LASER-RAMAN NOTES

BACKGROUND DECAY

On occasion, the Raman spectroscopist encounters high background which, in some samples, can be so intense that Raman scattering is thoroughly washed out. Although the background can arise in several ways, often fluorescence is the cause, populations at a higher energy level being excited by the intense laser beam. One way of dealing with this has already been described (1). Essentially, the method is to choose an exciting wavelength sufficiently removed from the fluorescence region so that the Raman-shifted spectrum is displaced from the fluorescence region. Intuition notwithstanding, some samples call for a short wavelength of excitation in order to skirt the fluorescence.

The intensity of fluorescence can frequently be reduced up to 10 times by bathing the sample in the laser radiation for an hour or so. To illustrate the effect, we chose two samples, one a liquid (indene), the other a solid (sheet of paper). Ar^+ radiation of 80 mW at 4880A was the source. As shown in Fig. 1, fluorescence of two samples of indene decayed at different rates. Further, sliding the capillary containing the indene to expose different portions had little effect on the fluorescence. Both of these can be explained by thermal mixing — molecular migration — of the liquid sample.

By contrast, decay of fluorescence in the solid sample was largely reproducible (Fig. 2). Not unexpectedly, it turned out to be exponential after a short conditioning period. When the paper was shifted to expose a new region to the laser, the initial intensity of fluorescence returned.

Despite the absence of an adequate explanation of the phenomenon, this drench-quench technique has proved so universally applicable that it should be tried on every sample exhibiting high levels of fluorescence.

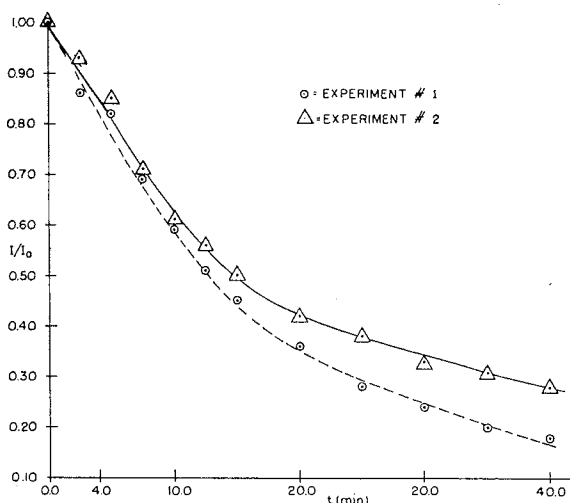1. J. R. Allkins, Spex RAMALOGS, Vol. 2, No. 4, 1969.

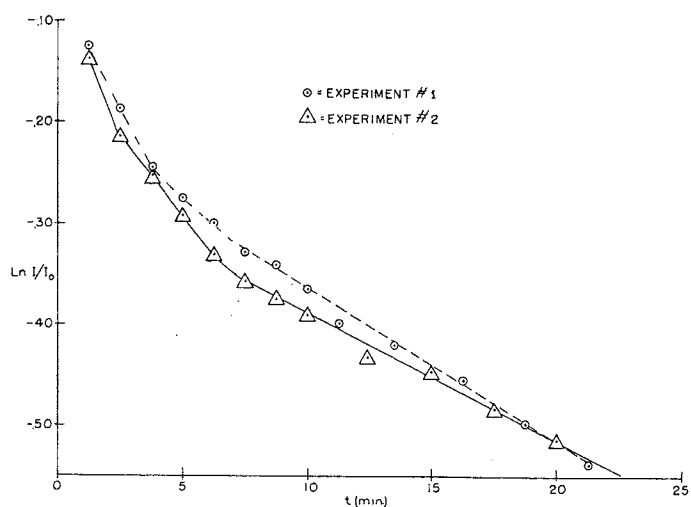Fig. 1   Fluorescence decay of liquid Indene in laser light is not reproducible

Fig. 2   Fluorescence decay of a solid, paper, in laser light is reproducible

THE RESOLUTION GAME

Like the traditional iron triplet in emission spectroscopy, carbon tetrachloride's 459 cm^{-1} structure has emerged as the standard of resolution in laser-Raman spectroscopy. Demonstrate four of the five isotopic peaks neatly separated and the spectrometer automatically passes. Hint at the fifth peak — however unreal — and the instrument is blue-ribboned as truly superb. Or so some enthusiastic sales engineers would have you believe.

Actually, things are decidedly more complex. First of all pure carbon tetrachloride does not yield as well resolved a spectrum as when it is diluted 70% with a non-polar solvent such as cyclohexane. Exactly why the theorists have not yet divulged but obviously it is related to interactions among CCl$_4$ molecules. The effect is unmistakingly clear as can be seen from Figures 1A and 1B. Taken under identical conditions within a few minutes of one another on the same instrument, the peak-to-valley distances of all four of the lines is considerably greater in the spectrum of the diluted material.

Another bit of sleight of handedness which one must be wary of is spectral slit width. Despite the fact that the minimum separation of the lines in the CCl$_4$ complex is around 3 cm^{-1}, reduction of spectral slit width to 0.5 cm^{-1} (21 microns in the Spex Model 1401 Double Spectrometer at 4880A) improves the resolution considerably. This can be seen in Fig. 2A and 2B identical with their Fig. 1 counterparts except that they were taken with 1 cm^{-1} spectral slit widths.
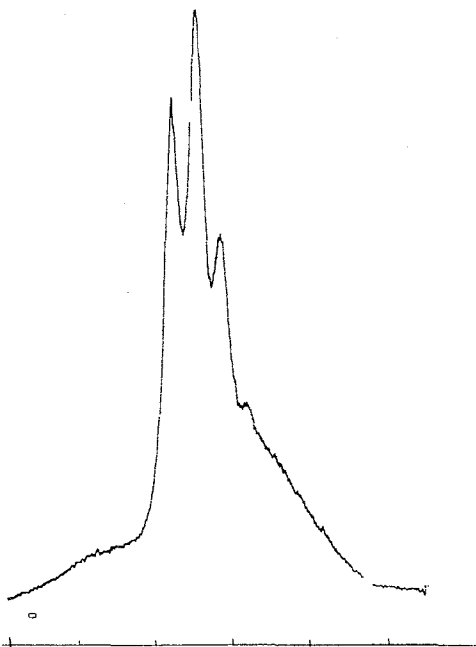

Fig. 1A   CCl$_4$, spectral slit width 0.5 cm^{-1}

Fig. 2A   CCl$_4$, spectral slit width, 1 cm^{-1}
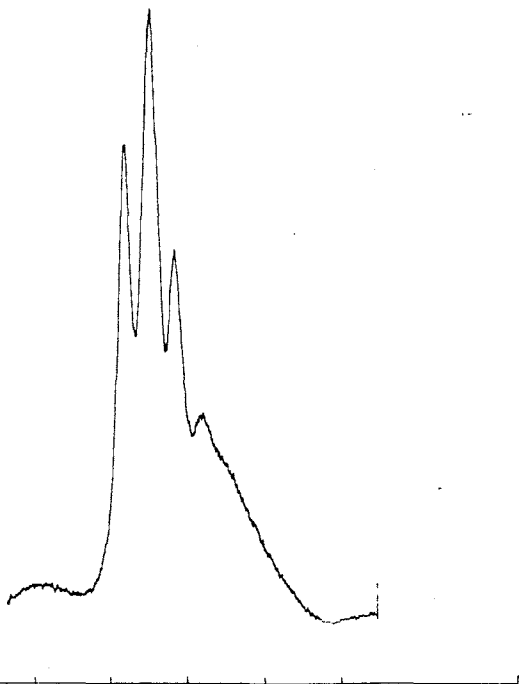
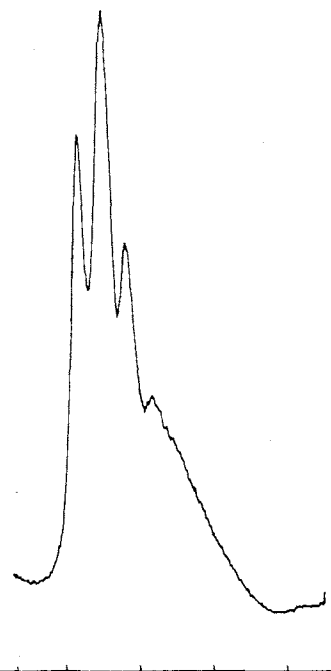**Fig. 1B   CCl$_4$, diluted, spectral slit width 0.5 cm^{-1}**

Fig. 2B   CCl$_4$, diluted, spectral slit width 1 cm^{-1}

In our opinion, carbon tetrachloride should be dethroned altogether as resolution standard bearer. Its discomforting smell its main deterrent, carbon disulfide appears to be a better choice. The reason relates to the concept of contrast in optical measurements. Known technically as modulation transfer function, the parameter measured is directly related to the ability of the optical system to detect a weak line in the presence of a strong one. Carbon tetrachloride, with its four towering peaks, is a measure of the spectrometric system to resolve lines of approximately equal intensity. On the other hand, carbon disulfide offers a much more stringent test: the ability of the optical system to measure a line about 2 cm^{-1} from a line about 4 times as intense. The arrow in Fig. 3A points to the CS_2 line in the 650 cm^{-1} complex taken with 0.5 cm^{-1} slits and Fig. 3B with 1 cm^{-1} slits.
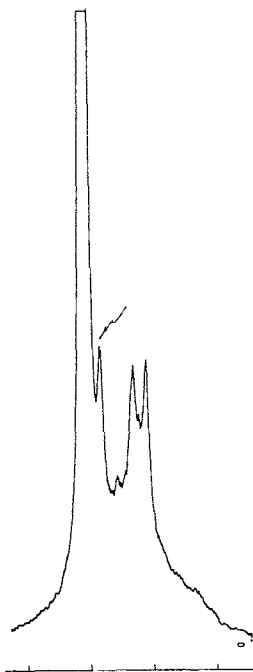

Fig. 3A   CS$_2$, spectral slit width 0.5 cm^{-1}

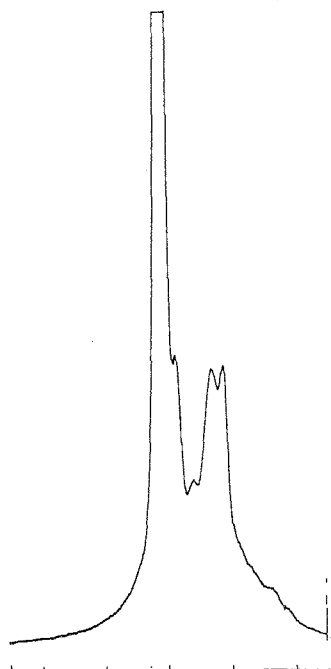**Fig. 3B   CS$_2$, spectral slit width 1 cm^{-1}**

SPURIOUS LINES

Before identifying a line as originating from the Raman effect — especially if the line is unusually sharp — the investigator should make sure that it is not spurious. Such lines can arise in at least four ways:

1) Extra lasing lines from high-power lasers;
2) Plasma, i.e., non-lasing lines, from lasers;
3) Grating ghosts;
4) Overhead fluorescent lights and sample fluorescence.

The subject of extra lasing lines is curious because it is so highly dependent on the individual laser. Some high-power Ar$^+$ lasers emit a line at 4889A in addition to the 4880A line. Neither the wavelength selecting prism in the laser itself nor the interference filter is capable of deliniating the 4880A, cleanly rejecting 4889A. As a result, 4889A can come through giving rise to a satellite on each Raman line. The intensity of the satellite can be as much as 10% of that of the parent line again depending on the individual laser. Another line noted is 5140A, appearing when 5145A is selected. This occurs only with Ar-Kr lasers, however, since it is a Kr lasing line. Should either line occur in the Raman spectrum, it can be largely filtered out by tipping the interefrence filter a few degrees thus moving its wavelength peak a few angstroms.

Plasma lines are generally removed entirely with an interference filter (and so can be distinguished from grating ghosts). It should be pointed out, however, that many interference filters are designed to block only the long wavelength—Stokes side. On the anti-Stokes side interference filters are generally open. Although interference filters can be made to block the anti-Stokes side as well as the Stokes side, their overall transmittance would suffer as a result.

Just as we were about to embark on a short project to provide plasma calibration lines (or interfering lines depending on the degree of one's optimism), we discovered the new book by Jack Loader, of Southampton University, England in which all the work has already been expertly documented. Compacted diligently into fewer than 100 pages, the book is called "Basic Laser Raman Spectroscopy," and is available from Sadtler Research Laboratories, Inc., Philadelphia, Pa. 19104 or Heyden & Son in England or Germany. Particularly helpful are the extensive tables of plasma lines with a He-Ne laser and an argon laser.

The newest gratings are essentially ghost-free. Older ones, however, do exhibit ghosts both close to the parent line and ones at a distance which can be much more treacherous. For example, older gratings made on B&L's non-interferometrically controlled ruling engine show a so-called Lyman (or worm) ghost at 1.25λ. This occurs at about 2906 cm^{-1} with 6328A excitation from a He-Ne laser but can easily be calculated for other excitation wavelengths. Ghosts can be detected by running a Raman spectrum of a roughened carbon pellet, which has no Raman spectrum, with and without an interference filter. Those lines whose intensity relative to that of the Rayleigh line does not change are either ghosts or extra lasing lines. By repeating the experiment at several excitation wavelengths, one can distinguish the ghosts from the extra lasing lines.

Occasionally lines are identified by unwary spectroscopists as Raman lines when they actually result from sample fluorescence or room lights. If you find lines at 18312, 17332 or 17270 cm^{-1} note that they are likely to be invariant in wavelength rather than wavenumber; turn out any fluorescent light in the area and check for sample fluorescence before attempting to theorize on their origin.

HELIUM-CADMIUM LASER EVALUATION

An RCA LD2148 He-Cd laser emitting 20 mW (15 mW nominal) at 4416A was tested as a potential source for laser-Raman spectroscopy. Except for the fact that power output was found to be too low for the analysis of weakly scattering gases, no faults were found with the laser. Raman spectra of powders, polymers, and pure liquids were recorded easily. Photodecomposition, expected because of the short wavelength, did not appear to be greater than that from Ar+ 4880A. Perhaps this should not have been surprising in that a great deal of work had been done in pre-laser days with Hg 4358A. Fluorescence when present was somewhat enhanced over that obtained from other wavelengths but in no way prevented the recording of perfectly acceptable spectra. Samples chosen for the investigation ranged from conjugated organics to long-chain polymers.

Some advantages of the helium-cadmium laser over, say, helium-neon as a source for Raman spectroscopy are:

1) Modern spectrometric systems designed to record Raman spectra have an almost linear response across the Raman range (0-4000 cm⁻¹ shift) when blue light is the source of excitation. This is due to the fact that the decrease in the photomultiplier response is largely offset by the increasing efficiency of the 5000A-blaze gratings. The result is a much truer representation of the intensities of the vibrations as compared to spectra recorded with red excitation.

2) Since the instrumental response (i.e., the combined factors of the grating reflectivity, photomultiplier response, fourth power scatter law, etc.) at 4416A is roughly five times that at 6328A, a system with a 15 mW He-Cd laser is equivalent to one with a 75 mW He-Ne laser.

3) More a convenience than an advantage is the fact that the emission spectrum from a He-Cd plasma in the Raman range is simpler than that from He-Ne and will therefore interfere less with the Raman spectrum. This requires less stringent specifications for the interference filter.

4) Apart from the cost saving of at least $2000, the prime advantage of the He-Cd laser over ion lasers is that it is air-cooled and requires standard power inputs (117V, 1φ). This in turn leads to simpler operation and less weight for the He-Cd.

The only disadvantages encountered with the He-Cd system are instrumental rather than spectroscopic. *Broadband dielectric* mirrors reflecting the laser beam from its source to the sample tend to transmit 4416A radiation when the radiation is linearly polarized and strikes the mirror at a 45° angle of incidence. The mirrors in the spectrometer are not affected since there the light is unpolarized and strikes the mirror at an angle of incidence much less than 45°. By substituting silvered mirrors for the dielectric mirrors in the external train, the transmission problem can easily be overcome.

The second disadvantage is that "Polaroid" analyzers for measuring depolarization ratios between 4800A and 8000A tend to pass some of the perpendicular component of the polarized radiation and thus give erroneous results between 4400A and 4800A. A replacement analyzer especially peaked for the 4000A region of the visible spectrum is therefore required.

To demonstrate clearly the capability of the He-Cd laser, Raman spectra of Teflon were recorded and are shown in Fig. a and b. The first spectrum was obtained with the RAMALAB, excited by an RCA LD2148 He-Cd Laser emitting at 4416A. Scan speed was 100 cm⁻¹/min with 10 cm⁻¹ slits. This spectrum is comparable to the second, obtained with the same instrument except with a Coherent Radiation Model 52 Ar+ laser emitting 400 mW at 4880A. Switching to the higher powered laser yielded a roughly equivalent spectrum at 2½ times less scanning time. That ratio is also roughly equivalent to the price ratio between the two lasers.

The initial investigation of the He-Cd laser has shown it to be amply suitable as a source for laser-Raman spectroscopy, especially valuable as a low-cost adjunct to a He-Ne laser. The higher Raman intensity and opportunity to analyze samples that absorb 6328A radiation should make the laser a valuable addition to any laboratory now limited to a He-Ne laser. And because both are almost identical, the same fine reliability can be expected from the new He-Cd laser. Pending long-term reliability checking, we can advise that all other properties — output stability, ease of operation and maintenance — are excellent.
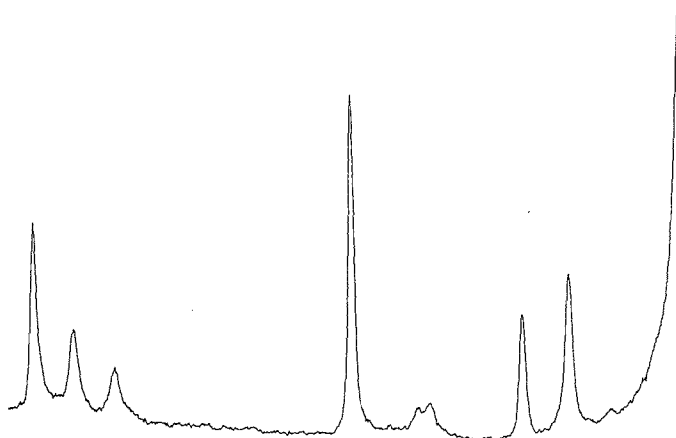

Fig. a Raman spectrum of a Teflon plate taken on a Spex RAMALAB with an RCA LD2148 He-Cd laser emitting 4416A (10 mW)
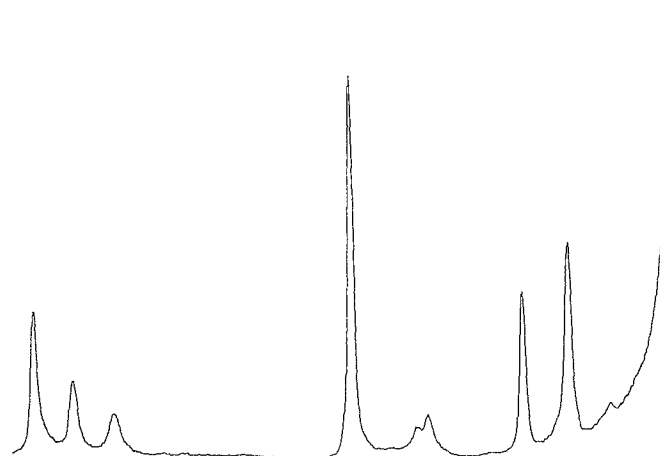

Fig. b Spectrum taken under identical conditions as (a) except for Ar+ laser emitting 4880A (400 mW) and 1/30 relative gain

A (GAIN 20 K)

190 CM⁻¹

SPECTROMETER

LASER

"DROP-OFF" FROM AN
EXCITATION LINE

A favorite "test" of prospective purchasers of laser-Raman equipment is to see how near one can approach the exciting line before the intensity of that line is great enough to mask Raman spectra. This test is often performed with a "typical" sample and little attention is paid to details such as slit widths, excitation frequencies or sample orientation.

Although conceptually this test is an excellent one, the theory that it represents the scattered light rejection properties of a spectrometer is misleading unless definite rigid guidelines are first laid down. To illustrate this point we have recorded spectra of the same sample (a white solid) oriented in three different ways to an incident laser beam. In each spectrum all conditions, such as laser power, slit width, excitation frequency, scan speed, etc., were fixed. Only the amplifier gain was changed.

In spectrum A the sample was illuminated by the standard pellet method, i.e., the sample was held at an angle of 20° to the direction of the laser beam and scattered light collected at 90° to the laser beam direction.

In spectrum B the laser beam was aimed to graze the face of the sample held parallel to the plane of the entrance slit of the spectrometer.

In spectrum C a small hole was drilled in the side of the sample still held in position B and the laser focused into this hole (see R.F. Schaufele, J.O.S.A. **57,** 105 (1967).

In each case, the method of illumination had a strong effect on the "drop-off" point from the excitation line. The degree and slope of the sample fluorescence background were equally affected. Results, therefore, reflect not so much quality of the instrumentation as the operator's knowledge of the various methods available for sample illumination.

B (GAIN 10K)

110 CM⁻¹

SPECTROMETER

LASER

C (GAIN 5K)

40 CM⁻¹

SPECTROMETER

LASER
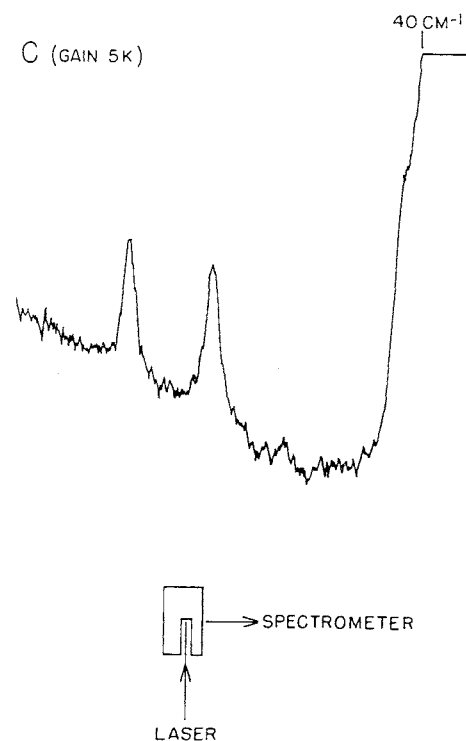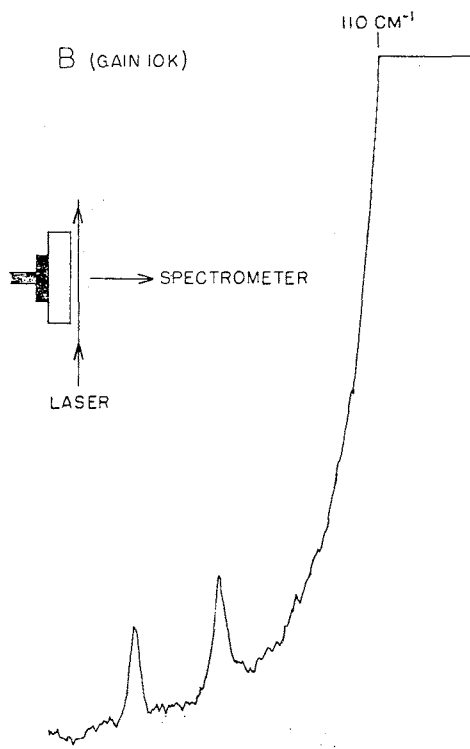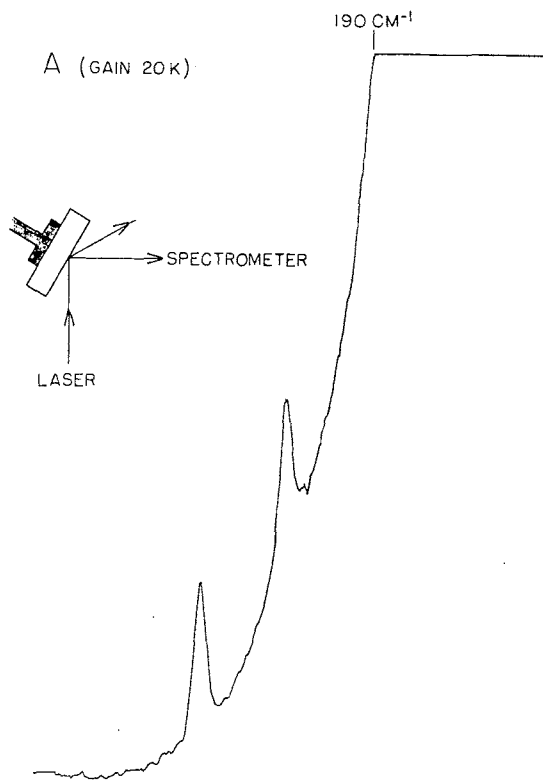
SPECTRA IN NO MAN'S LAND

If for no other reason than that it is there, the chasm between the far infrared and the ultrashort microwave region intrigues molecular spectroscopists. Eager to obtain spectra in this region, within 1 to 30 cm^{-1} of the exciting line where the Rayleigh scatter obstinately forces the recorder pen off scale, every Raman scientist cannot help but wonder what is hidden by the fog.

Two years ago, their curiosity aroused to the point where they did something about it, four Bell Labs researchers in Murray Hill found a means of clipping the Rayleigh wings. L. L. Chase, J. L. Davis, G. E. Devlin and S. Geschwind discovered that iodine vapor would filter out the green argon lasing line. By filling a cell around 50 mm long with hot iodine vapor, they produced a many-lined absorption filter which — serendipity violating Murphy's law — absorbed the Ar+ 5145A line. Because the absorption is so sharp, the laser must be single-moded with an etalon to squeeze its line inside that of the absorption line. In fact the iodine absorption lines which fall inside the Raman lines are so sharp

that with spectrometer slits opened even to 1 cm^{-1} the Raman spectrum appears perfectly normal.

What is decidedly better than usual is the drop-off frequency of the Rayleigh line. At the University of Oregon, Professor Warner Peticolas, Dr. Joseph Lippert, and Mr. Gary Hibler have been able to obtain Raman spectra of polycrystalline polymer samples to within 5 cm^{-1} of the Rayleigh line using this technique. Having already studied several polymers they report lines as close as 10 cm^{-1} off 5145A. They achieve 10^3 discrimination against the Rayleigh line. This value was obtained by observing the intensity of the 5145A Rayleigh line with the iodine filter in place and measuring the intensity maximum and minimum as the laser was tuned and detuned to one of the iodine rotational lines.

One of the disadvantages of the iodine vapor technique is that it appears to be limited to the 5145A Argon line. However, other diatomic gases might be useful for other lasing lines.
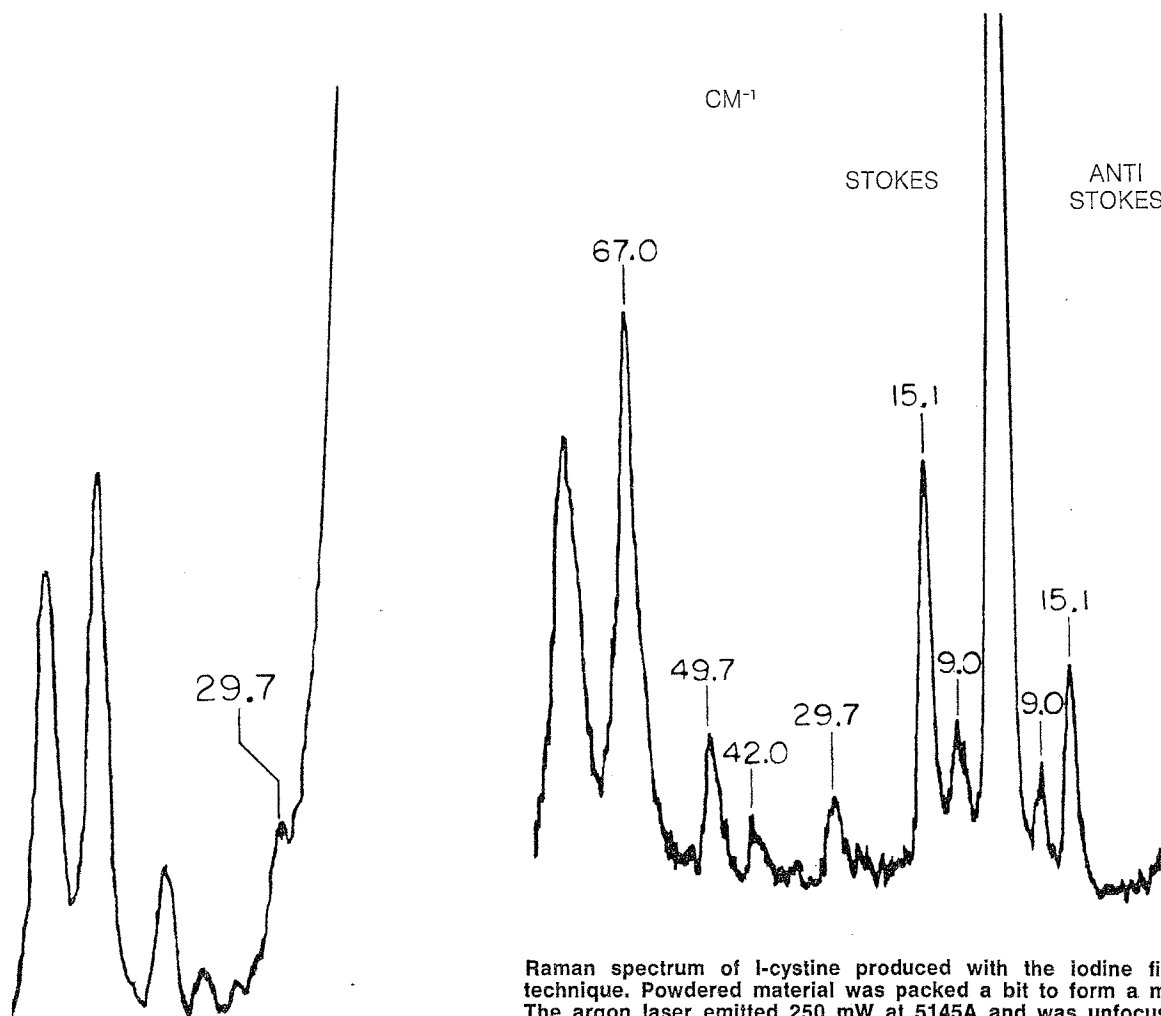
Raman spectrum of l-cystine taken without the iodine filter. Note that the drop-off is still not complete at 29.7 cm^{-1}; two Raman lines are hidden by scattering from the intense Rayleigh radiation.

Raman spectrum of l-cystine produced with the iodine filter technique. Powdered material was packed a bit to form a mat. The argon laser emitted 250 mW at 5145A and was unfocused on the sample. Scan rate was 0.24 cm^{-1}/sec with slits opened to 2 cm^{-1}. The photon counting scale was set to 1000 fs; a cooled FW-130 was the detector. The spectrometer was a Spex Model 1400-II with 1200 groove/mm gratings.

Note that the iodine filter blocks the exciting line so well that, not only does the 9 cm^{-1} line of the sample appear on both the Stokes and anti-Stokes sides, but the drop-off plunges nearly to the baseline at 2.3 cm^{-1}. (Courtesy Prof. W. L. Peticolas, University of Oregon.)

PROGRESS IN OUR HOME FRONT – WHO'S NEW?

In the Raman Lab

Whether the job is checking lasers or spurious lines, teasing ultimate resolution from the system, investigating a new theory or a less frequented region of the spectrum, running a familiar sample to convince an unfamiliar fellow or an unfamiliar material to push ahead one notch on the forefront of Raman spectroscopy it rests firmly on the talents of Dr. P. R. Reed, who joined Spex not long ago, having done eminently successful battle with the tools of this challenging trade at Lehigh University, Chemistry Department. And he is willing and able to take on yet other tasks.

It is nearly two years since we, somewhat hesitatingly, embarked on a program for commercial Raman analyses. Trouble is that service constantly loses customers to our instrument sales department, a fact that we mention with hardly a regret. But it is a fact that now leads us away from the meek, hesitating approach of 1968 to the reports in this issue, brimming with spectra evidencing an established technique, fulfilling its promises of revealing all sorts of molecular secrets. Our service laboratory is now equipped with both a RAMALOG and RAMALAB, as well as a variety of multicolored lasers, each poised to shed its light on your problem sample.

Call Bob Reed any time you suspect a sample of harboring an unknown information bit. For $45.00/hour, with a minimum charge of $90.00, you will be provided with a laser-Raman spectrum and report for your own interpretation.
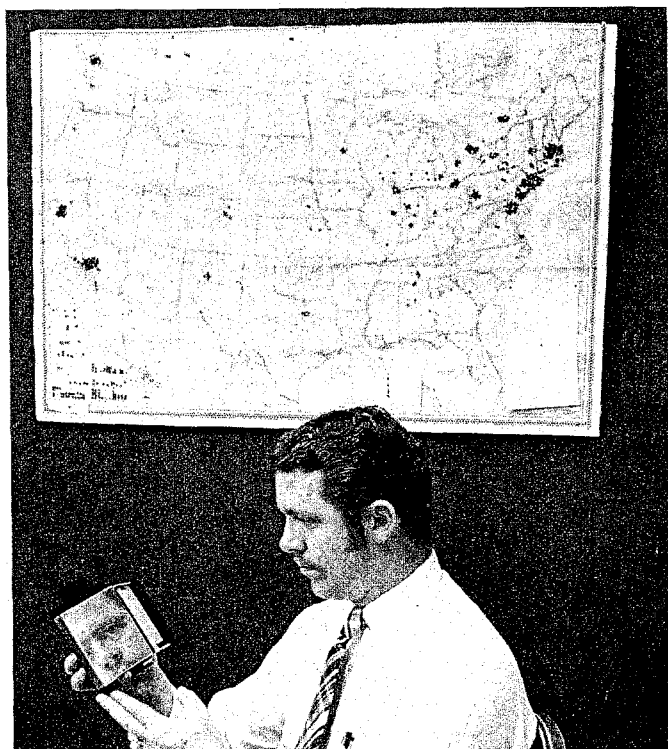
In the Performance Testing and Service Department

William J. Walker, practically an old timer being with us since May, trains his suspicious eye toward rejection of any imperfect mirrors or gratings, the likes of which might otherwise haunt a spectrometer. Having survived a rigorous apprenticeship in the Physics Department of Fordham University, where his graduate work under Prof. Alfons Weber involved high-resolution Raman studies of gases, Bill is now supervising our optical testing, installation and service activities.

Overhead is the department pin-up. Each dot is another Spex UVISIR spectrometer. Installations outside the USA are tacked in a cluster over the Pacific.
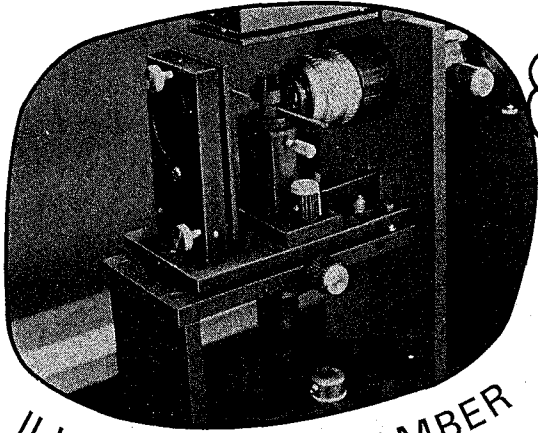
For Reference: Clipable Chart

MAXIMUM SCAN SPEEDS (A/min or cm⁻¹/min)

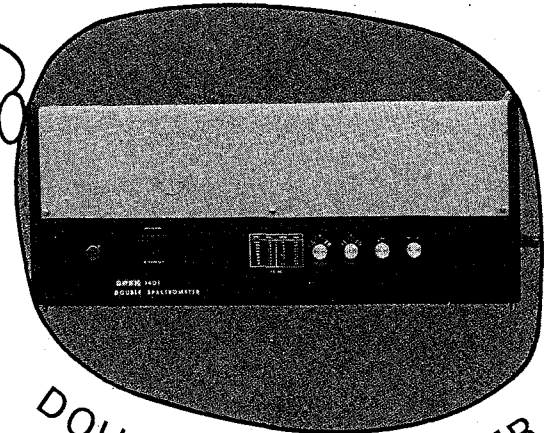| TC	RISE TIME	PERIOD	SPECTRAL SLIT WIDTH (A or cm⁻¹)				
—	Seconds	—	1	2	4	8	16
0.1	0.25	0.5	120	250	500	1000	2000
0.25	0.6	1.2	50	100	200	400	800
0.5	1.2	2.5	25	50	100	200	400
1.0	2.5	5.0	12.5	2.55	50	100	200
2.0	5.0	10.0	6.25	12.5	25	50	100
2.5	6.0	12.0	5	10	25	40	80
5	12	25	2.5	5	10	20	40
10	25	50	1.25	2.5	5	10	20
20	50	100	.625	1.25	2.5	5	10
25	60	120	.5	.1	2	4	8
50	120	250	.25	.5	1	2	4

Example: At a period 0.5 sec (equivalent to a rise time of 0.25 sec and a time constant of 0.1 sec) and a spectral slit width of 1 cm⁻¹, a maximum scan speed of 120 cm⁻¹/min is recommended. Survey spectra may be run at up to twice this speed.