

The

SPEX

INDUSTRIES, INC. • 3880 PARK AVENUE • METUCHEN, N. J., 08840 • ☎ (201)-549-7144

Speaker

LOW-FREQUENCY RAMAN SPECTROSCOPY

James F. Scott

Dept. of Physics and Astrophysics
University of Colorado

THE question is often asked: "How close to the exciting line can you measure Raman Spectra?" Of course, many answers are possible, depending on the experimental technique. In this article I would like to provide an answer within the context appropriate for most physicists and chemists, who employ low power gas lasers for excitation and a double grating spectrometer. Several examples taken largely from my own experiments are presented. They illustrate the performance which may be obtained within approximately 2-3A of the laser wavelength for scattering in crystals.

First, let us consider the kinds of experiments apt to yield spectra in this very low frequency region. The first category is that of structural phase transitions in solids. In displacive phase transitions which are second-order or nearly so, a "soft" or temperature-dependent phonon is generally observed whose frequency tends toward zero as the transition temperature is approached from above or below. This phenomenon was first observed in quartz by Sir C. V. Raman himself more than thirty years ago [1], and analyzed from a lattice dynamical standpoint by Bill Cochran [2]. Many good examples may be found in the literature now. In SrTiO_3 Paul Fleury, John Worlock and I were able to follow the soft modes [3] down to about 10 cm^{-1} (or 2.4A) from the laser. Fig. 1 shows spectra obtained for a very similar phase transition — that in LaAlO_3 . The lanthanum aluminate phase transition occurs at about 800K, where Raman measurements at low frequencies are generally hindered by large linewidths. The data in Fig. 1 were obtained with about 200 mW at 5145A with an alumina furnace available from Norton Company, Columbus, Ohio. (Price, including two 1/2" quartz windows mounted at the furnace center, about \$300.) The scattering geometry is shown in Fig. 2. These spectra, and those in SrTiO_3 , were obtained with a Spex 1400 double spectrometer and no "tricks" or modifications. It seems very likely that the addition of a third monochromator stage and/or an iodine filter would make possible soft-mode measurements much lower in frequency. This is an especially exciting prospect, since Alex Müller has shown recently [3] that within 20 or 30 degrees of the transition temperature, many crystals go from "classical" dynamics with a Curie-Weiss temperature dependence for their soft mode

$$\omega(T) = A[T_0 - T]^{1/2} \quad (1)$$

to "critical" behavior

$$\omega(T) = B[T_0 - T]^{1/3} \quad (2)$$

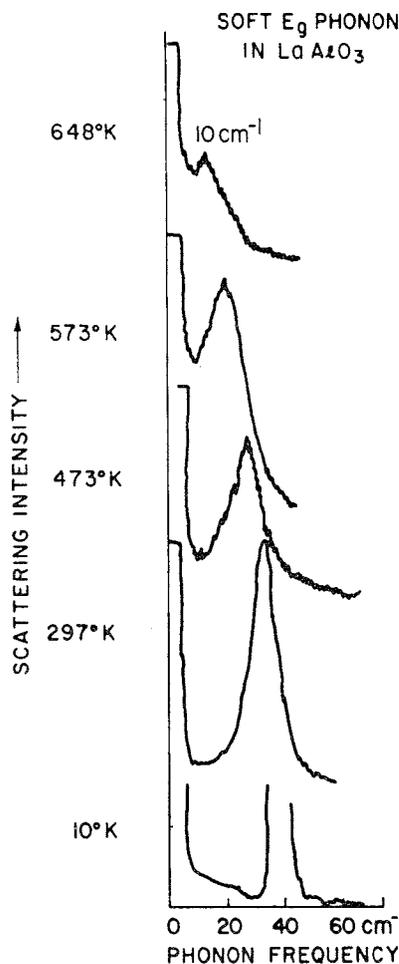


Fig. 1. E_g soft mode in LaAlO_3 (Ref. 3).

The occurrence of such a 1/3 exponent is well known in magnetic systems [4,5] and was first shown for phonons in some work done with quartz [6,7]. These interesting exponents are among the most important parameters Raman spectroscopists can extract from soft mode studies. To determine them accurately we need to be able to measure very low frequencies (5-10 cm^{-1}).

Very recently Riste's group at Kjeller, Norway has found [8] an anomalous "central component" centered at zero frequency in the neutron scattering from SrTiO_3 near $T_0 = 105.5\text{K}$. Edgar Steigmeier has reported [9] the detection of a similar feature in the Raman spectra of ferroelectric SbSI . SbSI spectra [9] of Steigmeier, Harbeke and Wehner are shown in Fig. 3. The central component, analogous to critical opalescence in liquid/gas systems, is prominent in the region 0-3A from the exciting line. Detection was by means of a Spex 1401. Again, insertion of a third monochromator stage and/or an iodine absorption cell would allow more detailed study of this phenomenon. The interpretation of these data is quite controversial.

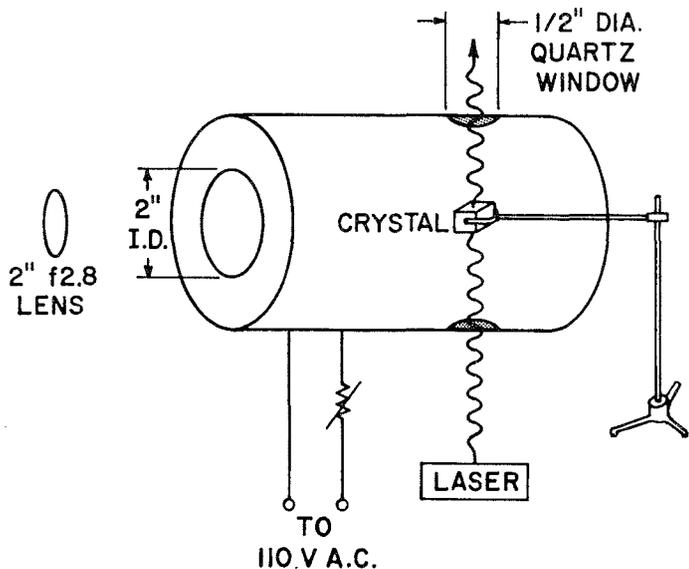


Fig. 2. Scattering geometry with Norton high temperature furnace.

Two other examples of very low frequency spectroscopy are shown in Figs. 4 and 5. Fig. 4 is that of the soft mode in CsH_2AsO_4 , an isomorph of the hydrogen-bonded ferroelectric KDP. All such crystals exhibit spectra centered at $\omega=0$. The spectra shown were obtained with a Spex 1401 and a low-power British argon laser (40 mW). Measurements could be made accurately down to 10 cm^{-1} (2.4Å). In fact, without the very low frequency lineshapes it would have been impossible for us to measure [10] the relaxation time for this mode (5.0×10^{-13} sec at 300K), which has a spectrum approximating that of a Debye relaxation. This was so because at higher frequencies the lineshape is severely distorted due to coupling with a phonon at 96 cm^{-1} . The analysis of the very low frequency spectra ($10\text{-}20 \text{ cm}^{-1}$) in CsH_2AsO_4 and KH_2AsO_4 was responsible for several important discoveries for this class of materials, namely, that the Lyddane-Sachs-Teller relation [11] failed [12,13] and that the soft-mode frequency did not go to zero, even though the transition was second-order.

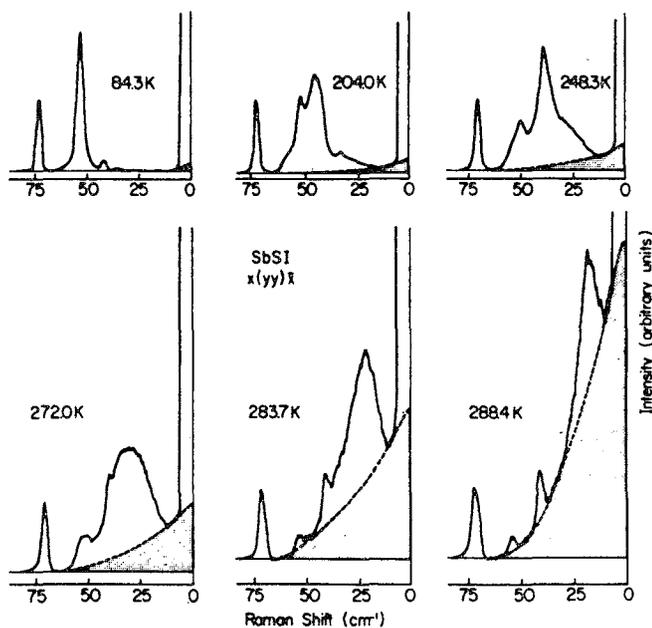


Fig. 3. Low-frequency spectra of SbSI (Ref. 9)

Fig. 5 illustrates the same kind of mode interaction, in this case, between an optic mode and an acoustic mode. This beautiful spectrum was obtained [14] by Paul Lazay and Paul Fleury, using a Spex 1401. It extends down to less than 1 cm^{-1} (or 0.2Å!!) from the argon laser exciting line. This work substantially clarified the BaTiO_3 phase transition.

To summarize, we have seen that crystals with structural phase transitions often exhibit important spectral features within 2 or 3Å of the laser line. Moreover, these features can be readily studied with a good double spectrometer. Perhaps of most importance, the development of third monochromator stages and iodine cells should allow the extension of studies of this sort to materials which are not available as large, transparent crystals — for example, the PZT ceramic ferroelectrics [15].

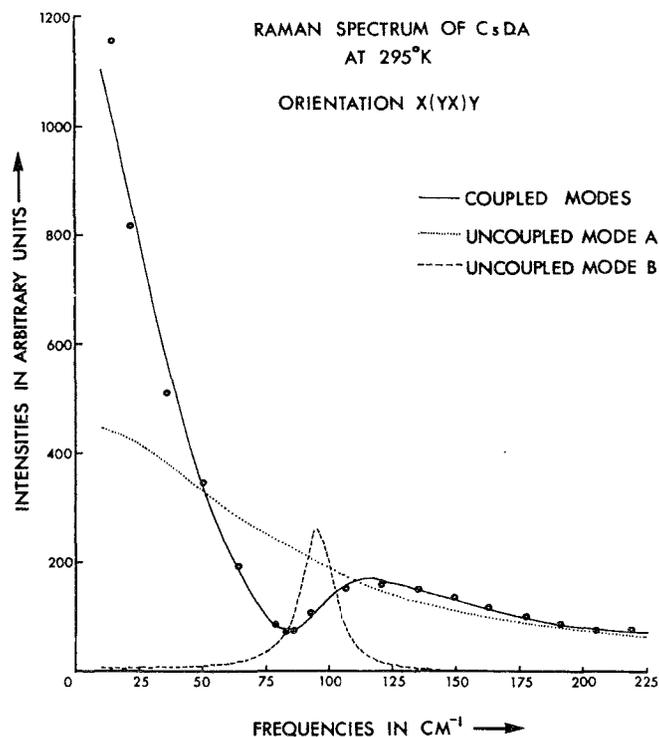


Fig. 4. Low-frequency spectra of CsH_2AsO_4 (Ref. 10).

Another class of very low frequency Raman spectra is that due to polaritons. Polaritons are transverse waves in crystals which are partially phonon-like and partly photon-like, i.e., the momentum is both electromagnetic and mechanical. A tutorial review covering light scattering from polaritons was given recently [16] in the American Journal of Physics.

Polaritons are interesting for many reasons. For example, stimulated Raman scattering from polaritons provides a tunable Raman laser source for the far infrared region of the spectrum, as demonstrated in LiNbO_3 , LiTaO_3 , and quartz [16]. Equally important is the fact that the relative magnitude and sign of deformation potential and electro-optic contributions of the Raman tensor can be determined from polariton intensities. This follows from a theory due to Rodney Loudon [17]. We write the polariton cross-section as

$$I(\omega) = \text{constant} \left[\frac{\partial \chi}{\partial u} \frac{du}{dE} + \frac{\partial \chi}{\partial E} \right]^2 \quad (3)$$

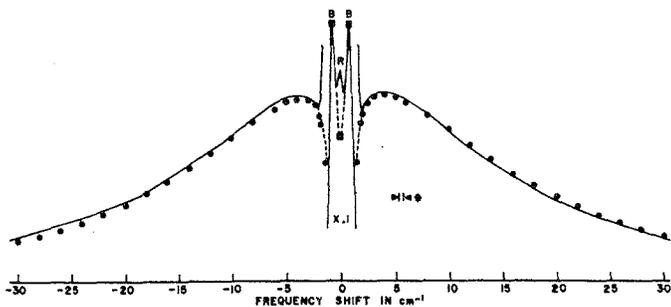


Fig. 5. Low-frequency spectra of BaTiO₃ (Ref. 14).

where u is the ionic displacement and E is the macroscopic field due to the phonon considered. u and E are related by the equation of motion

$$\mu \ddot{u} + ku = Ee^* \quad (4)$$

Assuming harmonic oscillator expressions for u and E , obtain from Eqs. (3) and (4)

$$I(\omega) = I(\omega_0) \left[1 + \frac{be^*}{a\mu} (\omega_{TO}^2 - \omega^2) \right]^2 \quad (5)$$

where $b = \frac{\partial \chi}{\partial E}$, $a = \frac{\partial \chi}{\partial u}$, e^* and

μ are the effective charge and mass for the mode, and

$$\omega_{TO} = \sqrt{\frac{k}{\mu}} \quad (6)$$

is the frequency at which the macroscopic field $E(\omega)$ vanishes.

From Eq. (5) it follows that the sign and magnitude of the ratio $be^*/a\mu$ can be obtained by measuring polariton intensities $I(\omega)$ at several frequencies. This has been done for ZnSe, ZnO and CdS [18]. For SrTiO₃ the polariton can be followed down to 5-8 cm⁻¹ (or about 2-3Å) with argon ion excitation and a double spectrometer as in Fig. 6. The data in

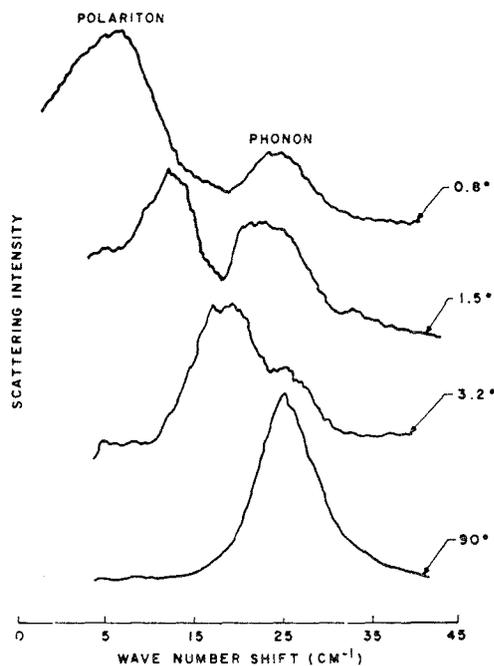


Fig. 6. Polariton spectra of SrTiO₃ (Ref. 19).

this figure are taken from a paper by Fleury, Worlock and myself [19]. Fitted to Eq. (5) they yield a ratio $be^*/a\mu$ which is negative and $\ll 1$ in magnitude. Polaritons can be studied by Raman spectroscopy in piezoelectric crystals via the geometry of Fig. 7, i.e. at small scattering angles, of the order of 1-2° of arc from directly forward.

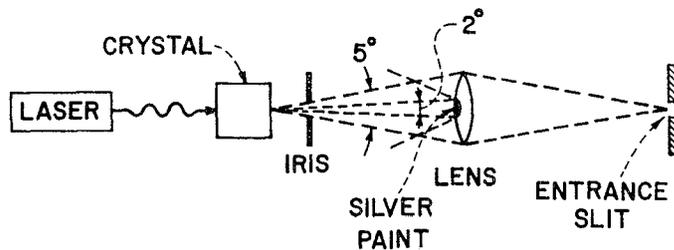


Fig. 7. Polariton scattering geometry.

The third class of very low frequency scattering which we can study with visible gas lasers and double spectrometers is that of electrons in wide-gap semiconductors. For Figs. 8 and 9 plasmon and spin-flip scattering were obtained [20,21] from inexpensive Eagle Picher samples of CdS and ZnSe, heavily doped with indium. They are not of particularly good optical quality.

The Plasmon spectra extend down to within 2Å of the exciting line. The ZnSe spin-flip scattering shows very well defined lines only 1Å from the laser. This spectrum from Spex 1401 with 20μ slits allowed us to determine the g-value of ZnSe (1.18 ± 0.03) for the first time.

A third monochromator stage and/or an iodine cell should allow such spin-flip studies to be made by scientists who have only electromagnets (8-30 kG) on hand, as opposed to our 100 kG superconducting solenoid.

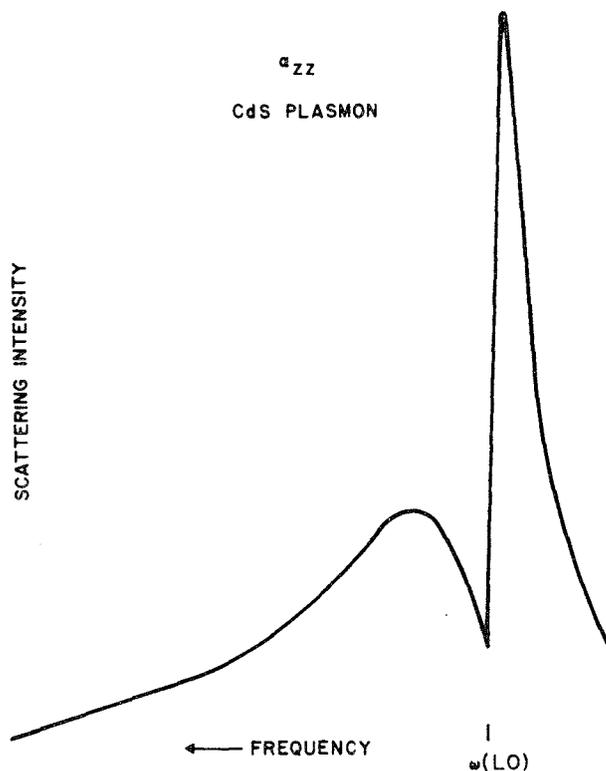


Fig. 8. Plasmon scattering spectra in CdS. (Ref. 20).

Figs. 1-9, then, indicate how low-frequency phonons, polaritons, plasmons, and spin-flip processes, can be studied with conventional excitation and a double spectrometer. The use of iodine absorption cells or a third monochromator stage would allow the extension of this work to materials of poorer optical quality.

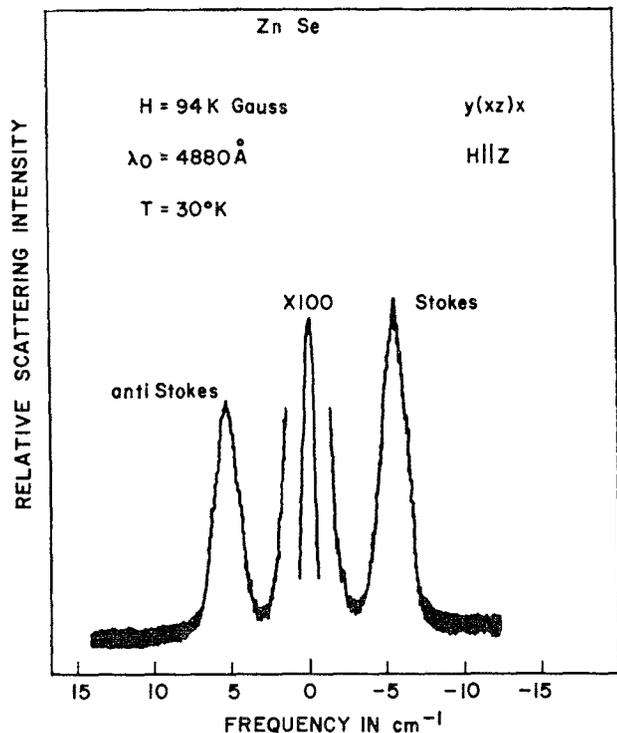


Fig. 9. Spin-Flip scattering spectra in ZnSe (Ref. 21).

REFERENCES

1. C.V. Raman and T.M.K. Nedungadi, *Nature* **145**, 147 (1940).
2. W. Cochran, *Advan. Phys.* **9**, 387 (1960).
3. P.A. Fleury, J.F. Scott and J.M. Worlock, *Phys. Rev. Letters* **21**, 16 (1968); J.F. Scott, *Phys. Rev.* **183**, 823 (1969); K.A. Müller and W. Berlinger, *Phys. Rev. Letters* **26**, 13 (1971).
4. P. Heller and G.B. Benedek, *Phys. Rev. Letters* **8**, 428 (1962).
5. P. Heller and G.B. Benedek, *Phys. Rev. Letters* **14**, 71 (1965).
6. J.F. Scott, *Phys. Rev. Letters* **21**, 907 (1968).
7. U. Hochli and J.F. Scott, *Phys. Rev. Letters* **26**, 1627 (1971).
8. T. Riste, E.J. Samuelson, K. Otnes, and J. Feder, *Sol. St. Comm.* **9**, 1455 (1971).
9. E. Steigmeier, *Proc. NATO Adv. Study Inst. on Soft Modes, Geilo, Norway, 1971*; and E. Steigmeier, G. Harbeke, and R.K. Wehner, "Light Scattering in Solids," M. Balkanski, ed., Flammarion, Paris, 1971, p. 396.
10. R.S. Katiyar, J.F. Ryan and J.F. Scott, *Phys. Rev.* **B4**, 2635 (1971).
11. R.H. Lyddane, R.G. Sachs and E. Teller, *Phys. Rev.* **59**, 673 (1941).
12. R.A. Cowley, G.J. Coombs, R.S. Katiyar, J.F. Ryan and J.F. Scott, *J. Phys.* **C4**, L203 (1971).
13. R. Blinc et al. (to be published).
14. P.D. Lazay and P.A. Fleury, *Light Scattering in Solids*, M. Balkanski, ed., Flammarion, Paris, 1971, p. 406.
15. G. Burns and B.A. Scott, *Phys. Rev. Letters* **25**, 1191 (1970).
16. J.F. Scott, *Am. J. Phys.* **39**, 1360 (1971).
17. R. Loudon, *Proc. Roy. Soc.* **A275**, 223 (1963).
18. J.F. Scott, T.C. Damen and Jagdeep Shah, *Optics Comm.* **3**, 384 (1971).
19. J.F. Scott, P.A. Fleury and J.M. Worlock, *Phys. Rev.* **177**, 1288 (1969).
20. J.F. Scott, T.C. Damen, R.C.C. Leite and Jagdeep Shah, *Phys. Rev.* **B1**, 4330 (1970).
21. P.A. Fleury and J. F. Scott, *Phys. Rev.* **B3**, 1979 (1971).

THE THIRD MONOCHROMATOR

D.O. Landon and P.R. Reed

THE need for sophisticated instrumentation in Raman spectroscopy arises largely from one problem: Rayleigh and Tyndall scattering at the excitation frequency are intense compared to Raman scatter, the inelastic scatter or frequency shifted light. With intensity disparities between elastic and inelastic scatter sometimes exceeding 10^9 , high spectral purity (high stray light rejection) is needed to unveil weak Raman features. The double spectrometer has nobly met this requirement for practical Raman spectroscopy. It has become apparent, though, that for certain experiments there is a need for even greater spectral purity than can be achieved with a double monochromator.*

Simply stated, spectral purity is the ability of a monochromator to distinguish light of a frequency to which it is tuned from light of another frequency. If monochromatic light from a laser were focused into a monochromator, to a first approximation, all of the light emerging at the exit slit would be concentrated in one spectral line with finite intensity. Actually, a small but measurable amount of light strays from its calculated spectral position and ultimately reaches the detector. With a properly designed instrument, the grating is the primary source of what is, obviously, "stray light."

Accordingly, when a monochromator is tuned to select a wavelength 100 cm^{-1} from the laser line frequency, a certain amount of stray light will spill over to this frequency. For a single monochromator the stray light intensity 100 cm^{-1} away from the laser frequency should be less than 10^5 of the parent peak intensity; for a double monochromator, the stray light should be less than 10^{10} . As expected, by tuning the monochromator closer to the laser frequency, stray light increases until an intensity maximum is attained at the laser frequency. The most significant property of a Raman spectrometer, then, is its ability to distinguish between the very weak Raman scatter and the stray light arising from Rayleigh and Tyndall scatter.

There are two principal manifestations of stray light in Raman spectroscopy. As indicated above, the first determines how close one can detect real spectra adjacent to the Rayleigh line. Fig. 1 qualitatively summarizes the situation for solids, liquids, gases, single crystal and powders.

The second manifestation, illustrated by the small spikes in Fig. 1, results from grating ghosts which appear as spurious features in a Raman spectrum. Ghosts are light of the excitation frequency scattered by grating imperfections. Only in the most recalcitrant samples are grating ghosts observed. Stray light of this sort is not a problem with most liquids, gases, and single crystals. When it is, one solution is to prevent the Rayleigh and Tyndall scatter from entering the Raman instrument by placing a filter between the sample and the double monochromator. The ideal device would be a narrow-band *rejection* filter (band width less than 2 cm^{-1}) with

*At one time the parliamentary linguists among us distinguished "monochromator" from "spectrometer." Like most others we apply the terms interchangeably.

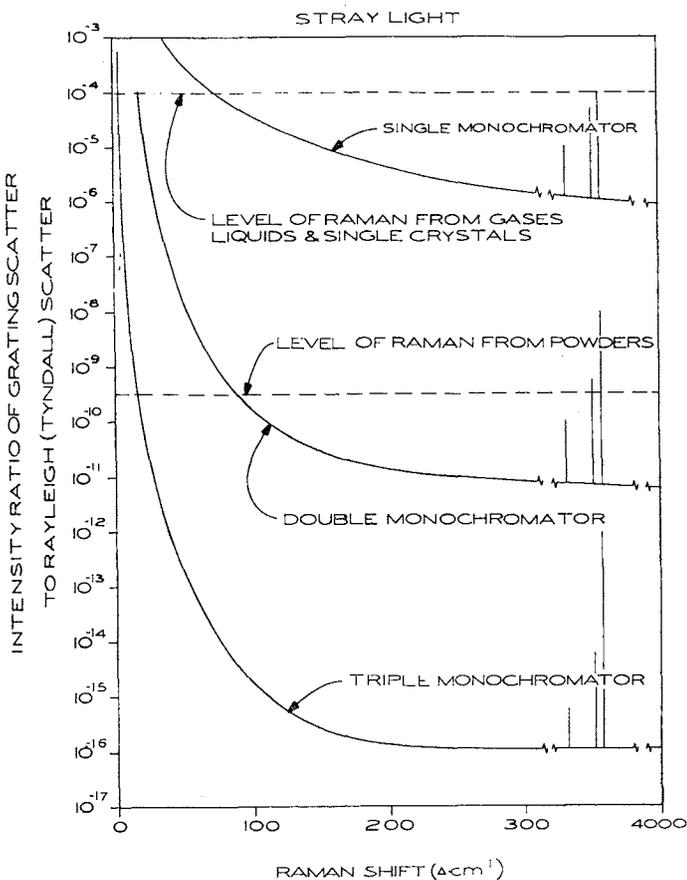


Fig. 1. Scattered light including ghosts appearing in a single, double, and triple monochromator. Although scattered light plunges to the square root in a double monochromator, interference with Raman spectra still occurs occasionally. In a triple monochromator, instrumental scatter has never been known to interfere with Raman scatter.

an optical density of 3 or 4. Though the problem may appear easy of solution, a narrow-band rejection filter counterpart to the bandpass interference filter has not been developed. Lacking such a filter, experimenters have tried other techniques. One takes advantage of the fact that interference filters reflect almost totally outside of their transmittance band. Tobin [1] suggested multi-reflecting the radiation from the sample between two interference filters which transmit the laser frequency (Fig. 2). On each reflection, a portion of the Rayleigh light is transmitted, but the Raman scattering outside the bandpass of the interference filter is reflected through the system. By assuming a 30% reflectivity of Rayleigh light and a 97% reflectivity outside the band pass, six reflections would diminish the Rayleigh component to 0.07%, and still transmit 83% of the Raman signal. Indeed, a fair trade off! Unfortunately this system has its drawbacks; because of the properties of interference filters, the spectrum below 50 cm^{-1} is rejected and the relatively small permissible aperture of the device severely restricts the solid angle at which scattering is collected from the sample. Furthermore, the optical quality of state-of-the-art interference filters can adversely affect the imaging properties of the collection optics, thereby degrading the performance of the monochromator.

Recently, an absorption filter has been shown to be successful for removing only the 5145A line of Ar^+ [2,3]. A heated iodine cell is placed between the sample and the spectrometer. Unshifted light is attenuated because an iodine

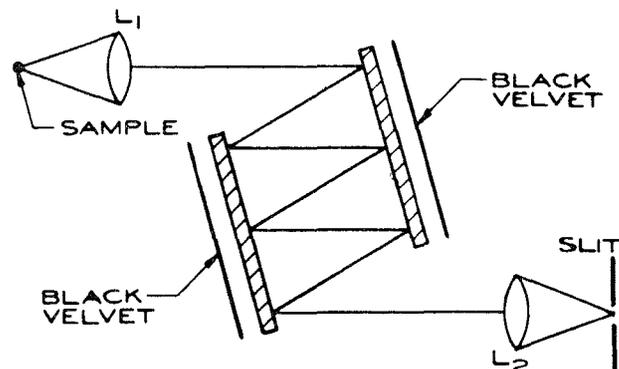


Fig. 2. Tobin's system for filtering out light of the excitation so it does not reach the monochromator relies on two facing interference filters with a bandpass at the excitation frequency. Light not passed is almost totally reflected to the slit.

vapor rotational line with half-bandwidth 0.01 cm^{-1} fortuitously coincides with a single mode ($\text{hbw} < 0.003 \text{ cm}^{-1}$, depending on the laser) under the 5145.4A gain curve of an argon ion laser. Though quite effective, iodine vapor has its own spectrum which interferes with spectra from weak Raman scatterers and limits its applicable spectral range. A highly stable single-mode argon laser is required and the iodine filter works at only one laser frequency.

The next category of efforts can be classified as differential electronic methods. The first was devised by Mooradian [4]. The exit beam from the Raman spectrometer is split into two equally intense components. One passes through an interference filter before continuing to the detector; the other goes directly to another detector. The two resulting signals are electronically subtracted to remove the Rayleigh component.

A related approach was tried by Landon [5] who showed that it is possible to decrease the Rayleigh component by selectively modulating the Raman scatter with a unique chopper placed between the sample and the spectrometer. The chopper is a silica disc coated as an interference filter over one half its aperture, while the other 180° is neutrally coated to equalize the transmission of the laser light through both halves. Rotating the chopper modulates only the Raman scattering for synchronous detection.

A third method under this category is a double beam sample technique proposed by Porto [6]. A small portion of the laser beam is deviated before being focused on the sample. The deviated beam passes through a Polaroid analyzer and is focused onto the spectrometer optics. Primary and deviated beams are modulated 180° out-of-phase with respect to each other by a three-bladed chopper. The intensities of the primary and reference beams are made equal by rotating the Polaroid analyzer which serves as a variable attenuator. As a result, only the Raman signal is modulated for synchronous detection.

The principal liability common to all three techniques is that the detectors are exposed to ever-increasing Rayleigh light as one scans closer to the Rayleigh line. Not only does this cause non-linear detection defects, there is danger of destroying the photomultiplier. In particular, the first technique cannot remove grating ghosts. A liability of the second technique is its inability to generate good square waves owing to the lack of uniformity in dielectric filters. The third

method relies too heavily on superimposing sample and reference beams. To prevent over or under cancellations, the laser image on the sample and the reference spot must present identical images on the entrance slit of the spectrometer, and both beams have to equally fill the spectrometer optics.

Another category of devices encompasses either a Michelson [7] or a multiple beam interferometer [8]. With the Michelson interferometer an actual rejection improvement of 100 was obtained in a Brillouin measurement. Conceivably, this apparatus could be adapted for a Raman experiment with a narrow band source. Along the same line is Porto's [8] multiple-beam interferometric filter with a rejection capability ranging from 100 to 1000. As with most interferometers, they are extremely sensitive to their environment and can tax their handler's patience and mechanical aptitude.

A most logical answer to the need for additional scattered light rejection is the addition of another grating monochromator, either fore or aft. Parker [9] et al. placed a 1/4-meter grating monochromator with fixed bandpass between the sample and the Raman spectrometer. The scattered light rejection achieved here could be as high as 10^4 with sharp cut-off characteristics. A separate monochromator cannot readily be synchronously scanned with the Raman spectrometer, however. Furthermore, its position requires a major change of sample illumination and collection optics each time it is inserted or removed.

An extension of the logic which led to the development of a double monochromator leads directly to a triple monochromator system for more severe cases of scattered light rejection. (Refer to Fig. 1). In upgrading from a single, to a double, to a true triple monochromator, the increase in optical and mechanical complexity must be emphasized. In particular, on going from a double to a triple spectrometer, one encounters severe difficulties in maintaining alignment because of the large number of additional optics required (14 or more elements in a triple vs. 8 in a double). Moreover, the diminution of throughput resulting from the increased number of optical surfaces, including the additional grating, is not warranted for every experiment. Even if the mirrors in the monochromator were assumed to be perfect reflectors the three gratings themselves would reduce throughput considerably. At the blaze wavelength, 70% of the light would be transmitted by the single monochromator. With a double 53% is transmitted, while only 37% is transmitted with a triple. Obviously, the more gratings there are in series, the lower the throughput. Away from the blaze, toward the red end of the spectrum, these losses become even more significant.

We have now considered all known techniques for minimizing stray light.* Taking the positive characteristics of each as performance targets, we developed THE THIRD MONOCHROMATOR, a variable bandpass, variable frequency filter.

*For the sake of completeness, another technique for reducing scattered light deserves mention. It is an acoustical filter, a solid-state device with a tunable bandpass which can be as small as 4Å. If this bandpass could be tracked with that of the double spectrometer, presumably the Rayleigh light would be rejected. To our knowledge, the acoustic filter is still under development and has not, as yet, been tried for this purpose.

Essentially, THE THIRD MONOCHROMATOR (TTM) is a modified Czerny-Turner spectrograph which attaches to the exit slit of another monochromator, its exit slit serving as the entrance slit of TTM. If we were to place a photographic plate at the focal plane of TTM and record a spectrum, the developed plate would reveal the same information as the photoelectrically recorded spectrum in this same spectral interval. By covering segments of the photographic plate, it would be possible to block out certain portions of the spectrum which would then be missing from the developed plate. This is exactly the function of THE THIRD MONOCHROMATOR.

Blocking is accomplished with the slit blades (Fig. 3). Lines 2 are transmitted, while lines 1 and 3 are rejected because they are outside the bandpass. The width of the spectral region passed by the TTM is determined by the slit width and the central frequency of this region is controlled by the angular orientation of the grating. Lines 1 and 3 could be transmitted by increasing the width between blades and/or by changing the grating angle. Thus, when added scattered light rejection is required in the low frequency Raman spectrum, TTM is tuned precisely so that the Rayleigh component is occulted by a knife edge, but the Raman spectrum is transmitted. The net effect is to reduce stray light by about three orders of magnitude.

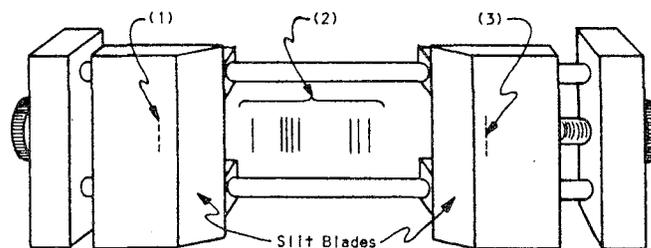


Fig. 3. Depiction from patent application of spectral lines transmitted (2) and rejected (1,3) by THE THIRD MONOCHROMATOR.

Fig. 4 presents scans of the low frequency region of l-cystine. The first trace was recorded with a double monochromator, the next with the I_2 filter and finally with TTM for comparison under nearly identical experimental conditions. In the latter cases additional lines are revealed at 15 and 9.7 cm^{-1} . A more impressive example is a duplication of efforts by Parker to record Raman spectra of metallic single

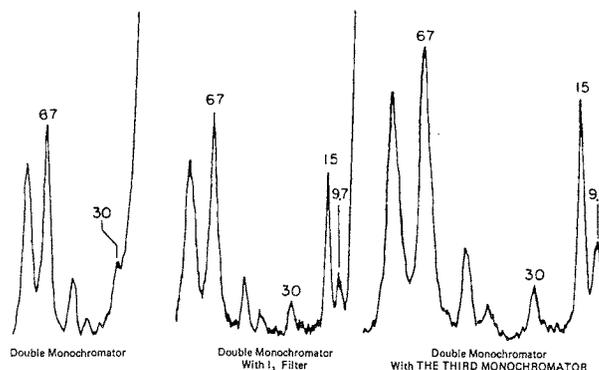


Fig. 4. Raman spectra of polycrystalline l-cystine. Note that two additional Raman features are revealed by scanning either with TTM or an iodine filter.

crystals. Our results for magnesium are in Fig. 5 where the top trace was recorded with just the double monochromator and reveals virtually no Raman shift of magnesium at 120 cm^{-1} , while with TTM this line is clearly observed.

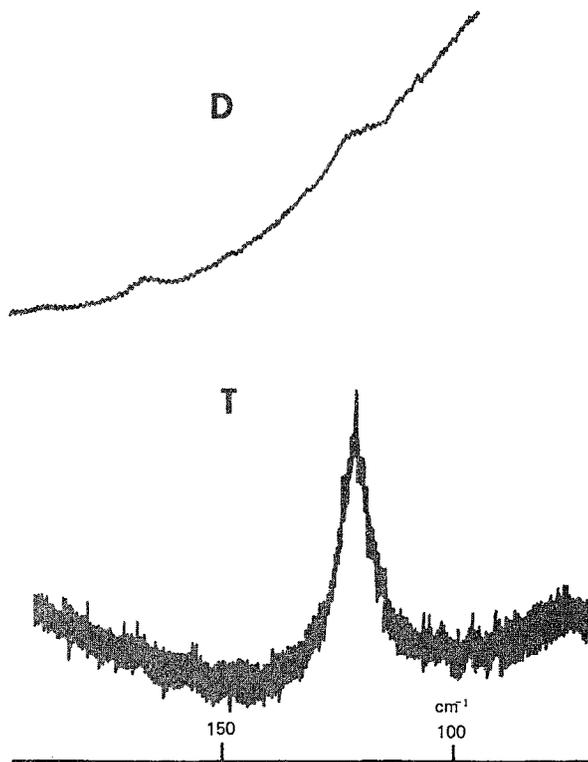


Fig. 5. When the grating is positioned in TTM, a magnesium Raman line appears at 120 cm^{-1} (Spectrum T). With the mirror in place, the system reverts to a double spectrometer and the line is no longer visible (Spectrum D). A 10X less sensitive scale is used in D.

This is actually one of three modes of TTM operation. The fixed frequency mode is particularly valuable for observing Raman features close to the exciting line. In Mode 2, the wavenumber position of TTM is electronically slaved to that of the double spectrometer as diagramed in Fig. 6. An incremental encoder connected to the leadscrew in the double monochromator sends pulses to a stepping motor which advances TTM. This mode is particularly valuable for removing spurious stray light observed at large wavenumber shifts from the excitation frequency, namely grating ghosts. For Fig. 7 we deliberately reflected 4880Å laser light into the double monochromator to record ghosts occurring at 1980 cm^{-1} . Then, with TTM connected, the same region was scanned. Not a trace of a ghost was observed, even at higher sensitivity. To demonstrate that TTM faithfully follows the double monochromator over the entire Raman region, we recorded the spectrum of cyclopentanone, Fig. 8.

Since a majority of samples do not require the much-improved stray-light rejection offered by TTM, a third mode of operation was incorporated to give nearly a two-fold increase in throughput (Fig. 9). In the mirror mode, TTM becomes an optical relay. By turning a knob on the top of

TTM, the grating is replaced with a 96%-reflectance mirror, minimizing signal losses when additional scattered light rejection is not required.

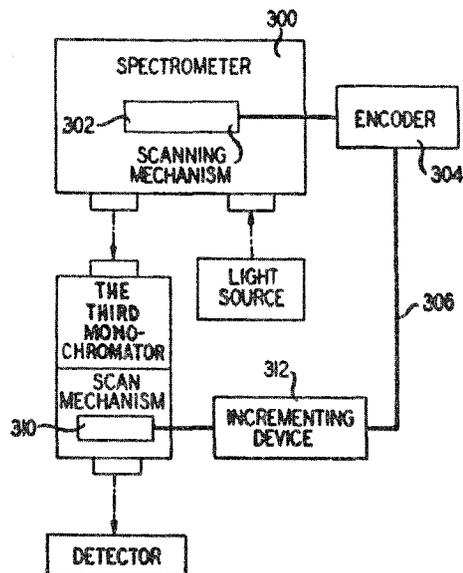


Fig. 6. To remove spurious stray light at large wavenumber shifts from the excitation frequency, TTM is electronically slaved to the double spectrometer's scanning drive.

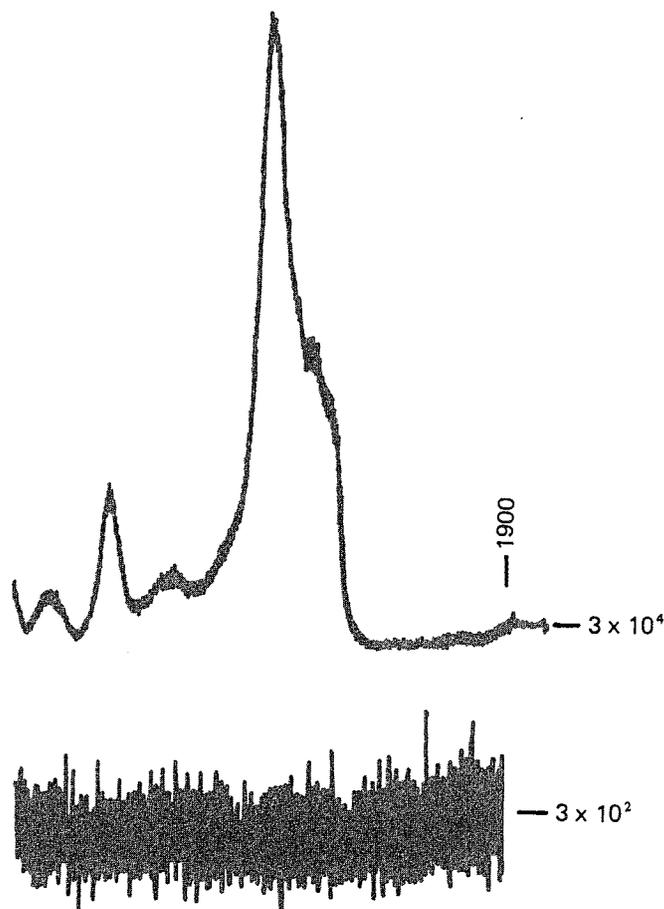


Fig. 7. Ghosts are also eliminated with TTM. Both spectra are of graphite, the upper with the mirror in TTM, the lower with the grating in place. The lines around 2000 cm^{-1} are ghosts.

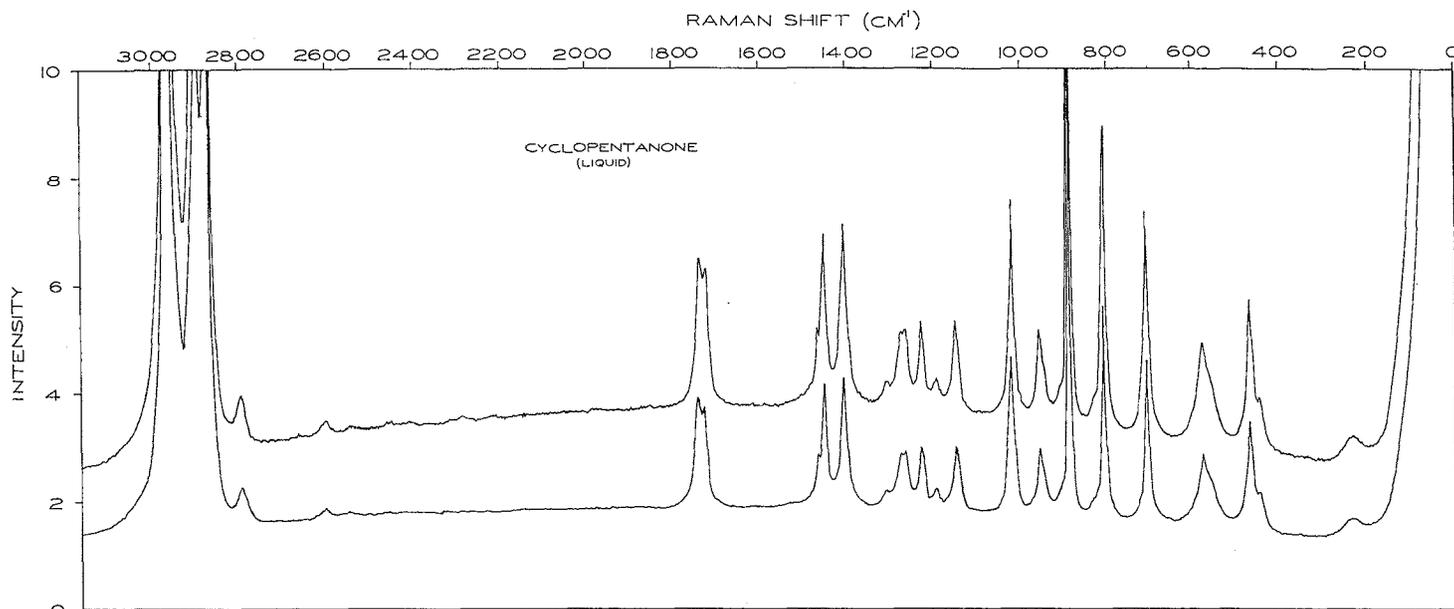


Fig. 8. That TTM tracks over the complete Raman range is evident from this normal appearing spectrum of cyclopentanone.

THE THIRD MONOCHROMATOR has thus emerged as the most universal answer to a need for greater stray light rejection. Though common in a triple spectrometer, problems with grating tracking will never happen with THE THIRD MONOCHROMATOR. It functions truly as a stray-light filter with far less mechanical and optical complexity than a triple spectrometer so the total price of TTM plus a double monochromator is less than that of a triple spectrometer. TTM retrofits any of the 250 plus Spex 1400 Series Spectrometers in the field and its parting virtue is that a 30-second effort removes its effects by restoring energy that would otherwise be lost in a triple spectrometer.

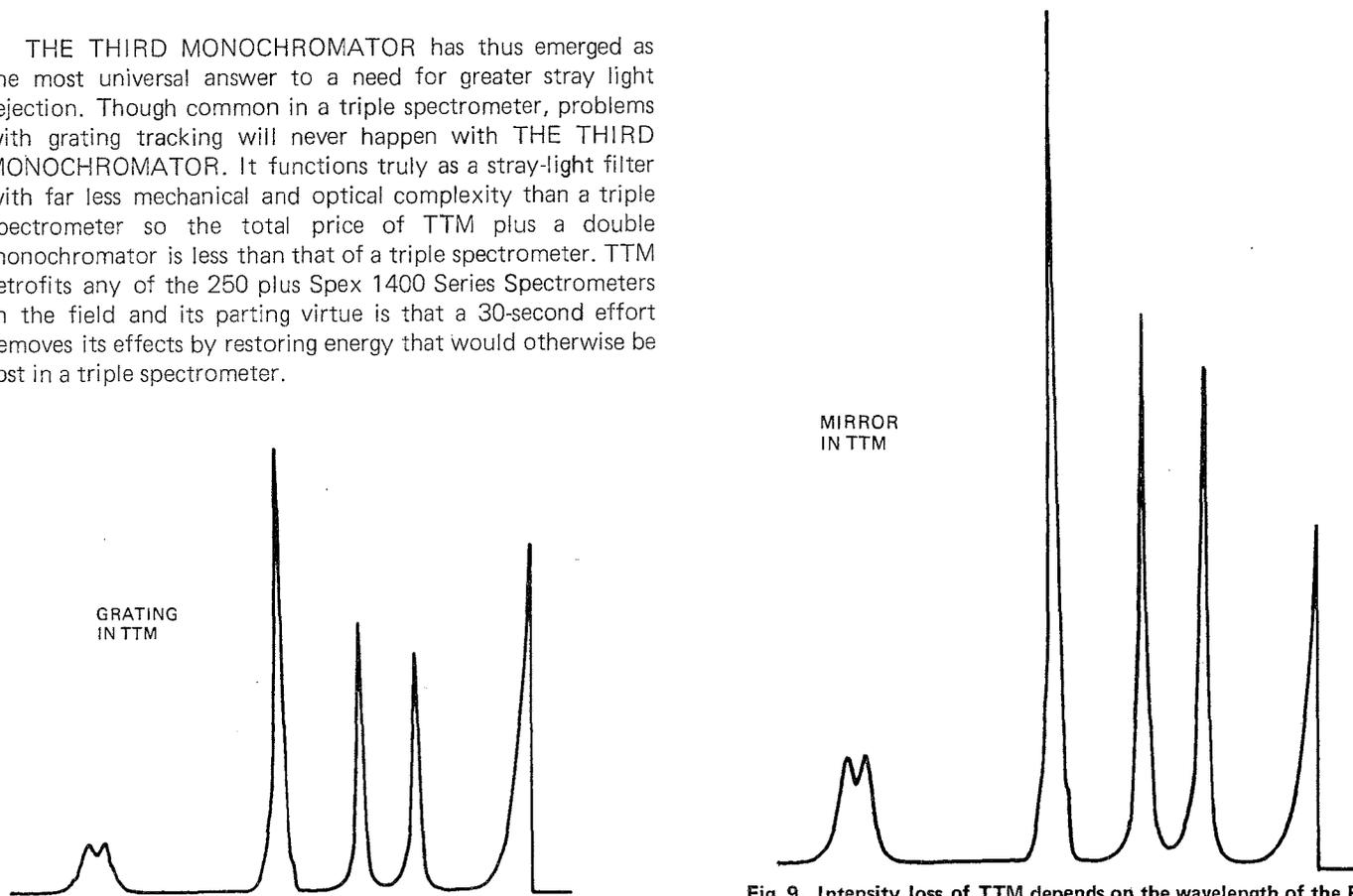


Fig. 9. Intensity loss of TTM depends on the wavelength of the Raman features and the blaze of the gratings. Loss of intensity, in this case of carbon tetrachloride taken with 4880A excitation, is typically about a factor of 2.

REFERENCES

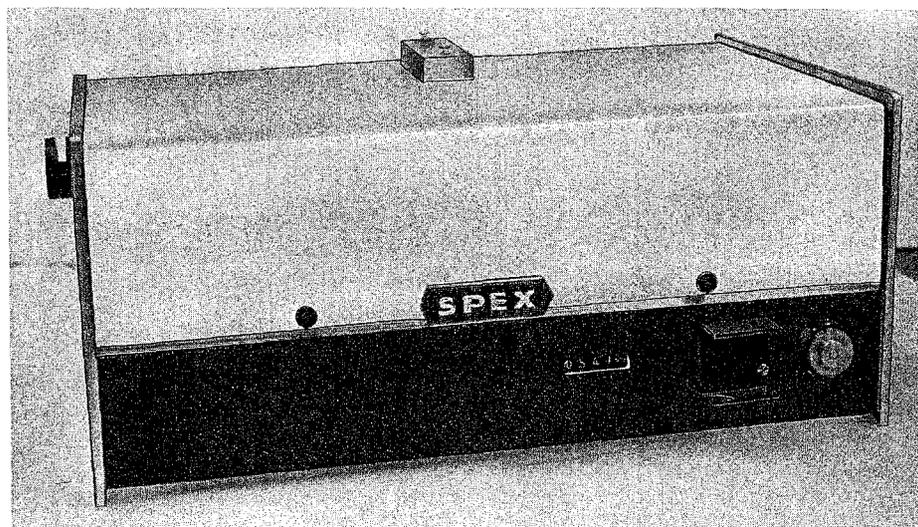
1. M.C. Tobin, *J. Opt. Soc. Am.* **49**, 850 (1959).
2. L.L. Chase, J.L. Davis, G.E. Devlin, S. Geschwind, *THE SPEX SPEAKER XV*, No. 3 (1970).
3. G. Hibler, J. Lippert, W.L. Peticolas, *THE SPEX SPEAKER XVI*, No. 1 (1971).
4. A. Mooradian, *Spex RAMALOGS Vol. 2*; No. 1 (1969).
5. D.O. Landon, *ibid.*
6. C.A. Arguello, D.L. Rosseau, & S.P.S. Porto, *ibid.*
7. K.H. Langley, & N.C. Ford, Jr., *J. Opt. Soc. Am.* **59**, 281 (1969).
8. W. Proffitt, L.M. Fraas, P. Ceruenka, and S.P.S. Porto, *Appl. Opt.* **10**, 531 (1971).
9. J.H. Parker, D.W. Feldman, & M. Ashkin, "Raman Scattering by Optical Modes of Metals," *Proceedings of the International Conference on Light Scattering*, New York University, New York, 1968.

DOUBLEMATE

MODEL 1672

The Doublemate is a unitized version of the "tandemized" Minimate monochromator system. As such, it maintains the same fast optical speed (f/4) and excellent scattered light characteristics (less than 10^{-9} that of the exciting line). At the same time it provides greater tracking accuracy (the ability of one grating to match wavelengths with another in double monochromator system) and, with optional narrow slits, greater resolution.

Optically the Doublemate is a Czerny-Turner mount with gratings arranged to provide double dispersion for maximum throughput. Input and output mirrors at 45° result in an in-line system. With 1200 grooves/mm gratings dispersion is 2 nm/mm over the range of the instrument. Proper choice of slits from the five pairs included allows bandwidths from 0.5 nm to 10 nm. Optionally, a high-performance model with $50\mu \times 5$ mm slits is available. It can achieve 0.1 nm resolution. The Doublemate, when combined with proper illumination systems serves as an ideal instrument for most fluorescence studies (at both excitation and emission positions) and for laser-Raman and other light scattering experiments.



SPECIFICATIONS (with 1200 groove/mm gratings)

Mounting: Czerny-Turner; in-line optics attained with internal 45° mirrors

Reciprocal Linear Dispersion: Approximately 2 nm/mm throughout wavelength range

Wavelength Range: 175 nm (with N_2 purging) to 1000 nm

Minimum Bandwidth: 0.5 nm for 1672; 0.1 nm for High Performance Model 1673 with 1200 g/mm gratings and 50μ slits

Wavelength Accuracy: 1 nm

Aperture Ratio: f/4

Focal Length: 220 mm

Wavelength Readout: Display on 4-digit counter accurate to 1 nm; graduations permit reproducing settings to 0.1 nm.

Slits: Five pairs all 10 mm high: 0.25, 0.50, 1.25, 2.5 and 5.0 mm (bandpass from 0.5 to 10 nm)

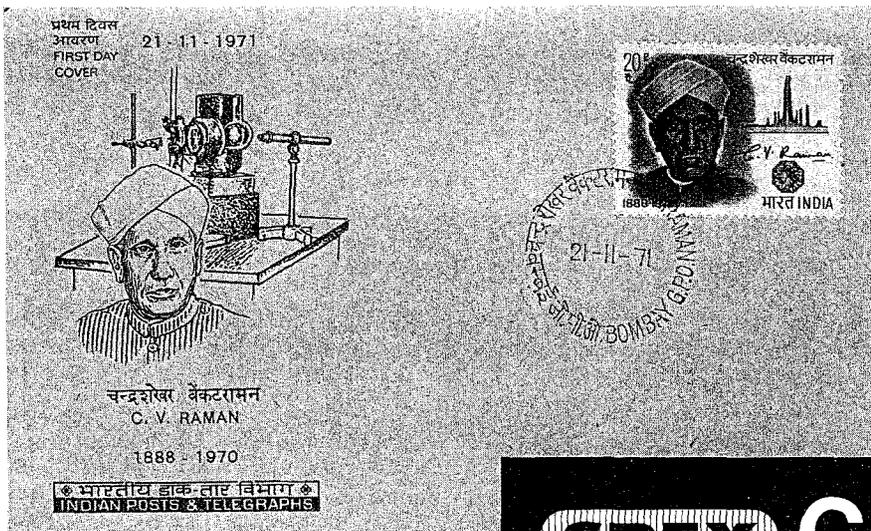
Near Stray Light (monochromatic source, slits 5 nm bandpass): Within 1.5 bandwidths—less than 10^{-3} ; Within 3.0 bandwidths—less than 10^{-4}

Far Stray Light (Greater than 10 bandwidths): Less than 10^{-9}

Motor (Optional): Speeds—12.5, 25, 50, 100 nm/min
Power—115 V, 60 Hz or 230 V, 50 Hz (specify)

Dimensions: 21-1/4 x 11-3/4 x 9"

Weight: 30 lb



SIR C.V. RAMAN

The late Nobel laureate, Sir C.V. Raman, discoverer of the light scattering effect named after him, has recently been further honored by his nation with the issuance of a stamp and first day cover, which is reproduced here. Note the Raman spectrum of carbon-tetrachloride on the background of the stamp and the reproduction of the spectroscope, through which the spectrum was first observed, on the background of the cover.

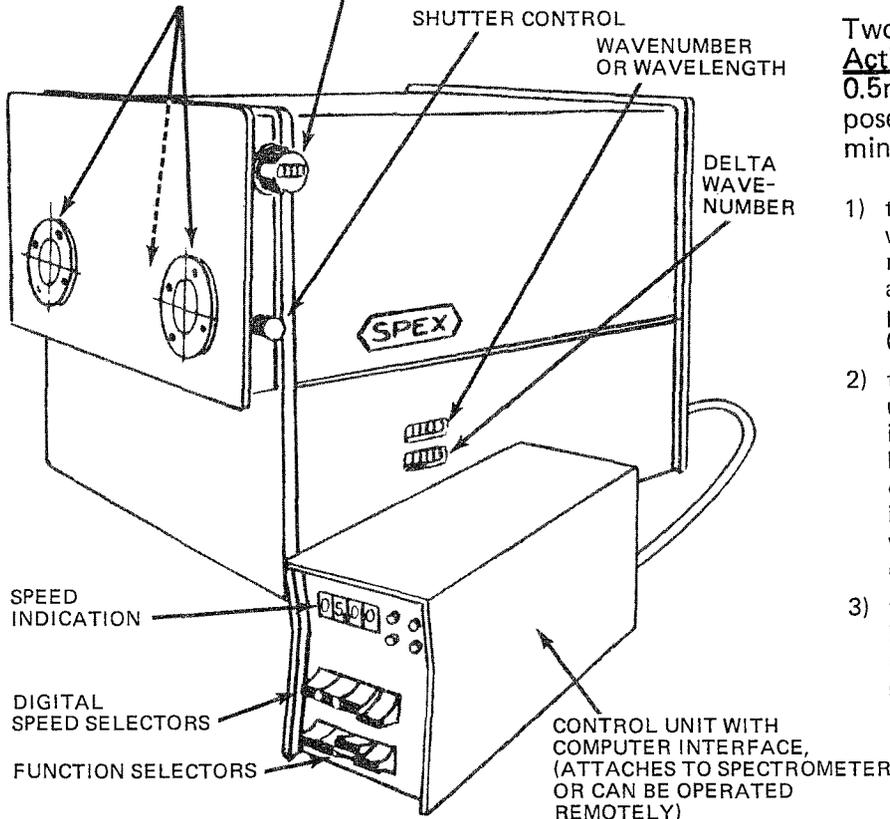
Spex is pleased to note that our double monochromators have had a very important role in expanding the acceptance of Raman spectroscopy as a diagnostic tool for the elucidation of the structure of matter.

SPEX CompAct

DOUBLE SPECTROMETER

1404 Wavelength or Wavenumber Model 1403

SLIT CONTROL, DIGITAL INDICATION
ALL THREE SLITS GANGED



Two new Spex CompAct (Computer Activated) Double Spectrometers of the 0.5m Czerny-Turner type, were purposefully designed with the following in mind:

- 1) the ever increasing number of scientists whose research requires an instrument with maximum scattered light rejection characteristics, but not the high resolution and precision offered by our famous 0.75m-0.85m instruments.
- 2) that the age of computerized instruments is upon us. Therefore the CompAct design incorporates a digital drive system that can be controlled not only by a suitable group of switches on the control panel of the instrument but also by means of a 4 bit word generated by a computer, connected directly through its I/O board.
- 3) that the supply of available research dollars is shrinking and therefore a moderately priced CompAct instrument will serve the scientific community very well.

SPEX INDUSTRIES, INC.

BOX 798, METUCHEN, N.J. 08840

☎ (201)-549-7144

All performance characteristics below are cast in terms of 1200 g/mm gratings in first order.

I OPTICAL SPECIFICATIONS

Double Spectrometer: 0.5-meter Czerny-Turner system, doubly dispersing.

Aperture: f/7.

Mirrors: Protected coatings, reflectivity exceeding 90%.

Gratings: 68x68x10 mm in kinematic quick change mounts with three orthogonal adjustments, 1200 groove/mm 5000A blaze standard. (Optionally, 1800 to 8 grooves/mm with blaze from 1500A to 112 microns). Efficiencies are typically greater than 70% at blaze; resolution typically 70-95% of theoretical. Standard 1200 g/mm gratings are essentially ghost-free with root structure almost undetectable in line images.

Spectral Purity: With a monochromatic source, I/I_0 is less than 10^{-11} at 100 cm^{-1} separation from input light.

Slits: Three, bilaterally opening from 10 microns to 3 mm. Height 2 to 20 mm. Ganged with direct reading in microns on digital counter.

WAVENUMBER MODEL

Spectral Coverage: 24,000 to $11,400\text{ cm}^{-1}$

Dispersion (Approx.): $20\text{ cm}^{-1}/\text{mm}$ at 15802 cm^{-1}

Resolution: At least 0.8 cm^{-1} at 17268 cm^{-1}

Readout: Two five digit, illuminated counters, one reading wavenumber, the second settable to display frequency difference (Δcm^{-1})

Accuracy: $1\text{ cm}^{-1}/1000\text{ cm}^{-1}$

Repeatability: $\pm 1\text{ cm}^{-1}$

WAVELENGTH MODEL

Spectral Coverage: 0 to 12,800A

Dispersion (Approx.): 8 A/mm at 6328A

Resolution: At least 0.25A at 5790A

Readout: Single five-digit direct reading illuminated counter.

Accuracy: 0.5A/1000A

Repeatability: $\pm 0.5A$

II SCANNING DRIVE SYSTEM

The CompAct spectrometers incorporate a digital (stepping) drive system that is operated directly either through its own control panel or a computer I/O board, a 4-bit word controlling speed; other words control other functions.

Speed Range: 15 selectable line-locked scanning speeds from 100 to 0.002 cm^{-1} (or A)/second in 10, 5, 2 - - - sequence. Rapid reverse and forward slewing at oscillator-controlled speed, approximately 30% faster than maximum scanning speed.

Drive Step Size: 0.02 cm^{-1} or 0.02A

Event Marker: Every 10 or 100 cm^{-1} (or A)

Controls: Speed select for 15 forward speeds, Execute switch, External - Internal select switch, Forward and Reverse slewing switch, Marker select switch (10-100-off), Manual rate and direction sensitive control for line peaking, Power on-off.

Numeric Display: Speed selected in $\text{cm}^{-1}/\text{sec}$ (or A/sec) 3-1/2 digit, + and - for direction.

Indicators: Power on, Left limit, Right limit, Manual controlled speed, Computer controlled speed, Forward and reverse slewing (+ and - flashers).

III GENERAL SPECIFICATIONS

Construction: Non-magnetic with the exception of small fittings and bearings.

Dimension: 48 cm high x 67 cm wide x 53 cm deep

Weight: 50 kg (approx.)

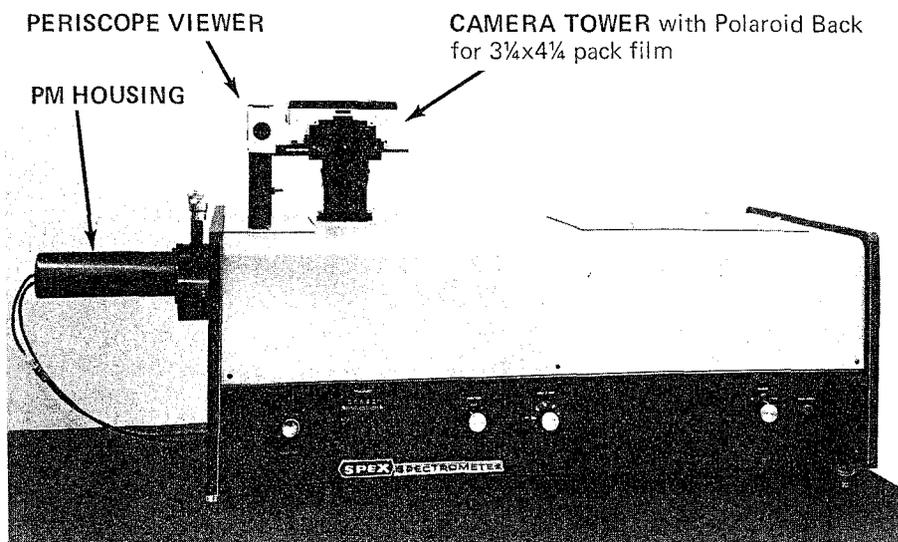
Power Required: 115V, 50-60 Hz.

Accessories: The following Spex catalog items are compatible with the CompAct to assure complete systems capability:

- 1419A Raman Illuminator and Sampling Accessories
- 1624E PM Housing and 1424B PM Bases
- 1427, 1428 IR Detector Housing and Detector
- 1522, 1522R Optical Bar and Riders
- 1550 Source Chamber and Accessories
- 1570 Experiment Chamber and Accessories
- 1527 Straight-through Optics
- 1630-11 PM Cryostat and Accessories
- 1730 Thermoelectric Cryostat and PMT's
- PC-1 Electronic Readout System

Czerny-Turner SPECTROMETERS**FOUR MODELS:**

- 3/4 OR 1-METER with WAVELENGTH OR WAVENUMBER DRIVE
- OPERATING IN OVER 1000 INSTALLATIONS
- VERSATILE • ACCURATE
- UV THROUGH FAR IR
- HIGH PRECISION OPTICS AND MECHANICS
- COMPUTER COMPATIBLE
- STEPPING/SYNCHRONOUS MOTOR
- 20 mm, 50 mm CURVED OR EXTRA-WIDE SLITS
- UNIQUE ENCODER EVENT MARKER
- KINEMATIC GRATING MOUNT
- EXTERNAL FOCUSING & ACCESSIBILITY TO OPTICS
- RUGGED NON-MAGNETIC CONSTRUCTION
- UP TO 20 TIMES HIGHER SPEED THAN CONVENTIONAL SPECTROGRAPHS
- 5-DIGIT ILLUMINATED COUNTER CALIBRATED TO 0.1Å or cm^{-1}
- 500:1 SCANNING SPEED RANGE STANDARD, EXTENDABLE TO 125,000:1 IN STEPPING MODE
- CONVERTIBLE SPECTROMETER/MONOCHROMATOR/SPECTROGRAPH
- ECONOMICAL • LIGHTWEIGHT

**PLUS CONVENIENCE ACCESSORIES:**

- MINIMATE OR MICROMATE PREDISPERSERS
- SOURCE AND EXPERIMENT CHAMBERS
- PERISCOPE VIEWER FOR ALIGNING MICROSCOPIC SAMPLES
- EXIT BEAM SPLITTER FOR RATIOING
- STRAIGHT THROUGH OPTICS
- IR THROUGH UV DETECTORS, PHOTOELECTRIC AND PHOTOGRAPHIC
- STEPPING MOTOR DRIVES AND COMPUTER INTERFACES



INDUSTRIES, INC. • BOX 798, METUCHEN, N.J. 08840

BULK RATE
U.S. POSTAGE
PAID
Permit No. 166
Plainfield, N.J.

Address Correction Requested