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HENRY DAVID BRANDT
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FAR INFRARED SPECTRA OF ROCHELLE SALT

APPROVED BY

John A. Smith
Richard Proctor
J. R. Burwell
William H. Huff
Robert M. St. John

DISSERTATION COMMITTEE

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TABLE OF CONTENTS

	Page
LIST OF TABLES	vi
LIST OF ILLUSTRATIONS.	vii
Chapter	
I. Introduction.	1
II. Fourier Transform Spectroscopy.	3
a. The Multiplex Principle.	3
b. The Fourier Transform.	4
c. Computation.	18
III. The Spectrometer.	24
a. The Vacuum Chamber	24
b. Electrical Connections to the Vacuum System	30
c. Mechanical Connections	30
d. Optics	31
e. The Carriage and Rails	34
f. The Beam Splitters	36
g. The Moire Fringe System.	40
h. The Detector	42
i. The Source and Filters	44
j. The Sample Holder.	46
k. Alignment.	49

TABLE OF CONTENTS (Continued)

Chapter	Page
1. Electronics	51
IV. Experimental Methods and Results	61
a. Check of the Instrument	61
b. Efforts on BaTiO_3	67
c. Growth and Preparation of Rochelle Salt Crystals.	68 71
d. Rochelle Salt Reflection Spectra.	72
e. Rochelle Salt Transmission Spectra.	86
V. Theory of Ferroelectricity in Rochelle Salt.	94
VI. Discussion	102
BIBLIOGRAPHY References	

LIST OF TABLES

Table	Page
I. Computer Program Listing.	20
II. Detector Comparison	43
III. Parts List for Chopper Driver - Amplifier	58
IV. Parts List for Phase-Lock Detector.	59
V. Parts List for DVM Read Command	60
VI. Correlation of the Point Groups C_2 and D_2	100

LIST OF ILLUSTRATIONS

Figure	Page
1. Scanning Functions	9
2. Main Vacuum Chamber - Top View	25
3. Main Vacuum Chamber - Elevation.	26
4. Detector Housing	28
5. Optical Arrangement.	32
6. Moving Carriage and Rails.	35
7. Beam Splitter.	39
8. Original Sample Holder	47
9. Sample Holder: Transmission	48
10. Sample Holder: Reflection	50
11. Electronic Block Diagram	52
12. Schematic for Chopper Driver - Amplifier	53
13. Schematic for Phase-Lock Detector.	54
14. Schematic for DVM Read Command	55
15. Absorption of Atmospheric Water Vapor.	62
16. Absorption of Methanol	64
17. Transmission of 125 Micron Beam Splitter	66
18. Background Spectrum for Reflection	73
19. Transmission Through 50 Microns of Rochelle Salt at 30°C (Including Background).	75

LIST OF ILLUSTRATIONS (Continued)

Figure		Page
20.	Transmission Through 50 Microns of Rochelle Salt at 19°C (Including Background).	76
21.	Transmission Through 50 Microns of Rochelle Salt at 27.5°C (Including Background).	77
22.	Transmission Through 1 mm Crystal Quartz Covered With Orange Shellac.	78
23.	Percent Transmission Through 50 Microns of Rochelle Salt at 30°C.	79
24.	Percent Transmission Through 50 Microns of Rochelle Salt at 19°C.	80
25.	Percent Transmission Through 50 Microns of Rochelle Salt at 27.5°C.	81
26.	Comparison of Transmission at 30°C, 27.5°C, 19°C . . .	82
27.	Comparison of Transmission at 30°C, 27.5°C, and 19°C Between 55 cm ⁻¹ and 75 cm ⁻¹	83
28.	Percent Transmission Through 0.4 mm of Rochelle Salt at 25°C	85
29.	Ferroelectric Structure of Rochelle Salt	89
30.	σ^2 vs (T - T _C) for the Lowest Frequency Band	97
31.	σ^2 vs (T - T _C) for the Second Lowest Band.	99

FAR INFRARED SPECTRA OF ROCHELLE SALT

CHAPTER I

INTRODUCTION

Fourier transform spectroscopy is the technique of determining a spectrum by Fourier transformation of an interferogram, which is the time dependent part of the intensity at the exit aperture of a two beam interferometer as the optical path between the two beams varies from zero path to some maximum displacement. The method is a refinement of the visibility technique that Michelson used in determining the separation of two closely spaced spectral lines. Much of the application of the principle, when it was first used in the modern sense, was in the area of near infrared night sky spectra by workers like Connes (1). The attractive feature was the high resolution attainable. Soon the method was extended to investigations of molecular rotational spectra by men like Gebbie (2) and Richards (3). The reason here was not only the high resolution, but the fact that Fourier transform spectroscopy makes very efficient use of available light. Thus the submillimeter region, previously difficult to work in due to weak sources, became much more accessible. These same reasons made the method attractive for solid state applications (4).

Theories of ferroelectric crystals had been on a phenomenological basis (summarized by Jona and Shirane (5)) through 1960. It was at this time that W. Cochran (6,7) suggested that ferroelectricity was connected with crystal stability. Only for those ferroelectrics with high symmetry (e.g. BaTiO_3) has this theory been worked out. The theory implies that a low frequency optic mode exists for such ferroelectric crystals with a specific temperature dependence.

The combination of an interesting new experimental method and the problem of finding such soft optic modes in ferroelectric crystals motivated the work presented here.

CHAPTER II

FOURIER TRANSFORM SPECTROSCOPY

The Multiplex Principle

Transform spectroscopy, which had been used almost exclusively for high resolution work in narrow spectral regions, was shown to have much wider use in 1951 with the publication of P. B. Fellgett's thesis at Cambridge University*. In regions where noise is overwhelmingly due to the detector rather than due to photon noise, the signal integrates in direct proportion to T , the time of observation, while the noise integrates in direct proportion to $\sqrt{T}$. Assuming that a total observation time T is available, one can compare the signal to noise ratio for a scanning spectrometer and one which detects all the spectral elements simultaneously. If m spectral elements are to be explored, each element would be observed for an average time T/m in sequential investigation, with a noise level of $\sqrt{T/m}$. A signal to noise ratio of $\sqrt{T/m}$ is the result. If these same m elements are to be explored by simultaneous investigation, each element is observed for a time T , resulting in a signal to noise ratio of $\sqrt{T}$. Assuming that the detectors are identical in the two cases and are illuminated

*The thesis itself has not been read by the writer, however it is generally accepted (1,8,9) that this was the first clear statement of the multiplex principle.

with the same solid angle of radiation, one sees that the signal to noise ratio due to simultaneous investigation is superior by a factor $\sqrt{m}$. When signal levels are very low, as in the far infrared region, Fellgett's multiplex gain is of great importance.

A further advantage, shown by P. Jacquinot, is that a Michelson interferometer has a greater energy throughput than a conventional spectrometer of the same resolution (8).

The Fourier Transform

If a two-beam interferometer, such as a Michelson, is illuminated by a parallel beam of light, the plane wave is divided by the beam splitter and then recombined after one beam has been subjected to a phase difference relative to the other since it has traveled over a different path length. At the exit side of the interferometer the electric field may be written as

$$E(t) = \mathcal{E}(t) + \mathcal{E}(t + \tau)$$

where $\mathcal{E}(t)$ is the field due to one beam and $\mathcal{E}(t + \tau)$ is the field due to the other beam. The intensity recorded by the detector is proportional to the time average of the square of the electric field strength,

$$I(\tau) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \left[\mathcal{E}^2(t) + \mathcal{E}^2(t + \tau) + 2\mathcal{E}(t)\mathcal{E}(t + \tau) \right] dt.$$

If the intensity of the incoming radiation is constant, then the first two terms of $I(\tau)$ are constants. The third term, a function of τ , is known as the autocorrelation function of the radiation incident on the interferometer. That part of the output signal which varies with τ is proportional to the autocorrelation function and is known as an inter-

ferogram. Since the time delay is usually measured in terms of the linear displacement of the moveable mirror, it is customary to write the interferogram as $I(x)$, where $x = c\tau$ is the optical path difference between the two beams.

Suppose an ideal Michelson interferometer is illuminated with strictly monochromatic, parallel light of intensity B and wave number σ_0 . The intensity of the light leaving the interferometer is due to two coherent sources that are out of phase. An ideal beam splitter divides the intensity equally, making the amplitude in each arm of the interferometer $\sqrt{B/2}$. Thus the resultant exit amplitude would be found by adding

$$y_1 = \sqrt{B/2} \sin(\omega t - \alpha_1)$$

$$y_2 = \sqrt{B/2} \sin(\omega t - \alpha_2)$$

where $\alpha_1 - \alpha_2 = \delta$, the phase difference between the two beams. The resultant amplitude $y = y_1 + y_2$ can be written as

$$y = A \cos \theta \sin \omega t - A \sin \theta \cos \omega t$$

where

$$A \cos \theta = \sqrt{B/2} (\cos \alpha_1 + \cos \alpha_2)$$

$$A \sin \theta = \sqrt{B/2} (\sin \alpha_1 + \sin \alpha_2).$$

Squaring and adding these equations one has

$$A^2 = B \left[1 + \cos(\alpha_1 - \alpha_2) \right] = B(1 + \cos \delta)$$

$$= B(1 + \cos 2\pi \sigma_0 x).$$

Thus, the interferogram for monochromatic light is given by

$$I(x) = B(\sigma_0) \cos 2\pi\sigma_0 x$$

that is, the detector registers a sinusoidal voltage with an amplitude proportional to the intensity of the incoming light. If the incoming signal contains several monochromatic lines, each one may be treated as in the above case of a single line and then added to yield the resulting signal. For the case of an arbitrary spectrum limited to the frequency range σ_1 to σ_2 , the interferogram becomes

$$I(x) = \int_{\sigma_1}^{\sigma_2} B(\sigma) \cos(2\pi\sigma x) d\sigma .$$

In order to obtain the spectrum $B(\sigma)$ when one has measured the interferogram $I(x)$ experimentally, one makes the inverse Fourier transform

$$\begin{aligned} B(\sigma) &= \int_{-\infty}^{\infty} I(x) \cos(2\pi\sigma x) dx \\ &= 2 \int_0^{\infty} I(x) \cos(2\pi\sigma x) dx . \end{aligned}$$

The last step is possible if $I(x)$ is an even function. The interferogram is symmetric about zero path position only in an ideal interferometer, which in actuality is achieved only to within certain limits. For example, dispersion in the beam splitter would result in the path difference x not being the same for all frequencies. The difference in the mathematics necessary for symmetric as against asymmetric interferograms is that the full Fourier transform needs to be taken in the asymmetric case rather than just the cosine transform. The simpler case of the cosine transform will usually be used in the

following.

A practical difficulty in obtaining the spectrum $B(\sigma)$ is encountered because the path difference x can be varied only over finite range having a maximum value L . The calculated spectrum is therefore not $B(\sigma)$, but rather

$$\begin{aligned} B'(\sigma) &= 2 \int_0^L I(x) \cos(2\pi \sigma x) dx \\ &= 2 \int_0^\infty I(x) D(x) \cos(2\pi \sigma x) dx \\ &= \int_{-\infty}^\infty I(x) D(x) \cos(2\pi \sigma x) dx \end{aligned}$$

where $D(x) = \begin{cases} 1 & -L \leq x \leq L \\ 0 & x > L, x < -L \end{cases}$. Let $f(\sigma)$ be the Fourier transform of $D(x)$.

The convolution $f * g$ of two functions f and g is defined by

$$f * g = \int_{-\infty}^\infty f(\xi) g(x - \xi) d\xi \quad (\text{ref. 41}).$$

Now,

$$\begin{aligned} B'(\sigma) &= \int_{-\infty}^\infty I(x) D(x) \cos(2\pi \sigma x) dx \\ &= \int_{-\infty}^\infty \left[\int_{-\infty}^\infty B(\sigma') \cos(2\pi \sigma' x) d\sigma' \right] D(x) \cos(2\pi \sigma x) dx \\ &= \int_{-\infty}^\infty \int_{-\infty}^\infty B(\sigma') D(x) \cos(2\pi \sigma' x) \cos(2\pi \sigma x) dx d\sigma' \\ &= 1/2 \int_{-\infty}^\infty B(\sigma') \left\{ \int_{-\infty}^\infty D(x) \left[\cos 2\pi(\sigma' - \sigma)x + \cos 2\pi(\sigma' + \sigma)x \right] dx \right\} d\sigma' \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{2} \int_{-\infty}^{\infty} B(\sigma) \left[f(\sigma_1 - \sigma) + f(\sigma_1 + \sigma) \right] d\sigma \\
&= \int_{-\infty}^{\infty} B(\sigma) f(\sigma_1 - \sigma) d\sigma = B(\sigma) * f(\sigma).
\end{aligned}$$

Hence, one sees that the calculated spectrum is the convolution of the true spectrum with the function $f(\sigma)$, which will be called the scanning function. Other names for $f(\sigma)$ also appear in the literature; such as apparatus function (1) and instrumental line-shape function (11).

The scanning function $f(\sigma)$ is the analog of the slit function for an ordinary spectrometer. The effect of the scanning function can be shown by supposing a δ -function input to the interferometer and determining the calculated output, $B'(\sigma_1)$.

$$\begin{aligned}
B'(\sigma_1) &= \int_{-\infty}^{\infty} B(\sigma) f(\sigma_1 - \sigma) d\sigma \\
&= \int_{-\infty}^{\infty} \delta(\sigma) f(\sigma_1 - \sigma) d\sigma = f(\sigma_1).
\end{aligned}$$

Further,

$$\begin{aligned}
f(\sigma_1) &= \int_{-\infty}^{\infty} D(x) \cos(2\pi\sigma_1 x) dx \\
&= \int_{-L}^L \cos(2\pi\sigma_1 x) dx \\
&= \frac{1}{2\pi\sigma_1} \sin(2\pi\sigma_1 x) \Big|_{-L}^L = 2L \frac{\sin(2\pi\sigma_1 L)}{2\pi\sigma_1 L}
\end{aligned}$$

Thus, a monochromatic input is calculated to have the shape of the solid line in Fig. 1. The large secondary maxima and minima are

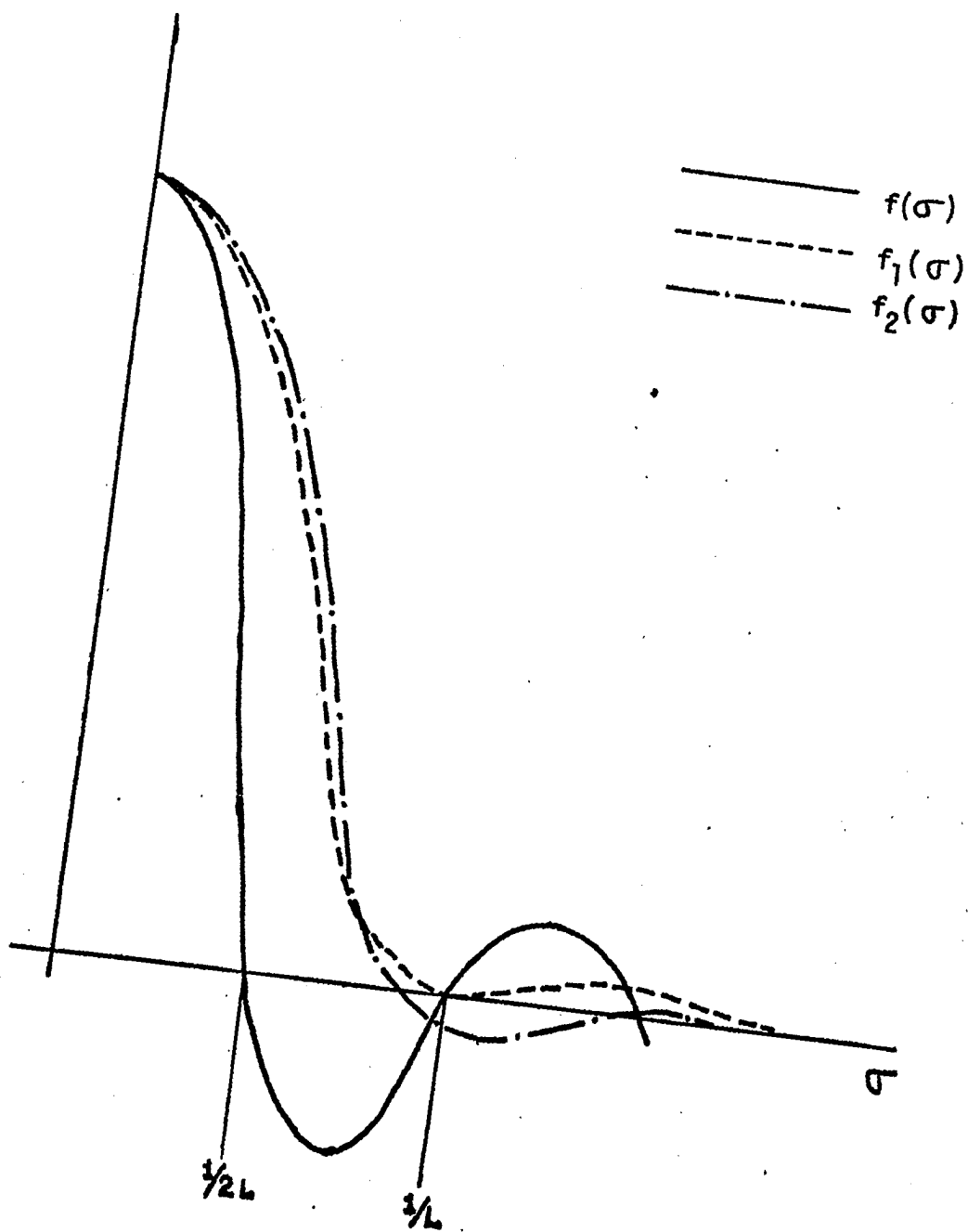


Figure 1. Scanning Functions (1).

undesirable, especially when sharp, closely spaced features are being investigated. If the spectra to be investigated are those with only broad features, any symmetric scanning function, even $f(\sigma)$, is satisfactory.

To overcome this difficulty, it is customary to multiply the interferogram by a weighting, or apodizing function. The calculated interferogram now becomes

$$\begin{aligned} B'(\sigma) &= \int_{-\infty}^{\infty} I(x) D(x) A(x) \cos(2\pi \sigma x) dx \\ &= \int_{-L}^L I(x) A(x) \cos(2\pi \sigma x) dx \end{aligned}$$

where $A(x)$ is the apodizing function. The property that all apodizing functions must have is to have a value of unity at $x=0$ and a value of zero at $x = L$. With this limitation in mind a number of functions have been used by various investigators. Gibbs and Gebbie (12) have used

$$A(x) = \cos^2\left(\frac{\pi x}{2nh}\right)$$

where h is the sampling interval. Two more commonly used functions are

$$A_1(x) = 1 - \left|\frac{x}{L}\right|, \quad |x| \leq L$$

$$A_2(x) = \left[1 - \left(\frac{x}{L}\right)^2\right]^2, \quad |x| \leq L$$

used by Vanasse (14) and Connes (1) respectively. The effect of multiplying by such a function is to change the shape of the scanning

function, that is, one now has a scanning function which is the Fourier transform of $D(x)A(x)$. The scanning functions corresponding to $A_1(x)$ and $A_2(x)$ respectively are given by Connes (1) as

$$f_1(\sigma) = \frac{L}{4} \frac{\sin^2(\pi \sigma L)}{(\pi \sigma L)^2}$$

and

$$f_2(\sigma) = \left[1 / (2\pi \sigma L)^{\frac{5}{2}} \right] J_{5/2}(2\pi \sigma L).$$

These functions are shown in Fig. 1. In both cases the side lobes are many times smaller than for the unapodized case. The price which must invariably be paid, however, is a widening of the central maximum and hence a decrease in resolution. We have followed the suggestion of Connes (1) and used $A_2(x)$ in this work. Apodization may be done physically rather than mathematically by shaping the aperture of the instrument to be different from round. This aspect, along with the whole subject of apodization, is treated in some detail by Jacquinet (13).

Limits of resolution in Fourier transform spectroscopy depend very much on the breadth of the scanning function. With no apodization, the first zero is at $1/2L$. If one can separate two lines which are such that the maximum of one falls at the minimum of the other, then $\Delta\sigma = 1/2L$ for the unapodized case. With the weighting function $A_1(x)$ or $A_2(x)$, $\Delta\sigma = 1/L$. Hence, one sees that the resolution is directly proportional to the maximum path difference L .

The sampling theorem of information theory states that: If a function $f(t)$ contains no frequencies higher than w hz, it is completely

determined by giving its ordinates at a series of points spaced $1/2w$ apart (15). An intuitive justification is that, if $f(t)$ contains no frequency higher than w , it cannot change to a substantially new value in time less than one-half cycle of the highest frequency, that is $1/2w$. In the case of Fourier transform spectroscopy being considered here, $f(t)$ is the interferogram $I(x)$ and the wave number σ is used instead of frequency w . One sees then that the interferogram needs to be sampled at only a finite number of points spaced a distance $h = 1/2 \sigma_M$ apart where σ_M is the highest frequency in the spectrum. Hence, instead of calculating the integral

$$B'(\sigma) = 2 \int_0^L I(x) A(x) \cos(2\pi \sigma x) dx$$

one needs to calculate the sum

$$\begin{aligned} B''(\sigma) &= h \left[I(0) A(0) + 2 I(h) A(h) \cos(2\pi \sigma h) + \cdots + 2 I(Nh) A(Nh) \cos(2\pi \sigma Nh) \right] \\ &= h \left[I(0) A(0) + 2 \sum_{n=1}^N I(nh) A(nh) \cos(2\pi \sigma nh) \right]. \end{aligned}$$

The outline of the following argument showing that the sum $B''(\sigma)$ determines the spectrum, given the proper choice of h , is primarily due to Connes (1). The above sum is equivalent to

$$B''(\sigma) = h \int_{-\infty}^{\infty} I(x) A(x) R_h(x) \cos(2\pi \sigma x) dx$$

where $R_h(x)$ is a Dirac distribution of interval h , that is

$$R_h(x) = \sum_{n=-\infty}^{\infty} \delta(x - nh)$$

That this integral reduces to the above mentioned sum is shown as follows:

$$\begin{aligned}
B''(\sigma_1) &= h \int_{-\infty}^{\infty} I(x) A(x) R_h(x) \cos(2\pi \sigma_1 x) dx \\
&= h \int_{-\infty}^{\infty} I(x) A(x) \left[\sum_{n=-\infty}^{\infty} \delta(x - nh) \right] \cos(2\pi \sigma_1 x) dx \\
&= h \sum_{n=-\infty}^{\infty} \int_{-\infty}^{\infty} I(x) A(x) \delta(x - nh) \cos(2\pi \sigma_1 x) dx \\
&= h \sum_{n=-\infty}^{\infty} I(nh) A(nh) \cos(2\pi \sigma_1 nh) \\
&= h \left[I(0)A(0) + 2 \sum_{n=1}^{\infty} I(nh) A(nh) \cos(2\pi \sigma_1 nh) \right]
\end{aligned}$$

which is the above mentioned sum. The integral representing this sum can be written

$$B''(\sigma_1) = \int_{-\infty}^{\infty} B(\sigma) F(\sigma_1 - \sigma) d\sigma$$

where $F(\sigma)$ is the Fourier transform of the product $A(x)hR_h(x)$. Thus, to see how $B''(\sigma_1)$ relates to the true spectrum $B(\sigma_1)$, one must determine $F(\sigma)$. The Fourier transform of $A(x)$ has already been determined, so it remains to find the Fourier transform of $R_h(x)$. This is done with the help of the theory of generalized functions. Lighthill (16) proves the following theorem:

The trigonometrical series

$$\sum_{n=-\infty}^{\infty} c_n \exp(in\pi x/l)$$

converges to a generalized function $f(x)$ if (and only if) c_n is on the order of $|n|^{-N}$ for some N as $n \rightarrow \infty$.

Since $R_h(x)$ is a generalized function, there exists a set of c_n such that

$$R_h(x) = \sum_{n=-\infty}^{\infty} c_n \exp(i 2 \pi n x / h) .$$

The ordinary integral which is usually used to evaluate Fourier coefficients cannot be used directly when generalized functions are involved because they cannot be integrated with finite limits. This difficulty may be overcome by introducing a special kind of function via the theorem (16):

A "unitary function" $U(x)$ can be found, which is a good function vanishing for $|x| \geq 1$ and such that

$$\sum_{n=-\infty}^{\infty} U(x + n) = 1$$

for all x .

The function

$$U(x) = \int_{|x|}^1 \exp\left[-\frac{1}{t(1-t)}\right] dt \bigg/ \int_0^1 \exp\left[-\frac{1}{t(1-t)}\right] dt$$

is shown in the proof by Lighthill to possess the necessary properties. If such "unitary functions" exist, then the idea of integrating $f(x)$ over a period to find the Fourier coefficients can be replaced by integrating $f(x) U(x/h)$ from $-\infty$ to ∞ . Such an integration is allowed in the theory of generalized functions and may be formally thought of as integrating $f(x)$ over a period. In other words, generally the Fourier coefficients are found from

$$c_m = \frac{1}{h} \int_{-\frac{h}{2}}^{\frac{h}{2}} f(x) \exp(i 2 \pi m x / h) dx .$$

Since generalized functions cannot be integrated with finite limits, this is replaced by

$$\begin{aligned}
 c_k &= \frac{1}{h} \int_{-\infty}^{\infty} f(x) U(x/h) \exp(-i2\pi kx/h) dx \\
 &= \int_{-\infty}^{\infty} f(x) U(x/h) \exp(-i2\pi kx/h) d(x/h) \\
 &= \sum_{n=-\infty}^{\infty} \int_{-n-1/2}^{n+1/2} f(x) U(x/h) \exp(-i2\pi kx/h) d(x/h) \\
 &= \sum_{n=-\infty}^{\infty} \int_{-1/2}^{1/2} f(x+nh) U\left(\frac{x}{h}+n\right) \exp(-i2\pi k\left(\frac{x}{h}+n\right)) d\left(\frac{x}{h}+n\right).
 \end{aligned}$$

The generalized function $f(x)$ is periodic with period h and the exponent has period 2π . Hence,

$$\begin{aligned}
 c_k &= \sum_{n=-\infty}^{\infty} \int_{-1/2}^{1/2} f(x) U\left(\frac{x}{h}+n\right) \exp(-i2\pi kx/h) d(x/h) \\
 &= \int_{-1/2}^{1/2} f(x) \left[\sum_{n=-\infty}^{\infty} U\left(\frac{x}{h}+n\right) \right] \exp(-i2\pi kx/h) d(x/h) \\
 &= \frac{1}{h} \int_{-\frac{h}{2}}^{\frac{h}{2}} f(x) \exp(-i2\pi kx/h) dx
 \end{aligned}$$

since $\sum_{n=-\infty}^{\infty} U(x/h+n) = 1$ for all x . The generalized form for calculating c_k is equivalent to the classical form which is used with ordinary functions. Now, the Fourier coefficients for $f(x) = R_h(x)$ are

$$c_k = \frac{1}{h} \int_{-\infty}^{\infty} R_h(x) U(x/h) \exp(-i2\pi kx/h) dx$$

$$\begin{aligned}
c_k &= \frac{1}{h} \int_{-\infty}^{\infty} \left[\sum_{n=-\infty}^{\infty} \delta(x - nh) \right] U(x/h) \exp(-i2\pi kx/h) dx \\
&= \frac{1}{h} \sum_{n=-\infty}^{\infty} \int_{-\infty}^{\infty} \delta(x - nh) U(x/h) \exp(-i2\pi kx/h) dx \\
&= \frac{1}{h} \sum_{n=-\infty}^{\infty} U(nh/h) \exp(-i2\pi knh/h) \\
&= \frac{1}{h} \sum_{n=-\infty}^{\infty} U(n) \exp(-i2\pi kn) = \frac{1}{h} \sum_{n=-\infty}^{\infty} U(n) = \frac{1}{h}
\end{aligned}$$

since $\sum_{n=-\infty}^{\infty} U(x + n) = 1$ for all x . Now $R_h(x)$ can be written in terms of a Fourier series, that is

$$R_h(x) = \sum_{n=-\infty}^{\infty} c_n \exp(i2\pi nx/h) = \frac{1}{h} \sum_{n=-\infty}^{\infty} \exp(i2\pi nx/h).$$

The Fourier transform of $R_h(x)$ is

$$\begin{aligned}
&\int_{-\infty}^{\infty} \left[\frac{1}{h} \sum_{n=-\infty}^{\infty} \exp(i2\pi nx/h) \right] \exp(-i2\pi \sigma x) dx \\
&= \frac{1}{h} \sum_{n=-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left[i2\pi \left(\frac{n}{h} - \sigma \right) x \right] dx \\
&= \frac{1}{h} \sum_{n=-\infty}^{\infty} \delta \left(\frac{n}{h} - \sigma \right) = \frac{1}{h} \sum_{n=-\infty}^{\infty} \delta \left(\sigma - \frac{n}{h} \right).
\end{aligned}$$

Hence, the Fourier transform of an infinite distribution of Dirac δ -functions is another infinite Dirac distribution of period $1/h$ instead of h .

Now it is possible to find $F(\sigma)$, the Fourier transform of

$hR_h(x)A(x)$. Here one needs to find the Fourier transform of a product in terms of the Fourier transforms of the two parts. This is the same problem encountered in evaluating $B'(\sigma)$ previously in this chapter. In that case it was found that the Fourier transform of the product of two functions is the convolution of the Fourier transform of the functions. Using that result here, one has

$$\begin{aligned}
 F(\sigma) &= \text{F.T.} [A(x) h R_h(x)] = [\text{F.T. } A(x)] * [\text{F.T. } h R_h(x)] \\
 &= \left[1/(2\pi\sigma L)^{5/2} J_{5/2}(2\pi\sigma L) \right] * \left[\sum_{n=-\infty}^{\infty} \delta(\sigma - \frac{n}{h}) \right] \\
 &= \int_{-\infty}^{\infty} 1/(2\pi\sigma L)^{5/2} J_{5/2}(2\pi\sigma L) \left[\sum_{n=-\infty}^{\infty} \delta(\sigma - \frac{n}{h} - \sigma_1) \right] d\sigma_1 \\
 &= \sum_{n=-\infty}^{\infty} \left[\frac{1}{2\pi L(\sigma - \frac{n}{h})} \right]^{5/2} J_{5/2} \left[2\pi L(\sigma - \frac{n}{h}) \right] .
 \end{aligned}$$

One sees that the new scanning function consists of a series of identical maxima occurring at intervals $\Delta\sigma = 1/h$. Each such maximum has the form of $f_2(\sigma)$. Thus, the discrete sum $B''(\sigma)$ will give the same result as the integral $B'(\sigma)$ if the intensity is zero everywhere except in the range $\Delta\sigma = 1/h$, that is, that a single scanning function maximum cover the entire spectrum. If the observed spectrum goes from $\sigma = 0$ to $\sigma = \sigma_M$, then $\Delta\sigma = \sigma_M$, and one has the condition stated by the sampling theorem, that $h = 1/2 \sigma_M$.

Another factor which effectively limits the resolution of a Michelson interferometer is deviation from complete parallelism of the light in the instrument. Such deviation is unavoidable since one must use a finite sized source. The solid angle Ω subtended by

the source which will allow a resolution $\Delta\sigma$ with a maximum frequency σ_M is given by $\Delta\sigma/\sigma_M$ (2).

Computation

The first attempts at calculating spectra from recorded interferograms were made by means of a computer program written in the manner suggested by Gibbs and Gebbie (12). This was used only for some of the initial scans of BaTiO_3 which were later discarded.

A more complete program, written by V. M. Cowan, Brock University, was used to calculate all of the spectra presented in this work. The program is designed to do several things beside the Fourier transform. First the constant level is subtracted from each recorded value, then the position of zero path is located, followed by numerical filtering and interpolation. Finally, the Fourier transform is performed to give the spectrum.

To obtain that part of the signal which is a function of path difference, the part which is not dependent on path difference must be subtracted out. This was done by averaging the first fifty and the last fifty points of a double-sided interferogram. A level, corresponding to the value on a straight line drawn between these two end averages, was subtracted from each point on the recorded interferogram to obtain the autocorrelation function.

The method for determining the position of zero path was suggested by Bosomworth and Gush (11). It is very unlikely that the phasing of the Moire fringe system will be adjusted so that a reading is taken precisely at the zero path position of the moving mirror.

This procedure is of importance when two or more scans are to be averaged since a correct average is obtained only if points at exactly the same path difference are added. The error in zero path position is deduced from the measured set of points by the second section of the computer program. The computer searches for a maximum with four points on either side of the maximum recorded point in the convolution,

$$S(x_1) = \int_{-L}^L I(x - \epsilon) C(x, -x) dx$$

where

$$C(x) = \begin{cases} \left[1 - \left(\frac{|x|}{X}\right)^2\right]^2, & -X \leq x \leq X \\ 0, & |x| > X \end{cases}$$

and $X = 0.04$ mm (corresponding to four points on either side of the recorded maximum). $C(x)$ has a shape somewhat like $I(x)$ in the region of zero path difference. A maximum in the convolution occurs when $x_1 = \epsilon$, the shift from zero path difference position.

The section of the program which does the numerical filtering and interpolation generates a new sequence of points from the recorded sequence, again following the approach of Bosomworth and Gush (11). High frequency noise is filtered out mathematically leaving a sequence of fewer points (approximately four times less) to be Fourier transformed to get the spectrum.

In the Fourier transform section the cosine transform, the sine transform, and the complete Fourier transform are computed and written out.

The complete program is listed in Table I.

Table I. Computer Program Listing

```

DIMENSION AVAINT(700),CONVOL(51),EPSLON(51),AINT(700),APOD(700),
1SYMPD(350),GNU(350),SUM(350)
REAL INT(1500),LOCATE(51)
DIMENSION ASYMPD(350),SUM1(350),SUM2(350)
DIMENSION BKG(350),SPCTRM(350)
C READ INTERFEROGRAM AND SUBTRACT CONSTANT LEVEL (MAY SLOPE SLIGHTLY)
IN=5
IOUT=6
1 READ(IN,2)NRUNS
2 FORMAT(15)
IF(NRUNS.EQ.0)GO TO 999
READ(IN,3)
3 FORMAT(72H
1
WRITE(IOUT,3)
READ(IN,4)WIDTH
4 FORMAT(F5,0)
READ(IN,5)IDENT,MODE1,MODE2
5 FORMAT(3A6)
DO 11 I=1,700
11 AVAINT(I)=0
DO 110 NTRACE=1,NRUNS
READ(IN,10)NPTS,NPTMIN,NPTMAX,NAVRGE,(INT(NPT),NPT=1,NPTS)
10 FORMAT(4I5/(15F5,3))
SUMPOS=0
SUMNEG=0
DO 20 J=1,NAVRGE
SUMPOS=SUMPOS+INT(NPTMAX-J+1)
20 SUMNEG=SUMNEG+INT(NPTMIN+J-1)
ENAVGE=NAVRGE
SUMPOS=SUMPOS/ENAVGE
SUMNEG=SUMNEG/ENAVGE
ENMID=NPTMAX-NAVRGE-NPTMIN
ENMIDL=NPTMIN+NAVRGE/2
SLOPE=(SUMPOS-SUMNEG)/ENMID
NPTSA=NPTMAX-NPTMIN+1
DO 30 J=NPTMIN,NPTMAX
AJ=J
JJ=J-NPTMIN+1
30 INT(JJ)=INT(J)-(AJ-ENMIDL)*SLOPE-SUMNEG
WRITE(IOUT,31) (INT(J),J=1,NPTSA)
31 FORMAT(//(15F7,3))
C LOCATE ZERO PATH DIFFERENCE
READ(IN,40)NPTZPD,EX
40 FORMAT(15,F5,0)
NEL=2,*EX+1.
NEX=EX+1.
EN1=50./WIDTH
DO 50 N=1,51
EN=N

```

Table I. (Continued)

```

EPSLON(N)=(EN-26.)/EN1
CONVOL(N)=0
DO 60 L=1,NEL
EL=L-NEX
REX=(EL-EPSLON(N))*3.141592/EX
IF(REX.EQ.0.)REX=1.0E-10
LOCATE(L)=(SIN(REX))/REX
60 CONVOL(N)=CONVOL(N)+LOCATE(L)*INT(NPTZPD-NEX+L)
50 CONTINUE
NMAX=1
DO 70 N=2,51
IF(CONVOL(NMAX).LT.CONVOL(N))NMAX=N
70 CONTINUE
SHIFT=EPSLON(NMAX)
WRITE(IOUT,61) SHIFT,(EPSLON(N),CONVOL(N),N=1,51)
61 FORMAT(/F10.5/( 6(F8.5,E12.5)))
C NUMERICAL FILTERING AND INTERPOLATION
READ(IN,80)GNUMIN,GNUMAX,DELNU,HO
80 FORMAT(3F10.1,F10.7)
H1=0.5/(GNUMAX-GNUMIN)
ENPTMX=NPTMAX
ZPD=NPTZPD
RANGEM=ZPD+SHIFT-1
RANGEP=ENPTMX-ZPD-SHIFT
RANGE=RANGEM
IF(RANGEM.GT.RANGEP)RANGE=RANGEP
CUTOFF=RANGE/20.
OFFCUT=1./CUTOFF
NPTZPA=(RANGE-CUTOFF)*HO/H1+1.
NPTMXA=2*NPTZPA-1
GNU2PI=6.283185*GNUMAX
DO 90 NPTA=1,NPTMXA
AMZPA=NPTA-NPTZPA
ENPT=AMZPA*H1/HO+SHIFT+ZPD
NSTART=ENPT-CUTOFF+1.
NEND=ENPT+CUTOFF
STMZPD=NSTART-NPTZPD
PD1=(STMZPD-SHIFT-AMZPA*H1/HO)*OFFCUT
XI1=PD1*CUTOFF*GNU2PI*HO
DELXI=HO*GNU2PI
COS0=2.*COS(DELXI)
SIN1=SIN(XI1)
SUMA=INT(NSTART)*SIN1*(1.-PD1**2)**2/XI1
PD1=PD1+OFFCUT
XI1=XI1+DELXI
SIN2=SIN(XI1)
SUMA=SUMA+INT(NSTART+1)*SIN2*(1.-PD1**2)**2/XI1
NSTRT2=NSTART+2
DO 100 NPT=NSTRT2,NEND
SIN3=SIN2*COS0-SIN1

```

Table I. (Continued)

```

PD1=PD1+OFFCUT
XI1=XI1+DELXI
IF(XI1.EQ.0.)GO TO 98
SUMA=SUMA+INT(NPT)*SIN3*(1.-PD1**2)**2/XI1
GO TO 99
98 SUMA=SUMA+INT(NPT)
99 SIN1=SIN2
100 SIN2=SIN3
    AINT(NPTA)=SUMA*2.*GNUMAX
90 AVAINT(NPTA)=AVAINT(NPTA)+AINT(NPTA)
    WRITE(IOUT,111) (AINT(NM),NM=1,NPTMXA)
110 CONTINUE
111 FORMAT(///(10F12.5))
    IF (NRUNS.EQ.1) GO TO 121
    ENRUNS=NRUNS
    DO 120 NPTA=1,NPTMXA
120 AVAINT(NPTA)=AVAINT(NPTA)/ENRUNS
    WRITE(IOUT,111)(AVAINT(N),N=1,NPTMXA
C    FOURIER TRANSFORM TO GIVE SPECTRUM
121 MAXPOS=NPTMXA-NPTZPA
    MAXNEG=NPTZPA-1
    ENZPMX=MAXPOS
    IF(MAXPOS.GT.MAXNEG)ENZPMX=MAXNEG
    DO 130 NPTA=1,NPTMXA
    PD=NPTA-NPTZPA
130 APOD(NPTA)=AVAINT(NPTA)*(1.-(PD/ENZPMX)**2)**2
    NZPMX=ENZPMX
    SYMPOD(1)=APOD(NPTZPA)
    DO 140 I=2,NZPMX
    ASYMPD(I)=(APOD(NPTZPA+I-1)-APOD(NPTZPA-I+1))
140 SYMPOD(I)=(APOD(NPTZPA+I-1)+APOD(NPTZPA-I+1))
    NNU=(GNUMAX-GNUMIN)/DELNU
    DO 150 N=1,NNU
    EN=N
    GNU(N)=GNUMIN+(EN-1.)*DELNU
    PHI=6.283185*GNU(N)*H1
    COS0=2.*COS(PHI)
    COS1=1
    COS2=COS(PHI)
    SIN1=0
    SIN2=SIN(PHI)
    SUM(N)=SYMPOD(1)+SYMPOD(2)*COS2
    SUM1(N)=ASYMPD(2)*SIN2
    DO 160 I=3,NZPMX
    COS3=COS2*COS0-COS1
    SIN3=SIN2*COS0-SIN1
    SUM(N)= SYMPOD(I)*COS3+SUM(N)
    SUM1(N)=ASYMPD(I)*SIN3+SUM1(N)
    SIN1=SIN2

```

Table I. (Continued)

```

      SIN2=SIN3
      COS1=COS2
160  COS2=COS3
      SUM(N)=SUM(N)*H1
      SUM1(N)=SUM1(N)*H1
      SUM2(N)=SQRT(SUM(N)**2+SUM1(N)**2)
150  CONTINUE
      WRITE(IOUT,170) (GNU(N),SUM(N),SUM1(N),SUM2(N),N=1,NNU)
170  FORMAT(/1X,26HFREQUENCY(CM-1) INTENSITY/(2(F10.1,3E13,5)))
      IF(IDENT.EQ." BKG")GO TO 180
      DO 200 I=1,NNU
200  SPCTRM(I)=SUM2(I)/BKG(I)
      WRITE(IOUT,3)
      WRITE(IOUT,210)MODE1,MODE2,(GNU(I),SPCTRM(I),I=1,NNU)
21-  FORMAT(9H FRACTION,2A6,35H AS FUNCTION OF FREQUENCY IN (CM-1)/(5(
      1F10.2,F10.5)))
      GO TO 1
180  DO 190 I=1,NNU
190  BKG(I)=SUM2(I)
      GO TO 1
999  STOP
      END

```

CHAPTER III

THE SPECTROMETER

Interferometers for the study of far infrared spectra have been designed and described by Bosomworth and Gush (11) and by Gebbie and Stone (17) among others. Both of these instruments were designed primarily for use with samples of gases at high pressures (up to about 130 atmospheres). The optics of the instrument presented here are similar to those used by Gebbie and Stone in order to avoid the off-axis paraboloids of Bosomworth and Gush and thus reduce the cost of the machine. It is somewhat more versatile than these instruments, however, in the sense that the sample is mounted externally to the main vacuum chamber, thus allowing any shape or size to be used.

The Vacuum Chamber

The main vacuum chamber (Figs. 2 and 3) housing the Michelson optics and the mercury arc was designed by the writer and constructed by the Boardman Co., Oklahoma City, Oklahoma. The main cylindrical body is of standard size black pipe, twenty inches inside diameter and one-half inch wall thickness. The top and bottom flanges were welded to the pipe and then machined flat and parallel. All flanges and

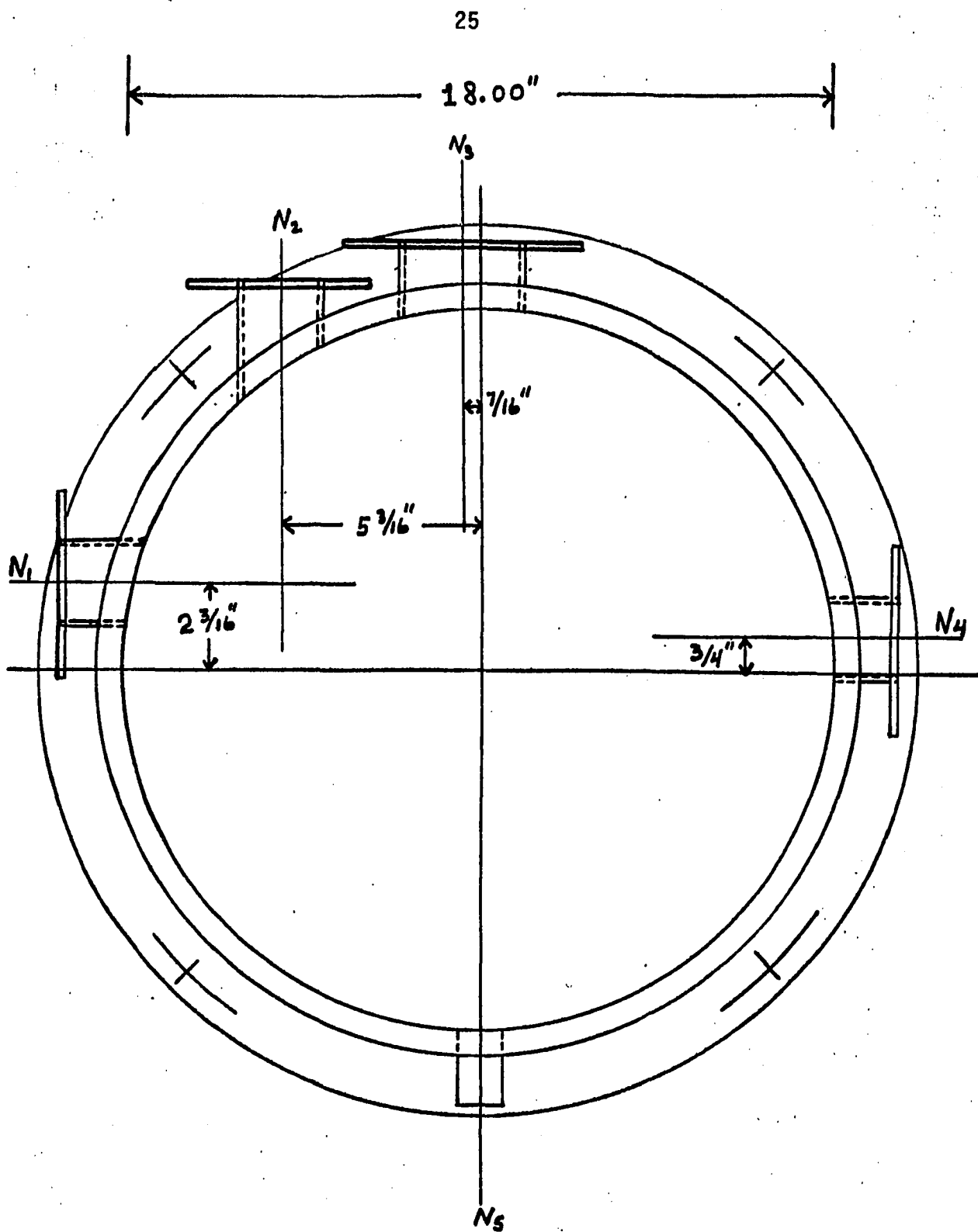


Figure 2. Main Vacuum Chamber - Top View.

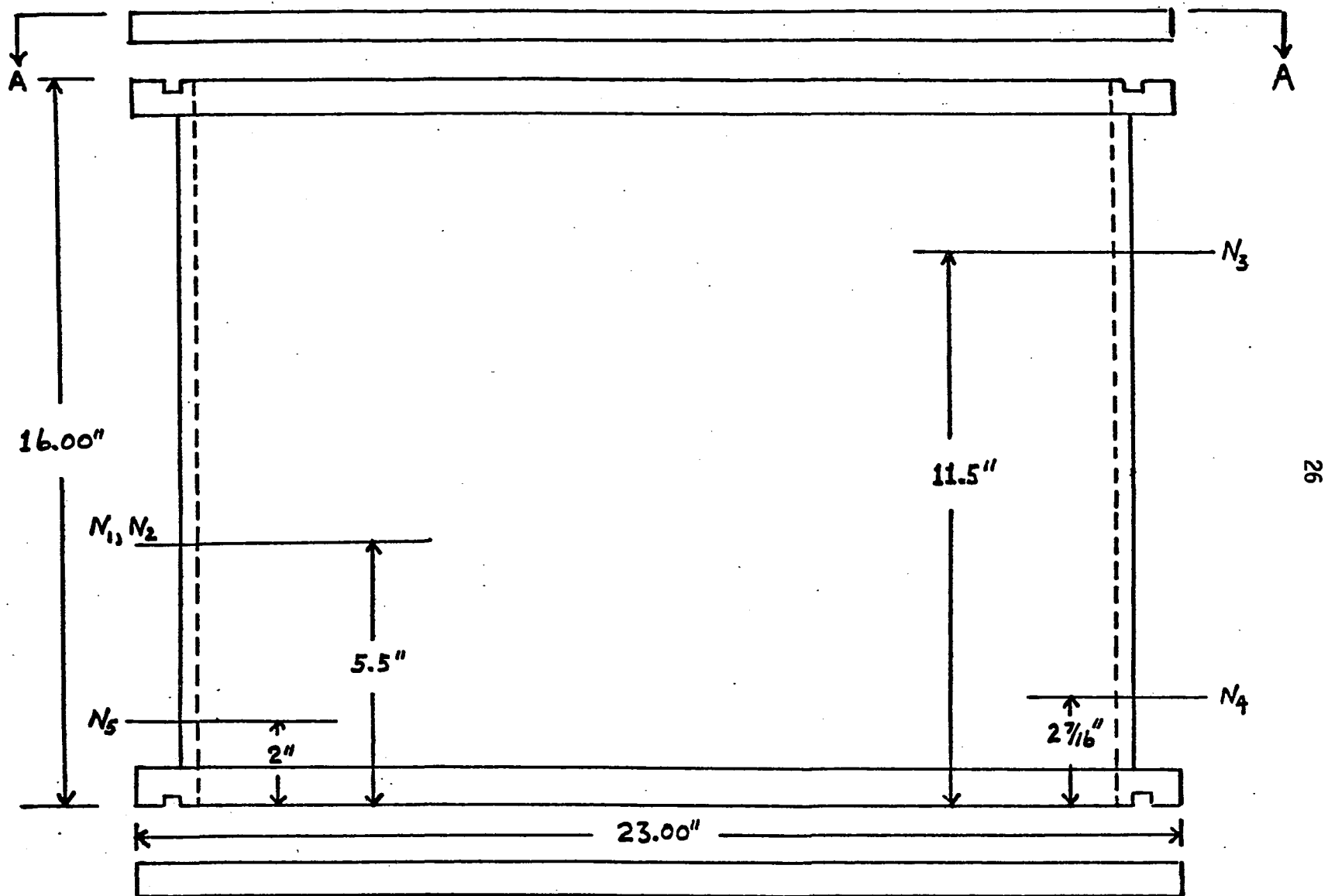


Figure 3. Main Vacuum Chamber - Elevation.

plates are of mild steel except the base plate, which is 3/4 inch hot rolled steel to give increased rigidity. All tolerances, except for O-ring grooves, are $\pm 1/16$ inch.

Originally the main chamber was intended to house only the Michelson optics with the source, detector, and pull-rod for the moving mirror being connected by means of an O-ring to the appropriate flange. With this in mind, two additional vacuum chambers were constructed. A chamber attached to port number N_2 housed the chopper, filters, and Golay detector. This tank was constructed of 3/8 inch aluminum in the instrument shop at Brock University, St. Catharines, Ontario. Due to its rectangular construction a great deal of difficulty was experienced in making the chamber free of leaks. The welds were liberally painted with Glyptol. The lid was finally made of 5/8 inch mild steel ground flat to provide a good seal against a 3/16 inch O-ring, which was fitted into a groove around the top. This chamber was later discarded when a change in the equipment set-up made it unnecessary. A second auxiliary chamber was designed to be attached to port number N_3 and to house the Golay detector. This chamber (Fig. 4) was also constructed in the instrument shop at Brock University.

The final arrangement, which allowed the large rectangular vacuum tank to be discarded, requires a connection only between the chamber housing the Golay cell (Fig. 4) and port number N_2 . The connection is made by means of highly polished 5/8 inch brass tubing with Cajon connectors providing a vacuum-tight seal on each end. The sample holder (to be described later) is between the detector and the

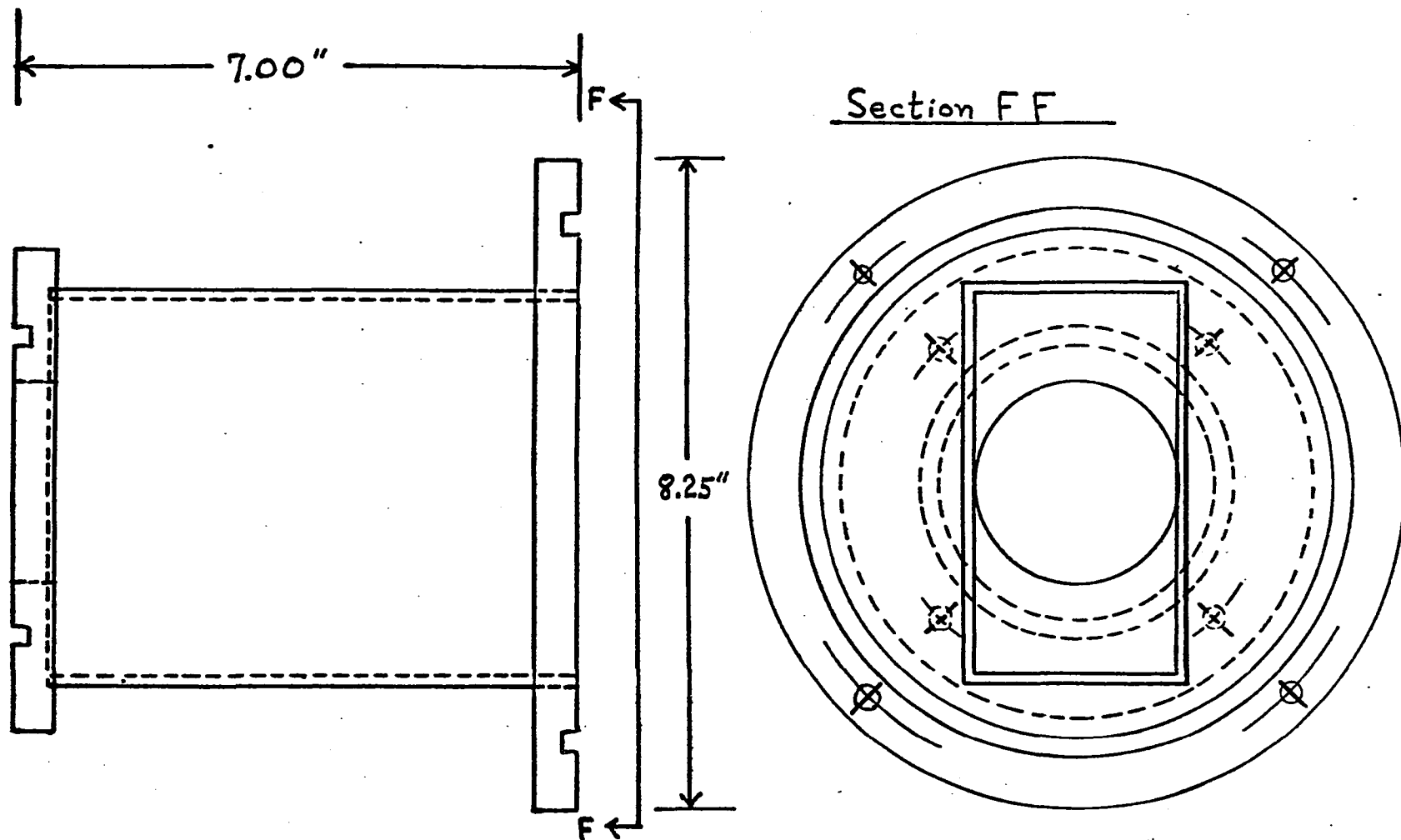


Figure 4. Detector Housing.

main vacuum chamber. The mercury lamp and a modified chopper are now inside the main vacuum chamber, allowing port N_3 to be covered with a flat plate, which has certain electrical and mechanical connections through it. At one point a lack of signal prompted some experimenting with different light pipes. In particular, 1/2 inch copper tubing was tried in place of brass because of the higher conductivity of copper. There was no detectable difference and hence the return to the more rigid brass tubing.

The pulling apparatus (to be discussed in detail later) is attached to port N_4 . Port N_1 is used for the electrical connections to the Moire fringe system, and when the cover is removed it allows the entrance of a helium-neon laser beam for alignment purposes. Port N_3 , originally designed to connect to the detector, is now used for electrical connections to the chopper and mercury arc, and water connections for cooling the mercury lamp.

When the instrument was first assembled it was discovered that the Moire fringe system, which was working properly when the tank was open, ceased to function when a vacuum was drawn. The reason for this malfunction was that the 3/4 inch base plate of the main vacuum tank was deforming under air pressure just enough to put the fringe system out of alignment. This problem was corrected with a modification in which the aluminum plate, on which all the optical components are mounted, was allowed to float rather than being firmly bolted to the base of the tank. This modification was implemented by V. M. Cowan, Brock University, at the suggestion of the writer.

Electrical Connections to the Vacuum System

Electrical connections to the moderate pressure mercury lamp, the Golay detector, the lamp for the Moire fringe system, and the silicon diode are all hermetically sealed BNC feed-throughs. The chamber is drilled and tapped so that the connectors are screwed directly into the walls of the chamber and are sealed with an O-ring. The only other electrical connections necessary are those for the 10 hz chopper mounted just ahead of the mercury lamp. These have all been made through a standard 7-pin connector with the pins potted in epoxy on one side. All of these connectors are sealed against the vacuum tank by means of O-rings.

Mechanical Connections

The drive used to pull the moving mirror presented several problems as the instrument developed. Initially a commercial feed-through manufactured by Consolidated Vacuum Corp. was installed at port N₄. Inside the tank the pull-rod was connected to the moveable carriage by two small universal joints from Boston Gear Co. Outside, the rod was connected similarly to a gear rack with 64 teeth per inch, which was then pulled by a one rev./hr. timing motor. It was soon discovered that this drive resulted in a very uneven pull. What one might call a "stick-slip" phenomenon was found to occur. Several different lubricants were tried unsuccessfully both in the feed-through, and between the gear rack and the slot in which it moved. After some time it was decided that this particular type feed-through was not

designed for smooth linear operation.

To correct the above problem, a micrometer screw was connected to the moveable carriage inside the tank. The feed-through now required only rotational motion. A system consisting of two O-rings and a smooth shaft provide the feed-through. The shaft is driven by a one rev./min. timing motor and a spur gear reduction system. This modification was made by V. M. Cowan of Brock University.

The only other mechanical connections into the vacuum system are the two pieces of 1/8 inch copper tubing used to carry water to the cooling coils around the mercury lamp. This is done by means of an O-ring which fits snugly around the tubing and is then pressed down onto the cover over port N₃ by means of a small flange.

Optics

The optical arrangement inside the main tank is shown in Fig. 5. The wavelengths of the radiation under investigation are many times longer than those of visible light, hence a mirror good to one-half wavelength in the visible region becomes an extraordinarily good mirror for the far infrared. Therefore, relatively inexpensive first surface mirrors ground to within one-half wavelength of visible light were obtained from Jaeger Optical Co., Lynbrook, N. Y. The two flat mirrors at right angles to each other and the two spherical mirrors are 4 1/2 inches in diameter, while the fifth mirror, situated at 45° with respect to the others, is 6 inches in diameter. The mirrors are mounted in simple rings with three spring loaded adjusting screws. These rings are then fastened to the base plate by an L-shaped bracket.

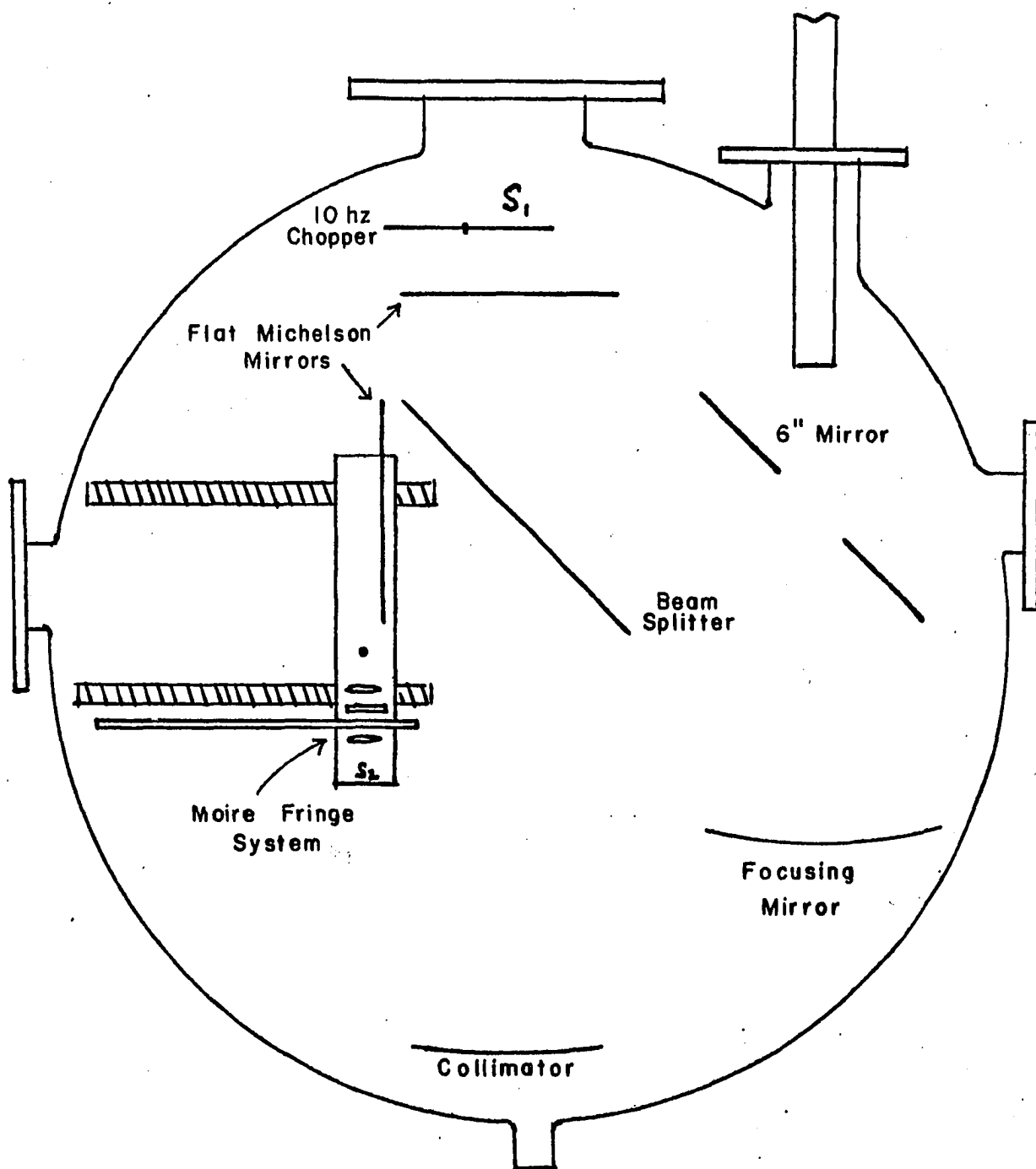


Figure 5. Optical Arrangement.

The 6 inch mirror (one inch in thickness) has a one inch hole through its center at 45° with respect to the mirror's normal direction. The mirror was purchased already aluminized, so the drilling of the hole had to be done with some care. First the front surface was coated with "black wax" dissolved in benzene. The benzene was allowed to evaporate leaving the protective coating of wax. A jig was constructed of wood to hold the mirror at 45° to the horizontal. Points of contact between jig and mirror were cushioned with balsa wood. The mirror was clamped into the jig, which had a tight-fitting one inch guide hole for about two inches above the mirror surface. A thin-walled, brass "cookie-cutter" was machined with a taper on the solid end which fitted directly into a drill press. A slurry of No. 80 carborundum and water was then used to slowly grind through the mirror. The actual drilling required about six hours. After the hole had been drilled, the black wax was washed off with benzene, leaving the mirror surface intact.

The solid angle subtended by the source is about $(1/32)^2$ since the diameter of the source is approximately $1/2$ inch and the focal length of the collimating mirror is 16 inches. Due to the tilt of the collimating mirror, the effective size of the source is increased somewhat. For a 10° tilt of the mirror, parallel light would be focused within a 0.45 inch area (18). Hence, the effective diameter of the source is approximately one inch. Using the criterion stated by Gebbie (2) this factor limits the resolution of the instrument to $\sigma_M / (32)^2$ which is 0.04 cm^{-1} if $\sigma_M = 50 \text{ cm}^{-1}$. The size of the exit aperture must be large enough to receive all the energy from the

focusing mirror. This is accomplished by the 5/8 inch brass tubing. The size of the beam is narrowed to 3/16 inch, the size of the Golay cell window, by a machined and polished brass cone.

The Carriage and Rails

The moving mirror is mounted on a mild steel carriage which slides along two stainless steel rails. The most important aspect of this assembly (Fig. 6) is the straightness of the rails. Any deviation from straightness affects the perpendicularity between the two flat mirrors of the Michelson optics. Due to this requirement, the rails were carefully ground and are straight to within 0.0005 inches over a seven inch length. Some deviation in parallelism of the rails with respect to each other and/or level of the rails with respect to the horizontal is permissible since this does not affect the perpendicular adjustment between the two mirrors. Hence, the rods are mounted parallel to each other to within 0.001 inches over a seven inch length and are in the same plane to within 0.001 inches over the seven inch length. The useable length of the rails is seven inches, which allows the carriage a maximum travel of 3.25 inches.

The problem of returning the carriage after being pulled through a scan by the drive mechanism was approached in several ways before the present arrangement was decided upon. Initially a coil spring (of the type used in alarm clocks) was mounted on the base holding the rails. The spring was used to rotate a drum which wound up two strings attached to the carriage. It was found that the spring had a tendency to stick in its housing, both while the carriage

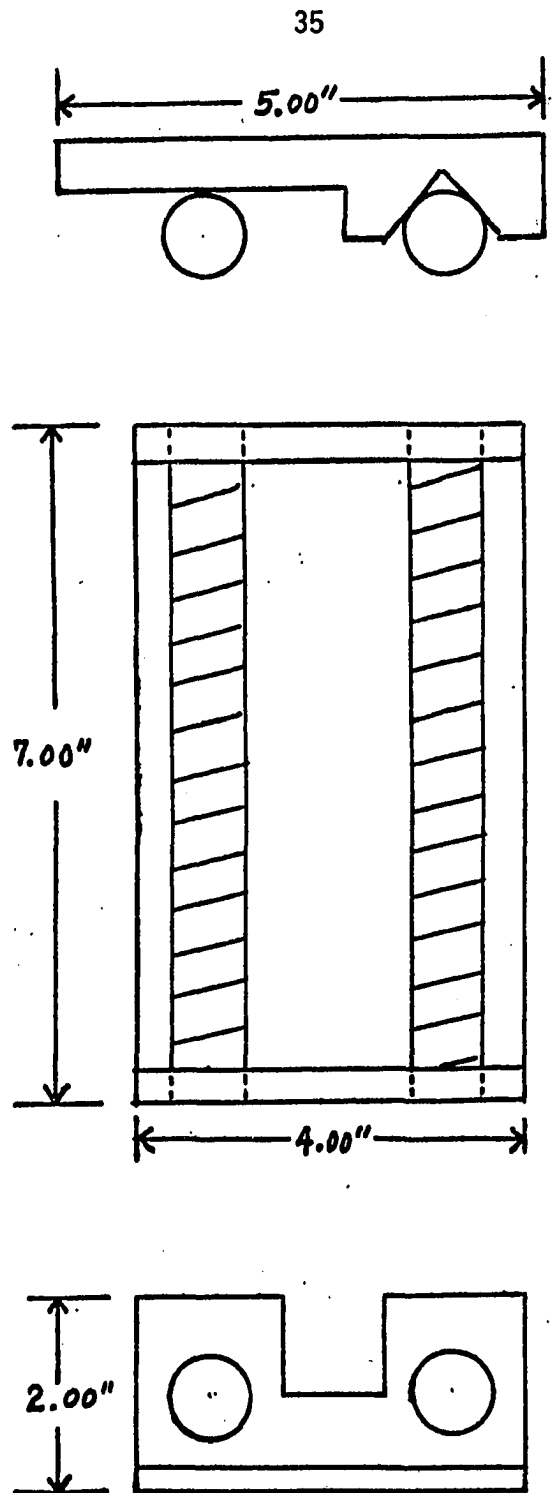


Figure 6. Moving Carriage and Rails.

was being pulled out by the drive as well as on the return. The result was an uneven scan and uncertainty whether the spring had actually returned the carriage to its starting position again or not. Thus, the spring was discarded. When the linear pull-rod was used to move the mirror it also served to return the carriage to the initial position. This worked well because of the rigid mechanical coupling achieved through the use of the universal joints. When this pulling method was replaced by the micrometer screw and rotary feed-through, another method was devised. A simple system of pulleys and weights now provides a constant restoring force on the carriage.

The carriage and rails were constructed in the instrument shop at the University of Oklahoma under the supervision of the late Mr. J. C. Hood.

The Beam Splitters

Primarily two types of beam splitting plates have been used to investigate the far infrared region. One is a fine wire mesh with spacing on the order of the wavelength being investigated. This has been used by Russell and Bell (19), and Vogel and Genzel (20). Other investigators such as Gebbie (17) and Gush (11) use the dielectric film beam divider. The work being presented here uses dielectric films, specifically, different thicknesses of Mylar (polyethylene terephthalate). No compensating plate is needed to obtain a symmetrical two beam interferogram as long as the film is uncoated (21). Some of

the early films used by Gebbie were coated with germanium, tellurium, or bismuth telluride, but this practice seems to have disappeared completely (2). These plastic films have a number of good properties such as low cost, mechanical strength, and simplicity.

The beam divider behaves as a dielectric, and absorption may be neglected as long as one uses a given film only within its first maximum (21). The thickness of a film is chosen so that maximum intensity will be transmitted through the interferometer at half the maximum frequency being investigated. It is found that a minimum is situated at σ_M when $2h\sigma_M n' \cos \theta' = m$ where σ_M = the maximum wavenumber being investigated, n' = the index of refraction of the film, θ' = the angle of refraction in the film, m is an integer, and h is the thickness of the film (21). This allows one to calculate the proper film thickness for a given spectral range. Ideally, the product of the energy transmitted and the energy reflected by a beam divider should be 0.25. Measurements made on a six micron thick sheet of Mylar at 45° angle of incidence gives a value of 0.23 (17), indicating a very high efficiency for these dielectric film beam dividers. The efficiency decreases slightly with thickness, due to absorption.

Four such beam splitters, having thicknesses of 25, 50, 75, and 125 microns, were constructed for use in the present work. Mylar of 12.5 microns is also on hand but has not been mounted because at present the investigations are limited to frequencies below those requiring a 12.5 micron beam splitter. With the four thicknesses presently mounted, the frequency range from about 5 cm^{-1} to 200 cm^{-1}

can be studied. The Mylar sheeting was obtained commercially from Cadillac Plastics, Dallas, Texas.

The rings holding the Mylar have been designed very much like those of Gebbie and Stone (17). The construction is of mild steel with an open area six inches in diameter (Fig. 7). Flatness of the defining ring (the lapped surface noted on Fig. 7) determines the flatness of the Mylar film. Therefore, after machining and annealing the ring, this defining ring was lapped plane to better than seven microns. The Mylar sheet was then stretched across this defining ring by an ordinary rubber O-ring, which was then pressed down by the hold-down ring. After the film had been mounted in this way, the entire assembly was placed in an oven at 165°C for about one half hour. This causes the Mylar to shrink leaving a flat, taut membrane. Machining and lapping of the rings was done in the instrument shop in the physics department at the University of Oklahoma.

Each of the four rings is mounted on three, half-inch steel balls which allow the beam splitter to be removed from the instrument and then replaced without affecting the optical alignment of the interferometer. The four rings are nearly identical, however some realignment of the interferometer is necessary in going from one beam splitter to another. Each beam splitter was set vertically by placing it on a flat granite plate and adjusting the screws attached to the three steel balls until the entire face was vertical compared to a machinist's square. The beam splitter rests on a base plate

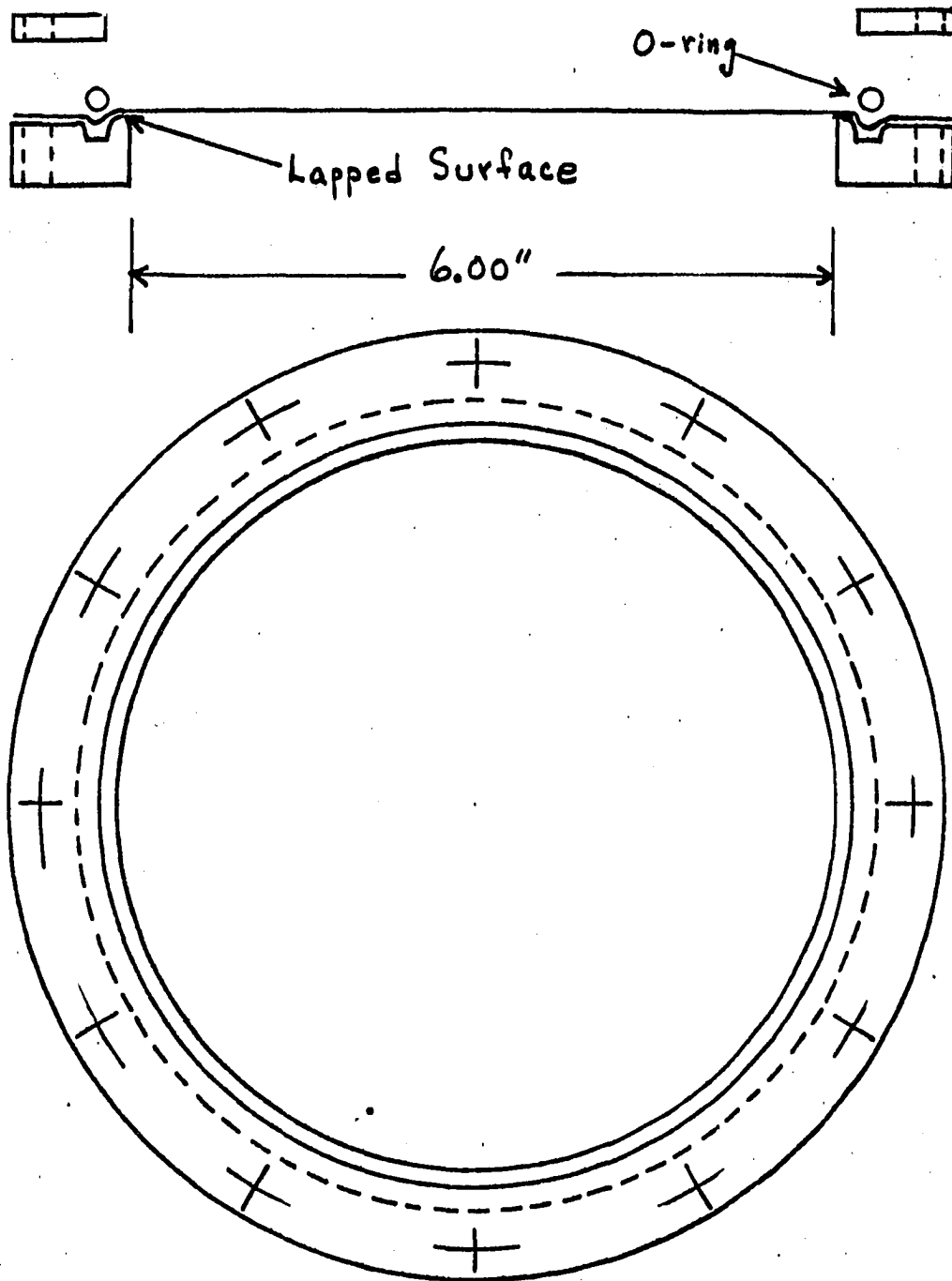


Figure 7. Beam Splitter.

which has two flats and a vee. This plate can be rotated about an axis through the plane of the film and the beam splitter is allowed one half inch of travel horizontally along the plate.

The Moire Fringe System

To obtain a correct interferogram, it is essential that the intensity be measured at exactly equal intervals of path difference. One might attempt this by using a well machined, fine screw to pull the moving mirror and then to take readings at equal time intervals. This would require workmanship in the screw that would make the price rather high. The alternative commonly used (17,11) is to measure the position of the moving mirror by means of two identical transmission gratings used in a Moire fringe system. It is this method which is used in this instrument. The principle of the method has been described by Guild (22). The gratings were purchased from Optical Measuring Tools, Ltd., Maidenhead, Berks., England, and have a spacing of 100 lines/mm.

One of the gratings is attached to the base of the vacuum tank, while the other is fixed to the moving mirror carriage. The gratings obtained were blazed for use at 0.85 microns and thus suitable for silicon photocells, whose sensitivity peaks sharply at 0.85 microns. The intensity contrast between light and dark fringes is highly dependent on the spacing between the gratings. A working gap of 0.0012 mm (0.005 inches) is considered normal by Ferranti Co. (manufacturers of Moire gratings). The change in intensity is impor-

tant in that it determines the size of the output signal from the photocell.

The gratings are mounted so that the lines of one are very nearly parallel to those of the other. If they were exactly parallel, the entire portion across both gratings would have the same intensity and would change from maximum to minimum as the gratings move relative to each other. Usually, in practice, a small skew angle exists between the lines of the gratings and a pattern of bright and dark bands moves across the gratings in a direction perpendicular to the relative motion of the gratings. This pattern moves one fringe when the gratings move a distance of the spacing between the lines. Thus, for the gratings used here, a shift of one fringe occurs for a movement of 0.01 mm by the carriage holding the moving mirror.

This alternating dark-light pattern moves across the face of a silicon photocell. The nearly sinusoidal output signal is amplified and fed into a trigger circuit which is used to command the digital voltmeter (DVM) to take a reading. The exact specifications of the photocell used are not known since it was found in the electronics stock at Brock University without any markings. The output voltage was taken across a 9K ohm resistor and has a peak-to-peak value of about 26 mv.

The light source is a GE47 bulb run at four volts. The light was collimated to pass through the gratings and then focused onto the sensitive area of the photocell.

The general arrangement of the Moire system may be seen as a part of Fig. 5.

The Detector

Various detectors have been used in the far infrared region. Until the early 1960's the only available detector was the Golay cell developed by Marcel Golay in 1947 (23). Recently, however, solid-state detectors have been put to use. The main advantage of these devices is their much faster response time compared to that of the Golay cell. The disadvantages are that the solid-state detectors must be operated at liquid helium temperatures and their range of usefulness is often quite restricted. The details for several types of detectors are listed in Table II.

The detector used in all of the experiments reported in this work is a Unicam Golay cell equipped with a diamond window. The cost of other solid-state detectors was considered prohibitive for this project. The Golay cell operates only on chopped radiation since the output signal is a measure of the difference in power seen by the detector between the radiation from the source and that from the blades of the chopper. Thus, the blades act as a reference signal and the radiation from them should be kept as constant as possible. This can be done by having a mirror surface on the chopper blades and reflecting the signal derived from a reference source maintained at a constant temperature. In these experiments no special reference was used, leaving the chopper blades at ambient temperature.

TABLE II: Detector Comparison

	Response Time	Operating Temperature	Sensitive Range
Golay Cell			
(23, 1, 17, 11)	20 msec	300 °K	Unlimited
n-type InSb	0.3 sec	4.2 °K	40 cm ⁻¹ - 2 cm ⁻¹
(24, 25)			
Ge:Ga Bolometer			
(26, 27)	1 msec	4.2 °K	250 cm ⁻¹ - 83 cm ⁻¹
Ge:In Bolometer			
(3)	1 msec	4.2 °K	200 cm ⁻¹ - 3 cm ⁻¹
Ge Bolometer			
(28)	1 msec	4.2 °K	110 cm ⁻¹ - 40 cm ⁻¹

It was discovered that when the chopper was placed close to the source, the signal would decrease gradually during approximately the first half hour, after which time it remained constant. This was attributed to a slight warming of the chopper blades due to their proximity to the mercury lamp.

The detector has a maximum response with a chopping speed of about 5 hz. The response drops to near zero at about 18 hz. A 10hz chopper manufactured by Eppley Laboratories was purchased for this purpose. Recently it was discovered by V. M. Cowan that the large table holding the interferometer had a natural vibration frequency very near 10 hz, resulting in a high level of noise. The problem has been remedied to a large extent by driving the chopper at 11 hz and mounting the interferometer on the floor.

The Source and Filters

It has been shown that in the far infrared region a moderate pressure mercury arc produces a source of radiation superior to that of a globar (17). Much of the literature consulted by the writer when this work was begun (e.g. 11, 29, 19) talked of using high pressure mercury arcs as sources. As a result the first lamp that was inserted as a possible source was a very high pressure mercury arc (9 atm. pressure). When this resulted in no signal being observed, a more thorough literature search was in order. Yoshinaga (29) showed that the useful far infrared radiation comes from both the mercury vapor as well as from the quartz envelope. At a wavelength of 100 microns,

the relative contribution from the vapor is about 40%. This increases rapidly as one goes to longer wavelengths. The amount of radiation that one sees at the very long wavelengths depends on the transmittance of the fused quartz envelope, which depends on the thickness of the envelope. The filters in the instrument had been designed to cut off all radiation of wavelength shorter than approximately 200 microns, hence the reason that no signal was observed is that the very high pressure lamp requires, for mechanical reasons, an envelope too thick to allow the far infrared radiation due to the vapor into the instrument. Subsequently, "high pressure" was interpreted to mean "moderate pressure", that is, on the order of one atmosphere. Several lamps were then purchased and tried. An Osram Hg/1, run with a proper ballast in the a-c lines, was selected because it had the greatest intensity.

Various types of filters have been used to eliminate the ultraviolet, visible, and middle infrared radiation also produced by the mercury arc. Fine wire mesh has been used by Yoshinaga (29), while Wettling and Genzel (30) have used frustrated total reflection. Investigations which go to somewhat higher frequencies than the present work make use of BaF_2 crossed restrahten filters (11). In the frequency region below 100 cm^{-1} , the writer has followed the suggestion of Bosomworth and Gush (11). The filter consists of a 6 mm thickness of crystalline quartz and a 1/8 inch thickness of high density polyethylene covered with turpentine soot. Crystalline quartz is transparent in the ultraviolet, visible, and far infrared,

but eliminates the middle infrared region. Turpentine soot filters the visible and the polyethylene cuts out the ultraviolet. It is important that high density rather than low density polyethylene is used. Except for an absorption band at 70 cm^{-1} , the transmittance of a 1/8 inch thickness of the former is greater than 60% throughout the far infrared region, whereas that of an equal thickness of low density polyethylene is only 30% (11). The beam splitter also does some filtering because of the rapid decrease in intensity of the secondary maxima relative to the first.

The Sample Holder

The initial sample holder was designed to fit into the light pipe between the main vacuum chamber and the auxiliary chamber housing the detector and chopper. The holder was constructed of brass and is shown in Fig. 8. A chromel-alumel thermocouple was inserted into the 1/2 inch brass flange to determine the temperature of the sample and a heating tape, run through a Variac, was wrapped around the outside of the holder. The intent was to investigate BaTiO_3 , and since the available crystals were such that the useful area was about 3/16 inch in diameter, the light pipe was narrowed from 5/16 inch to 3/16 inch by means of a brass cone, which was machined and then polished. The cone was found to reduce the intensity considerably. This design was abandoned due to inefficient heating and the inability to cool the sample below room temperature.

The cell shown in Fig. 9 was designed by V. M. Cowan. The

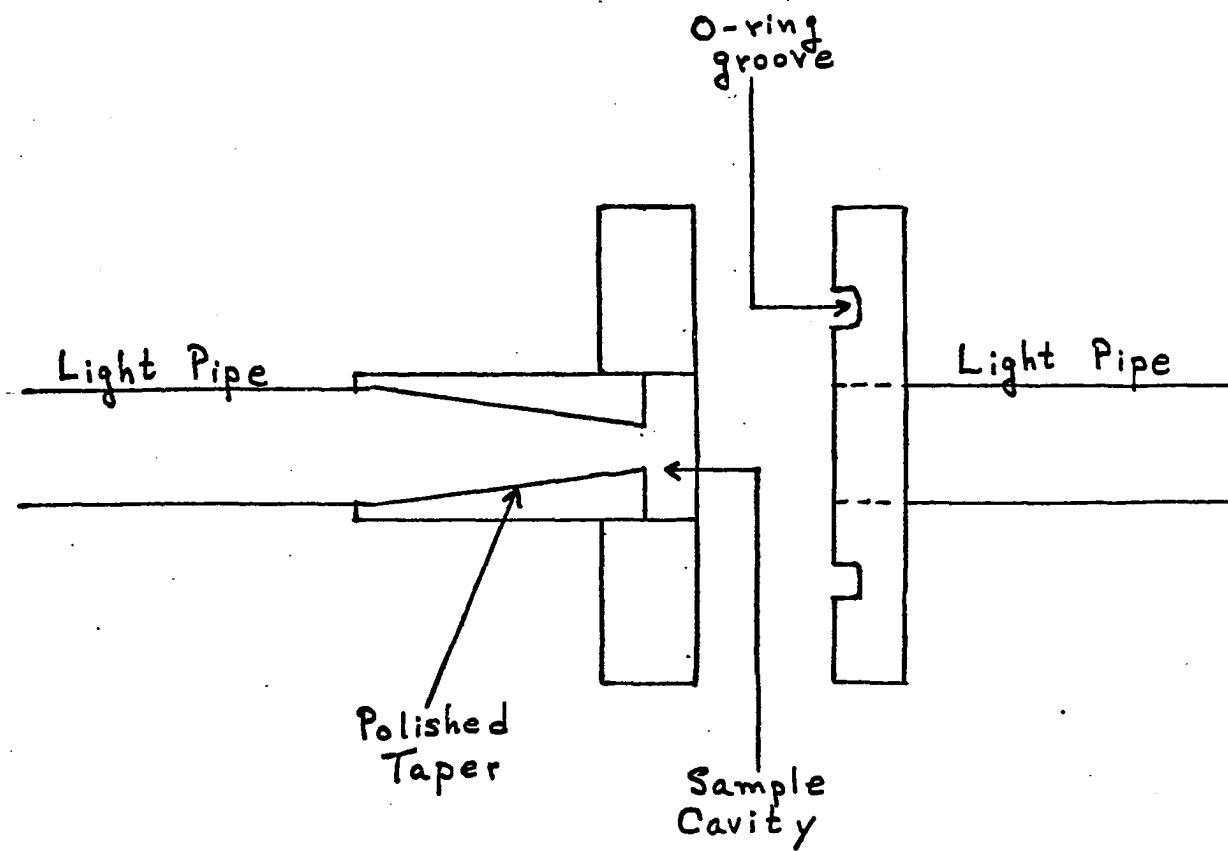


Figure 8. Original Sample Holder.

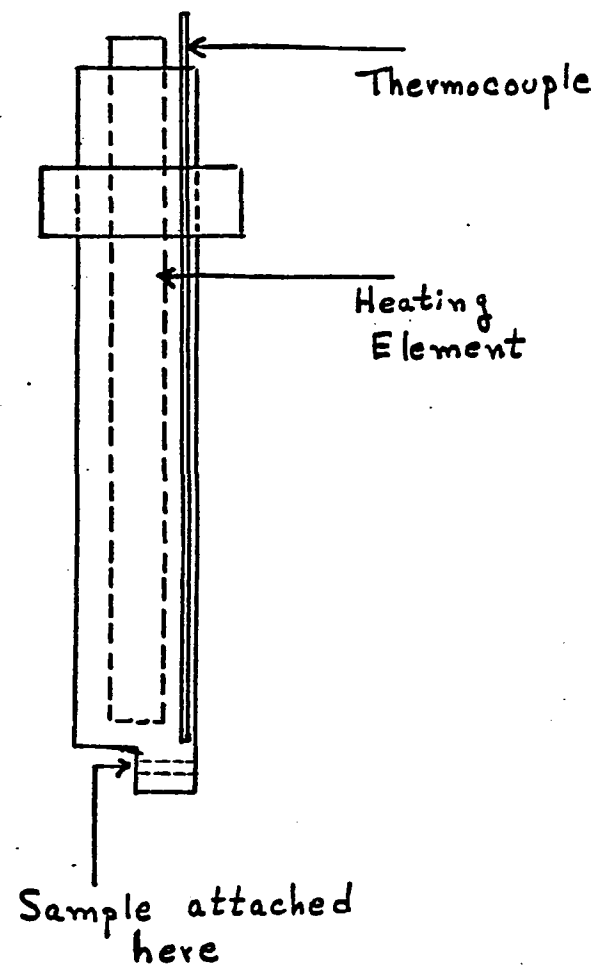
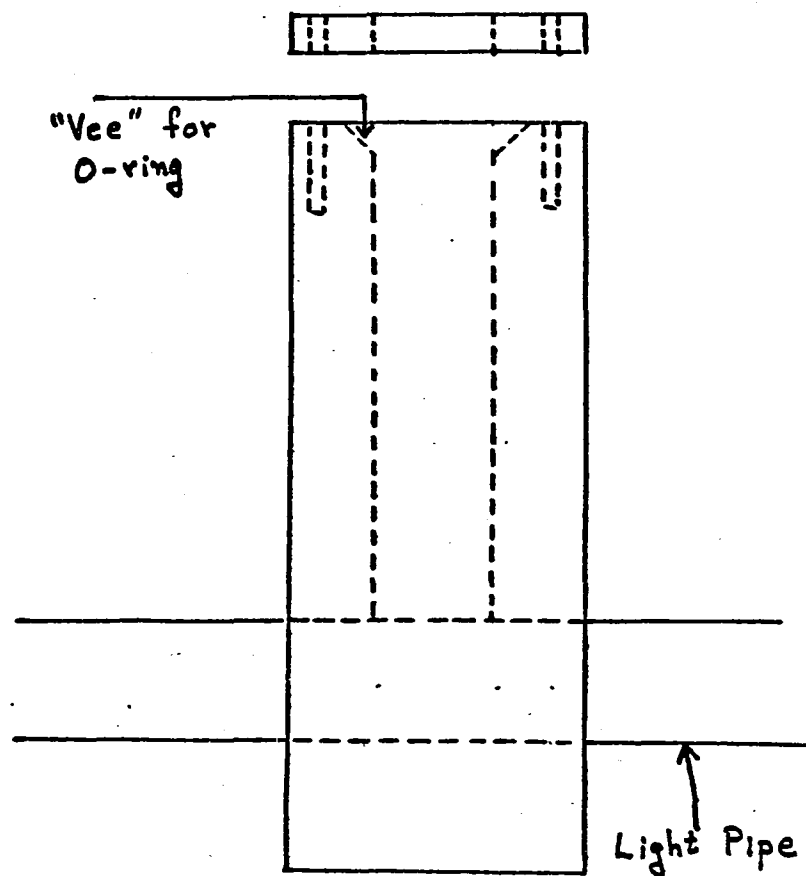


Figure 9. Sample Holder: Transmission.

heating wire is now inside the center finger and requires much less heat for a given temperature rise than the original sample holder. The thermocouple is attached to a groove in the side of the center finger by means of Sauereisen cement.

When it was decided to investigate Rochelle salt, it became necessary to operate at temperatures just above and below room temperature. Copper coils were cemented to the sides of the above holder to allow temperature controlled water to circulate around the brass holder and thus regulate the temperature of the sample.

Fig. 10 shows the details of a reflection cell which was constructed. In order to use this, the detector was swung around so that it again attached directly to the sample holder.

Alignment

To align the Michelson optics, the cover was taken from port N_1 on the main vacuum chamber. A helium-neon laser beam was then inserted horizontally into this open port. In order that this beam be allowed to fall on the beam splitter, the large six inch flat mirror had to be removed. (This design error could be corrected in future instruments by drilling through the six inch mirror again, but at 90° with respect to the first hole.) The Mylar beam splitter was quite adequate in splitting the laser beam nearly equally to the two Michelson mirrors. An ordinary plane mirror was then set at 45° with respect to the horizontal just ahead of the collimating mirror. The observer sees two series of spots in the plane mirror when viewed

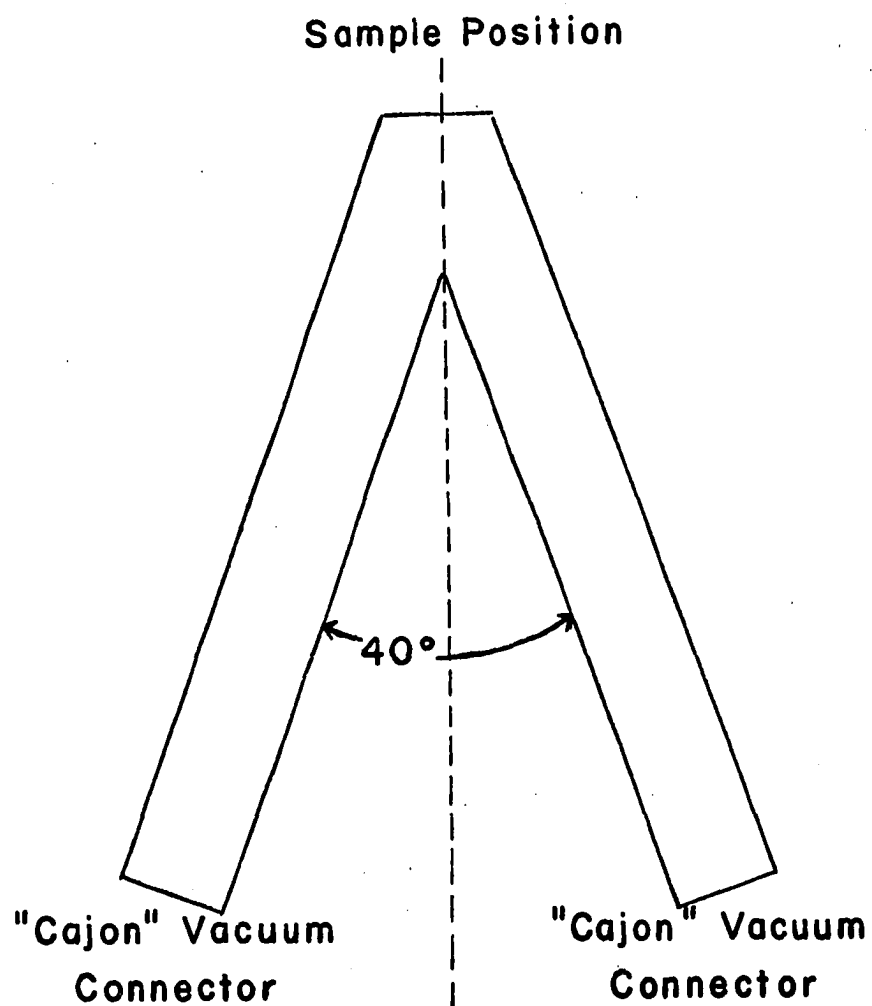


Figure 10. Sample Holder: Reflection.

from above the vacuum chamber. The two flat mirrors are then adjusted by means of three spring loaded screws until the two series of spots coincide. When this occurs, two or three interference fringes of the red laser light can be seen across the area of the beam. Since the Michelson optics showed fringes in the visible, it was assumed to be in very good alignment for the much longer wavelengths of the far infrared.

The collimating, focusing, and six inch flat mirrors were aligned by observing the light from the mercury arc and making adjustments so that all the energy, after alignment of the Michelson optics, was channeled into the exit aperture.

Electronics

An electronic block diagram is shown in Fig. 11. The source (mercury arc) is modulated at 10 hz by a modified Eppley chopper. The a-c component of the signal from the detector is amplified and then synchronously demodulated by a phase-sensitive detector. A filter (consisting of both active and passive components) smooths the output for measurement by an analogue to digital converter (Darcy Industries, Model DM440). The interferogram is recorded digitally on paper tape by a Hewlett-Packard 5050A printer.

The amplifier (Fig. 12), DVM read command (Fig. 13), and the phase-sensitive detector (Fig. 14) were designed and constructed by Mr. George Zibens of Brock University. The forms of these devices have undergone several modifications. One of these was due to the fact that numerous "extra points" were being recorded during the

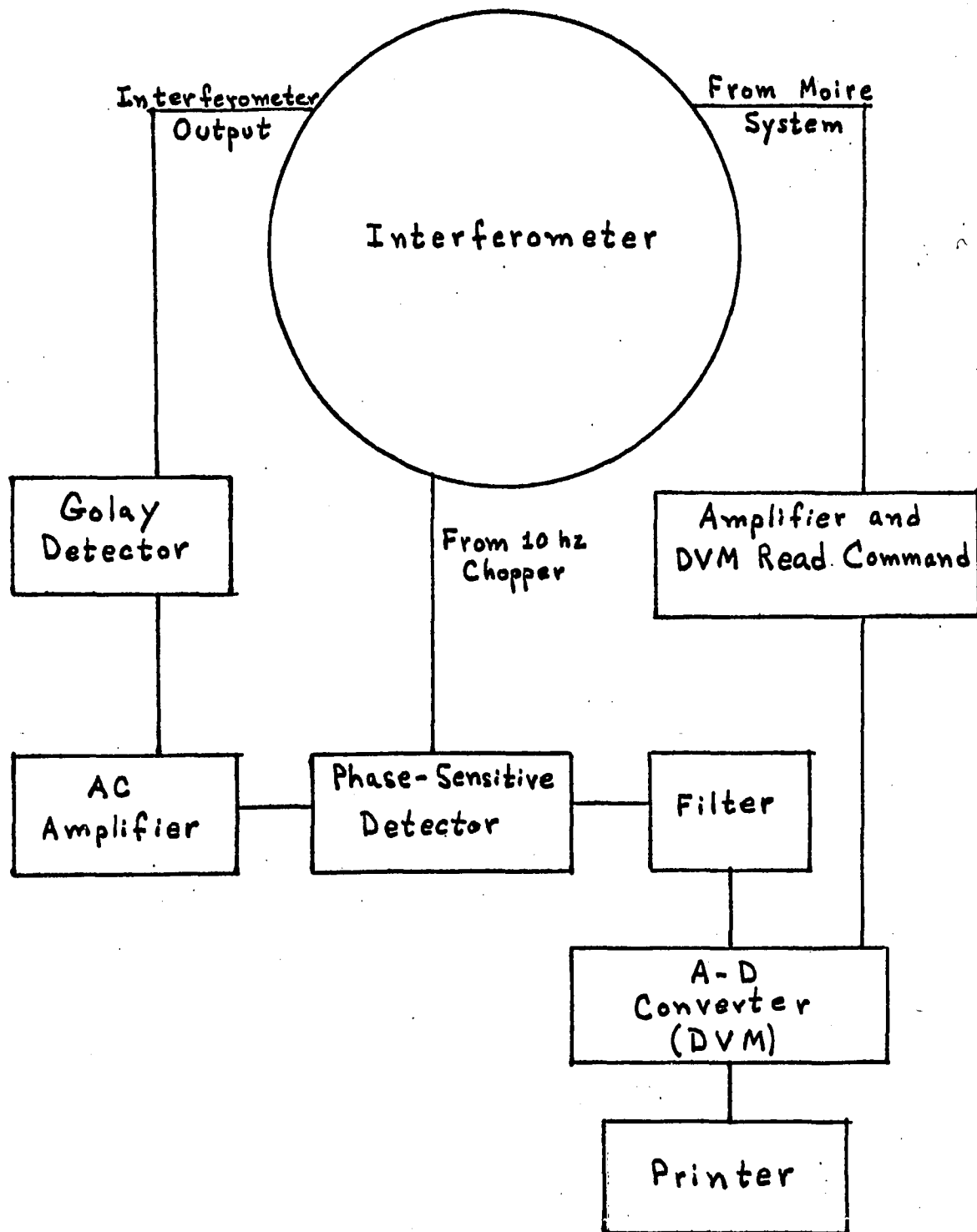
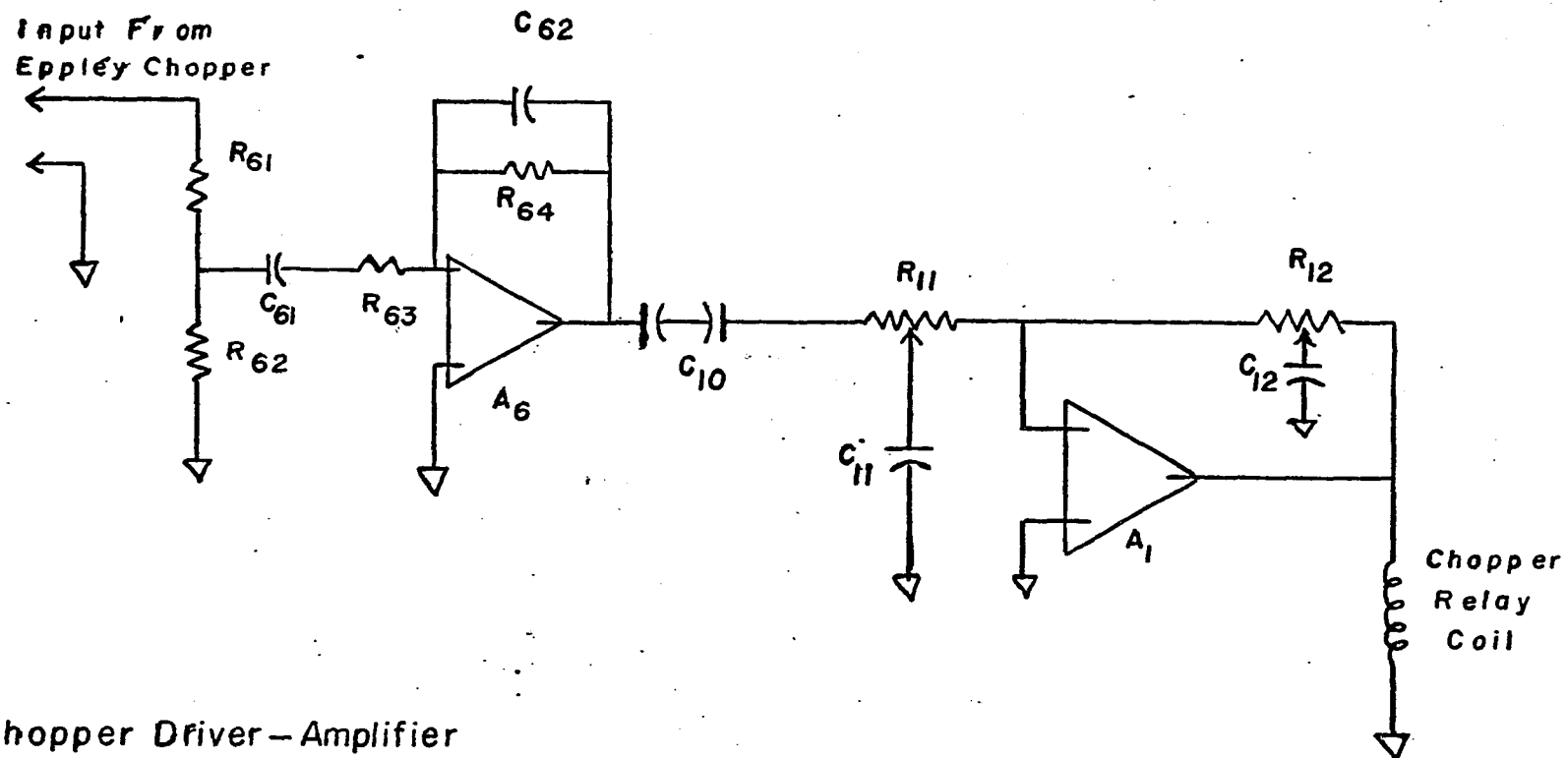


Figure 11. Electronic Block Diagram.



53

Chopper Driver - Amplifier

Brock Physics Electronics

Drawn By G. Zibens

19 Feb. 1971

Figure 12. Schematic for Chopper Driver - Amplifier.

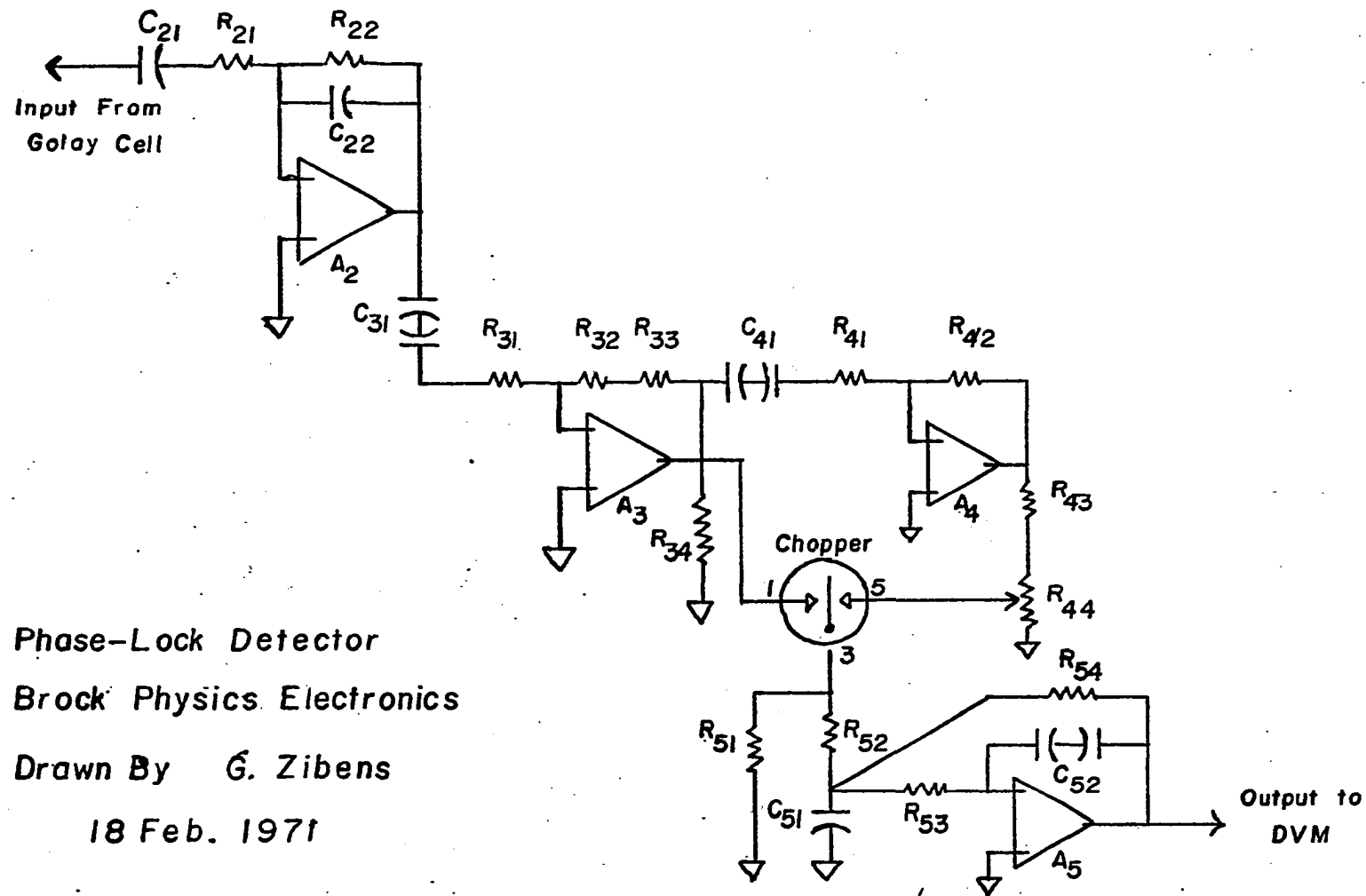
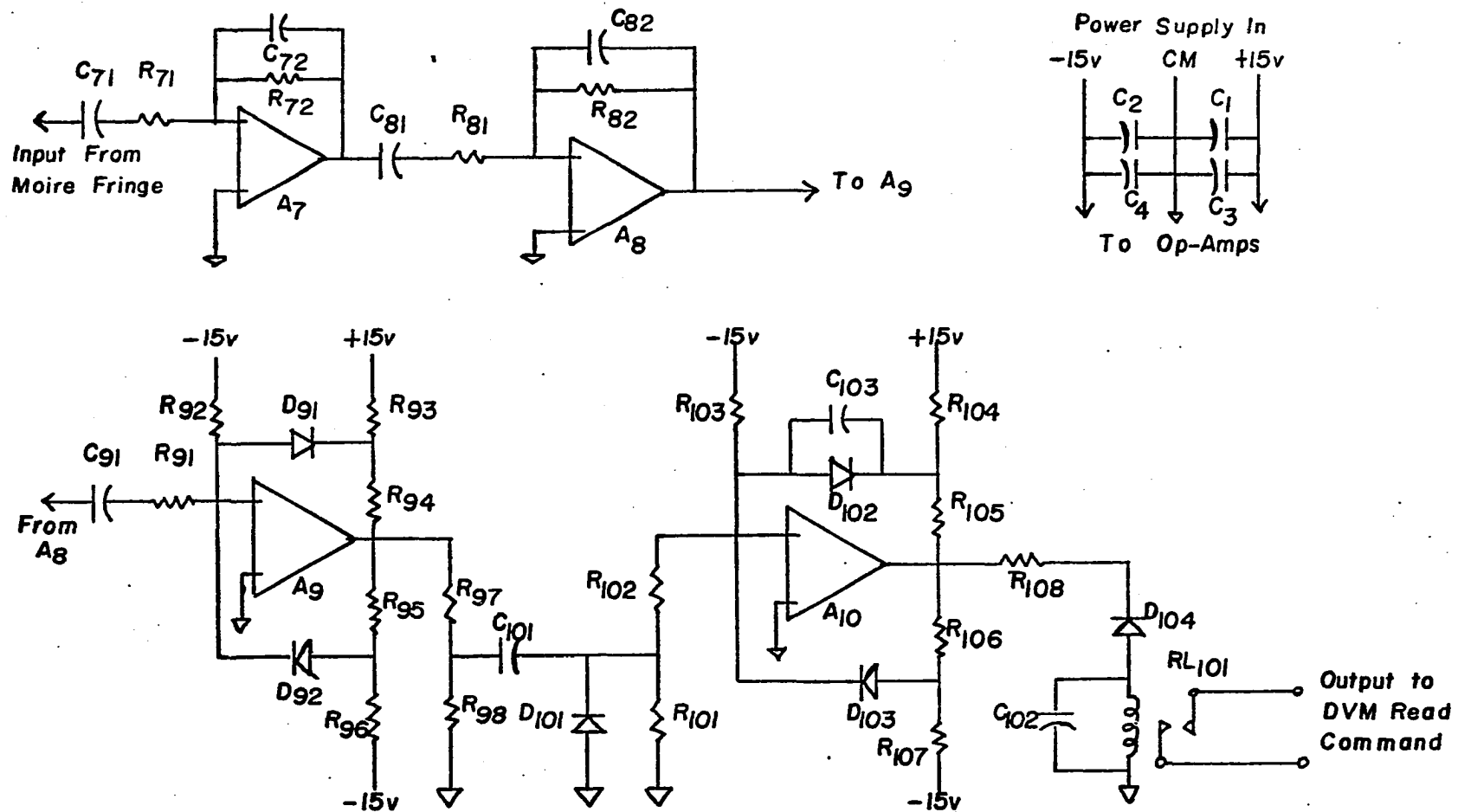


Figure 13. Schematic for Phase-Lock Detector.



DVM Read Command
 Brock Physics Electronics
 Drawn By: G. Zibens
 19 Feb 1971

Figure 14. Schematic for DVM Read Command.

early stages of this work. The digital volt meter reads when a relay in the DVM read command closes. The initial design was such that this relay remained closed for a period longer than the 110 millisecond cycle time of the digital voltmeter. As a result, spurious noise spikes were causing the DVM to read at times other than those specified by the Moire fringe system. The present DVM command has taken care of this problem by allowing only a momentary closure of the relay contacts.

The passive R-C filter has a nine second time constant which allows only very slow scans (about one point every six seconds). This was necessary due to the large amounts of noise present.

Some general notes referring to the schematic diagrams of Figures 12, 13, and 14 are:

- 1) The power supply for the operational amplifiers (op-amps) is a Hewlett-Packard Model 60153D, ± 15 volt, 0.2 amperes.
- 2) ± 15 volt and common op-amp power supply connections are not shown, for simplicity.
- 3) All op-amps use a 50K ohm 15 turn trimpot, (Beckman Helitrim, Part No. 79PR50K) as an external zero bias control.
- 4) Two useful handbooks are available from Burr-Brown Research Corp.
 - a) Handbook of Operational Amplifier Applications.
 - b) Handbook of Operational Amplifier Active RC Networks.
- 5) All circuits are mounted on Veroboards; copper clad, punched terminal boards.

Fig. 12 shows the electronics which amplify the signal from the photocell in the Eppley 10 hz chopper and then this signal goes to the mercury-wetted contact relay in the phase-sensitive detector. A complete parts list is given in Table III. A_1 , the second stage of amplification, is a lead-lag phase adjust circuit. Because the input (from the Eppley chopper) is a square wave rather than sine, this circuit does not provide phase adjustment but can be considered a "gain of one" buffer-driver, that is it isolates the input stage A_6 from the Clare chopper. It then drives the Clare chopper with the necessary voltage and current without transient feedback into A_6 and possibly into the "reference voltage" from the Eppley photocell.

The phase-lock detector (Fig. 13) takes its input from the Golay cell, amplifies the signal, and demodulates it by means of the mercury-wetted chopper relay. The output then goes through a filter network before feeding into the DVM. The ten turn Helipot, a gain adjust control, is front panel mounted. Electrical connections to the circuit are by means of Belden 2-wire "Beldfoil" shielded cable and chassis bulkhead feed-through connectors into the case. Both the phase-lock detector and chopper driver - amplifier are mounted on the same chassis. Table IV gives a parts list for the phase-lock detector.

The DVM read command (Fig. 14) provides a relay closure, which is what the DVM requires to commence taking a reading of the signal from the phase-lock detector. The input is taken across the 9K ohm resistor which is across the silicon photocell in the Moire fringe system. A complete parts list for the read command is given in Table V.

Table III. Parts List for Chopper Driver - Amplifier

Resistors:

R ₁₁	]	10K ohm potentiometer (15 turn trimming) Beckman Helitrim
R ₁₂		No. 78PR10K
R ₆₁	]	120K
R ₆₂		27K
R ₆₃	]	100K
R ₆₄		1 meg
		1/2 watt ± 2% metal oxide film, Welwyn type F20
		1/2 watt ± 5% cracked carbon, Philips series B830505N

Capacitors:

C ₁₀	2, 100 fd, 15 volt electrolytic back to back, Texas Inst. SCM-2
C ₁₁	] 0.1 fd, 63 volt ± 2% polystyrene, Philips series C295
C ₁₂	
C ₆₁	50 fd, 35 volt tantalum electrolytic, Texas Inst., SKM-2
C ₆₂	2700 pfd, disc ceramic

Operational Amplifiers:

A_1	]	Operational Amplifiers, Burr-Brown, 3077/12C
A_2		

Table IV. Parts List for Phase-Lock Detector

Resistors: Unless otherwise specified, all resistors are $\pm 2\%$,
metal oxide film made by Welwyn.

R ₂₁	100K	1/4 watt	R ₄₂	47K	1/4 watt
R ₂₂	470K	1/2 watt	R ₄₃	2.7K	1/2 watt
R ₃₁	1K	1/4 watt	R ₅₁	10K	1/2 watt
R ₃₂	4.7K	1/4 watt	R ₅₂	1K	1/2 watt
R ₃₄	47K	1/4 watt	R ₅₃	820K	1/2 watt
R ₄₁	10K	1/4 watt	R ₅₄	10K	1/2 watt
R ₃₃	100K	5 watt, $\pm 2\%$, $\pm 0.25\%$ linearity, 10 turn Beckman Helipot "A"			
R ₄₄	1K	15 turn Beckman Helitrim No. 77PR1K			

Operational Amplifiers:

A₁ to A₄ Burr-Brown No. 3077/12C

Capacitors:

C ₂₁	50 fd, 35 volt tantalum electrolytic, Texas Instr. No. SCM-11
C ₂₂	1200 pfd, disc ceramic
C ₃₁	2, 10 fd, 35 volt tantalum electrolytic, Texas Instr. No. SCM-2
C ₄₁	2, 50 fd, 35 volt " " " " No. SCM-11
C ₅₁	100 fd, 15 volt " " " " No. SCM-2
C ₅₂	2, 10 fd, 35 volt " " " " No. SCM-2

Miscellaneous:

Chopper - C. P. Clare, No. HGS-1084, mercury wetted contact relay

Table V. Parts List for DVM Read Command

Relay:

R_{L101} Dry reed relay, Wheelock Signals, Series 260A, 6 volt DC

Operational Amplifiers:

A_7 to A_{10} Burr-Brown, No. 3077/12C

Resistors: All resistors are 1/2 watt, $\pm 5\%$, cracked carbon, Philips series B8-305-05N

R_{71}	10K	R_{92}	1 meg	R_{97}	5.6K	R_{104}	15K
R_{72}	270K	R_{93}	15K	R_{98}	5.6K	R_{105}	10K
R_{81}	10K	R_{94}	10K	R_{101}	330K	R_{106}	3.3K
R_{82}	470K	R_{95}	3.3K	R_{102}	100K	R_{107}	15K
R_{91}	100K	R_{96}	15K	R_{103}	1 meg	R_{108}	680K

Capacitors:

C_{71}	150 fd, 15 volt, tantalum electrolytic, Texas Instr. No. SCM-2
C_{72}	0.47 fd, 250 volt, $\pm 10\%$, metalized foil, Philips Series C281
C_{81}	180 fd, 6 volt, tantalum electrolytic, Kemet No. 314J
C_{82}	0.47 fd, 250 volt, $\pm 10\%$, metalized foil, Philips Series C281
C_{91}	180 fd, 6 volt, tantalum electrolytic, Kemet No. 314J
C_{101}	0.25 fd, 600 volt, $\pm 10\%$, mylar, Sprague No. GPS-P25
C_{102}	1100 pfd, $\pm 10\%$, silver mica, Elmenco No. DM-15
C_{103}	100 pfd, $\pm 10\%$, silver mica, Elmenco No. DM-15
C_1	50 fd, 25 volt, aluminum electrolytic, Philips No. C425 ZZ/05
C_2	50 fd, 25 volt, aluminum electrolytic, Philips No. C425 ZZ/05
C_3 and C_4	120 pfd, disk ceramic

CHAPTER IV

EXPERIMENTAL METHODS AND RESULTS

Check of the Instrument

The instrument was checked against two other sets of information. The transmittance of water vapor between 17 cm^{-1} and 82 cm^{-1} with a resolution of 0.2 cm^{-1} has been published by Richards (3). The other standard used is the absorption spectrum of methanol (CH_3OH) between 29 cm^{-1} and 41 cm^{-1} due to Gebbie (2), taken with a resolution of 0.25 cm^{-1} . The corresponding spectra for this work were done under somewhat different conditions in both cases.

The water absorption shown in Fig. 15 was taken through approximately 0.5 meters of air at atmospheric pressure and room temperature. Five scans were averaged for the spectrum of air with water vapor as well as for the spectrum of a vacuum (used as the background). 250 points were recorded on either side of the zero path position, which corresponds to a path difference of 0.5 cm and thus to a resolution of 2 cm^{-1} . Richards' spectrum therefore shows much more detail due to its 0.2 cm^{-1} resolution. Between 36 cm^{-1} and 40 cm^{-1} Richards' spectrum shows four very intense absorptions along with some fine structure. This appears as an intense, broad absorption in Fig. 15 with some indication of the presence of more

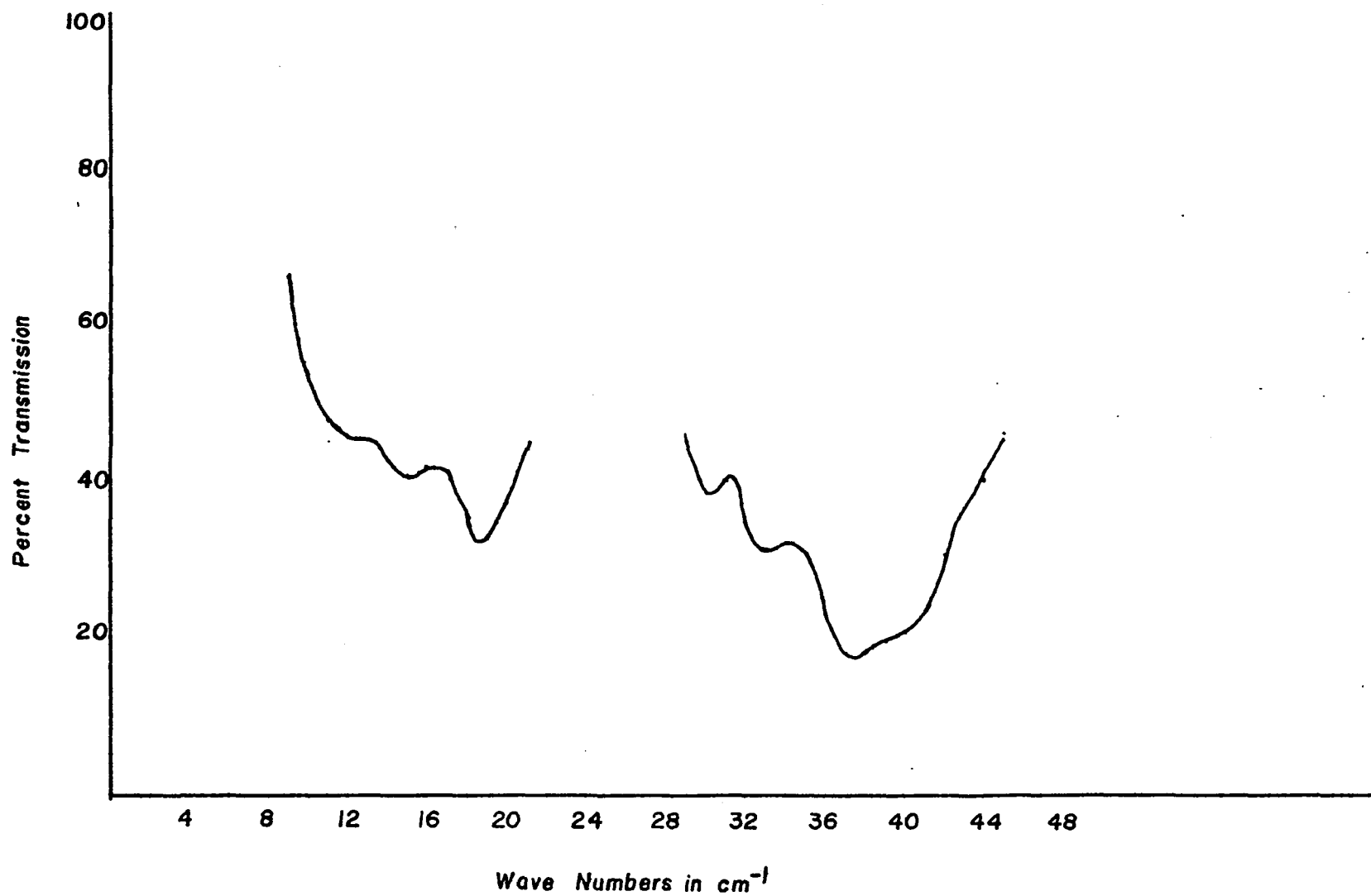


Figure 15. Absorption of Atmospheric Water Vapor.

than one band. The sharp, somewhat less intense band at 18.5 cm^{-1} in Richards' spectrum agrees well with the observed band at 18.5 cm^{-1} . The width of this band at half maximum intensity is approximately 2 cm^{-1} even though the band is actually shorter as one can see when the resolution is increased. The band at 25 cm^{-1} in Richards' spectrum is not seen in Fig. 15 because the minimum of intensity due to the beam splitter falls at that position. Richards' spectrum is of a 1.5 meter path of water vapor at 20 mm of mercury pressure, compared to the 0.5 meter path of air at atmospheric pressure used in the spectrum seen in Fig. 15. Assuming about 60% relative humidity of the air, this would correspond to a partial pressure of approximately 14.4 mm of mercury for the water vapor in the air. Agreement between the spectra is very good. It is difficult to see any difference at all in the position of the bands, and intensities agree qualitatively at least. Fig. 15 indicates that the resolution actually achieved with a 0.5 cm path difference is close to the theoretical limit of 2 cm^{-1} .

Gebbie's methanol spectrum (2) was taken with a cell length of 30 cm, a pressure of 11 mm of mercury, and a resolution of 0.25 cm^{-1} . The CH_3OH spectrum of Fig. 16 was taken by injecting enough methanol into the apparatus to achieve a pressure of 11 mm of mercury in a path length of about 75 cm. 720 points were taken on either side of zero path, which corresponds to a theoretical resolution of 0.7 cm^{-1} . The maximum width of the bands in Fig. 16 is again very close to this theoretical resolution, e.g. the band at 40 cm^{-1} has a width of about 0.5 cm^{-1} in Gebbie's spectrum and appears in Fig. 16 with a width of 0.8 cm^{-1} . The positions of the main bands agree very well

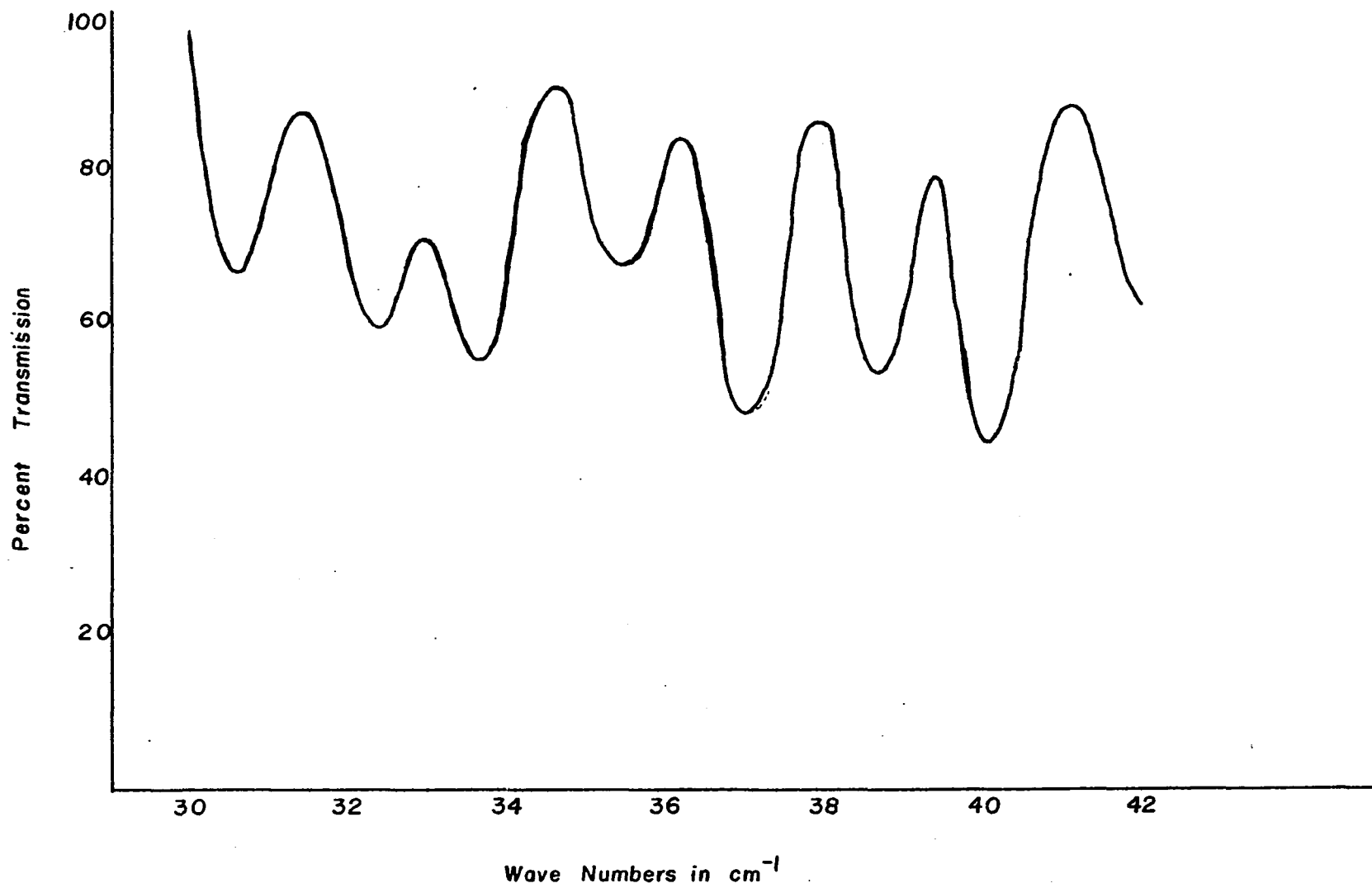


Figure 16. Absorption of Methanol.

with those of Gebbie. The intensity of the band at 35.5 cm^{-1} is not as large as that reported by Gebbie.

An example of a background spectrum is shown in Fig. 17. This is an average of five scans of 250 points on either side of zero path.

The results obtained agree well with published spectra of the same substances, within the limits of the resolutions used. Hence, the writer assumed that the instrument is a valid tool for investigation of far infrared spectra.

The spectra presented later in the chapter were taken at signal levels considerably lower than those obtained in the water and methanol spectra. For this reason twenty scans were averaged rather than five scans for the water spectrum and three scans for the methanol. The noise level, as seen by the digital voltmeter, was a range of approximately 50 mv. The average intensity when taking the water spectrum was in the vicinity of 500 mv whereas for the transmission spectra of Rochelle salt the average measured intensity varied between about 170 mv to 200 mv. This would drop the signal to noise ratio to between 3.4/1 and 4.0/1 compared with 10/1 for the water spectrum. Making use of the theory of errors as it applies to averaging independently obtained quantities (41), the effective signal to noise ratio for the water spectrum would be $10 \times \sqrt{5} = 22$ while for the Rochelle salt spectra it would be $4 \times \sqrt{20} = 18$. Then the Rochelle salt spectra would have an error of $\pm 5.5\%$ compared with $\pm 4.5\%$ for the water spectrum. Hence, if the water spectrum agrees with other accepted data, it is assumed that the Rochelle salt data is

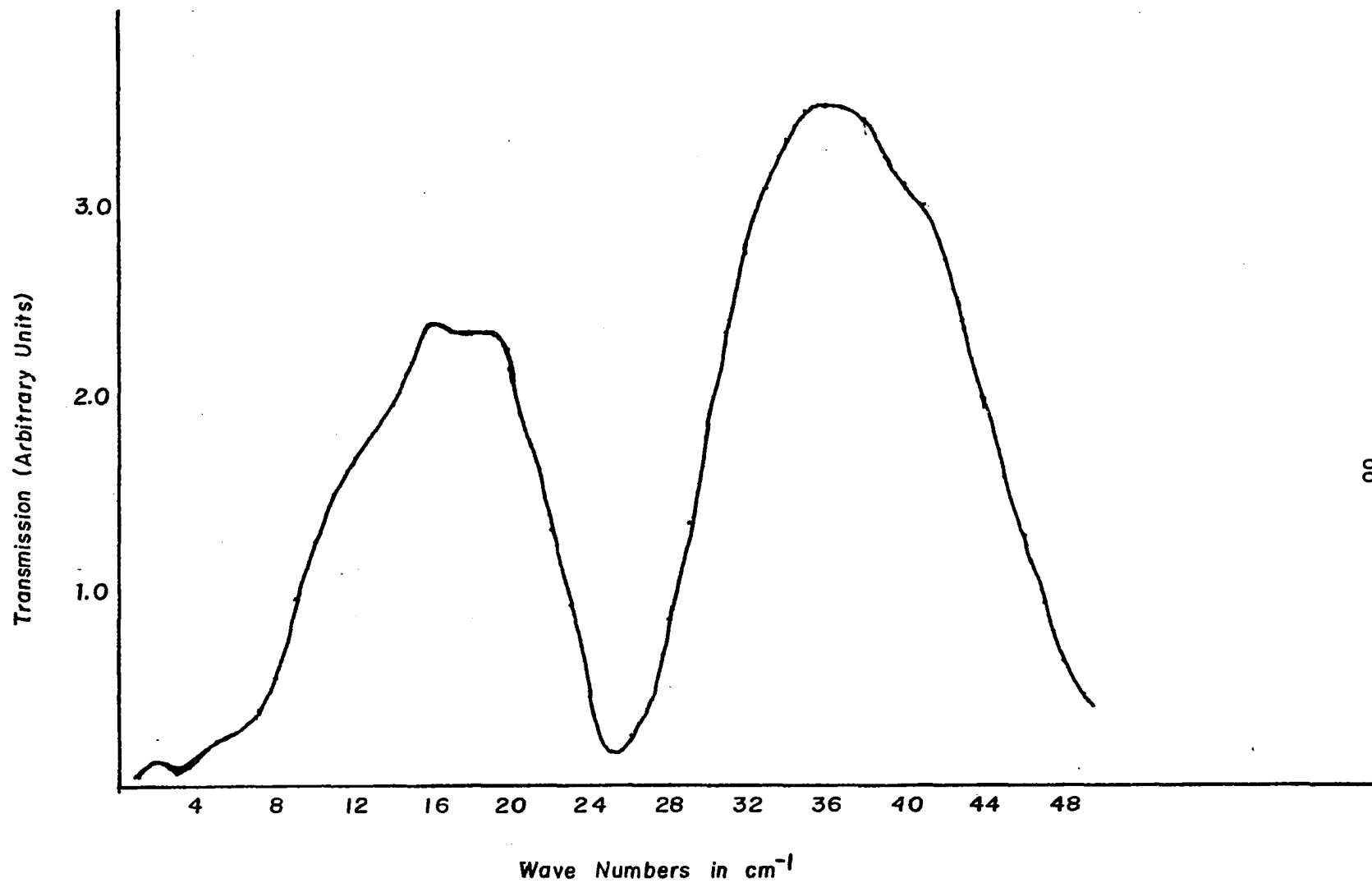


Figure 17. Transmission of 125 Micron Beam Splitter.

approximately within 1% of the same accuracy.

Efforts on BaTiO₃

The ideas for this work were first formulated in response to the theoretical work of Cochran (6,7); the purpose being to attempt a direct measurement of the soft optic mode in BaTiO₃ as a function of temperature in the vicinity of the Curie temperature T_C . Cochran (6) had given warning that this mode was overdamped. This is also evidenced by the "flat" curve of reflectivity vs. frequency determined by Ballantyne (31). In spite of this, the writer obtained four single crystals of BaTiO₃ from the Harshaw Chemical Co., Cleveland, Ohio.

The method outlined by Ballantyne (31) was used to prepare the crystals. The crystals are etched for at least a half hour in concentrated phosphoric acid at 150°C. This removes an anomalous surface layer due to the Remeika method of growth. Further etching is used to control thickness of the crystal. Two samples of thickness 0.165 mm and 0.120 mm were prepared in this manner.

These samples were inserted in the spectrometer and four scans were taken at each of four temperatures between 125°C and 160°C during the summer of 1969. The results were totally meaningless. At the time it was felt that BaTiO₃ was essentially opaque to far infrared radiation and hence reflection measurements seemed to be the only reasonable approach. The transmission measurements were made under very poor instrumental conditions. Shortly after this, it was discovered that the phase-sensitive detector was not completely in phase, which decreased the signal to noise ratio considerably. The averaging

of a much larger number of scans would have helped to overcome this to some extent. Also, it was discovered that the digital voltmeter was reading not only on command from the Moire fringe system, but also when certain electrical noise came through the system while the command to-read contacts on the trigger circuit were still closed. This design defect was then corrected. No attempts were made at polarizing the BaTiO_3 crystals.

Since the cause of the failure of these experiments was not known, BaTiO_3 was set aside, and investigation of another ferroelectric crystal (Rochelle salt) was undertaken. In retrospect, the writer feels that with the present instrument, another attempt at finding the BaTiO_3 spectrum might be warranted. In addition to the improved instrument, much thinner samples should be prepared (on the order of tens of microns).

Growth and Preparation of Rochelle Salt Crystals

Even before the failure of the BaTiO_3 spectra, a number of small Rochelle salt crystals had been grown, just to have a second ferroelectric crystal with an easily accessible Curie temperature (24°C) available. The following steps were followed in growing the crystals:

- 1) A room temperature saturated solution of $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ in distilled and deionized water was prepared.
- 2) The solution was slowly filtered to remove most of the particles which would serve as nuclei for crystallization to begin.
- 3) A clean flat dish was lined with an anti-wetting agent

(Dricote by Fischer Scientific Co.)

4) The solution was poured into the dish which was then nearly covered (to keep out dust and any other foreign matter), and allowed to slowly evaporate.

5) After about a day, a number of small crystals began to form on the bottom of the dish. The solution was then decanted into another clean dish (prepared just like the first one). Two of the small crystals begun in the first dish were inserted as seeds, and again slow evaporation was allowed to take place.

In about two weeks, one of the seed crystals had grown to a size approximately 1 cm X 2 cm X 4 cm. Ten or twelve somewhat smaller crystals had also formed during this time. The work presented here made use of these crystals. (At present, V. M. Cowan is preparing a much larger single crystal by beginning with a saturated solution at a temperature above room temperature and then slowly cooling the solution. Because the solubility of Rochelle salt in water is highly temperature dependent, a small change in temperature results in a relatively large amount of crystal growth. The advantages of this method are that one can exercise much better control over the crystal growth and the solution can be completely closed off from the atmosphere to prevent any foreign particles from entering.) Cady outlines various methods used in growing Rochelle salt crystals (32).

The first attempt at obtaining the temperature dependent spectrum of Rochelle salt was as unsuccessful as that of BaTiO_3 . The 0.25 mm thick sample was prepared, as suggested by Cady (32), by lapping the crystal on a damp silk cloth placed on a flat surface.

The sample was inserted so that it only partially covered the beam. Most of the energy which arrived at the detector was that which came from around the sides of the Rochelle salt sample. Two other types of samples were then prepared: 1) for reflection spectra, and 2) very thin samples for use in transmission work.

None of the crystals were large enough so that a slab, having faces perpendicular to the direction (001), could be cut to cover the entire opening of the reflection sample holder. Hence, three smaller pieces about one quarter inch thick were cut. The edges were lapped straight on damp cloth, the three pieces were then fitted together as closely as possible and potted in epoxy. When the epoxy had set, the surface was lapped until the three pieces formed a flat surface perpendicular in each case to the (001) direction. Small amounts of epoxy, which had seeped between the three pieces of crystal, were removed with a sharp razor blade.

When certain difficulties (to be discussed later) were encountered in obtaining reflection spectra, it was decided to prepare a very thin transmission sample of Rochelle salt. A slice of Rochelle salt was lapped on one side with a slurry of number 1000 carborundum and turpentine on ground glass. This flat side was then cemented with orange shellac to a 1 mm thick piece of crystal quartz, which had been similarly lapped flat. The other side of the Rochelle salt was then carefully lapped to the desired thickness. Using hand pressure and much patience, the sample was lapped to a thickness of 50 microns. The thickness was determined optically using crossed polarizers and known birefringence of Rochelle salt. The exposed surface was covered with

a thin coat of orange shellac so that the sample could be inserted into a vacuum without exposing the Rochelle salt, which rapidly loses the water molecules of crystallization in a vacuum.

Many of the chemical and physical characteristics of Rochelle salt are discussed by Cady (32).

Rochelle Salt Reflection Spectra

When attempts at obtaining transmission spectra of BaTiO_3 and Rochelle salt seemed to have failed, it was decided to obtain reflection data for Rochelle salt. A very simple sample holder (Fig. 10) was constructed for this purpose and a sample was prepared as described above. One factor which complicated reflection measurements was that, by the very nature of the measurements, no protective coating could be put on the Rochelle salt surface. This meant that the light pipe around the sample holder could not be evacuated and thus the strong absorption of atmospheric water had to be accounted for. The overall signal level was greatly reduced by this additional absorption to the point that the signal to noise ratio dropped to something near unity (probably a little less than unity). This meant that a large number of scans would be required to obtain meaningful data.

Two sets of 21 scans were made with the sample at 30°C , and one set of 25 scans was taken with the sample at 20°C . A few more sets of scans (about 10 to 12 scans each) were taken at 20°C and one at 30°C . No correlation was found to exist between any of the results except for a decrease in the reflectivity at 43 cm^{-1} found in both the 25 scan set

at 20°C and a 21 scan set at 30°C. The reasons for these incomprehensible results are not completely understood by the writer at this time. The background spectrum for each of the reflection spectra was obtained by replacing the sample by a polished copper plate. The result was what one would expect for a background modified by water vapor absorption, hence it was assumed that the sample holder was functioning properly. (This background spectrum is shown in Fig. 18). At a later date, it was discovered that rather large amounts of spurious electrical noise appeared in the system on occasion. If one recalls that one inordinately large point on the interferogram results in a sine wave superposed on the true spectrum, then even a few such "bad points" could greatly distort the spectrum. This effect would be enhanced by low signal levels and by averaging too small a number of scans. The failure to find consistency in the reflection data could be ascribed to this malfunction of the equipment.

Rochelle Salt Transmission Spectra

Having not succeeded in obtaining good reflection information, it was decided to again attempt transmission measurements, but with the sample much thinner than previously, and the 50 micron sample was prepared as described above. The overall signal level was considerably higher than with previous attempts using crystal thicknesses of about 0.25 mm. With the thick sample the highest percent transmission was about 12% at 8 cm^{-1} , whereas with the 50 micron sample approximately 70% was transmitted at 8 cm^{-1} . It was decided to take

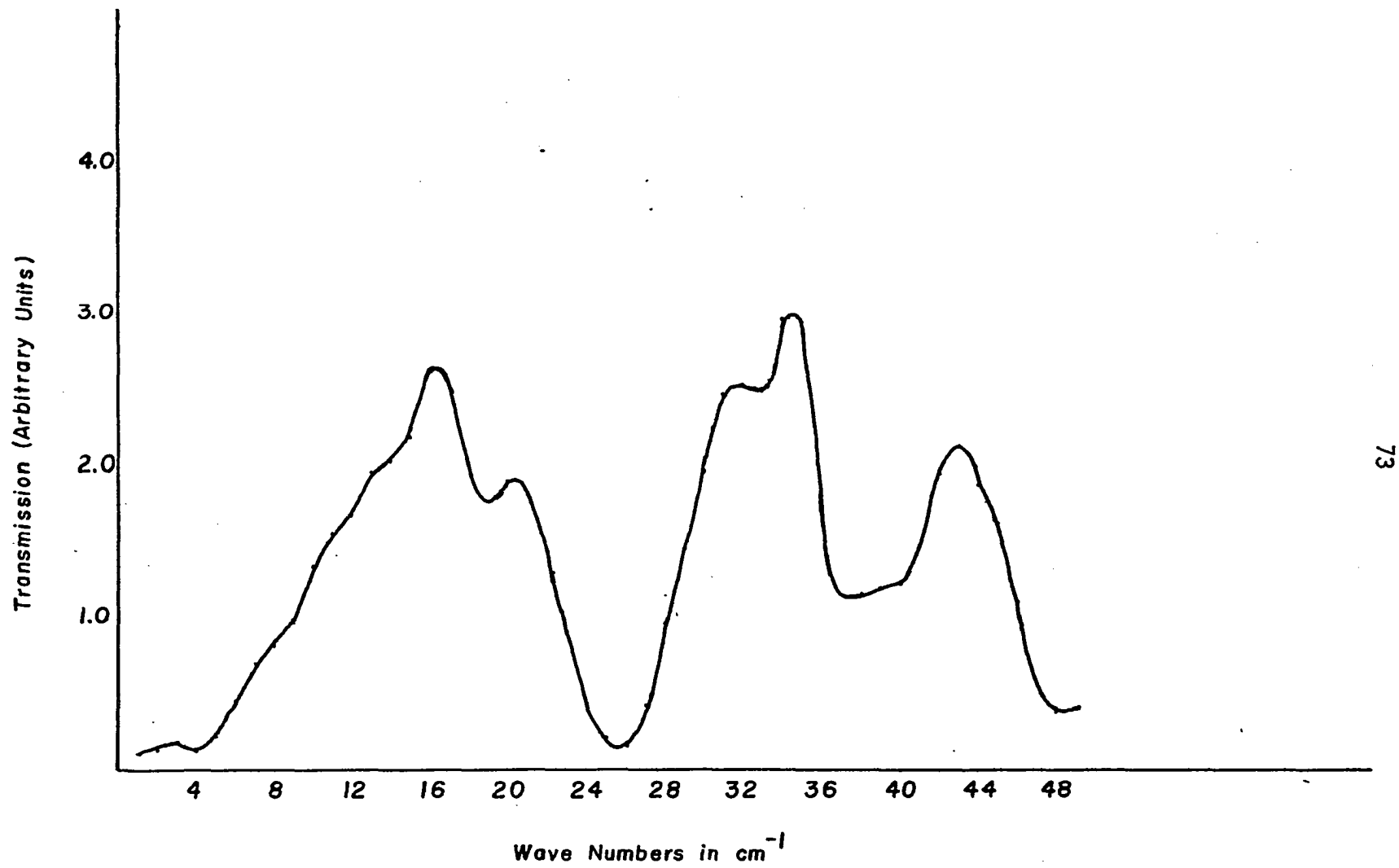


Figure 18. Background Spectrum for Reflection.

sets of 20 scans at 30°C, 19°C, and 27.5°C in that order. The corresponding spectra (without removing the background) are shown between 2 cm^{-1} and 49 cm^{-1} in Figures 19, 20, and 21. This region covers the first two maxima of the 125 micron beam splitter, which was in use during all of these measurements. The background spectrum (Fig. 22) was taken with a shellac covered piece of crystal quartz of the same thickness as the one used to mount the Rochelle salt inserted in the beam. Because of the increased signal to noise ratio, only seven scans were averaged to obtain the background spectrum. Figures 23, 24, and 25 show the percent transmission through the 50 micron slice of Rochelle salt. In every scan 250 points were recorded on either side of the zero path position of the interferometer. This corresponds to a path difference of 5 mm, and hence to a theoretical resolution of 2 cm^{-1} . Since no sharp bands are expected in such a spectrum of a solid, this was considered adequate to retrieve the information present. Fig. 26 is a superposition of Figures 23, 24, and 25 for purposes of comparison.

The system was supposedly designed to cut off all frequencies above 50 cm^{-1} . Allowing the computer to compute beyond this point revealed that some energy was getting through the interferometer at frequencies up to around 75 cm^{-1} . At each of the three temperatures under investigation there is an absorption of some kind around 56 cm^{-1} . At 69 cm^{-1} there is an absorption that increases in intensity with decreasing temperature. This part of the spectrum is shown in Fig. 27.

At no time during data acquisition of the transmission spectra presented in this work was any equipment malfunction detected. One

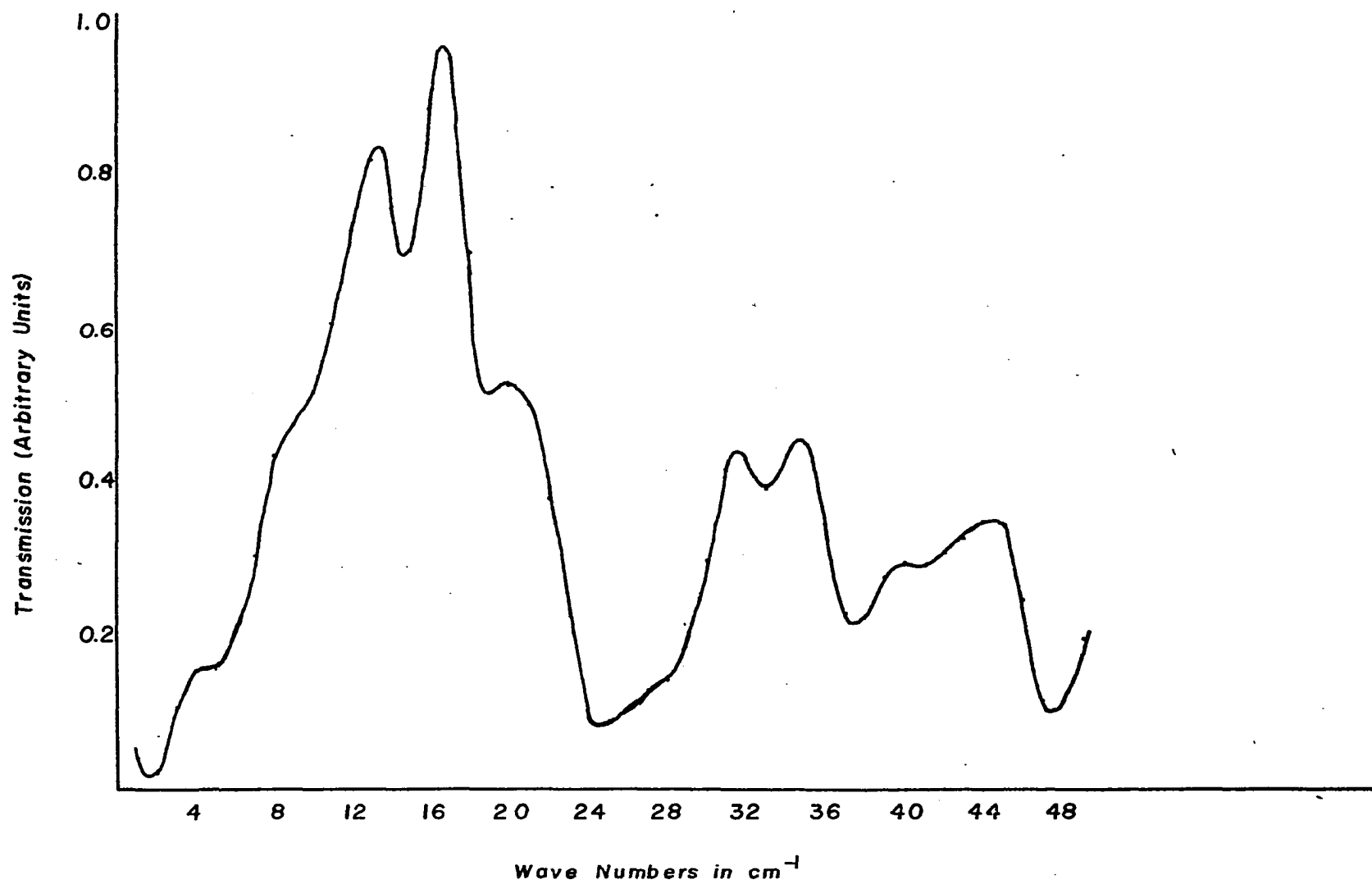


Figure 19. Transmission Through 50 Microns of Rochelle Salt at 30 °C (Including Background).

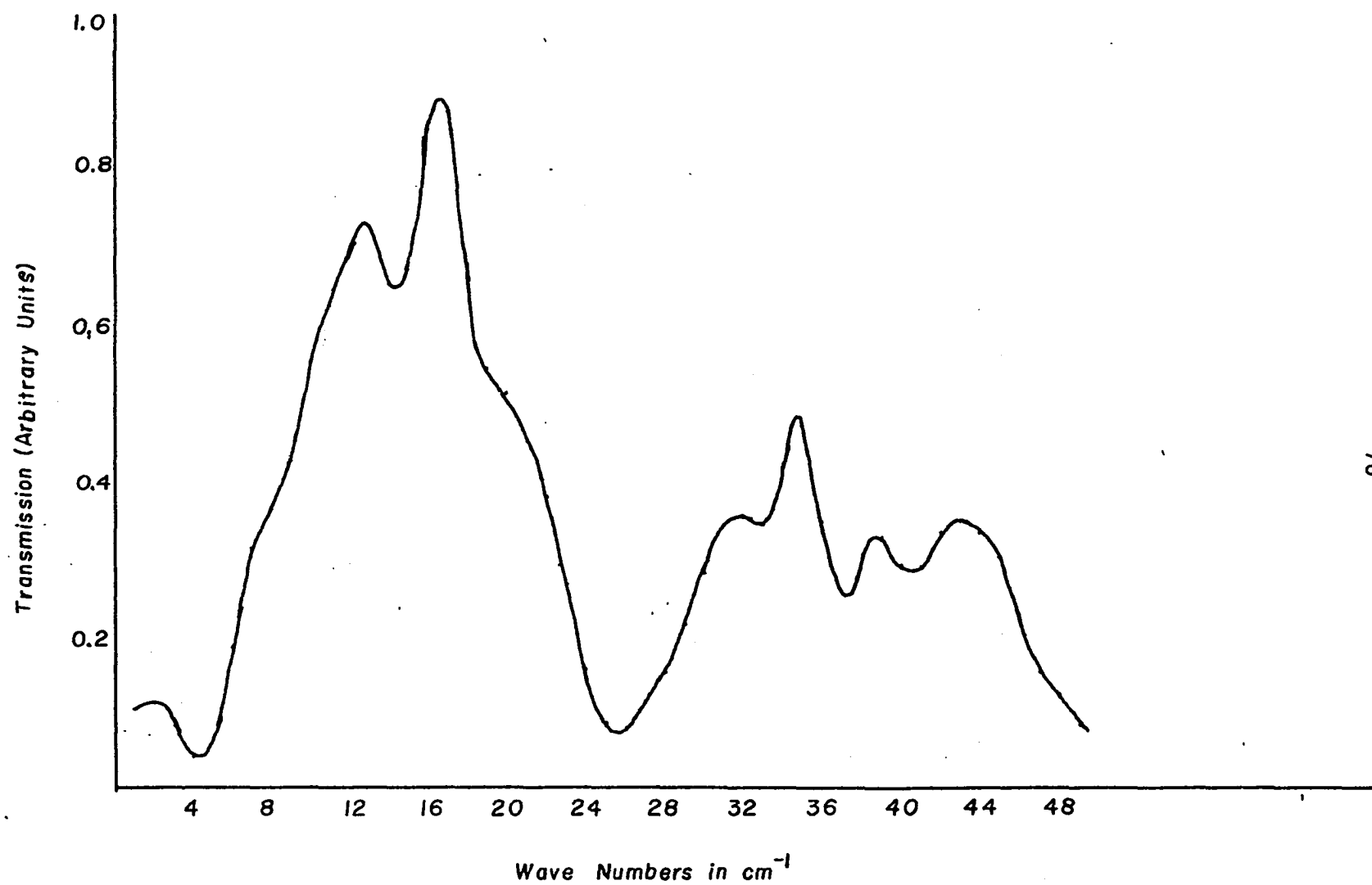


Figure 20. Transmission Through 50 Microns of Rochelle Salt at 19 °C (Including Background).

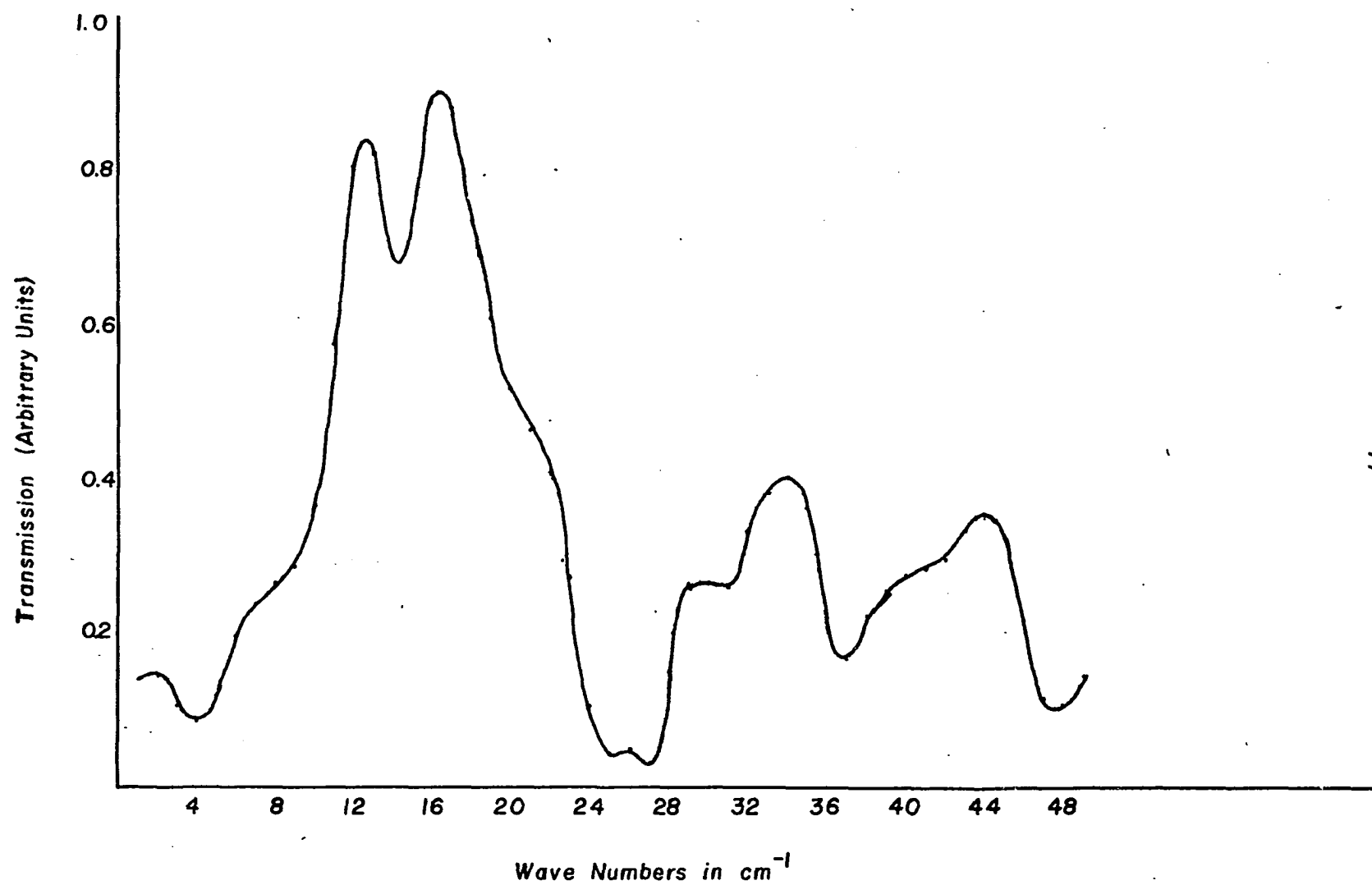


Figure 21. Transmission Through 50 Microns of Rochelle Salt at 27.5 °C (Including Background).

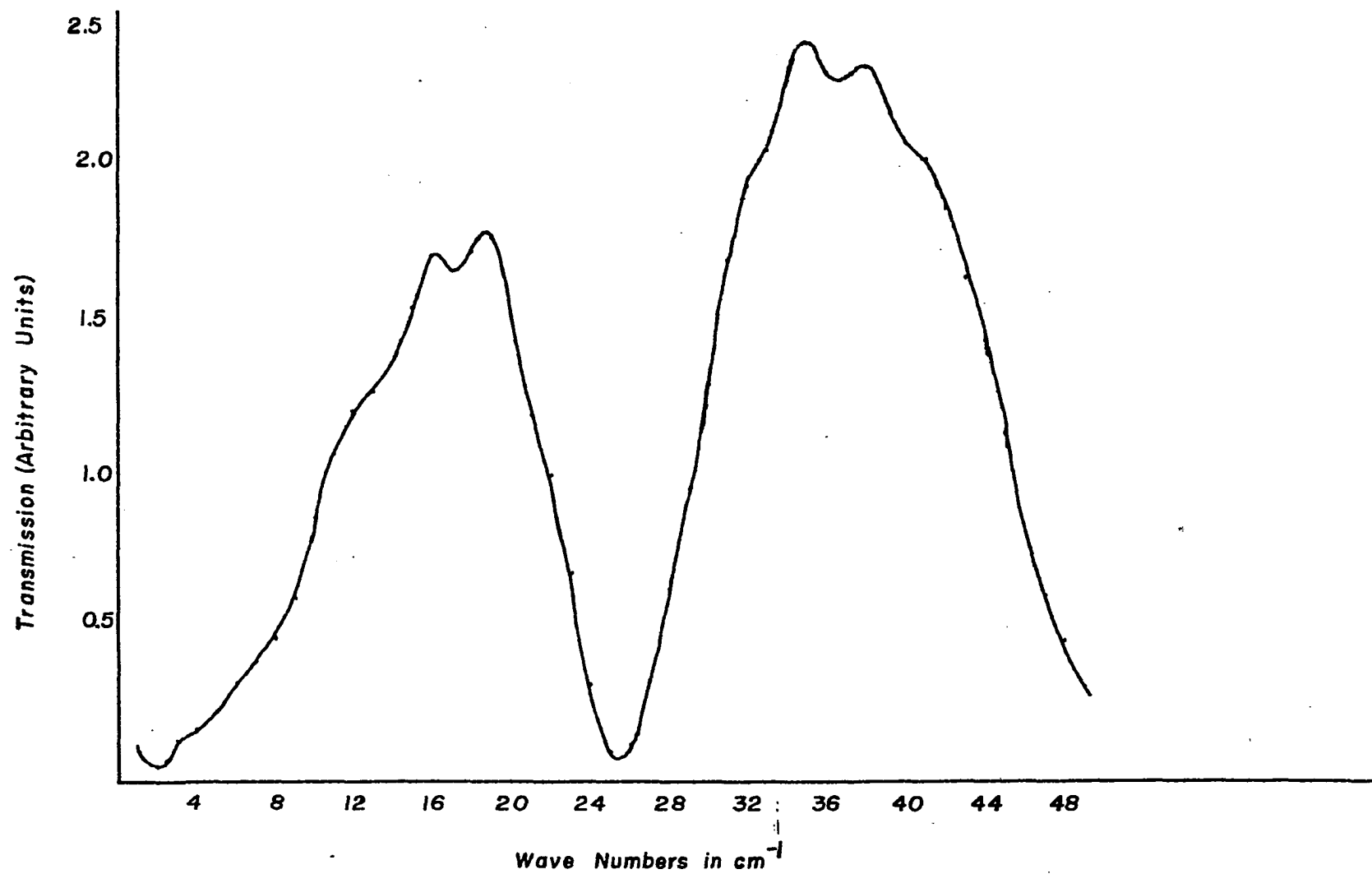


Figure 22. Transmission Through 1 mm Crystal Quartz Covered with Orange Shellac.

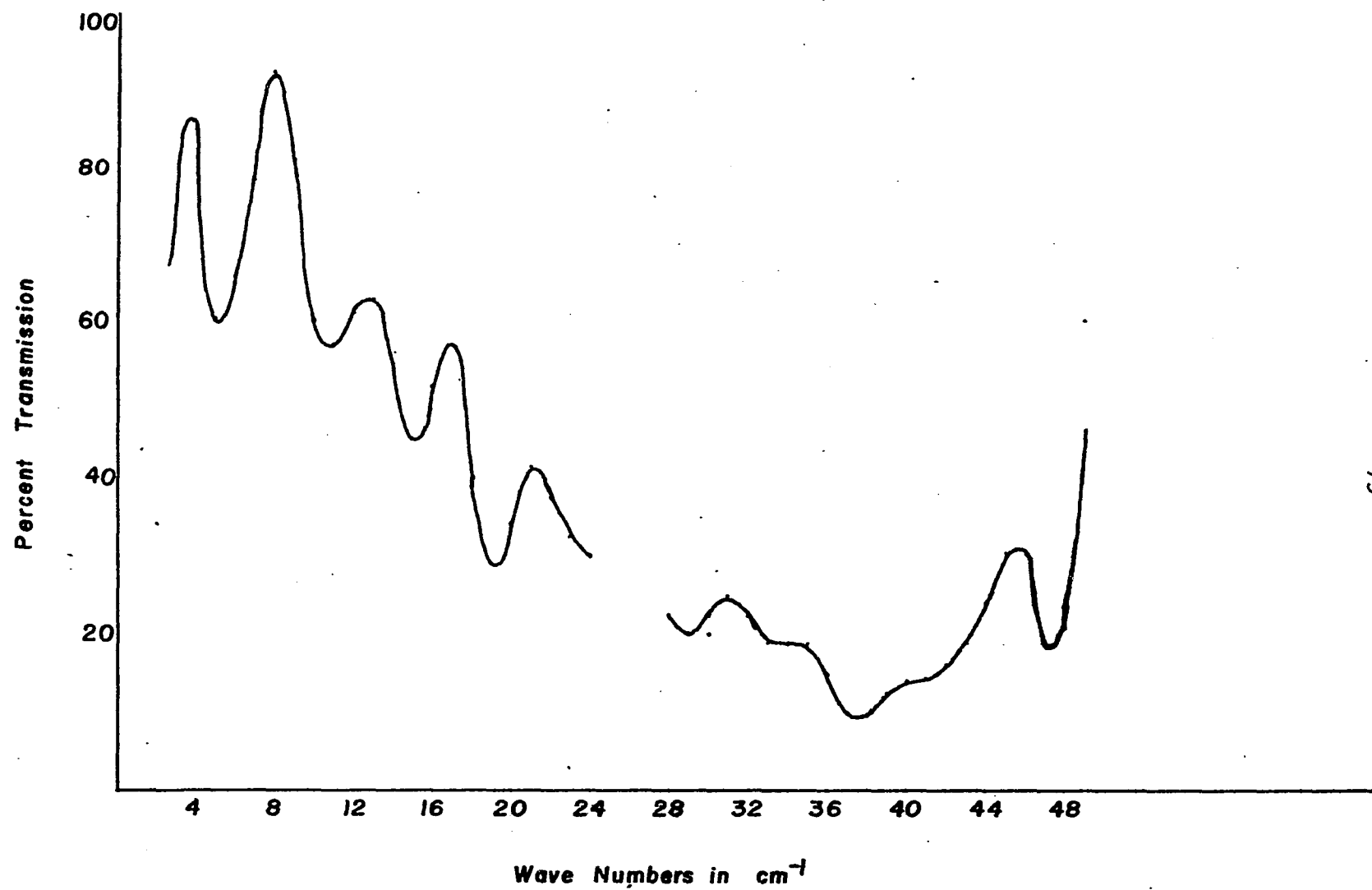


Figure 23. Percent Transmission Through 50 Microns of Rochelle Salt at 30 °C.

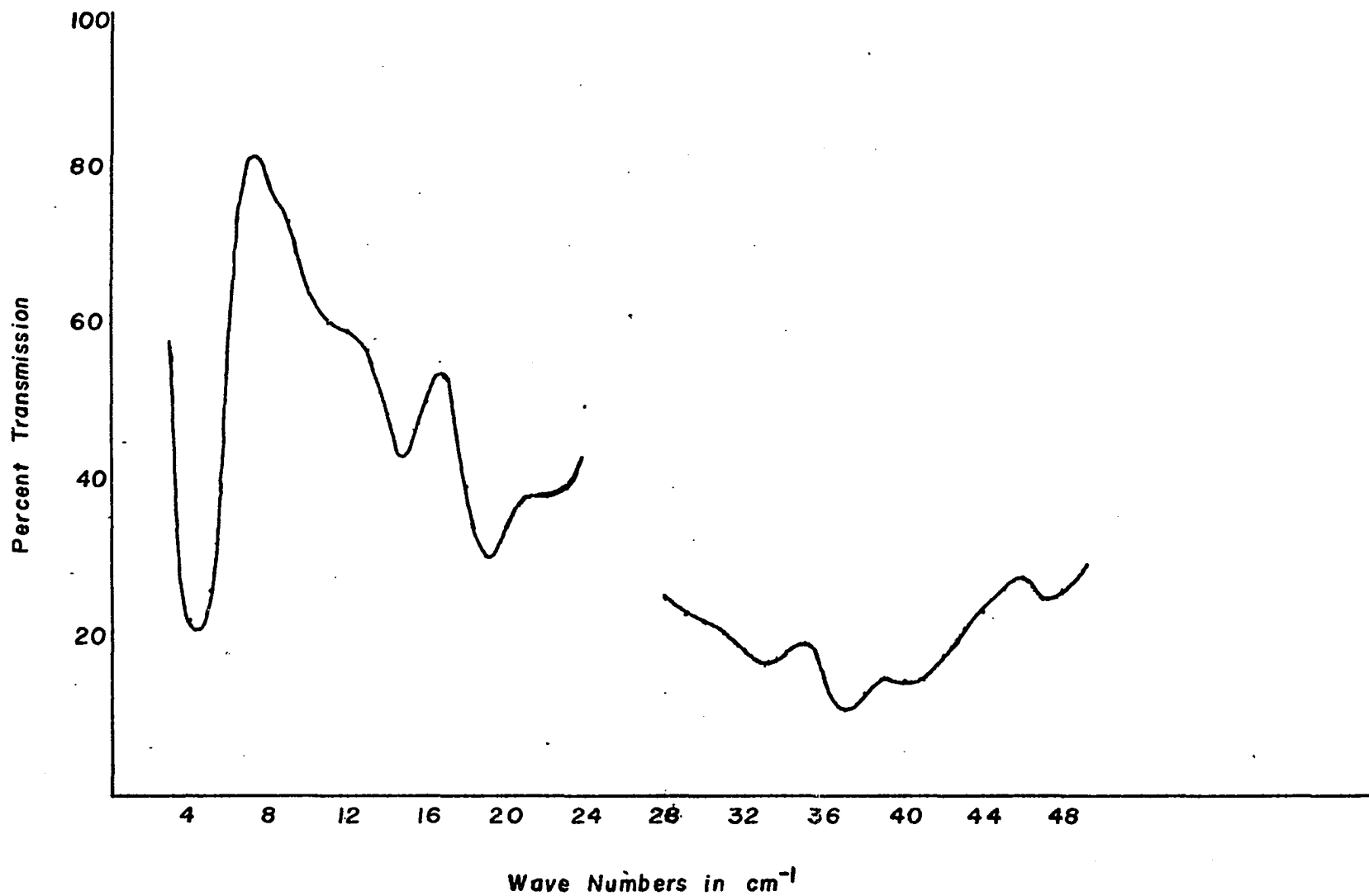


Figure 24. Percent Transmission Through 50 Microns of Rochelle Salt at 19 °C.

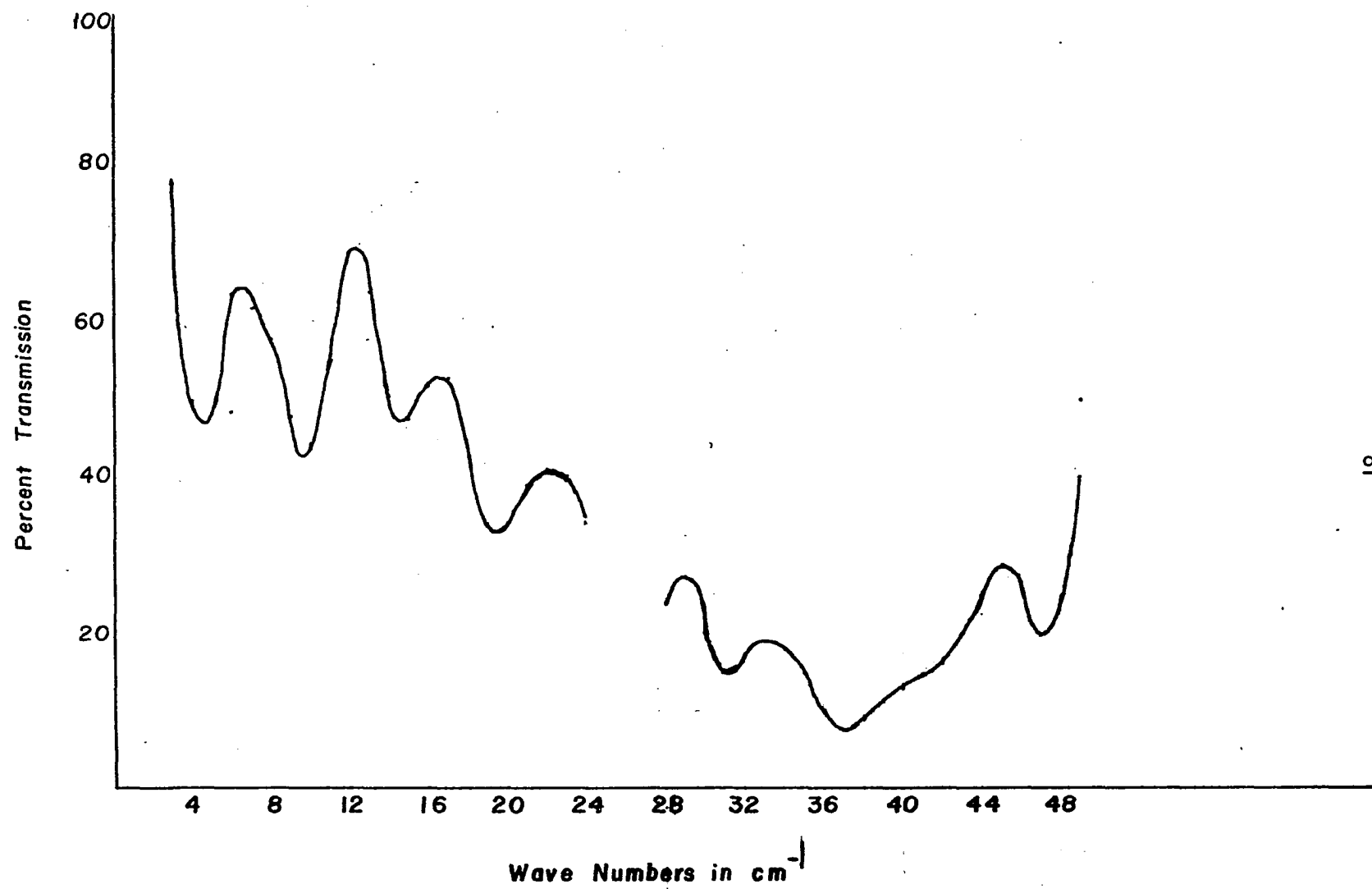


Figure 25. Percent Transmission Through 50 Microns of Rochelle Salt at 27.5 °C.

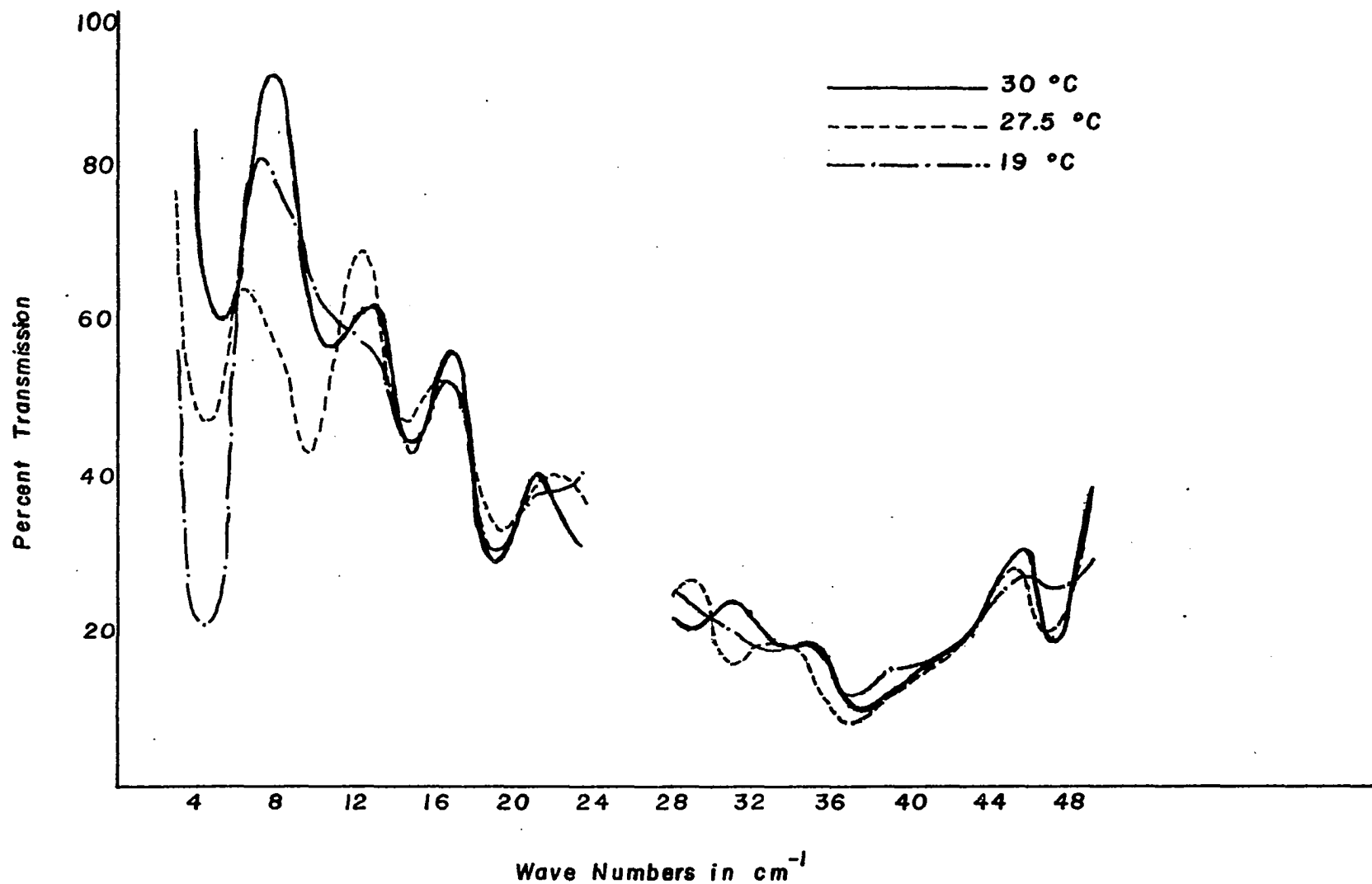


Figure 26. Comparison of Transmission at 30 °C, 27.5 °C, 19 °C.

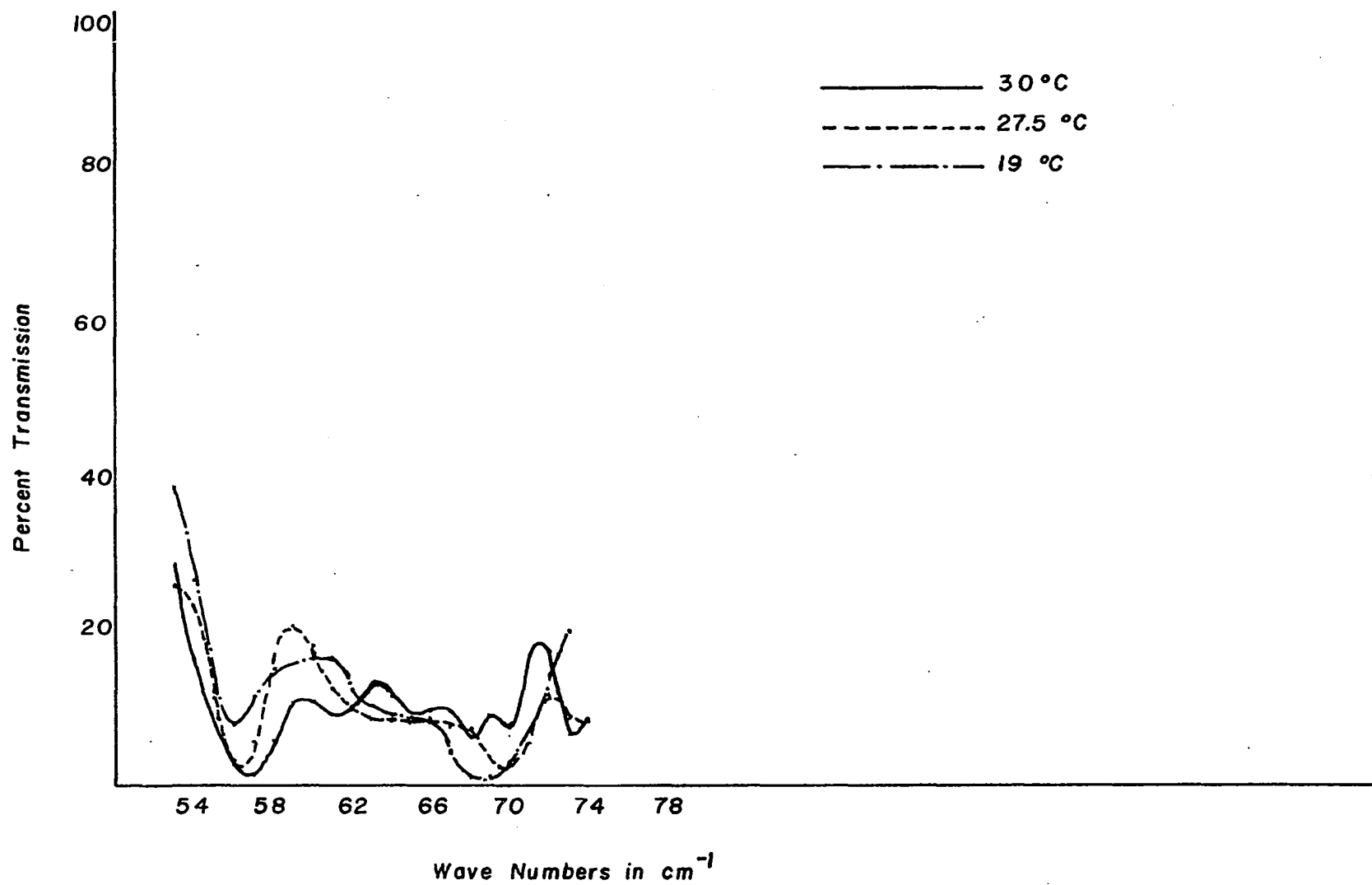


Figure 27. Comparison of Transmission at 30 °C, 27.5 °C, and 19 °C Between 55 cm^{-1} and 75 cm^{-1} .

set of 20 scans was divided into two sets of 10 scans. Each of these sets of 10 scans was individually processed and the results compared with each other and with the result when all twenty scans are used. The three computations were in agreement within the limits of experimental error.

After the above measurements had been made, it was intended to obtain the spectra at several more temperatures. However, in the process of the next set of 20 scans, the previously mentioned spurious noise returned with greater frequency and intensity. It was thought that the "bad points" could be identified during the course of transferring the interferogram to computer cards and averaging them into the adjacent values on the interferogram. This proved not to be feasible and it was decided to terminate the data gathering for this work.

In comparing the data from the 50 micron samples with some of the earlier transmission spectra of thicker samples (0.2 mm - 0.4 mm), it appeared that indeed most of the earlier spectra were marred by noise of some sort. However, it was noted that in every case the thicker samples showed an absorption at about 3.5 cm^{-1} and a broad general absorption centered near 37 cm^{-1} . These spectra were all taken at room temperature (approximately 25°C). A typical example of such a spectrum is shown in Fig. 28. The absorption around 37 cm^{-1} is very similar to that shown by the thinner samples at other temperatures, and the absorption at 3.5 cm^{-1} might have some relationship to the lowest frequency absorption at the other three temperatures. These are the only features that appear with consistency on all of the 25°C measurements.

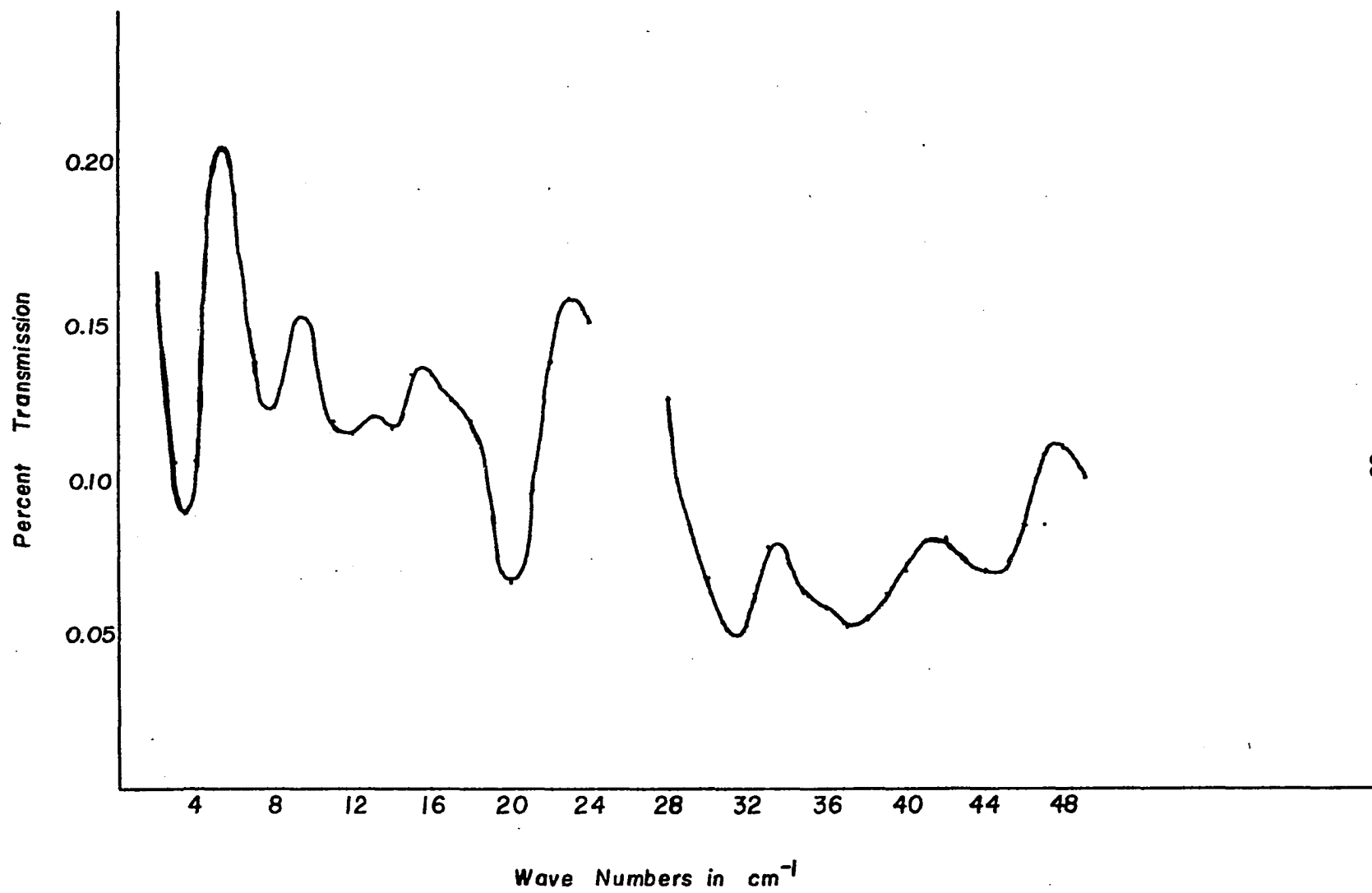


Figure 28. Percent Transmission Through 0.4 mm of Rochelle Salt at 25 °C.

CHAPTER V

THEORY OF FERROELECTRICITY IN ROCHELLE SALT

Ferroelectricity occurs in a number of crystals, some of which are structurally and chemically very different from each other. Theoretical treatments have therefore usually been restricted to dealing with one, or at most a few, ferroelectric crystals. Some attempts (e.g. Cady (32) and Devonshire (33)) have been made to arrive at a general theory of ferroelectricity. These are theories attempting to explain the anomalous dielectric behavior in terms of thermodynamic considerations. They are capable of describing the essential features of a ferroelectric transition of first or second order by assuming that the reciprocal dielectric susceptibility is temperature dependent. Such theories assume that:

- 1) All stresses are zero.
- 2) The polarization vector P is directed along one of the crystallographic axes.
- 3) The non-polar phase is centrosymmetric. The Helmholtz free energy of the crystal can then be written as

$$A(P) = \frac{1}{2} \chi^x P^2 + \frac{1}{4} \xi^x P^4 + \frac{1}{6} \zeta^x P^6$$

where the coefficients are temperature dependent. It must be remem-

bered that this kind of theory is admittedly only an approximation.

Extensions of this general theory have been made specifically for Rochelle salt by Mason (34), Devonshire (35), and Mitsui (36). These are considered the most successful attempts at phenomenological, theoretical treatments of ferroelectricity in Rochelle salt. The somewhat more recent work of Cochran (6,7) may ultimately prove to provide a better approach to the problem. Cochran attacks the whole problem of ferroelectricity from the standpoint of lattice dynamics and crystal stability. Details can be worked out only for crystals having rather high symmetry (such as BaTiO_3 , which is cubic in the non-polar phase). The orthorhombic symmetry of Rochelle salt prohibits the detailed application of Cochran's ideas, however some aspects may be helpful in this work and will be considered later in this chapter.

The work of Mitsui (36) is an expansion and improvement on the papers of Mason (34) and Devonshire (35). What follows is an outline of ferroelectric theory of Rochelle salt as proposed by Mitsui. The purpose is to develop a theory to explain the ferroelectric effect of Rochelle salt on the basis of a local field theory which uses order-disorder ideas of ferromagnetism. The earlier work of Mason (34) and Devonshire (35) used the X-ray analysis of Beevers and Hughes (37). This seemed to imply that the hydrogen bond between an oxygen atom and a water molecule was responsible for the ferroelectric dipole. More recent neutron diffraction studies (38) have showed that the orientation of a hydroxyl group of the tartrate molecule accounts for the primary contribution to the spontaneous polarization. The crystal is very complex and there may also be other smaller contribu-

tions. Mitsui's theory is based on the more recent neutron diffraction results. The essential feature of all of these theories consists in recognizing that these dipoles have two possible positions of equilibrium within the lattice, and that the dipole has different energies in the two positions.

The essential structure (for purposes of Mitsui's theory) is schematically given in Fig. 29. The arrows represent the dipoles labelled $(OH)_5$ by Beevers and Hughes (37). There are four chemical formula units in the unit cell. The symmetry of Rochelle salt in the paraelectric phase is that of the point group C_2 .

It will be assumed that $(OH)_5$ is a rotatable dipole with two equilibrium positions along the x-axis, and that the potential energy of the two positions is different. Hence, one set of dipoles has minimum energy when pointing in the positive x-direction, while another set has minimum energy when pointing in the negative direction. Mitsui chooses to call the polarizations due to the respective dipole sets, P_1 and P_2 . Any other dipoles induced by external and internal fields are written as P_{ei} ($i = 1, 2, \dots, n$) where n is one half the number of ions and atoms in the unit cell. Measurements of the properties of Rochelle salt indicate that all properties are normal except the clamped dielectric constant, i.e. the dielectric constant measured without any strains on the crystal. Therefore the theories of the ferroelectric effect in Rochelle salt are essentially theories of the clamped dielectric constant. If one assumes that the crystal is clamped, then the Helmholtz free energy per unit volume due to the polarization can be broken into four parts:

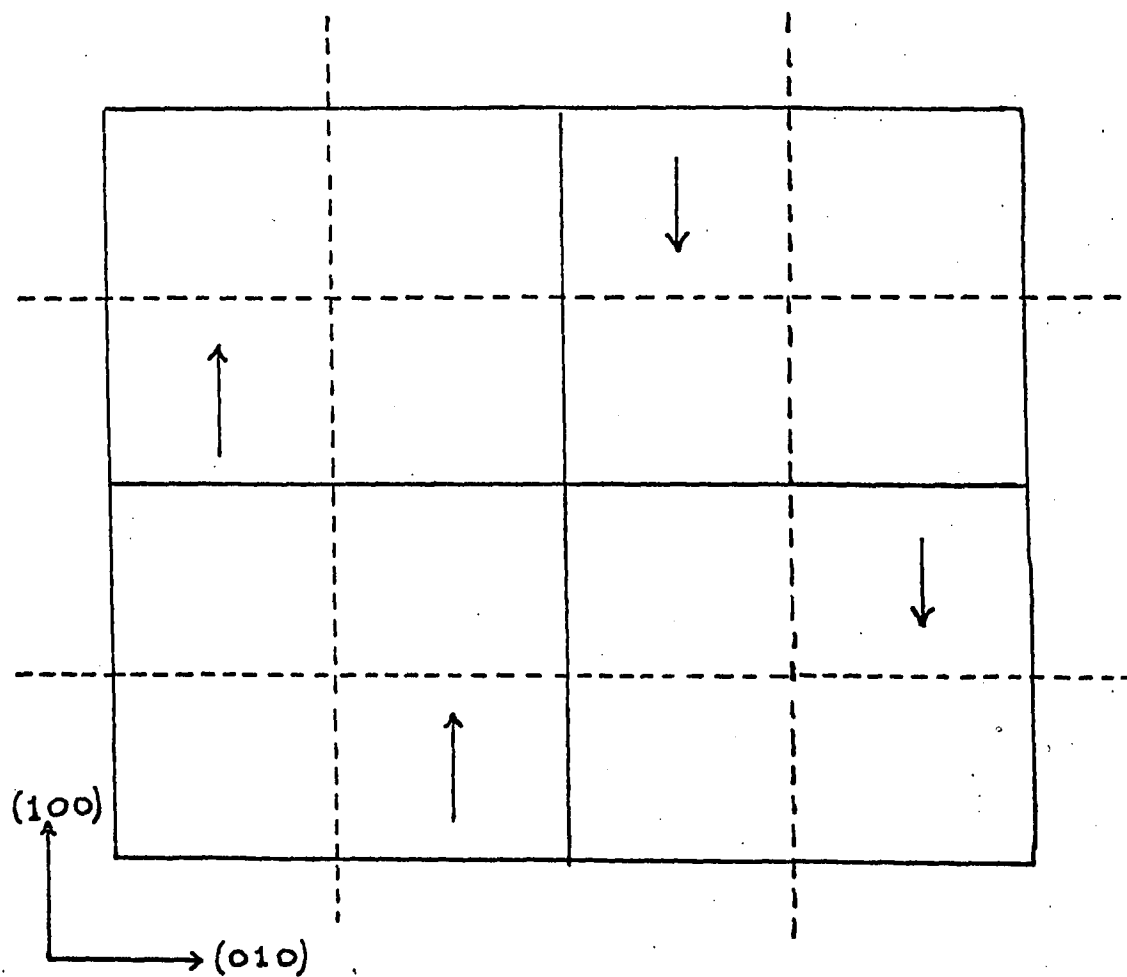


Figure 29. Ferroelectric Structure of Rochelle Salt.

- A_1 = the free energy of the induced dipoles,
 A_2 = the mutual interaction energy of the dipoles,
 A_3 = the potential energy of the rotatable dipoles,
 A_4 = the entropy terms of the rotatable dipoles.

These four parts can be written as

$$A_1 = \frac{1}{2} \sum v P_{ei} / \gamma_i$$

where v = one half the volume of the unit cell and γ_i is the polarizability of the i^{th} ion or atom.

$$A_2 = -\frac{1}{2} \sum_{i,j} \beta_{ij} P_{ei} P_{ej} - \sum_{i,j} \beta_{ij}^* P_{ei} P_j - \frac{1}{2} \sum_{i,j} \beta_{ij}^{**} P_i P_j$$

where β_{ij} , β_{ij}^* and β_{ij}^{**} are constants. This is equivalent to assuming that the local field on each dipole is a linear function of the polarizations.

$$A_3 = -V(N_{1+} - N_{1-}) + V(N_{2+} - N_{2-}) = \frac{-V}{p} P_1 + \frac{V}{p} P_2$$

where $2V$ is the difference between the potential energies at the two equilibrium positions, and N_{i+} and N_{i-} , ($i = 1, 2$), are the number of type i dipoles pointing in the $+x$ and $-x$ directions, respectively. The second expression results from the equation $p(N_{i+} - N_{i-}) = P_i$, ($i = 1, 2$) where p is the dipole moment of a single $(OH)_5$. The entropy term is written as

$$A_4 = \frac{1}{4} kNT \sum_i \left[(1 + \eta_i) \log (1 + \eta_i) + (1 - \eta_i) \log (1 - \eta_i) - 2 \log 2 \right]$$

where $\eta_i = 2P_i / (Np)$, ($i = 1, 2$), N is the number of $(OH)_5$ per unit volume, k is Boltzmann's constant and T is the temperature in degrees

Kelvin. Adding the four parts one has the total Helmholtz free energy A .

Using the relationships $E = \frac{\partial A}{\partial P_{ei}} = \frac{\partial A}{\partial P_i}$, Mitsui shows that

$$E = \chi_d P_d + \xi_d P_d^3$$

where $P_d = a(P_1 + P_2)$, (a is a constant depending on the β 's of A_4), χ_d and ξ_d are given in terms of N , p , k , T , β 's, and P_{10} which is the value of P_1 in the absence of both the electric field and the spontaneous polarization. Earlier the paper had argued that the free energy of a clamped crystal polarized along the x -axis could be written as

$$A = \frac{1}{2} \chi_1 P_x^2 + \frac{1}{4} \xi P_x^4$$

which leads to

$$E_x = \frac{\partial A}{\partial P_x} = \chi_1 P_x + \xi P_x^3$$

where χ_1 is the reciprocal susceptibility of the clamped crystal and ξ is a constant estimated to have a value between 6×10^{-8} and 10^{-6} in esu. Hence, Mitsui identifies the two equations and proceeds to calculate χ_1 and ξ in terms of atomic parameters.

All calculations were made in terms of a parameter

$$c = 2 x_0 \tanh^{-1} x_0 - 1,$$

where x_0 is the value of $x = 2P_{10}/Np$ at the temperature where the reciprocal susceptibility χ_1 is zero. Taking $c = 0.6$, the calculated $\chi_1(T)$ agrees quite well with experiment, especially near $T = 276^\circ\text{K}$, the temperature at which $\chi_1 = 0$. An estimate was also made on the quantity V/kT_0 , where $T_0 = 276^\circ\text{K}$, the temperature at which $\chi_1 = 0$. Using the values $N = 3.8 \times 10^{21} \text{ cm}^{-3}$ and $p = 1.51 \times$

10^{-18} esu, $V/kT_0 = 2.20$ for $c = 0.6$. Mitsui states that the order of magnitude is reasonable.

More recently, Cochran (6,7) has proposed another way of approaching the problem of ferroelectricity. The subject is considered from the standpoint of lattice dynamics and crystal stability. It is shown that, for ferroelectric crystals having high symmetry, one of the transverse optic modes becomes nearly unstable at the transition temperature, T_c , i.e. an anomaly in the static dielectric constant can obtain only if at least one frequency approaches zero. Also, this particular frequency, ω_T , may approach zero without the crystal becoming unstable against any other vibrational modes. At the end of his first paper (6), Cochran concludes that, with the possible exception of order-disorder transformations, the problem of the onset of ferroelectric properties is basically one in lattice dynamics. A few observations are made specifically concerning Rochelle salt. When a crystal of symmetry as low as that of Rochelle salt is considered, the full $3n \times 3n$ determinant must be used in solving the dynamics problem, because no one mode is constrained by crystal symmetry to be purely transverse or longitudinal. For this reason the frequencies of the optic vibrations in the long wavelength limit may not coincide with the dielectric dispersion frequencies. The only evidence that such a soft optic mode exists in Rochelle salt is the measurements of Akao and Sasaki (39) on the temperature dependence of the dielectric relaxation frequency of Rochelle salt. This frequency was in the region of 2×10^9 hz and seemed to vary according to $\frac{1}{\omega^2} \propto \epsilon_s$ where ϵ_s is the clamped dielectric constant and σ

is the lowest dispersion frequency. It appears that a low-lying optic mode which has a temperature dependence $\sigma^2 \propto (T - T_c)$ should exist for Rochelle salt, but not necessarily in the vicinity of 2×10^9 hz. It might be that such a mode would lie in the frequency region being investigated in the present work.

CHAPTER VI

DISCUSSION

The unit cell of Rochelle salt contains 112 atoms. This leads to an enormously complicated problem if one is to do a detailed lattice dynamical analysis. Data collected thus far on Rochelle salt has been interpreted in terms of the phenomenological theories of Mason (34), Devonshire (35), and Mitsui (36). The lattice dynamical work of Cochran (6,7) makes brief mention of Rochelle salt, with the suggestion that the low-lying optic mode discussed in detail for BaTiO_3 should also exist for Rochelle salt.

Temperature dependence in the spectra seems to appear primarily in the two lowest lying bands (between 3.5 cm^{-1} and 10 cm^{-1}). If the band between 4 cm^{-1} and 5 cm^{-1} is the absorption of the energy necessary to "flip" the lowest of the ferroelectric dipoles into the higher equilibrium state, then the potential barrier between the two states would be approximately 4 cm^{-1} . Mason (34), Mitsui (36), and Akao and Sasaki (39) all estimate this potential barrier to be at least 25 times greater. Such a large difference seems somewhat unlikely. It might be mentioned, however, that the tendency of the intensity of this band is correct, i.e. the intensity of absorption increases as the Curie temperature is approached, then, below T_c the absorption

again increases. This would indicate that as the temperature is decreased a larger number of the dipoles are in the lower of the two states of equilibrium. Mitsui, whose theory is the most recent of the phenomenological theories, does not predict any temperature dependence of this potential barrier, and hence the observed shift with temperature would not favor this interpretation. The band at 69 cm^{-1} (Fig. 27) whose intensity increases as the temperature decreases would be much more likely to be the energy necessary to flip the ferroelectric dipole from the lowest state into the higher equilibrium state of the asymmetric potential function. The energy of this band would begin to get close to the estimates made by Mitsui. In the region 54 cm^{-1} to 84 cm^{-1} the spectrum of water vapor is very rich and intense. Since the overall energy through the spectrometer in this region is low, it may be that the band at 69 cm^{-1} is due to residual water vapor in the system. The intensity anomaly could, in such a case, be due to different amounts of residual water vapor present at the different temperatures. Using the appropriate beam splitter and filters, the region from 50 cm^{-1} to 100 cm^{-1} should be investigated properly to verify this behavior.

Akao and Sasaki (39) found evidence for a temperature dependent dielectric relaxation frequency in the vicinity of $3 \times 10^9 \text{ hz}$ (0.1 cm^{-1}). Cochran cites this as evidence that the ferroelectricity of Rochelle salt is a problem in lattice dynamics, similar to the case of BaTiO_3 . If this is so, then there should also be a low-lying optic mode appearing as infrared absorption. Cochran (6) notes that no mode in Rochelle salt is constrained by crystal symmetry to be purely transverse

or longitudinal, therefore, the frequency of the optic vibrations for the long wavelength limit may not coincide with the dielectric dispersion frequencies. With this in mind, the writer investigated the nature of σ^2 vs $(T - T_c)$ just above the Curie temperature for the band in question. The points at 30°C and 27.5°C are taken from the data of Fig. 26, and the point at 25°C taken from Fig. 28. The results are shown in Fig. 30. The three points chosen lie almost exactly on a straight line, however the line does not pass through the origin as it should if σ^2 is strictly proportional to $(T - T_c)$. The slope of the line is $2.8 \text{ cm}^{-2}\text{deg}^{-1}$ and is considerably less than the slope predicted for BaTiO_3 by Cochran. Ballantyne (31) found that the actual measurements on BaTiO_3 resulted in much smaller shifts than those predicted by Cochran and attributed the difference to the fact that this mode was found to be highly damped whereas Cochran had assumed it to be only slightly damped. In the present work the mixing of transverse and longitudinal modes, along with a lack of information of all the normal mode frequencies, makes a quantitative comparison with dielectric measurements impossible. This can be done in principle by using the Lydane-Sachs-Teller relation

$$\frac{\epsilon(0)}{\epsilon(\infty)} = \prod_{j=2}^n \frac{(\sigma_l)_j^2}{(\sigma_t)_j^2}$$

and assuming that

$$\epsilon(0) = \frac{C}{T - T_c}$$

where $(\sigma_l)_j$ and $(\sigma_t)_j$ are the longitudinal and transverse lattice vibrational frequencies of the normal mode j , C is the Curie constant

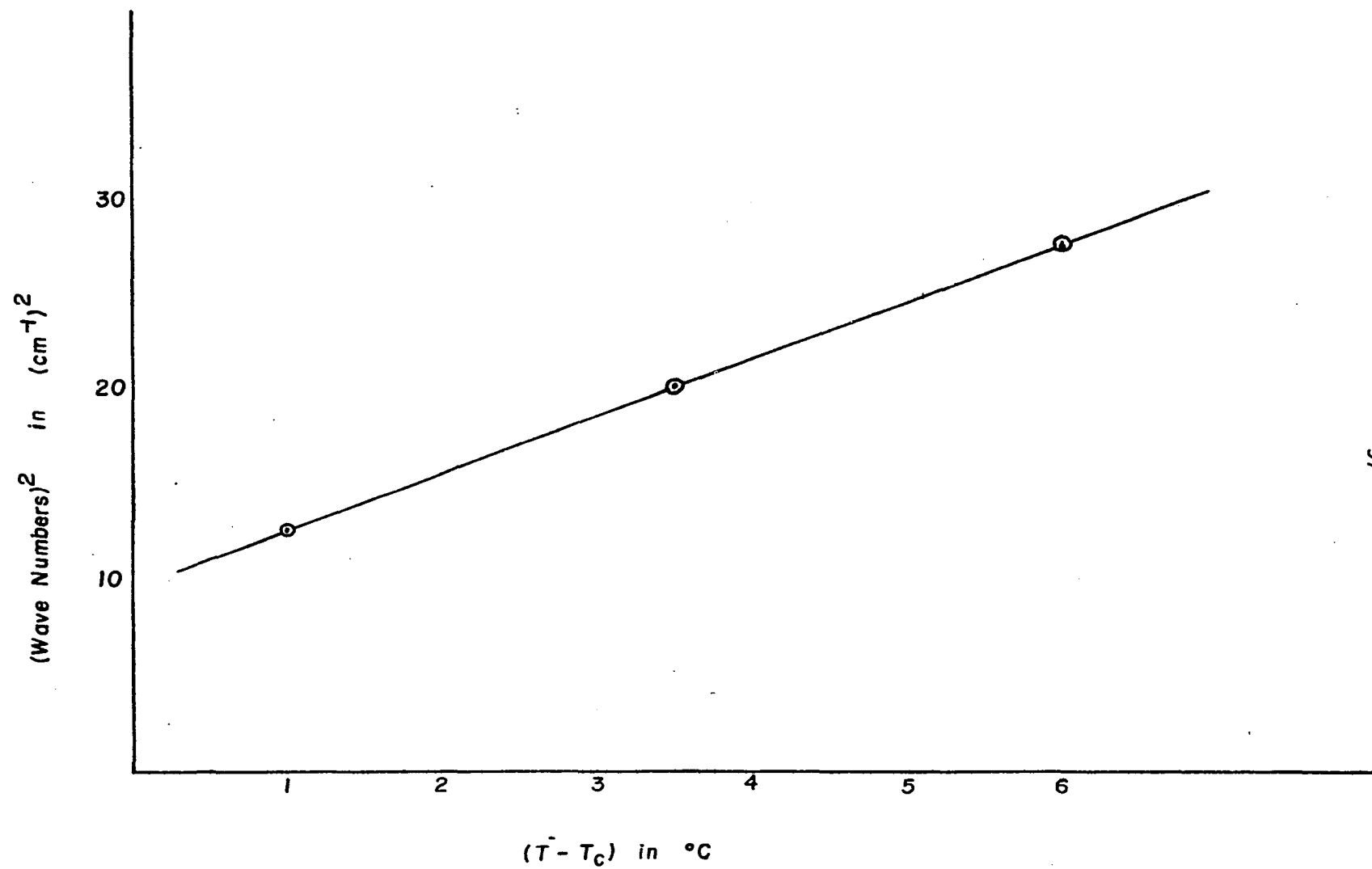


Figure 30. σ^2 vs $(T - T_c)$ for the Lowest Frequency Band.

and T_C is the Curie temperature. The linear relationship between σ^2 and $(T - T_C)$ leads to the conclusion that the band observed to lie between 3.5 cm^{-1} and 5.25 cm^{-1} is the soft optic mode predicted by Cochran to be responsible for ferroelectric crystals.

The next higher frequency band (8 cm^{-1} to 10.75 cm^{-1}) shifts with temperature in the same manner as the first band, and below T_C it disappears. The plot of σ^2 vs $(T - T_C)$ is also a straight line (Fig. 31), but the slope is increased to $10.9 \text{ cm}^{-2}\text{deg}^{-1}$.

In the paraelectric phase, Rochelle salt has the symmetry of the point group $D_2 = V$, whereas in the ferroelectric phase it has the lower monoclinic symmetry of the point group C_2 . The group D_2 has four species of normal vibrations, A_1 , B_1 , B_2 , B_3 (40). Of these, B_1 , B_2 , and B_3 are infrared active, however, since the plane of the crystal was perpendicular to the z-axis, only B_2 and B_3 , which transform like T_y and T_x , would be observed in the present spectrum. The group C_2 has only two species of normal vibrations, A and B. Correlation of the two groups is shown in Table VI. It is seen that with the change in symmetry, both B_2 and B_3 go to the species B. Only a single band would be expected below the Curie temperature, which is what has been observed in the present spectra. Thus, the band structure between 3 cm^{-1} and 11 cm^{-1} can be explained as low-lying lattice vibrations.

The bands at 15 cm^{-1} and 19 cm^{-1} have the same shape, intensity, and position at all three temperatures, within experimental error. One would conclude that they have no connection with the ferroelectric properties of Rochelle salt. Also, the two bands appear very similar to each other. This would indicate that they have similar origins.

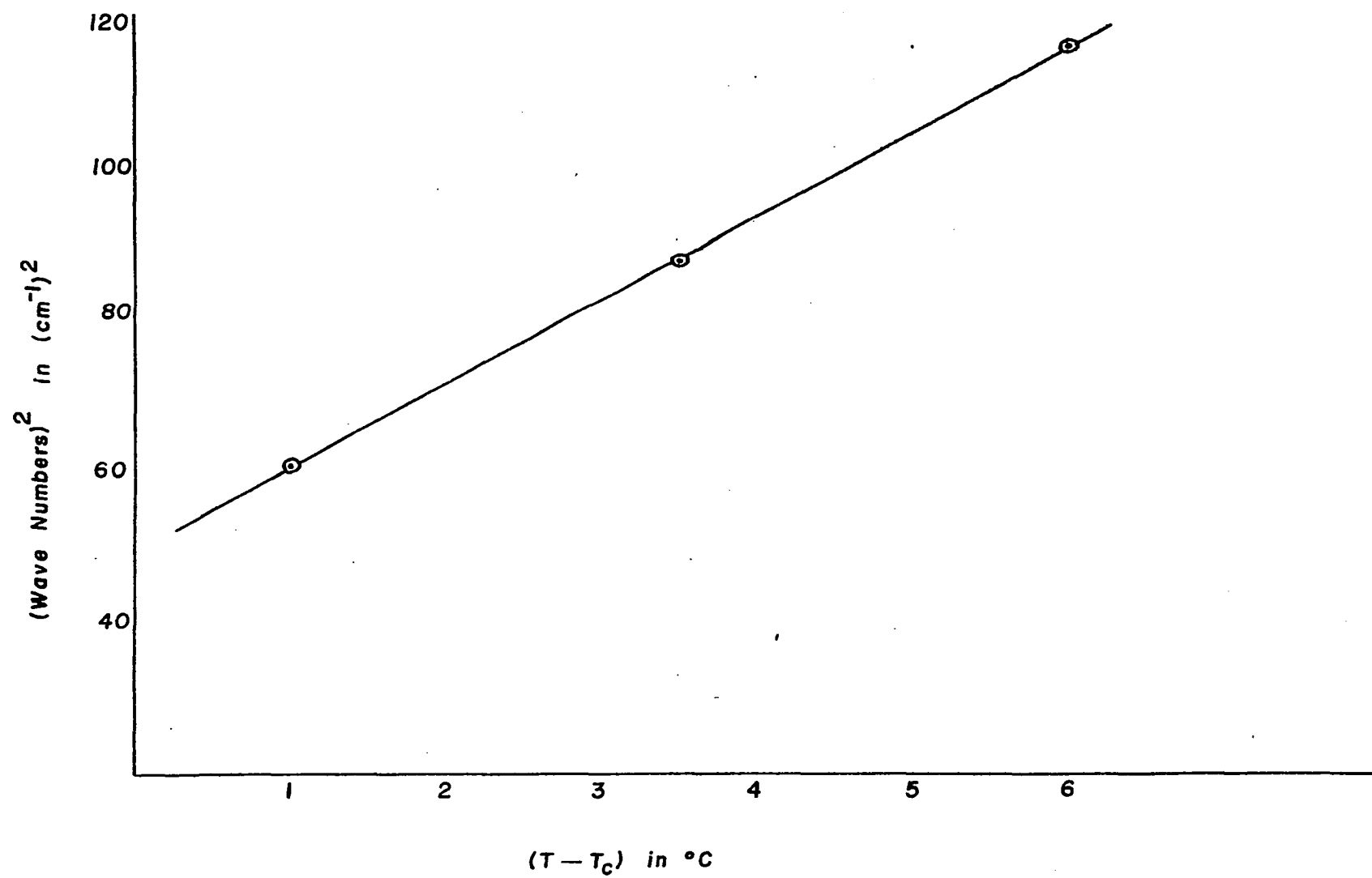


Figure 31. σ^2 vs $(T - T_c)$ for the Second Lowest Band.

Table VI. Correlation of the
Point Groups C_2 and
 D_2 (from ref. 40).

D_2	C_2
A	A
B_1	
B_2	B
B_3	

One possible explanation is that they are due to interactions between various dipoles in the crystal which do not contribute significantly to the ferroelectric properties of the crystal. The theory of Mason (34) was based on the hydrogen bond between $O_{(1)}$ and $(H_2O)_{(10)}$ (notation according to Beevers and Hughes) as being responsible for the ferroelectric properties of Rochelle salt. It has since been concluded that this bond does not play any significant part in the ferroelectricity of the crystal. Each unit cell has twelve water molecules in addition to the four $(H_2O)_{(10)}$. All of these dipoles in the crystal could undergo weak interactions with each other giving rise to the absorptions at 15 cm^{-1} and 19 cm^{-1} .

The intense, broad absorption centered at approximately 37 cm^{-1} was thought to be due to the effect of the thin sample. An index of refraction of 1.35 would allow the 50 micron crystal to provide a thickness of $1/4$ of the wavelength of the radiation in the crystal for $\sigma = 37\text{ cm}^{-1}$. This explanation does not seem very plausible,

however, since the same broad absorption was seen in the spectrum of the much thicker sample given in Fig. 28.

The band at 47 cm^{-1} again shows some temperature dependence in that the intensity decreases below the Curie temperature. This temperature dependence is not so large, however, that it might not be due to experimental error, especially since the band occurs near the end of the second beam splitter maximum. The present data would be inconclusive concerning whether this band shows an anomaly or not in passing through the Curie temperature.

The present work indicates that in the region from 3 cm^{-1} to 49 cm^{-1} , the band which appears as a doublet above T_c and as a single band in the ferroelectric phase, is the temperature dependent soft optic mode predicted by the work of Cochran (6) and observed as dielectric relaxation by Akao and Sasaki (39). Other observed bands are due to nonferroelectric effects.

If the behavior of the band at 69 cm^{-1} is really as it appears in Fig. 27, then it might be that the theory of Mitsui (36) as well as that of Cochran (6,7) is of importance in explaining Rochelle salt. Cochran makes no attempt at describing the mechanism by which the symmetry change takes place, but he does point out that in many ferroelectrics, including Rochelle salt, a lattice-dynamical instability occurs at the Curie temperature. Mitsui, on the other hand, attempts only to explain the mechanism for Rochelle salt rather than to formulate a more general theory. Thus, a more thorough investigation of the band at 69 cm^{-1} might lead to some definite numbers that could be used in substantiating the specific mechanism proposed by Mitsui.

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