

# FOURIER TRANSFORM SPECTROSCOPY

**T**he difficulties that always plague an experimental spectroscopist are those associated with resolving power, light-gathering ability, and wavelength and photometric accuracy. He sees a spectrum, such as that of atmospheric water vapor shown in Fig. 1, and deduces from it information about the atoms or molecules which gave rise to it. Such spectrograms can be taken at wavelengths from the far ultraviolet (about  $10^{-6}$  cm), through the visible (about  $10^{-4}$  cm), to the infrared ( $10^{-1}$  cm). They are made by passing a beam of white light through a sample of material and dispersing the light with a prism. The dispersed light, the spectrum, is then analyzed by moving a narrow slit across it and recording what passes through the slit with a suitable detector and recording system. If the slit is made narrow in order to see fine detail, then little light energy reaches the detector and the result is low signal-to-noise in the recording and low accuracy in the measured quantities. Over the past ten years there have been advances in spectroscopy that have greatly alleviated these difficulties when others are accepted in

their place. These advances came about largely as the result of the work of two men, P. Fellgett<sup>1</sup> and P. Jacquinot.<sup>2</sup>

Fellgett in 1952 showed that advantages can be obtained by doing multiplex spectroscopy; that is, examining the whole spectrum, all of the dispersed light, for all of the recording time as is done in a photographic spectrograph instead of recording one spectral element at a time with a narrow slit as is done in a scanning monochromator. In the infrared spectral region, where all detectors are small point detectors limited by noise which is independent of signal level, the multiplex method can result in a decrease in recording time by a factor equal to the number of resolved elements. Since the number of spectral elements may have values of many thousands, the advantages can be large. There are two commonly used instruments

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<sup>1</sup>P. Fellgett, "A Propos de la Théorie du Spectromètre Interférentiel Multiplex," *J. Phys. Radium* **19**, 1958, 187-191.

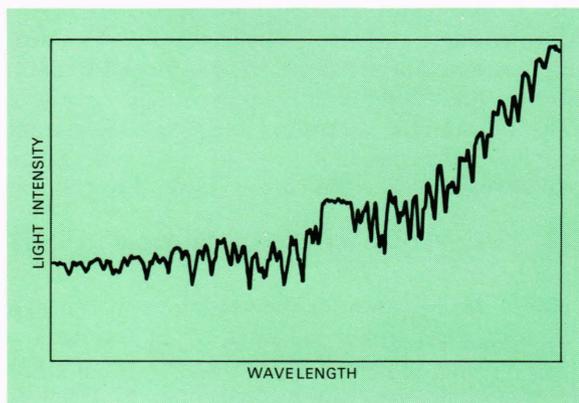
<sup>2</sup>P. Jacquinot, "New Developments in Interference Spectroscopy," *Reports on Progress in Physics* **23**, 1960, 267-312.

*About ten years ago, when large digital computers became widely available, an old spectroscopic method was revived. An interferometer invented by A. A. Michelson is used in a method called Fourier transform spectroscopy. The interferometer processes radiant energy into a Fourier transform of the spectrum which is then inverted by a digital computer. Because of the high light-gathering power of the interferometer and the efficient use of this energy, many problems are now being done which previously were considered possible only in theory.*

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which possess this advantage, the lamellar grating interferometer (a variable groove depth interferometer) and a Michelson interferometer.

Jacquinot in 1954 made the next advance when he compared the light-gathering power and resolution of prism and grating spectrometers and inter-



**Fig. 1—Six micron atmospheric water vapor band.**

ferometers. For identical size and resolving power, grating spectrometers are superior in light-gathering power to prism spectrometers and certain interferometers are superior to both. This increase in light-gathering power comes about because interferometers can use a large circular entrance aperture while spectrometers are limited by narrow slits. Here also there are two commonly used instruments that possess this advantage, the Fabry-Perot and the Michelson interferometers. Thus, it is seen that a Michelson interferometer possesses both the multiplex and the interferometric advantage.

As an example, let us calculate the expected gain of a Michelson interferometer over a commercial prism spectrometer when used at a wavelength of ten microns. The Fellgett advantage for scanning from 5 to 20 microns can be about fifty at moderately high resolution (the square root of the number of resolved elements), and the interferometric advantage can be as high as 200. The product of these, 10,000, might be reduced by losses of about an order of magnitude in a grating

instrument and still another order of magnitude if the interferometer has low transmission. However, a factor of one hundred in increased light-gathering ability still enables spectroscopic problems to be tackled that previously were not attempted.

In addition to these theoretical advantages, a Michelson interferometer is inherently free from stray light. In the far infrared this factor alone can justify the use of this method. In addition, if the interferometer is properly used it possesses high photometric accuracy. Interferometric techniques have the ability to measure wavelengths with unsurpassed accuracy and their resolution can be greater than for any conventional spectrometer.

With all of these advantages the reader might well ask why everyone does not use this method. At the present time, there are few commercial instruments available, and few people are willing to scrap the instruments they have for new, different, expensive, and not widely understood equipment. Since the output of a Michelson interferometer is the Fourier transform of the spectrum, rather than the spectrum itself, its use requires the availability of a large digital computer facility (or a smaller special purpose unit for this purpose alone). Available commercial instruments are very specialized and they provide precision performance only in the far infrared (past twenty microns) and give very low resolution in the near infrared. Thus, the usefulness of commercial interferometer spectrometers is somewhat restricted. If one decides to build an interferometer to cover a wide spectral range at high resolution, then the accuracy and precision required make the construction quite formidable. In the future more interferometers will undoubtedly be used, but at the present there are relatively few compared to conventional spectrometers.

## Theory

Figure 2 shows a simplified diagram of a Michelson interferometer. A broad source is viewed by a telescope through the interferometer. The light from the source is split by the divider plate, half going to each mirror. The light returns from the mirrors, is recombined at the divider plate and goes to the telescope. If one mirror is moved perpendicular to its surface, the beam from this mirror will vary in phase relative to the other beam.

If the addition of two beams of light of the same wavelength and amplitude is considered, the resultant intensity, which is the measured quantity, can be shown to be

$$I = 4E^2 \cos^2(\phi/2), \quad (1)$$

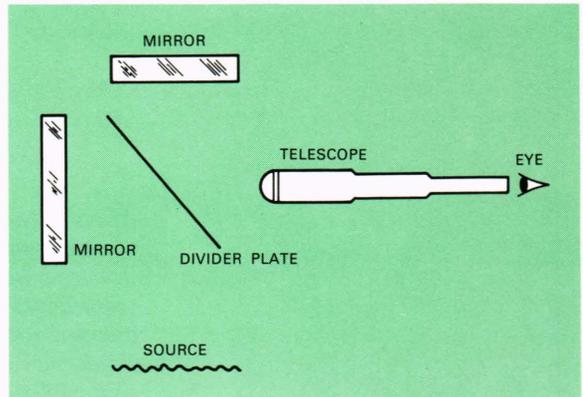


Fig. 2—Michelson interferometer.

where  $I$  is the intensity,  $E$  is the amplitude of the individual beams, and  $\phi$  is the phase difference between the two beams. In this and other equations constant multiplying terms are often omitted for simplicity.

The phase difference in a two-beam interferometer is given by

$$\phi = 2\pi D\sigma \cos \alpha, \quad (2)$$

where  $D$  is the optical path difference between the two beams (twice the distance the movable mirror is from an equilibrium position),  $\alpha$  is the angle between the beam direction and the viewing angle, and  $\sigma$  is the wave number

$$\sigma = 1/\lambda. \quad (3)$$

If the wavelength  $\lambda$  is expressed in centimeters,  $\sigma$ , the wave number, is in reciprocal centimeters ( $\text{cm}^{-1}$ ). When the telescope in Fig. 2 views a broad source of single wavelength light and  $D$  has a finite value not zero, a system of circular fringes is seen; this is due to the changing phase variation with viewing angle. When a Michelson interferometer is used as a spectrometer,  $\alpha$  is a small quantity so that the cosine of  $\alpha$  is approximately equal to one and only the variations in the central circular fringe are measured.

Putting Eq. (2), with  $\cos \alpha = 1$ , into Eq. (1) gives

$$I(D) = 2E^2 (1 + \cos 2\pi D\sigma). \quad (4)$$

This is the equation for the variations in the light intensity through a small aperture at the focus of the telescope objective. If the light is not a single frequency or wavelength then Eq. (4) must be integrated over all the wavelengths of light that are present. The single amplitude term is replaced

by the variable  $B(\sigma)$ , the intensity distribution in the spectrum, and the integral taken

$$I(D) = \int_0^\infty B(\sigma) d\sigma + \int_0^\infty B(\sigma) \cos 2\pi D \sigma d\sigma. \quad (5)$$

The first term is the total integrated light intensity reaching the detector and the second term is the variation in this intensity as the mirror is moved. This variation is the subject of interest here and is given by

$$\Phi(D) = \int_0^\infty B(\sigma) \cos 2\pi D \sigma d\sigma. \quad (6)$$

The variation,  $\Phi(D)$ , from the average energy value is called the interferogram. An inversion of the equation can be obtained with the theory of Fourier transformations to give the spectrum itself with the result

$$B(\sigma) = \int_0^\infty \Phi(D) \cos 2\pi D \sigma dD. \quad (7)$$

Equations (6) and (7) assume a perfect interferometer. The effects of deviations from this will be considered later.

In Fig. 3 are two assumed spectra and their interferograms. Figure 3a is a spectrum of a single frequency. Its interferogram is a cosine wave going from zero to infinity. Figure 3b shows the interferogram for a single broad spectral line. The interferogram in this case is a wave which is exponentially damped. The interferogram of complex spectra will be shown later.

We have so far considered the relationships between the optical path difference and the interferogram. Other theoretical considerations involve

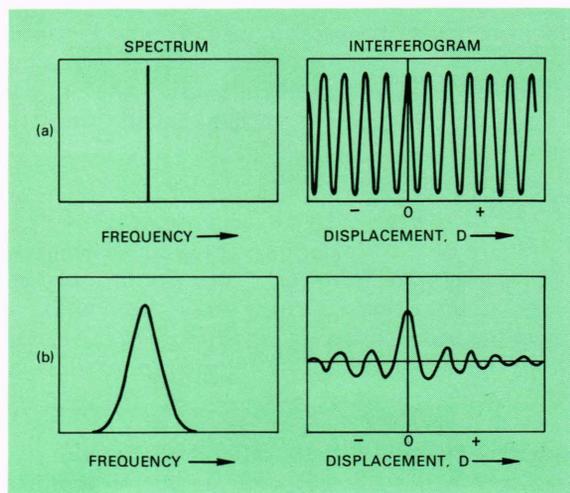


Fig. 3—Spectra and interferograms.

the relationships between resolution and light-gathering power. Resolution for a spectroscopic instrument is defined as

$$R = \lambda/\Delta\lambda = \sigma/\Delta\sigma, \quad (8)$$

where  $\lambda(\sigma)$  is the wavelength (wave number) involved and  $\Delta\lambda(\Delta\sigma)$  is the distance between two lines of equal intensity that are just resolved. Without going into the details of the definition of the point at which the lines are just resolved, let it suffice to say that two lines are resolved when the optical path difference in the interferometer is given by

$$D = 1/(2\Delta\sigma) \text{ or } \Delta\sigma = 1/(2D). \quad (9)$$

Jacquinot<sup>2</sup> has derived a relationship between light-gathering power and resolution for an interferometer which is usually written as

$$R\Omega = 2\pi, \quad (10)$$

where  $\Omega$  is the solid angle subtended by the source at the entrance optics. In a normal spectrograph it is the solid angle subtended by the slits at the collimating lens. In an interferometer the limiting aperture defines how much of the central circular fringe is allowed to enter the interferometer. This must be determined for the highest frequency (shortest wavelength) that is being analyzed.

Equations (8), (9), and (10), can be combined to show that

$$\Omega = \pi/(D\sigma)_{max} = \pi\lambda_{min}/D. \quad (11)$$

The allowable solid angle is thus inversely proportional to the product of the length of scan and the highest frequency in the spectrum.

## The Applied Physics Laboratory Interferometer

A Michelson interferometer spectrometer has been constructed for the investigation of infrared emission spectra of weakly emitting sources such as thermally excited gases, fluorescing solids, and gas discharges. Auxiliary apparatus permits the study of absorption spectra.

An instrument was needed to study low-intensity emission spectra which combined the requirements of high-light-gathering power for studying weak sources, wide spectral range, and small size comparable to conventional commercial infrared spectrometers. The instrument developed consists of reflection optics, mirrors to direct the light into the interferometer and out to the detector, the interferometer itself, and an auxiliary system for

alignment and path difference measurements. Any wavelength region between  $10^{-4}$  cm and  $10^{-1}$  cm can be examined by changing only the divider plates and light filters. The divider plates available at present are calcium fluoride for the near infrared and mylar for the far infrared. The detector in the instrument is a diamond window Golay pneumatic detector, although a thermocouple and a lead sulfide cell are also available.

The moving mirror of the interferometer rides on a  $45^\circ$ ,  $45^\circ$ ,  $90^\circ$ -glass prism mounted with the  $90^\circ$  angle up. This prism is 10 cm long and its faces are flat to one-quarter wavelength of visible light. The moving mirror does not tilt or tip more than one-twentieth of a wavelength of visible light over

through the interferometer and the  $5461\text{\AA}$  green line fringe system is recorded. The mercury arc fringe system drives a scaler circuit which applies a pip mark on the interferogram chart paper every 1, 2, 4, 8, or 16 fringes. This pip mark is made at a position known to within  $1/8$  wavelength in optical path difference or about  $0.07\mu$ . The mercury fringe system beam is also split by the beamsplitter and sent outside the instrument for monitoring and alignment purposes.

All of the optical components are mounted on top of a  $45 \times 90 \times 2.5$  cm aluminum plate. The chopper motors, the drive motor, and the screw drive system are mounted underneath. The whole assembly is enclosed in a one-inch-thick aluminum

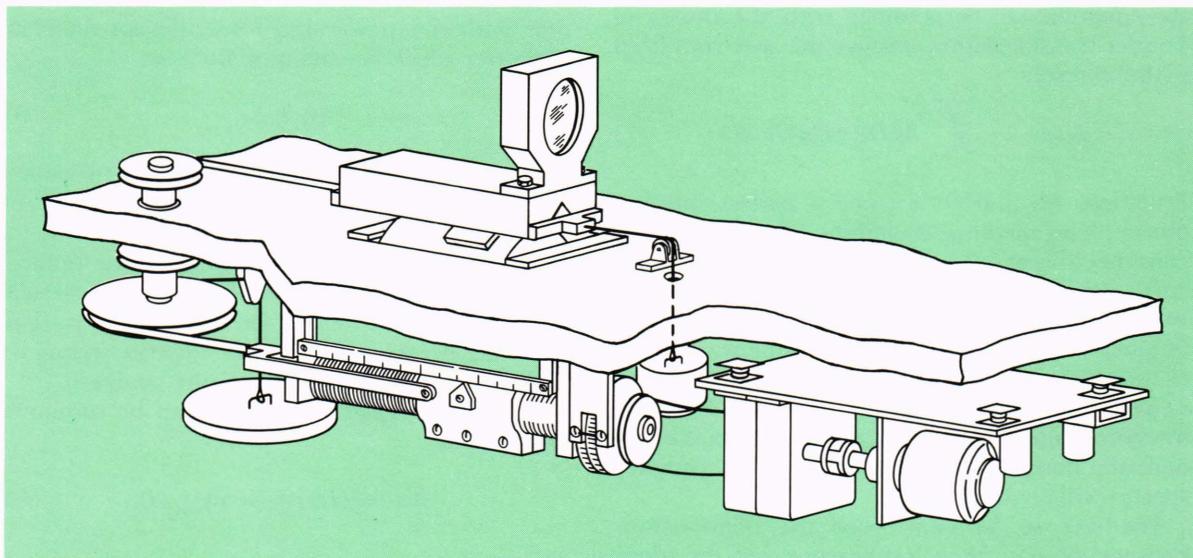


Fig. 4—Movable mirror and associated drive system.

an area of 1 cm diameter per mm of travel, and this error is easily corrected by adjustments in the stationary mirror. Figure 4 shows both the movable mirror and its associated drive system. The mirror can be moved through a distance slightly greater than  $5\frac{1}{2}$  cm for an optical path change from minus one to plus 10 cm.

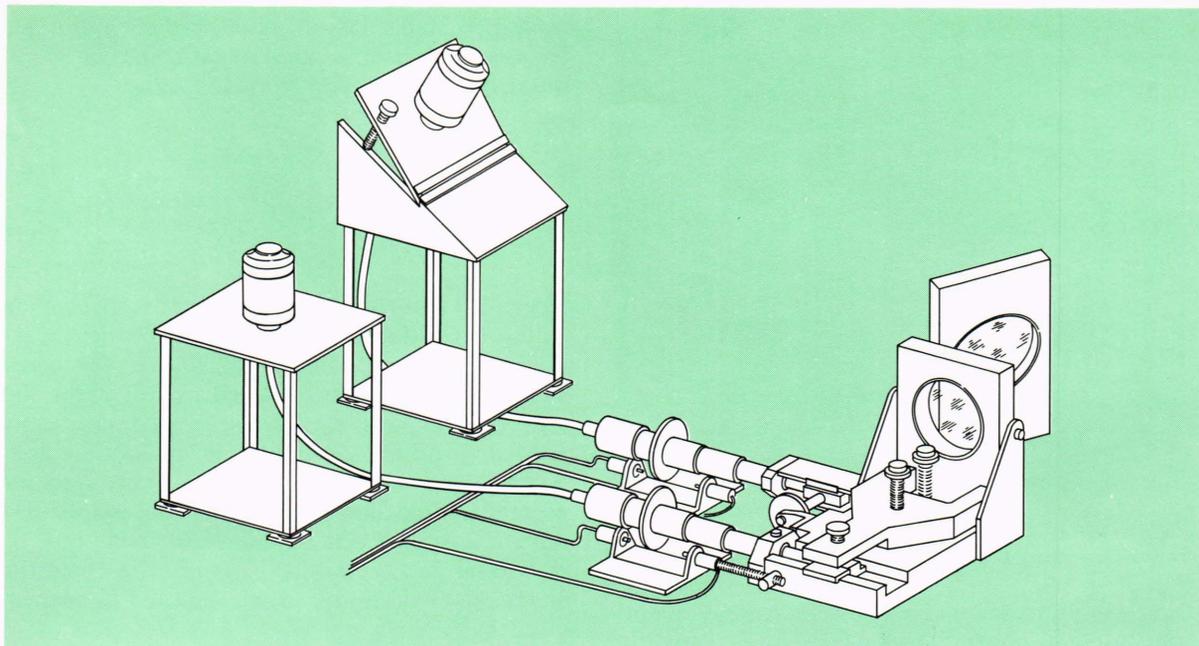
The stationary mirror, Fig. 5, is tipped and tilted by motor drives and can be adjusted while the instrument is in operation. The tip and tilt lines are carefully arranged so that they go through the mirror surface, so that these adjustments do not affect the optical path difference in the interferometer.

Even though the drive screw is of high precision, accurate to about one micron, the screw position is not used for the determination of the mirror position. Instead, light from a mercury lamp is sent

housing which measures approximately  $50 \times 50 \times 100$  cm. When running, the container is evacuated to less than 75 microns which eliminates atmospheric water vapor and carbon dioxide from the spectra.

### Typical Spectra

Figure 6 is a typical interferogram. The upper pip markers are from the scaler circuit and mercury lamp reference and the lower pip marks are from the screw drive microswitch. This is a relatively high signal-to-noise interferogram showing only the central peak, where the optical path difference is zero for all wavelengths, and about 550 microns of optical path difference on one side. Figure 7 is the transform of an interferogram of which Fig. 6 is the central section. This spectrum, which was taken during initial testing of instru-

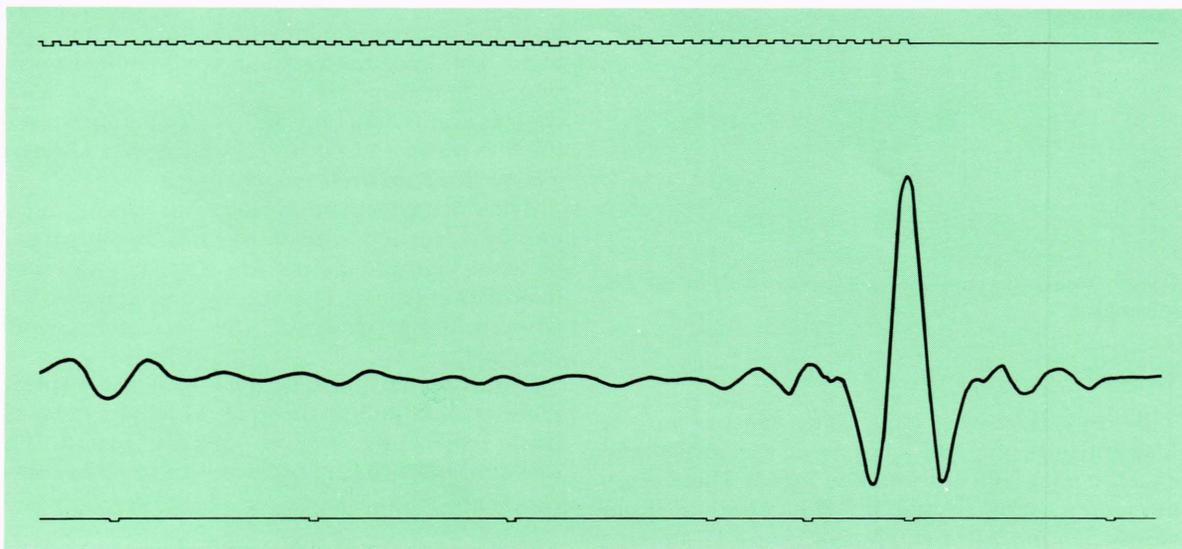


**Fig. 5—Stationary mirror with motor-driven tip and tilt control.**

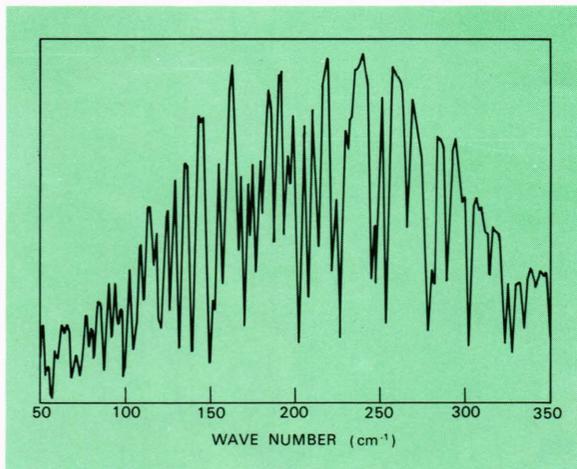
ment performance, is the spectrum of the water vapor contained in a 50-cm path of air at atmospheric pressure. For this experiment the source was a glowbar at a temperature of approximately 700°C. The total path difference was 5.5 mm and the interferogram was sampled every eighth fringe (approximately 4.4 microns). The expected resolution was  $1.8 \text{ cm}^{-1}$ . The observed resolution appears to be about 10 to 20% poorer.

Figure 8 is the pure rotational emission spec-

trum of HCl gas in the  $50$  to  $350 \text{ cm}^{-1}$  region at a resolution of  $4.5 \text{ cm}^{-1}$ . The gas was thermally excited to a temperature of only  $110^\circ\text{C}$  in a 30-cm cell at a pressure of 12 mm. Spectra of this type are ideally suited for interferometric spectroscopy as there is very little energy available and high resolution is required. In most cases where gaseous emission spectra have been recorded in the past, as in flames or electrical discharges, the gas was not in thermal equilibrium and the excitation condi-

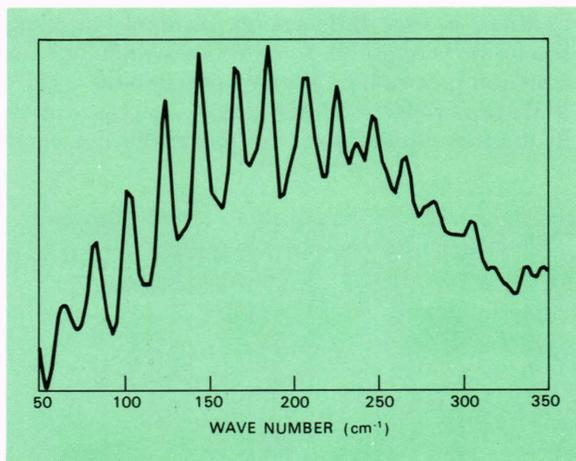


**Fig. 6—Typical interferogram of rotational spectrum of water.**



**Fig. 7—Rotational absorption spectrum of water vapor in the far infrared.**

tions were unknown. This has meant that quantities such as state populations and transition probabilities could not be obtained. These quantities can only be accurately determined if the gas is in thermal equilibrium at a low enough temperature so that neither excessive line broadening nor molecular dissociation takes place. This is the case for the HCl spectrum of Fig. 8.



**Fig. 8—Rotational emission spectrum of HCl in the far infrared.**

## Errors

Because this method of doing spectroscopy is new and different, an analysis of the errors and experimental difficulties will be made. Three types of error may be caused by (1) deviations from theory, (2) imperfect equipment, and (3) noise.

Errors due to deviation from theory cause three effects: error in the calculated frequencies, finite

resolution, and a loss in signal-to-noise ratio. The basic equation for digital transformation of an interferogram to a spectrum is

$$B(\sigma) = \sum_{n=0}^{n=D/\Delta D} [\Phi(n\Delta D) \cos(2\pi n\Delta D\sigma)], \quad (12)$$

where  $\Delta D$  is the incremental mirror displacement. In the derivation of this equation the field angle was assumed to be negligible; that is, the cosine factor in Eq. (2) was replaced by unity, the first term in its expansion. Because finite apertures are needed to admit a measurable amount of light,  $\alpha$  is not zero. This causes a phase error, since the average phase value over the aperture is recorded, not the assumed central value. By including the second term in the cosine expansion, a correction factor can be derived for the computed frequencies given by<sup>3</sup>

$$\sigma_{actual} = \sigma_{measured} / (1 - \Omega/4\pi). \quad (13)$$

The correction is usually negligible at long wavelengths (small  $\sigma$ ), but in the near infrared where  $\sigma$  reaches values in the thousands the correction can be quite appreciable.

The second effect is due to the integration or summation not extending from zero to infinity but only over a finite range of values of  $D$ . In Fig. 3a the interferogram of a single frequency is shown to be a cosine wave extending from zero to infinity. Consider for a moment the inverse, a cosine wave interferogram causing a spike. If the infinite interferogram is not taken, some of the information is lost, and this causes an uncertainty in the spectrum. This uncertainty shows up as limited resolution, or finite line width. This line width is called the apparatus function and is similar in effect to the line width caused by slit diffraction effects in a conventional spectrometer.

The third effect comes from digitizing a continuously recorded interferogram. Because data between digitized points are thrown away some information is lost. This can be overcome by stepwise scanning. However, this is experimentally difficult.

Digitizing must also be done with some care as there is a sampling theorem which dictates the point spacing for a given spectral region. This theorem states that in order not to have any spec-

<sup>3</sup>J. Connes, "Spectroscopic Studies Using Fourier Transformations," *Rev. Opt.* **40**, 1961, 45-79; 116-140; 171-190; 231-265.

tral region folded back on itself, the point spacing should be at least as short as one-half the shortest wavelength present in the spectrum as seen by the detector, not necessarily in the spectral region of interest. This and the dynamic range of the detector make short wavelength cutoff filters desirable. The availability of these filters leaves something to be desired.

The second type of error is associated with imperfect equipment. Several of these that can be corrected in computation are errors in selecting the correct zero phase point and lack of a perfectly compensated interferometer. These are simultaneously corrected by computing the phase error of a small section of interferogram located more or less symmetrically about zero  $D$ . The phase  $\xi$  of an interferogram is given by

$$\xi(\sigma) = \frac{\int_{-a}^{+a} \Phi(D) \sin 2\pi\sigma D dD}{\int_{-a}^{+a} \Phi(D) \cos 2\pi\sigma D dD} \quad (14)$$

If this function of the phase  $\xi$  is plotted against the frequency  $\sigma$ , a straight line of zero  $\xi$  will result if there is no correction. If this is not the case, then the interferogram is not symmetrical about the assumed zero and suitable correction factors have to be added.<sup>4</sup>

The equipment digitizing error due to skipping points that should be read cannot be corrected. This has the effect of giving spectra that are shifted with respect to one another.

Equipment errors can also arise in the analog operation of the electronics. These include dynamic range, nonlinearities, electronic noise, and drift. The last of these can be removed to some extent in the calculations by mathematically filtering the interferogram. Nonlinearity and electronic noise can be eliminated by careful design and workmanship. Dynamic range is a problem because the recording system needs a range greater than the ratio of total intensity to individual line intensity in order to detect the individual spectral lines. This is principally a difficulty in absorption spectroscopy where the background energy is usually large.

Imperfections in optical components, the most important of which are the interferometer surfaces, can produce errors. The errors in the interferometer optics show up as wavefront errors in the

light leaving the interferometer, and cause loss in modulation of the interferogram. An error of only one-tenth of a wavelength is serious as it causes a 30% loss in modulation. This type of error can come from defects in either the mirrors, the divider, or compensator plate, or in the more usual case, from the tip or tilt of the moving mirror as the optical path difference is changed.

An error arises from not knowing the position of the moving mirror with sufficient accuracy. Random inaccuracies will add noise to the spectrum while periodic inaccuracies will add ghosts in a manner similar to periodic errors in the ruling of diffraction gratings. In fact, for the same wavelengths and for the same ghost or noise intensity, the moving mirror position for an interferometer must be better controlled by an order of magnitude than the position of the ruled lines in a diffraction grating.

The third class of error is due to noise. With a conventional scanning monochromator the noise impressed on the spectrum is readily apparent. In a Michelson interferometer the data must undergo processing before the final spectrum is available. Even then it is difficult to see the relationship between interferogram noise and spectrum noise as one is the Fourier transform of the other. Several authors<sup>3,5</sup> have analyzed the problem of maximizing the signal-to-noise in the resultant spectrum but the answer depends heavily on the type of spectrum assumed. However, in most cases it does not pay to take an interferogram of longer length than needed for obtaining sufficient resolution, because the spectrum noise increases as the square root of the length of the interferogram while the signal, which is the modulation of the interferogram, is decreasing at a rapid rate. Hence, the signal-to-noise decreases as the resolution is increased. This is the same effect that is observed in all spectrometers. In a conventional spectrometer the resolution is increased by decreasing the slit width and this causes a decrease in the signal while the noise is constant. In an interferometer, since the Fourier transform of the noise is taken, the picture is not so clear but the same result is obtained.

## Acknowledgments

I wish to thank Charles F. Bradley for his able assistance in the design and construction of the interferometer and Joe T. Massey, Shelton M. Cannon, and John G. Montebaro for helping in the development of this project.

<sup>4</sup>M. Forman, W. Steel, G. Vanasse, "Correction of Asymmetric Interferograms Obtained in Fourier Spectroscopy," *J. Opt. Soc. Amer.* **56**, 1966, 59-63.

<sup>5</sup>J. Dowling, "Signal and Noise in Two-Beam Interferometry," *Appl. Optics* **6**, 1967, 1580-1581.