

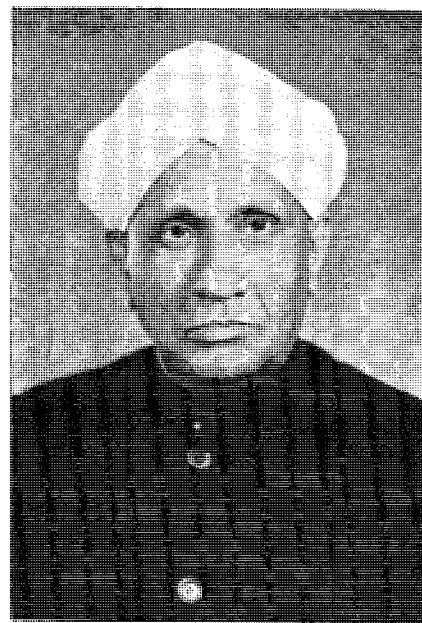
LASER RAMAN SPECTROSCOPY

FOREWORD

Looking back over many years of sustained scientific activity, I recall two periods, each of a few months, which stand out vividly in my memory by reason of their having opened new vistas of research which were later followed up. The first period was from September 1921 to February 1922. Experimental studies made during that time established the proposition that the molecular scattering of light in a transparent medium is a universal phenomenon exhibited in various degrees by all such materials, viz., crystalline solids, glasses, liquids and gases. It was thereby made evident that the study of the scattering of light is a fruitful pathway for the exploration of the structure of matter.

The second period was from September 1927 to February 1928. It began with my attempts to reconcile the apparent conflict between the ideas of wave-optics and Einstein's idea that light consists of discrete quanta of energy. That a reconciliation was possible between these two concepts of the nature of light was demonstrated by my success in deducing on the basis of the classical wave-principles, the existence, as well as the characters, of the two types of x-ray scattering, respectively with and without a change of frequency. This elucidation of the Compton effect suggested fresh experimental studies on the scattering of light making use of monochromatic radiation. These studies led to the discovery of the type of light-scattering in which a change of frequency manifests itself.

It may seem surprising but it was nevertheless the case that the new phenomenon was, in the first instance, observed visually. This was possible by reason of the availability in the mercury arc lamp of a powerful source of monochromatic light and because also of the extreme sensitivity of the human eye to feeble light under appropriate conditions. The observations which showed the universality of the phenomenon and revealed its origin were all made visually, using a pocket spectroscope of the direct-vision type. They were later confirmed using the photographically recorded spectra.



SIR C. V. RAMAN

C. V. Raman

MARCH 16, 1928 must have been an exciting day among scientists in Bangalore, India. It was the founding day of the South Indian Science Association and Prof. C. V. Raman of Calcutta University was to address the large assembly of distinguished scientists. He (1) included a number of simply implemented yet convincing demonstrations from the rostrum and described a phenomenon soon to bear his name, become one of the most powerful tools for the determination of molecular structure and win him the coveted Nobel Prize in Physics.

During the five years preceding this memorable address, already sure that "light scattering is . . . a meeting ground for thermodynamics, molecular physics and the wave theory of radiation." Prof. Raman had studied the blue opalescence of water, ice and the sky and demonstrated that, when a strong light is shone through clear glass, a similar bluish glow blazes its trail. Passing filtered sunlight from a heliostat-telescope through dozens of organic liquids, he discovered strange depolarization effects which were wavelength dependent. "Feeble fluorescence" seemed to be exhibited by every one of some 60

liquids investigated. Then the inspiration. Compton had just received the Nobel prize for his discovery of x-ray scattering with a resulting wavelength change. Was the ubiquitous optical "fluorescence" Raman had observed in reality analogous to x-ray scattering?

That the two were indeed similar in origin was theorized that March evening. When an intense beam of monochromatic light is passed through a transparent substance, the light viewed at right angles contains not only the original wavelength scattered in all directions but, in addition, weak spectral lines symmetrically displaced on both sides of the original wavelength. These Raman spectral lines are characteristic of the substance through which the light has passed and can serve to identify it unambiguously. Equally significant, the positions of the lines have a direct bearing on its molecular structure. Like x-ray diffraction patterns, infrared and micro-wave spectra, Raman lines can be put to work as a kind of molecular anatomical dissecting tool.

Raman, triumphing over years of what had seemed at the time to comprise unrelated, unmeaningful data now realized their implications. Several months following his address were devoted to even more fruitful experiments which led him and his colleague, K. S. Krishnan, to conclude:

1. For any given substance, the difference in frequency between the Raman lines and the exciting line was constant and independent of the frequency of the exciting line. Each substance displayed a characteristic scattering (Raman) spectrum.

2. The emitted lines were sharp and occurred in pairs uniformly separated in frequency units (or the more conveniently measured wavenumber) from the exciting line; lines on the low-frequency side were always more intense than their counterparts.

3. Emitted lines of benzene (the first material studied) were identical in wavenumber difference from the exciting line with the actual wavenumber of its strong infrared lines.

Apparently unknown to Raman was the treatment of scattering in Germany by Smekal (2), who had theorized that the interaction of light with molecules would give rise to line spectra. Although Raman was, unquestionably, the first to report finding the predicted lines, within a few months, two Russians Landsberg and Mandelstam (3) excited similar weak lines in quartz crystals.

Smekal's classical theoretical treatment was perfectly sound in view of the development of physics at the time but today Raman scattering is better discussed in quantum mechanical terms. Energies assumed by electrons are not continuous but distinct: they can exist at many different levels but not in between the levels. Electrons revolve about the nucleus only in discrete orbits corresponding to these energy levels. The absorption of external energy can jolt electrons from a rest orbit to an outer one from which they can return in either a single jump or in several, pausing momentarily for a spin in intervening orbits. Light of appropriate frequency multiplied by Planck's constant, h , is equivalent to an energy quantum capable of causing such orbital hops.

This is not to say that all of the light entering a transparent medium interacts with it. Most passes through unperturbed. Even in a completely clear medium, however, some light is Rayleigh scattered: a weak glow of the same color as the beam may be observed at all angles to the beam. In Rayleigh scattering electrons are first excited to a higher energy level than their ground or rest state then return with no net loss or gain of energy. This taking from one energy pocket and placing in another is indicated by the appearance of light of the same color. All light scattering intensity, incidentally, is proportional to the fourth power of the frequency. This accounts for the blueness of sky, water and ice and also, as will be seen later, favors the laser as a Raman source. Depending on the gas chosen and the geometry of the laser, hundreds of different wavelengths are now available as an excitation source.

In contrast to the constant-energy feature of Rayleigh scattering (Tyndall scatter is similar, the radiation bouncing off dust and colloidal particles rather than molecules), Raman scattering results from the sight-seeing stopovers by an electron on its way back home from a visit to a foreign orbit. Though most of the electrons wing back in express flights from the higher levels to the ground state, some return via local stop routes. Whenever they pause at a particular level, the energy corresponding to that hop appears as a Raman line. In Fig. 1 the origin of both the low-frequency excited (Stokes) line and

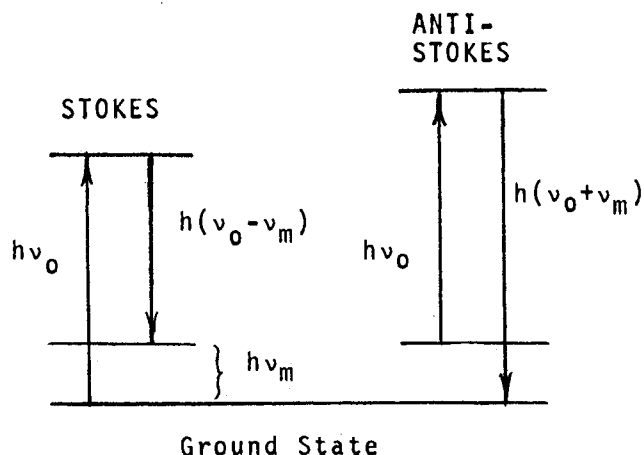


Fig. 1. Quantum mechanical representation of the origin of Stokes and anti-Stokes Raman pairs.

the high-frequency excited (anti-Stokes) line is explained in a quantum level diagram. A photon of energy $h\nu$, striking a molecule will raise it from its ground-state energy level by an amount equal to $h\nu$. If the molecule returns to a different energy state, it will do so with either the gain or loss of energy. The frequency of the exciting light will therefore be shifted; the intensity of the Raman line will be weak because so few molecules will be raised to this new energy level. As shown in Fig. 1, the anti-Stokes line originates when molecules in the new energy level, struck by a photon, are excited to an even higher level, and then return to the ground state. In both the Stokes and anti-Stokes transitions, the change in frequency is the same (ν_m). For the Stokes, the energy is lost, the frequency decreased; for the anti-Stokes, the energy is gained, the frequency increased. Since the population of excited states is usually lower than that of the ground state, the intensity of anti-Stokes lines is generally smaller than the corresponding Stokes lines. The ratio of intensities varies from almost unity to 10^{-6} . With increasing temperature, the population ratio increases as thermal energy is imparted to the molecule and the intensity ratio of the anti-Stokes to Stokes lines grows and so becomes a means of determining temperature. Anti-Stokes lines also serve to verify a Stokes line by, for example, distinguishing it from a grating ghost.

The explanation thus far of the origin of Raman spectra does not distinguish this phenomenon from fluorescence, yet there is a clear difference between them. Fluorescence requires that the quantum be absorbed first then reemitted. It is a two-step affair with a small but measurable (approx. 10^{-8} sec) time interval between the steps. Fluorescence can occur only when the exciting wavelength matches an absorption peak. With such an absorbing (colored) solution, of course, Raman spectroscopy is impossible, except by reflection.

While a comprehensive treatment of the origin of spectral lines from molecules is beyond the scope of this paper, we can indulge in some simplified generalizations. All lines originate from changes in periodic motions within the molecules and can be classified as 1) rotational in which the molecules spin on an axis; 2) vibrational in which the atoms oscillate much as a weight on the end of a coil spring; 3) electronic, i.e., the motion of electrons rather than atoms and molecular fragments; 4) interactions among the foregoing three.

Rotational energy changes are very small, involve gases ordinarily because the mean free path of molecules in liquids and solids is too small to permit rotation. In gases, the energy changes involve frequency shifts of around 1 cm^{-1} . Converted to wavelength, this represents 10^4 microns or 1 cm , in the heart of the microwave region. From rotational spectra can be derived the moment of inertia of a molecule from which, in turn, one can calculate the shape of a molecule, the angles and distances between atoms.

Vibrational spectra are generally in the infrared, $100\text{-}3500 \text{ cm}^{-1}$. Their uniqueness for each substance makes spectrophotometry one of the most powerful analytical tools.

The analogy between a helical spring and molecules oscillating in a stretching motion is so close that, to a first approximation, Hooke's Law applies. A large molecule can be viewed as a large number of masses linked by a number of coil springs. The number of possible vibrations or degrees of freedom equals $3N-6$ where N is the number of atoms in the molecule. Thus the more complex the molecule, the more complex the spectrum. Hooke's Law relates the frequency of oscillation to the force constant and masses of participating atoms. Knowing Raman or infrared frequencies thus immediately enables one to calculate force constants from which the thermodynamic properties of molecules can be derived.

Electronic spectra have been observed only quite recently (4) by the weak Raman spectra emitted by PrCl_3 crystals.

Until the advent of the laser, nearly all Raman spectroscopy was limited to vibrational spectra. Certain molecular characteristics can give rise to infrared spectra, others to Raman spectra, still others to both. Thus Raman and infrared techniques complement each other. A laboratory engaged in molecular structural studies is generally equipped with both types of measuring devices. For a particular molecular periodic motion to be either infrared or Raman active, a series of complex selection rules has been worked out. One rule will illustrate the way in which Raman and infrared spectroscopy can operate as a team.

When a molecule oscillates in a particular mode, it may create a dipole with the same frequency. Light at this frequency will be absorbed. If, on the other hand, the molecule in oscillating does not create an oscillating dipole then no absorption will appear at this frequency. N_2 and CO_2 are examples of both. N_2 is homonuclear, diatomic without a permanent dipole moment. When it oscillates it does not create a dipole moment so its vibrational frequency cannot be observed in absorption. By contrast, CO_2 is a linear, triatomic molecule with C at the center of the line linking the two O atoms. Like N_2 , CO_2 has no permanent dipole moment. When its two O atoms vibrate in a breathing mode, in phase towards and away from the C, the movement is symmetric and cannot be observed in absorption. However, the two O atoms can vibrate additionally in an asymmetric mode: out of phase, the two O atoms pulsating in the same direction at the same time. In this vibrational mode, a dipole moment is created and can be observed in absorption. N_2 is a transparent gas, can be used for purging infrared spectrometers while CO_2 has a sharp infrared band corresponding to its asymmetric vibrational mode.

While symmetric molecules exhibit no permanent dipole moment, one can be induced in them by an electrical field. Their electrons and protons are attracted in opposite directions, upsetting the charge symmetry and inducing polarization. An intense visible or ultraviolet monochromatic beam is one means of introducing an electrical field; that on which Raman spectroscopy is based. Donning its classical rather than its

quantum-mechanical hat, light consists of periodic electromagnetic waves. In a single cycle, the electrical field generated by the light surges and relaxes sinusoidally. This varying field induces a change in polarizability of even a symmetric mode to excite a Raman line.*

It turns out that all symmetric vibrations are Raman-active and, since all molecules present at least one symmetric mode, all emit characteristic Raman spectra. For molecules with a center of symmetry, therefore, those transitions allowed in Raman excitation are forbidden in infrared absorption; those that are Raman-forbidden are infrared-active. Measurements by both infrared and Raman are thus uniquely complementary for the determination of structure. They have shown, for example that N_2O is N-N-O rather than N-O-N while CS_2 is a symmetric S-C-S. Since for CS_2 all vibrations that are Raman active are infrared inactive and *vice versa*, while for N_2O the vibrations are simultaneously Raman and infrared active, one can conclude that N_2O has no center of symmetry while CS_2 does have one.

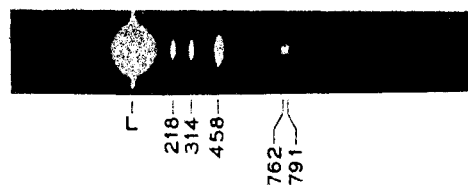


Fig. 2. Vibrational Raman spectrum of CCl_4 . All lines are infrared forbidden. A 7 mW He-Ne laser was the exciting source. A one-hour exposure was required on the optically slow spectrograph (12).

The rationale for assigning structure to a simple molecule like CCl_4 is quite straightforward. Four principal Raman lines (Fig. 2) appear, corresponding to the stretching vibrations among the Cl atoms themselves and between the C-Cl atoms. None of these infrared frequencies ($218, 314, 458, 791 \text{ cm}^{-1}$) is absorbed, from which one can immediately conclude that the molecule has a center of symmetry. Its carbon atom is centrally caged with chlorine atoms uniformly guarding it. Such a molecule can exist in but two configurations: a plane or a tetrahedron. It can be shown that if the CCl_4 molecule is tetrahedral it would have one completely polarized Raman line and three unpolarized Raman lines; if planar, it would have three polarized lines among its active Raman vibrations. By combining experiment with theory, it has been proved that CCl_4 is a tetrahedron with the Cl atoms at the vertices and the C at the center. The 458 cm^{-1} line is found to be polarized in the same direction as the laser excitation.

Clearly then, the intensity of Raman lines is a function of the polarizability of the particular transition. If the vibration is completely symmetric, the corresponding Raman scattered line will be polarized in the same direction as the exciting light. If asymmetric vibration is the origin, the scattered light will not be polarized in the same direction as the incident light.

*As first shown by E. U. Condon in 1934, an electric field can induce infrared absorption of a "forbidden" transition. A dipole moment is created in a vibrational mode which, at rest, has a dipole moment of zero. A variable density infrared filter is, thus, attainable.

The degree of symmetry of the vibration is best expressed in terms of the depolarization ratio, which is the intensity ratio of scattered light polarized perpendicular to the plane containing both the direction of the incident light and the direction of observation, to that parallel to this plane. Raman lines corresponding to totally symmetric vibrations have a depolarization ratio between 0 and 6/7. When the ratio equals the theoretical maximum of 6/7, the Raman line originates from an asymmetric vibration.

THE current glamour status of molecular activity displayed as Raman lines can be traced to the beautiful development of the continuous laser as a source, linked with the already-established attractive features of classical, i.e., Hg excited, Raman spectroscopy, namely:

1. Wavelength and intensity measurements are easily made because the region of the spectrum utilized (visible and ultraviolet) is amenable to photography and the lines produced are quite sharp.

2. A sample containing water absorbs obscuringly in the infrared but presents no problem with its Raman spectrum since that of water is so weak.

3. Measurements of concentration are facilitated by its linear relationship with intensity.

4. The complete range of vibrational frequencies can be spanned without instrumental change.

Disadvantages, however, are:

1. Colored samples absorb the exciting light and interfere with the Raman excitation.

2. Samples must be perfectly clear or Tyndall scatter interferes.

3. Samples must not fluoresce; any broad background will obliterate the weak Raman lines.

4. Even with a spectrometer of high optical speed hour-long exposures are often required.

5. The intense illumination may cause photodecomposition of the sample.

The key to the relative unpopularity, as an analytical tool, of Raman as compared with infrared spectroscopy has been the weak lines produced by Raman scatter. Few molecular physicists or analytical chemists have had the patience to wait an hour for a photographic spectrum, an understandable reluctance in view of the ten minutes or less required to obtain an infrared absorption spectrum. To detect the weak lines fast photographic emulsions are necessary. These tend to be heavily fogged and exhibit poor contrast. Quantitative interpretation on the basis of photographic density measurements of spectral lines often proves to be as hazy as the lines measured.

The continuous laser, by increasing the intensity of Raman lines has revived interest in the technique. Coupled with the concurrent advances in electronic detection devices, the increased laser output has made photo-electric readout feasible. In a few minutes a complete vibrational spectrum can be recorded in direct terms of intensity *vs.* wavelength. Since intensity is directly proportional to concentration, quantitative chemical analysis is greatly simplified.

Conveniences the continuous laser offers are:

1. A single frequency source replaces the multiple-lined Hg lamp. No filtering is necessary.

2. Raman lines, never narrower than the exciting line, are sharpest from a laser source. The half-width of a laser line is around 0.1 cm^{-1} , about half that produced by a spiral Toronto Hg lamp.

3. Because of the directionality of the laser beam, focusing and collimating are simplified.

4. The beam is polarized to the extent of 99.9%.

5. Because of the directionality, the fineness of the beam, and the single line emitted, a 100 mW He-Ne laser produces an energy density around 1000 times as great as a Hg source producing 1 W at 4358Å.

6. With an ionized noble gas laser refillable with Ar, Kr or Xe, dozens of lines may be selected from 4545Å to 1μ . Without changing the gas, different lines can be obtained simply by adjusting a prism external to the laser. Thus fluorescence and absorption of substances can often be successfully circumvented.

7. By eliminating the ultraviolet radiation from Hg sources, photodecomposition is avoided.

8. With a large choice of exciting frequencies, the problem of colored substances diminishes.

THE molecules comprising gases and liquids are free to roam about at random. In this respect they differ from solids whose molecules are firmly rooted. A single crystal of a solid offers an ideal specimen for Raman spectroscopy because its molecules are not only spatially fixed but all are similarly oriented. The laser pencil beam will penetrate a crystal along a fixed axis with respect to which all molecules in the crystal are uniformly positioned. For example, the laser beam, its light polarized in the crystal's x-axis, can be directed along the crystal's y-axis and the output scattering observed along the z-axis. Since the laser photons' electric field is in the x-direction of the crystal, some of the vibrations of the crystal will couple with the field to produce Raman lines; other vibrations will couple with fields in the z-axis. If the light field is in the x-direction and we observe the scattered light in the y-direction, there will be vibrations that are symmetric in relation to the x-axis and the Raman effect will also be polarized in the x-direction; on the other hand, if the vibration is asymmetric in relation to the x-axis, the Raman frequency may be polarized in the z-direction. For each of the 32 point groups to which any solid must belong, group theory has predicted the possible combinations of x, y, z polarizations of the incident of scattered beams. Laser Raman spectroscopy, in a few brief years, has thus become a tremendously powerful tool for crystallographic studies.

An example of the applicability of laser Raman spectroscopy to crystallography is zinc oxide, a substance to which a great deal of current experimentation is devoted because of its unique electrical properties. ZnO is extensively coated on papers for electrostatic copying; as far back as the days of crystal radio sets the "cat's whisker" benefited from the semiconductor property of ZnO; its electroluminescence converts an alternating electric field directly into light; its ability to convert infrared rays into visible light, thermoluminescence, is as yet unexploited as is candoluminescence—whereby ZnO emits brilliant red and blue lights at specific elevated temperatures. Photovoltaic also, ZnO, suspended in water, produces an electric current from light.

ZnO is hexagonal and belongs to the point group C_{6v} . For such a crystal, only one vibration (referred to as A₁) is completely symmetric and non-degenerate. This is to say that

in ZnO only one type of stretching or "breathing" vibration can occur. It means that the line corresponding to this vibration will be highly polarized in the same direction as the laser.

In mathematical terms, physicists state that the polarizability tensor components,

$$\alpha_{xx}, \alpha_{yy}, \alpha_{zz} \neq 0$$

for this vibrational mode. If the laser light is polarized in the x-direction to the crystal, the Raman frequency will be polarized in the same direction, a rule that holds true for the other two axes as well. For a material like ZnO, two other Raman lines will be excited for which

$$\alpha_{xx}, \alpha_{yy}, \alpha_{xy} \neq 0$$

This means that, if the laser light is x-polarized, the Raman frequency will have both x and y polarizations. There will also appear one line for which

$$\alpha_{xz}, \alpha_{yz} \neq 0$$

All of these lines have recently been observed (5) and the selection rules for the C_{6v} system were shown to be obeyed. If ZnO had been cubic instead of hexagonal, the polarizability selection rules would have been entirely different. Raman studies can thus help to establish the structure of a solid.

They can furthermore pinpoint the symmetry characteristics of any vibrations of a solid by determining which of the polarizability tensors are different from zero for a specific frequency. Investigations along these lines have recently been performed for a number of solids like calcite, quartz, rutile and gallium phosphide.

Zinc oxide was the medium through which another curious physical phenomenon was recently observed by Raman scattering: conservation of momentum of a phonon. An optical phonon is a vibration in a solid. It is a mechanical wave the speed of which is between that of sound and that of light. This is in contradistinction to a photon which is an electromagnetic wave moving at the speed of light. The momentum of a phonon is its mass multiplied by its velocity.

In a highly uniaxial crystal such as zinc oxide, the apparent phonon mass along the three axes is not constant. The configuration of the molecule along the three directions differs and so the molecule as seen by a phonon is different in mass in the three directions. Since the mass changes, the velocity of the phonon must change in inverse proportion for the momentum to be conserved. If the velocity changes, then the wavelength of the phonon will change proportionately.

The effect can be detected by interacting a photon with a phonon in a direction almost parallel to the exciting photon beam. In other words, by directing a laser beam down one of the axes of a crystal and pointing this almost but not quite along the optical axis of a spectrometer, the Raman line corresponding to the phonon in one crystal plane then another should change its wavelength. This was first observed at the Bell Labs in GaP by Henry and Hopfield (6) with a change of around 20% in the wavelength of the line.

More recently, Porto, Tell and Damen (7) found a shift of a much greater magnitude in ZnO by pointing their laser beam in a near-forward direction only 0.5° from the optical axis. In wavenumber units, the line shifted from 140 to 407 cm^{-1}

(Fig. 3). Of course, in ordinary Raman experiments, with the observation at right angles to the laser excitation, the line appears at its normal 407 cm^{-1} . The success of Porto's group stemmed from their examination of the radiation at tiny glancing angles, free from the normal interfering Rayleigh scatter, which had been unavoidable before a double spectrometer was substituted for a single one.

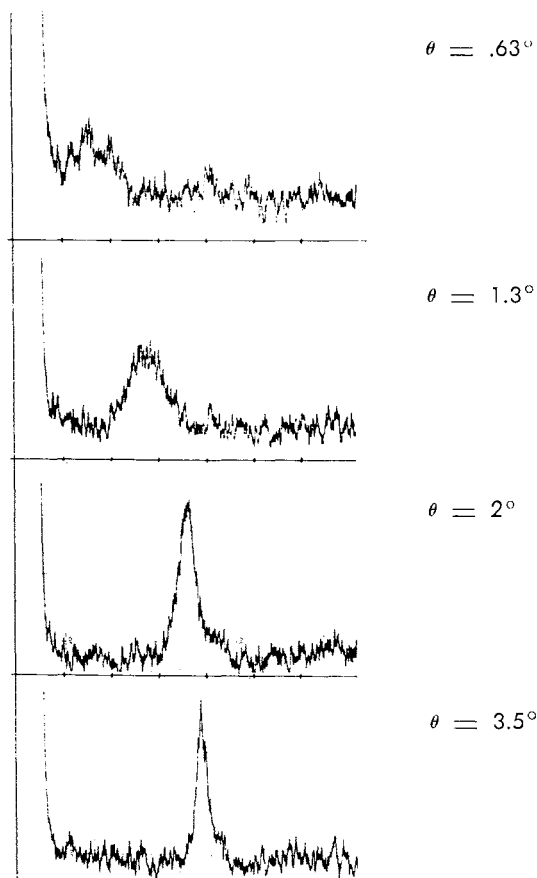


Fig. 3. Interaction of a phonon and a photon at very small, near-forward angles to the laser beam results in a shift of the ZnO Raman line normally seen at 407 cm^{-1} to a position within 140 cm^{-1} of the laser excitation frequency, as shown in top spectrum (7).

For the study of solids, the laser's unmatched directionality and complete polarization properties are thus exploited. For rotational spectra measurements, another property of laser light—its narrow line width—is put to work. Rotational band spectra consist of lines which are closely-spaced. Since an excited Raman line can be no narrower than that of its source, the laser has added another dimension to the observation of rotational spectra. Studies in this area which, heretofore, have required huge walk-in spectrographs of extremely high resolution are suddenly surging. Employing lab-bench size equipment, Porto, Cheesman, Weber and Barrett (8) were able to photoelectrically record rotational spectra $<1\text{ cm}^{-1}$ of the exciting line with signal:noise in excess of 100.

Current laser Raman spectroscopy is optimized by not only a continuous laser source but a double grating spectrometer which disperses the beam with vast reduction in scattered light over that in a single spectrometer. Especially chosen electronics, too, discriminate against noise while enhancing weak signals to permit instantaneous read-out.

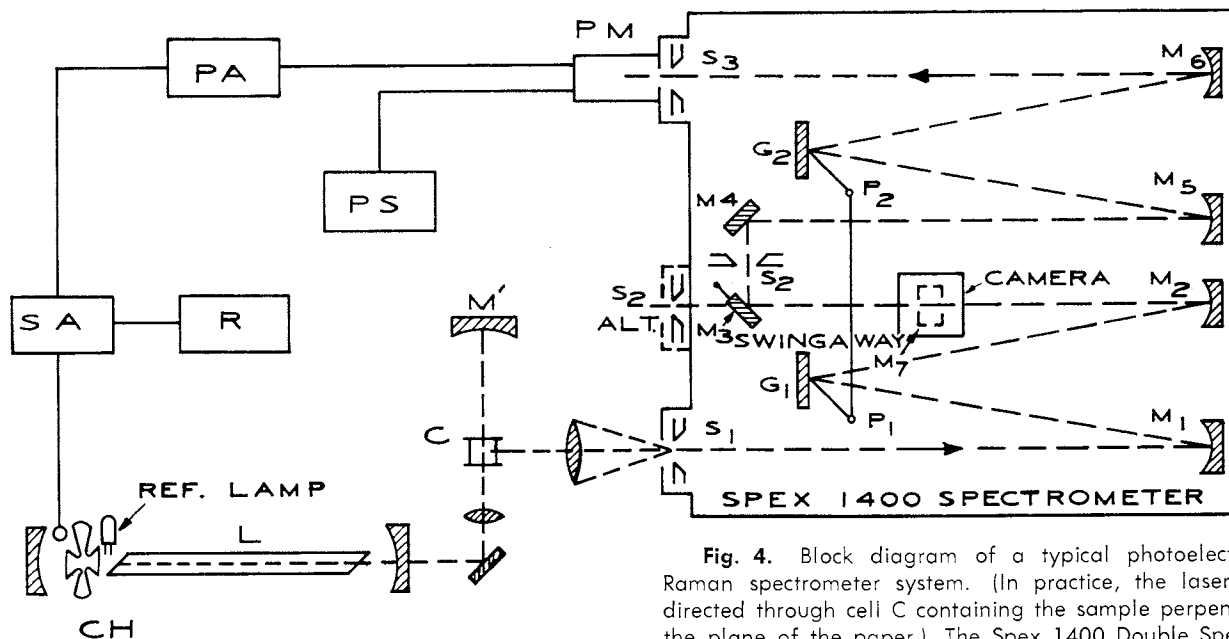


Fig. 4. Block diagram of a typical photoelectric laser-Raman spectrometer system. (In practice, the laser beam is directed through cell C containing the sample perpendicular to the plane of the paper.) The Spex 1400 Double Spectrometer may also be used photographically by swinging mirror M7 into position or as a single spectrometer by swinging M3 out of its kinematic indent.

A TYPICAL apparatus system (9) is shown in Fig. 4. Here a 70 mW He-Ne continuous laser 6328A beam is focused by means of a microscope objective set in reverse to produce a beam of about 0.05 mm diameter. This is passed through a cell containing the sample or, through a crystal itself. A mirror M' reflects the light back through the sample tube to double the exciting light intensity. At right angles (both the spectrometer and Raman optics are shown in plan view for ease of presentation) the light is focused on the entrance slit of spectrometer with a condensing lens of focal length calculated to fill the collimating mirror M1 also. The double grating system is shown schematically, a tie bar P1-P2 insuring that the gratings turn together. Only the monochromatic line of interest is allowed to pass through to the second or spectrometer half of the system. This, after traversing a second diffraction path emerges through the exit slit S3 to a photomultiplier. Depending on the wavelength of the exciting line, both the Amperex 150 CVP, S-1 response, and EMI 9558, S-20 response, photomultipliers have been found suitable but, to optimize the signal:noise, they must be cooled with liquid nitrogen. In the diagram, PA refers to a preamplifier and PS a high-voltage supply feeding the dynode network of the photomultiplier. SA is a synchronous amplifier, the timing signal (75-400 cps) to which is supplied by a chopper and reference lamp. The same chopper interrupts the laser beam which is then locked into the frequency of the reference signal. The incorporation of a fine-tuned discrimination circuit into the synchronous amplifier blocks out all noise except that which occurs at the selected frequency.

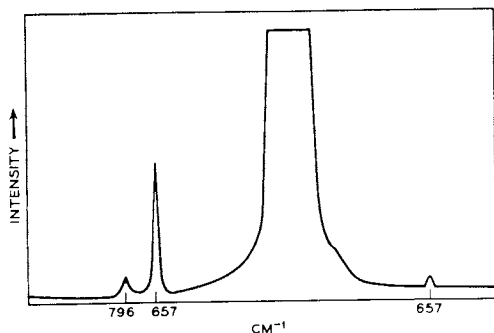


Fig. 5. Raman spectrum of CS₂ taken with a single spectrometer.

The overall advantages of the scheme are depicted in Fig. 5 and Fig. 6, both Raman spectra of CS₂, one taken with a single spectrometer the other with a double spectrometer. Note first the sharp enhancement of the two principal lines at 657 and 796 cm⁻¹; so strong are the signals in Fig. 6 that they are forbidden off scale. But, even more striking are the two "forbidden" lines, one clearly visible at 397 cm⁻¹, the other appearing as a slight rise above the noise at 1500 cm⁻¹. Forbidden lines are, according to selection rules, Raman inactive. Nevertheless, they can appear at exceedingly low intensity levels as a result of interactions among, rather than within, molecules. Forbidden lines would be expected from a liquid where molecules are crowded together but not from a gas where the population density is so much smaller. As with people, overcrowding tends to create problems.

Pushing sensitivity is the constant subject of attention in Raman work as elsewhere. The advent of the Spex 1400 has,

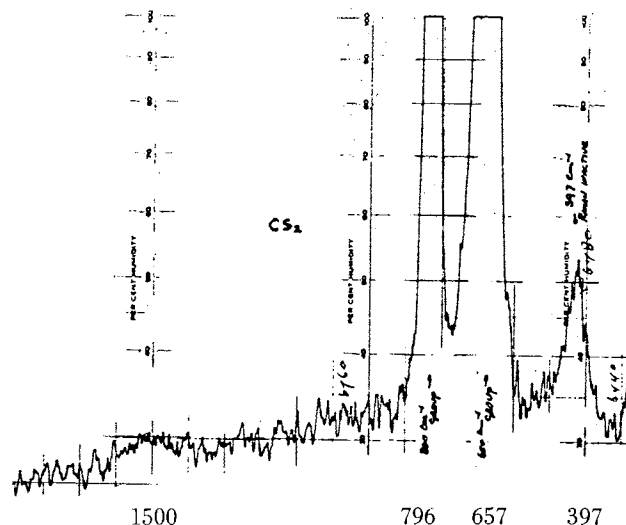


Fig. 6. Raman spectrum of CS₂ taken with a double spectrometer showing forbidden lines hidden behind the scattered light background in Fig. 5.

as shown in Fig. 6. put new brightness into the weak lines. This because of the long-known but heretofore untapped ability of a double spectrometer to reduce scattered light which originates almost entirely from the grating surface in a modern grating spectrometer.

Superimposed on a diffracted light beam at any particular angle is background resulting from spurious reflections caused by an imperfect grating. Gratings are ruled in evaporated aluminum and replicated in plastic. Both have a graininess or texture consisting of surface irregularities which reflect or scatter light randomly. In addition, any chatter by the diamond as it ploughs endlessly through the aluminum in the ruling process, and surface imperfections in the diamond itself, both introduce microscopic—electron microscopic to be more precise—roughness to the grating surface, resulting in scatter.

Such scattered or stray light generates a continuous background which, depending on its intensity, can mask some or all of the Raman lines. It is a subject of much current concern especially from the standpoint of methods for its reduction. Recently, Landon and Porto (10) compared the scattered light characteristics of a single spectrometer with a double one, both employing replica gratings from the same master. As shown in Fig. 7, the intensity of scatter in a single spectrometer drops to a constant value around 10^{-5} that of the monochromatic beam. As would be expected theoretically, the value plunges to 10^{-10} in a double instrument. Fig. 7 represents, succinctly and dramatically, the reasons for the acceptance of double spectrometers for Raman work. The problem of detection of lines grows increasingly difficult as they approach the parent line. For studies of close-spaced rotational Raman spectra where lines bunch up almost on top of the exciting line, a double instrument is a virtual necessity.

Grating ghosts also interfere with Raman lines not by forming a smokescreen like stray light but by posting line pairs that can easily be confused with the real things. Typi-

cally, the intensity of ghosts in B&L gratings is in the order of 0.003-0.03% which values are as strong or stronger than Raman lines produced in a single spectrometer. Fortunately, a double spectrometer reduces the ghost intensity exponentially exactly in the same manner as stray light.

Despite their resemblance to Raman lines, ghosts can be distinguished. First of all, ghost pairs are equidistant from the parent lines in wavelength terms while the Stokes and anti-Stokes twins are equidistant in wavenumber. The differences are easily measurable. For example, with a 6328Å (15,800 cm^{-1}) He-Ne laser line, a Raman pair 200 cm^{-1} distant would appear at 16,000 and 15,600 cm^{-1} . In wavelengths, these are at 6225Å and 6410Å, -103Å and +82Å, respectively, from the exciting laser line. Were they ghosts, the two wavelength differences would be identical.

Frequently, however, the anti-Stokes or matching ghost line is an uncooperative witness, too weak to testify. All is not yet lost. Another means of separating the two is based on the fact that a ghost is merely a displaced spectral line while a Raman line is one of a different wavelength than that of the exciting line. Insertion of a "spike" interference band-pass filter of the laser wavelength will not affect the intensity of a ghost but will, of course, reduce that of a Raman line.

If, after exhausting the possibility of ghosts, lines appear which are still unidentified, they may be due to Raman scatter of objects in the path of the laser beam: coatings, cement and glass of optics, fingerprints, etc.

LASERS are almost perfect polarizers, to the extent of about 99.9%, a property that simplifies molecular structural studies. Unfortunately, however, gratings polarize light, too. The latter subject has been little investigated until recently when a healthy sense of inquisitiveness prompted W. G. Nilsen and J. G. Skinner of the Bell Telephone Labs to run a polarization curve on their spectrometer for the purpose of obtaining what they expected would be a small, possibly insignificant, correcting term. Instead, they found sizable polarization effects for the one grating investigated, effects which were wavelength dependent and in some regions so great that the ratio of light transmitted in one direction was 10-20 times as great as the perpendicular component. Brought to our attention, their findings mystified us until Prof. G. Ascarelli of Purdue University pointed out similar prior findings tucked away in Appendix P of John Strong's "Concepts of Classical Optics," (11) for gratings ruled ten years ago at Johns Hop-

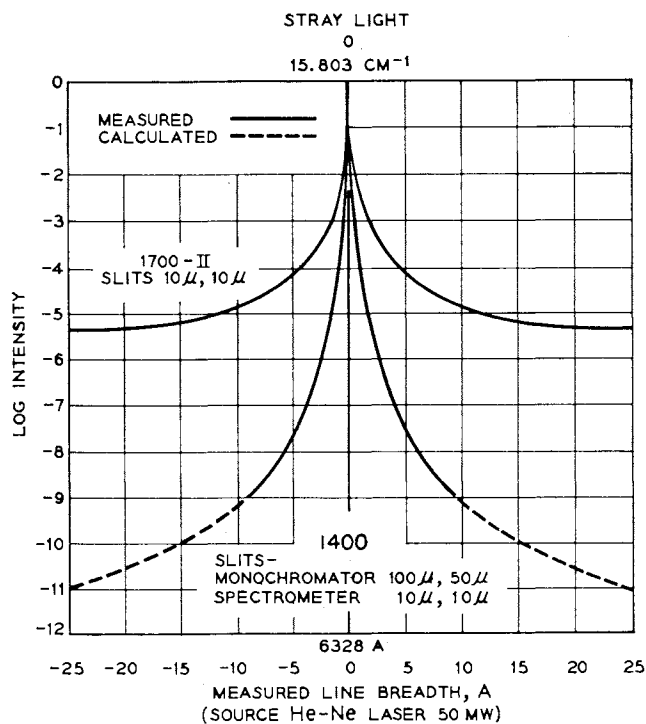


Fig. 7. Comparison of scattered light intensity between a single and double spectrometer (10).

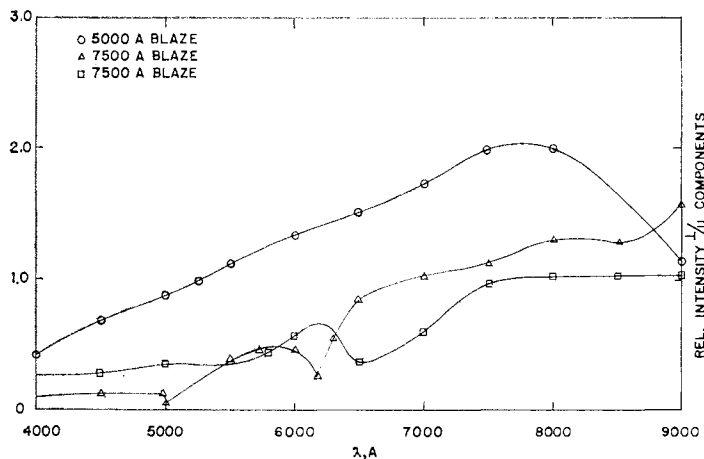


Fig. 8. Polarization vs. wavelength of three gratings. The two blazed at 7500Å are replicas from different masters.

1200 groove/mm

Grating polarization is indeed significant, as evidenced by the three curves shown in Fig. 8 taken on one spectrometer. Circles represent a grating with 1200 groove/mm blazed at 5000A (B&L Master 1041); triangles and squares are from two ~~7500~~ ⁷⁵⁰⁰ gratings replicated from different masters (B&L 2442 and 857, respectively). The remarkable differences among the three gratings surely warrant further study. Some tentative, and hopefully non-erroneous conclusions, have been drawn by D. O. Landon on the basis of these data plus measurements he has conducted on several other gratings:

1. Polarization appears to be minimal at the blaze wavelength and is independent of the groove spacing. The unity point on the graph may be a means of determining the blaze angle. The shape of the curve may be related to the efficiency curve of the particular grating.

7500 groove/mm

2. Above the blaze wavelength, the polarization curve is relatively smooth and unchanging. Polarization measurements of Stokes lines with either ~~7500~~ ⁷⁵⁰⁰ groove/mm grating depicted using a He-Ne laser source should not be hampered unduly once a cancelling correcting curve is applied.

3. Some reported grating anomalies—sharp dips in the intensity curve when measuring black body radiation—occur at the same wavelength as the dips in the polarization curves.

4. Replicas from the same master exhibit similar polarization curves.

The unexpected dovetailability of the continuous laser with Raman spectroscopy reaffirms the wisdom of conducting research for its own sake, unencumbered with a specific goal. Emerging from the heterogeneous laser investigations thus far are several casual applications in such areas as metrology—determination of distances and angles with extreme accuracy over great distances; or civil engineering—keeping tunnel diggers working along a straight line. And now, supplying the source which remodelled Raman spectroscopy into a busy tool, lasers help open a vista into basic physics.

ACKNOWLEDGMENT

GATHERING the latest reasonably-substantiated information at the brink of a trail-blazing frontier is not uncommonly associated with some degree of brain-tapping. Of this we confess doing our share. And for this we are grateful to each of the persons mentioned earlier.

To S. P. S. Porto of the Bell Telephone Laboratories, however, we are indebted for much more than the vast fund of information he shared with us, painstakingly translating it into terms we would understand. His enthusiasm for the subject, sparking the ingenuity and inspiration of so many of his colleagues, rubbed off on us as well.

We are grateful for the hours he spent with this manuscript and the good humor with which he offered comments, corrections and criticism. We trust he will catch up with any time missed at the chess board, bridge table, bowling alley, behind a fishing rod or in front of a spectrometer.

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—A.J.M.



1400 DOUBLE SPECTROMETER/MONOCHROMATOR SPECIFICATIONS*

A precision-built double Czerny-Turner mount with two ganged gratings, this instrument is designed primarily to minimize scattered light and so permit the detection of weak spectra (such as Romon lines) close to a strong line (such as 6328A from a He-Ne laser). It is capable of being used as a single or double monochromator, spectrometer or scanning spectrometer. The monochromator half may also be used as a rapid wavelength sweeping device or as a spectrograph, the latter by deflecting the light upward through an externally controlled 45° mirror.

FOCAL LENGTH: 750 mm

SPECTRAL COVERAGE: 1850A to 235 μ

APERTURE: f/6.8 in the U.V. (as the plane grating rotates to increase wavelength the effective aperture decreases from f/6.3 at the direct image to f/10 at maximum wavelength setting).

DISPERSION: (reciprocal linear) Constant at any one setting, it is a maximum of 11A/mm in the U.V., improving to about 6.5A/mm in the infrared .

TRACKING ACCURACY: wavelength matching ability of both halves of instrument $\pm 0.1A$ over any 5000A interval.

RESOLUTION: 0.09-0.12A at 6328A, half-width measurement
0.20-0.30A at 6328A, 1/10-width measurement

(Half-width measurements are significant for two bordering lines at approximately equal intensity; width at less than 1/2 intensity is meaningful for a weak line in proximity to a strong one.)

WAVELENGTH: Direct reading in angstroms

Range: Grating rotation 0-72°; 0-15700A with a 1200 groove/mm grating, 0-235 μ with an 8 groove/mm grating (Additional grating rulings available are 3600, 2400, 600, 300, 150, 75, 60, 40, 30, 20).

Accuracy: $\pm 1A$ over 6000A.

Periodic Error: $\pm 0.2A$ over 50A (one rotation of the lead screw).

Readability: $\pm 0.1A$. **Resetability:** $\pm 0.3A$.

SPECTRAL PURITY: with monochromatic source, 10⁻⁹ of the intensity of the 6328A laser line within 5A of the peak of that line, 3x10⁻¹¹ at greater than 50A. (Lumped together in the specification are all of the optical imperfections which allow improper wavelengths to emerge superimposed on the wavelength indicated by the counter. Scattered or stray light from the grating is the principal origin. The only acceptable technique for evaluating spectral purity is to use a monochromatic source, preferably a He-Ne 6328A gas laser. Continuous sources involve immense, uncontrollable variables such as spectral distribution, grating blaze and detector response. Any measurements made with a continuum are, therefore, difficult to interpret.)

*Although gratings are rapidly interchangeable, figures are normalized for a 1200 groove/mm grating in Order I, set for the U.V. unless otherwise specified.

SCANNING: Continuously variable, servo-controlled†; range either 0.25-1000A/min or 1-6000A/min; plug-ins for fixed speeds; limit switches at both ends of travel; event marker activating 1.5 watt 6 vdc pen marker every 5A. A wavelength take-off potentiometer is available for driving an X-Y recorder.

MIRRORS: are aluminized and overcoated with MgF₂ to maintain reflectivity above 90%.

GRATINGS:

Size: 102 x 102 x 16 mm or 102 x 150 x 25 mm for MIT-B&L gratings used for high angles

Ruling: 3600 to 8 groove/mm **Blaze:** 1500A to 112.5 μ

Efficiency: typically above 70%

Ghost Intensity: typically below 0.05%

Satellites (grass): root structure almost undetectable

Resolving Power: typically 70-95% of theoretical

Mounting: kinematic, instantly interchangeable

(World renowned for their performance and variety, Bausch & Lomb gratings are employed exclusively. Replicas are "pulled" from masters ruled on the B&L interferometrically-controlled engines as well as the MIT masters of extraordinarily-high resolution and low ghost intensity. Because no grating is perfect, we strive to choose ones whose performance best suits each application.)

SLITS: Bilaterally adjustable 18 mm straight or 50 mm curved; fishtail; shutter; 3-position Hartmann diaphragm.

CAMERAS: can either replace exit slit or be positioned topside for rapid changeover; 500A spectral range.

4" x 5" plate and Polaroid cut film

3-1/4" x 4-1/4" Polaroid roll film

REFRACTOR PLATE: 1/16", 1/8" or 1/4" rotates to display repetitive spectrum on oscilloscope; time resolution to 10⁻¹ sec/A; spectral coverage to 50 A; photoelectric trigger.

ADDITIONAL ACCESSORIES:

Readout electronics

Optical bar and riders

Photomultiplier attachments

Photomultiplier cryostat

Photographic shutter

Straight-through Optics to permit in-line source and detector.

CONSTRUCTION:

Materials: aluminum (non-magnetic with exception of hardware)

Size: 37" l. x 31" w. x 13" h.

Weight: 250 lbs. net (360 lbs. boxed)

POWER: 115v. 50-60 cycles, 100 watt
230v. 50-60 cycles, 100 watt

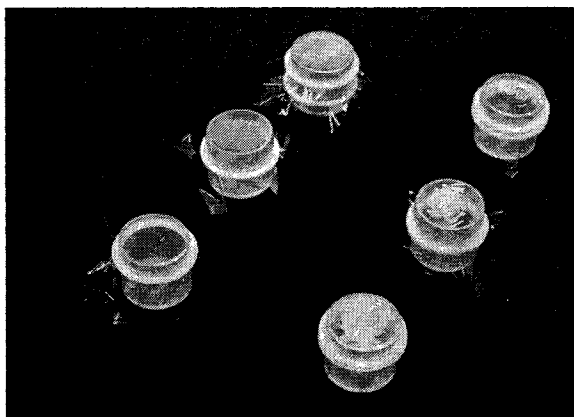
†Scanning controls in separate unit permit remote operation.

tricks of the trade

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2. Soon after we announced our Liquid Cells, John Johnson of Westinghouse's Commercial Atomic Power Department in Waltz Mill, Pa., complained that they were misnamed, being equally suited to the analysis of powders contained between two layers of Mylar film. The sandwich is prepared by first stretching the first layer of Mylar with a Teflon or polypropylene ring pushed down below the indenting shoulder. After the sample is spread, the top layer of Mylar is stretched with a 3514 polypropylene ring snapping it into the indent with a 2" dia. 3518 ring. If the Mylar is wrinkled, heating will iron it out.



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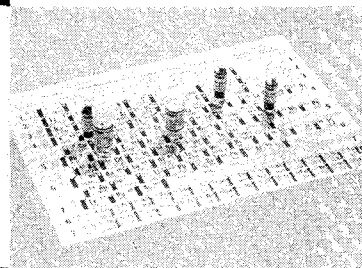
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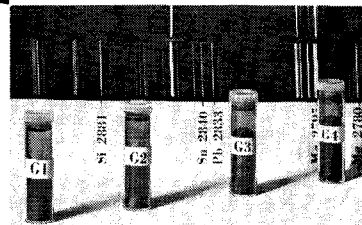
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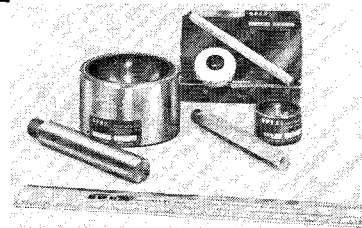
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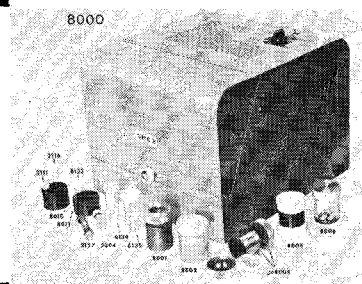
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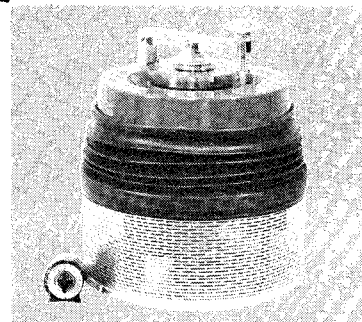
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