A MICROWAVE SPECTROSCOPE AND THE
MICROWAVE SPECTRA OF CHF₂Cl AND CHFCI₂

by
Cedric Robert Mann

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

in
PHYSICS

We accept this thesis as conforming to the
standard required from candidates for the
degree of DOCTOR OF PHILOSOPHY

Members of the Department of PHYSICS

THE UNIVERSITY OF BRITISH COLUMBIA
December, 1952
ABSTRACT

A microwave spectroscope is described which operates in the region 23,000 to 27,000 mc./sec. Measurement of the frequencies of rotational absorption lines is achieved by comparison of the frequency of the signal from the source oscillator with the frequency of one of a set of standard microwave signals generated with auxiliary apparatus. The frequency of each of the standard signals is known to be better than 1 part in $10^6$, and the frequency of a rotational absorption line can be measured to .05 mc./sec.

The spectroscope has been used to study the pure rotational spectra of the asymmetric top molecules CHF$_2$Cl and CHFCl$_2$. Thirty-two absorption lines have been observed for CHFCl$_2$ and the frequencies measured. Twenty absorption lines have been observed and the frequencies measured for CHF$_2$Cl. All the lines in CHF$_2$Cl are doublets, the separation of the two lines in each doublet varying from .59 mc./sec. to 6.18 mc./sec.

A graphical method of analyzing the spectrum of CHF$_2$Cl is developed and applied. The relative intensities of different types of transitions are calculated. It is shown that the strongest absorption lines observed should be due to transitions where $\Delta J = 0, \Delta T = +1$ and that the values of $J$ for the energy states between which these transitions occur should be greater than 12.

The hyperfine structure due to the quadrupole moment of the chlorine nucleus is calculated and it is shown that,
for $J$ greater than $12$, the hyperfine structure cannot be completely resolved. In this case, each line should appear as a doublet.

A method of using the hyperfine structure to help analyze the spectrum is given. By this means, the four lines centred around $26,441$ mc./sec. are identified as being the completely resolved hyperfine structure of the transition $10_{37} - 10_{47}$.

The frequency of the absorption lines due to the two transitions $11_{58} - 11_{48}$ and $9_{36} - 9_{46}$ are predicted to be approximately $20,500$ mc./sec. and $31,500$ mc./sec., and it is shown that if these lines are observed the moments of inertia of the molecule can be calculated.
THE UNIVERSITY OF BRITISH COLUMBIA
Faculty of Graduate Studies

PROGRAMME OF THE
FINAL ORAL EXAMINATION FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

of

CEDRIC ROBERT MANN
B.Sc. (New Zealand) 1947
M.Sc. (New Zealand) 1949

THURSDAY, DECEMBER 18th, 1952, at 3:00 P.M.
IN ROOM 301, PHYSICS BUILDING

COMMITTEE IN CHARGE
Dean H. F. Angus, Chairman
Professor A. M. Crooker Professor H. Hawthorn
Professor K. C. Mann Professor S. E. Jennings
Professor H. E. D. Scovil Professor J. J. R. Campbell
Professor G. M. Shrum Professor K. C. McTaggart

External Examiner: Professor A. van der Ziel,
University of Minnesota, Minneapolis, Minn.
GRADUATE STUDIES

Field of Study: Physics.

Atomic and Molecular Spectroscopy -- Professor A. M. Crooker
Electronics -- Professor A. van der Ziel
Theory of Measurements -- Professor A. M. Crooker
Special Relativity -- Professor W. Opechowski
Nuclear Physics -- Professor P. W. Burbidge
Quantum Mechanics -- Professor D. Brown

Other Studies:

Differential Equations -- Professor T. E. Hull
Application of Operational Methods to Engineering -- Professor W. D. Coulthard
Electrical Communications -- Dr. K. Kreilsheimer
A MICROWAVE SPECTROSCOPE AND THE MICROWAVE SPECTRA OF CHF$_2$Cl and CHFCI$_2$

A microwave spectroscope has been built which operates in the region 23,000 to 27,000 mc/sec. Measurement of the frequencies of rotational absorption lines is achieved by comparison of the frequency of the signal from the source oscillator with the frequency of one of a set of standard microwave signals generated with auxiliary apparatus. The frequency of each of the standard signals is known to be better than 1 part in $10^6$, and the frequency of a rotational absorption line can be measured to .05 mc/sec.

The spectroscope has been used to study the pure rotational spectra of the asymmetric top molecules CHF$_2$Cl and CHFCI$_2$. Thirty-two absorption lines have been observed for CHFCI$_2$ and the frequencies measured. Twenty absorption lines have been observed and the frequencies measured for CHF$_2$Cl. All the lines in CHF$_2$Cl are doublets, the separation of the two lines in each doublet varying from .59 mc/sec. to 6.18 mc/sec.

A graphical method of analyzing the spectrum of CHF$_2$Cl is developed and applied. The relative intensities of different types of transitions are calculated. It is shown that the strongest absorption lines observed should be due to transitions where $\Delta J = 0$, $\Delta \tau = +1$ and that the values of $J$ for the energy states between which these transitions occur should be greater than 12.

The hyperfine structure due to the quadrupole moment of the chlorine nucleus is calculated and it is shown that, for transitions between energy states whose $J$ values are greater than 12, the hyperfine structure cannot be completely resolved. In this case, each line should appear as a doublet.

The method of using the hyperfine structure to help analyze the spectrum is given. By this means, the four lines centred around 26,441 mc/sec. are identified as being the completely resolved hyperfine structure of the transition 10$_{37}$ - 10$_{47}$.

The frequency of the absorption lines due to the two transitions 11$_{58}$ - 11$_{48}$ and 9$_{36}$ - 9$_{46}$ are predicted to be approximately 20,500 mc/sec. and 31,500 mc/sec., and it is shown that if these lines are observed the moments of inertia of the molecule can be calculated.
ACKNOWLEDGEMENTS

The research described in this thesis has been supported by grants from the Defence Research Board of Canada.

I am personally indebted to the National Research Council for a scholarship held during 1951-52 and for a summer scholarship in 1952.

I wish to thank Dr. A van der Ziel under whom the project of building the spectroscope was started and Dr. W. Raudorf who suggested the investigation of the two Freons. I also wish to thank Mr. T. R. Hartz who built a considerable part of the equipment described and Dr. A. M. Crooker and Mr. W. M. Ross for their help in analysing the spectra.

C.R. Mann
TABLE OF CONTENTS

Introduction  1

Chapter I  The microwave spectroscope  6
  Molecular modulation  8
  The Stark effect spectroscope  9
  Source modulation  11
  The double modulation spectroscope  11
  The complete spectroscope  13
  The phase-sensitive detector  14

Chapter II  Frequency measurements  16
  Generation of standard frequencies  17
  Accuracy of measurement  18

Chapter III  The pure rotational spectra of the asymmetric rotor  21
  Asymmetry parameter and energy levels  21
  Selection rules  24
  Rotational absorption frequencies  25
  Intensities  26
  Hyperfine structure  27

Chapter IV  Analysis of the spectrum  30
<table>
<thead>
<tr>
<th>Chapter V</th>
<th>Rotational Spectrum of CHF$_2$Cl</th>
<th>34</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental results</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>Molecular structure</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Analysis of spectrum</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>Hyperfine structure</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>Summary</td>
<td>48</td>
</tr>
<tr>
<td>Chapter VI</td>
<td>Rotational spectrum of CHFCl$_2$</td>
<td>52</td>
</tr>
<tr>
<td>Appendix</td>
<td>Rearrangement of the King, Hainer and Cross tables</td>
<td>54</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>55</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figures</th>
<th>Description</th>
<th>Facing Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Block diagram of the microwave spectroscope</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>Illustration of two absorption lines</td>
<td>10</td>
</tr>
<tr>
<td>3-4</td>
<td>Photographs of complete spectroscope</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>The phase-sensitive detector</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>Illustration of increase in sensitivity with lower bandwidth</td>
<td>16</td>
</tr>
<tr>
<td>7</td>
<td>Block diagram of frequency standard</td>
<td>17</td>
</tr>
<tr>
<td>8</td>
<td>Energy level diagram for the asymmetric rotor</td>
<td>22</td>
</tr>
<tr>
<td>9</td>
<td>Illustration of an f-k diagram</td>
<td>31</td>
</tr>
<tr>
<td>10</td>
<td>Illustration of two absorption lines in CHF₂Cl</td>
<td>34</td>
</tr>
<tr>
<td>11</td>
<td>Model of CHF₂Cl</td>
<td>36</td>
</tr>
<tr>
<td>12</td>
<td>Thermal distribution of energy levels</td>
<td>39</td>
</tr>
<tr>
<td>13</td>
<td>Illustration of a transition ΔJ = -1</td>
<td>39</td>
</tr>
<tr>
<td>14</td>
<td>f-k diagram for CHF₂Cl</td>
<td>40</td>
</tr>
<tr>
<td>15</td>
<td>Illustration of hyperfine structure</td>
<td>42</td>
</tr>
<tr>
<td>16-17</td>
<td>Hyperfine structure for the 10\textsubscript{37} - 10\textsubscript{47} line in CHF₂Cl</td>
<td>48</td>
</tr>
</tbody>
</table>
INTRODUCTION

The microwave techniques developed during the war, almost exclusively for the purpose of radar, are very well suited for the construction of a spectroscope for the study of the pure rotational spectra of molecules. The first spectroscope using these techniques was built by Bleaney and Penrose in 1946 who studied the inversion spectrum of ammonia. Since this time progress in microwave spectroscopy has been rapid and the microwave spectroscope has come to be a very useful tool in Physics.

Of historical interest is the work of Cleeton and Williams in 1934 because it represents the first spectral measurements in the region between the optical and radio regions of the electromagnetic spectrum. These two investigators designed and built a set of split-anode magnetrons with which they were able to produce radiation at a wavelength as low as 1 cm., at that time the lowest wavelength obtained with a vacuum tube. The radiation was detected by an iron pyrites crystal and its frequency measured by use of a large diffraction grating. Four tubes were used to map the ammonia inversion spectrum at atmospheric pressures in the region 1.06 to 3.8 cm. wavelength. Previous to the war the only other known attempt was by Howe who used a cavity wavemeter to measure the frequency of the source.

The microwave region is generally taken as meaning that part of the electromagnetic spectrum between about 20 cm. wavelength and the long wavelength region of the infra-red where optical methods are used. The most suitable source of radiation for the purpose of spectroscopy in the microwave region
is the klystron oscillator. Compared to a magnetron the klystron generates relatively low power, but this is no particular disadvantage because of the saturation effect in molecules and because the sensitive silicon crystals used as detectors cannot detect high powers. The frequency of these oscillators may be swept repeatedly over a range of frequency from a few kilocycles to 30 or 40 megacycles by application of a repetitive voltage to one of the electrodes and this is a valuable feature for their use in spectroscopy. Each oscillator covers a comparatively small range usually about 5 kmc./sec. but a whole series is available to cover from 20 cm. down to .5 cm. wavelength. Radiation can be produced down to 2 mm. by use of harmonic generating crystals.

Higher power is obtainable with magnetrons than with klystrons but, since these oscillators are not in general as conveniently tuned, and since the most sensitive detectors are incapable of handling the high power obtained, they have not found wide use in microwave spectroscopy.

Cells in which to place the gas to be studied are made very conveniently from sections of rectangular waveguide with thin mica windows, which are transparent to the radiation, sealing the ends. Frequency measurements are accomplished by means of wavemeters to within about 5 mc./sec. and with frequency standards, one of which is described in this thesis, to within .05 mc./sec.

The usefulness of the microwave spectroscope lies in its ability to measure very small energy differences, that is to resolve lines which lie very close together. If one or more of
the atomic nuclei in the molecule has a quadrupole moment. Each rotational energy level is split into a number of levels lying close together. This results in narrow, hyperfine structures which can be resolved with the microwave spectroscope but which are beyond the resolving power of the best instruments in the infra-red or optical regions. From the number of components in the hyperfine structure and the frequency difference between them the spin of the nucleus and its quadrupole coupling constant may be determined.

The pure rotational spectra of asymmetric top molecules can be studied very effectively in the microwave region. There are a large number of rotational energy levels for this type of molecule and a large number of lines in their absorption spectra. The positions of the rotational energy levels can be determined, and from these the structure of the molecule found, by observation of the vibration-rotation bands in the infra-red. All too frequently, especially for the heavier asymmetric tops, these vibration-rotation bands cannot be resolved by the infra-red spectrometer and the rotational constants and geometry of the molecule cannot be determined.

The first chapter of this thesis is devoted to the description of a microwave spectroscope built partly by a former student and partly by the author. In the second chapter the measurement of the frequency of the rotational absorption lines is described. Chapter III is devoted to the theory of the pure rotational spectra of the asymmetric rotor and the theory of the perturbation of rotational energy states by the quadrupole interaction of a single nucleus. A method of analysing the
spectra of an asymmetric rotor is developed in Chapter IV.

An analysis of the microwave spectrum of CHF₂Cl in the region 23,000 to 27,000 mc./sec., which was measured using the spectroscope described, is presented in Chapter V.

The rotational absorption lines in the spectra of this, or for that matter any other asymmetric top of comparable molecular weight, are so profuse that it is beyond the capability of the infra-red spectrometer to resolve them so that it does not appear probable that the molecular structure can be determined by infra-red methods. The structure of the molecule was determined by Brockway in 1937, by means of electron diffraction, who obtained the interatomic distances to an accuracy of 2 percent. Brockway who at the same time investigated other halogen substituted methanes found that whenever two fluorines were attached to the carbon a shortening of the C-F bond was observed. A shortening of the C-Cl bond in CHF₂Cl and in CHFCl₂ was also indicated but the accuracy of measurement was not sufficient to confirm this.

The quadrupole coupling constants for the chlorine nucleus in the fluorochlora methanes has been determined by Livingston for the substances in the solid state. The quadrupole couplings, as determined by microwave spectroscopy, are 9.0 percent higher for CH₃Cl and 0.6 percent higher for CF₃Cl than Livingston's values. This indicated a change in the character of the carbon-halogen bond in going from the solid to the gaseous state.

If the rather complicated spectrum of CHF Cl can be analysed the accuracy to which the interatomic distances can be
can be determined (we should expect to obtain these to better than .5 percent) will be sufficient to confirm the electron diffraction results. It is also desirable to obtain the quadrupole coupling for the chlorine in this molecule in the gaseous state for comparison with the coupling in the solid state.

A few brief remarks are made about the microwave spectrum of CHFCl₂ which has also been measured in Chapter VI.
Chapter I

THE MICROWAVE SPECTROSCOPE

The operation of a microwave spectroscope can be described by the discussion of the simple and effective spectroscope which can be made with a klystron oscillator as source, a section of waveguide as absorption cell, a silicon crystal detector and a video frequency amplifier. The frequency of the klystron oscillator is repeatedly swept over a small region by application of a sawtooth voltage to the repeller electrode. If the gas in the cell has an absorption line in the region a sharp dip in the power reaching the detector occurs as the frequency reaches the absorption frequency. This power decrease will be superimposed on a gradual rise or fall of the power since the output from the klystron is dependent upon the repeller voltage. The rectified voltage appearing across the crystal is proportional to the input power (if this is low) and hence will have a waveform which contains the envelope of the absorption line and the power output of the klystron in the region swept. The signal from the detector is amplified and presented on the vertical deflection plates of a cathode-ray oscilloscope to whose horizontal plates is applied part of the sawtooth voltage used to sweep the klystron. This latter may be tuned manually over a much larger frequency range than it can be swept electrically and hence the whole region in which the
oscillator will function may be scanned in a search for absorption lines.

The sensitivity of this or any other spectroscope is ultimately limited by the noise inherent in the apparatus and thus will depend on the bandwidth of the amplifier which must be large enough to allow reproduction of the absorption line without distortion. The optimum bandwidth for minimum allowable distortion may be decreased by increasing the time taken to sweep over the absorption line, but to do this the rate of sweep and also the low frequency cut-off of the video amplifier must be lowered. Since the noise power generated in silicon rectifier crystals varies inversely with frequency the decrease in the noise due to the lower bandwidth is offset by the increase in the noise power output from the crystal detector at the lower frequency.

Amplification at a high frequency by an amplifier having a small bandwidth may be realized by producing a high frequency amplitude modulation of the microwave power reaching the detector (two methods of doing this are described later) and then amplifying the signal from the detector at the modulation frequency. The envelope of the high frequency signal from the amplifier will have a waveform which is the same as that of the voltage appearing across the crystal detector in the simple spectroscope and may be taken off by use of a second detector and displayed on an oscilloscope as before. With this arrangement the optimum bandwidth may be lowered by reducing the rate of sweep but in doing so it is not necessary to lower the cut-off frequency of the amplifier.
Molecular Modulation and the Stark Effect Spectroscope

Molecular Modulation

This type of modulation was first introduced by Hughes and Wilson. When the gas molecules in the absorption cell are subjected to an electric field the original absorption line is split into a number of components (Stark Effect). If the source oscillator is imagined tuned to a fixed frequency at some point on an absorption line and the gas is subjected to an alternating electric field the amount of power absorbed will change as the line shifts in frequency and the power reaching the detector will be modulated at the frequency of the alternating field. In practice the alternating field has the form of a square wave the base of which corresponds to zero field. The source klystron is swept over the absorption line at a frequency much slower than that of the applied field and, if the strength of the field is sufficiently great at the top of the square wave to completely separate the Stark components from the unperturbed line, the shape of the absorption line will be reproduced as the envelope of the burst of high frequency which appears at the output of the detector when the line is swept over. Similar bursts will occur when the Stark components themselves are swept over except the phase of the high frequency signal will differ from that obtained from the unperturbed line by 180°. This phase difference occurs because maximum and minimum absorption correspond to peak and base of the square wave for the unperturbed line whereas the opposite is the case for the Stark component.
FIG. 1. THE MICROWAVE SPECTROSCOPE

(BLOCK DIAGRAM.)
Stark Spectroscope

A spectroscope using the above principle has been constructed and is shown schematically in Fig. 1. (Imagine all the switches in position 'a', and the Stark cell used). The spectroscope is designed to operate in the K band and performs most satisfactorily in the range 23,000 to 27,000 mc./sec.

Two klystrons, Raytheon Type 2K33 and Raytheon Type QK140 are used to provide microwave power throughout the region. By adjusting the amplitude of the sawtooth voltage applied to the repeller electrodes the extent of the frequency range over which these klystrons are swept electrically may be varied between 0 and 45 mc./sec.

The absorption cell consists of three \(\frac{6}{2}\) ft. sections of waveguide, inside dimensions \(\frac{3}{8}\)" x 1", with an insulated brass conducting strip down the center whose broad face is parallel to the broadside of the guide. A cross section of the cell is shown inset in Fig. 1. The brass strip 1/32" thick is insulated and supported by lucite strips 3/32" wide by 1/16" thick which fit into slots cut in the wall of the guide, the brass strip itself fitting into slots 1/32" wide by 1/32" deep cut in the lucite. The three sections are joined by short lengths of the same size guide to give a cell whose effective length is 19\(\frac{1}{2}\) ft. The ends of the cell are made vacuum tight with mica windows and the whole assembly evacuated through a slot 1/16" x 3" cut in the center of the broad face of the guide. Matching to the standard K band waveguide, inside dimensions .420" x .170" is achieved by means of the taper sections. If a TE\(_{10}\) mode exists in the smaller waveguide the same mode will be propagated in the
Fig. 2. Illustration of two absorption lines as they appear on the Double Beam Oscilloscope. The signal from the 50 kc./sec. amplifier is shown on the lower trace and the signal from the phase-sensitive detector on the upper trace.
large guide if there are no discontinuities. The cell including the taper sections transmits 40% of the input power which corresponds to a loss of .25 db./ft. This is a factor of 10 greater than the attenuation of the waveguide without a central strip. Since losses in the dielectric could not account for this it appears that modes other than the TE\textsubscript{10} have been excited to which the detector will not respond.

A 50 kc./sec. square wave whose base is held at ground potential is applied between the central strip and the waveguide which is grounded, thus producing an alternating electric field whose E vector is parallel to the E vector of the microwave. The latter are detected with a conventional K band crystal detector using a IN26 crystal and the 50 kc./sec. signal which appears across the crystal when an absorption takes place is amplified by a 50 kc./sec. tuned amplifier with a 3 kc./sec. bandwidth. Following detection by a phase-sensitive detector the envelope of the 50 kc./sec. signal is displayed on the upper beam of a Cossor double beam oscilloscope. The phase-sensitive detector discriminates between signals which are 180° out of phase and the Stark components will appear inverted with respect to the unperturbed line. A picture of two of the lines of CHF\textsubscript{2}Cl are shown in Fig. 2. On the lower trace of the double beam oscilloscope the output from the 50 kc./sec. amplifier is displayed and on the upper trace the output from the phase-sensitive detector. The Stark components do not appear since in this case they are very weak.

The advantage of this type of spectroscope, particularly when searching for lines, is that a signal only appears
when an absorption line is present.

(b) Source Modulation and the Double Modulation Spectroscope

Source Modulation

The amplitude modulation of the microwave power may be achieved by suitably modulating the source. Upon the slowly varying sawtooth voltage is superimposed a voltage of much higher frequency which produces a frequency modulation of the microwaves. As an absorption line is slowly swept over, the oscillator makes rapid excursions in and out of regions of greater or less absorption and the gas thus acts as a discriminator converting the frequency modulation to an amplitude modulation. The absorption line (together with any reflections in the guide) appears in the envelope of the high frequency signal across the crystal detector.

The Double Modulation Spectroscope

This spectroscope, which operates on the above principle, was originally developed in this laboratory by Mr. T.R. Hartz.

It is shown schematically in Fig. 1. (Imagine all the switches at position 'b' and the double modulation cell used).

The sawtooth voltage applied to the repeller electrode has superimposed on it a 50 kc./sec. voltage wave which may have one of two forms. These are shown inset in Fig. 1 beside the R.F. generator. In type 'a' the sawtooth has superimposed a sine wave whose amplitude is such that the frequency swept over by the klystron in one period of the sine wave is much smaller than the width of the absorption line. This results in a differentiated line shape. The voltage applied in type 'b' is better described as a square wave with a sawtooth envelope, the bottom of the square wave remaining at a fixed level. With this type of modulation the
true line shape is obtained. The absorption cell is 30 ft. long and is constructed from K band waveguide, inside dimensions .140" x .170". The ends of the guide are made vacuum tight with mica windows and the guide is evacuated through a slit in its broad side.

The 50 kc./sec. signal from the crystal detector is amplified and detected, and the absorption line is displayed on an oscilloscope as in the Stark spectroscope.

There are two rather serious disadvantages associated with this type of spectroscope from the experimental viewpoint. Firstly, there is no discrimination between an absorption line and a reflection in the guide, which will also cause a change in power at the detector. The width of a reflection is usually much greater than that of an absorption line and thus the line appears superimposed in the reflection. In some cases however the reflections are quite narrow and, since they are usually much larger than an absorption line (if the line is weak), it is almost impossible to find the line. Secondly the power output from the klystron is never completely constant with a change in repeller volts as was mentioned above. Then when type 'b' modulation is used, a very large, 50 kc./sec., amplitude modulation of the microwaves occurs at the source, as well as the desired frequency modulation.

With the klystrons in use at the present time this effect produces a signal so much stronger than that due to a weak absorption line that the phase-sensitive detector is overloaded and the line cannot be observed. This large 50 kc./sec.
signal may be reduced by using a second cell, which does not contain gas, in parallel to the first. The microwave power is divided equally between the two cells and the 50 kc./sec. signal from the second cell subtracted from that from the first. If the cells are physically identical the 50 kc./sec. difference signal obtained is due only to the absorption in the gas. The method works successfully if both the cells and both the crystal detectors have exactly identical characteristics over a large frequency range. With our apparatus complete suppression of the unwanted 50 kc./sec. signal can only be obtained over a small range of frequencies, and this by tuning the detectors very carefully. When the frequency of the klystron is adjusted manually, in search of new lines, continual tuning of the detectors is necessary. The amplitude modulation of the microwaves at the source may be greatly reduced by use of type 'a' modulation since, in this case, the section of the mode swept over in one period of the 50 kc./sec. modulating voltage is very much smaller than in type 'b', and the amplitude modulation at the source is correspondingly reduced.

One advantage of this spectroscope is the simplicity of the absorption cell in comparison with the cell required for a Stark spectroscope. This allows very long cells to be constructed with a corresponding gain in sensitivity.

(c) Complete Spectroscope

By arranging that the frequency of the square wave used in the Stark spectroscope and the second modulating voltage superimposed on the sawtooth voltage in the double modulation spectroscope
Fig. 3. Rear view of the complete spectroscope

Fig. 4. Front view of the complete spectroscope.
have the same frequency, it is possible to use much of the same equipment for both types of instrument. Fig. 1 referred to above is a block diagram of the complete spectroscope, and back and front views of the apparatus are shown in Figs. 3 and 4.

The two cells are laid side by side on a long table with their front ends projecting under the instrument panel. The klystron and all the microwave components in the dotted block in Fig. 1 are mounted on a solid aluminum base which is grounded. This whole assembly may be shifted and connected to whichever cell it is decided to use. Thus to change from one type of modulation to the other it is only necessary to throw three switches and move the klystron assembly. Both cells are evacuated by a mercury diffusion pump backed by a Cenco rotary oil pump. It is usual to work at pressures of the order of .01 mm. of mercury and the cells are sufficiently vacuum tight to contain gas at this pressure for several hours.

(d) Phase Sensitive Detector

Before leaving the subject of the spectroscope, it is instructive to describe the phase-sensitive detector, since the narrow band widths, on which the sensitivity of the spectroscope depends are obtained in this part of the apparatus. The circuit of the detector is shown in Fig. 5, and is an adaptation of a circuit described by Chance.

A 50 kc./sec. reference voltage is applied across the points a, b of the diode bridge. When the point 'a' swings positive all the diodes conduct, the portion of the cycle in which
50 KC/SEC REFERENCE SIGNAL.

FIG.5. THE PHASE-SENSITIVE DETECTOR.
they conduct being limited by choice of the biasing combination $R_1C_1$. When a modulated 50 kc./sec. signal is applied to the input terminals of the detector c, d its action is such that the modulation, with a small ripple superimposed, appears across $C_2$. The amplitude of the signal across $C_2$ will be a maximum when the input signal and reference voltage are either in phase or out of phase; thus the detector will not respond to spurious signals which are not in the correct phase. The residual 50 kc./sec. ripple is removed by the resistance capacity combination RC. The time constant of this combination further serves to limit the bandwidth of the whole apparatus, the bandwidth being given by $\Delta f = 1/RC$. Hence for high sensitivity, RC should be as large as possible.

There is however one further restriction on RC. The signal which appears across $C_2$ will have a repetition time $T$, which is the same as that of the original sawtooth sweep, and a waveform which contains the envelope of the absorption line. The waveform may be considered as made up of a set of Fourier components the fundamental frequency of which is $1/T$. In order that the signal not be distorted, the reduction in amplitude and the phase shift of all the Fourier components, by the RC combination, must be the same. It is easy to show that if $V_1$ is the voltage across $C_2$, $V$ the voltage across $C$ and $\theta$ the phase difference between the two then

$$V = \frac{V_1}{(1 + \omega^2 R C^2)^\frac{1}{2}}$$

$$\tan \theta = \omega RC$$
Fig. 6. Illustration of the increase in sensitivity when a lower bandwidth is used. The photograph on the left is for a bandwidth of 500 cps, and the photograph on the right shows the same two lines when the bandwidth is 20 cps.
It follows from these two equations that for good reproduction
RC should be as small as possible. In practice the optimum value
of RC for a given rate of sweep must be a compromise between
maximum sensitivity and maximum allowable distortion.

The sweep rates in use on the spectroscope at present
are 1 cps., 7 cps., and 20 cps., and the RC combination used with
these rates give bandwidths of 20 cps., 200 cps. and 500 cps. The
two high frequency sweeps are used while generally searching the spec­
trum for absorption lines. The very slow sweep, which requires
the use of a long persistent screen in the oscilloscope is used
when a line is found and an increase in sensitivity is required.
Reproductions of two of the lines from CHF₂Cl, observed when the
sweep speeds are 7 cps. and 1 cps. and the respective bandwidths
are 500 cps. and 20 cps., are shown in Fig. 6. The decrease in
signal-to-noise ratio when the slow sweep and small bandwidth
are used is clearly illustrated.

Chapter II

FREQUENCY MEASUREMENTS

The method used to measure the absorption frequencies
is that devised by Unterberger and Smith. By use of a suitable
generator, to be described below, a set of harmonics of a
standard frequency are produced in the waveguide system, the
frequency difference between two consecutive harmonics being 90 mc./sec.
This set of harmonics is mixed with part of the output from the
FIG. 7. BLOCK DIAGRAM OF FREQUENCY STANDARD:

X-TAL OSC. → MULT. → MIXER → MULT → MULT → KLYSTRON. → 2970 MC.

200 KC. 4800 KC. 5 MC. 90 MC. 270 MC.

WWW COMM. REC. COMM. REC. COMM. REC.

X-TAL MIXER. HARMONIC GENERATING X-TAL

FROM SPECTROSCOPE.
klystron source of the spectroscope in a IN26 mixer crystal which is connected to the input of a communications receiver. The output of the receiver is taken to the Y2 deflection plates (lower beam) of the Cossor double beam oscilloscope (Fig. 1). While the klystron is being swept over a small range of frequencies, a point is reached in the sweep where the klystron frequency differs from that of one of the standard harmonics by an amount equal to the frequency at which the receiver is tuned. This produces a sharp 'marker pip' on the lower trace of the oscilloscope. By changing the setting of the communications receiver the pip may be moved along the trace and set to coincide with an absorption line. The frequency of the absorption line is then found by either adding or subtracting the receiver frequency from that of the harmonic used to obtain the beat. Whether the receiver frequency is to be added or subtracted can be determined by noting in which direction the pip moves along the trace when the receiver frequency is increased. To determine which of the harmonics is being used the frequency of the absorption line is first measured by use of a cavity wavemeter whose maximum error is approximately 20 mc./sec. (a) Generation of Standard Frequencies

A block diagram of the method is shown in Fig. 7. The secondary frequency standard used is a 200 kc./sec. ovencontrolled crystal. The 200 kc./sec. output is first multiplied to 4800 kc./sec. and is then mixed with part of the original 200 kc./sec. signal to give 5 mc./sec. This frequency is compared with one of the Standard frequencies broadcast
Further multiplication follows to 90 mc./sec. and 270 mc./sec. The output of the 270 mc./sec. multiplier is taken to a type 2K47 Sperry klystron, which is a velocity modulated tube designed for use as a frequency multiplier. The output resonator of this tube is tuned to the 11th harmonic (2970 mc./sec.) and the output is fed into a crystal multiplier in the waveguide system along with a 90 mc./sec. signal obtained from the 90 mc./sec. multiplier. Because of the non-linear nature of the crystal, a set of microwave signals, which are harmonics of 90 and 2970 mc./sec., and which have a wavelength shorter than the cut-off wavelength of the guide, are produced in the waveguide system. If the microwave system is correctly tuned then there will exist standard frequencies every 90 mc./sec. in the guide within its transmission band.

(b) **Accuracy of Measurement**

The accuracy of measurement depends on the following factors:

1. The accuracy to which the standard harmonics in the guide are known.
2. The accuracy to which the communications receiver frequency may be obtained.
3. Time delays or phase shifts in the amplifiers.
4. The accuracy to which the marker pip may be set on absorption line.

1. The 5 mc./sec. signal from the secondary standard is checked against the 15 mc/sec. signal from Station W.W.V. (which
has an accuracy of better than one part in $10^7$) by mixing the two signals in a communication receiver and observing the beat rate between them. The 200 kc./sec. crystal is sufficiently stable to hold the beat note to less than 3 cps. over a period which is much longer than that required to make a measurement. Thus the maximum error in the standard frequency is 1 cps. in 5 mc./sec. or approximately 5 kc./sec. in the region 25,000 mc./sec.

(2) The communications receiver used to measure the difference frequency is calibrated by use of a heterodyne frequency meter to better than 1 kc./sec. Thus this error is negligible compared with (1) above.

(3) Since the time required to sweep over an absorption line is comparatively small the difference in the time of transit of the two signals, one through the absorption cell and the following amplifier, and the other through the mixer crystal and communications receiver, is negligibly small. The error which may occur from distortion of the absorption line due to phase shifts in the amplifiers can be quite large. These phase shifts may occur either in the 50 kc./sec. amplifier, the phase-sensitive detector, or the audio amplifier. Distortion in the 50 kc/sec. amplifier will result in the modulation being shifted forward on the top of the wave and backward on the bottom or vice versa, so that this type of distortion may be checked quite easily by inspecting the 50 kc./sec. signal displayed on the screen of the oscilloscope. Distortion by the phase-sensitive detector and the low frequency amplifier may be checked by presenting the modulated 50 kc./sec. signal on the lower trace.
of the double beam oscilloscope and the output from the amplifier on the upper trace. If there is no distortion it should be possible to exactly superimpose the upper trace on the envelope of the 50 kc./sec. wave.

(4) The error in setting a marker pip on an absorption line depends on the sharpness of the line and its strength. This is essentially a personal error and may be reduced by repeated observations. For a weak line, of width .5 mc./sec. one should be able to superimpose the pip on the absorption line to within .05 mc./sec.
Chapter III

PURE ROTATIONAL SPECTRA OF THE ASYMMETRIC ROTOR

The fundamental theory of the asymmetric rotor has been given by several authors and equations defining the energy levels derived by various methods. Excellent compilations of the selection rules, symmetry properties, and tables which allow quick calculation of the intensities and rotational frequencies are given by King, Hainer and Cross in a series of papers in the Journal of Chemical Physics. Since it will be necessary to refer to the latter authors several times the author has taken the liberty of contracting their names to (KHC).

(a) Asymmetry Parameter and Energy Levels

The degree of asymmetry of an asymmetric rotor is conveniently given by use of the asymmetry parameter \( \kappa \), which is defined as

\[
\kappa = \frac{2b-a-c}{a-c}
\]

where

\[
a = \frac{h^2}{8\eta^2 I_a}, \quad b = \frac{h^2}{8\eta^2 I_b}, \quad c = \frac{h^2}{8\eta^2 I_c}
\]

\( I_a, I_b, I_c \) are here the principal moments of inertia taken so that \( I_a \leq I_b \leq I_c \). With this definition of \( \kappa \) we have, \(-1 \leq \kappa \leq 1\), the limit \( \kappa = -1 \) corresponding to the limiting prolate symmetric rotor, and the limit \( \kappa = +1 \) to the limiting oblate symmetric rotor.
FIG. 8. ENERGY LEVEL DIAGRAM.

PROLATE SYMMETRIC TOP

\( \kappa = -1 \)

J  K

\[
\begin{array}{cccc}
4 & 4 & 4 & 0 \\
4 & 3 & 4 & 1 \\
3 & 4 & 2 & 2 \\
2 & 4 & 1 & 3 \\
1 & 4 & 1 & 4 \\
0 & 4 & 0 & 4 \\
3 & 3 & 3 & 0 \\
3 & 2 & 3 & 1 \\
3 & 1 & 3 & 2 \\
3 & 0 & 3 & 3 \\
2 & 2 & 2 & 0 \\
2 & 1 & 2 & 1 \\
2 & 0 & 2 & 2 \\
1 & 1 & 1 & 1 \\
0 & 0 & 0 & 0 \\
\end{array}
\]

ASYMMETRIC TOP

\( \kappa = 0 \)

OBLATE SYMMETRIC TOP

\( \kappa = +1 \)
The energy of the asymmetric rotor in the form due to Ray¹⁰ is given by

\[ E(abc) = \frac{a+c}{2} J(J+1) + \frac{a-c}{2} E(\kappa) \]  

(1)

J is the total angular momentum quantum number. The factor \( E(\kappa) \), called the reduced energy, depends on \( a, b, c \), and \( J \) in a rather complicated manner, and for a given value \( J \) assumes \( 2J+1 \) values some of which are negative. The \( 2J+1 \) values of \( E(\kappa) \) for a given \( J \) are the roots of a secular determinant of degree \( 2J+1 \) which, fortunately, can be factored into a number of determinants of smaller degree, leading to algebraic equations. These equations the degree of which increases linearly with \( J \) express \( E(\kappa) \) in terms of \( \kappa \). Numerical solutions for \( \kappa = 0, -1, -2, \ldots, -1 \) have been obtained for \( J = 0 \) up to \( J = 12 \) by (KHC) and have been published in an exceedingly useful table ¹². By use of a simple relation, given in the tables, solutions for \( \kappa = 0, 1, 2, \ldots 1 \) may be obtained.

A qualitative diagram of the energy levels of the asymmetric rotor is given in Fig. 8. The energy levels for the completely asymmetric rotor \( (\kappa = 0) \) are plotted in the centre of the diagram, and the energy levels for the limiting prolate and oblate symmetric rotors plotted to the extreme left and right. The energy levels of the slightly asymmetric rotor for which each level of the limiting symmetric rotor is split into two components when \( \kappa \neq 0 \) are shown a little toward the inside.

There are two prevalent methods of labelling the \( 2J+1 \) sublevels. The first is to label each level \( J_\tau \) where \( J \) specifies the \( J \) set and \( \tau \) is an integer which assumes the \( 2J+1 \) values \(-J \leq \tau \leq J\); the level of lowest energy is \( J_{-J} \) and \( \tau \) increases
with increasing energy to give the highest level as $J_+$. This method is shown in the left hand column in the centre of Fig. 8.

A second method introduced by (KHC)$_{12}$ is to label each level with two subscripts $K_{-1}$ and $K_{+1}$, in this order. The first subscript $K_{-1}$ corresponds to the value of $K$ of the level in the limiting prolate symmetric top ($K = -1$), and the subscript $K_{+1}$ to the value of $K$ in the limiting oblate symmetric top ($K = +1$). Reference to Fig. 8 will show that $K_{-1}$ assumes the values 0, 1, 1, 2, 2 -- from the lowest to the highest level and $K_{+1}$ the values 0, 1, 1, 2, 2 --- from the highest to the lowest. With this method the symmetry of the level with respect to the behaviour of the rotational eigenfunctions under rotations of $180^0$ about the principal axes, may be inferred from the parity of the subscripts. For amplification of this the reader is referred to reference 12. This notation is very cumbersome algebraically, but it is particularly useful in labelling the initial and final levels of a particular transition, since the latter may be classified according to the change in the parity of the subscripts (see below).

In the following text the energy of a level, which is characterized by the quantum number $J$, and the pseudo quantum number $\tau$, will be written $E_J^{\tau}(abc)$ and the reduced energy will be written $E_J^{\tau}(\kappa)$.

Each energy level of a particular asymmetric top will be labelled according to the notation $J_{K_{-1}K_{+1}}$. With this
notation the value of \( \tau \) for the level can be obtained from the simple relation \( \tau = K_{-1} - K_{+1} \).

(b) **Selection Rules**

The selection rules for dipole radiation except for one which is only of importance when inversion doubling is not negligible, will be stated in terms of the \( J_{K_{-1}K_{+1}} \) notation. For the derivation of these the reader is referred to reference 12.

1. The selection rules for \( J \) are (as always for dipole radiation)

\[
\Delta J = Q_{\pm 1}
\]

2. If the permanent electric dipole moment of the molecule does not coincide with, or is not perpendicular to, one of the principal axes the only restriction is that "the parity of at least one of the two subscripts \( K_{-1}, K_{+1} \) must change".

In addition to these two rules the following three apply if the molecule has some symmetry.

3. If the permanent electric dipole moment lies parallel to the axis of least moment of inertia (a axis) "the parity of the \( K_{-1} \) subscript does not change".

4. If the permanent electric dipole moment lies parallel to the axis of greatest moment of inertia (c axis), only those transitions are allowed in which "the parity of the \( K_{+1} \) subscript does not change".
(5) If the permanent electric dipole moment lies parallel to the axis of intermediate moment of inertia (b axis), only those transitions are allowed in which "The parity of both the K subscripts change".

Transitions which are allowed by rule (3) are called a type transitions, those allowed by rule (4) c type transitions and those allowed by rule (5) b type transitions. If the dipole moment has components in two of the principal axes then the two corresponding types of transitions are both allowed.

It follows from the above rules that for b type transitions $\Delta \gamma$ is even and for a and c type $\Delta \gamma$ is odd. Reference to Fig. 8 will show this.

(c) Rotational Absorption Frequencies

The frequency of the radiation absorbed in any transition between two energy levels $J, \tau$ and $J', \tau'$ is given by

$$\nu = \frac{1}{\hbar} (E(abc) - E'(abc)) \quad \ldots \ldots \quad (2)$$

where $E(abc)$ is the energy of the level described by $J, \tau$ and $E'(abc)$ is the energy of the level described by $J', \tau'$. Substituting (1) in (2) gives, for a transition $\Delta J = +1$,

$$\nu = \frac{1}{\hbar} (a+c)(J+1) + \frac{a-c}{2} \left\{ E_{J+1}^{\gamma}(\kappa) - E_{J}^{\gamma}(\kappa) \right\} \quad \ldots \ldots \quad (3)$$

where $J$ is for the lower state.

In microwave spectroscopy it is convenient to calculate in units of $\text{Kmc./sec.}$ and, if $I_a$ is given in atomic mass and Angstrom units, (3) may be written

$$f_{\text{Kmc./sec.}} = (A+C)(J+1) + \frac{A-C}{2} \left\{ E_{J}^{\gamma}(\kappa) - E_{J}^{\gamma}(\kappa) \right\} \quad \ldots \ldots \quad (4)$$
where \( A_{\text{Kmc./sec.}} = \frac{505.425}{I_a(\text{amu.A}^2)} \), \( B_{\text{Kmc./sec.}} = \frac{505.425}{I_b(\text{amu.A}^2)} \),
\[
C_{\text{Kmc./sec.}} = \frac{505.425}{I_c(\text{amu.A}^2)}
\]
The value of \( h \) is taken as \( 6.6242 \times 10^{-27} \) erg.sec.
In this notation
\[
\kappa = \frac{2B-A-C}{A-C}
\]

(d) **Intensities**

The intensity of an absorption line for the transition \( n''; n' \) in the form given by (KHC)\(^{13} \), is
\[
I_{n''; n'} = \frac{8\pi^2}{3\hbar^2}Ng_{n''}(1-e^{-\frac{h\nu}{kT}}) \exp(-E_{n''}/kT) \sum \frac{\left| \mu_{n''; n'} \right|^2}{\hbar^2} \exp(-E_n/kT)
\]
where \( n \) stands for all the quantum numbers describing the state, \( N \) is the number of molecules per cc, \( E_{n''} \) is the energy of the lower state, \( g_{n''} \) is its weight factor, and \( \nu \) is the frequency of the absorption line. The last factor \( \left| \mu_{n''; n'} \right|^2 \) stands for \( \int \psi_{n''}^* \mu \psi_{n'} \, d\nu \), the square of the magnitude of the \( n''; n' \) element in the matrix of the dipole vector \( \mu \). Numerical values of this factor have been calculated by (KHC)\(^{13} \) for \( \kappa = -1, -0.5, 0, 0.5, 1 \) for \( J \) values up to \( J = 12 \). The strongest lines in the absorption spectrum of the asymmetric rotor occur when the corresponding transitions are permitted in the limiting symmetric rotor (i.e. \( \kappa = \pm 1 \)). This leads to a classification of the tables into permitted and forbidden sub-branches. Permitted sub-branches in the tables occur when the corresponding transition is permitted in either of two limiting symmetric rotors, forbidden sub-branches when it is not. Reference to Fig. 8 will show that a transition
will always fall in a forbidden sub-branch if $\Delta \tau \gg 5$. The intensity of this type of transition is relatively weak.

In using the intensities as an aid to assign transitions, the relative intensities rather than the absolute intensities suffice. Since the observed intensities are measured for the same sample under conditions of thermal equilibrium and at the same pressure some of the factors in \(\text{(5)}\) need not be evaluated. \(N, g_n \exp(-E_n/kT)\), and, if the spectrum covers a comparatively small range of frequencies, \(\gamma\) and \((1-e^{-\frac{\gamma}{kT}})\) may be taken as constants (whether the latter two factors may be taken as constant will depend on the accuracy to which the relative intensities are required). In this case \(\text{(5)}\) can be written as

\[
I_{n''}^{n'} = C g_n \exp(-E_n''/kT) \left| \mu_{n''} : n' \right|^2 \quad \ldots \quad \text{(6)}
\]

where

\[
C = \frac{8\gamma N}{3hc \sum g_n \exp(-E_n/kT)}
\]

With \(E_n''\) written in \(\text{Kmc.}/\text{sec.}\), \(k = 1.3807 \text{ erg.deg}^{-1}\) and \(T = 300^\circ \text{K}\) substitution of \(\text{(1)}\) into \(\text{(6)}\) yields

\[
I_{n''}^{n'} = C g_n \exp[-7.996 \times 10^{-5}(A+C)J(J+1)]
\times \exp[-7.996 \times 10^{-5}(A-C)E_r^J(k)] \left| \mu_{n''} : n' \right|^2 \quad \text{(7)}
\]

where both \(J\) and \(\tau\) are for the lower state.

(e) Hyperfine Structure

The theory of the interaction of Nuclear Electric Quadrupole Moments with Molecular Rotation, for Asymmetric Tops, has been worked out by Bragg and Golden. For a molecule containing only one nucleus where \(Q \neq 0\) the interaction energy,
in the notation of the first article, is given by

\[ E_{\text{quad}} = eQ \left\langle V_{zz} \right\rangle T(F) \]  \hspace{1cm} (8)

where \( Q \) = nuclear quadrupole moment.

\[ T(F) = \frac{3/4C(C+1) - J(J+1)I(I+1)}{2J(2J-1)I(2I-1)} \]

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

\[ C = F(F+1) - J(J+1) - I(I+1) \]

\[ \left\langle V_{zz} \right\rangle = \left( \frac{\partial^2 V}{\partial z^2} \right)_{A} \]

\( V \) = electrostatic potential at the quadrupole nucleus and \( A \) is a space-fixed axis.

Bragg and Golden show that the dependence of \( \left\langle V_{zz} \right\rangle \) on the rotational quantum numbers, and quantities which are constant for a given vibrational and electronic state, may be evaluated by use of the table of reduced energies given by \((\text{KHC})^{12}\). The expression for \( \left\langle V_{zz} \right\rangle \) derived in the second paper is

\[ \left\langle V_{zz} \right\rangle = \frac{1}{(2J+3)(J+1)} \left\{ V_{aa} \left[ J(J+1) + E_{E}^{J}(\kappa) - (J+1)\frac{J}{\kappa} \right] \right. \]

\[ + 2V_{bb} \frac{J}{\kappa} \left[ J^{2}(\kappa) - E_{E}^{J}(\kappa) + (\kappa-1)\frac{J}{\kappa} \right] \]

\[ \left. + V_{cc} \left[ J^{2}(\kappa) - E_{E}^{J}(\kappa) + (\kappa-1)\frac{J}{\kappa} \right] \right\}. \]  \hspace{1cm} (9)

where \( V_{aa}, \ V_{bb}, \ V_{cc} \) are components of the dyadic \( V E \) along the principal axes of the top.

By use of the relation \( V_{aa} + V_{bb} + V_{cc} = 0 \), which stems from Laplace's equation \( \nabla^2 V = 0 \), (9) may be rearranged to give
\[ \langle V_{zz} \rangle = \frac{1}{(2J+3)(J+1)} \left\{ V_{aa} \left[ J(J+1) + E^J_\tau(\kappa) - (\kappa+3)\frac{\partial E^J_\tau(\kappa)}{\partial \kappa} \right] + V_{cc} \left[ J(J+1) - E^J_\tau(\kappa) + (\kappa-3)\frac{\partial E^J_\tau(\kappa)}{\partial \kappa} \right] \right\} \tag{10} \]

It is convenient to rewrite (8) in the form

\[ E_{\text{quad}} = eQLU(F) \tag{11} \]

where from (9) and (10)

\[ L = \frac{\frac{1}{2}C(C+1) - J(J+1)I(I+1)}{2I(2I-1)J(J+1)2J-1)(2J+3)} \tag{11a} \]

\[ U(F) = \frac{\frac{1}{2}C(C+1) - J(J+1)I(I+1)}{2I(2I-1)J(J+1)2J-1)(2J+3)} \tag{11b} \]

The energy of a state characterized by the quantum numbers \( J, F \) and the pseudo quantum number \( \tau \) thus becomes

\[ E^{JF,\tau}_{\text{quad}} = E^{JF}_{\text{quad}} \tag{12} \]

where \( E^{JF}_{\tau}(abc) \) is the energy of the unperturbed state and the quadrupole interaction term \( E^{J}_{\tau,\text{quad}} \) takes on \( 2I + 1 \) values for \( J \ll I \).

For a transition between any two states we have the selection rule \( \Delta F = 0, \pm 1 \) in addition to those already imposed on \( J, K_- \) and \( K_+ \).

The relative intensities of the different hyperfine components of a given rotational transition may be determined from the weights \( 2F+1 \) of the upper and lower levels as in atomic spectra. Numerical values for the relative intensities up to \( J = 6 \) are given by White\textsuperscript{19} and the pertinent formula by Gordy\textsuperscript{1}. 
Chapter IV

ANALYSIS OF THE SPECTRUM

The best aid to assigning J values to the observed lines is by use of the Stark Effect. Methods of using both the number of Stark components and also the relative intensities of the components to identify the line are given by Golden and Wilson\(^1\). Use may also be made of the hyperfine structure in fixing the J value, particularly where only one nucleus has a quadrupole moment since in this case the observed pattern becomes relatively simple.

The pseudo quantum numbers \(\tau\) and \(\tau'\) for the initial and final states may be obtained if J can be determined but only if conditions are particularly favorable. For a heavy molecule such as that to be investigated the thermal distribution of rotational levels has a very broad maximum at high J values. This results in a very rich spectrum in which the strongest lines occur when J is large. The Stark effect, in this case, loses its usefulness because there are so many components \((J+1)\) for each \(J_{K-1}K_{+1}\) state, and \(2J+1\) if two states are degenerate. If this is the case one must have recourse to graphical methods of analysis. The particular graphical method used depends on the molecule investigated, and the amount of data available from other sources. The following method is applicable to a molecule where the values of the interatomic distances and bond angles are known to within certain limits, and where changes in these parameters do not result in large changes in the constants \(A, B, C\) and \(K\).
FIG. 9. ILLUSTRATION OF AN $\xi - \kappa$ (FREQUENCY-ASYMMETRY PARAMETER) DIAGRAM.
The allowed transitions are divided into three classes \( \Delta J = 0, +1 \) and 
-1. Lines where \( \Delta J = 0 \) are generally the
strongest and these are assigned first. For this type of
transition the frequency of the absorption line is given by

\[
f = x \left\{ E_J^x(\kappa) - E_J^y(\kappa) \right\}
\]

where

\[
x = \frac{A-C}{2}
\]  \hspace{1cm} (13)

The effect of a change in \( x \) or \( \kappa \) on a calculated spectrum is
quite different. Depending on whether \( x \) is too small, or too
large, the spectrum is either contracted and shifted to lower
frequencies, or expanded and shifted to higher frequencies.

If \( \kappa \) changes so does the character of the whole spectrum since
the change in \( E_J^x(\kappa) - E_J^y(\kappa) \) will depend on the changes in the
reduced energies \( E_J^x(\kappa) \) and \( E_J^y(\kappa) \), which will be different for
each level. Some transitions will shift to lower frequencies and
others to higher frequencies.

Maximum and minimum values are calculated for \( x \) and
from estimated error in the known structural parameters. Assuming
an intermediate value for \( x \), all the lines which fall in a
frequency range somewhat larger than that covered experimentally
are calculated for the maximum and minimum values of \( \kappa \). A plot
of frequency against \( \kappa \) is made for each line and presented on
what we will call the \( f-\kappa \) diagram. Fig.(9). The intensity of
each line is represented by a vertical line at the top of the
diagram, the height of the line representing the relative
intensity. The bounds of the region covered experimentally
are represented by \( f_a \) and \( f_b \), the extreme values of \( \kappa \) by \( \kappa_1 \) and \( \kappa_2 \).
If the original data is correct the spectrum of all the \( \Delta J = 0 \) lines must lie in the \( f-\chi \) diagram, either in an expanded or contracted form, along some line \( \chi = \text{const} \). A rider is made of transparent paper on which the observed spectrum is represented schematically, the frequency scale, which forms the base of the rider, being the same as that in the \( f-\chi \) diagram. Fig. (9). This rider is slid around on the diagram keeping its base parallel to the frequency axis until a position is found where the observed and calculated spectra are similar. As an illustration suppose \( f_1, f_2, f_3 \) are three observed lines and that a satisfactory position of the rider has been found. If \( f'_1, f'_2, f'_3 \) are the frequencies, as read from the diagram, at which the lines representing the plot of frequency against \( \chi \) for each of the assigned transitions cuts the base of the rider, then from equation (13) the following relations hold if the base of the rider lies along the correct line \( \chi = \text{constant} \) i.e. the position of the rider must be adjusted until the following relations are obtained

\[
\frac{f_1}{f'_1} - \frac{f_2}{f'_2} = \frac{f_3}{f'_3} - \frac{f_2-f_1}{f'_2-f'_1} = \frac{f_3-f_1}{f'_3-f'_1} = \frac{f_3-f_2}{f'_3-f'_2} = \frac{x''}{x'}
\]

where \( x' \) is the value of \( x \) used to plot the diagram and \( x'' \) is the correct value of \( x \) which is to be found. The correct value for \( \chi \) may be obtained from the \( \chi \) ordinate.

Once identification has been made \( x'' \) and \( \chi \) can be obtained more accurately by the following method. If \( f_1, f_2 \) are observed frequencies of two lines where \( \Delta J = 0 \) then from (13)
\[ \frac{f_1}{f_2} = \frac{E^J_{\tau}(\kappa) - E^J_{\tau'}(\kappa)}{E^J_{\tau''}(\kappa) - E^J_{\tau'''}(\kappa)} = \phi(\kappa) \quad \ldots \quad (14) \]

With the values of \( J, J', \tau, \tau', \tau'', \tau''' \), known the right hand side of this equation is a function of alone. Thus \( \phi(\kappa) \) may be plotted against \( \kappa \) by use of the (KHC) tables and \( \kappa \) determined. Once \( \kappa \) is known the numerator and denominator of (14) may be evaluated from the tables and substitution into the two equations for \( f_1 \) and \( f_2 \) yields the constants \( A \) and \( C \) and from the definitions of these two quantities \( I_a \) and \( I_b \). \( B \), and thus \( I_b \), may now be evaluated from the relation

\[ \kappa = \frac{2B-A-C}{A-C} \]

There will be more lines in the observed spectrum than have been assigned at this point, i.e. those due to transitions where \( \Delta J = \pm 1 \). Once the rotational constants have been determined by use of the above method a complete spectrum, including these types of transitions, may be calculated and should be the same as that observed. If incorrect assignments were made initially this will not result, thus in assigning transitions by the graphical method the test for the correctness of the assignments is that there is a calculated transition matching each of the observed transitions.
Fig. 10a. Illustration of the two absorption lines at 25,863.53 and 25,864.99 mc./sec. of CHF2Cl, using the Stark effect Spectroscope.

Fig. 10b. Illustration of the two absorption lines at 25,863.53 and 25,864.99 mc./sec. of CHF2Cl, using the double modulation spectroscope.
Microwave Spectrum of CHF$_2$Cl in the region 23,000-27,000 mc

Table I

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Rel. Intensity</th>
<th>Frequency</th>
<th>Rel. Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>23,333.84</td>
<td>18</td>
<td>25,933.65</td>
<td>2</td>
</tr>
<tr>
<td>23,335.39</td>
<td></td>
<td>25,934.54</td>
<td></td>
</tr>
<tr>
<td>23,837.43</td>
<td>7</td>
<td>26,021.35</td>
<td>2</td>
</tr>
<tr>
<td>23,838.46</td>
<td></td>
<td>26,022.45</td>
<td></td>
</tr>
<tr>
<td>24,234.23</td>
<td>10</td>
<td>26,439.36</td>
<td>8</td>
</tr>
<tr>
<td>24,235.37</td>
<td></td>
<td>26,439.95</td>
<td></td>
</tr>
<tr>
<td>24,925.79</td>
<td>5</td>
<td>26,443.70</td>
<td>8</td>
</tr>
<tr>
<td>24,926.65</td>
<td></td>
<td>26,444.33</td>
<td></td>
</tr>
<tr>
<td>24,993.78</td>
<td>5</td>
<td>26,469.88</td>
<td></td>
</tr>
<tr>
<td>24,995.61</td>
<td></td>
<td>26,471.50</td>
<td>7</td>
</tr>
<tr>
<td>25,621.01</td>
<td>4</td>
<td>26,585.64</td>
<td></td>
</tr>
<tr>
<td>25,622.44</td>
<td></td>
<td>26,587.48</td>
<td>7</td>
</tr>
<tr>
<td>25,753.04</td>
<td>6</td>
<td>26,691.00</td>
<td></td>
</tr>
<tr>
<td>25,755.23</td>
<td></td>
<td>26,691.88</td>
<td>3</td>
</tr>
<tr>
<td>25,796.44</td>
<td>18</td>
<td>26,823.13</td>
<td></td>
</tr>
<tr>
<td>25,798.26</td>
<td></td>
<td>26,825.02</td>
<td>3</td>
</tr>
<tr>
<td>25,863.53</td>
<td>20</td>
<td>27,044.32</td>
<td></td>
</tr>
<tr>
<td>25,864.99</td>
<td></td>
<td>27,046.54</td>
<td>3</td>
</tr>
<tr>
<td>25,894.23</td>
<td>3</td>
<td>27,267.16</td>
<td></td>
</tr>
<tr>
<td>25,897.86</td>
<td></td>
<td>27,273.34</td>
<td>8</td>
</tr>
</tbody>
</table>

To face page 34
(a) **Experimental Results**

The pure rotational spectrum of CHF$_2$Cl has been measured in the region 23,000 to 27,000 mc./sec. Twenty lines have been observed all of which appear as doublets; the two components of each doublet are of approximately equal intensity. The frequency of each line is determined to within .05 mc./sec. and the observed frequencies are given in Table I. See opposite page.

Three samples of Freon 22 were used, two being commercial samples as provided by Matheson & Co., the third, which was a highly purified sample, being kindly given to us by Dr. R.C. McHarness of the Jackson Laboratory, Delaware. All samples yielded the same spectrum. The frequencies were measured using the Stark Spectroscope but, since the lines were relatively weak, it was impossible to obtain a measure of the splitting of the Stark components with the applied field. Several of the lines were examined using the double modulation Spectroscope in an endeavor to further resolve each component of the doublets, but the resolving power of the instrument was not sufficient to provide further resolution. Photographs of the two strong lines at 25,863.53 and 25,864.99 mc./sec., as they appear on the screen of the oscilloscope, when both the Stark effect and double modulation spectroscope are used, are shown in Figs. 10a and 10b.

That the doublets are real and not due to a fault in the instrument can be seen with reference to Fig. 10b. When this
picture was taken, using the double modulation spectroscope, type 'a' modulation was used. (Chapt. I, section b). The two marker pips which occur with this type of modulation appear close together under one line. If one line is the image of the other there would be a marker pip under each line.

The measurements were made at a pressure of .01 mm. of mercury, the line widths, as measured, at this pressure were of the order of .5 mc./sec.

(b) Molecular Structure

The best values of interatomic distances and bond angles available were those from a study of the molecule by Electron Diffraction. The interatomic distances and bond angles as found by this method are, C-F = 1.36 Å, C-Cl = 1.73 Å, F-F = 2.24 Å, Cl-F = 2.56 Å. Bond angle FCF = 110° ± 1° and the angle FCCl = 110° ± 1°. The C-H distance and the angle HCCl were assumed to be 1.11 Å and 106°. The error in these two assumptions may be neglected in the following calculations since the mass of the hydrogen is much less than that of the chlorine and fluorine, and thus the contribution of the Hydrogen to the moments of inertia relatively small.

With the atoms occurring in their natural state the abundances of the isotopes are such that only contributions to the spectrum from the two forms \( ^{12}\text{C}^{1}H_{1}^{19}\text{F}_{2}^{35}\text{Cl}^{35} \) and \( ^{12}\text{C}^{1}H_{1}^{19}\text{F}_{2}^{37}\text{Cl}^{37} \) can be expected. The relative abundance of \( ^{35}\text{Cl} \) to \( ^{37}\text{Cl} \) is 75.4/24.6 hence the relative intensities of the lines from each form will be approximately 3:1.
FIG. II A. MODEL OF THE MOLECULE CHF₂Cl.

FIG. II B. MODEL OF CHF₂Cl WITH THE H, C, CL NUCLEI IN THE PLANE OF THE PAPER.
Using the foregoing data a model of the molecule was constructed and is shown in Figs. 11a and 11b. The molecule belongs to the point group $C_s$ having one plane of symmetry, namely that containing the H, C and Cl atoms. The centre of gravity and two of the Principal Axes must lie in this plane the third being perpendicular to it and passing through the centre of gravity. $X, Y, Z$ define a set of axes fixed to the molecule chosen so that the origin lies at the centre of gravity, and the $X, Y$ axes lie in the plane of symmetry, with the $Y$ axis parallel to the C-H bond. $\theta$ is the angle PCP, and $\phi$ the angle between the C-Cl bond and the perpendicular to the C-H bond which lies in the plane of symmetry. The constants $A, B, C$ and $\kappa$ were calculated for three different values of $\phi$ and two different values of $\theta$, the extreme values of which were chosen such that the molecule was distorted beyond the limits imposed by the estimated errors in the electron diffraction data. These values for the molecule $\text{C}^{12}\text{H}^1\text{F}^{19}\text{Cl}^{35}$ are given in Table II below.

The axis of intermediate moment of inertia is found to coincide with the $Z$ axis, and the axes of greatest and least moment of inertia to lie in the plane of symmetry, with the axis of greatest moment of inertia inclined at a small angle $\epsilon$ to the $Y$ axis.

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$\phi$</th>
<th>$A$ (Km/c)</th>
<th>$B$ (Km/c)</th>
<th>$C$ (Km/c)</th>
<th>$\kappa$</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>110.5°</td>
<td>14°</td>
<td>10.11592</td>
<td>4.88432</td>
<td>3.40562</td>
<td>-.55927</td>
<td>.72</td>
</tr>
<tr>
<td>110.5°</td>
<td>16°</td>
<td>9.76325</td>
<td>4.93400</td>
<td>3.47155</td>
<td>-.54511</td>
<td>2.28</td>
</tr>
<tr>
<td>110.5°</td>
<td>18°</td>
<td>9.72953</td>
<td>4.98777</td>
<td>3.50243</td>
<td>-.52294</td>
<td>3.87</td>
</tr>
<tr>
<td>106.0°</td>
<td>16°</td>
<td>10.17636</td>
<td>4.79760</td>
<td>3.47700</td>
<td>-.60576</td>
<td>1.56</td>
</tr>
</tbody>
</table>
(c) **Analysis of Observed Spectrum**

The spectrum obtained will actually be due to an interlacing of the spectra of the two isotopic species, thus some of the weaker lines may be expected to be due to the molecule $^{12}\text{C}^{1}\text{H}^{1}\text{F}_{2}^{19}\text{Cl}^{37}$. This must be kept in mind when analysing the spectrum.

Since the Stark components were too weak to be observed experimentally, and the hyperfine structure was apparently not completely resolved, recourse had to be made to graphical methods in an attempt to analyse the observed spectrum. Fortunately the constants $A$, $B$, $C$ and $\kappa$ can be evaluated to within reasonable limits, as inspection of Table II shows, and the method of analysis described in Chapt. III is applicable. An estimation of the relative intensities of the lines due to various types of transitions is in order at this point, since some types give very weak lines which will not have been observed.

In order to apply the three rules (3), (4), (5) Chapt. III(b), an approximation as to the orientation of the dipole moment with respect to the principal axes may be obtained by adding vectorially the individual bond moments (assumed to be along the internuclear lines), to obtain the resultant moment. Taking the individual moments in Debye Units as $\mu_{\text{C-H}} = .4$, $\mu_{\text{C-Cl}} = 1.5$, $\mu_{\text{C-F}} = 1.4^{16}$, the dipole moment is found to lie in the $XY$ plane at an angle of $30^0$ to the C-H bond. There is no component of the moment in the (b) axis, hence only a and c type transitions are allowed. The intensities of
lines arising from a and c type transitions will be proportional to the square of the component of the dipole moment in the a and c axes. With the above estimation of the orientation of the dipole moment the ratio of the square of the components of the dipole moment in the a and c axes is approximately 1/130. From the signal to noise ratio of the strongest lines observed it was estimated that lines whose relative intensity were less than 1/20 of the strongest lines would not be detected so that only c type transitions need be considered in the analysis. From Chapt. III(b) it follows that Δc must be odd.

To evaluate relative intensities equation (7) Chapt. III(d) will be used. The range of the frequency is 23 to 27 Kmc./sec., and use of (7) can lead to an error as large as 15% if a line at 27 Kmc./sec. is compared with a line at 23 Kmc./sec. However to begin with this error will be accepted, since the relative intensities have only been measured to an accuracy of 10%.

There is no axis of symmetry for this molecule and thus an exchange of the two identical nuclei (Fluorines) cannot be brought about by a simple rotation about one of the principal axes. The statistical weight factor g_I due to the spin of the nuclei will be the same for all levels and may be included in the constant C of (7). Assuming values of (A+C) = 13 Kmc./sec. and (A-C) = 6 Kmc./sec. and writing the statistical weight factor for each J level as

\[ g_n = 2J+1, \]

(7) becomes

\[ I_n'';n'' = C(2J+1) \exp\left[-.00103J(J+1)\right] \exp[-.00048 E^{J}_c(k)] \gamma \mu_n'';n'' \left| J_n'';n'' \right|^2 \quad (14) \]
FIG. 12. THERMAL DISTRIBUTION OF ENERGY LEVELS
FOR CH₂Cl.

FIG. 13. ILLUSTRATION OF A TRANSITION ΔJ = -1.
The first exponential term predominates in the above expression and the product of this and \((2J \ell)\) is plotted against \(J\). Fig. 12. It is to be remarked that the thermal distribution of levels is such as to be favorable for a transition over a very large range of \(J\).

The energy levels for this asymmetric top are spaced so that the transitions which could give a line in the observed region of the spectrum usually occur between levels where \(B_\ell^J(\kappa)\) is negative. This results in the exponent of the second exponential in \((14)\) becoming positive and the thermal distribution of energy levels being rather more favorable, particularly for high \(J\) values where \(B_\ell^J(\kappa)\) is large, than is indicated in Fig. 12.

For a transition of the type \(\Delta J = -1\) to occur in the observed region one of the higher levels of the lower \(J\) state must combine with one of the lower levels of the higher \(J\) state. Fig. 13. If one recalls the method of assigning it is apparent that will be large. All possible transitions of this type have been calculated up to \(J = 10\) and in every case \(\Delta \tau > 5\). As was stated in Chapt II(d) this type of transition is very weak and thus may be neglected.

The result of all this is that in the analysis of the spectrum we need only consider the transitions \(\Delta J = 0, \Delta \tau = 1, 3\) and \(\Delta J = +1, \Delta \tau = 1, 3\).

From the intensity considerations it appears that all the lines may arise from transitions involving \(J\) values beyond the extent of existing tables i.e. \(J > 12\) but, since it is only necessary to identify two lines to calculate the moments of inertia,
FIG. 14. THE J-K DIAGRAM FOR TRANSITIONS ΔJ=0. OF CH₄Cl.

RELATIVE INTENSITIES.

INTENSITIES ARE CALCULATED FOR K* = 5.

FREQUENCY KMC/SEC.

20 22 24 26 28 30 32 34 36 38

212 - 220

313 - 321

414 - 422

624 - 634

1234 - 1249

515 - 523

321 - 331

1138 - 1148

322 - 330

423 - 431

524 - 532

625 - 633

1037 - 1047

1146 - 1156

936 - 946

734 - 744

1248 - 1258

835 - 845
an attempt at an analysis was made.

Assuming a value of \( x = 3.2 \text{Kmc}, \text{eqn. 13} \), lines of the type \( \Delta J = 0 \), between 18,000 and 40,000 mc./sec., were calculated up to \( J = 12 \) from the (KHC) tables for \( \kappa = -0.4, -0.5, -0.6, -0.7 \). This resulted in what we have termed the \( f-\kappa \) diagram Fig. 14. A rider containing the observed spectrum on the same frequency scale is shown superimposed. Examination of the diagram shows that the rider may be placed in positions on the table such that none of the strong lines, which result when \( \Delta J = 0 \) and \( J \) is high, will be observed. If this is the case then some of the types of lines which we have neglected must be reconsidered, since the intensities of these, when \( J \) is large, may be sufficiently strong, due to a favorable Boltzmann factor, to compare in intensity with the lines given in the diagram where \( J \) is low (\( J < 7 \)) and the Boltzmann factor unfavorable. If however any of the strong lines do occur in the spectrum (and we note that at the most we can only expect two of them) they should be very marked. Inspection of the observed spectrum shows that there are three reasonably strong lines but it is impossible to fit these to any lines on the diagram.

It became imperative at this point to try and determine how many lines where \( \Delta J = 0 \) would be expected to occur in the diagram for \( J > 12 \) i.e. beyond the range of the available tables. By rearranging the existing tables it was possible by extrapolation to show that there would probably be one line of the types \( \Delta J = 0, \Delta \tau = 1 \) which would fall in the region of the diagram for every second \( J \) value 12 (see appendix). This being the case the strongest lines in the diagram will appear as the weaker lines
in the spectrum. This is the maximum amount of information available from the diagram in its incomplete form and attention was turned to the hyperfine structure itself.

(d) **Hyperfine Structure**

The spin of Cl being 3/2 and this being the only nucleus in the molecule whose spin is $>1$ then the hyperfine structure will only be caused by the quadrupole coupling of the chlorine nucleus. Inspection of the table of relative intensities for this case in White $^{19}$ shows that for high J values there will be four hyperfine components whose intensities are very much stronger than the others. For $\Delta J = 0$ these are the four transitions where $\Delta F = 0$, and for $\Delta J = +1$ where $\Delta F = 1$.

For example, for $\Delta J = 0$ and for $J = 9$ the ratio of the intensities of each of the four components where $\Delta F = 0$ to those where $\Delta F = \pm 1$ is approximately 1/50.

The strongest lines in the spectrum are expected to arise from transitions where $\Delta J = 0$ and $\Delta \tau = 1$ hence the hyperfine structure was calculated for this type of line. Since the spectrum is expected to be due to transitions where $J$ is high only the four strong components were considered. If the energies are written in units of $mc./sec.$ then, for transitions where $\Delta J = 0$, $\Delta \tau = 1$, the frequency of each of the hyperfine components, by use of (2) and (12), is given by

$$f_{mc./sec.} = \left\{ E_J^\tau(k) - E_J^\tau(k) \right\} + \left\{ E_{J,quad}^{JF} - E_{\tau,quad}^{JF} \right\} \quad \cdots (15)$$
FIG. 15. ILLUSTRATION OF THE FORM OF THE HYPERFINE STRUCTURE FOR TRANSITIONS WHERE $\Delta J = 0$ FOR CHFCl₂. ONLY THE FOUR STRONG COMPONENTS $\Delta F = 0$ ARE SHOWN.
If $\Delta f$ is the deviation of the hyperfine component from the unperturbed line, due to the quadrupole interaction, then from (15)

$$\Delta f = E_{\text{quad}} - E_{\text{quad}}$$

Substituting for $E_{\text{quad}}$ from (11) Chapt. II(e) we have for $\Delta J = 0$

$$\Delta F = 0$$

$$f = eQ(L_\tau,\tau - L_\tau) U(P) \quad \ldots \quad (16)$$

From this equation it is observed that the form of the hyperfine structure is given by the factor $U(P)$, since $(L_\tau,\tau - L_\tau)$ depends only on $J, \tau, \tau_h, I$ and is thus constant for the four hyperfine components of any transition.

Values of $U(P)$ are calculated for $J = 8$ to $J = 20$ and presented in table III (see below). Inspection shows that for each $J$ level the four components group into two pairs, thus resulting in a spectrum whose form will be as in Fig. 15. As $J$ increases the two pairs of lines move closer together and the separation of the two lines in each pair becomes smaller.

If $\Delta f_p$ is written as the shift in frequency of the hyperfine components from the unperturbed line, then, for $\Delta J = 0, \Delta F = 0$, the ratios

$$e = \frac{\Delta f_{J-3/2} - \Delta f_{J+1/2}}{\Delta f_{J+3/2} - \Delta f_{J-1/2}}, \quad f = \frac{\Delta f_{J-3/2} - \Delta f_{J+3/2}}{\Delta f_{J+3/2} - \Delta f_{J-1/2}}, \quad g = \frac{\Delta f_{J+1/2} - \Delta f_{J-1/2}}{\Delta f_{J+3/2} - \Delta f_{J-1/2}}$$

will depend only on $U(P)$, which may be calculated exactly. This immediately gives a very good method for fixing the $J$ value since these three ratios depend only on $J$ and $I$. Values of $e, f$ and $g$ have been calculated along with $U(P)$ in table (III)
### Table III

Hyperfine structure constants

<table>
<thead>
<tr>
<th>J</th>
<th>F</th>
<th>$U(F) \times 10^3$</th>
<th>$\epsilon$</th>
<th>$f$</th>
<th>$g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>19/2</td>
<td>1.4620</td>
<td>1.44</td>
<td>.218</td>
<td>.218</td>
</tr>
<tr>
<td>8</td>
<td>17/2</td>
<td>-2.0102</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>15/2</td>
<td>-1.3889</td>
<td>1.44</td>
<td>.218</td>
<td>.218</td>
</tr>
<tr>
<td>8</td>
<td>13/2</td>
<td>2.0833</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>21/2</td>
<td>1.1905</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>19/2</td>
<td>-1.5873</td>
<td>1.34</td>
<td>.169</td>
<td>.169</td>
</tr>
<tr>
<td>9</td>
<td>17/2</td>
<td>-1.1438</td>
<td>1.34</td>
<td>.169</td>
<td>.169</td>
</tr>
<tr>
<td>9</td>
<td>15/2</td>
<td>1.6339</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>23/2</td>
<td>0.9881</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>21/2</td>
<td>-1.2846</td>
<td>1.34</td>
<td>.169</td>
<td>.169</td>
</tr>
<tr>
<td>10</td>
<td>19/2</td>
<td>-0.9570</td>
<td>1.34</td>
<td>.169</td>
<td>.169</td>
</tr>
<tr>
<td>10</td>
<td>17/2</td>
<td>1.3158</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>25/2</td>
<td>0.8333</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>23/2</td>
<td>-1.0606</td>
<td>1.30</td>
<td>.151</td>
<td>.151</td>
</tr>
<tr>
<td>11</td>
<td>21/2</td>
<td>-0.8117</td>
<td>1.30</td>
<td>.151</td>
<td>.151</td>
</tr>
<tr>
<td>11</td>
<td>19/2</td>
<td>1.0823</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>27/2</td>
<td>0.7122</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>25/2</td>
<td>-0.8903</td>
<td>1.27</td>
<td>.137</td>
<td>.137</td>
</tr>
<tr>
<td>12</td>
<td>23/2</td>
<td>-0.6967</td>
<td>1.27</td>
<td>.137</td>
<td>.137</td>
</tr>
<tr>
<td>12</td>
<td>21/2</td>
<td>0.9057</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>29/2</td>
<td>0.6158</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>27/2</td>
<td>-0.7579</td>
<td>1.25</td>
<td>.126</td>
<td>.126</td>
</tr>
<tr>
<td>13</td>
<td>25/2</td>
<td>-0.6044</td>
<td>1.25</td>
<td>.126</td>
<td>.126</td>
</tr>
<tr>
<td>13</td>
<td>23/2</td>
<td>0.7692</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>31/2</td>
<td>0.5348</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>29/2</td>
<td>-0.6493</td>
<td>1.23</td>
<td>.116</td>
<td>.116</td>
</tr>
<tr>
<td>14</td>
<td>27/2</td>
<td>-0.5263</td>
<td>1.23</td>
<td>.116</td>
<td>.116</td>
</tr>
<tr>
<td>14</td>
<td>25/2</td>
<td>0.6578</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>33/2</td>
<td>0.4735</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>31/2</td>
<td>-0.5682</td>
<td>1.216</td>
<td>.108</td>
<td>.108</td>
</tr>
<tr>
<td>15</td>
<td>29/2</td>
<td>-0.4670</td>
<td>1.216</td>
<td>.108</td>
<td>.108</td>
</tr>
<tr>
<td>15</td>
<td>27/2</td>
<td>0.5747</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>F</td>
<td>(U(F) \times 10^3)</td>
<td>e</td>
<td>f</td>
<td>g</td>
</tr>
<tr>
<td>----</td>
<td>--------</td>
<td>----------------------</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>16</td>
<td>35/2</td>
<td>0.4202</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>33/2</td>
<td>-0.4989</td>
<td>1.20</td>
<td>.101</td>
<td>.101</td>
</tr>
<tr>
<td>16</td>
<td>31/2</td>
<td>-0.4151</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>29/2</td>
<td>0.5040</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>37/2</td>
<td>0.3754</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>35/2</td>
<td>-0.4416</td>
<td>1.19</td>
<td>.95</td>
<td>.95</td>
</tr>
<tr>
<td>17</td>
<td>33/2</td>
<td>-0.3714</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>31/2</td>
<td>0.4457</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>39/2</td>
<td>0.3196</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>37/2</td>
<td>-0.3729</td>
<td>1.18</td>
<td>.88</td>
<td>.88</td>
</tr>
<tr>
<td>18</td>
<td>35/2</td>
<td>-0.3166</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>33/2</td>
<td>0.3759</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>41/2</td>
<td>0.3049</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>39/2</td>
<td>-0.3530</td>
<td>1.17</td>
<td>.84</td>
<td>.84</td>
</tr>
<tr>
<td>19</td>
<td>37/2</td>
<td>-0.3022</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>35/2</td>
<td>0.3556</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>43/2</td>
<td>0.2769</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>41/2</td>
<td>-0.3184</td>
<td>1.16</td>
<td>.79</td>
<td>.79</td>
</tr>
<tr>
<td>20</td>
<td>39/2</td>
<td>-0.2747</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>37/2</td>
<td>0.3205</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The intensities of the four components have been calculated for \( J = 8 \) up to \( J = 12 \) and are given in Table IV (see below). The differences in the intensities of the four lines are small and decrease with increasing \( J \).

**Table IV**

Theoretical relative intensities of hyperfine components in transitions where \( \Delta J = 0 \) and \( \Delta F = 0 \)

<table>
<thead>
<tr>
<th>( J )</th>
<th>( F )</th>
<th>Rel. Int.</th>
<th>( J )</th>
<th>( F )</th>
<th>Rel. Int.</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>19/2</td>
<td>5659</td>
<td>11</td>
<td>25/2</td>
<td>13591</td>
</tr>
<tr>
<td>8</td>
<td>17/2</td>
<td>4949</td>
<td>11</td>
<td>23/2</td>
<td>12352</td>
</tr>
<tr>
<td>8</td>
<td>15/2</td>
<td>4373</td>
<td>11</td>
<td>21/2</td>
<td>11296</td>
</tr>
<tr>
<td>8</td>
<td>13/2</td>
<td>3931</td>
<td>11</td>
<td>19/2</td>
<td>10423</td>
</tr>
<tr>
<td>9</td>
<td>21/2</td>
<td>8189</td>
<td>12</td>
<td>27/2</td>
<td>17323</td>
</tr>
<tr>
<td>9</td>
<td>19/2</td>
<td>6937</td>
<td>12</td>
<td>25/2</td>
<td>15876</td>
</tr>
<tr>
<td>9</td>
<td>17/2</td>
<td>6217</td>
<td>12</td>
<td>23/2</td>
<td>14628</td>
</tr>
<tr>
<td>9</td>
<td>15/2</td>
<td>5647</td>
<td>12</td>
<td>21/2</td>
<td>13579</td>
</tr>
<tr>
<td>10</td>
<td>23/2</td>
<td>10434</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>21/2</td>
<td>9381</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>19/2</td>
<td>8508</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>17/2</td>
<td>7795</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To obtain the magnitude of the hyperfine splitting the factors \( V_{aa}, V_{cc} \) in (11) must be evaluated at the chlorine nucleus. Following Dr. C.H. Townes\(^20\) these may be estimated by assuming that the charge distribution in the vicinity of the
chlorine nucleus is symmetrical about the C-Cl bond and that the
component of $\nabla E$ along the bond is the same as that observed
experimentally in a similar molecule.

If the dyadic $\nabla E_{zz}$ is expressed in the charge symmetric
cordinate system $X', Y', Z'$, where $Z'$ lies along the C-Cl bond
and $X'$ is parallel to $I_B$, transformation from the $X', Y', Z'$
cordinates to those defined by the principal axes gives

$$V_{aa} = V_{Z'Z'} \cos^2 \alpha - 2V_{Z'Y'} \sin \alpha \cos \alpha + V_{Y'Y'} \sin^2 \alpha \quad (17a)$$

$$V_{cc} = V_{Z'Z'} \sin^2 \alpha + 2V_{Z'Y'} \sin \alpha \cos \alpha + V_{Y'Y'} \cos^2 \alpha \quad (17b)$$

where $\alpha = (\phi - \beta)$ is the angle between $a$ and $Z'$. See Fig. 11.

In the charge symmetric co-ordinates $(X', Y', Z')$ the
following relations hold

$$V_{Z'Y'} = V_{Y'Z'} = 0$$

$$V_{X'X'} = V_{Y'Y'} = -\frac{3}{2}V_{Z'Z'}$$

and substitution of these into $(17a)$ and $(17b)$ gives

$$V_{aa} = -\frac{3}{2}V_{Z'Z'}(1-3\cos^2 \alpha) \quad \ldots \quad (18a)$$

$$V_{cc} = -\frac{3}{2}V_{Z'Z'}(1-3\sin^2 \alpha) \quad \ldots \quad (18b)$$

Taking $\alpha = 16^\circ$ and $K = -0.5$ and substituting $(18a)$ and
$(18b)$ in $(11a)$ then $(11a)$ in $(16)$ we obtain

$$f = eQV_{Z'Z'}\left[1.26\left\{E^J_{\text{cm}}(k) - E^J_{\text{c}}(k)\right\} - \frac{\partial E^J_{\text{cm}}(k)}{\partial K} - \frac{\partial E^J_{\text{c}}(k)}{\partial K}\right] \ldots (19)$$
A value of \(-78.05\) mc./sec. is assumed for \(eQV_{z^2}\), this being the value obtained experimentally for the molecule \(\text{CF}_3\text{Cl}^{23}\). With \(K = -0.5\) the hyperfine splitting for five of the strong lines where \(J = 12\) which may occur in the region of the spectrum covered, are calculated and given in table V below.

**Table V**

Theoretical hyperfine splitting (\(\Delta_f\) mc./sec.) about the unperturbed line for transitions where \(\Delta J = 0\) and \(\Delta F = 0\)

<table>
<thead>
<tr>
<th>Transition</th>
<th>J-3/2</th>
<th>J+3/2</th>
<th>J-1/2</th>
<th>J+1/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>8(<em>{35}) - 8(</em>{45})</td>
<td>-4.14</td>
<td>-2.90</td>
<td>2.76</td>
<td>3.99</td>
</tr>
<tr>
<td>9(<em>{36}) - 9(</em>{46})</td>
<td>-2.96</td>
<td>-2.15</td>
<td>2.06</td>
<td>2.88</td>
</tr>
<tr>
<td>10(<em>{37}) - 10(</em>{47})</td>
<td>-2.62</td>
<td>-1.97</td>
<td>1.91</td>
<td>2.56</td>
</tr>
<tr>
<td>11(<em>{47}) - 11(</em>{57})</td>
<td>-3.09</td>
<td>-2.38</td>
<td>2.3</td>
<td>3.03</td>
</tr>
<tr>
<td>12(<em>{48}) - 12(</em>{58})</td>
<td>-2.66</td>
<td>-2.09</td>
<td>2.05</td>
<td>2.61</td>
</tr>
</tbody>
</table>

It is estimated for the observed spectrum that the spectroscope cannot resolve two lines which lie closer together than about .5 mc./sec. Inspection of table V shows that all these lines should be resolved completely, and that the spacing of the hyperfine components for the transition \(12_{48} - 12_{58}\) is verging on the limit of resolution. Since the spacing between hyperfine components should in general decrease with increasing \(J\), for \(J = 12\) the lines should be expected to appear as doublets, and the separation between the two lines of a doublet should be \(<4\) mc./sec. This is exactly what is observed (see Fig. 10 and table I) and confirms the calculations on line intensities and line frequencies, from which it appeared that the
Fig. 16. Photograph of the four lines which are the resolved hyperfine structure for the transition $^{10}_{37} - ^{10}_{47}$

To face page 48
observed spectrum arises from transitions involving values of \( J > 12 \).

By use of the \( f-K \) diagram it is apparent that at the most two of the transitions in table V. can appear in the spectrum. If the four lines at 26,441 mc./sec. are taken as the completely resolved components of one transition, then comparison of observed and theoretical values of \( e, f, \) and \( g \) results in assigning the transition 10\( _{37} \) - 10\( _{47} \) to this line, within the limits of experimental error. The experimental values of \( e, f, \) and \( g \) for this line are 1.325, .157, .168 respectively, and these are to be compared with the calculated values in table III. The oscilloscope trace of these four lines is shown in Fig.16 and the calculated and observed hyperfine components in Fig. 17. It is worth noting that the main discrepancy between observed and calculated values is in the scale factor. This factor can be expected to be incorrect since the calculated hyperfine structure is for a value of \( \kappa = -0.5 \) which is only an estimate and will not be correct.

If this assignment is made it is to be observed from the \( f-K \) diagram that there will be no other lines of the type \( \Delta \kappa = 0, \Delta J = 0 \) which will fall in the region 23,000 mc./sec. to 27,000 mc./sec. in which spectrum is observed.

(e) Summary

The analysis, as far as it has been taken, is by no means complete but this preliminary work is very promising. As has been shown it is possible to limit the number of probable transitions but until extensions to the (KHC) tables are available it will be impossible to make a complete analysis. It may be noted that if one identification can be made the analysis becomes
much simpler because this immediately restricts the movement of the rider on the $f-K$ diagram. (Fig. 14)

The most hopeful method of identifying lines appears to be by use of the hyperfine structure. In the 1st order calculation this is quite symmetrical for transitions where $\Delta J = 0$ and $J$ is high. The hyperfine structure for transitions where $\Delta J = +1$ has not been completely calculated but it may be remarked that for these lines there will again be four very strong components. In this case however the hyperfine structure should not be symmetrical, since the factor $U(F)$ in (11) will not be the same for the initial and final states, as is the case when $\Delta F = 0, \Delta J = 0$. If separations of hyperfine components can be measured with reasonable accuracy then it seems possible that the two types of transition may be identified from the form of the hyperfine structure.

Nothing has been said about the transitions $\Delta J = +1$ in the foregoing analysis. In the calculations which have been made for this type of line one point is worthy of note. The $2J+1$ levels in any $J$ set tend to group into pairs particularly at the two extremes of the set (see Fig. 8). The total number of levels is odd and there must be an odd line which occurs somewhere near the middle of the set; the levels in this region of the set do not pair off very strongly. The spacing between each pair is largest at the extremes and decreases towards the centre of the set. The result of this type of distribution of the levels is that all the transitions $J \to 0$ which could give rise to a line in the observed spectrum, occur in the region where there is little or no pairing of levels. This is not the case when $\Delta J = +1$, and thus, one would expect that
a natural consequence of the pairing of levels is that the absorption lines should run in pairs. For example the two transitions $9_{73} - 10_{65}$ and $9_{72} - 10_{64}$ should give rise to two lines separated by about $100$ mc./sec. In attemption to identify this type of line a search should be made for a similar line nearby.

It should be possible, if the correct assignment of the $10_{37} - 10_{47}$ transition has been made, to obtain the moments of inertia without an extension to the (KHC) tables. Reference to the $f - \kappa$ diagram (Fig. 14) will show that the lines due to the two transitions $11_{58} - 11_{48}$ and $9_{36} - 9_{46}$ should be observed at approximately $20,500$ mc./sec. and $31,500$ mc./sec., and reference to table V will show that the hyperfine structure of these two lines should be completely resolved. If these two lines can be obtained then the moments of inertia can be calculated. (See Chapt. IV). Unfortunately suitable klystrons were not available, in our laboratory, to extend the range of the spectroscope at the time this thesis was written.

The spin of Cl$^{37}$ is the same as that of Cl$^{35}$ (3/2) so that the table for the hyperfine structure constants (Table III) can be used for the analysis of the molecule $^{12}H_2^{19}F_2^{19}Cl^{37}$ as well as for $^{12}H_2^{19}F_2^{19}Cl^{35}$. It is then possible that the resolved line at $26,441$ mc./sec. could be due to the $10_{37} - 10_{47}$ transition in the molecule containing Cl$^{37}$. This is rather improbable however since reference to Fig. 12 and table I show that the observed relative intensity is approximately what one would expect for the transition in the molecule containing Cl$^{35}$. 
Finally it should be pointed out that the effects of centrifugal distortion have been neglected. The necessary theory for an asymmetric top has been worked out by Golden\textsuperscript{24}, who shows that the effect of this type of distortion is to increase the moments of inertia and change the asymmetry parameter ($\alpha$). Since this effect increases with $J$ it will have to be calculated to obtain an exact fit to the spectrum.
Chapter VI

THE ROTATIONAL SPECTRUM OF THE MOLECULE CHFCl₂

The pure rotational spectrum of CHFCl₂ was measured in the region 23,000 to 27,000 mc./sec. The observed lines are given in table VI (see following page). No attempt has been made to analyse the spectrum.

The model of the molecule will be similar to that for CHF₂Cl (Fig. 11), except that in this case the plane of symmetry will be the plane containing the H, C, and F atoms. Since the molecular weight of the molecule is larger than that of CHF₂Cl the moments of inertia will be larger and the observed transitions will probably involve high J values. The characteristic doubling of each line in CHF₂Cl will not appear in this case, since there are two quadrupole nuclei contributing to the quadrupole interaction (the two chlorine nuclei), and the hyperfine structure will be quite complicated. Only single lines were observed.

The observed lines were relatively weak and again no Stark components could be seen.
Microwave Spectrum of CHFCl\textsubscript{2} in the region 23,000-27,000 mc

Table VI

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Rel. Intensity</th>
<th>Frequency</th>
<th>Rel. Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>22,851.03</td>
<td>8</td>
<td>24,523.62</td>
<td>3</td>
</tr>
<tr>
<td>23,139.84</td>
<td>2</td>
<td>24,977.68</td>
<td>8</td>
</tr>
<tr>
<td>23,158.15</td>
<td>2</td>
<td>25,535.08</td>
<td>3</td>
</tr>
<tr>
<td>23,288.59</td>
<td>6</td>
<td>25,577.54</td>
<td>4</td>
</tr>
<tr>
<td>23,390.08</td>
<td>2</td>
<td>25,719.21</td>
<td>5</td>
</tr>
<tr>
<td>23,918.55</td>
<td>2</td>
<td>25,850.50</td>
<td>4</td>
</tr>
<tr>
<td>23,923.11</td>
<td>1</td>
<td>25,897.85</td>
<td>1</td>
</tr>
<tr>
<td>23,560.17</td>
<td>10</td>
<td>25,962.45</td>
<td>4</td>
</tr>
<tr>
<td>23,895.99</td>
<td>2</td>
<td>25,987.72</td>
<td>9</td>
</tr>
<tr>
<td>23,945.38</td>
<td>15</td>
<td>26,180.85</td>
<td>2</td>
</tr>
<tr>
<td>24,095.53</td>
<td>10</td>
<td>26,310.34</td>
<td>16</td>
</tr>
<tr>
<td>24,155.32</td>
<td>2</td>
<td>26,484.51</td>
<td>1</td>
</tr>
<tr>
<td>24,178.77</td>
<td>4</td>
<td>26,493.31</td>
<td>1</td>
</tr>
<tr>
<td>24,320.81</td>
<td>7</td>
<td>26,544.88</td>
<td>4</td>
</tr>
<tr>
<td>24,380.95</td>
<td>1</td>
<td>26,662.32</td>
<td>20</td>
</tr>
<tr>
<td>24,509.71</td>
<td>1</td>
<td>26,972.36</td>
<td>3</td>
</tr>
</tbody>
</table>
The (KHC) Tables are rearranged to give numerical values of \( \left\{ E_J^J(K) - E_J^J(\kappa) \right\} \) for values of \( J \) from 0 to 12 and of \( \kappa \) from 0 to -8, for \( \kappa = -0.5 \). The resulting table is split into two parts, one where \( J \) is even and the other where \( J \) is odd, only the first part is given here.

The value of \( J \) is given in the left hand column and the values of \( \kappa \) and \( \tau \) at the top of each column. The frequencies of transitions where \( \Delta J = 0, \Delta \kappa = 1 \) may be obtained by use of the relation

\[
f = \frac{A-C}{2} \left\{ E_J^J(K) - E_J^J(\kappa) \right\}
\]

The columns are classified as to the type of transition a or c. This is given at the head of each column.

<table>
<thead>
<tr>
<th>( J )</th>
<th>a</th>
<th>c</th>
<th>a</th>
<th>c</th>
<th>a</th>
<th>c</th>
<th>a</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5000</td>
<td>1.1056</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.3544</td>
<td>2.9997</td>
<td>4.9025</td>
<td>.3707</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.0032</td>
<td>5.6467</td>
<td>4.6276</td>
<td>1.3439</td>
<td>9.4950</td>
<td>.0798</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.4008</td>
<td>12.5651</td>
<td>2.9317</td>
<td>5.6472</td>
<td>8.8036</td>
<td>1.1530</td>
<td>14.6853</td>
<td>.0853</td>
</tr>
<tr>
<td>6</td>
<td>16.3136</td>
<td>8.9414</td>
<td>7.5782</td>
<td>2.5175</td>
<td>14.5909</td>
<td>.3097</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the molecule CHF₂Cl, \( \frac{A-C}{2} = 3.2 \text{Kmc./sec.} \) thus a transition should appear in the region of the spectrum covered i.e. in the region 23,000 to 27,000 mc./sec. when \( \left\{ E_J^J(K) - E_J^J(\kappa) \right\} = 8 \)

From the above table it is seen that a line can be expected from the transition 12₋₄ - 12₋₃ and, if the tables are extrapolated, lines are to be expected from the transitions 1₄₋₆ - 1₄₋₅ etc.

If only c type transitions are considered.
REFERENCES

19. H.E. White, Introduction to Atomic Spectra,  
21. S. Golden and E.B. Wilson, Jr.  