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SPEX DOUBLE SPECTROMETER—A PROGRESS REPORT

TWO years and some 60 instruments later, we propose to bring our readers up to date concerning an instrument which, we are proud to say, has nudged Raman spectroscopy another step forward in its painful march toward acceptance as a tool for both molecular structure studies and analytical chemistry. Ever since Sir C. V. Raman announced his discovery of wavelength-shifted scattered light, attempts have been made to devise commercial spectrographs capable of measuring the almost vanishingly weak line spectra. Hilger was probably the first to manufacture a series of high-aperture glass prism spectrographs, crowning one in the '50s with means for electronic readout. That the original photographic technique taking up to 24 hours exposure time could be reduced to direct reading on a stripchart recorder represented a long series of advancements of all phases of the instrumentation. Incorporating a high-intensity, spiral Toronto Hg arc, Applied Research Laboratories tried its hand at a three-prism spectrograph in the '40s. Probably the most successful from a commercial standpoint was Applied Physics Laboratories with its Model 81, an exquisitely complex, double grating Littrow spectrometer with complicated yet stable electronics and, recently, with provisions for substituting a laser for the blinding Toronto arc. Its pricetag—around \$50,000—was always a serious drawback, one that Perkin-Elmer has attempted to capitalize on, especially for routine analysis, with its compact LR-1 in which a single grating is double-passed in a Littrow mount.

Our own contribution is the Spex Model 1400 Double Spectrometer now in its second generation although the first instrument was delivered only one and one-half years ago. In 1962, S. P. S. Porto, having already discovered with D. L. Wood (1) that a pulsed ruby laser could excite Raman lines, began a series of what soon proved to be highly prolific investigations with the then brand-new continuous laser. Fortunately for him, his employer, Bell Telephone Laboratories, envisioned an even more promising future in the gas laser as a potential communications pipeline. For this application, a number of He-Ne lasers were constructed at BTL and Porto was able to borrow one plus a simple spectrometer and a roomful of electronics for his early experiments. Obstacles abounded but he systematically rooted out each, skillfully making an appropriate improvement.

As soon as his struggle for sensitivity began to look favorable, he found that extraneous light bouncing around within the spectrometer blocked the path to more effective measurements. Porto speculated correctly that the trouble was caused mainly by undiffracted light scattering from the face of the grating. He concluded that such stray light could be reduced significantly by arranging two spectrometers so that the output of one was purified by the second. Challenged to construct a suitable tandem instrument, we first took the easy way out by mechanically coupling two of our Model 1700 single Czerny-Turner spectrometers so one motor drove both lead screws

synchronously. Optical bridging was effectively if inelegantly accomplished with a pair of simple lenses and a pair of 45° mirrors.

Breadboarded though it was, the tandem spectrometer got off to a fine start. Working with it, Porto and Landon (2) showed that the scattered light compared with the exciting 6328Å line dropped from around 10^{-5} in a single instrument to 10^{-10} in the tandem. Small frequency Raman shifts previously buried beneath the debris of the exciting line began to emerge predictably. Porto's letters to Physical Review began to appear with increasing frequency as several molecular mysteries within crystals were successively clarified.

Apart from its crudity and the redundancy of its optics, the one-and-only tandem model soon demonstrated a more serious ailment—zigzagitis. Our spectrometers are so constructed that, with a 1200 groove/mm grating, one revolution of the lead-screw turns the grating through 50Å. No matter how carefully a leadscrew and nut are mounted, a certain amount of eccentricity will be measurable as a periodic wavelength error. (This, of course, is why gratings have ghost lines.) Since each of the tandem's two spectrometers was driven by an independent leadscrew, these errors would not necessarily appear in phase. Nicely obeying Murphy's law, the first grating zigged to a maximum positive wavelength error at the same time the other zagged to its maximum negative error. The result was a wavelength mismatch which forced Porto to open his slits to a bandpass that seriously hampered sensitivity and precluded high-resolution studies.

It was clear that one leadscrew had to go. In place of the tandem construction we ultimately wound up with a double spectrometer in which a single leadscrew drives two gratings linked together by a tiebar. Along with the discarded leadscrew went a slit—the exit slit of the first half of the instrument now serving as the entrance slit to the second half—and the pair of reimaging lenses.

Unlike the manufacturers who approached instrumental problems from the viewpoint of the analytical chemist, we continued to rely on research pioneers for advice, upgrading the 1400 to accommodate the relatively rare scientists engaged in the difficulties of trying to measure second-order interactions of light with molecular fragments, phonons, magnons, plasmons and electrons. During the past few years, we have had the good fortune of working closely with several resourceful individualists who generously enlightened us with their accomplishments. To name but a few, R. F. Schaufele of Esso Research and Development in Linden, N. J. found a cooperative manufacturer of photomultipliers who supplied him with a tube having a tiny cathode to knock down the tube-generated noise to a tolerable level. W. G. Nilsen and J. G. Skinner of BTL alerted us to the distinctive and disruptive polarization properties of individual gratings (3). Unless means

were incorporated within an instrument for compensating for grating polarization, unreliable depolarization ratio data would be obtained. G. B. Benedek of MIT's Lincoln Labs and Daniel Berger of Temple University's Skin and Cancer Hospital pointed out an optical scheme for optimizing excitation by pinpointing the laser radiation to maximize energy density rather than path length. J. H. R. Clarke of the University of Pennsylvania suggested that we direct the laser beam upward rather than downward to the sample to permit the analysis of molten salts and Dewar-contained materials. P. A. Franken, then of the University of Michigan, complained of instability in one of our early 1400s, thereby leading to appropriate design changes. Exploring the realm of signal:noise improvement we were led to consider an array of amplifying schemes including conventional dc, lock-in or synchronous frequency, signal correlation, photon counting and combinations thereof. The culmination of such combined efforts is our newly-designed Model 1400-II Double Spectrometer rounded out with the necessary auxiliary equipment to complete a laser-Raman package.

Progress in instrument design is a continuous thing. "Under-the-hood" changes are made so often that we sometimes wonder whether any two 1400s are identical. An early improvement in the spherical mirror mount facilitates focusing and alignment. Somewhere along the line our 1411 slits emerged from a need for convenience and a longer, wider opening capacity. 45° mirrors and an intermediate slit became a unit to aid alignment in both factory and laboratory. A new, low-reflecting black paint was found for the inside finish and provisions were made to accommodate the universally-accepted Zeiss-type triangular optical bar for which a large number of special optical mounts are available. On the grating mount a fine-pitched screw and a cam now simplify fine-tuning of wavelength and vertical alignment, respectively.

All of these revisions notwithstanding, our development people pocketed still more that eventually emerged in the 1400-II. Principally, these relate to the scanning drive and associated wavelength readout. In the original 1400, the wavelength counter hung obtrusively in front where its visibility under slit-mounted, elaborate and often makeshift experimental equipment was poor. In the 1400-II, the counter is recessed on the side and, to add further to its visibility in the darkened room that researchers seem to favor, it is illuminated. While we were at it, we changed to a new type counter which can be spun at a rate of 12,000 A/min without tearing the works apart. This permitted us to attach a handcrank for those impatient to see what's happening at 8000A within seconds after the instrument reads 6500A. And by virtue of an electrically-actuated clutch it is no longer necessary to disengage a gear manually before hand scanning.

Wavelength readout on a recorder is still a controversial subject, scientists dividing their vote between stripchart and X-Y recorders. Hedging our bet, we decided on improvements for both types. In place of the mechanical marker which tripped a microswitch riding on a 10-tooth sprocket wheel, a unique optical event marker was substituted. It consists of a disc with 10 equally spaced holes drilled near the edge. When light from a tiny pilot lamp passes through one of the holes, a light-actuated silicon-controlled rectifier switches on enough power to pulse the solenoid of an event marker pen on a stripchart recorder. One of the holes in the disc is doubled by masking off a central strip so two pulses are generated when this hole passes light to the LASC. Accessible from the outside, the disc is held on its shaft by a spring enabling it to be rotated with respect to the counter. If you care enough you can set the double hole to correspond exactly with, say, 6000A so the "blips" at 5A intervals will facilitate wavelength interpolation (Fig. 1 and 2).

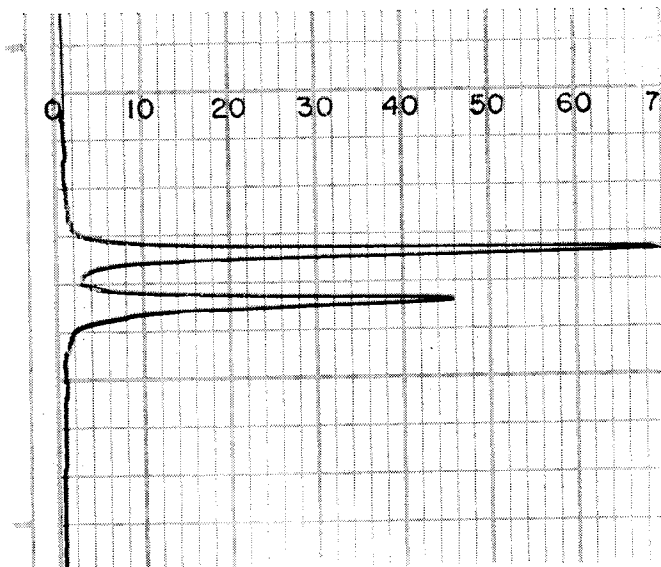


Fig. 1. Comparatively slow-speed scan of the Hg 3131A doublet (1200 groove/mm grating in order II) to illustrate event marks 2.5A apart for measuring spacing between close lines. Separation of the doublet is 0.28A.

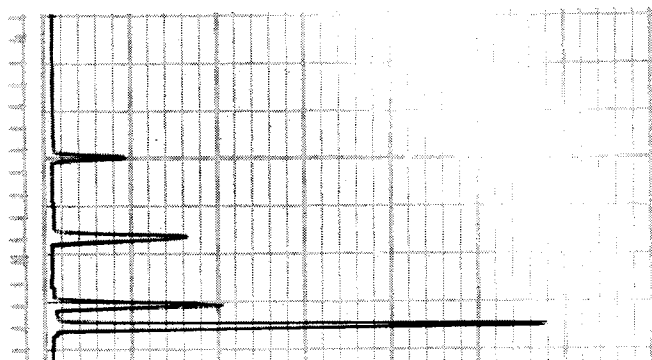


Fig. 2. A rapid scan of the 4200A region of the Ar spectrum. With a 1200 groove/mm grating in the second order the double marks are 25A apart for quick wavelength checks.

For the X-Y recorder proponents, we doubled the accuracy of the retransmitting potentiometer which, with the help of a stable, 15-volt power supply converts wavelength to an analog voltage. The 0.05% accuracy now exceeds that of the positioning control of the X or wavelength axis of commercial recorders although it is still not as accurate as that read out on the mechanical counter of the spectrometer. The signal can alternatively be directed to a digital voltmeter and from there be routed to a computer.

EVALUATION of lasers for Raman systems must account for several matters not the least of which is the state-of-the-art, a condition even more unstable than current international affairs. The fourth-power frequency dependence of scattering (the reason the sky appears blue) favors a laser emitting at the shortest possible wavelength. Yet so many organic materials fluoresce that a generally useful laser must emit light of sufficiently long wavelength to preclude such excitation. It takes no soothsayer to guess that several manufacturers are developing ideal ion lasers which will ultimately permit the rapid interchange of an argon and krypton tube to enable a switch from 4880A where almost half of the Ar⁺ laser's energy is concentrated to 6470A where 60% of the krypton's energy is concentrated.

Meanwhile, however, we must accept what is commercially available and at the moment a 50 mW He-Ne laser, conservatively rated, stable over long periods, essentially trouble-free and almost as simple to operate as an incandescent lamp appears to be the best compromise. Admittedly, a number of well-funded physicists have opted for a 2-watt Ar⁺ laser. The fourth-power law favors Ar⁺ 4880Å over He-Ne 6328Å by a factor of around 3.5. The difference in laser power between the two lines ups the advantage a further 20 times. Still another factor of 2 is achieved courtesy of the relative quantum efficiency of S-20 photomultipliers at the two wavelengths. Together, they mean a better than 100-fold increase in Raman line intensity when a 2W Ar⁺ laser is substituted for a 50 mW He-Ne laser. Especially tempting is this factor for high-resolution studies or those involving even weaker scattering effects than Raman. But for day-to-day jobs, where there is little choice over samples He-Ne is as yet the most practical and versatile. Already over 25 are operating in conjunction with our Model 1400.

In an optical system (Fig. 3) designed to excite Raman spectra and project the scattered light into the double spectrometer, the laser itself is placed on a shelf high enough to permit occasional adjustment but low enough to feed its output into the bottom end of the Model 1430 Sample Illuminator. The spectrometer is located on a customary laboratory bench for ease in working with it. To accommodate the system to the layout and size of the room, the cylinder holding the entrance window and first mirror is rotatable about a vertical axis. The laser can then be located if desired at right angles to the entrance beam, in line with, or underneath the spectrometer.

Within the Sample Illuminator, the laser beam first passes through a non-fluorescing silica window sealing the periscope tube from dust, one of the worst offenders against laser intensity. The beam is then reflected upwards by a dielectrically-coated mirror M with a reflectivity of greater than 99% throughout the visible region. This mirror, incidentally, is ac-

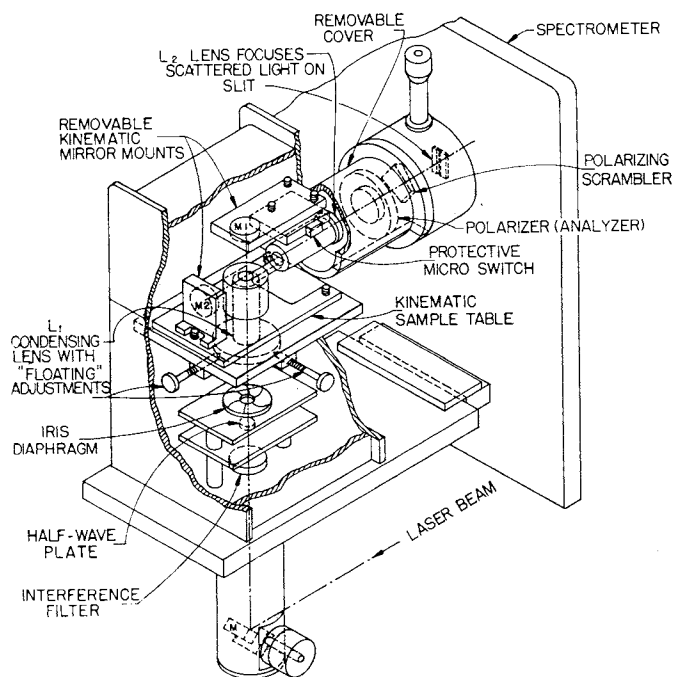


Fig. 3. Schematic of the Spex 1430 Sample Illuminator.

cessible from the bottom of the tube by rotating it downward and removing an end cap so it can be examined or cleaned, if necessary. The laser beam proceeds through a "spike" filter passing more than 80% of the light at 6328Å with a half-width of 20Å. A door provides access to this filter so it can be removed when non-lasing Ne lines are to be passed for wavelength calibration. Above the filter is a half-wave plate of quartz which rotates the plane of polarization through a right angle. (Some laser tubes are axially rotatable through a right angle so that their output, conventionally polarized vertically, emerges horizontally instead. If this can be done, the half-wave plate is unnecessary and is removed.) Next in line is a variable iris diaphragm which helps scrape diverging, non-lasing illumination from the beam. The laser beam is then condensed with a microscope objective set in reverse so that an intense, diffraction-limited point source finally excites the sample. Accurate horizontal adjustment of the objective is accomplished through a "floating" mount with external controls. The beam is focused with another external knob.

Having been directed, filtered, "extruded" and condensed, the laser beam is now ready to act on the sample. Liquid or solid, (but not gas which has insufficient molecular density for this type of excitation unless an Argon Laser is used) the sample is placed on a kinematic, removable table and aligned with the focused laser beam. For liquids a rectangular, 2 ml silica cell is provided. All six sides are fused and the cell is filled through a side tube capped with a Teflon plug. Above is a condensing mirror which, by returning the beam to the focus point, theoretically doubles the Raman scatter. This mirror also serves to protect the operator's eye. Inadvertently, he might try to look down at the sample. As an additional safety feature, M1, itself kinematically mounted for ease of replacement, engages a microswitch controlling the input power to the laser. Since for certain experiments, e.g., those requiring a Dewar, it is necessary to remove M1, a parallel key-operated switch is provided. The experimenter is then unprotected against eye injury but for a warning sign.

L2 is an f/1.8 condensing lens which, in association with mirror M2, focuses the scattered light on the entrance slit. A polarizing analyzer with rotational stops at 0 and 90° and a polarizing scrambler complete the optical components. The analyzer passes light polarized in one direction only. In order that this polarized light not be distorted by polarizing effects of the gratings, the scrambler effectively depolarizes the light before it enters the spectrometer.

Apparently this illuminator design is not widely known as yet; in most other schemes the laser beam is multi-passed through a liquid to excite as many molecules as possible by sheer strength of path length alone. For that purpose, ingenious wedged cells have been devised to reflect the beam repeatedly from the inside walls so the resulting path extends to many times that of the cell length. By contrast, our approach pinpoints the radiation so its density rather than path length is maximized. This has the advantage of being compatible with fluid micro samples, with more conventional larger samples as well as with crystals and powders. Compared to a single pass of a collimated laser, Raman scattering is increased by a factor of about 10 by the focused laser.

As described in greater detail by Benedek and Fritsch (4), the factor limiting this mode of illumination is set by the slit width and therefore the resolution requirements. Once the latter is established, the parameters of the lenses are automatically assignable. In the following treatment, we assume a 50 μ slit width throughout the Model 1400 which, with 1200 groove/mm gratings, is equivalent to a resolution of around 0.6 cm⁻¹.

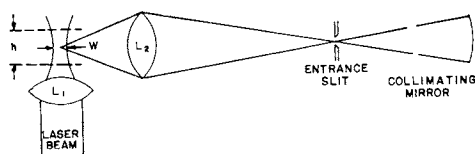


Fig. 4. Optical path of the Laser beam in the Sample Illuminator.

If the condensing lens L2 is such that it collects the optimum solid angle at the source and its angle of convergence matches our spectrometer it will have a magnification of 5 and the width W of the source of illumination is related to the slit width W_1 by the magnification factor M (Fig. 4).

$$W = W_1/M$$

The focal length f of L1 is related to the laser beam diameter a (about 2 mm) and the wavelength λ (6328Å) by

$$f = \frac{Wa}{\lambda} = 30 \text{ mm}$$

The projected height h of the source image on the slit under these conditions

$$h = 3 \lambda M (f/a)^2 = 2.0 \text{ mm}$$

These calculations should be considered approximations only since they depend on a somewhat crude calculation of the dimensions of the pinched cylinder. In general terms they relate to a one-half power value. If a 30 mm microscope objective focuses the laser on a sample and a 5X magnifier directs its image on a 50 μ wide slit, then about one-half of the total scattered light collected by the lens will be accommodated. Of course, reducing the slit width to 25 μ will result in a 50% loss of illumination.

By selecting L2 as an $f/1.8$ projection lens, about 1/4 steradian of the light scattered by the sample is directed to the slit. Its scattered counterpart behind the sample cell is added to the energy by mirror M2.

In earlier Spex articles (Spex Speaker XI, No. 1 and No. 2) we pointed out that gratings are known to respond unequally to light polarized in different directions. The intensity distribution varies widely depending on the individual grating master. Having examined several, the only conclusion we have reached is that the cross-over point (where intensity for parallel and perpendicular rays is equal) is at the blaze wavelength and, as a matter of fact, is just about the best way of determining the exact blaze wavelength.

Since depolarization ratios are important in determining the origin of spectra, one obvious out is to provide means to correct for the grating disparity. Fig. 5 shows how serious the effect is and how it would be necessary to provide correction factors for each wavelength for them to be meaningful. Obviously, this procedure at best would be inconvenient and time-consuming. A better way of coping with grating polarization is to present essentially depolarized light to the entrance slit. Depending on the origin of the scattered radiation, light emerging from the sample will be polarized or depolarized. If at this point in the optical train a polarizing scrambler is added, it will essentially prevent the grating effect.

A polarizing scrambler consists of a quartz wedge which functions by varying the retardation across its face. What emerges is light of every conceivable degree of polarization. The scattered Raman radiation is so scrambled across the face of the grating that the net effect is almost the same as though completely depolarized light were impinging.

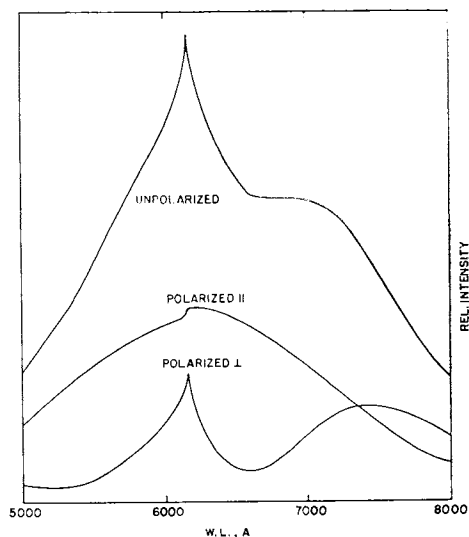


Fig. 5. Illustration of the polarizing effect of gratings in the Spex Double Spectrometer. With an unpolarized incandescent lamp incident on the slit, the response of an S-20 photomultiplier is given in the upper trace. Interspersing a parallel polarizer before the entrance slit, the middle trace is obtained. Similarly, the lower trace results from turning the polarizer to a perpendicular position. The sharp peak at around 6200Å is a grating anomaly that is not well understood. The cross-over between the two orthogonal polarizing traces occurs at the blaze wavelength of the grating.

The accurate measurement of depolarization ratios depends on the avoidance of all instrumental effects; note the aid in this regard of the polarizing scrambler (Table I). Three values are reported for the CCl_4 459 cm^{-1} line. Without the polarizing scrambler the ratio turns out to be 0.05. That is, light excited at this wavelength in a direction perpendicular to the electric vector is 0.05 as great as that in a direction parallel to the electric vector. With a 1/4-wave plate interposed between the analyzer and the spectrometer, the depolarization ratio drops to 0.013—closer to but still about twice the accepted value. Clearly, circularly polarized light created by the 1/4-wave plate is only partially effective in counteracting the polarizing by the gratings. When, however, the quartz polarizing scrambler is inserted, the value drops to an acceptable 0.010, well within the range reported in the literature. Some ratios are as low as 0.005; theoretically, the value should be zero.

TABLE I

INSTRUMENTAL EFFECT		
DEPOLARIZATION RATIOS I_{\perp}/I_{\parallel}		
$\text{CCl}_4 \bar{\nu} = 459$		
No correction	1/4 wave sheet	Quartz depolarizer
0.05	0.013	0.010

THE natural choice of photomultiplier is one with a tri-alkali (antimony-sodium-potassium-cesium) photocathode. Such tubes have an S-20 response, peaking at around 4500Å and fading to 10% of their peak response at 7500Å, a 2470 cm^{-1} shift from the 6328Å exciting line. Of those tested, the most satisfactory in terms of signal:noise has a tiny effective cathode (around 3 mm dia.) so that errant electrons originating from the cathode face are minimized. Noise is so low that, except

for the most exacting work with very weak signals, cooling of the photomultiplier is not needed. Fortunately, this tube has found a sizable market as a star tracker. By magnetically sweeping its sensitive spot over all four quadrants, it functions as a guide in space exploration vehicles. The tube is produced therefore in large enough quantities to permit us to select ones with low dark counting rates for the special requirements of Raman spectroscopy.

The so-called S-20 cathode is the most sensitive surface ever formulated. Remarkably similar to the sensitivity curve of the human eye, it has about a 20% peak quantum efficiency and some tubes have been produced, luckily to be sure, with a quantum efficiency approaching 50%. Phrased more dramatically, for every two 4500Å photons impinging on the cathode one dislodges an electron which can then be amplified and detected.

If photons were the only source of electrons, an S-20 photomultiplier would be a near-perfect transducer. Unfortunately, several other sources of electrons have been discovered, one contributor being the cathode itself. The applied potential between cathode and first dynode is enough to pull away a small number of thermally-agitated electrons which then comprise the dark noise. Were this perfectly uniform, it would do us no harm. Naturally, the facts are to the contrary. Aver-

aging around 250 electrons/sec/cm² of cathode, the thermionic dark noise fluctuates statistically and cannot be distinguished from real photon-generated electrons. The noise-component being proportional to effective cathode diameter, the photomultiplier with a 3 mm diameter cathode is about 15 times better than tubes with a 50-mm cathode face. Cooling either S-20 tube to dry-ice temperatures can reduce the dark signal 10- 100 times but for routine work is a continuing chore and expense.

A second source of photomultiplier noise can, fortunately, be distinguished from real light signals. Down the dynode string, an occasional electron will fall into the current stream. Unlike electrons originating from the cathode, these downstream electrons undergo less multiplication and produce a smaller anode pulse (Fig. 6). Photon counting offers a means of discriminating against them.

Photon counting—more generally known as pulse counting—is an electronic amplification technique whereby high-speed circuitry actually counts every anode pulse. It may be thought of as a digital amplifier as contrasted with conventional analog amplifiers. In our ER-3 photon counting component up to 100,000 pulses/sec can be counted before straining the circuitry so it begins to lag behind. The main advantage of photon counting is not the ability to count, however—dc am-

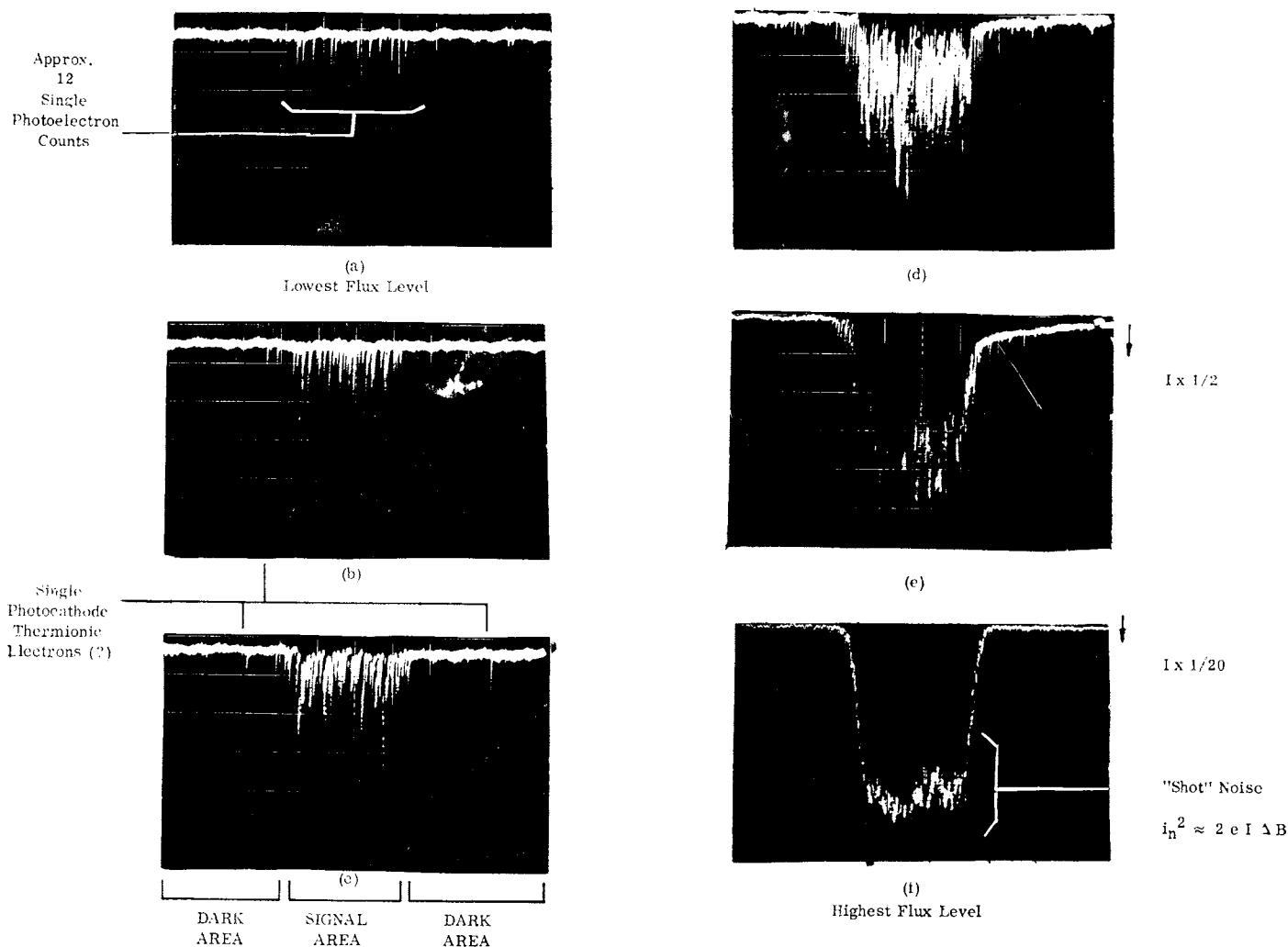


Fig. 6. Oscilloscope tracings of an S-20 photomultiplier at decreasing signal levels. In (f) the signal is sufficiently intense to preclude counting; the shot noise fluctuations are small with respect to the average current. At a lower flux intensity the shot noise breaks up into single electron pulses. Finally, at (a) the flux intensity is so low that only single electron pulses are present. At such low light levels, typical of Raman emission spectra, digital (i.e. photon counting) amplification techniques are superior to analog (i.e. conventional dc or lock-in) methods. Photograph courtesy E. H. Eberhardt, ITT Industrial Laboratories.

plifiers can average out the counts over a far wider range—but its associated discrimination networks. One type of discrimination fabricates an energy window through which the signal must pass to be counted. If the lower energy level is biased to a value above that attainable by any but electrons originating from the cathode, all downstream electrons are effectively denied entrance. At the same time the high-energy side may be blocked out to ward off pulses originating from cosmic rays and radioactivity. A second type of discrimination rejects all signals which do not have appropriate rise-time characteristics.

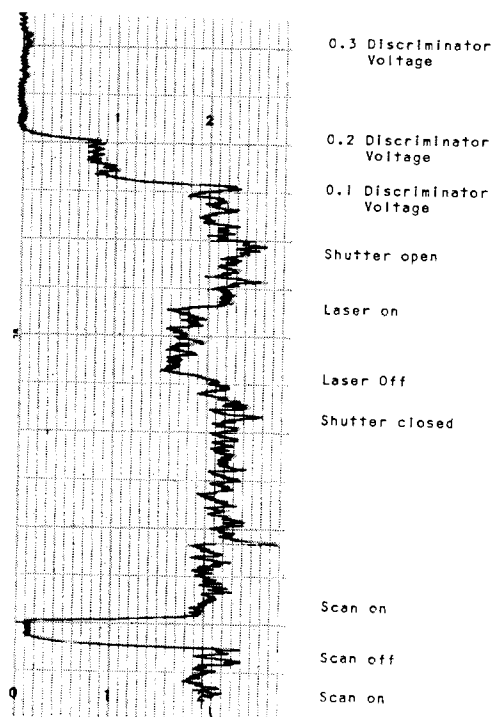


Fig. 7. Effect of biasing discriminator voltage to reduce background noise response.

How effective such discrimination can be is illustrated in Fig. 7. The stripchart tracing was started at the bottom with no signal entering the photomultiplier. Both the laser and scanning drive of the spectrometer were on, however, and air-borne radiation pickup from these was sufficiently intense to be detectable. First the scanning drive motor was switched off causing a considerable drop in counting rate. After the scan was turned back on, the laser was turned off. It, too, added to the background noise. Closing the shutter, incidentally, had no effect proving that none of the current recorded came from light. When a discriminating voltage of 0.1 was biased into the circuitry, a drop to around one-half of the recorder current was evident. Increasing this to 0.2 V dropped the current to almost zero. With higher amplification, 0.4 V bias can be shown to be optimum.

To evaluate the advantage of photon counting over straight dc amplification, the 459 cm^{-1} line of CCl_4 was run at high resolution. Normally seen as a single line in ordinary chemical analysis, the CCl_4 isotope interactions can be isolated by trimming the slits of the 1400-II down to 50μ (0.6 cm^{-1}). The fine structure of the 459 cm^{-1} line originates from molecules containing different combinations of C^{135} and C^{137} which have a natural abundance of around 75% and 25%, respectively. Five different lines representing five combinations can appear as shown in Table II.

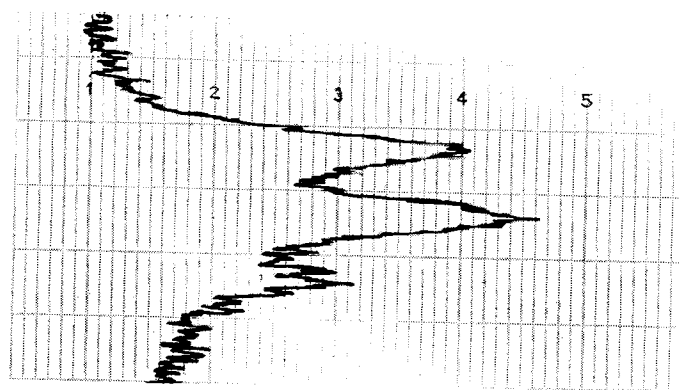


Fig. 8A. The 459 cm^{-1} line of CCl_4 with dc electrometer detection.

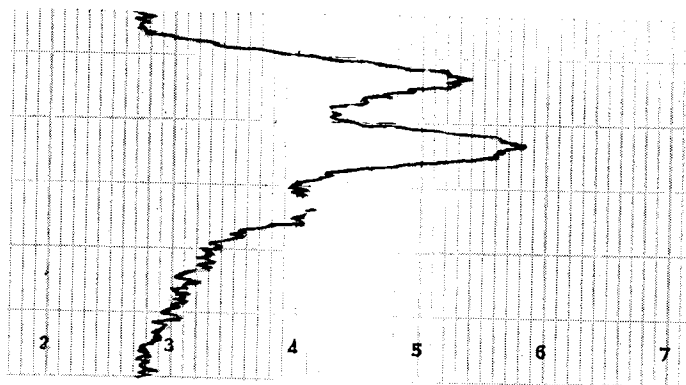


Fig. 8B. The 459 cm^{-1} line of CCl_4 with photon counting detector, without any discriminator bias.

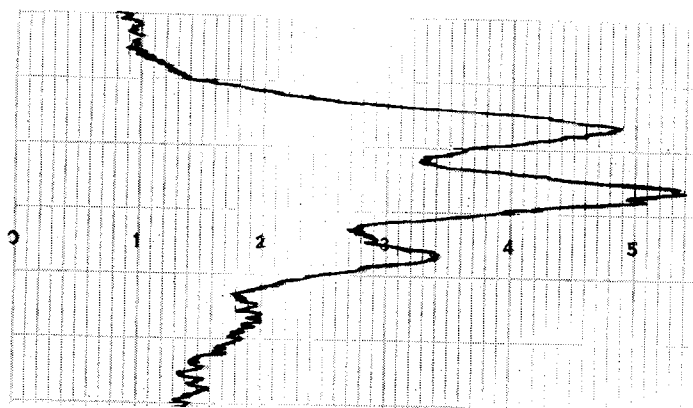


Fig. 8C. The 459 cm^{-1} line of CCl_4 with photon counting including a 0.4 V discriminator.

TABLE II
ISOTOPE STRUCTURE CCl_4 459 cm^{-1}

Line, Decreasing ν	Origin	Predicted Intensity
1	CCl^{135}_4	81
2	$\text{CCl}^{135}_3\text{Cl}^{137}_1$	108
3	$\text{CCl}^{135}_2\text{Cl}^{137}_2$	54
4	$\text{CCl}^{135}_1\text{Cl}^{137}_3$	12
5	CCl^{137}_4	1

The line of lowest frequency represents the symmetrical breathing mode in a molecule containing all four C^{137} atoms with carbon and should be weakest because only one-quarter of the total number of chlorine atoms are present in this isotope. Since there are three times as many C^{135} atoms as C^{137} , the most abundant molecule is No. 2. Simple probability theory indicates that, if the least abundant molecule (No. 5) is taken as unity, then the most abundant is 108 times greater or, put differently, the line it emits is 108 times more intense. Although no attempt has been made to compare integrated intensities, the lines appear qualitatively in the predicted order.

In Fig. 8A, the dc amplifier section of our ER-3 was set to the 10^{-9} amp scale and the line scanned at a rate of around $6 \text{ cm}^{-1}/\text{min}$. Only three components are visible, the third so noisy that it can be mistaken for a doublet. Measuring its frequency accurately would hardly be possible.

In Fig. 8B, the amplifier was switched to photon counting but without discrimination; all other conditions remained the same. Somewhat less noise is apparent, the frequency of the third line can be measured fairly accurately but there is no evidence of two weaker lines.

In Fig. 8C, the discrimination bias was turned up to 0.4 V. At once the three lines attain a crisper shape, a fourth line appears on the noise horizon and one can even see a fifth line, albeit with some imagination.

Although few would quarrel with the inescapable conclusion that photon counting is better than dc amplification for measuring Raman scattering, tagging this improvement with a quantitative figure of merit does represent a

problem. One way of tackling it is by ratioing the peak of the weakest line seen with dc above what would be the baseline noise to the average of the valley-to-peak displacement above the noise. Here we get figures of about 3 for dc, 5 for photon counting without discrimination and 15 for photon counting with discrimination (Fig. 8C). An improvement of roughly 5 is what we thus calculate but we shall leave the raw data for the reader to interpret as he sees fit.

ECLUSIVE for 30-odd years, the Raman effect seems finally to have found a partner in the laser, making for exciting times for those of us engaged in this research. Raman first demonstrated the effect with strong sunlight in a darkened room. Our contribution may well be exemplified by our impromptu demonstration last March at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. As anyone who has ever attended (and who hasn't?) one of these conclaves will testify, experimental conditions are hardly ideal. Voltage skitters, dust flies, cigarette smoke settles in a low cloud, people are everywhere and everything rattles. James Carter, University of Pittsburgh, however, challenged us with a fluorinated sample that had defied infrared analysis by dissolving the cells on contact. He was rewarded in short order with a stripchart record of its Raman spectrum.

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LASER-RAMAN SYSTEM

Although the Spex laser-Raman package may vary in price depending upon the application, we are listing below a typical system for chemical analysis of liquids to furnish our readers with a "ball-park" figure. As outlined, the instrumentation is complete, requiring only a source of ac power, an air-conditioned room and two benches. It is recommended that for convenience of operation the spectrometer be placed on a standing-height bench. The laser is then placed on a sitting-height bench. The 1430 Illuminator is so designed that the laser can be in-line with or at right angles to the optical path, thus allowing for versatility of room layouts.

SOURCE—He-Ne laser, 50 mW, with power meter... \$ 8,935.00

SPECTROMETER—Model 1400-II with straight slits,
two 1200 groove/mm gratings, scanning
drive \$11,491.00

SAMPLE ILLUMINATOR—Model 1430 \$ 2,360.00

DETECTION PACKAGE—Consisting of ER-3 with
photon counting and dc amplification, a
premium quality S-20 photomultiplier with
Spex cryostat, focusing optics and electronic
circuitry \$ 9,334.00

WE ARE NOT FASHION-CONSCIOUS, BUT:

Comes a time in the life of an instrument when it can benefit from experience. Our 1700-III single and 1400-II double spectrometer have emerged fresh from several design changes for improved performance.

1) The wavelength counter has been moved from the front to the side, glass enclosed and illuminated for better visibility. It is a new counter with a speed rating about 2-1/2 times that of the older unit. It is thus protected against damage from rapid hand-scanning; the vernier and larger numerals are also easier to read.

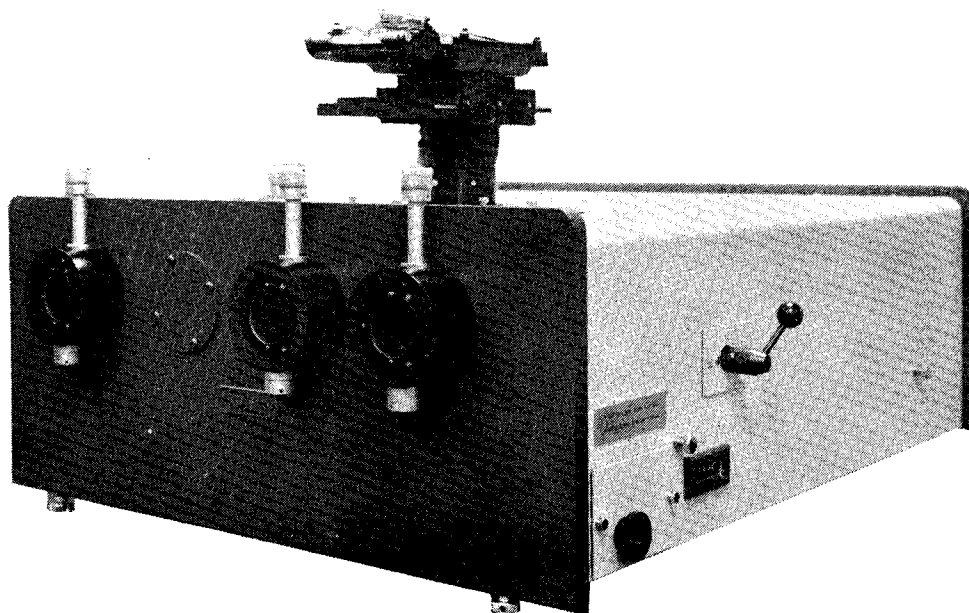
2) The mechanical event marker has been retired in favor of one photoelectrically actuated and adjustable. With a 1200g/mm grating a pulse is generated every 5A and to further facilitate measurement, a double pulse appears every 50A. It can be set to make its mark starting at, say, 3000A precisely or wherever else is desired.

3) The scanning speed range has been extended at both ends. For a 1200g/mm grating it is now 0.13 to 2000A/min.

4) For fast or fine hand-scanning the necessity of manually disengaging motor gears has been eliminated with a magnetic clutch which uncouples automatically when the electrical scanning drive is turned off.

5) More precise wavelength tuning of the kinematic grating mount is now accomplished with an 80 thread/inch adjustment screw.

6) Several convenience features such as a main switch, outlet pilot light and fuse have been added. All connections are now located on the rear plate providing access to interior without the necessity of unplugging electrical connectors.



SPEX 1400-II DOUBLE SPECTROMETER



INDUSTRIES INC.

P. O. Box 798
Metuchen, New Jersey 08840

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