of alternating layers of ZnS and cryolite. Undesirable interference because of luminescence of various optical path of the apparatus (lenses, prisms, windows) was suppressed by the use of quartz instead of glass. The spectra were excited with an argon laser and recorded photographically or photoelectrically. In the photoelectric technique a double monochromator (Spex-Double Instruments) and a photon counter were used.

The apparatus just described was employed in a study of the electronic Raman spectra of gaseous NO. The results obtained should be compared with those yielded when the same spectrum was studied with a gas-discharge lamp. In the latter case the exposure was 12 h. The spectrum was complicated by the hyperfine structure of the 4358 Å line. This structure limited the resolution to 0.3 cm⁻¹. Laser excitation (even in the case of multimode operation of the laser) increased the resolution twofold and reduced the exposure to 2 h. The multipath cuvette used by Rich and Welsh^[20] made it possible to make observations in the forward direction. Consequently, it should be possible to reduce the line broadening to the impact component, which would increase the resolution up to ~0.001 cm⁻¹, subject to any limitations imposed by other parts of the apparatus and, particularly, of the spectroscopic instrument.

3. HIGH-TEMPERATURE SPECTROSCOPY OF VAPORS. STRUCTURE APPLICATIONS

This method was developed for the study of nonvolatile inorganic substances in the vapor phase. The vibrational spectra of such substances are very important in connection with their structure, and qualitative and quantitative compositions of the vapor phase. They are also important as a source of data for the calculation of the thermodynamic functions. Until recently this information has been obtained from infrared spectra.^[21] However, the infrared method imposes certain restrictions of basic and technical nature. In particular, this method fails to give the complete set of the vibrational frequencies. Therefore, the development of the high-temperature Raman spectroscopy and improvement of its methods has become of exceptional importance. Investigations in the vapor phase should help in the understanding of the physics of such fundamental processes as the resonance Raman effect and luminescence. A special section of the present review will deal with this subject.

Systematic investigations of the Raman spectra of vapor-phase molecules were started in 1969.^[22] In the last few years about 60 single-phase and two component systems were investigated. These systems were mainly halides of elements in groups II–VIII. The Raman spectra of about 50 such systems were identified reliably. The results of these investigations demonstrate the unique capabilities of the Raman spectroscopy method. Before we give a brief review of the typical data obtained in this way, we must describe the experimental method.

The principal part of the apparatus used to obtain the infrared spectra of vapors is a high-temperature oven which also acts as a cuvette. Many such ovens have been developed and different methods and principles of heating are employed. The heating technique continues to improve and it is already possible to reach temperatures above 2500° K and to investigate some of the substances at these temperatures.^[21]

One of the major difficulties encountered in high-temperature infrared spectroscopy is the need to employ thick (up to 200 mm) layers of a uniformly heated gas. Moreover, crystal windows transparent at infrared wavelengths must work under difficult conditions. The experimental situation in the Raman spectroscopy is

much easier. Since the excitation wavelengths lie in the visible part of the spectrum, a cuvette can be made of materials which are more easily available. In the pulsed excitation of the spectra, which has not yet been realized experimentally, it should be possible—at least in principle—to use an open oven-cuvette. In many cases the volume of the vapor being investigated need not exceed 1–2 ml. All these circumstances make it easy to build high-temperature apparatus for the study of the Raman spectra. However, the published investigations were carried out at temperatures not exceeding 1000°C and vapor pressures not less than 0.75 Torr. Much lower pressures can be used in the infrared method.

Thus, the infrared and the Raman methods for investigating vapors of nonvolatile compounds differ in the experimental features, supplement each other, and can be used in combination to obtain full information.

The simplest systems studied at high temperatures are the vapors of molecules formed from identical atoms (phosphorus, arsenic, antimony, sulfur, and selenium).^[23-25] The spectra of these and other systems can be excited by argon laser radiation of wavelengths 4880 and 5145 Å, which are partly absorbed only by selenium. Temperatures employed in these investigations lie in the range ~ 200–1000°C.

In the case of phosphorus, arsenic, and antimony it was possible to obtain easily the conventional and the polarized Raman spectra and to identify the bands belonging to the P₂, P₄, As₂, As₄, and Sb₂ molecules. It was established that the P₂ and P₄ molecules, like the As₂ and As₄ molecules, coexist in the gaseous phase at high temperatures (1000°C). Similar investigations were carried out on a mixture of phosphorus with arsenic and of phosphorus with antimony^[25] in connection with the question of halogen exchange in the gaseous phase. It was found that molecules of the P_nAs_{4-n} type (n = 0–4) formed in the first system and SbP₃ molecules formed in the second system. These conclusions were checked by calculating the frequencies using a central-force model and the data on the elastic constants taken from the results of previous investigations of the tetrahedral molecules P₄ and As₄.^[23,24]

The situation in sulfur vapor was no less complex than in the case of single-component phosphorus and antimony systems. In good agreement with the published data on the Raman spectra of solid sulfur and its solutions and melts, the spectra of the sulfur vapor indicated the presence of vibrations of S₈, S₆, and especially S₇ molecules. Sulfur molecules with fewer atoms were expected at the highest available temperatures and the lowest vapor pressures. However, the experimentally obtained spectra were very complex, typical of the resonance Raman scattering and luminescence.

Other investigations were performed in order to establish the composition of the gaseous phase and the geometry of the nuclear configuration of its components. For example, it was shown in^[26] that the molecules of NbOCl₃ were monomeric in the vapor phase and had pyramidal symmetry. The absence of polymerization was reported also for the Te molecules, which had a different symmetry (C₁).^[27] Very interesting observations were reported by Perry and Beattie,^[28,29] who investigated some of the tin, lead, germanium, and tellurium halides. The spectrum of SnCl₂ was found to have two strong polarized lines. This observation was

compatible only with the bent shape of the SnCl₂ molecules. Similar results were obtained also for GeCl₂. However, in the presence of excess germanium vapor, there was some spectroscopic evidence for GeCl₄. In the case of PbCl₂ the necessary vapor pressure could not be established even at 1000°C. For this reason only the resonance luminescence was observed. In the presence of excess Cl₂ vapor the resonance luminescence spectrum transformed into the conventional Raman spectrum containing two polarized lines. Therefore, it was interpreted using a bent model of the triatomic molecule PbCl₂. For the same reasons a similar structure was ascribed to the TeCl₂ molecule. An investigation of a mixture of a small amount of SnBr₂ with a large amount of SnCl₂ revealed the presence of mixed SnClBr molecules. The resonance luminescence interfered strongly in the study of the Raman spectra of vapors of group IV bromides and iodides.^[29] A weak Raman spectrum on a resonance luminescence background (attributed tentatively to Br₂) was observed only in the case of PbBr₂ molecules in the presence of excess Br₂.

Vapors of pure and mixed zinc and mercury halides, gallium chloride with an excess of gallium, and of the two-component system GaCl₃ + GaBr₃ were investigated in^[30]. None of the zinc or mercury compounds exhibited deformation vibrations and hence it was concluded that the ZnX₂ and HgX₂ molecules were linear (X = Cl, Br, I). A very large frequency shift (~ 50 cm⁻¹) was observed on transition from the molten to the vapor state but no satisfactory interpretation of this shift was provided. An investigation of gallium dichloride with the nominal formula GaCl₂ revealed spectroscopic evidence for the presence of GaCl and GaCl₃ molecules. The compounds GaBr₂Cl and CaCl₂Br were found in the high-temperature phase of the GaCl₃ + CaBr₃ mixture.

Beattie and Horder^[22] used the Raman spectra of aluminum, gallium, and indium halide vapors to follow the dissociation of dimeric molecules and their conversion into monomers, which was influenced by temperature. Spectral bands representing monomers were identified reliably for the first time. Some of the bands in the spectra of iodides were due to the resonance luminescence of traces of I₂, which formed as a result of dissociation of the molecules present originally.

The Raman spectroscopy of nonvolatile substances is in its early stages of development. The experimental technique will be improved and much will be borrowed from the experience accumulated in infrared spectroscopic studies. The purpose of the present brief review of the results obtained is to draw attention to this new and promising direction of studies.¹⁾

4. MATRIX ISOLATION METHOD

This method was first applied to the electronic and infrared spectra over 15 years ago. Subsequently, it has been developed very considerably and improved. It has provided solutions to some very fine problems in the spectroscopy and structure of matter. The essence of the method is the dispersion of a very small amount of the investigated substance in an inert solid matrix which is kept at such a low temperature that the probability of collisions between the particles of the investigated substance, and, consequently, their aggregation

¹⁾A complete review of the relevant material is given in [7].

or recombination is extremely low. The matrix isolation method provides a unique technique for investigating species which are normally unstable. Such species include, for example, NaCl molecules which tend to polymerize forming finally an ionic lattice, molecules which tend to aggregate via hydrogen bonds, and free radicals of various types and origin.^[31-33] Nitrogen and inert gases are usually employed as the matrix materials. The molar ratio of the matrix to the investigated substance is usually several hundreds. The apparatus used in the matrix isolation method is described in, for example,^[34]

The first experiments in which the matrix isolation method was applied to the Raman spectroscopy were carried out practically simultaneously in 1971 by two different groups of investigators.^[35,36] Boal and Ozin^[36] investigated sulfur hexafluoride and chloroform, which were precipitated on a platinum mirror in 4 h at temperatures from 4 to 20° K. A cylindrical lens was used to collect the exciting radiation on a sample 4 mm high. The radiation sources were argon and krypton lasers with output powers of 1 W and 500 mW, respectively (4880, 5145, and 6471 Å). The Raman spectrum of sulfur hexafluoride, obtained for a sample with the molar ratio $M_{\text{argon}}/M_x = 500$, contained all three Raman-active lines. The frequencies of these lines were close to those observed in the gas phase. The spectrum of chloroform (concentration 1 : 100–200) consisted of seven lines. Once again a reasonable correspondence was obtained with the frequencies of the same substance in the gas phase. An attempt was made to detect the presence of free radicals, resulting from photolysis of chloroform, with the aid of the Raman spectra. However, this attempt was not successful because of the strong luminescence of the system under investigation. Boal and Ozin^[36] embedded, in a xenon matrix, the XeCl₂ molecules formed under the action of a discharge in the reaction chamber. A comparison with the spectrum of chlorine showed that the spectrum of the matrix included an additional strong band which was attributed to the vibration of the XeCl₂ molecules. The absence of the deformation vibration band indicated that the XeCl₂ molecule was linear. The ratio of the intensities of the bands of the XeCl₂ and Cl₂ molecules showed that both molecules were present in the matrix in approximately the same amounts.

Further development of the matrix isolation method was reported in^[37-39]. Claassen and Huston^[37] studied the structure of the normally unstable molecules XeO₃F₂ using the Raman and the infrared absorption spectra. The results of the matrix isolation method were particularly interesting in the Raman spectroscopy of the vapors of inorganic compounds.^[38,39] We shall consider these results in greater detail.

Boal et al.^[38] studied a system formed by the SeO₂ molecules. Less than 1% of these molecules was introduced into a CO₂ matrix kept at liquid helium temperature. The temperature was then raised gradually to 30–90° K and the changes in the spectra were followed with the aim of observing the formation of (SeO₂)_n polymers. The nature of the spectra of the isolated substance and the comparison with the published data for the vapor and crystal phases indicated that initially the SeO₂ molecules were completely isolated and, therefore, they existed in the monomer form. However, at

30–90° K new lines appeared in the spectra and these were attributed to dimers. Further heating of the matrix produced trimers and more complex polymers. A detailed analysis of the experimental data led Boal et al.^[38] to the conclusion that dimers had the trans-centrosymmetric structure with two bridging oxygens.

Further examples of the capabilities of the matrix isolation method were described by Hüber et al.^[39] They investigated the SnBr₂ and PbCl₂ molecules as well as their mixtures. The matrices were solid krypton and nitrogen. The concentrations of the investigated substances were 0.1–1% and the working temperatures were 4.2 and 20° K. The spectra contained all three active bands. Aggregation of the molecules was observed in the SnBr₂ + PbCl₂ mixture when the temperature was raised. The fine structure of the bands made it possible to identify the PbCl₂ molecule with isotopic chlorine atoms. This demonstrated that the sensitivity and the resolution of the matrix isolation method in combination with the Raman spectroscopy were not inferior to the corresponding parameters of the infrared technique. The polarized Raman spectra of isolated substances were obtained but these were analyzed only qualitatively.

Very recently the matrix isolation method was used to obtain the Raman spectra of the Br₃ and LiO₂ radicals^[40,41] and to investigate isolated molecules of CS₂, CCl₄, CH₄, and COS.^[42] In the latter investigation the stray scattering was reduced considerably by the use of a triple monochromator.

The reported results show that the matrix isolation method presents the investigator with new opportunities. It is unlikely to become a routine method but further development of the method should be worthwhile.

5. RESONANCE EFFECTS

Secondary radiations excited in any system of particles can be of different nature and origin. Therefore, it is extremely important to identify the secondary radiation. Sometimes this is a very difficult task and the difficulties increase under sharp resonance conditions. The identification is easiest in the cases of gases and vapors because of the availability of discrete absorption and emission spectra.

In the most general case the nature and, therefore, the classification of secondary radiation (such as luminescence, Rayleigh scattering, or Raman scattering) is deduced from very closely related properties, which include the dependences of the frequency, width, and profile of the secondary emission lines on the corresponding parameters of the exciting line (one of the effects is the frequency correlation or the "memory"), the influence of the characteristics of the electron cillator on the spectrum, the behavior of the system after instantaneous removal of the excitation source (the presence or absence of afterglow), and the reaction to quenching agents.²⁾

The question of classification of secondary radiations has a fairly long history. There has been continuous change in the criterion adopted, which can be one of those listed above or some other factor. For example, according to Vavilov, the principal distinguishing characteristic of the luminescence is the afterglow of short-

²⁾The anisotropy of the Doppler line profile can be used to separate the Raman effect from the luminescence. [18].

ter or longer duration resulting from the occurrence of intermediate processes between the excitation and de-excitation stages (these intermediate processes are responsible for the quenching phenomena).^[43] This criterion is extremely useful and it has helped in the correct interpretation of many observations.

Stepanov and Apanasevich have drawn attention to the difficulty and the ambiguity of the Vavilov criterion in the separation of the luminescence from the radiation generated in systems with negative absorption coefficients and from the radiation emitted under resonance excitation conditions (see^[44]). Initially, Stepanov and Apanasevich considered the problem from the classical point of view. They concluded that in the classical approximation the scattering and the luminescence are accompanied by afterglow. Therefore, both the scattering and the luminescence can be quenched by, for example, the addition of foreign gases. According to Stepanov and Apanasevich, the application of quantum electrodynamics shows that the only difference between these two secondary radiations is the point whether the photon absorption and creation events occur immediately one after the other or whether they are separated by intermediate processes.

Thus, according to the classical analysis given in^[44] a prolonged afterglow and the possibility of quenching are equally likely to occur in the scattering and luminescence phenomena. If a rigorous approach is used, all that can be said reliably that the luminescence is characterized by a redistribution of the excitation energy, i.e., by the occurrence of intermediate processes in the excited state. Thus, the problem of establishing particular criteria for specific types of secondary radiation (such criteria will not necessarily be valid in all cases but will be capable of experimental verification) reduces to the solution of the more general but in practice very difficult problem, which is the mechanism of generation of a given radiation. The problem of identification of stimulated radiations can be settled by appeal to other properties which are characteristic only of stimulated emission: small divergence of the light beams, monochromaticity, universal coherence, and oscillation thresholds. Similarly, the luminescence and the scattering phenomena can be separated.^[45]

A qualitative description (which is in agreement with experimental data) of the evolution of the properties of the secondary radiation with the spectral composition of the exciting light and the special features of these molecular scattering system was given by Shorygin and Krushinskii^[46] and later by Shorygin alone.^[47] This general picture was developed on the basis of the Placzek criterion characterizing the sharpness of the resonance,^[48] the Heitler analysis of the resonance effects,^[49] and the extensive experimental material on this subject obtained primarily by Shorygin and his colleagues.

If the frequency of a narrow exciting line is separated from the maximum of a wide absorption band of molecules by an interval exceeding typical values of the vibrational frequencies, the Raman spectrum is simply enhanced. The distribution of the energy between the various lines is normal. The positions of the displaced lines can be deduced in an unambiguous manner from the frequency of the excited line. There is practically no afterglow. As the exciting line penetrates into the

absorption band, so that its separation from the maximum of this band becomes comparable with the width of the explicit or latent vibrational structure, the secondary radiation acquires some of the features of the luminescence. These features are in the form of anomalously strong intensities of harmonics of various orders, which coincide approximately with the components of the vibrational structure of the absorption band.

When the harmonics in the secondary emission spectrum become narrower, the signs of the luminescence begin to appear and, particularly, the dependence of the positions of the lines on the frequency of the exciting light becomes weaker or disappears completely. At the same time the afterglow becomes more important and, consequently, the secondary radiation can be quenched more easily. Finally, when the spectrum is excited in the region of the components of the rotational structure of freely orientable molecules, the importance of the afterglow becomes even greater, the depolarization of the lines increases, and the spectrum as a whole acquires all the other features of the luminescence.

Thus, depending on the spectral properties of the exciting radiation and the scattering system, the secondary emission can exhibit features of the luminescence, of the resonance Raman effect, or of intermediate processes with a mixture of features of both kinds. The general theory of the processes of transformation of the radiation by simple systems characterized by sets of fairly narrow levels was developed by Sushchinskii.^[50] We shall not discuss the many details of this theory but we shall mention simply that it can describe not only the luminescence and the resonance Raman effect but also mixed cases of simultaneous excitation of both these radiations.

A specific feature of gases and vapors is the free quantized rotation of molecules. This is reflected in the theory of the interaction between radiation and matter, especially in the case of sharp rotational resonance. In particular, it is necessary to refine and make more specific the formulas describing the state of polarization of the lines in the secondary radiation spectra.

This task is undertaken in a recent theoretical treatment.^[51] This treatment is concerned with isolated freely rotating molecules. Three quantum numbers J , J' , and J'' —representing the rotational levels of molecules in the initial, final, and intermediate states—are introduced explicitly into the dispersion formula. This splits the scattering tensor into two parts. One of them represents the internal properties of the molecules and the other is related to the rotation. The formulas become extremely simple and the results are very easy to understand in the case of a sharp rotational-vibrational resonance when the treatment can be restricted to just one intermediate state. In this case any given value of J corresponds to nine combinations of the other two quantum numbers for which the scattering tensor does not vanish. Consequently, the limiting degree of the depolarization of the spectral lines (ρ for $J \rightarrow \infty$) can be assumed to be $1/3$, $3/4$, and 2 . The first value is obtained for $J' = J'' = J$.

The first laser investigation of the resonance Raman effect in gases was carried out by Holzer et al.^[52] The excitation source was an argon laser (5145, 5017, 4965, 4880, and 4765 Å) with an output power from 1 W to 50 mW. Holzer et al. investigated gaseous Cl_2 , Br_2 , I_2 ,

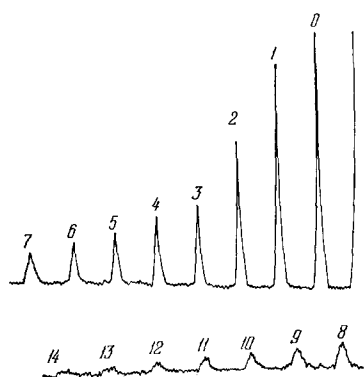


FIG. 5. Typical resonance Raman spectrum of I_2 vapor obtained under the following conditions: vapor pressure 15 torr; slit width 7.5 cm^{-1} ; exciting line $\lambda = 4880 \text{ \AA}$. The symbol 0 represents the fundamental vibration (213 cm^{-1}); 1-14 are the harmonics of this vibration.

Table I

Gas	Wavelengths of exciting lines, \AA				
	5145	5017	4965	4880	4765
Cl_2	SRE	SRE	SRE	SRE, RL	SRE
Br_2	RL	RSRE	RSRE	RSRE	RSRE
I_2	RL	RL	RSRE	RSRE	RSRE
$BrCl$	RSRE	RSRE	RSRE	RSRE	RSRE
ICl	RSRE	RSRE	RSRE	RSRE	RSRE
IBr	RSRE	RSRE	RSRE	RSRE	RSRE

$BrCl$, ICl , and IBr . The spectra were recorded photoelectrically by photon counting. The observations were made at an angle of 90° . The slit widths ranged from 2.5 to 7.5 cm^{-1} .

Holzer et al.^[52] observed secondary radiations whose properties varied strongly with the experimental conditions. In some cases the spectra recorded at low gas pressures (a few Torr) consisted of well-resolved doublets and an irregular sequence of harmonics. The radiation was depolarized. When the gas pressure was increased, the intensity of the spectrum as a whole fell, i.e., quenching was observed, and the sharp doublets changed into multiplets. Similar changes occurred under the influence of admixtures of a foreign gas. In other cases (at pressures of 15–100 Torr) the vibrational lines had wide Q branches and rotational wings, a sequence of overtones of systematically increasing width (right up to the 14-th harmonic in the case of I_2) and a decreasing peak intensity was observed, and all the lines were strongly polarized ($\rho < 0.45$); when the pressure was increased, the intensity of these harmonics increased but there was no significant change in their profiles. This case is illustrated in Fig. 5.

Thus, the two types of radiation were characterized by different profiles of the spectral lines and a different structure of the harmonics as well as by different states of polarization and different reactions to an increase in the gas pressure. All these features could result from one- and two-quantum processes. Consequently, the former radiation could be identified as a resonance luminescence and the latter as the resonance Raman effect.

A very important result established by Holzer et al.^[52] was that the transition from the resonance luminescence to the resonance Raman effect occurred in a narrow range of the excitation frequencies. For example, when the excitation wavelength was $\lambda = 5145 \text{ \AA}$ it was found that gaseous bromine emitted the resonance

luminescence but at $\lambda = 5017 \text{ \AA}$ it exhibited the resonance Raman effect. In the case of iodine the excitation with the $\lambda = 5017 \text{ \AA}$ produced the resonance luminescence and the excitation with the $\lambda = 4965 \text{ \AA}$ gave rise to the resonance Raman effect. The results of all the various experimental investigations of halogens and halides under resonance excitation conditions are collected in Table I, where the following notation is used: SRE denotes the spontaneous Raman effect, RL denotes the resonance luminescence, and RSRE denotes the resonance spontaneous Raman effect.

In discussing the principal problem of the physics of the transition from the resonance Raman effect to the resonance luminescence and back again, Holzer et al.^[52] draw the attention to the observation that, for example, in the case of Br_2 a strong continuous absorption is observed in the region where the resonance Raman effect is excited by the $\lambda = 4880 \text{ \AA}$ line. The limit of convergence of the absorption lines is located approximately at 5108 \AA and a discrete spectrum is observed at longer wavelengths. However, it is known that the excitation of a secondary radiation within line-like bands gives rise to the resonance luminescence. This is associated with the excitation of discrete molecular states which are manifested in the resonance luminescence in the form of real (long-lived) states. The true absorption of the radiation of $\lambda = 4880 \text{ \AA}$ would have caused dissociation of the molecules. Consequently, under these conditions the resonance luminescence is impossible and only the resonance Raman effect is observed. In other words, it is assumed that when a secondary radiation is excited in the region of the continuum, the competing one-quantum process cannot take place and therefore the resonance Raman effect is observed. This qualitative explanation is in agreement with the quenching influence of the gas pressure as a result of which the resonance luminescence is transformed into the resonance Raman effect. Thus, it would seem that the resonance Raman effect in gases appears if the energy of the exciting quanta is greater than the dissociation energy. However, it should be pointed out that in the case of liquid solutions the resonance Raman spectra are usually excited on the long-wavelength side of the absorption band.

Kiefer and Schrötter^[53] studied the resonance Raman effect in gases: their aim was to excite simultaneously both types of secondary radiation. They studied bromine and the spectrum was excited with radiation of much longer wavelength which was provided by a quasi-cw ruby laser ($\lambda = 6943 \text{ \AA}$) with an average output of about 200 mW.

Important features appeared in the secondary radiation spectrum at a gas pressure of 150 Torr. It was found that the fundamental vibration line as well as the first and second harmonics consisted of two components of comparable intensity. A polarized-light spectrum was obtained for the fundamental vibration and it was found that one of these components (301 cm^{-1}) was depolarized, whereas the other (319 cm^{-1}) was polarized. The doublet structure of the lines appeared even more clearly when a foreign gas (krypton), which increased the pressure to 1 atm, was added to the cuvette. It was then found that a fine structure was exhibited also by the third harmonic. These observations were attribu-

Table II

Exciting line	Fundamental vibration		First harmonic		Second harmonic		Third harmonic		Identification
	ν	ρ	ν	ρ	ν	ρ	ν	ρ	
6943 Å	308	0.8	616	—	923	—	1229	—	RL
	319	0.2	636	—	953	—	1270	—	RSRE
4880 Å	318.5	0.25	638	0.35	953	0.37	1268	0.35	RSRE

ted, as before, to the quenching effect of krypton. All the data, including those taken from^[52], are collected for convenience in Table II, which gives the information on the secondary radiation spectra of gaseous Br₂ obtained under different excitation conditions.

These observations make it possible to attribute the line sequence 301, 616, ... to the resonance luminescence and the line sequence 319, 636, ... to the resonance Raman effect. This interpretation is confirmed, in particular, by the observation that the degree of the depolarization of the 308 cm⁻¹ line decreases systematically with increasing pressure, i.e., a gradual transition from the resonance luminescence to the resonance Raman effect takes place.

One may immediately ask what is the reason for the fairly sharp differences between the frequencies of each of the lines in a sequence and why the luminescence is relatively weak. Kiefer and Schrötter^[53] answered these questions using the following hypothetical model. They drew attention to the observation that the 4880 Å excitation line is located in the region of a strong absorption band (³Π_{ou}⁺) whereas the 6943 Å line is located within a much weaker absorption band (³Π_{1u}). It is then assumed that in the latter case the resonance luminescence still occurs and the ³Π_{ou}⁺ state is excited as a result of "hot" transitions from very high vibrational levels of the normal electronic state. This explains the weakening of the luminescence. If we assume that the Raman effect involves a vibrational transition between much lower levels, we can explain the change in the line frequencies bearing in mind the mechanical anharmonicity. However, it is not clear which of these two states is active in the resonance Raman effect.

According to^[54] the continuum in the absorption spectrum of the molecular Br₂ has two clear maxima: a strong one at ~ 24 000 cm⁻¹ and a weak one at ~ 20 000 cm⁻¹. Ignoring a possible interpretation of these maxima, which is considered also in^[55], we shall note that even the second of these maxima can be reached by ruby laser quanta (14 400 cm⁻¹) from at least the 18-th vibrational level of a low electron state. Population of such high levels is negligible and it cannot ensure an effective resonance Raman effect. On the other hand, the attributes of a sharp resonance (a sequence of strong harmonics in the spectrum) are incompatible with the assumption that the scattering is due to transitions from lower vibrational levels.

Thus, the model assumed in^[53] lacks internal consistency and cannot explain satisfactorily even the mechanism of the excitation of the resonance Raman effect, although the coexistence of the resonance luminescence and the resonance Raman effect in gases has been established quite reliably and is of great interest. In this connection it is worth noting that the simultaneous excitation of the luminescence and the resonance Raman

effect in liquid solutions was first discovered and described by Shorygin and Ivanova back in 1958.^[56] This effect is typical also of semiconductor crystals, as reported in^[57-60]. All these observations can be understood if we use the theory of Sushchinskii^[50] mentioned above.

Beattie et al.^[24] investigated vapors of the natural Se₂ and of its isotope Se₂⁸⁰ and obtained spectra which were extremely rich in lines (particularly in the case of natural selenium). The distribution of intensities in these spectra, the degree of depolarization of the lines, and the fact that the experiments were carried out at very low vapor pressures (amounting to a fraction of a torr) led Beattie et al. to the conclusion that the spectra were due to the resonance luminescence and not the resonance Raman effect. The relationship between these two phenomena and the conditions for the transition from one to the other were investigated in detail using iodine vapor as the model substance. The results obtained were in full agreement with those reported by Holzer et al.^[52] and they showed that the resonance luminescence changed to the resonance Raman effect when the excited molecules were deactivated, i.e., when the luminescence was quenched effectively by the addition of a foreign gas (argon) to iodine vapor. The criteria of the transition were the general nature of the spectrum and the state of polarization of the lines. It was found that as the pressure was increased right up to 30 atm, the degree of depolarization gradually decreased from 0.8 to ~ 0.3. The latter value was typical of the resonance Raman spectra of liquid solutions of iodine.

Thus, investigations considered above established that an increase in the gas pressure, which was accompanied by the deactivation of the excited molecules, unavoidably transformed the resonance luminescence into the resonance Raman effect. In other words, only the resonance luminescence could be quenched.

The extremely rapid progress in the technique of resonance experiments has stimulated corresponding theoretical developments. Jacon et al.^[61] drew attention to the incorrectness of the usual representations limited to an allowance for the contribution of just the resonance state to the scattering. They considered the excitation of secondary radiations in the region of the continuum and concluded that it is necessary to allow also for near-resonance virtual states which make contributions of the same order of magnitude as the resonance state. This approach is used to deal with the gradual transition, in discrete part of the spectrum, of the resonance luminescence into the resonance Raman effect under the influence of increasing pressure.

The unsatisfactory nature of the available theories of resonance processes is demonstrated in^[62] by precision measurements of the frequency dependence of the cross sections for the resonance Raman effect stimulated within the continuum of the vapor phase of I₂. The excitation was provided by seven lines of a high-power argon laser. The instrumental factors affecting the results of measurements were carefully considered and allowed for. In particular, the temperature of the vapor was measured by two methods. The areas under the spectral lines, recorded using monochromator slits 0.5 cm⁻¹ wide, were measured by planimetry. The re-

Table III

Ref. cross section of RSRE, σ	Wavelengths of exciting lines, Å						
	4965	4880	4765	4727	4658	4579	4545
σ_{meas}	1.20	1	0.61	0.48	0.33	0.30	0.28
σ_{theor}	1.40	1	0.49	0.32	0.10	0.02	0.01

sults were compared with the modified formulas given in^[63,64].

The results are presented in Table III which gives the frequency dependence of the cross sections for the resonance Raman effect in the spectrum of I₂ vapor. We can see that the measured values deviate systematically from the theoretical ones and that the sign of the deviation is compatible with the ideas put forward in^[61]. It is pointed out that some role might be played by the photodissociation and recombination of I₂ molecules (this point requires further study).

We have mentioned earlier that the theory of the resonance emission refined in^[61] makes an allowance for the contribution of the neighboring states to the s scattering. The cases of a continuum and of discrete levels adjoining the resonance state are not distinguished sharply. Only the method of allowance for their presence (integral or sum over the states) is affected. This approach seems to be greatly oversimplified. We shall try to refine it later.

At the beginning of the present section we mentioned a theoretical treatment which yielded, in the one specific case of a sharp rotational resonance, explicit formulas for the dependence of the degree of depolarization ρ of the vibrational lines on the rotational quantum numbers of the initial, final, and intermediate states. The calculations gave limiting values of 1/3, 3/4, and 2 for ρ . The first of these values corresponds to the invariance of all three rotational quantum numbers in a scattering event. Such values of ρ are in fact typical of the resonance Raman effect. On the other hand, the resonance luminescence is characterized by higher values of ρ up to about 0.8. From the physical point of view this result may mean that the rotational state of a molecule does not have a chance to change in an elementary scattering event. If we assume, in accordance with the published data, that the lifetime of a virtual state under resonance conditions is 10^{-11} – 10^{-12} sec and the rotational relaxation time of gaseous molecules is 10^{-12} sec, we find that this indeed is true. The situation is reversed in the resonance luminescence process: during the lifetime of a real excited state (10^{-6} sec) a molecule may undergo many rotational transitions. This is in good agreement with the criteria of the resonance luminescence and the resonance Raman effect that have been discussed above. The excitation of a secondary radiation within a continuum lying above the dissociation limit of molecules is, in the opinion of the present author, described quite satisfactorily by the model suggested by Jacon et al.^[61] However, the case when the frequency of the exciting line is located within the discrete part of the spectrum requires further refinement. We shall use the published work and try to picture the physical aspects of the processes which occur in this case.

We shall assume that the natural width of the ab-

sorption lines of the vapor phase of I₂ is very small. Therefore, at low vapor pressures the profiles of these lines can be described completely by the Doppler broadening. This broadening is of the same order of magnitude as the width of the excitation lines provided by an argon laser ($\sim 0.1 \text{ cm}^{-1}$). In this situation we may encounter intermediate processes of the type described by Heitler^[49] or due to interference between real and virtual states.^[50,65] Therefore, it is no longer physically meaningful to consider separately the resonance luminescence and the resonance Raman effect, each of which is defined by its own set of criteria. When the pressure is increased, we finally reach such a strong broadening of the Doppler line profiles that the role of the intermediate processes becomes negligible and the importance of the resonance Raman effect in the secondary radiation rises strongly because of the quenching of the resonance luminescence and the activation of a large number of centers which give rise to a homogeneous impact broadening of the lines. However, the broadening need not be monotonic. In fact, it is reported in^[16,17] that when the pressure of hydrogen is increased, the rotational lines first become narrower because of reduction in the translational velocity and then the lines begin to broaden. This may probably be explained satisfactorily by the properties of the secondary radiation. If the excitation is provided by even narrower spectral lines (for example those generated by a single-frequency laser), i.e., by lines which are much narrower than the Doppler profiles of the components of the absorption spectrum of the iodine molecules, it may be necessary to make an allowance for the distribution of the molecular velocities and the phenomena will occur in restricted molecular ensemble so that the physical picture will become much more complex.

Thus, experimental investigations of freely orientable molecules under resonance conditions have yielded much valuable information and have established certain general relationships. The most interesting feature is the observed dependence of the processes transforming the incident radiation on the pressure of gases and vapors and on the part of the absorption spectrum (discrete or continuous) in which the excitation is applied. This makes it necessary to consider other systems characterized by discrete absorption.

Back in 1952 Shpol'skiĭ et al.^[66] showed that rapid crystallization of dilute solutions of aromatic compounds in normal hydrocarbons produces systems characterized by quasilinear absorption and emission spectra. Since that time the Shpol'skiĭ effect has become the subject of comprehensive investigations and the source of information on the structure of molecules and their energy spectra that could not be obtained in any other way.^[67,68] In particular, attempts have been made to use the Shpol'skiĭ effect in preparing new media which would be active in the stimulated Raman scattering. However, only strong discrete stimulated luminescence has been excited.^[45] This may be due to the inhomogeneous nature of the broadening of separate lines in the Shpol'skiĭ spectra. Since this broadening can, within limits, be controlled by, for example, altering the concentration of a substance or the rate of freezing a sample, investigations should be made of the conditions for the appearance of both types of secondary radiation.

Such investigations could also yield new information on the vibrational spectra of the Shpol'skiĭ systems which would be important for the better understanding of the Shpol'skiĭ effect itself.

Thus, there is every reason to expect further successes in the detailed studies of the fundamental problem of the modern spectroscopy which is the nature and mechanisms of resonance conversion of radiation in matter.

6. APPLICATIONS OUTSIDE THE LABORATORY: LIDAR STUDIES OF THE ATMOSPHERE, PLASMA DIAGNOSTICS, AND OTHER POSSIBLE APPLI- CATIONS OF REMOTE SPECTROSCOPY

The microwave radar technique has been used for a long time for ranging purposes. The development of high-power Q-switched lasers has made it possible to apply the radar methods in the visible part of the spectrum. The small divergence of laser beams and their high power can ensure a high sensitivity of the optical radar (lidar). The spatial resolution is governed by the duration of laser pulses.

We shall understand the laser optical ranging to be the qualitative and quantitative determination of the composition of the atmosphere including its natural and man-made components (pollutants), and the height at which these components are located. Such determinations are very important in the control of atmospheric pollution in the vicinity of major cities and they would be also very useful in tackling the problems encountered in atmospheric physics. Information on changes in the concentration of nitrogen, oxygen, and water vapor with time can be used to determine the conditions for the formation of clouds and are of great interest in meteorology and aerodynamics. By analogy with radar, the laser optical ranging is denoted by the acronym lidar from the initial letters of "Light Detection and Ranging."

The first use of lidar in investigations of the atmosphere, including its higher layers, was published in 1963. Initially, the return signals were due to the molecular (Rayleigh) and the Mie backscattering by large particles. However, because of their very nature these signals are not shifted in the frequency. Therefore, in this application of lidar the separate components of the atmosphere are difficult to identify and such identification is not always certain. In fact, the Rayleigh and the Mie scattering gives the overall pattern rather than detailed information. The situation is quite different in the spontaneous Raman effect because it gives rise to frequency-displaced lines which are specific of given molecules. Therefore, the Raman lidar is completely free of the disadvantages of the Rayleigh and Mie scattering but it can give little information on the size and shape of the aerosol particles.

A typical lidar unit consists of a pulsed laser which can usually generate a sequence of high-power pulses (this is important for continuous monitoring), a telescope which expands the exciting light beam, i.e., reduces its divergence, a telescope which collects the scattered radiation on the entry slit of a spectroscopic instrument or simply on an array of specially selected narrow-band and cutoff interference filters and a sys-

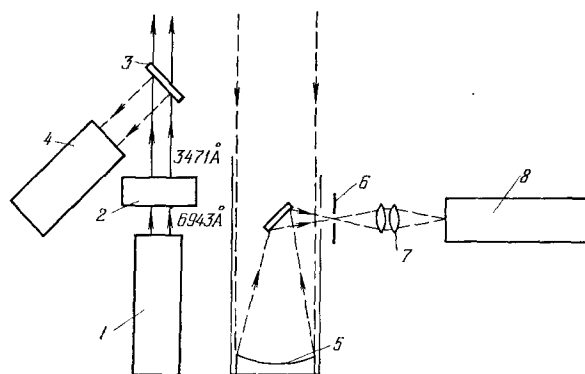


FIG. 6. Schematic diagram of a typical lidar: 1—pulsed ruby laser; 2—crystal acting as frequency doubler; 3—light-splitting mirror; 4—photodiode used to measure the pulse energy; 5—mirror of receiving telescope ($D = 400$ mm); 6—stop; 7—illumination optics; 8—double monochromator with a photomultiplier, an amplifier, and a recording system.

tem for data reception, recording, and analysis (Fig. 6). All these parts of a lidar unit are mounted in a stable manner at some fixed place or in the body of a truck or a van, which makes the apparatus mobile.^[69,70]

The pioneering work of this kind was carried out by Leonard,^[71] who used a high-power pulsed nitrogen laser just developed by Leonard and Gerry (see review^[8]). The pulses emitted by this laser were of 10-nsec duration, the output power at $\lambda = 3371 \text{ \AA}$ was 100 kW, and the repetition frequency was 100 Hz. Other workers^[72-77] used the fundamental-frequency radiation ($\lambda = 6943 \text{ \AA}$) of a Q-switched ruby laser although this would seem to go against the law $I_{\text{scatt}} \propto 1/\lambda^4$ and the low sensitivity of the detector photocathodes. Subsequently, it has become usual to employ the second harmonic of the ruby laser.^[78-82] More recently, there has been a tendency to carry out Lidar investigations employing the second and fourth harmonics of neodymium-glass lasers and of lasers utilizing neodymium-doped yttrium aluminum garnet crystals (wavelengths ~ 5320 and 2660 \AA , respectively).^[69,70,83] The latter wavelength is favorable for the attainment of the resonance condition in the excitation of the spontaneous Raman effect, is not absorbed very strongly by the lower layers of the atmosphere,³⁾ and lies in the spectral region where the sky radiation is negligible at moderate altitudes. This makes it possible to carry out 24-h observations, which is a very important practical point (the same problem can be solved by the stroboscopic technique).

The method of reception and recording of the incoming signal plays a very important role in the lidar technique. Two methods can be used. In the first method the Raman spectra are excited by giant pulses, the scattered signal is subjected to wide-band amplification and passed to an oscillograph. In the second method one uses spatial storage and excites the spectra by a train of pulses. The sensitivity is much lower in the first method than in the second. However, the first method is characterized by a much higher spatial resolution. For typical lidar units the spatial resolution in these

³⁾The absorption is primarily due to the ozone molecules in higher layers of the atmosphere.

two methods is 5 m and 1 km, respectively.^[78] The method is selected in accordance with the problem to be tackled.

As mentioned above, in some cases we do not need a spectroscopic instrument. This approach was used by Leonard,^[71] who used a set of interference filters displaced from their normal positions to select the required part of the spectrum from the scattered beam. It is more usual to employ monochromators or polychromators which make it possible to tune the lidar unit to several spectral lines representing different components of the atmosphere. This part of the lidar units, like all the other parts, was developed to a high level by Hirschfeld and Klainer.^[82]

A complex system for the reception (in the absence of a Vidicon tube), spectral transformation, and recording of weak instantaneous (up to 10 nsec) signals was developed by the French firm of Coderg.^[84] The system is based on new principles and it makes it possible to record simultaneously a number of signals in a fairly wide range of wavelengths.

In this system the spectral conversion is performed by a double monochromator working as a spectrograph (with a wide intermediate slit and without an exit slit). This makes it possible to select a bright undisplaced line and to reduce the level of optical strays. The image of the investigated part of the spectrum is projected on the screen of an image converter with three-stage amplification of the brightness. The image is transferred, for the purpose of time scanning and recording, to a Vidicon television tube which is connected to a tape recorder and an oscillograph. The schematic diagram of the apparatus is shown in Fig. 7. The apparatus is capable of recording processes of duration not less than 10 μ sec but without time resolution. Such resolution can be provided, at the 10 nsec level, if additional time scanning of the image is performed along the spectral slit with a rotating mirror or a prism.

When short-wavelength laser radiation is used for excitation purposes in lidars, one must bear in mind that the atmospheric losses due to the Rayleigh scattering increase when the wavelength is reduced. If the radiation frequency is fixed, these losses determine the optimal height at which measurements can be performed. This problem has been considered theoretically in^[85].

A detailed description of the construction of a typical meteorological lidar unit is given in^[86]. The problem of the ultimate capabilities of this unit is analyzed in that paper with an allowance for the special features of the detection and measuring channels. The results reported in^[86] can be applied fully to the Raman Lidars in which we are interested.

Calibration of lidars requires the knowledge of the Raman scattering cross sections of various gases. Measurements of these cross sections have been carried out recently. The related problem is the resonant increase in the cross sections, which opens up the possibility of using the resonance effect in probing of the atmosphere. Schwiesow and Derr^[87] used an argon laser to excite the spectra of an artificial $\text{SO}_2 + \text{N}_2$ mixture and found that sulfur dioxide scattered light much more strongly than nitrogen. However, they gave no

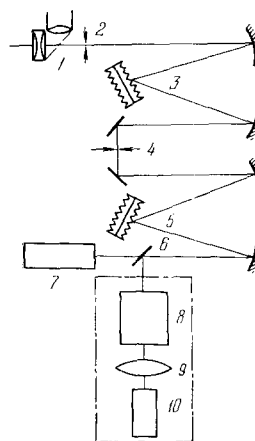


FIG. 7. Schematic diagram of a spectroscopic unit made by the firm of Coderg for investigation of fast processes: 1—entry optics (interchangeable illuminating objective and a sighting unit); 2—entry slit (0.2 mm) of the spectroscopic instrument; 3—diffraction gratings of the first monochromator (1221 and 305 lines/mm); 4—intermediate slit (0.15 mm); 5—diffraction gratings of the second monochromator (161 and 610 lines/mm); 6—rotating mirror; 7—photomultiplier; 8—three-stage image converter and amplifier; 9—intermediate optics; 10—Vidicon television tube. The slits are driven electrically. A rotating mirror or prism is inserted in front of the entry slit (not shown in the figure). The double monochromatization of light follows the Czerny-Turner scheme. Each of the monochromators can be used with different combinations of gratings in which the dispersion is added or subtracted. The maximum amplification provided by the image converter and amplifier is 10^5 . The output signal is applied to an oscillograph and a tape recorder.

numerical values. The relative cross sections of N_2 , O_2 , CO , CO_2 , SO_2 , and H_2S were measured by Fouche and Chang.^[88] They used an argon laser ($\lambda = 5145 \text{ \AA}$) and the nitrogen served as the standard. They obtained the following relative values of the cross sections: 1 for N_2 , 1.2 for O_2 , 0.91 for CO , 1.5 for CO_2 ($\nu = 1388 \text{ cm}^{-1}$), 5.5 for SO_2 , and 6.6 for H_2S . The absolute scattering cross section of nitrogen was found to be $(2.6 \pm 1) \times 10^{-31} \text{ cm}^2/\text{sr}$. When the spontaneous Raman effect was excited by the radiation produced by a pulsed nitrogen laser ($\lambda = 3371 \text{ \AA}$), Leonard^[89] obtained the same results, $\sigma_{\text{NO}}/\sigma_{\text{N}_2} = 0.5 \pm 0.1$ and $\sigma_{\text{SO}_2}/\sigma_{\text{N}_2} = 2.4 \pm 0.3$, for two gases NO and SO_2 irrespective of the direction of observation (90 and 180°); these results were obtained using nitrogen as the internal standard. A comparison with the preceding values shows that the approach to the resonance excitation conditions reduces the difference between the Raman scattering cross sections of gaseous SO_2 and N_2 . Che-Jen Chen and Wu^[90] measured the Raman scattering cross section of N_2O_4 using an excitation wavelength $\lambda = 6943 \text{ \AA}$; this cross section was $1.4 \times 10^{-31} \text{ cm}^2$. Holzer et al.^[52] determined the relative intensities of the spectral lines of gaseous halides, relative to nitrogen and methane. The Raman spectra were excited by an argon laser ($\lambda = 4880 \text{ \AA}$). They reported the following sequence of values: $I_{\text{methane}} = 1$, $I_{\text{Cl}_2} = 1.65$, $I_{\text{Br}_2} = 3.30$, and $I_{\text{I}_2} = 100$. Since methane was transparent to the argon laser radiation, these values represented primarily the resonant increase in the Raman scattering cross sec-

tion, at least for the last two gases.⁴⁾ Thus, under real conditions the Raman scattering cross section can increase by about one order of magnitude because of resonance.

Let us now consider some specific results of probing of the atmosphere with Raman lidars. Cooney^[72] studied the density of the atmosphere at heights up to 3 km. He obtained nitrogen distribution curves which did not agree with those expected theoretically. In a later paper,^[81] Cooney extended this method to a study of the water vapor. Nitrogen was used as the internal standard and it was assumed that the concentration of nitrogen in the atmosphere was known. Melfi et al.^[79] determined the profile of the distribution of the water vapor at heights up to 2 km. Strauch et al.^[92] utilized the lidar method in the measurement of the fluctuations of the temperature of the atmosphere by an indirect method in which use was made of the backscattered Raman signal of the N₂ molecules located at a fixed height. Control experiments, in which the temperature was measured independently, demonstrated the great promise of the method.

Inaba and Kobayasi^[75-78] investigated mainly the problem of the qualitative and quantitative diagnostics of pollutants in the atmosphere. Several of their experiments were carried out under conditions simulating the atmospheric situation. They demonstrated that it should be possible to identify the presence of such components as SO₂, CO, and CO₂ (Fig. 8). An investigation of a city atmosphere established the presence of CO₂ in concentrations 50 times higher than normal. Measurements of the nitrogen and oxygen concentrations under different meteorological conditions enabled Inaba and Kobayasi to determine the ratio of the intensities of the shifted and unshifted lines I_S/I_U . The published intrinsic value of I_U was employed in a calculation of the Raman scattering cross section of oxygen, which was in good agreement with the theory. The results reported by Inaba and Kobayasi in^[78] were of exceptional interest in relation to the construction and the selection of parameters of Raman lidars. They established the minimum power for the return signal in the case of excitation of the spontaneous Raman effect by the second harmonic of the ruby laser under different experimental conditions. They found that in the case of direct recording this minimum power was 6.2×10^{-11} W whereas in the case of storage and photon counting this power could be as low as 3.1×10^{-14} W. Inaba and Kobayasi reported also absolute data on atmospheric interference in the form of sky radiation. On a clear night this radiation represented 5.6×10^{-16} W, at twilight it was 10^{-14} – 1×10^{-11} W, and on a cloudy day it was 1×10^{-11} – 1×10^{-9} W. These were the values that limited the threshold sensitivity of Raman lidars operating in the near ultraviolet (it was not clear whether Inaba and Kobayasi^[78] used the stroboscopic technique).

In one particular case (CO₂), Inaba and Kobayasi determined the threshold concentration of gas by instantaneous measurement at heights of several tens of me-

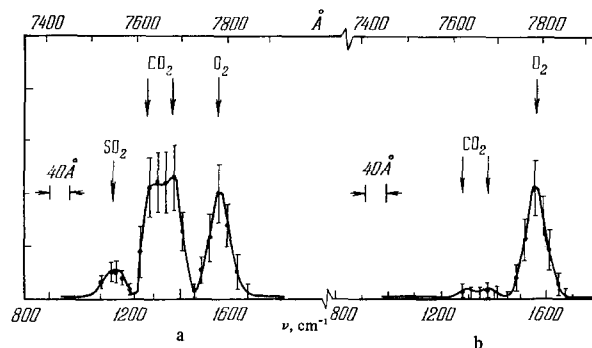


FIG. 8. Comparison of the Raman spectra of a polluted (a) and clean (b) atmosphere, recorded with a lidar unit. The vertical lines represent the scatter of the experimental points.

ters. This concentration was 3×10^{12} molecules/cm³. The storage method was found to be much more sensitive at higher altitudes (1 km or higher).

A very careful laboratory and field investigation of about 200 liquid and gaseous substances, carried out by Hirschfeld and Klainer,^[80] yielded all the initial data necessary for the construction of lidars and estimates of the threshold capabilities. These results were taken into account in the construction of the final version of the apparatus. Some of the data on the sensitivity of the measurements were tabulated. It was found that the sensitivity at distances up to 250 m was within the range 1.2×10^{12} – 1.7×10^{14} molecules/cm³. This was in general agreement with the aforementioned estimate for gaseous CO₂.

Zaromb et al.^[83] determined the concentrations of ozone at heights of 2–3 km and obtained 1.5×10^{11} molecules/cm³. These values were obtained under resonance conditions (the exciting radiation used by Zaromb et al.^[83] was of 2660 Å wavelength, i.e., of wavelength lying in the region of the fundamental absorption of the O₃ molecules). Zaromb et al. determined also the maximum concentration of SO₂, which was 1.5×10^{12} molecules/cm³, and they found that other components could be discovered only at low heights (30–300 m) and only if present in higher concentrations.

The problem of plasma diagnostics has recently attracted many investigators working on the Raman effect. The diagnostics implies local determination of the components and temperatures of flowing gases. The available diagnostics methods include luminescence, Rayleigh, and Thomson scattering. However, each of these methods has its own limitations and cannot provide full information. Therefore, investigators turned to the remote Raman spectroscopy. Investigations of this kind were carried out by Widhopf and Lederman.^[88] Such investigations are still in the laboratory stage but the results are worth detailed consideration.

Widhopf and Lederman excited the Raman spectra with a Q-switched ruby laser. The pulse power was up to 100 MW. The spectral lines were selected with a simple diffraction-grating monochromator by a system of interference filters. A photomultiplier was used as a detector and the signals were displayed on an oscillograph. Widhopf and Lederman studied model gases at room temperature—N₂, O₂, and CO₂—as well as their mixtures at pressures from 3 to 760 torr.

⁴⁾The influence of the frequency of the incident light on the intensity of the Raman lines of water vapor was investigated by Derr and Schwiesow.^[91] Unfortunately, the results of this investigation are not available in an easily accessible form.

In all cases Widhopf and Lederman found a linear, i.e., theoretical, dependence of the line intensity on the gas concentration (to within $\pm 10-20\%$). This provided the basis for the proposed plasma diagnostics method. Data were obtained on the threshold power needed in the case of CO_2 this power was 10^{-9} W. In the case of excitation by the second harmonic of the laser the scattered power should be 10^{-11} W. This value was obtained by extrapolation and it was quite close to the estimate of Inaba and Kobayashi,^[78] particularly when the results were normalized to the same excitation power. The example of O_2 molecules at a pressure of 760 torr was used to demonstrate that the method was capable of yielding the vibrational temperature. The conditions for measurements of this temperature should be much more favorable in a hot plasma.

The apparatus used by Widhopf and Lederman could be improved considerably. The ways in which this can be done are quite clear. Therefore, the Raman spectroscopy method can be regarded as a promising plasma diagnostics technique.

In conclusion you must draw attention to other possible, at least in principle, applications of the remote Raman spectroscopy. It can be used in industry as a method for monitoring, and, to some extent, control of certain chemical processes. This is due to the high selectivity and the satisfactory sensitivity of the method and the circumstance that the scattered Raman signal does not require troublesome preparations in the form of selection of suitable concentration of the substance and thickness of the working layer (these operations take much time). The optimal conditions for the return Raman-scattering signal are achieved automatically. Therefore, if giant laser pulses are used, the Raman signal can be obtained practically instantaneously. Consequently, a necessary command can be sent to the control apparatus immediately. This combination of properties cannot be found in any other molecular spectroscopy method. Moreover, it is likely that the remote Raman spectroscopy will provide a method for indicating dangerous concentrations of firedamp gas in pits. Finally, there are no doubts about the suitability of the method in structural and other investigations of explosive substances in any aggregate state.

Note added in proof. The Raman spectroscopy of weakly interacting molecules continues to develop very rapidly. The first applications of a single-mode argon laser in high-resolution spectroscopy are described in [94]. The matrix isolation method has been extended to the molecules of S_2 , [95] H_2O_3 , H_2O_4 , and O_3 . [96] Spectra of isolated molecules of LiO^{16} , NaO^{16} , NaO^{16-18} and NaO^{18} , were obtained by Hatzenbuehler et al. [97] and the signal/noise ratio was improved by the use of a computer in time averaging of the spectra. The degree of depolarization of the spectral lines of Br_2 and I_2 vapors was determined under resonance conditions. [98] A comparative analysis of the remote spectroscopic method for investigating the atmosphere, including the Raman method, is given in [99]. A mobile Raman lidar was tested under field conditions and its sensitivity limits were determined. [100] The relative cross sections of the Raman effect of gaseous O_3 , CH_4 , C_3H_8 , NO , N_2O , and H_2 were determined. [101] The remote Raman spectroscopy method was applied to the determination of the temperature of a hydrogen flame. [102]

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Translated by A. Tybulewicz