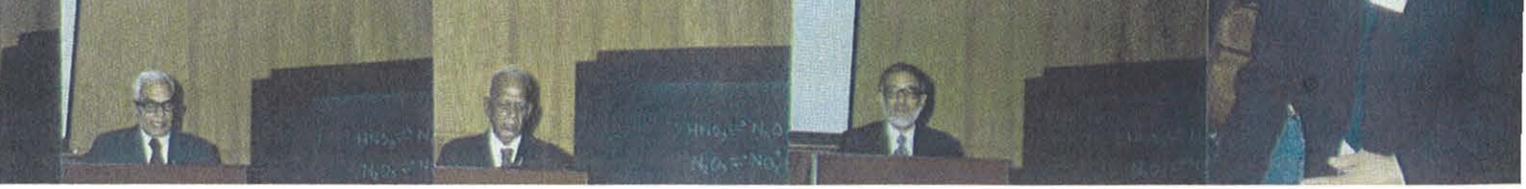
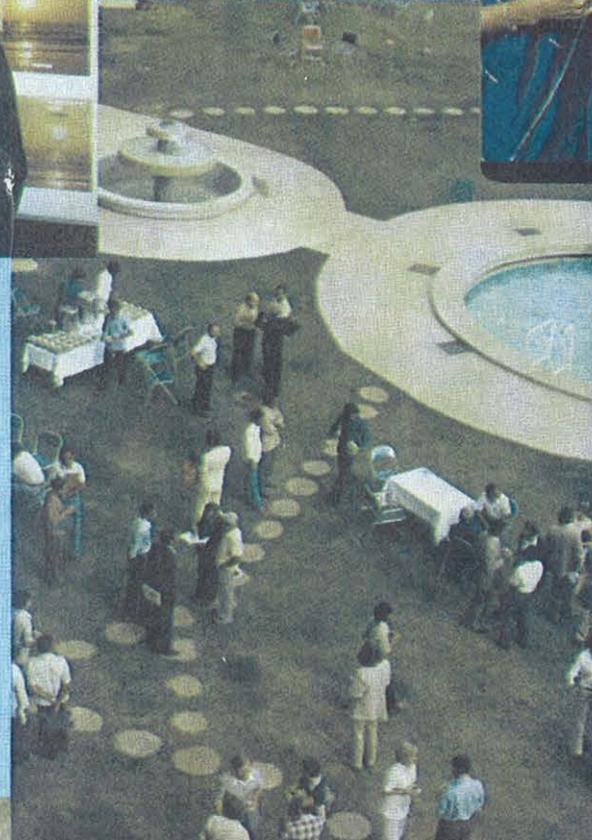


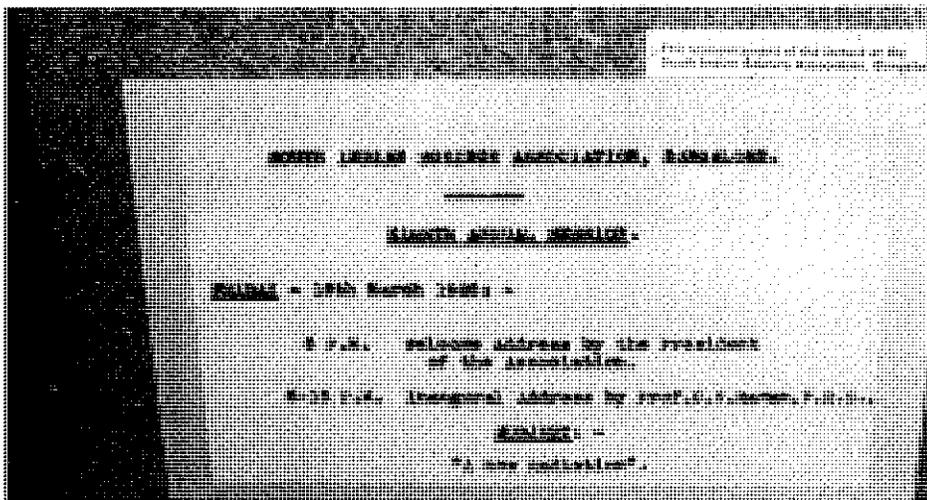
The SPEX Speaker

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RAMAN ANNIVERSARY ISSUE

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GOLDEN JUBILEE OF THE RAMAN EFFECT

Situated at a cool altitude of around 1000 meters in south central India, Bangalore was the historic setting for last September's Sixth Raman Conference commemorating the 50th anniversary of the discovery of the effect. Here C.V. Raman moved from Calcutta where his pioneering discovery was made, and here he continued his research for more than 40 years at the institute constructed for him and named in his honor.

The conference amply portrayed the vast scope and ongoing contributions of Raman spectroscopy. Subject matter of the 47 invited and over 250 contributed papers covered investigations in chemistry, solid state physics, and biochemistry. Although the advent of the laser was the single most important event contributing to the proliferation of research in Raman, such recently introduced tools and techniques as resonance Raman, time-dependent processes and coherent anti-Stokes Raman spectroscopy (CARS) were shown to be emerging as highly significant means for furthering the progress of Raman successes. Certainly, Raman could not have anticipated that his first modest experiment with benzene would constitute the cornerstone of an entirely new technology in which thousands of researchers are engaged, unlocking an increasing amount of fundamental scientific information and practical applications.

Sir Raman's initial experiments were spartan and simple. Sunlight, a large glass condensing lens, a glass flask, and a direct-vision spectroscope comprised his entire analytical system; purified benzene, his sample. Little more than toys by today's standards, they were all the tools he needed to spot the incredibly weak, shifted spectral lines emitted by benzene. But he was careful as well as resourceful: before issuing his momentous article to Nature in early 1928, he substituted a mercury lamp for the capricious sun. With this he was able to conclude that the shifted lines were uniquely characteristic of the substance being irradiated. Soon, Raman found that a prism spectrograph was better than a

spectroscope. In conjunction with the lamp, he could run long exposures and photograph the resulting spectra for publication. That spectrograph, incidentally—a wooden box perhaps one meter long, studded with brackets, screws, and mounting holes, and patched with black, self-adhesive tape—is still preserved and operated at the Indian Institute of Science in Bangalore.

The Raman Institute, a museum, laboratory, and home, established in Bangalore for the first Indian scientist to win the Nobel Prize, tells much about Raman the man. Throughout his life, light in its varied manifestations fascinated him. In one section is a large display of fluorescent minerals that he collected from all over the world. Under ultraviolet radiation, the sleeping stones awaken to display surprisingly vivid colors.

In another section of the Institute's museum is a portion of Raman's collection of diamonds. Hundreds are on display, in all

FRONT:

N.A. Narasimham, India
Mrs. S. Dhawan, India
Mrs. D.A. Long, UK
D.A. Long, UK
S. Bhagavantam, India
T. Shimanouchi, Japan
F.A. Miller, USA
E.D. Becker, USA
O. Thomas, UK
Mrs. W. Peticolas, USA
W. Peticolas, USA

B.P. Stoicheff, Canada
C.H. Wang, USA
W. Kiefer, W. Germany

C.K. Subramanian, India
P.S. Narayanan, India
T.S. Krishnan, India

S. Bhagavantam, India
K.R. Ramanathan, India
M.G.K. Menon, India
E.D. Schmid, W. Germany

sizes, shapes, colors, and quality. Soon after he discovered shifted lines in liquids, Raman turned his attention to solids and, according to a co-worker, Dr. S. Bhagavantam whose lecture spear-headed the Conference, one of the first solids to be analyzed was the diamond in Raman's brother's wedding ring. Sure enough, it emitted a sharp Raman band. But, as Raman was to learn over the next few decades, the spectra of all diamonds are not identical. So intrigued did he become by diamonds that he embarked on a collection effort, pursued for the remainder of his life. One was even borrowed from a wealthy Maharaja, a modest 140-carat stone, the spectrum of which was published together with a description of the stone and its weight followed by several exclamation points.

How did Raman become interested in looking at spectral scattering from benzene in the first place? A book on a shelf in a lighted cabinet in the Institute is probably an important clue. Opened to its title page, the book is concerned with the color of water. Trained and educated as a natural scientist, Raman was surprised to learn that there were no rational explanations for the obviously different hues and shades displayed by different bodies of water. He set out to find reasons and from his interest and curiosity stemmed the discovery 600 of us traveled to remote Bangalore to celebrate.

Sidetracked by technical, business and frivolous distractions, our camera roamed sporadically, capturing only a few of the attendees. Should you wish to identify any familiar face, herewith follows our list of martyrs reading from left to right starting at upper left.

BACK:

A.J. Mitteldorf, USA
J.R. Durig, USA
S. S. Mitra, USA
W.G. Fateley, USA
R.K. Chang, USA
J.H. Nicola, USA
J. F. Scott, USA
E. Castellucci, Italy

A.L. Verma, India
L.A. Rebane, USSR
K.K. Rebane, USSR
M.N. Dixit, India

D.J. Lockwood, Canada
J. Shamir, Israel
J. Schnur, USA
Mrs. J. Schnur, USA

H.M. Mitteldorf, USA
E.M. Anastassakis, Greece
Mrs. G.R. Wilkinson, UK
G.R. Wilkinson, UK
H.D. Bist, India
V. Bhargava, India
R.M. Pick, France

PHYSICISTS VIEW FIFTY YEARS OF RAMAN SPECTROSCOPY

J. Brandmüller, University of Munich

and

W. Kiefer, University of Bayreuth

In Calcutta on February 28, 1928 the line spectrum of a new radiation was imaged on the eye of C.V. Raman for the first time [1]. Shortly afterwards, Raman and Krishnan [2] published the first Raman spectra of benzene and toluene. These liquids were irradiated with the indigo blue line (435.8 nm) of a mercury lamp and the scattered light was dispersed with a spectrograph. Once it became clear that the new spectral lines were not components of the excitation source, but were actually characteristic of the scattering medium, Raman immediately submitted a note titled "A Change of Wave-length in Light Scattering" to Nature on March 8, 1928 [3]. This note was the culmination of more than seven years of experimental studies of light scattering in transparent media of all kinds.

Chandrasekhara Venkata Raman was born on November 7, 1888 in Trichinopoly, South India. He studied physics at the University of Madras and though he finished at the top of his class with a gold medal, he couldn't find work in his field so he had to settle for a position with the finance department in Calcutta which he held from 1907 to 1917. During this period, he found time for research at the laboratory of the Indian Association for the Cultivation of Science and in 1917 he was appointed physics Professor at the University of Calcutta. It wasn't until 1921, however, that Raman, while voyaging to Europe, experienced the marvelous opalescence of the Mediterranean. The sight of the wonderful blue color so impressed him that he decided to devote his future to the study of light scattering in liquids [4].

In 1923, Compton [5], while scattering x-rays from a graphite block, discovered the effect that bears his name. Two scattered components were detected: one corresponding to the incident beam, the other shifted in frequency by an amount that depended on the scattering angle, but was independent of the initial wavelength. Learning of Compton's discovery, Raman began a search for an optical analog of the phenomenon. A short publication submitted to Nature [6], just two weeks before the first Raman spectrum was photographed, indicates how persistently Raman pursued evidence for the existence of frequency-shifted components in the spectra of scattered light. And he was not alone in his search.



The original Raman apparatus, Indian Institute of Science, Bangalore.

On March 23, 1928 Brillouin delivered a report to the French Academy of Science concerning a note published by Rocard in Comptes Rendues [7]. Rocard [8] had investigated the effect of an oscillating dipole moment on the scattering process and he came to the conclusion that the scattered light must have a different spectral structure than that of the incident light. He would have postponed the publication of these results until experimental verification, but after Raman's discovery it appeared advisable to reveal his calculations immediately. Rocard went on to interpret the frequency-shifted scattered light as an optical modulation caused by the various vibrational frequencies of the electrical dipole moment of the oscillating molecules. He was able to describe quantitatively the scattered radiation at about 500 nm that was observed by Raman in liquids such as pentane and octane when irradiated by the 435.8 nm mercury line. (Nowadays we would speak of the C-H stretch at about 3000 cm^{-1} .) One week later, Fabry reported to the French Academy on a note by Cabannes [9]. As early as 1924, Cabannes predicted the effect of "optical beating"; however, since that time he had tried vainly to verify his prediction through a study of light scattering in gases. His checkmate ("échec") was the very low scattering intensity of a gas under normal conditions. Because the intensity of scattered light is

proportional to the number of scattering molecules, one would more likely observe the effect in compressed gases or in liquids. Yet the spectacular point of his paper is that Cabannes had recognized the condition for the existence of pure rotational Raman lines: the finite optical anisotropy of the molecules under investigation. Meanwhile in Moscow, at the Institute for Theoretical Physics, Landsberg and Mandelstam [10], while performing molecular light scattering experiments on solids, wondered whether there existed a change in wavelength that could be explained on the basis of the Debye theory of specific heat¹.

When the 253.6, 312.6 and 365 nm mercury lines impinged on quartz and calcite crystals, the frequency-shifted lines were found in different spectral regions than expected from Debye's theory. On May 6th, 1928, the Russians submitted their results as a letter ("Zuschrift") to the German journal Naturwissenschaften. They included a possible explanation:

"bei der Zerstreung des Lichtes können einige eigene ultrarote Frequenzen des Quarzes auf Kosten der Energie des zerstreuten Lichtes angeregt werden und dadurch würde die Energie der zerstreuten Quanten und folglich ihre Frequenzen um die Grösse der entsprechenden infraroten Quanten abnehmen."² The principal difference between infrared absorption and Raman scattering was not recognized at that time. Landsberg and Mandelstam mentioned in their paper that they could not judge "ob und wieweit die von uns beobachtete Erscheinung mit der von Raman (und Krishnan [6, 3]) erst kürzlich beschriebenen im Zusammenhang steht, ... weil seine Schilderung zu summarisch ist."³

¹"... was man nach der Debyeschen Theorie der spezifischen Wärme vermuten kann."

²"When light is scattered by quartz, some of the crystal's own infrared frequencies can be excited at the cost of the energy of the scattered light and the scattered quanta; hence their frequencies decrease by the amount of the respective infrared quanta."

³"Whether and how far the effect observed by us is equivalent to the one which was recently described by Raman and Krishnan [6, 3] because his discussion is too brief."

The conclusive publication by Raman [2] was therefore unknown to Landsberg and Mandelstam when they composed their letter to *Naturwissenschaften*. At a meeting of the French Academy of Sciences, July 9, 1928, Cotton reported on a note by Landsberg and Mandelstam [11]. In this publication the relationship between the frequency-shifted lines and the eigenfrequencies of the crystal is clearly demonstrated. Thus, Raman was the first to publish a spectrum of scattered light containing frequency-shifted spectral lines and on December 11th, 1930, he received the Nobel prize in physics "for his work on the 'diffusion' of light and for the discovery of the effect which bears his name." (In Russian-speaking countries one often refers to combination scattering radiation instead of Raman scattering.) In 1933, Raman became Professor and Director of the Indian Institute of Science in Bangalore, South India. In 1948, he founded the Raman Research Institute in Bangalore where he became Director. He also founded the Indian Academy of Sciences, of which he was President. Raman was made a knight of the English crown in 1929 and much later he received the Lenin Medal during a visit to Moscow.

Very often a short note, published by the Austrian physicist Smekal [12] in 1923, the year Compton discovered the effect which bears his name, is evaluated as a prediction of the Raman effect. An important observation later derived from this note is the fact that all elementary excitations, which are associated with quantized excitation energies can give rise to a Raman effect. This became significant when the Raman effect on phonons, polaritons, magnons, excitons, etc. in solids was studied.

Placzek [13] characterized the developments that followed. "Encouraged by Smekal's note, Kramers and Heisenberg [14] showed how the origin of this modified scattering radiation can be understood classically, and after this, they were able to derive their quantum-theoretical scattering formula by combining the correspondence principle with the classical theory of electro-magnetic radiation. The importance of this investigation by far exceeds this field of problems: it was the origin of modern quantum mechanics." In 1927 Dirac [15] developed a quantum-mechanical scattering theory from which he derived the formulas for the intensity of scattered radiation. Thus the theory for the Raman effect was firmly established one full year ahead of its experimental discovery.

The quantum-mechanical expression for the intensity of Raman-scattered light causes difficulties when applied to most concrete questions since numerical calculation of the Raman intensity requires knowledge of all eigenstates of the scattering system, i.e., a molecule or a crystal. Even for the simplest

molecules, the challenge remained to gather all this information. In 1934, Placzek [13] led the way, to everyone's advantage. In his polarizability theory he introduced a semiclassical approach. To calculate a Raman intensity he considered the nuclei of the molecule as being fixed and then examined how the scattered radiation was modified when the nuclei are moved. He concluded that the polarizability is a function only of the position of the nuclei, not of their velocity, provided the following three conditions are fulfilled:

- 1) The frequency of the exciting light must be so far away from all electronic transition frequencies that the difference is large compared to the splitting and displacement of the electronic ground state caused by the nuclear frequency. Within the applicability of the polarizability theory, this condition excludes the so-called resonance Raman effect (see for instance Behringer [16, 17]) where the exciting frequency nearly or actually coincides with the frequency of an allowed electronic absorption transition. In the case of resonance excitation, the rigorous quantum-mechanical theory, recently tested successfully with simple systems [18, 19], also applies.
- 2) The second condition for validity of the polarizability theory is that the exciting frequency must be large compared to the nuclear frequency of the electronic ground state.
- 3) Finally, the electronic ground state should not be essentially degenerate.

With these assumptions, Placzek derived an expression for the intensity of the scattered radiation which only contains quantities related to the electronic ground state. The influence of all other states is contained in the polarizability and in its derivatives with respect to the nuclear coordinates. An invaluable advantage of the polarizability theory, however, is that the selection rules for the Raman effect may be defined simply by applying group-theoretical methods. These selection rules can be derived from the symmetry behavior of the polarizability which is a tensor of rank two. Except for special cases, this tensor is symmetric. It was only recently that further development of the theory of the Raman effect became necessary. Then the increasing significance of the resonance Raman effect required a return to the quantum-mechanical scattering theory [17]. Furthermore, the introduction of the laser as the light source in Raman spectroscopy drew attention to nonlinear effects (see for instance Flytzanis [20] and Yariv [21]).

International Experimentation

Let us go back to the early days of Raman spectroscopy, following up the experimental work performed immediately after the discovery. At that time it was customary to repeat newly reported effects and to try to look for new aspects. At various places in the world the Raman effect was recognized

by physicists as well as chemists to be a powerful tool for structural investigations. In the United States the history of the Raman effect [22] began when R. W. Wood read Raman and Krishnan's publication in *Nature* [6] and checked his own file of spectroscopic plates, taken during a study of resonance fluorescence of various simple molecules. Noting clear evidence of the Raman effect, he hastily assembled a temporary Raman apparatus and photographed the spectrum of a quartz crystal. His results were cabled as a short note to *Nature* [23]. Wood also introduced the term "anti-Stokes" referring to the Raman lines on the high energy side. A great amount of valuable experimental detail, including reproductions of the spectra of many substances, were published shortly after his cable in an extensive paper [24]. Wood subsequently published some thirty articles on the Raman effect in the decade beginning in 1928. We cannot go into detail here to describe all of his work, but would like to emphasize that the modern theory of resonance Raman scattering in gases [17] and current experiments with the same gases studied by Wood at the beginning of the century [18, 25, 26] point to an interpretation of resonance fluorescence as a special case (discrete resonance Raman scattering) of a more general Raman scattering process. In this light, Wood observed the Raman effect as early as 1906, in the well-known resonance fluorescence series of iodine vapor. Of course, this close relation between resonance fluorescence and the Raman effect went unnoticed at that time. We may mention at this point that the relation of resonance Raman to resonance fluorescence has been discussed extensively [27]. Recent studies in semiconductors [28] clearly indicate that resonance fluorescence and Raman scattering can be identical. This was demonstrated by the observation of interference of the two emissions, leading to the famous Fano interference line-shape. We have already mentioned the beginning of Raman spectroscopy particularly in France and Russia where it remains a topic of continuous study. Numerous other people should be included here and although it is not possible for us to single out everyone in every country who contributed fruitfully to the developing field of molecular spectroscopy, we are taking the liberty of noting just a few: Mathieu [29] in Paris, Shorygin [30] and Sushchinskii [31] in Moscow, Woodward [32] in Oxford, all of whom applied Raman scattering to clarify molecular structure. As for the extension of the method to chemistry, it is now well known that Wilson, Decius and Cross [33] wrote the book which turned out to be a standard in the field. Herzberg [34] in Canada wrote three classic texts which contain a great deal of molecular spectroscopy data. In Italy, Bonino, as well as Carrelli [35], devoted themselves very

early to the Raman effect. Bonino's first article appeared in 1929 [36] and by 1976 more than 400 articles came from this group [37]. In December 1928, Dadiou [38] reported, at a Colloquium of the Physical Institute at the Technical University in Graz/Austria, on the previously mentioned article by Wood. After his presentation, Dadiou suggested to the Director of the Institute, Prof. Kohlrusch, that he abandon ultraviolet spectroscopy and devote his energy to the far more promising Raman effect. "From the start, Kohlrusch was determined to explain the entire phenomenon physically, that is to say, to determine with the aid of Raman spectra the complete vibrational modes of the molecules under observation" [39]. On the first anniversary of Raman's discovery, Dadiou and Kohlrusch submitted their first paper to the Austrian Academy of Science. The following years and decades brought an abundance of papers by the Graz Raman School that opened up the field of Raman spectroscopy for research in molecular structure and applications in chemistry. These results were summarized in the invaluable work published by Kohlrusch between 1931 and 1943 [40]. The first group in Germany to study the Raman effect was the one around Pringsheim [41] in Berlin. Schaefer [42] in Breslau and his co-workers Matossi and Aderhold were engaged with Raman spectroscopy of crystals. Goubeau [43] in Göttingen, and later in Stuttgart, began his studies of the Raman effect in 1932.

Goubeau was the founder of the Raman Colloquia which took place in Stuttgart in 1955 and 1958 and in Freudenstadt/Black Forest in 1964. The next Raman colloquium was organized by Kriegsmann in Magdeburg. These colloquia may be regarded as predecessors of the International Raman Conferences which started in Ottawa 1969, followed by Oxford 1970, Reims 1972, Brunswick 1974, and Freiburg 1976. The sixth conference in this series, held in September 1978 in Bangalore, India, had a special significance: it commemorated the 50th anniversary of the reporting of the Raman effect by C.V. Raman. Simon and Féher [44] began studies with Raman spectroscopy in Dresden in 1935. Their investigations were continued by Féher and Baudler in Cologne, by Steger in Dresden and Kriegsmann in East Berlin. In the chemical industry, Matz found early applications of this significant analytical tool.

Gerlach, from whose group — in a broad sense — the authors of this article originate, began Raman investigations in 1928 as Director of the Physical Institute of the University in Tübingen and continued this work after his nomination to the same position at the University in Munich. His first

"On the width of spectral lines of Raman-scattered light in benzene."

article "Über die Breite der Spektrallinien der Raman-Streustrahlung von Benzol"⁴ was submitted in December 1928 [45]. Further articles on crystallized nitrate salts followed [46]. In spite of the chaos during World War II, a complete Raman apparatus from the Steinheil Söhne Company, Munich, survived at his Institute and it was on April 1st, 1949, that Prof. Gerlach charged one of us (J.B.) with renewing the investigations in Raman spectroscopy that had been interrupted for so long. At that time, there was no interest in the Raman effect among physicists. Information on molecular structure which could not be obtained from infrared spectroscopy alone (a method of increasing importance in that epoch) attracted only chemists; however, even among them, Raman spectroscopy was far from popular because convenient equipment was not as available as it was for infrared. Nevertheless, one of us (J.B.) as a physicist had good reasons to devote himself to the Raman effect. During World War II military needs spurred the development of photomultipliers to replace the photographic plate and by 1952 Raman spectra benefitted from the linear response of photoelectric recording [47]. During the fall of 1953, Professor Shorygin from Moscow presented a paper on the resonance Raman effect at a meeting in Gmunden, Austria and introduced a new concept. Hitherto Raman spectroscopy had been limited to substances which do not absorb the excitation wavelength. To excite colored materials, special light sources were developed mainly by Stammreich and his coworkers in Brazil [48]. Shorygin showed that excitation within the region of electronic absorption (resonance Raman) has distinct advantages. Colored substances [49] could be examined and very small concentrations, characteristic of biological samples, became manageable [50].

The Laser

The most decisive discovery, however, was the laser, and it brought a renaissance of Raman spectroscopy. In 1960, Maiman [51] observed the first stimulated emission in a ruby crystal at 694.3 nm. On the occasion of a lecture, given by Schawlow at the National Research Council in Ottawa in January 1961, Herzberg and Stoicheff suggested the ruby laser as a light source for Raman spectroscopy. Porto and Wood [52] reported at the Columbus meeting in 1961 on the first results. They photographed the Raman spectra of carbon tetrachloride and benzene excited by approximately 50 to 100 laser pulses. At the same time Stoicheff [53] was also successful. It was true that the first laser-excited Raman spectra could not compete with the then customary mercury-line-excited Raman spectra recorded photoelectrically [54]. These experiments, however, paved the way for unforeseen developments in Raman

spectroscopy. This evolution took two directions.

Experiments involving linear Raman spectroscopy surged ahead with the advent of continuously emitting gas lasers. In 1963 Leite and Porto [55] were able to photoelectrically record Raman spectra of carbon tetrachloride, carbon disulfide and benzene with excitation by a 10 mW He-Ne laser. Scattering was observed from a liquid cell placed inside the laser resonator. Koningstein and Smith [56] showed that laser excitation combined with photoelectric techniques was also possible when the cell is placed outside the laser cavity.

In our time the laser has completely replaced the mercury lamp as an excitation source. The high degree of collimation and polarization, as well as the high power density of the laser beam, are exploited particularly for solid state research where observation of the Raman effect on phonons is facilitated. Many articles and books on light scattering by phonons have been published as a consequence. Some of them are cited in Refs 57-61. With backscattering geometries, excitation of opaque crystals (e.g. semiconductors, see for example Ref 59) was also possible. The proliferation of lasers has also opened a whole range of other excitation possibilities in the solid state. Raman scattering on polaritons is such an example. Born and Huang [62] claimed the existence of elementary excitations corresponding to mixed states of mechanical and electromagnetic energy. Henry and Hopfield confirmed this experimentally by Raman scattering from cubic GaP [63]. Hopfield [64] christened these coupled excitation states polaritons. Scott, Cheesman and Porto [65] investigated the polariton spectrum of the uniaxial α -quartz crystal. Further developments are discussed in detail in the comprehensive articles by Scott [66] and by Claus, Merten and Brandmüller [67]. Light scattering on magnons was reported in the antiferromagnetic crystals MnF₂ and FeF₂ by Fleury and Porto [68]. Poppinger [69] has measured the profiles of two-magnon bands in MnF₂ and has calculated them theoretically. Koningstein [70] photoelectrically recorded electronic Raman scattering by Yb, Eu and Nd ions in Y-Ga garnets. Raman scattering by plasmons in GaAs was demonstrated experimentally by Mooradian [71] in 1966. Slusher et al. [72] detected Raman scattering by Landau levels in InSb. These experiments also showed Raman scattering by the spin-flip transition, which later became important for the production of magnetically tunable infrared laser sources. There are also some review articles [73-77], which discuss the influence the laser had on the spectroscopy of the spontaneous, linear Raman effect.

The laser has extended the field of Raman

spectroscopy in another direction as well. The very high electrical fields now available could stimulate nonlinear effects from the interaction of light with matter. This stimulated Raman effect was first observed by Woodbury and Ng [78] in 1962. They created giant pulses from a ruby laser by filling a Kerr cell with nitrobenzene and placing it inside the laser cavity to act as an optical switch. Analyzing the spectrum of the laser light, they found the laser wavelength at 694.3 nm and another strong line at 767 nm. The wavenumber difference between these two lines corresponds exactly to the strongest Raman line of nitrobenzene (1345 cm⁻¹). An interpretation of this new line was given by Eckhardt [79], who studied molecular spectroscopy in Frankfurt/Main under Czerny. (With Turner, Czerny developed the spectrometer optical design bearing their name.) More than a hundred years ago Lommel [80] had claimed that sum and difference frequencies have to be present in the scattered spectrum of an anharmonic damped oscillator. Schaefer [81] resurrected Lommel's idea in 1929. Thus, quite early in spectroscopic history nonlinear effects had been taken into consideration to describe the scattering phenomenon of electromagnetic waves on matter. However, it was soon recognized that it is not necessary to consider nonlinearities in the treatment of the spontaneous linear Raman effect and the nonlinear scattering effects were not observed before 1962 when the high field strength of laser beams made it possible. Since that time, tremendous development has taken place in this field. Primary applications range from the generation of new laser frequencies (Raman laser) [82] to the measurement of vibrational relaxation times [83].

Nonlinear Raman Effects

Let us briefly present a semi-classical treatment of those nonlinearities where the scattering system — in the simplest case of a molecule — is described quantum-mechanically, and the radiation is treated classically. The justification for this simplified model is that rigorous quantum-mechanical theory yields the same result. According to the theory of Hertz, the relation between the total intensity (I) of the radiation field of an oscillating dipole is given by:

$$I = \frac{2}{3c^2} \langle |\ddot{\vec{p}}_{if}|^2 \rangle \quad (1)$$

where $\langle |\ddot{\vec{p}}_{if}|^2 \rangle$ is the time average of the square of the absolute magnitude of the second derivative (with respect to time) of the dipole moment for the transition of the

molecule between state i and state f. In the linear approximation, the dipole moment is related to the polarizability α and the electric field \vec{E} by:

$$\vec{p} = \vec{\mu} + \alpha \vec{E} \quad (2)$$

Here $\vec{\mu}$ is a permanent electric dipole moment which may be present in addition to the induced dipole moment $\alpha \vec{E}$. The polarizability α is a function of the eigenfrequencies of the molecule. According to Piaczek's polarizability theory [13] this relationship can be calculated by expanding the polarizability into a Taylor series with respect to the normal coordinates q_j .

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q_j} \right)_0 \cdot q_j \quad (3a)$$

For the dipole moment it takes the form:

$$\vec{p} = \vec{\mu}_0 + \left(\frac{\partial \vec{p}}{\partial q_j} \right)_0 \cdot q_j \quad (3b)$$

Breaking off after the linear term, (i.e., neglecting higher powers of q_j) restricts the relationship to first-order Raman scattering (over and combination frequencies are eliminated). The frequency dependence of q_j follows from the equation of motion of a free harmonic oscillator.

$$\ddot{q}_j + \omega_j^2 q_j = 0 \quad (4)$$

$$q_j = q_{j0} \cdot \cos \omega_j t \quad (5)$$

For the electric field of the exciting light we have (neglecting the phase, which does not play any role in spontaneous processes):

$$\vec{E} = \vec{E}_0 \cdot \cos \omega_e t \quad (6)$$

Combining Eq 3, 5, and 6 with 2 we have:

$$\vec{p} = \vec{\mu}_0 + \left(\frac{\partial \vec{p}}{\partial q_j} \right)_0 \cdot q_{j0} \cdot \cos \omega_j t$$

Radiation in IR

$$+ \alpha_0 \vec{E}_0 \cdot \cos \omega_e t \quad (7)$$

Rayleigh Scattering

$$+ \left(\frac{\partial \alpha}{\partial q_j} \right)_0 \cdot q_{j0} \vec{E}_0 \cdot \cos \omega_e t \cdot \cos \omega_j t$$

Raman Scattering

The last term in Eq 7 gives rise to Raman Scattering since:

$$\cos \omega_e t \cdot \cos \omega_j t = \quad (8)$$

$$\frac{1}{2} [\cos(\omega_e - \omega_j)t + \cos(\omega_e + \omega_j)t]$$

In order to calculate the radiation intensity from Eq 1, we have to evaluate the absolute magnitude of the vector \vec{p} and then perform the time averaging. Because of this averaging, only the terms containing the square of the cosine function will be different from zero, so a definite physical explanation for the various terms in Eq 7 can be given.

For high electric field strength, as can be achieved with laser sources, the linear relation given in Eq 2 is no longer sufficient and higher terms in the series have to be considered for a single molecule. This results in the expression:

$$\vec{p} = \vec{\mu} + \alpha \vec{E} + \beta \vec{E} \vec{E} + \gamma \vec{E} \vec{E} \vec{E} + \dots \quad (9)$$

where β , γ etc. are the hyperpolarizabilities, which are tensors of rank 3, 4, etc., respectively. $\vec{E} \vec{E}$ is the dyadic product of two electric fields. For β we can expand as in Eq 3. Assuming excitation with two different frequencies ω_1 and ω_2 , we have:

$$E_\sigma = E_{\sigma\sigma} (\cos \omega_1 t + \cos \omega_2 t)$$

$$E_\tau = E_{\sigma\tau} (\cos \omega_1 t + \cos \omega_2 t)$$

where ρ , σ , τ represent a Cartesian coordinate system. We see that the inclusion of the second-order induced dipole moment yields additional terms. In the following we give only those time-dependent factors which, after time-averaging, contribute to the scattering intensity I:

$$\cos 2\omega_1 t, \cos 2\omega_2 t$$

hyper-Rayleigh scattering

$$\cos(2\omega_1 - \omega_j)t + \cos(2\omega_1 + \omega_j)t$$

$$\cos(2\omega_2 - \omega_j)t + \cos(2\omega_2 + \omega_j)t$$

hyper-Raman scattering

$$\cos(\omega_1 - \omega_2)t + \cos(\omega_1 + \omega_2)t \quad (10)$$

difference and sum frequency

$$\cos(\omega_1 - \omega_2 - \omega_j)t + \cos(\omega_1 - \omega_2 + \omega_j)t$$

hyper-Raman scattering at difference frequency

$$\cos(\omega_1 + \omega_2 - \omega_j)t + \cos(\omega_1 + \omega_2 + \omega_j)t$$

and sum frequency

All these effects are coupled to the group-theoretical selection rules (e.g. hyper-Rayleigh scattering is forbidden for molecules having a center of inversion).

Classically, the hyper-Raman effect, hyper-Rayleigh scattering, etc., can be regarded as modulations of the excitation light, as was the case for the linear Raman effect, though the spontaneous hyper-Raman effect is extremely weak. The first hyper-Raman spectrum was observed in water by Terhune, Maker and Savage [85] in 1965. In principle, the hyper-Raman effect is very attractive to the molecular spectroscopist because of its different selection rules compared to the linear Raman effect. As an example, in tetrachloroethylene, the normal vibration with symmetry A_u cannot be observed in either the infrared absorption or Raman scattering spectrum, whereas this line is allowed for hyper-Raman scattering, and is found at 106 cm^{-1} [86]. Due to the extremely weak scattering efficiency, the hyper-Raman effect is limited in its application to physical problems in molecular spectroscopy. This is somewhat disappointing. However, the study of this effect has proved valuable since some fundamental theoretical aspects have arisen.

Above, we discussed the general case where excitation was provided by two waves of different frequencies ω_1 and ω_2 . Treating only one frequency, the quantum-mechanical calculation of the matrix elements by Aitmann and Strey [87] led to a different result than when the limit $\omega_2 \rightarrow \omega_1$ was taken. A discrepancy of a factor of two was found between these calculations [88] and Strey showed that the coherence property of the incident light is responsible for this. Another fundamental result is that natural light in nonlinear optics can be alternatively represented by superposing linearly or circularly polarized light waves as in linear optics, but with the important modification that an infinite number of incoherent components should be superposed instead of only two of them [87].

In the linear Raman effect spherical molecules have no pure rotational Raman spectrum, although this is allowed in the hyper-Raman effect. The first pure rotational hyper-Raman spectrum of methane was recorded and analyzed by Maker et al [89] in 1966. Since then the general theory for rotational and rotational-vibrational hyper-Raman scattering has been worked out [90].

The spontaneous hyper-Raman effect on crystals was studied by Vogt [91] who showed that the longitudinal and transversal phonons in CsI which are forbidden in the normal Raman effect, can be detected in the hyper-Raman spectrum at 90 and 60 cm^{-1} respectively.

In the spontaneous processes, either linear or nonlinear, discussed above, scattering from different scattering centers (e.g. molecules) occurs independently and is non-correlated (out of phase). This is not

the case for stimulated scattering processes, which take place at higher laser power. Here, the molecular vibrations remain in phase over a long path length and it is no longer sufficient to describe the scattering as from a single molecule. The theory has to be expanded to a macroscopic scale and instead of the microscopic relation 9, we have:

$$\vec{P} = \chi^1 \vec{E} + \chi^2 \vec{E}\vec{E} + \chi^3 \vec{E}\vec{E}\vec{E} + \dots \quad (11)$$

Here, \vec{P} is the dielectric macroscopic polarization and χ^n the dielectric susceptibility of order n . The latter can be calculated from the equation of motion of a driven oscillator. Eq 11 then determines \vec{P} , which is put into Maxwell's equation to derive the electric field \vec{E}_M in the medium. In this case, the scattering intensity is calculated from:

$$I = \langle |\vec{S}| \rangle \sim |\vec{E}_M|^2 \quad (12)$$

where \vec{S} is the Poynting vector. Stimulated scattering processes require a fulfillment of the phase relation between the electric fields involved in the scattering process (conservation of momentum). In the case where χ^3 becomes effective we have:

$$2\vec{k}_L = \vec{k}_S + \vec{k}_{as} \quad (13)$$

where \vec{k}_L is the wave vector of the laser beam with frequency ω_L , \vec{k}_S the wave vector of the scattered Stokes, and \vec{k}_{as} the wave vector of the scattered anti-Stokes beam. Scattering processes based on χ^3 are the already mentioned stimulated Raman effect and the inverse Raman effect. This was discovered by Stoicheff [92] in 1963, where under certain conditions a Raman transition can be observed as an absorption line in a continuum on the anti-Stokes side. Of particular interest is the process christened CARS (Coherent anti-Stokes Raman scattering). Maker and Terhune drew attention to this effect in 1965. The material is irradiated with light of a fixed frequency ω_L . Then a second light source having a frequency ω_s that differs from ω_L by exactly the vibrational frequency ω of the molecule or a crystal ($\omega_L - \omega_s = \omega$) generates an intense radiation on the anti-Stokes side ($\omega_L + \omega$) in a direction determined via Eq 13. With the development of tunable dye lasers, CARS sparked great interest [93, 94] since it claims a resolution of 0.02 cm^{-1} or better. Resolution is no longer determined by the Raman spectrometer, but by the line-width of the laser beams. Examples of high resolution CARS spectra of the Q branches of some simple gases are given in Ref 95.

The second order susceptibility χ^2 in Eq 11 describes the generation of the second harmonic and of sum and difference frequencies. It is hard to say whether these processes can be regarded as Raman effects. It is not easy to draw a definite line. The mechanism for generation of a sum

frequency, for instance, is not essentially different from that of the stimulated Raman effect. Both processes are due to the interaction of light with matter and what is or is not called a Raman effect becomes a question of convention or history.

Development in Instrumentation

Finally, we may mention that all the progress in linear and nonlinear Raman spectroscopy would have been impossible without enormous strides in instrumentation. It may even be said that instrumental advances sparked much experimental creativity, starting with the large glass-prism spectrographs of Hilger & Watts in England and Steinheil in Germany back in the days of 24-hour exposures. Replacing the simple mercury lamp in 1952, the spiral Toronto arc [96] reduced day-long exposures to hours before efficient photomultipliers with multi-alkali then GaAs photocathodes offered a hundred times greater sensitivity than the fastest photographic plates.

Adding photon-counting (pc) detection further increased the signal-to-noise ratio over that of picoammeters (dc detection), while gratings evolved from painstakingly ruled originals to better-blazed replicas and finally to holographic versions virtually devoid of ruling "ghosts" and spurious lines.

The introduction of image-intensifier phototubes placed in the focal plane of spectrographs permitted simultaneous recording of a large spectral region [97]. Studies of a variety of problems in physics and chemistry which require time-resolved and space-resolved Raman spectra could then be performed [98].

Coupled with the development of powerful monochromatic sources and photoelectric recording Raman instruments has been the development of digital computers that are now readily available to most spectroscopic laboratories. Linking these two approaches further improved the quality of Raman spectra [99].

Let us conclude this discussion by saying that as a consequence of the invention and development of the laser, the Raman effect, 50 years after its discovery, has found a broad field of application and forms a common point of view for all processes which are due to interaction of light with matter.

So far, we — as physicists — have only discussed a few of the new aspects introduced into physics through the exploitation of the Raman effect. Many other exciting results, which we could not describe in this short survey, were also obtained in other fields, mainly chemistry, biology and medicine. In References 100-103 we cite some books in which the missing information can be found.

The wide range of topics covered by the Sixth International Conference on Raman Spectroscopy, held this year in Bangalore where Raman spent the last four decades of his life, vividly testifies to the universal applicability of the Raman effect and to the number of scientific observations this effect was able to contribute to the broad field of natural sciences [104]

Munich/Bayreuth, December, 1978.

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GLOSSARY

SPONTANEOUS, LINEAR RAMAN EFFECT The normal Raman effect: an inelastic light-scattering phenomenon in which the scattering mechanism produces a change in the polarizability tensor associated with each scattering system. Light of frequency ω_0 incident on matter produces scattered light with the same frequency (Rayleigh scattering) and additional, weak spectral lines (Raman scattering) with frequencies $\omega_0 \pm \omega_s$, where ω_s is an eigenfrequency of the scattering system (e.g. vibrational frequency in a molecule, phonon in a crystal). Linear because of the linear relationship between induced dipole moment and electric field ($\vec{p} = \alpha \vec{E}$).

COMBINATION SCATTERING RADIATION Russian synonym for the spontaneous, linear Raman effect.

NONLINEAR RAMAN EFFECT A change in the frequency of intense monochromatic exciting light as a result of nonlinear interaction with a system. The nonlinearity is due to the relation between induced dipole moment and electric field:

$$\vec{p} = \alpha \vec{E} + \beta \vec{E} \vec{E} + \gamma \vec{E} \vec{E} \vec{E} + \dots$$

(Examples of nonlinear Raman effects: Hyper-Raman effect, Inverse Raman effect, Stimulated Raman effect, CARS.)

VIBRATIONAL RAMAN EFFECT Spontaneous, linear Raman effect where the change of frequency is due to a vibrational quantum. Oldest kind of Raman effect known. Can be simply understood as a modulation of the polarizability tensor components by a vibration of the molecule. Frequency shift $\sim 100-4400 \text{ cm}^{-1}$.

ROTATIONAL RAMAN EFFECT The change of frequency is due to a rotational quantum. When the molecule rotates, the polarizability viewed in a laboratory system changes relative to the direction of polarization of the incident light, assuming the polarizability is not a sphere. Frequency shift $\sim 5-400 \text{ cm}^{-1}$.

BRILLOUIN SCATTERING An incoming photon scattered at a displaced frequency by propagating pressure fluctuations (sound or acoustic waves). Conservation of momentum must be taken into consideration. Frequency shift $\sim 0.1-0.5 \text{ cm}^{-1}$.

RAYLEIGH SCATTERING Incident light is scattered without a change in frequency.

RAYLEIGH WING SCATTERING Anisotropic Raman scattering in liquids due to molecules rotating in a viscous medium. Similar to the rotational Raman effect but instead of discrete levels, the Raman spectrum is a low frequency continuum around the exciting frequency.

HYPER-RAYLEIGH SCATTERING Nonlinear scattering process where, due to the high electric field of the exciting radiation with frequency ω_0 , the nonlinear terms in the expression for the induced dipole moment become significant and lead to second and third harmonic light scattering at the frequencies $2\omega_0$ and $3\omega_0$, respectively.

HYPER-RAMAN SCATTERING Under the same conditions for Hyper-Rayleigh scattering, nonlinear inelastic light scattering at frequencies $2\omega_0 \pm \omega$ and $3\omega_0 \pm \omega$ can occur, where ω is the frequency of an elementary excitation in the material (vibration, rotation, phonon, etc.). An extremely weak scattering process.

STIMULATED RAMAN EFFECT Nonlinear Raman effect where the elementary scattering process involves four photons as described by the wave vector relation $2\vec{k}_i = \vec{k}_s + \vec{k}_{as}$

(i: incident, s: Stokes, as: anti-Stokes). This coherent radiation is excited by laser light with high electric field strengths. In contrast to the linear Raman effect, only a very few lines and their harmonics are generated. The intensity of these lines is on the order of the Rayleigh-line intensity.

INVERSE RAMAN EFFECT Also called Stoicheff absorption. A medium is irradiated simultaneously by intense monochromatic light and by a continuum. Then sharp absorption lines can be observed on the anti-Stokes side. Under the influence of the continuum and the laser, vibrational quanta are absorbed from the continuum, which leads to an "absorption spectrum"

ELECTRONIC RAMAN EFFECT Scattering of light by a system in which energy is conserved by the quantum jump of an electron from one electronic state to another. Observed in gases and solids.

SECOND-ORDER RAMAN SCATTERING This scattering generates two quanta (vibrational overtones or combination bands in liquids or gases, two phonons in crystals) that produce a modulation in the polarizability and hence a Raman process. In most cases, higher-order Raman processes give rise to weaker lines than first-order scattering.

RESONANCE RAMAN EFFECT When the exciting frequency ω_0 is close to or coincides with the absorption frequency ω_e , the scattering intensity is enhanced since the polarizability α , from which the intensity is derived, contains the denominator $1/(\omega_e - \omega_0)$

DISCRETE RESONANCE RAMAN SCATTERING Resonance Raman scattering where the exciting frequency ω_0 coincides with an absorption transition between discrete levels (e.g. rotational-vibrational levels in a molecule in the gas phase).

CONTINUUM RESONANCE RAMAN SCATTERING Here ω_0 coincides with a continuum of excited states (e.g. the continuum above the dissociation limit of the excited state, or the continuum of a repulsive state, or the continuum in a semiconductor).

RESONANCE FLUORESCENCE Same as discrete resonance Raman scattering.

CARS Coherent Anti-Stokes Raman Scattering. A nonlinear Raman process generated via the third-order nonlinear susceptibility of the material by simultaneous excitation with two lasers of frequencies ω_1 and ω_2 . Coherent radiation is produced at frequency $\omega_3 = 2\omega_1 - \omega_2$ whenever $\omega_1 - \omega_2$ coincides with a quantized state ω of the medium. ($\omega_3 = \omega_1 + \omega$ anti-Stokes radiation with respect to ω_1).

HORSES Higher Order Raman Spectral Excitation Studies. Similar to CARS (four-wave mixing process) HORSES is regarded as a higher-order process: e.g. six-wave or second-order four-wave mixing.

RIKE Raman Induced Kerr Effect. A laser pulse can be made to induce a Kerr effect only at Raman-shifted frequencies. In RIKE, an intense polarized, monochromatic pump beam at frequency ω_0 induces complex, anisotropic changes in the refractive indices experienced by a weaker probe beam at frequency ω . These changes exhibit resonances when $|\omega_0 - \omega|$ is near the frequency of a Raman-active vibration in the scattering medium. Experimentally, the probe beam intensity is first blocked by an analyzer after the sample cell in the absence of the pump beam. When the latter is admitted, transmission of probe beam through the analyzer is brought about by RIKE.

RAMAN GAIN Similar to CARS, this process is generated via the third-order, nonlinear susceptibility. However, instead of creating an anti-Stokes signal, the intensity of one of the two incident laser beams (the probe) is enhanced by energy from the other (the pump). This technique offers ultra-high resolution ($<0.001 \text{ cm}^{-1}$) when two cw, single-frequency lasers are applied. Raman Gain is also known as cwSRGS: continuous wave Stimulated Raman Gain Spectroscopy

RAMAN OPTICAL ACTIVITY Small differences in the intensity of Raman scattered light from right and left circularly polarized incident light.

CID Circular Intensity Differential. A relevant quantity in measurements of Rayleigh and Raman optical activity is the dimensionless CID:

$$\Delta = (I^R - I^L) / (I^R + I^L)$$

where I^L and I^R are the scattered intensities from left and right circularly polarized incident light.

RAMAN SCATTERING BY PHONONS Scattering of light by a wave propagating in a crystal. This wave, characterized by a discrete phase velocity v , frequency ω and a wave propagation vector k , is called a phonon (normal mode of the crystal). Since $|k| \neq 0$, we must take into consideration momentum conservation (which is not necessary for liquids).

BY POLARITONS Light scattering by elementary excitations corresponding to mixed states of mechanical and electromagnetic energy. These coupled excitation states, generated by interaction of the electromagnetic radiation with the mechanical vibration, exist only for very small values of $|k|$; so to scatter from them, the Raman effect has to be observed in the forward or near-forward direction.

BY MAGNONS Magnons are quantized states of spin waves. In ferromagnetic materials the spins of all atoms have the same orientation as the magnetic field, while in antiferromagnetic materials the spins are oriented antiparallel. In a ferrimagnet the spins are also antiparallel but of different magnitude. Oriented spins are coupled and disturbance by a phonon, for instance, creates a spin wave which travels through all the spins. One-magnon and two-magnon-scattering can be observed.

BY PLASMONS Light scattering by quantized plasma oscillations. The electrons in a plasma congregate around configurations of minimum free energy and oscillations around this equilibrium are possible. Disturbance by a photon creates a wave propagating through the plasma that is called a plasmon.

BY PLASMARITONS Light scattering by coupled photon-phonon-plasmon states (polariton-plasmon).

BY LANDAU LEVELS Light scattering by quantized (so called) cyclotron orbits inside a crystal. If a magnetic field is applied to a conductor or semiconductor, the translations of free electrons are superimposed with rotations at cyclotron frequencies. The quantized states are called Landau levels.

BY EXCITONS Light scattering by quantized states in electron systems (semiconductors or insulators) which are connected with the formation of a bound electron-hole pair. These excitons are mobile, excited states that propagate as waves through the crystal and can be initiated by photons.

BY SOFT MODES Light scattering by an unstable or "soft" optical phonon, whose frequency decreases substantially as the transition temperature of a structural phase transition is approached from above or below.

SPIN-FLIP TRANSITION A transition between Landau levels (see above) with a change in quantum number by two. The spin of the electron state flips between two opposite directions and the Raman frequency is $\omega_s = \omega_0 - 2\omega_c$, where ω_0 is the incident frequency, $\omega_c = eB/m^*c$ the cyclotron frequency of electrons.

SPIN-FLIP RAMAN LASER Magneto-Raman Laser: Stimulated spin-flip Raman transitions lead to coherent, tunable Raman scattering. Tuning is achieved by a change of the magnetic field B .

FERMI RESONANCE Coupling between two excitations (of the same symmetry) in a molecule: one is a one-quantum level, and the other a two-quantum state. The intensity of the normally weak second-order Raman line is enhanced by "borrowing" intensity from the fundamental.

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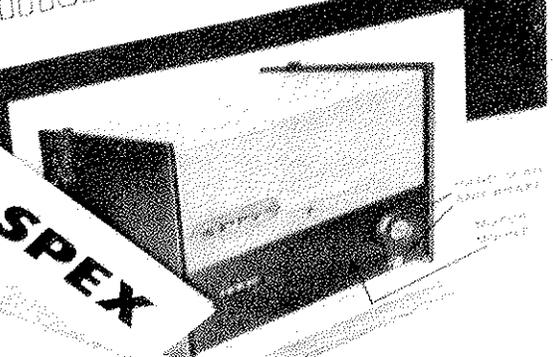
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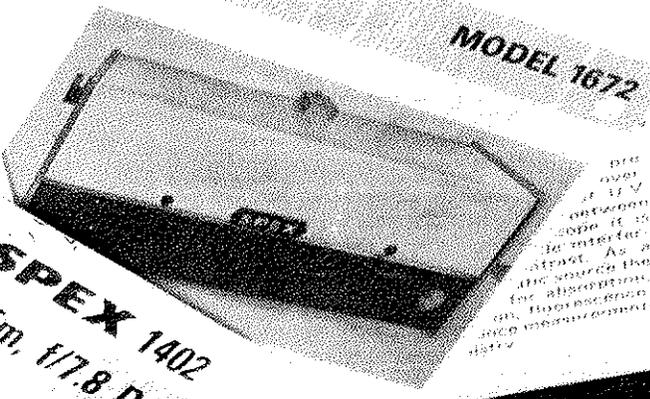
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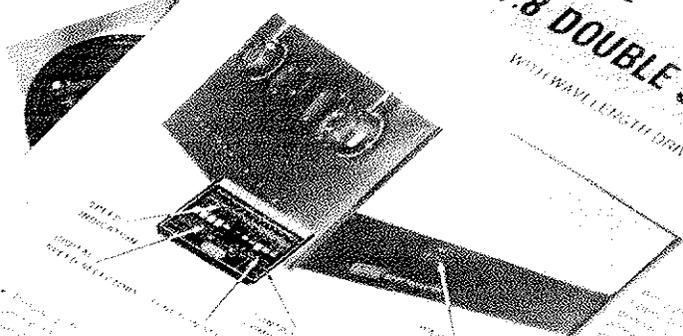
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