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The SPEX Speaker

INDUSTRIES, INC. • BOX 798, METUCHEN, N.J. 08840 • ☎ (201) 549-7144

# THE RAMALAB, 1970

THE RAMALAB®, a benchtop laser-Raman spectrometric system, is designed specifically for the busy laboratory where a dozen or so samples are lined up day after day. The system is considerably more compact and easier to operate than others including the Spex RAMALOG. Yet it is capable of generating spectra well within the stringent Coblentz Society's Class II criteria for the infrared (Table 1). Samples in the form of liquids, solids, single crystals at ambient, elevated and $LN_2$ temperatures may be handled by the standard instrument. For the analysis of gases, where the Raman scattering level ranges several orders of magnitude below that for liquids and solids, a high powered laser and a special cooled photomultiplier are available.

Depending on the particular sample, Raman spectra can be decisive in assigning molecular structure or serve as a powerful complement to infrared absorption measurements. It turns out that those group vibrations associated with weak absorption spectra often give rise to strong Raman spectra and vice versa. Identification of vibrations, such as C—C, C=C, C≡C, S—S, etc., is best achieved through Raman spectroscopy.

Inorganic and organo-metallic compounds containing heavy metal ions usually generate their most characteristic bands in the far infrared, a region normally shunned because of severe instrumental limitations. Raman spectroscopy nicely circumvents the problem by producing all of its data—corresponding to near infrared, infrared and far infrared—as visible light. In a single tracing, without change of optics, detector or source, a Raman spectrum encompasses the broad region from around 20-4000 $cm^{-1}$.

Designed for rapid analysis, the RAMALAB combines many unique features:

- A ready-to-operate system can be purchased for under $23,000.
- Spectra equivalent to Coblentz Society Class II research grade infrared spectra are traced in 3 to 30 minutes depending on sample and laser power.
- The RAMALAB is tabletop-compact; controls are simplified; electronics are modularized, conditioning optical components are stored in turret holders; all three slits are ganged.
- Presentation of wavenumber is identical with that from infrared spectrophotometers for overlaying spectra.
- An optional component permits the operator to trace infrared spectra and Raman spectra on the same preprinted chart—formats are identical. This device also couples the recorder and wavenumber drives allowing a repeat Raman spectrum to be superimposed. This feature is especially convenient for depolarization presentations.
- An optional Variable Temperature Assembly permits samples to be run at temperatures from 77°K to 200°C.
- All-digital computer-controlled performance is assured with the standard stepper/synchronous motor; an optional stepper motor control is already on hand. Photon counting yields direct digital intensity data.
- The spectrometer section is thermostatted above ambient to maintain accuracy of wavenumber readout despite room temperature variations.

**Table 1.**

| | CLASS II COBLENTZ IR SPECIFICATION | SPEX RAMALAB SPECIFICATION |
|---|---|---|
| Resolution, $cm^{-1}$ | Spectral slit width 2 $cm^{-1}$ over at least 80% of spectral range | 1 $cm^{-1}$ over entire Raman range |
| Wavenumber Accuracy and readability, $cm^{-1}$ | ±5 in region 2000-4000<br>±2 in region below 2000 | ±2 over entire Raman range |
| Fiduciary marks | Specified to guard against paper shrinkage and chart/spectrometer mismatch | Standard event marker |
| Noise level | less than 1% peak-to-peak | less than 1% peak-to-peak |
| Spectral range, $cm^{-1}$ | 400-3800 | 10-4000 |
| Time constant, sec | Variable for compatibility with scan rate and spectral slit width | 0.5-15 |

## Laser

THE least costly laser suggested for the RAMALAB is the RCA LD2148, a He-Cd laser emitting 15 mW at 4416A. The unit is placed externally on the bench alongside the RAMALAB. Although more than adequate for most analytical applications, the laser may be readily replaced by more powerful ones. The fact that it is located externally rather than inside of the console is important for changing or servicing the laser; experience has taught that laser optics must be cleaned periodically to maintain power output at or above rated values.

The RAMALAB is so constructed that any continuous laser is compatible. Ar, Ar/Kr and He-Ne lasers may be expedient depending on the proposed application.

## Sample Illuminator

THE illuminator supplied is identical with that in the more sophisticated Spex RAMALOG. The same wide versatility in sampling, the same high utilization of weak Raman scatter and the same simplicity of operation are offered. The laser beam is reflected into the instrument by a high reflectance mirror. Entry is through an opening in the rear panel located near the floor of the sample chamber. The beam passes toward the front of the instrument where an identical mirror reflects it upward through the sample illuminator. The 99% reflectance mirrors, unlike prisms, do not require readjustment when the exciting color is changed since the angle of total reflectance of mirrors does not vary with wavelength. After passing through double turreted wheels in which polarization rotators, neutral density and interference filters may be stacked with standbys permanently mounted and waiting to be flipped into or out of the optical path, the laser beam is brought to a diffraction-limited focus at the sample position. To further increase the effective laser power and maximize the Raman scatter, the beam is multi-

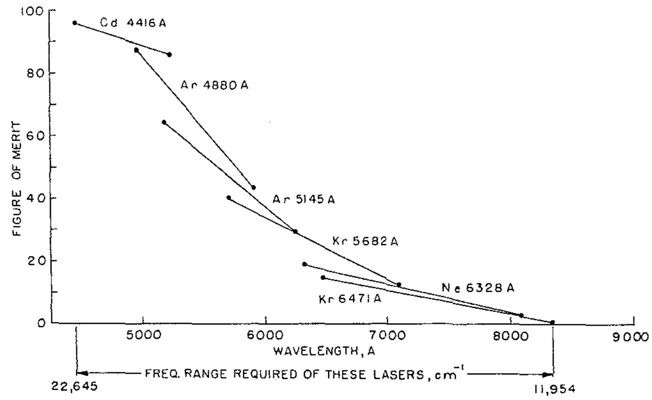
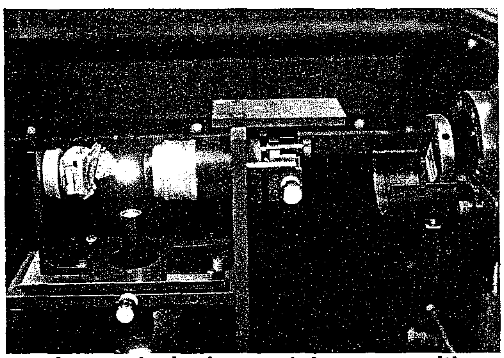



**Fig. 1 Depiction of scattering intensity excited by lasers commonly applied to Raman spectroscopy. The solid bars cover the usual Raman range (Delta=0-3500 $cm^{-1}$). As an example, at 3500 $cm^{-1}$ a He-Cd laser excites a Raman line with about 80 times as much intensity as does a $Kr^+$ laser set for 6471A.**

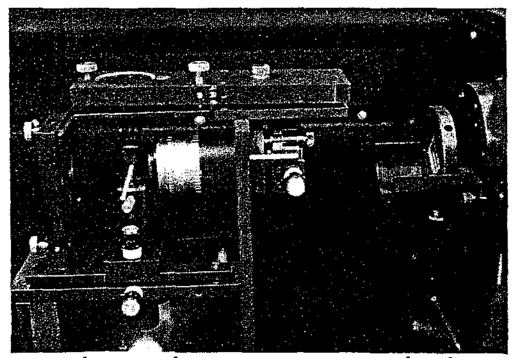
passed through the sample by two kinematically mounted mirrors above and behind it.

The module includes a table for liquids or powders, also kinematically mounted. Samples may be loaded into melting point capillaries or a 1 ml silica cylindrical cell. Additional sample mounts are available for solids, single crystals, and low temperature studies. A quick change 180° viewing system is optional.

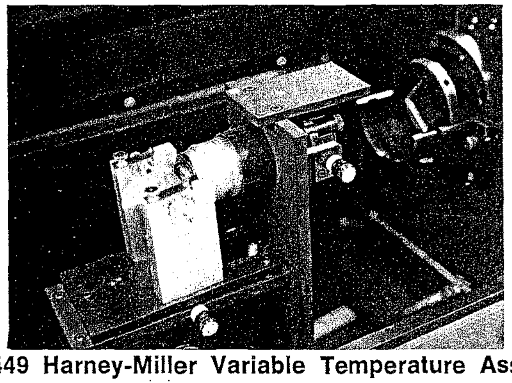
A highly efficient photographic f/0.95 lens gathers the Raman radiation scattered at 90° to the incident laser beam directing it to the spectrometer via a polarization analyzer to determine depolarization ratios and a scrambler to overcome grating bias for polarized light. Proper determinations of depolarization, e.g. 0.006 for $CCl_4$ at 459 $cm^{-1}$, are assured.



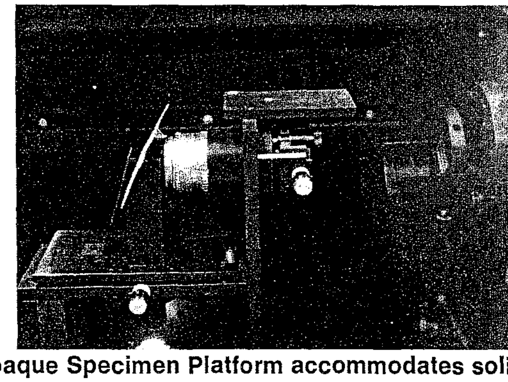
**Small samples and single crystals are positioned on a goniometer which is kinematically interchangeable with the other mounts.**



**Liquids, powders and gases are conveniently contained in a melting point capillary, the axis of which is the focus of the laser beam.**



**The 1449 Harney-Miller Variable Temperature Assembly provides temperatures from −196°C to +200°C and holds the same general-purpose capillaries shown upper-right.**



**An Opaque Specimen Platform accommodates solids such as plastic sheets and, like the others, is kinematically repositionable.**

The Sample Illuminator module bolts to the floor of the 17″ x 12″ x 13″ h chamber. Removal of two bolts frees the module so it can be lifted out leaving the open space for experiments with, say, very large samples, Dewars, or high-temperature furnaces. Exact return of the illuminator is provided for by an indexing fence.

### Spectrometer

THE spectrometer is a double, symmetrical Czerny-Turner design laid out for double dispersion. It achieves the low instrumental scatter characteristic of an instrument where the radiation is dispersed serially by two separate gratings. At the same time, double (additive) dispersion—in sharp contrast with subtractive dispersion—achieves at least twice the luminosity or instrumental throughput. Simply phrased, double dispersion means that slits may be opened twice as far for equivalent spectral bandpass. The effect is that signal levels from a 15 mW laser equal those from a 30 mW laser with a spectrometer whose optical components are laid out for subtractive dispersion.

Scanning is through a synchronous/stepper type motor. On normal ac mains it provides smooth, uniform scans for recorder readout. When interfaced to a digital computer, the motor steps along as directed.

### Detection and Amplification

FOR argon or He-Cd lasers the standard S-11 photomultiplier, with its low dark count even at room temperatures, is a wisely economical choice. A red-sensitive tube becomes important for yellow or red laser light, however, so the FW-130 plus a thermoelectric cooler are offered as options to provide a detector range from 4416A to 6471A as may be required with He-Cd and $Ar^+/Kr^+$ lasers. And to protect the easily upset photomultiplier which reacts to excessive light by breaking out in a temporary high dark count, its high voltage supply has been programmed to reduce its output when sensing that the anode current is approaching the danger level.

The already digitized output from photon counting amplification provides the intensity values in a form directly acceptable by a computer. For the x-axis—that is wavenumber presentation—the Spex Model 1751 Stepper Motor Control serves as the necessary interface to a computer. Through a power amplifier, it takes the 5 V computer pulses and drives the scanning motor in increments of 0.01 to 0.1 $cm^{-1}$.

### Recorder

THE high cross-chart speed recorder has a 10 $cm^{-1}$ interval marker and push-button gear changes for spreading out spectra when needed for detailed study. The optional Recorder Coupler which must be factory installed at the time of purchase serves three unique purposes:

1—The chart drive is mechanically coupled to the wavenumber drive;

2—At 2000 $cm^{-1}$, an automatic gear change halves the speed of the chart paper drive;

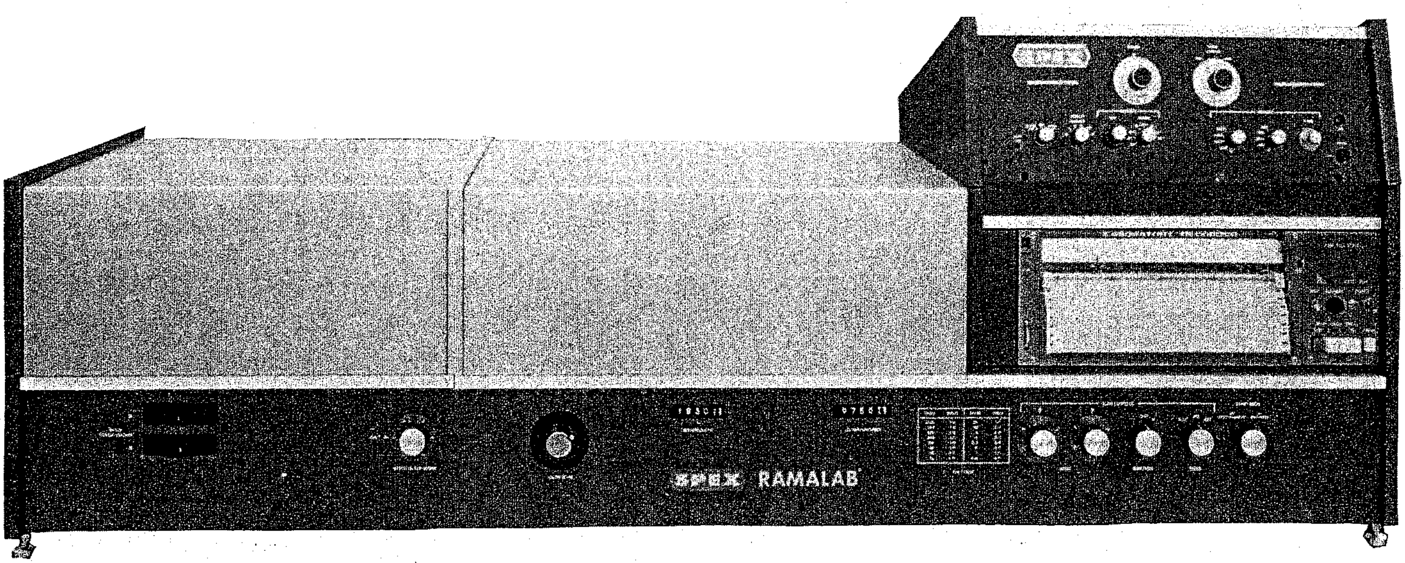
3—At 4000 $cm^{-1}$ both the scanning drive and chart paper drive are automatically shut off.

The first feature is most convenient for polarization measurements. After a run is completed, the operator merely scans back to delta-zero (manually, or electrically at 5000 $cm^{-1}$/min). The polarization analyzer is rotated 90° and the scan is repeated. Both tracings appear exactly juxtaposed. This same feature is exceedingly useful for repetitive scans over a short wavenumber range. One may want to check stability of the sample, study effects of orientation or segregation, or do "poor man's" signal averaging (repetitive, superimposed scans), etc.

The second feature establishes the system's infrared compatibility. Many modern infrared spectrometers employ preprinted chart paper with the format: 100 $cm^{-1}$/25 mm up to 2000 $cm^{-1}$ and 200 $cm^{-1}$/25 mm between 2000 and 4000 $cm^{-1}$. Spex is supplying identical pre-printed chart paper, Z-folded and perforated between individual charts. Simply by switching to "Spectrometer Coupled" the operator achieves infrared-matched format. After obtaining a Raman spectrum he can place the chart on his infrared spectrometer. Together, Raman spectra in both polarization planes and the infrared spectrum provide compact, comprehensive characterization of the material under study. Alternatively, of course one can uncouple the spectrometer and recorder drives, for example, to spread out a short spectral region for evaluating subtle spectral features.

### Exemplary Spectra

THE test of laser-Raman Spectroscopy is in the wealth of information its spectra can provide rapidly and reliably. Hard-working pioneers of the past few years have already sparked a spreading endorsement of Raman for accurate fingerprinting of a host of materials that defy infrared analysis.



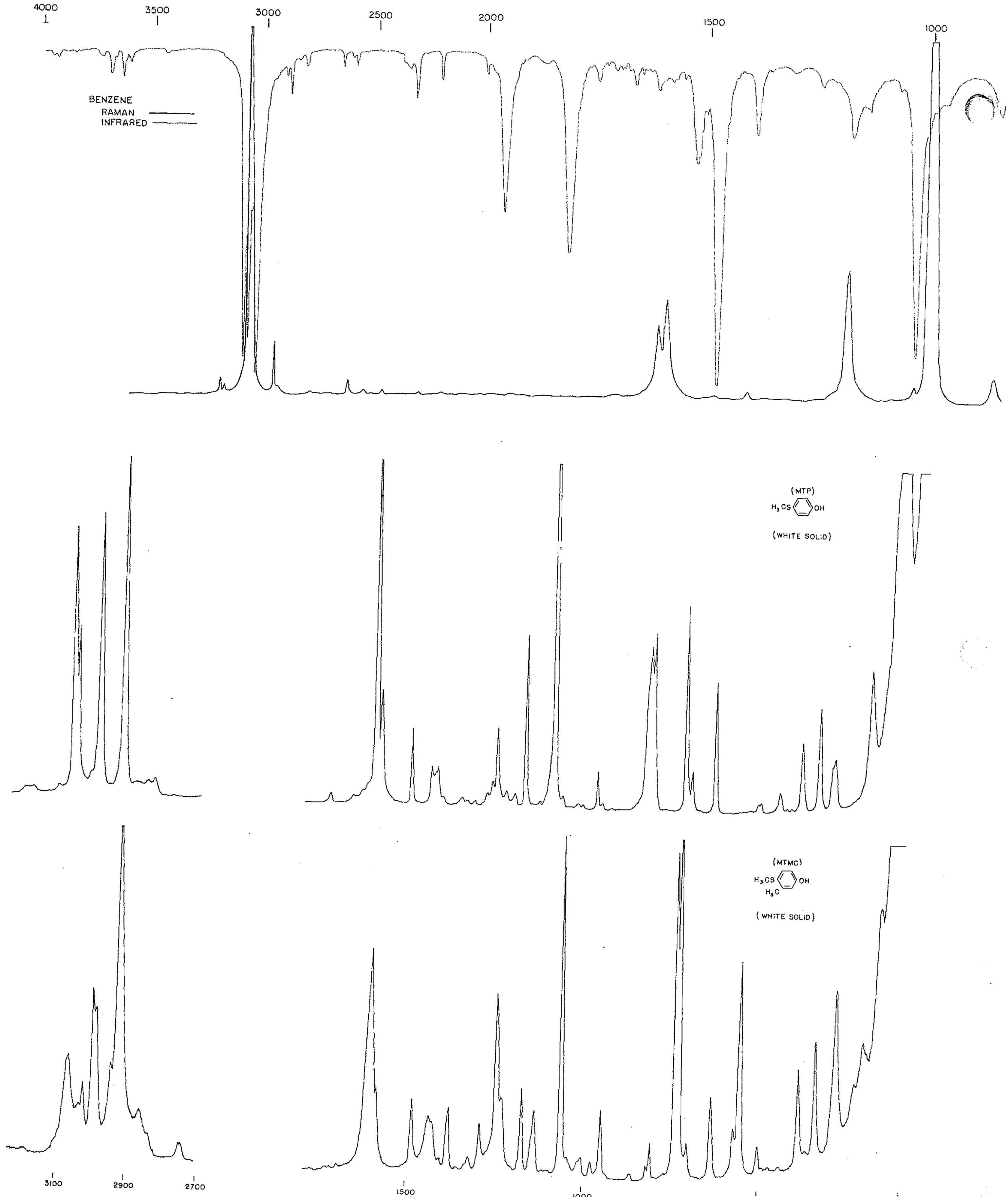



**Fig. 3 Differences in the Raman spectra of 4-(methylthio)-m-cresol and 4-(methylthio) phenol resulting from the addition of one methyl group to the system. (Samples courtesy of Crown Zellerbach, Carnas, Washington.)**

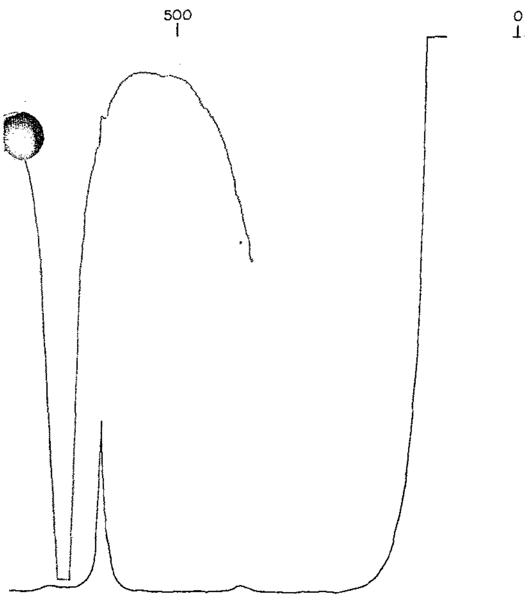



**Fig. 2 Being identical in wavenumber format Raman and IR spectra can be traced on a single sheet. Because of the centro-symmetric nature of benzene, it is an excellent compound to illustrate the complementary nature of Raman and IR. All strong Raman bands are forbidden in IR and vice versa. For a full vibrational picture of benzene, therefore, one must have both spectra. The strong Raman line at 991 $cm^{-1}$ is characteristic only of aromatic rings. The structure in both Raman and IR just beyond 3000 $cm^{-1}$ denotes aromatic C-H stretching. The fact that no strong lines in both spectra coincide is indicative of the centrosymmetric benzene structure.**

An extension of the ability to detect different molecular species of similar formula is evidenced by Fig. 3. The addition of one methyl group to MTP to form MTMC results in a complete change in the Raman spectrum. One rapid method of determining whether MTP has been converted to MTMC is therefore to record a spectrum of the reaction mixture. Since Raman scattered radiation is, to a first approximation, linearly proportional to the concentration of the sample a fair idea of the extent of the conversion can also be gained. And, unlike the hydrophobic infrared region, water will not ruin the sample nor adversely affect the quality of a Raman spectrum.

When a component is separated from a mixture on a thin-layer chromatography plate, it is ultimately concentrated in a small area on the surface. By illuminating this with a laser beam and focusing the scattered light into a spectrometer, the Raman spectrum of the component **in situ** can be easily obtained. This technique is still in the experimental stage and leaves definite room for improvement. In Fig. 4 the background fluorescence probably arises from the support material, which, if changed, might well remove this problem.

That Raman spectra appear as shifted emission lines in the visible region of the electromagnetic spectrum is an advantage illustrated in Fig. 5. With a normal infrared instrument all of the information below 250 $cm^{-1}$ in the spectrum of this organometallic complex would be lost. Laser-Raman, however, lends itself to the detection of low-frequency vibrations which often arise from bonding between heavy metal atoms involving a high degree of covalency. Since heavy metal complexes are becoming increasingly important in catalysis and biochemistry, this simple method of detecting and studying metal-metal and metal-ligand bonding is appealing. The richness of the common steroid spectrum in Fig. 6 and the ease with which it can be run indicate the promises Raman can fulfill for biochemical analysts.

Unlike infrared systems, Raman sample chambers require no evacuation or dry air flushing to obtain low-frequency vibrational region spectra, nor does Raman suffer from any lack of excitation energy at the longer wavelengths. It takes only one instrument to scan the entire vibrational region equivalent to the far infrared through and beyond the mid-infrared.

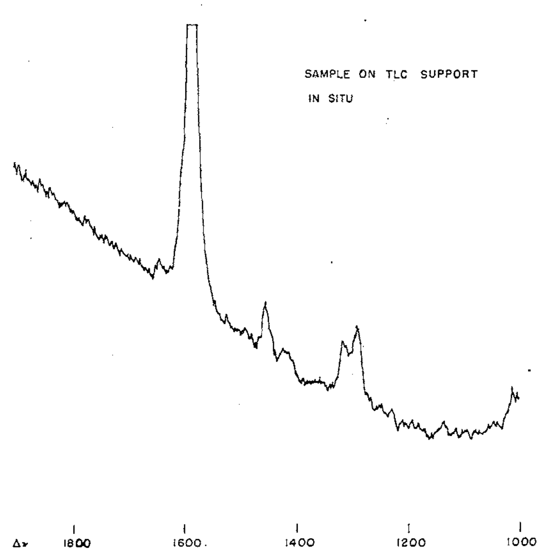



**Fig. 4 Raman spectrum of a component "in situ" on a TLC plate.**

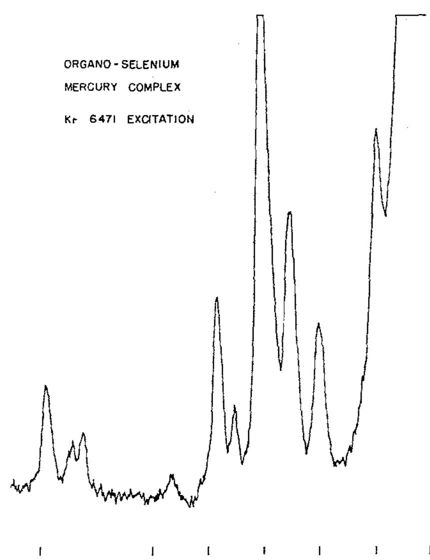



**Fig. 5 Low-frequency spectrum of a mercury-selenium complex excited by the red line (Kr 6471) of a mixed gas laser.**

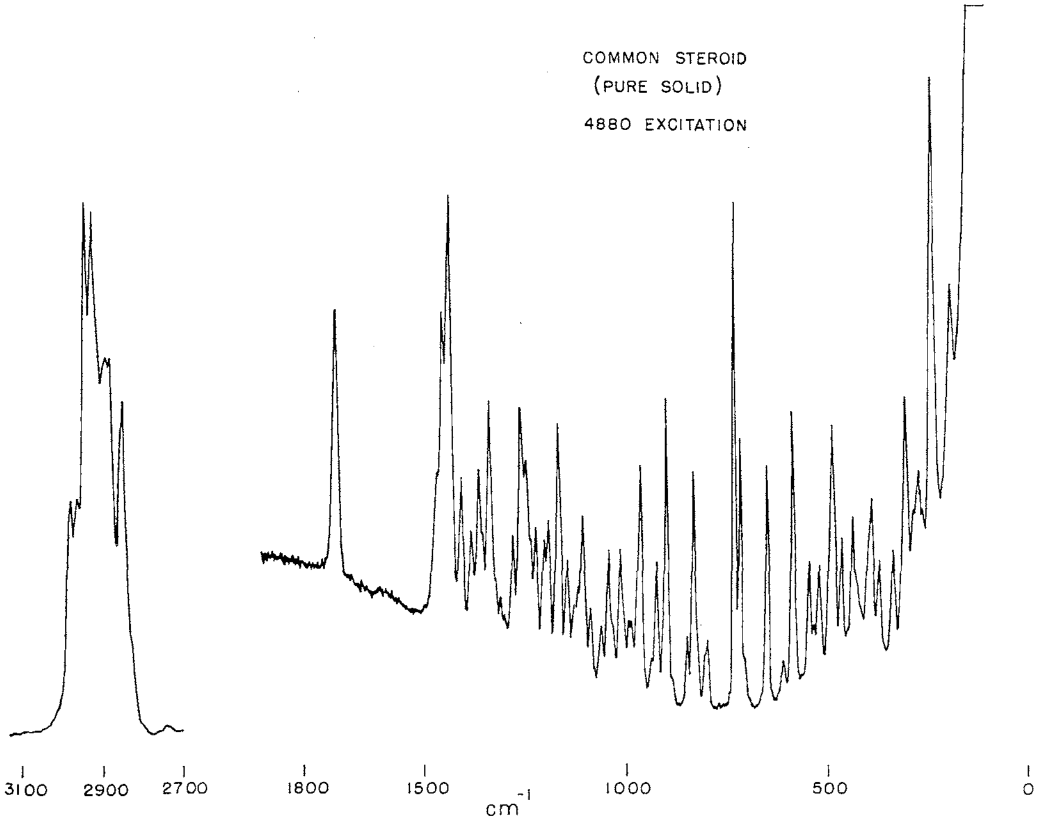



**Fig. 6 Raman spectrum of a common steroid excited by 4880A excitation.**

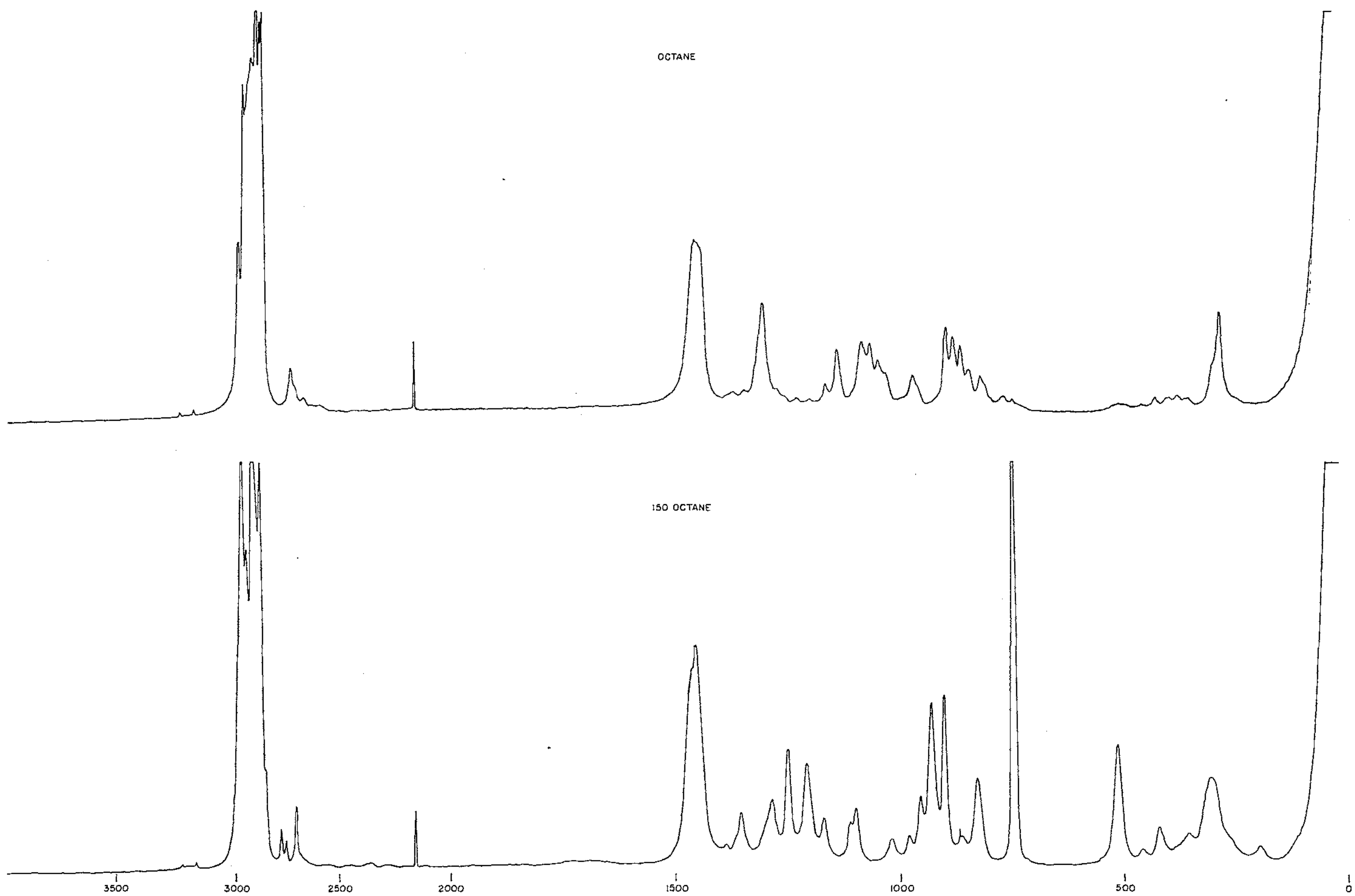



**Fig. 7 Illustrating the ease with which two isomers may be identified, apart or in the presence of each other, the difference between the octane and iso-octane in these Raman spectra will be of particular interest to those in the petrochemical industry. IR spectra, by contrast, are quite similar.**

# RAMALAB OUTLINE SPECIFICATIONS

**Sample Illuminator**

**Optics**

| | |
|---|---|
| Objective | 30 mm fl condensing lens focuses laser on sample |
| Collecting Lens | f/0.95 |
| Multipassing | Two spherical mirrors, above and behind sample |

**Sampling (standard)** The basic RAMALAB comes equipped with all necessary components for the analysis of liquids and powder samples including a kinematically positioned platform for capillary and 1 ml cells as well as 100 capillaries and one fused silica cell. In addition, a single interference filter (specify laser line) is included.

**Sampling (accessories)**

| | |
|---|---|
| Liquids | Micro (12 $\mu$l capacity) cell; semi-micro (50 $\mu$l capacity) cell; interference filters for all lasing wavelengths; neutral filters. |
| Solids | Kinematic platform takes samples from $\phi$ 0.5″ to about 2″ square. |
| Single Crystals | Kinematic platform accepts standard ACA goniometer |
| Parr Pellet Press | For preparing $\phi$ 3/16″ pellets from powders |
| Variable Temperature Cell | Harney-Miller type; 77°K to 200°C (Appl. Spec. **24**, 291, 1970) |
| 180° Viewing Platform | For enhancing Raman spectra with certain samples |
| Polarization Rotator | For crystal orientation studies (specify laser excitation) |
| Dimensions | 60″l x 21.5″w x 23.5″h |
| Weight | 300 lb (approx) |
| Electrical | 115V, 50-60 Hz (specify); 100W including heater in thermostat |
| Water | Individual lasers may require water-cooling; optional thermoelectric cooler for PM tube requires 10 gal/hr |

**Spectrometer** (double, symmetrical, Czerny-Turner)

| | |
|---|---|
| **Focal Length** | 0.5m |
| **Aperture** | f/7 |
| **Resolution** | 1 cm$^{-1}$ with 4416A (He-Cd) excitation; 0.7 cm$^{-1}$ at 6471A (Kr) excitation |

**Wavenumber**

| | |
|---|---|
| Range | 10,000 to 31,000 cm$^{-1}$ |
| Accuracy | 1 cm$^{-1}$ over Raman range |
| Presentation | Two five-digit, illuminated counters, one reading wavenumber; the second can be set to zero at any excitation frequency and displays the Raman shift |

**Scanning**

| | |
|---|---|
| Method | Electrical through stepper / synchronous motor; clutch disengages motor for manual scanning |
| Speeds | Nine synchronous speeds, from 0.5 to 5000 cm$^{-1}$/min forward and reverse |

**Spectral Purity** Better than 10$^{-11}$ for a monochromatic line at a shift of at least 100 cm$^{-1}$ from that line

**Gratings**

| | |
|---|---|
| Size | 64 x 64 mm ruled area |
| Constant | 1200 grooves/mm blazed at 5000A |
| Efficiency | Above 70% at blaze |
| Ghosts | Not measurable in Raman spectroscopy; $<10^{-13}$ |

**Slits**

| | |
|---|---|
| Type | Entrance, intermediate and exit slits are on a fused silica substrate; they are ganged for operation with a single lever. |
| Widths* | 1, 2, 4, 8 cm$^{-1}$ bandpass |
| Height | 10 mm |

**Photomultiplier**

| | |
|---|---|
| Standard | Special bi-alkali recommended for excitation at 4416A, 4880A or 5145A. |
| Optional | For maximum responsivity as well as compatibility with yellow and red lasing lines, the FW-130 (extended S-20 response) photomultiplier is recommended. When cooled in the Spex 1730 thermoelectric cryostat, exceedingly low levels of Raman scatter may be measured. |

**Photomultiplier Power Supply**

| | |
|---|---|
| Type | Programmable; voltage automatically drops upon overload of anode current |
| Range | 200-2200V |
| Control | 20V steps |
| Stability | 0.01% |

**Amplification**

| | |
|---|---|
| Type | Photon counting for low light levels; dc for higher levels |
| Range | 30-2,000,000 pps |
| Zero Suppression | Covers entire dynamic range |
| Period** | 0.5 to 60 sec for photon counting |

**Recorder**

| | |
|---|---|
| Type | 10″ wide potentiometric, stripchart |
| Sensitivity | 10 mV FS |
| Chart Drive Speeds | 0.25, 0.5, 1, 2.5, 5 and 10 cm/min through push-buttons |
| Cross-chart Speed | 0.5 sec |
| Zero Adjust | Full scale |
| Chart Paper | Z-fold (IR compatible pre-printed charts are available) |
| Event Marker | Pulses every 100 cm$^{-1}$ |

*Because the dispersion of a Czerny-Turner spectrometer improves towards longer wavelengths, values given are for 4416A, the shortest excitation wavelength likely to be used. At 6471A, bandpass values are narrower, about 70% of those specified. In other words, resolving power gets better with redder excitation.

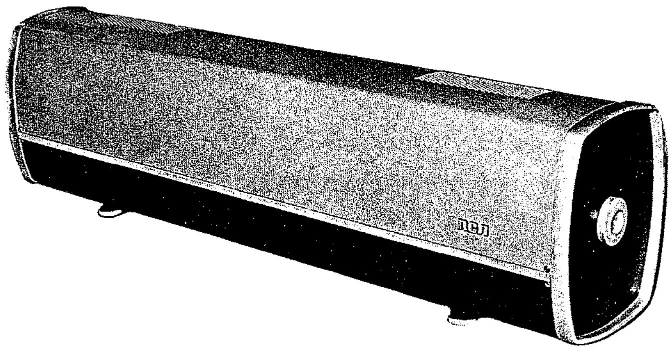
**Period equals 4.4 time constants and represents the time to sweep from 0 to 99% of full scale.

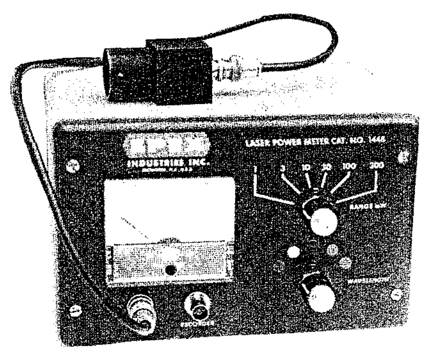
## He-Cd LASER

The RCA Model 2148 He-Cd laser is the least expensive laser recommended in conjunction with the RAMALAB. Emitting 15 mW at 4416A, it produces a Raman spectrum equivalent in intensity to that of a 100 mW He-Ne laser. The principle reason for this is the response of the photomultiplier which peaks around 4000A.

Raman spectroscopists who own a He-Ne laser and are handicapped by its single red excitation line will find that the purchase of the relatively inexpensive Model 2148 will greatly expand the number of compounds that can be analyzed. Those that absorb at 6328A, or fluoresce in the red or that scatter weakly will often produce excellent spectra with the He-Cd laser. Backed by the reputation and service facilities of RCA worldwide, the Model 2148 promises to be as reliable a work-horse as the well-known 50 mW He-Ne lasers, a welcome violet complement.

**RCA 2148 LASER**, He-Cd, 15 mW at 4416A, 115V, **$3,500.00**, (specify) 50 or 60 Hz.





**Specifications**

Sensing element — self-powered silicon photovoltaic cell
Measuring ranges — 1, 3, 10, 30, 100, 300 mW
Wavelength settings —

| | | |
|---|---|---|
| 4416A | 4880A | 5145A |
| 5682A | 6328A | 6471A |

**1448 Laser Power Meter** .................................................. **$400.00**

## 1448 LASER POWER METER

For running Raman spectra a laser power meter is a practical necessity. At the start of an experiment or when the wavelength of the laser is changed, one must be able to maximize the output at the laser by adjusting the prism and Brewster mirrors.

Additionally, a panel of experts recommends that, among operating parameters specified when submitting spectra for publication or comparison, the power at the sample be stated.

Until now, most commercially available laser power meters read correctly in energy units only at a specified wavelength, say 6328A. For other wavelengths, a calibration chart is provided.

The Spex 1448 Laser Power Meter greatly simplifies things. It contains built-in attenuators so set that the energy readout is correct regardless of the color of the laser. Set to the color of the laser emission, the instrument reads out directly in mW, up to 250. With the 20% neutral filter included, its range is extended above 1W.

Automatic compensation is provided for the variation in color sensitivity of the sensor. Values read are traceable to NBS standards and are correct to about ±10% of absolute. An output jack permits recorder monitoring.