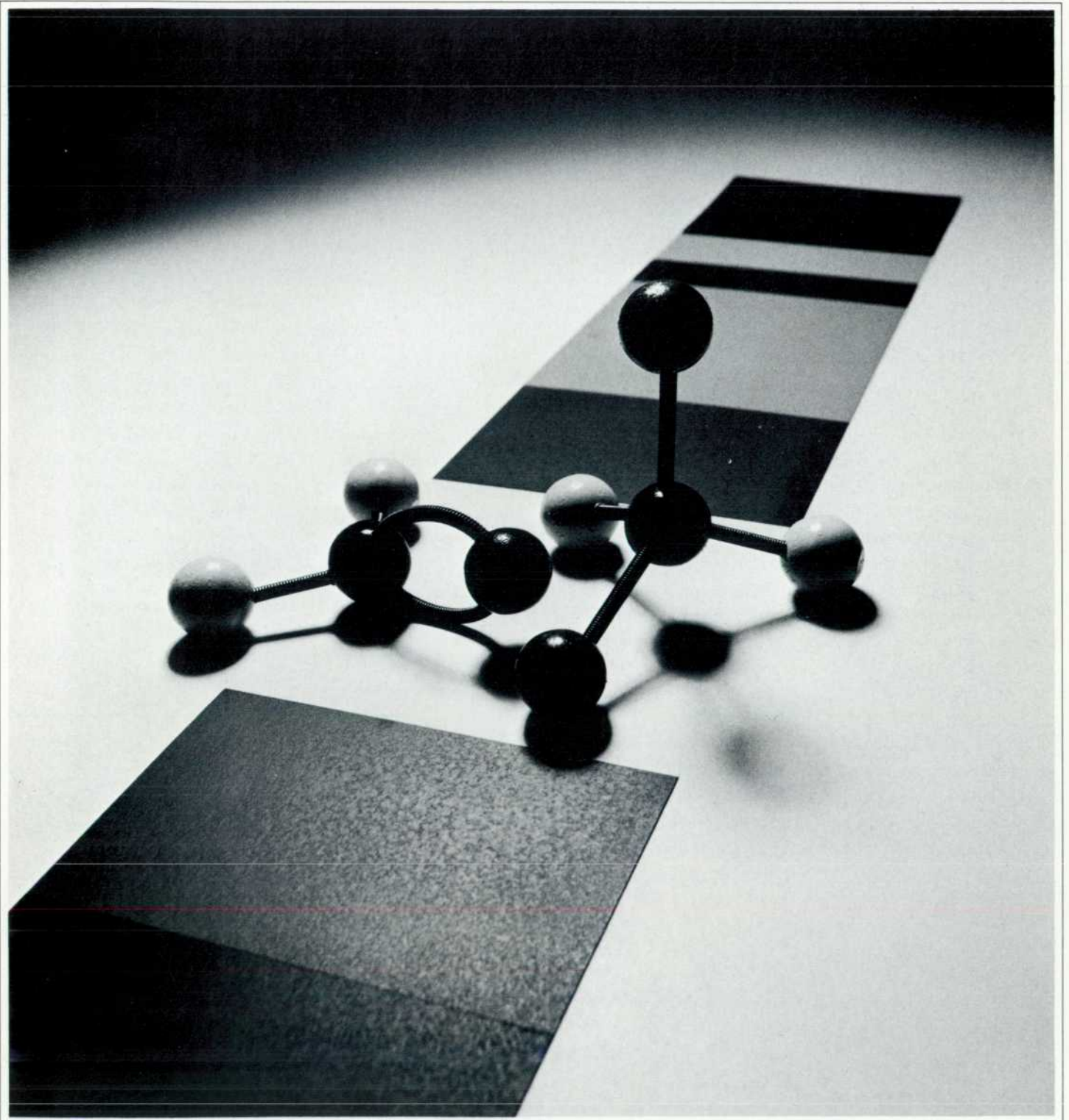# HEWLETT-PACKARD JOURNAL

JUNE 1971

The Routine
Rotational Microwave Spectrometer

*For the first time, it's now a simple matter to get high-quality
data using this 30-year-old technique. A new spectrometer makes the centimeter-
wavelength region of the spectrum available for routine analytical work.*

By Howard W. Harrington, John R. Hearn, and Roger F. Rauskolb

SPECTROSCOPY—the study of how matter interacts with the electromagnetic spectrum—has for over a century been providing scientists with solutions to some of the knottiest problems of physics and chemistry. The ultraviolet and visible segments of the spectrum were the first to be used routinely. Scientists didn't thoroughly understand the exact nature of the interaction between the radiation and the sample, but spectrometers were easy to build and operate, and they provided a wealth of data from which useful empirical rules were deduced. As technology advanced, the infrared and X-ray portions of the spectrum began to be used for spectroscopy, and again routine use preceded a complete understanding of the interaction between the radiation and the sample. Abundant, easy-to-acquire data, combined with the ingenuity of the scientist-detective, yielded useful solutions to analytical problems. Understanding of the interactions developed gradually.

Quite a different story applies to rotational microwave spectroscopy, which uses the centimeter-wavelength region of the electromagnetic spectrum. Here there exists a nearly complete understanding of how gas molecules which have unsymmetrical electric-charge distributions will, at low pressures, absorb microwave energy at highly distinctive frequencies as they increase their rates of rotation.[1, 2, 3, 4] Measurements of the frequencies and intensities of the absorptions yield detailed information about molecular structure and serve to identify molecules beyond a shadow of a doubt, even when they're parts of complex mixtures. This kind of spectroscopy is thirty years old and has reached a certain maturity as a research technique. Yet unlike ultraviolet, visible, or infrared, the absorption spectroscopy of low-pressure polar gases in the centimeter-wavelength region hasn't become a routine analytical tool. Why not? The chief reason is that recording microwave absorption spectra hasn't been a routine matter. Most spectrometers have been home-made, narrow-band instruments. Building and operating one successfully has typically called for considerable engineering skill. Only a small portion of the available wavelength range could be examined at any one time, and gathering any significant amount of data required constant tuning of the microwave source
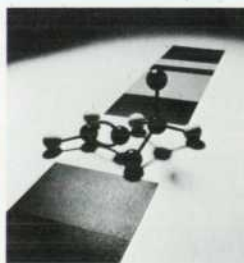
Cover: Rotational microwave spectroscopy, operating in the centimeter-wavelength region of the electromagnetic spectrum, gives exact information about the structures of molecules. But spectrometers haven't been as easy to use as those for other regions of the spectrum. Hence there's been a gap, but it's now bridged by the HP 8460A MRR Spectrometer described in this issue.
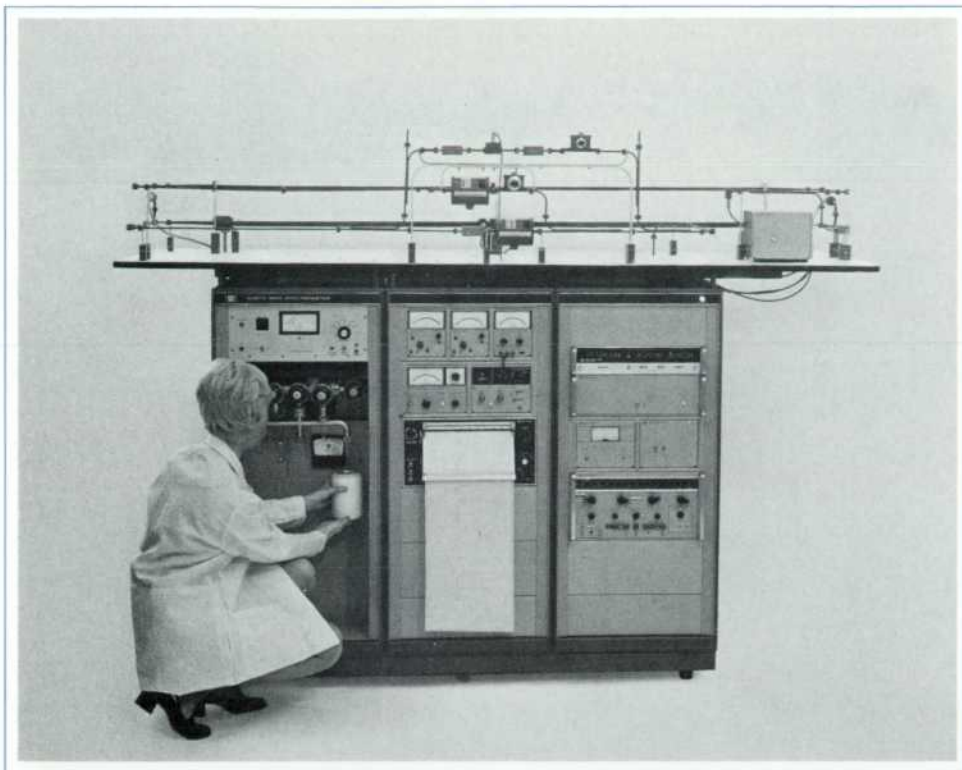
Fig. 1. *New HP 8460A MRR Spectrometer is the first rotational microwave spectrometer that's really easy to operate. 'Table tops,' which hold all the microwave circuitry already mounted and ready for use, make it easy to change frequency bands.*

and detector. All of this served to defer the interest of many potential users.

This story is about to change. A new spectrometer, incorporating the latest microwave and solid-state technology, makes rotational microwave spectra as easily accessible as spectra in other wavelength regions of the electromagnetic spectrum. With the HP 8460A MRR* Spectrometer (Fig. 1), no engineering skill is required to observe, measure, and reproduce spectra over a wavelength range of 3.75 to 0.75 centimeters. For the first time, therefore, the unique sensitivity, resolution, and specificity of rotational microwave spectroscopy are available for routine use.

But that isn't the whole story. As often happens when an advanced instrument is developed, the new spectrometer has begun to change our notions of what microwave spectroscopy is. An important recent development that wouldn't have been possible without this sensitive, broadband instrument is the discovery that rotational microwave spectra exist for many large molecules that weren't previously thought to have such spectra. These 'band spectra' can only be seen easily with a spectrometer that's capable of sweeping wide frequency ranges rapidly, something early spectrometers couldn't do. Also

new and significant are improved methods for measuring absorption intensities. Accurate intensity measurements are essential for quantitative mixture analysis. Much of the work on band spectra and intensity measurements has been done by HP.

What Makes a Rotational Microwave Spectrometer Routine?

Development of a routine spectrometer wasn't a simple matter. The low-pressure gas samples have absorptions ranging from narrower than 0.1 MHz to wider than 100 MHz.* Samples may have only a few absorptions or hundreds of absorptions in a particular wavelength range. These can be very weak, absorbing only 10^{-5} per cent of the incident microwave radiation, or they can be as much as 10^6 times stronger. Absorption lines can be as close as a few MHz or separated by tens of thousands of MHz. The routine spectrometer has to observe and measure these absorptions quickly, accurately, and reproducibly.

Like any spectrometer, a rotational microwave spectrometer has four basic parts (Fig. 2): a source of radiation (microwave in this case), a sample cell in which the radiation interacts with the sample, a detector to

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* 'MRR' stands for molecular rotational resonance, a term coined by HP mainly because it's descriptively accurate, and it's a lot easier to write and say 'MRR' than 'rotational microwave spectroscopy.' MRR also has the interesting property that molecular moment of inertia, to which MRR is especially sensitive, has the same units ($I = mr^2$)!

* In the microwave region one generally refers to frequency rather than wavelength [$frequency = \frac{velocity\ of\ light}{wavelength}$]. A frequency of 30,000 MHz or 30 GHz has a wavelength of one centimeter.

Everything You Always Wanted To Know About Rotational Microwave Spectroscopy

Rotational microwave spectrometers detect and record the absorption spectra of low-pressure gases or vapors at microwave frequencies. A spectrum recorded by one of these instruments is a graphic plot of the electromagnetic energy absorbed by the sample as a function of the frequency of the energy. The processes which lead to the absorption of radiation by the sample are governed by quantum-mechanical laws, and as a consequence a given substance will absorb energy only at discrete frequencies. A typical spectrum, therefore, consists of many very narrow peaks called absorption lines.

In general, microwave energy affects the slow end-over-end rotation of the molecules of the sample. When a molecule absorbs energy its rate of rotation increases. But its rotational energy is quantized—only certain energies are allowed. Absorptions occur when the frequency ν of the microwave energy and the energy difference ΔE between two allowed rotational energies satisfy the quantum relationship $\Delta E = h\nu$, where h is Planck's constant.

For a molecule to absorb radiation, the radiation must exert a force on the molecule. With few exceptions, this force is a torque exerted by the electric-field component of the radiation on a permanent electric dipole moment fixed in the molecule. A molecule has such a dipole moment if the centroid of all of its negative electric charges doesn't coincide with the centroid of all of its positive electric charges. The electric field exerts forces in opposite directions on opposite electric charges and thereby applies a torque to the molecule. Not all molecules have permanent electric dipole moments, although most do, including many common air pollutants, which are mostly small, light gas molecules. Sulfur dioxide (SO_2), for example, has a microwave spectrum. Carbon dioxide (CO_2), on the other hand, doesn't.

The general features of a rotational spectrum are determined by the moments of inertia of the molecule. The moment of inertia I about any axis of rotation is a function of the masses m_i of the atoms in the molecule and the distances r_i of the atoms from the axis of rotation, that is, $I = \Sigma m_i r_i^2$. Rotational spectra are extremely sensitive to changes in a molecule's moments of inertia. Substitute for one of the atoms an atom of a different isotope of the same material and the spectrum changes radically. Change the angle of one bond or the distance of one atom from the axis and you get a totally different spectrum. This sensitivity makes rotational microwave spectroscopy a valuable tool for determining exact molecular structure, that is, the exact angles of interatomic bonds and exact interatomic distances. Take for example a simple linear molecule like carbonyl sulfide (OCS), which looks like

$$O = C = S$$

Knowing the masses of the three atoms from other experiments, microwave spectroscopists have measured the frequencies of absorption lines in the rotational spectrum of OCS and have determined that the distance between the O and C atoms is 1.1552×10^{-8} centimeters and the distance between the C and S atoms is 1.5653×10^{-8} centimeters.

How is this done? Spectroscopists calculate quantities called rotational constants from microwave spectra. For a linear molecule the rotational constant is $B = h/8\pi^2 I$. The laws of quantum mechanics show the allowed rotational energies of such a molecule to be $E_J = hBJ(J + 1)$, where J is an integer (0, 1, 2, . . .) called the principal rotational quantum number. Because of quantum-mechanical restrictions, or selection rules, the microwave radiation can induce transitions only between energies whose values of J differ by one unit. The transition frequencies, the frequencies where absorptions occur, are then $\nu(J \to J + 1) = 2B(J + 1)$. This equation describes the rotational spectrum of a rigid linear molecule. It's a series of equally spaced lines starting at a frequency 2B and occurring at higher frequencies at intervals of 2B. Thus it's easy to determine B by measuring the frequency difference between lines. One measurement, of course, isn't enough to determine two distances. But two measurements, made on the very different spectra of two different isotopic combinations, $^{16}O^{12}C^{32}S$ and $^{18}O^{12}C^{32}S$, are quite sufficient and lead to the values given above for the bond distances.

Normally the situation is more complex than it is for the rigid linear molecule. Three moments of inertia are needed to describe the rotation of rigid asymmetric nonlinear molecules. Sometimes computers are needed to help interpret the observed spectra. But the mathematics are highly developed and it's a straightforward task, following along the lines of our linear example. For many molecules, extensive tabulated data are available.

Also complicating the situation is the fact that no molecule is truly a rigid rotor. To a spectroscopist, however, deviations from the rigid-rotor spectrum are often the most important aspects of a spectrum, since they provide additional fundamental information about molecular properties.

An untapped application area with great potential is analysis of complex mixtures by rotational microwave spectroscopy. The high-resolution absorption lines are extremely narrow. They occur at absolutely constant frequencies and lines for different molecules almost never overlap. Thus this kind of spectroscopy is highly specific. A molecule's spectrum is a distinctive fingerprint which identifies it beyond a shadow of a doubt, even when it's part of a complex mixture. With an easy-to-use instrument like the HP 8460A, quantitative as well as qualitative mixture analysis is straightforward.

For more information about theory and applications than it's been possible to give in this necessarily brief and elementary discussion, we suggest the following:

1. G. M. Barrow, 'Introduction to Molecular Spectroscopy,' McGraw-Hill Book Co., Inc., 1962. This is suitable for general reading. The other four books are more advanced.
2. T. M. Sugden and C. N. Kenney, 'Microwave Spectroscopy of Gases,' D. Van Nostrand Co., 1965.
3. A. L. Schawlow and C. H. Townes, 'Microwave Spectroscopy,' McGraw-Hill Book Co., Inc., 1955.
4. J. E. Wollrab, 'Rotational Spectra and Molecular Structure,' Academic Press, Inc., 1967.
5. W. Gordy and R. L. Cook, 'Microwave Molecular Spectra,' Interscience, 1970.
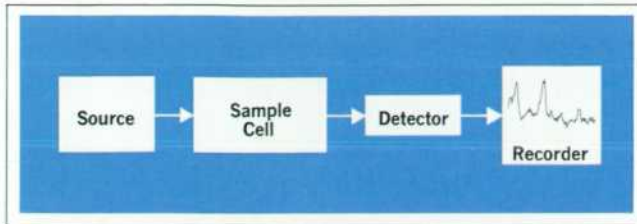
Fig. 2. *Like all spectrometers, the HP 8460A has four basic parts: a source of radiation, a sample cell where the radiation interacts with the sample, a detector to monitor the power absorbed by the sample and a recorder to plot absorbed power versus frequency.*

monitor the power absorbed in the sample cell, and a recorder to plot the absorbed power as a function of frequency. In a microwave spectrometer the sample cell, or absorption cell, must function well as a microwave transmission line in addition to holding the low-pressure sample (sample-cell pressures are typically 10^{-5} to 10^{-4} atmospheres).

Design of such an instrument is primarily a microwave measurement problem. This is HP's business, of course, or a large part of it. Yet it's safe to say it challenged HP's microwave technology to build this instrument. Here are the high points of how it was done.

The Microwave Source

The source of microwave radiation must have considerable versatility to cope with the wide variety of absorptions expected. Formerly, klystron tubes were the most commonly used sources. These tubes generate sufficiently monochromatic microwave radiation, but have to be tuned manually to cover a wide frequency range. Also, it isn't a simple matter to measure their frequencies precisely; yet precise knowledge of the frequency of the source is necessary for accurate measurements of absorption frequencies.

The source in the new spectrometer is a backward-wave oscillator (BWO), which is electronically tuned. For stability, the BWO is continuously phase-locked to a harmonic of a stable 400–420 MHz reference oscillator; this ensures an output sufficiently close to monochromatic. The stability of the reference oscillator comes from a 10 MHz crystal. Reference frequencies of 400 to 420 MHz are synthesized digitally from the crystal frequency, and therefore have the same percentage stability and frequency accuracy as the crystal.

Because its outputs are synthesized, the reference oscillator's output frequency can't be tuned continuously. Instead, it's programmed in 1-Hz steps. To cover the spectrometer's frequency range of 8.0 to 40.0 GHz, reference-oscillator harmonic numbers of 20 to 100 are

used, and this means that the BWO frequency is varied in steps of 20 to 100 Hz. These steps are small compared to the narrowest absorption lines expected, and the stepping rate is fast enough so the effect approaches a continuous sweep.

Four BWO's are needed to cover the entire 8.0 to 40.0 GHz range. BWO's are changed by exchanging plug-in modules in the source power supply mainframe. Each BWO corresponds to a standard microwave band (X, P, K, and R).

The user will find the spectrometer source easy to operate. All of the control settings are of the fingertip type and are located on the front panel of the microwave source sweep control unit (Fig. 3). The operator can select arbitrary frequency limits in 0.001 MHz steps merely by dialing them on thumbwheel switches. These limits, F1 and F2, can enclose any part or all of a particular microwave band. The user can also select one of 13 different scan rates between 10 MHz per second and 0.001 MHz per second, and he can rest assured that the sweep rates will be linear because the source is digitally controlled. He can also read the frequency continuously with 0.001 MHz resolution from the digital display on the control unit.
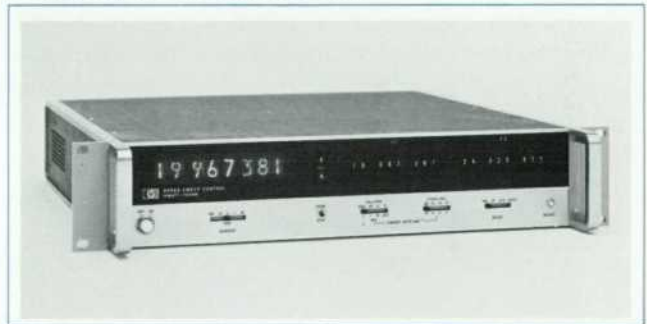

Fig. 3. *The HP 8460A has a specially designed source, sample cell, and detector, which don't require any engineering skill to operate. This is the source control unit, used for setting sweep limits and sweep rates. The display reads the instantaneous microwave frequency.*

There's additional flexibility in the choice of operating modes. In the CW mode the output frequency will be F1 and will be stable within less than 5 parts in 10^9 per day. In the UP mode the source will sweep from F1 to F2 linearly at the specified sweep rate and stop at F2. In the U/D mode the source will sweep from F1 to F2 and back to F1 and stop. Again, this will be at the specified sweep rate. The auto mode will produce a back-and-forth sweep between F1 and F2.

The operator can change the sweep rate at any time during a scan without affecting the frequency. In the event that some interesting spectral feature is discovered

during a sweep, the sweep can be interrupted by changing a front-panel toggle switch to STOP. The region above and below the frequency where the sweep was interrupted can then be investigated by pressing a frequency rocker switch. The operator can then return the toggle switch to its original position and the sweep will continue. For convenience, frequency markers with selectable spacing will be printed on the record chart.

Quite a bit of advanced microwave technology had to be applied to make this specially designed source this easy to operate. Yet there are no unnecessary frills. All these features are necessary if it's to be a routine matter to obtain accurate and reproducible spectral data.

A feature of the source that isn't absolutely necessary but is often convenient is compatibility with computers or other remote control units. The source can be remotely controlled by way of a rear-panel connector.

The Absorption Cell and Stark Modulator

While the 8460A user will be required to set the various sweep conditions himself, he will find that he all but ignores the absorption cell. The same cell is used for all four microwave bands. No tuning or other adjustments are required while operating in any of these bands.

Nevertheless, the cell is a critical spectrometer component and required considerable design effort to assure its performance in the dual role of sample chamber and microwave transmission path. As a sample holder, it must be air tight because the sample pressure is generally between 10 and 100 millitorr (7.6×10^5 millitorr is atmospheric pressure). There also must be minimum interaction between the surface of the absorption cell and the sample. To that end, the entire inside of the 8460A absorption cell is gold plated. The cell must also be a high-performance microwave transmission device; this is essential for uniform sensitivity over the 8.0 to 40.0 GHz frequency range. Microwaves can be temperamental. Unless great care is taken in the design and manufacture of the transmission path there will be reflections and significant losses which will degrade the performance of the spectrometer.

Complicating the microwave design problem is the spectrometer's use of the Stark modulation technique invented by Wilson at Harvard in 1947.[5,6] This technique greatly improves spectrometer sensitivity. The Stark effect, that is, the dependence of molecular energies on an electric field, is used to modulate the molecular microwave absorption process. An electric field, sometimes as high as 4,000 volts per centimeter, is applied across the sample and switched on and off (at

a 33.333 kHz rate in the 8460A). When the field is applied, rotational quantum levels are shifted and split. What is observed is that a single absorption line with no field applied is shifted in frequency in the presence of the field, or more often, is split into separate lines called Stark components. Whenever the spectrometer is being swept through an absorption, whether zero-field or a Stark component, the microwave power will be modulated at the Stark modulation rate because the absorption frequency is being shifted by the presence and absence of the applied electric field. The spectrometer detection system is tuned exactly to this modulation frequency. In the 8460A a synchronous detection system is used. A reference signal from the modulator is applied to the synchronous detector, which sees only signals at the 33.333 kHz rate and rejects spurious noise.

New HP Division for Physics and Physical Chemistry

The Hewlett-Packard Scientific Instruments Group is a new organization formed by the combination of two major projects from Hewlett-Packard Laboratories and the former scientific instruments group of the Microwave Division. Its function is to design, manufacture and market measuring instruments in the fields of physics and physical chemistry. It operates in conjunction with the Avondale Division, which produces a range of routine analytical and research instruments.

The 8460A MRR Spectrometer was the new group's first product. It has been followed by the 8330A/8334A Radiant Flux Meter and Detector, the 5930A Mass Spectrometer and the 5950A ESCA X-Ray Photo-Electron Spectrometer. Watch these pages for more articles from this new HP division.

All of this adds another dimension to the Stark cell microwave transmission path design problem. First, the Stark electrode, or septum, is inside the Stark cell and runs the entire length of the cell. The septum must be insulated from the cell body. Furthermore, the high alternating Stark fields can produce mechanical distortions in the cell body if the walls are not reinforced, and such distortions are a source of synchronous noise. These problems have been minimized in the 8460A, and the Stark cell is a smooth transmission path over the 8.0 to 40.0 GHz range.

In the 8460A there are two Stark cells, each three feet in length. Thus the total length is six feet. Since spectrometer sensitivity increases with increasing absorption-path length, the Stark cells were made as long as possible within the limitations of the machining processes necessary to guarantee that the cells have good

transmission characteristics. So important are these transmission characteristics that the 8460A has better broadband sensitivity than some spectrometers with Stark cells 15 feet or more in length.

The Stark cells are constructed with care to keep reflections to a minimum. The cells are basically three-foot pieces of 8 GHz waveguide, but they have walls several times thicker than regular waveguide so mechanical motions that might cause errors are minimized. The insides are broached to give precise internal dimensions and to create grooves to hold the septum. The septum is inserted in the grooves with a small piece of teflon tape around the edges for high-voltage insulation. Mica windows at the ends of each Stark cell act as vacuum seals, but allow microwave power to pass through. Two windows spaced approximately one-quarter wavelength apart are used at each end of each cell; this minimizes reflections. Transition pieces adapt the same Stark cells for use in different frequency bands. The total volume of the two Stark cells is approximately 500 cc.

The modulator itself plays an important role in insuring uniform sensitivity. Some absorptions are very sensitive to the applied field, shifting over wide frequency ranges for relatively small applied fields. In these cases, the off portion of the applied Stark field must be very close to zero or these first-order lines will be greatly distorted or missing altogether. The sensitivity of the system will be significantly degraded no matter how good the source or the Stark cell or the detector may be. The 8460A solid-state Stark modulator unit has a special circuit which insures adequate zero-basing over the complete range of modulating voltages.

The Microwave Detector

Like the absorption cell, the 8460A detector requires little or no operator attention. The detector requires no tuning at all. It's a rugged, selected, high-efficiency point-contact silicon crystal diode mounted in a broadband ridged-waveguide configuration. In the past, spectrometer detectors required manual tuning every few MHz and, in spite of this tuning, their performance was highly frequency dependent. Such tuning and frequency dependence are not characteristic of the 8460A detector.

For maximum sensitivity the microwave crystal detector output is synchronously detected to eliminate random noise. When absorption occurs, there is a 33.333 kHz component in the rectified crystal output due to the Stark modulation. The crystal output is fed into a tuned preamplifier, which is followed by a crystal filter that narrows the noise bandwidth. After the filter comes
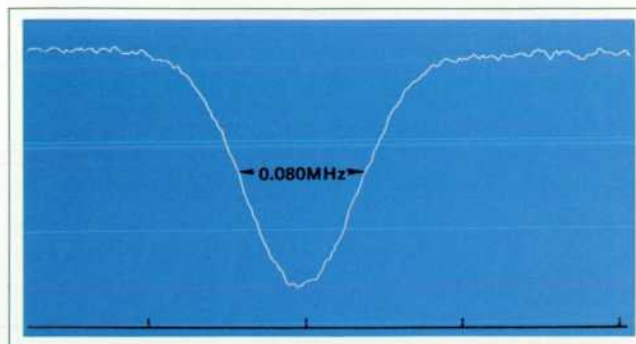

Fig. 4. This is an absorption line only 80 kHz wide at a center frequency of about 36,489 MHz. That's a resolution of about two parts per million—orders of magnitude higher resolution than infrared spectroscopy.
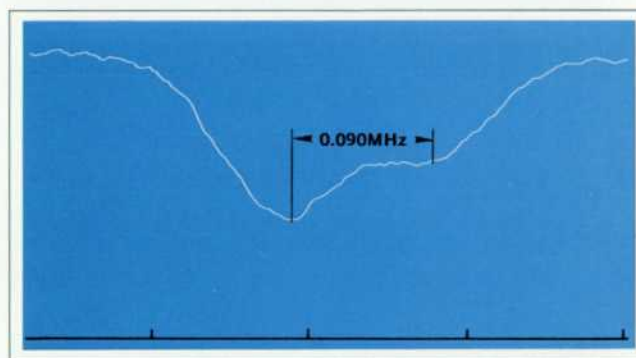

Fig. 5. HP 8460A can resolve two absorption lines only 90 kHz apart at microwave frequencies.

the synchronous detector, synchronized with the 33.333 kHz Stark modulation. This detector rejects spurious noise that isn't synchronous with the modulation rate.

The Total Spectrometer

Model 8460A MRR Spectrometer requires only a low level—a few milliwatts—of microwave radiation, which doesn't degrade the sample or pose a health hazard to the operator. Very small samples—a few micrograms—are needed. If a liquid, the sample is injected into the spectrometer with a microliter syringe. If a gas, it's introduced through a half-inch quick-connect input port. The Stark cell is purged with a single small mechanical pump and an ion pump, both of which are standard parts of the instrument.

A unique, removable table-top design makes it easy to change waveguide systems when going from one of the four frequency bands to another. The table-tops contain all the microwave circuitry—except the Stark cell, which isn't changed*—already mounted and ready for use. Three of the waveguide systems—those for frequencies above 12.4 GHz—come in two versions, one a standard 'in-line' system for measuring absorption frequencies and unsaturated intensities, and the other a

* The low-pressure sample can even stay in the Stark cell when changing table-tops.

microwave bridge system with more intensity-measurement capability. For the 8-to-12.4-GHz band, only the standard in-line type of system is available. The bridge-type waveguide system makes it possible for the user to vary the power in the Stark cell and keep the crystal detector current constant at the same time. This is required for absolute intensity measurements and intensity-law measurements.

What the Routine Spectrometer Can Do

Centimeter-wavelength measurements made easily available by the HP 8460A MRR Spectrometer fall into three categories. High-resolution spectroscopy includes all the more traditional applications. Exact molecular structure determination (bond angles and bond distances), studies of intramolecular forces (vibration-rotation interaction, nuclear quadrupole interactions), and dipole-moment determination from the Stark effect are all in the high-resolution category. Qualitative mixture analysis also belongs in this category. Fast-scan spectroscopy is the study of band spectra. This recent development is used for characterizing molecules larger than those generally considered suitable for study by microwave spectroscopy. The third category, intensity measurements, includes all applications that call for the precise measurement of the microwave absorption rate. Uses range from spectral assignment and line-shape studies to quantitative analysis of complex mixtures.

High-Resolution Spectroscopy

High-resolution rotational microwave spectroscopy has produced a wealth of very detailed, accurate information which has helped to clarify many puzzling situations.[1,2,3,4] Its contributions include exact molecular structural determination, accurate dipole-moment measurements, analysis of internal rotation barriers, specification of various molecular conformational preferences, and structure analysis of new molecules. Since this technique looks at the molecule between collisions, isomeric forms which interchange on collision can be caught and studied in stop action. The data generated in this field has been drawn on by theorists to test their models of chemical bonding. It is safe to predict that as more and more rotational absorption data become available, the impact on chemistry will be enormous.

How high is high resolution? Fig. 4 shows an absorption line that's only 0.08 MHz wide at a center frequency of about 36,489 MHz. The energy in this particular transition can be measured to better than 10^{-6} wave numbers. Compare this with infrared spectroscopy,
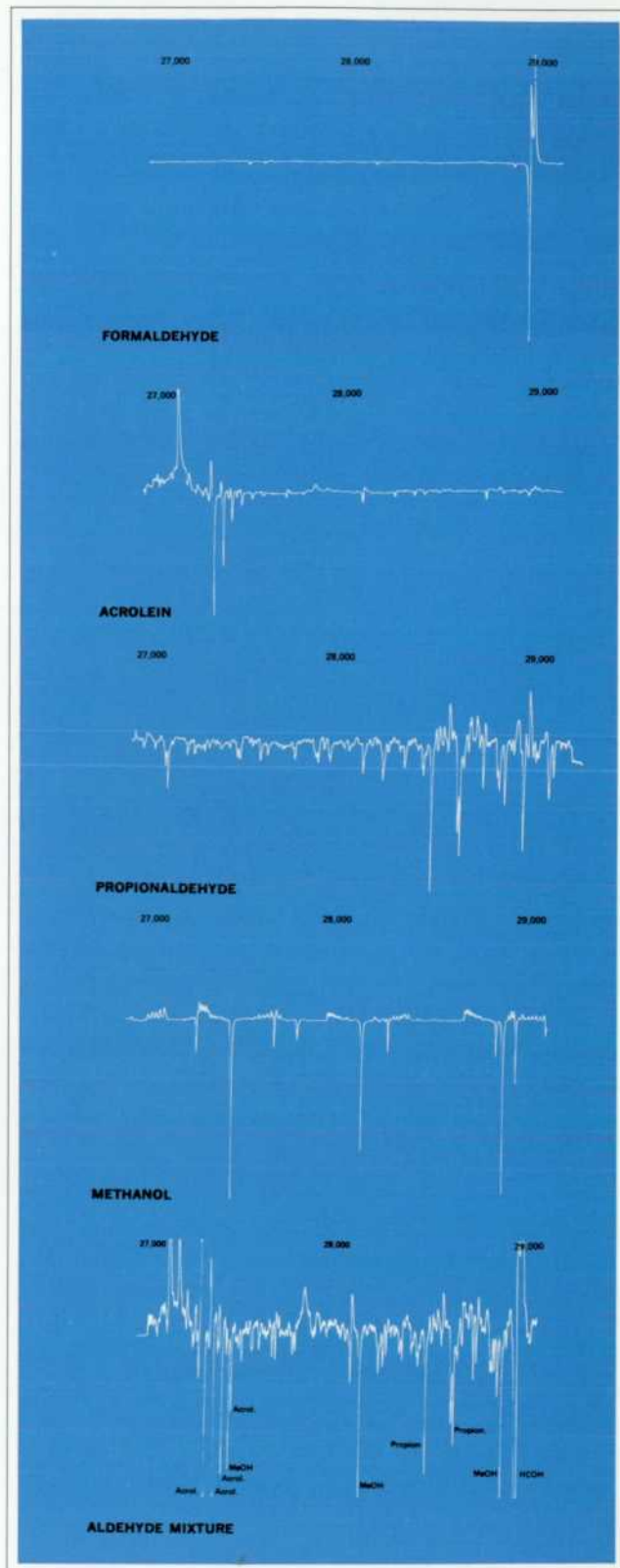

Fig. 6. *Mixture analysis—qualitative and quantitative—is an important application of high-resolution rotational microwave spectroscopy. For example, given the individual spectral fingerprints of these four compounds it's easy to spot them in the mixture.*

for example, which typically gives measurements to within one wave number or so. How far apart must two peaks be before they are distinguishable? Fig. 5 shows a trace of two peaks separated by about 0.090 MHz. These traces were recorded on a standard 8460A with no manual tuning of the source, cell, or detector.

Qualitative Mixture Analysis

Here is a largely untapped application area with significant potential. Once a molecule has been fingerprinted by rotational microwave spectroscopy, it can always be recognized no matter what kind of mixture it's in. The peak frequencies of the narrow absorption lines do not depend on the mixture composition, that is, these frequencies have no solvent effects. The full impact of this statement is easy to underestimate. Imagine being able to dial in the fingerprint-frequency of a molecule to a few parts in 10^7 and being certain to find an absorption if the molecule is present. If one requires even more evidence, he can dial in another known frequency to double check; molecules generally have several absorptions in a given microwave band. With the 8460A, it's as easy to dial in a frequency thousands of megahertz away as it is to check an absorption line which is only a few MHz away.

Other advantages of this technique are the low level of microwave radiation (milliwatts) which prevents degradation of the sample, the very low sample pressures which minimize chemical interactions between mixture components, and the fact that rare and valuable samples can easily be recovered.

Fig. 6 shows the absorption spectra of four organic molecules—formaldehyde, acrolein, propionaldehyde, and methanol—and the spectrum of a mixture of these substances. These traces cover only a small portion—27,000 to 29,000 MHz—of the microwave R-band region. Yet it's easy to see what's in the mixture.

Suppose a mixture contains various istopically substituted combinations of the same molecule. For example, there might be $DH_2C\text{-}CH=CH_2$, $H_3C\text{-}CD=CH_2$, $H_3C\text{-}CH=CHD$, and so on. Each of these can be individually identified in a mixture. They are distinguishable because their moments of inertia are different, even though they have the same chemical formula, C_3H_5D. Isomeric forms of a molecule are also easily distinguishable for the same reason, even though they're impossible to separate chemically.

Fast-Scan Spectroscopy

This new technique greatly expands the scope of rotational microwave spectroscopy. If the 8460A is swept in its fastest scan rate, 10 MHz per second, and the spectra are compressed into about three feet of recorder chart paper, then a surprising number of organic molecules show spectra like those shown in Fig. 7. These are band spectra for three bromoethylbenzene molecules which have the same empirical chemical formula, C_8H_9Br. Band spectra have been observed in the past but only for a few molecules. Now it turns out that they exist for many types of molecules, including fairly asymmetric types.

Quick inspection of these traces reveals an orderly series of strong bands which are broader—50 to 100 times broader—than the usual high-resolution absorption lines. One quickly notices that these band patterns are simple in appearance, and there is obviously a significant pattern change as the bromine atom is relocated in the ethylbenzene molecule. One also quickly notices that the bands appear in doublet pairs, each member having the same shape and intensity, at least qualitatively. This is especially clear in the 1-bromoethylbenzene and p-bromoethylbenzene spectra.
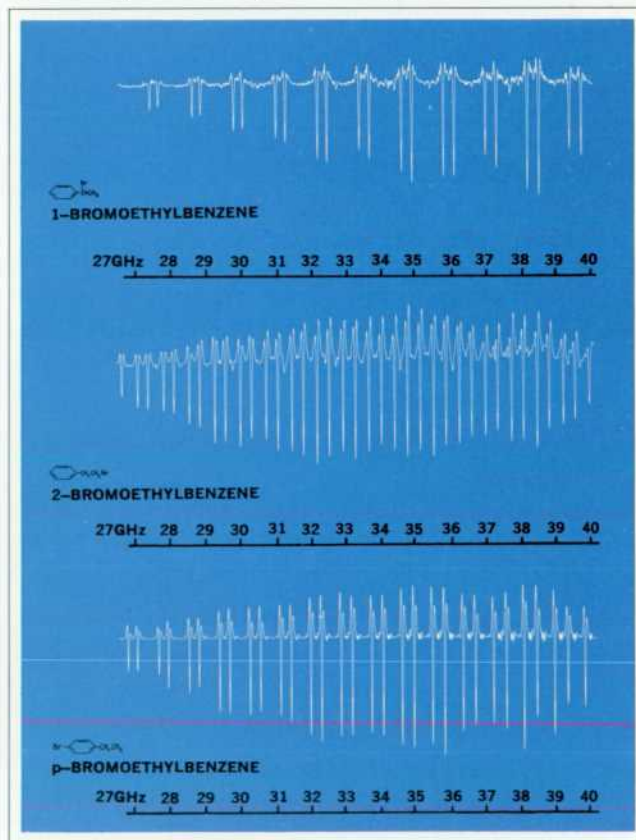

Fig. 7. *These are band spectra, recorded by scanning a broad frequency range quickly. The absorption bands here are 100 times wider than high-resolution absorption lines like those of Fig. 6. Such spectra have been found to exist for many more molecules than were previously thought to have them.*

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The intensity and simplicity of the appearance of band spectra is initially surprising to the spectroscopist. A general rule of thumb is that the more atoms a molecule has, the greater the number of individually weaker lines. But instead we find that a large number of large molecules—we have nearly 100 examples so far—give significantly stronger, simpler-appearing spectra than this rule of thumb predicts. These bromoethylbenzene spectra are good examples.

Interpretation of band spectra isn't difficult. Each of the three shown in Fig. 7 consists of two regular series of bands separated in frequency by $\Delta\nu = B^*(J+1)$ where $\Delta\nu$ is the frequency difference between any two consecutive band members, J is the angular momentum quantum number, and B^* is an average rotational constant which contains the molecular structural information. In the case of the 1-bromoethylbenzene, there are two B^*'s, one for each of the two bromine isotopes, [81]Br and [79]Br. These two isotopes are nearly equal in natural abundance and account for the doublet band structure. This slight molecular mass difference alters the moment of inertia enough to cause the large frequency difference between members of each doublet. Relocating the bromine atom in the molecule has an even more noticeable effect on the spectrum. The number of bands changes significantly. Hence even though these bands are broad, the isotope effect and isomeric forms are still easily visible.

How useful are these spectra? Glance at Fig. 8, the band spectrum of crotonic acid, a solid material yet with sufficient vapor pressure to observe the rotational spectrum at room temperature. Two sets of bands are observed and two B^*'s can quickly be evaluated from the spectrum. Drawing upon the structural data (bond angles and distances) of past high-resolution microwave research, one can calculate the Cartesian coordinates for the atoms of crotonic acid, then calculate the B^*
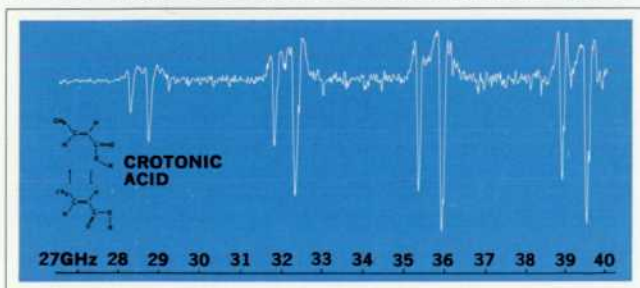

Fig. 8. *The two conformations of crotonic acid shown here are impossible to separate chemically, but the band spectrum clearly shows two series of bands, one for each conformation. This is why rotational microwave spectroscopy is valuable for determining molecular structure, its principal use to date.*

associated with that particular geometry and compare this with the measured B^*'s. In this way, we can conclude that the two band series of crotonic acid arise from the s-trans and s-cis isomeric forms. This is a simple way to characterize these two inseparable conformations.

The fast-scan mode can also be a real time saver for the high-resolution spectroscopist. This is elegantly illustrated in the spectrum of N-methylaniline, Fig. 9. The fast-scan spectrum shows a series of bands with considerable fine structure, but if an 80-MHz part of the center of the band at 38,000 MHz is examined under high-resolution conditions, there is no recognizable pattern. Twenty minutes of time invested in scanning the spectrum in the fast-scan mode makes sense out of an apparently meaningless spectrum.

Quantitative Analysis

Microwave absorption intensity-coefficient measurements contain valuable molecular information. However, the intensities of the absorption lines have historically been difficult to measure accurately.[7] No other consideration has affected the design of the HP 8460A as much as an intensity-measurement requirement.

While work is still in progress on the intensities of band spectra, HP has investigated in depth the intensity of high-resolution absorptions with the objective of quantitatively analyzing mixtures like that of Fig. 6. This is a three-fold problem. One, relating the observed spectrometer signal to an intensity coefficient. Two, interpreting the intensity coefficient in terms of the partial pressure of the molecules absorbing the radiation. Three, determining the percentage of each constituent from a total sample pressure measurement.

HP has done considerable investigation on the first two stages of this problem. There are accurate pressure gauges available commercially which operate in the millitorr region and which satisfy the third requirement.

A simple measurement of the spectrometer output corresponding to a peak in the spectrum doesn't necessarily yield the information that's needed, which is the partial pressure of a particular component in the mixture. The area under a peak under low-power conditions *is* a measure of the partial pressure which is independent of the mixture composition, but this area is difficult to measure except for strong absorption lines, the reason being that with low incident power one approaches the noise level where accuracy is a problem.

Several years ago HP investigated the possibility of intensity measurements at a single microwave frequency,
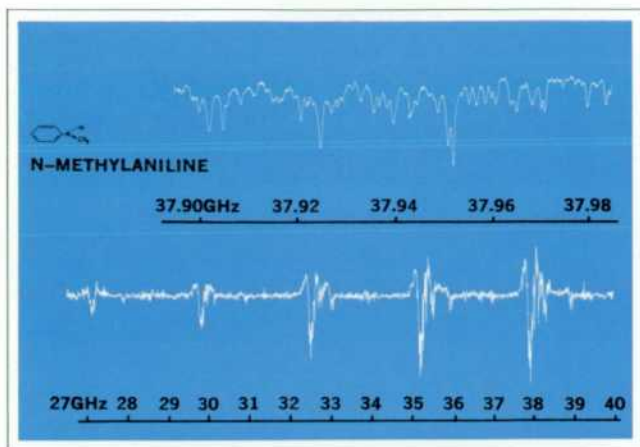
Fig. 9. *The band spectrum (top) often makes sense when the high-resolution spectrum doesn't. Both can be recorded with a sensitive, broadband spectrometer like the HP 8460A.*

the peak frequency, which would be proportional to the partial pressure of the absorbing species and independent of the sample composition. The results of this research have been published elsewhere.[8,9] An intensity coefficient was found which had the required quantitative properties. It's defined as $\Gamma = \Delta Pg / LP_0^{1/2}$, where ΔPg is the power absorbed by the sample, L is the length of the sample cell, and P_0 is the incident power. It was discovered that Γ varied with the incident microwave power P_0 as shown in Fig. 10. The maximum in this curve is directly proportional to the partial pressure of the absorbing molecular species. What's more, Γ_{max} is constant for a given concentration of the absorbing species, independent of the remaining mixture components.

The observed spectrometer output signal is directly proportional to Γ provided the crystal detector current is kept constant while P_0, the incident power to the sample cell, is varied. The crystal current can be kept constant using an optional microwave bridge arrangement on the 8460A. This capability is possible between 12.4 and 40.0 GHz.

This investigation was carried a step further. It was found that a plot of log Γ versus log P_0 (and when using the microwave bridge, log S versus log P_0, where S is the observed spectrometer output signal) gives a curve shape that depends only on the microwave power density distribution in the sample. The incident power level, the mode of microwave propagation, reflections, and the absorption-cell insertion loss all affect this power distribution. The 8460A Stark cell has been designed to minimize moding and reflections over its operating microwave range. However, there can be variations in the cell insertion loss with frequency. This insertion loss

is measured by the operator using standard microwave power measurement techniques and an intensity measurement is easily corrected for it. Thus accurate information from intensities is readily available.

There are many applications of intensity measurements. Mixture analysis is only one. Intensities can be an aid to spectral assignment. Another use is exemplified by the spectrum of conformations such as axial and equatorial cyclohexyl fluoride. From a measurement of the relative intensities of lines from each of these species one can calculate the energy difference between the two conformations.[10] Another application is line-width studies from which intermolecular effects can be determined.
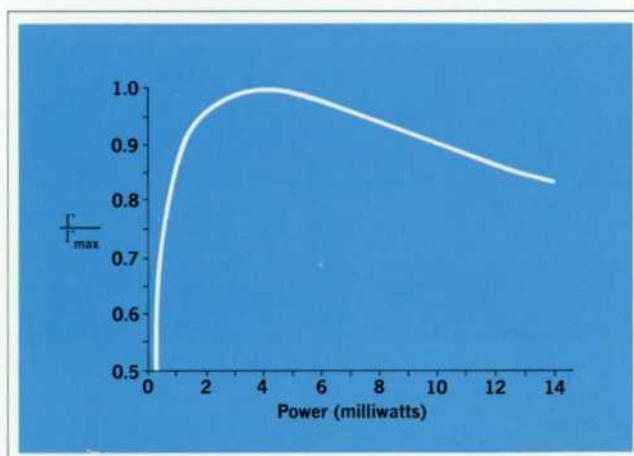

Fig. 10. *Intensity coefficient Γ_{max}, readily measured with an HP 8460A MRR Spectrometer bridge option, is a measure of the partial pressure of a mixture component independent of mixture composition. It's useful for quantitative mixture analysis.*

Acknowledgments

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HP 8460A
MRR Spectrometer

John R. Hearn

John Hearn, engineering manager of the HP Scientific Instruments Group, is a 1956 graduate of the University of Southhampton with a B.Sc. (Honours) degree in physics. When he joined HP in 1961 he was the first development engineer at Hewlett-Packard Limited in the United Kingdom. Later he was chief engineer there. He transferred to the HP Microwave Division in 1966 as a project leader and assumed his present position in 1968. John is a member of the Institute of Physics and the holder of several patents. As for diversions, John says he likes 'travel, good cars, and steam railways!'

Howard W. Harrington

Howard Harrington has to be one of the world's most enthusiastic microwave spectroscopists. He came to HP in 1962 to initiate the rotational microwave spectrometer project out of which has come the 8460A. He's the author of several fundamental papers on microwave spectroscopy and holder of two patents. He's now product manager for the 8460A. Howard received his AB degree in chemistry from Hope College in 1957 and his PhD degree in physical chemistry in 1962 from the University of California at Berkeley. He's a member of several scientific organizations. Art collecting is another of his passions; music and skiing are for relaxation. Lately, Howard's been spending much of his spare time helping his wife fill orders for an ecology handbook she helped organize for the American Association of University Women. So far, 40,000 copies have been sold in five months.

Roger F. Rauskolb

Roger Rauskolb received his Diplom Ingenieur degree from the Technical University of Darmstadt in 1961 and his MSEE degree from Stanford University in 1965. At HP since 1962, he put together the first of HP's highly successful automatic network analyzer systems. He was project leader for the 8460A and is now group leader for the 5950A ESCA Spectrometer. He's published three papers in Germany. Roger enjoys music, photography, and skiing, but more important to him are the discussion groups he and his wife lead with the objective of helping to make the world better through awareness of its problems.

An Easy Way to Analyze Graphs

By Dean C. Millett and Ivar W. Larson

DATA FROM STRIP CHARTS, X-Y plots, oscilloscope photos and even contour maps can be converted into digital form and fed to the Model 9100 desktop calculators for analysis. The Hewlett-Packard Model 9107A Digitizer, Fig. 1, a new calculator peripheral, has three main components: a hand-held cursor, the digitizing surface, and the electronics package. The free-moving cursor contains a transmitting coil and is used to trace the graphic material. Graphs or charts are mounted on a platen, or digitizing surface, which contains a precise grid of conductive strips. An audio-frequency ac field produced by the cursor coil induces voltages in the matrix. Circuitry in the electronics package converts the signals from analog to digital. These digital signals are the X and Y coordinates of the cursor position on the platen.

Resolution of the Digitizer is 0.01 inch (0,25 mm). Tracing speed can be up to 150 inches per second. When set in the continuous sample mode, the Digitizer can feed up to 100 pairs of points per second to the calculator. However, this rate may be limited if a printer or plotter is used. Either a keyboard command or program control of the calculator initiates transfer of coordinate data to the X and Y registers of the calculator.

Four operating control buttons are on the cursor. An (O) button enables the operator to set the origin anywhere on the digitizing surface, for four-quadrant digitizing. Single points may be sampled by pressing the single sample (S) button. Continuous sample mode (C) is used when tracing lines or curves for analysis. The fourth button on the cursor (H) sets the hold.

Any flat non-magnetic material less than 0.025 inch (0,63 mm) thick may be used as graphic media for digitizing without loss of accuracy. The cursor may be lifted 0.04 inch (1 mm) above the platen before data lockout. If this happens, a small 'beep' notifies the user that lockout has occurred.

The 'beep' is also programmable and may be used to give the operator an audible indication that a predetermined condition has been met. For example, the operator may not remember the starting point when he is tracing around an irregular shape to determine the area. The digitizing system may be programmed to 'beep' when the operator reaches the starting point.

The HOLD button can be used to translate the origin. When HOLD is pressed, and the cursor is moved to a new point, and HOLD is pressed again, the new point assumes the coordinate values of the last point digitized. Using this technique, charts larger than the 17 x 17 inch area of the digitizing area can be analyzed.

Applications of the Digitizer

Strip Chart Recordings

Strip chart recorders have been used for many years to provide permanent records for various phenomena. The reduction of this data into useful form has presented the recorder user with a tedious and time consuming task, particularly if the recording is not linear in either axis. The digitizer may be used to transform the recording in almost any manner, limited only by the imagination of the user.

For example, an accelerometer response curve might be digitized and replotted to a different scale as the first step in the data reduction. The digitizer is then used to retrace the curve. Plotting the first and second integrals will yield the velocity and displacement diagrams respectively.
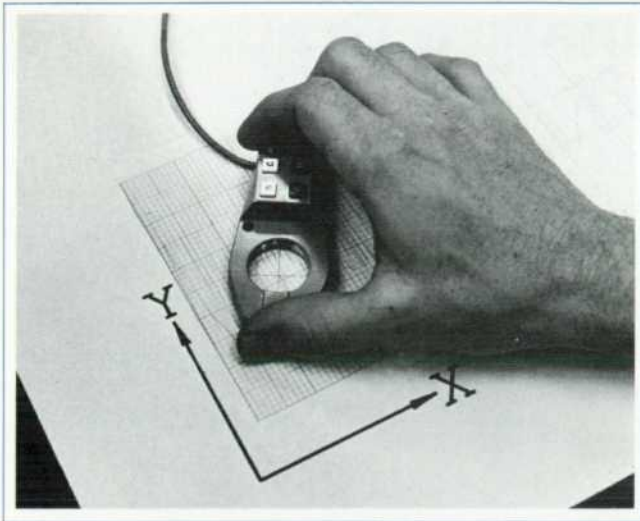
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Fig. 1. *In using the Model 9107A Digitizer, the graphic data to be analyzed is placed on the platen. The cursor is placed over the chart and the curves traced as shown. Coordinate pairs under the cross hairs are automatically entered into the X and Y registers of the Model 9100 calculators.*

Analysis of X-rays

For example, the determination of cardiac output and ventricular volume has presented the cardiologist with several data reduction problems. An accurately measured quantity of an opaque (to x-rays) dye is rapidly injected into the heart. A high speed (about 50 frames per second) x-ray camera records the heart in various states of expansion (diastole) and contraction (systole). One technique used to determine the ventricular volume is the length-area method. The ventricle is approximated by an ellipsoid of revolution.

The x-ray is digitized to determine the area and the length of the major axis. The mathematical relationship between length of the major axis and area gives the length of the minor axis. The volume is easily computed by revolving the resulting ellipse through 180 degrees. The program calculates systolic volume, diastolic volume, stroke volume, ejection fraction, and heart muscle mass.

Photo Analysis

Photographs including oscilloscope photos may be easily analyzed with the digitizer. The photograph is placed directly on the digitizing surface. Calibration to allow for photographic distortion may be incorporated into any program by digitizing the known distance between two points to obtain a scale factor. Since the digitizer always reads the X, Y coordinates directly in inches, the scale factor will be applied to all input values. Additional scaling can also be used to plot on any graph paper.

Typical Applications

Statistical Analysis of Data
Curve fitting—regression analysis
Analysis of strip-chart recordings
Histogram analysis—probability density functions
Mathematical models of families of curves

Analysis of Irregular Shapes
Calculate areas within or under irregular shapes
Calculate centroid
Calculate moments of inertia
Determine distance between points over irregular path and lengths of curved and irregular lines

Analysis of Irregular Waveforms
Harmonic analysis—determine Fourier coefficients
Find area under curves
Transient analysis from oscilloscope photos or plots

Teaching Mathematical and Statistical Concepts
Illustrate integration and differentiation by plotting on calculator plotter as curve is traced

Contour Maps
Determine volumes of earth that must be moved for road building or site planning

Scaling with Plot
Trace curve and plot to different scale
Change from logarithmic plot to linear or vice-versa

Coordinate Transformation
Scaling
Rotation
Translation

Fourier Analysis

A periodic signal can be defined mathematically by the following equation. Because the waveform repeats itself at regular intervals:

$$f(t) = f(t + nT) \qquad n = 1, 2, 3 \ldots$$

where T is the time required for one complete cycle. Periodic signals can be rewritten as

$$f(t) = \frac{a_0}{2} + \sum_{n=1}^{\infty} \left(a_n \cos \frac{2n\pi t}{T} + b_n \sin \frac{2n\pi t}{T} \right) \quad (1)$$

where

$$a_n = \frac{2}{T} \int_{t_0}^{t_0 + T} f(t) \cos \frac{2n\pi t}{T} \, dt \qquad (2)$$

$$b_n = \frac{2}{T} \int_{t_0}^{t_0 + T} f(t) \sin \frac{2n\pi t}{T} \, dt \qquad (3)$$

Now, f(t) is sampled at discrete values of t over a complete cycle. The next task is to evaluate the coefficients a_n and b_n by carrying out the integrations of Eqs. 2 and 3.
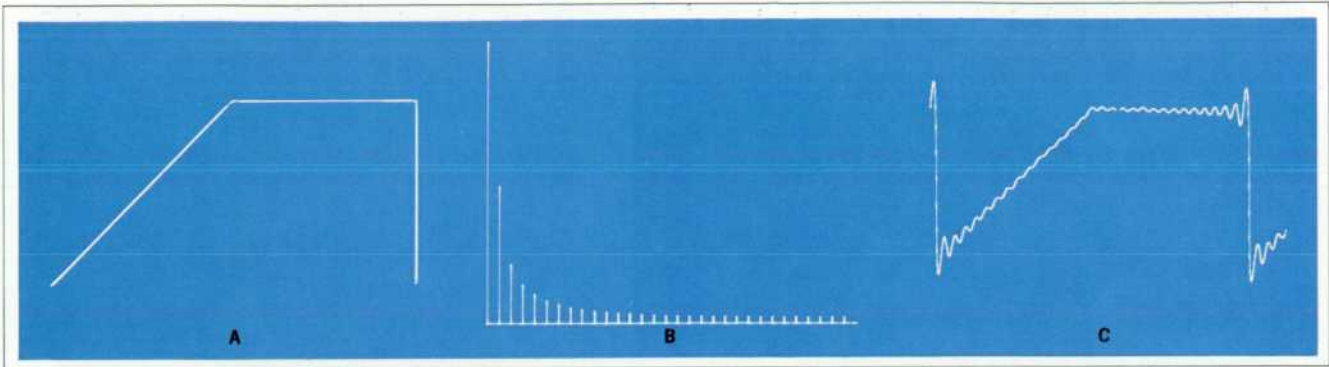
Fig. 2. *The time function (A) is digitized, and the frequency spectrum (B) is the resulting plot of the Fourier analysis. Plotting the reconstructed f(t) from the computed coefficients gives an approximation of the original time function (C).*
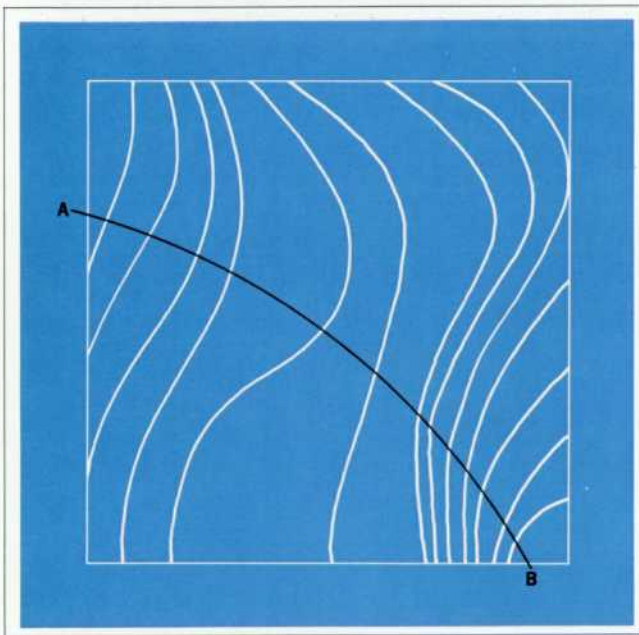

Fig. 3. *Contour map used for preliminary studies of most economical freeway route AB. Alternatives may be investigated without sending surveying crews into the field.*

Contour Map Analysis

Highway road building and subdivision layout almost always involve moving volumes of earth. Earth volumes can be calculated from contour maps and surveying data with the digitizer and calculator combination.

Preliminary cost and time studies may be performed using the digitizer, plotter and extended memory. The proposed roadway centerline is drawn on the contour map as shown by the line AB in Fig. 3. The map scale and contour interval, as well as the desired scale for horizontal and vertical distance to be plotted, are entered into the calculator by the operator. The digitizer is then used to enter data at each point where the centerline of the roadway crosses a contour line. This data is scaled in the calculator and is used to plot the existing profile shown in Fig. 4. The proposed grade is drawn on the same plot thus indicating the vertical distance to the existing ground level in either cut or fill at any point along the roadway.
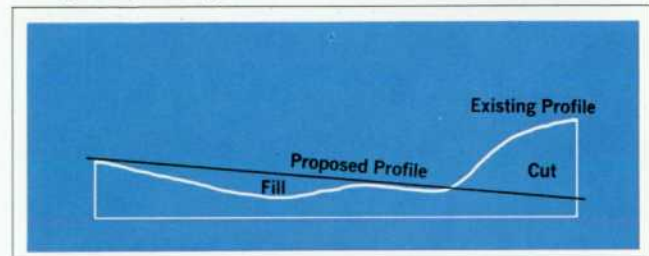

Fig. 4. *Profile section shows areas of cut and fill. Successive sections are used to compute the volume of earth to be moved.*

Stations are taken at desired intervals along the centerline and existing elevations are recorded. Successive end areas, or cross-sections, are used to determine the total amount of cut and fill required.

A Fourier series analysis associated with a time function may be performed with the 9100A/B digitizer system to obtain up to 35 sine and cosine coefficients. The waveform in Fig. 2(A) is traced with the cursor to obtain the discrete $f(t)$ values for given t values. The program computes the coefficients and plots the frequency spectrum as shown in Fig. 2(B). The representative Fourier series may be expressed as Eq. 1. This function is reconstructed and plotted, Fig. 2(C), using the derived coefficients, and may be compared to the original function.

We should like to give credit for technical assistance in designing the Calculator-Digitizer interface to Mr. Robert E. Childs of Bendix and Mr. Edward L. Miller of Hewlett-Packard.

Ivar W. Larson

Ivar is a graduate of the University of Colorado with a B.S. in Applied Mathematics Engineering. He received his MSEE from Bradley University in 1967.

Ivar joined the Hewlett-Packard Loveland Colorado Division in 1967 and has worked on the design and development of advanced calculators and equipment. He is presently Applications Engineering Manager.

A member of Phi Kappa Phi, Ivar's hobbies include woodworking, hunting, fishing and painting.

Dean C. Millett

Dean has had extensive experience in the field of mass spectrometry, thin-film deposition equipment and programmable calculators before joining Hewlett-Packard. He joined HP in 1968 in calculator sales, and transferred to the Loveland, Colorado Division as applications engineer early in 1970. He is now Product Manager for calculator peripherals.

Dean has a BSME from Heald Engineering College, San Francisco, 1961. He also attended the University of California at Berkeley.

His hobbies include fishing and raising quarter horses.

PARTIAL SPECIFICATIONS
HP Model 9107A
Digitizer

ACTIVE DIGITIZING AREA: An area of 17 x 17 inches (431,8 x 431,8 mm)

RESOLUTION: 0.010 inch (0,254 mm)

ACCURACY: ±0.010 inch ($\pm0,254$ mm) per axis from 15°C (59°F) to 30°C (86°F)
±0.030 inch ($\pm0,762$ mm) per axis from 30°C (86°F) to 50°C (122°F) and 0°C (32°F) to 15°C (59°F)

ORIGIN: Can be placed anywhere on the digitizing surface

MAXIMUM TRACING SPEED: 150 inches (3810 mm) per second

RECORD MODES: Single (S) — Digitizes one point at a time
Continuous (C) — Digitizes up to a miximum of 110 points per second

LOCKOUT: Cursor may be lifted 0.040 inch (1,0 mm) above platen before data lockout. Data lockout is indicated by an audible tone of approximately 0.75 second.

HOLD: Pressing the hold button locks in the coordinates of the last digitizer position on the platen. These coordinates may become the initial coordinates for a subsequent cursor position on the platen by locating the cursor over the new coordinates and pressing the hold button again. Coordinates digitized thereafter continue from the locked-in coordinates.

COMPATIBILITY: Operates with all HP 9100A/B Calculators and peripherals.

GRAPHIC MEDIA: Flat non-magnetic material less than 0.025 inch (0,64 mm) thick may be digitized without loss of accuracy.

POWER: 50–60 Hz, 75 Volt Amps, 115/230 V, $\pm10\%$

DIMENSIONS:
Electronics Package:
5½ inches high (139,7 mm)
17 inches wide (431,8 mm)
18½ inches deep (469,9 mm)
Platen:
22 inches deep (558,8 mm)
22 inches wide (558,8 mm)
2 inches high (50,8 mm)

WEIGHT:
Electronics Package:
24 lbs. (10,9 kg)
Platen:
13 lbs. (5,9 kg)

PRICE: $5900

OPTIONS: 001 Digitizing System — Includes 9107A Digitizer and 9100A Calculator

Price: $9850
002 Digitizing System — Includes 9107A Digitizer and 9100B Calculator

Price: $10,800

MANUFACTURING DIVISION: LOVELAND CALCULATOR DIVISION
Loveland, Colorado 80537