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Infrared High-Resolution Grating Spectrometer

Earle K. Plyler and Lamdin R. Blaine

An infrared grating spectrometer which can be used as a single- or double-pass instrument has been built and set in operation. The collimating mirror has a focal length of 235 centimeters and the instrument has the highest resolution from 1,600 to 3,500 cm^{-1}. In order to have flexibility in scanning the spectra at different speeds, a special drive mechanism has been built which is made of spur gears and worm gears. The speeds range from 2.5 to 200 minutes of time per degree of rotation. Examples of the spectra resolved by the instrument are given. Lines separated by 0.05 cm^{-1} are completely resolved and two lines separated by 0.025 cm^{-1} are partially resolved.

1. Introduction

In recent years, cooled lead sulfide detectors have been made of high signal to noise ratio. By the use of these cooled PbS cells, much smaller slits can be used on the spectrometer and the diffracting grating may be the limiting factor in the resolution of the instrument. By double passing the radiation on a high-grade grating, a resolution approaching the theoretical resolving power has been obtained by Rank and his coworkers [1] in the region of 5,000 cm^{-1}. The instrument that is described in the present work is best suited for measurements in the region from 1,600 to 3,500 cm^{-1}, and partial resolution of 0.025 cm^{-1} has been obtained in this region.

2. Description of Instrument

A spectrometer has been designed which can be used as a single- or double-pass instrument. Two optical systems have been used for double passing the grating. One arrangement of the optical components is shown in figure 1. After the radiation has passed through the entrance slit it falls on an on-axis paraboloidal mirror (focal length 235 cm) and is rendered parallel. The mirror has a diameter of 16 in., and by using 7 in. on one side of the center it is effectively equal to a 3° off-axis system. From the grating, the parallel beam is intercepted by the optical flat and is reflected back to the grating where the beam almost retraces the incident path and falls on the second slit. The single-pass diffraction beam also falls on the second slit but its wavelength is slightly different from that of double-pass radiation. For the optical arrangement of figure 1, the dispersion is almost equal in the single- and double-pass spectra and is different only due to the inequality of the angle of the incident and reflected rays; and the wavelength regions are so close together that they cannot be separated by the transmission filters. In order to separate the two spectra, the optical flat is tilted a few minutes of arc from the vertical so that the two spectra are focused on the second slit with one above the other. The exit slit is then masked so that only the double-pass spectrum reaches the detector. When the instrument is used single pass, the optical flat is screened and the mask on the second slit is removed. The receiving surface of the lead sulfide cell is 2.5 by 0.2 mm and the radiation on 18 mm of the height of the slit is detected by the use of an ellipsoidal mirror giving a 7 to 1 reduction of image size.

[1] J. N. Shearer, T. A. Wiggins, A. H. Guenther, and D. H. Rank, J. Chem. Phys. **25**, 924 (1956).

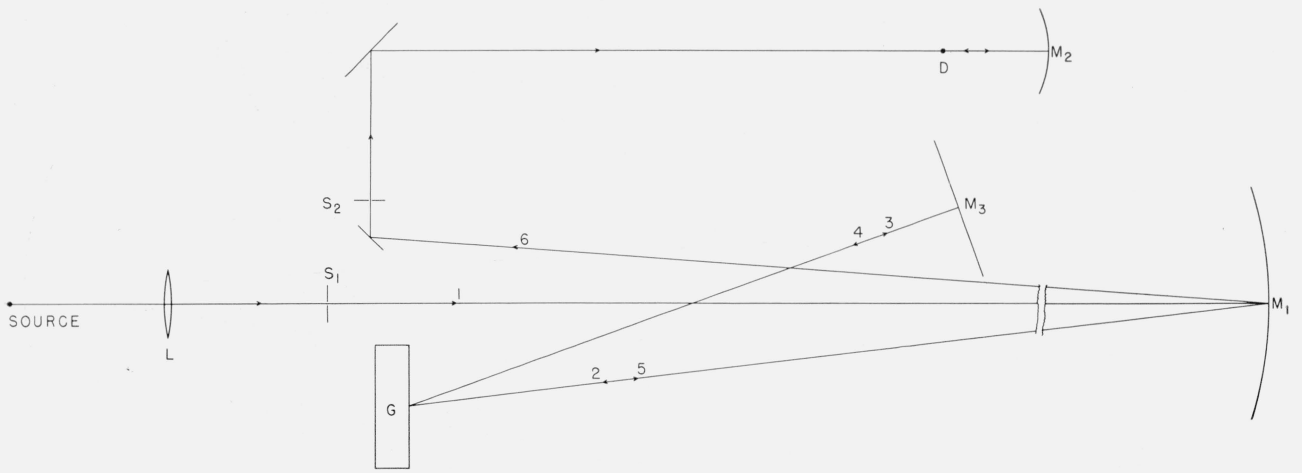

FIGURE 1. *The optical arrangement for the double-pass spectrometer using an optical flat* M_3.

M_1 is a paraboloidal mirror of 235 cm^{-1}, and M_2 is an ellipsoidal mirror with foci of 15 and 105 cm^{-1}.

The second optical system for double passing the radiation is shown in figure 2. The essential part of this system is the two small plane mirrors behind the entrance slit which send the energy back to the grating the second time. In order to remove the single-pass radiation, the beam is chopped in front of one of the small 45° mirrors. In this system the dispersion is, for all practical purposes, identical to its single-pass dispersion as the angle of the incident and reflected radiation are practically equal. The image on the second slit for single pass is curved. The two mirrors reverse the image and its curvature so that the double-pass image on the second slit is approximately straight.

In addition to the optical parts of the spectrometer, a number of auxiliary components are used. These consist of sources, filters, absorption cells, Fabry-Perot interferometers, PbS and PbTe photodetecting cells, amplifiers, and recorder. From 1 to 3.6 μ, a 300-w Sylvania enclosed zirconium arc is used for the source, and from 3.6 to 6 μ, a Nernst glower is used. In order to remove the higher order spectrum, transmission filters are set into the path of the radiant energy in front of the entrance slit of the spectrometer. A silicon filter is used from 1.2 to 2 μ, a germanium filter from 2 to 3.5 μ, and transmission filters made by Baird-Atomic from 3.5 to 6 μ. The filters transmit about 90 percent of the energy and are used instead of a foreprism arrangement. The absorption cell is 1 m in length and with the use of mirrors a 6-m path is obtained. Fluorite windows are used and the transmission of the cell for the 6-m path length is about 75 percent.

The spectrum is recorded on a two-pen recorder. One pen is used for the interferometer fringe system and the other pen records the absorption spectrum. The method of measuring the spectra from the charts has been described previously.[2] A disk chopper is used to modulate the radiation at 90 cps. The radiation falling on the cooled PbS cell is amplified by a 90-cps Wilson narrow-band-pass type amplifier[3] of low noise level. The spectrum is scanned by rotating the grating and for the highest resolution slow speeds are required. For example, in the region of 3,020 cm^{-1}, about 30 min of time is required to scan one wavenumber for the best formation of the lines. In order to adequately survey different regions of the spectrum under different levels of resolution a versatile drive system is desirable. A large number of speeds are possible by use of a gear box between the motor and the worm gear attached to the grating mount. A synchronous motor of 900, 1,800, and 3,600 rpm of about 1/30 hp is attached to a 10-to-1 reduction gear, which drives a four-speed gear box with reductions of 1 to 4, 1 to 1, 3 to 1, and 5 to 1. The gear box is reduced by a 60-to-1 precision worm, which then drives a pair of precision worms on the grating turn table which have reductions of 120 to 1, and 180 to 1. This arrangement of gears makes it possible to rotate the grating mount at 12 different speeds, the fastest speed being 2.5 min of time per degree of rotation and the slowest being 200 min/deg. Additional speeds which are faster and slower than those described above, can be obtained by changing the gears in the first reducer.

The uniformity of rotation of the system has been checked by the regularity of interference fringes of about 0.3-cm^{-1} spacing. The variation of the distance between successive fringes is less than 4 percent, which indicates that the irregularities of the drive do not introduce errors in measurement greater than 0.006 cm^{-1}. For rapid scanning or for moving from one spectral region to another, an auxiliary motor of 1,800 rpm can be automatically coupled directly to the output of the transmission gear box, which provides a rotational speed of 1° per half minute of time.

[2] Earle K. Plyler, L. R. Blaine, and E. D. Tidwell, J. Research NBS **55**, 279 (1955) RP2630.

[3] R. C. Nelson and W. R. Wilson, Proc. Nat. Elec. Conf. 3 (1947).

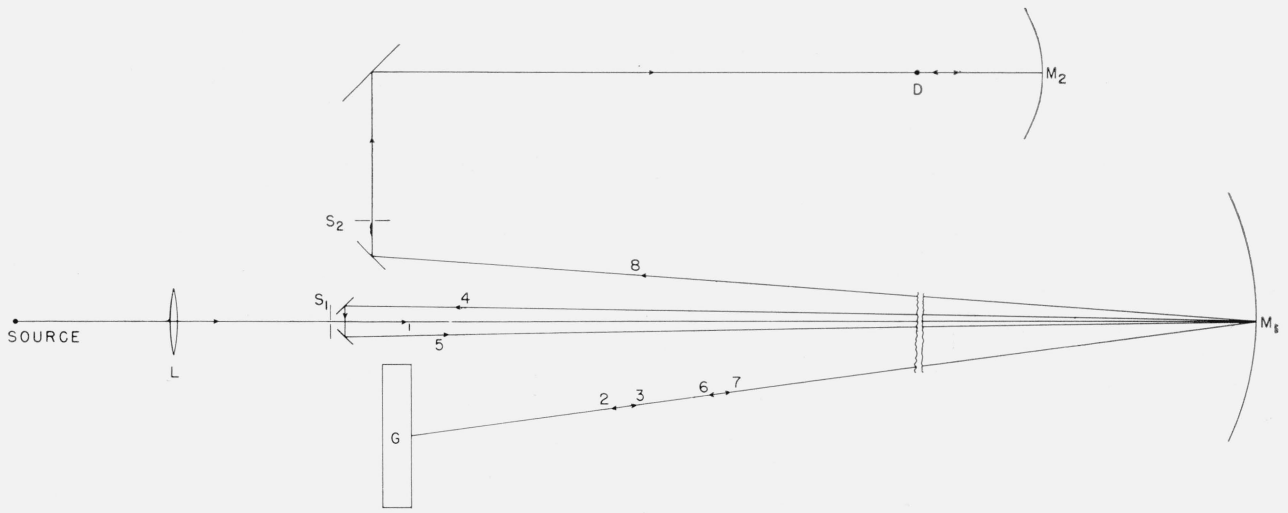

FIGURE 2. *The optical system for double pass using two small mirrors behind the entrance slit.*

The other mirrors are the same as those represented in figure 1.

3. Examples of Spectra Measured

The spectrometer has been in operation for about a year and some bands of several molecules such as methane, ethylene, ethane, ammonia, and cyclopropane have been measured. The classification of these spectra and the calculation of the molecular constants are now being made and the results will be given in other publications.

Some examples of the high resolution obtained by the instrument are given of parts of bands observed with slow scanning speeds. Figure 3 shows the P13 lines of methane as observed with a 10,000 lines/in. Bausch and Lomb grating using the optical system represented in figure 1. The pressure used was 0.1 mm (Hg) and the path length was 6 m. As the resolution of the instrument is increased, lower pressures of the gas can be used. When the P–13 transition of methane was measured on a single-pass spectrometer the last three lines were not so well separated and for the same maxima of absorption about 1 mm (Hg) pressure was necessary. The last two lines are separated by 0.055 cm^{-1} and the line widths at half intensity are about 0.023 cm^{-1}.

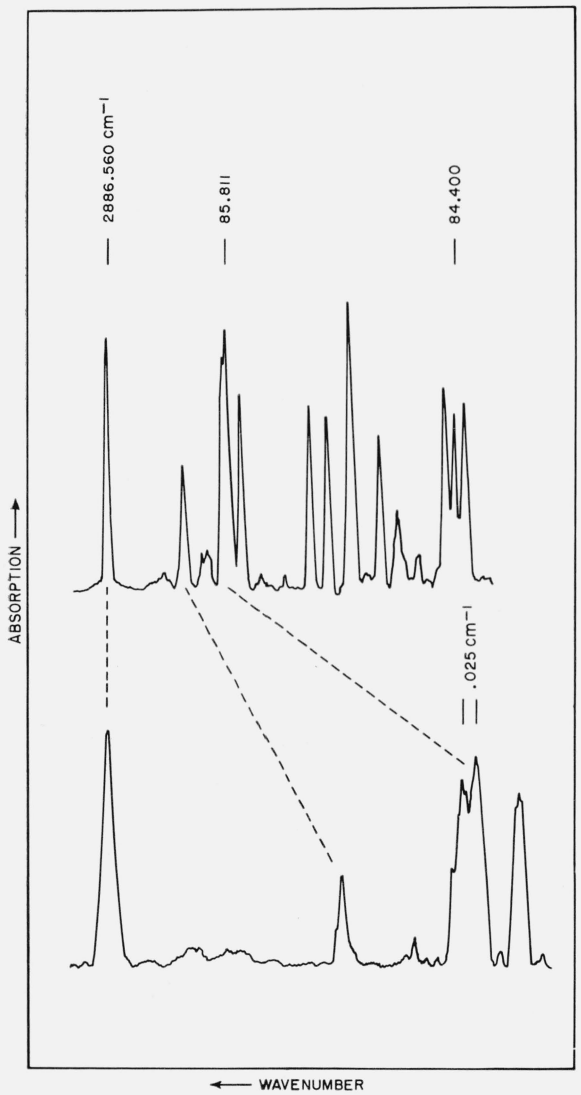

FIGURE 3. *The fine structure of the P13 line of the ν_3 band of methane.*

The lower curve is a part of the P13 line of methane scanned at the slowest rate of the drive. The two partially resolved lines are separated by 0.025 cm^{-1}. The pressure was 0.1 mm (Hg) and the path length 6 m. A grating with 10,000 lines/in. was used.

The lower part of the figure shows a slower scan (one-third speed) of several lines of the upper spectrum. The separation of the two partially resolved lines is 0.025 cm^{-1}. It is believed that the optical system is capable of still higher resolution, but until the noise of the electronics and the detector is reduced, the limit of resolution of the gratings and the optics cannot be determined.

An example of pressure broadening is shown in figure 4. Part of the ν_3 band of ammonia at 3,500 cm^{-1} overlaps the atmospheric absorption lines of water vapor. The width of the water vapor lines is about 0.15 cm^{-1} and the observed width of the ammonia lines at 2-mm pressure (Hg) is 0.03 cm^{-1}. On account of the large difference in line widths of the two substances it is easy to identify the two spectra. The spectra shown in figure 4 were observed with a Babcock 15,000 lines/in. grating which had a total of 120,000 lines.

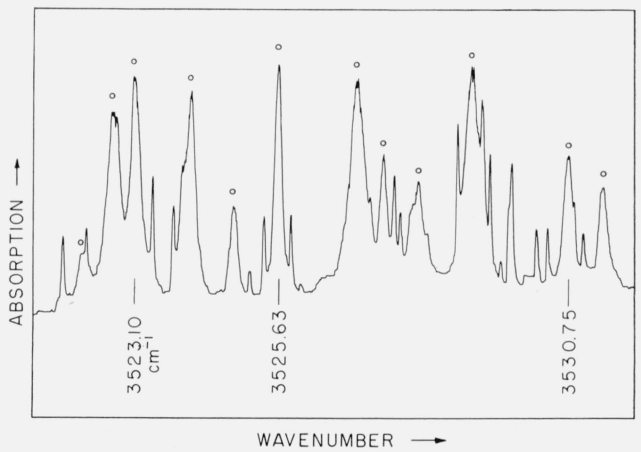

FIGURE 4. *The absorption spectrum of ammonia 2 mm* (Hg) *pressure, in the region of* 3,500 cm^{-1}.

The broad lines, marked with a circle over them, are produced by the atmospheric absorption of water vapor.

The actual limit of resolution of the instrument at the present time under the best conditions appears to be about 0.02 cm^{-1}. Larger gratings or more sensitive detectors, or both, will be required to make a further improvement in resolution.

The authors are indebted to Horace Babcock for making available to them one of his 15,000 lines/in. gratings.

WASHINGTON, September 29, 1958.