



Spectroscopy at Extreme Infra-Red Wavelengths. I. Technique

D. Bloor; T. J. Dean; G. O. Jones; D. H. Martin; P. A. Mawer; C. H. Perry

Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, Vol. 260, No. 1303 (Mar. 21, 1961), 510-522.

Stable URL:

<http://links.jstor.org/sici?sici=0080-4630%2819610321%29260%3A1303%3C510%3ASAEIWI%3E2.0.CO%3B2-X>

Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences is currently published by The Royal Society.

Your use of the JSTOR archive indicates your acceptance of JSTOR's Terms and Conditions of Use, available at <http://www.jstor.org/about/terms.html>. JSTOR's Terms and Conditions of Use provides, in part, that unless you have obtained prior permission, you may not download an entire issue of a journal or multiple copies of articles, and you may use content in the JSTOR archive only for your personal, non-commercial use.

Please contact the publisher regarding any further use of this work. Publisher contact information may be obtained at <http://www.jstor.org/journals/rsl.html>.

Each copy of any part of a JSTOR transmission must contain the same copyright notice that appears on the screen or printed page of such transmission.

JSTOR is an independent not-for-profit organization dedicated to creating and preserving a digital archive of scholarly journals. For more information regarding JSTOR, please contact support@jstor.org.

Spectroscopy at extreme infra-red wavelengths

I. Technique

BY D. BLOOR, T. J. DEAN, G. O. JONES, D. H. MARTIN, P. A. MAWER
AND C. H. PERRY

Department of Physics, Queen Mary College (University of London), London, E. 1

*(Communicated by N. Kurti, F.R.S.—Received 5 October 1960—
Read 26 January 1961)*

[Plate 25]

Improved spectroscopic techniques are described for the difficult and relatively unexplored region of the extreme infra-red (between $70\ \mu$ and 1 mm wavelength), in which good sources of radiation do not exist. The improvements include the development and application of a superconducting bolometer, whose detectivity is about 100 times superior to that of the best room-temperature detector sensitive at these wavelengths.

INTRODUCTION

The properties of solids in the extreme infra-red (or submillimetre) part of the spectrum have hardly yet been explored. In this region lie the resonances of many crystal lattices and the excitations of electrons in superconductors, and we may expect to find here also other phenomena characteristic of collective oscillations in solids, such as the resonances of antiferromagnetics and of other coupled-spin systems.

The reasons for the deficiencies of spectroscopic technique between, say, $50\ \mu$ and 1 mm are well known. The methods of microwave spectroscopy, using powerful coherent sources, have of course very high sensitivity. There is, however, great difficulty in the progressive extension of the technique to shorter wavelengths. Although sources of 1 mm radiation have been available for ten years the only work so far reported at wavelengths less than 1 mm has been the accurate determination of frequencies of rotation of certain molecules. The technique employs harmonics derived from sources of radiation in the millimetre range and does not yet seem suitable for less specialized spectroscopic investigations, where an unknown spectrum is to be determined over a wide range of frequencies.

Recently the techniques of grating spectrometry using hot untuned sources have been extended to the extreme infra-red beyond $150\ \mu$ (McCubbin & Sinton 1950; Oetjen, Haynie, Ward, Hansler, Schauwecker & Bell 1952; Genzel & Eckhardt 1954; Yoshinaga, Fujita, Minami, Mitsuishi, Oetjen & Yamada 1958; Dean, Jones, Martin, Mawer & Perry 1958) and the pure rotation lines of a number of simple molecules have been recorded. Sensitive detectors are essential because the energy from a hot source falls off rapidly with increasing wavelength (only one part in 10^8 of the total emission of a black body at 10000 °K lying between, say, 150 and $350\ \mu$). Further, the energy in the various orders reflected from an

echelette grating in a given direction varies as the cube of the order number for unfiltered incident black-body radiation, so that extremely effective filtering is necessary if the intrusion of high-order spectra is to be avoided. In the present paper we describe the improved techniques with which we are now studying the spectral properties of solids down to 4 °K. The improvements include methods of testing directly the spectral purity of the radiation issuing from the grating monochromator, and development of a superconducting bolometer for use in place of the conventional Golay detector when higher resolution is desired. In another paper (Jones, Martin, Mawer & Perry 1961) we give results of a comprehensive study of the lattice resonances of the heavier ionic crystals.

DESIGN AND OPERATION OF THE SPECTROMETER

The optical design of the spectrometer is illustrated in the ray diagram of figure 1 in which the monochromator unit is shown in conjunction with a Golay detector mounted for a measurement of transmission at room temperature. The

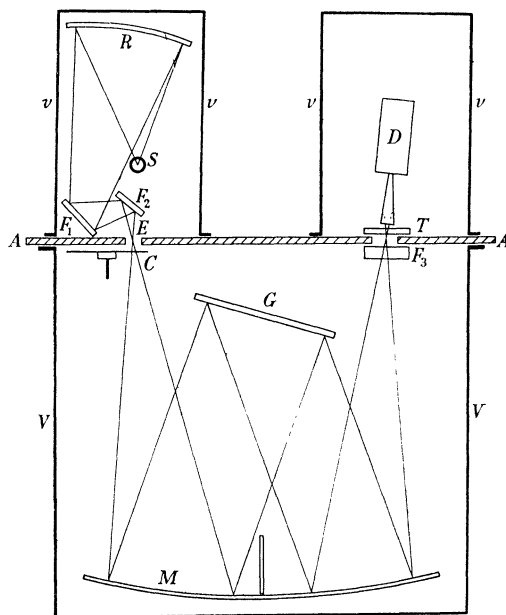


FIGURE 1. Ray diagram of the spectrometer.

Ebert optical arrangement was chosen for its simplicity, compactness and relative freedom from aberration. The design allows in a convenient way the use of large mirrors and monochromator slits, and the evacuation of the spectrometer. The main vacuum tank, VV , for example is a cylinder of diameter only 20 in. and length 20 in.

The source S is a high-pressure mercury discharge lamp in a quartz envelope, forming an image at the entrance slit E after reflexion by the parabolic reflector R and the aluminium reflectors F_1 and F_2 , which may be polished or ground or constructed as 'rejector' gratings to diffract out of the beam radiation of just

shorter wavelength than that required. Just below the entrance slit (at C) the radiation is 'chopped' mechanically at the frequency (10 c/s) to which the detector amplifier is tuned (a photoelectric cell incorporated in the chopper unit provides a reference signal for the phase-sensitive amplifier).

The large spherical mirror M of focal length 15 in. and aperture $f/1$ serves both as collimator and condenser. The grating G is a 6 in. square echelette selected from a series of six, having between 12 and 250 lines to the inch, as required to cover the range from 70 to 1500 μ . Such gratings are known to concentrate most of the diffracted energy into one order. We have no reason to think, from examination of the spectra obtained, that our resolution is at present limited by the quality of the grating, although they were cut in Duralumin on an ordinary planing machine using a steel tool. On leaving the exit slit the radiation is passed through the appropriate combination of filters F_3 having as sharp a cut-off as possible at the short-wavelength end of the first-order range of the grating (see below). The radiation passes through (or is reflected from) the specimen under examination T and is led up to the detector D through a conical light-tube of copper, easily alined, and giving a gain in energy flux density of $\times 8$. The effective aperture of the spectrometer is $f/2.2$.

The monochromator unit is mounted inside the blackened cylindrical vessel VV which is evacuated to eliminate the heavy selective absorption by water vapour. We have used an unconventional vertical mounting. The optical components are all supported by the horizontal face-plate AA and can easily be lifted bodily out of the vacuum vessel for alinement or grating changes. Smaller cylindrical vacuum chambers vv are used to enclose the source and detector, the seals in each case being made by rubber rings of O-section.

When a measurement of the transmission through a sample at a low temperature is to be made with the Golay detector (which operates at room temperature) a simple absorption cell is used which is in the form of a stainless steel light-tube, 2 cm in diameter, passing right through a liquid-helium cryostat. The sample is mounted at the centre of the tube where it passes through the liquid-helium bath. Three radiation shields of quartz (which are opaque between 4 and 40 μ) or of black polyethylene are mounted in the entrance and in the exit ends of the tube, and are maintained at the temperatures of liquid air, hydrogen and helium, respectively. Narrow slots milled in the wall of the light-tube, between the radiation shields, increase its thermal impedance so that its length may be kept down to 15 cm. With the inner surface plated with copper the total reflexion loss at the walls of the tube then does not exceed 50%. The radiation is focused on the entrance to the light-tube on leaving the monochromator, and, after traversing the sample and emerging at the other end, is collected by a conical condenser mounted on the Golay detector-head. (A somewhat different arrangement is used with the superconducting bolometer, which operates at about 3.7 °K, and is described later.)

Spectra are obtained by automatic recording, the grating being rotated slowly by a shaft passing through the face-plate and having an arrangement of pivoted arms which makes the record linear in wavelength. A smoothing circuit is used in the final stage before the pen recorder to give a selection of time-constants up to

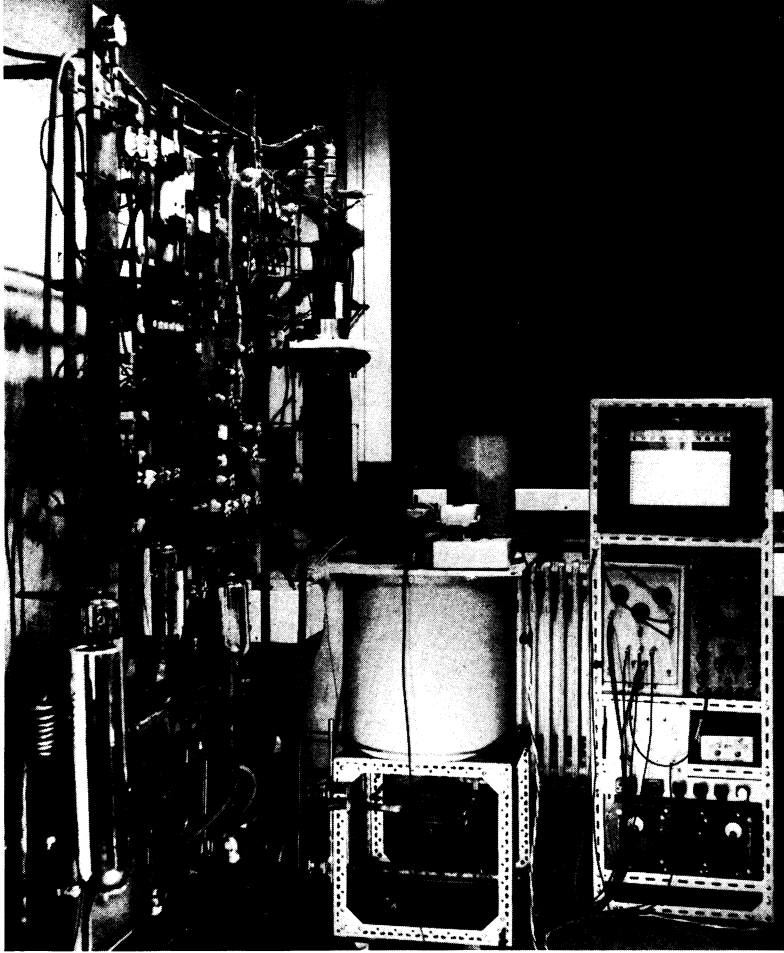


FIGURE 10. Arrangement of helium cryostat, spectrometer and amplifier.

40 s in order to increase the signal/noise ratio. With 40 s as time-constant about 3 h are required to scan the range of one grating—about one octave. An automatic system can be used to reverse the sense of rotation of the grating and to change the specimen so that the spectrometer may work unattended for long periods.

In figure 10, plate 25, is shown the spectrometer (centre) being used in conjunction with the helium liquefier-cryostat (left).

THE SUPERCONDUCTING BOLOMETER

The most widely used detector in the extreme infra-red has been the pneumatic detector (Golay & Zahl 1946). Photoconductive detectors, which have made possible the attainment of resolutions of the order of one part in 10^6 in the near infra-red region, gain their superior sensitivity, compared with thermal detectors, at the expense of a reduced range of wavelengths to which they will respond. Photoconductive detection has recently been employed beyond 10μ , and as far into the infra-red as 40μ , by using doped semiconductors. It seems unlikely, however, that simple photoconductive detectors will ever be available for the extreme infra-red, say beyond 140μ . The Golay detector is a thermal detector and responds uniformly throughout the spectrum and has been developed to the stage where it is less than ten times inferior to an idealized thermal detector operating at room temperature and is in fact equal to the very best room temperature bolometers and thermocouples. The low intensity of hot-body sources of radiation in the extreme infra-red, however, prevents the attainment of resolutions exceeding about one part in 10^2 using grating spectrometers and these room temperature thermal detectors. This is inadequate for the resolution of sharp absorptions such as those associated with magnetic resonances and the resonances of ionic lattices which we have observed at 4°K . One promising approach towards improved techniques has been the recent use of interferometers, which increase the effective exposure time (Strong & Vanasse 1959; Gebbie 1958). We have aimed instead at improving the detection in the spectrometer by developing the superconducting bolometer.

The superconducting bolometer makes use of the high value of the temperature coefficient of resistance (dR/dT) of a superconducting metal in the neighbourhood of its transition temperature. The resistivity of a tin sample, for example, even when in the form of an evaporated film, falls to zero at about 3.7°K over a temperature interval of less than 0.05°K . It is not difficult to make a film a few square millimetres in area, which has a resistance of, say, 50Ω and dR/dT equal to about $5 \times 10^3\Omega\text{ deg}^{-1}$ at 3.7°K . This is several orders of magnitude greater than dR/dT for normal metals at room temperature. In spite of the potentially very high sensitivity of a bolometer whose element is a superconductor at its transition temperature (Andrews, Brucksch, Ziegler & Blanchard 1942), no previously constructed bolometer of this type has warranted its use in spectrometry. We now describe a superconducting bolometer and a mode of operation which have made this possible, and give examples of the greatly improved performance obtained.

A typical bolometer is shown in figure 2. The main feature is the sensitive element E made of tin evaporated on to a very thin (about $1\ \mu$) strip of mica. The area of the element is a few square millimetres and it is supported by nylon threads TT (about $10\ \mu$ diameter) on which lead is evaporated. In use the space surrounding the bolometer is evacuated. The films are maintained on their superconducting transitions using a liquid-helium manostat. The influence of rapid fluctuations in the bath temperature is reduced by the introduction of a thermal resistance (the nylon bush B in the figure) between the helium reservoir H and the brass cylinder S which serves as a thermal sink for the bolometer. Though the lead deposited on the nylon threads must be thin in order to keep the thermal conductance low, it provides electrical contact without resistance because it is in the superconducting state throughout, and this avoids the generation of heat in the leads.

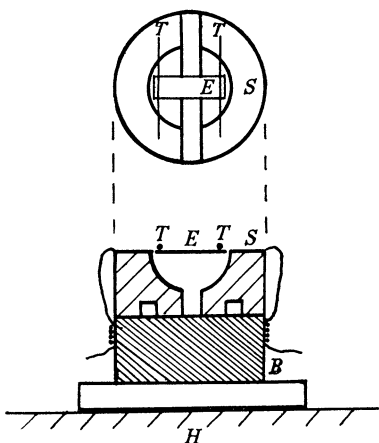


FIGURE 2. Mounting of the superconducting bolometer.

Because the main source of noise at present is the amplifier and not the bolometer itself, the bolometer is designed for maximum responsivity, r , defined as the ratio of the alternating potential difference across the bolometer to the amplitude of the chopped incident signal power. For a bolometer element of thermal capacity c linked through a thermal conductance to a sink at constant temperature the responsivity is given by

$$r = \frac{a}{2\{\omega^2\tau^2 + (1-b)^2\}^{\frac{1}{2}}} \left(\frac{\tau b}{c} \frac{dR}{dT} \right)^{\frac{1}{2}}, \quad (1)$$

where a is the absorptivity of the receiving surface, ω is the angular frequency of chopping, τ the thermal time constant (equal to the ratio of the thermal capacity to the thermal conductance to sink), and \sqrt{b} is the ratio of the current in the bolometer to that current for which the Joule heating would be sufficient to render the bolometer unstable. It follows that c and ω should be as small, and b and dR/dT as large, as practicable; a must be as close to unity as possible, while τ has an optimum value equal to $(1-b)/\omega$ with respect to changes in τ effected by varying the conductance to the sink.

A convenient value for ω is $2\pi \times 10$ rad s^{-1} in view of the rapid increase at low frequencies of flicker noise and similar effects in the vacuum tubes and circuit components of electronic amplifiers. To avoid risk of instability we find it convenient to operate the bolometer with a current well below the critical value so that b is generally less than $\frac{1}{2}$. The optimum value of τ is then about 0.01 s and time constants in this range are obtained by adjusting the thermal conductance to sink.

We are able to determine a value for the expected responsivity of a typical bolometer with the aid of equation (1). Using $\omega = 2\pi \times 10$ rad s^{-1} , $b = 0.5$, $\tau = 0.01$ s, $c = 5 \times 10^{-8}$ J deg^{-1} , $dR/dT = 100 \Omega \text{ deg}^{-1}$ (as determined in ancillary experiments, Martin & Bloor 1961) and assuming for the moment $a = 0.1$, we obtain

$$r = 230 \text{ V/W of incident radiation.}$$

This is about two orders of magnitude greater than that of ordinary bolometers or thermocouples, and it is this feature which enables us to gain some advantage from the use of low temperatures in spite of the noise originating in the parts of the apparatus at room temperature.

The output from the bolometer must be amplified greatly before recording becomes possible. Because the noise-equivalent resistances of the best vacuum valve amplifiers are about 0.1 M Ω at low frequencies and our bolometer resistance is about 1.0 Ω at 4 °K, at least one stage of amplification by transformer is necessary before the output is applied to an amplifier driving a pen-recorder. The bolometer forms one arm of a bridge which is fed by an 800 c/s source. The off-balance current, which is amplitude-modulated at 10 c/s as a result of the chopping of the incident radiation, is amplified first by a transformer which operates in the liquid-helium bath and has a strip-wound core of a special nickel-iron alloy having an initial permeability of 7000 at 4 °K, and then by a low-noise 800 c/s amplifier. The rectified output alternates at 10 c/s and is applied to a phase-sensitive detector which derives its reference phase from the chopper unit in the spectrometer. The final stage before the pen-recorder is a smoothing circuit providing a selection of time-constants up to 40 s. We shall see that, although the bolometer has a high responsivity and the transformers as high gain as is practicable, the major source of the noise in the final record is the vacuum-valve amplifier.

The high value of dR/dT necessary for the operation of the detector is exhibited only over the narrow region of the superconducting transition which extends over about 0.02 °K. It is desirable, therefore, to have a clear and continuous indication of the resistance of the bolometer, so that the optimum working conditions can be readily obtained. This is provided directly by the steady amplitude of the 800 c/s carrier current from the bolometer bridge, which is displayed by the output meter of the amplifier. This output also serves another most important purpose; it is used to control the current which is passed through a heater wound upon the bolometer sink, so that the operating temperature of the bolometer *element* remains approximately constant in the face of the large variations in the power falling upon the element as the spectrometer scans through its blaze. (An interesting effect we have observed, for example, is that in the absence of the thermostatic control the bolometer cools considerably whenever it sees an image of itself in a reflecting surface

at room temperature—whenever the grating of the spectrometer moves into the peak of its blaze for instance.)

To concentrate the radiation emerging from the monochromator on to the detector it is convenient to use, instead of a mirror, a segmented light-tube *LLL* in the form of a 6 in. cone tapering from 1 cm diameter at aperture down to 2 mm diameter at the bolometer element *E* as shown in figure 3. The bolometer is shielded from the short-wave thermal radiation from the spectrometer by cooled windows of quartz *Q* mounted inside the cone. The bolometer and first transformer *T* are arranged inside a lead-coated superconducting box *S* cooled by liquid helium to protect them from electromagnetic interference. A quartz vacuum window *W* separates the cryostat from the monochromator.

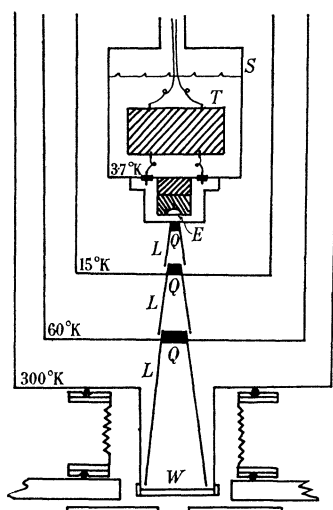


FIGURE 3. Arrangement of cooled light-tubes used with the superconducting bolometer.

As a test of the improvement in signal/noise ratio shown by a superconducting bolometer over that obtained with the best room-temperature thermal detectors we have recorded a number of lines of the mercury emission spectrum in the *visible* and *near infra-red* region (figure 4). The lower trace was obtained with a Golay detector and the upper trace with a superconducting bolometer of roughly the same sensitive area and used under identical optical operating conditions. The right-hand section of the trace due to the superconducting bolometer was taken more than an hour after the left-hand section, during which time the bolometer was in continuous use, and this illustrates the effectiveness of the temperature-control system in maintaining the detector in its sensitive condition. The gain in signal/noise ratio over that of the Golay detector is more than $\times 40$. The Golay detector had been calibrated for the near infra-red using a black-body source, and the record indicates that for a signal/noise ratio of unity this superconducting bolometer (of area 3 mm^2 and with an overall response time constant equal to 1.25 s) required an incident signal of less than $1.2 \times 10^{-12} \text{ W}$.

Similar comparisons of superconducting bolometers and Golay detectors at a wavelength of 1 mm show that the former can be at least 100 times more sensitive than the conventional detectors.* Absolute calibrations are impracticable in the extreme infra-red, but ancillary investigations into the transmissivities of the absorbing films, used in Golay detectors, strongly suggest that the best of these detectors have sensitivities in the extreme infra-red roughly equal to those measured absolutely in the near infra-red (Martin & Bloor 1961). We conclude that

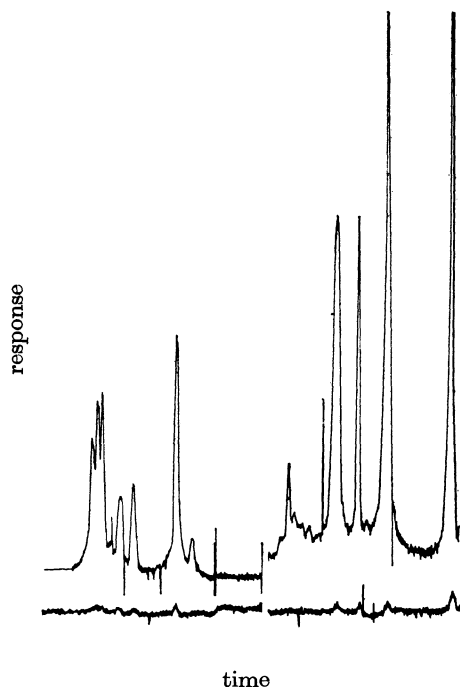


FIGURE 4. Emission spectra obtained with the Golay detector and superconducting bolometer at optical and near infra-red wavelengths.

our superconducting bolometers have an approximately constant sensitivity throughout the range from 1 to 1500μ with a minimum detectable signal appreciably less than 10^{-12} W, falling on an area of 3 mm^2 when the overall time constant of the system is 1.25 s. An example of a spectrum obtained in the extreme infra-red with the superconducting bolometer is shown later.

Special problems are met in the use of the superconducting bolometer in optical systems of large aperture, as is necessary in the extreme infra-red. Sufficient background energy from those parts of the apparatus at room temperature reaches the detector to maintain it well above its transition temperature, unless suitable cooled filters are provided in the conical condenser. We have used 1 mm thick plates of lithium fluoride and of caesium halides for work beyond

* Carbon bolometers of the type used recently in the extreme infra-red by Ginsburg & Tinkham (1960) operate at 1.5°K , and are also more sensitive than Golay detectors, but insufficient information on these has yet been published for a comparison with our bolometers to be made.

500 μ , and combinations of thin films of various alkali halides can be used as band-pass filters for shorter wavelengths.

Almost all the noise in the records obtained with the superconducting bolometer has its origin in the vacuum-valve amplifier. We calculate that the signal equivalent to the Johnson noise and the fluctuations of temperature in the bolometer itself is two orders of magnitude less than the present minimum detectable signal. Apart from the improved performance which might therefore follow from refinements in the electronic circuits, there is also the possibility of increasing the absorptivity of the receiving surface of the bolometer. Most of our measurements have so far been made with the untreated surfaces of the superconducting metals. We are now investigating a number of ways of increasing the absorptivity, including the use of gold black, of evaporated films of ionic crystals which absorb strongly over restricted spectral ranges, and of thin metallic films tuned to free space. Complications arise, of course, because low-temperature operation is required. The bolometer must also be modified so that the superconducting element does not provide a complete high-frequency short-circuit of the absorbing layer at these long wavelengths.

CALIBRATION AND TESTS OF SPECTRAL PURITY AND RESOLUTION

Clear and well-spaced landmarks exist in our spectral range in the pure rotation spectra of simple dipolar molecules such as HCl, HI, NH₃ and N₂O. For HCl, for example, the transitions $J = 0$ to $J = 1$, $J = 1$ to $J = 2$ and $J = 2$ to $J = 3$ correspond respectively to 479, 240 and 160 μ . A part of the spectrum of HCl recorded with the Golay detector is shown in figure 5. Several sharp absorption lines are seen superimposed upon the 'blaze'—the broad peak which dominates any spectrum obtained with an echelette grating. To obtain the spectral transmissivity of a sample the intensity at each wavelength in a record of the type shown in figure 5 must be divided by the intensity recorded in the absence of the sample. An example of such a spectrum, obtained with the superconducting bolometer, is shown in figure 6. This is the spectrum of N₂O which has a larger molecular moment of inertia and a smaller dipole moment than HCl; the corresponding absorption lines therefore occur at much longer wavelengths and are much less intense. The sensitivity needed to resolve the lines of N₂O beyond 600 μ (which, so far as we know, have not previously been recorded by infra-red techniques) required the use of the superconducting bolometer.

These simple spectra follow a sequence governed approximately by the formula $\lambda = 4\pi^2 cI/Jh$ for the wavelength of the rotational transition $J \rightarrow (J - 1)$, where I is the molecular moment of inertia. The constant wave-number separation apparent in figure 6 follows from this formula, which is based upon the selection rule $\Delta J = \pm 1$. The wavelengths of the lines can be deduced with high accuracy from vibration-rotation spectra in the near infra-red and microwave data, and these gases therefore provide the means for direct and simple calibration of the instrument.

These spectra also allow us to judge how effective has been the filtering-out of short-wave radiation. In figure 5, for example, no second-order lines can be seen.

With less efficient filtering alternate second-order lines appear between the first order lines, that is at $192\ \mu$, $137\ \mu$, etc., on the scale, so that it is clear from figure 5 that the filter used has absorbed efficiently up to the short-wavelength end of the octave under study. We find also that the transmission at the peak of a strong

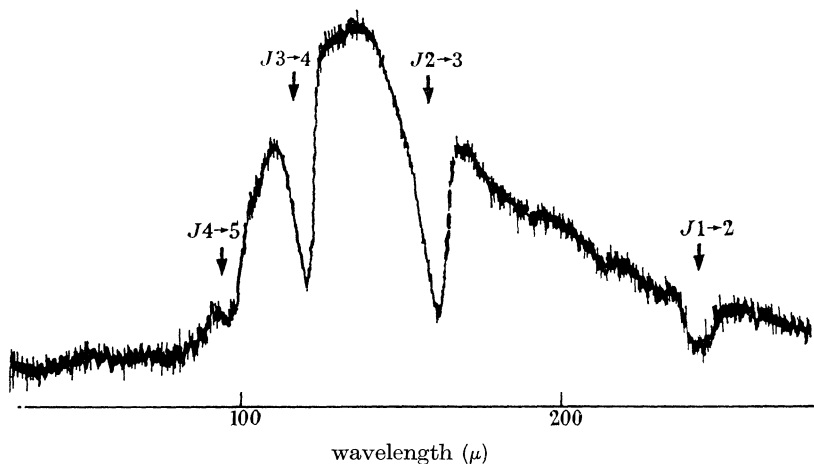


FIGURE 5. Pure rotation spectrogram of HCl between 100 and $250\ \mu$.

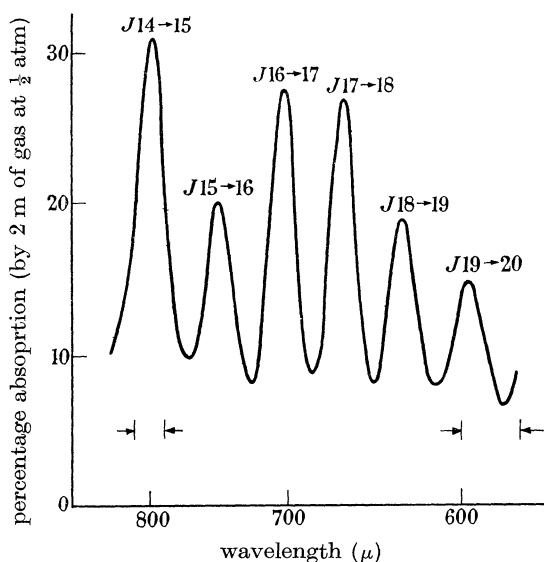


FIGURE 6. Pure rotation spectrum of N_2O between 600 and $800\ \mu$ obtained with the superconducting bolometer. Spectral slit widths are indicated.

absorption line, of an alkali halide film for example, can be as low as 3% without apparent distortion of the line. We conclude that unwanted radiation amounts to less than 3%, at least at the short-wavelength end of our range.

To cover the range from 70 to $1000\ \mu$ several methods of filtering are required. First, rejector gratings having two and three times as many lines to the inch as the main grating are used for all wavelengths greater than $150\ \mu$ (in positions F_1 and F_2

of figure 1). When working between 70 and 150μ we have found abraded aluminium reflectors effective, as shown by curve *C* in figure 7 which records the measured reflectivity of an aluminium plate which had been abraded with 150 Carborundum powder. We have also employed restrahlen reflexion filters. Using KBr, for example, we find that plates made by compressing power in a small hydraulic press have reflectivities only a few per cent different from that of a single crystal.

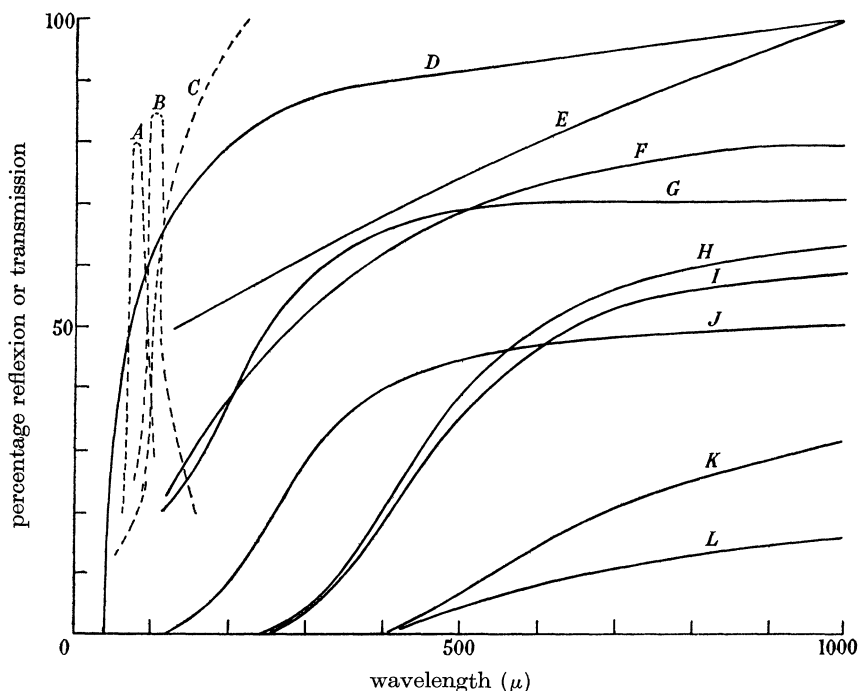


FIGURE 7. Approximate reflexion and transmission curves of filters used in the extreme infra-red. ----, Reflectivity; —, transmissivity. *A*, Pressed plate of KBr; *B*, pressed plate of RbBr; *C*, aluminium plate ground with grade 150 carborundum powder; *D*, 1 mm crystal quartz; *E*, 0.015 mm mica; *F*, 1 mm soot in polyethylene; *G*, 1 mm 5% soot in paraffin; *H*, 1 mm KBr or 1 mm RbCl; *I*, 1 mm RbBr; *J*, 1 mm 15% soot in paraffin; *K*, 1 mm RbI; *L*, 1 mm TiCl.

Since it is clear therefore that single crystals are not essential, a wide range of wavelengths can be easily covered using pressed plates of the halides of sodium, potassium, rubidium, caesium and thallium. In figure 7 are included the reflexion curves of pressed plates of some of these salts.

The combinations we have found most useful in absorption filters are 0.5 mm plates of black polyethylene (containing lamp-black) for use when studying the 70 to 100μ region; quartz (1 mm) with paraffin wax (1 mm) containing lamp-black in a proportion adjusted to suit the range of interest (see figure 7) from 100 to 500μ ; 1 mm pressed plates of the alkali halides, in addition to the quartz and paraffin wax, beyond 500μ . The reflexion and transmission curves for some of our filter materials are collected in figure 7, where it can be seen that good filtering is possible when working in the range just above 100μ , but that the

rather broad cut-off of our filters for use above 300μ limits the spectral purity obtained there and removes much of the energy falling in the range of interest.

The construction of interference filters for this range is by no means out of the question and we are investigating this possibility. In fact, interference in optical components provides a special problem at these wavelengths. Figure 8 shows transmission maxima and minima, superimposed on the blaze of the grating,

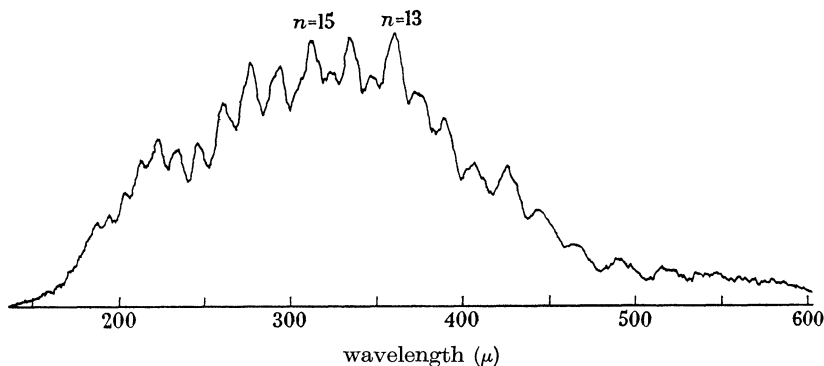


FIGURE 8. Structure due to interference in optical components.

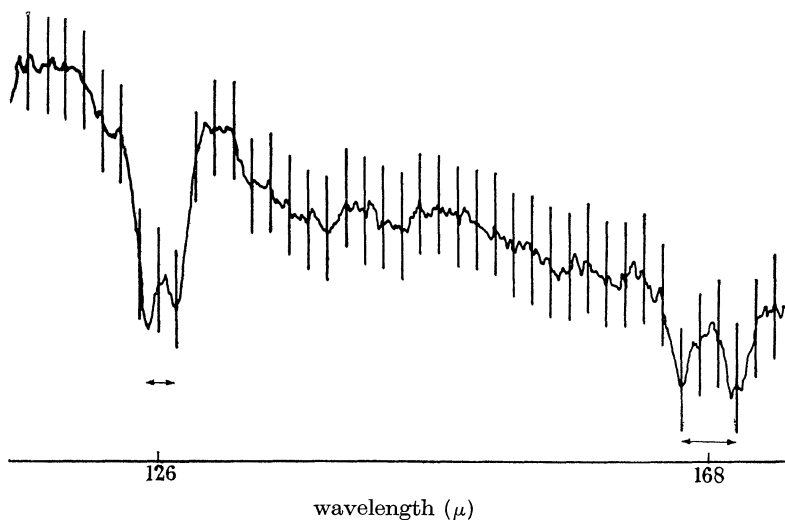


FIGURE 9. Spectrogram of ammonia with inversion splitting.

arising from interference in a quartz window of 1 mm thickness. Such maxima and minima may confuse the interpretation of spectra, but can be eliminated to some extent by employing wedge-shaped windows, and we have found this especially desirable for the windows of the Golay detector. (The standing waves in figure 8 permit the real part of the refractive index of quartz to be determined, and we find this to be 2.34 for crystalline quartz, and constant within $\frac{1}{2}\%$ over the range from 150 to 600μ .)

The pure rotation spectrum of ammonia provides a very convenient test of the resolution obtained with the spectrometer because each rotational line is a doublet

due to inversion splitting. The separations of these doublets in our region of the spectrum are of the order 1.5 cm^{-1} and can be accurately deduced from the results of microwave and near infra-red measurements. Figure 9 shows that the splitting of the lines at 126 and 168μ (1.45 and 1.51 cm^{-1} respectively), and beyond, can be readily resolved by the Golay detector. With the filtering required to reduce the intrusion of short-wave radiation to less than 5%, we can obtain an energy-limited resolution with the Golay detector which is certainly better than 1 cm^{-1} throughout our range. We are at the moment using the superconducting bolometer at the millimetre end of the range. Its effectiveness is illustrated by the rotation spectrum of N_2O shown in figure 6, where the rather weak lines which are separated by 0.84 cm^{-1} are well resolved at 800μ . We find, in fact, that a signal/noise ratio of 20 can be obtained at 1 mm when the spectral slit width of the monochromator is set at the limiting resolution of the 6×6 in. grating, which is approximately 0.15 cm^{-1} .

We acknowledge useful discussions with Dr G. Wilkinson of King's College, London, on questions of infra-red techniques, and the assistance of Mr A. D. Young of this Department in many experiments. We are indebted to the Department of Scientific and Industrial Research for research studentships awarded to three of us (D.B., T.J.D., P.A.M.) and for a substantial grant-in-aid, and to the Central Research Fund of the University of London for the loan of apparatus.

REFERENCES

- Andrews, D. H., Brucksch, Jr., W. F., Ziegler, W. T. & Blanchard, E. R. 1942 *Rev. Sci. Instrum.* **13**, 281.
Dean, T. J., Jones, G. O., Martin, D. H., Mawer, P. A. & Perry, C. H. 1958 *Physica Suppl.* **24**, S 151.
Gebbie, H. A. 1958 *J. Phys. Radium.* **19**, 230.
Genzel, L. & Eckhardt, u. W. 1954 *Z. Phys.* **139**, 578.
Ginsburg, D. M. & Tinkham, M. 1960 *Phys. Rev.* **118**, 990.
Golay, J. E. & Zahl, H. A. 1946 *Rev. Sci. Instrum.* **17**, 511.
Jones, G. O., Martin, D. H., Mawer, P. A. & Perry, C. H. 1961 *Proc. Roy. Soc. A*, **261**, 10.
Martin, D. H. & Bloor, D. 1961 *Cryogenics* (in the Press).
McCubbin, Jr., T. K. & Sinton, W. M. 1950 *J. Opt. Soc. Amer.* **40**, 537.
Oetjen, R. A., Haynie, W. H., Ward, W. M., Hansler, R. L., Schauwecker, H. E. & Bell, E. E. 1952 *J. Opt. Soc. Amer.* **42**, 559.
Strong, J. D. & Vanasse, G. A. 1959 *J. Opt. Soc. Amer.* **49**, 844.
Yoshinaga, M., Fujita, S., Minami, S., Mitsuishi, A., Oetjen, R. A. & Yamada, Y. 1958 *J. Opt. Soc. Amer.* **48**, 315.