JOURNAL OF RESEARCH of the National Bureau of Standards—C. Engineering and Instrumentation
Vol. 67C, No. 3, July-September 1963

A Far-Infrared Vacuum Grating Spectrometer

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(March 4, 1963)

A far-infrared vacuum grating spectrometer has been designed, built and tested at the National Bureau of Standards. This instrument has been in operation and under constant improvement for the past two years. Its useful range of operation is from 30 to 400 cm^{-1}. The detecting and dispersing elements are a Golay pneumatic detector and a series of $2\frac{1}{4} \times 3$ in. plane gratings. A spectral resolution of from 0.5 to 1.0 cm^{-1} has been attained in the region between 30 and 200 cm^{-1}.

The far-infrared absorptions of several halogenated ethanes in the liquid state have been observed and measured. The absorptions observed were: pentachloroethane, 175.5 cm^{-1}, 164.5 cm^{-1}, and 85 cm^{-1}; symmetric-tetrachloroethane, 172.0 cm^{-1} and 87 cm^{-1}; 1 bromo-2-chloroethane, 202.0 cm^{-1} and 123 cm^{-1}.

1. Introduction

In recent years a renewed and enlarged interest has been aroused in the direct measurement of spectra below 200 cm^{-1}. It is in this low frequency region that one observes absorption bands arising from the bending and twisting modes of complex molecules.

This work is primarily concerned with the construction of an instrument of medium resolution that would be capable of observing and measuring these low lying frequencies.

2. Equipment

In order to design a vacuum instrument that would possess the convenience and adaptability necessary for the numerous phases of infrared research, four basic aims were used as guides: (1) the maintaining of a maximum level of source energy, (2) the use of window mounts that could easily be adapted to many situations, (3) the accessibility of optical components for convenient adjustment and interchange, and (4) the allowance for subsequent improvements on the instrument, both in size and quality.

2.1. Instrument Housing

The instrument housing as shown in figures 1 and 2 is divided into four separate chambers, each of which is accessible through one or more cover plates. These chambers are interconnected by three focal plane windows. Each window and cover plate is O-ring sealed and has its mounting holes indexed for rapid interchange and adaptation.

The main section, composed of chambers C2 and C3, was fabricated from $\frac{5}{16}$-in. aluminum plate. The plate was rolled into a cylinder 72 in. long ×22 in. in diameter. All of the joints were heli-arc welded. Chambers C1 and C4 were fabricated from the same material and can be detached from the main housing.

Chamber C1 houses the source and source optics (fig. 2). It may be flushed with a dry inert gas or evacuated as the research allows. Liquid or gas absorption cells up to 10 cm in length may be placed in the path between M2 and W1.

Chamber C2 is essentially a variable path gas absorption cell. The path length may be varied from 2 to 6 m. The reflector, MR, is a six-position turret that is controlled from cover A3. On this turret plane reflectors are mounted and selected as needed.

The monochromator chamber C3 is of sufficient size to house a spectrometer having a focal length of 60 cm. At present a modified monochromator section of a Perkin-Elmer Model 12 single-beam spectrometer is being used. The grating turntable is driven by an externally located synchronous motor. An O-ring sealed shaft transmits the power through the vacuum wall at cover A8. The monochromator slits are driven by an electric motor located within the vacuum chamber. Slit motor and detector leads are brought outside through the Kovar seals in cover A7. Cover A6 provides for access to the grating and contains a glass window for observation purposes. Between C2 and C3 there is a separating window W2, which can be removed or installed as the research demands. This allows one to make use of the added path length of the monochromator whenever noncorrosive gases are being studied.

Chamber C4 is used specifically to house the Golay pneumatic detector and may be flushed with dry nitrogen or evacuated. The cover of this chamber is hinged and is fitted with Kovar seals for signal and power connections. In this chamber liquid and gas absorption cells up to 15 cm in length may be introduced into the optical path at window W3.

The vacuum system is composed of a forepump, oil diffusion pump, and strategically located cold traps (fig. 1). Chambers C2 and C3 are evacuated through 4-in. copper tubing beginning at covers A2 and A5 and joining at the cold trap T1. Preceding the cold trap T1, there is a 4-in. 300 liter/sec oil diffusion pump P1. Preceding P1 is a packless

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[1] This work was done in partial fulfillment of the requirements for the degree of Master of Science for the Graduate School of the University of Maryland.

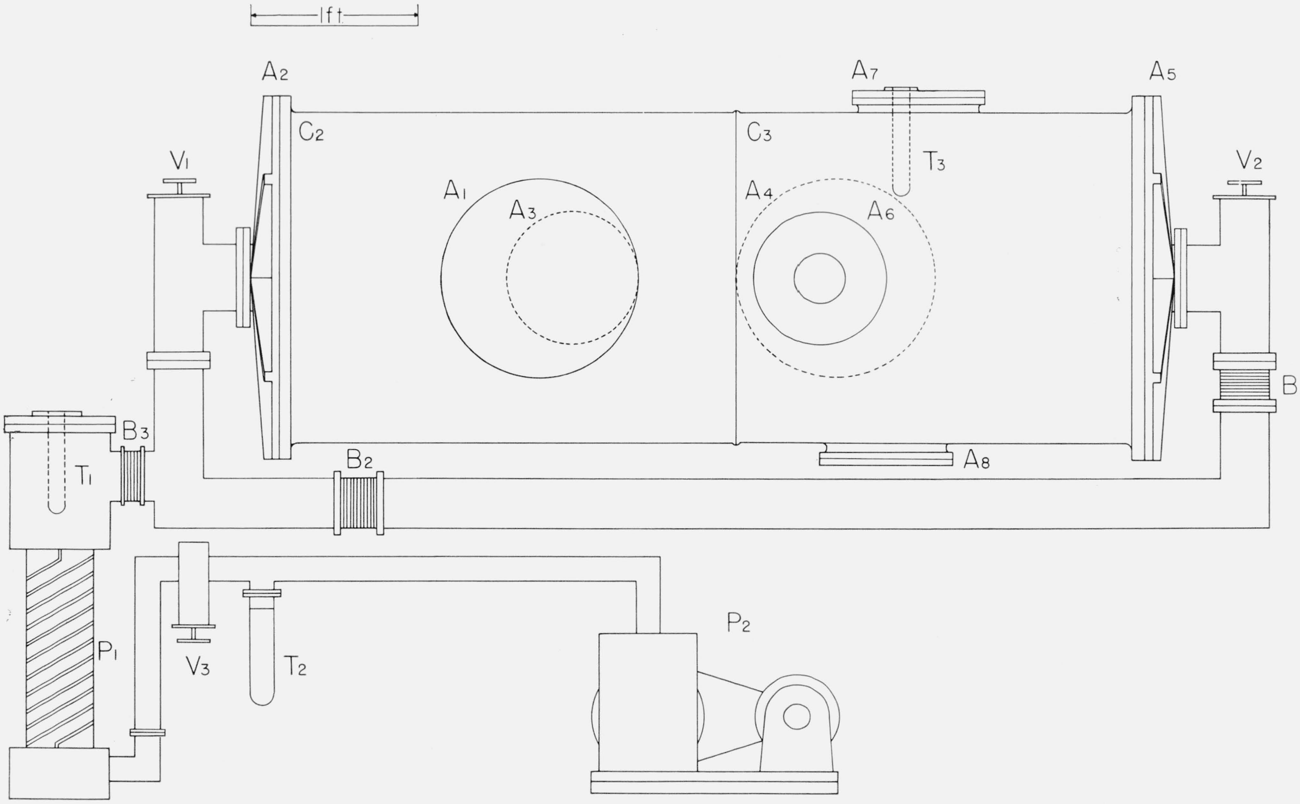

FIGURE 1. *Instrument housing and vacuum system.* (*side view*)

valve V3, a cold trap T2, and a forepump P2. An additional cold trap in the form of a cold finger, T3, is suspended in the monochromator chamber, C3, at cover plate A7.

This vacuum system has been found adequate for the removal of atmospheric absorption with respect to the present path length and resolution of the instrument.

2.2. Optical System

The optical system is divided into four sections: source optics, absorption cell optics, monochromator optics, and detector optics (fig. 2).

a. Light Path

The light is first modulated at 10 c/s at the source S by the chopper C, passes to reflector M1, to spherical mirror MS1, to plane mirror M2 and is then focused on the plane of window W1.

On entering chamber C2 it is reflected from plane mirror M3 to spherical mirror MS2 and then to one of the six plane reflectors on the turret MR. From this point it is reflected into the spherical mirror MS3 and into the mirror system of the multipass absorption cell. This is composed of several small plane mirrors, M4, M5, M6, M7, and one spherical mirror MS4, having a 50-cm radius of curvature. A path length of up to 6 m is available by changing the arrangement of the multipass mirrors. These are prepositioned on a plate that can be changed as a unit. This operation can be performed through cover plate A3. After leaving the multipass cell, the light passes to plane mirror M8, spherical mirror MS5, plane mirror M9, and through the exit window W2.

From the window W2, the light is brought to a focus on the monochromator entrance slit S1. It then passes through a standard Littrow-type f/4.5 grating monochromator. The monochromator exit slit, S2, is then focused on the window W3 by the plane mirrors M11 and M12 and the spherical mirror MS6.

After entering chamber C4 the light may pass either to toroidal mirror MT, or to a 90-deg-off-axis ellipsoidal mirror ME, and then be focused into the Golay receiver D. The toroidal mirror with its short focal length leaves space only for short liquid and gas absorption cells up to 2 cm in thickness. The ellipsoidal mirror, however, has conjugate focal distances of 3 and 21 cm and will allow absorption cells up to 15 cm in length to be placed between window W3 and the ellipsoid ME.

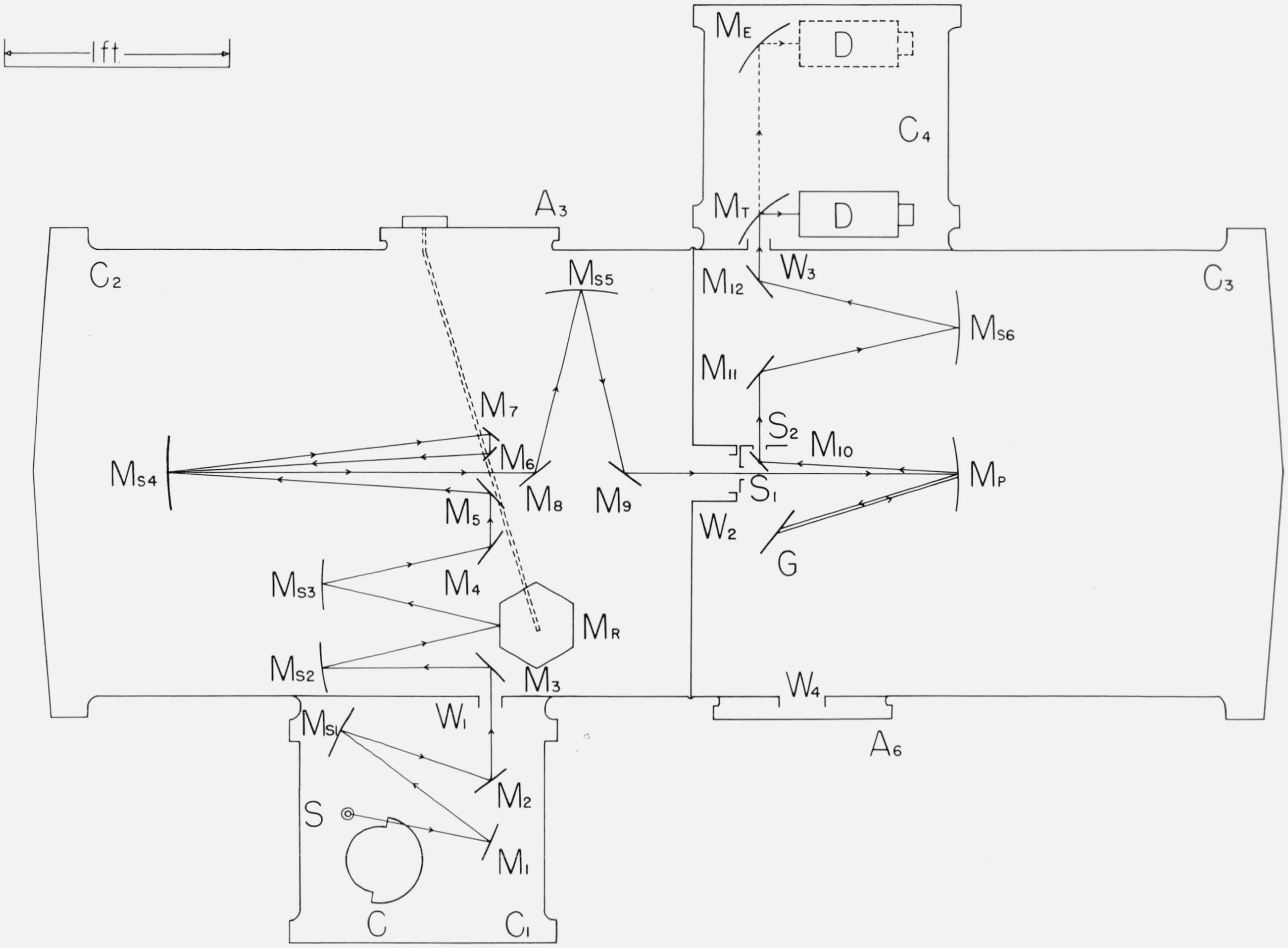

FIGURE 2. *Optical system.*

b. Monochromator and Modifications

(1) *Grating drive.* The P.E. 12 is a prism instrument and its Littrow mirror is rotated by a sine bar which allows only 10 deg of angular rotation. In order to eliminate this inconvenience and obtain 360 deg of rotational freedom the sine bar was removed and a precision worm gear substituted. Connection was then made to the power shaft at A8. The prism table was removed and a suitable grating mount was substituted for the standard Littrow mirror mount.

The grating turntable driving system consists of a synchronous motor, standard three-speed transmission, several precision worm gears, a rotation counter, an O-ring sealed drive shaft, and an independent rapid traverse drive motor. The synchronous motor having a variable speed-reducer gives a range of scanning speeds from 1.2 to 0.16 deg of arc per minute of time. This provides scanning speeds compatible with the time constants of the detector system.

The rapid traverse drive is specifically designed for rapid positioning of the grating and gives a scanning rate of 31.4 deg/min of time.

(2) *Slits.* The bilateral slits are geared to an electric motor which is located within the vacuum chamber C3, and controlled from an outside switch panel. A Veeder-Root rotation counter located in the gear train enables one to determine the slit width to within a few microns. This counter is readily observed through the window in cover A6.

(3) *Optical modification.* In order that the Golay detector could be placed in chamber C4, under atmospheric pressure, the standard optical system behind the monochromator exit slit, S2, had to be rearranged so as to focus the image of S2 on the window W3. This was accomplished by installing the plane mirrors M11 and M12 and the spherical mirror MS6.

(4) *Electrical system.* Controls for the slit drive, grating drives and vacuum gages are mounted on a control panel which is located on the instrument support frame. The electric motors that power these components are single phase ratio-motors [2] having a rating of approximately 1/100 hp. Power or signal

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[2] Electric motors equipped with a built-in speed reducer.

leads that pass in and out of the individual chambers are fed through the cover plates with Kovar seals.

The signal detection system[3] consists of a Golay pneumatic detector and associated equipment so that the signal is amplified and ultimately recorded on a strip chart.

3. Spectroscopy in the Far Infrared

3.1. Sources

The choice of a good source for far infrared absorption studies is somewhat limited. The region from 400 to 100 cm^{-1} is efficiently covered by the globar. Below 100 cm^{-1} a high pressure mercury arc is used.

The source being used in this work is a 100 w high pressure mercury arc. This arc is enclosed in two envelopes, an inner one of fused quartz and an outer one of glass. The fused quartz is transparent to radiation below 100 cm^{-1} but the glass is opaque to this radiation and is therefore removed for this work. Figure 3 gives the transmission characteristics of fused and crystal quartz and the emission curve of excited mercury vapor filtered by the fused quartz envelope. The curve 3d shows the relative level of a globar continuum in the 100 cm^{-1} region. The arc is unique in that it has an intense emission continuum below 100 cm^{-1}. This emission covers a region roughly from 100 to 10 cm^{-1} and reaches a maximum at approximately 80 cm^{-1}. Although the fused quartz envelope is transmitting only about 15 percent at 90 cm^{-1}, the arc is still emitting a factor of 3 over a standard globar.

3.2. Order Separation

As one works at successively lower frequencies, the problem of obtaining spectra free of overlapping orders becomes very severe. The root of this problem is seen in an examination of the Planck radiation law for an ideal blackbody. Consider, as an illustrative example, a blackbody at a temperature of about 1,500 °K. The radiation curve for this source has a peak at about 3,000 cm^{-1}. We are interested in the region around 30 cm^{-1}. The intensity at 30 cm^{-1} is down by a factor of 5×10^{-4} from that at the peak. This suggests the required efficiency of one's filtering techniques. The emission characteristics of the mercury arc would lead one to believe that such a source would simplify the order separation problems in the far infrared, but the heat produced by the arc maintains the quartz envelope at a temperature of about 900 °C, and the emission then produced by the envelope, not being filtered by the quartz, must still be eliminated.

Black polyethylene has been quite effective in this filtering problem. Essentially, it is a dispersion of carbon in polyethylene. As shown by figure 5, it greatly attenuates the visible and near infrared wavelengths and passes the longer. Previously, one was forced to smoke a piece of window material with turpentine or camphor soot.

This difficulty can be considerably lessened by working in the first order, well away from the grating blaze. Thus the relatively short (high order) wavelengths, which are very sensitive to the blaze, will be efficiently concentrated in other regions and the longer (first order) wavelengths which are not sensitive to the blaze will be left less contaminated. Good quality gratings used as zero order selective reflectors offer another efficient filtering device [1].[4] When several are properly used in series their reflection edge can be as sharp as the transmission edge of crystal quartz with the added feature of control. Figure 4 gives the reflectivity curves of three good quality gratings.

Another widely used filtering technique makes use of the transmission properties of various crystals. In addition to a sharp high frequency absorption edge, a low frequency transmission edge is also present in these crystals which is usually not sharp enough to serve as an efficient filter. Only crystal quartz seems to fulfill this requirement. This transmission edge, however, can be sharpened and controlled by impregnating polyethylene with one or more of these crystals in powdered form [2].

Probably the most efficient filtering technique is that of using the reststrahlen of various crystals.

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[3] Manufactured by Eppley Laboratory Inc., Newport, R.I.

[4] Figures in brackets indicate the literature references at the end of this paper.

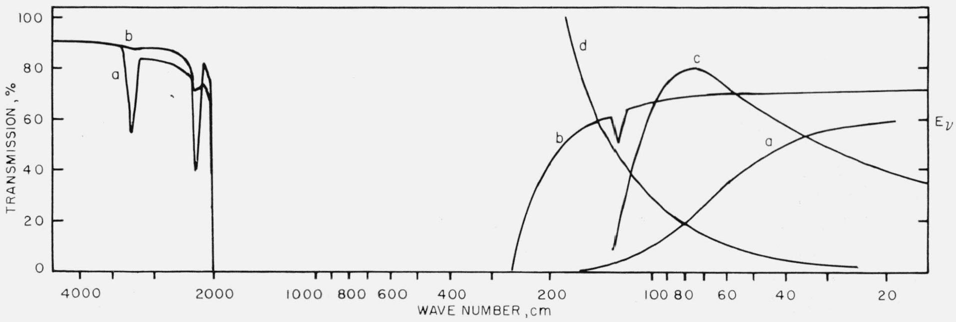

FIGURE 3. *Properties of quartz and the mercury arc.*

(a) Transmission of fused quartz. (b) Transmission of crystal quartz. (c) Spectral output of a high pressure mercury arc filtered by 1 mm of fused quartz. (d) Spectral output of a globar.

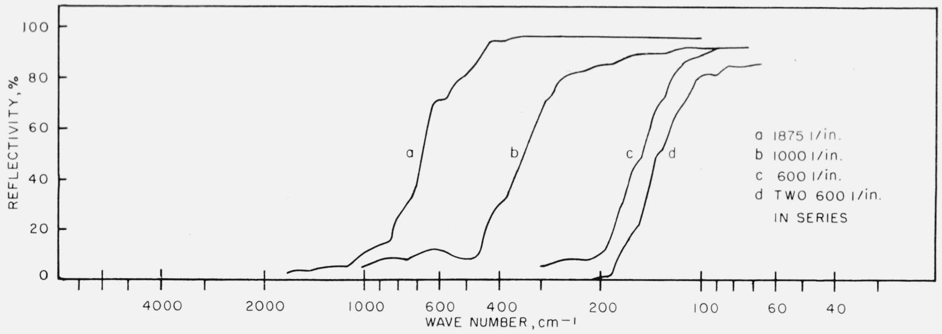

FIGURE 4. *Regular reflection of three gratings.*

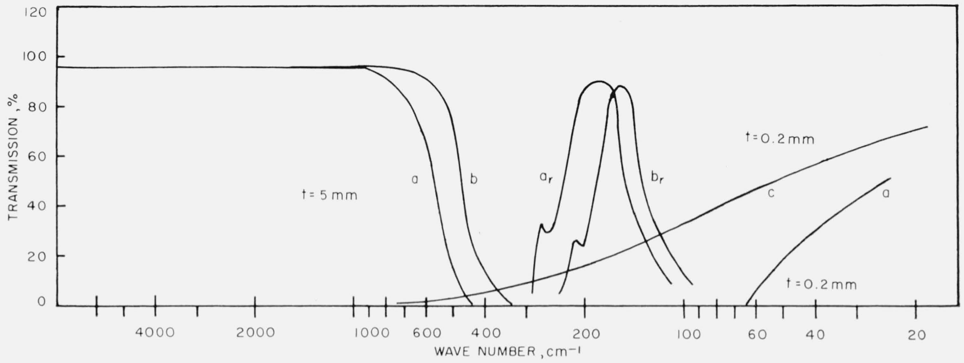

FIGURE 5. *Transmission and reflection properties.*

(a) NaCl, (b) KCl, (c) black polyethylene.

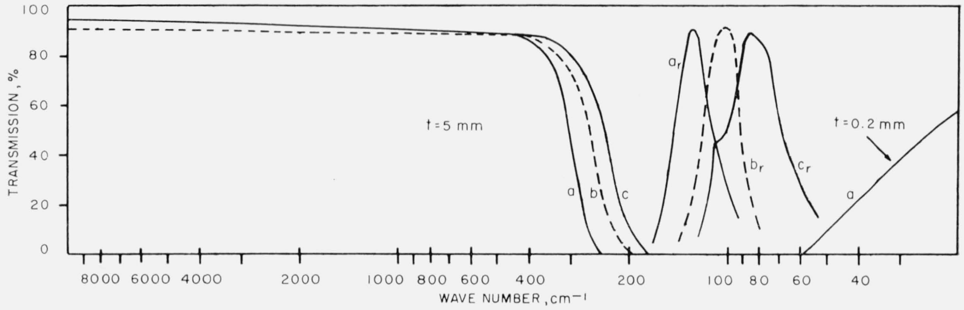

FIGURE 6. *Transmission and reflection properties.*

(a) KBr, (b) RbBr, (c) CsBr.

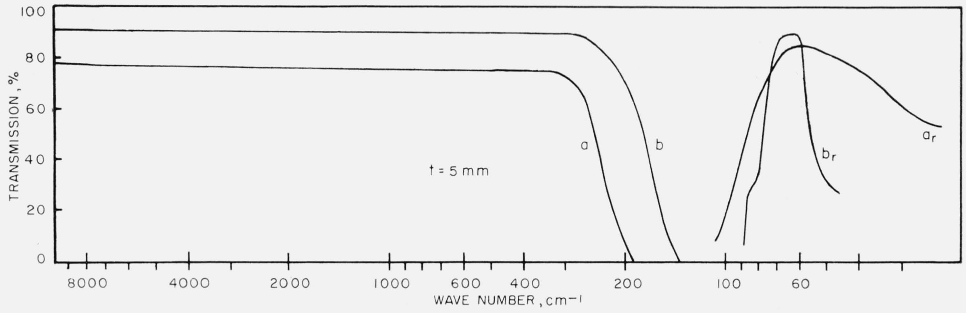

FIGURE 7. *Transmission and reflection properties.*

(a) KRS-5, (b) CsI.

Many of these crystals have a peak reflectivity of 90 percent and cover a reasonably narrow spectral interval.

In all cases the separation of spectral orders requires strategic use of the reflective, scattering, and transmissive properties of many materials. Figures 5, 6, and 7 give a sequence of transmission and reflection curves for a number of materials. They are arranged in order of their usefulness with respect to decreasing frequency.

3.3. Calibration and Measurement

Calibration is accomplished by measuring the pure rotation absorption spectrum of water vapor or other gases. Water vapor lines are obtained by reducing the flush rate of chambers C1 and C4. In the case of other gases (NH_3, HCl, HCN) a 5-cm absorption cell at the appropriate pressure is placed in the beam.

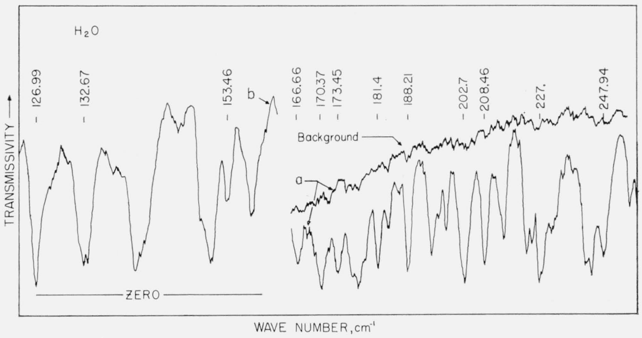

Figure 8. *Absorption spectrum of water vapor from 248 to 126 cm^{-1}.*

Conditions: (a) 600 1/in. dispersion grating, 0.05 mm black polyethylene, one NaCl reflection, one 1,800 1/in. scatter plate. (b) 320 1/in. dispersion grating, 0.1 mm black polyethylene, 0.5 mm crystal quartz, two 1,200 1/in. scatter plates.

First approximation measurements are made by applying the standard grating formula

$$\nu = \frac{n}{2d \cos \frac{1}{2}\alpha} \frac{1}{\sin \theta},$$

where ν is the wave number, d is the grating groove separation in cm, n is spectral order, and θ is the angular separation of the central image and the spectral line in question. The angle α is that angle subtended by the two slits at the center of the collimating mirror. The angle θ is determined by means of a rotation counter that is mounted in the gear train. A microswitch automatically activates a fiducial marker on the recorder every 500 counts. This system, without special calibration, will determine a relative frequency to 1 part in 1,000. A more accurate calibration is made by measuring the positions of several standard lines and from them determining an average central image position. By this procedure, and variations of it, frequencies of sharp symmetric lines can be measured to 1 part in 4,000. Figures 8 through 13 show recordings of the water lines between 200 and 30 cm^{-1}. Their latest accepted frequencies are indicated.[5] Figure 16 illustrates a case where the band to be measured has been bracketed by the calibrating lines. In this case a short air path was left unflushed before and after the band was recorded.

The task of measuring the center frequencies of the broad bands that are found in liquids and solids

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[5] Frequencies of pure rotational water lines were kindly supplied by Dr. W. S. Benedict. These are calculated values derived from the best available energy levels.

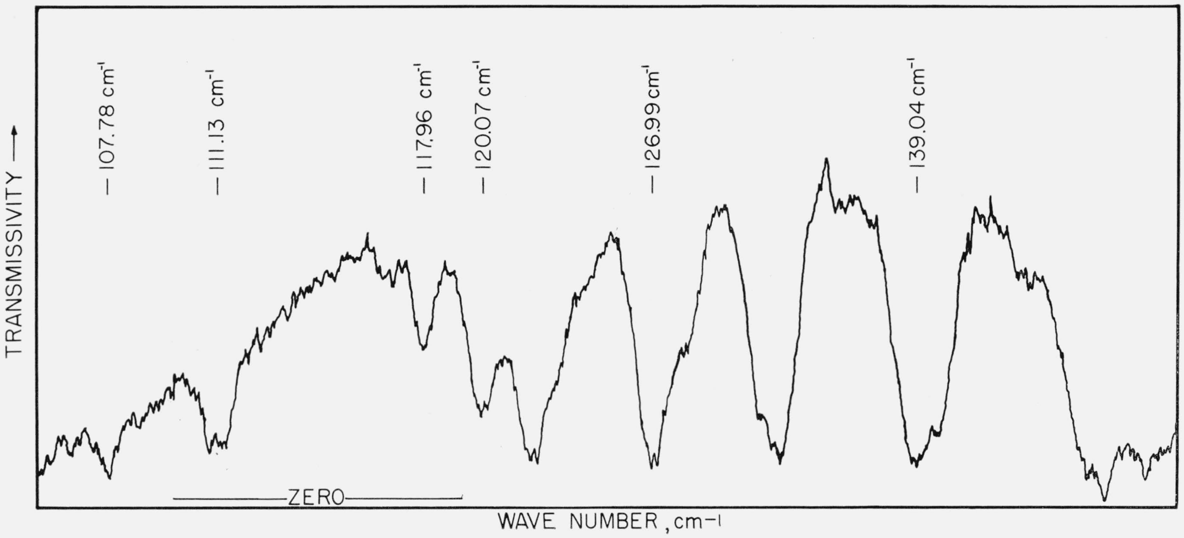

Figure 9. *Absorption spectrum of water vapor from 150 to 105 cm^{-1}.*

Conditions: 320 1/in. dispersion grating, 0.1 mm black polyethylene, 0.5 mm crystal quartz, one KBr reflection, one 600 1/in. scatter plate.

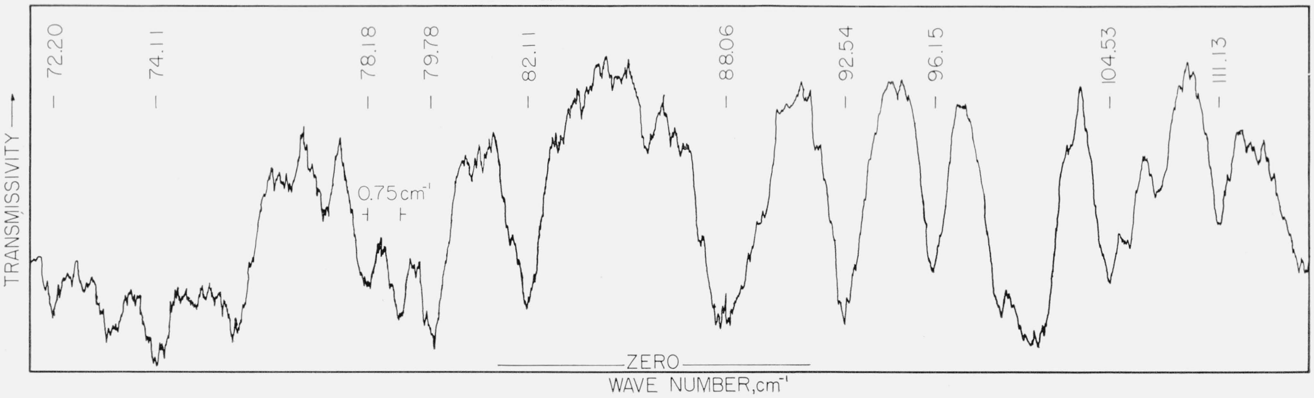

FIGURE 10. *Absorption spectrum of water vapor from 115 to 70 cm*$^{-1}$.

Conditions: 320 1/in. dispersion grating, 0.1 mm black polyethylene, 1.0 mm crystal quartz, one CsBr reflection, two 600 1/in. scatter plates.

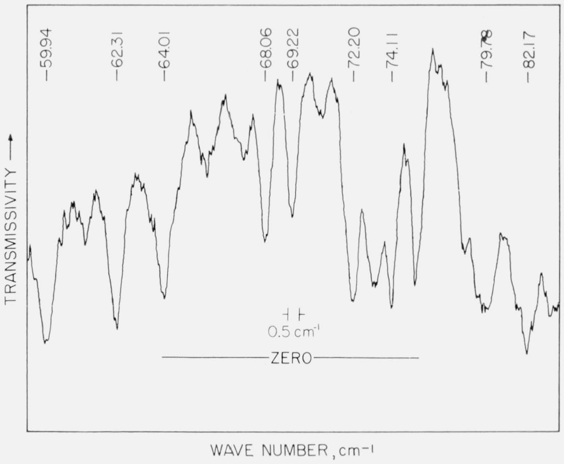

FIGURE 11. *Absorption spectrum of water vapor from 92 to 59 cm*$^{-1}$.

Conditions: 180 1/in. dispersion grating, 0.2 mm black polyethylene, 1.0 mm crystal quartz, one KRS-5 reflection, two 320 1/in. scatter plates.

presents a difficulty which greatly reduces the precision and accuracy of measurement. Those bands having widths[6] between 5 and 20 cm^{-1} are in general no problem except in that their width makes it impossible to determine their centers precisely. A special problem is presented by those bands having widths greater than 20 cm^{-1}. This is due to the fact that in regions where the reststrahlen of a crystal are a necessary part of the filtering technique, the energy contour is usually no wider than the absorption band to be measured. In many cases the band contour is never directly observed, but must be obtained by subtracting out the reststrahlen background. The band center is then measured from a plotted contour. This greatly reduces the attainable precision and accuracy.

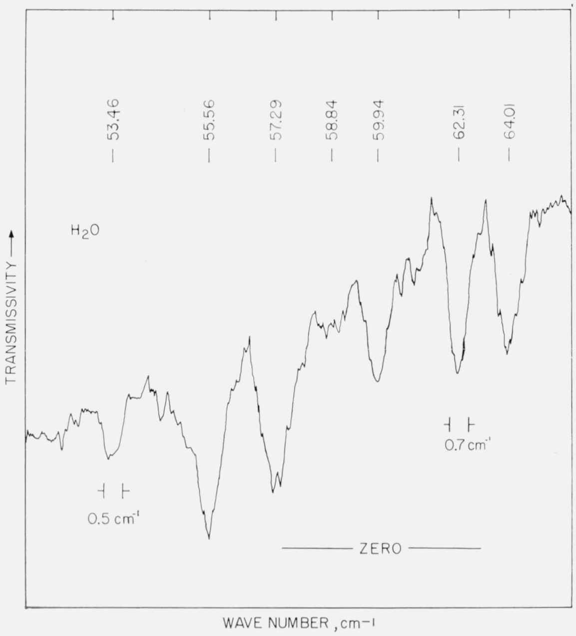

FIGURE 12. *Absorption spectrum of water vapor from 64 to 50 cm*$^{-1}$.

Conditions: 180 1/in. dispersion grating, 0.2 mm black polyethylene, 1.0 mm crystal quartz, 0.5 mm LiF, one KRS-5 reflection, two 320 1/in. scatter plates.

4. Observations and Measurements

In addition to the spectra of water vapor, the low lying absorptions of some haloethanes were observed. The compounds (Eastman Kodak) examined were of high purity. The high purity was affirmed by an examination of their infrared spectrum from 4,000 to 150 cm^{-1}.

The compounds observed were: pentachloroethane, 1-bromo-2-chloroethane, and symmetric-tetrachloroethane. The bands observed are listed in table 1. Those bands that were directly observable are shown in figures 14, 15, and 16 and are given to ±0.5 cm^{-1}. The lower frequency bands, however, were extremely broad (25 to 50 cm^{-1}) and are correspondingly less precise.

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[6] Line widths = full line width at half intensity.

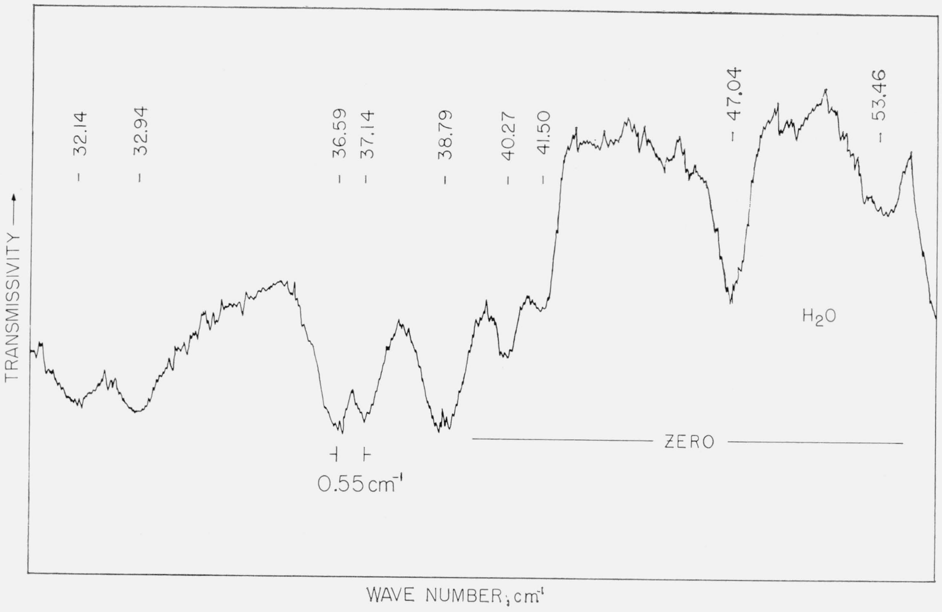

FIGURE 13. *Absorption spectrum of water vapor from 54 to 31 cm*$^{-1}$.

Conditions: 100 1/in. dispersion grating, 0.2 mm black polyethylene, 1.0 mm crystal quartz, 0.2 mm NaF-TlCl-polyethylene filter, one KRS-5 reflection, two 240 1/in. scatter plates. (This filter was kindly furnished by Hiroshi Yoshinaga of Osaka University in Japan.)

TABLE 1. *Observed bands of halogenated ethanes*

Compound	cm^{-1}
Cl_3C-$CHCl_2$	85. ±1.5 164.5±0.5 175.5±0.5
ClH_2C-CH_2Br	123. ±1.0 202.0±0.5
Cl_2HC-$CHCl_2$	87. ±1.0 172.0±0.5

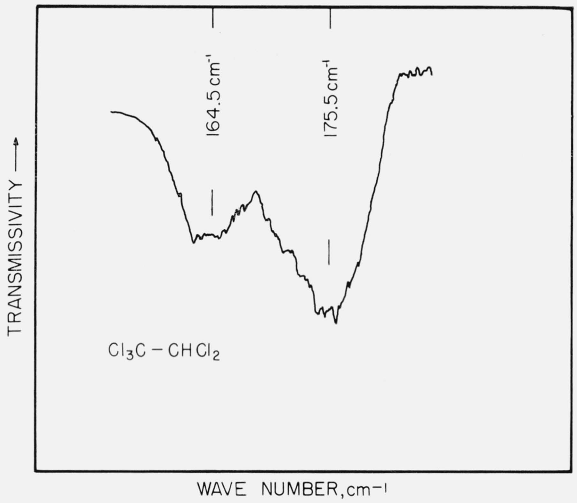

FIGURE 14. *Absorption of* Cl_3C–$CHCl_2$ *at 164.5 and 175.5 cm*$^{-1}$.

Cell thickness=1.5 mm; Concentration=1:3 (by volume) of compound in CCl_4.

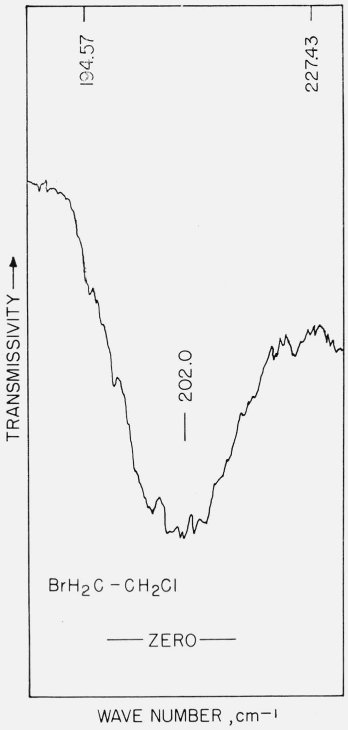

FIGURE 15. *Absorption of* BrH_2C–CH_2Cl *at 202 cm*$^{-1}$.

Cell thickness=1.5 mm; Concentration=1:30 (by volume) of compound in CCl_4.

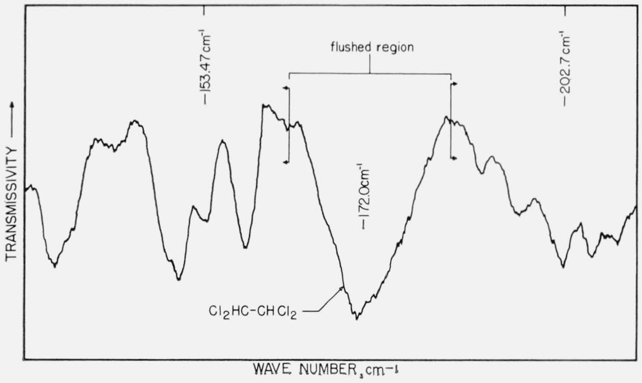

FIGURE 16. *Calibration of the 172.0 cm^{-1} absorption band of* Cl_2HC*-*$CHCl_2$*.*

Cell thickness = 1.5 mm; Concentration = 1:10 (by volume) of compound in CCl_4.

5. Discussion

The far infrared offers many challenging problems that must be solved before high quality data will be available from this spectral region.

Quality is judged first in spectral resolution and second in accuracy and precision of measurement. Using the high quality work produced in the near infrared as a guide, the goal would be a spectral resolution of 0.03 cm^{-1} and a precision of approximately 0.005 cm^{-1}. By using the scanning techniques presently used in the near infrared, it is feasible that the goal of precision could be attained. The goal of resolution however is more challenging.

Considering first an f/4.0 single pass optical system, using 12×8 in. high quality grating and a high quality collimating mirror, one would have a system capable of attaining the 0.03 cm^{-1} spectral resolution. Thus it is seen that the optical system does not represent the major obstacle. The highest resolution attained with grating spectrometers by recent workers is of the order of 0.25 cm^{-1}, which is a factor of about 8 less than that expected. In order to reduce the spectral width to the 0.03 cm^{-1} mentioned above, one would have to accept a loss by a factor of 64 in detector output. This deficiency must be made up by more powerful sources, more efficient filtering techniques, and more sensitive detectors.

A study of the high pressure mercury arc to determine the origin of its long wavelength emission could possibly lead to more efficient sources. Also research in plasmas, high temperature blackbodies, and emissivities should be profitable.

A small factor may possibly be realized in more efficient filtering methods. The use of the reststrahlen of crystals still remains the most dependable method at present. These, teamed with good gratings as scatter plates, should be highly efficient in eliminating stray radiant energy. The development of an automatic crystal and grating changer may prove to be not only the most convenient but also the most efficient solution.

By far, the greater effort will have to be applied to detector development. Presently work is being done on supercooled bolometers and related devices [3]. Indications are that factors of 40 could be expected in this area.

The problem of maintaining spectral purity in the far infrared coupled with that of measuring the centers of the very broad bands of many liquids could be solved by the construction of a large high vacuum double-beam–single-beam spectrometer having an automatic crystal and grating changer. An instrument built along these lines would serve as a valuable tool in far infrared research.

The author expresses thanks to E. K. Plyler for his cooperation and helpful discussions, and to W. Koepper and M. Myers for the machining and welding done on this instrument.

6. References

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(Paper 67C3–131)