MICROWAVE MASER SPECTROSCOPY

by

M. W. LONG

and others.

Department of the Navy
Office of Naval Research
Contract No. NNonr-991(07)
Project No. NR 372-781

Project A-390

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia
1958 - 63
CONTENTS

Status Report.

Long, M. W.
March 15, 1960.
May 1, 1961.

Semi-Annual Status Report.

No. 1-2 by Long, M. W.

Annual Summary Report.

Long, M. W.
December 12, 1962.


No. 1-2 by Long, M. W.

No. 3. by Johnson, R. C.

No. 4. by Long, M. W. and Butterworth.
Dr. Arnold Shostak  
Head, Electronics Branch  
Office of Naval Research  
Washington 25, D. C.

Subject: Status Report on Contract No. Nonr-991(07)

Dear Dr. Shostak:

Current work on the subject contract is devoted to two major phases, (1) an evaluation of detector noise and means for reducing this noise and (2) a study of centrifugal distortion in symmetric top molecules. The status of this work is described below.

DETECTOR NOISE

The work on determining detector noise and the effect of this noise on systems required to detect a small decrement, $\Delta P$, in the relatively large amount of power, $P$, has continued since the publication of a previous report. Emphasis is being placed on barretters because the full capability of these devices has not been realized.

Approximations regarding crystal noise and conversion gain exist in the literature but constants evaluated for the appropriate equations differ greatly. Even if the values were well known they would not describe the region between square law and linear. Crystals have been investigated with a synchronous detection system which provides a novel means for determining the figure of merit $\Delta P/P$ as a function of $P$; results are included in Figure 1.


\[\text{By: } \mathbb{A}\text{390} \quad \text{3-18-60}\]
The synchronous detection system has also been used for the evaluation of barretter characteristics and a typical sensitivity curve obtained for barretters is included in Figure 1. Research has been initiated on the use of a barretter mounted in an evacuated chamber; this may reduce the barretter noise if it is generated by uneven heating along the element and should also increase the change in resistance per unit change in r-f power. A 30 cps modulation rate will be used because evacuation will increase the thermal time constant.

A paper entitled "Detectors for Microwave Spectrometers" (or any other system which the parameter to be measured is a small change in a relatively large power level) is nearing completion and will soon be mailed to the editor of the Review of Scientific Instruments. This paper outlines principles limiting the performance of detecting systems, includes data in Figure 1, describes the system for detecting weak CFCl\textsubscript{3} lines reported in Technical Report No. 1, and describes conditions for which spectrometer output is linearly dependent on the intensity of lines.

**CENTRIFUGAL DISTORTION COEFFICIENTS**

Centrifugal distortion and the effects of nuclear quadrupole interaction on the microwave spectrum of CFCl\textsubscript{3} were reported in reference 1. This report also describes measurements on the J = 1 \rightarrow 2 transition of CHCl\textsubscript{3} and a comparison of the results for CFCl\textsubscript{3} with previous work on CHCl\textsubscript{3}. The measurements of the very complex J = 2 \rightarrow 3 spectrum reported\textsuperscript{2} by Wolfe were used to assist with the analysis. This spectrum was measured by me last summer and only small differences were observed. The line K of Table II, reference 2,  

<table>
<thead>
<tr>
<th>Curve</th>
<th>Detector</th>
<th>Signal Frequency</th>
<th>Modulation Frequency</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LN26</td>
<td>24,000 Mc</td>
<td>1 kc</td>
<td>Computed from Johns Hopkins data*</td>
</tr>
<tr>
<td>2</td>
<td>LN23E</td>
<td>10,000 Mc</td>
<td>1 kc</td>
<td>Typical of LN23 data</td>
</tr>
<tr>
<td>3</td>
<td>LN23B</td>
<td>10,000 Mc</td>
<td>1 kc</td>
<td>Most sensitive of diode data</td>
</tr>
<tr>
<td>4</td>
<td>LN23E</td>
<td>10,000 Mc</td>
<td>85 kc</td>
<td>Computed from manufacturer's data and confirmed by CFCl₃ measurements</td>
</tr>
<tr>
<td>5</td>
<td>610B</td>
<td>10,000 Mc</td>
<td>1 kc</td>
<td>Typical of 610B barretter data</td>
</tr>
<tr>
<td>6</td>
<td>Theoretical limit</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

reported by Wolfe as weak but not accounted for in his analysis was sufficiently
strong that on a relative basis it should be classed as being of medium inten-
sity. The shape of the most intense line at low pressures suggests that this
line is the sum of two lines. The above observations are consistent with the
analysis of reference 1.

Results of the work on CFCl₃ and CHCl₃ were prepared in the form of a
paper entitled "Microwave Spectrum of CFCl₃" for the Journal of Chemical
Physics. Minor modifications suggested by the referee were made and the
paper has been returned to the editor.

Effects of centrifugal distortion in symmetric top molecules are expressed by the distortion coefficients D_J and D_JK in

\[ f/2(J+1) = B - D_{JK} K^2 - 2D_{J}(J+1)^2. \]

As previously mentioned, analysis indicates that CFCl₃ and CHCl₃ have negative
values of D_{JK} and negative values of D_J. Effort has been devoted to this
subject because previous investigations have yielded only positive values
of D_J and some authors have surmised that D_J must be positive for all symmetric
tops. The negative values of D_{JK} also seemed unusual. This investigation has
revealed that for XY₃ and XYZ₃ molecules, reported values of D_{JK} are negative
for molecules with center of mass within the "umbrella" and are positive for
molecules with center of mass outside the umbrella. D_J is generally called


a centrifugal distortion constant but $D_j$ depends on $J$ for the low $J$-value data of CFCl$_3$ and CHCl$_3$. It seems that the negative $D_j$ values are caused by reduction of moment of inertia about the molecular symmetry axis with increased angular momentum $J$. The work is described in a note entitled "Centrifugal Distortion in Symmetric Top Molecules", to be published in the March 1960 issue of the Journal of Chemical Physics.

It would seem that the unusual effect of distortion on $D_j$ for CFCl$_3$ and CHCl$_3$ might also exist for CClF$_3$ because of the similarity of bonding. CClF$_3$ has been investigated by others, but not in sufficient detail for determining centrifugal distortion coefficients with certainty. The center of mass for this molecule is outside the umbrella and it is therefore expected that $D_{JK}$ is positive. That $D_{JK}$ is positive has been confirmed by recent measurements under this contract, but further work is required before the sign of $D_j$ can be determined with certainty. The work on CClF$_3$ is being carried out by Mr. R. C. Johnson and it will be used as part of his thesis for the Ph.D. in physics.

FUTURE PLANS

Work planned for accomplishment between now and 15 September 1960, which concludes the present contractual period, includes (1) the determination of minimum detectable signals obtainable with evacuated barretters operating at 30 cps, (2) the determination of centrifugal distortion coefficients of CClF$_3$, (3) completion of the paper on detectors for microwave spectrometers, and (4) further work on isolating barretter noise caused by various sources.

Very truly yours,

M. W. Long
Project Director
Dr. Arnold Shoestak  
Head, Electronics Branch  
Office of Naval Research  
Washington 25, D.C.

Subject: Status Report  
Contract N00019-61-C-0710

Reference: NR 372-761

Dear Dr. Shoestak:

Current work on the subject contract is devoted to two major phases:

1. an evaluation of detector noise and means for reducing this noise, and
2. a study of centrifugal distortion in asymmetric-top molecules. Progress on the work since 15 September 1960 is reviewed below.

DETECTOR NOISE

The investigations on detectors have been extended beyond those discussed in the last report¹ which indicates that, for certain specialized detection applications, fine-wire bolometers (barretters) are more sensitive than crystals. In principle, it would seem that even greater sensitivity could be attained because the excess noise level from good barretters far exceeds that to be expected from Johnson noise. Recently, it has been found that barretter sensitivity is increased by operation in an environment of reduced air pressure; therefore, effects of evacuation on barretter performance are being studied in detail. As a result of this work, the performance² of a


direct detection 4-mm radiometer being used on another Georgia Tech program
has been greatly enhanced by operating a barretter in an evacuated holder.

During the last several months, R. E. Pidgeon of Georgia Tech has made
theoretical calculations for a heat-sensitive element which has a resistivity
that can be approximated by a linear function of temperature over the
operating range and in which the heat loss is predominantly from the supported
ends of the element. It would seem that these conditions are good approxi-
mations for a microwave barretter operating in an evacuated environment.
Calculations on responsivity and time constant have been completed, but
further theoretical work needs to be accomplished on noise power. Bolometers
have been previously analyzed for the case in which the heat loss is by
radiation and conduction to the surrounding gas with no loss by end
conduction; but these calculations are not applicable to microwave
barreteres. Some measurements of responsivity and time constant have been
made, but further analysis must be accomplished before the study can be com-
pleted.

Measurements have been made on minimum detector power and excess noise
as functions of pressure. Evacuation results in a 10-db improvement in
minimum detector power for an X-band barretter operating as a video detector;
this indicates that the ratio of responsivity to noise power has increased by
a factor of 100. Barretter sensitivity measurements have also been made for
the case of detecting a small change in a relatively large amount of power.
The sensitivity measurements were made as a function of air pressure and as
a function of the unmodulated component of power. As expected from the video

3. R. A. Smith, F. E. Jones, and R. P. Chasmar, "The Detection of Infrared
detection data, evacuation improves the sensitivity by 10 db if the unmodulated component is small, but evacuation produces less improvement for large levels of constant power. Plans have been made for further theoretical and possibly further experimental studies so that a better understanding can be had of the mechanisms which produce excess barretter noise.

CENTRIFUGAL DISTORTION IN SYMMETRIC-TOP MOLECULES

R. C. Johnson has continued his research on centrifugal distortion in symmetric-top molecules. He is presently completing a technical report \(^4\) entitled, "Centrifugal Stretching in Symmetric-top Molecules and the Stark Effect of Chlorotrifluoromethane"; this will also be used as a thesis for the Ph.D. degree in Physics. The abstract for this report follows.

The effects of centrifugal distortion in symmetric-top molecules are usually predicted through the use of distortion constants, \(D_{jj}\) and \(D_{jk}\). It is expected that \(D_{jj}\) will always be positive and that \(D_{jk}\) may be either positive or negative. Recently, \(\text{CCl}_3\) and \(\text{CHCl}_3\) were each reported to have a negative \(D_{jj}\) which varies with the rotational quantum number \(J\). This prompted further studies of distortion effects in other symmetric tops. Detailed calculations of distortion constants were made for three molecules:

(a) \(\text{CH}_3\text{Cl}\), a typical methyl halide; (b) \(\text{CCl}_3\text{F}\), a molecule with bonding similar to that of \(\text{CCl}_3\text{F}\); and (c) \(\text{CHF}_3\), a molecule with its center of mass within the \(\text{CF}_3\) tetrahedron. All three were found to obey existing distortion theory within the limits of experimental error. The \(J = 1\rightarrow 2\) through \(1\rightarrow 5\) transitions for \(^{12}\text{C}\text{Cl}\) were measured. Absorption lines for \(J = 2\rightarrow 3\) and \(3\rightarrow 4\) have been reported previously; however, the \(2\rightarrow 3\) data are believed

to be slightly in error. Present data yield $B_0 = 3335.596$ mc,
$sqq = -77.98$ mc, $D_{yj} = 0.59$ kc, and $D_{jk} = 2.06$ kc. Theoretical dis-
tortion constants can be calculated from the molecular structure and the
molecular force constants. A comparison of measured and theoretical
constants for nine symmetric-top molecules shows reasonable agreement for
all except CC1$_3$F and CIC1$_3$, which are the only molecules considered having
three identical nuclei with quadrupole moments. From Stark effect
measurements on the $J = 1 \leftrightarrow 2$ transition, the molecular dipole moment of
$C^{12}$Cl$_3$F$_3$ was assigned the value $0.50 \pm 0.01$ debye.

Funds Remaining

It is estimated that funds allocated to the subject contract will be
exhausted upon completion of Technical Report No. 3, "Centrifugal Stretching
in Symmetric-top Molecules and the Stark Effect of Chlorotrifluoromethane,”
during June 1961. Additional funds will soon be requested to continue the
program.

Very truly yours,

M. W. Long
Project Director
SEMIA-ANNUAL STATUS REPORT NO. 1

PROJECT NO. A-390

MICROWAVE MASER SPECTROSCOPY

COVERING THE PERIOD
15 JUNE THROUGH 15 DECEMBER 1958

Department of the Navy
Office of Naval Research
Contract No. N00r-991(07)
Project No. NR 372-781

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia
ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

SEMI-ANNUAL STATUS REPORT NO. 1
PROJECT NO. A-390

MICROWAVE MASER SPECTROSCOPY
Prepared by
M. W. Long

COVERING THE PERIOD
15 JUNE THROUGH 15 DECEMBER 1958

Department of the Navy
Office of Naval Research
Contract No. N0onr-991(07)
Project No. NR 372-781
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. INSTRUMENTATION</td>
<td>2</td>
</tr>
<tr>
<td>A. Conventional Spectrometers</td>
<td>2</td>
</tr>
<tr>
<td>B. Sensitivity of Spectrometers</td>
<td>2</td>
</tr>
<tr>
<td>C. Coherent First Detector</td>
<td>5</td>
</tr>
<tr>
<td>D. Frequency of Stark Modulation</td>
<td>6</td>
</tr>
<tr>
<td>E. Detection Systems</td>
<td>6</td>
</tr>
<tr>
<td>1. Crystal Detector with Video Amplifier</td>
<td>6</td>
</tr>
<tr>
<td>2. Bolometer with Video Amplifier</td>
<td>9</td>
</tr>
<tr>
<td>3. Superheterodyne with Microwave Bridge</td>
<td>12</td>
</tr>
<tr>
<td>III. MICROWAVE SPECTRUM OF FLUOROTRICHLOROMETHANE</td>
<td>15</td>
</tr>
<tr>
<td>A. Description of Fluorotrichloromethane</td>
<td>15</td>
</tr>
<tr>
<td>B. Three Equivalent Nuclei with Quadrupole Moments</td>
<td>16</td>
</tr>
<tr>
<td>C. Theoretical Calculations on the J = 1→2 Transition</td>
<td>17</td>
</tr>
<tr>
<td>IV. PROGRAM FOR FUTURE WORK</td>
<td>19</td>
</tr>
<tr>
<td>V. BIBLIOGRAPHY</td>
<td>20</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

This is a semi-annual status report for a research program which was initiated 15 June 1958. Under this program the contractor will design instrumentation techniques and will collect and analyze spectrographic data in the 4,000 mc to 16,000 mc frequency range. These data will be collected and analyzed with a view toward extending the range of quantum-mechanical devices.

During this report period emphasis has been placed on determining instrumentation techniques and making comparisons between performances which can be obtained within the 4,000 mc to 16,000 mc region with those obtainable within the 20,000 mc to 40,000 mc region which is normally used for spectrographic investigations. Although the strengths of rotational lines for a given molecule decreases rapidly with frequency, worthwhile research results can be obtained at the lower frequencies.

Lines for the rotational transitions $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ have been recorded for fluorotrichloromethane. These frequencies occur at approximately 9800 mc and at 14,700 mc, and the absorption coefficients appear to be of the order of $10^{-10}$/cm. Calculations are presently being made to determine the quadrupole coupling constant and a centrifugal distortion constant. The calculations are difficult because the problem involves three identical nuclei with quadrupole moments. No previous measurements have been reported for this molecule.
II. INSTRUMENTATION

A. Conventional Spectrometers

Conventional microwave spectrometers consist of a klystron, a waveguide which contains the molecules under investigation, and a video detector. The klystron is slowly swept in frequency and the detector output is recorded so as to provide molecular absorption as a function of frequency. The waveguide is constructed so that a voltage can be applied which subjects the molecules to an electric field, thereby causing splitting and shifting of absorption lines by the Stark effect. Hughes and Wilson (8) were the first to introduce the idea of using Stark modulation. The Stark modulation frequency most often used is 6 kc and is almost always between 1 kc and 100 kc. The transmission loss through the waveguide is modulated by this technique; thereby providing a modulated detector output which is amplified by a tuned amplifier having a center frequency equal to the modulation frequency. Phase sensitive detectors are used to provide linear second detection and to further reduce bandwidth. Because the phase sensitive detector is linear and is designed to have a much narrower bandwidth that that of the tuned amplifier, the effective bandwidth for detection is equal to the bandwidth of the phase sensitive detector. The bandwidth of a phase sensitive detector can be made as small as desired by increasing the time constant of the r-c output network.

B. Sensitivity of Spectrometers

In comparing the sensitivity of various types of microwave receivers for use in microwave spectroscopy one must recognize the basic differences in the types of signals which are detected and amplified. In many appli-
cations the signal consists of a weak pulse of microwave power. In microwave spectroscopy the signal is in the form of a small decrement in a relatively large amount of power. A decremental signal which varies in power by the amount $\Delta P$ can be synthesized by the sum of a relatively large signal of power $P$ and weak periodic pulses which are in phase with the large signal. Let $P'$ represent the peak power of the weak pulses. It can be shown that

$$P' = \frac{(\Delta P)^2}{4P}$$

provided that $P'$ is much smaller than $P$. The problem of calculating the minimum detectable decrement of power in microwave spectroscopy then reduces to calculating the minimum detectable pulses having power $P'$. The minimum noise power, that due to Johnson noise, referred to the input of a receiver is

$$P_n = kT\Delta \nu$$

where $\Delta \nu$ is the effective bandwidth. At room temperature this becomes

$$P_n = 4 \times 10^{-21} \Delta \nu \text{ watts.}$$

If the minimum detectable signal is defined as the signal having power $P'$ equal to noise power $P_n$, the minimum detectable decrement of power is

$$\Delta P_{\text{min}} = 2 \sqrt{P \cdot P'}_{\text{min}} = 1.26 \times 10^{-12} \sqrt{P \Delta \nu} \text{ watts.}$$

If waveguide attenuation is neglected, $\Delta P$ in terms of the absorption coefficient of the gas, $\gamma$, for a cell of length $L$ is
\[ \Delta P = \gamma LP. \]

Therefore the minimum detectable absorption coefficient is

\[ \gamma_{\text{min}} = \frac{1.26 \times 10^{-10}}{L} \frac{\Delta \nu}{P}. \]

If we assume that \( \Delta \nu \) is 0.01 cps, \( P \) is \( 10^{-3} \) watt and \( L \) is 350 cm, the minimum detectable absorption coefficient is about \( 10^{-12} \)/cm. The example cited above assumed noiseless components, a very narrow but usable pass band, a somewhat higher power \( P \) than is normally used and a typical cell length. A greater cell length was not used because substantial improvement in minimum detectable absorption coefficient would result only through use of very unwieldy lengths.

Large effective lengths are theoretically obtainable by the use of cavity type absorption cells. These cells will not be discussed because we have been unable to find suitable means for applying a Stark field to a high-Q cavity.

Based on a graph given by Townes*, 95 percent of all lines measured between 20,000 and 30,000 mc have intensities less than \( 10^{-7} \)/cm. Since intensities of microwave lines increase with frequency approximately as \( \nu^3 \), equipment capable of detecting lines having absorption coefficients as weak as \( 10^{-9} \) cm should be suitable for most research down to 3000 mc. As far as we know, the weakest measured lines are from \( \mathrm{CF}_3\mathrm{I} \) and reported

by Sterzer (13). He calculated an intensity of $3.3 \times 10^{-10}$ cm for his weakest line which occurred at about $3400$ mc. Lines for the $J = 1 \rightarrow 2$ rotational transition of CFCI$_3$ being investigated under this contract have comparable intensities; they are briefly discussed in Chapter III.

C. Coherent First Detector

One of the most promising methods for detecting microwave power is the coherent first detector. This detector (2, 3) is like the superheterodyne detector with the exception that the local oscillator frequency is derived from the same source as the incoming signal. If these two signals are in phase, the equation representing detection is the same as that for the superheterodyne having an intermediate frequency of zero; the amplifier following the detecting element is tuned to the repetition frequency of the signal pulses. Richmond (12) reported minimum detectable signals of $0.5 \times 10^{-12}$ watt using X-band bolometers or crystals with a 4-cps pass band. Use of coherent first detectors represents a major step in the improvement of sensitivity over video detection techniques.

It is interesting to compare the coherent first detector with the conventional Stark modulation scheme used in spectroscopy. In Section II B we synthesized the signal out of the Stark cell with two small signals of the same frequency. Thus it can be seen that the conventional Stark system which is often referred to as a video system is in actuality a coherent first detector, simply a superheterodyne which has zero intermediate frequency. Once it is recognized that the Stark system is a superheterodyne, spectrometers can be analyzed by using known results for the superheterodyne.
D. Frequency of Stark Modulation

Stark cells are usually constructed out of standard waveguide having as large a cross-section area as practicable; this is for the purpose of minimizing power density. Reduction of power density permits higher spectrometer sensitivity because higher signal powers can be used for equal broadening of lines due to power saturation. The Stark electrode consists of a conducting sheet which is isolated from the waveguide by insulating tape. The conducting sheet runs the length of the waveguide cell and is mounted parallel to the broad side of the waveguide. Ratios of width to height of standard waveguides are approximately 2:1. For this reason the capacitance of Stark cells are not strongly dependent on waveguide size. In general the cross-sectional area of Stark cells will be increased with increase in wavelength. On this basis a larger Stark voltage will be required across the cell for a given electric field strength at a lower frequency than at a higher frequency. The higher power requirements for Stark modulators can be offset by the use of low Stark modulation frequencies. For this reason we have devoted considerable effort to the design of a sensitive spectrometer which performs well with a low modulation frequency. The bolometer detector provides an excellent means for accomplishing this task.

E. Detection Systems

1. Crystal Detector and Detector Amplifier. Crystal rectifiers are used almost exclusively for detectors of microwaves in spectroscopy. Though the rectifying properties vary from crystal to crystal, their characteristics can be roughly divided into a square-law region where the rectified
current I is proportional to P (holds for $P < 10^{-5}$ watts) and the linear region where I is proportional to $\sqrt{P}$ (holds for $P > 10^{-4}$ watts).

In spectrometers the resonance signal usually appears as a small modulation of a comparatively large carrier reaching the detector. Because of the carrier, a rectified current flows in the crystal. This current produces a frequency dependent noise which can be represented \(^{(4)}\), in the square-law region, by

$$P_n = \left(\frac{SP^2}{2} + 1\right)KDF$$

where $f$ is the frequency around which the pass band $\Delta f$ is centered and

where

$\beta = 5 \times 10^{14}$ watt$^{-2}$ sec$^{-1}$

for the type LN23C crystal. The conversion gain in the square-law region can be represented by $G = SP$ where $S$ was found for the LN23C crystal to be approximately 500 watt$^{-1}$. For signal levels such that crystal noise greatly exceeds amplifier noise, crystal noise is proportional to $P^2$. The change in power in the output of the Stark cell is proportional to $P$ and consequently, since the crystal output power is proportional to the square of the input power, the signal within the amplifier also varies as $P^2$. Thus for small variations of the input power such as is produced by gas absorption, the minimum detectable gas absorption coefficient is independent of power within the Stark cell provided this power is sufficiently large to produce crystal noise greatly exceeding amplifier noise and sufficiently small so that the crystal is operating in its square-law region.
As the carrier power reaching the detector is increased, $P_n$ increases. However when the input power is a few tenths of a milliwatt, the crystal behaves as a linear detector and, in spite of the additional noise, becomes more sensitive than it is as a square-law detector. Because of the increase in noise and increase in backward current through the crystal, the sensitivity decreases as the input power exceeds a milliwatt. From theory on superheterodyne receivers we know that the detector output voltage due to a small pulsed signal is always proportional to the incident electric field of this signal provided the large signal is much greater than the small signal. Therefore, regardless of whether the crystal is behaving as a linear detector or a square-law detector, the output voltage is proportional to $\sqrt{P}$ and consequently the output voltage of a spectrometer is always proportional to $\Delta P$ provided the system is linear beyond the first detector.

The noise power of a crystal in the linear region can be represented by (4)

$$P_n = \left( \frac{2P}{f} + 1 \right) kT\Delta f$$

where $\gamma \approx 10^{11}$ watt$^{-1}$ sec$^{-1}$ for a type LN23C crystal. The conversion gain $G$ of a type LN23C crystal in the linear region is approximately 0.3. This equation yields a noise power of $4.8 \times 10^{-18}$ watt per cycle of bandwidth at 85 kc for one milliwatt incident upon the crystal. Using the 0.3 value for conversion gain, minimum detectable $P'$ would be $16 \times 10^{-18}$ watt. The detectable decrement of power at one milliwatt level is then

$$P' = 16 \times 10^{-18} = \frac{(\Delta P)^2_{\text{min}}}{4 \times 10^{-3}}$$
\[ (\Delta P)_{\text{min}} = 2.5 \times 10^{-10} \text{w}. \]

for 1 cps bandwidth. Measurements using the Georgia Tech 85-kc spectrometer and a type 1N23B crystal indicated agreement, within experimental error, with this value of \((\Delta P)_{\text{min}}\) when normalized for a 1 cps bandwidth. This result indicates

\[ (\Delta P)_{\text{min}} = 2.4 \times 10^{-9} \text{w}. \]

with 1 cps bandwidth and a 1-kc system operating at the one milliwatt level.

The internal impedance of crystal rectifiers is of the order of thousands of ohms in the square-region and is reduced with increase in incident power. In the linear region this impedance is down to several hundred ohms. Because of the high impedance in the square-law region, input circuits for spectrometers usually have a high impedance at the modulation frequency; this is often accompanied by too-large a d-c resistance for crystal current. In order to minimize noise and conversion loss when operating in the linear region, the d-c resistance \(14\) external to the crystal should be reduced to less than 100 ohms.

2. Bolometer and Detector Amplifier. The bolometers discussed in this section are commercially available detecting elements which consist of short lengths of wire of low thermal time constants. The useful property of these elements is that resistance is a function of the amount of power absorbed. Bolometers are normally biased with direct current to an operating resistance of 200 ohms; the addition of r-f power to the element increases the element
resistance above this bias point. Analyses of detector sensitivities using bolometers are easier than for crystals because bolometer noise is essentially independent of microwave power. Theoretically the noise is that of a 200 ohm resistor at the elevated temperature, due to the bias current, of the bolometer. Based on typical sensitivities in ohms per milliwatt and an operating temperature consistent with typical temperature coefficients of expansion, and estimate of minimum detectable change in power is

$$\Delta P = 10^{-10} \sqrt{\Delta \nu} \text{ watt.}$$

Recall that the minimum $\Delta P$ for a 1-kc system using the type 1N23C crystal operating at a one milliwatt level is

$$\Delta P = 2.4 \times 10^{-9} \sqrt{\Delta \nu} \text{ watt.}$$

Because the noise from a bolometer is that of a resistance at an elevated temperature, bolometer noise is of the order of Johnson noise. For this reason low noise amplifiers are required for use with bolometers. On the other hand, the noise power of crystals at frequencies in the kilocycle region are thousands of times Johnson noise and consequently amplifier noise figure is of less importance. For the same reasons, klystron noise is of more importance when using bolometers. The above consideration is not applicable to conventional microwave superheterodyne receivers employing intermediate frequencies in the megacycle region.

A 1-kc spectrograph has been constructed for determining pitfalls associated with bolometer systems. Modulation frequencies must be low
because of bolometer thermal time constants; 1 kc is sufficiently low for most bolometers. This frequency was selected so that commercially available low-noise detector amplifiers could be employed. The work required the design and construction of a phase sensitive detector, recorder amplifier, and 1-kc Stark modulator.

Minimum detectable signals were first determined by measuring 1-kc square wave pulses from a klystron. By interchanging commercial amplifiers, differences of 15 db after normalizing to a specific bandwidth were measured for minimum detectable signals with so-called low-noise amplifiers. This was particularly disturbing because minimum detectable signal level with a square law detecting element varies as the square root of noise figure; this indicated noise figures differing by a factor of 1000. The amplifier giving the best performance was improved by using a d-c heater supply and battery bias for the bolometer. The amplifier noise figure appears to be less than 2 with this arrangement.

Minimum detectable signal with the best amplifier and many commercial bolometers was measured. The better bolometers gave minimum detectable signals corresponding to

\[ \Delta P = 4 \times 10^{-10} \sqrt{\Delta v} \]

This result is encouraging in that it provides a minimum \( \Delta P \) which is only a factor of 4 greater than the theoretical value. The results are still puzzling through, because this factor indicates noise of bolometer plus amplifier which is 16 times Johnson noise.
The next problem with the bolometer system was klystron noise; little data exist on this noise. It was found that an X-12 klystron operating at 15 kmc and delivering 2-3 milliwatts to the bolometer doubled bolometer plus amplifier noise. Comparable noise was observed with the two available X-12 klystrons. X-13 and X-13B klystrons in the 10 kmc region contributed almost negligible noise to the system when delivering 2-3 milliwatts to the bolometers.

It should be relatively simple to reduce klystron noise by connecting two bolometers in push-pull to the input of a bolometer amplifier. In this arrangement one bolometer would be connected to the absorption cell and the other would be supplied with comparable power from the klystron. The addition of the second bolometer doubles bolometer noise, but because bolometers are square detectors, minimum detector signal exclusive of klystron noise is reduced only by $\sqrt{2}$. This technique for klystron noise reduction has not been tested; consequently the practical problems associated with the criticalness of unbalance are still unknown.

3. Superheterodyne with Microwave Bridge. Initial investigations under this contract were devoted to the conventional superheterodyne receiver having an intermediate frequency in the megacycle region. The advantage of a high intermediate frequency is the reduction of crystal noise because of its $1/f$ dependence. At higher frequencies where detector power must be small to avoid molecular saturation, the superheterodyne provides a means for operating crystals at high enough power levels to obtain minimum conversion loss.

Conventional superheterodyne detection requires an auxiliary oscillator which is kept at a constant frequency difference from the signal generator.
This local oscillator may be made to follow the signal oscillator by a discriminator and automatic frequency-control system. The need for a local oscillator signal makes the superheterodyne more complicated than the simple detector using a crystal or bolometer. Moreover the local oscillator may be an additional source of noise, although most of this noise can be eliminated by the use of a balanced mixer. To reduce the carrier relative to the useful signal, a balanced bridge is required. This bridge permits the use of superheterodyne detection without overloading the intermediate frequency amplifiers and will reduce the signal oscillator noise.

Little information could be found in the literature regarding actual sensitivities that have been obtained with superheterodyne detectors in microwave spectrometers, although Townes and Schawlow do indicate (see page 492 of reference 15) that sensitivities on the order of $10^{-8}$ cm$^{-1}$ have been obtained. In pursuance of the present research, an X-band bridge was constructed and used with an existing i-f amplifier modified for the present application. The center frequency of the i-f amplifier is 140 mc and the bandwidth is 40 mc. Use of the wide bandwidth amplifier removes the need for an afo as long as searching is restricted to narrow frequency limits. The noise figure of the amplifier is 10 db; this is a large noise figure (because of transit-time effects), but it was considered suitable for indoctrination into problems associated with bridge type superheterodyne systems. The results of this work were discouraging in that the sensitivities obtained were seriously limited by available bridge stabilities and the many other complicating features of such a system. Sensitivities over short time intervals were comparable to those obtained with the 85-ke crystal system.
operating at a one milliwatt level but because of many types of instabilities the practical limit on sensitivity was less than with the 85-kc crystal system. Use of a less noisy i-f amplifier would improve the system sensitivity, but the resulting improvement would not be adequate to justify the use of the superheterodyne system. After this rather frustrating attempt to obtain high sensitivities, the work of Misra (10) on sensitivity of paramagnetic resonance spectrometers was discovered. Although it is believed that his choice of a superheterodyne system for high sensitivity was based on erroneous analyses of crystal and bolometer systems, his thesis vividly displays problems which are encountered in attempts to use this type of spectrometer. The availability of high detector powers for gaseous spectroscopy in the $\frac{1}{4}$ to $16$ kmc region through the use of absorption cells having large cross-sectional areas and the necessity for frequency tuning of the detection system makes the practical application of bridge type superheterodyne systems even more unlikely than in the field of paramagnetic resonance. One of the major problems that would have to be overcome is the development of a suitably linear second detector. This problem is serious because of the large ratio of required i-f bandwidth, because of short term local oscillator instabilities, to video bandwidth. The effective noise bandwidth for a large square-law detector is $\sqrt{f_1 f_2}$ where $f_1$ represents the intermediate frequency bandwidth and $f_2$ represents the narrow video bandwidth preceding the recorder. Conventional diode detectors when operated under optimum conditions are good linear detectors, but still some loss in effective noise bandwidth is expected.
III. MICROWAVE SPECTRUM OF FLUOROTRICHLOROMETHANE

During this report period lines for the rotational transitions $J = 1 \to 2$ and $J = 2 \to 3$ have been recorded for CFCI$_3$. Accurate measurements on the frequencies of the $J = 1 \to 2$ lines have been made with a secondary frequency standard. Two relatively strong lines which are almost equal and several smaller lines were observed. The two stronger lines were observed at 9859.44 ± 0.06 mc and 9864.20 ± 0.03 mc. Absorption coefficients of these lines appear to be of the order of $10^{-10}$/cm. Calculations are presently being made to determine the quadrupole coupling constant based on these frequencies. Frequency measurements will soon be made for the prominent features of the $J = 2 \to 3$ lines so that a centrifugal distortion constant can be evaluated; a combination of the data will provide a good estimate of the rotational constant. No previous measurements have been reported for this molecule.

A. Description of Fluorotrichloromethane

Fluorotrichloromethane is composed of three identical chlorine atoms arranged in an equilateral triangle, a carbon atom equidistant from the chlorine atoms, and a fluorine atom which is closer to the carbon than to the plane of the chlorine atoms and which is along the symmetry axis bisecting the pyramid formed by the chlorine and carbon. The chlorine atoms possess nuclear electric quadrupole moments which interact with the gradient of the average electric field of the molecule. Absorption lines are weak because the molecule has a large moment of inertia about its symmetry axis, it has a small electric dipole moment, the rotation lines are split into a
complex hyperfine structure due to nuclear interaction, and use of low frequencies is required to permit analysis of the complex hyperfine spectrum.

B. Three Equivalent Nuclei with Quadrupole Moments

The problem of three nuclei with quadrupole moments has been investigated by Bersohn (1) who obtained matrix elements for the interactions and by Mizushima and Ito (11) who used Bersohn's work to calculate the effect of quadrupole interaction for the \( J = 0 \to 1 \) rotational transition and for cases for which the three nuclei have spins of \( 1, 3/2, 2 \) and \( 5/2 \). Also, a theoretical investigation of the expected hyperfine structure of ND₃ was undertaken by Hadley (5). The first experimental work reported is that of Kojima et al (9) on bromoform in an effort to employ the theoretical calculations of Mizushima and Ito for the \( J = 0 \to 1 \) rotational transition. The spectrum reported was proved later (6) to be of spurious origin. Wolfe (16, 17) was the first person to make a valid comparison of the spectrum of a molecule with three nuclei having quadrupole moments with a calculated spectrum. Wolfe measured the \( J = 2 \to 3 \) rotational spectrum of the abundant symmetric top species of chloroform and calculated the spectrum by use of the procedure outlined by Bersohn. More recently Herrmann (7) made measurements on ND₃ and compared these with the theoretical work of Hadley.

The calculation of energies and intensities for three nuclei with quadrupole moments is laborious. For the case that Wolfe considered, \( J = 2 \to 3 \) transition and \( 3/2 \) for spin of each nucleus, hundreds of transitions are possible between the two rotational levels. Because of the large number of overlapping lines it is difficult to find the result of
superimposing the components on the basis of a reasonable physical assumption of line shape. As pointed out by Wolfe, with his assumption of rectangular shapes, the positions of prominent features can be shifted somewhat from their true values, except in cases for which one component is considerably more intense than its neighbors. A complicating feature of the analysis results because centrifugal distortion allows different pattern "centers" for the hyperfine patterns corresponding to each value of K, where \( \vec{K} \) is the component of angular momentum resolved along the symmetry axis of the molecule. Neglecting the \( K = 0 \) spectrum because only second order Stark shifting applies to this transition, \( K = 1 \) and \( K = 2 \) spectra had to be investigated. Wolfe handled this problem by shifting the relative positions of his calculated \( K = 1 \) and \( K = 2 \) patterns to obtain a best fit with his measured composite pattern. This technique provided a value for the quadrupole coupling constant and a value of the centrifugal distortion constant \( D_{JK} \).

C. Theoretical Calculations on the \( J = 1 \rightarrow 2 \) Transition

A theoretical calculation is being made using the procedure outlined by Bersohn to determine the \( J = 1 \rightarrow 2 \) rotational spectrum for nuclei of spin \( 3/2 \). There are a total of 34 energy levels for \( J = 1 \) and 82 energy levels for \( J = 2 \); because of certain selection rules and molecular symmetries, the number of energy levels are reduced to 11 for \( J = 1 \) and 16 for \( J = 2 \). For these energy levels there are a total of 104 possible transitions but many of them have small transition probabilities. The calculation of several of the energy levels and many of the intensities is delayed until a table containing certain needed Racah coefficients is found. As suggested by Dr.
M. E. Rose of Oak Ridge National Laboratory, Dr. W. T. Sharp of Chalk River Project, Ontario, Canada, has been contacted in regard to the needed coefficients.

Comparisons of the $J = 1\rightarrow 2$ measurements with the calculated spectrum should provide a direct determination of the quadrupole coupling constant for CFCl$_3$. With this coupling coefficient and a measurement of the separation between the two strongest lines in the $J = 2\rightarrow 3$ transition, the centrifugal distortion constant $D_{JK}$ can be determined. Having a value for $D_{JK}$ a good estimate of the rotational constant can then be determined through use of the $J = 1\rightarrow 2$ transition data.
IV. PROGRAM FOR FUTURE WORK

Investigations applicable to the 4 kmc to 16 kmc region on techniques for attaining high sensitivity in spectrometers will be continued. Major considerations will be devoted to means for reducing klystron noise in bolometer systems and means for increasing the effective length of absorption cells. A theoretical quadrupole spectrum for three identical nuclei with spin 3/2 will be calculated for the J = 1→2 rotational transition. This spectrum and the J = 2→3 spectrum already calculated by Dr. P. N. Wolfe will be used to analyze experimental data on CFCl3. If time permits, spectra between 4,000 mc and 10,000 mc of molecules having large absorption coefficients will be measured.

Very truly yours,

M. W. Long
Project Director

Approved:

A. L. Bennett, Chief
Physical Sciences Division
V. BIBLIOGRAPHY


March 20, 1962

Dr. Arnold Shostak
Head, Electronics Branch
Office of Naval Research
Washington 25, D. C.

Subject:  Semi-annual Status Report, Contract Nnr-991(07)
Reference: NR 372-761

Dear Dr. Shostak:

This is a status report for the period 15 September 1961 to 15 March 1962; the present contract period ends 15 September 1962. The last status report was dated 1 May 1961 and at that time the contract funds were virtually exhausted. Supplementary material to that status report was included in the 18 May 1962 letter requesting additional funds. Since additional funding was not obtained at that time, the letters adequately describe progress up to 15 September 1961. Technical Report No. 3 and three papers, the research for which was partly supported under this contract, were reproduced since preparation of the May 1961 status report. These documents are as follows:


As stated in previous correspondence, the efforts of CNR personnel on matters pertaining to my accident and to my Great Britain visit were gratefully appreciated. The visit arrangements permitted me to gather worthwhile information at the Admiralty, the Admiralty Surface Weapons Establishment and the Royal Radar Establishment on my trip which was not made at the expense of the Government. This vacation trip permitted me to spend an interesting day at the Research Division of CSF, located a short distance from Paris, on matters pertaining to the generation, detection and propagation of millimeter and submillimeter waves. Things learned at RRE and CSF substantiated my feelings on the importance of the planned work for the subject contract.

**PROGRESS SINCE 15 SEPTEMBER 1961**

Effort since 15 September 1961 has been directed toward trying to conceive of economically feasible means for making sensitivity measurements as a function of wavelength for detectors in the $4 \text{ mm}$ to $1 \text{ mm}$ region. This is a formidable task because means of measuring very low-power levels are required and coherent sources for the region are virtually nonexistent. A few low-power coherent sources are available, but they are costly and operate only over limited frequency intervals within the region of interest.

The appendix to this letter outlines the principles of operation for a new type of interference modulation device. Development of the techniques disclosed therein should represent a major step toward instrumenting for the lower millimeter and submillimeter region.
CURRENT STATUS AND FUTURE PLANS

Detailed planning is underway for the development of an interference modulation device operating in the general vicinity of 4 mm, but the techniques used will be restricted to those which can be readily extended to shorter wavelengths. This region was selected because 4-mm components and component techniques are relatively well developed; consequently, it is the only band shorter than 8 mm for which any experimental work could be accomplished with the limited budget available under the subject contract.

It is believed that the instrument depicted by Figure 1 (see appendix) can be designed, built and debugged before 15 September 1962, which is the end of the present contract period. In addition, it is hoped that the sensitivity of several detectors, such as a few crystal diodes, barretters, and a Golay cell, can be measured with the new device.

Information learned in the course of developing and operating the 4-mm instrument should be directly applicable to shorter wavelengths, and it is planned that the work will eventually be extended to the far less explored wavelengths.

Respectfully submitted,

M. W. Long, Chief
Electronics Division

M/6:ivp
Attachment
cc: Addressee
S/E Area Representative
SENSITIVITY OF DETECTORS IN LOWER MILLIMETER REGION

There are many technological difficulties associated with determining sensitivity of detectors as a function of wavelength, even for wavelengths in the well-developed part of the microwave spectrum. Little quantitative sensitivity data\(^1\) are available for the lower millimeter and submillimeter region because of severe equipment limitations. The following discussion is directed toward only the problems uniquely associated with measurements in this more difficult region. Basically, the new problems stem from the unavailability of sources of coherent radiation over a wide frequency region for which the power level must be accurately known. Even if well-developed crystal multipliers were available for supplying power for the wide spectral region under consideration, a power meter would be required which is far more sensitive than the calorimetric type\(^2\) currently used.

Another approach to the problem would be to employ the combination of a noise source and a narrow passband filter for which the center frequency could be adjusted. Though power per unit bandwidth would be small, a heated matched load of known thermometric temperature in combination with a known width of the passband would serve as a power standard. Thus, availability of an ideal, adjustable passband filter and a calibrated noise source would in principle fulfill all requisites for determining detector sensitivity as a function of frequency. Characteristics of microwave filters, even those

\(^1\)M. V. Long and W. K. Rivers, Jr., "Submillimeter Wave Radiometry", Proceedings of the IRE 49, 1024 (June 1961)

with the best of out-of-band rejection capabilities, are such that the out-
of-band energy passed through the filter would be at least comparable to the
in-band energy because of the very wide spectrum of a heated load.

INTERFERENCE MODULATION DEVICE

The fact that there is a one-to-one correspondence between mechanical
speed and the frequency of Doppler components provides an interesting new
concept\(^3\) for microwave instrumentation. Assume that the moving short in
Figure 1 could maintain a constant speed, \(v\); then an interference modulation
frequency, \(f_1\), is produced which is uniquely related to the wavelength within
the waveguide, \(\lambda_g\), by the equation

\[ f_1 = 2 \frac{v}{\lambda_g} \quad (1) \]

Thus, the tuned audio amplifier of Figure 1 would in effect serve as a pass-
band filter because its output would be proportional to only those frequency
components corresponding to \(\lambda_g\) of Equation 1. If a fixed tuned amplifier
were used with the arrangement in Figure 1, characteristics of microwave
devices could be determined as a function of frequency by simply varying the
speed of the short circuit, and the power would be known from the theromeric
load temperature and the microwave bandwidth which is controlled by the
audio bandwidth. The actual spectral purity of the Doppler components is

\(^3\)Use of the interference principle to produce the effect of a waveguide filter
was suggested as a result of discussions with W. K. Rivers, Jr. This is re-
lated to his ideas on developing a highly efficient submillimeter spectrometer
by an imaginative combination of microwave and optical techniques.
Figure 1. Interference Modulation Device
a complicated function of the reversing action of the short circuit, and
design work is currently underway to minimize signal degradation caused
by the necessity of reciprocating motion.

Power Measurements

Frequently, the power levels available in the lower millimeter region
are too low to be determined by current power-measuring techniques. One
example of a severe power level problem is that of determining the power
available at 1 mm by crystal harmonic generators driven with an 8-mm
klystron. The harmonic power might well be less than 1 microwatt.

The harmonic output could be detected by replacing the noise source
of Figure 1 with the harmonic generator. Suppose that, by comparison with
a heated load of known temperature, the harmonic generator was determined
to produce an output from the amplifier equivalent to that of a $10^6 \cdot K$ load.
The harmonic power could then be determined by simply ascertaining the
equivalent noise power contained in the bandwidth region at 1 mm which
Corresponds to the amplifier audio bandwidth. For example, with a center
frequency of 30 cps and a bandwidth of 1 cps, the equivalent r-f noise
bandwidth is 1/30 of the signal frequency, or $10^{-10}$ cps. Thus, from the
well-known relationship

$$ P = kTB = 1.38 \times 10^{-23} \, \text{TB}, $$

the power level would be

---

\[^1\] In Reference 2, Thaxter and McGowan report a minimum detectable signal of
50 microwatts with a 20-second response time for their calorimeter designed
for a somewhat lower frequency region.
\[ P = 1.38 \times 10^{-23} \times 10^6 \times 10^{10} = 0.138 \text{ microwatt} \]

This example illustrates how an interference power meter might be used for levels much smaller than those measurable by conventional techniques. Based on the use of existing detectors\(^1\), it presently seems that the minimum detectable signal for a power meter having the above parameters should be about \(10^{-3}\) microwatt for a response time of only one second.

**Measurements of Detector Sensitivity as a Function of Frequency**

In addition to the capability of the system illustrated in Figure 1 for measuring the power level of weak coherent sources, the instrument is a self-contained device for determining the sensitivity of detectors versus frequency. The great flexibility of the device should be noted along with the fact that it does not in any way require the use of a coherent source, even in the design stages, and that a power meter, per se, is never required.

Assuming audio amplifier characteristics are fixed at a center frequency of 30 cps and a bandwidth of 1 cps, r-f resolution would be equal to \(1/30\) of the center frequency. The center frequency would be determined and controlled by the velocity of the short circuit. Thus, the minimum detectable power as a function of frequency would be determined from attenuator readings and the measured (thermometer) temperature of the heated matched load.
Dr. Arnold Shostak  
Head, Electronics Branch  
Office of Naval Research  
Washington 25, D.C.

Subject: Annual Summary Report on Contract NONR-991(07)  
Reference: NR 372-731

Dear Dr. Shostak:

This letter reviews progress for the period 16 September 1961 through 15 September 1962; the last status report was dated 20 March 1962. In addition, progress for much of the report period was thoroughly outlined in a letter dated 21 August 1962 which requested an extension of the subject contract; a formal reply to the 21 August letter has not as yet been received.

During the report period, the following articles resulting from research under the subject contract were published:


R. C. Johnson, T. L. Weatherly, and G. Williams, "Dipole Moment of CClF_3", Journal of Chemical Physics 33, 2261 (December 1961)

I. RESEARCH RESULTS SINCE 15 SEPTEMBER 1961

Effort began on 15 September 1961 in trying to conceive of an economically feasible means for making sensitivity measurements as a function of wavelength for detectors in the 4-ma to 1-ma region. This was a formidable task because means of measuring very low-power levels are required, and coherent sources for the region are virtually nonexistent. A few low-power coherent sources are available, but they are costly and operate only over limited frequency intervals within the region of interest. Because of this, many tubes would be required, and those available would provide only partial coverage of the 4-ma to 1-ma region.

The novel techniques developed permitted the construction and operation of a very flexible interference modulation device which is, in essence, a continuously tunable, electromechanical, band-pass filter. An experimental device has already been successfully operated throughout the very wide frequency range of 50 kmc to 90 kmc.
Preliminary results obtained with the new instrument were thoroughly outlined in the 21 August 1962 letter requesting extension of the subject contract. Since preparation of that letter, the techniques conceived for determining the sensitivity of detectors and for determining the power of weak coherent sources have been refined. The more recent work has substantiated the fact that the interference device provides a convenient means for determining absolute values for detector sensitivity, but further effort is required before the device will serve as a simple means for determining the power of very low energy sources. Recent work has also included theoretical and experimental studies on the effects of higher order waveguide modes on system accuracy. Indications are that these effects will be negligible when waveguide mounted detectors are employed.

II. CURRENT STATUS AND FUTURE PLANS

The interference device will be described in a paper on 8 January 1963 at the "Millimeter and Submillimeter Conference" to be held in Orlando, Florida. A written version of the paper will be prepared as a technical report for the subject contract.

As soon as additional funding is received, effort will be directed toward developing a technique which will enable the interference device to be used as a convenient means for determining power of weak coherent sources. Measurements will also be continued on determining the absolute sensitivity of detectors. After completion of this work, the research program will be directed toward the development of a system which will extend operation to frequencies above 90 mc.

Respectfully submitted,

R. W. Long, Chief
Electronics Division

MML:wp
cc: Addressee
S/E Area Representative

bcc: GTRI
Library (2)
A-330 File
Sensitivity of Microwave Spectrometers and Hyperfine Spectra of CFCl₃

DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH
CONTRACT NO. N0AR-991 (07)

15 June 1959

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia
SENSITIVITY OF MICROWAVE SPECTROMETERS AND HYPERFINE SPECTRA OF CFCl₃

by

M. W. Long

Department of the Navy
Office of Naval Research
Contract No. N0nr-991 (07)

15 June 1959
ACKNOWLEDGEMENTS

The work reported here is the result of the contributions of several people at the Georgia Institute of Technology. The experience of Dr. J. Q. Williams with spectroscopy and his adept ability with experimental physics were invaluable. The author is greatly indebted to Dr. Williams for his contributions as thesis adviser. Dr. T. L. Weatherly assisted greatly with the problem of nuclear quadrupole interactions and other theoretical aspects of molecular phenomena. The work of Mr. E. R. Flynt on many of the electronic instrumentation problems was also significant to the success of the program.

This report also constitutes a thesis presented to the Georgia Institute of Technology by Maurice W. Long in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics. Reproduction in whole or in part is permitted for any purpose of the United States Government.

Submitted: 

Approved:

M. W. Long / Project Director
A. L. Bennett, Chief
Physical Sciences Division

Approved:

J. E. Boyd, Director
Engineering Experiment Station
ABSTRACT

Comparisons based on theoretical and experimental investigations are made on the following detection systems for use with Stark spectrographs: crystal diodes and tuned amplifiers, bolometers and tuned amplifiers, and superheterodynes in conjunction with a microwave bridge. Equipment modifications are described which provide improved sensitivity for detecting small decrements in a relatively large amount of power; the modified equipment is sensitive to signal changes of one part in $10^{10}$. Absorption lines at X-band having a calculated absorption coefficient at room temperature of $4 \times 10^{-11}$ cm$^{-1}$ were measured. It is believed that these are the weakest lines ever reported.

A theoretical calculation is made for the hyperfine structure of the $J=1 \rightarrow 2$ rotational transition for symmetric top molecules having three identical nuclei of spin $3/2$. This calculation is used to analyze the CFCl$_3^{35}$ transition at 9.86 km/m, and provides the quadrupole coupling constant with respect to the molecular symmetry axis. Frequencies of the most intense lines in the $J=1 \rightarrow 2$ transitions for CFCl$_3^{35}$ and CFCl$_2^{35}$Cl$_{37}$ are used to determine the molecular structure of CFCl$_3$. The work on nuclear electric quadrupole interaction is used to assist with analysis of higher rotational transitions which were measured. This analysis indicates that the centrifugal distortion constant $D_J$ is negative and changes with $J$. Previous investigations for other molecules had yielded only positive values for $D_J$, and some authors have surmised that this parameter is a positive constant.
TABLE OF CONTENTS

ACKNOWLEDGEMENTS .................................................. 11
ABSTRACT ........................................................................... iii
LIST OF TABLES ................................................................. vi
LIST OF ILLUSTRATIONS ................................................ vii

Chapter

I. INTRODUCTION ............................................................. 1

II. INSTRUMENTATION ...................................................... 4

   Sensitivity of Spectrometers ........................................... 4

   Detection Systems ....................................................... 8

      Crystal Detector and Amplifier ................................... 8

      Bolometer and Amplifier ........................................... 11

      Superheterodyne with Microwave Bridge .................... 14

      Results on Detection Systems .................................. 16

   Experimental Techniques Used to Investigate Fluorotrichloromethane ........................................ 18

III. MICROWAVE SPECTRUM OF FLUOROTRICHLOROMETHANE .................................................. 23

   Description of Fluorotrichloromethane .......................... 23

   Molecular Rotation Theory ............................................ 25

      Symmetric Rotor ...................................................... 25

      Asymmetric Rotor ................................................... 27

   Structure of Fluorotrichloromethane ............................ 31

   Nuclear Quadrupole Interaction Theory .......................... 35

   Calculations for the $J = 1 \rightarrow 2$ Quadrupole Interaction Spectrum ............................................. 43
# TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental Results</td>
<td>47</td>
</tr>
<tr>
<td>$J = 1 \rightarrow 2$ Spectrum</td>
<td>50</td>
</tr>
<tr>
<td>$J = 2 \rightarrow 3$ Spectrum</td>
<td>56</td>
</tr>
<tr>
<td>Other Rotational Transitions</td>
<td>66</td>
</tr>
<tr>
<td>Quadrupole Coupling Constant</td>
<td>71</td>
</tr>
<tr>
<td>Discussion of Results</td>
<td>75</td>
</tr>
</tbody>
</table>

**IV. CONCLUSIONS** ........................................... 79

**V. RECOMMENDATIONS** ........................................ 82

**APPENDICES**

A. **DERIVATION FOR ADDITION OF TWO IN-PHASE WAVES** . . . . . . . 84

B. **CORRECTION TO MOMENTS OF INERTIA FOR SPECIES II** ........... 86

C. **RACAH COEFFICIENTS** ....................................... 88

D. **CALCULATIONS FOR $J = 1 \rightarrow 2$ TRANSITION** ........ 90

E. **PREDICTED PROMINENCES FOR $J = 2 \rightarrow 3$ TRANSITION** .. 98

**BIBLIOGRAPHY** ................................................ 101
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Symmetry Properties of the Asymmetric Rotor Energy Levels</td>
<td>26</td>
</tr>
<tr>
<td>2.</td>
<td>Observed and Predicted J = 1→2 Transitions in Fluorotrichloromethane</td>
<td>31</td>
</tr>
<tr>
<td>3.</td>
<td>Observed and Calculated Features of the J = 1→2 Hyperfine Spectrum</td>
<td>54</td>
</tr>
<tr>
<td>4.</td>
<td>Observed and Calculated Features of the J = 2→3 Hyperfine Spectrum</td>
<td>61</td>
</tr>
<tr>
<td>5.</td>
<td>Frequencies for the Strongest Line in Various Spectra</td>
<td>69</td>
</tr>
<tr>
<td>6.</td>
<td>The Quadrupole Coupling Constant of Cl(^{35}) in the Methyl Chlorides.</td>
<td>72</td>
</tr>
<tr>
<td>7.</td>
<td>Various Chloroform Lines</td>
<td>74</td>
</tr>
<tr>
<td>8.</td>
<td>Matrix Elements for J = 1</td>
<td>91</td>
</tr>
<tr>
<td>9.</td>
<td>J = 1, K = 1 Eigenvalues</td>
<td>92</td>
</tr>
<tr>
<td>10.</td>
<td>J = 2, K = 1 Eigenvalues</td>
<td>93</td>
</tr>
<tr>
<td>11.</td>
<td>Intensity Factors for J = 1→2, K = 1</td>
<td>94</td>
</tr>
<tr>
<td>12.</td>
<td>Racah Coefficients Needed for Intensities</td>
<td>95</td>
</tr>
<tr>
<td>13.</td>
<td>Calculated Spectrum, J = 1→2, K = 1</td>
<td>96</td>
</tr>
<tr>
<td>14.</td>
<td>Predicted Prominences for J = 2→3, K = 1</td>
<td>99</td>
</tr>
<tr>
<td>15.</td>
<td>Predicted Prominences for J = 2→3, K = 2</td>
<td>100</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>The Fluorotrichloromethane Molecule.</td>
<td>24</td>
</tr>
<tr>
<td>2.</td>
<td>Graphical Description of Secular Determinants for J = 1 and for J = 2.</td>
<td>44</td>
</tr>
<tr>
<td>3.</td>
<td>Predicted Quadrupole Interaction Spectrum for J = 1→2 Transition</td>
<td>48</td>
</tr>
<tr>
<td>4.</td>
<td>J = 1→2 Transition in CFCl$_3^{35}$ at 60 µ Pressure</td>
<td>51</td>
</tr>
<tr>
<td>5.</td>
<td>J = 1→2 Transition in CFCl$_3^{35}$ at 25 µ Pressure</td>
<td>52</td>
</tr>
<tr>
<td>6.</td>
<td>Predicted Hyperfine Pattern, J = 2→3, K = 1</td>
<td>58</td>
</tr>
<tr>
<td>7.</td>
<td>Predicted Hyperfine Pattern, J = 2→3, K = 2</td>
<td>59</td>
</tr>
<tr>
<td>8.</td>
<td>J = 2→3 Transition in CFCl$_3^{35}$ at 20 µ Pressure</td>
<td>60</td>
</tr>
<tr>
<td>9.</td>
<td>J = 2→3 Transition in CFCl$_3^{35}$ at 75 µ Pressure</td>
<td>63</td>
</tr>
<tr>
<td>10.</td>
<td>Observed and Calculated Features of the J = 2→3 Transition in CFCl$_3^{35}$</td>
<td>67</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

A theoretical and experimental investigation was made on the abundant symmetric top species of fluorotrichloromethane (CFCl₃). The rotational absorption lines for this molecule are very weak because the molecular dipole moment is small and because lines are split by interaction of the quadrupole moments of the three chlorine nuclei with the gradient of the electric field of the molecule. The molecular hyperfine spectra due to this interaction are very complex; the complexity increases rapidly with increase in the angular-momentum quantum number, J. For this reason the spectrum was investigated at the lowest practical frequency because of the complexity of the hyperfine structure, even though line strengths decrease rapidly with frequency. For the reasons stated above a spectrograph having optimum sensitivity was a primary objective.

Theoretical and experimental research which was devoted to the determination of optimum equipment sensitivities is discussed. Spectrographic equipment is described which was developed for operation between 8,000 mc and 18,000 mc. Little gaseous spectroscopy has been performed at these frequencies because spectroscopists have been able to find all molecular phenomena of interest at higher frequencies where line strengths are large. Use of measured sensitivity of the developed spectrograph was made to compare calculated absorption coefficients with measured values. To the best of the writer's knowledge this investigation has disclosed weaker absorption lines than ever previously reported.
A theoretical and experimental investigation of the most abundant symmetric top species of fluorotrichloromethane is discussed. No microwave data have been previously reported for this molecule. The hyperfine structure has been critically analyzed for the $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ transitions. The spectra occur at 9.86 kmc and 14.79 kmc, respectively. The theoretical calculation for the $J = 1 \rightarrow 2$ spectrum follows Bersohn's theory for nuclear quadrupole interaction and is similar to the work of Wolfe for the $J = 2 \rightarrow 3$ hyperfine spectrum of chloroform. The calculation results in 11 energy levels for $J = 1$ and 16 for $J = 2$; there are 99 possible transitions. The $J = 2 \rightarrow 3$ spectrum was compared with Wolfe's calculations. This work gives the quadrupole coupling constant with respect to the molecular symmetry axis, $eQV_{zz}$, and a centrifugal distortion constant, $D_{JK}$. Use of higher rotational transitions was made to assist in the analysis of the $J = 2 \rightarrow 3$ transition for fluorotrichloromethane which was particularly complex because of interference of Stark components with the hyperfine structure. The $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ data for $K = 1$ lines indicate that $D_J$ is negative. Frequencies for the rotational transitions $J = 3 \rightarrow 4$ through $J = 6 \rightarrow 7$ were experimentally determined. These data indicated that $D_J$ changes with $J$; they also indicated that $D_J$ is negative. Previous investigations for other molecules have yielded only constant positive values for $D_J$. The rotational constant, $B$, was determined by a least squares fit of $J = 1 \rightarrow 2$ through $J = 6 \rightarrow 7$ data and the value of $D_{JK}$ obtained from the $J = 2 \rightarrow 3$ analysis.

Frequencies of the most intense lines in the $J = 1 \rightarrow 2$ transitions for $\text{CFCl}_3^{35}$ and $\text{CFCl}_2^{35}\text{Cl}^{37}$ were used to determine the molecular structure of $\text{CFCl}_3$. The data were analyzed by assuming these two molecular species to be rigid rotors.
The quadrupole coupling constant with respect to the C-Cl bond axis, $eQ_{aa}$, was calculated under the assumption that extranuclear charge is symmetric about the bond axis. This coupling constant is compared with those obtained from previous investigations for other methyl chlorides in gases and in solids. The calculated value for CFCI$_3$ appears too large in comparison with the other data. The only other molecule with three nuclei of spin 3/2 for which $eQ_{aa}$ has been previously determined is CHCI$_3$; this was determined by Wolfe from $J = 2 \rightarrow 3$ data. The $J = 1 \rightarrow 2$ hyperfine spectrum of CHCI$_3$ was examined in the present investigation; this investigation indicated a large quadrupole coupling constant which is only slightly smaller than the value obtained for CFCI$_3$. From a review of Wolfe's data and CHCI$_3$ data for other rotational transitions, it appears that this value of $eQ_{aa}$ for CHCI$_3$, obtained in the present investigation, is also applicable to the $J = 2 \rightarrow 3$ transition. This analysis indicated that $D_J$ is also negative for CHCI$_3$ and that the magnitude depends on $J$.

Since the details of the measured $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ hyperfine spectra match the predicted spectra, the large values of $eQ_{aa}$ obtained for CFCI$_3$ and CHCI$_3$ indicate one of the following difficulties: (1) the quadrupole interaction theory is in error by a multiplicative factor, or (2) the usual assumption of charge symmetry about the C-Cl bond is not valid for the case of three nuclei. Existence of an error in the quadrupole coupling theory might also explain large values of $D_{JK}$, negative values of $D_J$, and dependence of $D_J$ on $J$. 
CHAPTER II

INSTRUMENTATION

Conventional microwave spectrometers consist of a klystron, a waveguide which contains the molecules under investigation, and a video detector. The klystron is slowly swept in frequency and the detector output is recorded so as to provide molecular absorption as a function of frequency. The waveguide is constructed so that a voltage can be applied which subjects the molecules to an electric field, thereby causing splitting and shifting of absorption lines by the Stark effect. Hughes and Wilson (1) were the first to introduce the idea of using Stark modulation. The Stark modulation frequency most often used is 6 kc and is almost always between 1 kc and 100 kc. Absorption by the gas is modulated by this technique; this provides a modulated detector output which is amplified by a tuned amplifier having a center frequency equal to the modulation frequency. A phase sensitive detector is used to provide linear second detection and to further reduce bandwidth. Because the phase sensitive detector is linear and is designed to have a much narrower bandwidth than that of the tuned amplifier, the effective bandwidth for detection is equal to the bandwidth of the phase sensitive detector. The bandwidth of a phase sensitive detector can be made as small as desired by increasing the time constant of the RC output network.

Sensitivity of Spectrometers

In comparing the sensitivity of various types of microwave receivers for use in microwave spectroscopy one must recognize the basic
differences in the types of signals which are detected and amplified. In many applications the signal consists of a weak pulse of microwave power. In microwave spectroscopy the signal is in the form of a small decrement in a relatively large amount of power. A decremental signal which varies in power by the amount $\Delta P$ can be represented as the sum of a relatively large signal of power $P$ and weak periodic pulses of power $P'$ which are in phase with the large signal. Let $P'$ represent the peak power of the weak pulses. The derivation in Appendix A shows that

$$P' = \frac{(\Delta P)^2}{4P}$$

provided that $P'$ is much smaller than $P$. The problem of calculating the minimum detectable decrement of power in microwave spectroscopy can then be accomplished by calculating the minimum detectable pulses having power $P'$. The minimum noise power, that due to Johnson noise, referred to the input of a receiver is

$$P_n = kT\Delta v$$

where $\Delta v$ is the effective bandwidth. At room temperature this becomes

$$P_n = \frac{k}{4} \times 10^{-21} \Delta v \text{ watts.}$$

If the minimum detectable signal is defined as the signal having power $P'$ equal to noise power $P_n$, the minimum detectable decrement of power is

$$\Delta P_{\min} = 2\sqrt{P P'_{\min}} = 1.26 \times 10^{-10} \sqrt{P'\Delta v} \text{ watts.}$$
\( \Delta P \) in terms of the absorption coefficient of the gas, \( \gamma \), for a cell length \( L \) can be approximated as

\[
\Delta P = \gamma LP.
\]

Therefore the minimum detectable absorption coefficient is

\[
\gamma_{\text{min}} = \frac{1.26 \times 10^{-10}}{\sqrt{L/P}} \sqrt{\Delta \nu}.
\]

Under the assumption that \( \Delta \nu \) is 0.01 cps, \( P \) is \( 10^{-3} \) watt and \( L \) is 350 cm, the minimum detectable absorption coefficient is about \( 10^{-12} \) cm\(^{-1}\). The example cited above assumed noiseless components, a very narrow but usable pass band, a somewhat higher power \( P \) than is normally used and a typical cell length. A greater cell length was not used because substantial improvement in minimum detectable absorption coefficient would result only through use of very unwieldy lengths. The above equations show the well-known fact that any sensitivity is available if one is willing to restrict \( \Delta \nu \) to a small enough value. This means that the response time of the system must become very long and the data-taking time accordingly lengthened.

Large effective lengths are theoretically obtainable by the use of cavity type absorption cells (2). These cells are not discussed because a suitable means for applying a Stark field to a high-\( Q \) cavity was not found.

Based on a graph given by Townes and Schawlow (3), 95 percent of all lines reported between 20,000 and 30,000 mc have intensities greater than \( 10^{-7} \) cm\(^{-1}\). Since intensities of microwave lines increase with fre-
quency approximately as \( v^3 \), equipment capable of detecting lines having absorption coefficients as weak as \( 10^{-9} \text{ cm}^{-1} \) should be suitable for most research down to 3000 mc. As far as we know, the weakest line measured prior to this research is from \( \text{CF}_3\text{I} \) and reported by Sterzer (4). He calculated an intensity at room temperature of \( 3.3 \times 10^{-10} \text{cm}^{-1} \) for his weakest line which occurred at about 3400 mc. The weakest line reported in this investigation for the \( J = 1 \rightarrow 2 \) rotational transition of \( \text{CFCl}_3 \) has a calculated intensity at room temperature of less than \( 10^{-10} \text{cm}^{-1} \).

One of the most promising methods for detecting microwave power is the coherent first detector. This detector (5, 6) is like the superheterodyne detector with the exception that the local oscillator frequency is derived from the same source as the incoming signal. If these two signals are in phase, the equation representing detection is the same as that for the superheterodyne having an intermediate frequency of zero; the amplifier following the detecting element is tuned to the repetition frequency of the signal pulses. Richmond (7) reported minimum detectable signals of \( 0.5 \times 10^{-12} \text{ watt} \) using X-band bolometers or crystals with a 4-cps pass band. Use of coherent first detectors represents a major step in the improvement of sensitivity over video detection techniques.

It is interesting to compare the coherent first detector with the conventional Stark modulation scheme used in spectroscopy. The signal out of the Stark cell is represented in Appendix A as two signals of the same frequency. Thus it can be seen that the conventional Stark system which is often referred to as a video system is in actuality a coherent first detector, simply a superheterodyne which has zero intermediate
frequency. Once it is recognized that the Stark system is a superheterodyne, spectrometers can be analyzed by using known results for the superheterodyne.

Stark cells are usually constructed out of standard waveguide having as large a cross-section area as practicable; this is for the purpose of minimizing power density. Reduction of power density permits higher spectrometer sensitivity because higher signal powers can be used for equal broadening of lines due to power saturation. The Stark electrode consists of a conducting sheet which is isolated from the waveguide by insulating tape. The conducting sheet runs the length of the waveguide cell and is mounted parallel to the broad side of the waveguide. Ratios of width to height of standard waveguides are approximately 2:1. For this reason Stark-cell capacitance is not strongly dependent on waveguide size. In general the cross-sectional area of Stark cells will be increased with increase in wavelength. On this basis a larger Stark voltage will be required across the cell for a given electric field strength at a lower frequency than at a higher frequency. The higher power requirements for Stark modulators can be offset by the use of low Stark modulation frequencies. The bolometer detector provides a sensitive means for using low modulation frequencies.

Detection Systems

Crystal Detector and Amplifier.--Crystal rectifiers are used almost exclusively for detectors of microwaves in spectroscopy. Though the rectifying properties vary from crystal to crystal, their characteristics can be roughly divided into a square-law region where the rectified current $I$ is proportional to $P$ (holds for $P < 10^{-5}$ watts) and the linear
region where $I$ is proportional to $\sqrt{P}$ (holds for $P > 10^{-4}$ watts).

In spectrometers the resonance signal usually appears as a small modulation of a comparatively large carrier reaching the detector. Because of the carrier, a rectified current flows in the crystal. This current produces a frequency dependent noise which can be represented (8), in the square-law region, by

$$P_n = \left( \frac{\beta P^2}{f} + 1 \right) kT \Delta \nu$$

where $f$ is the frequency around which the pass band $\Delta \nu$ is centered and where

$$\beta \approx 5 \times 10^{14} \text{ watt}^{-2} \text{ sec}^{-1}$$

for the type 1N23C crystal. The conversion gain in the square-law region can be represented by $G = SP$ where $S$ was found for the 1N23C crystal to be approximately 500 watt$^{-1}$. For signal levels such that crystal noise greatly exceeds amplifier noise, crystal noise is proportional to $P^2$. The change in power in the output of the Stark cell is proportional to $P$ and consequently, since the crystal output power is proportional to the square of the input power, the signal within the amplifier also varies as $P^2$. Thus for small variations of the input power such as is produced by gas absorption, the minimum detectable gas absorption coefficient is independent of power within the Stark cell provided this power is sufficiently large to produce crystal noise greatly exceeding amplifier noise and sufficiently small so that the crystal is operating in its square-law region.
As the carrier power reaching the detector is increased, $P_n$ increases. However when the input power is a few tenths of a milliwatt, the crystal behaves as a linear detector and, in spite of the additional noise, becomes more sensitive than it is as a square-law detector. Because of the increase in noise and increase in backward current through the crystal, the sensitivity decreases as the input power exceeds a few milliwatts. From the theory of superheterodyne receivers it is known that the detector output voltage due to a small pulsed signal is always proportional to the incident electric field of this signal provided the large signal is much greater than the small signal. Therefore, regardless of whether the crystal is behaving as a linear detector or a square-law detector, the output voltage is proportional to $\sqrt{P}$ and consequently the output voltage of a spectrometer is always proportional to $\Delta P$ provided the system is linear beyond the first detector.

The noise power of a crystal in the linear region can be represented by (8)

$$P_n = (\gamma P + 1)kT\Delta v$$

where $\gamma \approx 10^{11}$ watt$^{-1}$ sec$^{-1}$ for a type LN23C crystal. The conversion gain $G$ of a type LN23C crystal in the linear region is approximately 0.3. This equation yields a noise power of $4.8 \times 10^{-18}$ watt per cycle of bandwidth at 85 kc for one milliwatt incident upon the crystal. Using the value of 0.3 for conversion gain, minimum detectable $P'$ is $16 \times 10^{-18}$ watt. The detectable decrement of power at one milliwatt level is then
\[ P' = 16 \times 10^{-18} = \frac{(\Delta P)^2_{\text{min}}}{4 \times 10^{-3}} \]

or

\[ (\Delta P)^2_{\text{min}} = 2.5 \times 10^{-10} \text{ w} \]

for 1 cps bandwidth. Measurements using the Georgia Institute of Technology 85-kc spectrometer and a type 1N23E crystal indicated agreement, within experimental error, with this value of \((\Delta P)^2_{\text{min}}\) when normalized for 1 cps bandwidth. This result indicates

\[ (\Delta P)^2_{\text{min}} = 2.4 \times 10^{-8} \text{ w} \]

with 1 cps bandwidth and a 1-kc system operating at the one milliwatt level.

The internal impedance of crystal rectifiers is of the order of thousands of ohms in the square-region and is reduced with increase in incident power. In the linear region this impedance is down to several hundred ohms. Because of the high impedance in the square-law region, input circuits for spectrometers usually have a high impedance at the modulation frequency; this is often accompanied by too-large a d-c resistance for crystal current. In order to minimize noise and conversion loss when operating in the linear region, the d-c resistance (9) external to the crystal should be reduced to less than 100 ohms.

Bolometer and Amplifier.--The bolometers discussed in this section are commercially available detecting elements which consist of short lengths
of wire of low thermal time constants. The useful property of these elements is that resistance is a function of the amount of power absorbed. Bolometers are normally biased with direct current to an operating resistance of 200 ohms; the addition of r-f power to the element increases the element resistance above this bias point. Analyses of detector sensitivities using bolometers are easier than for crystals because bolometer noise is essentially independent of microwave power. Theoretically the noise is that of a 200 ohm resistor at the elevated temperature, due to the bias current, of the bolometer. Based on typical sensitivities in ohms per milliwatt and an operating temperature consistent with typical temperature coefficients of expansion, an estimate (10) of minimum detectable change in power is

$$\Delta P = 10^{-10} \sqrt{\Delta \nu} \text{ watt.}$$

Recall that the minimum $\Delta P$ for a 1-kc system using the type LN23C crystal operating at a one milliwatt level is

$$\Delta P = 2.4 \times 10^{-8} \sqrt{\Delta \nu} \text{ watt.}$$

Because the noise from a bolometer is that of a resistance at an elevated temperature, bolometer noise is of the order of Johnson noise. For this reason low noise amplifiers are required for use with bolometers. On the other hand, the noise power of crystals at frequencies in the kilocycle region is thousands of times Johnson noise and consequently amplifier noise figure is of less importance. For the same reasons, klystron noise is of more importance when using bolometers. The above considera-
tion is not applicable to conventional microwave superheterodyne receivers employing intermediate frequencies in the megacycle region.

A 1-kc spectrograph has been constructed for determining pitfalls associated with bolometer systems. Modulation frequencies must be low because of bolometer thermal time constants; 1 kc is sufficiently low for most bolometers. This frequency was selected so that commercially available low-noise detector amplifiers could be employed. The work required the design and construction of a phase sensitive detector, recorder amplifier, and 1-kc Stark modulator.

Minimum detectable signals were first determined by measuring 1-kc square wave pulses from a klystron. By interchanging commercial amplifiers, differences of 15 db after normalizing to a specific bandwidth were measured for minimum detectable signals with so-called low-noise amplifiers. This was particularly disturbing because minimum detectable signal level with a square law detecting element varies as the square root of noise figure; this indicated noise figures differing by a factor of 1000. The amplifier giving the best performance was improved by using a d-c heater supply and battery bias for the bolometer. The amplifier noise figure appears to be less than 2 with this arrangement.

Minimum detectable signal with the best amplifier and many commercial bolometers was measured. The better bolometers, Narda type N-610B, gave minimum detectable signals corresponding to

\[ \Delta P = 4 \times 10^{-10} \sqrt{\Delta f}. \]

This result is encouraging in that it provides a minimum \( \Delta P \) which is only a factor of 4 greater than the theoretical value.
The next problem with the bolometer system was klystron noise; little data exist on this noise. It was found that an X-12 klystron operating at 15 kmc and delivering 2-3 milliwatts to the bolometer doubled bolometer plus amplifier noise. Comparable noise was observed with the two available X-12 klystrons. X-13 and X-13B klystrons in the 10 kmc region contributed almost negligible noise to the system when delivering 2-3 milliwatts to the bolometers.

**Superheterodyne with Microwave Bridge.**--Initial investigations on equipment sensitivity were devoted to the conventional superheterodyne receiver having an intermediate frequency in the megacycle region. The advantage of a high intermediate frequency is the reduction of crystal noise because of its f⁻¹ dependence. At higher frequencies where detector power must be small to avoid molecular saturation, the superheterodyne provides a means for operating crystals at high enough power levels to obtain minimum conversion loss.

Conventional superheterodyne detection requires an auxiliary oscillator which is kept at a constant frequency difference from the signal generator. This local oscillator may be made to follow the signal oscillator by a discriminator and automatic frequency-control system. The need for a local oscillator signal makes the superheterodyne more complicated than the simple detector using a crystal or bolometer. Moreover the local oscillator may be an additional source of noise, although most of this noise can be eliminated by the use of a balanced mixer. To reduce the carrier relative to the useful signal, a balanced bridge is required. This bridge permits the use of superheterodyne detection without overloading the intermediate frequency amplifiers and will reduce the signal oscillator noise.
Little information could be found in the literature regarding actual sensitivities that have been obtained with superheterodyne detectors in microwave spectrometers, although Townes and Schawlow do indicate (11) that sensitivities on the order of $10^{-9} \text{ cm}^{-1}$ have been obtained. In pursuance of the present research, an X-band bridge was constructed and used with an existing i-f amplifier modified for the present application. The center frequency of the i-f amplifier is 140 mc and the bandwidth is 40 mc. Use of the wide bandwidth amplifier removes the need for an afc as long as searching is restricted to narrow frequency limits. The noise figure of the amplifier is 10 db; this is a large noise figure, but it was considered suitable for indoctrination into problems associated with bridge type superheterodyne systems. Results of this work were discouraging in that the sensitivities obtained were seriously limited by available bridge stabilities and the many other complicating features of such a system. Sensitivities over short time intervals were comparable to those obtained with the 85-kc crystal system operating at a one milliwatt level but because of many types of instabilities the practical limit on sensitivity was less than with the 85-kc crystal system. Use of a less noisy i-f amplifier would improve the system sensitivity, but the resulting improvement would not be adequate to justify the use of the superheterodyne system. After this rather frustrating attempt to obtain high sensitivities, the work of Misra (12) on sensitivity of paramagnetic resonance spectrometers was discovered. Although it is believed that his choice of a superheterodyne system for high sensitivity was based on erroneous analyses of
crystal and bolometer systems, his thesis vividly displays problems which are encountered in attempts to use this type of spectrometer. The availability of high detector powers for gaseous spectroscopy in the 4 to 16 kmc region through the use of absorption cells having large cross-sectional areas and the necessity for frequency tuning of the detection system makes the practical application of bridge type superheterodyne systems even more unlikely than in the field of paramagnetic resonance. One of the major problems that would have to be overcome is the development of a suitably linear second detector. This problem is serious because of the large ratio of required i-f bandwidth, because of short term local oscillator instabilities, to video bandwidth. The effective noise bandwidth for a square-law detector is $\sqrt{f_1 f_2}$, where $f_1$ represents the intermediate frequency and $f_2$ represents the narrow video bandwidth preceding the recorder. Conventional diode detectors when operated under optimum conditions are good linear detectors, but still some loss in effective noise bandwidth is expected because of the large ratio of $f_1$ to $f_2$ required.

**Results on Detection Systems.**--Based on a pass band of one cycle per second, a spectrograph employing noiseless components, an ideal second detector, and a Stark cell of reasonable length would have a noise level corresponding to an absorption coefficient of $10^{-11}$ cm$^{-1}$. Analysis shows that the conventional Stark spectrograph introduced by Hughes and Wilson in 1947 is equivalent to the coherent first detector. This detector, which is analogous to the superheterodyne having an intermediate frequency of zero, is today considered to be one of the most promising methods for detecting microwave power.
Because of the similarity of the Stark spectrograph to the superheterodyne, greatest sensitivity can be achieved with crystal diodes and bolometers if operated at higher microwave power levels than is usually used with spectrographs. At these power levels, a Stark cell having a large cross-sectional area is required to prevent molecular saturation. The noise power of crystal diode detectors varies inversely with Stark modulation frequency. The measured noise level of an 85-kc Stark spectrograph operated in this manner corresponds to an absorption coefficient of $6 \times 10^{-10}$ cm$^{-1}$ for a one cycle per second pass band. Under similar operating conditions but with a 1,000 cps modulation frequency, the best sensitivity obtained with a bolometer system corresponds to an absorption coefficient of $10^{-9}$ cm$^{-1}$.

In general greater Stark modulator power is required at the lower microwave frequencies to provide comparable Stark fields because larger waveguide is used. The higher power requirements for Stark modulators can be offset by the use of the low Stark modulation frequencies suitable for bolometers. Based on the $1/f$ dependence of noise power for crystal diodes, the noise level of a crystal diode system operating with a 1,000 cps modulation frequency is expected to have a noise level corresponding to an absorption coefficient of $6 \times 10^{-9}$ cm$^{-1}$ for a one cycle per second pass band.

The superheterodyne detector with intermediate frequency in the megacycle region provides a means for reducing crystal noise because of the $1/f$ dependence. Conventional superheterodyne detection requires an auxiliary oscillator which is kept at a constant frequency difference
from the signal generator. The need for such a local oscillator signal makes the superheterodyne more complicated than the simple detector using a crystal or bolometer. Moreover the local oscillator may be an additional source of noise, although most of this noise can be eliminated by the use of a balanced mixer. Also, a balanced microwave bridge is required to reduce the carrier relative to the useful signal. The instabilities and sources of noise introduced from the additional components substantially limit system performance. Under the most suitable conditions, measured sensitivities never exceeded the value obtained with the simple crystal and tuned amplifier operating at 85 kc. The superheterodyne in conjunction with the microwave bridge does, however, provide a means for operating crystals at high enough power levels to obtain minimum conversion loss without subjecting the sample molecules to high power levels.

Ninety-five percent of all lines reported between 20,000 and 30,000 mc have intensities greater than $10^{-7}$ cm$^{-1}$. Since intensities of microwave lines vary with frequency approximately as frequency cubed, equipment capable of detecting lines having absorption coefficients as weak as $10^{-9}$ cm$^{-1}$ should be suitable for most research down to 3,000 mc. A simple crystal diode system was used in this research to measure very weak absorption lines which occur at about 9850 mc; the absorption coefficients are approximately $10^{-10}$ cm$^{-1}$.

Experimental Techniques Used to Investigate Fluorotrichloromethane

The spectrometer used in the investigation of CFCl$_3$ consists of a conventional Stark-modulation system (13), modified for use with relatively high power incident upon the crystal diode detector. This system
employs an 85-kc square-wave modulator which applies an electric field in
the waveguide region occupied by the gas. The applied square-wave voltage
is clamped so that it alternates between zero and an adjustable negative
voltage. The square wave can readily be unclamped so that it swings
with equal positive and negative potentials. This provides a test as
to whether or not an output deflection is actually an absorption line.
Second detection is accomplished by a phase sensitive detector with an
output network having a time constant of several seconds.

The input circuit of the pre-amplifier was modified to reduce the
d-c resistance for crystal current; this minimizes noise and conversion
loss for high power operation (see section entitled Crystal Detector
and Amplifier). The modification consists of replacing the 125 mh
choke coil and 1000 ohm resistor which shunts the diode input shown on
page 60 of reference 13 with a 10 mh ferrite core coil having a resis-
tance of 28 ohms. The microwave power for measuring the lower transi-
tions was usually such that the rectified crystal current* was between
one-half and two milliamperes, corresponding to a few milliwatts of
microwave power. Objectionable 85-kc pickup was found to exist as a
result of current flow along the walls of the Stark cell and to the
crystal detector through the crystal holder. The pick-up was removed
by isolating the crystal holder from the cell by using a thin Mylar
spacer between waveguide flanges and Nylon connecting screws.

*This measurement was made with a low resistance meter, so that
the measured current is essentially the short-circuit current.
Microwave power is supplied by reflex klystrons which were slowly swept through the frequency range of interest by mechanically tuning with one of several slow speed motors and a variable speed gear reducer.

The X-band cell has inside cross-sectional dimensions of 0.900 inch by 0.400 inch and was made with the general fabrication techniques used with the S-band cell described below. The X-band cell is, however, made of two sections and has a total length of 20 feet. The S-band cell consists of a 0.040 inch by 140 inches brass sheet for a Stark electrode mounted in a 12-foot length of waveguide. The guide is standard type RG48/U which has inside cross-sectional dimensions of 2.84 inches by 1.34 inches. Each side of the electrode is supported by 93-mil Teflon tape. To minimize interface reflections of the microwaves, the ends of the Teflon tape and Stark electrode are tapered. The cell is sealed at each end by a 10 mil Mylar window compressed with an O-ring between waveguide flanges. A gas port is located at each end for passing gas through the cell. The ports consist of 4-inch slits having a width of 1/8 inch. Standard 1/2-inch copper tubing is used for connecting the cell to the gas handling system. A wooden framework lined with polyfoam encloses the cell. This serves as a heat insulator to facilitate cooling the cell with dry ice.

For measurements on each transition, microwave power is divided into two parts: one portion is supplied to a crystal diode associated with the frequency measuring system, where its frequency is determined approximately by a wavemeter and then more precisely by comparison with standard markers from a secondary frequency standard. The remainder of the power passes through the absorption cell to a second crystal diode which serves as a detector.
A crystal controlled secondary frequency standard compared with WWV generates standard microwave frequencies 30 mc apart at the terminals of a crystal diode. Beat frequencies are also produced in this diode which are the differences between the standard frequencies and the unknown klystron frequency. These are detected by a National HRO receiver. Absorption lines are observed by two methods. For the \( J = 1 \rightarrow 2 \) and \( J = 2 \rightarrow 3 \) transitions a long time constant RC network was used at the output of the phase sensitive detector. Because of this the klystron frequency was slowly varied and the spectrograph output was indicated on a chart recorder. For the higher transitions the klystrons were swept in frequency by applying a sawtooth voltage to the repeller at a rate of 15 cps; sometimes the chart recorder was used to study line detail. The recorded \( J = 1 \rightarrow 2 \) and \( J = 2 \rightarrow 3 \) spectra were calibrated in frequency by manually actuating the side pin of the chart recorder at intervals of one megacycle, as determined by listening for a beat note between the frequency standard and the mechanically swept klystron on the HRO receiver. More accurate frequency determinations were made for the major prominences by measuring the difference frequency at the time that the recorder indicated a peak signal. To reduce errors resulting from long filter time constants, the frequency obtained for increasing klystron frequency was averaged with that obtained for decreasing klystron frequency. The reported frequencies are averages of repeated measurements of this type and the ranges indicated for the measurements are probable errors associated with the ensemble of frequency determinations for a single prominence under the assumption that frequency differences are normally distributed about their means. For
the higher transitions the klystron frequency was swept electronically and the absorption line displayed on an oscilloscope. Frequencies were determined by superimposing a difference frequency marker on the observed absorption line and averaging data for sweeping the klystron up in frequency with that for sweeping the klystron down in frequency.

Major components used in observing data for each rotational transition are listed below.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Frequency (kmc)</th>
<th>Klystron</th>
<th>Stark Cell</th>
<th>Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→2</td>
<td>9.86</td>
<td>X-13</td>
<td>S-band</td>
<td>1N23E</td>
</tr>
<tr>
<td>2→3</td>
<td>14.79</td>
<td>X-12</td>
<td>S-band</td>
<td>1N70B</td>
</tr>
<tr>
<td>3→4</td>
<td>19.73</td>
<td>QK-306</td>
<td>X-band</td>
<td>1N26</td>
</tr>
<tr>
<td>4→5</td>
<td>24.66</td>
<td>2K33</td>
<td>X-band</td>
<td>1N26</td>
</tr>
<tr>
<td>5→6</td>
<td>29.59</td>
<td>QK-289</td>
<td>X-band</td>
<td>1N26</td>
</tr>
<tr>
<td>6→7</td>
<td>34.52</td>
<td>QK-291</td>
<td>X-band</td>
<td>1N26</td>
</tr>
</tbody>
</table>

The Stark cell was kept at dry ice temperature by filling the insulated framework with dry ice. The sample CFCl₃ was cooled by surrounding the sample holder with a dry ice and acetone solution contained in an insulated flask. The sample holder was connected to the input port of the Stark cell through two stopcocks separated by a small volume consisting of a short section of glass tubing. Gas was introduced into the small volume by opening and closing the stopcock closest to the sample holder with the other stopcock closed. The second stopcock was then opened and closed, providing a Stark cell pressure suitable for high pressure operation. Lower pressures were obtained by removing gas from the output port with a diffusion pump.
CHAPTER III

MICROWAVE SPECTRUM OF FLUOROTRICHROMETHANE

Description of Fluorotrichloromethane

The fluorotrichloromethane employed as a sample in this investigation was purchased from The Matheson Company, Inc. This gas, which has the trade name of "Freon 11", has a purity of 99.9 percent. A sketch of the molecule is shown in Figure 1.

Isotopic abundances and nuclear spins for C, F, and Cl follow (13):

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass Number</th>
<th>Abundance (percent)</th>
<th>Nuclear Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>12</td>
<td>98.88</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>1.12</td>
<td>1/2</td>
</tr>
<tr>
<td>F</td>
<td>19</td>
<td>100</td>
<td>1/2</td>
</tr>
<tr>
<td>Cl</td>
<td>35</td>
<td>75.4</td>
<td>3/2</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>24.6</td>
<td>3/2</td>
</tr>
</tbody>
</table>

Nuclear quadrupole moments, through interaction with the gradient of the electric field, contribute a hyperfine structure to the rotational spectrum. It is well established that there is no electric quadrupole moment for nuclei with spin 0 or 1/2. Therefore it is expected that the only nuclear multipole moments which need to be considered are the electric quadrupole moments of the three chlorine atoms.

Since the natural abundance ratio Cl$^{35}$:Cl$^{37}$ is approximately 3:1, one has the following abundances for the four species of fluorotrichloromethane:
Figure 1. The Fluorotrichloromethane Molecule.
Species I \[ \text{CFCl}_3^{35} \] \[ 27/64 \]
Species II \[ \text{CFCl}_2^{35} \text{Cl}^{37} \] \[ 27/64 \]
Species III \[ \text{CFCl}_2^{35} \text{Cl}^{35} \] \[ 9/64 \]
Species IV \[ \text{CFCl}_3^{37} \] \[ 1/64 \]

Molecular Rotation Theory

**Symmetric Rotor**.--Symmetric-top molecules have equal moments of inertia about two of their three principal axes. The total angular momentum is constant in magnitude as well as in direction, and its component in the direction of the symmetry axis is constant in magnitude. The symmetry axis rotates at a constant angle and at a constant frequency about the total angular momentum vector.

The quantum mechanical solution for the rotational energies of a rigid symmetric-top molecule can be expressed as

\[
E = \frac{J(J+1)\hbar^2}{2I_B} + \frac{1}{2} \left[ \frac{1}{I_C} - \frac{1}{I_B} \right]\hbar^2 K^2
\]

where \( I_C \) is the moment of inertia about the symmetry axis, and \( I_B = I_A \) is the moment of inertia about the other two perpendicular principal axes. \( J \) is the total angular momentum quantum number, and \( K \) is the component of angular momentum along the symmetry axis.

The above equation applies to a rigid molecule. For a non-rigid molecule corrections must be applied for centrifugal distortion. It is usual to express these corrections in terms of the distortion coefficients \( D_J \), \( D_K \), and \( D_{JK} \). The energies of a non-rigid symmetric top molecule are given by
\[ \frac{E}{h} = BJ(J+1) + (C-B)K^2 - DJ^2(J+1)^2 - DK^2(J+1)K^2 - DJ_K K^4 \]

where
\[ B = \frac{\hbar}{8\pi^2I_B} , \quad C = \frac{\hbar}{8\pi^2I_C} . \]

Because of the symmetry there can be no dipole moment component perpendicular to the symmetry axis, and hence the electric fields associated with radiation cannot exert a torque about this axis. Therefore for electric dipole radiation one has the selection rule \( \Delta K = 0 \). The selection rule for the quantum number \( J \) for electric dipole radiation is the usual \( \Delta J = 0, \pm 1 \). Therefore, the frequencies of the absorption lines for the \( J \rightarrow J + 1 \) rotational transitions are given by
\[ f = 2(J+1)(B-JK^2) - hD_J(J+1)^3 . \]

Because \( D_J \) and \( DJ_K \) are small constants a series of almost equally spaced absorption lines, separated by \( 2B \), is to be expected.

The main effect of the centrifugal distortion is to remove the degeneracy of the different \( K \) states. Without the distortion only one line would appear for each different transition of the principal quantum number, \( J \), because of the \( \Delta K = 0 \) selection rule.

The two symmetric isotopic species of \( \text{CFCl}_3 \) contain three identical chlorine nuclei which interact with the average gradient of the electric field produced by the rest of the molecule. This interaction is sufficiently large to produce a hyperfine structure. The frequencies
of the absorption lines for the J→J+1 rotational transition including the effect of quadrupole interaction may be expressed as

\[ f = 2(J+1)(B-D_{JK}K^2) - 4D_J(J+1)^3 + \Delta \nu_Q. \]  

All terms in Equation 1 are defined above with the exception of \( \Delta \nu_Q \), which represents the frequency shift resulting from nuclear quadrupole interaction.

**Asymmetric Rotor.**—The allowed rotational energies of an asymmetric top molecule \((I_A < I_B < I_C)\) are considerably more difficult to obtain than are those for linear and symmetric-top molecules \((14)\). The energies for asymmetric rotors can be expressed in closed form for low values of \( J \) only. There are \( 2J+1 \) sub-levels of energy for each \( J \) of an asymmetric top. These are labeled \( J_\tau \) where \( \tau \) takes on \( 2J+1 \) integral values \((-J \leq \tau \leq J)\). The sub-levels are numbered in order of increasing energy, the lowest level being \( J_{-J} \) and the highest level being \( J_{+J} \).

Symmetry properties of the levels \( J_\tau \) can be specified \((14)\) in terms of the behavior of the corresponding wave functions with respect to rotations by \( \pi \) about the \( C \) axis \((C_{2C})\) and about the \( A \) axis \((C_{2A})\). These properties, with the corresponding values of \( K \) for the prolate and oblate limiting cases are given in Table 1.

Species I and IV of fluorotrichloromethane, being symmetric tops, have their permanent electric dipole moments along the \( C \) axis. Therefore, it is expected that the slightly asymmetric top resulting from the substitution of a different isotope for one species will still have its permanent dipole moment lying almost along the \( C \) axis. In addition to
Table 1. Symmetry Properties of the Asymmetric Rotor Energy Levels

<table>
<thead>
<tr>
<th>J</th>
<th>$\tau$</th>
<th>$K_{\text{prolate}}$</th>
<th>$K_{\text{oblate}}$</th>
<th>$C_{2C}$</th>
<th>$C_{2A}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>2</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-2</td>
<td>0</td>
<td>2</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>
the selection rule $\Delta J = 0, \pm 1$, the symmetry selection rules for this case are (14)

$$++ \leftrightarrow + - \text{ and } - + \leftrightarrow --.$$ 

For the energy levels shown in Table 1, these selection rules correspond to $\Delta K$ (oblate) = 0. The energies, $E^J_\tau$, for the states listed in Table 1 are:

$$E^2_0/h = 2A + 2B + 2C + 2 \sqrt{(B-C)^2 + (A-C)(A-B)}$$

$$E^2_1/h = 4A + B + C$$

$$E^2_0/h = A + 4B + C$$

$$E^2_{-1}/h = A + B + 4C$$

$$E^2_{-2}/h = 2A + 2B + 2C - 2 \sqrt{(B-C)^2 + (A-C)(A-B)}$$

$$E^1_1/h = A + B$$

$$E^1_0/h = A + C$$

$$E^1_{-1}/h = B + C$$

$$E^0_0/h = 0.$$ 

From these values of energy and the selection rules, the frequencies corresponding to the $J = 1 \rightarrow 2$ transitions in Species II and III are:

$$f(\tau = 1 \rightarrow 2) = A + B + 2C + 2 \sqrt{(B-C)^2 + (A-C)(A-B)}$$

$$f(\tau = 0 \rightarrow 1) = 3A + B$$

$$f(\tau = -1 \rightarrow 0) = A + 3B.$$
For slightly asymmetric tops the centrifugal distortion effects are approximately the same as for the symmetric top. Because of this, effects of centrifugal distortion need not be considered in determining the molecular structure which was obtained from $J = 1 \to 2$ transition data for species I and species II.

Wolfe (15) has shown that the most intense nuclear quadrupole hyperfine structure component for the transition $J \to J + 1$, in a molecule with three identical quadrupolar nuclei of spin $3/2$, has $K = 1 \to 1$. His expression for frequency, when modified to be in terms of the quadrupole coupling constant $eQV_{zz}$ (see section entitled Nuclear Quadrupole Interaction Theory), is

$$\Delta \nu_Q = \beta(J) eQV_{zz}.$$ 

$\Delta \nu_Q$ is the frequency by which the most intense hyperfine component of the $J \to J + 1$ transition is shifted because of quadrupole interaction. To account for the shift in the most intense component of species II, an effective nuclear quadrupole coupling constant is employed,

$$(eQV_{zz})_{\text{effective}} = \left[ N_{35} + N_{37} \left( q^{37}/q^{35} \right) \right] \frac{eQV_{zz}}{3}.$$ 

Here $N_{35}$ is the number of Cl$^{35}$ nuclei in the molecule, $N_{37}$ is the number of Cl$^{37}$ nuclei. From the work of Livingston (16), $q^{37}/q^{35} = 0.788$. Therefore, for species II

$$(eQV_{zz})_{\text{effective}} = \left[ 2 + 1(0.788) \right] \frac{eQV_{zz}}{3} = 0.929 \ eQV_{zz}.$$
Structure of Fluorotrichloromethane

The structure of fluorotrichloromethane was determined from experimental $J = 1 \rightarrow 2$ data for the most intense line of species I and the most intense lines of the transitions $J_x = 1_0 \rightarrow 2_1$ and $J_x = 1_1 \rightarrow 2_0$ for species II.

Results given in the section on experimental data indicate that the most intense line in the $J = 1 \rightarrow 2$ spectrum for species I is lowered by 2.26 mc, i.e.,

$$\Delta v_Q(I) = -2.26 \text{ mc}.$$ 

Based on $(\varepsilon Q_{zz})_{\text{effective}}$ and $\Delta v_Q(I)$ it is expected that the most intense lines of the various transitions for species II are shifted by

$$\Delta v_Q(II) = -2.10 \text{ mc}.$$ 

Relatively low Stark fields (about 160 volts/cm) were employed throughout this investigation. As a consequence, $K = 0$ components were not observed since these possess no first-order Stark effect. The available Stark field was not large enough to observe the frequency $f(1_1 \rightarrow 2_2)$, which corresponds to $K = 0$ in the limiting case of a symmetric top.

Table 2 gives the observed frequencies and corresponding frequency expressions in terms of rotational constants.

**Table 2. Observed and Predicted $J = 1 \rightarrow 2$ Transitions in Fluorotrichloromethane**

<table>
<thead>
<tr>
<th>Species</th>
<th>$f$(Observed)</th>
<th>$f$(Predicted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$9859.30 \pm 0.04$ mc</td>
<td>$\frac{1}{2}B(I) - 2.26$ mc</td>
</tr>
<tr>
<td>II</td>
<td>$9786.05 \pm 0.20$ mc</td>
<td>$3A(II) + B(II) - 2.10$ mc</td>
</tr>
<tr>
<td></td>
<td>$9656.62 \pm 0.10$ mc</td>
<td>$A(II) + 3B(II) - 2.10$ mc</td>
</tr>
</tbody>
</table>
The data in Table 2 yield

\[ A(I) = B(I) = 2465.39 \text{ mc} \]
\[ A(II) = 2463.22 \text{ mc} \]
\[ B(II) = 2398.50 \text{ mc}. \]

The relation

\[ I_A (A^2 \text{Amu} A \text{mc}) = 5.05531 \times 10^5 \]

was employed to convert between moments of inertia and rotational constants.

Based on the following atomic masses,

F: \[ 19.00450 \]
C\(^{12}\): \[ 12.00382 \]
Cl\(^{35}\): \[ 34.97867 \]
Cl\(^{37}\): \[ 36.97750 \],

the principal moments of inertia, in units of Angstroms-squared times atomic mass units, are:

Species I:

\[ I_A = I_B = I_{xx} = I_{yy} = 52.46801 a^2 + 16.34774 b^2 + 29.33931 ab \cos \beta \]
\[ - 28.53255 a^2 \cos^2 \beta \]
\[ I_C = I_{zz} = 104.93601 a^2 \sin^2 \beta \]

Species II:

\[ I_A = I_{xx} - \Delta, \text{ where} \]
\[ I_{xx} = 52.46801 \ a^2 + 16.38624 \ b^2 + 29.46494 \ ab \cos\beta \]
\[ - 28.43006 \ a^2 \cos^2\beta, \]
\[ \Delta = \frac{I_{xz}^2}{(I_{zz} - I_{xx})}, \]
\[ I_{xz} = -0.27538 \ ab \sin\beta - 0.44932 \ a^2 \sin\beta \cos\beta, \]
and
\[ I_{zz} = 106.90588 \ a^2 \sin^2\beta. \]
\[ I_B = I_{yy} = 54.43787 \ a^2 + 16.38624 \ b^2 + 29.46494 \ ab \cos\beta \]
\[ - 30.39993 \ a^2 \cos^2\beta. \]

In these equations \( a \) and \( b \) are the C-Cl and C-F bond distances, respectively, and \( \beta \) is the angle between a C-Cl bond direction and the symmetry axis, \( z \). For species I, the C axis is parallel to the C-F bond, with the A and B axes arbitrary but perpendicular to each other and to C.

For species II, the C axis lies almost parallel to the C-F bond, in the plane C-F-Cl. The A axis is in this plane and is perpendicular to C. The B axis lies perpendicular to the plane of A and C.

The term \( \Delta \) is an approximate correction to \( I_A \) due to the tipping of axis C in the asymmetric species (see Appendix B). For the structural parameters involved

\[ \Delta = 0.0115 \ A^2 \ Amu, \]

and \( I_{xx} \) is approximately \( 205 \ A^2 \ Amu \).
The structure was determined from the moments of inertia calculated from experimental data: \( I_A(I), I_A(II), \) and \( I_B(II) \). Substitution of \( I_A(II) \) into \( I_B(II) \) with \( \Delta = 0.0115 \) yields a value for \( \alpha \) as a function of \( \beta \); this relation was used to eliminate \( \alpha \) from \( I_A(I) \) and \( I_B(II) \). Values of \( b \) were then obtained from the equations for \( I_A(I) \) and \( I_B(II) \) for assumed values of \( \beta \). The solution for \( \beta \) was selected as the value which results in equal values of \( b \) from these equations. \( \beta \) was determined to be 70°40'. The geometry of the molecule yields the following relation between the angle \( \beta \) and the angle Cl-C-Cl, defined as \( 2\alpha \),

\[
\cos 2\alpha = \frac{1}{2} (3 \cos^2 \beta - 1).
\]

This analysis gave the following structural parameters for fluorotrichloromethane:

\[
\begin{align*}
C-Cl &= a = 1.76 \text{ A} \\
C-F &= b = 1.33 \text{ A} \\
\text{Cl-C-Cl} &= 2\alpha = 109°40'.
\end{align*}
\]

Electron diffraction data (17) for this molecule indicate C-Cl: 1.76 A, C-F: 1.40 A and Cl-C-Cl: 111.5°. There seems to be a discrepancy between the data for the C-F length; however, microwave data for C-F distances in other molecules (18) are as follows.

\[
\begin{align*}
\text{CF}_3\text{Cl}^{35} &: 1.32 \text{ A} \\
\text{CF}_3\text{Br}^{79} &: 1.33 \text{ A} \\
\text{CF}_3\text{I} &: 1.33 \text{ A} \\
\text{CF}_3\text{H} &: 1.332 \text{ A} \\
\text{CH}_3\text{F} &: 1.39 \text{ A}.
\end{align*}
\]
In addition, the Cl-C-Cl angle determined from the present investigation is approximately tetrahedral (109°28').

Nuclear Quadrupole Interaction Theory

The problem of three identical nuclei with quadrupole moments has been investigated by Bersohn (19) who obtained matrix elements for the interactions and by Mizushima and Ito (20) who used Bersohn's work to calculate the effect of quadrupole interaction on the $J = 0 \rightarrow 1$ rotational transition for a molecule with three identical nuclei with spins of 1, 3/2, 2, and 5/2. Also a theoretical investigation of the expected hyperfine structure of ND$_3$ was undertaken by Hadley (21). The first experimental work reported was that of Kojima et al (22) who applied the theoretical calculations of Mizushima and Ito to the $J = 0 \rightarrow 1$ rotational transition of bromoform (CHBr$_3$). The spectrum reported was proved later (23) to be of spurious origin. Wolfe (24) was the first to make a valid comparison of observed and calculated spectra for a molecule having three identical nuclei with quadrupole moments. Wolfe measured the $J = 2 \rightarrow 3$ rotational spectrum of the abundant symmetric top species of chloroform (CHCl$_3^{35}$) and calculated the spectrum by use of the procedure outlined by Bersohn. More recently Herrmann (25) made measurements on ND$_3$ (three nuclei of spin 1) and compared these with the theoretical work of Hadley.

The calculation of energies and intensities for three nuclei with quadrupole moments is laborious. For the case that Wolfe considered, the $J = 2 \rightarrow 3$ transition with spins of 3/2, hundreds of transitions are possible between the two rotational levels. Because of the large number of overlapping lines it is difficult to find the result of superimposing
the components on the basis of a reasonable physical assumption of line shape. As pointed out by Wolfe, with his assumption of rectangular shapes, the positions of prominent features can be shifted somewhat from their true values, except in cases for which one component is considerably more intense than its neighbors. A complicating feature of the analysis results because centrifugal distortion allows different "centers" for the hyperfine patterns corresponding to each value of K. The quantum numbers K = 0, K = 1, and K = 2 are permissible for the J = 2→3 transition. Wolfe investigated CHCl₃ experimentally with relatively weak Stark fields in order to prevent second order Stark components from being sufficiently displaced to interfere with nuclear quadrupole hyperfine components. As a consequence, K = 0 components are not observed since these possess no first order Stark effect. Wolfe handled the problem of two values of K by shifting the relative positions of his calculated K = 1 and K = 2 patterns to obtain a best fit with his measured composite pattern. This technique provided a value for the quadrupole coupling constant and a value of the centrifugal distortion constant DJK. Analysis of the J = 1→2 transition for fluorotrichloromethane is even more difficult than the analysis of the chloroform spectrum. This is because the absorption coefficients of the lines are smaller and because the dipole moment of the molecule is so small that with usable electric fields the Stark components interfere with all but the strong lines. Analysis of the CFCl₃ spectrum required a theoretical calculation of the quadrupole splitting of the J = 1→2 transition.

By means of the interactions of the nuclear quadrupole moments with the electric field gradient, the nuclear spin angular momenta, I₁,
1, 2, 3, are coupled with the rotational angular momentum, \( J \), of the molecule to produce a resultant total angular momentum, \( F = J + I_1 + I_2 + I_3 \). As a consequence, the rotational energy levels of the symmetric top are split into several components by the nuclear quadrupole interaction. The line splitting due to nuclear quadrupole interaction with three identical nuclei produces very complex hyperfine spectra, with complexity increasing rapidly with \( J \).

The following discussion of nuclear quadrupole interaction follows Wolfe (15). His work on quadrupole interaction was specialized for the case of three identical nuclei of spin \( 3/2 \); he used the general procedure outlined by Bersohn (19) for determining quadrupole fine structure of molecular rotational spectra. In addition, Wolfe predicted a spectrum for the \( J = 2 \rightarrow 3 \) rotational transition of chloroform.

In order to follow the method of Bersohn, which makes use of Racah algebra (26), in determining the perturbation energy \( E^1 \) due to the nuclear quadrupole interaction, the following unsymmetrical-appearing coupling scheme is employed in writing the nuclear-rotational wave functions:

\[
I_1 + I_2 = L, \quad L = I_1 + I_2, \quad I_1 + I_2 - 1, \ldots, I_1 - I_2
\]

\[
I_1 + I_3 = L, \quad I = L + I_3, \quad L + I_3 - 1, \ldots, L - I_3
\]

\[
I + J = F, \quad F = I + J, \quad I + J - 1, \ldots, I - J.
\]

The required nuclear-rotational wave functions are then

\[
<1_1I_2I_3;LJKFM>.
\]
they describe the states corresponding to the coupled nuclear spin angular momenta, $I_1^i$, $i = 1, 2, 3$, and the rotational angular momentum, $J$. These wave functions can be expressed as

$$<I_1^1 I_2^2 I_3^3 LLJKFM| = \sum_{m_1, m_2, m_3, m_J} (I_1^1 I_2^2 m_1 m_2 | L m_L)(I_3^3 m_3 | L m_L)$$

$$\times (IJm_J | FM)\varnothing(Jkm_J')\varnothing(I_1^1 m_1)\varnothing(I_2^2 m_2)\varnothing(I_3^3 m_3).$$

$J$ and $I$ were defined in this section; $I$ times $m_1$, $m_2$, $m_3$, $L$, $I$, $J$, and $F$ on a space-fixed $Z$ direction ($m_1 = I_1^1$, $I_1^1 - 1$, ..., $-I_1$; $m_2 = J, J-1, ...$, $-J$; etc.). $\varnothing(Jkm_J')$ is the normalized rotational wave function for a rigid symmetric top, and $\varnothing(I^i_1 m_1)$, $i = 1, 2, 3$, is the normalized nuclear wave function for the $i^{th}$ chlorine nucleus in the state expressed in its argument. The quantities $(abcd | ef)$ are the vector-addition or Clebsch-Gordan coefficients, and are numerical functions of their arguments.

Perturbation theory specifies the $E^1$ as roots of the secular determinant

$$|E_{rr'}^1, - E^1 s(rr')| = 0,$$

where $H^1$ is the nuclear quadrupole interaction Hamiltonian, $r$ specifies the state $<I_1^1 I_2^2 I_3^3 LLJKFM|$, and $r'$ the state $<I_1^1 I_2^2 I_3^3 L'I'J K'F'M'|$.

A classical consideration (19) of the electrostatic interaction between the nuclear quadrupoles and the electric field of the remainder of the molecule shows that $H^1$ may be written as the scalar product of two tensor operators of order two:
\[ H^1 = \sum_{i=1}^{n} \left[ Q(i) \cdot \nabla E(i) \right], \]

where \( n \) is the number of quadrupolar nuclei in the molecule. \( Q(i) \) is called a quadrupole moment tensor and is a function of quantum number \( I_i \); \( \nabla E(i) \) is the gradient of the electric field at the \( i \)th nucleus due to the remainder of the molecule and is a function of quantum numbers \( J \) and \( K \). Matrices for products such as are contained in the quadrupole interaction Hamiltonian were developed by Racah (26).

A partial diagonalization of the perturbation energy matrix can be made by taking into account the identity of the three quadrupolar nuclei. The group of permutations on three identical things has three irreducible representations: \( A_1, A_2, \) and \( E \). \( A_1 \) is the one-by-one identity representation, \( A_2 \) is the one-by-one alternating representation and \( E \) is two-by-two. Since three identical nuclei are involved in this problem the nuclear states, \( < LI \mid \), must belong to one or more of these representations, and the quadrupole Hamiltonian is invariant under their exchange and therefore commutes with the operators of the group. Hence it is possible to perform a transformation from the \( < LI \mid \) nuclear representation to a representation \( < SI \mid \), \( S = A_1, A_2, E \), in which the energy matrix elements are diagonal in \( S \). This follows because the \( S \) states are mutually orthogonal. When these transformations are employed, the non-vanishing matrix elements of \( H^1 \) diagonal in \( J \) and \( K \) become:

\[ \langle SIJKF|H^1|SI'JKF \rangle = (-1)^{F-J+\frac{1}{2}} \lambda(SII') G(JK) W(IJI'J;F2). \]  (3)
The $\lambda(SII')$ are related to Clebsch-Gordan coefficients used to express the wave functions as linear orthogonal combinations of the states $S$. Wolfe (Table 6 of reference 24) gives values of $\lambda(SII')$ required for analysis of molecules having three identical nuclei of spin $3/2$. $W$ is the Racah coefficient and is discussed in Appendix C. The coefficient $G(JK)$ can be expressed as:

$$G(JK) = g(JK) \, eQ \, V_{zz},$$

where

$$g(JK) = \frac{3K^2 - J(J+1)}{2(J+1)} \left[ \frac{5(2J+2)(2J+1)}{(2J+3)(2J+1)} \right]^{1/2}.$$ 

eQ is the electric quadrupole moment of the chlorine nucleus and $V_{zz}$ is the second partial derivative of the electric potential at the chlorine nucleus (due to extranuclear charges), with respect to $z$, the symmetry axis of the molecule.

The total wave function for a molecule may be considered to be the product of three component wave functions:

$$\psi(\text{total}) = \psi(\text{electronic}) \, \psi(\text{vibrational}) \, \psi(\text{nuclear-rotational}).$$

For a molecule containing three identical nuclei the behavior of $\psi(\text{total})$ with respect to permutations of these three nuclei is then the product of the behaviors of the three component wave functions.

*The sign for $G(JK)$ is incorrect in Equation 3 of reference 15; it is given correctly in Equation 17 of reference 24. Because of the error in Equation 3, the sign is also incorrect in Equation 6 of reference 15. These differences in sign were confirmed by personal communication with the author.
The great majority of molecules have totally symmetric, $A_1$, ground electronic states. Fluorotrichloromethane is assumed to be no exception and consequently the symmetry property of $\psi$ (electronic) does not enter into the determination of the behavior of $\psi$ (total).

The following symmetry properties of the symmetric top wave functions are known (27). For the ground vibrational state, which is twofold because of the possibility of inversion of the molecule at its center of mass, $\psi$ (vibrational) will be of species $A_1$ or $A_2$. The rotational wave functions, $\psi(JKm_j)$, for $K = 1$ and $K = 2$ states are of species $E$. $K = 0$ will not be considered in the $J = 1 \rightarrow 2$ calculation because it does not give rise to first order Stark effect, and therefore was not observed.

According to Fermi-Dirac statistics obeyed by nuclei of half-integral spin, such as chlorine, $\psi$ (total) must be antisymmetric in the three nuclei, that is, it must be of species $A_2$. Hence $\psi$ (nuclear-rotational) must be of species $A_1$ or $A_2$, dependent upon whether the species of $\psi$ (vibrational) is $A_2$ or $A_1$. In other words, one of the following conditions must be satisfied for $\psi$ (total) and $\psi$ (electronic) to be $A_2$ and $A_1$, respectively:

1. If $\psi$ (vibrational) is $A_1$, $\psi$ (nuclear-rotational) must be $A_2$.
2. If $\psi$ (vibrational) is $A_2$, $\psi$ (nuclear-rotational) must be $A_1$.

The nuclear-rotational wave functions involve products of the $\psi(JKm_j)$ and the nuclear wave functions. Since the $\psi(JKm_j)$ are of species $E$ for the values of $K$ under consideration, $K = 1$ and $K = 2$, the permissible nuclear states are of species $E$, otherwise the nuclear-rotational wave functions could not be of species $A_1$ or $A_2$. 
Relative intensities of the various hyperfine components of a given transition, J→J + 1, are computed as the square of the matrix elements of the Z-component of the permanent electric dipole moment of the molecule, between the initial and final nuclear-rotational states involved in the transition. This computation yields (15) the following selection rules for the transitions J→J + 1:

\[ \Delta K = 0 \]

\[ S \rightarrow S \]

\[ \Delta F = 0, \pm 1, \]

\[ \Delta M = 0. \]

The intensities are summed over M because the hyperfine splitting is independent of this quantum number.

Wolfe determined an expression for the frequency shift of the most intense hyperfine component for any J→J + 1 transition. This expression provides useful results from rotational-transition data for which the hyperfine spectrum has not been calculated. He found that the most intense component belongs to the set K = 1 and is specified by \( \mathbf{F} = J + \frac{7}{2} \rightarrow J + \frac{9}{2} \). Wolfe was able to obtain an expression in closed form because the energy matrices are always diagonal for these states and involve only the solution of one-by-one determinants. His expression, when modified to be in terms of the quadrupole coupling constant \( \epsilon Q_{zz} \), is

\[ \Delta \nu_Q = \beta(J) \epsilon Q_{zz} \]  \[ \text{where} \]

\[ \beta = - \frac{3}{4} \frac{(J+1)(J+2) + (4J+7)}{(2J+5)(2J+3)(J+2)(J+1)}. \]
is the frequency by which the most intense hyperfine component of the $J \rightarrow J + 1$ transition is shifted because of quadrupole interaction. The $J = 0 \rightarrow 1$ transition, having only $K = 0$ components, does not satisfy this relation.

Calculations for the $J = 1 \rightarrow 2$ Quadrupole Interaction Spectrum

Matrix elements $H_{tr}^1 / \mathcal{G}(JK)$ were computed from Equation 3,

$$(SIJKF|H^1|SI'JKF)/\mathcal{G}(JK) = (-1)^F-J+\frac{1}{2} \lambda(SII') W(IJI'J;F2),$$

and values of $\lambda(SII')$ obtained by Wolfe (24). The Racah coefficients were obtained by the methods discussed in Appendix C. The values of $\lambda(SII')$ and the matrix elements are listed in Table 5 (Appendix D). The three spin angular momenta are aligned parallel for $I = 9/2$; therefore the corresponding nuclear wave function is not permissible for a symmetric top molecule because it is symmetrical in the three nuclei (species $A_1$). The forms of the secular determinants for $J = 1$ and $J = 2$ are illustrated in Figure 2. The heavy outline is for $J = 1$; the $J = 2$ determinant includes elements enclosed by the dotted lines in addition to the elements applicable to $J = 1$. Diagonalization of the matrices involves the solution of one linear equation, 2 quadratic equations, and 2 cubic equations for a total of 11 roots for $J = 1$; one linear equation, 2 quadratic equations, one cubic equation and 2 quartic equations for a total of 16 roots for $J = 2$. Roots obtained in the present work for $J = 1$ are listed in Table 9 and those obtained by Wolfe for $J = 2$ are included in Table 10. These roots will be indicated by an index $\mathcal{T}$. 
Figure 2. Graphical Description of Secular Determinants for $J = 1$ and for $J = 2$. 
The nuclear quadrupole interaction energy is obtained by multiplying the above roots by $G(JK)$ defined in Equation 4. Equation 4 gives:

\[ G(11) = 0.61237 \ e\nu_{zz} \text{ and} \]
\[ G(21) = -0.66815 \ e\nu_{zz}. \]

The eigenvalues of the quadrupole interaction energy for the allowed nuclear states for $J = 1$ and 2, $K = 1$ are given in Tables 9 and 10. Also included in these tables are approximate coefficients $B_{\text{TT}}$ of the transformation matrices which accomplish the diagonalization. These coefficients are used in computing intensities.

A transition from a lower state, of energy

\[ E_1(JKTF) = E_{1}^0(JK) + E_{1}^1(JKTF), \]

to an upper state, of energy

\[ E_2(J+1K'T'F') = E_{2}^0(J+1K) + E_{2}^1(J+1K'T'F'), \]

is induced by radiation of frequency

\[ f = (E_2 - E_1)/\hbar = f_0 + \Delta \nu_q, \]

where $f_0 = \left[ E_{2}^0(J+1K) - E_{1}^0(JK) \right]/\hbar$ is the unperturbed rotational frequency, $2B(J+1)\lambda$, and

*The sign given for $G(11)$ in Table 9 of reference 24 is incorrect; this was confirmed by personal communication with the author.*
\[ \Delta v_Q = \left[ E_2^{K+1}(J+1K'T'F') - E_1^J(JKT) \right] / \hbar \]

is the correction to \( f_0 \) caused by the nuclear quadrupole interaction perturbation. When \( eQV_{zz} \) is stated in units of frequency rather than energy, the factor \( \hbar \) is omitted from the last expression:

\[ \Delta v_Q = E_2^J(J+1K'T'F') - E_1^J(JKT). \] (6)

According to Wolfe (24) the relative intensity, \( N \), of a given \( J = 1 \rightarrow 2 \) transition for which \( K = l \) is

\[ N = \left[ \sum I B_{T'I} B_{T'I} R_1^{(FF')} \right]^2 \] (7)

where

\[ R_1^{(FF')} = \sqrt{(2F+1)(2F'+1)} W(1F2F',1l). \]

Values of \( R_1 \) for \( J = 1 \rightarrow 2 \), \( K = l \) are listed in Table 11. Most of the required Racah coefficients were calculated by hand using the techniques of Sharpe et al (see Appendix C); these are given in Table 12.

By means of the frequency relation, Equation 6, and the intensity expression, Equation 7, the data in Tables 9, 10, 11, and 12 give the frequencies and intensities of the \( J = 1 \rightarrow 2 \), \( K = 1 \), \( \Delta F = 0 \pm 1 \) transitions. There are a total of 99 hyperfine components but many of them are relatively weak. The increase in frequency, \( \Delta v_Q \), in terms of \( eQV_{zz} \) and the relative intensity of these hyperfine components are listed in Table 13. These hyperfine components indicate two major prominences shifted in
frequency by approximately \(-0.0607 \, \text{e} Q_{zz}^2\) and \(+0.0643 \, \text{e} Q_{zz}^2\). Components contributing to these prominences are large compared to neighboring components. Therefore, a spectrum was calculated by using a half width for individual components, in terms of the experimentally determined value of \(e Q_{zz}^2\), which gives line widths comparable to measured widths. Figure 3 shows the sums of intensities at intervals of 0.001 \(e Q_{zz}^2\). These intensities were summed by assuming that each component is Gaussian in shape and has a width between one-half intensity points of 0.015 \(e Q_{zz}^2\).

Experimental Results

Theoretical and experimental examinations were made for the hyperfine structure of the \(J = 1 \rightarrow 2\) and \(J = 2 \rightarrow 3\) transitions of \(\text{CFCl}_3\). The frequency of the most intense prominence in the transitions \(J = 3 \rightarrow 4\) through \(J = 6 \rightarrow 7\) were experimentally determined. No previous microwave data have been reported for this molecule. Analysis of the \(J = 1 \rightarrow 2\) spectrum provided a determination of the quadrupole coupling constant with respect to the molecular symmetry axis, \(e Q_{zz}^2\), and the rotational constant \(B\) in terms of the centrifugal distortion constants \(D_{JK}\) and \(D_J\). Based on the results of the \(J = 1 \rightarrow 2\) investigation it was possible to interpret the very complex \(J = 2 \rightarrow 3\) transition. This provided values for the distortion constants \(D_{JK}\) and \(D_J\). Frequencies of the most intense prominences for the transitions \(J = 3 \rightarrow 4\) through \(J = 6 \rightarrow 7\) were used to verify the assignment for the most intense prominence of the \(J = 2 \rightarrow 3\) spectrum.

In principle the analysis performed for the \(J = 2 \rightarrow 3\) transition can be made without \(J = 1 \rightarrow 2\) data. The following practical problems prohibit this:
Figure 3. Predicted Quadrupole Interaction Spectrum for $J = 1 \rightarrow 2$ Transition.
(1) the lines are so weak that only the stronger prominences of the $J = 2 \rightarrow 3$ hyperfine structure could be identified, and

(2) the molecular dipole moment is so small that the maximum usable Stark field (limited by electrical breakdown of the waveguide cell) is not sufficiently large to remove the Stark components from the $J = 2 \rightarrow 3$ hyperfine structure.

Analysis of the $J = 1 \rightarrow 2$ data provided a determination of the quadrupole coupling constant $eQV_{zz}$. Knowledge of this constant permitted recognition of the major prominences in the $J = 2 \rightarrow 3$ spectrum. With this information it was possible to determine a value for the centrifugal distortion constant $D_{JK}$ from the $J = 2 \rightarrow 3$ spectrum.

The Stark effect in symmetric top molecules with nuclear quadrupole coupling has been treated by Low and Townes (26). Their work yields displacement frequencies of

$$2\mu F_{mK}/\hbar (J+1)(J+2)$$

(8)

for the $J \rightarrow J + 1$ transition, spread slightly by the quadrupole interactions. The maximum usable Stark voltage is limited by electrical breakdown of the gas in the cell. Lowering the pressure will allow the use of higher Stark voltages but will reduce the intensity of absorption lines. Stark fields ranging between 160 v/cm and 640 v/cm were used in studying the $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ spectra. For a dipole moment of 0.45 debye (29) for CFCl$_3$ and a Stark field of 160 v/cm, the above expression gives ± 12 mc for the minimum $J = 1 \rightarrow 2$ displacement frequency. No Stark interference was observed for the $J = 1 \rightarrow 2$ transition. For the $J = 2 \rightarrow 3$ spectrum and the range of Stark fields used, Stark components
are expected between ± 3 mc and ± 12 mc, ± 6 mc and ± 24 mc, and ± 12 mc and ± 48 mc. The three frequency ranges correspond to \( m_J = 1, 2 \) for \( K = 2 \) and \( m_J = 1 \) for \( K = 1 \). For this reason, only data from the strong \( J = 2 \rightarrow 3 \) prominences at the center of the hyperfine spectrum could be used with any assurance to investigate the molecule.

**J = 1→2 Spectrum.**—In an attempt to verify the predicted hyperfine structure and to evaluate the quadrupole coupling constant, \( eQV_{zz} \), the \( J = 1→2 \) transition of the most abundant symmetric top species of fluorotrichloromethane was examined repeatedly, under various conditions of pressure and Stark field. Typical results are shown in the recorder tracings of Figures 4 and 5.

Two relatively strong lines which are almost equal in intensity and several smaller lines were observed. Based on about thirty measurements for each line taken at pressures of 30 μ or less, the two stronger lines were observed at 9859.30 ± 0.04 mc and 9863.96 ± 0.05 mc. The indicated errors are probable errors under the assumption that the errors are normally distributed about the mean frequencies.

From Table 13 it is seen that the quadrupole interaction produces a shift in frequency of -0.06071 eQV_{zz} in the most intense line and +0.06429 eQV_{zz} in the other strong line. Therefore the frequency difference of these lines is 0.1250 eQV_{zz}. The difference in measured frequencies is 4.66 ± 0.06 mc. This gives

\[
eQV_{zz} = 37.3 ± 0.5 \text{ mc}.
\]

Assuming that the \( K = 0 \) transition is not observable, the only value of \( K \) which is permissible is \( K = 1 \). The spectrum in absence of the quadrupole interaction would then be a single line frequency \( f_1 \), where
Figure 4. J = 1 → 2 Transition in CFCl$_3^{35}$ at 60$\mu$Hg Pressure.
Figure 5. $J = 1 \rightarrow 2$ Transition in $\text{CFCl}_3$ at $25\mu$ Pressure.
\[ f_1 = f - \Delta v_Q = (9859.30 \pm 0.04) - (-0.06071)(37.3 \pm 0.5) \quad (9) \]

\[ = 9861.56 \pm 0.05 \text{ mc.} \]

Use of Equation 1 and Equation 8 gives

\[ B_{DK} - B_{D_J} = 2469.39 \pm 0.01 \text{ mc.} \quad (10) \]

Frequency \( f_1 \) of Equation 9 and \( eQ_{zz} \) of \( 37.3 \pm 0.5 \text{ mc} \) were used to calculate frequencies for major prominences of Figure 3. Comparisons between the calculated and observed frequencies are given in Table 3.

The relative intensities given in this table for prominences consisting of more than one line were taken from Table 13, Appendix D. Prominences marked weak were not observed on all recordings; there may be other weak prominences of comparable intensity not recorded in Table 3.

The absorption of a spectral line at its maximum is generally expressed for a temperature of \( 300^\circ \text{K} \). For symmetric top molecules and a line width of \( 25/\text{mc mm pressure} \), this absorption may be expressed (30) as

\[ \gamma = 4.94 \times 10^{-22} \sqrt{\hbar} \mu^2 \nu^3 \left[ 1 - \frac{K^2}{(J+1)^2} \right] \text{ cm}^{-1}. \quad (11) \]

In this expression

\[ \mu = \text{dipole moment in debye units (} 10^{-18} \text{ esu/cm)} \]

\[ \nu = \text{the frequency in megacycles} \]

\[ C = \text{the rotational constant about the figure axis in megacycles} \]

\[ = 10^{-6}h/8\pi^2I_0. \]
<table>
<thead>
<tr>
<th>Designation</th>
<th>Observation</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Frequency mc</td>
<td>Intensity cm(^{-1})</td>
</tr>
<tr>
<td>α</td>
<td>9853.68 ± 0.08</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β</td>
<td>9855.60 ± 0.20</td>
<td>Weak</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ</td>
<td>9859.30 ± 0.04</td>
<td>3.3 × 10(^{-10}) (Strong)</td>
</tr>
<tr>
<td>δ</td>
<td>9860.60 ± 0.10</td>
<td>Medium</td>
</tr>
<tr>
<td>ε</td>
<td>9861.80 ± 0.30</td>
<td>Weak</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ζ</td>
<td>9863.96 ± 0.05</td>
<td>3.0 × 10(^{-10}) (Strong)</td>
</tr>
<tr>
<td>η</td>
<td>9865.00 ± 0.20</td>
<td>Weak</td>
</tr>
<tr>
<td>θ</td>
<td>9866.69 ± 0.11</td>
<td>7.4 × 10(^{-11}) (Medium)</td>
</tr>
<tr>
<td>ρ</td>
<td>9870.50 ± 0.20</td>
<td>Medium</td>
</tr>
<tr>
<td>κ</td>
<td>9875.00 ± 0.25</td>
<td>Weak</td>
</tr>
<tr>
<td>λ</td>
<td>9877.00 ± 0.25</td>
<td>Weak</td>
</tr>
</tbody>
</table>
This formula holds for one particular value of k. In case k is not zero, transitions corresponding to +k and -k are always superimposed, thus the expression must be doubled to account for this effect in the J = 1→2 transition. The rotational constant C was calculated for the molecular dimensions obtained in the present research, and was found to be 1747 mc. For a ν of 9860 mc, μ of 0.45 debye (29), J and K of unity, Equation 11 gives

\[ \gamma = 6.0 \times 10^{-8} \text{ cm}^{-1}. \]

The intensities when calculated as above must be modified to take into account the following effects:

1. depletion due to less than 100 per cent abundance of the isotopes giving rise to the absorption, and

2. splitting of the line into hyperfine components.

From the description of fluorotrichloromethane we know that 27/64 of the molecules are of species CFCl\textsuperscript{13}\textsuperscript{15}. Therefore if no splitting of the line into hyperfine components occurred, the maximum absorption coefficient would be

\[ \gamma = 2.53 \times 10^{-8} \text{ cm}^{-1}. \]

The multiplicative factor by which the most intense line is reduced because of quadrupole interaction was determined from Table 13. This factor was obtained by dividing the sum of intensities of components contributing to the major prominence, \( \gamma \) in Figure 3, by the sum of all intensities in Table 13. The resultant calculated intensity for room temperature of the most intense line is
\[ \gamma = 4.5 \times 10^{-10} \text{cm}^{-1}. \]

Other calculated intensities were obtained from the intensity of \( \gamma \) by using the relative intensities indicated by Figure 3; these are included in Table 3.

The absorption coefficients of three relatively strong lines \((\gamma, \zeta, \theta)\) were also determined by comparing the line strengths with the measured noise level of the spectrograph, expressed in terms of absorption coefficient. This comparison, which was made for the gas at dry-ice temperature, indicated absorption coefficients of \( 9 \times 10^{-10} \) \( \text{cm}^{-1} \), \( 8 \times 10^{-10} \), and \( 2 \times 10^{-10} \) \( \text{cm}^{-1} \). Line intensity for a symmetric top molecule varies \((27)\) with temperature as \( T^{5/2} \). Results of the absorption coefficient measurements expressed for room temperature are given in Table 3. The agreement between calculated and measured absorption coefficients is good in view of errors which necessarily exist for sensitivity measurements of the type required for this problem.

**J = 2→3 Spectrum.**--Problems associated with analysis of the \( J = 2→3 \) rotational spectrum are reduced significantly if only data on the more intense lines are required. Because of this, the centrifugal distortion constant \( D_{JK} \) was evaluated through a determination of the difference in the frequencies of the most intense line for \( K = 1 \) and the most intense line for \( K = 2 \) in the \( J = 2→3 \) spectrum. Calculations of the predicted frequencies for this transition are based on the work of Wolfe.

The data in Tables 14 and 15 give the frequencies and intensities for the \( J = 2→3, K = 1 \) and \( K = 2 \) transitions, respectively. These tables were computed from the calculations of Wolfe \((31)\) by simply mul-
tiplying his data by -2.8688, the constant which converts frequencies in terms of quadrupole coupling constant with respect to the bond axis to frequencies in terms of quadrupole coupling constant with respect to the molecular symmetry axis, $eQ_{zz}$. Figures 6 and 7 show the sums of the intensities in Tables 14 and 15 at intervals of 0.005 $eQ_{zz}$, each sum containing all components which lie within 0.005 $eQ_{zz}$ of its center. The summation of components within 0.005 $eQ_{zz}$ was required to obtain the correspondence between measured and predicted hyperfine spectra shown in Figure 10.

Figure 8 is typical of recordings made using pressures of 30 $\mu$ or less. Equipment sensitivity was such that 10 $\mu$ was the lowest pressure for which prominences C, E, and F could be seen in a recording. Results of repeatedly measuring frequencies of the major prominences are given in Table 4. Figure 9 illustrates a typical spectrum measured with pressures between 60 $\mu$ and 150 $\mu$. The frequency of the second-strongest prominence, C of Figure 9, corresponds to that of the strongest prominence, C, for the low pressure case illustrated in Figure 8. The largest prominence (E,F) of Figure 9 corresponds to a frequency intermediate to prominences E and F of Figure 8, indicating that the strongest high-pressure prominence contains components E and F. A comparison of Figure 8 with Figures 6 and 7 suggests that the largest component, C, corresponds to the strongest component (designated as e in Figure 6 and Table 14) of the predicted spectrum for $K = 1$.

From data similar to Figure 9, it was seen that the smallest Stark displacement is 2.9 mc for a nominal field of 180 volts/cm. These data
Figure 6. Predicted Hyperfine Pattern, $J = 2 \rightarrow 3$, $K = 1$. 
Figure 7. Predicted Hyperfine Pattern, J = 2 → 3, K = 2.
Figure 8. $J = 2 \rightarrow 3$ Transition in CFC$_3^{35}$ at 20$\mu$ Pressure.
Table 4. Observed and Calculated Features of the J = 2→3 Hyperfine Spectrum

<table>
<thead>
<tr>
<th>Designation</th>
<th>Frequency (mc)</th>
<th>Intensity</th>
<th>Calculated Frequency (mc)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>unobserved</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>14,784.75 ± 0.10</td>
<td>M*</td>
<td>14,784.25 ± 0.16</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>14,785.64 ± 0.14</td>
<td></td>
<td>14,786.02 ± 0.11</td>
<td>26</td>
</tr>
<tr>
<td>unobserved</td>
<td></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>14,790.46 ± 0.08</td>
<td>W</td>
<td>14,789.59 ± 0.07</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>14,790.24 ± 0.06</td>
<td></td>
<td>14,790.52 ± 0.07</td>
<td>99</td>
</tr>
<tr>
<td>C</td>
<td>14,792.80 ± 0.06</td>
<td>S</td>
<td>14,792.94 ± 0.07</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>14,793.00 ± 0.06</td>
<td></td>
<td>14,793.24 ± 0.06</td>
<td>46</td>
</tr>
<tr>
<td>D</td>
<td>14,793.92 ± 0.08</td>
<td>W</td>
<td>14,793.59 ± 0.06</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>14,793.95 ± 0.06</td>
<td></td>
<td>14,794.66 ± 0.08</td>
<td>118</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>14,795.26 ± 0.08</td>
<td>S</td>
<td>14,795.14 ± 0.07</td>
<td>195</td>
</tr>
<tr>
<td>G</td>
<td>14,796.25 ± 0.10</td>
<td>W</td>
<td>14,796.29 ± 0.08</td>
<td>58</td>
</tr>
</tbody>
</table>

*Intensities are S, strong; M, medium; W, weak.
Table 4. Observed and Calculated Features of the $J = 2 \rightarrow 3$

Hyperfine Spectrum (Continued)

<table>
<thead>
<tr>
<th>Designation</th>
<th>Frequency (Mc)</th>
<th>Intensity</th>
<th>K</th>
<th></th>
<th>Frequency (Mc)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>14,797.12 ± 0.10</td>
<td>M</td>
<td>1</td>
<td>λ</td>
<td>14,796.84 ± 0.08</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>8</td>
<td>14,797.02 ± 0.09</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>9</td>
<td>14,797.32 ± 0.09</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>m</td>
<td>14,797.77 ± 0.09</td>
<td>65</td>
</tr>
<tr>
<td>I</td>
<td>14,799.50 ± 0.30</td>
<td>W</td>
<td>1</td>
<td>n</td>
<td>14,799.28 ± 0.11</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>o</td>
<td>14,799.85 ± 0.11</td>
<td>31</td>
</tr>
<tr>
<td>unobserved</td>
<td>2</td>
<td></td>
<td>10</td>
<td>10</td>
<td>14,800.58 ± 0.11</td>
<td>19</td>
</tr>
<tr>
<td>unobserved</td>
<td></td>
<td></td>
<td>1</td>
<td>p</td>
<td>14,802.38 ± 0.14</td>
<td>29</td>
</tr>
<tr>
<td>J</td>
<td>14,803.40 ± 0.30</td>
<td>W</td>
<td>2</td>
<td>11</td>
<td>14,803.18 ± 0.14</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>12</td>
<td>14,803.98 ± 0.15</td>
<td>97</td>
</tr>
<tr>
<td>unobserved</td>
<td>2</td>
<td></td>
<td>13</td>
<td>13</td>
<td>14,807.98 ± 0.20</td>
<td>78</td>
</tr>
<tr>
<td>unobserved</td>
<td>2</td>
<td></td>
<td>14</td>
<td>14</td>
<td>14,809.45 ± 0.21</td>
<td>39</td>
</tr>
<tr>
<td>unobserved</td>
<td>2</td>
<td></td>
<td>15</td>
<td>15</td>
<td>14,811.09 ± 0.23</td>
<td>58</td>
</tr>
</tbody>
</table>
Figure 9. $J = 2 \rightarrow 3$ Transition in CFC1$_3^{35}$ at 75\$\mu$ Pressure.
and Equation 8 yield a value of dipole moment which gives approximate agreement with the value of 0.45 debye obtained by low frequency measurements (28).

The following calculation was used to determine the approximate frequency of the most intense $J = 2 \rightarrow 3$ component based on the $J = 1 \rightarrow 2$ data and the predicted $J = 2 \rightarrow 3$ hyperfine spectrum. Use of Equation 1 evaluated for $J = 2, K = 1$ yields

$$ f = 6(B - D_{JK}) - 108D_J + \Delta \nu_Q = 6(B - D_{JK} - 8D_J) - 60D_J + \Delta \nu_Q. \quad (12) $$

Equation 5 for $J = 2$ and $eQV_{zz}$ equal to $37.3 \pm 0.5$ mc gives

$$ \Delta \nu_Q = -1.00 \pm 0.01 \text{ mc}. \quad (13) $$

The result of substituting Equations 10 and 13 into Equation 12 is

$$ f = 14,791.34 - 60D_J \pm 0.06. $$

Because it appeared that no major prominence* had a frequency corresponding to this expected frequency (based on the $J = 1 \rightarrow 2$ spectrum), considerable effort was devoted to measuring spectra corresponding to larger values of $J$. According to the work described in the section which follows, prominence C in Figure 5 is the only line that can correspond to the strongest line in the $K = 1$ spectrum. On the basis of the above, prominence E must indeed correspond to component e of the predicted spectrum because prominence C is (a) the strongest component observed at low

---

*A negative value of $D_j$ is required to obtain agreement in frequency; previous investigations for other molecules have yielded only positive values (32).
pressures, and (b) the only observed prominence having a frequency compatible with measured components of other rotational spectra.

On the basis of the relative intensities of major components in the predicted spectra, prominence E is expected to correspond to the most intense component in the \( K = 2 \) spectrum (designated as \( b \)) and prominence F is expected to correspond to the second-most intense component in the \( K = 1 \) spectrum (designated as \( j, k \)). At the lower pressures, the frequency of the peak of \((j, k)\) is due almost entirely to component \( j \) of Table 14. If this assignment of components is correct, the frequency of prominence F, according to Table 4, will exceed that of prominence C by 0.0626 eV. By using 37.3 ± 0.5 mc for eV (obtained from the \( J = 1 \rightarrow 2 \) spectrum) and 14,792.80 ± 0.06 mc for C, it is then predicted that the component corresponding to the second-most intense component of the \( K = 1 \) spectrum will be located at 14,795.14 ± 0.07 mc. This must correspond to the observed feature F at 14,795.26 ± 0.08 mc.

The assumption, based on relative intensities, that E corresponds to the most intense component of the \( K = 2 \) spectrum can be tested by comparing a predicted spectrum, obtained by adding the two predicted spectra, with the observed composite spectrum.

The amount that the \( K = 2 \) spectrum must be shifted with respect to the \( K = 1 \) spectrum, because of centrifugal distortion, is calculated below. For the most intense component in the \( K = 1 \) spectrum

\[
6b - 6d_{JK} - 108d_j - 0.02679 (37.3 \pm 0.5) = 14,792.80 \pm 0.06,
\]

and for the most intense component in the \( K = 2 \) spectrum

\[
6b - 24d_{JK} - 108d_j - 0.07143 (37.3 \pm 0.5) = 14,794.66 \pm 0.08.
\]
A combination of these equations gives

\[ D_{jk} = -196 \pm 6 \text{ kc.} \]

Figure 10 shows a comparison of the measured prominences with the predicted prominences; the general agreement in line structure indicates a valid assignment of components. Table 4 contains calculated frequencies for all components listed in Tables 14 and 15. These calculated frequencies are compared with the frequencies corresponding to the measured prominences. Although several of the weaker components were not identified, a sufficient number of other prominences were identified to verify that the value of \( eQV_{zz} \) obtained for the \( J = 1 \rightarrow 2, K = 1 \) spectrum is valid for the \( J = 2 \rightarrow 3, K = 1 \) and 2 spectra.

The absorption coefficient of the most intense component of the \( J = 2 \rightarrow 3 \) spectrum was calculated by the same method used for the most intense component of the \( J = 1 \rightarrow 2 \) spectrum. Equation 11 and data from Table 14 provide an absorption coefficient of \( 2.5 \times 10^{-8} \text{ cm}^{-1} \); the corresponding coefficient for the \( J = 1 \rightarrow 2 \) transition is \( 4.5 \times 10^{-10} \text{ cm}^{-1} \). The increased absorption coefficient for the \( J = 2 \rightarrow 3 \) over the \( J = 1 \rightarrow 2 \) value is offset by a lower spectrometer sensitivity. The sensitivity is lower because the LN78B crystal detectors used for the \( J = 2 \rightarrow 3 \) region are less efficient than the LN23E crystals used for the \( J = 1 \rightarrow 2 \) region.

Other Rotational Transitions.—Measurements were made for the frequencies of the largest resolvable prominence at pressures of about 25 \( \mu \) for each of the rotational transitions \( J = 3 \rightarrow 4 \) to \( J = 6 \rightarrow 7 \), inclusive. The
Figure 10. Observed and Calculated Features of the $J = 2 \rightarrow 3$
Transition in $\text{CFC}_3^{35}$. 
measurements were used to assist in the assignment of the major prominences in the $J = 2\rightarrow 3$ hyperfine spectrum. The results were analyzed with Equation 5,

\[
\Delta \nu_Q = \beta(J) eQV_{zz},
\]

where

\[
\beta(J) = -\frac{3}{4} \left[ \frac{(J+1)(J+2)+(4J+7)}{(2J+5)(2J+3)(J+2)(J+1)} \right].
\]

$\Delta \nu_Q$ is the frequency by which the largest individual line is shifted as a result of quadrupole interaction. Results of the measurements and calculations, including those for the $J = 1\rightarrow 2$ and $J = 2\rightarrow 3$ spectra, are given in Table 5. Because the strongest component is expected to correspond to $K = 1$, Equation 1 may be expressed as

\[
\frac{f_{-\Delta \nu_Q}}{2(J+1)} = (B-D_{JK}) - 2D_J(J+1)^2. \tag{14}
\]

The values in the right-hand column for the $J = 1\rightarrow 2$ and $J = 3\rightarrow 4$ transitions assist in assigning the frequency of the largest measured prominence in the $J = 2\rightarrow 3$ hyperfine spectrum at low pressures to the frequency corresponding to the largest individual line in the predicted spectrum. The frequency of this $J = 2\rightarrow 3$ component is expected to occur within the limits of frequencies corresponding to the values of $(f_{-\Delta \nu_Q})/2(J+1)$ for the $J = 1\rightarrow 2$ and $J = 3\rightarrow 4$ spectra. Based on Table 5, it should lie between 14,791.3 mc and 14,793.3 mc; prominence C (Table 4) is the only observable prominence within these limits.
Table 5. Frequencies of the Strongest Line in Various Spectra

<table>
<thead>
<tr>
<th>Transition</th>
<th>Measured Frequency, f, of Strongest Line</th>
<th>β(J)</th>
<th>Δν_Q*</th>
<th>( \frac{f-Δν_Q}{2(J+1)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→2</td>
<td>9,859.30 ± 0.04</td>
<td>-0.0607</td>
<td>-2.26 ± 0.03</td>
<td>2465.39 ± 0.01</td>
</tr>
<tr>
<td>2→3</td>
<td>14,792.80 ± 0.06</td>
<td>-0.0268</td>
<td>-1.00 ± 0.01</td>
<td>2465.63 ± 0.01</td>
</tr>
<tr>
<td>3→4</td>
<td>19,725.17 ± 0.01</td>
<td>-0.0148</td>
<td>-0.55 ± 0.01</td>
<td>2465.72 ± 0.00</td>
</tr>
<tr>
<td>4→5</td>
<td>24,657.26 ± 0.03</td>
<td>-0.0093</td>
<td>-0.35 ± 0.00</td>
<td>2465.76 ± 0.00</td>
</tr>
<tr>
<td>5→6</td>
<td>29,588.95 ± 0.01</td>
<td>-0.0063</td>
<td>-0.23 ± 0.00</td>
<td>2465.76 ± 0.00</td>
</tr>
<tr>
<td>6→7</td>
<td>34,520.42 ± 0.01</td>
<td>-0.0046</td>
<td>-0.17 ± 0.00</td>
<td>2465.76 ± 0.00</td>
</tr>
</tbody>
</table>

\[ Δν_Q = β(J)eν_{Q_{zz}}, \text{ where } β(J) = -\frac{3}{4} \frac{(J+1)(J+2)+(4J+7)}{(2J+5)(2J+3)(J+2)(J+1)} \]

*eν_{Q_{zz}} = 37.3 ± 0.5 mc based on J = 1→2 data.
The increasing value of \((f - \Delta v_q)/2(J+1)\) with increasing \(J\) is a strange effect, if one assumes that it is the result of centrifugal stretching, because it implies a negative value of \(D_j\). Calculations based on Table 5, the \(J = 1 \rightarrow 2\) data and the \(J = 2 \rightarrow 3\) through \(J = 6 \rightarrow 7\) data yield for \(D_j\) the values: \(-0.024 \pm 0.002\) mc, and \(-0.014\) mc, \(-0.009\) mc, \(-0.006\) mc, and \(-0.004\) mc with probable errors less than \(0.001\) mc. A least squares fit for the various rotational spectra permitted the determination of a single value of \(D_j\) which provides a good prediction for locating the frequencies corresponding to the \(J = 1 \rightarrow 2\) through \(J = 6 \rightarrow 7\) spectra. This analysis gives

\[
(B - D_{JK}) = 2465.6\ mc\ and
\]

\[
D_j = -6.6\ kc.
\]

Use of \(D_{JK}\) obtained from analysis of the \(J = 2 \rightarrow 3\) spectrum gives

\[
B = 2465.4\ mc,
\]

\[
D_{JK} = -196 \pm 6\ kc,\ and
\]

\[
D_j = -6.6\ kc.
\]

The standard deviation of the frequencies predicted by the equation

\[
f = 2(J+1)(B-D_{JK}K^2) - hD_j(J+1)^3 + \Delta v_q,
\]

where

\[
\Delta v_q = -\frac{3}{4} \frac{(J+1)(J+2)(4J+7)}{(2J+5)(2J+3)(J+2)(J+1)} eqV_{zz},
\]
and

$$eQV_{zz} = 37.3 \text{ mc},$$

from the set of measured frequencies in Table 5 is 0.5 mc. With this fit
the largest discrepancy occurs for $J = 1$; the measured frequency is ap-
proximately one megacycle lower than is predicted with the constants ob-
tained by the least squares fit.

**Quadrupole Coupling Constant.**—In order to compare the quadrupole cou-
pling constant of fluorotrichloromethane with that of other methyl
chlorides, it is convenient to express the field gradient at the chlorine
nucleus $V_{zz}$ in terms of $V_{aa}$, where $a$ is the C-Cl bond direction. If it
is assumed that the field gradient is due entirely to a cylindrically
symmetric charge distribution about the C-Cl bond, then (15)

$$V_{zz} = (\cos 2\alpha) V_{aa} = \frac{1}{2}(3 \cos^2 \beta - 1) V_{aa},$$

where $2\alpha$ is the angle Cl-C-Cl and $\beta$ is the angle between a C-Cl bond and
the molecular symmetry axis. The value $109^\circ 40'$ for $2\alpha$ gives

$$eQV_{aa} = -110.8 \pm 1.5 \text{ mc}$$

for the quadrupole coupling constant of CFCl$_3$. Table 6 lists the quadru-
pole coupling constants obtained from both microwave spectra and pure
quadrupole resonance studies for various methyl chlorides. Where neces-
sary for the derivation of $eQV_{aa}$, the assumption of axial symmetry of
charge about the C-Cl bond was made.
Table 6. The Quadrupole Coupling Constant of C{l}^{35} in the Methyl Chlorides

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Gas ( eQV_{aa} )</th>
<th>reference</th>
<th>Solid ( eQV_{aa} )</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)Cl</td>
<td>-75.50 mc</td>
<td>(33)</td>
<td>68.40 mc</td>
<td>(35)</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>-78.4 ± 2</td>
<td>(34)</td>
<td>72.47</td>
<td>(35)</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>-80.39 ± 0.22</td>
<td>(15)</td>
<td>76.98</td>
<td>(35)</td>
</tr>
<tr>
<td></td>
<td>-102.5 ± 1.4</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CFCl(_3)</td>
<td>-110.8 ± 1.5</td>
<td>*</td>
<td>79.63</td>
<td>(35)</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>81.85</td>
<td></td>
<td>(35)</td>
<td></td>
</tr>
</tbody>
</table>

*Present investigation

The coupling constant for fluorotrichloromethane obtained in the present investigation does not fit the empirical sequences apparent in the table.

The possible discrepancy between the coupling constant obtained in this investigation for CFCl\(_3\) and the constant obtained by Wolfe in an analysis of the \( J = 2 \rightarrow 3 \) spectrum of CHCl\(_3\), the only previously investigated molecule with three nuclei with spin 3/2, was particularly disturbing. For this reason the \( J = 1 \rightarrow 2 \) spectrum of the most abundant symmetric top species of chloroform was examined; the measurements were made with the sample at dry ice temperature. The hyperfine structure for this spectrum was found to have the same general features as that of CFCl\(_3\). The two relatively strong lines were repeatedly measured; the strongest line occurred at 13,204.32 ± 0.04 mc and the second strongest line occurred at 13,208.89 ± 0.05 mc. In accordance with the discussion of the \( J = 1 \rightarrow 2 \) spectrum for CFCl\(_3\), the frequency difference of these lines is 0.1250 \( eQV_{zz} \). This provides
\[ eQV_{zz} = 36.3 \pm 0.5 \text{ mc}. \]

Use of the conversion based on the assumption of charge symmetry about the C-Cl bond direction and the Cl-C-Cl angle of 110°55' (15) gives

\[ eQV_{aa} = -102.5 \pm 1.4 \text{ mc}. \]

There is a general agreement in the ratio of quadrupole coupling constant of CFCl₃ to that of CHCl₃ obtained from the pure quadrupole resonance data and the ratio of the much larger constants obtained in this investigation.

Experience with the analysis of the \( J = 2 \rightarrow 3 \) spectrum of CFCl₃ had indicated that it would have been virtually impossible to analyze this spectrum without the value of \( eQV_{zz} \) from the \( J = 1 \rightarrow 2 \) spectrum and with data from higher rotational transitions. On this basis it was decided that Wolfe's frequency data should be reviewed to ascertain if they represent a definite discrepancy with the \( J = 1 \rightarrow 2 \) data.

Table 7 compares measured frequencies of lines in several spectra for chloroform and the values of \( f - \Delta \nu_Q / 2(J+1) \) similar to Table 5. The lowest measured frequency for the \( J = 2 \rightarrow 3 \) transition was taken from Table 2 of reference 15 to indicate that this line is indeed the most intense line for a more completely resolved spectrum. That this can happen may be seen by a comparison of Figures 8 and 9 for CFCl₃. Wolfe's measured spectrum has two large prominences similar to those in Figure 9. If it is assumed that the lowest frequency reported by Wolfe corresponds to that of the most intense component for \( K = 1 \), then the second most intense \( K = 1 \) line would occur at 19,812.86 ± 0.06 mc (if
\( \varepsilon Q_{zz} = 36.6 \pm 0.5 \text{ mc} \); the frequency of the strongest prominence in Wolfe's data was 19,812.92 ± 0.10 mc. The analysis above makes use of \( K = 1 \) lines only. Wolfe based his analysis on the least squares fit of lines identified with the \( K = 2 \) spectrum; this analysis provided the position of his most intense line. Because it was not known why the quadrupole coupling constant might change with \( K \) (or \( J \)), and since such a change was not evident in the analysis of the \( J = 2 \rightarrow 3 \) spectrum of CFCl₃, Wolfe's frequency data were further reviewed.

Table 7. Various Chloroform Lines

<table>
<thead>
<tr>
<th>Transition</th>
<th>Measured Frequency</th>
<th>Ref.</th>
<th>( \Delta \nu_Q^* )</th>
<th>( \frac{f-\Delta \nu_Q}{2(J+1)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→2</td>
<td>13,204.32 ± 0.04</td>
<td>**</td>
<td>-2.22 ± 0.03</td>
<td>3301.64 ± 0.01</td>
</tr>
<tr>
<td>2→3</td>
<td>19,812.92 ± 0.10</td>
<td></td>
<td>-0.98 ± 0.01</td>
<td>3302.32 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>19,810.57 ± 0.05</td>
<td>(15)</td>
<td>-0.98 ± 0.01</td>
<td>3301.93 ± 0.01</td>
</tr>
<tr>
<td>6→7</td>
<td>46,227.2 ± 0.15</td>
<td>(36)</td>
<td>-0.17 ± 0.00</td>
<td>3301.96 ± 0.01</td>
</tr>
</tbody>
</table>

\(*\varepsilon Q_{zz} = 36.6 \pm 0.5 \text{ mc based on } J = 1 \rightarrow 2 \text{ data}

**Present Investigation

A good fit to most of Wolfe's data can be made with the assignment discussed above for the \( K = 1 \) spectrum (Figure 6) if the \( K = 2 \) spectrum (Figure 7) is shifted by \( \Delta \nu_Q/\varepsilon Q_{zz} \) equal to 0.09878. This shift corresponds to \( D_{JK} = -200.9 \pm 2.9 \text{ kc} \). With this assignment relatively weak lines corresponding to 13, 14, 15 (Figure 7) would occur at 19,824.66 mc, 19,826.31 mc and 19,827.77 mc; these are outside the range of frequencies reported by Wolfe. That there is a good possibility these lines actually exist may be seen by referring to the recorded spectrum in Figure 18 of
reference 24. As expected for a spectrum as complex as this one, a perfect fit will not be obtained with this procedure. It was, however, reassuring to notice that a prominent line observed by Wolfe at 19,808.28 ± 0.12 mc but not positively identified in his assignment (see Figure 21 of reference 24) corresponds to line d (Figure 6), which in the present assignment is located at 19,808.34 ± 0.06 mc.

The present investigation indicates no definite discrepancies between the eQV$_{zz}$ for the J = 1→2 and the J = 2→3 spectra of CFCl$_3$ or CHCl$_3$. The values of eQV$_{sa}$ obtained under the assumption of charge symmetry about the C-Cl bonds seem too large in comparison with the pure quadrupole data. Therefore one must conclude that the quadrupole interaction calculations common to the J = 1→2 and J = 2→3 spectra for three nuclei are in error by a multiplicative factor or the assumption of charge symmetry about the C-Cl bond is not valid for the case of three nuclei.

Discussion of Results

The existence of what has appeared to be a negative value of D$_J$ is interesting because previous investigations have yielded only positive values (32), and D$_J$ has been expected to always be positive because centrifugal stretching due to rotation about any given axis will always tend to increase the moment of inertia about that axis (32). Thomas, Cox, and Gordy (37) have, however, presented an argument which permits the existence of a negative D$_J$. They argue that the molecular distortion comes about principally by a change in the nature of the C-Cl bond in CHCl$_3$ with a change in angle β (Figure 1). Such
a mechanism might make the C-F bond (and the C-H bond) shorter and $D_J$ negative. CFCl₃ and CHCl₃ are the only molecules with three nuclei of spin 3/2 to which the theory of quadrupole interaction has been applied; they are also the only molecules for which negative values of $D_J$ have been obtained. Effects which might produce the strange values calculated for $D_J$ are discussed below.

One might surmise that the increasing value of $f - \Delta \nu_Q / 2(J+1)$ with increasing $J$ is caused by increasingly larger permissible $K$ with $J$. Since $D_{JK}$ is negative and $D_J$ is expected to be small, this might shift the peak of the unresolved components of different $K$ toward higher frequencies. Equation 14

$$\frac{f - \Delta \nu_Q}{2(J+1)} = (B - D_{JK}K^2) - 2D_J(J+1)^2$$

may be helpful to the reader. A misleading peak could result from a summation of hyperfine components of different $K$ in a manner similar to that which causes the misleading peak in Figure 9. This explanation is untenable because of the negative value of $D_J$ which is obtained in comparing the $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ spectra, for which the major $K = 1$ components are indeed resolved for both spectra.

The validity of using Equation 5 to calculate the frequency shift of the most intense line in each rotational transition might be questioned because of the large values obtained for $eQ_{aa}$. However, from an inspection of Tables 13 and 14 it can be seen that this equation does predict the same shifts that were calculated from Equation 5 for the $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ spectra. Since the measured spectra closely
resemble the spectra predicted from the matrix elements of Equation 3, Equation 5 in conjunction with the determined values of $eQV_{zz}$ does indeed predict the correct frequency shift of the most intense line ($K = 1$) from the center of each hyperfine spectrum. This will be true even if the values of $eQV_{zz}$ so obtained are in error by a multiplicative constant because of an error in the theoretical calculations.

The above discussion does not rule out the possibility that the center of each hyperfine spectrum may be shifted with respect to their respective rotational lines. If each $K = 1$ hyperfine spectrum were shifted downward in frequency by an amount that decreases with increasing $J$, the spacing between adjacent $K = 1$ spectra would change so as to give the effect of a negative value of $D_J$. The large and almost equal negative values of $D_{JK}$, obtained in the analysis of the $J = 2 \rightarrow 3$ spectra for CFCl$_3$ and CHCl$_3$, might then indicate that there exists a shift in the centers of the hyperfine spectra which is dependent on $K$ in addition to $J$.

The fundamental vibrational levels (38) for CFCl$_3$, expressed in inverse centimeters are $\omega_1 = 1085$, $\omega_2 = 534$, $\omega_3 = 351$, $\omega_4 = 846$, $\omega_5 = 400$, and $\omega_6 = 245$. The first three are nondegenerate and of species $A_1$, and the last three are doubly degenerate and of species $E$. These vibrational levels are distributed so that a relatively large number of molecules are in the first-excited vibrational state, even at dry ice temperature. The ground ($\omega_0$) and first excited ($\omega_6$) states have the following approximate populations:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\omega_0$</th>
<th>$\omega_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$27^\circ C$</td>
<td>25%</td>
<td>15%</td>
</tr>
<tr>
<td>$-78^\circ C$</td>
<td>57%</td>
<td>19%</td>
</tr>
</tbody>
</table>
The lack of knowledge of the rotational constants for the excited vibrational states makes it impossible to quantitatively take into account the possible effects of interference from this source. Unpredicted weak recorder deflections may be produced by vibrational effects but they may also be produced by lines from other isotropic species or by weak reflections in the spectrometer.
CHAPTER V

CONCLUSIONS

A conventional Stark spectrograph is analogous to a superheterodyne detector with intermediate frequency of zero. Because of this, a crystal diode detector operated at a higher microwave power level than is usual for spectrographs will provide improved sensitivity. A crystal diode detector operating at a one to two milliwatt power level can be used at X-band with an 85-kc Stark modulation system to detect lines having absorption coefficients less than $10^{-10}$ cm$^{-1}$.

Approximate rotational constants of CFCl$_3$ are

$$A(I) = B(I) = 2465.39 \text{ mc}$$

for CFCl$_3^{35}$, and

$$A(II) = 2463.22 \text{ mc}$$

$$B(II) = 2398.50 \text{ mc}$$

for CFCl$_2^{35}$Cl$^{37}$. The structural parameters for CFCl$_3$ are:

$$\text{C-Cl} = 1.76 \text{ A},$$

$$\text{C-F} = 1.33 \text{ A}, \text{ and}$$

$$\text{Cl-C-Cl} = 109^\circ 40'.$$

Based on the quadrupole coupling theory, the quadrupole coupling constant with respect to the molecular symmetry axis, $eQ_{zz}$, of CFCl$_3^{35}$
is 37.3 ± 0.5 mc. The quadrupole coupling constant in CFCl$_3^{35}$ with respect to the C-Cl bond, eQ$_{aa}$, is -110.8 ± 1.5 mc under the usual assumption that extranuclear charge is symmetric about the bond axis. The quadrupole coupling constant in CHCl$_3^{35}$ with respect to the symmetry axis is 36.6 ± 0.5 mc; eQ$_{aa}$ under the assumption of charge symmetry is -102.5 ± 1.4 mc.

Details of the measured $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ hyperfine spectra for CFCl$_3^{35}$ and CHCl$_3^{35}$ match the predicted hyperfine spectra. The magnitudes of the eQ$_{aa}$ obtained for CFCl$_3$ and CHCl$_3$ are large compared with data from other methyl chlorides. There is a general agreement in the ratio of quadrupole coupling constant of CFCl$_3$ to that of CHCl$_3$ from pure quadrupole resonance data and the ratio of the larger eQ$_{aa}$ obtained in this investigation.

Based on the existing quadrupole interaction theory, the centrifugal distortion constant D$_J$ is negative for K = 1 lines and the magnitude decreases with increasing $J$. Frequencies for which the maximum absorption occurs in the $J = 1 \rightarrow 2$ through $J = 6 \rightarrow 7$ rotational transitions of CFCl$_3^{35}$ indicate that the rotational constant B and the centrifugal distortion constants D$_J$ and D$_{JK}$ are

$$(B - D_{JK}) = 2465.6 \text{ mc and}$$

$$D_J = -6.6 \text{ kc.}$$

Use of D$_{JK}$ obtained from the $J = 2 \rightarrow 3$ spectrum gives

$$B = 2465.4 \text{ mc,}$$

$$D_{JK} = -196 \text{ kc, and}$$

$$D_J = -6.6 \text{ kc.}$$
The large values of $eQV_{aa}$ obtained for CFCl$_3$ and CHCl$_3$ indicate one of the following difficulties: (1) the quadrupole interaction theory is in error by a multiplicative factor, or (2) the usual assumption of charge symmetry about the C-Cl bond is not valid for this molecule. Existence of an error in the quadrupole coupling theory might explain the large values of $eQV_{aa}$ and $D_{JK}$, the negative values of $D_J$, and the dependence of $D_J$ on $J$. 
CHAPTER VI

RECOMMENDATIONS

The $J = 0 \rightarrow 1$ spectrum of a molecule having three nuclei of spin $3/2$ should be investigated. CHCl$_3$ is preferable to CFCI$_3$ for this purpose because the larger dipole moment results in a greater absorption coefficient and a larger Stark displacement for the same electric field. Equipment required for the $K = 0$ spectrum must supply a large electric field because the Stark effect for $K = 0$ is of second order. Because of this the equipment should consist of a Stark modulator operating at 1000 cps or less to provide an adequate electric field strength without excessive power requirements on the Stark modulator. At this modulation frequency a bolometer detector will provide greater sensitivity than would be obtainable with a crystal detector.

Data which are better resolved than Wolfe's should be experimentally obtained for the $J = 2 \rightarrow 3$ hyperfine spectrum of CHCl$_3$.$^{35}$

Details of the $J = 3 \rightarrow 4$ and higher rotational transitions of CFCI$_3$ or CHCl$_3$ should be further investigated. It may be possible to associate frequencies corresponding to centers of the $K = 2$ hyperfine spectra. These frequencies, with the $K = 1$ data from the present investigation, will provide insight into a possible dependence of $D_{JK}$ on $J$.

The theory of quadrupole interaction should be reinvestigated with a view toward explaining the large values of $eQ_{aa}$ and $D_{JK}$, the negative values of $D_J$, and the dependence of $D_J$ on $J$. 
APPENDICES
APPENDIX A

DERIVATION FOR ADDITION OF TWO IN-PHASE WAVES

For convenience let the transmitted microwave power from the signal oscillator be represented by a voltage defined so that \( V^2 = ZP \), where \( P \) is the power and \( Z \) is the guide impedance. \( V \) is the rms voltage of the wave. To further simplify the rotation, let \( Z = 1 \). Let a much smaller voltage, \( \delta V \), from the same oscillator be added in phase with \( V \). The power contained in the wave having amplitude \( V + \delta V \) is then

\[
P + \Delta P = (V + \delta V)^2 = V^2 + 2V(\delta V) + (\delta V)^2.
\]

Since \( V^2 = P \), the above equation gives

\[
(\delta V)^2 + 2V(\delta V) - \Delta P = 0.
\]

Since \( \Delta P \) and \( \delta V \) must have the same sign, use of the quadratic equation gives

\[
\delta V = -V + \sqrt{V^2 + \Delta P} = -\sqrt{P + \frac{\Delta P}{P}} \left[ 1 + \frac{\frac{\Delta P}{P}}{\frac{1}{2}} \right].
\]

Expansion of the second term by the binomial series gives

\[
\delta V = -\sqrt{P} + \sqrt{P} \left[ 1 + \frac{1}{2} \left( \frac{\Delta P}{P} \right) - \frac{1}{8} \left( \frac{\Delta P}{P} \right)^2 + \ldots \right].
\]

\( P/\Delta P \) will exceed \( 10^6 \) for the cases to be considered. Then

\[
\delta V \approx \frac{1}{2} \frac{\Delta P}{\sqrt{P}}.
\]  \( \text{(15)} \)
Since \((8V)^2\) is the power of the wave having amplitude \(8V\), \(P'\), squaring Equation 15 gives

\[
P' = \frac{(\Delta P)^2}{4P}.
\]  

(16)

To clarify the meaning of Equation 16 consider the following example of its application to the fields in a Stark cell. Let \(\Delta P\) be the power absorbed by the gas and let \(P\) be the input power to a cell having negligible attenuation. Then \(P'\) is the small amount of unbalanced power which would exist due to an absorption line if one were to use r-f balancing to cancel the power when the oscillator was not at the frequency of an absorption line.
APPENDIX B

CORRECTION TO MOMENTS OF INERTIA FOR SPECIES II

Principal moments of inertia are obtained by determining the roots of the secular equation (39)

\[
\begin{vmatrix}
I_{xx} - I & I_{xy} & I_{xz} \\
I_{xy} & I_{yy} - I & I_{yz} \\
I_{xz} & I_{yz} & I_{zz} - I
\end{vmatrix} = 0.
\]

The origin in the coordinate system selected is at the molecular center of mass, \( z \) is along the molecular symmetry axis, \( x \) is in the C-F-Cl\(^{37} \) plane and perpendicular to \( z \), and \( y \) is perpendicular to \( x \) and \( z \). The secular equation for this coordinate system reduces to

\[
\begin{vmatrix}
I_{xx} - I & 0 & I_{xz} \\
0 & I_{yy} - I & 0 \\
I_{xz} & 0 & I_{zz} - I
\end{vmatrix} = 0.
\]

In the notation for asymmetric top molecules \( I_A < I_B < I_C \), the principal moments of inertia obtained from the secular equation are

\[
I_A = \frac{(I_{xx} + I_{zz}) - (I_{xx} - I_{zz})}{2} \sqrt{1 + \frac{4I_{xz}^2}{(I_{xx} - I_{zz})^2}}
\]
\[ I_B = I_{yy} \]

\[ I_C = \frac{(I_{xx} + I_{zz})}{2} + \frac{(I_{xx} - I_{zz})}{2} \sqrt{1 + \frac{I_{xz}^2}{(I_{xx} - I_{zz})^2}}. \]

Let

\[ \Delta = \frac{I_{xz}^2}{(I_{xx} - I_{zz})^2}; \]

then for \( \Delta \ll 1 \), the principal moments of inertia are

\[ I_A = I_{xx} - \frac{I_{xz}^2}{(I_{zz} - I_{xx})}, \]

\[ I_B = I_{yy}, \] and

\[ I_C = I_{zz} + \frac{I_{xz}^2}{(I_{zz} - I_{xx})}. \]
APPENDIX C

RACAH COEFFICIENTS

Most of the coefficients used for calculation of the $J = 1 \rightarrow 2$ spectrum were obtained from published tables \(^{(40,41)}\). The remainder were obtained by hand from Equation 17 below and the tables by Sharpe et al \(^{(40)}\). The following discussion was taken from the aforementioned report by Sharpe.

The Racah coefficient $W_{\text{abcd},ef}$ arises in the relationship between different ways of combining the vectors $a$, $b$, and $d$ to give a resultant $c$. In terms of Clebsch-Gordan coefficients, this relationship is:

$$(ab|e)(ed|c) = \sum_f (2e+1)^{1/2} (2f+1)^{1/2} (bd|f)(af|c)W_{\text{abcd},ef}.$$

As this relationship is independent of the magnetic quantum numbers, these have been suppressed in writing the Clebsch-Gordan coefficients.

An algebraic formula for $W_{\text{abcd},ef}$ has been given by Racah \(^{(26)}\):

$$W_{\text{abcd},ef} = \Delta(abe) \Delta(ode) \Delta(acf) \Delta(bdf) w_{\text{abcd},ef} \quad (17)$$

where

$$w_{\text{abcd},ef} = \sum_z \left\{ \frac{(-1)^{a+b+c+d+z}(z+l)!}{(z-a-b-e)! (z-c-d-e)! (z-a-c-f)! (z-b-d-f)!} \times \frac{1}{(a+b+c+d-z)! (a+d+e+f-z)! (b+c+e+f-z)!} \right\}.$$

The "triangle coefficient" $\Delta(abc)$ is defined by
\[
[\Delta(abc)]^2 = \frac{(a+b-c)!(b+c-a)!(c+a-b)!}{(a+b+c+1)!}
\]

provided \(a, b, c\) form the sides of a triangle with integral sum. \(\Delta\) is symmetrical with respect to permutations of \(a, b, c\). The sum runs over all integral values of \(z\) that do not make the arguments of factorials in the denominator negative. From either formula it follows that the Racah coefficient is defined only if each of the four triads \((abe), (cde), (acf), (bdf)\) form the sides of a triangle and have integral sum. The algebraic formula also exhibits the symmetries of \(W\):

\[
W(abcd,ef) = W(badc,ef) = W(cdab,ef) = W(acbd,fe) = (-1)^{e+f-a-d} W(efcb,ad)
\]

\[
= (-1)^{e+f-b-c} W(efbd,ec).
\]

Any particular \(W\) can be computed rapidly using the algebraic formula together with the table of factorials in factored form given in the tables by Sharpe et al. The quantities tabulated in these tables are rational fractions which, for the ranges of parameters considered, contain prime factors larger than 19 only in exceptional cases. Since the computations required involve multiplications and divisions, this notation enables these operations to be carried on quickly.
APPENDIX D

CALCULATIONS FOR J = 1→2 TRANSITION
Table 8. Matrix Elements for J = 1

<table>
<thead>
<tr>
<th>F</th>
<th>S</th>
<th>I</th>
<th>I'</th>
<th>λ(SII')</th>
<th>W(III'1;F2)</th>
<th>(F - J + 1/2)</th>
<th>H'_{rr}/G(11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9/2</td>
<td>E</td>
<td>7/2</td>
<td>7/2</td>
<td>0.92582</td>
<td>0.044096</td>
<td>4</td>
<td>0.040825</td>
</tr>
<tr>
<td>7/2</td>
<td>E</td>
<td>7/2</td>
<td>7/2</td>
<td>0.92582</td>
<td>0.125988</td>
<td>3</td>
<td>-0.116642</td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>5/2</td>
<td>5/2</td>
<td>0.13094</td>
<td>0.044543</td>
<td>3</td>
<td>-0.005832</td>
</tr>
<tr>
<td></td>
<td>7/2</td>
<td>5/2</td>
<td>5/2</td>
<td>-0.90712</td>
<td>0.094491</td>
<td>3</td>
<td>0.085715</td>
</tr>
<tr>
<td>5/2</td>
<td>E</td>
<td>7/2</td>
<td>7/2</td>
<td>0.92582</td>
<td>0.094491</td>
<td>2</td>
<td>0.087482</td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>5/2</td>
<td>5/2</td>
<td>0.13094</td>
<td>0.142539</td>
<td>2</td>
<td>0.016664</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>3/2</td>
<td>3/2</td>
<td>1.40000</td>
<td>0.040825</td>
<td>2</td>
<td>0.057155</td>
</tr>
<tr>
<td></td>
<td>7/2</td>
<td>5/2</td>
<td>5/2</td>
<td>-0.90712</td>
<td>0.146385</td>
<td>2</td>
<td>-0.132789</td>
</tr>
<tr>
<td></td>
<td>7/2</td>
<td>3/2</td>
<td>3/2</td>
<td>1.38564</td>
<td>0.182574</td>
<td>2</td>
<td>0.252982</td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>3/2</td>
<td>3/2</td>
<td>1.20000</td>
<td>0.100000</td>
<td>2</td>
<td>0.120000</td>
</tr>
<tr>
<td>3/2</td>
<td>E</td>
<td>5/2</td>
<td>5/2</td>
<td>0.13094</td>
<td>0.124721</td>
<td>1</td>
<td>-0.016331</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>3/2</td>
<td>3/2</td>
<td>1.40000</td>
<td>0.163299</td>
<td>1</td>
<td>-0.228619</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>0.00000</td>
<td>--</td>
<td>1</td>
<td>0.000000</td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>3/2</td>
<td>3/2</td>
<td>1.20000</td>
<td>0.187082</td>
<td>1</td>
<td>-0.224498</td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>1/2</td>
<td>1/2</td>
<td>-0.64803</td>
<td>0.223606</td>
<td>1</td>
<td>0.144915</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>1/2</td>
<td>1/2</td>
<td>0.69282</td>
<td>0.091287</td>
<td>1</td>
<td>-0.063245</td>
</tr>
<tr>
<td>1/2</td>
<td>E</td>
<td>3/2</td>
<td>3/2</td>
<td>1.40000</td>
<td>0.204124</td>
<td>0</td>
<td>0.285774</td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>1/2</td>
<td>1/2</td>
<td>0.69282</td>
<td>0.288675</td>
<td>0</td>
<td>0.200000</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>--</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 9. $J = 1$, $K = 1$ Eigenvalues

<table>
<thead>
<tr>
<th>$F$</th>
<th>$E_{1}^{1}/G(11)$</th>
<th>$R_{T}^{7/2}$</th>
<th>$R_{T}^{5/2}$</th>
<th>$R_{T}^{3/2}$</th>
<th>$R_{T}^{1/2}$</th>
<th>$E_{1}^{1}/eG_{zz}$</th>
<th>$T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9/2</td>
<td>0.04083</td>
<td>1.00</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.02500</td>
<td>a</td>
</tr>
<tr>
<td>7/2</td>
<td>0.04083</td>
<td>0.48</td>
<td>0.88</td>
<td>0</td>
<td>0</td>
<td>0.02500</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>-0.16330</td>
<td>-0.88</td>
<td>0.48</td>
<td>0</td>
<td>0</td>
<td>-0.10000</td>
<td>c</td>
</tr>
<tr>
<td>5/2</td>
<td>0.32659</td>
<td>0.74</td>
<td>-0.06</td>
<td>0.67</td>
<td>0</td>
<td>0.19999</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td>0.12249</td>
<td>-0.30</td>
<td>0.86</td>
<td>0.41</td>
<td>0</td>
<td>0.07501</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>-0.28578</td>
<td>-0.60</td>
<td>-0.51</td>
<td>0.62</td>
<td>0</td>
<td>-0.17500</td>
<td>f</td>
</tr>
<tr>
<td>3/2</td>
<td>0.23169</td>
<td>0</td>
<td>0.71</td>
<td>-0.42</td>
<td>0.56</td>
<td>0.14188</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>-0.10404</td>
<td>0</td>
<td>-0.43</td>
<td>0.36</td>
<td>0.83</td>
<td>-0.06371</td>
<td>h</td>
</tr>
<tr>
<td></td>
<td>-0.37260</td>
<td>0</td>
<td>-0.55</td>
<td>-0.83</td>
<td>0.07</td>
<td>-0.22817</td>
<td>i</td>
</tr>
<tr>
<td>1/2</td>
<td>0.38869</td>
<td>0</td>
<td>0</td>
<td>0.89</td>
<td>0.46</td>
<td>0.23802</td>
<td>j</td>
</tr>
<tr>
<td></td>
<td>-0.10291</td>
<td>0</td>
<td>0</td>
<td>-0.46</td>
<td>0.89</td>
<td>-0.06302</td>
<td>k</td>
</tr>
</tbody>
</table>
Table 10. $J = 2$, $K = 1$ Eigenvalues
(E States)

<table>
<thead>
<tr>
<th>$F$</th>
<th>$E_{2/0}^{1/2}$</th>
<th>$B_T^{7/2}$</th>
<th>$B_T^{5/2}$</th>
<th>$B_T^{3/2}$</th>
<th>$B_T^{1/2}$</th>
<th>$E_{2}/eG_{zz}$</th>
<th>$T'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11/2</td>
<td>0.05345</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td>-0.03571</td>
<td>A</td>
</tr>
<tr>
<td>9/2</td>
<td>0.05345</td>
<td>0.57</td>
<td>0.82</td>
<td></td>
<td></td>
<td>-0.03571</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>-0.13363</td>
<td>0.82</td>
<td>-0.57</td>
<td></td>
<td></td>
<td>0.00528</td>
<td>C</td>
</tr>
<tr>
<td>7/2</td>
<td>0.23445</td>
<td>0.43</td>
<td>0.42</td>
<td>0.80</td>
<td></td>
<td>-0.15665</td>
<td>D</td>
</tr>
<tr>
<td></td>
<td>0.06009</td>
<td>-0.56</td>
<td>0.82</td>
<td>-0.13</td>
<td></td>
<td>-0.00407</td>
<td>E</td>
</tr>
<tr>
<td></td>
<td>-0.21382</td>
<td>0.71</td>
<td>0.39</td>
<td>-0.59</td>
<td></td>
<td>0.14286</td>
<td>F</td>
</tr>
<tr>
<td>5/2</td>
<td>0.21264</td>
<td>-0.57</td>
<td>0.60</td>
<td>-0.38</td>
<td>0.42</td>
<td>-0.14208</td>
<td>G</td>
</tr>
<tr>
<td></td>
<td>0.02070</td>
<td>0.66</td>
<td>0.24</td>
<td>0.15</td>
<td>0.69</td>
<td>-0.01383</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>-0.11756</td>
<td>0.24</td>
<td>0.77</td>
<td>0.26</td>
<td>-0.54</td>
<td>0.07855</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td>-0.27613</td>
<td>0.43</td>
<td>0.00</td>
<td>-0.87</td>
<td>-0.22</td>
<td>0.18450</td>
<td>J</td>
</tr>
<tr>
<td>3/2</td>
<td>0.26226</td>
<td>0.66</td>
<td>-0.52</td>
<td>0.57</td>
<td>0.15</td>
<td>-0.17523</td>
<td>K</td>
</tr>
<tr>
<td></td>
<td>0.08794</td>
<td>-0.40</td>
<td>0.15</td>
<td>0.42</td>
<td>0.79</td>
<td>-0.05876</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>0.00000</td>
<td>0.68</td>
<td>0.59</td>
<td>-0.29</td>
<td>0.34</td>
<td>0.00000</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>-0.24330</td>
<td>-0.05</td>
<td>0.56</td>
<td>0.66</td>
<td>-0.50</td>
<td>0.16256</td>
<td>N</td>
</tr>
<tr>
<td>1/2</td>
<td>0.30590</td>
<td>-0.34</td>
<td>0.94</td>
<td></td>
<td></td>
<td>-0.20439</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>-0.06538</td>
<td>0.94</td>
<td>0.34</td>
<td></td>
<td></td>
<td>0.04368</td>
<td>P</td>
</tr>
<tr>
<td>$\Delta F$</td>
<td>$F(J=1)$</td>
<td>$R_{7/2}$</td>
<td>$R_{5/2}$</td>
<td>$R_{3/2}$</td>
<td>$R_{1/2}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+1</td>
<td>9/2</td>
<td>1.540</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7/2</td>
<td>-1.110</td>
<td>1.415</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>0.653</td>
<td>-0.102</td>
<td>0.127</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>0</td>
<td>0.610</td>
<td>-0.916</td>
<td>1.095</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0.578</td>
<td>-0.817</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>9/2</td>
<td>0.880</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7/2</td>
<td>-1.010</td>
<td>0.755</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>0.876</td>
<td>-0.855</td>
<td>0.600</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>0</td>
<td>0.748</td>
<td>-0.653</td>
<td>0.366</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0.577</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>9/2</td>
<td>0.394</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7/2</td>
<td>-0.652</td>
<td>0.309</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5/2</td>
<td>0.897</td>
<td>-0.490</td>
<td>0.200</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>0</td>
<td>0.634</td>
<td>-0.258</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 12. Racah Coefficients Needed for Intensities

<table>
<thead>
<tr>
<th>( W(1F2F';I1) )</th>
<th>( I = 7/2 )</th>
<th>( I = 5/2 )</th>
<th>( I = 3/2 )</th>
<th>( I = 1/2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( W(1{3\over 2} 2 {1\over 2}; I1) )</td>
<td>0</td>
<td>0.224</td>
<td>-0.091</td>
<td>0</td>
</tr>
<tr>
<td>( W(1{3\over 2} 2 {3\over 2}; I1) )</td>
<td>0</td>
<td>0.187</td>
<td>-0.163</td>
<td>0.091</td>
</tr>
<tr>
<td>( W(1{3\over 2} 2 {5\over 2}; I1) )</td>
<td>0</td>
<td>0.125</td>
<td>-0.187</td>
<td>0.224</td>
</tr>
<tr>
<td>( W(1{5\over 2} 2 {3\over 2}; I1) )</td>
<td>0.183</td>
<td>-0.100</td>
<td>0.048</td>
<td>0</td>
</tr>
<tr>
<td>( W(1{5\over 2} 2 {5\over 2}; I1) )</td>
<td>0.146</td>
<td>-0.143</td>
<td>0.100</td>
<td>0</td>
</tr>
<tr>
<td>( W(1{5\over 2} 2 {7\over 2}; I1) )</td>
<td>0.094</td>
<td>-0.146</td>
<td>0.183</td>
<td>0</td>
</tr>
<tr>
<td>( W(1{7\over 2} 2 {5\over 2}; I1) )</td>
<td>-0.094</td>
<td>0.045</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( W(1{7\over 2} 2 {7\over 2}; I1) )</td>
<td>-0.126</td>
<td>0.094</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( W(1{7\over 2} 2 {9\over 2}; I1) )</td>
<td>-0.124</td>
<td>0.158</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( W(1{9\over 2} 2 {7\over 2}; I1) )</td>
<td>0.044</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( W(1{9\over 2} 2 {9\over 2}; I1) )</td>
<td>0.088</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( W(1{9\over 2} 2 {11\over 2}; I1) )</td>
<td>0.141</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( W(1{1\over 2} 2 {3\over 2}; I1) )</td>
<td>0</td>
<td>0</td>
<td>0.204</td>
<td>-0.289</td>
</tr>
<tr>
<td>( W(1{1\over 2} 2 {1\over 2}; I1) )</td>
<td>0</td>
<td>0</td>
<td>0.289</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 13. Calculated Spectrum, J=1→2, K=1

<table>
<thead>
<tr>
<th>Transition (TT')</th>
<th>$\Delta \nu_q/eQV_{zz}$</th>
<th>Intensity</th>
<th>Transition (TT')</th>
<th>$\Delta \nu_q/eQV_{zz}$</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>j0</td>
<td>-0.44241</td>
<td>0.24</td>
<td>h0</td>
<td>-0.14068</td>
<td>0.00</td>
</tr>
<tr>
<td>jK</td>
<td>-0.41325</td>
<td>0.08</td>
<td>eL</td>
<td>-0.13377</td>
<td>0.01</td>
</tr>
<tr>
<td>dK</td>
<td>-0.37522</td>
<td>0.17</td>
<td>dI</td>
<td>-0.12144</td>
<td>0.09</td>
</tr>
<tr>
<td>dD</td>
<td>-0.35664</td>
<td>0.08</td>
<td>kK</td>
<td>-0.11221</td>
<td>0.08</td>
</tr>
<tr>
<td>g0</td>
<td>-0.34627</td>
<td>0.00</td>
<td>hK</td>
<td>-0.11152</td>
<td>0.01</td>
</tr>
<tr>
<td>dG</td>
<td>-0.34207</td>
<td>0.24</td>
<td>gP</td>
<td>-0.09820</td>
<td>0.21</td>
</tr>
<tr>
<td>gK</td>
<td>-0.31711</td>
<td>0.01</td>
<td>eH</td>
<td>-0.08884</td>
<td>0.10</td>
</tr>
<tr>
<td>jL</td>
<td>-0.29678</td>
<td>0.00</td>
<td>eE</td>
<td>-0.07908</td>
<td>0.00</td>
</tr>
<tr>
<td>gG</td>
<td>-0.28396</td>
<td>0.14</td>
<td>hG</td>
<td>-0.07837</td>
<td>0.12</td>
</tr>
<tr>
<td>dL</td>
<td>-0.25875</td>
<td>0.04</td>
<td>jN</td>
<td>-0.07346</td>
<td>0.35</td>
</tr>
<tr>
<td>eK</td>
<td>-0.25024</td>
<td>0.01</td>
<td>eM</td>
<td>-0.07501</td>
<td>0.20</td>
</tr>
<tr>
<td>jM</td>
<td>-0.23802</td>
<td>0.10</td>
<td>gI</td>
<td>-0.06333</td>
<td>0.01</td>
</tr>
<tr>
<td>eD</td>
<td>-0.23166</td>
<td>0.01</td>
<td>aB</td>
<td>-0.06071</td>
<td>0.25</td>
</tr>
<tr>
<td>eG</td>
<td>-0.21709</td>
<td>0.14</td>
<td>bB</td>
<td>-0.06071</td>
<td>0.52</td>
</tr>
<tr>
<td>dH</td>
<td>-0.21382</td>
<td>0.37</td>
<td>aA</td>
<td>-0.06071</td>
<td>2.37</td>
</tr>
<tr>
<td>dE</td>
<td>-0.20406</td>
<td>0.14</td>
<td>dF</td>
<td>-0.05713</td>
<td>0.08</td>
</tr>
<tr>
<td>gL</td>
<td>-0.20064</td>
<td>0.12</td>
<td>cD</td>
<td>-0.05665</td>
<td>0.29</td>
</tr>
<tr>
<td>dM</td>
<td>-0.19999</td>
<td>0.19</td>
<td>cG</td>
<td>-0.04208</td>
<td>0.06</td>
</tr>
<tr>
<td>JP</td>
<td>-0.19434</td>
<td>0.03</td>
<td>bH</td>
<td>-0.03883</td>
<td>0.02</td>
</tr>
<tr>
<td>bD</td>
<td>-0.18165</td>
<td>0.01</td>
<td>dN</td>
<td>-0.03743</td>
<td>0.01</td>
</tr>
<tr>
<td>aD</td>
<td>-0.18165</td>
<td>0.00</td>
<td>bE</td>
<td>-0.02907</td>
<td>0.67</td>
</tr>
<tr>
<td>bG</td>
<td>-0.16708</td>
<td>0.12</td>
<td>aE</td>
<td>-0.02907</td>
<td>0.05</td>
</tr>
<tr>
<td>gH</td>
<td>-0.15571</td>
<td>0.35</td>
<td>dJ</td>
<td>-0.01549</td>
<td>0.00</td>
</tr>
<tr>
<td>gM</td>
<td>-0.14188</td>
<td>0.01</td>
<td>fK</td>
<td>-0.00023</td>
<td>0.15</td>
</tr>
<tr>
<td>k0</td>
<td>-0.14137</td>
<td>0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 13. Calculated Spectrum, J=1→2, K=1 (Continued)

<table>
<thead>
<tr>
<th>Transition (TT')</th>
<th>$\Delta v_q/eQ_{zz}$</th>
<th>Intensity</th>
<th>Transition (TT')</th>
<th>$\Delta v_q/eQ_{zz}$</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>eI</td>
<td>0.00354</td>
<td>0.32</td>
<td>bJ</td>
<td>0.15950</td>
<td>0.02</td>
</tr>
<tr>
<td>kL</td>
<td>0.00426</td>
<td>0.50</td>
<td>fH</td>
<td>0.16117</td>
<td>0.03</td>
</tr>
<tr>
<td>hL</td>
<td>0.00495</td>
<td>0.01</td>
<td>iL</td>
<td>0.16941</td>
<td>0.04</td>
</tr>
<tr>
<td>fD</td>
<td>0.01835</td>
<td>0.01</td>
<td>fE</td>
<td>0.17093</td>
<td>0.06</td>
</tr>
<tr>
<td>gN</td>
<td>0.02068</td>
<td>0.14</td>
<td>fM</td>
<td>0.17500</td>
<td>0.07</td>
</tr>
<tr>
<td>io</td>
<td>0.02378</td>
<td>0.10</td>
<td>cI</td>
<td>0.17855</td>
<td>0.06</td>
</tr>
<tr>
<td>fc</td>
<td>0.03292</td>
<td>0.18</td>
<td>cC</td>
<td>0.18928</td>
<td>0.17</td>
</tr>
<tr>
<td>gJ</td>
<td>0.04262</td>
<td>0.23</td>
<td>iH</td>
<td>0.21434</td>
<td>0.01</td>
</tr>
<tr>
<td>hh</td>
<td>0.04988</td>
<td>0.26</td>
<td>kN</td>
<td>0.22558</td>
<td>0.02</td>
</tr>
<tr>
<td>iX</td>
<td>0.05294</td>
<td>0.27</td>
<td>hN</td>
<td>0.22627</td>
<td>0.23</td>
</tr>
<tr>
<td>bI</td>
<td>0.05355</td>
<td>0.02</td>
<td>iM</td>
<td>0.22817</td>
<td>0.15</td>
</tr>
<tr>
<td>kM</td>
<td>0.06302</td>
<td>0.03</td>
<td>cF</td>
<td>0.24286</td>
<td>0.60</td>
</tr>
<tr>
<td>hM</td>
<td>0.06371</td>
<td>0.00</td>
<td>hJ</td>
<td>0.24821</td>
<td>0.08</td>
</tr>
<tr>
<td>bC</td>
<td>0.06428</td>
<td>1.32</td>
<td>fT</td>
<td>0.25355</td>
<td>0.10</td>
</tr>
<tr>
<td>aC</td>
<td>0.06428</td>
<td>0.52</td>
<td>fP</td>
<td>0.27185</td>
<td>0.07</td>
</tr>
<tr>
<td>cB</td>
<td>0.06429</td>
<td>1.25</td>
<td>cJ</td>
<td>0.28450</td>
<td>0.06</td>
</tr>
<tr>
<td>eF</td>
<td>0.06785</td>
<td>0.02</td>
<td>fF</td>
<td>0.31786</td>
<td>0.10</td>
</tr>
<tr>
<td>iG</td>
<td>0.08609</td>
<td>0.21</td>
<td>iI</td>
<td>0.30672</td>
<td>0.01</td>
</tr>
<tr>
<td>ch</td>
<td>0.08617</td>
<td>0.17</td>
<td>fN</td>
<td>0.33756</td>
<td>0.06</td>
</tr>
<tr>
<td>eN</td>
<td>0.08755</td>
<td>0.03</td>
<td>fJ</td>
<td>0.35950</td>
<td>0.30</td>
</tr>
<tr>
<td>CE</td>
<td>0.09593</td>
<td>0.04</td>
<td>iN</td>
<td>0.39073</td>
<td>0.01</td>
</tr>
<tr>
<td>kP</td>
<td>0.10670</td>
<td>0.01</td>
<td>iJ</td>
<td>0.41287</td>
<td>0.35</td>
</tr>
<tr>
<td>hP</td>
<td>0.10739</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>eJ</td>
<td>0.10949</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fL</td>
<td>0.11624</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>eF</td>
<td>0.11786</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bF</td>
<td>0.11786</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hH</td>
<td>0.14226</td>
<td>0.61</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX E

PREDICTED PROMINENCES FOR J = 2→3 TRANSITION
Table 14. Predicted Prominences for J = 2→3, K = 1

<table>
<thead>
<tr>
<th>$\Delta \nu_Q/eQV_{zz}$</th>
<th>Relative Intensity</th>
<th>Designation</th>
<th>$\Delta \nu_Q/eQV_{zz}$</th>
<th>Relative Intensity</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.25822</td>
<td>3</td>
<td></td>
<td>0.00275</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>-0.25277</td>
<td>2</td>
<td></td>
<td>0.00516</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>-0.24864</td>
<td>4</td>
<td></td>
<td>(0.00410)</td>
<td>(118)</td>
<td>i</td>
</tr>
<tr>
<td>(-0.25283)</td>
<td>(9)</td>
<td>a</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.21903</td>
<td>2</td>
<td></td>
<td>0.03575</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td>-0.21496</td>
<td>5</td>
<td></td>
<td>0.03563</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>-0.20873</td>
<td>11</td>
<td></td>
<td>(0.03586)</td>
<td>(195)</td>
<td>j</td>
</tr>
<tr>
<td>-0.20521</td>
<td>5</td>
<td></td>
<td>0.04464</td>
<td>83</td>
<td>k</td>
</tr>
<tr>
<td>-0.19554</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0.20653)</td>
<td>(26)</td>
<td>b</td>
<td>0.08162</td>
<td>46</td>
<td>ℓ</td>
</tr>
<tr>
<td>-0.11395</td>
<td>22</td>
<td></td>
<td>0.10632</td>
<td>65</td>
<td>m</td>
</tr>
<tr>
<td>-0.11091</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0.11294)</td>
<td>(33)</td>
<td>c</td>
<td>0.14559</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>-0.08781</td>
<td>99</td>
<td>d</td>
<td>0.14794</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>(-0.11697)</td>
<td>(34)</td>
<td></td>
<td></td>
<td></td>
<td>n</td>
</tr>
<tr>
<td>-0.02679</td>
<td>238</td>
<td>e</td>
<td>0.16074</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>-0.02143</td>
<td>59</td>
<td>f</td>
<td>0.16562</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>(-0.16232)</td>
<td>(31)</td>
<td></td>
<td></td>
<td></td>
<td>o</td>
</tr>
<tr>
<td>-0.01498</td>
<td>46</td>
<td>g</td>
<td>0.22322</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>-0.00897</td>
<td>2</td>
<td></td>
<td>0.23022</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>-0.00886</td>
<td>1</td>
<td></td>
<td>0.24035</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>-0.00620</td>
<td>14</td>
<td></td>
<td>0.24187</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>-0.00559</td>
<td>7</td>
<td></td>
<td>(0.22999)</td>
<td>(29)</td>
<td>p</td>
</tr>
<tr>
<td>-0.00496</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0.00574)</td>
<td>(35)</td>
<td>h</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Close multiplets are grouped and are considered as a single component whose intensity is the sum of the component intensities, and whose frequency is the intensity-weighted mean of the component frequencies. The resultant frequency and intensity for these groups are given in parentheses beneath the group.
Table 15. Predicted Prominences for J = 2→3, K = 2

<table>
<thead>
<tr>
<th>$\Delta v_Q/eQ_v^{zz}$</th>
<th>Relative Intensity</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.40878</td>
<td>19</td>
<td>1</td>
</tr>
<tr>
<td>-0.35045</td>
<td>39</td>
<td>2</td>
</tr>
<tr>
<td>-0.31327</td>
<td>78</td>
<td>3</td>
</tr>
<tr>
<td>-0.28415</td>
<td>58</td>
<td>4</td>
</tr>
<tr>
<td>-0.11751</td>
<td>39</td>
<td>5</td>
</tr>
<tr>
<td>-0.07143</td>
<td>214</td>
<td>6</td>
</tr>
<tr>
<td>-0.02766</td>
<td>58</td>
<td>7</td>
</tr>
<tr>
<td>-0.00815</td>
<td>78</td>
<td>8</td>
</tr>
<tr>
<td>0.00000</td>
<td>39</td>
<td>9</td>
</tr>
<tr>
<td>0.08735</td>
<td>19</td>
<td>10</td>
</tr>
<tr>
<td>0.15710</td>
<td>58</td>
<td>11</td>
</tr>
<tr>
<td>0.17855</td>
<td>97</td>
<td>12</td>
</tr>
<tr>
<td>0.28573</td>
<td>78</td>
<td>13</td>
</tr>
<tr>
<td>0.32512</td>
<td>39</td>
<td>14</td>
</tr>
<tr>
<td>0.36899</td>
<td>58</td>
<td>15</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY


27. Townes and Schawlow, *Microwave Spectroscopy*.
32. Townes and Schawlow, *Microwave Spectroscopy*, p. 79.


Technical Report No. 2
Project No. A-390

Detectors for Microwave Spectrometers

DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH
CONTRACT NO. NOnr-991 (07)

REVIEW
PATENT 3-Y 1961 BY
FORMAT 19 BY
23 February 1961

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia
Detectors for Microwave Spectrometers

MAURICE W. LONG

Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia

(Received March 26, 1960; and in final form, August 30, 1960)

The sensitivity of detectors used in sample modulated microwave spectrometers is investigated. Characteristics of crystal diodes and barretters as functions of microwave power are compared with an ideal detector operating at room temperature. A spectrograph is described which was used to measure a CFCI line having a calculated absorption coefficient of $3.9 \times 10^{-8}$ cm$^{-1}$. The relationship between recorder deflection and absorption coefficient is discussed.

INTRODUCTION

CONVENTIONAL microwave spectrometers consist of a klystron, a waveguide which contains the molecules under investigation, and a detector. The klystron is slowly swept in frequency and the detector output is recorded so as to provide a graph of molecular absorption as a function of frequency. The waveguide is constructed so that the molecules under investigation are subjected to an electric or magnetic field, thereby causing splitting and shifting of absorption lines. Absorption by the molecules is modulated by this technique; this provides a modulated microwave detector output which is amplified by a tuned amplifier having a center frequency equal to the modulation frequency. A phase-sensitive detector is often used to provide linear second detection and to further reduce bandwidth. Because the phase-sensitive detector is linear and is designed to have a much narrower bandwidth than that of the tuned amplifier, the equivalent noise bandwidth is that of the phase-sensitive detector.

MINIMUM DETECTABLE SIGNAL

The microwave signal out of a sample holder is in the form of a small decrement $\Delta P$ in a relatively large amount of power $P$. In terms of the absorption coefficient of molecules $\alpha$ and a cell of length $L$, $\Delta P$ can be approximated as

$$\Delta P = \alpha L P,$$

where $P$ is the power at the detector without resonant absorption by the molecules. The relatively large constant signal of power $P$ modulated so that the power level changes by $\Delta P$ can be represented by the sum of $P$ and weak periodic pulses of power $P'$ which are in phase with the large signal. The relationship between these power levels is

$$P' = (\Delta P)^2 / 4P,$$

where $P'$ is much smaller than $P$. Then an equivalent circuit, as far as the detector is concerned, is illustrated in Fig. 1. The conversion gain normally specified for crystal diodes is applicable to the signal of power $P'$, instead of the signal $\Delta P$.

The minimum detectable value of $P'$ is ultimately determined by the noise power $kT\Delta v$, where $k$ is Boltzmann's constant, $T$ is the absolute temperature of the system, and $\Delta v$ is the over-all system bandwidth. Actual noise will be larger, and for room temperature it may be expressed as

$$P_n = 4 \times 10^{-21} N \Delta v,$$

where $N$ is called "noise ratio" and accounts for excess noise contributed by the detector, amplifier, and klystron. The signal power $P'$ of Eq. (1) must be comparable to $kT N \Delta v$ to be discernible in thermal noise; therefore, a small change in power $\Delta P$, which we wish to detect, must be considerably larger than $kT N \Delta v$ if it is to be detected. For example, if $P = 10^{-4}$ w and $P'$ is $10^{-10}$ w, then $\Delta P$ is $2 \times 10^{-8}$ w.

For square-wave modulation, the total sideband power at the fundamental frequency is $(2/(2\pi))^2 P'$. If a tuned amplifier following the microwave detecting element passes the repetition frequency, the signal power to be amplified is $G(2/(2\pi))^2 P'$, where $G$ is defined as conversion gain of the detector, ratio of output to input power. If $G(2/(2\pi))^2 P'$ is assumed to be equal to $P_n$, the minimum detectable absorption coefficient $\alpha_n$ can be expressed in the form

$$\alpha_n = 2.81 \times 10^{-11} (\Delta P)^4 / (P L)^2,$$

(2)

The ratio $\Delta P / P$ is descriptive of the detector sensitivity providing $P'$ is much smaller than $P$. Then an equivalent circuit, as far as the detector is concerned, is illustrated in Fig. 1. The conversion gain normally specified for crystal diodes is applicable to the signal of power $P'$, instead of the signal $\Delta P$.

The minimum detectable value of $P'$ is ultimately determined by the noise power $kT\Delta v$, where $k$ is Boltzmann's constant, $T$ is the absolute temperature of the system, and $\Delta v$ is the over-all system bandwidth. Actual noise will be larger, and for room temperature it may be expressed as

$$P_n = 4 \times 10^{-21} N \Delta v,$$

where $N$ is called "noise ratio" and accounts for excess noise contributed by the detector, amplifier, and klystron. The signal power $P'$ of Eq. (1) must be comparable to $kT N \Delta v$ to be discernible in thermal noise; therefore, a small change in power $\Delta P$, which we wish to detect, must be considerably larger than $kT N \Delta v$ if it is to be detected. For example, if $P = 10^{-4}$ w and $P'$ is $10^{-10}$ w, then $\Delta P$ is $2 \times 10^{-8}$ w.

For square-wave modulation, the total sideband power at the fundamental frequency is $(2/(2\pi))^2 P'$. If a tuned amplifier following the microwave detecting element passes the repetition frequency, the signal power to be amplified is $G(2/(2\pi))^2 P'$, where $G$ is defined as conversion gain of the detector, ratio of output to input power. If $G(2/(2\pi))^2 P'$ is assumed to be equal to $P_n$, the minimum detectable absorption coefficient $\alpha_n$ can be expressed in the form

$$\alpha_n = 2.81 \times 10^{-11} (\Delta P)^4 / (P L)^2,$$

(2)

The ratio $\Delta P / P$ is descriptive of the detector sensitivity

![Fig. 1. Equivalent circuit for detector input.]

* Supported by the Office of Naval Research.


3 R. L. Cosgrove, Antenna Laboratory, Ohio State University Research Foundation, Tech. Rept. 487-5 (December 1953).

4 Equations differing only negligibly from Eq. (2) appear elsewhere; this equation corresponds to the result of equating Eq. (3) of reference 1 to unity.
for sample modulated spectrometers. It is expected that the maximum power gain in a detector is 0.5. The theoretical limit for \( \Delta P/P \) based on a 1-cps effective bandwidth, \( G \) equal to 0.5, and \( N \) equal to unity is shown in Fig. 2.

**CRYSTAL DIODES**

The most common detector for microwaves is the crystal diode. Though the rectifying properties vary from crystal to crystal, their characteristics can be roughly divided into a square-law region where the rectified current \( I \) is proportional to \( P \) (holding for \( P < 10^{-3} \) w) and the linear region where \( I \) is proportional to \( P^4 \) (holding for \( P > 10^{-4} \) w).

The rectified current produces a frequency dependent noise which can be represented, by a noise ratio

\[
N = \left[ (\beta P^2/f) + 1 \right],
\]

where \( f \) is the frequency around which the pass band \( \Delta f \) is centered. For a given crystal, \( \beta \) is approximated by a constant. The conversion gain in the square-law region can be represented by \( G = \alpha P \), where \( \alpha \) is also a constant. Only a small amount of data exists in the literature for \( \alpha \) and \( S \) and some of the values differ widely. Cosgriff has found a \( P^4 \) instead of a \( P^3 \) dependence for some crystals. Cosgriff had also observed a plateau in \( N \) as a function of \( P \) for some crystals.

The noise ratio of a diode in the linear region can be represented by

\[
N = \left[ (\gamma P^2/f) + 1 \right].
\]

For a given diode, \( \gamma \) is a constant. A great deal of data is available for diodes operating at \( f = 1 \) Me because this is the usual operating level for superhet receiver designers. Values of \( G \) and \( N \), at \( f = 30 \) Mc are given in Table I. Equation (4) and the data in Table I can be used to calculate \( \gamma \) and \( N \), as a function of \( P \) and \( f \).

The data given in Table I on conversion gain and noise ratio are minimum and maximum values, respectively, with exception of the 1N23E data. Actual values will in general be better than listed. The 1N23E data were obtained through personal communications with R. T. DiBona of Microwave Associates, Inc., and are reported representative of more than 99% of the type 1N23E diodes produced.

If \( \gamma, \beta, \) and \( S \) were known, \( \Delta P/P \) could be calculated by substituting the corresponding values of \( G \) and \( N \) into Eq. (2). However, these constants would not provide sufficient information for determining sensitivity in the region not clearly defined as either square-law or linear. A method for determining \( \Delta P/P \) as a function of \( P \) with a synchronous detection system is described in the following.

The system illustrated in Fig. 1 provides a method for determining detector sensitivities as a function of \( P \). Figure 3 illustrates implementation of Fig. 1. If the signal in channel 1 is the signal desired for detection, the circuit would be called a synchronous detection system. For our purposes, channel 2 supplies \( P \) and channel 1 supplies \( P' \), \( P'' \), and \( P \) added in phase develop \( \Delta P \). Results of calculating \( \Delta P \) from Eq. (1) and Georgia Tech and Johns Hopkins measurements are given in Fig. 2. The results are expressed in terms of minimum detectable signal per cycle second of amplifier bandwidth. Minimum detectable \( \Delta P \) increases linearly with \( (\Delta f)^4 \), where \( \Delta f \) is amplifier

---

bandwidth. Measurements were made on several type 1N23B and 1N23E diodes. It is interesting that the most sensitive diode measured was a 1N23B, instead of a 1N23E.

Many of the commercially available 1000-cps amplifiers have noise figures considerably in excess of unity. The author used a Scientific-Atlanta, Inc. 1-kc amplifier as a low noise preamplifier to drive a commercially available standing wave amplifier; this provided a noise figure of 2 or less.

Equation (2) with Eqs. (3) and (4) predicts that $\Delta P/P$ is independent of $P$ providing the amplifier and klystron noises are small compared to diode noise; $\Delta P/P$ varies as $1/P$ at the lower values of $P$ where amplifier noise is predominant. The measured 1N23 characteristics agree with these predictions.

BARRETTERS

The useful property of barretters is that resistance is a function of the amount of power absorbed. Barretters are normally biased with direct current to an operating resistance of 200 ohms; the addition of r.f. power to the element increases the element resistance above this bias point.

The signal voltage $\delta V$ which exists across the barretter is $\Delta R$. $R$ is the barretter resistance and $I$ is the current bias on the barretter which should be kept constant for a maximum voltage change $\delta V$. Since

$$\frac{dR}{dP} = \frac{\delta R}{\delta P} = (\Delta P/P) \frac{\Delta R}{\Delta P}$$

then

$$\delta V = I e \Delta P (1 - eP)^{-1},$$

where $e = dR/dP$. In assuming the barretter resistance follows the modulation so that the output voltage is a square wave, and that a narrow band amplifier is used, the rms value of the fundamental component $\sqrt{2}\delta V/\pi R$ is the level of voltage to be amplified. The minimum detectable signal obtained by solving the equation

$$(\sqrt{2}\delta V/\pi)^2 R^{-1} = k T \Delta p N$$

simultaneously with Eq. (5) is

$$\Delta P = \frac{\pi (1 - eP)(RkT\Delta p N/2)^4}{eP}.$$  \hspace{1cm} (6)

The result of substituting $T = 300^\circ K$ and the manufacturers' specifications from Table II for the type 610B barretter into Eq. (6) is

$$\Delta P = 3.3 \times 10^{-11} (\Delta p N)^4.$$  \hspace{1cm} (7)

Modulation frequencies must be low because of barretter thermal time constants; 1 kc is sufficiently low for most barretters. With the arrangement of Fig. 3, the most sensitive of the barretters investigated, type 610B, gave minimum detectable signals corresponding to

$$(\Delta P)_{\text{min}} = 4 \times 10^{-10} (\Delta p N)^4.$$

This corresponds to the values of $\Delta P/P$ of Fig. 2 for the lower values of $P$. The $(\Delta P)_{\text{min}}$ obtained with other amplifiers or with other barretters were sometimes less sensitive by a factor of 10 or more.

For the lower power levels of Fig. 2, $\Delta P/P$ varies as $1/P$ independent of the ratio of barretter noise to amplifier noise. At higher levels, $\Delta P/P$ increases [see Eq. (2)] because of klystron noise and increased barretter temperature due to the microwave power; this effect may be seen in Fig. 2.

Equation (6) was determined without using $P$ or $P'$ explicitly. This was done because barretter noise (absolute temperature) is essentially independent of microwave power. In the case of crystals, microwave power level must be considered and it becomes convenient to use the concept of power gain for the signal $P'$. The power gain $G$ of a barretter is included here for comparison to the crystals,

$$G = \frac{(\delta V)^2 / R}{P'} r \left(1 - eP' \right)^{-1}.$$  \hspace{1cm} (8)

Based on the foregoing manufacturer's specifications, Eq. (8) gives for the type 610B barretter $G = 72.1 P$, where $P$ is in watts.

SPECTROGRAPH USED FOR CFCl3 LINES

This section describes the Stark spectrograph used to accomplish measurements of which the author is particu-

<p>| Table II: Barretter characteristics. |
|-----------------|-----|-----|-----|-----|</p>
<table>
<thead>
<tr>
<th>Type</th>
<th>$R$ (ohms)</th>
<th>$I$ (ma)</th>
<th>$\epsilon$ (ohms/mw)</th>
<th>Frequency (Mcy</th>
</tr>
</thead>
<tbody>
<tr>
<td>821B</td>
<td>200</td>
<td>8.75</td>
<td>4.5</td>
<td>0 to 12 400</td>
</tr>
<tr>
<td>610B</td>
<td>200</td>
<td>8.75</td>
<td>4.5</td>
<td>0 to 18 000</td>
</tr>
<tr>
<td>614</td>
<td>200</td>
<td>4.5</td>
<td>10</td>
<td>12 400 to 26 500</td>
</tr>
<tr>
<td>617</td>
<td>200</td>
<td>4.5</td>
<td>10</td>
<td>18 000 to 40 000</td>
</tr>
</tbody>
</table>

* M. W. Long, Tech. Rept. No. 1 (June 1959); ASTIA No. AD 216 615.
larly proud. The lines are those of the hyperfine spectrum of the $J = 1 \rightarrow 2$ rotational transition of CFC$_3$ which occur at 9860 Mc and the weakest line measured has a calculated absorption coefficient of $3.9 \times 10^{-11}$ cm$^{-1}$.

The spectograph used consists of a conventional Stark-modulation system, modified for use with relatively high power (1kw) incident upon a type 1N23E diode. This system employs an 85-kc square-wave modulator which applies an electric field in the waveguide region occupied by the gas. Second detection is accomplished by a phase-sensitive detector with an output network having a time constant of 3 sec. Microwave power was supplied by a type X-13 reflex klystron. The Stark cell consists of a 350-cm brass sheet for a Stark electrode mounted in type RG-48/u waveguide. Measurements were made with the cell at dry ice temperature.

The input circuit of the preamplifier was modified to reduce the dc resistance for crystal current for minimizing noise and conversion loss for high power operation. Objectionable 85-kc pickup was produced by current flow along the walls of the Stark cell and to the crystal detector through the crystal holder. The pickup was removed by isolating the crystal holder from the cell by using a thin Mylar spacer between waveguide flanges and nylon connecting screws.

Parameters pertinent to the system sensitivity are as follows:

- $f = 85$ kc
- $\Delta v = 1/\pi T = 1/\pi 3 = 0.106$ cps
- $L = 350$ cm
- $N_e = 1.25$ at 30 Mc
- $P = 10^{-4}$ w
- $G = 0.35$

From Table I and Eq. (4) we find that $\gamma = 7.5 \times 10^6$. By substituting $\gamma$ into Eq. (4) we find that the crystal noise ratio at 85 kc is 89.2. This noise ratio far exceeds noise figures of amplifiers of reasonable design, thus

$$N = N_e = 89.2.$$  

The result of substituting $\Delta n$, $N$, $P$, $G$, and $L$ into Eq. (2) is $(\Delta P/P) = 4.7 \times 10^{-6}$, and

$$\alpha_m = 1.33 \times 10^{-10} \text{ cm}^{-1}.$$  

Absorption coefficients for symmetric top molecules vary with temperature as $T^4$ but absorption coefficients of molecules are conventionally expressed for 300 K.

The absorption coefficient of the weakest CFC$_3$ line measured with this spectrometer is then

$$\alpha = \left(\frac{195}{300}\right) = 4.5 \times 10^{-11} \text{ cm}^{-1}.$$  

The agreement between the calculated sensitivity (noise power equal to signal power) of $4.5 \times 10^{-11}$ cm$^{-1}$ and the calculated absorption coefficient of $3.9 \times 10^{-11}$ cm$^{-1}$ for the weakest line actually observed is good, if not remarkable.

**RELATIVE VALUES OF ABSORPTION COEFFICIENT**

Frequently the relative absorption of neighboring lines within a complex spectrum is of importance. It is convenient to employ the analogy between the sample modulated system and the synchronous detector (a superheterodyne with intermediate frequency of zero) to show that the output deflection of a recorder is linearly proportional to absorption coefficient. From the theory of synchronous detection it is known that the detector output voltage due to a small signal $P'$ is proportional to the incident electric field of this signal provided the large signal $P$ is much greater than the small signal. This is true regardless of whether the detector is operating within the linear region or the square-law region. Therefore the output voltage is always proportional to $(P')^4$. Then from Eq. (1) it is seen that the output voltage of a spectrograph is always proportional to $\Delta P$ provided the amplifiers are linear beyond the first detector. Since driving amplifiers are designed so that recorder deflections are proportional to impressed voltage, the recorded output is linearly proportional to $\Delta P$ or absorption coefficient $\alpha$, if $P$ and the detector conversion gain are constant.

Frequently the relative amount of absorption of lines within a group such as those resulting from quadrupole splitting are of interest. If the lines are closely spaced, but adequately resolved, relative values of absorption coefficient are given by direct comparison of the recorded line heights. One must not forget that the conversion gain of a detector and the klystron output power will change with all but small changes in frequency.

**ACKNOWLEDGMENTS**

The author expresses his appreciation to E. R. Flynt and W. K. Rivers for many profitable discussions regarding this paper and to J. B. Chastain for performing the synchronous detection measurements.
Centrifugal Stretching in Symmetric-Top Molecules and the Stark Effect of Chlorotrifluoromethane

DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH
CONTRACT NO. N001-991 (07)

2 May 1961

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia
CENTRIFUGAL STRETCHING IN SYMMETRIC-TOP
MOLECULES AND THE STARK EFFECT
OF CHLOROTRIFLUOROMETHANE

by

R. C. Johnson

Department of the Navy
Office of Naval Research
Contract No. N00r-991 (07)

2 May 1961
ACKNOWLEDGMENTS

The author is grateful to Drs. Maurice W. Long, Thomas L. Weatherly, and J. Q. Williams for their suggestions and contributions during this investigation.

This report also constitutes a thesis presented to the Georgia Institute of Technology by Richard C. Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics. Reproduction in whole or in part is permitted for any purpose of the United States Government.

Submitted:

R. C. Johnson
Research Physicist

Approved:

M. W. Long, Chief
Electronics Division

Approved:

J. E. Boyd, Director
Engineering Experiment Station
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>11</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>vi</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>viii</td>
</tr>
<tr>
<td>Chapter</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. INSTRUMENTATION</td>
<td>3</td>
</tr>
<tr>
<td>III. SYMMETRIC-TOP MOLECULES</td>
<td>7</td>
</tr>
<tr>
<td>Rigid Rotor</td>
<td>8</td>
</tr>
<tr>
<td>Centrifugal Stretching</td>
<td>11</td>
</tr>
<tr>
<td>Quadrupole Hyperfine Structure.</td>
<td>11</td>
</tr>
<tr>
<td>Rotational Spectra</td>
<td>14</td>
</tr>
<tr>
<td>Analysis of Microwave Data</td>
<td>16</td>
</tr>
<tr>
<td>Quadrupole Coupling Constant, eqQ</td>
<td>16</td>
</tr>
<tr>
<td>Distortion Constant, $D_{JK}$</td>
<td>17</td>
</tr>
<tr>
<td>Distortion Constant, $D_{JJ}$</td>
<td>18</td>
</tr>
<tr>
<td>Rotational Constant, $B$</td>
<td>19</td>
</tr>
<tr>
<td>Molecular Models</td>
<td>19</td>
</tr>
<tr>
<td>IV. ROTATIONAL DISTORTIONS IN SYMMETRIC-TOP MOLECULES</td>
<td>22</td>
</tr>
<tr>
<td>Chloromethane, CH₃Cl</td>
<td>23</td>
</tr>
<tr>
<td>Chlorotrifluoromethane, CClF₃</td>
<td>24</td>
</tr>
<tr>
<td>Trifluoromethane, CHF₃</td>
<td>40</td>
</tr>
<tr>
<td>Higher-Order Distortion Constants and CCl₃F</td>
<td>44</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical Rotational Distortion Constants</td>
<td>46</td>
</tr>
<tr>
<td>Summary of Results</td>
<td>51</td>
</tr>
<tr>
<td>V. STARK EFFECT OF CHLOROTRIFLUOROMETHANE</td>
<td>56</td>
</tr>
<tr>
<td>VI. CONCLUSIONS AND RECOMMENDATIONS</td>
<td>72</td>
</tr>
<tr>
<td>APPENDICES</td>
<td></td>
</tr>
<tr>
<td>A. DISTORTION COEFFICIENTS</td>
<td>76</td>
</tr>
<tr>
<td>B. BOND ANGLES IN XYZ₃ MOLECULES</td>
<td>80</td>
</tr>
<tr>
<td>C. MOMENTS OF INERTIA IN XYZ₃ MOLECULES</td>
<td>82</td>
</tr>
<tr>
<td>D. HYBRIDIZATION WITH QUADRICOVALENT ATOMS</td>
<td>85</td>
</tr>
<tr>
<td>E. TABLES FOR CALCULATION OF ROTATIONAL DISTORTION CONSTANS</td>
<td>88</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>94</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Measured Hyperfine Line Frequencies for C(^1)(^2)Cl(^3)F(_3)</td>
<td>37</td>
</tr>
<tr>
<td>2. Frequencies of the Strongest Line (K=1) in Various</td>
<td>45</td>
</tr>
<tr>
<td>Transitions for C(^1)(^2)Cl(^3)F(_3)</td>
<td></td>
</tr>
<tr>
<td>3. Molecular Dimensions of Some XCYZ(_3) Molecules</td>
<td>52</td>
</tr>
<tr>
<td>4. Force Constants of Some XCYZ(_3) Molecules</td>
<td>53</td>
</tr>
<tr>
<td>5. Calculated and Observed Rotational Distortion</td>
<td>55</td>
</tr>
<tr>
<td>Constants for Some XCYZ(_3) Molecules</td>
<td></td>
</tr>
<tr>
<td>6. Stark Line Frequencies for C(^1)(^2)Cl(^3)F(_3)</td>
<td>70</td>
</tr>
<tr>
<td>7. The [^{\text{i}}]_{\text{q}}_o for an Axially Symmetric</td>
<td>89</td>
</tr>
<tr>
<td>XYZ(_3) Molecule</td>
<td></td>
</tr>
<tr>
<td>8. Force Constant Symbols for XCYZ(_3) Molecules</td>
<td>90</td>
</tr>
<tr>
<td>9. The f Matrix</td>
<td>91</td>
</tr>
<tr>
<td>10. The U and U’ Matrices</td>
<td>92</td>
</tr>
<tr>
<td>11. The F Matrix</td>
<td>93</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1.</td>
<td>Simplified Block Diagram of the Stark Effect Microwave Spectrometer.</td>
</tr>
<tr>
<td>2.</td>
<td>Vector Relations of Rotational Angular Momenta for a Symmetric-Top Molecule.</td>
</tr>
<tr>
<td>3.</td>
<td>Vector Relations of Angular Momenta for a Symmetric-Top Molecule With ( \text{IJ-Coupling} )</td>
</tr>
<tr>
<td>4.</td>
<td>Distortion Constants of ( {\text{C}}^{12}\text{H}<em>3\text{Cl}</em>{35} )</td>
</tr>
<tr>
<td>5.</td>
<td>Weighted Distortion Constants of ( {\text{C}}^{12}\text{H}<em>3\text{Cl}</em>{35} )</td>
</tr>
<tr>
<td>6.</td>
<td>Distortion Constants of ( {\text{C}}^{12}\text{Cl}_{35}\text{F}_3 ) (Using Data From Coles and Hughes)</td>
</tr>
<tr>
<td>7.</td>
<td>Weighted Distortion Constants of ( {\text{C}}^{12}\text{Cl}_{35}\text{F}_3 ) (Using Data From Coles and Hughes)</td>
</tr>
<tr>
<td>8.</td>
<td>Distortion Constants of ( {\text{C}}^{12}\text{Cl}_{35}\text{F}_3 ) (Using Present Data)</td>
</tr>
<tr>
<td>9.</td>
<td>Weighted Distortion Constants of ( {\text{C}}^{12}\text{Cl}_{35}\text{F}_3 ) (Using Present Data)</td>
</tr>
<tr>
<td>10.</td>
<td>Recording of the ( J = 0 \rightarrow 1 ) Transition of ( {\text{C}}^{12}\text{Cl}_{35}\text{F}_3 )</td>
</tr>
<tr>
<td>11.</td>
<td>Theoretical Hyperfine Structure of the ( J = 1 \rightarrow 2 ) Transition of ( {\text{C}}^{12}\text{Cl}_{35}\text{F}_3 )</td>
</tr>
<tr>
<td>12.</td>
<td>Theoretical Hyperfine Structure of the ( J = 2 \rightarrow 3 ) Transition of ( {\text{C}}^{12}\text{Cl}_{35}\text{F}_3 )</td>
</tr>
<tr>
<td>13.</td>
<td>Theoretical Hyperfine Structure of the ( J = 3 \rightarrow 4 ) Transition of ( {\text{C}}^{12}\text{Cl}_{35}\text{F}_3 )</td>
</tr>
<tr>
<td>14.</td>
<td>Major Components of the Theoretical Hyperfine Structure of the ( J = 4 \rightarrow 5 ) Transition of ( {\text{C}}^{12}\text{Cl}_{35}\text{F}_3 )</td>
</tr>
<tr>
<td>15.</td>
<td>Distortion Constants of ( {\text{C}}^{12}\text{H}_3\text{F}_3 )</td>
</tr>
<tr>
<td>16.</td>
<td>Weighted Distortion Constants of ( {\text{C}}^{12}\text{H}_3\text{F}_3 )</td>
</tr>
<tr>
<td>17.</td>
<td>An ( \text{XYZ}<em>3 ) Molecule Belonging to the ( \text{C}</em>{3v} ) Group</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>18. Vector Diagrams for the Stark Effects on Symmetric-Top Molecules With Nuclear Quadrupole Coupling.</td>
<td>57</td>
</tr>
<tr>
<td>19. Graphical Illustration of the Hamiltonian Matrix for ( J = 1, K = 1, ) and ( I = 3/2 )</td>
<td>61</td>
</tr>
<tr>
<td>20. Graphical Illustration of the Hamiltonian Matrix for ( J = 2, K = 1, ) and ( I = 3/2 )</td>
<td>62</td>
</tr>
<tr>
<td>21. Stark Energy Versus Field Intensity for ( \text{C}^{12}\text{Cl}^{35}\text{F}_3 ) With ( J = 1 ) and ( K = 1 )</td>
<td>65</td>
</tr>
<tr>
<td>22. Stark Energy Versus Field Intensity for ( \text{C}^{12}\text{Cl}^{35}\text{F}_3 ) With ( J = 2 ) and ( K = 1 )</td>
<td>66</td>
</tr>
<tr>
<td>23. Recording of the ( J = 1 \leftrightarrow 2 ) Transition of ( \text{C}^{12}\text{Cl}^{35}\text{F}_3 ) Illustrating Stark Line Separation.</td>
<td>67</td>
</tr>
<tr>
<td>24. Stark Line Separation Versus Field Intensity for the ( J = 1 \leftrightarrow 2, K = 1 ) Transition of ( \text{C}^{12}\text{Cl}^{35}\text{F}_3 ).</td>
<td>69</td>
</tr>
<tr>
<td>25. Bond Angles in an ( \text{XYZ}_3 ) Molecule</td>
<td>81</td>
</tr>
<tr>
<td>26. Structural Parameters of an ( \text{XYZ}_3 ) Molecule</td>
<td>83</td>
</tr>
<tr>
<td>27. Hybridization in ( \text{XYZ}_3 ) Molecules</td>
<td>87</td>
</tr>
</tbody>
</table>
SUMMARY

The effects of centrifugal distortion in symmetric-top molecules are usually predicted through the use of distortion constants, $D_{JJ}$ and $D_{JK}$. It is expected that $D_{JJ}$ will always be positive and that $D_{JK}$ may be either positive or negative. Recently, CCl₃F and CHCl₃ were each reported to have a negative $D_{JJ}$ which varies with the rotational quantum number $J$. This prompted further studies of distortion effects in other symmetric tops. Detailed calculations of distortion constants were made for three molecules: (a) CH₃Cl, a typical methyl halide; (b) CClF₃, a molecule with bonding similar to that of CCl₃F; and (c) CHF₃, a molecule with its center of mass within the CF₃ tetrahedron. All three were found to obey existing distortion theory within the limits of experimental error. The $J = 1\rightarrow2$ through $4\rightarrow5$ transitions for $^{12}$Cl$^{35}$F₃ were measured. Absorption lines for $J = 2\rightarrow3$ and $3\rightarrow4$ have been reported previously; however, the $2\rightarrow3$ data are believed to be slightly in error. Present data yield $B_o = 3335.596 \text{ mc}$, $eqq = -77.98 \text{ mc}$, $D_{JJ} = +0.59 \text{ kc}$, and $D_{JK} = +2.06 \text{ kc}$. Theoretical distortion constants can be calculated from the molecular structure and the molecular force constants. A comparison of measured and theoretical constants for nine symmetric-top molecules shows reasonable agreement for all except CCl₃F and CHCl₃, which are the only molecules considered having three identical nuclei with quadrupole moments. From Stark effect measurements on the $J = 1\rightarrow2$ transition, the molecular dipole moment of $^{12}$Cl$^{35}$F₃ was assigned the value $0.50 \pm 0.01$ debye.
CHAPTER I

INTRODUCTION

The effects of centrifugal distortion in symmetric-top molecules, neglecting electric quadrupole splitting, are usually predicted (1) through the use of two rotational distortion constants, $D_{JJ}$ and $D_{JK}$. It has been surmised by some authors (2) that $D_{JJ}$ will be positive for all symmetric tops, while $D_{JK}$ may in principle be either positive or negative. It was pointed out that all molecules of the $YZ_3$ type which have so far been examined have $D_{JK}$ negative, while molecules of the $XYZ_3$ type have $D_{JK}$ positive.

A recent investigation (3, 4) on $CCl_3F$ and $CHCl_3$ yielded negative values for both $D_{JJ}$ and $D_{JK}$. In addition, it was found that $D_{JJ}$ is a function of $J$ for the low $J$-value data which were considered. Long (4) also pointed out that the centers of mass for previously reported $XYZ_3$ molecules are outside the $YZ_3$ tetrahedron and the centers of mass for $CCl_3F$, $CHCl_3$, and all $YZ_3$ molecules are within the $YZ_3$ tetrahedron.

The unexpected results of the above investigation (3, 4) invited further study of distortion effects in other symmetric tops. It was decided to calculate distortion effects of $CClF_3$ in detail because the bonding is similar to that of $CCl_3F$. In addition, it was decided to compare the results with those of $CH_3Cl$, a typical methyl halide, and of $CHF_3$, a molecule with its center of mass toward the base of the $YZ_3$ tetrahedron. It was found that all three molecules can be described,
within the limits of experimental errors, by existing rotational distortion theory (i.e., the distortion constants $D_{JJ}$ and $D_{JK}$ are not functions of $J$ or $K$).

The theoretical rotational distortion constants, $D_{JJ}$ and $D_{JK}$, can be calculated (5, 6) from the molecular structure and the molecular force constants; the former is calculated from microwave spectra and the latter are calculated from Raman and infrared spectra. A comparison of the theoretical and observed distortion constants for nine symmetric-top molecules provided an interesting link between spectra in the microwave and infrared regions. There was reasonable agreement for all except CCl$_3$F and CHCl$_3$, the only molecules considered which have three identical nuclei with quadrupole moments. The disagreement was serious in these two cases.

The electric dipole moment of CClF$_3$ was evaluated by Birnbaum (7) using a cavity method to determine the nonresonant, or Debye type, absorption. It was later evaluated by Beeson (8) by measuring and analyzing the Stark effect for the $J = 2 \rightarrow 3$ transition. The latter determination was not considered very accurate because of difficulty in resolving the Stark components. It was decided to evaluate the dipole moment by measuring and analyzing the Stark effect for the $J = 1 \rightarrow 2$ transition since the Stark spectrum is considerably less complex for this transition.
CHAPTER II

INSTRUMENTATION

The microwave spectrometer used in this investigation is illustrated in the simplified block diagram of Figure 1. It is a Stark modulation type similar to that introduced by Hughes and Wilson (9).

Basically, the equipment consists of a klystron with power supply, a Stark cell, and a crystal detector. Absorption of the gas is modulated by a zero based, 85 kc, square wave, Stark generator, and the signal is amplified by an 85 kc amplifier. A phase sensitive detector is used to reduce effective bandwidth and to distinguish absorption lines from the Stark components.

When using an oscilloscope display, as illustrated in Figure 1, the klystron frequency, the display oscilloscope, and the power monitor oscilloscope are swept in synchronism. The absorption lines appear as upward displacements and the Stark components appear as downward displacements. When the setting of the cavity wavemeter is within the band of frequencies swept by the klystron, the wavemeter frequency appears as a dip on the power monitor oscilloscope; it can be used to determine the absorption line frequency within a few megacycles.

The absorption line frequency is accurately determined through the use of a fixed marker generator, whose oscillator is adjusted to zero beat with the National Bureau of Standards Station, WWV. The generator produces a family of markers spaced every 30 mc apart; its output is mixed with a sample of the klystron signal and the beat frequency is
Figure 1. Simplified Block Diagram of the Stark Effect Microwave Spectrometer.
measured by a calibrated National HRO receiver. When the beat frequency corresponds to the setting of the calibrated receiver, a marker pip appears on the display oscilloscope. By tuning the calibrated receiver, the marker pip can be varied until it is superimposed on the absorption line being measured. The frequency of the absorption line is then determined by adding (or subtracting) the calibrated receiver frequency to the appropriate fixed marker frequency, as determined by the wavemeter. Several measurements are made as the klystron is swept from low to high frequencies, and then several measurements are made while sweeping from high to low frequencies. These measurements are averaged in order to eliminate errors due to time delays or nonlinearities in the sweep circuits.

The klystron frequency can be swept slowly through the use of a variable, low speed, mechanical drive mechanism, while the signal from the phase sensitive detector is displayed on an Easterline-Angus recorder. With this slow sweep, a very large filter time constant can be used in the output of the phase sensitive detector, thereby reducing effective bandwidth and increasing signal-to-noise ratio.

Either of two Stark cells is available for use, depending upon the operating frequency. The X-band cell has inside cross-sectional dimensions 0.900 inch by 0.400 inch and a length of 17 feet; the S-band cell has inside cross-sectional dimensions 2.84 inches by 1.34 inches and a length of 12 feet. The operating frequencies are approximately 8.2 to 45 kmc for the X-band cell and 2.6 to 16 kmc for the S-band cell. Both cells have a brass Stark electrode which is supported by insulating strips of teflon along the inner wall of each side of the waveguide. In
this manner, the applied Stark field is parallel to the electric field of
the incident microwave energy. Each cell is housed in a wooden framework
lined with polyfoam which serves as an insulator to facilitate cooling
the cell with dry ice.

A small quantity of the sample gas is admitted into the Stark cell
through a stopcock on the manifold of the vacuum system. An oil diffusion
pump followed by a mechanical vacuum pump is used to pump the gas out of
the system until the desired operating pressure is reached, as indicated
by a Pirani gauge.
CHAPTER III

SYMMETRIC-TOEP MOLECULES

The moments of inertia of a molecule (or any rigid system of masses) may be represented by an ellipsoid whose orientation is fixed in the molecule and whose center coincides with the center of mass. If the coordinate system is oriented so that x, y, and z are along the principal axes of the ellipsoid of inertia, the equation for the ellipsoid may be written as

\[ x^2I_{xx} + y^2I_{yy} + z^2I_{zz} = 1 \]  

(1)

where \( I_{xx} \), \( I_{yy} \), and \( I_{zz} \) are the moments of inertia along the principal axes. The moment of inertia about any other axis is equal to the square of the reciprocal of the radius vector from the origin to the ellipsoid of inertia measured along the axis of interest. The three principal moments of inertia are usually arranged in increasing order of size and designated \( I_A \), \( I_B \), and \( I_C \). In the most general case, all three moments of inertia are different, \( I_A < I_B < I_C \), and the molecule is called an asymmetric top. In the case where two of the moments of inertia are equal and different from the third, the molecule is called a symmetric top.

The prolate type has \( I_A < I_B = I_C \) (momental ellipsoid elongated along the symmetry axis), and the oblate type has \( I_A = I_B < I_C \) (momental ellipsoid flattened along the symmetry axis). Usually the z-axis is chosen along the symmetry axis. Then, \( I_A \) and \( I_C \) are the moments of inertia along the
symmetry axis for prolate and oblate tops, respectively, and $I_B$ is the moment of inertia about an axis through the center of mass and perpendicular to the symmetry axis.

Rigid Rotor

The quantized rotational energy levels for a rigid symmetric-top molecule were first obtained by Dennison (10) with matrix mechanical methods and later by Reiche and Rademaker (11) and by Kronig and Rabi (12) with the Schrödinger Equation. The quantized energies for a prolate top can be expressed as

$$W = \frac{J(J+1)\hbar^2}{8\pi^2I_B} + \left(\frac{h^2}{8\pi^2I_A} - \frac{h^2}{8\pi^2I_B}\right)K^2.$$  \hspace{1cm} (2)

By defining the rotational constants

$$A = \frac{h}{8\pi^2I_A} \quad \text{and} \quad B = \frac{h}{8\pi^2I_B},$$  \hspace{1cm} (3)

Equation 2 can be written

$$\frac{W}{\hbar} = J(J+1)B + K^2(A-B),$$  \hspace{1cm} (4)

where $\hbar$ is Planck's constant, $J$ is the rotational angular momentum quantum number, and $K$ is the quantum number specifying the component of rotational angular momentum along the molecular symmetry axis. For an oblate top, the rotational constant $A$ is replaced by $C$, where

$$C = \frac{h}{8\pi^2I_C}. \hspace{1cm} (5)$$
In microwave spectroscopy, rotational constants are most often expressed in megacycles. Therefore, W/h in Equation 4 expresses the quantized energies in units of megacycles.

The quantum mechanical treatment of the symmetric top involves three quantum numbers,

\[ J = 0, 1, 2, \ldots \]
\[ K = 0, \pm 1, \pm 2, \ldots, \pm J \]
\[ M_J = 0, \pm 1, \pm 2, \ldots, \pm J \]

which have the following significance. The total rotational angular momentum has the magnitude \( \sqrt{J(J+1)} \hbar \), the \( z \)-component of rotational angular momentum is \( K \hbar \), and the \( z \)-component of rotational angular momentum is \( M_J \hbar \), where \( \hbar = h/2\pi \). Figure 2 illustrates the vector relations of rotational angular momenta for a symmetric-top molecule. Selection rules for the symmetric rotor, involving no quadrupole interaction, are

\[ \Delta J = 0, \pm 1 \]
\[ \Delta K = 0 \]
\[ \Delta M_J = 0, \pm 1 \]

For an absorption transition with the Stark field parallel to the electric field of the microwave radiation, the selection rules for \( J \) and \( M_J \) are

\[ \Delta J = \pm 1 \]
\[ \Delta M_J = 0 \]

In the absence of an external field, the selection rule for \( M_J \) is unimpor-
Figure 2. Vector Relations of Rotational Angular Momenta for a Symmetric-Top Molecule. The XYZ system is fixed in space, and the xyz system is fixed in the molecule with z along the symmetry axis.
tant since the rotational energy expressed in Equation 2 is independent of $M_J$.

Centrifugal Stretching

The above discussion is applicable to a rigid molecule. When the effects of centrifugal distortion are included (1), the quantized energy levels can be expressed as

$$\frac{\hbar}{W} = J(J+1)B + K^2(A-B) - J^2(J+1)^2D_{JJ} - J(J+1)K^2D_{JK} - K^4D_{KK}$$

where $D_{JJ}$, $D_{JK}$, and $D_{KK}$ represent distortion constants which are small compared with $A$ or $B$.

The absorption frequency resulting from a rotational transition $J \rightarrow J+1$ and $\Delta K = 0$ is

$$\nu = 2(J+1)B - k(J+1)^3D_{JJ} - 2(J+1)K^2D_{JK}$$

For a rigid molecule, the absorption lines are equally spaced; and for a given transition of $J$, all possible values of $K$ give identical frequencies.

For a nonrigid molecule, the degeneracy is removed because of the $D_{JK}$ distortion constant, as may be seen in Equation 9. A high-resolution microwave spectroscopic can usually resolve the lines involving different $K$'s, so that $D_{JK}$ can be evaluated.

Quadrupole Hyperfine Structure

For most molecules in the electronic ground state, the magnetic fields produced by various electronic orbitals almost completely cancel,
resulting in zero or a very small magnetic field at the nucleus and therefore a negligible hyperfine structure. However, the electric quadrupole interactions in molecules may give rise to a sizable hyperfine structure.

If the electric charge of a nucleus is not spherically symmetric, which is usually the case when the nuclear spin \( I \neq 1 \), the nucleus has an electric quadrupole moment \( Q \) which can couple the nuclear axis to the molecular framework by interaction with the average electric field gradient of the molecule at the nucleus. Vectorially, the nuclear spin angular momentum \( \vec{I} \) and the rotational angular momentum \( \vec{J} \) can be regarded as forming a resultant total angular momentum \( \vec{F} \), fixed in space, about which both \( \vec{I} \) and \( \vec{J} \) precess. The vector relations of angular momenta for a symmetric-top molecule with \( \text{IJ-coupling} \) are illustrated in Figure 3. The quantum conditions on \( F \) and \( M_F \) are

\[
F = J + I, J + I - 1, \ldots, \left| J - I \right| \\
M_F = 0, \pm 1, \pm 2, \ldots, \pm F,
\]

and the quantum number \( I \) is fixed for a particular nucleus. The nuclear spin angular momentum has the magnitude \( \sqrt{I(I+1)} \), the total angular momentum has the magnitude \( \sqrt{F(F+1)} \), and the Z-component of total angular momentum is \( M_F \).

The nuclear quadrupole energy, expressed in units of frequency, for a nucleus on the molecular axis of a symmetric top can be expressed as (13)

\[
\frac{W_Q}{\hbar} = eQ f(I,J,F) g(J,K),
\]
Figure 3. Vector Relations of Angular Momenta for a Symmetric-
Top Molecule With IJ-Coupling. The XYZ system is
fixed in space, and the xyz system is fixed in the
molecule with z along the symmetry axis.
where $e$ is the charge of one proton, $q$ is the second partial derivative of the electric potential (resulting from extranuclear charges) with respect to the molecular symmetry axis evaluated at the nucleus considered, $Q$ is the electric quadrupole moment of the nucleus, and

$$f(I,J,F) = \frac{(3/4)C(C+1) - I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)}$$

(12)

$$C = F(F+1) - I(I+1) - J(J+1)$$

$$g(J,K) = \frac{3K^2}{J(J+1)} - 1$$

(13)

The quantity $eqQ$ is called the quadrupole coupling constant. A table of Casimir's function, $f(I,J,F)$, and relative intensities of hyperfine components (14) is helpful when calculating energies resulting from nuclear quadrupole interactions.

Rotational Spectra

In the above discussion, three kinds of energy in a rotating symmetric-top molecule have been considered. In order of decreasing magnitude, they are (a) rotational energy, (b) quadrupole coupling energy, and (c) distortion energy. The latter is closely related to rotational energy.

In a rotational absorption transition, the molecule goes from an initial state to a final state, each of which can be specified by the quantum numbers $J$, $K$, $I$, and $F$. The selection rules for a symmetric top, not involving quadrupole interaction, are given in Equation 7; selection rules for a symmetric top having quadrupole interaction are
\[ \Delta J = 0, \pm 1 \]
\[ \Delta K = 0 \]
\[ \Delta I = 0 \]
\[ \Delta F = 0, \pm 1 \]
\[ \Delta M_F = 0, \pm 1 \]

For an absorption transition with the Stark field parallel to the electric field of the microwave radiation, the selection rules for \( J \) and \( M_F \) are

\[ \Delta J = +1 \]
\[ \Delta M_F = 0 \]

The absorption frequency is determined by the difference between the initial and final state energies. Let the following definitions apply to the energy differences expressed in megacycles:

- \( \nu \) absorption line frequency,
- \( \nu_R \) rotational energy difference which assumes a rigid molecule,
- \( \nu_D \) distortion energy correction term which accounts for a nonrigid molecule, and
- \( \nu_Q \) quadrupole energy term which accounts for the interaction between the nuclear quadrupole moment and the average field gradient at the nucleus.

The absorption frequency for the transition \( J \rightarrow J+1, \Delta K = 0, F_i \rightarrow F_f \) (i and f refer to initial and final states) is

\[ \nu = \nu_R + \nu_D + \nu_Q \]
where
\[ \nu_R = 2(J+1)B \]  \hspace{1cm} (16)
\[ \nu_D = -4(J+1)D_{JJ} - 2(J+1)K^2D_{JK} \]  \hspace{1cm} (17)
\[ \nu_Q = eqQ \left[ g(J+1,K)f(I,J+1,F_1) - g(J,K)f(I,J,F_1) \right] \]  \hspace{1cm} (18)

The functions \( f \) and \( g \) are defined in Equations 12 and 13.

Analysis of Microwave Data

Referring to Equations 15 through 18, one sees that it is necessary to evaluate four constants; they are the rotational constant \( B \), the distortion constants \( D_{JJ} \) and \( D_{JK} \), and the quadrupole coupling constant \( eqQ \). The various terms of Equation 15 are functions of the quantum numbers, as indicated in the following:

\[ \nu(J,K,I,F_1,F_1') = \nu_R(J) + \nu_D(J,K) + \nu_Q(J,K,I,F_1,F_1') \]  \hspace{1cm} (19)

Assume that as many lines as possible have been measured and identified by the quantum numbers of the initial and final states. Evaluation of the constants can proceed as follows.

Quadrupole Coupling Constant, \( eqQ \).--To evaluate the quadrupole coupling constant, choose a group of lines involving the same \( J \) and \( K \), but different combinations of \( F_1 \) and \( F_1' \). Designate lines by numerical subscripts; then a pair (e.g., numbers 1 and 2) can be used as follows:

\[ \nu_1 = \nu_R(J) + \nu_D(J,K) + \nu_Q(J,K,I,F_{11},F_{11}') \]
\[ \nu_2 = \nu_R(J) + \nu_D(J,K) + \nu_Q(J,K,I,F_{12},F_{12}') \]
Subtracting gives

\[ \Delta \nu_{12} = \nu_1 - \nu_2 = \nu_Q(J,K,I,F_{i1},F_{f1}) - \nu_Q(J,K,I,F_{i2},F_{f2}) \]

or

\[ \eq Q = \Delta \nu_{12} + \left\{ \left[ g(J+1,K) f(I,J+1,F_{f1}) - g(J,K) f(I,J,F_{12}) \right] - \left[ g(J+1,K) f(I,J+1,F_{f2}) - g(J,K) f(I,J,F_{12}) \right] \right\} \]  \hspace{1cm} (20)

If the constant \( \eq Q \) is evaluated for every possible pair of lines in each group involving the same \( J \) and \( K \), a weighted average can be taken and assigned as the quadrupole coupling constant, \( \eq Q \), for the molecule. If it is assumed that each line is measured with identical accuracy, then \( \Delta \nu \) is a reasonable weighting factor. A faulty frequency measurement can often be detected by examining the "spread" of the individual calculations.

**Distortion Constant, \( D_{JK} \).**--After the quadrupole coupling constant has been evaluated, the quadrupole energy contribution \( \nu_Q \) to each line can be calculated. Define the unsplit line frequency as

\[ \nu' = \nu - \nu_Q = \nu_R + \nu_D \]  \hspace{1cm} (21)

If the unsplit line frequency is calculated for each measured absorption line, a weighted value can be assigned to each group involving the same \( J \) and \( K \). This is the theoretical frequency that would be observed if quadrupole coupling were not present. A logical weighting factor is the relative line intensity.

Equation 21 can be written as

\[ \nu' = 2(J+1)B - 4(J+1)^3 D_{JJ} - 2(J+1)^2 D_{JK} \]
or

\[
\frac{\nu'}{2(J+1)} = B - 2(J+1)^2D_{JJ} - K_{JK}^2.
\]  

(22)

Evaluate \(\nu'/2(J+1)\) for each unsplit line frequency; choose pairs involving the same \(J\) but different \(K\) (designated by numerical subscripts, e.g., 1 and 2). From Equation 22,

\[
\frac{\nu_1'}{2(J+1)} = B - 2(J+1)^2D_{JJ} - K_{JK}^2
\]

\[
\frac{\nu_2'}{2(J+1)} = B - 2(J+1)^2D_{JJ} - K_{JK}^2.
\]

Subtracting the above equations, the distortion constant is found to be

\[
D_{JK} = \frac{\frac{\nu_1'}{2(J+1)} - \frac{\nu_2'}{2(J+1)}}{K_2^2 - K_1^2}.
\]  

(23)

If estimated errors have been assigned to each unsplit line frequency, then estimated errors can be assigned to each calculation of \(D_{JK}\), and a weighted average can be taken for the molecule. A logical weighting factor is the reciprocal of the estimated error for each calculation.

**Distortion Constant, \(D_{JJ}\)** -- The evaluation of the distortion constant \(D_{JJ}\) is similar to that for \(D_{JK}\). After \(\nu'/2(J+1)\) has been evaluated for each unsplit line frequency, choose pairs involving the same \(K\) but different \(J\) (designated by numerical subscripts, e.g., 1 and 2). From Equation 22,

\[
\frac{\nu_1'}{2(J_1+1)} = B - 2(J_1+1)^2D_{JJ} - K_{JK}^2.
\]
and
\[ \frac{v_1^2}{2(J_2+1)} = B - 2(J_2+1)^2D_{JJ} - K^2D_{JK} \ . \]

Subtracting the above equations, the distortion constant is found to be
\[ D_{JJ} = \frac{v_1^1 - v_2^1}{2(J_1+1)^2 - 2(J_2+1)^2} \ . \]  \hspace{1cm} (24)

Estimated errors can be assigned for each calculation as they were for
\( D_{JK} \) and a weighted average can be taken for the molecule.

**Rotational Constant, B.** After the quadrupole coupling constant and dis-
tortion constants have been evaluated, the rotational energy difference,
\[ \nu_R = \nu - \nu_Q - \nu_D \ , \]  \hspace{1cm} (25)
can be evaluated for each measured line, and an average value can be
taken for those involving the same \( J \). The rotational constant can then
be evaluated for each \( J \) transition by
\[ B = \frac{\nu_R}{2(J+1)} \ . \]  \hspace{1cm} (26)

If estimated errors have been assigned to each rotational energy differ-
ence, then estimated errors can be assigned to each calculation of \( B \),
and a weighted average can be taken for the molecule.

**Molecular Models**

Some authors attempt to explain the magnitude and algebraic sign
of measured distortion constants by referring to simple molecular models.
Most arguments, however, which attempt to give the reader a simple "picture" of what is happening, are incomplete and therefore unacceptable. To be complete, the model must be capable of predicting energy levels for each quantum state; then from the calculation of allowed transition frequencies between states, the distortion constants can be evaluated. The energy levels should include the total energy—the kinetic energy due to rotation about both axes and the potential energy which is stored in the stretched bonds. Arguments which do not include total energy are not acceptable.

In the course of a discussion concerning the positive value of $D_{JK}$ for methyl halides, Thomas, Cox, and Gordy (16) suggested a method whereby $D_{JJ}$ might be negative. The argument, which concerns hybridization of the bonding orbitals, is as follows. An increase in angular momentum about the symmetry axis tends to make the $\text{CH}_3$ group more nearly planar, and hence to increase the $S$ character in the three $C$ orbitals which bond to hydrogen. For a completely planar structure, each of these orbitals would have 33 per cent $S$ character; whereas, the usual tetrahedral bonding has 25 per cent $S$ character (see Appendix D). As a consequence, the $C$ orbital bonding to the halogen must be reduced for proper normalization. This tends to make the $C$-$H$ bonds stronger, the $C$-Hal bond weaker, and $D_{JK}$ positive. By similar arguments, one might conclude that end over end rotation, because it tends to decrease the $H$-$C$-$H$ angle (see Appendix C), will decrease the $S$ character of the $C$-$H$ bonds and consequently increase the $S$ character of the $C$-Hal bond; this tends to make the $C$-Hal bond stronger and $D_{JJ}$ negative. The argument is interesting because it suggests the possibility of a negative $D_{JJ}$;
however, the argument is incomplete because it does not consider the kinetic energy due to rotation about the symmetry axis and the potential energy stored in the bonds.

A more satisfactory approach for calculating distortion constants theoretically was undertaken by Slawsky and Dennison (1). They applied the theory of the semi-rigid rotor, which was developed by Wilson and Howard (18), to the symmetric molecules $YZ_3$ and $XYZ_3$. It was found that the change in rotational energy, caused by centrifugal distortions, can be expressed in terms of the quantum numbers $J$ and $K$ and as a function of the potential constants and the molecular dimensions. More recently, the calculation of rotational distortion constants for some axially symmetric $XYZ_3$ molecules was considered by Dowling, Gold, and Meister (5, 6). Explicit equations were written for the rotational distortion constants $D_{JJ}$, $D_{JK}$, and $D_{KK}$ in terms of the masses, internuclear distances, interbond angles, and the molecular force constants. This method is discussed further in the next chapter.
CHAPTER IV

ROTATIONAL DISTORTIONS IN SYMMETRIC-TOP MOLECULES

Effects of centrifugal distortion in symmetric-top molecules, neglecting electric quadrupole splitting, are expressed by the distortion constants $D_{JJ}$ and $D_{JK}$ in the equation,

$$\frac{\nu}{2(J+1)} = B - 2(J+1)^2 D_{JJ} - K^2 D_{JK},$$

(27)

for a transition $J\rightarrow J+1$ and $\Delta K = 0$. It has been surmised by some authors (2) that $D_{JJ}$ will be positive for all symmetric tops, while $D_{JK}$ may in principle be either positive or negative. It was also pointed out that all molecules of the type $YZ_3$ which have so far been examined have $D_{JK}$ negative, while molecules of the type $XYZ_3$ have $D_{JK}$ positive.

A recent investigation (3, 4) of CCl$_3$F and CHCl$_3$ yielded negative values for both $D_{JJ}$ and $D_{JK}$. In addition, it was found that $D_{JJ}$ is a function of $J$ for the low J-value data which were considered. Long (4) also pointed out that the centers of mass for previously reported $XYZ_3$ molecules are outside the $YZ_3$ tetrahedron, and the centers of mass for CCl$_3$F, CHCl$_3$, and YZ$_3$ molecules are within the $YZ_3$ tetrahedron. It has since been pointed out that CHF$_3$ has its center of mass within the $YZ_3$ tetrahedron and was reported (15) to have $D_{JJ}$ positive and $D_{JK}$ negative. A search, in conjunction with M. W. Long, for reported values of $D_{JK}$, for YZ$_3$ and $XYZ_3$ molecules, yielded two distinct groups. Group I has the center of mass outside the $YZ_3$ tetrahedron and $D_{JK}$ positive, while
Group II has the center of mass within the YZ₃ tetrahedron and DJK negative.

<table>
<thead>
<tr>
<th>Group I</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃Br</td>
<td>CClF₃</td>
<td>F₃GeCl</td>
<td></td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>CF₃I</td>
<td>PF₃S</td>
<td></td>
</tr>
<tr>
<td>CH₃F</td>
<td>H₃BCO</td>
<td>SiF₃Cl</td>
<td></td>
</tr>
<tr>
<td>CH₃I</td>
<td>H₃CCCI</td>
<td>SiF₃Br</td>
<td></td>
</tr>
<tr>
<td>CBrF₃</td>
<td>F₃CCCH</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group II</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₃</td>
<td>NH₃</td>
<td>PH₃</td>
<td></td>
</tr>
<tr>
<td>CHF₃</td>
<td>ND₃</td>
<td>AsF₃</td>
<td></td>
</tr>
<tr>
<td>CCl₃F</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is interesting to note that the signs of DJK calculated later (see Table 5) also agree with this grouping.

The unexpected results of Long's work concerning distortion constants of CCl₃F and CHCl₃ invited further investigations of the subject. It was decided to study distortion effects of CClF₃ in detail because the bonding is similar to that of CCl₃F. Since the center of mass for this molecule is outside the YZ₃ tetrahedron, it was expected that DJK would be positive. In addition, it was decided to compare the results with those of CH₃Cl, a typical methyl halide, and of CHF₃, a molecule with its center of mass toward the base of the YZ₃ tetrahedron.

Chloromethane, CH₃Cl

The microwave absorption spectrum of methyl chloride (chloromethane) has been analyzed and reported by Thomas, Cox, and Gordy (16). The
resolved hyperfine lines, reported in Reference 16, for the $J = 3\to 4$ and $J = 5\to 6$ transitions were used to calculate distortion constants for all possible combinations of the hypothetical unsplit lines. The results are illustrated in Figures 4 and 5. It was necessary to select an arbitrary estimated error for the unsplit lines of only $\pm 0.03$ mc in order to have good agreement among the various calculations of $D_{JJ}$ and $D_{JK}$. This estimated error is quite low considering that the line frequencies were approximately 106 kmc and 159 kmc.

The weighted averages, based on this author's calculations, are

$$D_{JJ} = + 17.7 \text{ kc}$$

and

$$D_{JK} = + 198.5 \text{ kc} ;$$

whereas, the values reported by Thomas, Cox, and Gordy are

$$D_{JJ} = + 18.1 \pm 0.5 \text{ kc}$$

and

$$D_{JK} = + 198.0 \pm 5.0 \text{ kc} .$$

It is possible that the values reported by Thomas, Cox, and Gordy are based on additional data. This author's calculations were made to see if the individual $D_{JJ}$ and $D_{JK}$ calculations were consistent.

Chlorotrifluoromethane, $\text{CClF}_3$

The microwave absorption spectrum of chlorotrifluoromethane has been reported for the $J = 2\to 3$ and $J = 3\to 4$ transitions by Coles and Hughes (17). Using their data, the distortion constants $D_{JJ}$ and $D_{JK}$ were calculated for all combinations of hypothetical unsplit line frequencies.
<table>
<thead>
<tr>
<th>K</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>198.0 ±7.5</td>
<td>199.5 ±1.9</td>
<td>198.7 ±0.8</td>
<td>17.7 ±0.2</td>
<td>198.0 ±7.5</td>
<td>200.0 ±2.5</td>
<td>198.8 ±0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>199.5 ±1.9</td>
<td>200.0 ±2.5</td>
<td>198.0 ±1.5</td>
<td>17.6 ±0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>198.7 ±0.8</td>
<td>198.8 ±0.9</td>
<td>198.0 ±1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>17.7 ±0.2</td>
<td>198.5 ±1.3</td>
<td>198.7 ±0.6</td>
<td>198.3 ±0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>198.5 ±1.3</td>
<td>198.7 ±0.6</td>
<td>198.8 ±1.0</td>
<td>198.3 ±0.4</td>
<td>197.9 ±0.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4. Distortion Constants of $^{12}$HCl. The calculations are based on data reported by Thomas, Cox, and Gordy (16). The constant $D_{11}$ appears in the large blocks along the diagonal, and the constant $D_{22}$ appears in the off-diagonal blocks. Each constant was computed from the two transitions which designate its row and column.
Figure 5. Weighted Distortion Constants of $^{12}$H,$^{35}$Cl. The calculations are based on data reported by Thomas, Cox, and Gordy (16). The dotted lines indicate the weighted averages, and the horizontal lines indicate the estimated error of the individual calculations.
The hyperfine lines for the $J = 1 \rightarrow 2$ transition were measured (see Figure 11 and Table 1), and the data were used to make additional calculations of distortion constants. The appropriate blocks in Figure 6 illustrate that the results were inconsistent; and, in fact, a negative $D_{JJ}$ was calculated using the $J = 1 \rightarrow 2$, $K = 1$ and the $J = 2 \rightarrow 3$, $K = 1$ transitions. An attempt was made to measure the hyperfine lines for the $J = 0 \rightarrow 1$ transition; however, the lines were not completely resolved from their Stark components (see Figure 10).

In a further effort to clear up the inconsistencies in the distortion calculations, the hyperfine lines for the $J = 4 \rightarrow 5$ transition were measured (see Figure 14 and Table 1). The data were used to make additional calculations of distortion constants which are illustrated in the appropriate blocks in Figure 6. The results were still inconsistent and showed no particular trend.

An arbitrary estimated error for the unsplit lines of ±0.02 mc (based on numerous measurements, this estimated error seems to be realistic) was selected, and weighted values of the distortion constants were calculated. The results are illustrated in Figure 7. Referring to Figures 6 and 7, it can be seen that the calculated values for distortion constants are consistent for all calculations except those involving the $J = 2 \rightarrow 3$ transition, which was reported by Coles and Hughes (17). This suggested that a remeasurement should be undertaken to check their data.

The hyperfine lines for the $J = 2 \rightarrow 3$ and $J = 3 \rightarrow 4$ transitions (see Figures 12 and 13) were measured and compared with those reported by Coles and Hughes (see Table 1). Good agreement was found for the $3 \rightarrow 4$ transition; however, slight differences were found for the $2 \rightarrow 3$ transition. Some of the weaker lines of the $J = 3 \rightarrow 4$ transition, which were reported
<table>
<thead>
<tr>
<th>J = 1→2</th>
<th>J = 2→3</th>
<th>J = 3→4</th>
<th>J = 4→5</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>0</td>
<td>+4.3 ±10</td>
<td>-2.4 ±0.8</td>
<td>+0.8 ±0.3</td>
</tr>
<tr>
<td>1</td>
<td>-2.4 ±0.8</td>
<td>+4.5 ±2.2</td>
<td>+3.1 ±0.4</td>
</tr>
<tr>
<td>2</td>
<td>+4.5 ±2.2</td>
<td>+2.4 ±0.4</td>
<td>+1.4 ±0.2</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>+0.8 ±0.3</td>
<td>+3.1 ±0.4</td>
<td>+1.2 ±1.7</td>
</tr>
<tr>
<td>2</td>
<td>+2.4 ±0.4</td>
<td>+1.2 ±1.7</td>
<td>+1.6 ±1.0</td>
</tr>
<tr>
<td>3</td>
<td>+1.4 ±0.6</td>
<td>+1.6 ±1.0</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>+0.6 ±0.2</td>
<td>+1.6 ±0.2</td>
<td>+0.4 ±0.3</td>
</tr>
<tr>
<td>2</td>
<td>+1.4 ±0.2</td>
<td>+0.7 ±0.3</td>
<td>+3.1 ±1.3</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>+0.8 ±0.5</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>+2.2 ±0.3</td>
</tr>
</tbody>
</table>

Figure 6. Distortion Constants of $C_{12}Cl_{35}F_2$. The calculations are based on data for $J = 2→3$ and $3→2$ reported by Coles and Hughes (17) and data for $J = 1→2$ and $4→5$ measured in the present investigation. The constant $D_{JK}$ appears in the large blocks along the diagonal, and the constant $D_{JJ}$ appears in the off-diagonal blocks. Each constant was computed from the two transitions which designate its row and column.
Figure 7. Weighted Distortion Constants of $^{12}\text{Cl}^{35}\text{F}_3$. The calculations are based on data for $J = 2 \rightarrow 3$ and $3 \rightarrow 4$ reported by Coles and Hughes (17) and data for $J = 1 \rightarrow 2$ and $4 \rightarrow 5$ measured in the present investigation. The dotted lines indicate the weighted averages, and the horizontal lines indicate the estimated error of the individual calculations. Calculations involving the $J = 2 \rightarrow 3$ transition are indicated by empty circles.
<table>
<thead>
<tr>
<th></th>
<th>$J = 1 \rightarrow 2$</th>
<th>$J = 2 \rightarrow 3$</th>
<th>$J = 3 \rightarrow 4$</th>
<th>$J = 4 \rightarrow 5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K = 0$</td>
<td>5.5 ±1.0</td>
<td>1.2 ±0.8</td>
<td>0.8 ±0.3</td>
<td>0.6 ±0.2</td>
</tr>
<tr>
<td>$J = 1 \rightarrow 2$</td>
<td>1.2 ±0.8</td>
<td>1.1 ±2.2</td>
<td>0.5 ±0.4</td>
<td>0.4 ±0.2</td>
</tr>
<tr>
<td>$J = 2 \rightarrow 3$</td>
<td>1.1 ±2.2</td>
<td>0.6 ±0.4</td>
<td>0.6 ±0.2</td>
<td></td>
</tr>
<tr>
<td>$J = 3 \rightarrow 4$</td>
<td>0.8 ±0.3</td>
<td>1.7 ±1.7</td>
<td>1.7 ±0.6</td>
<td>0.4 ±0.3</td>
</tr>
<tr>
<td>$J = 4 \rightarrow 5$</td>
<td>0.6 ±0.4</td>
<td>1.7 ±1.0</td>
<td>0.6 ±0.3</td>
<td></td>
</tr>
<tr>
<td>$J = 5 \rightarrow 6$</td>
<td>0.4 ±0.2</td>
<td>1.3 ±0.3</td>
<td>3.1 ±1.3</td>
<td>2.2 ±0.3</td>
</tr>
<tr>
<td>$J = 6 \rightarrow 7$</td>
<td>0.6 ±0.2</td>
<td>0.6 ±0.3</td>
<td>3.1 ±1.3</td>
<td>1.8 ±0.3</td>
</tr>
<tr>
<td>$J = 7 \rightarrow 8$</td>
<td>0.6 ±0.3</td>
<td>2.3 ±0.5</td>
<td>1.8 ±0.8</td>
<td>2.1 ±0.6</td>
</tr>
<tr>
<td>$J = 8 \rightarrow 9$</td>
<td></td>
<td>2.2 ±0.3</td>
<td>2.0 ±0.3</td>
<td>2.1 ±0.6</td>
</tr>
</tbody>
</table>

Figure 8. Distortion Constants of $\text{C}_{\text{12}}\text{Cl}_{\text{35}}\text{F}_7$. The calculations are based on present data from Table 3. The constant $D_{JK}$ appears in the large blocks along the diagonal, and the constant $D_{JJ}$ appears in the off-diagonal blocks. Each constant was computed from the two transitions which designate its row and column.
Figure 9. Weighted Distortion Constants of \( C^{12}Cl^{35}F_2 \). The calculations are based on present data from Table 1. The dotted lines indicate the weighted averages, and the horizontal lines indicate the estimated error of the individual calculations. Calculations involving the \( J = 2 \to 3 \) transition are indicated by empty circles.
Figure 10. Recording of the J = 0→1 Transition of $\text{C}^{12}\text{Cl}^{35}\text{F}_3$. 
Figure 11. Theoretical Hyperfine Structure of the $J = 1-2$ Transition of $^{35}\text{Cl}^{35}\text{F}_2$. The major $K = 0$ line is shown dashed.
Figure 12. Theoretical Hyperfine Structure (Neglecting K = 0 Lines) of the J = 2→3 Transition of \( ^{12}\text{C}^{35}\text{F}_3 \).
Figure 13. Theoretical Hyperfine Structure (Neglecting K = 0 Lines) of the $J = 3\rightarrow 4$ Transition of $^{12}\text{C}^{35}\text{Cl}^{3}\text{F}_3$. 
Figure 14. Major Components of the Theoretical Hyperfine Structure (Neglecting $K = 0$ Lines) of the $J = 4 \rightarrow 5$ Transition of $\text{C}^{12}\text{Cl}^{35}\text{F}_3$. 
Table 1. Measured Hyperfine Line Frequencies for $^{12}$Cl$^{35}$F$_3$.\(^a\)

<table>
<thead>
<tr>
<th>J</th>
<th>K</th>
<th>F</th>
<th>Theoretical(^b)</th>
<th>Measured Present</th>
<th>Measured Coles and Hughes (17)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>0</td>
<td>$3/2+5/2$</td>
<td>13,344.03</td>
<td>13,344.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$5/2+7/2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>$3/2+5/2$</td>
<td>13,327.59</td>
<td>13,327.59</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$5/2+7/2$</td>
<td>13,347.09</td>
<td>13,347.11</td>
<td></td>
</tr>
<tr>
<td>2-3</td>
<td>1</td>
<td>$1/2+3/2$</td>
<td>20,015.46</td>
<td>20,015.53(^c)</td>
<td>20,015.77(^c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3/2+5/2$</td>
<td>20,010.59</td>
<td>20,010.65(^c)</td>
<td>20,010.84(^c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$5/2+7/2$</td>
<td>20,010.73</td>
<td>20,010.69(^c)</td>
<td>20,010.84(^c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$7/2+9/2$</td>
<td>20,015.59</td>
<td>20,015.53(^c)</td>
<td>20,015.77(^c)</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>$3/2+5/2$</td>
<td>20,013.47</td>
<td>20,013.39</td>
<td>20,013.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3/2+3/2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$5/2+7/2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$5/2+5/2$</td>
<td>19,999.55</td>
<td>19,999.57</td>
<td>19,999.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$5/2+3/2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$7/2+9/2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$7/2+7/2$</td>
<td>20,019.04</td>
<td>20,019.04</td>
<td>20,019.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$7/2+5/2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-4</td>
<td>1</td>
<td>$3/2+5/2$</td>
<td>26,684.74</td>
<td>26,684.72</td>
<td>26,684.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$5/2+7/2$</td>
<td>26,682.79</td>
<td>26,682.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$7/2+9/2$</td>
<td>26,683.80</td>
<td>26,683.80</td>
<td>26,683.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$9/2+11/2$</td>
<td>26,685.75</td>
<td>26,685.73</td>
<td>26,685.73</td>
</tr>
</tbody>
</table>

(Continued)
Table 1. Measured Hyperfine Line Frequencies for $^{12}$Cl$^{35}$F$_3$
(Continued).

<table>
<thead>
<tr>
<th>J</th>
<th>K</th>
<th>F</th>
<th>Theoretical b</th>
<th>Measured Present</th>
<th>Measured Coles and Hughes (17)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3→4</td>
<td>2</td>
<td>3/2→5/2</td>
<td>26,690.12</td>
<td>26,690.12$^c$</td>
<td>26,690.14$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5/2→5/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5/2→7/2</td>
<td>26,682.32</td>
<td>26,682.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7/2→7/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7/2→9/2</td>
<td>26,679.59</td>
<td>26,679.58</td>
<td>26,679.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9/2→9/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9/2→11/2</td>
<td>26,687.39</td>
<td>26,687.38</td>
<td>26,687.38</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>3/2→5/2</td>
<td>26,699.09</td>
<td>26,699.10</td>
<td>26,699.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5/2→7/2</td>
<td>26,681.55</td>
<td>26,681.53</td>
<td>26,681.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5/2→5/2</td>
<td>26,674.72</td>
<td></td>
<td>26,674.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7/2→9/2</td>
<td>26,672.57</td>
<td>26,672.58</td>
<td>26,672.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7/2→7/2</td>
<td>26,670.17</td>
<td></td>
<td>26,670.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9/2→9/2</td>
<td>26,696.93</td>
<td></td>
<td>26,697.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9/2→11/2</td>
<td>26,690.11</td>
<td>26,690.12$^c$</td>
<td>26,690.14$^c$</td>
</tr>
<tr>
<td>4→5</td>
<td>1</td>
<td>5/2→7/2</td>
<td>33,355.50</td>
<td>33,355.42$^c$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7/2→9/2</td>
<td>33,354.53</td>
<td>33,354.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9/2→11/2</td>
<td>33,355.39</td>
<td>33,355.42$^c$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>11/2→13/2</td>
<td>33,356.36</td>
<td>33,356.40</td>
<td></td>
</tr>
</tbody>
</table>

(Continued)
Table 1. Measured Hyperfine Line Frequencies for $\text{C}^{12}\text{Cl}^{35}\text{F}_3$
(Continued).

<table>
<thead>
<tr>
<th>$J$</th>
<th>$K$</th>
<th>$F$</th>
<th>Theoretical $^b$</th>
<th>Measured Present</th>
<th>Measured Coles and Hughes (17)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4→5</td>
<td>2</td>
<td>5/2→7/2</td>
<td>33,357.81</td>
<td>33,357.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7/2→9/2</td>
<td>33,353.91</td>
<td>33,353.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9/2→11/2</td>
<td>33,353.34</td>
<td>33,353.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>11/2→13/2</td>
<td>33,357.24</td>
<td>33,357.27</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5/2</td>
<td>5/2→7/2</td>
<td>33,361.64</td>
<td>33,361.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7/2→9/2</td>
<td>33,352.87</td>
<td>33,352.95</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9/2→11/2</td>
<td>33,349.93</td>
<td>33,349.91</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>11/2→13/2</td>
<td>33,358.70</td>
<td>33,358.71</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5/2</td>
<td>5/2→7/2</td>
<td>33,367.03</td>
<td>33,367.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7/2→9/2</td>
<td>33,351.43</td>
<td>33,351.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9/2→11/2</td>
<td>33,345.16</td>
<td>33,345.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>11/2→13/2</td>
<td>33,360.76</td>
<td>33,360.72</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Line frequencies are in megacycles per second.

$^b$ Theoretical line frequencies were calculated from the constants $E = 3335.596$ mc, $eqQ = -77.98$ mc, $D_{JJ} = +0.59$ kc, and $D_{JK} = +2.06$ kc, which were evaluated from the present data.

$^c$ Unresolved lines.
by Coles and Hughes (17), were not remeasured because of the good agreement found for the other lines of this transition. The calculations for the distortion constants using measurements made by this author are illustrated in Figures 8 and 9. It should be noted that all calculations are now consistent; for this reason, the $J = 2 \rightarrow 3$ data reported by Coles and Hughes (17) is believed to be slightly in error. If this is the case, then $^{12}\text{Cl}^{35}\text{F}_3$ obeys Equation 27 within the limits of experimental errors.

Using present data from Table 1, the following constants were calculated:

- $B = 3335.596$ mc
- $eqQ = -77.98$ mc
- $D_{JJ} = +0.59$ kc
- $D_{JK} = +2.06$ kc

Values reported by Coles and Hughes (17) are

- $B = 3335.56$ mc
- $eqQ = -78.05$ mc

**Trifluoromethane, CHF$_3$**

The microwave absorption spectrum of trifluoromethane has been analyzed and reported by Burrus and Gordy (15). It should be noted that the atoms in this molecule have no quadrupole moment; therefore, no hyperfine splitting occurs. The center of mass for this molecule is well within the $YZ_3$ tetrahedron and $D_{JK}$ turns out to be negative as expected. The resolved lines, reported in Reference 15, for the $J = 3 \rightarrow 4$, $J = 6 \rightarrow 7$, and $J = 8 \rightarrow 9$ transitions were used in all possible combinations to calculate distortion constants.
In order to extend the investigation lower in J-values, the J = 0→1 transition was measured by this author and found to occur at

\[ 20,697.72 \text{ mc} \]

This datum was used in conjunction with data on the other transitions to calculate additional values for the distortion constant \( D_{JJ} \). The complete results are illustrated in Figure 15. The estimated errors were obtained by assigning ±0.03 mc to the J = 0→1 transition and using other estimated errors as reported in Reference 15. All evaluations of the distortion constants are consistent within the limits of experimental errors.

The weighted values of distortion constants for Cl2HF3 were found to be

\[ D_{JJ} = +11.37 \text{ kc} \]

and

\[ D_{JK} = -18.05 \text{ kc} \]

as illustrated in Figure 16. These compare well with the values reported by Burrus and Gordy (15),

\[ D_{JJ} = +11.3 \text{ kc} \]

and

\[ D_{JK} = -18.0 \text{ kc} \]

For Figure 16, the estimated errors of the line frequencies reported by Burrus and Gordy have been reduced by a factor of ten, and consistent results were still obtained. This seems to indicate that their assignment of estimated errors may be too generous.
<table>
<thead>
<tr>
<th>K</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Figure 15. Distortion Constants of $^{12}$HF. The calculations are based on data for $J = 3/2^+$, $6/2^+$, and $8/2^+$ reported by Burrows and Gordy (15) and data for $J = 0^+$ measured in the present investigation. The constant $D_{JK}$ appears in the large blocks along the diagonal, and the constant $D_{JJ}$ appears in the off-diagonal blocks. Each constant was computed from the two transitions which designate its row and column.
Figure 16. Weighted Distortion Constants of $^{12}$HF$_2$. The estimated errors for the lines reported by Burrus and Gordy (15) have been reduced by a factor of ten.
Higher-Order Distortion Constants and CC\textsubscript{13}F

In the recent investigation (3) of CC\textsubscript{13}F, the J = 1→2 and 2→3 transitions were analyzed in detail, and measurements were made for the frequencies of the largest resolvable prominence for each of the rotational transitions J = 3→4 through 6→7. The frequency shift of the most intense hyperfine component for any J→J+1 transition belongs to the set K = 1 and is specified by F = (J+7/2)→(J+9/2). The expression for the frequency shift (32) is

\[ \nu_Q = \beta(J) q \frac{Q}{Q} , \]

where

\[ \beta(J) = -\frac{3}{4} \frac{(J+1)(J+2) + (4J+7)}{(2J+5)(2J+3)(J+2)(J+1)} \]

and q is the second partial derivative of the electric potential at the chlorine nucleus (resulting from extranuclear charges) with respect to z, the symmetry axis of the molecule. Results of the measurements are given in Table 2.

The increasing value of (\nu - \nu_Q)/\nu_{J+1} with increasing J in Table 2 is a strange effect, if one assumes that it is the result of centrifugal stretching, because it implies a negative value of D_{\text{JJ}}. Calculations (3) based on the J = 1→2 data and the J = 2→3 through 6→7 data yield for D_{\text{JJ}} the values: -24 ± 2 kc and -14 kc, -9 kc, -6 kc, and -4 kc with probable errors less than ±1 kc. The observed variation of D_{\text{JJ}} with J suggests a possible need for considering higher-order distortion constants.
Table 2. Frequencies of the Strongest Line \((K=1)\) in Various Transitions for \(\text{Cl}_2\text{Cl}_3\text{F}\).\(^a\)

<table>
<thead>
<tr>
<th>Transition (J\rightarrow J+1)</th>
<th>Measured Frequency, (v), of Strongest Line (mc)</th>
<th>(\nu^b)</th>
<th>(\nu^b - \nu^Q) (\frac{1}{2(J+1)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→2</td>
<td>9 859.30 ± 0.04</td>
<td>- 2.26 ± 0.03</td>
<td>2465.39 ± 0.01</td>
</tr>
<tr>
<td>2→3</td>
<td>14 792.80 ± 0.06</td>
<td>- 1.00 ± 0.01</td>
<td>2465.63 ± 0.01</td>
</tr>
<tr>
<td>3→4</td>
<td>19 725.17 ± 0.01</td>
<td>- 0.55 ± 0.01</td>
<td>2465.72 ± 0.00</td>
</tr>
<tr>
<td>4→5</td>
<td>24 657.26 ± 0.03</td>
<td>- 0.35 ± 0.00</td>
<td>2465.76 ± 0.00</td>
</tr>
<tr>
<td>5→6</td>
<td>29 588.95 ± 0.01</td>
<td>- 0.23 ± 0.00</td>
<td>2465.76 ± 0.00</td>
</tr>
<tr>
<td>6→7</td>
<td>34 520.42 ± 0.01</td>
<td>- 0.17 ± 0.00</td>
<td>2465.76 ± 0.00</td>
</tr>
</tbody>
</table>

\(^a\) From Reference 3.

\(^b\) \(\nu^Q = 37.3 \pm 0.5\) mc based on \(J = 1\rightarrow 2\) data.

If the third-order terms of a Taylor's expansion of the energy are retained, the equivalent of Equation 27 for a transition \(J\rightarrow J+1\) and \(\Delta K = 0\) becomes

\[
\frac{\nu'}{2(J+1)} = B - 2(J+1)^2D_{JJ} - K^2D_{JK} - (J+1)^2(3J^2+6J+4)D_{J^3J} - 2(J+1)^2K^2D_{JJK} - K^4D_{JJK^2} \tag{28}
\]

where \(\nu' = \nu - \nu^Q\) is the unsplit line frequency and \(D_{JJJ}, D_{JJK},\) and \(D_{JKK}\) are defined as second-order distortion constants (see Appendix A). An effort was made to fit the \(\text{CCl}_3\text{F}\) data to Equation 28, and the data was found to be inconsistent.

In Appendix A, it is shown that any nonrigid symmetric-top molecule should obey Equation 28, or a similar equation including additional higher
order terms. However, it seems highly unlikely that the energy expression, as a function of J and K, has a higher-order "wrinkle" for low J-values.

It is more conceivable that higher-order distortion constants are required for high J transitions; this fact has been observed by Cowan and Gordy (33) while investigating Br$^8$CN for transitions involving $J = 47\rightarrow 48$, $J = 51\rightarrow 52$, and $J = 55\rightarrow 56$.

The fact that the CCl$_3$F data cannot be described by Equation 28 seems to indicate that the unsplit line frequencies of Table 2 are incorrect. If so, this would indicate either (a) an error in determining the frequencies of the strongest hyperfine lines or (b) an error in the calculated quadrupole frequency shift. Both of these possibilities have been discussed by Long (34); however, no suitable explanation could be found. It is interesting to note that, if the $\Omega$ is arbitrarily increased by a factor of $5/3$, the unsplit line frequencies are well behaved and indicate a rotational constant D$_{JJ}$ approximately equal to zero. However, this is unsatisfactory because the quadrupole coupling constant, assuming extranuclear charge symmetry about the C-Cl bond, is already large compared to values obtained for other molecules.

Theoretical Rotational Distortion Constants

A theoretical approach for calculating distortion constants was undertaken by Slawsky and Dennison (1). They applied the theory of the semi-rigid rotor, which was developed by Wilson and Howard (18), to the symmetric molecules YZ$_3$ and XYZ$_3$. It was found that the change in rotational energy, caused by centrifugal distortions, can be expressed in terms of the quantum numbers J and K and as a function of the potential constants and the molecular dimensions. The numerical calculations,
however, are rather involved and laborious. Agreement between theoretical values, based on calculations of this type, and experimental values for distortion constants were fair for most molecules considered.

More recently, the calculation of rotational distortion constants for some axially symmetric XYZ₃ molecules was considered by Dowling, Gold, and Meister (5, 6). Explicit equations were written for the rotational distortion constants D JJ, D JK, and D KK in terms of the nuclear masses, bond lengths, bond angles, and the molecular force constants.

For axially symmetric molecules of the XYZ₃ type, the principal symmetry axis passes through the X and Y atoms as illustrated in Figure 17. Molecules of this type are said to belong to the C₃ᵥ point group (19, 20); the subscript 3v means that there are three vertical planes of symmetry and that the covering operations consist of three reflections and three rotations.

The rotational distortion constants of a molecule belonging to the C₃ᵥ point group can be written (5) in the form

\[ D_{JJ} = \frac{\epsilon t_{xxxx}}{8(I_{xx}^0)^4} \]  \hspace{1cm} (29)

\[ D_{JK} = -2D_{JJ} + \frac{\epsilon(t_{xxzz} + 2t_{xzzz})}{4(I_{xx}^0)^2(I_{zz}^0)^2} \]  \hspace{1cm} (30)

and

\[ D_{KK} = -D_{JJ} - D_{JK} + \frac{\epsilon t_{zzzz}}{8(I_{zz}^0)^4} \]  \hspace{1cm} (31)

where I_{xx}^0 is the xx-component of the moment of inertia tensor evaluated
Figure 17. An $XYZ_3$ Molecule Belonging to the $C_{3v}$ Group.
at equilibrium for a molecule in its center of mass, principal axis system. The \(t_{\alpha \beta \gamma \delta}'s\) may be written as

\[
t_{\alpha \beta \gamma \delta} = \sum_{i} \left[ J_{\alpha \beta}^{i} \right]_{0} (F^{-1})_{i k} \left[ J_{\gamma \delta}^{k} \right]_{0},
\]

where \(\left[ J_{\alpha \beta}^{i} \right]_{0}\) is the partial derivative (evaluated at equilibrium) of the \(\alpha \beta\)-component of the moment of inertia tensor with respect to the \(i^{th}\) symmetry coordinate and \((F^{-1})_{i k}\) is an element of the matrix inverse to the potential energy matrix written in terms of the symmetry coordinates. The \(\left[ J_{\alpha \beta}^{i} \right]_{0}\) are given in Table 6 of Appendix E. In general, the \(F\) matrix will be factored in blocks along the diagonal and therefore so will the \(F^{-1}\) matrix. For an \(XYZ_3\) molecule of \(C_{3v}\) symmetry, \(F^{-1}\) will consist of three \(3 \times 3\) matrices, two of which will be identical. The constant \(\varepsilon\) multiplying each \(t_{\alpha \beta \gamma \delta}\) is \(6.7731 \times 10^5\) \(\text{kc/sec}\), if the masses are in atomic mass units, the internuclear distances are in Angstroms, the \(F\) matrix elements corresponding to the stretching bonds and the interaction between the stretching of bonds are in millidyne/Angstrom, the \(F\) matrix elements corresponding to the interaction between bending and stretching are in millidyne/radian, and the \(F\) matrix elements corresponding to bending and the interaction between bending and bending are in millidyne Angstrom/radian^2.

If one assumes harmonic motion of small amplitude for the nuclei, the expression for the potential energy \(V\) of the molecule can be written (31) in the form

\[
2V = \sum_{i,j} r_{i} r_{j} r_{i} r_{j},
\]

(33)
where \( f_{ij} = f_{ji} \) are force constants related to the internal coordinates, \( r_i \) and \( r_j \). But the potential energy can also be expressed in terms of the symmetry coordinates by means of the equation

\[
2V = \sum_{ij} F_{ij} R_i R_j ,
\]

(34)

where \( F_{ij} \) are force constants related to the symmetry coordinates \( R_i \) and \( R_j \). In matrix notation, these equations are

\[
2V = \mathbf{r}' \mathbf{f} \mathbf{r}
\]

(35)

and

\[
2V = \mathbf{R}' \mathbf{F} \mathbf{R}
\]

(36)

where \( \mathbf{r}' \) and \( \mathbf{R}' \) are the transposes of the \( \mathbf{r} \) and \( \mathbf{R} \) matrices. The \( r_i \) and \( R_i \) coordinates transform as

\[
\mathbf{R} = \mathbf{U} \mathbf{r}
\]

(37)

or

\[
\mathbf{r} = \mathbf{U}' \mathbf{R}
\]

(38)

where \( \mathbf{U}' \) equals \( \mathbf{U}^{-1} \), the inverse of \( \mathbf{U} \). From the above

\[
\mathbf{R}' \mathbf{F} \mathbf{R} = \mathbf{r}' \mathbf{f} \mathbf{r} = \mathbf{R}' \left( \mathbf{U} \mathbf{f} \mathbf{U}' \right) \mathbf{R} ,
\]

or

\[
\mathbf{F} = \mathbf{U} \mathbf{f} \mathbf{U}'
\]

(39)

The \( \mathbf{F} \), \( \mathbf{f} \), \( \mathbf{U} \), and \( \mathbf{U}' \) matrices are defined in Appendix E.

It is now possible to calculate the distortion constants if the following parameters are known: nuclear masses, bond lengths, bond
angles, and the appropriate force constants. The required parameters for several \( \text{XCZ}_3 \) molecules are given in Tables 3 and 4. The calculated and observed rotational distortion constants are given in Table 5. Agreement between calculated and observed constants is fair for all molecules except \( \text{CHCl}_3 \) and \( \text{CCl}_3\text{F} \), the only ones considered having three identical nuclei of spin \( 3/2 \). The disagreement was very great in these two cases; this suggests a need for further investigations of these molecules.

Summary of Results

Because of the apparent violation of existing distortion theory by the molecules \( \text{CHCl}_3 \) and \( \text{CCl}_3\text{F} \), detailed calculations of distortion constants were made for three other symmetric tops: \( \text{CH}_3\text{Cl}, \text{CClF}_3 \), and \( \text{CHF}_3 \). All three were found to obey existing distortion theory, within the limits of experimental errors, using first-order distortion constants. An attempt was made to fit the \( \text{CCl}_3\text{F} \) data from Reference 3 using distortion constants through second order, and the data were found to be inconsistent. In addition, the theoretical and observed distortion constants for nine symmetric tops were compared. Agreement was fair for all molecules considered except \( \text{CHCl}_3 \) and \( \text{CCl}_3\text{F} \); the disagreement was very large in these two cases.
Table 3. Molecular Dimensions of Some XCl₃ Molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>C-X</th>
<th>C-Z</th>
<th>Z-C-Z</th>
<th>X-C-Z</th>
<th>B₀</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃</td>
<td>1.073</td>
<td>1.767</td>
<td>110°24'</td>
<td>108°32'</td>
<td>3301.94</td>
<td>22</td>
</tr>
<tr>
<td>CHF₃</td>
<td>1.098</td>
<td>1.332</td>
<td>108°48'</td>
<td>110°8'</td>
<td>10,348.74</td>
<td>22</td>
</tr>
<tr>
<td>CH₃Br₇⁹</td>
<td>1.9391</td>
<td>1.113</td>
<td>111°14'</td>
<td>107°39'</td>
<td>9568.40</td>
<td>23</td>
</tr>
<tr>
<td>CH₃Cl₃⁵</td>
<td>1.7610</td>
<td>1.113</td>
<td>110°31'</td>
<td>108°24'</td>
<td>13,292.89</td>
<td>23</td>
</tr>
<tr>
<td>CH₃I</td>
<td>2.1392</td>
<td>1.113</td>
<td>111°25'</td>
<td>107°27'</td>
<td>7501.25</td>
<td>23</td>
</tr>
<tr>
<td>CCl₅F₃</td>
<td>1.740</td>
<td>1.328</td>
<td>108°</td>
<td>110°54'</td>
<td>3335.56</td>
<td>24,25b</td>
</tr>
<tr>
<td>CCl₅F₇⁹</td>
<td>1.33</td>
<td>1.76</td>
<td>109°40'</td>
<td>109°16'</td>
<td>2465.39</td>
<td>3</td>
</tr>
<tr>
<td>CF₃Br₇⁹</td>
<td>1.908</td>
<td>1.330</td>
<td>108°</td>
<td>110°54'</td>
<td>2098.06</td>
<td>25</td>
</tr>
<tr>
<td>CF₃I</td>
<td>2.134</td>
<td>1.332</td>
<td>108°</td>
<td>110°54'</td>
<td>1523.23</td>
<td>25</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
M_C &= 12.001 \\
M_{Cl} &= 35.000 \\
M_H &= 1.008 \\
M_{Br} &= 79.000 \\
M_F &= 19.000 \\
M_I &= 127.00
\end{align*}
\]

\(^a\) Bond lengths are in Angstroms, masses are in atomic mass units and rotational constants are in megacycles per second.

\(^b\) The bond lengths were calculated in Reference 24 assuming tetrahedral angles; the bond lengths recorded here were given in Reference 25 assuming Z-C-Z = 108°, a more probable value.
Table 4. Force Constants of Some XeZ\textsubscript{3} Molecules\textsuperscript{a}.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( f_{x} )</th>
<th>( f_{z} )</th>
<th>( f_{zz} )</th>
<th>( f_{xx} )</th>
<th>( f_{zz}^{x} )</th>
<th>( f_{xz}^{x} )</th>
<th>( f_{zz}^{x} )</th>
<th>( f_{zz} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCCl\textsubscript{3}</td>
<td>4.8002</td>
<td>3.4580</td>
<td>1.1621</td>
<td>0.92126</td>
<td>0.08800</td>
<td>0.63846\textsuperscript{b}</td>
<td>0.30760</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>HCF\textsubscript{3}</td>
<td>5.0323</td>
<td>6.2460</td>
<td>2.1523</td>
<td>0.94632</td>
<td>0.25305</td>
<td>0.26428\textsuperscript{b}</td>
<td>0.87900</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>BrCH\textsubscript{3}</td>
<td>2.8631</td>
<td>5.1199</td>
<td>0.53534</td>
<td>0.62871</td>
<td>0.05890</td>
<td>0.00000</td>
<td>0.25970</td>
<td>-0.00781</td>
<td>28</td>
</tr>
<tr>
<td>ClCH\textsubscript{3}</td>
<td>3.40025</td>
<td>5.14435</td>
<td>0.54894</td>
<td>0.77495</td>
<td>0.08800</td>
<td>0.00000</td>
<td>0.33000</td>
<td>-0.00169</td>
<td>29</td>
</tr>
<tr>
<td>ICH\textsubscript{3}</td>
<td>2.2467</td>
<td>5.0541</td>
<td>0.54775</td>
<td>0.57410</td>
<td>0.063509</td>
<td>-0.13676\textsuperscript{b}</td>
<td>-0.0254</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>ClCF\textsubscript{3}</td>
<td>3.4580</td>
<td>6.2460</td>
<td>2.1329</td>
<td>1.1408</td>
<td>0.70843</td>
<td>-0.73068\textsuperscript{b}</td>
<td>0.87900</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>FCCl\textsubscript{3}</td>
<td>4.9447</td>
<td>3.4580</td>
<td>1.1621</td>
<td>1.6580</td>
<td>0.90713</td>
<td>-0.13733\textsuperscript{b}</td>
<td>0.30760</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>BrCF\textsubscript{3}</td>
<td>3.0352</td>
<td>6.2460</td>
<td>2.1329</td>
<td>0.73841</td>
<td>0.71247</td>
<td>-0.26499\textsuperscript{b}</td>
<td>0.87900</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>ICF\textsubscript{3}</td>
<td>2.2890</td>
<td>6.2460</td>
<td>2.1329</td>
<td>0.51360</td>
<td>0.63250</td>
<td>-0.3640\textsuperscript{b}</td>
<td>0.87900</td>
<td>31</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Bond stretching and bond interaction constants are in units of md/A (millidyne/Angstrom); angle-bond interaction constants are in md/rad; angle bending and angle interaction constants are in md A/rad\textsuperscript{2}.

\textsuperscript{b} This force constant is \( f_{xx}^{zz} - f_{xx}^{xz} \).

(Continued)
Table 4. Force Constants of Some XCl\textsubscript{3} Molecules (Continued).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$f_{zz}^2$</th>
<th>$f_{zz}'$</th>
<th>$f_{xz}$</th>
<th>$f_{xz}'$</th>
<th>$f_{xz}$</th>
<th>$f_{xz}'$</th>
<th>$f_{zz}$</th>
<th>$f_{zz}'$</th>
<th>$f_{xz}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC\textsubscript{3}Cl</td>
<td>0.36434</td>
<td>-0.27281</td>
<td>0.18601</td>
<td>-0.16400</td>
<td>0.028235</td>
<td>0.00000</td>
<td>0.08503</td>
<td>0.27305</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>HC\textsubscript{3}F</td>
<td>0.41959</td>
<td>-0.2244</td>
<td>0.43933</td>
<td>-0.21967</td>
<td>0.31008</td>
<td>0.00000</td>
<td>0.52869</td>
<td>0.17901</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Br\textsubscript{3}CH</td>
<td>0.15645</td>
<td>-0.06855</td>
<td>0.06965</td>
<td>-0.05535</td>
<td>0.01000</td>
<td>0.00000</td>
<td>-0.01600</td>
<td>-0.01516</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Cl\textsubscript{3}CH</td>
<td>0.18000</td>
<td>-0.08000</td>
<td>0.26000</td>
<td>-0.09100</td>
<td>0.06464</td>
<td>-0.00236</td>
<td>-0.01616</td>
<td>0.05789</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>IC\textsubscript{3}H</td>
<td>0.22912</td>
<td>-0.09777</td>
<td>0.40936</td>
<td>0.18676</td>
<td>0.015916</td>
<td>0.00000</td>
<td>-0.017934</td>
<td>-0.001256</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Cl\textsubscript{3}CF</td>
<td>0.41770</td>
<td>-0.22339</td>
<td>0.30557</td>
<td>-0.15278</td>
<td>0.060827</td>
<td>0.00000</td>
<td>0.52392</td>
<td>-0.022689</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>FC\textsubscript{3}Cl</td>
<td>0.36434</td>
<td>-0.27281</td>
<td>0.30940</td>
<td>-0.22571</td>
<td>0.06236</td>
<td>0.00000</td>
<td>0.08503</td>
<td>0.22668</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Br\textsubscript{3}CF</td>
<td>0.41770</td>
<td>-0.22339</td>
<td>0.24665</td>
<td>-0.09272</td>
<td>0.0500</td>
<td>0.00000</td>
<td>0.57700</td>
<td>-0.23225</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>IC\textsubscript{3}F</td>
<td>0.41770</td>
<td>-0.22339</td>
<td>0.29545</td>
<td>-0.11430</td>
<td>0.0300</td>
<td>0.00000</td>
<td>0.6392</td>
<td>-0.28590</td>
<td>31</td>
<td></td>
</tr>
</tbody>
</table>
Table 5. Calculated and Observed Rotational Distortion Constants for Some $X\text{C}_3\text{Z}_3$ Molecules.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$D_{JJ}$ Calculated</th>
<th>$D_{JJ}$ Observed</th>
<th>$D_{JK}$ Calculated</th>
<th>$D_{JK}$ Observed</th>
<th>Observed Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl\textsubscript{3}\textsuperscript{35}</td>
<td>1.44\textsuperscript{b}</td>
<td>4.12</td>
<td>-2.39\textsuperscript{b}</td>
<td>55</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>-1.8\textsuperscript{c}</td>
<td></td>
<td>-201</td>
<td></td>
<td>4,3</td>
</tr>
<tr>
<td>CHF\textsubscript{3}</td>
<td>11.4\textsuperscript{b}</td>
<td>11.3</td>
<td>-18.2\textsuperscript{b}</td>
<td>-18.0</td>
<td>15</td>
</tr>
<tr>
<td>CH\textsubscript{3}Br\textsuperscript{79}</td>
<td>9.7\textsuperscript{b}</td>
<td>9.9</td>
<td>103\textsuperscript{b}</td>
<td>128.3</td>
<td>16</td>
</tr>
<tr>
<td>CH\textsubscript{3}Cl\textsuperscript{35}</td>
<td>18.2\textsuperscript{b}</td>
<td>18.1</td>
<td>179\textsuperscript{b}</td>
<td>198</td>
<td>16</td>
</tr>
<tr>
<td>CH\textsubscript{3}I</td>
<td>6.45</td>
<td>6.28</td>
<td>55.9</td>
<td>98.5</td>
<td>16</td>
</tr>
<tr>
<td>CCl\textsubscript{3}F\textsubscript{3}</td>
<td>0.55</td>
<td>0.59</td>
<td>2.00</td>
<td>2.06</td>
<td>Present</td>
</tr>
<tr>
<td>CCl\textsubscript{3}F</td>
<td>0.46</td>
<td>-4\textsuperscript{d}</td>
<td>-0.50</td>
<td>-196</td>
<td>3</td>
</tr>
<tr>
<td>CF\textsubscript{3}Br\textsuperscript{79}</td>
<td>0.26\textsuperscript{b}</td>
<td></td>
<td>1.22\textsuperscript{b}</td>
<td>1.26</td>
<td>25</td>
</tr>
<tr>
<td>CF\textsubscript{3}I</td>
<td>0.17\textsuperscript{b}</td>
<td></td>
<td>0.88\textsuperscript{b}</td>
<td>0.6</td>
<td>25</td>
</tr>
</tbody>
</table>

\textsuperscript{a} In units of kc/sec.

\textsuperscript{b} From Reference 5.

\textsuperscript{c} Calculations using $J = 1\rightarrow 2$ and $2\rightarrow 3$ data yield -14.5; calculations using $J = 1\rightarrow 2$ and $6\rightarrow 7$ data yield -1.8.

\textsuperscript{d} Calculations using the $J = 1\rightarrow 2$ data and the $J = 2\rightarrow 3$ through $J = 6\rightarrow 7$ data yield for $D_{JJ}$ the values: $-24 \pm 2$ and $-14$, $-9$, $-6$, and $-4$ with probable errors less than $\pm 1$. 
CHAPTER V

STARK EFFECT OF CHLOROTRIFLUOROMETHANE

Stark effects are changes in the spectrum of a system when the system is subjected to an electric field. The rotational spectrum of a molecule which has an electric dipole moment may be expected to be modified when the molecule is in an electric field, since the field exerts torques on the molecular dipole and thereby changes its rotational motion. A measurement and analysis of the Stark effect allows one to evaluate the molecular dipole moment.

The Stark effect of the symmetric top, chlorotrifluoromethane (CClF$_3$), is affected by the quadrupole coupling of the chlorine nucleus to the average gradient of the molecular electric field. The theory of Stark effects on symmetric-top molecules with nuclear quadrupole coupling has been developed by Low and Townes (35). They found it convenient to discuss three types of conditions: weak field, strong field, and intermediate field.

In the weak field case, the Stark energy is small compared to the quadrupole coupling energy. In this case, the rotational wave functions and the hyperfine structure are only slightly perturbed by the electric field. Expressed classically, the precession of the molecule due to the Stark field is so slow that the interaction between the nucleus and the molecule is very little disturbed. A vector diagram of the weak field case is illustrated in Figure 18. The molecular symmetry axis precesses rapidly about the rotational angular momentum vector $\mathbf{J}$. The nuclear
Figure 18. Vector Diagrams for the Stark Effects on Symmetric-Top Molecules With Nuclear Quadrupole Coupling.
quadrupole moment couples to the average molecular field, causing the rotational angular momentum vector \( \vec{J} \) and the nuclear spin angular momentum vector \( \vec{I} \) to precess slowly about the total angular momentum vector \( \vec{F} \). The Stark field, oriented along the Z-axis, couples to the molecular dipole moment causing a precession, much slower than the previous two, about the Z-axis. The molecular state is satisfactorily specified by the quantum numbers, \( J, K, I, F, \) and \( M_F \). Each hyperfine line is split by the Stark effect into various components according to the value of \( M_F \), and this splitting is small compared with the hyperfine splitting.

In the strong field case, the Stark energy is large compared to the quadrupole coupling energy. The molecule is precessed so violently by the external field that the nuclear orientation cannot follow the motion; the vectors \( \vec{J} \) and \( \vec{I} \) are said to be decoupled. A vector diagram of the strong field case is also illustrated in Figure 18. The rapid precession of the molecular symmetry axis about \( \vec{J} \) is not affected appreciably by the Stark field. The average value of the molecular dipole moment along \( \vec{J} \) couples to the strong external field and causes \( \vec{J} \) to precess about the Z-axis at a rapid rate. The nuclear quadrupole moment couples to the average molecular field along the Z-axis causing \( \vec{I} \) to precess slowly. The molecular state is satisfactorily specified by the quantum numbers \( J, K, I, M_J, \) and \( M_I \). The quantum number \( M_F \) can be used, but it is related to \( M_J \) and \( M_I \) by \( M_F = M_J + M_I \). The rotational line is split into Stark levels according to the values of \( M_J \), and the quadrupole coupling gives a hyperfine splitting of each Stark level according to the value of \( M_I \). The hyperfine splitting is small compared to the separation between Stark levels.
In the intermediate field case, the Stark energies and hyperfine energies are comparable in size. In this case, F, M₁, and M₇ are not good quantum numbers, and a satisfactory vector diagram for the intermediate case cannot be drawn. Determination of the energy levels is generally rather complex because it involves the diagonalization of the perturbing Hamiltonian $H_Q + H_S$, where $H_Q$ is the quadrupole coupling Hamiltonian and $H_S$ is the Stark effect Hamiltonian.

Chlorotrifluoromethane, CClF₃, has the trade name "Freon-13." The sample used in this experiment was obtained from the Matheson Company, and it is reported to have a purity of 99.0 per cent.

The electric dipole moment of C¹²Cl¹³F₃ was evaluated by Beeson (8) by measuring and analyzing the Stark effect for the $J = 2 \rightarrow 3$ transition. The dipole moment obtained was not considered to be very accurate because of the difficulty of resolving the Stark components. It was decided to reevaluate the dipole moment by measuring and analyzing the Stark effect for the $J = 1 \rightarrow 2$ transition since the Stark spectrum is considerably less complex for this transition. Best results were obtained with the Stark cell at dry ice temperature and with a gas pressure of about 0.07 mm of mercury.

In order to determine the energy levels in the presence of the Stark field, it was necessary to determine the eigenvalues of the Hamiltonian matrix, $H_0 + H_Q + H_S$, where $H_0$ is the unperturbed rotational Hamiltonian and $H_Q$ and $H_S$ are the quadrupole and Stark Hamiltonians, respectively. The matrix elements can be computed from either of two sets of wave functions: (a) the weak field wave functions characterized by J, K, I, F, and $M_p$ or (b) the strong field wave functions characterized by J, K,
\( I, M_J, \) and \( M_I \). It appears most convenient to select the latter since expressions for calculating the matrix elements of both \( H_Q \) and \( H_S \), for the strong field wave functions, exist in the literature.

Since \( J, K, \) and \( I \) are good quantum numbers in both the weak and strong field cases, it may be surmised that they are good in the intermediate field case. Thus, the Hamiltonian will be diagonal in \( J, K, \) and \( I \); and, for particular values of \( J, K, \) and \( I \), the secular equation is

\[
\left| \langle JKIM_J M_I | H_Q + H_S | JKIM_J M_I \rangle - \frac{\mu E}{J(J+1)} \right| = 0 .
\]  

(40)

It may also be surmised that \( M_F = M_J + M_I \) is a good quantum number; thus, the Hamiltonian will also be diagonal in \( M_F \). In other words, the Hamiltonian matrix consists of submatrix blocks, dependent on \( M_F \), along the diagonal as illustrated in Figures 19 and 20.

The matrix of the Stark Hamiltonian is diagonal in \( M_J \) and \( M_I \); the elements are (36)

\[
\langle JKIM_J M_I | H_S | JKIM_J M_I \rangle = \mu E \frac{K M_J}{J(J+1)} .
\]  

(41)

The matrix elements of the quadrupole Hamiltonian (35) are *

\[
\langle JKIM_J M_I | H_Q | JKIM_J M_I \rangle = \frac{\mu Q}{2I(2I-1)(2J-1)(2J+3)} \left[ \frac{3K^2}{J(J+1)} - 1 \right] \langle M_J M_I | F | M_J M_I \rangle ,
\]  

(42)

* The factor \((2J+3)\) should be included in Equation 2 of Reference 35.
Figure 19. Graphical Illustration of the Hamiltonian Matrix for $J = 1$, $K = 1$, and $I = 3/2$. Non-zero terms appear only in the blocks along the diagonal.
Figure 20. Graphical Illustration of the Hamiltonian Matrix for $J = 2$, $K = 1$, and $I = 3/2$. Non-zero terms appear only in the blocks along the diagonal.
where

\[ F = 3(\mathbf{I} \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I} \cdot \mathbf{J}) - I(I+1)J(J+1) \quad (43) \]

The operator \( F \) has the following nonzero matrix elements (37):

\[ < M_J M_I | F | M'_J M'_I > = \frac{1}{2} \left[ 3M^2_I - I(I+1) \right] \left[ 3M^2_J - J(J+1) \right] \quad (44) \]

\[ < M_J M_I | F | M'_J M'_I = \frac{3}{4} (2M_J+1)(2M_I+1) \]

\[ \left[ (J^\dagger M_J)(J^\dagger M_J+1)(I^\dagger M_I)(I^\dagger M_I+1) \right]^{1/2} \quad (45) \]

and

\[ < M_J M_I | F | M'_J M'_I = \frac{3}{4} \left[ (J^\dagger M_J)(J^\dagger M_J-1)(I^\dagger M_I)(I^\dagger M_I+2) \right] \]

\[ (I^\dagger M_I)(I^\dagger M_I-1)(I^\dagger M_I+1)(I^\dagger M_I+2) \right]^{1/2} \quad (46) \]

The Hamiltonian matrices for the two cases--(1) \( J = 1, K = 1, \]
\( I = 3/2 \) and (2) \( J = 2, K = 1, I = 3/2 \)--are illustrated in Figures 19 and
20. The quadrupole coupling constant, \( \text{eqQ} \), was assigned the value
\(-77.98 \text{ mc} \), as previously measured by this author, and the molecular
electric dipole moment, \( \mu \), was assigned the value 0.50 debye* as reported
by Beeson (8). The Hamiltonian matrix was calculated for each case at
several values of Stark field intensity. The energy eigenvalues were
obtained with the aid of an electronic digital computer and the results

* 1 debye = \( 10^{-18} \) esu cm.
are illustrated in Figures 21 and 22. The electric field intensity in the Stark cell is related to the cell voltage by assuming an electrode spacing of 0.466 cm, as calibrated by measurement of the Stark effect of the OCS molecule.

It appears that the molecule behaves according to the strong field case for field intensities greater than about 400 volts/centimeter; the Stark levels are split according to the values of $M_J$, and the hyperfine structure is split according to the values of $M_I$. Recordings of the $J=1\rightarrow2$ transition at various voltages above 400 volts/centimeter indicated a widely separated pair of Stark lines symmetrically located on each side of the group of rotational lines (see Figure 23) as might be expected. Assuming the strong field selection rules for absorption,

$$
\Delta J = 1
$$

$$
\Delta K = 0
$$

$$
\Delta M_J = 0
$$

$$
\Delta M_I = 0
$$

it was found that each Stark line was composed of a group of four unresolved hyperfine lines, and the separation between the groups was a unique function of the electric field intensity.

The evaluation of the molecular dipole moment proceeded then as follows: (a) Stark energy levels versus electric field intensity were calculated, using intermediate field theory (7), for several assumed values of molecular dipole moment in the neighborhood of 0.500 debye. (b) Using the strong field selection rules, a family of curves, one for each assumed value of dipole moment, was constructed illustrating the
Figure 21. Stark Energy Versus Field Intensity for $\text{C}^{12}\text{Cl}^{35}\text{F}_3$ with $J = 1$ and $K = 1$. 
Figure 22. Stark Energy Versus Field Intensity for $\text{C}^{12}\text{O}^{35}\text{P}_3$ with $J = 2$ and $K = 1$. 
Figure 23. Recording of the $J = 1 \rightarrow 2$ Transition of $\text{C}^{12}\text{Cl}^{35}\text{F}_3$
Illustrating Stark Line Separation.
theoretical frequency separation versus field intensity for the pair of Stark lines. Each Stark line was assumed to be the average of its four unresolved hyperfine components. (c) The frequency of each of the pair of Stark lines was accurately measured at two values of electric field intensity: 657 and 1100 volts/centimeter. From these measurements, the frequency separation was found for both values of field intensity.

(d) With a large scale graph of the family of curves from Step b and the two experimental points from Step c, the molecular electric dipole moment for \( \text{C}^{12}\text{Cl}^{35}\text{F}_3 \) was assigned the value

\[ \mu = 0.50 \pm 0.01 \text{ debye}. \]  

Most of the estimated error in this result is attributed to an uncertainty of the electrode spacing in the Stark cell. A graph of the theoretical Stark line separation versus electric field intensity for the above value of \( \mu \), along with the two experimental points, is shown in Figure 24.

The evaluation of \( \mu \) was essentially independent of the assumed value of eqQ since the quadrupole coupling produced only a small perturbation on the Stark splitting and the individual hyperfine lines were not resolved. By using the measured separation between the pair of Stark lines, the evaluation of \( \mu \) was made independent of the rotational constant B and effects such as molecular polarization and second-order Stark energies which tend to shift both lines equally in the same direction.

It was desirable, however, to compare the individual measured Stark line frequencies with the theoretical frequencies; the comparison is illustrated in Table 6. The second-order Stark energy (38) was calculated from the equation,
Figure 24. Stark Line Separation Versus Field Intensity for the \( J_{1} = 1 \rightarrow 2, K = 1 \) Transition of \( ^{12}\text{C}^{35}\text{Cl}^{35}\text{F}_{3} \).
Table 6. Stark Line Frequencies for C\textsuperscript{12}Cl\textsuperscript{35}F\textsubscript{3}.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Stark Field Intensity (volt/cm)</th>
<th>M\textsubscript{J}</th>
<th>M\textsubscript{I}</th>
<th>1st Order Stark Displacement</th>
<th>Average 1st Order Stark Displacement</th>
<th>2nd Order Stark Displacement</th>
<th>Theoretical Stark Line Frequency</th>
<th>Measured Stark Line Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>657</td>
<td>+1</td>
<td>+3/2</td>
<td>+56.34</td>
<td>-55.30</td>
<td>0.33</td>
<td>13,398.1</td>
<td>13,398.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+1/2</td>
<td>+54.54</td>
<td>+55.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-1/2</td>
<td>+55.14</td>
<td>+55.40</td>
<td>+0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-3/2</td>
<td>+55.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>657</td>
<td>-1</td>
<td>+3/2</td>
<td>+54.37</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>+1/2</td>
<td>+56.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-1/2</td>
<td>+55.71</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-3/2</td>
<td>+55.30</td>
<td>-55.40</td>
<td>+0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>+1</td>
<td>+3/2</td>
<td>+92.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>+1/2</td>
<td>+91.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-1/2</td>
<td>+92.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-3/2</td>
<td>+92.76</td>
<td>+92.44</td>
<td>+0.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>-1</td>
<td>+3/2</td>
<td>-91.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>+1/2</td>
<td>-93.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-1/2</td>
<td>-92.84</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-3/2</td>
<td>-92.15</td>
<td>-92.44</td>
<td>+0.94</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} The transitions are J = 1\textsuperscript{\textminus}2, K = 1, I = 3/2, \Delta M\textsubscript{J} = 0, \Delta M\textsubscript{I} = 0; the electric dipole moment is 0.50 debye; the rotational energy is 2B(J+1) = 13,342.40 mc. Frequencies are given in megacycles.
\[ \Delta \omega_2 = \frac{u_2^2 E^2}{2 \hbar} \left\{ \frac{(J^2-K^2)(J^2-M^2)}{J^3(2J-1)(2J+1)} - \frac{(J+1)^2-K^2}{(J+1)^3(2J+1)(2J+3)} \right\} \]  

(49)

Polarization of the molecule and higher-order Stark effects were neglected. Comparison of the measured and theoretical frequencies is considered to be quite good since the Stark lines were on the order of three megacycles wide.
CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

This investigation of distortion constants was prompted by the recent work (3, 4) on CCl$_3$F and CHCl$_3$. The results for these molecules were unusual in three respects: (a) the measured values for the rotational distortion constants $D_{JJ}$ and $D_{JK}$ do not agree with the theoretical values calculated from the molecular structure and force constants; (b) the value of $D_{JJ}$ is negative and is a function of $J$; and (c) the quadrupole coupling constant, assuming extranuclear charge symmetry about the C-Cl bond, is large compared to values observed in other molecules. These two molecules are the only known symmetric tops, having three identical nuclei with quadrupole moments, for which the hyperfine spectra have been analyzed and reported. The centers of mass for these molecules are inside the YZ$_3$ tetrahedron; whereas the centers of mass for previously reported XYZ$_3$ molecules, other than CHF$_3$, are outside the YZ$_3$ tetrahedron.

The unusual behavior of the distortion constants is particularly disturbing since it is a violation of existing distortion theory, as expressed in Equation 27. For this reason, detailed calculations of distortion constants were made for three other symmetric tops: (a) CH$_3$Cl, a typical methyl halide; (b) CClF$_3$, a molecule with bonding similar to that of CCl$_3$F; and (c) CHF$_3$, a molecule with its center of mass well within the YZ$_3$ tetrahedron.

The hyperfine absorption spectrum of CH$_3$Cl has previously been analyzed and reported (16). The resolved hyperfine lines for the $J = 3-4$
and $J = 5\rightarrow 6$ transitions were used to calculate distortion constants for all possible combinations of the hypothetical unsplit lines. The molecule was found to obey Equation 27 with no apparent inconsistencies.

The hyperfine absorption spectrum of $\text{CClF}_3$ has been reported (17) for the $J = 2\rightarrow 3$ and $J = 3\rightarrow 4$ transitions. The hyperfine lines of the $J = 1\rightarrow 2$ and $J = 4\rightarrow 5$ transitions were measured in the present work, and all possible combinations of the hypothetical unsplit lines were used to calculate distortion constants. Several inconsistencies were observed for calculations involving the $J = 2\rightarrow 3$ transition. The $J = 2\rightarrow 3$ and $J = 3\rightarrow 4$ transitions were remeasured and compared with the reported values. Good agreement was found for the $3\rightarrow 4$ transition; however, slight differences were found for the $2\rightarrow 3$ transitions. Using data from the present work, the molecule was found to obey Equation 27 with no apparent inconsistencies. For this reason, the $J = 2\rightarrow 3$ data reported by Coles and Hughes (17) is believed to be slightly in error. A detailed calculation of distortion constants, for all possible combinations of unsplit lines, appears to be a good method for finding inconsistencies in experimental data.

Based on data from the present investigation for the $J = 1\rightarrow 2$ through $J = 4\rightarrow 5$ transitions, the following constants were calculated for $\text{CClF}_3$:

$$B = 3335.596 \text{ mc}$$
$$eq\eta = - 77.98 \text{ mc}$$
$$D_{JJ} = + 0.59 \text{ kc}$$
$$D_{JK} = + 2.06 \text{ kc}.$$  

The absorption spectrum of $\text{CHF}_3$ has previously been analyzed and reported (15). In order to extend the investigation lower in $J$-values,
the $J = 0 \rightarrow 1$ transition was measured in the present work. Data from the $J = 0 \rightarrow 1$, $3 \rightarrow 4$, $6 \rightarrow 7$, and $8 \rightarrow 9$ transitions were used to calculate distortion constants for all possible combinations of absorption lines. The molecule was found to obey Equation 27 with no apparent inconsistencies.

The theoretical rotational distortion constants for nine symmetric-top molecules were calculated using the molecular structures and the molecular force constants; the former are calculated from microwave spectra and the latter are calculated from Raman and infrared spectra. A comparison of the theoretical and observed distortion constants provides an interesting link between spectra in the microwave and infrared regions. Agreement between the calculated and the observed constants was fair for all molecules considered except CHCl$_3$ and CCl$_3$F.

From a Taylor's expansion of the energy, expressed as a function of $J$ and $K$, it is clear that all molecules should have constant distortion coefficients, particularly if additional terms are included as in Equation 28. An attempt was made to fit the reported CCl$_3$F data using distortion constants through second order; however, the data were found to be inconsistent.

All molecules considered in this investigation, except CHCl$_3$ and CCl$_3$F, obey existing distortion theory and show fair agreement with infrared data. The two exceptional molecules, CHCl$_3$ and CCl$_3$F, should be studied further; and, in particular, the theory of quadrupole interaction involving three identical nuclei with spin $3/2$ should be re-examined.

The dipole moment of $^{12}$Cl$^{35}$F$_3$ was evaluated by measuring and analyzing the Stark effect for the $J = 1 \rightarrow 2$ transition; the result was

$$\mu = 0.50 \pm 0.01 \text{ debye}.$$
By measuring the separation between the pair of strong Stark lines at various electric field intensities, the results were made independent of the quadrupole coupling constant, second-order Stark effects, and molecular polarization. Most of the estimated error in the evaluation of the dipole moment is the result of an uncertainty of the electrode spacing in the Stark cell. A more accurate calibration of the electrode spacing would enable a more significant evaluation of the dipole moment.

In the present work, an electronic digital computer was utilized to calculate the theoretical distortion constants and to diagonalize matrices in the study of the Stark effect in CClF$_3$. Many of the standard calculations in microwave spectroscopy, although simple in principle, are laborious to carry out. It is felt that several of these calculations can be handled conveniently with electronic computer routines. For example, the theoretical absorption frequencies for symmetric-top molecules can be calculated from the constants $B$, $e$,$\tilde{\alpha}$, $D_{JJ}$, and $D_{JK}$ or the constants can be evaluated from the measured absorption frequencies. Utilizing computer routines can free the experimenter from many of the time-consuming calculations.
APPENDIX A

DISTORTION COEFFICIENTS

Centrifugal stretching of symmetric tops is somewhat complicated because it involves both angular momentum quantum numbers J and K. The problem can be handled quite simply, however, if the following three assumptions are made.

(1) Assume that each energy level (neglecting quadrupole interactions) for a nonrigid rotor is determined by the quantum numbers J and K. The total energy is the sum of the kinetic energy of rotation of the distorted molecule and the potential energy stored in the stretched bonds; however, each of these are functions of J and K. Hence, the total energy for each level is determined by J and K.

(2) Assume that the amount of centrifugal distortion of the molecule does not depend on the sign of the angular rotation (e.g., whether it is clockwise or counterclockwise). Then, the energy levels must be functions of only even powers of the momentum, such as the square of the total angular momentum $J(J+1)\hbar^2$ or the square of the component of momentum along the symmetry axis $K^2\hbar^2$.

(3) Assume that the total energy function $W'[J(J+1),K^2]$, where $W' = W/\hbar$ is the energy expressed in units of frequency, is analytic at the origin ($J = 0$ and $K = 0$) and that quantum mechanics specifies the allowed values of J and K.

In order to simplify the notation, make the following associations:
\[ x \to J(J+1) \]
\[ y \to K^2 \]

Then, use Taylor's theorem to make an expansion about the origin (i.e., \( J = 0, K = 0 \)). The result is

\[ W'(x,y) = W'_0 + W'_x x + W'_y y \]
\[ + \frac{1}{2} W'_{xx} x^2 + W'_{xy} xy + \frac{1}{2} W'_{yy} y^2 \]
\[ + \frac{1}{6} W'_{xxx} x^3 + \frac{1}{2} W'_{xxy} x^2 y + \frac{1}{2} W'_{xyy} xy^2 + \frac{1}{6} W'_{yyy} y^3 + \ldots \]

where, for example, \( W'_x = (\partial W' / \partial x) \) evaluated at \( x = 0 \) and \( y = 0 \).

The constant term \( W'_0 \) may arbitrarily be set equal to zero. Identify the various derivatives in the following manner:

\[
\begin{align*}
W'_x & \to B \\
W'_y & \to A - B \\
W'_{xx} & \to -2JJ \\
W'_{xy} & \to -JK \\
W'_{yy} & \to -KK \\
W'_{xxx} & \to -6JJJ \\
W'_{xxy} & \to -2JJK \\
W'_{xyy} & \to -2JKK \\
W'_{yyy} & \to -6KKK, \text{ etc.}
\end{align*}
\]

Then, the energy of the level, specified by the quantum numbers \( J \) and \( K \), can be expressed as
\[ W' = \frac{W}{\hbar} = J(J+1)B + K^2(A-B) \]
\[ - J^2(J+1)^2D_{JJ}^2 - J(J+1)K^2D_{JK}^2 - K^4D_{KK}^4 \]
\[ - J^3(J+1)^3D_{JJJ}^3 - J^2(J+1)K^2D_{JJK}^2 - J(J+1)K^4D_{JKK}^4 \]
\[ - K^6D_{KKK}^6 + \ldots \]

In the expansion of the energy function \( W' \), A and B are first-order coefficients; \( D_{JJ}, D_{JK} \), and \( D_{KK} \) are second-order coefficients; \( D_{JJJ}, D_{JJK}, D_{JJK}, \) and \( D_{KKK} \) are third-order coefficients; etc. In the field of microwave spectroscopy, A and B are defined as rotational constants; \( D_{JJ}, D_{JK}, \) and \( D_{KK} \) are defined as distortion constants; and other D's are referred to as higher-order distortion constants. In order to be more specific when referencing distortion constants, the following definitions have been used here: A and B are rotational constants; \( D_{JJ}, D_{JK} \), and \( D_{KK} \) are first-order distortion constants; \( D_{JJJ}, D_{JJK}, D_{JJK}, \) and \( D_{KKK} \) are second-order distortion constants; etc. Defining the order of the distortion constants in this manner seems to be the most satisfactory method, even though the order of the distortion constant does not correspond to the order of the coefficient in the expansion, Equation 52.

The energy of the level specified by \( J+1 \) and \( K \) can be expressed in a manner similar to Equation 52. Then, the frequency for the transition \( J \rightarrow J+1 \) and \( \Delta K = 0 \) can be expressed as

\[ \nu = 2(J+1)B - 4(J+1)^3D_{JJJ} - 2(J+1)K^2D_{JKK} \]
\[ - 2(J+1)^3(3J^2+6J+4)D_{JJJ}^3 - 4(J+1)^3K^2D_{JJK}^2 - 2(J+1)K^4D_{JKK}^4 + \ldots \]

which is identical to that given by Costain (39). It is often more
convenient to divide both sides by $2(J+1)$ which yields

\[
\frac{v}{2(J+1)} = B - 2(J+1)^2 D_{JJ} - K^2 D_{JK} - (J+1)^2 (3J^2 + 6J + 4) D_{J\bar{J}J} - 2(J+1)^2 K^2 D_{JJ\bar{K}} - K^4 D_{J\bar{K}K} + \ldots .
\]  

(54)

It should be noted that $B$ and the $D$'s are constants by definition.

If the basic assumptions are valid, any spectrum (neglecting quadrupole interactions) can be represented by Equation 54 if enough terms are included; usually the first three terms are sufficient.
APPENDIX B

BOND ANGLES IN XYZ₃ MOLECULES

Consider an XYZ₃ molecule as illustrated in Figure 25. Using elementary trigonometric formulae for triangles, the following are obtained:

\[
\cos \alpha = \frac{2d^2 - 3a^2}{2a^2} \tag{55}
\]

\[
\cos \beta = \frac{-b}{d} \tag{56}
\]

\[
\cos \gamma = \frac{b}{d} \tag{57}
\]

Since \(a^2 = d^2 - b^2\),

\[
\cos \alpha = \frac{3b^2 - d^2}{2d^2} \tag{58}
\]

From Equations 57 and 58, the angles \(\alpha\) and \(\gamma\) are related as follows:

\[
\cos \alpha = 3 \cos^2 \gamma - 1 \tag{59}
\]

\[
\cos \gamma = \sqrt{2 \cos \alpha + 1} \tag{60}
\]
Figure 25. Bond Angles in an $XYZ_3$ Molecule.
APPENDIX C

MOMENTS OF INERTIA IN XYZ_3 MOLECULES

Consider an XYZ_3 molecule with fixed bond lengths and a configuration as illustrated in Figure 26. The moments of inertia can be expressed as a function of the angle \( \gamma \).

The location of the center of mass is

\[
\ell = \frac{3m_z b - m_X d}{M},
\]  

(61)

where \( M = m_X + m_Y + 3m_Z \). The moment of inertia about the \( y \)-axis is

\[
I_{yy} = m_X (D + \ell)^2 + m_Y \ell^2 + 3m_Z (b - \ell)^2 + \frac{3}{2} m_Z a^2 .
\]

(62)

From Equations 61 and 62 and the relations \( a = d \sin \gamma \) and \( b = d \cos \gamma \),

\( I_{yy} \) can be expressed as a function of \( \gamma \); the result is

\[
I_{yy} = \left( m_X D^2 + \frac{3}{2} m_Z a^2 - \frac{m_X D^2}{M} \right) + \left( \frac{6m_Z m_X a}{M} \right) \cos \gamma
\]

\[
+ \left( \frac{3}{2} m_Z a^2 - \frac{9m_Z^2 a^2}{M} \right) \cos^2 \gamma .
\]

(63)

The moment of inertia about the \( z \)-axis is

\[
I_{zz} = 3m_Z a^2
\]

(64)

or

\[
I_{zz} = 3m_Z a^2 \sin^2 \gamma .
\]  

(65)
Figure 26. Structural Parameters of an $XYZ_3$ Molecule.
The derivatives of the moments of inertia with respect to \( \gamma \) are

\[
\frac{dI_{yy}}{d\gamma} = 6m_z d \left( l - \frac{b}{2} \right) \sin \gamma \tag{66}
\]

and

\[
\frac{dI_{zz}}{d\gamma} = 6m_z d^2 \sin \gamma \cos \gamma \tag{67}
\]

From Equation 67, it is seen that \( I_{zz} \) increases with \( \gamma \) as expected. From Equation 66, however, it is seen that \( I_{yy} \) increases with \( \gamma \) if \( l \) is greater than \( b/2 \); but it decreases with an increase of \( \gamma \) if \( l \) is less than \( b/2 \). Centrifugal forces due to rotation about any given axis will always tend to increase the moment of inertia about that axis. Therefore, rotation about an axis perpendicular to the molecular symmetry axis will tend to increase the angle \( \gamma \) if the center of mass is in the lower half \((l > b/2)\) of the \( YZ_3 \) tetrahedron, and it will tend to decrease the angle \( \gamma \) if the center of mass is above the mid-point \((l < b/2)\) of the \( YZ_3 \) tetrahedron.
APPENDIX D

HYBRIDIZATION WITH QUADRICovalent Atoms

Stable bonds are formed only with the use of stable atomic orbitals—the 1s orbital for hydrogen, the 2s and 2p orbitals for the first-row atoms, and so on. The various stable orbitals of an atom which can be used for bond formation do not differ much in their radial dependence; however, they may show a great difference in their angular distribution. For tetrahedral bond orbitals, the angular parts of the wave functions are

\[ s = 1 \]
\[ p_x = 3 \sin\theta \cos\phi \]
\[ p_y = 3 \sin\theta \sin\phi \]
\[ p_z = 3 \cos\theta \]

where \( \theta \) and \( \phi \) are the angles in spherical polar angles. These functions are normalized to \( 4\pi \): the integral of the square of the function taken over the surface of the unit sphere has the value \( 4\pi \).

Treating the electronic wave functions as vectors, the hybrid bond functions can be written as

\[ \phi_1 = d_{1s} + cp_z \]
\[ \phi_2 = d_{2s} + ap_x - bp_z \]
\[ \phi_3 = d_{2s} - \frac{a}{2} p_x + \frac{\sqrt{3}}{2} ap_y - bp_z \]
\[ \phi_4 = d_{2s} - \frac{a}{2} p_x - \frac{\sqrt{3}}{2} ap_y - bp_z \]
where $a$, $b$, $c$, $d_1$, and $d_2$ are arbitrary constants. Requiring the wave functions to be orthonormal and evaluating the coefficients results in

$$
\psi_1 = \frac{\sqrt{2}}{\tan \gamma} s + \sqrt{1 - \frac{2}{\tan^2 \gamma}} p_z \quad (70)
$$

$$
\psi_2 = \sqrt{\frac{1}{3} - \frac{2}{3 \tan^2 \gamma}} s + \sqrt{\frac{2}{3}} p_x - \frac{\sqrt{2/3}}{\tan \gamma} p_z
$$

$$
\psi_3 = \sqrt{\frac{1}{3} - \frac{2}{3 \tan^2 \gamma}} s - \frac{1}{2} \sqrt{\frac{2}{3}} p_x + \frac{\sqrt{2}}{2} p_y - \frac{\sqrt{2/3}}{\tan \gamma} p_z
$$

$$
\psi_4 = \sqrt{\frac{1}{3} - \frac{2}{3 \tan^2 \gamma}} s - \frac{1}{2} \sqrt{\frac{2}{3}} p_x - \frac{\sqrt{2}}{2} p_y - \frac{\sqrt{2/3}}{\tan \gamma} p_z
$$

From Appendix B,

$$
\cos \gamma = \frac{1 + 2 \cos \alpha}{3}
$$

or

$$
\tan^2 \gamma = \frac{2 - 2 \cos \alpha}{1 + 2 \cos \alpha} \quad (71)
$$

Therefore, the percentage of hybridization in the Y-Z bonds is

$$
\frac{1}{3} \left( 1 - \frac{1 + 2 \cos \alpha}{1 - \cos \alpha} \right) 100\% \quad (72)
$$

as illustrated in Figure 27. Hybridization for tetrahedral bond angles is 25 per cent; if the YZ$_3$ atoms form a planar structure, the hybridization is 33 per cent.
Figure 27. Hybridization in $XYZ_3$ Molecules
APPENDIX E

TABLES FOR CALCULATION OF
ROTATIONAL DISTORTION CONSTANTS
Table 7. The $\mathbf{J}_{\alpha\beta}^{(1)}$ for an Axially Symmetric XYZ$_3$ Molecule.$^a,^b$

<table>
<thead>
<tr>
<th>( R_1 )</th>
<th>( \mathbf{J}_{xx}^{(1)} )</th>
<th>( \mathbf{J}_{zz}^{(1)} )</th>
<th>( \mathbf{J}_{xz}^{(1)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2 m_1 (D + l) )</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( \sqrt{3} m_3 (d (1 + l^2) + 2 l c) )</td>
<td>( 2 \sqrt{3} m_3 d s^2 )</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( \sqrt{6} m_3 d s k (\frac{d c}{2} + l) )</td>
<td>( -\sqrt{6} m_3 d^2 s k )</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( \frac{-\sqrt{6}}{2} m_3 d s^2 )</td>
<td>0</td>
<td>( -\sqrt{6} m_3 s (d c + l \mathbf{I}_{yy}^x) )</td>
<td></td>
</tr>
<tr>
<td>( \mathbf{R}_{ca} )</td>
<td>0</td>
<td>0</td>
<td>( \frac{1}{3} m_3 (D + l) 2 \mathbf{I}_{yy}^x )</td>
</tr>
<tr>
<td>( \mathbf{R}_{3a} )</td>
<td>( \frac{\sqrt{2}}{2} m_3 d^2 s^2 )</td>
<td>0</td>
<td>( -\sqrt{2} m_3 d s (d c + l) \mathbf{I}_{yy}^x )</td>
</tr>
</tbody>
</table>

\( R_{1b}, R_{2b}, R_{3b} \) | 0 | 0 | 0 |

$^a$ From References 5 and 6. Some of the symbols have been changed for this presentation.

$^b$ The symbols are defined as follows: \( c = \cos \beta; s = \sin \beta; \beta = X-Y-Z \) angle; \( m_1 \) = mass of \( X \) atom; \( m_3 \) = mass of \( Z \) atom; \( D = X-Y \) bond distance; \( d = Y-Z \) bond distance; \( \Gamma = \sec \delta \), where \( \delta \) is the angle between the \( X-Y \) bond and the normal to the \( Z-Y-Z \) plane; \( \delta = \frac{\pi}{2} - \arctan \left( \frac{\sin \beta}{2 \cos \beta} \right) \); \( l = M^{-1} (m_1 D + 3 m_3 d \cos \beta) \); \( M = \Sigma_1 m_i; \mathbf{I}_{yy}^x = \mathbf{I} \mathbf{I}_{yy}^{-1} \), where \( \mathbf{I}_x = \Sigma_1 m_i x_i^2 \); and \( k = -\frac{\cos \alpha/2}{\sqrt{3} \cos \beta} \), where \( \alpha = Z-Y-Z \) angle.
Table 8. Force Constant Symbols for XZ$_3$ Molecules.$^a$

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_x$</td>
<td>C-X stretching</td>
</tr>
<tr>
<td>$f_z$</td>
<td>C-Z stretching</td>
</tr>
<tr>
<td>$f_{zz}$</td>
<td>Z-C-Z bending</td>
</tr>
<tr>
<td>$f_{xz}$</td>
<td>X-C-Z bending</td>
</tr>
<tr>
<td>$f_{x}^z$</td>
<td>C-X, C-Z interaction</td>
</tr>
<tr>
<td>$f_{x}^{zz}$</td>
<td>C-X, Z-C-Z interaction</td>
</tr>
<tr>
<td>$f_{x}^{xx}$</td>
<td>C-X, X-C-Z interaction</td>
</tr>
<tr>
<td>$f_{z}^z$</td>
<td>C-Z interaction between different bonds</td>
</tr>
<tr>
<td>$f_{z}^{zz}$</td>
<td>C-Z, Z-C-Z interaction with C-Z forming one side of angle</td>
</tr>
<tr>
<td>$f_{z}^{zz'}$, $f_{z}^{zz''}$</td>
<td>C-Z, Z-C-Z interaction with C-Z different from bonds forming angle</td>
</tr>
<tr>
<td>$f_{z}^{xz}$</td>
<td>C-Z, X-C-Z interaction with C-Z forming one side of angle</td>
</tr>
<tr>
<td>$f_{z}^{xx'}$</td>
<td>C-Z, X-C-Z interaction with C-Z different from bonds forming angle</td>
</tr>
<tr>
<td>$f_{zz}$</td>
<td>X-C-Z, Z-C-Z interaction with C-Z bond common to both angles</td>
</tr>
<tr>
<td>$f_{zz'}$</td>
<td>X-C-Z, Z-C-Z interaction with no bond common to both angles</td>
</tr>
<tr>
<td>$f_{zz''}$</td>
<td>Z-C-Z interaction</td>
</tr>
<tr>
<td>$f_{xz}$</td>
<td>X-C-Z interaction</td>
</tr>
</tbody>
</table>

$^a$ The xz symbolism is more recent; it was introduced in Reference 40. All force constants in the Ddαβ symbolism are in units of md/A; to convert numerically to the more modern xz symbolism, bond stretching and bond interactions go directly, multiply bond angle interactions by d, and multiply angle bending and angle interactions by d$^c$, where d is the equilibrium length of the C-Z bond.
### Table 9. The f Matrix.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>( \Delta x )</th>
<th>( \Delta z_1 )</th>
<th>( \Delta z_2 )</th>
<th>( \Delta z_3 )</th>
<th>( \Delta x z_1 )</th>
<th>( \Delta x z_2 )</th>
<th>( \Delta x z_3 )</th>
<th>( \Delta z z_{12} )</th>
<th>( \Delta z z_{23} )</th>
<th>( \Delta z z_{31} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta x )</td>
<td>( f_x )</td>
<td>( f_x )</td>
<td>( f_x )</td>
<td>( f_x )</td>
<td>( f_x )</td>
<td>( f_x )</td>
<td>( f_x )</td>
<td>( f_x )</td>
<td>( f_x )</td>
<td>( f_x )</td>
</tr>
<tr>
<td>( \Delta z_1 )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
</tr>
<tr>
<td>( \Delta z_2 )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
</tr>
<tr>
<td>( \Delta z_3 )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
<td>( f_z )</td>
</tr>
<tr>
<td>( \Delta x z_1 )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
</tr>
<tr>
<td>( \Delta x z_2 )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
</tr>
<tr>
<td>( \Delta x z_3 )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
<td>( f_{xz} )</td>
</tr>
<tr>
<td>( \Delta z z_{12} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
</tr>
<tr>
<td>( \Delta z z_{23} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
</tr>
<tr>
<td>( \Delta z z_{31} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
<td>( f_{zz} )</td>
</tr>
</tbody>
</table>

\(^{a}\) The matrix is symmetric.
Table 10. The $U$ and $U^*$ Matrices.

\[ U_{A1} = \begin{bmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1\sqrt{3} & 1\sqrt{3} & 1\sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1\sqrt{6} & -1\sqrt{6} & -1\sqrt{6} & 1\sqrt{6} & 1\sqrt{6} & 1\sqrt{6}
\end{bmatrix} \]

\[ U_E = \begin{bmatrix}
0 & 0 & 1\sqrt{2} & -1\sqrt{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1\sqrt{2} & -1\sqrt{2} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1\sqrt{2} & 0 & 1\sqrt{2}
\end{bmatrix} \]

\[ U_{A1}^* = \begin{bmatrix}
1 & 0 & 0 \\
0 & 1\sqrt{3} & 0 \\
0 & 1\sqrt{3} & 0 \\
0 & 1\sqrt{3} & 0
\end{bmatrix} \quad \text{and} \quad \begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
1\sqrt{2} & 0 & 0 \\
-1\sqrt{2} & 0 & 0
\end{bmatrix} \]

\[ U_E^* = \begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
1\sqrt{2} & 0 & 0 \\
0 & -1\sqrt{2} & 0
\end{bmatrix} \quad \text{and} \quad \begin{bmatrix}
0 & 0 & -1\sqrt{2} \\
0 & 0 & 0 \\
0 & 0 & 1\sqrt{2} \\
0 & 0 & 0
\end{bmatrix} \]
Table 11. The F Matrix.\textsuperscript{a}

For type A\textsubscript{1} vibrations:

<table>
<thead>
<tr>
<th></th>
<th>(R_1)</th>
<th>(R_2)</th>
<th>(R_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_1)</td>
<td>(f_x)</td>
<td>(\sqrt{3}f_{xz}^2)</td>
<td>(\frac{\sqrt{6}}{2}(f_{xz}^2 - f_{xz}))</td>
</tr>
<tr>
<td>(R_2)</td>
<td>(f_z + 2f_z^z)</td>
<td>(\frac{\sqrt{2}}{2}(2f_{zz}^z + f_{xz}^z - 2f_{zz}^z - f_{xz}^z))</td>
<td></td>
</tr>
<tr>
<td>(R_3)</td>
<td></td>
<td></td>
<td>(\frac{1}{2}(f_{zz} - f_{xz}^z + 2f_{xz}^z))</td>
</tr>
</tbody>
</table>

For type E vibrations: \textsuperscript{b}

<table>
<thead>
<tr>
<th></th>
<th>(R_{1a})</th>
<th>(R_{2a})</th>
<th>(R_{3a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_{1a})</td>
<td>(f_z - f_z^z)</td>
<td>(f_{xz} - f_{xz}^z)</td>
<td>(f_{zz}^z - f_{zz})</td>
</tr>
<tr>
<td>(R_{2a})</td>
<td></td>
<td>(f_{xz} - f_{xz}^z)</td>
<td>(f_{zz}^z - f_{zz})</td>
</tr>
<tr>
<td>(R_{3a})</td>
<td></td>
<td></td>
<td>(f_{zz} - f_{zz}^z)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Both submatrices are symmetric.

\textsuperscript{b} The same submatrix is obtained for \(R_{1b}\), \(R_{2b}\), and \(R_{3b}\).
BIBLIOGRAPHY


36. Townes and Schawlow, op. cit., p. 250.


38. Townes and Schawlow, op. cit., p. 251.


New Technique
for
Microwave Radiometry
NEW TECHNIQUE FOR MICROWAVE RADIOMETRY

by

M. W. Long and J. C. Butterworth

Department of the Navy
Office of Naval Research
Contract No. N0nr-991(07)

3 May 1963
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. ABSTRACT</td>
<td>1</td>
</tr>
<tr>
<td>II. INTRODUCTION</td>
<td>2</td>
</tr>
<tr>
<td>III. THEORY OF INTERFERENCE MODULATION</td>
<td>4</td>
</tr>
<tr>
<td>A. Principles of Operation</td>
<td>4</td>
</tr>
<tr>
<td>B. System Resolution and Useful Source Power Available</td>
<td>8</td>
</tr>
<tr>
<td>IV. EXPERIMENTAL RESULTS</td>
<td>11</td>
</tr>
<tr>
<td>A. Modulation Device</td>
<td>11</td>
</tr>
<tr>
<td>B. Detector Sensitivity Measurements</td>
<td>19</td>
</tr>
<tr>
<td>C. Detectors</td>
<td>22</td>
</tr>
<tr>
<td>D. Power Measurements</td>
<td>24</td>
</tr>
<tr>
<td>E. Effects of Higher Order Waveguide Modes</td>
<td>25</td>
</tr>
<tr>
<td>V. CONCLUSIONS</td>
<td>29</td>
</tr>
<tr>
<td>VI. ACKNOWLEDGMENTS</td>
<td>30</td>
</tr>
<tr>
<td>VII. APPENDIX. MICROWAVE POWER AT DETECTOR VERSUS PATH LENGTH</td>
<td>31</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Equivalent Circuit of Interference Modulation Device</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Block Diagram of Interference Modulation Device as First Constructed</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>Trombone Version of Interference Device</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>Amplifier Output Versus Time</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>Response of System to Transmission Through High-Pass Filter</td>
<td>17</td>
</tr>
<tr>
<td>6</td>
<td>Amplifier Output Versus Time (One Second per Division)</td>
<td>21</td>
</tr>
<tr>
<td>7</td>
<td>Mode Chart for RG-98/U</td>
<td>27</td>
</tr>
</tbody>
</table>
I. ABSTRACT

An interference modulation technique for microwave radiometry is described. Use of the technique is considered for the development of a radiometer for tuning over a wide range of frequencies, a radiometric device for determining the absolute sensitivity of detectors over a wide range of frequencies, and a means for determining the power level of coherent sources as a function of frequency. A device using this technique does not require the use of a coherent source, and the technique is applicable to wavelengths well into the low millimeter region.

A tunable radiometer using interference modulation has been operated as a measurements system within the 50-90 gc region. Successful performance required the use of a sensitive detector which consisted of a barretter operated in an evacuated atmosphere. A noise source having known temperature was used as the source of microwaves for determining the sensitivity of detectors as a function of frequency. It has been found that the sensitivity of barretters is greatly improved by a reduction in air pressure and that, when evacuated, a commercially available barretter will provide a sensitivity of approximately 6 x 10^-11 watt for an audio bandwidth of 1 cps. The technique discussed provides the opportunity for developing a calibrated power meter for millimicrowatt levels from coherent sources.
II. INTRODUCTION

A continuously tunable measurements device based on an interference technique has been operated throughout the 50-90 gc region. The instrument, which does not require the use of a coherent source, is useful for making transmission measurements as a function of wavelength, and detector sensitivity measurements can be made without the use of a power meter, per se. In fact, the technique used should also serve for measuring the output power of weak coherent sources.

Determination of detector sensitivity versus frequency throughout the low millimeter region by other techniques is a formidable task because of the low power levels (harmonics) available, and the difficulty of obtaining harmonics throughout all of the lower millimeter region. Transmission measurements have not been possible with superheterodynes in much of the lower millimeter region because suitable coherent sources (and sensitive fast detectors) are unavailable. Use of direct-detection systems is limited by the need for a continuously tunable, band-pass filter for microwaves. The effect of a tunable filter is accomplished in the present system through the use of an interference technique and filtering in the audio range.

The heart of the new instrument is, in essence, a continuously tunable, electromechanical, band-pass filter. It has been operated throughout the 50-90 gc region where 4-mm components could be used, but the technique used should be useful throughout the low millimeter-wave region. Operation is based on the fact that there is a one-to-one correspondence between mechanical speed and the frequency of Doppler components. Power from a microwave source is divided between two paths by a waveguide T and is recombined with a T before reaching the detector. Doppler components are produced by varying one of the paths with a
trombone-shaped section which is moved back and forth by the drive rod at a nearly constant speed. Thus, an interference modulation frequency is produced which is uniquely related to the wavelength within the waveguide. The audio frequency modulation spectrum at the detector for a wide-band microwave source will be continuous; thus, a tuned audio amplifier (or other frequency analyzer) in conjunction with the varying path length will serve as a band-pass filter.
III. THEORY OF INTERFERENCE MODULATION

A. Principles of Operation

The fact that there is a one-to-one correspondence between mechanical speed and the frequency of Doppler components provides an interesting new concept for microwave instrumentation. Assume that the difference in path length between Paths 1 and 2 of Figure 1 is varied at a constant speed, $s$; then an interference modulation frequency, $f_a$, would be produced which is related to the wavelength within the waveguide, $\lambda_g$, by the equation

$$f_a = \frac{s}{\lambda_g} \quad (1)$$

Thus, the tuned audio amplifier in conjunction with the varying path length will serve as a microwave band-pass filter because the amplifier output will depend only on those frequency components corresponding to $\lambda_g$ of Equation 1.

In order to visualize amplifier waveform, assume that the difference in lengths of Paths 1 and 2 is varied at a nearly constant rate by alternately lengthening and shortening one of the paths. With this arrangement the Doppler frequencies will be unchanged except during the short time required for reversing the motion. It is shown in the appendix that detector power from a noise source depends on the difference in lengths of Paths 1 and 2 and that the maximum power occurs when the paths are of equal length. When operated at low-power levels (square-law region), detector output voltage, $V_d$, is related to incident microwave power, $P_d$, by

$$V_d = RP_d \quad (2)$$
Figure 1. Equivalent Circuit of Interference Modulation Device.
For a given detector the responsivity, \( R \), is approximated by a constant. Thus, the voltage waveform out of a tuned amplifier following the detector will contain pulses occurring periodically, and these pulses will have a maximum each time the path length difference is zero.

For the special case of the narrow microwave pass band \( B \) considered in the appendix, amplifier output would be independent of audio bandwidth provided that all Doppler frequencies are within the amplifier pass band. Conversely, the output of a tuned amplifier is independent of microwave bandwidth if the audio amplifier pass band is contained within the complete Doppler spectrum. Assume that (1) the frequency limits of the amplifier pass band correspond exactly to the two Doppler frequencies for the edges of the microwave band \((F - B/2, F + B/2)\), and (2) that the detector responsivity, \( R \), is constant over the frequency interval \( B \). Under these conditions, and for the realistic condition of a microwave source spectrum wider than \( B \), Equations 2 and 17 can be used to express amplifier waveform for the hypothetical case of a constant change in the path length difference. Thus, if time zero is defined so that it exists each time the path difference is zero, the voltage out of the tuned amplifier with center frequency \( f_a \) and unity gain may be expressed as

\[
v = \frac{1}{2} RkTB \left[ \frac{\omega_t}{F} \right] \frac{\sin \left[ \frac{\omega_a t}{B} \right]}{\cos \frac{\omega_a t}{B}} \cos \omega_a t = g(t) \cos \omega_a t \quad . \tag{3}
\]

The radian frequency of the output wave is \( \omega_a \), and it is equal to the center
frequency of the tuned amplifier. Notice that the argument of the sine term of Equation 3 differs from that of the cosine term by the fraction B/2F. The ratio B/F is the system resolution factor, and it might typically be of the order of 0.1 or less. Thus, the effect of g(t) is to slowly modulate the envelope of the cosine output wave.

In practice, the difference in lengths of Paths 1 and 2 is changed at a nearly constant rate by alternately lengthening and shortening one of the paths. The path length change is such that equal path lengths occur approximately midway between the path length extremes. In this arrangement pulses described by g(t) occur periodically and reach a maximum each time the difference between path lengths is zero. The pulses described by g(t) exist throughout the sweep period, but with reduced amplitude. Thus, if Equation 3 is to be valid, the sweep period must be sufficiently long that effects of sweep-to-sweep interference are negligible. Near each envelope peak where values of t are sufficiently small (by definition) that

\[
\sin \left( \left( \frac{\omega t}{a \frac{B}{F}} \right) \frac{B}{2} \right) \text{can be approximated by} \left( \frac{\omega t}{a \frac{B}{F}} \right) \frac{B}{2},
\]

amplifier output voltage may be expressed as

\[
v = R \frac{1}{2} kT B \cos \omega t.
\]

Notice that Equation 4 indicates that the magnitude of the peaks in amplifier waveform will be directly proportional to the power (kT) contained in the microwave band B; recall that for a wide-band noise source, B is determined by the bandwidth of the tuned audio amplifier. Also recall that the
center of the band to which the system responds is determined by the rate of change in path length and/or amplifier center frequency. Thus, the band of microwaves to which the system is tuned can be controlled solely by the characteristics of the audio amplifier.

Since the magnitude of the peaks in the amplifier output caused by a coherent source will also be proportional to source power, comparison of peak output with that caused by a calibrated noise source provides a convenient method for determining the power level of a weak coherent source. In principle, power measuring devices can be calibrated as a function of frequency with a modulated noise source and a tunable microwave band-pass filter. Such measurements are not currently possible in the low millimeter region because band-pass filters with variable, but known, center frequency and effective bandwidth are not available.

B. System Resolution and Useful Source Power Available

As stated above, the magnitude of the peaks in the amplifier waveform is directly proportional to the power contained in a microwave band of width \( B \) which is determined by the bandwidth of the tuned audio amplifier. Let \( f_1 \) and \( f_2 \) be the lower and upper frequency limits of the audio pass band, respectively. Then the lower and upper microwave frequency limits to which the amplifier responds, \( F_1 \) and \( F_2 \), may be expressed as

\[
\left[ F_2 \left( \frac{\lambda_2}{\lambda g_2} \right) - F_1 \left( \frac{\lambda_1}{\lambda g_1} \right) \right] \frac{c}{g} = f_2 - f_1
\]

where
\( \lambda_1 \) and \( \lambda_2 \) are free space wavelengths for the frequencies \( F_1 \) and \( F_2 \),

\( \lambda g_1 \) and \( \lambda g_2 \) are guide wavelengths for the frequencies \( F_1 \) and \( F_2 \),

\( s \) is the rate of change in path length, and

\( c \) is the free space propagation velocity.

Let \( F \) represent the center of the microwave spectrum, for which the Doppler frequency equals amplifier center frequency \( f_a \), and let \( B \) and \( B_a \) represent the microwave and audio bandwidths, respectively. Since the pass bands of interest are narrow, it is reasonable to assume that \( \lambda_1 / \lambda g_1 \) equals \( \lambda_2 / \lambda g_2 \).

With this assumption, it is seen that the relation

\[
\frac{B}{F} = \frac{B_a}{f_a}
\]  

(5)

is a good approximation for narrow pass bands. In other words, the percentage microwave bandwidth resolved by the system is equal to the percentage audio bandwidth.

For a constant rate of change of path length and a coherent source, detector power (see Equation 16) modulated so that it passes an amplifier tuned to the Doppler frequency, \( \omega_a \), may be expressed \( (P_s/2) \cos \omega_a t \). \( P_s \) is the power level of the unmodulated coherent source. From Equation 4 it may be seen that detector power from an incoherent source during the interval of maximum output is \( (kT B/2) \cos \omega_a t \). Noise power from a matched microwave load can be determined from the approximation\(^1\)

\(^1\)This approximation is usually valid for the millimeter region; it causes only a small error in calculations for the submillimeter region providing low temperatures are not involved, and it is not usually valid for infrared. For example, see C. R. Nicoll, "The Measurement of Thermal and Similar Radiations at Millimetre Wavelengths," Proceedings of the IEE 104, 519-527 (September 1957).
\[ P = kTB, \] (6)

where \( k \) is Boltzmann's constant \((1.38 \times 10^{-23} \text{ joule per degree Kelvin})\), \( T \) is the temperature of the load in degrees Kelvin, and \( P \) is the power in watts available in the bandwidth \( B \) in cycles per second. Thus, equivalent source power for the case of an incoherent source is equal to the total noise power, \( kTB \), contained within the resolution of the system.

This paper describes a system which uses an audio amplifier having a center frequency of 28.5 cps and a bandwidth of 4 cps. Assume that the change in path length and audio amplifier center frequency is such that the system responds to a band centered at 70 gc; then from Equation 5 we find that the system responds to a microwave band \( B \) as follows:

\[ B = \frac{B_a}{F_a} F = 9.8 \text{ gc}. \]

Under these conditions and with the noise source employed \((14,500^\circ K)\), the equivalent power, \( kTB \), is \( 2 \times 10^{-9} \) watt. In comparison with power levels for coherent sources, the equivalent power is small but useful if a sensitive detection system is employed.
IV. EXPERIMENTAL RESULTS

A. Modulation Device

Figure 2 illustrates the microwave circuit of the modulation device as first constructed and operated. The moving short circuit was driven back and forth in a waveguide at a nearly constant speed except for a short reversal time. The period of the mechanical motion was 2 seconds, i.e. pulses occurred at the rate of one per second. With this drive mechanism, tuning to a desired microwave frequency of observation was accomplished by adjusting the length of the travel of the short without changing the period. Length of travel was continuously adjustable over the range of 1/2 inch to 6 inches; the corresponding velocities with the short circuit mounted in RG-98/U waveguide provide 30-cycle Doppler modulation for wavelengths as long as 6 mm and extending throughout the lower millimeter region. Thus, a noise source, a 30-cycle amplifier, a waveguide system similar to that illustrated in Figure 2, in conjunction with appropriate detectors and noise sources could, in principle, be used to make measurements over all of the lower millimeter region.

The system as outlined above was operated with a commercially available 4-mm noise source\(^2\) and a PRD-634 barretter mounted in an evacuated PRD-632 holder. System performance was poor outside the design region of the hybrid ring, and a somewhat wider bandwidth was later obtained by replacing the hybrid ring with a magic T.

\(^2\)Noise Source Model GNW-V18, for which the noise temperature was given as $14,500^\circ K \pm 1800^\circ K$ in private communications with R. White, Roger White Electron Devices, Inc.
Figure 2. Block Diagram of Interference Modulation Device as First Constructed.
Figure 3 shows a new system which has been operated over the 50-90 gc region with the 4-mm noise source and evacuated barretter. A trombone type device provides the variable path length required for the circuit illustrated in Figure 1. Power is divided by waveguide T's, and path length is changed with a sliding trombone made of circular waveguide.

The power dividers are E-plane T's in which the output branches near the junction are half the height of the input branch. The output branches are gradually tapered up to the size of RG-98/U guide. The movable section of the trombone is constructed of round tubing with an inside dimension of 0.189 inch. Tubing was used because of the availability of slide fit telescoping brass tubing and the relative ease of fabricating a bend. Operation of the system could be limited by the presence of higher order modes that might be generated within the bend. For this reason, a rectangular trombone was constructed. The movable section was fabricated of RG-98/U waveguide and it slides over rectangular waveguide fabricated of 0.003-inch brass stock. No discernible differences were observed between the system performance obtained with the circular and rectangular trombone sections.

Figure 4 is a recording of output voltage versus time of the audio amplifier which had a center frequency of 28.5 cps and a 4 cps bandwidth. The trombone modulator, the Roger White noise source, and an evacuated barretter were used to obtain Figure 4. The waves under the envelopes with large peaks occurring at 1-second intervals are produced by the interference phenomenon; the waves under the smaller (and unevenly spaced) envelopes are produced by amplifier and detector noise that passes the tuned amplifier. As expected, a change in temperature of the noise source changes the average level of the periodically
Figure 3. Trombone Version of Interference Device.
Figure 4. Amplifier Output Versus Time.
occurring envelopes but does not modify the average for the envelopes produced by amplifier and detector noise. Equation 3 describes the waves produced by the interference phenomenon; by definition, 1 equals zero in Equation 3 each time a large peak is produced by constructive interference.

System resolution can be determined from Figure 4 without explicit knowledge of amplifier bandwidth or center frequency. There are about 14 cycles under the major envelopes of Figure 4; thus, Equation 3 indicates that 2F/B is 14, or that the ratio of center microwave frequency to microwave bandwidth is approximately 7. Parenthetically, note that the indication of an average value meter depends only on envelope peak amplitude because envelope width is controlled only by audio amplifier bandwidth. Since 2F/B is equal to 2f_a/B_a (Equation 5), it can be seen that envelope width is 2/B_a seconds.

Figure 5 includes data measured with the trombone system, the Roger White noise source, the evacuated barreter, and the audio amplifier described above. The output of the amplifier was observed on a meter whose deflection is proportional to the average value of audio amplifier output voltage. Since the pulse lengths are independent of microwave frequency, average voltage output depends on microwave power contained in the bandwidth corresponding to the system resolution, 14 per cent for the operating conditions described above. Care should be taken in interpreting Figure 5 because (1) output voltage is proportional to input microwave power (for example, a change of 10 dB in amplifier output corresponds to a change of 5 dB in r-f input), and (2) a constant percentage system resolution means that resolution expressed in gigacycles (and thus available noise power) is directly proportional to center microwave operating frequency.
Figure 5. Response of System to Transmission Through High-Pass Filter.
The solid curve of Figure 5 indicates signal-to-noise ratio at the amplifier output versus frequency with a PRD-634 barretter mounted in a fixed tuned, evacuated holder (PRD-632). This curve provides data required to determine relative detector sensitivity versus frequency. Similar detector measurements have also been made with a tunable holder developed at Georgia Tech. If tuned for maximum response at each frequency, sensitivities can be made comparable to that at 55 gc (Figure 5) for frequencies up to approximately 75 gc. This type of measurement would be difficult to accomplish by conventional techniques.

The dashed curve of Figure 5 was measured by inserting a waveguide designed for cut-off at 60 gc in the setup used to obtain the solid curve; thus, transmission loss introduced by the waveguide can be determined by taking the difference between the two curves. Because the detector operates in the square-law region, waveguide insertion loss expressed in decibels is one-half the difference between the two curves. Within a first approximation, the waveguide cut-off frequency is that frequency for which the difference in the two curves is 6 db, and system resolution is two times the difference between the 6-db frequency and the frequency for which insertion loss is essentially zero. System resolution obtained in this manner indicates a bandwidth of about 9 gc, which is in approximate agreement with that predicted Equation 5.

---

3 For example, minimum detectable temperature at 50 gc is 6 db smaller than at 75 gc. Thus, since percentage resolution is constant, minimum detectable power at 50 gc is approximately 8 db smaller than at 75 gc.

4 A 1-inch length of 0.099 by 0.074 inch guide was used to obtain a high-pass filter with a cut-off at 60 gc. One-inch linear H-plane tapers are used as transitions to RG-98/U dimensions.
In conclusion, the experimental system shown in Figure 3 was constructed in accordance with the diagram of Figure 1. Figure 5 illustrates average amplifier output obtained with the system as a function of trombone speed -- alternatively, average output voltage as a function of center frequency for a fixed percentage bandwidth. The solid curve contains data on detector sensitivity versus frequency; the dashed curve was obtained with a high-pass waveguide filter inserted at the output of the noise tube. Thus, the difference between the solid and dashed curves provides a direct measurement of microwave resolution without the use of a coherent source. Percentage microwave resolution determined by this method agrees with the resolution calculated from Figure 4 (same as percentage bandwidth of the audio amplifier).

B. Detector Sensitivity Measurements

The interference device provides a convenient instrument for measuring the absolute sensitivity of detectors operating in the square-law region. This has previously been a formidable task because sensitive power standards and coherent sources to cover a wide spectrum are expensive and sometimes difficult to obtain.

In certain cases, detector sensitivity may be too poor to measure by the direct method that will be described below. In that case, it is possible to measure the output power level from a harmonic generator with the interference device and determine sensitivity by usual techniques. This in itself provides some extension in the state of the art because the interference device will serve as a highly sensitive power meter.

For this paper, minimum detectable change in power, $\Delta P_{\text{min}}$, is defined as that change in signal power for which the rms value of signal voltage out
of the tuned amplifier is equal to the rms value of output noise. From Equation 4, the rms voltage out of a unity gain amplifier near a peak in envelope from the interference modulation device is \((R/2\sqrt{2})kT\). For the purpose of using the interference device to determine detector sensitivity applicable to other systems, let \(S/N\) represent the ratio of rms value of signal voltage to rms value of noise voltage, \(V_N\). Then we have

\[
\frac{R}{2\sqrt{2}} kT = \left(\frac{S}{N}\right) V_N .
\]  

(7)

Calculations for \(\Delta P_{\text{min}}\) made below will be applicable to square-wave modulation, whether it be random noise square-wave modulated at the rate \(f_a\), or coherent power that is square-wave modulated at the rate \(f_a\). The rms voltage out of a unity gain amplifier tuned to the fundamental frequency is \((\sqrt{2}/\pi) v_{\text{peak}} = (\sqrt{2}/\pi) R A P\), where \(v_{\text{peak}}\) is the magnitude of the square voltage pulse out of the detector. \(\Delta P_{\text{min}}\) for square-wave modulation can be expressed in terms of rms noise voltage as

\[
\frac{\sqrt{2}}{\pi} R A P_{\text{min}} = V_N .
\]  

(8)

Substituting the value of \(V_N\) from Equation 7 into Equation 8 gives

\[
\Delta P_{\text{min}} = \frac{\pi}{4} kT \left(\frac{N}{S}\right) .
\]  

(9)

Figure 6 shows a recording of system output consisting of several sweeps of the type shown in Figure 4. Parameters pertinent to the system sensitivity are as follows:

20
Figure 6. Amplifier Output Versus Time (One Second per Division).
\[ T = 14,500^\circ K \quad f_a = 28.5 \text{ cps} \]
\[ F = 55 \text{ gc} \quad B_a = 4 \text{ cps}. \]

From Equations 5 and 6, we find that \( B \) is 7.7 gc and \( kTB \) is \( 1.5 \times 10^{-9} \) watt.

Measurements of the positive peaks of Figure 6 indicate an average height of 3.1 divisions with an rms fluctuation of 0.37 division. The rms signal corresponding to an average height of 3.1 divisions is 2.2 divisions. Thus \( S/N \) is 5.9. Then from Equation 9,
\[
\Delta P_{\text{min}} = \frac{\pi}{4} \cdot 1.5 \times 10^{-9} \left( \frac{\frac{1}{5.9}}{\frac{1}{5.9}} \right) = 2 \times 10^{-10} \text{ W}
\]

For a detector operating in the square-law region, minimum detectable power, \( \Delta P_{\text{min}} \), varies as
\[
\Delta P_{\text{min}} = K \sqrt{B_a}
\]

where \( K \) is the minimum detectable change in power referred to a 1-cps audio bandwidth, and \( B_a \) is the audio bandwidth. Since the audio bandwidth used is 4 cps, minimum detectable change in power referred to a 1-cps audio bandwidth is approximately \( 10^{-10} \) watt. The measurement described above includes ohmic losses in the waveguide and losses due to mismatches at the various junctions. An estimate based on limited measurements of the average loss in the waveguide over the pass band of 2-3 db gives a minimum detectable power referred to a 1-cps audio bandwidth for the evacuated barretter of \( 6 \times 10^{-11} \) watt.

C. Detectors

Evacuated PRD-632 barretters are used because they are more sensitive than individual crystal diodes (1N53, 1N2792, and MA441) available to us; in fact, crystal diodes tested are too insensitive to detect the signal from
the interference device. Sensitivity measurements were made at 70 gc with a harmonic generator. The diode units, when tuned for optimum performance, are 10-18 db (minimum detectable power) less sensitive than evacuated barretters. Furthermore, diodes and their holders are more frequency sensitive than is desirable for this application. For the comparative measurements, the barretter was mounted in a tunable holder developed at Georgia Tech.

The input circuit for the 30-cps amplifier uses a Triad model G10 transformer. For these measurements, no d-c bias was used with the diodes, and the diodes were connected so that their load impedance was that of the transformer primary. D-C bias did not improve sensitivity for the crystal diodes because 1/f noise is excessive at 30 cps.

Improvements of approximately 14 db in minimum detectable power have been obtained with PRD-634 barretters mounted in PRD-632 holders which have been evacuated to a pressure of 50 microns or less; this is a somewhat greater improvement than has been reported5 for an X-band barretter. Minimum detectable power for evacuated barretters has been as low as 6 x 10^-11 watt (Figure 6), but the barretter presently in use is about 1 db less sensitive. Results obtained with the currently used barretter and the 30-cps amplifier, which has a noise figure of about 2 db, are given below. The barretter is biased with direct current to an operating resistance of about 200 ohms; when evacuated, bias current is reduced from the nominal 4 ma to 1 ma to prevent burn-out and to maintain resistance at 200 ohms. Noise power contributed to amplifier

output by the barretter is 20 db for atmospheric pressure and is reduced to 7 db when evacuated. The above data indicate an improvement in signal-to-noise ratio of 28 db, and 15 db of this improvement results from increased responsivity caused by evacuation.

D. Power Measurements

As previously noted, the magnitude of the peaks in the amplifier waveform are directly proportional to the noise source power contained in a microwave band determined by the bandwidth of the audio amplifier. Since the magnitude of the peaks in the amplifier output caused by a coherent source is also proportional to source power, comparison of peak signal with that caused by a calibrated noise source should provide a convenient method of determining the power level of a weak coherent source. Power meters are sometimes required which are far more sensitive than the calorimetric type currently used. An example of a severe power-level problem is that of determining the power available from crystal harmonic generators.

Video detectors are more sensitive than water calorimeters, but normally they are not used for absolute power measurements because of calibration difficulties. The power-measuring technique described herein uses the sensitivity available from video detectors, and calibration is obtained by comparison with a noise source of known temperature. It is possible to specify available power from knowledge of source temperature because the interference

---

device serves as a band-pass filter for microwaves. Thus, the power level of a coherent source can be determined by comparing the relative levels of the peaks caused by the coherent source (many peaks will occur periodically within a single sweep for this mode of operation) with those caused by the noise source.

It should be possible to develop a simple, highly sensitive power meter based on interference modulation. Variability of detector characteristics could be calibrated out if a noise source were made an integral part of the instrument. However, care must be taken in accounting for reflection losses because the average loss for a band of frequencies may differ from that for a single frequency. The peaks of Figure 6 were produced by an input power of 1.5 x 10^{-9} watt. With a power level of one millimicrowatt, the "probable" error\(^7\) in the peaks due to noise would be about 1/2 db.

E. Effects of Higher Order Waveguide Modes

Thus far the analysis has been made as if the noise source radiates only the dominant mode \((TE_{01})\), and with the assumption that the radiation temperature is independent of frequency. Errors can be introduced in the system as a result of the noise source radiating higher order modes or by higher order modes being generated from the dominant mode by waveguide discontinuities. In principle, each mode generated by the source can have a radiation temperature which approaches source temperature. However, since gaseous noise sources are

---

\(^7\)For the peaks of Figure 6, the average is 3.1 units and the standard deviation (independent of microwave power) is 0.37 unit. Thus probable error, defined as 0.67 times standard deviation for a Gaussian distribution, is 0.25 unit. Since meter deflection is proportional to microwave power, a one-millimicrowatt power level would produce peaks with an average level of 2.0 units -- thus, the probable error would be about 1/2 db.
designed to maximize radiation temperature for the dominant mode, it would seem likely that the temperatures for higher modes are substantially less than that of the dominant mode. The temperatures for higher order modes generated by waveguide discontinuities are less than the temperature of the dominant mode because the higher order mode energy is obtained by conversion from the dominant mode.

Figure 7 shows guide wavelength for RG-98/U (inside dimensions of 0.148 x 0.074 inch) versus frequency for several modes. For each mode there exists a frequency for which guide wavelength is equal to guide wavelength for the dominant mode at a lower frequency; thus, there are Doppler frequencies associated with higher modes which are produced by path-length changes that are equal to those for the dominant mode. Equation 5 is invalid near cut-off because \( \lambda/\lambda_g \) changes rapidly within the bandwidth B. The rapid change in \( \lambda/\lambda_g \) near cut-off results in a smaller microwave bandwidth for a given audio bandwidth. Higher order contributions are also reduced because waveguide attenuation is large for modes near the cut-off frequency.

The condition of simultaneously having the lengths of Paths 1 and 2 in Figure 1 equal electrically for all modes is satisfied only if the paths are physically identical. For example, if the trombone (part of Path 1) is constructed of circular guide and Path 2 is made entirely of rectangular guide, peaks for higher modes will be displaced from the strong, dominant mode peak. It is conceivable that such a displacement would be useful for effecting a significant minimization of higher mode contributions. Two trombones have been used with the system described herein, one was constructed from RG-98/U and the other constructed from circular waveguide. No differences have been
Figure 7. Mode Chart for RG-98/U.
observed between the results obtained from the two trombones; thus, the contributions due to higher order modes are not prohibitive for this system.

Probably the greatest minimization of the effects of higher order modes is due to detector design. The barretter and other waveguide mounted detectors are designed for optimum performance for the $TE_{01}$ mode. It is expected that such detectors are quite insensitive to higher order modes.
V. CONCLUSIONS

An interference modulation technique for microwave radiometry is described. Operation is based on the fact that there is a one-to-one correspondence between mechanical speed and frequency of Doppler components. One of the attractive features of the technique is that it is applicable to wavelengths throughout much of the low millimeter region where coherent sources are virtually nonexistent. The complete system consists of simple microwave components, a detector, and a tuned audio amplifier.

A radiometer using interference modulation has been operated as a measurements system within the 50-90 gc region. Microwave performance of this instrument is consistent with theoretical predictions. A commercially available noise source having a known temperature was used as the source of microwaves for determining the sensitivity of detectors as a function of frequency. It has been found that the sensitivity of a commerically available barretter evacuated so that the air pressure is 50 microns or less is approximately $6 \times 10^{-11}$ watt for an audio bandwidth of 1 cps. From the detector investigation it has been learned that signal-to-noise ratio at the detector output is improved by 28 db by evacuating the barretter, and that minimum detectable power for evacuated barretters is 10-18 db smaller than for available crystal diodes.

The interference modulation technique provides the opportunity for developing a highly sensitive power meter for coherent sources. However, there are numerous details to be solved before a simple, highly sensitive power meter can be made commercially available. Present indications are that it should be possible to develop a calibrated power meter for millimicrowatt levels from coherent sources.
VI. ACKNOWLEDGMENTS

The authors express their appreciation to E. R. Flynt and W. K. Rivers, Jr., for numerous profitable discussions regarding this work. Mr. Rivers introduced the authors to the subject of interference modulation, and Mr. Flynt assisted with many instrumentation problems.

Respectfully submitted:

M. W. Long, Chief
Electronics Division
VII. APPENDIX

MICROWAVE POWER AT DETECTOR VERSUS PATH LENGTH

Assume that power from the microwave source of Figure 1 is divided equally between Paths 1 and 2, and is recombined before reaching the detector. Let the difference in lengths of Paths 1 and 2 be designated \( \delta \). Then for any single microwave frequency, power reaching the detector, \( P_d \), expressed in terms of source power, \( P_s \), is

\[
P_d = \frac{P_s}{2} \left[ 1 + \cos \frac{2\pi \delta}{\lambda_g} \right]
\]

where \( \lambda_g \) is the guide wavelength corresponding to the microwave frequency, \( f \). For an air-filled waveguide, guide wavelength and frequency are related by the well-known equation

\[
\lambda_g = \frac{c/f}{\sqrt{1 - \left(\frac{c/f}{\lambda_c}\right)^2}}
\]

where \( c \) is free space propagation velocity, and \( \lambda_c \) is guide cut-off wavelength. Notice that the detector power is equal to the total source power when the path difference is zero, and that it changes periodically with path length.

If the microwave source is a noise tube filtered so that only frequencies within a bandwidth \( B \) about the center frequency \( F \) are passed, power incident
upon the detector can then be expressed as

\[ P_d = \frac{kT}{2} \int_{F - B/2}^{F + B/2} \frac{T(f)}{F - B/2} \left[ 1 + \cos \left( \frac{2\pi \delta}{\lambda_g} \right) \right] df \quad , \quad (12) \]

where \( k \) is Boltzmann's constant and \( T(f) \) is effective noise temperature which may depend on frequency. Integration of Equation 12 is not simple because of the dependence of \( \lambda_g \) on \( f \). It may be seen, however, that for the special case in which path length \( \delta \) is zero, detector power is equal to total source power.

Guide wavelength, \( \lambda_g \), can be expressed in terms of free space propagation velocity and frequency as

\[ \lambda_g = \left( \frac{\lambda_g}{\lambda} \right) c/f \quad . \]

The factor \( \lambda_g/\lambda \) is always greater than unity in waveguide, and is less than 1.7 within the recommended bands for the various standard waveguides. Since pass bands of interest are narrow (\( B/f \) small), it is reasonable to assume that \( \lambda_g/\lambda \) and \( T(f) \) are constant over \( B \). Then Equation 12 becomes

\[ P_d = \frac{kT}{2} \int_{F - B/2}^{F + B/2} \left[ 1 + \cos \left( \frac{2\pi \delta}{c} \left( \frac{\lambda}{\lambda_g} \right) f \right) \right] df \quad . \quad (13) \]

The result of integrating Equation 13 is

\[ P_d = \frac{1}{2} kT \left[ B + \frac{c}{2\pi \delta} \left( \frac{\lambda_g}{\lambda} \right) \left[ \sin \left( \frac{2\pi \delta}{c} \left( \frac{\lambda}{\lambda_g} \right)(F + B/2) \right) - \sin \left( \frac{2\pi \delta}{c} \left( \frac{\lambda}{\lambda_g} \right)(F - B/2) \right) \right] \right] \quad . \quad (14) \]
Use of the identity

\[ \sin(\alpha + \beta) - \sin(\alpha - \beta) = 2 \cos \alpha \sin \beta \]

in Equation 14 gives

\[
P_d = \frac{1}{2} kTB \left[ 1 + \sin \left( \frac{2\pi \delta}{c} \left( \frac{\lambda}{\lambda_g} \right) \right) \cos \left( \frac{2\pi \delta}{c} \frac{\lambda}{\lambda_g} \right) \right].
\]

(15)

Notice that Equation 15 indicates that \( P_d \) is equal to the total source power \( kTB \) only if the path-length difference, \( \delta \), is zero. From Equation 10 for a coherent source, it was seen that detector power is equal to total source power if \( \delta \) is zero, but it also reaches this value periodically with changes in \( \delta \). For both types of microwave sources, detector power consists of a constant term which is equal to one-half the source power plus a term which depends on \( \delta \).

For the incoherent source and the limit of large path differences, Equation 15 indicates that detector power is equal to the constant term only, i.e., one-half the total source power.

Assume that the difference in paths, \( \delta \), is varied at a constant speed, \( s \). Let time, \( t \), be defined as zero when \( \delta \) is zero, i.e., let \( \delta \) be expressed as \( \delta = st \). Then Equation 10 becomes

\[
P_d = \frac{P_s}{2} \left[ 1 + \cos \left( \frac{2\pi st}{\lambda_g} \right) \right] = \frac{P_s}{2} \left[ 1 + \cos \left( \frac{\omega d t}{\lambda_g} \right) \right].
\]

(16)

The interference modulation rate for a band of frequencies which is produced by a constant change in \( \delta \) may be obtained from Equation 15. It can be seen
that the term \( \frac{1}{c} \frac{\lambda}{\lambda_g} \) \( F \) is equal to \( \lambda^* \), where \( \lambda^* \) is the guide wavelength corresponding to the microwave center frequency \( F \). Thus, for uniform change in \( \delta \), the microwave power incident upon the detector may be expressed as

\[
P_d = \frac{1}{2} kTB \left[ 1 + \frac{\sin \left( \frac{\omega_a t}{F} \frac{B}{2} \right)}{\left( \frac{\omega_a t}{F} \frac{B}{2} \right)} \cos \omega_a t \right]
\]

(17)

Notice that the magnitude of the periodic peaks caused by a coherent source of power \( P_s \) (see Equation 16) are the same as the peak for an incoherent source (\( t = 0 \) in Equation 17) for which \( kTB \) is equal to \( P_s \).