FOURIER SPEGTROSCOPY IN THE FAR INFRARED
by
RONALD MURRAY STROHMAIER
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Physics

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Department of PHYSICS

The University of British Columbia Vancouver 8, Canada

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## ABSTPACT

An infrared Fourier spectrophotometer has been set up in the solid state labaratory of the University of British Columbia.

A cryostat has been built and adapted to the spectrometer.
A computer program to analyze the data and plot the spectrum has been written.

As a demonstration of the system's capability, the transmission spectrum from $40 \mathrm{~cm}^{-1}$ to $330 \mathrm{~cm}^{-1}$ of boron doped silicon was obtained for the sample at liquid helium temperature. This spectrum was compared to earlier work done by Colbow in the region $240 \mathrm{~cm}^{-1}$ to $330 \mathrm{~cm}^{-1}$.

A spectrum of boron and indium doped silicon was investigated in the hope of finding $\mathrm{B}^{-}$and $\mathrm{In}^{+}$ionized centres. These were not found at the impurity concentrations and temperatures used.

A transmission spectrum of intrinsic silicon at liquid helium temperature was obtained for the region $40 \mathrm{~cm}^{-1}$ to $330 \mathrm{~cm}^{-1}$.

A comparison of the above spectra suagests that the low energy tail of the boron doped and boron and indium doped samples is due to a frequency dependant value of reflectivity as is seen from the spectrum for intrinsic silicon.

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## INTRODUCTION

1. Spectroscopy in the Far Infrared

The infrared region of the electromagnetic spectrum is subdivided into the near ( $500 \mathrm{~cm}^{-1}$ to $12.500 \mathrm{~cm}^{-1}$ ), mid ( $200 \mathrm{~cm}^{-1}$ to $500 \mathrm{~cm}^{-1}$ ) and far ( $10 \mathrm{~cm}^{-1}$ to $200 \mathrm{~cm}^{-1}$ ) infrared regions.

Photographic methods, whereby the spectrum is spacially dispersed and the effect on a photographic film is studied, is prohibited in most of the infrared spectrum. The reason for this is the lack of a photographic film or other similar device which is sensitive to wavelengths longer than 1 micron.

For optical studies in the infrared, there are several spectographic means available. These are the conventional prism and grating spectrometers and also interferometric spectrometers, such as those employing a Fabry-Perot or a Michelson interferometer.
2. Advantages and Disadvantages of a Michelson Interferometer

In the infrared spectral region, the conventional spectrometer generally employs a grating rather than a prism, since a significantly greater flux and resolving power may be obtained. In the far infrared, the lack of materials with high dispersive powers dictates the use of gratings as the dispersive element.

A disadvantage associated with gratings is the presence of other overlapping orders of diffraction. The optical filtering required to eliminate these also reduces the intensity
of useful radiation. This becomes a decided disadvantace in the energy limited far infrared.

In the infrared spectral region, detector noise is usually very much greater than any other source of noise. This type of noise is of a random nature and is essentially independent of the signal level:.

For the same resolving power. the amount of radiation admitted by the slit of a grating spectrometer is much less than for a Michelson, Fabry-Perot, or lamellar grating spectrometer. In the infrared spectral region, we can increase the overall $\mathrm{S} / \mathrm{N}$ (signal to noise) ratio by using one of the above interferometric spectrometers. since the detector noise does not increase appreciable when the amount of radiation falling on the detector is increased. This is known as the Jacquinot advantage.

If $N$ spectral elements are observed in a time interval T, then the grating or Fabry-Perot spectrometer samples each element for a time, $t=T / N$. When a Michelson interferometer is employed, the full time of observation is affordo ed each spectral element. For random noise, such as that which is characteristic of infrared detectors, this means an increased $S / N$ ratio by a factor of $\sqrt{N}$. This advantage was first pointed out by Fellgett ${ }^{1}$ and is now referred to as Fellgett's advantage.

In order to double the resolution of the Michelson interferometer, we must double the maximum displacement of the moveable mirror. If we wish to retain the same $\mathrm{S} / \mathrm{N}$ ratio, then the time required to sample the spectrum must be twice
as long. To double the resolution using a grating spectrometer, both entrance and exit slit widths must be halved. The flux of radiation available to the detector is then $\frac{1}{4}$ of the original value. For a detector signal which is time integrated, the pure signal varies proportional to the time and any random noise signal varies proportional to the square root of the time. To retain the same $\mathrm{S} / \mathrm{N}$ ratio would then require a time 16 times greater than the original spectrum.

For high resolution or for obtaining a spectrum over a large range of frequencies where the intensity is low, the Michelson interferometer is of particular use. It does have the drawback that $1 t$ requires the use of a computer to do the Fourier transforms. When computing facilities are available, the Micheison interferometer is a particularly good instrument to cover the far and mid infrared regions.

## 3. Other Interferometric Spectrometers

Closely related in principle to the Michelson interferometer is the interferometric modulator ${ }^{2}$, which employs a lamellar grating with a variable depth. Because of mechanical difficulties, this type of interferometer is generally used in the long wavelength regions.

The SISAM ${ }^{3}$ (Spectrometre Interferential à Selection par l'Amplitude de Modulation) is essentially a Michelson interferometer in which the mirrors are replaced by gratings. These gratings are inclined at equal angles to the radiation incident from the beam splitter. This method scans selectively through the spectrum and does not, therefore, possess
the Fellgett advantage.
4. History and Use of the Michelson Interferometer in the Infrared

The Michelson interferometer was first developed and used by Michelson around the turn of the century. The work carried out by Michelson was in the visible region of the electromaznetic spectrum.

The first application of the Michelson interferometer to infrared spectroscopy was by Rubens and Wood in 1911.

A further brief history of the use of the Michelson interferometer for spectroscopic studies in the infrared spectrai region is given by Jacquinot ${ }^{3}$.

The developmental work on the Michelson interferometer as applied to infrared spectroscopy was carried out at four major centres: National Physics Laboratory, Teddington. Middlesex, U. K.; Johns Hopkins University, Baltimore, Maryland. U.S.A.; Université de Paris, Paris, France; and C.N.R.S. (Centre National de la Recherche Scientifique). Bellevue, France.

This type of instrument is used for research in a wide variety of chemical and physical studies in the infrared. Some of the types of studies where it is employed are: lattice vibrations, magnetic resonance, superconductivity, astronomy, optical constants, electronic effects in semiconductors, meteorology, molecular spectroscopy, and the study of plasmas.

## THEORY OF THE MICHELSON INTERFEROMETER

1. The Interferocram Function

Consider a monochromatic plane wave normally incicent upon an ideal Michelson interferomenter, operating in a vacuum.


Figure 1. Michelson Interferometer
When the two mirrors are equidistant from the beam splitter, there is no phase difference between the two beams upon recombining. This position of mirror M2 is designated as the zero path difference $(x=0)$ and all path differences. which are twice the mirror displacement from zero path difference, are measured with respect to this origin.

If:

```
t = the transmission coefficient of the beam
                splitter
r = the reflection coefficient of the beam splitter
R = the reflection coefficient of mirrors M1
        and M2
a = twice the distance from either mirror to the
        beam splitter, at zero path difference
x = path difference
```

then, upon recombining, the electric vector is of the form:
$|\vec{E}|=\left(r t R E_{o}\right)(\cos (w t-2 \pi k a)+\cos (w t-2 \pi k(a+x))$

$$
\begin{equation*}
=\left(r t R E_{o}\right) \operatorname{Re}(\exp (i(w t-2 \pi k a))(\exp (-i 2 \pi k x)+1)) \tag{1}
\end{equation*}
$$

Let us consider a plane polarized monochromatic plane wave for which $|\vec{E}|=|\vec{H}|$ and $\vec{E} \perp \vec{H}$.

The intensity of an electromagnetic wave is given by the time average of the Poynting vector, $\vec{S}$. We therefore have:

$$
\begin{equation*}
I=\langle S\rangle_{t}=(c / 8 \pi)\left(\overrightarrow{E x} \vec{H}^{*}\right)=(c / 4 \pi)\left(r t R E_{0}\right)^{2}(I+\cos (2 \pi \mathrm{kx})) \tag{2}
\end{equation*}
$$

We now consider an unpolarized plane wave which will have different coefficients of reflection and transmission for the sigma and pi polarizations at the bean splitter. The reflection coefficients for the mirrors M1 and M2 are the same for each polarization since the wave is normally incident.

Allowing also the wave to be heterochromatic with a spectral distribution of intensities which is not constant, then $E$ will vary with frequency. In general, the product (rtR) may also be frequency dependent. We therefore write:

$$
\begin{align*}
& \left.(\mathrm{c} / 4 \pi)(\mathrm{rtRE})_{\pi}^{2}+(\mathrm{c} / 4 \pi)(\mathrm{rtRE})_{0}\right)_{\sigma}^{2}=I(k)  \tag{3}\\
& \\
& \text { We then have, for any path difference } \mathrm{x}:  \tag{4}\\
& I(x)=\int_{0}^{\infty} I(k)(1+\cos (2 \pi k x)) d k=\int_{0}^{\infty} I(k) d k+\int_{0}^{\infty} I(k) \cos (2 \pi k x) d k  \tag{5}\\
& \\
& \quad \text { For } x=0 \text {, we have: } \\
& I(0)=2 \int_{0}^{\infty} I(k) d k
\end{align*}
$$

and for $\mathrm{x}=\infty$ we have:

$$
\begin{equation*}
I(\infty)=\int_{0}^{\infty} I(k) d k \tag{6}
\end{equation*}
$$

Equation 6 is derived from equation 4 when the cosine term goes to zero. This follows, since for very large values of $x, \cos 2 \pi k x$ is a very rapidly varyine function of $k$ and the average value of $I(k) \cos 2 m k x$ over any cycle will be zero.

From equations 4 and 6 , we have:

$$
\begin{equation*}
I(x)=I(\infty)+\int_{0}^{\infty} I(k) \cos (2 \pi k x) d k \tag{?}
\end{equation*}
$$

From equations 5 and 6:

$$
\begin{equation*}
I(\infty)=\frac{1}{2} I(0) \tag{8}
\end{equation*}
$$

We may define a function:

$$
\begin{equation*}
F(x)=I(x)-\frac{1}{2} I(0)=I(x)-I(\infty)=\int_{0}^{\infty} I(k) \cos (2 \pi k x) d k \tag{9}
\end{equation*}
$$

In applying the interferometer to spectroscopy, filters are applied, so that $I(k)=0$ for $k \geqslant K$, where $K$ is the maximum wave number of interest. We therefore have:

$$
\begin{equation*}
F(x)=\int_{0}^{K} I(k) \cos (2 \pi k x) d k \tag{10}
\end{equation*}
$$

In practice, the ideal and perfectly alioned interferometer is not realized. As a consequence, there is an additional phase difference, $\varnothing(k)$. introduced. Therefore:

$$
\begin{align*}
F(x) & =\int_{0}^{\infty} I(k) \cos (2 \pi k x-\phi) d k  \tag{11}\\
& =\int_{0}^{k} I(k) \cos \phi \cos (2 \pi k x) d k+\int_{0}^{k} I(k) \sin \phi \sin (2 \pi k x) d k
\end{align*}
$$

2. Fourier Transforms

The exponential Fourier transform is defined by:

$$
\begin{align*}
g(k) & =\int_{-\infty}^{\infty} f(x) \exp (i 2 \pi k x) d x  \tag{12}\\
& =\int_{-\infty}^{\infty} f(x) \cos (2 \pi k x) d x+i \int_{-\infty}^{\infty} f(x) \sin (2 \pi k x) d x \tag{12a}
\end{align*}
$$

The inverse transform is siven by:

$$
\begin{align*}
f(x) & =\int_{-\infty}^{\infty} g(k) \exp (-i 2 \pi k x) d k  \tag{13}\\
& =\int_{-\infty}^{\infty}(k) \cos (2 \pi k x) d k-i \int_{-\infty}^{\infty} g(k) \sin (2 \pi k x) d k \tag{13a}
\end{align*}
$$

If $f(x)$ is an even function, that is $f(-x)=f(x)$,
then from 12a we have that:

$$
\begin{equation*}
g(k)=\int_{-\infty}^{\infty} f(x) \cos (2 \pi k x) d x=2 \int_{0}^{\infty} f(x) \cos (2 \pi k x) d x \tag{14}
\end{equation*}
$$

This is referred to as the Fourier cosine transform.
Likewise, is $f(x)$ is an odd function of $x$, that is.
$f(-x)=-f(x)$, then:

$$
\begin{equation*}
g(k)=i \int_{-\infty}^{\infty} f(x) \sin (2 \pi k x) d x=2 i \cdot \int_{0}^{\infty} f(x) \sin (2 \pi k x) d x \tag{15}
\end{equation*}
$$

This is called the Fourier sine transform with a multiplying factor of 1 .

We may write equation $12 a$ as: $g(k)=c(k)+i s(k)$, where $c$ and $s$ refer to the cosine and sine transforms respectively.

Tables of calculated Fourier transforms may be found in Cambell and Foster ${ }^{4}$ or Bateman ${ }^{5}$.

## 3. Calculating the Spectrum

If we consider $F(x)$ as the function $f(x)$ in a Fourier transform, then from equation 11:

$$
\begin{align*}
c\left(k_{I}\right) & =\int_{-\infty}^{\infty} F(x) \cos \left(2 \pi k_{1} x\right) d x \\
= & \int_{0}^{k}(k) \cos \phi\left\{\int_{-\infty}^{\infty} \cos ^{\infty}\left(2 \pi k_{1} x\right) \cos (2 \pi k x) d x\right\} d k \\
& +\int_{0}^{k}(k) \sin \phi\left\{\int_{-\infty}^{\infty} \cos \left(2 \pi k_{1} x\right) \sin (2 \pi k x) d x\right\} d k \tag{16}
\end{align*}
$$

Now:

$$
\begin{align*}
& \int_{-\infty}^{\infty} \cos \left(2 \pi k_{1} x\right) \cos (2 \pi k x) d x \\
& =\frac{1}{2} \int\left(\exp \left(i 2 \pi\left(k+k_{1}\right) x\right)+\exp \left(i 2 \pi\left(k-k_{1}\right) x\right)\right) \\
& =\frac{1}{2}\left(\delta\left(k+k_{1}\right)+\delta\left(k-k_{1}\right)\right) \tag{17}
\end{align*}
$$

where $\delta$ is the Dirac delta function, and is defined by:

$$
\begin{equation*}
\delta(k+L)=\int_{-\infty}^{\infty} \exp (i 2 \pi(k+L) x) d x \tag{18}
\end{equation*}
$$

In equation 16, we also have:

$$
\begin{equation*}
\int_{-\infty}^{\infty} \cos \left(2 \pi k_{1} x\right) \sin (2 \pi k x) d x=0 \tag{19}
\end{equation*}
$$

since the integrand is an odd function of $x$.

$$
\begin{align*}
& \text { Therefore: } k \\
& \begin{aligned}
c\left(k_{1}\right) & =\frac{1}{2} \int I(k) \cos \phi\left\{\delta\left(k+k_{1}\right)+\delta\left(k-k_{1}\right)\right\} d k \\
& \left.=\frac{I\left(k_{1}\right)}{2}\right) \cos \phi
\end{aligned}
\end{align*}
$$

since $I(k)=0$ for $k \geq k$ and we also have $k=\frac{1}{\lambda} \geq 0$. Similarly:

$$
\begin{equation*}
S\left(k_{1}\right)=\left(I\left(k_{1}\right) / 2\right) \sin \phi \tag{21}
\end{equation*}
$$

Thus:

$$
\begin{equation*}
\left|g\left(k_{1}\right)\right|=\left(c^{2}\left(k_{1}\right)+s^{2}\left(k_{1}\right)\right)^{\frac{1}{2}}=\frac{1}{2} I\left(k_{1}\right)\left(\sin ^{2} \phi+\cos ^{2} \phi\right)^{\frac{1}{2}} \tag{22}
\end{equation*}
$$

and then:

$$
\begin{equation*}
I\left(k_{1}\right)=2\left|g\left(k_{1}\right)\right|=2\left(c^{2}\left(k_{1}\right)+s^{2}\left(k_{1}\right)\right)^{\frac{1}{2}} \tag{23}
\end{equation*}
$$

If we are only interested in relative intensities,
we may drop the factor of 2 and write:
$I\left(k_{1}\right)=\left(c^{2}\left(k_{1}\right)+s^{2}\left(k_{1}\right)\right)^{\frac{1}{2}}$
If the interferogram function, $F(x)$, is symmetric about $x=0$, that is, $\varnothing(k)=0$, then:

$$
\begin{equation*}
S(k)=0 \text { and } I(k)=C(k) \tag{25}
\end{equation*}
$$

In this case, it would only be necessary to record $I(x)$ on one side of the zero path difference. In the case when $\phi(k) \neq 0$, it would also be possible to obtain all the necessary information by recording one side only, if we knew the exact position of the zero phase difference.
4. Finite Integration Limits

In practice, the interferogram is obtained over a limited range of path differences. The range of the integration limits then becomes $\pm X$, rather than $\pm \infty$, where $\pm X$ is the maximum positive and negative path difference.

To examine the effect of the finite integration limits, we consider the case of a monochromatic plane wave of wave number $k_{1}$ in an ideal interferometer.

From equation 9, therefore:

$$
\begin{equation*}
F(x)=I\left(k_{I}\right) \cos \left(2 \pi k_{I} x\right) \tag{26}
\end{equation*}
$$

The Fourier transform of $F(x)$ over the finite range of $x$ may be written as:

$$
\begin{equation*}
\int_{-\infty}^{\infty} I\left(k_{1}\right) \cos \left(2 \pi k_{1} x\right) \exp (i 2 \pi k x) T(x) d x \tag{27}
\end{equation*}
$$

where:

$$
\begin{aligned}
T(x) & =0 & \ddots & |x|>X \\
& =1 & & |x| \leq X
\end{aligned}
$$

We now make recourse to the convolution theorem, which may be stated as follows:

The Fourier transform of the product of two functions, $f(x)$ and $g(x)$ is the convolution of their transforms $F(y)$ and $G(y)$, where the convolution is defined by:

$$
\begin{equation*}
F * G=\int_{-\infty}^{\infty} G(t) F(y-t) d t \tag{28}
\end{equation*}
$$

The Fourler transform of $T(x)$ is:
$\int_{\infty}^{\infty} \mathrm{T}(\mathrm{x}) \exp (\mathrm{i} 2 \pi \mathrm{kx}) \mathrm{dx}=\int_{-X}^{X} \exp (\mathrm{i} 2 \pi \mathrm{kx}) \mathrm{dx}$
$=\int_{-X}^{x}(\cos (2 \pi k x)+i \sin (2 \pi k x)) d x=\left.\left(\frac{\sin (2 \pi k x)}{2 \pi k}-\frac{i \cos (2 \pi k x)}{2 \pi k}\right)\right|_{-x} ^{x}$

$$
\begin{equation*}
\equiv \frac{2 \sin (2 \pi k X)}{2 \pi k} \tag{29}
\end{equation*}
$$

The Fourier transform of $F(x)$ is:
$\int_{-\infty}^{\infty}\left(k_{1}\right) \cos \left(2 \pi k_{1} x\right) \exp (i 2 \pi k x) d x$
$=\frac{1}{2} \int_{-\infty}^{\infty} \mathrm{I}\left(\mathrm{k}_{1}\right)\left(\exp \left(i 2 \pi k_{1} x\right)+\exp \left(-i 2 \pi k_{1} x\right)\right) \exp (i 2 \pi k x) d x$
$=\frac{1}{2} \int_{-\infty}^{\infty}\left(k_{1}\right)\left(\exp \left(i 2 \pi\left(k+k_{1}\right) x\right)+\exp \left(i 2 \pi\left(k-k_{1}\right) x\right)\right) d x$
$=\frac{1}{2} I\left(k_{I}\right)\left(\delta\left(k+k_{I}\right)+\delta\left(k-k_{I}\right)\right)$
The convolution of the transforms is then:
$\int_{-\infty} 2\left(\frac{\sin (2 \pi t X)}{2 \pi t}\right)\left(\frac{I\left(k_{1}\right)}{2}\left(\delta\left(k+k_{1}-t\right)+\delta\left(k-k_{1}-t\right)\right) d t\right.$
$=I\left(k_{1}\right) X \frac{\sin \left(2 \pi\left(k+k_{1}\right) X\right)}{2 \pi\left(k+k_{l}\right) X}+\frac{\sin (2 \pi(k-k}{2 \pi\left(k-k_{1}\right)} \frac{X)}{2 \sin \theta}$
The maximum value of the function $\frac{\sin \theta}{\theta}$ is unity and occurs when $\theta=0$. If $\theta=2 \pi\left(k-k_{1}\right) X$, then the
maximum occurs at $k=k_{1}$.
If we now consider the contribution to the spectrum from the term $\theta=2 \pi\left(k_{1}+k\right) x$, we find that its maximum value occurs for $k=-k_{1}$. This is not a physically realizable situation since $k=\frac{1}{\lambda} \geq 0$. We may see a small contribution from values of $k \geq 0$, but these will be negligible for $k_{1}$ greater than $10 \mathrm{~cm}^{-1}$. We see this by considerine the maximum value of $\frac{\sin 2 \pi\left(k_{1}+k\right) X}{2 \pi\left(k+k_{1}\right) X} \leq \frac{1}{2 \pi\left(k+k_{1}\right) X}$. for positive values of $k$. For $k=k_{1}=10 \mathrm{~cm}^{-1}$, we have a maximum value for this term of $\frac{1}{40 \pi x}$. Even for an extremely small value of $X$, such as 1 cm , we still only have $\frac{1}{4 \pi}$ which is small in comparison to unity, the contribution of the other term. The effect of this term becomes even less important as $k$ and/or $k_{1}$ increases.

The monochromatic line is thus spread out and its frequency spectrum is modulated by $\frac{\sin \theta}{\theta}$, where $\theta=$ $2 \pi\left(k-k_{1}\right) X$.

This function is referred to as the spectral window. The form of this function is shown by curve a in Figure 2.

curve a
$n=1$
$\theta=2 \pi(R-R)$, curve $b$
$n=2$
$\theta=\pi\left(k-k_{1}\right) x$

Figure 2. Spectral Windows
5. Apodization

The form of the spectral window may be modified by using a different truncating function, $\mathrm{T}^{1}(\mathrm{x})$. This amounts to multiplying $F(x)$ by another function before multiplying by $T(x), t_{\infty}$ that is:

$$
\begin{align*}
& \int_{-\infty}^{\infty} \exp (i 2 \pi k x)(F(x) G(x)) T(x) d x \\
& =\int_{-\infty}^{\infty} \exp (i 2 \pi k x) F(x) T^{I}(x) d x \tag{32}
\end{align*}
$$

Where $\begin{aligned} T^{1}(x)=G(x) T(x) & =G(x) & & |x| \leq X \\ & =0 & & |x|>X\end{aligned}$
This process is called apodization and its use can result in the reduction of the height of the side lobes, at the cost of a reduction in resolution.

A common apodization function is given by:

$$
\begin{align*}
T^{1}(x) & =0 \quad|x| \geq X \\
& =1-\frac{|x|}{X} \quad x \leq X \tag{33}
\end{align*}
$$

The spectral window is given by $F(k) \not T^{1}(k)$.
The Fourier transform of $T^{1}(x)$ is:

$$
\begin{align*}
& \int_{-X}^{x}\left(1-\frac{|x|}{\bar{x}}\right) \exp (i 2 \pi k x) d x=\frac{2 \sin (2 \pi k x)}{2 \pi k}-\frac{1}{\bar{x}} \int_{-X}^{x} x \cos (2 \pi k x) d x \\
& =\frac{2 \sin (2 \pi k x)}{2 \pi k}-\left.\frac{2}{x}\left(\frac{x \sin (2 \pi k x)}{2 \pi k}+\frac{\cos (2 \pi k x)}{(2 \pi k)^{2}}\right)\right|_{0} ^{x} \\
& =2\left(\frac{1-\cos (2 \pi k X)}{(2 \pi k)^{X} X}=\frac{4 X \sin ^{2}(2 \pi k X)}{(2 \pi k)^{2} X^{2}}=X\left(\frac{\sin (\pi k X)}{\pi k X}\right)^{2}\right. \tag{34}
\end{align*}
$$

If. $F(x)$ is as before, then:

$$
\begin{align*}
& F(k) * T^{I}(k)=\int_{-\infty}^{\infty} X\left(\frac{\sin (\pi k X)}{\pi k X}\right)^{2}\left(\frac{I\left(k_{1}\right)}{2}\right)\left(\delta\left(k+k_{1}-t\right)+\delta\left(k-k_{1}-t\right)\right\rangle d t \\
& \simeq \frac{I\left(k_{1}\right)}{2} X\left(\frac{\sin \left(\pi\left(k-k_{1}\right) X\right.}{\pi\left(k-k_{1}\right) X}\right)^{2} \tag{35}
\end{align*}
$$

where the term $\left(\frac{\sin \theta}{\theta}\right)^{2}$ for $\theta=\pi\left(k+k_{1}\right) x$ is negligible as before.

The form of this spectral window is shown by curve
$b$ of Figure 2.
Gebbie and Twiss ${ }^{5}$ have shown that this has the effect of reducing the side bands to approximately $5 \%$ of the height of the main peak, as compared to $15 \%$ for the orieinal spectral window.

It will be noted that. for the apodization function given above, the height of the main peak is reduced by a factor of 2. If the sample spectrum is to be ratioed with a reference spectrum, then the intensities obtained are not affected, other than a broadening of the bands. The integrated intensity over a band should remain the same.
6. Maximum Path Difference Limitations on Resolution

The resolution of an optical instrument is its ability to dinstinguish between two spectral lines which are close together. The minimum separation of two lines of equal intensity which can be distinguished is called the resolution.

The most common method of calculating the theoretical resolution of an instrument is to consider two monochromatic lines. For curves $a$ and $b$ of Figure 2. Jacquinot ${ }^{3}$ defines the resolution as the distance between the first two zeros. For the unapodized case (curve a), the resolution $1 s$ the $1 / 2 \mathrm{X}$. For the apodized case (curve b). the resolution is given by $1 / \mathrm{X}$.

Martin? points out that this is somewhat naive, since in practice we never deal with pure monochromatic spectral lines, but a distribution of frequencies about a
central peak value. Martin chooses a Gaussian distribution $e^{-b\left(k_{1}-k\right)^{2}}$ for which the interferogram would be $B e^{-\pi^{2} x^{2} / b} \cos 2 \pi k, x$, where $b$ and $B$ are constants.

We now consider two such peaks, of equal intensity and of half-width w, which are separated by w. We find that the sum of the intensities is a doublet (Figure 3). which suffers a dip of approximately $7.3 \%$ at the mid-point between the two peaks.


Figure 3. Resolution for a Gaussian Distribution

The half-width is given by $w=(2.77 / b)^{\frac{1}{2}}$. We see that the envelope of the interferogram will be reduced to $e^{-\pi^{2} / 2.77}=.028$ when $x=1 / w$ and decreases rapidly as $x$ increases. If we obtain the interferogram up to $x=1 / w$, the calculated spectrum is essentially the same as the true spectrum, since the contribution, to the transform, from $x=1 / w$ to $\infty$ is negligible. Martin quotes a value of $5 \%$ for the dip under this condition. which is still sufficient for the two peaks to be distinguished.

The value obtained for the resolution using the above condition is given by:

$$
\begin{equation*}
w=1 / x \tag{36}
\end{equation*}
$$

In the case where the apodization function discussed earlier is used, the resolution is given by $\sqrt{2} /$ X. $^{8}$

If we are looking at broad band spectra. for which the width of the spectral line is much lareer than the resolution, We see from the above that we do not have the problem of side lobes in the transformed spectra. In this case, there is then no need to apodize.
7. Admission Angle and Resolving Power

Until now, we have only considered a plane wave which is normally incident upon the interferometer. We now consider the effect of a plane wave incident at an angle $\theta$.

The optical arrangement being considered is shown in Figure 4.


Figure 4. Michelson Interferometer

For the purpose of calculating the path differences between rays 1 and 2 , the optical system may be considered as shown in Figure 5.

$x=2 d ; b \cos \theta=d ; b \sin \theta=a / 2 ; a \sin \theta=c$
Figure 5. Equivalent Ray Diagram for the Interferometer The path difference between rays 1 and 2 is given by:

$$
\begin{align*}
\text { p.d. } & =2 b-c=2 b-a \sin \theta=2 b-2 b \sin ^{2} \theta \\
& =2(d / \cos \theta)\left(1-\sin ^{2} \theta\right)=2 d \cos \theta \tag{37}
\end{align*}
$$

For a monochromatic plane wave incident at angle $\theta$ we then have:

$$
F(x)=I\left(k_{1}\right) \cos \left(2 \pi k_{1} x \cos \theta\right)
$$

The Fourier transform of $F(x)$ is given by:

$$
\begin{align*}
& g(k)=\int_{-\infty}^{\infty} F(x) T(x) \exp (i 2 \pi k x) d x  \tag{38}\\
& =G(k) * t(k) \text { where } G(k) \text { and } t(k) \text { are the Fourier }
\end{align*}
$$

transforms of $F(x)$ and $T(x)$ respectively.
Now:

$$
\begin{align*}
G(k) & =\int_{-\infty}^{\infty}\left(k_{1}\right) \cos \left(2 \pi k_{1} \cos \theta x\right) d x \\
& \left.=\frac{I\left(k_{1}\right)}{2}\right)\left(\exp \left(i 2 \pi k_{1} \cos \theta x\right)+\exp \left(-i 2 \pi k_{1} \cos \theta x\right)\right) \exp (i 2 \pi k x) d x \\
& \left.=\frac{I\left(k_{1}\right.}{2}\right)\left(\delta\left(k+k_{1} \cos \theta\right)+\delta\left(k-k_{1} \cos \theta\right)\right) \tag{39}
\end{align*}
$$

For a uniformly radiating disc of solid angle $\Omega$.
the contribution from various angles of incidence between $\theta$ and $\theta+d \theta$ is proportional to the corresponding
solid angle $d \Omega=2 \pi \sin \theta d \theta=-2 \pi d(\cos \theta)$.
We now consider a source such as described above, when used with the Michelson interferometer. Then:

$$
\begin{aligned}
& \mathrm{cos} \theta=\cos \theta_{m} \\
& G(k)=A I\left(k_{1}\right) \int\left(\delta\left(k+k_{1} \cos \theta\right)+\delta\left(k-k_{1} \cos \theta\right)\right) d(\cos \theta) \\
& =A I\left(k_{1}\right) \text { if } k= \pm \mathrm{k}_{1} \cos \theta
\end{aligned}
$$

$$
\text { for some } \cos \theta^{\prime} \text { such that } 0 \leq \operatorname{coses}_{m} \leq \cos \theta^{\prime} \leq 1
$$

$$
=0 \text { otherwise }
$$

where $A=$ constant
$\theta_{\mathrm{m}}$ corresponds to the total solid angle $\Omega$
As before, we will neglect $k<0$.
$G(k)$ is then a step function, having a constant, non-zero value for $k_{1} \cos \theta_{m} \leq k \leq k_{1}$, and zero otherwise.

Neglecting the effect of finite integration limits and considering only small values of $\theta$, we now consider the resolution of two frequencies with wave numbers $k_{1}$ and $k_{2} . G(k)$ is shown in Figure 6, for two elements which are easily resolved.


Figure 6. Angular resolution
To be resolved, $\mathrm{k}_{2} \cos \theta_{\mathrm{m}}$ must be greater than $k_{1}$. For calculation purposes, we may assume that they are Just resolved when $k_{2} \cos \theta_{\mathrm{m}}=\mathrm{k}_{1}$. Then:

$$
\Delta k=k_{2}-k_{1}=k_{1}\left(1 / \cos \theta_{m}-1\right)=k_{1} \frac{\left(1-\cos \theta_{n}\right)}{\cos \theta_{m}-}
$$

The resolving power is defined as ${ }^{m_{R}}=k / \Delta k$, where
$k$ is the average value of the wave numbers of the two
frequencies just resolved. Thus:

$$
\begin{array}{ll}
k=\frac{k_{1}+k_{2}}{2}=\frac{k_{1}}{2} \frac{\left(1+\cos \theta_{m}\right)}{\cos \theta_{m}} \quad \text { and } \\
R=\frac{1+\cos \theta_{m}}{2\left(1-\cos \theta_{m}\right)} \simeq \frac{1}{1-\cos \theta_{m}} \quad \text { for small } \theta_{m}
\end{array}
$$

Now:

$$
\begin{equation*}
\Omega=-2 \pi \int_{\cos \theta=1}^{\cos \theta}(\cos \theta)=2 \pi\left(1-\cos \theta_{\mathrm{m}}\right) \tag{41}
\end{equation*}
$$

Therefore. we have the result which Jacquinot ${ }^{3}$
gives, that is:
$R \Omega=2 \pi$

## 8. Resolution

There are two factors which govern the resolution, namely the maximum path difference and the admission ansle. The true resolution will be less than the sum of these resolutions calculated independently of each other and greater than either of them individually. The admission angle is chosen such that the resolution calculated for the maximum wave number of interest is less than the resolution determined by the maximum path difference. The resolution is then within a factor of 2 as calculated using the maximum path difference.

If we consider a monochromatic source with an admission angle which allows a maximum angle of incidence onto the interferometer of $\theta \mathrm{m}$, then:
for $\theta_{\mathrm{m}}$ small.

$$
\begin{align*}
& F(x) \propto \int_{k_{1}} \cos \cos \theta_{m} \\
&=\frac{1}{\pi x}\left\{\cos \left(\frac{2 \pi k_{1}}{2} 1-\frac{x}{2 \pi x}+\sin \left(2 \pi k_{1} x\right)-\sin \left(2 \pi k_{1} \cos \theta_{m} x\right)\right)\right. \\
& \approx\{l /(\pi x)\}\left\{\cos \left(2 \pi k_{1} x\right) \sin \left(\frac{\pi k_{1}}{2} \frac{x \theta_{1}^{2}}{2}\right)\right\}  \tag{43}\\
& \text { small. }
\end{align*}
$$

Since the arguement of the cosine term is larger than the arguement of the sine term. we have a cosine variation which has an envelope of $\frac{1}{\pi x} \sin \frac{\pi k_{1} x \theta_{m}^{2}}{2}$ This envelope tends to zero as $x$ tends to $\frac{2}{k_{1} \theta_{\mathbb{Z}}^{2}}$. Since we have $R=\frac{k}{\Delta k}=k X$ and

$$
\begin{array}{ll}
\Omega=2 \pi\left(1-\cos \theta_{m}\right) \simeq \pi \theta_{\mathrm{m}}^{2} & \text { then } \\
\mathrm{R} \Omega=\mathrm{kX} \pi \theta_{\mathrm{m}}^{2}=2 \pi & \text { and } \\
X=2 /\left(k \theta_{\mathrm{m}}^{2}\right) &
\end{array}
$$

We see that for a given wave number, the resolution as defined by $1 / X$ is limited by the choice of the admission angle.

The theoretical resolution is not always realized in practice. When the fluctuations in $F(x)$ become comparable to the noise, then it is useless to sample the interferogram beyond this value.

For high resolution, the admission ande must be reduced, hence reducing the amount of radiation avallable. In the case of strong absorption or reflection, the $\mathrm{s} / \mathrm{N}$ ratio may be such that it dictates that the sampling of the interferogram be terminated. It is then the $\mathrm{S} / \mathrm{N}$ ratio which limits the resolution attainable.

## 9. False Energies

In order to be able to calculate the intensity at the maximum frequency of interest, we must sample at least twice per cycle. In the spacial variation, this means:

$$
\begin{equation*}
\left(2 \pi k x^{\prime}-2 \pi k x\right)=\pi \quad \text {; that is, } 2 \Delta x=I / K \tag{44}
\end{equation*}
$$

where $\Delta \mathrm{X}$ is the spacial sampling interval and $K$ is the
maximum frequency of interest.
The effect of digitization is that the integrals
must be approximated by sums, that is:

$$
\begin{align*}
c\left(k_{i}\right)= & \int_{-x}^{x} F(x) \cos \left(2 \pi k_{i} x\right) d x \approx \frac{1}{2}\left(F(0)+F(\Delta x) \cos \left(2 \pi k_{i} \Delta x\right)\right) \Delta x \\
+ & \frac{1}{2}\left(F(\Delta x) \cos \left(2 \pi k_{i} \Delta x\right)+F(2 \Delta x) \cos \left(2 \pi k_{i} \Delta \Delta x\right)\right) \Delta x+\cdots \cdots \\
+ & \frac{1}{2}\left(F((N-1) \Delta x) \cos \left(2 \pi k_{i}(N-1) \Delta x\right)+F(N \Delta x) \cos \left(2 \pi k_{i} N \Delta x\right)\right) \Delta x \\
+ & \frac{1}{2}\left(F(0)+F(-\Delta x) \cos \left(2 \pi k_{i} \Delta x\right)\right) \Delta x+\cdots \cdots \cdots \cdots \cdots \cdots \cdots \\
+ & \frac{1}{2}\left(F(-(N-I) \Delta x) \cos \left(2 \pi k_{i}(N-1) \Delta x\right)+F(-N \Delta x) \cos \left(2 n k_{i} N \Delta x\right) \Delta x\right. \\
= & \Delta x\left(F(0)+\frac{(F(N \Delta x)+F(-N \Delta x)) \cos \left(2 \pi k_{i} N \Delta x\right)}{2}\right. \\
& \left.+\sum_{m=1}^{A-1}\left(\frac{F\left(m_{\Delta} x\right)+F(-m \Delta x)}{2}\right) \sin \left(2 \pi k_{i} m \Delta x\right)\right) \tag{45}
\end{align*}
$$

and similarly:

$$
\begin{align*}
s\left(k_{i}\right)= & \Delta x\left\{\frac{(F(N \Delta x)-F(-N \Delta x)) \sin \left(2 \pi k_{i} N \Delta x\right.}{2}\right. \\
& \left.+\sum_{m=1}^{N-1} \frac{(F(m \Delta x)-F(-m \Delta x))}{2} \sin \left(2 \pi k_{i} m \Delta x\right)\right\} \tag{45}
\end{align*}
$$

where $\pm N \Delta x= \pm X$.
Because of the finite sampling interval and consequent approximation of the integrals by sums, there are "false energies" introduced at $k_{i}$ due to radiation with frequercies greater than $K$ and equal to $2 n K-k_{1}$ and $2(n-1) K-k_{1}$ where $n \geq 1$ and is integral.

This may be seen from the following:

$$
\begin{equation*}
2 \pi\left(2 n K-k_{i}\right) m \Delta x=2 \pi m n-2 \pi k_{i} m \Delta x \tag{47}
\end{equation*}
$$

since $K=\frac{1}{2}(1 / \Delta x)$.

## Therefore:

$$
\begin{align*}
& \cos \left(2 \pi\left(2 n K-k_{i}\right) m \Delta x\right) I\left(2 n K-k_{i}\right) \\
& =I\left(2 n K-k_{i}\right)\left(\cos (2 \pi m n)+\cos \left(2 \pi k_{i} m \Delta x\right)\right) \\
& =I\left(2 n K-k_{i}\right)\left(I+\cos \left(2 \pi k_{i} m \Delta x\right)\right. \\
& =I\left(2 n K-k_{i}\right)+I\left(2 n K-k_{i}\right) \cos \left(2 \pi k_{i} m \Delta x\right) \tag{48}
\end{align*}
$$

Thus, upon Fourier analysis, this radiation of higher frequencies becomes indistinguishable from that of $\mathrm{k}_{1}$ and these terms will contribute to the calculated values of $c\left(k_{1}\right)$ and $s\left(k_{1}\right)$.

In order to eliminate these false energies, it is necessary to reduce $I(k)$ to zero for $k \geq K$.

## SECTION III

## INSTRUMENTATION OF THE SPECTROMETER

## 1. The Spectrometer

The spectrometer used for the work in this thesis is a FSo720 Fourier spectrophotometer, employing a stepping motor drive. The unit is manufactured by Beckman RIIC Limited. A ray diagram for the instrument, taken from the instruction manual. is given in Figure 7.

In order to eliminate water vapour absorption of the infrared radiation, the spectrometer is held under a vacuum during the course of an experiment. The vacuum is produced using a Precision Scientific model 150 pump, rated at 150 i1tres/minute free air displacement. This produces an ultimate vacuum of approximately 10 microns after one hour of pumping. A cold trap is incorporated into the pumping line to prevent back streaming of oil vapour from the pump. since it is extremely important that oil. which absorbs very strongly, does not collect on the optical components of the spectrometer.

A vacuum connection has been installed on one side of the source module, to which a pirani gauge is normally attached. This connection serves also to employ a mass spectrometer leak detector.

The electronics of the spectrometer are operated from a regulated power supply (Stabiline 1E 5101).
2. Source


Work in the infrared is limited by the availability of sources of sufficient intensity. There are two types of sources commonly avallable, namely grey hot bodies, for which the emissivity is a constanc less than unity, and mercury arcs.

Grey hot bodies are best used for wave numbers greater than $100 \mathrm{~cm}^{-1}$. Shown in Figure $8^{9}$ is a comparison of the performance of a mercury arc lamp (working pressure of 3 atmospheres) and a globar (operated at $1200^{\circ} \mathrm{K}$ ). The lamp used was the same type as is employed in the FS-720, a Phillips' $H P K, 125 \mathrm{~W}$ lamp.

The high pressure of the mercury vapour in the lamp broadens the discrete emission lines and a broad band spectra is obtained. The intensity of the emitted radiation is pressure dependent, increasing with pressure.

The envelope of the lamp is of fused quartz, which absorbs the infrared radiation of the arc above $200 \mathrm{~cm}^{\boldsymbol{- 1}}$. The main source of infra radiation above $200 \mathrm{~cm}^{-1}$ is then due to the hot envelope 1tself. The surface of the envelope is "dimpled" to reduce interference effects.

Cooling of the lamp is provided by a water cooled lamp housing. The lamp is protected asainst overheating by a thermostat which cuts off the lamp power supply if the temperature of the lamp base exceeds $65-75^{\circ} \mathrm{C}$.


Figure 8. Comparison of a Mercury Lamp to a Globar

## 3. Beam Splitter

The interchangeable beam splitters are made from mylar (polyethylene terephalate) and are of thicknesses 6, 12, 25, 50 and 100 microns.

The transmitted radiation through the interferometer depends on the product of squares of the transmission and reflection coefficients, $t$ and $r$ respectively, of the beam splitter. If no absorption occurs, then $|r|^{2}+|t|^{2}=1$ and the maximum of the product $|r|^{2}|t|^{2}$ occurs when $|r|^{2}=|t|^{2}=0.5$ and $|r t|^{2}$ is then 0.25 . This product may be very much less depending on the polarization, as is shown in Appendix A. This is a serious drawback and is one of the main reasons why the lamellar grating interferometer is superior in the very far infrared region of very low intensity radiation.

Figure 9, taken from the instruction manual, shows the relative beam splitter efficiencies, neglecting absorption. The diagram is erroneous in that the correct condition for a maximum is $\mathrm{Bd}=\left(\mathrm{N}-\frac{1}{2}\right) \pi, \quad(\mathrm{N}=1,2,3 \ldots)$ that is, $k=\frac{\left(N-\frac{1}{2}\right)}{2 n d\left(1-1 / 2 n^{2}\right)^{\frac{1}{2}}}$ as is shown in Append $1 \times \mathrm{A}$ (In the Appendix, $k=\frac{2 \pi}{\lambda}$, here $k=\frac{1}{\lambda}$ ). Likewise, the condition for a minimum is $k=\frac{N}{2 n d\left(1-1 / 2 n^{2}\right)^{\frac{1}{2}}} \cdot$ For $n=1.6 . \quad\left(1-1 / 2 n^{2}\right)^{\frac{1}{2}}=.9$. The correct locations of the maxima and minima are then shifted to $1 /(.9)^{2}=1.23$ times the values shown in Figure 9.

In regions of low efficiency, the $\mathrm{S} / \mathrm{N}$ ratio decreases and the beam splitter size must therefore be chosen for the


FIGURE 9: RELATIVE REAM SPLITTER EFFICIENCIES
appropriate spectral range. A number of separate spectra may be needed to cover the spectral region of interest, especially in the lower energy end of the spectrum.

Since the radiation is not normally ineident upon the beam splitter, the sigma and pi coefficients of reflection and transmission are different, resulting in the beam being strongly polarized. A calculation of this polarization is given in Appendix A.
4. Admission Angle and Resolving Power

The collimating mirror for the source is an
f:1.7 surface alumnized offoaxis paraboloid. The focal length is given by $f=$ (f number) (linear diameter of entrance pupil).

For the FS-70:

$$
\begin{equation*}
f \simeq(1.7)(3 \times 2.54) \simeq 13.0 \mathrm{~cm} \tag{49}
\end{equation*}
$$

From equation 42 , the theoretical resolving power is given by:

$$
\begin{equation*}
\mathrm{R}=\frac{2 \pi}{\Omega} \simeq \frac{2 \pi}{\pi}\left(\frac{2 f}{d}\right)^{2}=8\left(\frac{f}{d}\right)^{2} \tag{50}
\end{equation*}
$$

where:
$\Omega=$ the solid angle subtended by the source at the centre of the collimating mirror
$f=$ the focal length of the collimating mirror
$d=$ the linear diameter of the source.
The source aperture of the FS-720 is variable in
steps of 3,5 and 10 mm diameter. We therefore have theoretical resolving powers of $1.48 \times 10^{4}, 5.4 \times 10^{3}$ and $1.35 \times 10^{3}$ respectively for the above apertures.

In order to maintain these theoretical resolving
powers, we require the admission angle of the detector to be as large as or larger than the largest solid angle subtended by the source. since the effective admission angle, that is, that through which radiation from the interferometer enters the detector, is the same as the anale subtended by the source.

## 5. Drive

The position of the moveable mirror is controlled by a stepping motor. The mirror may be moved either to the left or right of zero path differences in steps of 5 . 10. 20,40 and 80 microns path difference. From equation 44, this would allow maximum calculateable wave numbers of 1000. 500. 250.125 , and $62.5 \mathrm{~cm}^{-1}$ respectively for the above stepfing intervals.

The maximum path difference is $X= \pm 5 \mathrm{~cm}$ from which the maximum obtainable resolution as defined by equation 36 is $.2 \mathrm{~cm}^{-1}$.

The gating times or time periods between samples are $0.53,1.07,2.13 .4 .27,8.53 .17 .06$ and 34.13 seconds.
6. Detector

The detector employed in the FS-720 is a Golay, fitted with a 3 mm diameter diamond window and is manufactured by Unicam Instruments Limited.

The Golay cell is a pneumatic chamber, sealed at one end by a radiation absorbine film and at the other by a mirror membrane. The cell contains xenon gas which, when
warmed by the absorbing film, expands and causes a distortion of the flexible mirror membrane. The distortion of the mirror is converted into an electrical signal by means of an optical system which reflects light off the mirror surface onto a photomultiplier. The amount of light incident on the photomultiplier depends on the distortion of the mirror membrane. The operating point of the detector is chosen such that the signal of the photomultiplier bears a linear relationship to the mirror displacement.

Light from the source is chopped at 15 . HZ by a rotating blade. This produces a corresponding oscillation in the mirror membrane and hence in the electrical signal from the photomultiplier. The radiation signal received from the rotating blade of the chopper becomes the zero reference signal when the output signal of the detector is demodulated and amplified. The ambient radiation does not then appear in the amplified signal.

The pneumatic chamber has a small leak connecting it with a ballasting chamber on the far side of the mirror membrane. The time required for the two chambers to reach equilibrium pressure is of the order of several seconds. and therefore has little effect on the signal due to the chopped radiation from the source. The response of the cell is shown in Figure 10, taken from the Golay instruction manual.

The leak between the two chambers prevents slow changes in the ambient temperature from affecting the signal.


Figure 10. Response of the Golay Detector

A comprehensive description of a Golay detector is given by Hadni ${ }^{2}$.

The root mean square equivalent noise input at any frequency and in a certain bandwidth is defined as the r.m.s. signal at the same frequency which would equal the r.m.s. noise in the same bandwidth. For the detector used in the FS-720, the quoted value of the R.M.S.E.N.I. is $4 \times 10^{-11}$ watts at 15 Hz in a bandwidth of 0.1 Hz .

The sensitivity in this system is defined as the
ratio:

$$
\frac{\text { R.M.S. volts }(15 \mathrm{~Hz}) \text { Output }}{\text { R.M.S. watts }(15 \mathrm{~Hz}) \text { radiation Input }}
$$

This has an approximate value of $2 \times 10^{5}$ volts/watt for the detector employed with the FS-720.

The absorbing membrane in the detector employed is quoted as having a constant response for all wavelengths in the range 1 to 1000 microns.

The diamond window of the detector transmits approximately $50-60 \%$ of the incident radiation in the range $10-1000 \mathrm{~cm}^{-1}$.

Below $40 \mathrm{~cm}^{-1}$. Perry, Geik and Youns ${ }^{8}$ note that the S/N ratio for a Golay detector rapidly decreases and it then becomes advantageous to use a detector which has a greater
detectivity.
In the very far infrared; there are only three other detectors which are used appreciably, all of which require operation at low temperatures. These are the carbon bolometer, germanium bolometer and indium antirinide photodetector. A comparison of the response of the above detectors is given in the paper mentioned above.
7. Electronics

The voltage signal produced by the Golay detector bears a linear relationship to the radiation intensity incident upon the detector. This relationship is given by the sensitivity.

The voltage signal is amplified, demodulated. integrated and filtered before being fed into an analogue to digital converter. A full description of the above system is given in the instruction manual.
8. Filtering

As previously discussed, filtering is necessary to eliminate "false energies". Filtering is also required to prevent unwanted short wavelength radiation from overloading the detector to the extent that the low intensity far infrared radiation may not be measureable because the dynamic range of the analogue to digital converter is not sufficient for the detection of this weak sienal against the background of high intensity short wavelength radiation (see Section IV).

Black polyethylene acts as an optical filter. strongly attenuating frequencies of wave number greater than $500 \mathrm{~cm}^{-1}$. The condensing lens of the detecting system is made of black polyethylene and thus serves as a filter as well as a lens.

Other optical filters, supplied by Beckman Instruments, with different cut-off frequencies, are used. Transmission curves for these are shown in Figure 11.

Electronic filtering is employed in the amplifying circuitry. The value of the time constant in the RC filter is appropriately chosen to filter out the unwanted high frequencies, as well as the residual ripple of the demodulated 15 Hz frequency due to chopping.

If the highest frequency of interest has a wave number $K$ and we sample at least twice per cycle for this maximum frequency, then we require a time, $2 \Delta t$, to sample one complete cycle. The time required for each sample is $\Delta t$ 。

Therefore:

$$
\begin{equation*}
w_{\max }=2 \pi f=2 \pi /(2 \Delta t)=\pi /(\Delta t) \tag{51}
\end{equation*}
$$

In order that frequencies of interest are not appreciable attenuated and that the unwanted high frequencies are strongly attenuated, we require that:

$$
\begin{equation*}
\tau_{w_{\max }} \simeq 1 \tag{52}
\end{equation*}
$$

that is, the 3 db point.
Therefore:

$$
\begin{equation*}
\tau=\frac{\Delta t}{\pi} \tag{53}
\end{equation*}
$$

The FS-720 has time constants of $0.5,1,2,4,8$ and

(\%) noissthswuil

## SECTION IV

## DYNAMIC RANGE

Since the Fourier transform is a linear operation, we may regard the interferogram as a noise interferogram plus a signal interferogram. that is:
$F(x)=F(x)_{N}+F(x)_{S}$ for noise of a random nature. In order to observe the signal interferogram, we require that:

$$
\frac{F(x)_{S}}{F(x)_{N}}>\frac{N}{S} \quad \text { that is: } S / N>\frac{F(x)_{N}}{F(x)_{S}}
$$

The dynamic ranse, or distinguishable signal levels, of the analogue to digital converter must be greater than $\frac{F(x)_{N}}{F(x)_{S}}$ in order to fully utilize the signal. The FS-720 has a 12 bit binary $A / D$ converter and can therefore distinguish 1 bit in $4,096$.

A large portion of the d.c. interferogram signal. $I(\infty)$, may be subtracted before being fed to the $A / D$ converter, by adjusting the "zero offset" voltage. The entire range of the $A / D$ converter may then be filled with the varying portion of the signal, $F(x)$.

Mertz ${ }^{10}$ has shown that:

$$
\frac{\bar{s}}{\left(\bar{n}_{I}^{1}\right)^{1 / 2}}=\sqrt{\frac{\Delta \nu_{n}}{\Delta \nu_{s}}} \frac{I_{0}}{\sqrt{\bar{n}_{I}} \sqrt{N}}
$$

where:

$$
\begin{aligned}
\mathbf{s} & =\text { the average spectral intensity } \\
\sqrt{\overline{n_{1}^{2}}} & =\text { the r.mos. noise per unit abscissa of the } \\
& \text { interferogram } \\
\sqrt{\overline{n_{s}^{2}}}= & \text { the r.m.s. noise per unit abscissa of the } \\
& \text { spectrum }
\end{aligned}
$$

$\Delta \nu_{s}=$ the spectral bandwidth
$\Delta V_{n}=$ the noise bandwidth
$I_{0}=$ the amplitude of the peak to peak envelope of the central fringes of the interferogram
$N=$ the number of resolved elements in the spectrum.

The ratio $s / \sqrt{\sqrt{n_{s}^{2}}}$ may be improved by decreasing $\Delta \nu_{s}$ by filtering and by decreasing $n_{I}$ using longer integrating times.

If the spectrum consists of a background and a very narrow line, then the dynamic range and $S / N$ ratio must be greater than the ratio of the area under the background spectral curve to the area under the line curve in order that the narrow feature can be distinguished.

## SECTION V

## ADAPTATIONS FOR LOW TEMPERATURE WORK

A cryostat was constructed which may be attached to the spectrometer sample chamber, after removing the top cover plate of the chamber.

A stand with an adjustable height setting was built in order to support the cryostat. such that it did not place any weight on the spectrometer.

The cryostat consists of an outer brass shell. containing two dewars. Both dewars are suspended from the top of the outer shell by stainless steel tubing, in order to reduce heat flow into the inner part of the cryostat.

The outermost dewar is a brass jacket containing liquid nitrogen, A $15 / 8^{\prime \prime} 0 . D$. copper tube extends downward from the bottom of this container and surrounds the tail of the inner dewar, thus acting as a radiation shield. At the lower end of the shield are two diametrically opposite 7/8" diameter holes. which allow the radiation from the interferometer to pass to the sample and then out again to the detector.

The inner dewar is a one litre stainless steel
can. A thin 1 " diameter stainless steel tube extends downward from the bottom of the can and is sealed at the lower end by a copper plug. which is threaded to accept a copper sample holder, shown in Figure 12. An indium pad is placed between the plug and sample holder to provide a good thermal contact.


Material: Copper


Figure 12. Sample Holder

The stainless steel tube also extends approximately $2 / 3$ of the way up into the inner dewar. This facilitates easy conversion to a variable temperature cryostat. (Reference: R.W. MacPherson ${ }^{11}$ ).

In order to prevent heat leaks due to conduction and convection, the space between the various components of the cryostat must be evacuated. Since the spectrometer pumping system could not produce a sufficiently low pressure for the cryostat to operate effectively, it was necessary to isolate the two systems. A diffusion pump was used to pump the cryostat to a lower pressure than the spectrometer. The isolation of the system was initially accomplished by means of two $\frac{1}{4}$ " thick soft polyethylene windows with a cryostat tailpiece. This was found to be unsatisfactory due to strong signal absorption, especially
at high energies. Finally, the spectrometer "purge kit" unit was used. This unit is the same as the standard sample cell module except that it has a vacuum tight $\frac{1}{4}$ " thick hard polyethylene window, covering the entrance aperture。

The spectral distribution for the spectrometer using the purge kit and a 25 G ( 6 micron) beam splitter is shown in Figure 13.

A holder for the optical filters was made. which fits on the cryostat tailpiece.

The arrangement of the helium return and vacuum system pumping lines is shown in Figure 14.

INTENSITY



FIGURE 14: HELIUM RETURN AND PUMPING LINES

## THEORY OF IONIZED CENTRES IN DOUBLE DOPED SILICON

If a group III atom replaces a silicon atom in a perfect lattice, a hole state is produced. This hole state is loosely bound to the impurity site. The hole in the ground state of the impurity atom may be excited by electromapnetic radiation. These excitations can therefore be investigated by means of absorption spectra.

Boron doped silicon has been studied by Colbow ${ }^{12}$.
Shown in Figure 15 are the normal ground state energy levels for the individual impurities. Besides the ground state, there are excited hole states which are bound and lie between the ground state and the valence band.
V.B.


$$
\begin{aligned}
& x=\text { electron } \\
& 0-\text { hole } \\
& T \approx 4^{\circ} \mathrm{K}
\end{aligned}
$$

Figure 15. Ground States of Singly-Doped Silicon

It is believed that, when silicon is doped with both boron and indium, ionized impurity atoms could be formed. This is illustrated in Figure 16.


Figure 16. Possible Ground States of Doubly-Doped silicon

The $\mathrm{B}^{-}$ion resembles a $\mathrm{H}^{-}$like ion, for which only the ground state exists. The $\mathrm{In}^{+}$also resembles a $\mathrm{H}^{-}$ like ion, only with the charges of the nucleus and electron reversed. We assume, then, that no excited hole states exist when the impurity centres are ionized.

In order to calculate the electronic energy of the $B^{-}$ion in the lattice, we assume that the ratio of this energy to the binding energy of the boron atom in the lattice is the same as the ratio of the binding energy of the free $\mathrm{H}^{-}$ion to the binding energy of the Hydrogen atom, that is:

$$
\frac{E_{B}-}{E_{B}}=\frac{E_{H^{-}}}{E_{H}} \quad \text { Therefore: } \quad E_{B}-=E_{B}\left(\frac{E_{H}-}{E_{H}}\right)
$$

We then have, for the binding energy of the $\mathrm{B}^{-}$
ion:

$$
\begin{aligned}
E_{B}-=(.045)\left(\frac{.75}{13.6}\right) \mathrm{ev} & =2.48 \times 10^{-3} \mathrm{ev} \\
& \simeq 7.4 \mathrm{~cm}^{-1}
\end{aligned}
$$

In a similar manner:

$$
\begin{aligned}
\mathrm{EInt}_{\mathrm{In}}=(.155)\left(\frac{.75}{13.6}\right) \mathrm{ev} & =8.55 \times 10^{-3} \mathrm{ev} \\
& =69 \mathrm{~cm}^{-1}
\end{aligned}
$$

The $\mathrm{B}^{-}$impurity is optically inactive; however. the In $^{+}$ion is optically active. Therefore, in order to determine whether the ionization does occur, we look for continuous optical absorption for frequencies with wave numbers greater than $70 \mathrm{~cm}^{-1}$. This energy is well below the energy of excitations of the ground state of boron and indium and should therefore be distinguishable from them.

## SECTION VII

## EXPERIMENTAL PROCEDURE AND RESULTS

1. Sample Preparation and Mounting

All samples were polished using 600 mesh abrasive on astomet cloth.

Before obtaining a spectrum, the samples were ultrasonically degreased in toluene and then in ethyl alcohol.

To ensure a good thermal contact with the sample holder, a small amount of vacuum grease mixed with powdered silver was placed between the sample and the holder. The grease was used on one end of the sample only, to avoid introducing strains across it when the grease froze.

The front plate of the sample holder was fastened down just sufficiently to hold the sample against the back face of the sample holder (see Figure 12).

A small amount of vacuum grease mixed with powdered silver was also placed on the threads of the copper plug, at the bottom of the $1^{\prime \prime}$ diameter stainless steel tube, to ensure a good thermal contact between it and the sample holder.
2. Temperature of the Sample

After the helium boils off in the $1 "$ diameter stainless steel tube to which the sample holder is attached, the sample may be warmed slightly by the incident radiation.

From the spectra obtained, it is seen that there is no dependance of the absorption on $\lambda^{2}$ and it is therefore assumed that the temperature of the samples was sufficiently low that free carrier absorption did not have any appreciable
effect on the spectra.
3. Results

Shown in Figure 17 is the absorption spectrum of boron-doped silicon at liquid helium temperature. The boron impurity concentration is approximately $1.3 \times 10^{16}$ atoms $/ \mathrm{cm}^{3}$. The thickness of the sample is 1.02 mm .

From Colbow ${ }^{12}$, the ratio of the transmission of the reference to the sample spectrum is:

$$
\text { Rat10 }=1 / T=\frac{1-R^{2} \exp }{(1-R)^{2} \exp \left(\frac{2 \alpha d}{(-\alpha d}\right)}
$$

Where $R$ is the reflection coefficient of the sample and $\alpha$ the absorption coefficient. The reference used here is the spectrum obtained with no sample in the beam, all other conditions being the same as for a sample spectrum.

Since $R$ is fairly constant (see below), the peaks were due to absorption effects.

We observed peaks 1 through 4 at the same frequencies as did Colbow ${ }^{12}$.

An absorption spectrum of silicon doubly doped with boron $\left(N_{B}=2.6 \times 10^{16}\right.$ atoms $\left./ \mathrm{cm}^{3}\right)$ and indium $\left(N_{I}=1.8 \mathrm{x}\right.$ $10^{17}$ atoms $/ \mathrm{cm}^{3}$ ), was obtained at liquid helium temperature for a sample 1.67 mm thick. This spectrum is shown in Figure 18.

The spectrum may be seen to be basically the same as that of the boron-doped silicon, except that the absorption lines are broadened due to impurity concentration effects.

Shown in Figure 19 is the spectrum of a 2.04 mm thick sample of intrinsic silicon at liquid helium temperature.


FIGURE 17: BORON DOPED SILICON


FIGURE 18: DOUBLE DOPED SILICON


PTOLRE 19: TNTRTNSTC ETTITCON

There is an oxygen impurity concentration of $5 \times 10^{17}$ to $10^{18}$ atoms $/ \mathrm{cm}^{3}$. These impurities do not affect the spectrum in the region observed here.

For this spectrum we have:
Ratio $=1 / T=\frac{1+R}{1-R}$. since $\alpha=0$
For a constant value of the reflectivity, $1 / \mathrm{T}$ does not vary with wave number. As is seen in the spectrum obtained, $1 / T$ varies with wave number. It is thought, therefore, that the reflectivity may be frequency dependant.

Comparing the three spectra described above, we are led to suspect that the low energy tail below $240 \mathrm{~cm}^{-1}$ in the spectra of the doped silicon samples was due to the reflection characteristic of silicon.

Using the FS-720 Michelson interferometer, we were able to obtain the absorption peaks observed by Colbow in boron-doped silicon for the spectral region $240 \mathrm{~cm}^{-1}$ to $330 \mathrm{~cm}^{-1}$. We were also able to extend the spectral reaion down to $40 \mathrm{~cm}^{-1}$.

We were unable to observe any absorption edge which would be indicative of the existence of ionized $B^{-}$and In ${ }^{+}$centres, at the impurity concentrations and temperatures with which we were working.

Comparing the spectrum of the intrinsic silicon with that of the impurity doped silicon samples, we were led to suspect that the low energy tail of the doped silicon spectra was due to a frequency dpdendence of the reflection coefficient of silicon. In order to confirm this, reflectivity measurements should be made using a special reflectance attachment, available from the manufacturer of the spectrometer.

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## APPENDIX A

## POLARIZATION

Consider a non-absorbing film of refractive index $n_{f}$ with radiation incident at an angle $\theta$ as shown below:


From Snell's law:

$$
\begin{equation*}
n_{1} \sin \theta=n_{f} \sin \psi=n_{2} \sin \phi \tag{1}
\end{equation*}
$$

stone ${ }^{13}$ shows that for both the pi and sigma

## polarizations:

$$
\begin{array}{ll}
E_{1}+E_{r}=E_{+}+E_{-} & Y_{1}\left(E_{i}-E_{r}\right)=Y_{f}\left(E_{+}-E_{-}\right) \\
E_{+} e^{i \beta d}+E_{-} e^{-1 \beta d}=E_{t} & Y_{f}\left(E_{+} e^{i \beta d}-E_{-} e^{-i \beta d}\right)=Y_{2} E_{t} \tag{2}
\end{array}
$$

Where the E's are electric vectors associated with the corresponding wave vector of the diagram.

$$
\begin{equation*}
\mathcal{\beta}=n_{f} k_{o} \cos \psi \tag{3}
\end{equation*}
$$

and:

$$
\begin{array}{lll}
Y_{1 \pi}=\frac{n}{\cos \theta}- & Y_{f \pi}=\frac{n}{\cos \psi} & Y_{2 \pi}=\frac{n_{2}}{\cos \phi} \\
Y_{1 \sigma}=n_{1} \cos \theta & Y_{f \sigma}=n_{f} \cos \psi & Y_{2 \sigma}=n_{2} \cos \phi \tag{4}
\end{array}
$$

Stone further shows that $E_{+}$and $E_{\text {. }}$ may be eliminated in equations 2 to give:

$$
\begin{equation*}
E_{i}+E_{r}=\left(\cos \beta d-i \cdot \bar{Y}_{f} \sin \beta d\right) E_{t} \tag{5}
\end{equation*}
$$

$$
\begin{align*}
& Y_{1}\left(E_{i}-E_{r}\right)=\left(-i Y_{f} \sin \beta d+Y_{2} \cos \beta d\right) E_{t}  \tag{6}\\
& \text { If } \theta=T / 4, n_{1}=n_{2}=1 \text { and } n_{f}=1.5 \text {, then: } \\
& \sin \theta=\sin \phi=\cos \theta=\cos \phi=1 / \sqrt{2} \tag{7}
\end{align*}
$$

and : $\quad \cos \psi=\left(1-\sin ^{2} \psi\right)^{\frac{1}{2}}=\left(1-\frac{1}{1.5^{2} \sqrt{2}}{ }^{2} \frac{1}{2} \approx .9\right.$
For the pi component, we then have:
$Y_{1}=\sqrt{2} \quad Y_{2}=\sqrt{2} \quad Y_{f}=1.6 / .9=1.78$
Adding equations 5 and 6 and using equations 7,8
and 9, we have:

$$
\begin{equation*}
2 E_{i}=\left(2 \cos \beta \mathrm{~d}-i\left(\frac{\sqrt{2}}{1.78}+\frac{1.78}{\sqrt{2}}\right) \sin \beta \mathrm{d}\right) E_{t} \tag{10}
\end{equation*}
$$

or: $\quad E_{i}=(\cos \beta d-i(1.025) \sin \beta d) E_{t}$
and therefore:

$$
\begin{align*}
\left|t_{\pi}\right|^{2}=\left|\frac{E_{t}}{E_{i}}\right|_{\pi}^{2} & =\frac{2}{\cos \beta d+(1.025)} 2 \sin ^{2} 2 \bar{d} \\
& =\frac{1}{1+.05 \sin \beta d} 2- \tag{11}
\end{align*}
$$

For the sigma component, we have:
$Y_{1}=1 / \sqrt{2} \quad Y_{2}=1 / \sqrt{2} \quad Y_{f}=(1.6)(.9)=1.44$
Adding equations 5 and 6 as before, we have:

$$
\begin{equation*}
2 E_{i}=\left(2 \cos \beta \mathrm{~d}-i\left(\sqrt{2}(1.44)+\frac{1}{\sqrt{2}(1.44)}\right) \sin \beta \mathrm{d}\right) \mathrm{E}_{\mathrm{t}} \tag{13}
\end{equation*}
$$

Therefore:

$$
\begin{align*}
& \left|t_{\sigma}\right|^{2}=\left|\frac{E_{t}}{E_{i}}\right|_{\sigma}^{2}=\frac{1}{\cos } 2 \frac{1}{\beta d+(1.26)} 2 \frac{}{\sin \beta \mathrm{~d}} \\
& =\frac{.05 \sin ^{2} \beta \mathrm{~d}}{\left(1+.05 \sin ^{\beta} \mathrm{d}\right)} 2- \tag{14}
\end{align*}
$$

For a non-absorbing film, $|r|^{2}+|t|^{2}=1$.
Therefore:

$$
\begin{equation*}
|r t|^{2}=|t|^{2}\left(1-|t|^{2}\right) \tag{15}
\end{equation*}
$$

For the pi polarization, we have:

$$
\begin{align*}
|\mathrm{rt}|^{2} & =\frac{1}{(1+.05 \sin \beta \mathrm{~d})} 2 \frac{.05 \sin ^{2} \beta \mathrm{~d}}{(1+.05 \sin \beta \mathrm{~d})} 2 \\
& =\frac{.05 \sin ^{2} \beta \mathrm{~d}}{(1+.05 \sin } 2 \frac{\beta \mathrm{~d})}{}^{2-} \tag{16}
\end{align*}
$$

The maximum of the expression occurs when $\sin \beta d=1$. that is:

$$
\begin{equation*}
\beta d=\pi\left(n+\frac{1}{2}\right) \quad n=0,1,2,3, \ldots \tag{17}
\end{equation*}
$$

By a similar analysis, the same condition for a maximum of $|r t|^{2}$ applies to the sigma polarization.

For the sigma polarization:

$$
\begin{align*}
|r \mathrm{t}|^{2} & =\frac{}{(1+.58 \sin } 2 \frac{1}{\beta \mathrm{~d})}\left(\frac{.58 \sin ^{2} \beta \mathrm{~d}}{1+.58 \sin } 22 \mathrm{~d}\right) \\
& =\frac{.58 \sin ^{2} \beta \mathrm{~d}}{\left(1+.58 \sin ^{2}\right.} 2 \frac{\mathrm{\beta d}}{}^{2}- \tag{18}
\end{align*}
$$

If unpolarized radiation is incident upon the interferometer, the percentage polarization in the sigma direction after the two beams recombine is given by:

$$
\begin{equation*}
\frac{|r t|_{\sigma}^{2}-\left.\left.\right|_{r}\right|_{\pi} ^{2}}{|r t|_{\sigma}^{2}+|r t|_{\pi}^{2}} \times 100 \% \tag{19}
\end{equation*}
$$

In order to obtain some 1dea of the degree of polarization, we consider an example where the value of $|r t|^{2}$ for both sigma and pi polarization is a maximum. In this instance we have:

$$
\begin{aligned}
& |\mathrm{rt}|^{2}=\frac{.05}{(1+.05)^{2}}=\frac{.05}{1.10}=.045 \\
& |\mathrm{rt}|^{2}=\frac{.58}{(1+.58)^{2}}=\frac{.58}{2.50}=.232
\end{aligned}
$$

and the percentage polarization is:

$$
\begin{equation*}
\frac{.232-.045}{.232+.045} \times 100 \%=66.5 \% \tag{20}
\end{equation*}
$$

## APPENDIX B

## COMPUTER PROGRAM

The computer program to process the data is written for an IBM model $360 / 67$ computer and an off-line calcomp plotter.

The program contains four subprograms:
(a) FTTAPE: This program converts the binary output to digital form. When the paper tape output is converted to magnetic tape, a value of 256 is placed between the conversion of individual tapes and a value of 512 at the end of the last tape converted.

The code used on the paper tape is 12 bit binary and requires three frames for each output value. This is shown below:
$1^{\text {st }}$ frame index $\rightarrow$ O
The parity channel is punched in such a manner that each frame is of odd parity; should a frame be of even parity. the PTAPE routine returns a negative valued integer rather than a positive one.

The zero channel is punched whenever a frame is completely empty of data. This serves as a check that the actual value is zero, rather than that a malfunction of the equipment has occurred.

The conversion to masnetic tape reads each frame separately and is strictly binary.
(b) CASJU6: This program arranges the data for RHARM (see below), calls RHARM and computes the intensity and wave number values from the output of RHARM. In the case where spectra are ratioed, the subroutine checks that the reference spectrum has as many or more useable input points as the sample spectrum.
(c) RHARM: This is an IBM scientific subroutine which finds the Fourier coefficients of onedimensional real data. It requires $2(2)^{n}$ input values and returns $2^{n}+2$ output, values, where $n$ is an integer.
(d) WBPLOT: Provides for the plotting of the transformed data.

There are three modes of operation of the program:
Mode 1: Each interferogram is transformed and the output is plotted as intensity vs. wave number. For each spectrum, the cards required to obtain the transform are: 1. Title
2. Comp - which may be any additional information
3. Mode, NFT, NAPOD, MOVE, LPAGE, XMAX, XMIN
4. DINIT, DFINAL, DZERO, DELX

Mode 2: The sample and reference interferograms are transformed. The ratio of the reference to the sample transmission is calculated and plotted as a function of wave number. The program requires that the reference interferogram be transformed with as many or more points either side of zero path difference as is used for the
sample.
The cards 1 - 4 used for Mode 1 are used, where card 4 contains values for the sample interferogram. These are followed by card 5 which is the same as card 4 except that it contains the data for the reference run.

Mode 3: This is the same as Mode 2 except that a number of different sample spectra may be ratioed against the same reference spectra.

The cards used are $1-5$ as for fode 2, followed by 1-4 for each subsequent sample spectrum.

Calculations under Mode 1.2 or 3 may be made in one complete run. provided the reference spectrum is always preceded by a sample spectrum when running under Mode 2 or 3. Subsequent sample spectrum are ratioed against the last reference spectrum when running under Mode 3.

In the program, the scale on the wave number axis is read in as LPAGE. In order to be compatible with the calcomp routines, it must be $1,2,4,5,8$ or one of these times any integer power of 10.

A flow diagram for the main program and the CASJU6 subroutine are included to aid in understanding the operation of the program.
$\operatorname{THAN}$




## CASJKG




| 78 | 15 | CONTINUE |
| :---: | :---: | :---: |
| $) 9$ |  |  |
| 10 |  | DDIFF=DFINAL-DLAST |
| \1 |  | WRITE(PAPER,209)RX(1), RX(RNDATA), DDIFF |
| 12 | 209 | FORMAT(IHO,'REFERENCE PATH DIFFERENCES. FIRST ONE IS ',F8.4, ${ }^{\prime}$ C: |
| 13 |  | 1 FINAL ONE IS',F3.4, ${ }^{\prime} \mathrm{CM}$. FINAL DRUM READING OBSERVED-CALCULATE: |
| 14 |  |  |
| 15 | C | \%*\%*:CALCULATE THE INTENSITY FUNCTION F(I) = SSIG(I)-INF, OR |
| 16 | C | *****F(I)=RS16(I)-INF $\%$ \% $\%$ \% |
| 1.7 | 16 | $\operatorname{INF}=(\operatorname{IPINF}(1)+\operatorname{IPINF}(2)+\operatorname{IPINF}(3)+\operatorname{IPINF}(4)+\operatorname{IPINF}(5)+\operatorname{IPINF}(6)) / 6.0$ |
| 1.8 |  | WRITE(PAPER,210) INF |
| 19 | 210 | FORMAT(1H0, 'IMTENSITY AT PLUS INFINITY IS',F10.4) |
| ? |  | GO TO(17,18), ITIS |
| $\geq 1$ | 17 | DO $19 \mathrm{I}=1$, SNDATA |
| $\geq 2$ |  | $F(I)=S S 16(I)-I N F$ |
| $\geq 3$ | 19 | CONTINUE |
| 24 |  | GO TO 101 |
| $\geq 5$ | 18 | $00.20 \mathrm{I}=1$, RNDATA |
| 5 |  | F(I) $=$ RSI6(1)-INF |
| $? 7$. | 20 | CONTINUE |
| $\bigcirc 8$ | C | ***** READY TO F.T. F(I). WI TH SX(I) OR RX(I) |
| $\bigcirc 9$ | 101 | GO TO(105,106), ITIS |
| 30 | 105 | CALL CASJU6(F,SX,SNDATA,SINT,NU, \&107, \&4l2) |
| 31 | 106 | CALL CASJUG(F,RX,RNDATA,RINT,NU, \&107, \&412) |
| 32 | 107 | CONTINUE |
| 33 | C | \%梀米**F. TRANSFORM COMPLETED |
| 34 |  | GO TO (30,50,92), MODE |
| 35 | C |  |
| 36 | C | \% \% $* * *$ RETURN OR EXIT $* * * * *$ |
| 37 | 30 | GO TO(44, 134), NFT |
| 58 | 44 | G0 10(400,401), 1115 |
| 39 | 401 | NDATA =RNDATA |
| ¢0 |  | GO TO 33 |
| +1 | 400 | NDATA = SNDATA |
| +2 | C |  |
| + 3 | 33 | $\mathrm{I}=\mathrm{NDATA}+1$ |
| 44 | 42 | WRITE (PAPER,212). TITLE |
| +5 | 212 | FORMAT (1H1,20A4) |
| 46 |  | WRITE (PAPER,213) COMP |
| +7 | 213 | FORMAT(1HO,20A4) |
| +8 |  | GO TO (408,414), NABORT |
| +9 | 414 | WRITE(PAPER,231) |
| 30 | 231 | FORMAT (IHO, DATA COULD NOT BE RATIOED, SAMPLE RESULTS PRINTED F: |
| il |  | IT, REFERENCE RESULTS FOLLOW') |
| ;2 | 408 | WRITE (PAPER,214) |
| ;3 | 214 |  |
| 34 |  | 1 'WAVE/CM', $5 \times$, 'INTENSITY AT NU') |
| ; 5 | C | \%\%\%\%* LINES PER PAGE COUNTER TO ZERO ***** |
| 56 |  | NPC $=0$ |
| ;7 |  | IF (I-NDATA-1)34,35,36 |
| ; 8 | 36 | CALL PLOTND |
| ;9 |  | WRITE(PAPER,258)NG |
| j0 |  | STOP 222 |
| ;1 | 35 | DO $34 \mathrm{l}=1$, NDATA |

    IFTI-NONUT 38,38.40
    GO TO ( 74,403),ITIS
    WRITE(PAPER,215)SS16(I),SX(I),NU(I),SINT(I)
    GO TO 41
    403 WRITE (PAPER,215)RS16(I),RX(I),NU(I),RINT(I)
        GO TO 41
    215 FORMATIIH,9X,F9.4,1IX,F8.4,IIX,F7.2,7X,EI2.5)
    4 0
    406
    WRITE(PAPER,217) RS16(I),RX(I)
    217 FORMAT(1H,9X,F9.4,11X,F8.4)
        NPC =NPC + +1
        IF(52-NPC)34,42,34
    34 CONTINUE
    134 CONTINUE
    C 米***CALL PLOTTING ROUTINE, NU IS X AXIS, SINT OR RINT IS Y AXIS
        GO TO (409,410),ITIS
    409 CALL NBPLOT(NU,SINT,NONU)
        NG=NG+1
        WRITE (PAPER,218)
    218 FORMAT(1HO,'SINT PLOTTED')
        GO TO 411
    410 CALL WBPLOT(NU,RINT,NONU)
        NG=NG+1
        WRITE (PAPER,230)
    230 FORMAT (1HO,'RINT PLOTTED')
    411 GO TO (412,413),NABORT
    C %%***CHECK FOR FURTHER RUNS. LAST=8888 IF MORE RUNS
    C ***** 9999IF NO MORE RUNS. ******
        ITIS=1
        IF(LAST-9999) 23,43,23
    413 ITIS=2
        NABORT=1
        GO TO }10
        C 米**** MODE=2 IF SAMPLE DATA PROCESSED GO BACK AND PROCESS
        C ***** REFERENCE DATA WITH ITIS=2 THEN CALCULATE RATIO
        C ***** AND PRINT AND PLOT RESULTS ******
        50 GO TO (51,52),ITIS
        51.". ITIS=2
        GO TO 24
        5 2 ~ D O ~ 5 3 ~ I = 1 , N O N U
            54 WRITE(PAPER,220) NU(I),RINT(I)
            220 FORMAT(1HO,'AT',F7.2,'WAVE/CM RINT=',E12.5,'IS NEGATIVE OR ZERIG:
            RATIO(I) =0.0
            GO TO 53
            55 IFISINT(I;)56,56,57
            56 WRITE(PAPER,221)NU(I),SINT(I)
            221 FORMAT(1HO,'AT',F7.2,'WAVE/CM SINT=',EI2.5,'IS NEGATIVE OR ZERIM:
            RATIO(I) =0.0
            GO TO 53
            57 RATIO(I)=RINT(I)/SINT(I)
            5 3 ~ C O N T I N U E
    ```
\begin{tabular}{|c|c|c|}
\hline 16 & & NRITEPPAPER,222ISNDATA, RNDATA, NQNU \\
\hline 17 & 222 & FORMAT(IHO, 'SNDATA=1, I4,' RNDATA = , I4,' NONU=', I4) \\
\hline 18 & c & *****SS16,SX,RSIG,RX,NI,SINT, RINT,RATIO CALCULATED AND READY FOR \\
\hline 1.9 & C & *****PRINTING AND PLOTTING WHERE NEEUED \(\%\) :\% \% \% \\
\hline \(\geq 0\) & 540 & GO TO(63,533)NFT \\
\hline ?1 & 63 & NDATA \(=\) MAXO(SNDATA,RNDATA, NONU) \\
\hline 2 & \(\bigcirc\) & F****PAGE HEADINGS AND SET I TO GET PAST FIRST IF \%**** \\
\hline \(\geq 3\) & & \(\mathrm{I}=\mathrm{NDATA}+1\) \\
\hline \(\geq 4\) & 88 & WRITE(PAPER,2.2)title \\
\hline 25 & & WRITE(PAPER,213)COMP \\
\hline 26 & & WRITE(PAPER,223) \\
\hline \(\geq 7\) & 223 & FORMAT(1H0,4X,'SS16(X)', 6x, 'SX/CM', 5x, 'RSSI6(X)', 6x, 'RX/CM', \\
\hline T8 & &  \\
\hline \(\bigcirc 9\) & c & \% \(\%\) \% \\
\hline 30 & & NPC \(=0\) \\
\hline 31 & & IF (I-NDATA-1) \(64,65,66\) \\
\hline 32 & 66 & CALL PLOTND \\
\hline 33 & & STOP 333 \\
\hline 34 & 65 & D0 \(641=1\), NDATA \\
\hline 35 & & IF(I - NONU)69,69,68 \\
\hline 36 & 69 & IF(1 - SNDATA \(170,70,84\) \\
\hline 37 & 70 & IF(I - RNDATA)71,71,87 \\
\hline 38 & 71 & WRITE(PAPER,224)SS16(I), SX(I),RSI6(I),RX(I),NU(I), SINT(I), \\
\hline 39 & & 1 RINT(I),RATIO(I) \\
\hline ¢0 & 224 &  \\
\hline +1 & & 1E12.5,3X,F8.41 \\
\hline +2 & & GO TO 80 \\
\hline 3 & 68 & IF (I - SNDATA)73,73,83 \\
\hline 14 & 73 & IF(I - RNDATA) \(77,77,78\) \\
\hline +5 & 77 & WRITE(PAPER,224)SS16(I), SX(I),RS16(I), RX(I) \\
\hline 16 & & GT 1080 \\
\hline 17 & 78 & WRITE(PAPER,224)SS16(I), SX(I) \\
\hline 18 & & GO TO 80 \\
\hline 19 & 83 & WRITE(PAPER,228)RS16(I);RX(I) \\
\hline ; & 228 & FORMAT(1H, 26X,F9.4,3X,F8.4) \\
\hline i1 & & G0 T0 80 \\
\hline , & 81 & WRTTETPAPER, 227SSI6(1),SX(I),NUIT,SINTIT, RINTTI), RATIO IT \\
\hline 13 & 22.7 & FORMAT(1H , 3X,F9.4,3X,F8.4,28X,F8.2,3X,E12.5,3X,E12.5,3X,F8.4) \\
\hline ; 4 & & G0 T0 80 \\
\hline 5 & 84 & IF(I - RNDATA) \(85 ; 85,86\) \\
\hline 6 & 85 & WRITE(PAPER, 225)RSI6(I),RX(I),NU(I);SINT(I),RINT(I), RATIO(I) \\
\hline 7 & 225 & FORMAT(1H, 26X,F9.4,3X,F8.4,5X,F8.2,3X,E12.5,3X,E12.5,3X,F8.4) \\
\hline 8 & & 601080 \\
\hline 9 & 86 & WRITE(PAPER,226)NU(I), SINT(I),RINT(I),RATIO(I) \\
\hline 0 & 226 & FORMAT(1H , 51X,F8.2,3X,E12.5,3X,E12.5,3X,F8.4) \\
\hline 1 & 80 & \(N P C=N P C+1\) \\
\hline , 2 & & IF (52-NPC 164,88,64 \\
\hline 3 & 64 & continue \\
\hline 4 & 533 & Cuntinue \\
\hline 5 & c & ****: CALL PLOTting routine to plot nu(i) as y axis \\
\hline 6 & C & ***** AGAINST RATIO(I) AS X AXIS \% \(\begin{aligned} & \text { \% }\end{aligned}\) \\
\hline 7 & & Call wbplot (nu,ratio,nonu) \\
\hline 8 & & \(N G=N G+1\) \\
\hline 9 & & WRITE(PAPER,229) \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|}
\hline \(70^{-}\) & 229 & FURMATTIHO, RRATIOVS NU PLOTTED' ... \\
\hline 71 & & GO TO (412,412,415), MODE \\
\hline 72 & 415 & NMODE3 \(=\) NMODE \(3+1\) \\
\hline 73 & & GOTO 412 \\
\hline 74 & C &  \\
\hline 75 & C & ***** REFERENCE DATA. IF NMODE3=1 OR MORE GO THROUGH MODE=2 \({ }^{\text {\% }}\) \% \\
\hline 76 & 92 & TF(NMTTOE3-1)93,52,52 \\
\hline 77. & 93 & NMODE3 \(=\) NMODE3+1 \\
\hline 78 & & ITIS \(=2\) \\
\hline 79 & & GOTO 24 \\
\hline 80 & 43 & CALL PLOTND \\
\hline 31 & & HRITE(PAPER,258)NG \\
\hline 82 & 258 & FOTRPAT (THO, \(44, \mathrm{GRAPH}\) (S) PLOTTED' \\
\hline 33 & & STOP 999 \\
\hline 34 & & END \\
\hline 35 & C & *****SUBROUTINE TO ARRANGE DATA FOR RHARM, CALLRHARM, AND TO \\
\hline 86 & C & *****CALCULATE INT (NU) AND NU FROM RESULTS OF RHARM. ALSO TO \\
\hline 37 & C & ***** ENSURE THAT SAMPLE AND REFERENCE DATA ARE TRANSFORMED WITH \\
\hline 88 & C & *****THE SAME NUMBER OF POINTS. ***** \\
\hline 89. & & SUBROUTINE CASJUG(F,FX,NUM,FINT, NU, *,*) \\
\hline Э० & & DIMENSION FTDATA(16388), FINT(8193), F(9000), FX(9000), INV(2048) \\
\hline 91 & & 1,S(2048) \\
\hline 72 & & REAL NU(8195) \\
\hline 93 & & INTEGER PAPER \\
\hline 94 & & COMMON COMP (20), TITLE(20), MODE, ITIS, NMODE3,NAPOD, NABOR T, RESOL, \\
\hline 75 & & 1 NONU, DELX,LPAGE, XPAGE,NG, MOVE, XMAX;XMIN \\
\hline 36 & & PAPER \(=6\) \\
\hline 97 & & \(N P=0\) \\
\hline \(\ni 8\) & & \(N Z=0\) \\
\hline 39 & & NM \(=0\) \\
\hline 50 & & \(004 \mathrm{I}=1\), NOM \\
\hline J1 & & IF(FX(1) \(5,6,7\) \\
\hline )2 & 5 & \(N M=N M+1\) \\
\hline J3 & & GO TO 4 \\
\hline 34 & 6 & \(N Z=N Z+1\) \\
\hline 35. & & GO TO 4 \\
\hline 56 & 7 & \(N P=N P+1\) \\
\hline )7 & 4 & CONTINUE \\
\hline 38 & C & \%*\%*\% FOR SPECTRA TO BE RATIOED AGAINST EARLIER SPECTRA SET \\
\hline 39 & C & \% \(* * *\) THINGS UP SO THAT WE HAVE THE SAME NUMBER OF POINTS TAKEN \\
\hline 10 & C & \%**** ON EACH \(* * * * *\) \\
\hline 11 & & GO TO (1,2,3), MODE \\
\hline \([2\) & 2 & G0 1011,701, 1115 \\
\hline 13 & 70 & IF (NP-NM) 71,72,72 \\
\hline 14 & 71 & NROSS \(=2 * N P+N Z\) \\
\hline 15 & & GO TO 73 \\
\hline 16 & 72 & NROSS \(=2 \div\) NM \(+2 * N Z\) \\
\hline 17 & 73 & NFS \(=2 * N\) \\
\hline [8 & & IF(NROSS-NFS)74,41,41 \\
\hline 19 & 74 & WRITE(PAPER,201) MODE, NMODE 3 \\
\hline \(? 0\) & 201 & FORMAT (1HO,'INSUFFICIENT POINTS TAKEN. MODE= ', I4,' NMODE3=1, I4, \\
\hline \(\geq 1\) & & GO TO 42 \\
\hline \(\geq 2\) & 41 & WRITE (PAPER,204)MODE, NMODE3 \\
\hline \(\geq 3\) & 204 &  \\
\hline
\end{tabular}

\begin{tabular}{|c|c|c|}
\hline 18 & \(C\) &  \\
\hline 79 & C & RETURNED FROM RHARM IN FTDATA, LNPOI + 2VALUES.CALCULATE IMTENSIT: \\
\hline 80 & C & Fint at nonu frequencies from this \\
\hline 81 & & CALL RHARM (FTDATA,IFT, INV, S, IFERR) \\
\hline 82 & & MFIN = LNPOI + 2 \\
\hline 83 & & WRITE(PAPER,209)N,NPOINT,LNPOI, NONU \\
\hline 84 & 209 &  \\
\hline 85 & & \(J=0\) \\
\hline 86 & & DO \(35 \mathrm{I}=3, \mathrm{MFIN}, 2\) \\
\hline 87 & & \(\mathrm{J}=\mathrm{J}+1\) \\
\hline 88 & & \(\operatorname{FINT}(J)=S Q R T(F T D A T A(I) * * 2+F T D A T A(I+1) * * 2)\) \\
\hline 89 & 35 & Continue \\
\hline 90 & C & W*** CALCULATE RESOLUTION, AND FREQUENCTES AT THICH MTENSTIES \\
\hline 91 & C &  \\
\hline 92 & & RESOL \(=10000 /(\mathrm{N} * \mathrm{DELX})\) \\
\hline 93 & & GO TO (53,52), NAPOD \\
\hline 94 & 53 & RESOL \(=\) RES OL \(* 2 * * .5\) \\
\hline 95 & 52 & DELNU \(=5000.0 /(N P O I N T * D E L X)\) \\
\hline 96 & C &  \\
\hline 97 & & WRITE(PAPER,200) NMIS,NAPOD \\
\hline 98 & 200 & FORMAT(1HO,'THE FOLLOHING FX POINTS WERE NOT NOT USED IN THE TEP \\
\hline 99 & & IFORM.', I4,' ZERO POINTS WERE ADDED. NAPOD=1, I4,' \(11=A P O D I S E, 2=\) \\
\hline 00 & & 2 NOT APODISE)' \\
\hline 01 & & MPONE \(=N \cap P-M-1\) \\
\hline O2 & & TFA -GT.MPDNE)GU TO 61 \\
\hline 03 & & WRITE(PAPER,207) FX(1),FX(MPONE) \\
\hline 04 & 46 & CONTINUE \\
\hline 05 & & IF (NTNEG •GT •NUA ) GO TO 62 \\
\hline 06 & & WRITE(PAPER,207) FX(MNEG), FX(NUM) \\
\hline 07 & 45 & CONTINUE \\
\hline 08 & 207 & FORMAT(1H0,F9.4, ' T0 1,F9.4) \\
\hline 09 & 62 & WRITE(PAPER,208) LNPOI, NONU, DELNU,RESOL \\
\hline 10 & 208 & FORMAT(1HO, I5,' POINTS USED IN TRANSFORM, INTENSITIES CALCULATET \\
\hline 11 & & 1 ', I4,' FREQUENCIES',F6.3, 'WAVE/CM APART. RESOLUTION IS ASOUT'\% \\
\hline 12 & & 2F6.3,' WAVE/CM') \\
\hline 13 & & GO TO ( \(36,37,38), \mathrm{MODE}\) \\
\hline 14 & 36 & DO \(391=1\), NPOINT \\
\hline 15 & & NU(I) \(=\) DELNU*I \\
\hline 16 & 39 & CONTINUE \\
\hline 17 & & GO TO 40 \\
\hline 18 & 37 & GO TO \((36,40)\), ITIS \\
\hline 19 & 38 & IF (NMODE3-1)36,40,40 \\
\hline 20 & 40 & RETURN I \\
\hline 21 & & END \\
\hline 22 & C & ***** SUBROUTINE TO PLOT RATIO OR INTENSITY AS A \\
\hline 23 & C &  \\
\hline 24 & . & SUBROUTINE WBPLOT (XFN, YFN, NDATA) \\
\hline 25 & & DIMENS ION \(\mathrm{XFN}(8195)\), YFN (8195), XA (8195), YA (8195), XR(8195) :YB(819] \\
\hline 26 & & COMMON COMP (20), TTTLE(20), MODE, ITIS, NMTODE3, NAPOU, NAEORT, NESOL, \\
\hline 27 & & INONU, DELX, LPAGE, XPAGE, NG, MOVE, XMAX, XMIN \\
\hline 28 & & LDATA \(=0\) \\
\hline 29 & & DO \(51 \mathrm{I}=1\), NDATA \\
\hline 30 & & IF(XFN(I).GT.XMAX) GO TO 63 \\
\hline 31 & & LDATA = LDATA +1 \\
\hline
\end{tabular}


20 LPAGE = 2WLPAGE
GO TO 61
END
        2\% \% \% SUBROUTINE TO READ PAPER TAPE OUTPUT
        SUBROUTINE FTTAPE(IPINF,XSI6,M,LAST)
        DIMENSIUN IT (27024), OU(9008), XS16(9000),IK(200)
        COMMON COMP (20), TITLE(20), TODE, ITIS, NHTDE 3, NAPOD, MAEDGA: FSOL.
        1 INONU, DELX,LPAGE,XPAGE,NG,MOVE, XMAX,XMIN
        REAL IPINF(6)
        DO \(33 \mathrm{~K}=1,200\)
        CALL PTAPE(I)
        \(\operatorname{IK}(K)=I\)
        IF (IK (K).EQ.0) GO TO 33
        GO TO 14
        33 CONT INUE
        \(14 \quad M=0\).
        LAST \(=8888\)
        DO \(10 \mathrm{~J}=1: 27024,3\)
        CALL PTAPE(1)
        \(\operatorname{IT}(J)=I\)
        IF(IT(J).EQ.256)GO TO 19
        IF(IT(J).EO.512)GO TO 21
        GO TO 22
10
11 22 IF(IT(J).EQ.-255)GO TO 4
12. 81 IF(IT(J).GE.128)GO TO 5
13
14
15
16
17
18
19
20
\(\geq 1\)
\begin{tabular}{lll}
+0 & 6 & CONTINUE \\
+1 & 100 & RETURN \\
+2 \\
JF FILE & END
\end{tabular}

NOFF```

