

The discovery of combinational scattering of light (the Raman effect)

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Soon after research on molecular scattering of light began in the Soviet Union, Landsberg and Mandel'shtam made one of the most important discoveries in physics in this century: combinational scattering of light (or the "Raman effect," as it is known outside the Soviet Union. Transl. ed. note). In this paper, the history of Soviet research on this subject is briefly outlined. Research in other countries is discussed only briefly and only to the extent necessary for an objective description of the course of events. Use is made of archival material, including one of the first spectrograms obtained by Landsberg and Mandel'shtam that has been preserved, which clearly shows a combinational-scattering line. This spectrogram, obtained on February 23–24, 1928, constituted the first observation of the new effect anywhere, but the results were published only with considerable delay. Translations into Russian of the complete texts of the first papers on the subject by Raman and Krishnan and by Landsberg and Mandel'shtam are presented (only the references to original papers are given in the English edition). Some early descriptions of the effect and some early comments on it (by Born, Rutherford, etc.) are given. Current trends in the development and applications of combinational scattering are outlined very briefly at the end of the paper.

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1. INTRODUCTION

Combinational scattering of light was discovered in 1928, approximately simultaneously, by the Soviet physicists G. S. Landsberg and L. I. Mandel'shtam¹⁻⁵ working in Moscow and the Indian physicists C. V. Raman and K. S. Krishnan⁶⁻⁹ working in Calcutta. This proved to be one of the major discoveries in physics in this century.

Landsberg and Mandel'shtam were studying the spectrum of light scattered by crystals in an attempt to find new discrete lines due to modulation of the scattered light by thermal elastic waves with frequencies on the acoustic branch of the dispersion curve. Instead, they found new lines resulting from a modulation of the scattered light by higher frequencies, lying on the optical branch of the dispersion curve. This was combinational scattering of light.

Raman and Krishnan were seeking in light scattered by liquids and vapors light of an altered frequency, under the assumption that an optical analog of the Compton effect exists, when they discovered combinational scattering of light. Ironically, in even earlier work the French physicists Rocard, Cabannes, and Daure¹⁰⁻¹³ had deliberately looked for combinational scattering of light in gases but had not found it. The problem was

that at the time they were not able to detect light at the low intensities involved.

The aim of this paper is to review the development of the research in the Soviet Union which ultimately led to the discovery of combinational scattering of light.

The work by the Indian physicists will be discussed only briefly, exclusively on the basis of their publications, and only to the extent necessary for an objective account of the research in its earliest stages in 1928.

We emphasize that all three groups which were studying the molecular scattering of light at the time (in the Soviet Union, India, and France) were working completely independently of each other.

The effect can be summarized as follows. The spectrum of the scattered light contains, in addition to the Rayleigh scattering at the frequencies of the exciting light, additional lines, which lie on the long-wavelength and short-wavelength sides of each spectral line of the exciting light. These satellites (the "Stokes" satellites on the long-wavelength side and the "anti-Stokes" satellites on the short-wavelength side) are characteristic of intramolecular, intermolecular, or lattice vibrations, which are sometimes also manifested in infrared absorption spectra.

When Landsberg and Mandel'shtam, in their delicate and laborious experiments, definitely proved the existence of a new optical effect and recorded combinational lines in the spectrum on February 21, 1928, they understood the nature of the effect correctly. They calculated the frequencies which should be emitted by the substances being investigated and demonstrated complete agreement with their experiment.¹⁾ It was not until April of that year, however, that Landsberg reported his work with Mandel'shtam on the subject, at an optics seminar in Moscow. Below we will also discuss the order in which the papers on this new effect appeared.

Landsberg's report of the new effect to the Moscow optics seminar made a very strong impression on the audience. In fact, one of the physicists present said, "This can't be correct, because it would mean that we were 'hearing a molecule talk'" (according to the recollection of a scientist present at the seminar). The listeners had good reason to be surprised at the report. Indeed, this was the first instance in which interaction of light with matter, "passive" and immobile in the absence of an external electric or magnetic field, had led to the appearance in the spectrum of additional spectral lines. Today, the effect is familiar to anyone who had taken a general course in physics, and is accepted as natural, but fifty years ago it seemed nothing short of miraculous.

But even at the time it was accepted as natural by a very few: among them were Einstein, Kramers, Heisenberg, Smekal, Born, and perhaps a few others. But we will return to this point later.

There was no miracle involved. Landsberg and Mandel'shtam were actually "hearing a molecule talk," and they understood its "speech" correctly. Landsberg later wrote²⁾, "Just as we hear someone speak into a microphone when we receive modulated vibrations, when we observe the combinational scattering of light we are in a sense hearing a molecule tell about the processes occurring in itself." Landsberg and Mandel'shtam understood the meaning of their discovery, and they also had a good idea of the extremely important role which this effect would come to play in physics, chemistry, and biology. The applications of the effect actually turned out to be so varied that they could not all have been foreseen at the time.

Any research carried out by Landsberg and Mandel'shtam was always very careful and thorough, guided by a clear understanding of the effect under study, and they did not rush to publish their results.

¹⁾ The additional lines which appear are combinations of the frequencies of the exciting light and the frequency of natural modes of the substance, so Landsberg and Mandel'shtam called this new effect "combinational scattering of light." It was apparently in France¹¹⁻¹³ that this effect was first called the "Raman effect." This name was then adopted in India, and this is the name which has become established outside the Soviet Union and which is in fact frequently used inside the Soviet Union. Raman has stated¹⁴ that he first saw a combinational-scattering line on February 28, 1928.

More than that, after some particular study had been carried out, and even after a paper had been written for publication, they did not immediately send it off to a journal; instead they let it sit in a desk drawer for a while. While the paper was sitting in the drawer another idea could be added or, if necessary, the shades of meaning of some expression could be refined or changed. In general, it was necessary to let everything settle; then the paper could be submitted for publication. Their style was directly opposite to the tendency frequently seen today: to publish rapidly in order to "stake a claim" on an actual or only a possible "discovery." It might be more accurate to say that such haste was incompatible with their physiological makeup. All these admirable qualities are fully reflected in the research which is the subject of the present paper.

I would not be honest, however, if I were to claim that I did not regret their delay in publishing their observation of this new effect, which they saw and understood earlier than anybody else. Furthermore, although I worked with Landsberg for 20 years and discussed various aspects of the discovery with him on many occasions, I never heard him give any hint that he in any way regretted their procedure in studying the new effect and in publishing their results.

There are not many physical effects which have found the widespread scientific and practical application that combinational scattering has. There is not enough room here even simply to list the applications which have already been made in studying molecular structure, intermolecular interactions, critical phenomena, polaritons, and several other effects, along with the analytic applications. Many thousands of original papers have been published on the subject, dozens of books and many review articles have been written, and the work continues to expand, to the point that journals have been founded which deal with nothing else. The *Journal of Raman Spectroscopy* and the *Raman News Letters* have been published for several years now. High-power laser pulses have led to the discovery of stimulated combinational scattering, which has opened up new opportunities for studying the interaction of light with matter and which has generated new research methods.

In the present paper, as we mentioned earlier, we will be concerned with only the earliest stage of the work and we will restrict the discussion to work carried out primarily in 1928; only toward the end of the article we will briefly mention those applications which were not foreseen by the discoverers of the effect.

We now go back to the time already far in the past, when the new field of physical optics—the study of molecular scattering of light—was beginning to gather momentum, and the subsequent development of which gave birth to combinational scattering of light.

2. THE BEGINNING OF THEORETICAL RESEARCH ON MOLECULAR SCATTERING OF LIGHT

The earliest work in the field which is now known as molecular scattering of light is generally credited to

Rayleigh,¹⁵ who carried out calculations for the scattering of light by molecules of low-density gases in the atmosphere. In this case each molecule is a radiator of secondary waves which acts independently of the other molecules, and the intensity of the scattered light can be found simply by summing the secondary radiation of all the molecules.

For condensed media, on the other hand, in which the mean free path of a molecule or the average distance between particles is much smaller than the wavelength of the light, the situation is completely different.

What the situation is in these really important cases, remained unclear for a long time. Only after Smoluchowski,¹⁶ in studying critical opalescence, concluded that this strong light scattering was due to the appearance of large density fluctuations near the critical point did the reason for the optical inhomogeneity of an optically pure medium become clear. Smoluchowski's idea that an optical inhomogeneity resulted from fluctuations turned out to be extremely fruitful. Since fluctuations result from the statistical nature of the motion of the particles of the medium, it was found possible to speak in terms of the scattering of light due to fluctuations in the density and orientation and, in solutions, additionally due to fluctuations in the concentration. Furthermore, fluctuations also exist which lead to a distortion of a mirror-finish surface of a material or of an interface between two media in equilibrium.

The scattering of light due to fluctuations of various origins today constitutes the scientific field called the "molecular scattering of light." The first statistical theory which made possible the calculation of the intensity of the light scattered by density and concentration fluctuations in an isotropic medium belongs to Einstein.¹⁷ Treating fluctuations as being responsible for the optical inhomogeneity, Einstein for computational purposes expanded the density or concentration perturbation in a three-dimensional Fourier series. In this work the harmonic components of the series were not yet called waves or even "gratings," but each term in the Fourier series was in fact a three-dimensional diffraction grating. Three years later, Mandel'shtam¹⁸ solved the problem of light scattering by an interface between two media for the case in which an ideal plane interface at equilibrium is distorted by thermal fluctuations.

To calculate the intensity of the light scattered from such a surface, which is "rough on the molecular scale," Mandel'shtam expanded the roughness in a two-dimensional Fourier series. Although he used some important results found by Einstein,¹⁷ he was of course solving an independent and difficult problem. He treated each term of the two-dimensional series as a diffraction grating, as he stated directly: "Each term in series (3) can be thought of as a cross-shaped grating." Later, he was the first to point out that the scattered light is none other than the light diffracted by these gratings. This is essentially already the modern understanding of the nature of molecular scattering, not only at a surface but also in the interior of a

substance. At this point, however, these static gratings and the terms of the Fourier series are not yet waves. However, the motion of the gratings is of no significance in a calculation of the intensity integrated over the frequency. We should once more emphasize, however, that this treatment of the light-scattering process as a process of diffraction by Einstein and Mandel'shtam gratings was a very important step toward understanding the mechanism of the effect.

Prior to the work on light scattering by a surface whose roughness is due to fluctuations, Mandel'shtam carried out a series of fundamental studies on the theory of oscillations and wireless telegraphy and other questions of radio physics.

Mandel'shtam's wide-ranging scientific interests led him to a study of optical problems. According to Papaleski,¹⁹ "...foremost among these problems were those dealing with the scattering of light, which Mandel'shtam studied throughout his life, beginning with his professional dissertation, 'Optically Homogeneous and Turbid Media' (1907)." In reviewing Mandel'shtam's research, Papaleksi¹⁹ noted, "The series of optical studies on topics arising from analogies with radiotelegraphy was very ingenious and of fundamental importance. This work included a study of the damping of the natural vibrations of glowing sodium vapor (1910) and the radiation from a source at a distance comparable to the wavelength from the interface between two media (1914)."

Mandel'shtam could thus clearly imagine what would happen in the spectrum of light if the light were modulated by some time-dependent periodic process. But, as has already been pointed out, in the papers by Einstein and Mandel'shtam the gratings at which the diffraction occurred were still static gratings, and for the time being no mention was made of a time-dependent periodic process modulating the scattered light. Already before the calculation of the intensity of light scattered by density and concentration fluctuations, Einstein²⁰ took a step of fundamental significance in the development of a theory of the specific heat of solids. The equation derived by Einstein gave a good description of the specific heat of a solid at constant volume everywhere except at very low temperatures.

In an effort to improve Einstein's theory, Debye²¹ adopted a model for a solid in the form of a continuum in which elastic waves were propagating in all possible directions, with frequencies ranging from zero to a frequency of the order of the ratio of the sound velocity to the lattice constant, i.e., the maximum frequency of the Debye spectrum. The idea of representing the energy of thermal motion as the energy of elastic waves proved fruitful and allowed Debye to formulate his familiar law stating that the specific heat at low temperatures is proportional to the cube of the absolute temperature. The question of the specific heat was solved, but Debye did not mention the problem of light scattering in that paper. But density fluctuations reduce to pressure fluctuations, if entropy or temperature fluctuations which are small in a solid are ignored.

Such fluctuations cannot remain in one place; instead, they travel through the solid. A random pattern of condensations and rarefactions due to fluctuations is equivalent to a set of elastic waves of all possible frequencies (up to a maximum) which are propagating in all possible directions in the crystal.

In expanding the density fluctuations and the surface irregularities in three-dimensional and two-dimensional Fourier series, Einstein¹⁷ and Mandel'shtam¹⁸ said nothing about the specific heat. At the time it was apparently not so easy to see the correspondence between the terms of the Fourier series and the Debye elastic waves.

Only five years later, this point became clear to Mandel'shtam. When he understood it, however, he also realized that a standing wave or a grating would lead not only to diffraction but also, because of the time-dependent change in the density in the standing wave, to a periodic change in the refractive index, so that the scattered light would be modulated at the frequency of the elastic thermal wave.

In this case the scattered light would contain components shifted by an amount $\Delta\nu$ from the fundamental frequency of the exciting light, ν :

$$\nu' = \nu \pm \Delta\nu, \quad (1)$$

where $\Delta\nu = f$, and f is the frequency of the Debye thermal wave. It is easy to show that this frequency is (see, for example, Ref. 25)

$$f = \frac{v}{\Lambda} = \frac{v \cdot 2n \sin(\theta/2)}{\lambda}. \quad (2)$$

Here v , Λ , λ , and θ are the velocity and wavelength of the sound, the wavelength of the light, and the scattering angle, respectively.

It follows from (1) and (2) that

$$f = \Delta\nu = \pm 2n\nu \frac{v}{c} \sin \frac{\theta}{2}, \quad (3)$$

where c is the speed of light in vacuum.

The same result is found for a traveling wave, from which light is reflected as it would be from a mirror moving at a velocity v (Ref. 25). It is difficult to say now precisely when the entire picture of the molecular-scattering spectrum became so clear to Mandel'shtam that he was able to write equations for the shifts of the components of a spectral line. He had a perfect grasp of the theory of oscillations, radio physics, and radio engineering, having been one of the founders of these fields, so as soon as it was found that the modulation should exist he could of course immediately derive all the equations.

Landsberg²² wrote the following about Mandel'shtam's work: "This type of investigation had been completed by Mandel'shtam as early as 1918, although the corresponding note ('Light scattering in an inhomogeneous medium')²³ appeared much later, in 1926, by which time some of the results found by Mandel'shtam had already been published by Brillouin (1922)."²⁴ Equation (3) is referred to as the "Mandel'shtam-Brillouin equation."

The physical picture of the effect and the necessary

equations had now been found, all the necessary calculations had been carried out, and the next step was an experimental study of the predictions.

It remains unclear why Mandel'shtam, who had completely understood the effect of the modulation of scattered light by the frequencies of the acoustic branch of the dispersion curve, said nothing about modulation at the higher frequencies of the optical branch, whose effects were the first to be discovered. The same comment can be applied to Brillouin.

3. FIRST EXPERIMENTS ON MOLECULAR SCATTERING OF LIGHT

A cursory look at the origins of research on molecular scattering of light, discussed in part in the preceding section of this paper, shows that the most important achievement at this stage was the determination of the physical nature of the optical inhomogeneities which led to light scattering. These inhomogeneities of the refractive index were caused by fluctuations of various origins. The fluctuational origin of optical inhomogeneities and the theoretical progress pointed out a clear direction for laboratory experiments, in the interior of pure substances and at the interfaces, and they later led to spectroscopic investigations in various media. The first quantitative experiments on scattered light refer to the pure atmosphere of the Earth. They were carried out by Cabannes (1915), Dember (1916), Strutt (1918), and Wood (1920). These measurements yielded Avogadro's number, through the use of the Rayleigh equation for the light intensity, which follows as a particular case from the Einstein equation for liquids. In laboratory experiments, spectrally undecomposed light scattered by gases and condensed media was studied by Cabannes in France, Strutt in England, Martin in the US, Raman in India, and by Gans in Germany. Also in Germany, in the laboratory of F. Braun, experiments were carried out by Mandel'shtam¹⁸ on light scattering at the interface between two media and near the critical mixing point of solutions.

A detailed description of the results goes beyond the scope of the present paper. Here it is important to emphasize that the earlier work had established a significant depolarization of scattered light in liquids, which are, on the whole, isotropic media. The light scattered by density and concentration fluctuations is completely linearly polarized, so the depolarization of the scattered light meant that a significant part of the scattered light was light scattered because of anisotropy fluctuations. It was not a simple matter to calculate the corresponding intensity. This calculation was first carried out by Leontovich²⁸ in 1941, and the work was developed by Rytov.²⁹ The depolarized-scattering spectrum was found simultaneously by Cabannes and Daure¹¹ and Raman and Krishnan³⁰ in 1928, after the discovery of combinational scattering. Here we wish to emphasize two points: while the spectrum of polarized scattering in a liquid is confined to a spectral interval $\sim 1 \text{ cm}^{-1}$ (30 GHz), the width of the depolarized spectrum can exceed 300 cm^{-1} (9000 GHz). The de-

polarized light scattered by many ordinary organic liquids is more intense than the polarized scattering: by a factor of five in liquids such as nitrobenzene and a factor of two in benzene. The difference is less in other cases.

Study of molecular scattering of light in the Soviet Union began after 1925, at Mandel'shtam's initiative.

Mandel'shtam began his scientific activity in the laboratory of F. Braun in Strasbourg, working initially in radio physics and the theory of oscillations and later in optics. This work earned Mandel'shtam an international reputation. After the Strasbourg period, he worked in Odessa at the Polytechnical Institute and then in Leningrad at the Central Radio Laboratory. In 1925 he was invited to work at Moscow State University (at the time, the First Moscow State University), where he began to teach and do research in the Department of Physics and Mathematics. G. S. Landsberg had been working in this department since 1923 on certain aspects of photometry and questions related to solar eclipses.

The collaboration between Mandel'shtam and Landsberg began the moment Mandel'shtam arrived in Moscow, and it continued essentially to Mandel'shtam's death in 1944. Landsberg became not only a colleague but also a friend of Mandel'shtam. For the first joint effort, Landsberg and Mandel'shtam formulated a problem for studying the spectrum of molecular light scattering in solids. Solids were chosen because it was believed that the damping of high-frequency elastic waves in liquids would be severe [Eq. (2)]. Beginning at this time, Landsberg carried most of the burden of experimental work in this field, which was perhaps the most difficult field in experimental optics at the time.

The immediate purpose of this work was to detect displaced components of spectral lines due to a modulation of the scattered light by the thermal elastic waves which had been predicted by Mandel'shtam back in 1918.

The problem was difficult for several reasons. First, the magnitude of the displacement, $\Delta\nu$ [Eq. (3)], is proportional to the ratio of the sound velocity to the speed of light, i.e., of the order of $10^{-5}\nu$. It was very difficult to detect a frequency change of one-thousandth of 1%, but not absolutely impossible. The second difficulty was that the intensity of the light scattered by a good crystal was expected to amount to only a small fraction of the intensity of the primary light (a relative intensity of the order of 10^{-8}), and it was necessary not only to detect but also to study the spectrum of this light. Finally, no one knew at the time whether it would be possible to find a crystal, or even a region of a crystal, in which most of the scattered light would be molecular scattering, rather than parasitic scattering due to various inclusions or various other defects. The first sample chosen for study was crystalline quartz, which is very common in nature and which has excellent optical properties. At the time, very little study had been made of this crystal, but even so there was

already a fair amount of confusion. The first physicist to study light scattering in quartz had been Strutt.²⁶ He reached the conclusion that the scattered light which he observed was due to impurities. In a brief note in *Nature*, Raman²⁷ asserted that Strutt's data referred to molecular scattering. The first task was thus to reliably determine the actual relationship between the parasitic light and the molecular scattering in a good quartz crystal. This problem was resolved by Landsberg, in work beginning in 1926. In the Soviet Union at that time there was no optical instrumentation industry, and nobody needed quartz crystals (perhaps some might be found in the Mineralogical Museum).

The investigators were thus confronted with a serious problem: to find a quartz single crystal of good quality. Landsberg and Mandel'shtam knew that former families of Russian nobility had not only their own coats of arms but also their own seals, which were generally made of the better-quality pieces of rock crystal, in other words, crystalline quartz. It is difficult to trace the movements of these quartz seals, but they ended up in antique shops and pawn shops. That was where Landsberg looked for them and bought them, raising a few eyebrows among the salespeople and others who might see his purchases. (Who needed these crystal seals, especially someone else's?) Landsberg had to keep on shopping, however, because it was only after he returned to the laboratory, placed his most recent purchase in immersion fluid, and illuminated it with an intense light beam in a dark room that he was able to make out the coarse defects. Putting this unsuccessful purchase aside, he continued his search and purchases. All these purchases, of course, were at his own expense. One of these seals, which was not used, is shown in Fig. 1. Landsberg's career as a "collector" had its share of irritating misadventures. Some dishonest tradesmen had furnished their clients glass seals instead of the quartz seals paid for. As long as the seal was not cracked by the hot sealing wax, its owner would never suspect that it was made of glass. In the laboratory, the question could be resolved quickly, but in a shop it was not possible to distinguish quartz from glass, and Landsberg suffered some annoying losses for this reason. If these sharp dealers could have known what injury they would be inflicting on science in general and on the personal finances of



FIG. 1. Photograph of one of the many quartz seals acquired by G. S. Landsberg. Seals of this type were used to prepare samples for experiments on molecular scattering of light. (Photo by L. V. Sukhov)

one scientist in particular, they might have acted differently. At any rate, several suitable seals were ultimately found, and samples were cut from them for study.

The first quantitative results on the study of light scattering in quartz were reported by Landsberg to the Fifth All-Russian Congress of Physicists in late 1926. In 1927 Landsberg published two papers in *Zeitschrift für Physik*.³¹ The basic result of this work was Landsberg's determination, on the basis of a study of the temperature dependence of the scattering intensity, that, in the better samples, only 25% of the scattered light was independent of the temperature and thus due to foreign inclusions, while the other 75% was a linear function of the temperature and by implication the result of molecular scattering. At this point it became possible to start the spectroscopic experiments; suitable samples were already available. In 1927, Landsberg and Mandel'shtam started their spectroscopic work on molecular light scattering in the better quartz samples at their disposal.

While this extremely important work was going on, Landsberg and his students and colleagues continued their study of molecular scattering in quartz³² and rock salt³³ crystals. They measured the absolute intensity of molecular scattering in these substances, and later they also made an experimental study of light scattering in a nonuniformly heated solid.³⁴

4. FIRST OBSERVATIONS AND FIRST INTERPRETATIONS OF THE NEW EFFECT

As we have seen, already by 1927 Landsberg had suitable quartz samples and could begin spectroscopic study of the scattered light. His second paper reached the editorial office of *Zeitschrift für Physik* on August 10, 1927, so the second half of this year was free for spectroscopic work. As mentioned in the Introduction, the goal of the first spectroscopic experiments was to detect spectral components which were shifted from the exciting line and which were due to a modulation of the scattered light by thermal elastic waves—the effect predicted by Mandel'shtam.

Landsberg and Mandel'shtam began their preliminary experiments with a study of the spectrum of the light scattered in two quartz samples. One of the quartz samples exhibited fluorescence, while the other did not. The scattered light was excited by light from a mercury lamp (Heareus, 110 V) and analyzed with a quartz spectrograph (Fuess, Model B).

Near several lines, after long exposures, they observed additional lines, or satellites, which were not in the spectrum of the exciting light. These satellites were particularly apparent near the most intense resonant line of the mercury spectrum, $\lambda = 2536 \text{ \AA}$. The shift of these satellites was much larger than that expected on the basis of modulation of the scattered light by thermal elastic waves. The experimental results were unexpected and surprising. It was necessary to prove that the observed satellites were real. At the beginning, only the "red" or "Stokes" satellites,

which are strong, were observed in exposures of 15 h.

Many experiments of various kinds were carried out. They proved that the experimentalists were dealing with real spectral lines, rather than spurious signals produced by the many reflecting surfaces of the optics system used. Finally, Mandel'shtam and Landsberg felt it necessary to carry out a decisive experiment. In the path of the scattered light before the spectrograph they placed a resonant filter: a quartz vessel filled with nonemitting mercury vapor. By adjusting the temperature, they found the density at which the light in the resonant line was completely absorbed after passing through the entire length of the filter. When this resonant filter was then placed in the path of the scattered light, the light corresponding to the resonant line would be completely removed, leaving only the light at the new wavelength.

This experiment was carried out, and the satellites remained. All these many, tedious, and complicated (especially at the time) experiments convinced Landsberg and Mandel'shtam that they were dealing with real additional spectral lines and thus a new optical effect. They had spent a lot of time on the subject, but they did not begrudge the time spent to prove that the effect was authentic. As soon as this new effect had been firmly established, it was correctly understood by Landsberg and Mandel'shtam, and their simple quantum explanation of the effect remains valid today, as does their original classical interpretation, which they offered somewhat later.

Figure 2a (see insert) shows a print made from an original spectrogram which has been preserved. The negative was obtained on February 23-24, 1928. All the writing on the negative is Landsberg's handwriting. To allow for the possibility of imperfect reproduction of the original photograph in the present article (on the long-wavelength side of the fundamental resonance line, $\lambda = 2536 \text{ \AA}$, a satellite is clearly visible on the spectrogram of the scattered light at an exposure time of 15 h), we also show a microdensitometer trace (prepared recently) of a part of the spectrum including $\lambda = 2536 \text{ \AA}$ for the scattered light (exposure of 15 h) and a reference spectrum (the light from a mercury lamp scattered by black velvet, with an exposure time of 3 sec) (Figs. 2b and 2c).

Landsberg and Mandel'shtam understood and stated the reason for the observed effect. It results from a modulation of the scattered light, not by thermal elastic waves, as expected, but by the higher-frequency infrared vibrations of the material. Synchronized with the infrared vibrations of the nuclei of molecules of the crystal lattice there a deformation of the electron cloud occurs, which leads to a periodic change in the polarizability and thus in the electric moment induced by the light wave. If the time-dependent part of the incident light wave, of frequency ν , is written $E = E_0 \cos \nu t$, the induced moment in the simplest case, in which the system has a single vibration frequency, is

$$P = \alpha(\nu) E_0 \cos \nu t, \quad (4)$$

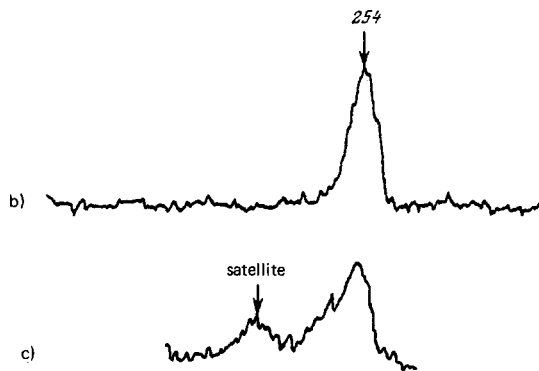
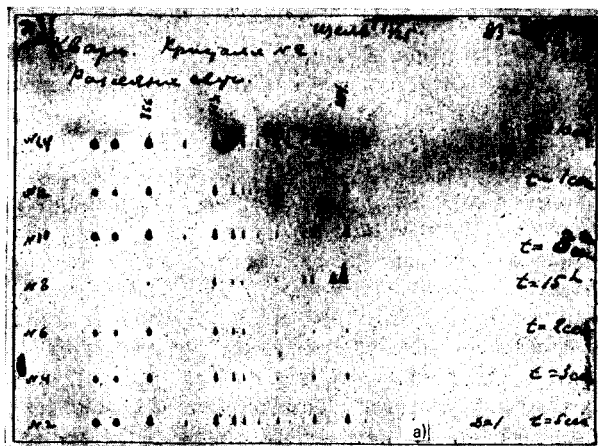


FIG. 2. a: Spectrogram of the scattered and exciting light obtained by G. S. Landsberg and L. I. Mandel'shtam on February 23-24, 1928 [seen on the spectrogram of the scattering light (No. 8) with the exposure of 15 h is the Stokes satellite to the left of the Rayleigh-scattering line, above which "254" is written. Above it is the spectrum of a mercury arc reflected from velvet. The print was made from the original spectrogram by L. V. Sukhov]. b: Microdensitometer trace of the spectral line of the exciting light at $\lambda = 2536 \text{ \AA}$. c: Microdensitometer trace of the spectrum of the scattered light, made by A. A. Sychev (the prints and the microdensitometer traces were prepared for the present paper. [Translator's note. The Russian words in the top left corner of the spectrogram are "Quartz Crystal No. 2. Light scattering." The word at the top center of the spectrogram is "slit." The units for the exposure times at the right are seconds, except in the fourth row, where the units are hours.]

where $\alpha(q)$ is the polarizability as a function of the coordinates of the elements of the vibrating system. In general, this is a tensor quantity. Ignoring the subtle features stemming from the tensor nature of $\alpha(q)$ and, for example, from a possible rotation of the molecule, we assume that $\alpha(q)$ can be written in the following form as the result of infrared sinusoidal vibrations of the system with small deviations from $q = 0$:

$$\alpha(q) = \alpha(0) + \frac{\partial \alpha}{\partial q} q_0 \cos(\nu' t + \varphi), \quad (5)$$

where φ is an arbitrary phase, which differs for the different vibrating elements (e.g., molecules), and ν' is the infrared vibration frequency of the system.

Substituting (5) into (4), and carrying out the elementary trigonometric manipulations, we find

$$P = \alpha(0) E_0 \cos \nu t + \frac{1}{2} \frac{\partial \alpha}{\partial q} q_0 E_0 \{ \cos[(\nu + \nu') t + \varphi] + \cos[(\nu - \nu') t - \varphi] \}. \quad (6)$$

Since the radiation of secondary waves or, more simply, the light scattering is governed by the induced moment P , the light at the original frequency, ν , will be accompanied in the scattered light by light at new frequencies: $\nu + \nu'$ and $\nu - \nu'$. For a system which has i vibration frequencies, this result is easily generalized, and it immediately becomes clear that satellites with frequencies $\nu \pm \nu_i$ should appear in the scattered light.

This was essentially the explanation given by Landsberg and Mandel'shtam for the effect which they observed. We also note that since the phase φ is arbitrary the radiation by the various molecules or the various parts of the system will be incoherent.

It follows from the early papers by Raman and Krishnan⁶⁻⁸ and Raman's inaugural address to the South Indian Science Association¹⁴ that these investigators were seeking scattered light at a shifted frequency

under the assumption that an optical analog of the Compton effect should exist.²⁾ In his speech, Raman told how Dr. Ramanathan and Mr. Krishnan had studied 80 different liquids and, in their opinion, had found a faint luminescence in all of them. Raman stated that, "... a powerful impetus to further research was provided when I conceived the idea that the effect was some kind of optical analogue to the type of x-ray scattering discovered by Professor Compton, for which he recently received the Nobel Prize in Physics. I immediately undertook an experimental re-examination of the subject in collaboration with Mr. K. S. Krishnan..."

This was the specific concept which led the Indian physicists to search for a new type of radiation with a new frequency.

To let the reader reach his own conclusions regarding the earliest steps, the first results, and the first explanations of the observed effect, we consider it to be useful to reproduce here the complete texts, translated into Russian by the author of the present article, of the first brief reports of the Soviet and Indian physicists. These brief reports have never before been published in Russian translation. The report by Landsberg and Mandel'shtam¹ dated May 6, 1928, appeared in the

²⁾ The Compton effect can be summarized as follows. In the scattering of x rays, photons of both the original energy and of a lower energy can be detected in the scattered flux. In the case of scattering by light elements (aluminum, boron, carbon, paraffin, etc.), i.e., in the case of essentially free-electron scattering, the increase in the wavelength is independent of the substance but dependent on the scattering angle θ . This increase is

$$\Delta \lambda = 2 \Delta \lambda_0 \sin^2 \frac{\theta}{2},$$

where $\Delta \lambda_0 = 0.021 \text{ \AA} = h/m_0 c$. In an "optical analog" of the Compton effect we should thus expect the wavelength change to be smaller by a factor of thousands.

German journal *Naturwissenschaften* dated July 13, 1928. Here is its text (translated from the Russian text appearing in Fabelinskii's review rather than directly from the original German of Ref. 1).

A NEW EFFECT IN THE SCATTERING OF LIGHT IN CRYSTALS

In a study of the molecular scattering of light in solids which we undertook in order to determine whether there is a change in wavelength, as could be expected on the basis of the Debye theory of specific heats, we found a new effect, which we believe will be of definite interest.

This effect consists of a change in wavelength, but the change is of an order of magnitude different from what we expected, and it is of an entirely different origin.

In the experiments, an intense light beam from a quartz mercury lamp was passed through a quartz crystal. The light reflected at an angle of 90° with respect to the incident beam was studied with a quartz spectrograph. The standard measures were taken to combat spurious light signals.¹ A reference spectrum was obtained by reflecting light from black velvet. The exposure time was 2-14 h.

Experiments were carried out with two different quartz samples. On all the spectrograms, all the mercury lines were accompanied by clearly defined satellites at a slightly higher wavelength. In addition, near each line we found a hint of two or three less well defined lines.

No traces of these satellites were found in the reference spectrum.

One of the spectrograms is shown in the figure.³⁾ Approximate measurements from the spectrogram show that the wavelength for the brightest satellites behaves as indicated in the accompanying table. We carried out a variety of control experiments to establish firmly that the observed lines were not due to spurious light signals.

We believe that the following experiment was decisive. Between the scattering quartz crystal and the spectrograph slit we placed a quartz vessel filled with mercury vapor, which absorbed all the light at 2536 Å. On the spectrogram we did not find this line—only the satellites.

This experiment was solid proof that the satellites were in fact at a wavelength different from that of the fundamental line.

At this point we think it is too early to give a definite explanation of the observed effect.

One of the possible theoretical explanations runs as follows: Certain natural infrared frequencies of quartz may be excited, at the expense of the energy of the scattered light. The energy of the scattered quantum and thus its frequency will decrease by amounts cor-

³⁾(Note added by ILF:) This spectrogram is not reproduced here, because important details would likely be lost in the reproduction. See instead Fig. 2 (on insert).

TABLE I.

$\lambda, \text{Å}$	$\Delta\lambda, \text{Å}$	
	Observation	Calculation
2536	About 30	30.8
3126	» 47	47.0
3650	» 63	64

responding to an infrared quantum. When we start from the frequency corresponding to the wavelength² $\lambda = 20.7 \mu$, we find good agreement between the calculated and measured values (see the accompanying table).

At present we cannot say how closely this effect is related to the effect described by Raman,³ because Raman's description was so brief.

G. Landsberg and L. Mandel'shtam Moscow, Institute of Theoretical Physics, First University, May 6, 1928

Note Added in Proof. More recently, we have studied light scattering in Iceland spar and have observed the same effect. The change in the wavelength is greater in this material than in quartz. The change corresponds to an infrared frequency, for which the corresponding wavelength is $\lambda = 9.1 \mu$.

¹Landsberg, G.—Zs. Phys., 1927 Bd., 43, S. 773; Bd. 45, S. 442.

²Rubens, Nichols.—Ann. d. Phys., 1927, Bd. 60, S. 418. The value $\lambda = 20.7 \mu$ is used uncorrected, since this refers to our preliminary measurements.

³Raman, C. V., Khrishnan, K. C.—Nature, 31 March 1928, v. 121, p. 501; 21 April 1928, *ibid.*, p. 619.

This note was followed immediately by a brief note in the journal *Zhurnal Russkogo Fiziko-Khimicheskogo Obshchestva*, dated May 10, 1928, i.e., four days after the note given above. In this second note we now find a clear assertion: "The analogy with the Compton shift (in the red direction) is striking, but the mechanism for the change in wavelength should, in all probability, be different." Then the interpretation given in the first note was repeated. The phrasing used by Landsberg and Mandel'shtam reflects their extreme caution in discussing the nature of this new effect. This caution is seen in all their papers. But we know perfectly well that if they said that "...the mechanism...should, in all probability, be different" and then went on to say precisely what this mechanism should be, there can be no doubt that they had more than enough evidence to support their interpretation and that their assertions, even in this form, would always stand up. This particular case was no exception. Here they not only used the words ("...the mechanism...should, in all probability, be different") but also gave a table of the observed and calculated frequencies of the infrared vibrations, which were in good agreement, and which even today do not require any important corrections.

We will now reproduce the text of the first brief report by C. V. Raman and K. S. Krishnan,⁶ dated February 16, 1928, which was published in *Nature* on March 31, 1928.

A NEW TYPE OF SECONDARY RADIATION

If we assume that the x-ray scattering of the 'unmodified' type observed by Professor Compton corresponds to the normal or average state of the atoms and molecules, while the 'modified' scattering of altered wavelength corresponds to their fluctuations from that state, it would follow that we should expect also in the case of ordinary light two types of scattering, one determined by the normal optical properties of the atoms or molecules, and another representing the effect of their fluctuations from their normal state. It accordingly becomes necessary to test whether this is actually the case. The experiments we have made have confirmed this anticipation, and shown that in every case in which light is scattered by the molecules in dust-free liquids or gases, the diffuse radiation of the ordinary kind, having the same wavelength as the incident beam, is accompanied by a modified scattered radiation of degraded frequency.

The new type of light scattering discovered by us naturally requires very powerful illumination for its observation. In our experiments, a beam of sunlight was converged successively by a telescope objective of 18 cm. aperture and 320 cm. focal length, and by a second lens of 5 cm. focal length. At the focus of the second lens was placed the scattering material, which is either a liquid (carefully purified by repeated distillation *in vacuo*) or its dust-free vapour. To detect the presence of a modified scattered radiation, the method of complementary light-filters was used. A blue-violet filter, when coupled with a yellow-green filter and placed in the incident light, completely extinguished the track of the light through the liquid or vapour. The reappearance of the track when the yellow filter is transferred to a place between it and the observer's eye is proof of the existence of a modified scattered radiation. Spectroscopic confirmation is also available.

Some sixty different common liquids have been examined in this way, and every one of them showed the effect in greater or less degree. That the effect is a true scattering and not a fluorescence is indicated in the first place by its feebleness in comparison with the ordinary scattering, and secondly by its polarisation, which is in many cases quite strong and comparable with the polarisation of the ordinary scattering. The investigation is naturally much more difficult in the case of gases and vapours, owing to the excessive feebleness of the effect. Nevertheless, when the vapour is of sufficient density, for example with ether or amylene, the modified scattering is readily demonstrable.

C. V. Raman, K. S. Krishnan, 210 Bowbazar Street, Calcutta, India, February 16.

In this first work of Raman and Krishnan, the scattered light was excited by a continuous spectrum (sunlight), glass filters were used for the spectral study, and the observations were visual. Naturally, in this experiment, in which white light was used to excite the scattering, no additional spectral lines were observed, and none could have been observed. Further-

more, it is now a well-established fact that the sum total of combinational scattering in a liquid amounts to a few percent of the Rayleigh scattering. Estimates³⁶ show that the actual figure is ~3% for pentane and hexane and ~2% for heptane and octane. We should expect roughly the same values for other liquids. Since the coefficient for Rayleigh scattering in liquids is usually of the order of 10^{-5} – 10^{-6} cm^{-1} , the coefficient for combinational scattering must be of the order of 10^{-7} – 10^{-8} cm^{-1} . In other words, combinational scattering is produced by only 10^{-8} of the exciting light. Raman and Krishnan were indeed brave to assert that the light they observed was radiation of an altered frequency (a new type of secondary radiation), and not luminescence, not the wing of the Rayleigh line (mentioned above), and, finally, not a consequence of an imperfection of fluorescence of the filters themselves—all this on the sole basis of their first experiment,⁶ in which the observations were only visual observations, and glass filters were used.

Incidentally, the intensity of combinational scattering in quartz is more than 30% of the Rayleigh intensity.

In a second note,⁷ dated March 8, 1928, and published in the April 21 *Nature*, Raman stated that light from a mercury lamp was used as well as the continuous sunlight spectrum to excite the scattered light, and he asserted that new lines had been observed with a spectroscope. In this note he says, "The preliminary visual observations appear to indicate that the position of the principal modified lines is the same for all substances, though their intensity and that of the continuous spectrum does vary with their chemical nature." This note reported that the spectra were being photographed and measured.

This constancy of the positions of the shifted lines from one substance to another could be taken as evidence supporting the authors' idea of an optical analog of the Compton effect. In the first study by Landsberg and Mandel'shtam,¹ on the other hand, the measurements showed that the positions of the altered or shifted lines observed experimentally for different materials were very sensitive to the nature of the material (quartz and Iceland spar). In this second note,⁷ Raman concluded "... that the radiations of altered wavelength from neighbouring molecules are coherent with each other," but combinational scattering is incoherent, as mentioned above, and this incoherence is an important aspect of the new effect. These two notes by Raman in *Nature* were cited in the first paper by Landsberg and Mandel'shtam.¹ It may be precisely because in the first of these notes it was stated that shifted lines could not be observed, while in the second it was stated that the line positions were independent of the substance and that the radiation was coherent, that Landsberg and Mandel'shtam wrote, in their characteristically careful words, "At present we cannot say how closely this effect is related to the effect described by Raman, because Raman's description was so brief." This comment is also found in a paper²⁷ published in *Zhurnal Russkogo Fiziko-Khimicheskogo Obshchestva* where there is now also a reference to a third paper by

Raman and Krishnan,⁹ dated March 22, 1928, published in the May 5 *Nature*, and entitled "The Optical Analogue of the Compton Effect." At the end of this note, Raman and Krishnan stated that the position of the shifted lines depends on the substance and that the magnitude of the shift is far larger than in the Compton effect with x rays. They noted that the shift "... is of the same order of magnitude as the frequency or the molecular infra-red absorption line." The title of the paper and certain of the statements in it are nevertheless confusing. Raman and Krishnan were still talking about an optical analog of the Compton effect, while Landsberg and Mandel'shtam¹⁻⁵ believed that the explanation should be different, and offered a different explanation.

The next paper by Landsberg and Mandel'shtam,⁴ a long paper submitted to *Zeitschrift für Physik* and dated July 9, 1928, contained a thorough description of the apparatus, the detailed results of a study of the combinational scattering spectra in quartz and Iceland spar crystals, and a very clear explanation of the effect, based on the elementary quantum-mechanical arguments set forth briefly in Ref. 1. In the experiments described in this paper, the spectrograph slit was much narrower, and the exposure time was increased to 100 h. As a result, five groups of combinational lines, with a total of 82 lines, were observed in quartz, while two groups (18 lines) were observed in Iceland spar. All the quantitative data were summarized in seven tables. All the observed lines were measured very carefully, and the rule $\Delta\nu = \text{const}$ was confirmed. In the text of the paper is the following interesting comment regarding the overall picture of the effect. "We established the following result, which we believe is extremely important. In addition to the 'red' satellites there are also 'violet' satellites in the scattered light. The positions of the red and violet satellites are symmetric with respect to the fundamental lines, but the violet satellites are much fainter and can be clearly identified only for the most intense of the fundamental lines." They also give an explanation for the overall picture of the effect, based on elementary considerations, but still perfectly rigorous, so that this explanation remains equally valid today.

"It clearly follows from the tables that each system of satellites is characterized by a constant frequency difference with respect to the corresponding fundamental lines.

In terms of the theory of light quanta, which is extremely convenient here, this assertion is known to have the following meaning.

If $h\nu$ is the energy of the incident quantum and $h\nu'$ is that of the scattered quantum, then $h\nu - h\nu'$ is the energy transferred to the crystal. Since this energy is constant for each system of satellites, it can be assumed that we are dealing with the excitation of some natural vibration mode of the crystal, with a frequency

$$\nu_i = \nu - \nu'. \quad (1)$$

If, on the other hand, the natural vibration mode transfers a quantum to the incident light, we would

have a violet satellite, and Eq. (1) would be written $\nu' - \nu = \nu_i$. For the entire set of satellites we thus have the relationship $\nu' = \nu \pm \nu_i$. Incidentally, this conclusion agrees with arguments advanced many years ago by Smekal,³⁷ regarding the scattering of light by individual molecules.

The theory of Kramers and Heisenberg³⁸ is known to lead to the same frequency relations. In our case the effect may be due partially to natural vibration modes of atomic complexes and partially to lattice vibrations."

In summary, it can definitely be concluded that in the first half of 1928 Landsberg and Mandel'shtam had carried out a complete experimental study, that they understood their results correctly, and that their quantitative results were explained quantitatively in quite a modern manner. With regard to the frequencies and positions of the lines, the problem had been completely solved. In Ref. 4 Landsberg and Mandel'shtam discussed the intensities of the red and violet satellites and offered a correct qualitative explanation, which subsequently found quantitative theoretical development in the work of Mandel'shtam, Landsberg, and Leontovich³⁹ and in the quantum theory of Tamm.⁴⁰

These early theories led to the following equations for the intensities of the red (Stokes) and violet (anti-Stokes) satellites:

$$I_{\text{red}} = A(1 - e^{-h\nu'/kT})^{-1},$$

$$I_{\text{viol}} = A'(1 - e^{-h\nu'/kT})^{-1} e^{-h\nu/kT},$$

where $(A/A') \sim [(\nu - \nu')/(\nu + \nu')]^4$. It follows from these equations that as the temperature approaches absolute zero the intensity of the red satellite approaches some constant limit, while that of the violet satellite approaches zero, and the ratio of the satellite intensities is

$$\frac{I_{\text{red}}}{I_{\text{viol}}} = \frac{A}{A'} e^{h\nu/kT}.$$

This relationship was verified experimentally by Landsberg and Mandel'shtam, but this took place in the following year, 1929, and we should perhaps restrict the discussion here to the experimental work of the initial stage, which was published in 1928.

Raman and Krishnan published several other papers in this first stage. One of them, entitled "The Negative Absorption of Radiation," was published in *Nature* on July 7, 1928 (Ref. 9). In this work Raman and Krishnan observed the violet satellites of combinational scattering. They discussed these violet satellites as a manifestation of "negative absorption" in the sense in which Einstein used this phrase in the paper devoted to deriving the Planck equation.^{42,43}

Today, with negative absorption used so widely in laser science and technology, there is no point in discussing in detail the confusion which was caused at the time, especially since the incorrectness of this assertion by Raman has been pointed out elsewhere.⁴¹

It is difficult for us to determine just when Raman stopped asserting that he had found an optical analog of the Compton effect, and it is difficult to say whether he reached this conclusion independently or was influ-

enced by the papers of the French authors, by other papers, or by some other factors, but already in his papers in *Nature* on July 7, 1928, and later he gave the observed effect the same explanation as given by Landsberg and Mandel'shtam and by the French authors in their papers in *Comptes Rendus*, about which we will have more to say later. In a subsequent publication of a speech⁴⁾ by Raman in the *Indian Journal of Physics* we already find the outline of a correct explanation of the effect, and we find that frequencies had been measured and detailed tables had been compiled on the basis of an extensive study of several organic liquids (the work was particularly thorough in the case of benzene).⁴⁴ In Raman's speech,¹⁴ in the part where he was talking about his experiments with Krishnan seeking the new type of radiation, he said that "... the new type of secondary radiation is also observable in crystals such as ice, and in amorphous substances."

We have already mentioned that this research was carried out completely independently in India and the Soviet Union, without any exchange of information.

When the first papers by Landsberg and Mandel'shtam appeared, however, Raman wrote a letter to Mandel'shtam. Since this letter is unique and constitutes the entire correspondence between the two groups, it is useful to present its text here.

The letter was typewritten on Raman's personal stationary and dated August 7, 1928. After the standard greeting, Raman wrote as follows (since the original letter was unavailable to the translator, the editor has retranslated the passage from the Russian text).

"My attention has been brought to two recent papers on light scattering in crystals which you have published together with Dr. Landsberg in *Naturwissenschaften* on July 13, 1928, and in *Comptes Rendus* on July 8, 1928, which were received in Calcutta in the last mail delivery. In *Naturwissenschaften* I found a reference to two letters to the editor of *Nature* in which the discovery of a new type of secondary radiation and its spectral composition were reported from Calcutta. But in none of your communications have I found any mention of my speech of March 15, 1928, entitled "A New Radiation" and published in the *Indian Journal of Physics*. In this speech, which was published on March 31, 1928, the phenomenon of a change of wavelength upon scattering in crystals was clearly described and explained. Your University library regularly receives the *Indian Journal of Physics* by exchange, and over the past three months this paper has been cited several times by Cabannes and Daure and other authors who had published in *Comptes Rendus* and with whose articles you are evidently familiar. Therefore the absence of any reference to prior publication of the discovery of this effect in crystals, made in Calcutta, is somewhat unexpected. I trust that this omission will

⁴⁾ In a note in Ref. 14 it is stated that this speech had been published in a separate pamphlet on March 31, 1928. The author of the present paper had no opportunity to examine this pamphlet.

be corrected in your future publications on the subject.

Thanking you in advance, Respectfully yours,
C. V. Raman."

The papers by the French authors which Raman mentioned in his letter to Mandel'shtam, and which we mentioned in the Introduction to the present paper, are of considerable historical interest. It follows from Rocard's paper,¹² submitted on April 23, 1928, that it had been clear to Rocard for a long time before the experimental detection of this effect that the effect should exist. Working theoretically, Rocard reached the conclusion that the vibration of a molecule should modulate the scattered light, and he stated directly that if the modulation by a molecule could be described by $A[1 + \epsilon \sin(\alpha t + \varphi)]$, and if the light wave could be described by $\sin \omega t$, then the scattered light would contain, in addition to the frequency ω , the frequencies $\omega + \alpha$ and $\omega - \alpha$. Rocard also stated that there should be a frequency change in the scattered light because of rotational motion of molecules. A week later, on April 30, there was a paper by Cabannes¹⁰ in *Comptes Rendus* in which Cabannes also reported that since 1924 he had been trying to observe combinational light scattering but had not been successful. To support his arguments that such an effect should exist, he gave precisely the same arguments and equations as Rocard.¹²

Cabannes explained the reason for his lack of success by the fact that he was working with gases, for which the scattering intensity is so low as to be undetectable. With the appearance of the first papers by Raman and Krishnan,^{7,8} however, with reports of new lines and a discussion of them as an optical analog of the Compton effect, Rocard and Cabannes realized immediately that the effect in question was the one which they had predicted and which one of them had unsuccessfully sought.

In a later paper¹¹ in the June 4, 1928, *Comptes Rendus* Cabannes and Daure reported a study of combinational light scattering. Using a Fabry-Perot interferometer, they detected the wing of the Rayleigh line. This study led Landsberg and Mandel'shtam to state that their own observations and those of Raman and Krishnan were of basically the same effect. Landsberg and Mandel'shtam wrote,⁴ "It is extremely likely, especially in view of the observations recently reported by Cabannes and Daure,¹¹ that it is basically the same effect which is involved in the two cases."

Everything, or nearly everything, had thus been clarified. A new effect had been discovered and explained, but in all these questions which were studied theoretically and experimentally there were some very unusual circumstances, not characteristic of other important discoveries. The usual course of events is that either 1) an effect is predicted theoretically, and the prediction is then used to design a special experiment, in which the effect is observed (this was the case, for example, in the discovery of the positron or the deflection of a light beam in the gravitational field of a massive object), or 2) an unexpected experimental discovery is made, and a theoretical explanation is

subsequently found for it (for example, the Zeeman effect or the discovery of the wavelike properties of the electron).

The course of events in the case of combinational scattering does not fit either of these scenarios. As it turned out, the theoretical predictions of the new effect, made many years before its actual discovery, had absolutely no influence on the discovery.

The first prediction of this new effect—combinational scattering of light—was offered by Smekal³⁷ (1923) on the basis of quantum-mechanical considerations. Credit for the complete quantum-mechanical theory goes to Kramers and Heisenberg,³⁸ whose paper appeared two years later. It turns out that none of the people who were doing experiments on light scattering paid any attention to these theoretical papers. It is impossible to understand why this happened in the various countries. One possible explanation is that Landsberg and Mandel'shtam were seeking another effect, involving modulation of the scattered light by thermal elastic waves, while Rocard, Cabannes, and Daure were seeking scattered light modulated by vibrations of nuclei in molecules. As was mentioned earlier, combinational scattering can be predicted and understood on the basis of classical arguments, if the modulation mechanism is used, and from the start the experimentalists ignored the existing quantum-mechanical theories of the effect, although as their work progressed they of course mentioned the work by Smekal, Kramers, and Heisenberg (see, for example, Ref. 4).

Raman and Krishnan were caught up in a search for an optical analog of the Compton effect, and they also turned their attention to the quantum-mechanical theory only after the effect had already been discovered. Once the effect had been explained from the classical and quantum standpoints, the theoretical and, especially, experimental work began to accelerate at an unusually high rate. The reader is referred to the comprehensive monographs^{35, 45-50, 55, 69, 70} for information on the development of this field or of only some of its aspects.

A question naturally comes to mind: what happened to the effect (the modulation of scattered light by thermal elastic waves) which Landsberg and Mandel'shtam were looking for when they began their work?

Their discovery of combinational scattering of course distracted them from their original problem, and it was only two years later that they returned to it. The apparatus at their disposal was not suited to the problem, and even the use of a resonant mercury filter failed to improve the chance of success, but the work was begun and pursued energetically. The desire to use apparatus more suitable for the problem brought Landsberg and Mandel'shtam to appeal to Leningrad, to D. S. Rozhdestvenskii, who had high-resolution spectroscopes. Rozhdestvenskii immediately grasped the importance of the problem, and he assigned a Michelson echelon grating and the young scientist E. F. Gross to the resolution of the problem (see Ref. 51 for more details). Work continued in Moscow and

Leningrad and met with complete success. Landsberg²² has written the following: "The principal experimental difficulty was that the scattered light was extremely faint, so that it was extremely difficult to use high-resolution spectroscopic equipment. Nevertheless, the expected effect, a modulation of the appropriate order, was observed in experiments by L. I. Mandel'shtam and the present author. The effect was even better observed in experiments by E. F. Gross,⁵² carried out at our suggestion." The development of this field, primarily by Mandel'shtam and M. A. Leontovich, laid the foundation of an entire new field of molecular acoustics (see, for example, Ref. 25).

5. FIRST COMMENTS ON THE DISCOVERY OF THE NEW EFFECT

The importance of the discovery of combinational scattering was immediately recognized by many physicists. The discovery attracted much interest in many countries, and a major effort was undertaken to pursue the study of the effect.

Naturally, there was also much interest in the initial stage of the research and in its history.

Some people who were at the time working along with Landsberg and Mandel'shtam in the laboratory have orally stated that the first lines corresponding to this new effect had been observed earlier, in the fall of 1927, but that the investigators feared that they were seeing possible parasitic reflections in the optical system. Mandel'shtam apparently did not consider these first observations to be convincing enough to be labeled the beginning of the discovery of the new effect, as can be seen from correspondence between Mandel'shtam and O. D. Khvol'son which began in December 1928. On a postcard dated December 7, 1928, Khvol'son wrote Mandel'shtam, "Please inform me whether you gave a report (in Moscow) on the new effect of light diffusion before May 6 of this year, and if so, on what day." On the same card, Khvol'son congratulated Mandel'shtam "on the well-deserved honor of election to the Academy." Without waiting for a reply, but having received from Mandel'shtam copies of the papers in which he was interested, Khvol'son sent another card, on which he asked another question: "Could you specify when you first saw the new lines? I am writing a paper, and this information would be very important for me."⁵³

In his first letter, dated December 14, 1928, Mandel'shtam thanked Khvol'son for the congratulations, and wrote "I myself have not presented a paper in Moscow. G. S. Landsberg gave a report on the new effect of light diffusion, based on our joint work, on

⁵³ The "paper" to which Khvol'son was referring was apparently a section which he was writing for the second edition of his book *Contemporary Physics*.⁵³ In a preface to the second edition Khvol'son wrote, "I have added two articles, "A clue to the nebular question" and "The effect of Raman, Mandel'shtam, and Landsberg." Another possibility is that Khvol'son was referring to Ref. 54.

April 27 of this year, at an optics colloquium at the Institute of Physics of the People's Commissariat of Public Health."

In a letter dated December 18, 1928 Mandel'shtam responded to the second postcard from Khvol'son and the other question on it: "With regard to your further question I can report the following. We first noted the appearance of the new lines on February 21, 1928. On a negative from an experiment of February 23-24 (exposure time of 15 h), the new lines were clearly visible. Our apparatus had a low transmission, so we decided to switch to a higher-transmission apparatus to pursue the study. For various extraneous reasons, our work was delayed. Really good negatives were obtained using the new apparatus in mid-April. From these photographs we established the rule $\Delta\nu = \text{const}$ for the various fundamental lines, and we determined the relationship between $\Delta\nu$ and the infrared frequency of quartz."⁶⁾

Figure 2 shows a copy of the spectrogram from the experiment of February 23-24, 1928, cited by Mandel'shtam.

Raman, at the end of his speech,¹⁴ stated, "The line spectrum of the new radiation was first seen on the 28th February, 1928. The observation was given publicity the following day."

Landsberg and Mandel'shtam were thus perfectly justified in writing,⁴ "...we observed the appearance of satellites in the scattered light in quartz before the publication by Raman and Krishnan,^{6-8,59} who described a change in the wavelength in light scattered by certain vapors and liquids."

In the second and all later editions of his book *Contemporary Physics*, Khvol'son⁵³ wrote, after a lengthy introduction, "We can now turn to a description of a remarkable new optical effect which was discovered in early 1928. This discovery was made approximately simultaneously, and of course independently, by the Indian physicist C. V. Raman and his student K. S. Krishnan, working in Calcutta, and our own professors L. I. Mandel'shtam and G. S. Landsberg, working in Moscow. Raman promptly published a report of his discovery (on March 31). He had observed the new effect in various liquids. The Russian scientists, unfortunately, were in no hurry to report their discovery of the effect, which they studied in crystalline quartz and calcite, i.e., in solids. News of discovery reached print only in July." Khvol'son adds this comment "If our scientists had reported their discovery promptly, the term "Mandel'shtam-Landsberg effect" would probably have become preserved in science forever." Khvol'son also made the justified comment that "...the achieve-

⁶⁾ This passage is quoted from a rough draft preserved among the personal papers of Mandel'shtam. V. Ya. Frenkel' devoted much time, at my request, to finding Mandel'shtam's answer to Khvol'son among the latter's personal papers, but the effort was unsuccessful. Judging from Khvol'son's statements in his book, he did receive an answer along the lines of the one printed here. I thank V. Ya. Frenkel' for the assistance.

ments of our Russian scientists are well known outside the country," and he then went on to outline the effect.

In 1928, the Association of Russian Physicists held its Sixth Congress, which was a brilliantly well-organized affair, primarily thanks to the efforts of A. F. Ioffe. The participants of the Congress were very representative and were many in number. Twenty-one of the four hundred participants were foreign scientists. Among the foreign guests were Born, Brillouin, Darwin, Debye, Dirac, Phol, Pringsheim, Ph. Frank, Scheel, and many others.^{5,56} Landsberg and Mandel'shtam reported the discovery of the new effect to this Congress in a paper entitled "A New Effect Accompanying the Scattering of Light." The Congress began on August 5, 1928, in Moscow and ended on August 15 in Saratov. From Moscow, the participants traveled to Nizhniĭ Novgorod (now Gor'kii), and the day after their arrival there was a large plenary session at the University. Then a steamboat took the participants down the Volga River and stopped at Kazan', where the Congress held another session. The foreign participants had special praise for the hospitality afforded them and for the major impression made on them by this old Tartar city. Continuing down the Volga, the steamboat stopped at several picturesque places. Several papers, including one by Debye and Frank, were read while the steamboat was under way. The closing session of the congress was held in Saratov. Then the participants went on a steamboat excursion to Tsarytsin (later renamed Stalingrad; now Volgograd), by train and car to Tiflis (now Tbilisi), and then home.

Enthusiastic accounts of this Congress were published by Born⁷⁾ in *Naturwissenschaften*⁵⁷ and Darwin in *Nature*.⁵⁸ These accounts paid special attention to Landsberg and Mandel'shtam's report of the new light-scattering effect.

Born wrote, "At the center of the second general session were reports by R. Ladenburg (Berlin) on an experimental demonstration of negative dispersion, by G. Landsberg and L. Mandel'shtam (Moscow) on a new effect in light scattering in quartz and feldspar crystals, and by R. Pringsheim (Berlin) on the Raman effect and bands in the infrared spectrum." He continued, "The effect discovered by Landsberg and Mandel'shtam in crystals is essentially identical to the effect observed by Raman and his colleague Krishnan in liquids. Russian physics can justly take pride in the fact that this important discovery was made by the Moscow researchers independently of the Indians and nearly simultaneously (February 20, 1928). This coincidence is one more demonstration of the international nature of our science, which now spans the entire world." In his paper, Darwin⁵⁸ also drew attention to the report by Landsberg and Mandel'shtam and men-

⁷⁾ A Russian translation of Born's report was published in the journal *Telegrafiya i telefoniya bez provodov* [Vol. 9, p. 718 (1928)]. There the Russian-speaking reader can see the impressions of this guest—one of the most eminent physicists of the twentieth century.

tioned that their discovery was made independently of Raman's research. Both these theoreticians, Born⁵⁷ and Darwin,⁵⁸ drew attention to the fact that this effect had been predicted long before its discovery on the basis of the quantum theory of Smekal³⁷ and Kramers and Heisenberg.³⁸ We have already discussed this point.

We see that the Soviet and other physicists were well informed on the research on the spectra of scattered light. This widespread familiarity with the effect, due in part to the Sixth Congress of the Association of Russian Physicists but mostly to the published papers on the subject, was achieved in the same year as the discovery: 1928. In 1929, however, the fame of this discovery continued to increase, along with the number of papers on it. In November 1919, Rutherford, who was then the president of the Royal Society, devoted much space to the discovery of the new effect in his annual report.⁶⁰ After outlining the effect and noting that groups of new spectral lines had been observed on both the low-frequency and high-frequency sides of the original line in the incident light, Rutherford wrote:

"An excellent account of these beautiful experiments was given this year by Raman and Krishnan in our 'Proceedings.' Similar effects were observed by Landsberg and Mandel'shtam by examining the light scattered by certain crystals. Such experiments are not easy, for the scattered light is very feeble, and long exposures with intense sources of light are necessary to bring out the relatively faint new lines. An examination of the results showed that the changes of frequency depend on characteristic frequencies of the molecule, connected with its vibrational states."

Rutherford went on to give a qualitative quantum-mechanical explanation for the new effect—the same as that offered by Landsberg and Mandel'shtam⁴—and also cited the theory of Kramers and Heisenberg.³⁸ Rutherford pointed out the importance of the discovery itself, and he outlined the broad range of applications. In particular, he mentioned that this new effect would make it a comparatively simple matter to find much information which could be obtained only with great difficulty by infrared absorption spectroscopy. Rutherford later expressed the thought that the new effect would find a variety of applications. "This new discovery, of great interest in itself, thus promises to open up a new field of experimental enquiry and throw valuable light on the modes of vibration and constitution of the chemical molecule. This discovery has attracted much attention, and a number of papers dealing with it have been published in all parts of the scientific world. It is naturally of great interest to consider the processes occurring in the molecule that give rise to these scattered radiations."

We believe that the comments which we have just read regarding this new effect and the value assigned to it by well-known physicists demonstrate clearly that this effect is of major scientific importance and that its discovery can be credited in equal measures to Raman and Krishnan and to Landsberg and Mandel'shtam, as was well known to the physicists and chemists of the time.

In 1930, however, the Nobel Prize in physics was awarded to Raman alone for the discovery of combinational scattering.

This outstanding achievement of Soviet physics—the discovery of combinational scattering of light by Landsberg and Mandel'shtam—has never been recognized with an international or national prize.

The discovery itself, however, has had very fortunate consequences, and we could hardly hope for a better fate for this exceedingly important discovery. We have already mentioned the various applications which this new effect found in various fields of science and the various practical applications which were found even during the lifetime of the discoverers. Beginning in 1928, after the discovery of the combinational scattering of light, Landsberg was involved in many physical problems, but his primary fields of research were the scientific and practical applications of combinational scattering. His major contributions in both fields earned him a worldwide reputation. Over the course of many years Landsberg and his students and colleagues studied the various aspects of intermolecular interactions, in particular, the hydrogen bond. The series of studies in this field serves as a standard of excellence. The most fundamental of these papers are included in the volume of his selected works.

An important field which was developed by Landsberg and his students in collaboration with his chemist colleagues is the analytic use of combinational scattering. The results obtained in this field were published in books^{61,62} during Landsberg's lifetime and after his death, and his students are still working in this field.⁶³

6. A FEW WORDS ON THE FUTURE DEVELOPMENT OF RESEARCH ON COMBINATIONAL SCATTERING

The appearance of laser light sources in the 1960's led not only to important progress in the traditional research on combinational scattering, but, more significantly, it led to the discovery and study of new effects and the development of new experimental methods.^{79,94}

Much work was carried out with gas lasers, but it was the use of high-power ruby lasers that led to the discovery of stimulated combinational scattering.

Remarkably, this new effect was also an unexpected discovery, by Woodbury and Ng.⁷¹ In experiments in which a ruby laser was Q-switched by means of a Kerr cell filled with nitrobenzene, they found not only the laser output at $\lambda = 6943 \text{ \AA}$ but also an intense directed beam at a wavelength of about 7500 \AA . An investigation soon revealed that stimulated combinational scattering was occurring in the nitrobenzene and that the additional radiation corresponded to a line of thermal⁸⁾

⁸⁾ Ordinary combinational scattering is frequently called "spontaneous" scattering, by analogy with the spontaneous emission of atoms and molecules, to distinguish it from stimulated combinational scattering. This is an unfortunate analogy, however, because any scattering is a process induced by an external field. We will accordingly refer to this ordinary scattering, due to thermal vibrations of the molecules, as "thermal."

combinational scattering, with $\nu = 1345 \text{ cm}^{-1}$. In contrast with the thermal scattering, the stimulated scattering is coherent.

The use of lasers to study thermal and stimulated combinational scattering has been reviewed in many books and review articles, and it would be impossible to attempt here to summarize even briefly these applications. We should, however, discuss briefly at least two or three (arbitrarily chosen) examples; we will simply mention certain other new fields (but by no means all of them). We hope that in a few words we can demonstrate to the reader that research on thermal and stimulated combinational scattering is still in a stage of rapid development and that many interesting and important discoveries lie in the future.

The use of the intense lines emitted by gas lasers, with a narrow spectrum and a small divergence, made it possible to detect combinational scattering by polaritons and to study polaritons. These are electromagnetic waves which propagate in crystals under conditions such that their propagation is strongly affected by mechanical vibrations, e.g., in ionic crystals. To study polaritons it is important to take into account the frequencies and the wave number (the spatial dispersion).⁷²⁻⁷⁵

For observation of combinational scattering by polaritons, the light scattered at small angles is imaged on the spectrograph slit in such a manner that the light corresponding to the scattering angle $\theta = 0$ reaches the slit at half its height, while the light scattered at larger angles arrives on the two sides of this midpoint. Since the dispersion direction of the spectrograph is perpendicular to the spectral image of the slit, the polariton branch should be "traced out" on the spectrum. Figure 3, taken from Ref. 73, is an

excellent example of this effect. Polaritons are under study by many investigators in various countries.^{64-66,73,75,77} Long chapters of books have been devoted to the theory of this effect (see, for example, Refs. 74-77). Progress in the development of tunable lasers has led to a large number of interesting studies of resonant combinational scattering (see, for example, Refs. 65 and 67).

The first fundamental work on resonant Rayleigh scattering, or "selective scattering of light," as it was known at the time, was carried out by Landsberg and Mandel'shtam,⁷⁸ who observed resonant scattering of the light from a zinc arc in mercury vapor. All the work on resonant scattering is based on a principle which was used 42 years ago in Ref. 78. Laser light sources and the dramatically improved double and triple spectrometers which use holographic gratings and multiple-pass Fabry-Perot interferometers⁷⁹ have made it possible to obtain spectra with extremely high contrast values $I_{\text{max}}/I_{\text{min}}$, from 10^7 to 10^{13} . This development has made it possible to study thermal combinational scattering in metals; to study the interaction of photons with many other excitations,⁸⁰ e.g., magnons, plasmons, and surface polaritons; to study combinational scattering by impurities and other defects in crystals; and to study spin flipping and the electronic spectra of combinational scattering.^{64-68,77,80}

Combinational scattering has proved an extremely effective tool for studying phase transitions.

Particularly important results on phase transitions were obtained with a new apparatus after Ginzberg⁶¹ (see also Ref. 82) was the first to point out that a phase transition should be accompanied by an oscillation, whose frequency should decrease with approach to the transition temperature, and that the corresponding com-

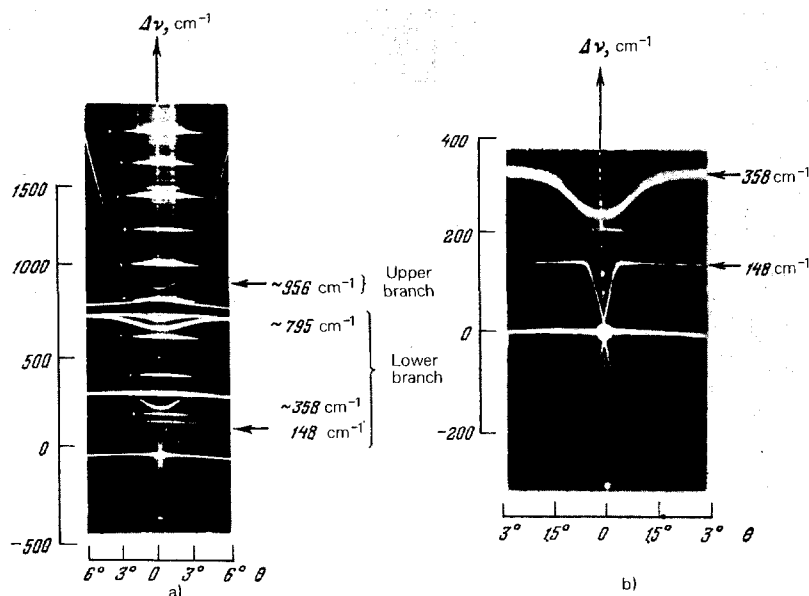


FIG. 3. Polariton spectrum of the LiIO_3 crystal (the frequency of the Raman scattering line $\Delta\nu$ as a function of the scattering angle in the crystal, θ). The arrows show the frequencies of transverse optical phonons. The points at the left indicate parasitic lines of the fluorescence of iodine vapor, used to attenuate the exciting light at $\lambda = 5145 \text{ \AA}$. a, b) Two different relative positions of the crystallographic axes and the propagation vectors of the scattered light.⁷³

binational-scattering line should merge with the Rayleigh line having the frequency of the exciting light. Such oscillation frequencies have been observed in a crystal, and the corresponding combinational-scattering lines are called "soft modes."^{764,69,77,82}

Interestingly, the first experimental observation of a soft mode was actually made back in 1929, by Landsberg and Mandel'shtam,⁸³ when they detected a pronounced change in a satellite in quartz corresponding to the wavelength $\lambda = 48 \mu$. Above the transition temperature (900°K), this satellite vanished completely. In that work, Landsberg and Mandel'shtam were of course not able to study all the subtle details which can be studied with modern experimental apparatus, but they considered their observations deserving of a special preliminary report. This publication means that they thought this effect was extremely important. The number of theoretical and experimental papers which have now been published on this effect is extremely large (see, for example, Refs. 64-68).

Stimulated combinational scattering, which we mentioned earlier, results from the application of intense light to a material in a very short pulse. While the exposure times required to detect thermal combinational scattering ranged up to 100 h at the time of its discovery, a stimulated-scattering line can be obtained in 10^{-7} - 10^{-11} sec. Because of the particular features of stimulated scattering, the methods used previously in the case of thermal scattering cannot be used in this case to study the shape and other characteristics of the lines. The special approaches which have accordingly been worked out are described in many books and reviews.^{49,84-91}

The method of the Kerr effect induced by combinational-scattering lines—a method proposed by Hellwarth⁹² and used by Hellwarth *et al.*⁹³—has proved to be a particularly effective method, in which it is possible to obtain, not simply one or two scattering lines as in the stimulated-scattering method, but the entire group of combinational lines characteristic of a given substance.

Lasers generating picosecond pulses have made it possible to develop direct methods for measuring fast processes and, in particular, the lifetimes of molecules in excited vibrational states in condensed media. It has become possible to carry out direct measurements of times of the order of 10^{-12} - 10^{-13} sec. The time evolution of the intensity of thermal-scattering and stimulated-scattering lines has been studied in several cases, and the decay times of these lines have been determined. These methods provide important opportunities for studying various subtle processes which occur in molecules and crystals and for studying the kinetics of intermolecular interactions.

The progress in the development of tunable lasers has led to a new method, which may be called "coherent anti-Stokes scattering" for brevity. The idea of the method and its first use are credited to Terchune.⁹⁵ In a sense, this method occupies a position intermediate between the thermal and stimulated

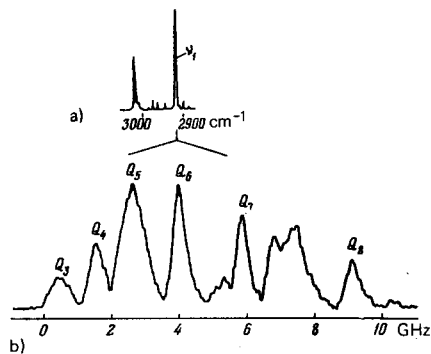


FIG. 4. Spectrum of the thermal Raman scattering in methane. a) Raman scattering spectrum in methane at the customary resolution; b) part of the spectrum corresponding to the Q branch and ν_1 in part a, found by the method of coherent anti-Stokes scattering. The resolution is 40 MHz ($\sim 10^{-3} \text{ cm}^{-1}$). The gas pressure is 20 torr. (Ref. 96).

combinational scattering. We outline this method.

We assume that a thermal-scattering line corresponding to a transition from a state 1 to a state 2 (or the opposition transition) in a molecule is characterized by a frequency ν' . Two laser beams, with frequencies ν_L and ν_S such that $\nu_L - \nu_S = \nu'$, are directed into a medium consisting of such molecules. The nonlinear interaction of the incident beams in the nonlinear-interaction region gives rise to a polarizability-derivative "wave." The anti-Stokes scattering which occurs in this case is coherent, in contrast with thermal scattering.

In this method, the intensity of the anti-Stokes line is measured as the laser producing the ν_S beam is tuned. The frequency ν_S is varied in such a manner that the difference $\nu_L - \nu_S$ is varied slightly around the frequency ν' . This method permits a precise study of the shape of the anti-Stokes combinational-scattering line without a spectrometer.

The resolution in this case depends on the width of the spectral lines of the two lasers. Figure 4, taken from Ref. 96, shows an excellent example of the use of this method, for the Q branch of methane. In this case the resolution is 40 MHz or about 10^{-3} cm^{-1} .

This brief list does not, of course, cover everything that has been done by the students, colleagues, and successors of G. S. Landsberg and L. I. Mandel'shtam in the Soviet Union. Certainly, we have not covered everything which has been done throughout the world. This effect which was discovered 50 years ago is still being studied and is still finding new fields of application.

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