

# INTERFERENCE SPECTROSCOPY AND SOME OF ITS APPLICATIONS IN THE FAR INFRARED AND IN THE NEAR INFRARED

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## INTRODUCTION

The use of interference techniques in spectroscopy in the visible and ultra-violet is familiar through the use of the Fabry Perot apparatus and the Lummer plate to investigate the fine structure of a few lines within a narrow range of a spectrum produced by a prism or grating. The method of interference spectroscopy to be described here requires no prism or grating as a dispersing element. Instead, a Michelson interferometer produces an interferogram which is converted into a conventional spectrum by a digital computer and some ancillary equipment. The apparatus described here was developed at the National Physical Laboratory by Dr H. A. Gebbie, and the work described is entirely due to him and his associates.

The original idea of producing an interferogram and deriving the spectrum from it by harmonic analysis is due to Michelson<sup>1</sup>. Some crude experiments were made over 50 years ago by Rubens and Wood<sup>2</sup> in the far infrared (150 to 200 microns). Fellgett<sup>3</sup> was largely responsible for reviving interest in this method, stressing particularly the advantages to be gained from processing all wavelengths simultaneously instead of scanning them successively as in the conventional spectrometer. The theory of this method of interference spectroscopy has been most carefully investigated by Jacquinot<sup>4</sup> who has shown very clearly that (in common with several other methods of interference spectroscopy) one of its greatest advantages is the high luminosity or light gathering power. It is this factor which makes such spectrometers attractive for absorption spectra in the far infrared or emission spectra from low temperature sources in the near infrared.

## PRINCIPLES

The principle of the method is best understood by reference to a diagram of the apparatus (*Figure 1*). Radiation from a source is made parallel by a mirror and falls onto a beam splitter to form the two beams of a Michelson interferometer. These beams are recombined on the detector, which in the NPL apparatus is a Golay cell for the far infrared and a photoconductive cell for the near infrared. Suppose that the incident radiation is monochromatic and the path difference between the two beams is zero, the detector then records a maximum of energy, and, if one of the mirrors is slowly moved, a series of maxima and minima would be recorded by the detector,

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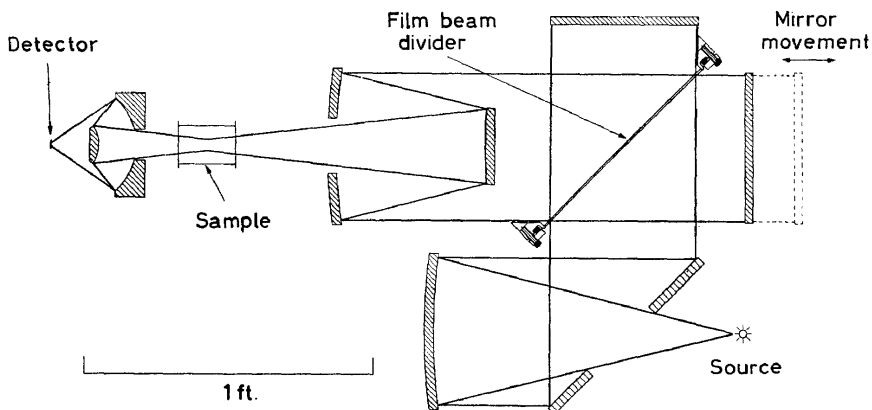


Figure 1. Plan of Michelson interferometer arrangement for infrared spectroscopy

as in Figure 2a. If the incident radiation consists of a doublet, then the interferogram (intensity at the detector *v.* path difference between the two beams) would be as shown in Figure 2b or 2c.

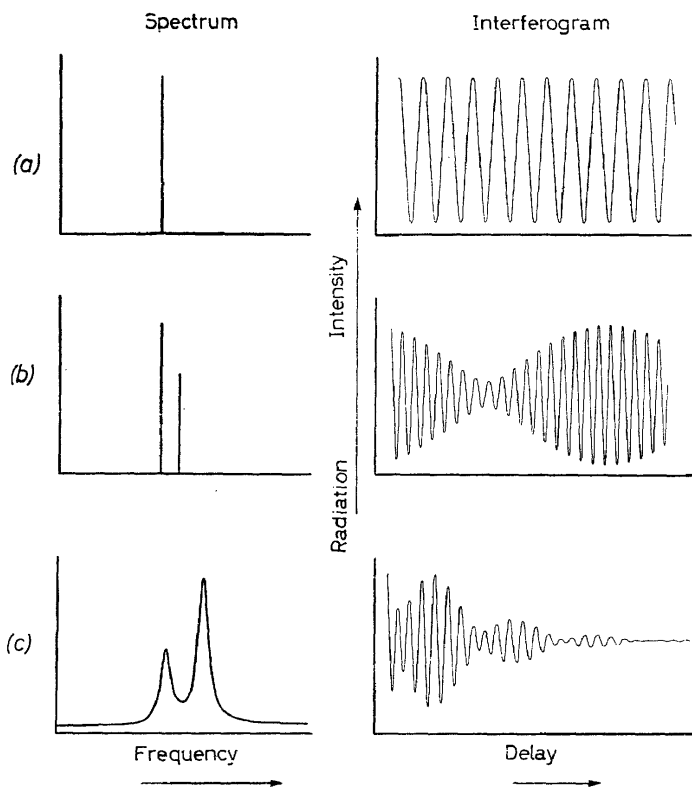


Figure 2. Interferograms of line spectra: (a) top pair for single monochromatic line; (b) middle pair for two monochromatic lines; (c) lowest pair for two lines which are not quite monochromatic

## INTERFERENCE SPECTROSCOPY

The interferogram is in fact the Fourier transform of the required spectrum. Mathematically, this is expressed by the following transformation for the spectral intensity  $G(k)$  at frequency  $k$  (in  $\text{cm}^{-1}$ )

$$G(k) = \sum_0^X I(x) \cos 2\pi kx \Delta x \quad (1)$$

Where  $I(x)$  is the intensity at the detector for a path difference of  $x$  (in cm) between the two beams, and  $X$  is the maximum path difference (in cm).

This last quantity is a primary factor in determining the resolving power of the instrument, as it is in all forms of spectroscopy. Jacquinot<sup>4</sup> has shown that the maximum resolving power  $R_0$  is given by

$$R_0 = \frac{k}{\Delta k_0} = \frac{X}{\lambda} \quad (\lambda \text{ in cm}) \quad (2)$$

It follows that the limit of spectral resolution  $\Delta k_0$  (in  $\text{cm}^{-1}$ ) is given by

$$\Delta k_0 = \frac{1}{X} \quad (3)$$

Thus, to resolve two lines differing in frequency by  $0.5 \text{ cm}^{-1}$ , it is necessary to record the interferogram while the movable mirror increases the path difference between the two beams from 0 to 2 cm.

In order to perform the summation of the Fourier series, it is necessary to decide on the sampling interval  $\Delta x$  for  $I(x)$ . This is obviously related to the highest frequency in the spectral range being investigated, since the fringe system becomes finer the higher the frequency of the incident radiation. The maximum sampling interval  $\Delta x_m$  is given by

$$\Delta x_m = \frac{1}{2k_0} \quad (4)$$

where  $k_0$  is the highest frequency in which we are interested. This frequency is determined by the problem under investigation and is controlled by a high frequency cut-off filter introduced at some convenient part of the apparatus. Thus, if a spectrum is to be investigated over a range from 0 to  $k_0 \text{ cm}^{-1}$  with a spectral resolution of  $\Delta k_0$ , the minimum number of sampling points,  $N$ , at which  $I(x)$  has to be measured is given by

$$N = \frac{X}{\Delta x_m} = \frac{2k_0}{\Delta k_0} \quad (5)$$

For the range 0 to  $500 \text{ cm}^{-1}$  and a spectral resolution of  $1 \text{ cm}^{-1}$ , this means 1000 points. However, in the near infrared, *e.g.* the range  $5000$  to  $7000 \text{ cm}^{-1}$ , the minimum number of points would be 4000 for the same resolution. It is obvious that the Michelson interferometer is not a practicable proposition for general spectroscopic work in the visible and ultraviolet regions, although it could be used over very narrow ranges of wavelength.

There is one other factor which is very important in the performance of a Michelson interferometer as a spectrometer, *viz.* the admissible solid angle, since this is what really limits the resolving power of the instrument. From (3) above, it might appear at first sight that the resolving power is unlimited since there is no physical obstacle to increasing  $X$  indefinitely. However, because the interferometer must have a finite aperture (if it is to admit any radiation at all), the path difference will be slightly different for two rays entering the interferometer from the extreme edges of the aperture, even when the mirrors are set to give no path difference for a ray from the centre of the aperture. As  $X$  becomes larger, this path difference due to the finite aperture must eventually set a practical limit to the resolving power which can be achieved.

Jacquinet<sup>4</sup> has shown that the relation between the admissible solid angle  $\Omega$  and the maximum resolving power  $R_0 = X/\lambda$  is given by

$$\Omega R_0 = 2\pi \quad (6)$$

Thus, if we attempt to increase  $R_0$  by increasing  $X$ , then the aperture has to be reduced by reducing  $\Omega$ .

Combining (6) and (2), we obtain

$$\Omega = \frac{2\pi\Delta k_0}{k_0} \quad (7)$$

Note that  $\Omega$  is determined not only by the spectral resolution  $\Delta k_0$  but also by the highest frequency in which we are interested, since the aperture must be set for the highest frequency, *i.e.* the closest fringe system. An alternative way of writing (7) is to express the resolving power in terms of the physical constants of the apparatus, thus

$$R_0 = \frac{k_0}{\Delta k_0} = \frac{2\pi}{\Omega} = \frac{2\pi f^2}{\pi r^2} = 2\left(\frac{f}{r}\right)^2 \quad (8)$$

where  $r$  is the radius of the exit pupil and  $f$  is the focal length of the focussing mirror of the interferometer.

It should be added that in the above discussion a convention has been used in defining the resolving power. In practice, the resolving power can be made a little higher by apodization<sup>4, 5</sup>.

### SOME PRACTICAL POINTS

Descriptions of the NPL apparatus for the long wave region have been given by Gebbie<sup>5, 6</sup> and for the near infrared by Gebbie *et al.*<sup>7</sup>.

In the instrument for the far infrared,  $f$  and  $r$  (equation 8) are respectively 10 cm and 0.15 cm giving a maximum theoretical resolving power of nearly 9000 at 500  $\text{cm}^{-1}$ . In practice, the highest resolving power so far attained is about 1000, *i.e.* a spectral resolution of about 0.1  $\text{cm}^{-1}$  near 100  $\text{cm}^{-1}$  (Figure 3). There have been so many interesting problems to investigate in which it was quite unnecessary to have a resolving power of much more than

# INTERFERENCE SPECTROSCOPY

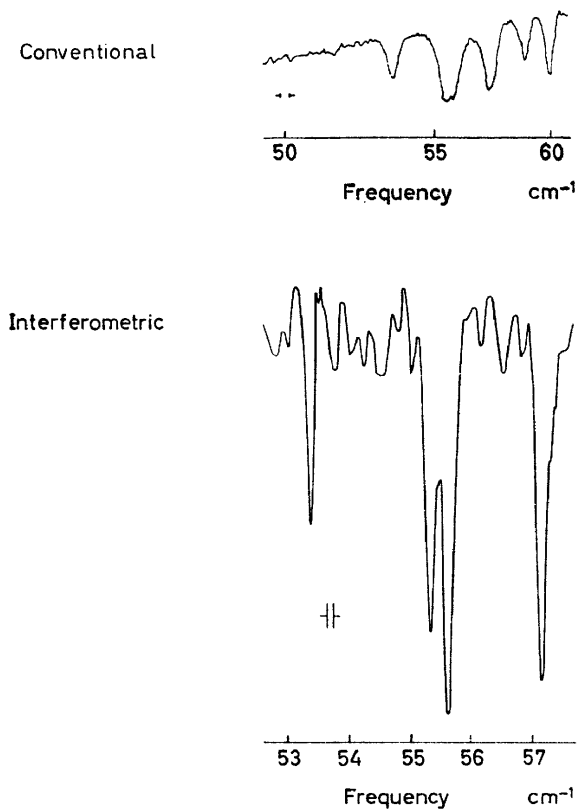


Figure 3. Resolution of lines in the pure rotation spectrum of water vapour

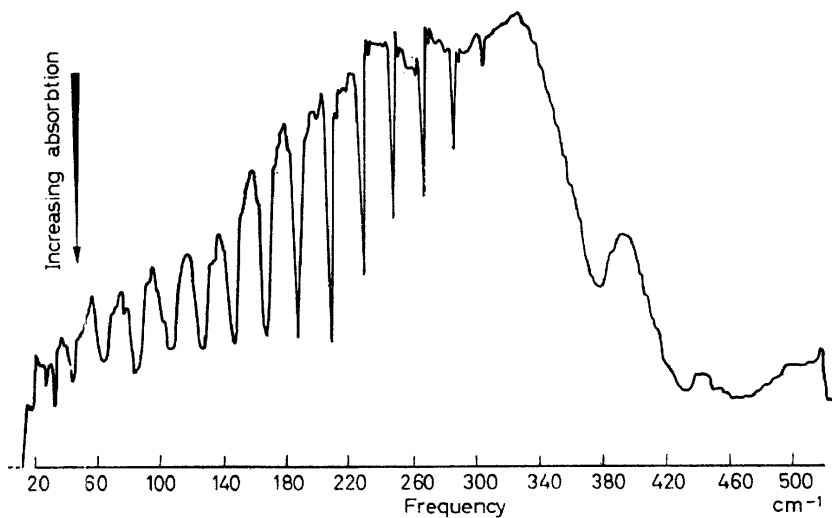


Figure 4. Pure rotation spectrum of gaseous HCl (the bands above  $350 \text{ cm}^{-1}$  are due to the material used for the beam divider)

1000 that we do not yet know the practical limit of this apparatus. The most valuable property of the interference spectrometer is the capacity to cover the range from  $20\text{ cm}^{-1}$  to over  $400\text{ cm}^{-1}$  in one run with a spectral resolution of about  $4\text{ cm}^{-1}$  (*Figure 4*). The time occupied in obtaining the interferogram is then about 20 minutes and the time for the conversion of the interferogram (in the form of punched tape) to a plotted spectrum by the NPL ACE computer is about 3 minutes. The limiting factor in this operation is the speed of the Brown recorder on which the curve is plotted. The computer time could probably be reduced by a factor of nearly 10 if an IBM 7090 computer were used. The cost of computer time is therefore not a major factor for institutions which possess reasonably modern computers.

In one of the instruments for the near infrared ( $1000$  to  $10,000\text{ cm}^{-1}$ ) the optical path difference can be as great as  $30\text{ cm}$  giving the possibility of resolving power of  $300,000$ . In the other, the maximum path difference is  $1\text{ cm}$  with a corresponding limit of  $10,000$ .

## APPLICATIONS

A few examples will now be given of the application of this type of interference spectroscopy to various spectroscopic problems.

### Methyl alcohol

The far infrared spectrum of methyl alcohol is of particular interest because of the phenomenon of hindered rotation of the OH group about the main symmetry axis of the molecule. In spite of much previous work in other regions of the spectrum, the absence of any data for the range  $20$  to  $50\text{ cm}^{-1}$  and the inadequacy of the existing data for the range  $50$ – $70\text{ cm}^{-1}$  made an investigation of the spectrum of methanol vapour between  $20\text{ cm}^{-1}$  and  $80\text{ cm}^{-1}$  very desirable.

The spectrum was obtained without serious difficulty with a spectral resolution of about  $0.25\text{ cm}^{-1}$ . It is illustrated in *Figure 5*. The discussion of this spectrum has been given by Gebbie *et al.*<sup>8</sup>

### Lattice vibrations in solid hydrogen halides

A similar situation existed here in that no observations had been made on the spectra of the hydrogen halides in the crystalline state below about  $300\text{ cm}^{-1}$ . This meant that interpretations of the partial spectra were tentative. In *Figure 6* are shown the spectra of HCl and HBr between  $20\text{ cm}^{-1}$  and  $340\text{ cm}^{-1}$ . The low frequency doublets between  $40$  and  $110\text{ cm}^{-1}$  are particularly interesting as these were quite unpredictable. It will be noticed that they are unaffected at the transition temperature, in contrast to the higher frequency doublet near  $250\text{ cm}^{-1}$ . These spectra have been discussed in a preliminary way by Anderson *et al.*<sup>9</sup>.

### Pressure broadening in the pure rotation spectrum of HCl

Studies have been made of the effect of pressure on the shape and position of the first five lines in the pure rotation spectrum of HCl. The partial pressure of HCl was  $40\text{ mm}$  of Hg while helium, argon, krypton and xenon were used as perturbing gases with pressures ranging between  $7$  and  $40$

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## Far i.r. spectrum of methanol

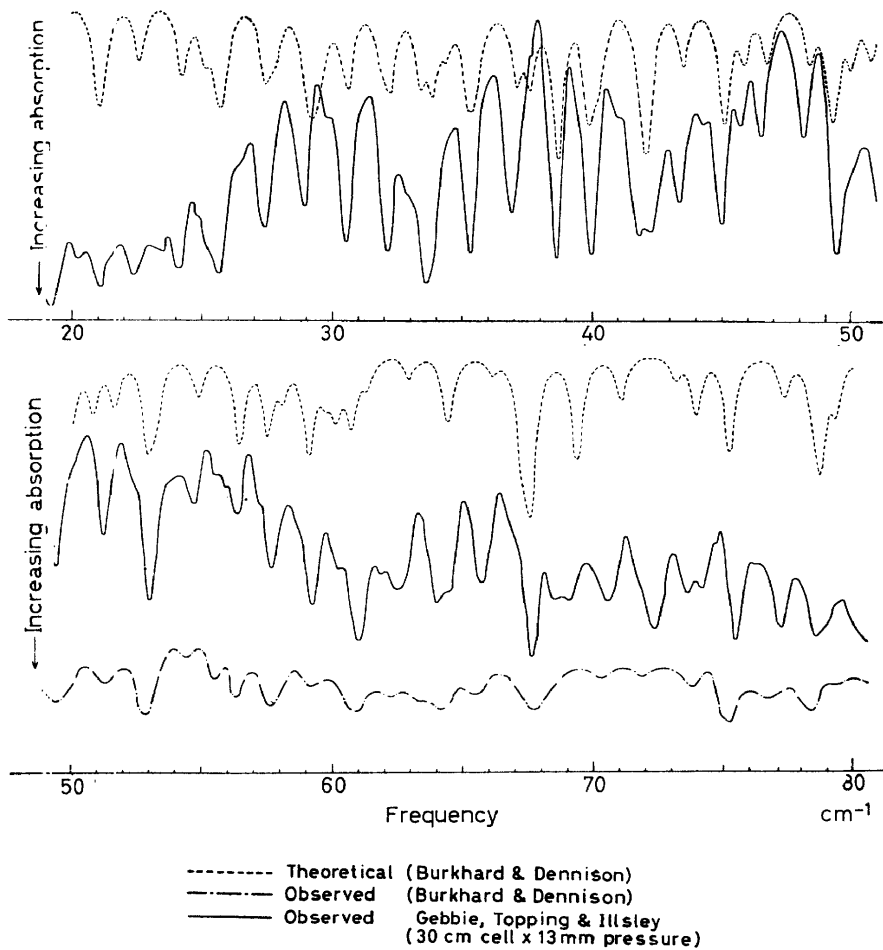


Figure 5. Part of the far infrared spectrum of methanol

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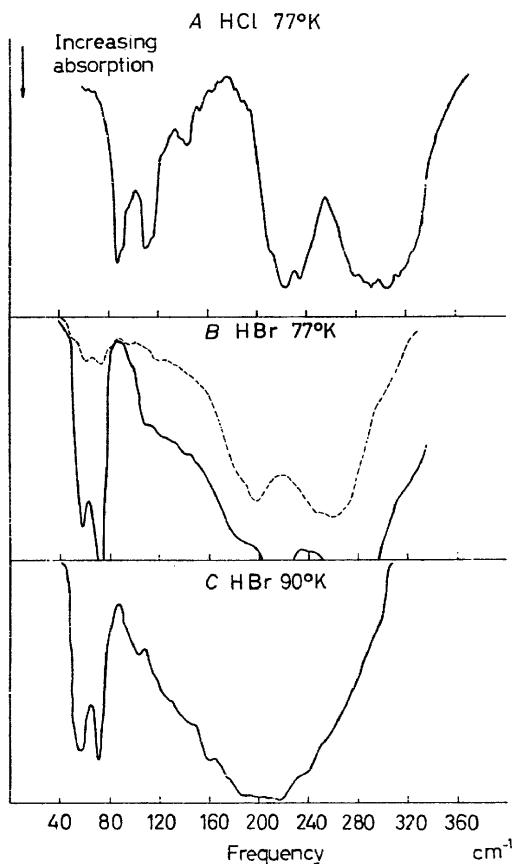


Figure 6. Spectra of solid HCl and HBr

atmospheres. In *Figure 7* are shown results on the  $J = 0$  to  $J = 1$  line broadened with krypton at 15 atmospheres. The shift in the centre of the line is about  $0.013 \text{ cm}^{-1}$  per atmosphere<sup>10</sup>.

### Pressure-induced absorption in nitrogen

It has been known for some time that vibration spectra in the infrared can be obtained from homo-nuclear molecules,  $X_2$ , by compressing them sufficiently to induce dipole moments during the collision process. Less familiar are the corresponding pure rotational spectra of such molecules occurring in the far infrared. A study has been made of such a spectrum for  $N_2$  at 120 atmospheres by Gebbie *et al.*<sup>11</sup>. It is illustrated in *Figure 8* which shows a broad band extending from  $20 \text{ cm}^{-1}$  to about  $250 \text{ cm}^{-1}$ . The spectral resolution was  $2 \text{ cm}^{-1}$  and no sign of rotational structure was found, although the spacing predicted is  $8 \text{ cm}^{-1}$  for a selection rule of  $\Delta J = 2$ .

### Far infra spectra of various molecules

In collaboration with the National Chemical Laboratory studies have been

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$J$  0 $\rightarrow$ 1 LINE OF HCl

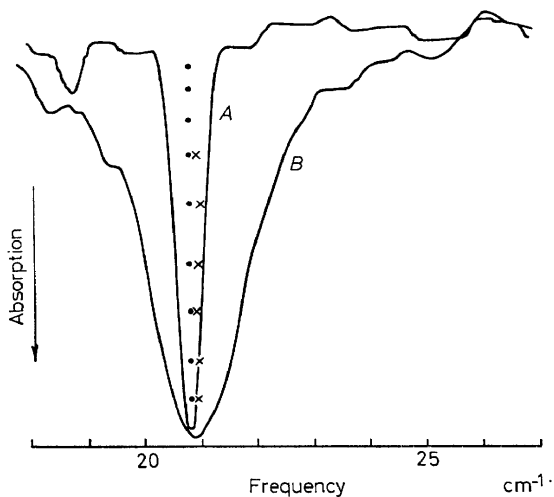


Figure 7. Broadening of the first line in the pure rotation spectrum of HCl under pressure of a foreign gas

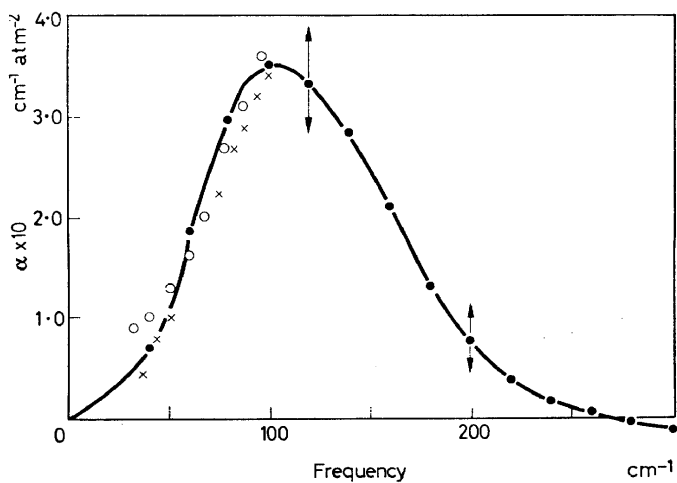


Figure 8. Pressure-induced pure rotation spectrum of nitrogen

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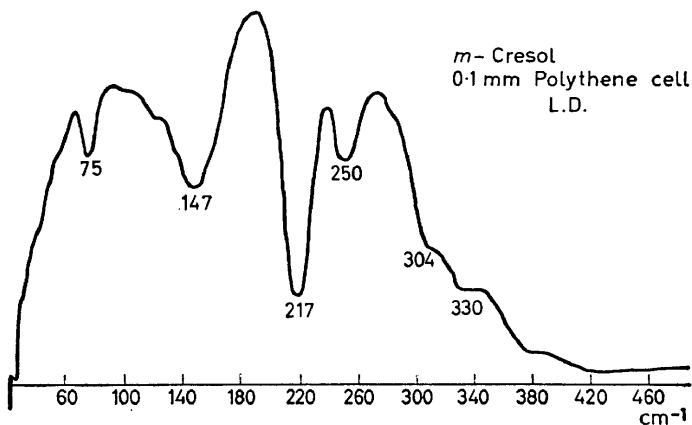


Figure 9. Far infrared spectrum of *m*-cresol

PART OF  $\nu_2$  BAND OF NH<sub>3</sub> IN EMISSION

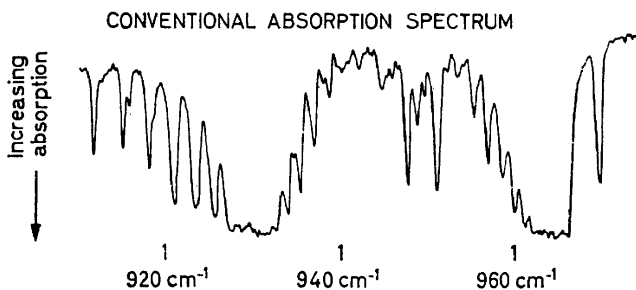
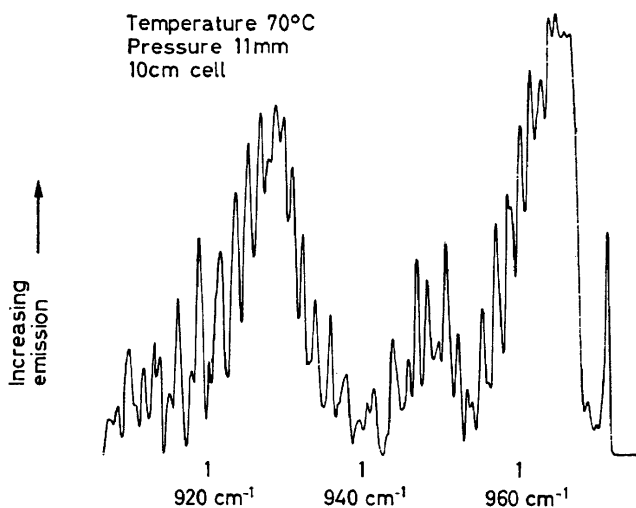


Figure 10. Part of the emission spectrum of ammonia with the corresponding absorption spectrum

## INTERFERENCE SPECTROSCOPY

made of the spectra of a number of liquid organic compounds in the range between  $20\text{ cm}^{-1}$  and  $500\text{ cm}^{-1}$ . Such studies are valuable in completing frequency assignments and also in investigating hydrogen bonding. In *Figure 9* is shown the spectrum of *m*-cresol in which the broad band near  $150\text{ cm}^{-1}$  is probably connected with hydrogen bonding<sup>12</sup>.

A special class of inorganic compounds, *viz.* those involving metal—halogen bonds have also been studied very profitably in the far infrared<sup>13</sup>.

### Emission spectrum of ammonia

The emission spectrum from ammonia gas at a temperature of  $70^\circ\text{C}$  has been recorded with a spectral resolution of less than  $0.4\text{ cm}^{-1}$  (*Figure 10*). The spectral resolution is probably close to  $0.1\text{ cm}^{-1}$  but the pressure of the gas (11 mm) makes it impracticable to achieve this figure because of line broadening<sup>14</sup>.

### Planetary spectra

The spectrum of the solar radiation reflected from Venus has been recorded between 1.2 and 2.5 microns, showing part of the vibration rotation spectrum of  $\text{CO}_2$ <sup>15</sup>.

### Luminescence spectra

The spectrum of the luminescence from uranium doped calcium fluoride (a laser material) has been obtained<sup>16</sup> in the region of 2.2 microns with a spectral resolution of about  $10\text{ cm}^{-1}$ .

The foregoing examples should make it clear that interference spectroscopy based on the Michelson interferometer is a practical and powerful method for the infrared region of the spectrum.

*I am much indebted to Dr H. A. Gebbie and his colleagues for allowing me to quote some of their results in advance of publication.*

### References

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