

THE MICROWAVE SPECTRUM OF CHClF_2
AND THE
STARK EFFECT OF CHClF_2 , CClF_3 , and NOCl

A THESIS

Presented to
the Faculty of the Graduate Division

By

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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy in the School of Physics

Georgia Institute of Technology

June 1960

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Date Approved by Chairman: May 10, 1960

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ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. T. L. Weatherly, his advisor, and to Dr. J. Q. Williams for suggesting topics for the thesis and for the many helpful consultations. The author acknowledges the help of the Southern Fellowships Fund for the Faculty Fellowship which he held during the 1958-1959 academic year which helped make the creation of this thesis possible. Dr. I. E. Perlin is thanked for several fruitful discussions with the author. Louise, the author's wife, who helped with her typing and encouragement, and the many other people whose efforts contributed to make this thesis possible are sincerely thanked.

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SUMMARY

Microwave spectroscopy provides a useful and accurate means of measuring absorption transitions between the rotational energy levels of gas molecules when the molecules have permanent electric dipole moments or magnetic dipole moments. From the microwave absorption spectrum one can determine much information about molecules including the nuclear quadrupole coupling constants, the rotational constants, and in some cases, the molecular structure. The Stark spectrum can be analyzed to determine the molecular electric dipole moment.

This research had several objectives in addition to the primary one of determining molecular constants of specific molecules. One of these was to determine the usefulness of microwave spectroscopy for measuring molecular constants in the case of a complex asymmetric molecule. Another objective was to determine the validity and usefulness of the existing theories which are applied to microwave spectroscopy for the analysis of the Stark spectra of symmetric and asymmetric molecules when they are complicated by nuclear quadrupole interactions. Finally, it was desired to determine how important the effects of near-degeneracy of energy levels are in the case of a nearly-symmetric rotor when analyzing the Stark effect to determine the electric dipole moment.

A Stark effect microwave spectrometer was used for measuring the rotational spectrum of CHClF_2 and for measuring the Stark effect of CHClF_2 , CClF_3 and NOCl . The spectrometer employs the principle of modulation of the absorption of the microwave energy by alternately turning an electric field on and off in the absorption cell by the use

of a square wave generator. The modulation of the absorption makes it possible to greatly increase the sensitivity of the spectrometer and to eliminate detection of extraneous signals. The frequencies of rotational absorption lines or Stark lines can be measured to a fraction of a megacycle.

Part of the spectrum of the asymmetric molecule chlorodifluoromethane has been observed by other workers, but the spectrum has not been previously analyzed. The dipole moment has been estimated but it is not clear how the estimate was obtained without analysis of the Stark spectrum. Part of the work described here was concerned with investigations of the absorption spectrum of CHClF_2 in the microwave region between 14,000 and 37,000 Mc. The spectrum is very complicated because of the existence of two isotopic species of chlorine in the molecule, and because the asymmetric rotor has a much more complicated spectrum than linear or symmetric rotors. Several transitions were identified by analysis of the hyperfine structure. The identified transitions are: $J_{\tau} = 0_0 - 1_1, 1_0 - 2_1, 1_{-1} - 2_0, 2_{-2} - 3_{-1},$ and $3_1 - 3_2$. These transitions were observed for both isotopic species of the molecule. The quadrupole coupling constants were accurately determined by means of a "maximum likelihood" calculation for both species of molecule. The quadrupole coupling constants were found to be $\chi_{aa} = -64.30$ Mc, $\chi_{bb} = +35.28$ Mc, $\chi_{cc} = +29.02$ Mc for $\text{CHCl}^{35}\text{F}_2$ and $\chi_{aa} = -51.02$ Mc, $\chi_{bb} = +28.04$ Mc, $\chi_{cc} = +22.98$ Mc for $\text{CHCl}^{37}\text{F}_2$. The rotational constants were determined from the measurements of the $J_{\tau} = 1_0 - 2_1, 1_{-1} - 2_0$ and $2_{-2} - 3_{-1}$

transitions. The rotational constants evaluated were $A = 10,234.68$ Mc, $B = 4,861.22$ Mc and $C = 3,507.68$ Mc for $\text{CHCl}^{35}\text{F}_2$ and $A = 10,233.84$ Mc, $B = 4,717.14$ Mc and $C = 3,432.44$ Mc for $\text{CHCl}^{37}\text{F}_2$. Ray's asymmetry parameters are $k = -0.598$ for $\text{CHCl}^{35}\text{F}_2$ and $k = -0.622$ for $\text{CHCl}^{37}\text{F}_2$. Calculations were made to determine the bond distances and angles between the atoms. The results were $d(\text{C} - \text{Cl}) = 2.10$ A, $d(\text{C} - \text{H}) = 1.09$ A, $d(\text{C} - \text{F}) = 1.25$ A, and $\text{F} - \text{C} - \text{H} = 101^\circ$, angle $\text{F} - \text{C} - \text{Cl} = 91^\circ$ and angle $\text{F} - \text{C} - \text{F} = 120^\circ$. These bond distances and angles do not agree with those found by electron diffraction. The discrepancies may be caused by centrifugal distortion and/or errors in the moments of inertia. More accurate determination of the structure can be accomplished by measurements of other isotopic species. It is difficult to make enough measurements with sufficient accuracy to obtain accurate structures for complicated molecules, and it may be difficult to solve the equations for the structure. The Stark effect of the $J_\tau = 0_0 - 1_1$ transition of chlorodifluoromethane was analyzed, and the components of dipole moment calculated were $\mu_a = 0.12 \pm .02$ Debye and $\mu_c = 1.45 \pm .02$ Debye.

The spectrum of the symmetric top chlorotrifluoromethane has been investigated by other workers. Several transitions were identified, and the rotational constants, molecular structure and quadrupole coupling constants were evaluated, but the electric dipole moment was not measured. This thesis describes further investigations of chlorotrifluoromethane. The Stark effect of the $J = 2 - 3$ transition was analyzed, and the dipole moment was found to be $0.50 \pm .05$ Debye. The

theories for the Stark effect of the symmetric and asymmetric molecule with quadrupole interaction are adequate, but the labor required for the calculation of the Stark effect in the symmetric case can be reduced by making a different choice for the wave functions required in the analysis of the problem than that recommended by other workers. This less laborious method is strongly recommended.

Nitrosyl chloride, an asymmetric rotor which is nearly a symmetric top, has been investigated by microwave spectroscopy by other workers who found the rotational constants and quadrupole coupling coefficients but gave only an estimate of the electric dipole moment. This thesis presents the results of the analysis of the Stark effect of nitrosyl chloride. The effects of the near-degeneracy of the energy levels of the nearly-symmetric rotor were included in the calculation. The results prove that it is necessary to include the effects of near-degeneracy of energy levels in the calculations in order to obtain the correct value of dipole moment; otherwise, large errors may result. Only one component of dipole moment could be obtained; the value was $\mu_a = 1.86 \pm .02$ Debye. Transitions that were sensitive to the other component could not be found.

CHAPTER I

INTRODUCTION

Microwave spectroscopy began with the measurement of the absorption spectrum of microwave radiation in ammonia by Cleeton and Williams in 1933 (1). Since that time much progress has been made. Improvements in instrumentation have markedly increased the sensitivity and resolving power of available spectrometers. The theory of molecular spectra which is applied to microwave spectroscopy has grown with the advances in equipment, and at this time there is a suitable theory for almost every kind of molecule. Most modern microwave spectrometers use the principle of Stark modulation which was introduced by Hughes and Wilson in 1947 (2). The Stark effect spectrometer has the advantages of greatly increased signal-to-noise ratio, elimination of detection of power variations caused by reflections in the waveguide and elimination of other spurious responses. It can be used to measure the Stark spectrum which is an aid in the identification of transitions and provides a means of measuring electric dipole moments.

The microwave spectrometer is usually employed for measuring absorption transitions between rotational energy levels of molecules in the gaseous state. If the rotational spectrum of a molecule is to be observed, the molecule must have a permanent electric dipole moment or a permanent magnetic dipole moment. Microwave spectroscopy has yielded much valuable information concerning the structure of molecules. In some cases molecular structures can be completely determined by its use.

Quadrupole coupling constants can be determined from the hyperfine structure which they produce. All these molecular constants are useful to the theoretical chemist who is interested in chemical bonds.

Diatomic molecules are usually easy to analyze by microwave spectroscopy; next in order of difficulty come symmetric top molecules, then asymmetric top molecules. The first molecules investigated were those having the smallest number of atoms and the simplest structures. They had fairly simple spectra which were easily interpreted and the early investigations were often very fruitful for that reason. Further progress in investigations of more complex molecules has become increasingly difficult. Analysis of the spectra of many symmetric top molecules has been accomplished, but comparatively few asymmetric top molecules have been investigated, particularly where the spectra are complicated by hyperfine structure resulting from nuclear quadrupole interactions. The molecular properties of the asymmetric molecules are just as interesting as those of the symmetric type, but because of the complex spectra of the asymmetric molecules their constants are more difficult to obtain. One purpose of the present investigation was to determine the usefulness of microwave spectroscopy for measuring molecular constants in these more difficult cases.

The microwave spectrum of chlorodifluoromethane was measured and analyzed in order to determine the rotational constants, nuclear quadrupole coupling constants, molecular structure and electric dipole moment. The spectrum is very complicated because of the asymmetry of the molecule. The rotational absorption lines appear throughout the microwave region investigated, and they do not fall into easily identified groups.

The presence of two isotopic species of chlorine in the molecules of gas in the naturally occurring ratio of 75.4 per cent Cl^{35} to 24.6 per cent Cl^{37} increases the complexity of the spectrum by two-fold. The spectrum of the Cl^{37} species of the molecule is somewhat weaker than that of the Cl^{35} species but is still comparable in intensity. The rotational spectrum predicted by using values of interatomic distances measured by electron diffraction was not precise enough to identify correctly the observed groups of lines because of the comparatively large possible errors in the interatomic distances and bond angles of the molecule. The theoretically predicted hyperfine structure for the different transitions made it possible to identify the different observed groups of lines by comparing the relative intensities and splittings of lines in a measured group with the theoretically predicted patterns. The actual measured frequencies of many hyperfine lines were used in a "maximum likelihood" calculation to determine the quadrupole coupling coefficients. These coefficients were then used in a similar type calculation to determine the unperturbed rotational line frequencies of several transitions which, in turn, were used to make accurate calculations of the rotational constants.

The Stark effect of the $J_{\tau} = 0_0 - 1_1$ transition of chlorodifluoromethane was measured and analyzed in order to determine the electric dipole moment. In order to test the adequacy of the existing theories for dealing with the Stark effect of symmetric and asymmetric tops, and to determine the practicality of using the Stark effect to determine dipole moments, the molecules nitrosyl chloride and chlorotrifluoromethane were investigated also.

The rotational spectrum of NOCl has previously been investigated by Rogers (3). The rotational constants and quadrupole coupling constants were determined, but the electric dipole moment given by Rogers was only an estimate. The NOCl molecule is nearly a symmetric top and therefore the rotational energy levels tend to be degenerate in pairs. Previous experience with nitrosyl bromide (4) indicated that this near degeneracy must be taken into account in the calculations for the Stark effect. The Stark effect of the $J_{\tau} = 1_1 - 2_0$ transition was analyzed, and one component of the dipole moment was determined. Calculations were made by the method of Mizushima (5) and correction for near-degeneracy of rotational levels was made using the theory of Golden and Wilson (6).

The microwave spectrum of CClF₃ has been investigated previously by Coles and Hughes (7) to the extent of determining the rotational constant B_0 , quadrupole coupling constants and molecular structure. They did not report any determination of the dipole moment. The Stark effect of CClF₃ was measured, and the dipole moment was calculated using the theories of Low and Townes (8).

CHAPTER II

EXPERIMENTAL TECHNIQUES

The microwave spectrometer used in the investigations reported here is similar to that described by Hughes and Wilson (2). A block diagram of the spectrometer is shown in Figure 1. The main absorption cell is a 20 foot section of X-band waveguide with a brass septum mounted on electrical insulating strips of Teflon inside the waveguide. An electric field is produced in the waveguide by the application of a zero-based 85 kc square wave between the guide wall and the septum. This field is essentially parallel to the electric vector of the microwave radiation.

The Stark effect is produced by the interaction between the molecular electric dipole moment and the electric field. This interaction splits each rotational energy level into several levels with the result that each spectral line is split into several Stark components. The microwave energy is obtained from a klystron oscillator. The frequency can be varied electronically by changing the klystron reflector voltage, or it can be varied mechanically by means of a tuning shaft which changes the internal dimensions of the klystron when the shaft is rotated. Energy from the klystron is transmitted through the waveguide to the crystal detector. When the microwave is tuned to the frequency of a rotational transition in the gas molecules being investigated, the molecules will absorb some of the microwave energy. If the Stark field is then turned on, the rotational line will be split into Stark components and the microwave energy will pass through the gas either without any loss or at least with smaller loss. The Stark field is turned on and off in the

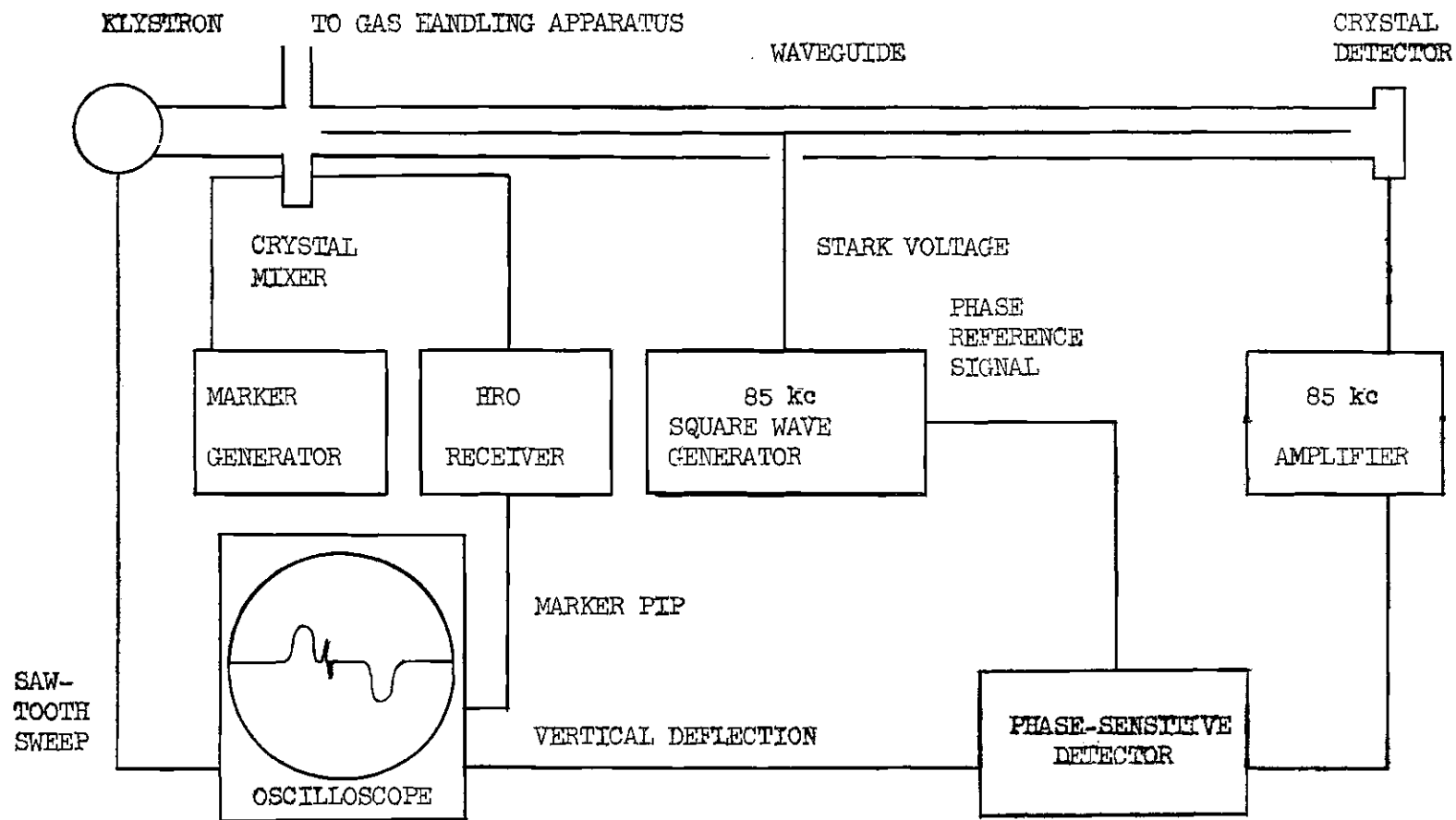


Figure 1. Block Diagram of Stark Effect Microwave Spectrometer.

waveguide at a frequency of 85 kc by a square wave generator. The crystal detector output is amplitude modulated at 85 kc when the microwave is tuned to a rotational transition frequency. It is amplitude modulated also when the microwave is tuned to the frequency of a Stark component; i.e. energy will be absorbed when the Stark field is on and there will be no absorption when the Stark field is off. The crystal detector output will be modulated at 85 kc in the event of a pure rotational transition or in the event of a Stark transition, but with a phase difference of 180° between the two cases. In the absence of either a pure rotational transition or a Stark transition in the gas, there will be no 85 kc modulation of the output of the crystal detector. The crystal detector output signal is applied to a narrow-band amplifier tuned to 85 kc. The amplifier responds only when an actual pure rotational transition or a Stark transition occurs; otherwise, there is no signal. The amplitude of the 85 kc signal depends upon the intensity of the absorption line in the spectrum. The signal from the 85 kc amplifier is applied to a phase-sensitive detector.

The phase-sensitive detector is a circuit that is designed to separate the signals in a modulated wave. Modulation of a time function $e_1(t)$ by another time function $e_2(t)$ is a nonlinear process. The resulting modulated wave contains frequencies that were not present in the original time functions. The components present in the frequency spectrum of the output depend upon the circuit and the degree of nonlinearity. The phase-sensitive detector makes use of symmetry to eliminate undesired frequency components. A simple basic circuit is shown in Figure 2. For the sake of simplicity, let us assume that e_1 has the same phase and polarity in the primary and in each half of the secondary of the transformer. The important point to

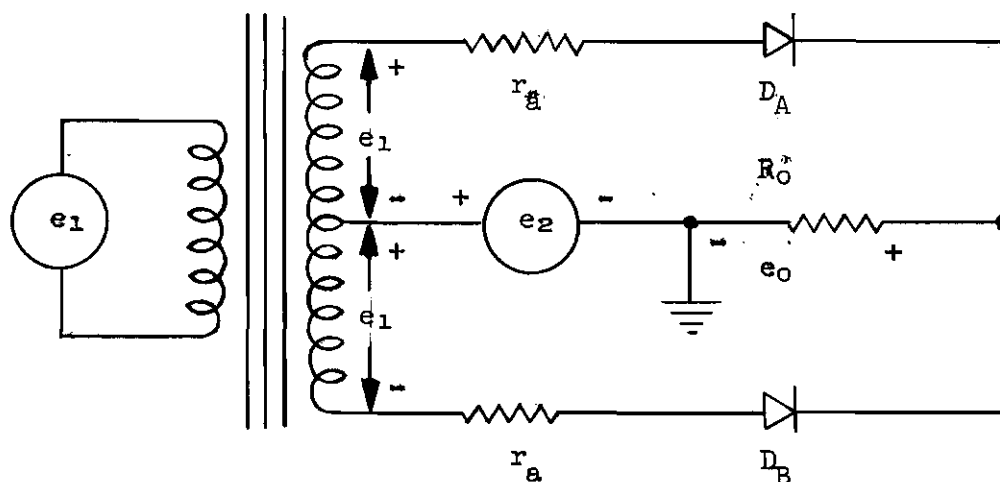


Figure 2. Schematic Diagram of a Simple Phase-Sensitive Detector.

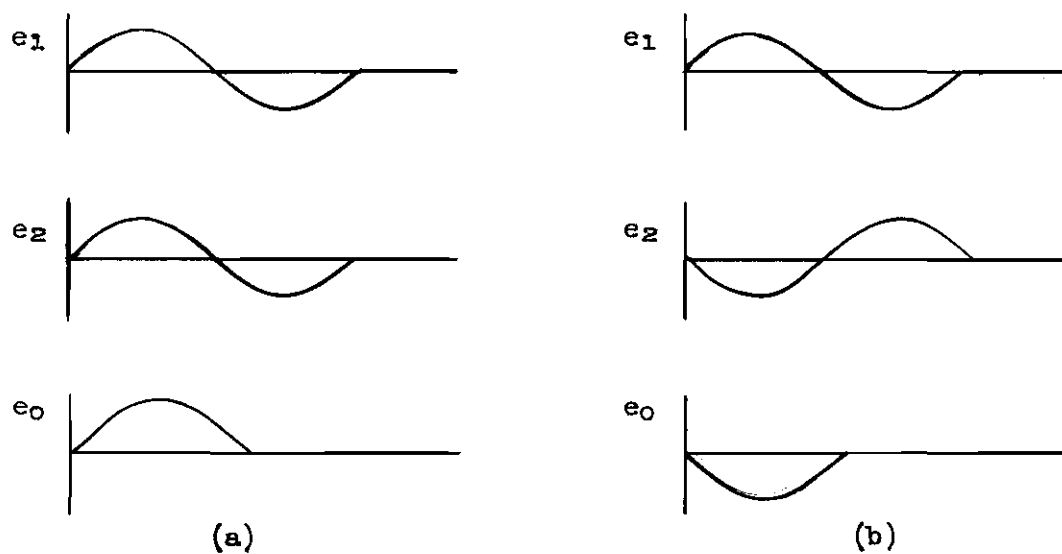


Figure 3. Voltage Waveforms in a Phase-Sensitive Detector.

observe is that one input is applied to the diodes symmetrically whereas the other is applied antisymmetrically. In the circuit shown, e_2 drives the diodes on and off simultaneously while e_1 alternately causes conduction through one diode and then the other. With e_2 alone applied, e_0 is a half-wave rectified version of e_2 . With both e_1 and e_2 applied to the circuit at the same time, we note that conduction through diode D_A depends on $(e_1 + e_2)$ whereas conduction through diode D_B depends on $(e_1 - e_2)$ (9). Now let e_1 be a reference signal from the square-wave generator, and let e_2 be the amplified signal from the microwave detector. If e_1 and e_2 are in phase, the wave forms will be as in Figure 3(a) and if e_1 and e_2 are out of phase, the wave forms will be as shown in Figure 3(b). Now the polarity of e_1 is determined by whether the Stark voltage is on or off in the waveguide. The voltage e_1 determines the polarity of the output voltage e_0 . Let us say e_1 is positive when the Stark voltage is off and negative when the Stark voltage is on. The output voltage e_0 will be positive when a pure rotational transition occurs and negative when a Stark transition occurs. The value of e_0 is zero when no transition occurs. It is clear that the polarity of e_0 indicates whether a signal is due to an unperturbed rotational transition or to a Stark transition. The output signal e_0 consists of half-wave rectified 85 kc pulses. The pulses are filtered by a filter which has variable time constants. The effective bandwidth of the system, i.e., the band from which noise is received, is just half the reciprocal of the time constant, assuming that the time constants furnish the smallest bandwidth of the system (10). The effective bandwidth can be reduced and the signal-to-noise ratio increased simply by increasing the filter time constants.

The output from the filter can be displayed on an oscilloscope. When this is done the oscilloscope sweep is synchronized with the electronic frequency sweep for the klystron. This gives a visual presentation of the absorption spectrum on the oscilloscope with the negative deflection indicating a Stark transition and positive deflection indicating an unperturbed rotational transition. Very large filter time constants can be used giving much greater signal-to-noise ratio if a very slow frequency sweep is used. An electric motor drives an appropriate speed reduction gear which turns the klystron tuning shaft to obtain the desired slow frequency sweep. The spectrum obtained by using the slow mechanical sweep is displayed by recording the filtered output of the phase-sensitive detector on paper with an Esterline-Angus recording meter as the klystron frequency is varied. In either case, the Stark lines are displayed as a deflection in the opposite direction from that of the rotational lines.

The gas to be analyzed is admitted in small amounts into the evacuated waveguide through a stopcock on the manifold of the vacuum system. An oil diffusion pump followed by a mechanical vacuum pump is used to pump the gas out of the system until the desired operating pressure is reached as indicated by a Pirani gauge. The waveguide is maintained at low temperature by filling the space inside an insulated box surrounding the waveguide with dry ice. This reduction in gas temperature increases the relative populations of the lower rotational energy levels and increases the intensities of the transitions between the lower rotational energy levels. These levels are usually the most desirable ones to observe, because they have comparatively simple hyperfine structure.

A cavity absorption-type wavemeter is used to obtain a frequency measurement of an absorption line within a few megacycles. The exact frequency is determined by using a frequency marker generator which produces a family of marker frequencies spaced 30 Mc apart. The marker generator is maintained at standard frequency by adjusting its oscillator to zero beat with a radio signal from the National Bureau of Standards station WWV. The marker generator output is mixed with a small portion of the klystron output by use of a crystal mixer and produces a beat frequency between 15 and 30 Mc. The beat frequency is measured by a calibrated National HRO receiver, and the audio output of the receiver is superimposed on the oscilloscope display of the spectrum. The receiver audio output signal increases when the difference between the klystron frequency and a marker frequency is equal to the frequency to which the receiver is tuned, and a visible pip is produced on the oscilloscope as the klystron frequency is swept. By tuning the HRO receiver, the frequency at which the pip appears is changed, and the pip can be superimposed on the absorption line being measured. Several measurements are made as the klystron is electronically swept from low to high frequency, and several measurements are then made as the klystron is swept from high to low frequency. These measurements are averaged in order to eliminate errors due to time delays in the detector and frequency measuring circuits. The exact frequency of the measured absorption line is then determined by adding the beat frequency to or subtracting it from the known frequency of the appropriate marker as determined by the cavity wavemeter. When the slow mechanical frequency sweep is employed to ob-

tain the greatest sensitivity, the absorption frequencies are accurately determined by listening to the HRO receiver for the beat note as the klystron is tuned. The receiver frequency at which the beat note is heard is noted, and simultaneously the margin of the recording is marked with the auxiliary marking pen of the recorder.

CHAPTER III

THE MICROWAVE SPECTRUM OF CHLORODIFLUOROMETHANE

The chlorodifluoromethane used in the experiments described was obtained from the Matheson Company, Incorporated. The compound is also known by the trade name "Freon-22", and is reported to have a purity of 97.0 per cent.

Experiments have been carried out by Brockway (11) to determine the structure of CHClF_2 by electron diffraction. The bond distances measured in Angstroms and bond angles obtained were as follows:

$$d(\text{C} - \text{Cl}) = 1.73(0.03) \text{ \AA}, \quad d(\text{C} - \text{F}) = 1.36(0.03) \text{ \AA},$$

angle $\text{Cl} - \text{C} - \text{F}$ greater than angle $\text{F} - \text{C} - \text{F}$.

The above dimensions were used to obtain moments of inertia for use in predicting the rotational spectrum. Tetrahedral angles were assumed in the initial calculations of the moments of inertia. An isometric drawing of the molecule is shown in Figure 4 in which coordinates of the atoms are drawn to scale and tetrahedral angles are assumed. Rectangular coordinate axes are chosen so the C and F atoms are in the $\text{Y}'\text{Z}'$ plane, and the C, Cl and H atoms are in the $\text{X}'\text{Z}'$ plane. The XYZ axes are along the principal axes of inertia and have their origin at the center of mass of the molecule. A straightforward calculation yielded the principal moments of inertia. The angle between X (the axis of least moment of inertia) and X' was found to be 49.7° . The rotational constants, which are inversely proportional to the moments of inertia, I, were found using the relation

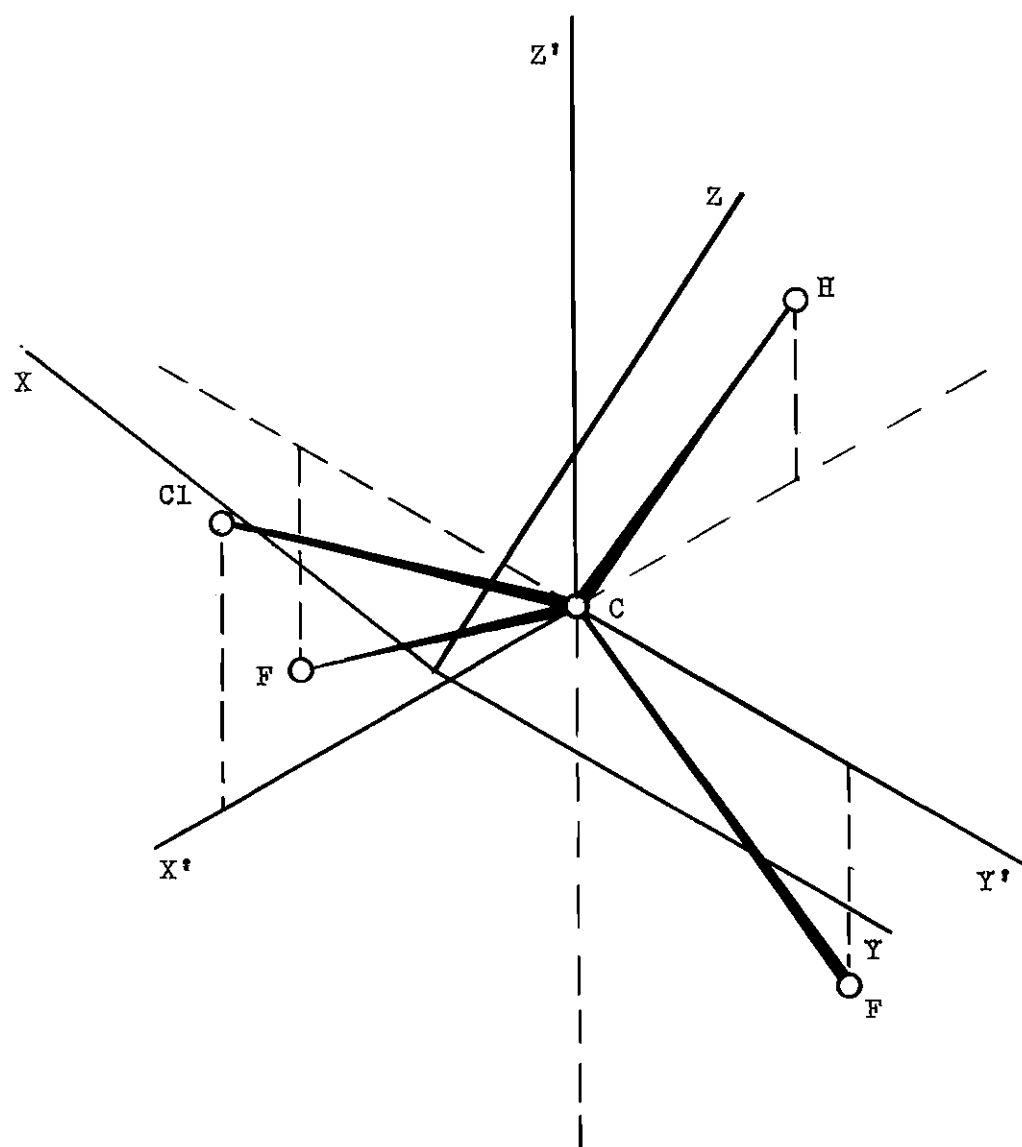


Figure 4. Estimated Structure of Chlorodifluoromethane.

$$BI = 5.05531 \times 10^5 \text{ Mc/amu } \text{\AA}^2,$$

where Mc represents megacycles, amu atomic mass units, and A Angstroms.

The calculated values for the principal moments of inertia, rotational constants A, B and C and Ray's asymmetry parameter k $\left[k = (2B-A-C)/(A-C) \right]$ are given in Table 1.

Table 1. Estimated Principal Moments of Inertia, Rotational Constants and Asymmetry Parameters for Chlorodifluoromethane

	$\text{CHCl}^{35}\text{F}_2$	$\text{CHCl}^{37}\text{F}_2$
I_a	51.4107 amu \AA^2	51.4145 amu \AA^2
I_b	101.5245	104.6265
I_c	143.8358	146.9341
A	9833.18 Mc	9832.47 Mc
B	4979.40	4831.77
C	3514.64	3440.53
k	-0.5364	-0.5647

Rotational energies were calculated using the expression of King, Hainer and Cross (12)

$$W = \frac{1}{2}(A + C)J(J + 1) + \frac{1}{2}(A - C)E_\tau(k) \quad (1)$$

where J is the rotational quantum number, τ is the integer used to specify the order of the energy among the $2J + 1$ different sublevels of the same J for an asymmetric top, and $E_\tau(k)$ is the reduced energy of a rigid rotor as defined and tabulated by King, Hainer and Cross. A more complete

tabulation of $E_{\tau}(k)$ is given by Townes and Schawlow (13). The rotational energy levels were used to calculate the rotational transition frequencies after the allowed transitions were determined from the selection rules for the asymmetric rotor.

The selection rules for J and M are the same as for the symmetric top, that is $\Delta J = 0, \pm 1$ and $\Delta M = 0, \pm 1$. However, the selection rules for the asymmetric top are further complicated, partly by the increased number of separate levels, and partly because of their dependence on the direction of the dipole moment with respect to the principal axes of inertia. Additional selection rules are obtained in terms of the symmetry properties of the wave functions. The momental ellipsoid of an asymmetric molecule is symmetric with respect to a rotation of 180° about any principal axis, even though the molecule itself may not have this symmetry. Hence, the wave function for an asymmetric rotor must be either symmetric (+) or antisymmetric (-) with respect to such a rotation. In the case of a symmetric rotor the component of \vec{J} (the molecular angular momentum excluding electron and nuclear spin) along the axis of symmetry is given by the integer K in units of Planck's constant divided by 2π . The quantum number K cannot be used to specify the rotational state of an asymmetric top, but it is related to τ in the following manner:

$$\tau = K_{-1} - K_1 ,$$

where K_{-1} is the K value of the limiting prolate symmetric top and K_1 is the K value for the limiting oblate symmetric top. Examination of the wave functions shows that any asymmetric top wave function $\psi_{K_{-1}K_1}$ is

symmetric with respect to rotation of 180° about the axis of ~~smallest~~ moment of inertia, a, when K_{-1} is even and antisymmetric when K_{-1} is odd. Also $\psi_{K_{-1}K_1}$ is symmetric with respect to rotation of 180° about the axis of greatest moment of inertia, c, when K_1 is even and antisymmetric when K_1 is odd. The symmetry for rotation of 180° about the intermediate axis, b, is derivable from the symmetry for the a and c axes; it is just such that it will counteract the effect of rotation about a and c. Therefore, it is sufficient to know the symmetries for the a and c axes only.

A transition $J\tau M \rightarrow J'\tau'M'$ is allowed if any one of the matrix elements of the space-fixed components of the dipole moment is different from zero. The vanishing or non-vanishing of these matrix elements can be determined by considering the direction of the molecular dipole moment and the symmetries of the initial and final state wave functions under rotation through 180° about the a and c axes. If the dipole moment does not lie along any principal axis, it may be resolved into components along the three axes, and the allowed transitions are the sum of those allowed for each component (14). The molecule CHClF_2 has no component of dipole moment along the b axis because of its symmetry about the XZ plane. Therefore, no transitions occur due to the b component of dipole moment. Allowed transitions for CHClF_2 resulting from interactions between the radiation field and components of dipole moment are given below in terms of the symmetries of the initial and final state wave functions.

Component of Dipole Moment	Allowed Transitions in Terms of Wave Function Symmetry with Respect to Rotation About Axes c and a
	c a c a
a	+ + \leftrightarrow - +
	- - \leftrightarrow + -
c	+ + \leftrightarrow + -
	- - \leftrightarrow - +

Best experimental results were obtained at gas pressures of about 17 to 18 microns of mercury with the absorption cell at dry ice temperature. The observed spectrum was so complicated that it was impossible to identify transitions from the predicted frequencies of rotational transitions found as described above. It was necessary to identify the transitions by their hyperfine structures caused by the interaction of the chlorine nuclear quadrupole moment with the electric field gradient.

The first order quadrupole interaction Hamiltonian (15) is given by the equation

$$\frac{eQ \left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{av} \left[3(\vec{I} \cdot \vec{J})^2 + \frac{3}{2}(\vec{I} \cdot \vec{J}) - \vec{I}^2 \vec{J}^2 \right]}{2J(2J - 1)I(2I - 1)} . \quad (2)$$

Here e is electronic charge, Q is the nuclear quadrupole moment, and $\left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{av}$ is a quantum mechanical average of the electric field gradient at the nucleus which can be obtained for asymmetric top molecules from the formula given by Bragg (16):

$$eQ \left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{av} = \frac{2J}{(2J+1)(2J+3)} \sum_{\tau} \left[\chi_{aa} \lambda_{J\tau, J\tau}^a + \chi_{bb} \lambda_{J\tau, J\tau}^b + \chi_{cc} \lambda_{J\tau, J\tau}^c \right] . \quad (3)$$

The λ 's are tabulated line strengths defined by Cross, Hainer and King (17). The quadrupole coupling coefficients are defined by the relations:

$$\chi_{aa} = eQ \frac{\partial^2 V}{\partial X^2} ,$$

$$\chi_{bb} = eQ \frac{\partial^2 V}{\partial Y^2} ,$$

$$\chi_{cc} = eQ \frac{\partial^2 V}{\partial Z^2} .$$

For the purpose of identifying lines the χ 's can be estimated from the molecular configuration by the following method suggested by Townes (15). If cylindrical symmetry of the charge distribution about the bond axis is assumed, the following relation holds:

$$\frac{\partial^2 V}{\partial X_1^2} = \frac{\partial^2 V}{\partial \xi^2} \left(\frac{3 \cos^2 \alpha_{x_1 \xi} - 1}{2} \right), \quad i = 1, 2, 3. \quad (4)$$

The $\alpha_{x_1 \xi}$ are the angles between the bond axis ξ and the principal axes x_1 . From known values of the quadrupole coupling in other molecules, we can assume for Cl³⁵

$$eQ \frac{\partial^2 V}{\partial \xi^2} = 78 \text{ Mc.}$$

From the previously estimated structure of $\text{CHCl}^{35}\text{F}_2$ one then obtains the estimated values:

$$\chi_{aa} = - 71 \text{ Mc},$$

$$\chi_{bb} = + 39 \text{ Mc},$$

$$\chi_{cc} = + 32 \text{ Mc}.$$

The bracketed factor in equation (2) is given by

$$\frac{3}{4} C(C + 1) - I(I + 1)J(J + 1)$$

where

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

and

$$F = J + I, J + I - 1, \dots, |J - I|.$$

After carrying out the calculations mentioned, the hyperfine structures of $\text{CHCl}^{35}\text{F}_2$ were predicted for transitions shown in Table 2 which are low J-number transitions allowed by the selection rules.

The predicted hyperfine structures were compared with the recorded spectrum, and by comparing ratios of frequency differences between predicted lines and measured lines some of the different groups were identified. The hyperfine structure was also observed in the case of each of the identified transitions for $\text{CHCl}^{37}\text{F}_2$ which was another check on the identification of the transitions.

Table 2. Calculated Transitions

Component of Dipole Moment		a	c
Transition	$J_r =$	$1_1 - 2_0$	$0_0 - 1_1$
		$2_1 - 3_0$	$1_1 - 2_2$
		$2_0 - 3_{-1}$	$1_0 - 2_1$
		$2_{-1} - 3_{-2}$	$1_{-1} - 2_0$
		$2_{-2} - 3_{-3}$	$2_0 - 3_1$
		$3_{-1} - 4_{-2}$	$2_{-1} - 2_2$
			$2_{-2} - 3_{-1}$
			$3_1 - 3_2$
			$3_{-1} - 4_{-4}$
			$3_{-2} - 3_1$

Only transitions attributable to μ_c , the component of dipole moment along the principal axis of largest moment of inertia, could be observed. A search was made for transitions due to the component μ_a but none were found.

The quadrupole coupling constants were determined by the "maximum likelihood" method described by Clayton (18). This method is a statistical data-smoothing or averaging process which provides for proper weighting of individual frequency measurements. It affords a strong determination of the quadrupole couplings by allowing the fitting of the hyperfine structures of several transitions simultaneously. The maximum likelihood calculation was carried out using the best 25 measured frequencies of hyperfine lines for the $\text{CHCl}^{35}\text{F}_2$ molecule and the best 24 measured

frequencies for the $\text{CHCl}^{37}\text{F}_2$ molecule. These calculations yielded the coupling constants given in Table 3.

Table 3. Quadrupole Coupling Constants of Chlorodifluoromethane

	$\text{CHCl}^{35}\text{F}_2$	$\text{CHCl}^{37}\text{F}_2$
χ_{aa}	-64.30 Mc	-51.02 Mc
χ_{bb}	+35.28	+28.04
χ_{cc}	+29.02	+22.98

The best measurements of hyperfine components for each transition were used then with the above mentioned values of χ_{aa} and χ_{cc} in a weighted average calculation to determine the unperturbed rotational frequencies for the transitions which could most easily be used in calculating exact values of rotational constants. The frequencies determined are shown in Table 4.

Table 4. Unperturbed Rotational Transition Frequencies for Chlorodifluoromethane

	$\text{CHCl}^{35}\text{F}_2$	$\text{CHCl}^{37}\text{F}_2$
$J_{\tau} = 0_0 - 1_1$	15,095.96	14,951.05
$1_0 - 2_2$	35,565.25	35,418.66
$1_{-1} - 2_0$	24,818.33	24,385.27
$2_{-2} - 3_{-1}$	35,288.15	34,525.41

The rotational energy levels are given explicitly in terms of rotational constants for low J values by Gordy (19). The energies, $E_{J\tau}$, for the levels involved in the above transitions are

$$E_{3-1} = 5A + 5B + 2C - 2\sqrt{4(A-B)^2 + (A-C)(B-C)},$$

$$E_{21} = 4A + B + C,$$

$$E_{20} = A + 4B + C,$$

$$E_{2-2} = 2A + 2B + 2C - 2\sqrt{(B-C)^2 + (A-C)(A-B)},$$

$$E_{11} = A + B,$$

$$E_{10} = A + C,$$

$$E_{1-1} = B + C.$$

The frequencies of the unperturbed rotational lines, $\nu_0 (J\tau - J'\tau')$, found from the energy levels are

$$\nu_0 (0_0 - 1_1) = A + B, \quad (5)$$

$$\nu_0 (1_0 - 2_1) = 3A + B, \quad (6)$$

$$\nu_0 (1_{-1} - 2_0) = A + 3B, \quad (7)$$

$$\begin{aligned} \nu_0 (2_{-2} - 3_{-1}) = 3A + 3B - 2\sqrt{4(A-B)^2 + (A-C)(B-C)} \\ + 2\sqrt{(B-C)^2 + (A-C)(A-B)}. \end{aligned} \quad (8)$$

Equations (6) and (7) give values of A and B, and C is determined by solving the quadratic equation obtained from equation (8). The quadratic equation is

$$C^2 - C(A+B) + \left\{ AB + 4(A-B)^2 + \left[\frac{3(A-B)^2}{\nu_0 - 3(A+B)} + \frac{\nu_0 - 3(A+B)}{4} \right]^2 \right\} = 0. \quad (9)$$

The above equations yielded the actual values for the rotational constants and asymmetry parameters which are shown in Table 5.

Table 5. Rotational Constants and Asymmetry Parameters for Chlorodifluoromethane

	$\text{CHCl}^{35}\text{F}_2$	$\text{CHCl}^{37}\text{F}_2$
A	10,234.68 Mc	10,233.84 Mc
B	4,861.22	4,717.14
C	3,507.68	3,432.44
k	-0.598	-0.622

A check on the correctness of the values for A, B and C is given by comparing frequencies for all measured lines with frequencies calculated from the constants given in Tables 3 and 5. In Figures 5 and 6 calculated hyperfine structures of four rotational groups of $\text{CHCl}^{35}\text{F}_2$ are shown by solid lines with the actual measured hyperfine structures shown by dashed lines. These calculated structures were obtained by using the best evaluation of the quadrupole coupling coefficients and rotational constants and give a clear idea of the degree of precision of the fit of measured and calculated frequencies. The lengths of the solid lines are

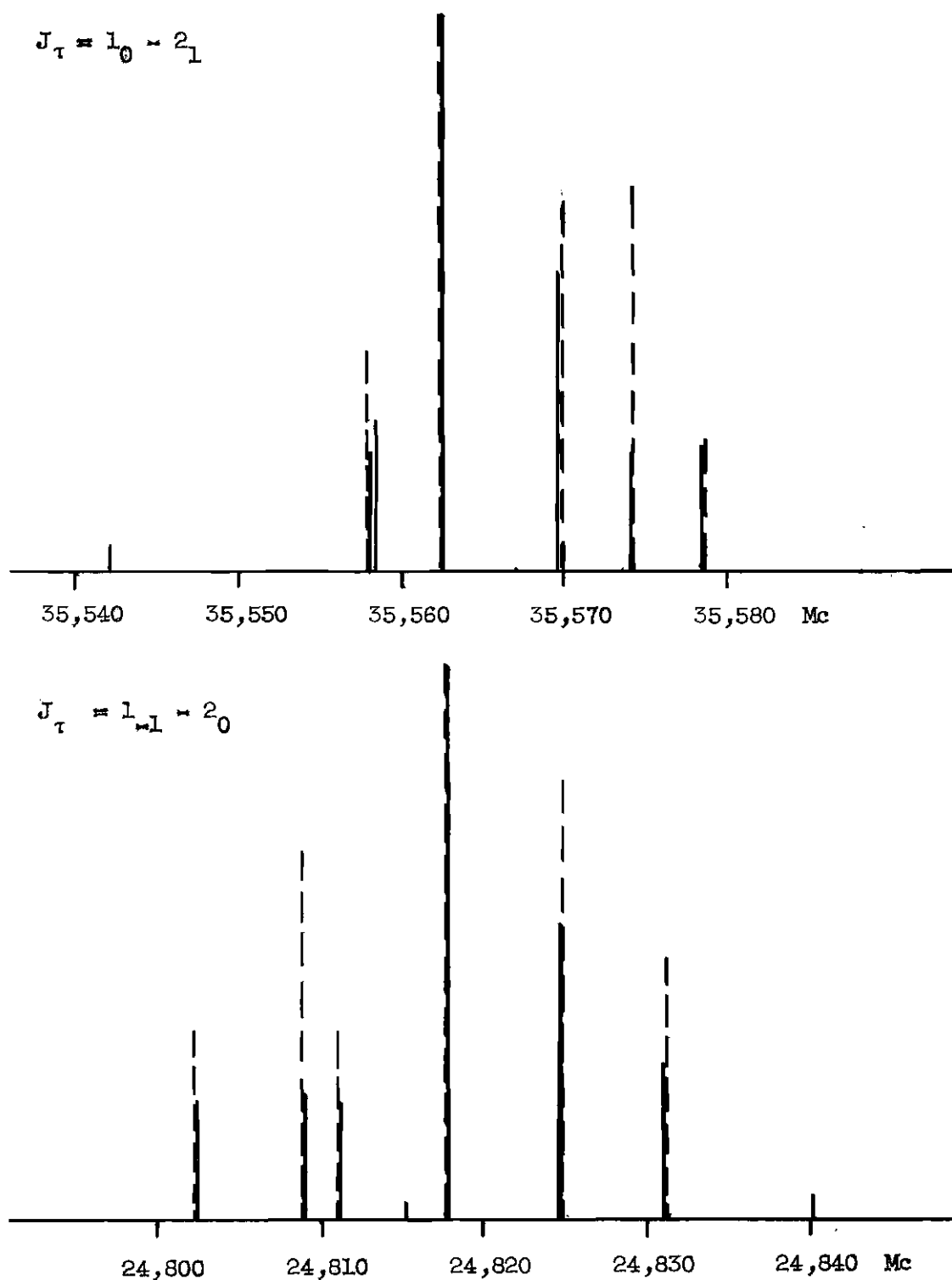


Figure 5. Hyperfine Structure of $\text{CHCl}^{35}\text{F}_2$. Predicted Structure is Indicated by Solid Lines and Measured Structure by Dashed Lines.

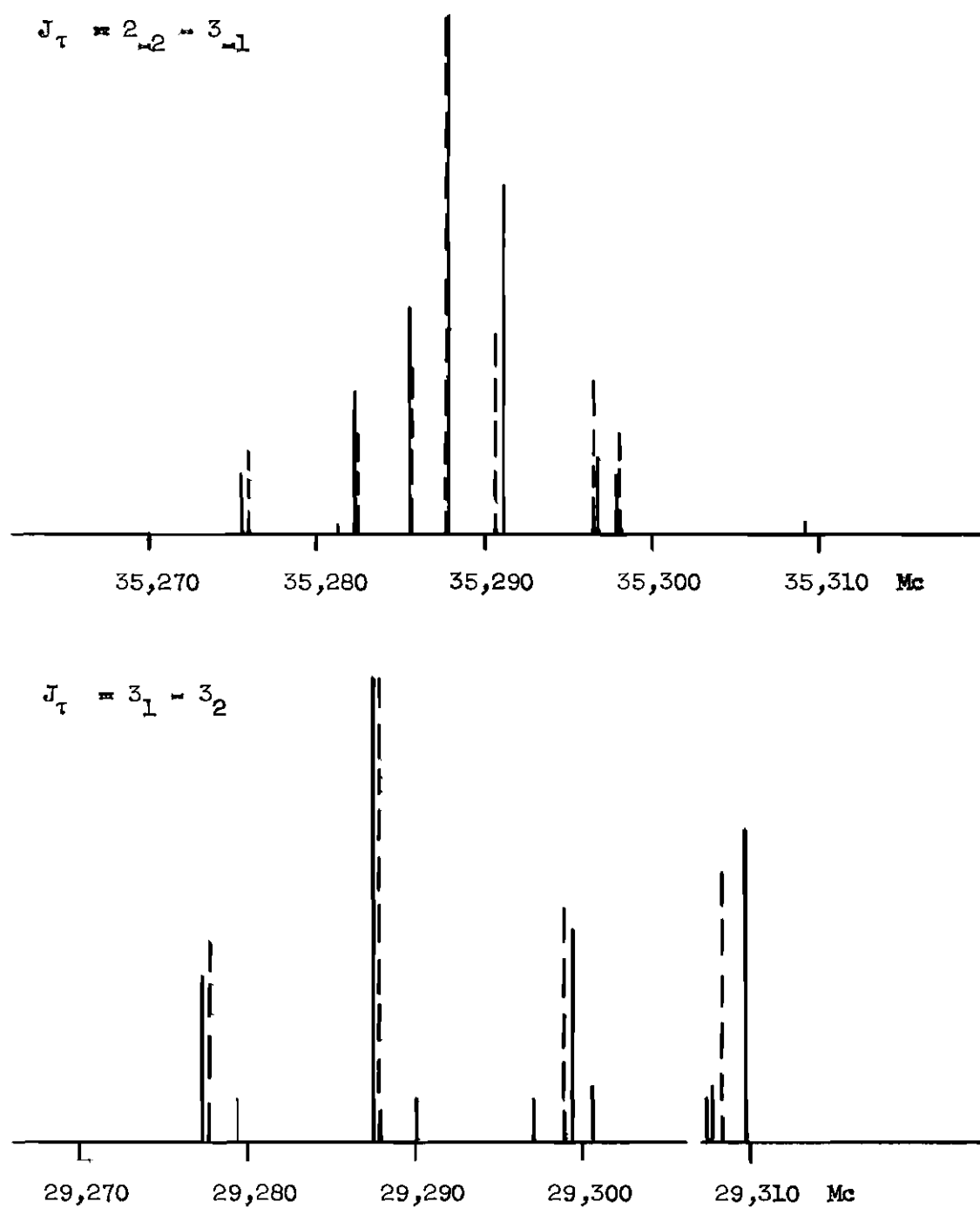


Figure 6. Hyperfine Structure of $\text{CHCl}^{35}\text{F}_2$. Predicted Structure is Indicated by Solid Lines and Measured Structure by Dashed Lines.

proportional to the relative theoretical intensities. The lengths of the dashed lines are proportional to the observed intensities, and the lengths are scaled so the length of the strongest measured line coincides with the length of the line which represents the greatest theoretical intensity. However, because the spectrometer is not well adapted to the accurate measurement of intensities, the observed intensities are not very reliable. Tables 6, 7 and 8 show the measured and final calculated frequencies for the transitions which were identified.

Table 6. The Microwave Spectrum of the $J_{\tau} = 0_0 - 1_1$ and $1_0 - 2_1$ Transitions of CHClF_2

$0_0 - 1_1$ Transition

Measured Group Center Frequency 15,095.96 Mc for $\text{CHCl}^{35}\text{F}_2$, 14,951.05 Mc for $\text{CHCl}^{37}\text{F}_2$

Calculated Group Center Frequency 15,095.90 Mc for $\text{CHCl}^{35}\text{F}_2$, 14,950.98 Mc for $\text{CHCl}^{37}\text{F}_2$

F_0	F_1	Theoretical Relative Intensity	$\text{CHCl}^{35}\text{F}_2$ Calculated Frequency (Mc)	$\text{CHCl}^{35}\text{F}_2$ Measured Frequency (Mc)	$\text{CHCl}^{37}\text{F}_2$ Calculated Frequency (Mc)	$\text{CHCl}^{37}\text{F}_2$ Measured Frequency (Mc)
3/2	1/2	16.7	15,088.64	15,088.57	14,945.24	14,945.20
3/2	5/2	50.0	15,094.45	15,094.51	14,949.83	14,949.91
3/2	3/2	33.3	15,101.70	15,101.91	14,955.58	14,955.75

$1_0 - 2_1$ Transition

Measured and Calculated Group Center Frequency 35,565.25 Mc for $\text{CHCl}^{35}\text{F}_2$, 35,418.66 Mc for $\text{CHCl}^{37}\text{F}_2$

F_1	F_2	Theoretical Relative Intensity	$\text{CHCl}^{35}\text{F}_2$ Calculated Frequency (Mc)	$\text{CHCl}^{35}\text{F}_2$ Measured Frequency (Mc)	$\text{CHCl}^{37}\text{F}_2$ Calculated Frequency (Mc)	$\text{CHCl}^{37}\text{F}_2$ Measured Frequency (Mc)
1/2	1/2	8.33	35,557.99	35,557.95 ¹	35,412.91	35,413.06 ¹
3/2	3/2	10.7	35,558.19	35,557.95 ¹	35,413.05	35,413.06 ¹
5/2	7/2	40.0	35,562.42	35,562.18	35,416.42	35,416.40
3/2	5/2	21.0	35,569.68	35,570.03	35,422.16	35,422.12
1/2	3/2	8.33	35,574.07	35,574.24	35,425.07	35,425.57
5/2	5/2	9.00	35,578.50	35,578.51	35,429.17	*35,429.5-

¹Lines not resolved.

*Not used in maximum likelihood calculation.

Table 7. The Microwave Spectrum of the $J_{\tau} = 1_{-1} - 2_0$ and $2_{-2} - 3_{-1}$ Transitions of CHClF_2

$1_{-1} - 2_0$ Transition Measured and Calculated Group Center Frequency 24,818.33 Mc for $\text{CHCl}^{35}\text{F}_2$, 24,385.27 Mc for $\text{CHCl}^{37}\text{F}_2$						
F_1	F_2	Theoretical Relative Intensity	$\text{CHCl}^{35}\text{F}_2$ Calculated Frequency (Mc)	$\text{CHCl}^{35}\text{F}_2$ Measured Frequency (Mc)	$\text{CHCl}^{37}\text{F}_2$ Calculated Frequency (Mc)	$\text{CHCl}^{37}\text{F}_2$ Measured Frequency (Mc)
1/2	3/2	8.33	24,802.25	24,802.14	24,372.51	24,372.46
5/2	5/2	9.00	24,808.81	24,808.77	24,377.71	24,377.70
1/2	1/2	8.33	24,811.07	24,810.99	24,379.52	24,379.50
5/2	7/2	40.0	24,817.63	24,817.60	24,384.72	24,384.61
3/2	5/2	21.0	24,824.89	24,824.96	24,390.47	24,390.37
3/2	3/2	10.7	24,831.19	24,831.43	24,395.48	24,395.75
$2_{-2} - 3_{-1}$ Transition Measured and Calculated Group Center Frequency 35,288.15 Mc for $\text{CHCl}^{35}\text{F}_2$, 34,525.41 Mc for $\text{CHCl}^{37}\text{F}_2$						
F_2	F_3	Theoretical Relative Intensity	$\text{CHCl}^{35}\text{F}_2$ Calculated Frequency (Mc)	$\text{CHCl}^{35}\text{F}_2$ Measured Frequency (Mc)	$\text{CHCl}^{37}\text{F}_2$ Calculated Frequency (Mc)	$\text{CHCl}^{37}\text{F}_2$ Measured Frequency (Mc)
7/2	7/2	4.08	35,275.56	35,275.99	34,515.16	34,515.28
1/2	3/2	10.0	35,282.29	35,282.42	34,521.07	34,520.84
3/2	5/2	16.0	35,285.71	35,285.73	34,523.40	34,523.22
7/2	9/2	35.7	35,287.89	35,287.75	34,525.22	34,525.29
5/2	7/2	24.5	35,291.17	35,290.59	34,527.55	34,527.50
5/2	5/2	5.22	35,296.86	35,296.61	34,532.25	34,532.71
3/2	3/2	4.00	35,297.91	35,298.21		not resolved

Table 8. The Microwave Spectrum of the $J_{\tau} = 3_1 - 3_2$ Transition of CHClF_2

$3_1 - 3_2$ Transition		Measured Group Center Frequency 29,294.62 Mc for $\text{CHCl}^{35}\text{F}_2$, 29,944.82 Mc for $\text{CHCl}^{37}\text{F}_2$. Calculated Group Center Frequency 29,295.03 Mc for $\text{CHCl}^{35}\text{F}_2$, 29,944.54 Mc for $\text{CHCl}^{37}\text{F}_2$				
F_3	F_3	Theoretical Relative Intensity	$\text{CHCl}^{35}\text{F}_2$ Calculated Frequency (Mc)	$\text{CHCl}^{35}\text{F}_2$ Measured Frequency (Mc)	$\text{CHCl}^{37}\text{F}_2$ Calculated Frequency (Mc)	$\text{CHCl}^{37}\text{F}_2$ Measured Frequency (Mc)
3/2	3/2	11.4	29,277.08	*29,277.70	29,930.29	29,931.57
9/2	9/2	32.7	29,287.55	29,287.96	29,938.60	29,939.42
5/2	5/2	14.7	29,299.52	29,298.81	29,948.10	29,948.25
7/2	7/2	21.8	29,309.99	29,308.29	29,956.42	29,955.57

*Not used in maximum likelihood calculation.

CHAPTER IV

THE STRUCTURE OF CHLORODIFLUOROMETHANE

The development of microwave spectroscopy has made it possible to determine many interesting properties of the molecules whose spectra are observed. After the absorption spectrum of a molecule has been analyzed and the rotational constants determined as described previously, it is often possible to determine accurately the structure of the molecule. This is done by determining the coordinates of the atomic masses required to give the observed principal moments of inertia that are obtained from the rotational constants. Except for diatomic molecules and a few asymmetric top molecules, the moments of inertia of one isotopic species of a molecule are not sufficient to determine the molecular configuration. When sufficient information is available concerning the moments of inertia of a molecule, it becomes possible to determine the molecular configuration completely. The principal moments of inertia were found for two isotopic species of chlorodifluoromethane. This asymmetric top molecule is composed of five atoms, so it has a fairly complex structure. One purpose of carrying out this research was to determine the feasibility of analyzing the structure of complicated molecules by use of microwave spectroscopy. It seemed that it would be an interesting problem to find out as much as possible about the structure of chlorodifluoromethane by using the moments of inertia of the two isotopic species. It must be realized that, in general, increasing the number of atoms increases the

complexity of the problem, and if several isotopic species cannot be measured, it may be impossible to determine the molecular structure at all because of lack of sufficient information.

Before taking up the actual determination of molecular structure, it is appropriate to point out that all spectroscopic measurements are made on vibrating molecules. Even in the lowest or ground state, the atoms have a certain amount of vibrational energy, the so-called zero-point energy. Because of this vibration, the analysis of a rotational spectrum gives rotational constants which are essentially reciprocals of the moments of inertia averaged over a rotational state. The moments of inertia computed from these rotational constants are effective moments of inertia. The effective moment of inertia will not be equal to the equilibrium moment of inertia. This follows for two reasons. In the first place, if r represents the distance of a given atom from an axis of rotation, the moment of inertia is proportional to the average value of r^2 , i.e., to $(r^2)_{av}$. Since $(r^2)_{av}$ is not equal to $(r_{av})^2$, the effective moment of inertia will not be equal to the equilibrium moment of inertia. In the second place, the vibrations are anharmonic so the equilibrium distance is not equal to r_{av} . When it is necessary to use different isotopic species of a molecule to complete the structural determination, it is assumed that the structural parameters are the same in all isotopic species of the molecule. This assumption is true only for the equilibrium structural parameters. In some cases, it is possible to compute the equilibrium rotational constants and from these the equilibrium positions of the atoms. However, it has not been possible in the majority of cases to

do so. If, for lack of sufficient information, it is necessary to use effective moments, not only will the calculated structural parameters differ from the equilibrium parameters, but they may not exactly fit all the isotopic species measured (20).

When the moments of inertia of two different isotopic species of a molecule are known, it is possible to find the coordinates in the principal axis coordinate system of an atom of mass m in the original molecule which is replaced by an isotope of mass $m + \Delta m$. This can be done by a method described by Kraitchman (20) which is followed in the present discussion. Let I_x, I_y, I_z be the principal moments of inertia of $\text{CHCl}^{35}\text{F}_2$ and I'_x, I'_y, I'_z be the principal moments of inertia of $\text{CHCl}^{37}\text{F}_2$ such that $I_x < I_y < I_z$ and $I'_x < I'_y < I'_z$. The coordinates for the substituted atom in a nonplanar asymmetric top can be found by using the following relation:

$$\begin{aligned}
 |X| &= \left\{ \frac{1}{2\mu} \left[(I'_y - I_y) + (I'_z - I_z) - (I'_x - I_x) \right] \right. \\
 &\quad \times \left[1 + \frac{(I'_x - I_x) - (I'_y - I_y) + (I'_z - I_z)}{2(I_x - I_y)} \right] \\
 &\quad \times \left. \left[1 + \frac{(I'_x - I_x) + (I'_y - I_y) - (I'_z - I_z)}{2(I_x - I_z)} \right] \right\}^{\frac{1}{2}}, \quad (10)
 \end{aligned}$$

where $\mu = \frac{m\Delta m}{m + \Delta m}$. A cyclic permutation can be used to get suitable equations for $|Y|$ and $|Z|$.

The CHClF_2 molecule is a nonplanar asymmetric top, but careful investigation of the relations governing the principal moments of inertia shows that the following equation holds:

$$(I'_y - I_y) - (I'_x - I_x) - (I'_z - I_z) = 0. \quad (11)$$

A derivation of this equation is given in Appendix A. For this equation to hold, it is necessary that the Y principal axis be perpendicular to the plane of symmetry of the molecule for each isotopic species, and the Cl atom must lie in the plane of symmetry (the plane of the C, H and Cl atoms) for each isotopic species. When equation (11) is substituted into equation (10), the latter reduces to the equations given by Kraitchman for the case of a planar asymmetric top, namely:

$$|Z| = \left\{ \frac{1}{\mu} (I'_x - I_x) \left[1 + \frac{I'_z - I_z}{I_z - I_x} \right] \right\}^{\frac{1}{2}}, \quad (12)$$

$$|X| = \left\{ \frac{1}{\mu} (I'_z - I_z) \left[1 + \frac{I'_x - I_x}{I_x - I_z} \right] \right\}^{\frac{1}{2}}. \quad (13)$$

The moments of inertia, which were experimentally determined for CHClF_2 and are not actually the equilibrium moments, are

$$\begin{array}{ll} I_x = 49.3939 \text{ amu } \text{\AA}^2, & I'_x = 49.3980 \text{ amu } \text{\AA}^2, \\ I_y = 103.9926 \text{ amu } \text{\AA}^2, & I'_y = 107.1689 \text{ amu } \text{\AA}^2, \\ I_z = 144.1210 \text{ amu } \text{\AA}^2, & I'_z = 147.2806 \text{ amu } \text{\AA}^2. \end{array}$$

It is realized that the accuracy of the experimental results does not warrant the retention of all these digits, but they are kept in order to reduce computational errors. The coordinates of the Cl^{35} atom found by substituting these moments of inertia in equations (12) and (13) are

$$\begin{aligned} |Z| &= 0.0470 \text{ \AA}, \\ |X| &= 1.2930 \text{ \AA}. \end{aligned}$$

Actual substitution of the moments of inertia in equation (11) gives the value 0.0127 amu \AA^2 instead of zero. This gives some indication of the error that can be expected in determination of the coordinates; for example, if the error in the quantity $(I'_x - I_x)$ were 0.0127 , it would mean the existence of a possible error of 157 per cent in the determination of $|Z|$, but it would lead to an error of only 0.62 per cent in the determination of $|X|$. Consideration of these possible errors has an influence on the method adopted for solution of the molecular structure.

Equations which can be solved to determine the unknown coordinates of the other atoms are needed. The moments of inertia of the molecule can be expressed in terms of the coordinates of all the atoms, and it may be possible to solve these equations for the coordinates. To obtain a suitable system of equations which are simpler than those for the moments of inertia, it is more convenient to use a symmetric dyadic, \underline{P} , called the planar dyadic (20). The planar dyadic is defined by

$$\underline{P} = \sum_i m_i \vec{r}_i \vec{r}_i - \frac{\left(\sum_i m_i \vec{r}_i \right) \left(\sum_i m_i \vec{r}_i \right)}{\sum_i m_i}, \quad (14)$$

for the case of a free rotating body when the origin of the coordinate system is not at the center of mass. If the origin of the coordinate axes is at the center of mass, \underline{P} reduces to

$$\underline{P} = \sum_i m_i \vec{r}_i \vec{r}_i . \quad (15)$$

The diagonal elements of \underline{P} are often called planar moments of inertia. The nondiagonal elements, except in choice of sign, are equivalent to the products of inertia. Relations between elements of \underline{P} and principal moments are

$$P_X = (1/2)(I_Y + I_Z - I_X) ,$$

$$I_X = P_Y + P_Z .$$

With the coordinate system chosen as the principal axis system (origin at center of mass, of course) the elements of the planar dyadic take the form:

$$\begin{aligned} P_{xy} &= \sum_i m_i x_i y_i = 0, & P_X &= \sum_i m_i x_i^2 , \\ P_{xz} &= \sum_i m_i x_i z_i = 0, & P_Y &= \sum_i m_i y_i^2 , \\ P_{yz} &= \sum_i m_i y_i z_i = 0, & P_Z &= \sum_i m_i z_i^2 . \end{aligned} \quad (16)$$

Notice that each of the planar moments of inertia is a function of only one coordinate. Let the hydrogen, carbon, chlorine and fluorine atoms have the subscripts 1, 2, 3 and 4 respectively. The equations (16) and the equations for the center of mass become:

$$m_1x_1z_1 + m_2x_2z_2 + m_3x_3z_3 + 2m_4x_4z_4 = 0, \quad (17)$$

$$m_1x_1^2 + m_2x_2^2 + m_3x_3^2 + 2m_4x_4^2 = (1/2)(I_y + I_z - I_x), \quad (18)$$

$$2m_4y_4^2 = (1/2)(I_x + I_z - I_y), \quad (19)$$

$$m_1z_1^2 + m_2z_2^2 + m_3z_3^2 + 2m_4z_4^2 = (1/2)(I_x + I_y - I_z), \quad (20)$$

$$m_1x_1 + m_2x_2 + m_3x_3 + 2m_4x_4 = 0, \quad (21)$$

$$m_1z_1 + m_2z_2 + m_3z_3 + 2m_4z_4 = 0. \quad (22)$$

The magnitudes of x_3 and z_3 have been previously determined, so this leaves seven unknowns in the six equations. The equation (19) determines y_4 . This leaves five equations in the unknown quantities x_1 , x_2 , x_4 , z_1 , z_2 and z_4 . These equations are nonlinear, and there are no general theorems concerning the existence or uniqueness of solutions of simultaneous nonlinear equations. Every such system of equations must be treated as a separate problem. The variables x_4 and z_4 were eliminated for a reason that will be apparent later. The equations obtained after eliminating x_4 and z_4 are

$$Ax_1^2 + Bx_2^2 + 2E_1x_1 + 2E_2x_2 + 2E_3x_1x_2 + F_1 = 0, \quad (23)$$

$$Az_1^2 + Bz_2^2 + 2E_4z_1 + 2E_5z_2 + 2E_3z_1z_2 + F_2 = 0, \quad (24)$$

$$\begin{aligned} Ax_1z_1 + Bx_2z_2 + E_1z_1 + E_2z_2 + E_4x_1 + E_5x_2 \\ + E_3(x_1z_2 + x_2z_1) + F_3 = 0. \end{aligned} \quad (25)$$

The coefficients which appear here are given by the following relations:

$$A = \frac{m_1}{2m_4} \left(1 + \frac{m_1}{2m_4} \right),$$

$$B = \frac{m_2}{2m_4} \left(1 + \frac{m_2}{2m_4} \right),$$

$$E_1 = \frac{m_1m_3x_3}{(2m_4)^2},$$

$$E_2 = \frac{m_2m_3x_3}{(2m_4)^2},$$

$$E_3 = \frac{m_1m_2}{(2m_4)^2},$$

$$E_4 = \frac{m_1m_3z_3}{(2m_4)^2},$$

$$E_5 = \frac{m_2m_3z_3}{(2m_4)^2},$$

$$F_1 = \frac{m_3x_3^2}{2m_4} \left(1 + \frac{m_3}{2m_4} \right) - \frac{I_y + I_z - I_x}{4m_4},$$

$$F_2 = \frac{m_3z_3^2}{2m_4} \left(1 + \frac{m_3}{2m_4} \right) - \frac{I_x + I_y - I_z}{4m_4},$$

$$F_3 = \frac{m_3x_3z_3}{2m_4} \left(1 + \frac{m_3}{2m_4} \right).$$

In order for there to be any possibility at all of solving the system of equations (23), (24) and (25) in four unknowns, it is necessary to have more information. One piece of information as yet unused is the

equation for I_y' . Equation (23) represents an ellipse in the x_1x_2 plane, and equation (24) represents a similar ellipse in the z_1z_2 plane. The semi-axes of both ellipses are rotated the same amount with respect to their coordinate axes. Equation (25) along with any other appropriate equation may be considered as a transformation which maps a point in the x_1x_2 plane to a point in the z_1z_2 plane or vice versa. The problem is to find an appropriate point on the x_1x_2 ellipse which maps over into a point on the z_1z_2 ellipse, if such a point exists, and to determine the correct point if more than one exists.

The first attempt to solve the equations failed. Points were chosen on the appropriate segment of the z_1z_2 ellipse, and points were obtained that traced out a curve on the x_1x_2 plane. This curve did not intersect the x_1x_2 ellipse when using parameters which gave a reasonable C - H bond distance because of the experimental error in determination of z_3 . A solution was obtained by treating z_3 as a variable and using an estimated C - H bond distance. The C - H bond distance was estimated to be 1.09 Å by examining C - H bond distances for other molecules. This estimated value provides the following relation in addition to the previous equations:

$$(x_2 - x_1)^2 + (z_2 - z_1)^2 - (1.09)^2 = 0. \quad (26)$$

The reason for estimating the length of the C - H bond follows from the fact that the H atom has about 1/35 the mass of the Cl atom. From this

fact it is easy to see that a small error in the previously determined position of the Cl atom causes a very large error in the determination of the position of the H atom. For this reason the estimated C - H bond distance is at least as good as that which could be obtained from an exact calculation based upon the probably erroneous position assigned to the Cl atom. When the C - H distance is estimated it is possible to solve the system of four second degree equations in the four unknowns x_1 , x_2 , z_1 and z_2 . An estimated position of the H atom can be used to give a quite accurate position for the heavier atoms. The coordinates of the F atoms were eliminated from the equations under consideration because they are not involved in expressions for the C - H bond distance. A later determination of the F coordinates is quite simple.

The plan of solution finally adopted was an iterative process in which an IBM 650 digital computer was employed. The value of z_3 determined from experimental data was not used because of the large possible error involved. Steps taken in the solution of the problem by the computer were as follows:

1. Choose a value of x_1 and determine x_2 from equation (23). The x_1x_2 ellipse is fixed by x_3 and the other constants defined previously.
2. Use equations (25) and (26) to find

$$z_1 = \frac{(Bx_2 + E_3x_1 + E_2) \sqrt{F_4 - (x_1 - x_2)^2 - (E_4x_1 + E_5x_2 + F_3)}}{(A + E_3)x_1 + (B + E_3)x_2 + E_1 + E_2} \quad (27)$$

At this point z_1 is a function of z_3 because E_4 , E_5 , and F_3 are functions of z_3 .

3. Find z_2 as a function of z_3 from the equation

$$z_2 = z_1 - \sqrt{F_4 - (x_1 - x_2)^2} . \quad (28)$$

4. Substitute z_1 and z_2 in equation (24) to find z_3 . Each different value of z_3 determines a different ellipse in the z_1z_2 plane.

5. Find numerical values of z_1 and z_2 by substituting z_3 in equations (27) and (28). These values of z_1 and z_2 are the coordinates of a point on the z_1z_2 ellipse.

6. Find x_4 and z_4 from the center of mass relations:

$$x_4 = - \frac{1}{2m_4}(m_1x_1 + m_2x_2 + m_3x_3) , \text{ and} \quad (29)$$

$$z_4 = - \frac{1}{2m_4}(m_1z_1 + m_2z_2 + m_3z_3) . \quad (30)$$

7. Calculate the moment of inertia of $\text{CHCl}^{37}\text{F}_2$ about the Y axis of the molecule by substituting the coordinates calculated above into the following relation which was obtained by translating the coordinate system to the center of mass of the $\text{CHCl}^{37}\text{F}_2$ molecule:

$$\begin{aligned} I'_{Y_c} = & m_1(x_1^2 + z_1^2) + m_2(x_2^2 + z_2^2) + M_3(x_3^2 + z_3^2) + 2m_4(x_4^2 + z_4^2) \\ & - \frac{(\Delta m)^2}{M} (x_3^2 + z_3^2) . \end{aligned} \quad (31)$$

Here M_3 is the mass of Cl^{37} and M is the mass of the $\text{CHCl}^{37}\text{F}_2$ molecule.

8. Test I'_{Y_c} to find out if it is different from the measured moment of inertia; if so, vary x_1 by increments until the difference is a minimum.

The coordinates obtained for the atoms are given below.

$$x_1 = -1.620000 \text{ \AA}, \quad y_1 = 0, \quad z_1 = + 1.101041 \text{ \AA},$$

$$\begin{aligned}
 x_2 &= -0.752367 \text{ \AA}, & y_2 &= 0, & z_2 &= + 0.441258 \text{ \AA}, \\
 x_3 &= +1.293037 \text{ \AA}, & y_3 &= 0, & z_3 &= - 0.000056 \text{ \AA}, \\
 x_4 &= -0.909415 \text{ \AA}, & y_4 &= \pm 1.08195 \text{ \AA}, & z_4 &= - 0.168045 \text{ \AA}.
 \end{aligned}$$

Notice that the value for z_3 lies within the previously mentioned experimental error. These coordinates give moments of inertia for the CHClF_2 molecule as follows:

$$\begin{aligned}
 I_x &= 49.3939 \text{ amu \AA}^2, & I'_x &= 49.3939 \text{ amu \AA}^2, \\
 I_y &= 103.9926 \text{ amu \AA}^2, & I'_y &= 107.2567 \text{ amu \AA}^2, \\
 I_z &= 144.1210 \text{ amu \AA}^2, & I'_z &= 147.3850 \text{ amu \AA}^2.
 \end{aligned}$$

The values calculated for I_x , I_y , and I_z are the same as those determined from the rotational constants. The values of I'_x , I'_y , and I'_z are slightly inconsistent with the values determined from experimental data. The inconsistencies could arise because equilibrium moments of inertia were not obtained for use in the calculations. No compensation was made for the effects of centrifugal distortion, and there are possible errors in the moments of inertia. The structure found by microwave spectroscopy is shown below for comparison with the structure found by electron diffraction.

Table 9. Structure of CHClF_2

	Microwave	Electron Diffraction
$d(\text{C} - \text{Cl})$	2.10 \AA	1.73 \AA
$d(\text{C} - \text{F})$	1.25 \AA	1.36 \AA
$d(\text{C} - \text{H})$	1.09 \AA	-
$\angle \text{Cl} - \text{C} - \text{F}$	91°	greater than $\angle \text{F} - \text{C} - \text{F}$
$\angle \text{F} - \text{C} - \text{H}$	101°	-
$\angle \text{F} - \text{C} - \text{F}$	120°	-

Figure 7 shows the calculated structure of chlorodifluoromethane. The disagreement in the structures obtained is considerable. Errors in structural determination by microwave spectroscopy could arise because of small errors in the moments of inertia. A small error in the position of one atom can result in large errors in positions of other atoms determined from the first one, and the errors grow worse as the number of atoms in the molecule increases.

A summary of the method used to determine the structure may be useful. First the coordinates of the substituted atom (Cl) were determined from the moments of inertia of the two isotopic species of molecule. Equations for the elements of the planar dyadic and center of mass were written, and two coordinates of atoms were eliminated from these equations by algebraic methods. The remaining system of nonlinear equations was solved by an iterative process. Finally, the coordinates which had been eliminated were found by use of the center of mass equation.

The results obtained for this molecule indicate that the measured moments of inertia will not give an accurate determination of molecular structure. It seems likely that for most molecules of this type three or four isotopic species will have to be investigated in order to determine the structure accurately.

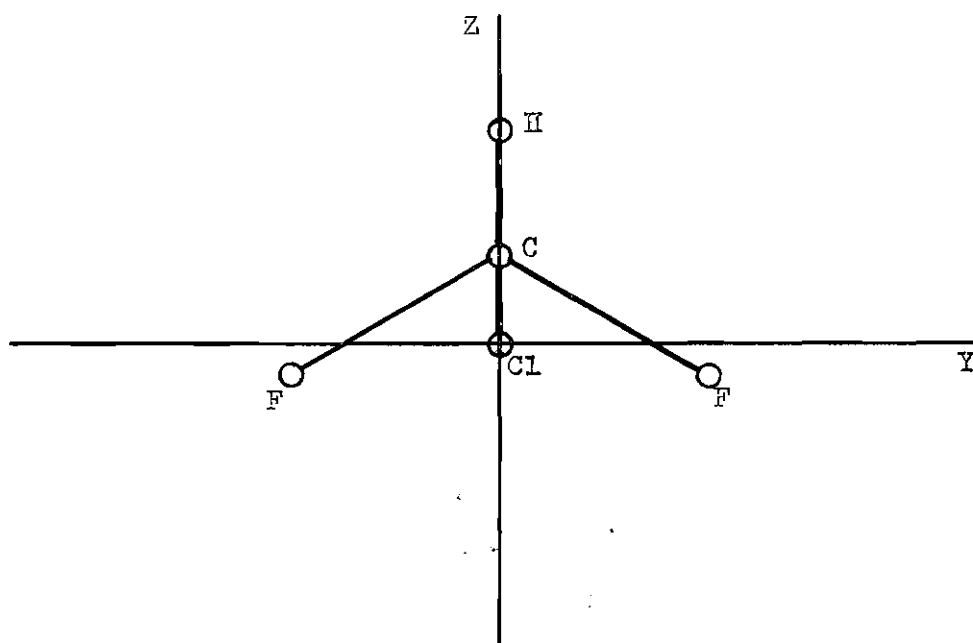
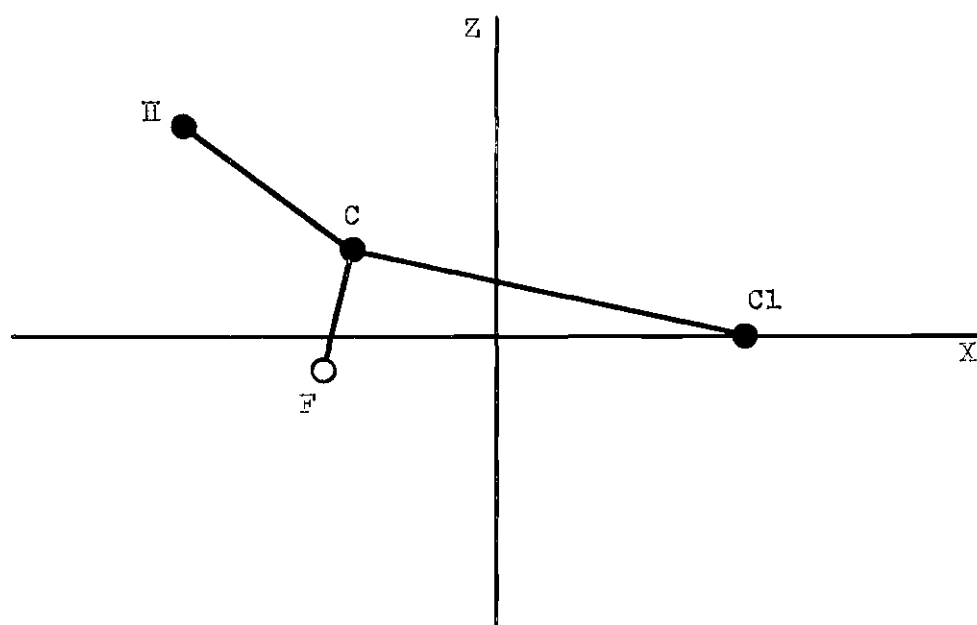


Figure 7. Calculated Structure of Chlorodifluoromethane.

CHAPTER V

THE STARK EFFECT OF CHLORODIFLUOROMETHANE

The Stark effect for the $J_{\tau} = 0_0 - 1_1$ transition of chlorodifluoromethane was measured. Experiments were performed on this particular transition because it has the simplest possible hyperfine structure, it exhibits well-resolved Stark components, and it occurs at a convenient operating frequency. Measurements of the Stark components at different voltages indicated that the Stark displacements were of the same order of magnitude as the quadrupole splittings. This information was used in choosing the method which was employed in the analysis of the Stark effect. The rotational energy levels for the transition are separated enough that the effects of near-degeneracy can be ignored. If the molecule were more nearly a symmetric top, it would be necessary to take into account the effects of near-degeneracy of the energy levels. Because of the similarity in magnitude of the Stark displacements and quadrupole splittings, the stronger field case of Mizushima (5) was chosen for calculating the Stark effect. Mizushima's theory does not include the effects of near-degeneracy.

The Stark energies, E , were found by solving the following secular equation:

$$\left| \frac{eQ \left\langle \frac{\partial^2 V}{\partial z^2} \right\rangle_{av} \left\langle JIm_{Jm_I} \left| 3(\vec{I} \cdot \vec{J})^2 + \frac{3}{2}(\vec{I} \cdot \vec{J}) - \vec{I}^2 \vec{J}^2 \right| JIm'_{Jm'_I} \right\rangle}{2I(2I-1) J(2J-1)} + \left(W_{J,\tau,I=0, m_J} - E \right) \delta_{m_J m'_J} \delta_{m_I m'_I} \right| = 0. \quad (32)$$

The component of \vec{J} along the external field is m_J and the component of \vec{I} along the external field is m_I . The Stark effect energy $W_{J,\tau,I=0,m_J}$ is obtained from the equation for $W_{J,\tau M}$ given by Golden and Wilson (6) by replacing M by m_J . This gives

$$\begin{aligned}
 W_{J,\tau,I=0,m_J} = & \sum_{g=abc} \mu_g^2 \mathcal{E}^2 \left[\frac{J^2 - m_J^2}{4J^2(4J^2 - 1)} \sum_{\tau'} \left\{ \frac{[(\phi_{Zg})_{J\tau J - 1\tau'}]^2}{W_{J\tau}^0 - W_{J-1\tau'}^0} \right\} \right. \\
 & + \frac{m_J^2}{4J^2(J+1)^2} \sum_{\tau' \neq \tau} \left\{ \frac{[(\phi_{Zg})_{J\tau J\tau'}]^2}{W_{J\tau}^0 - W_{J\tau'}^0} \right\} \\
 & \left. + \frac{(J+1)^2 - m_J^2}{4(J+1)^2(2J+1)(2J+3)} \sum_{\tau'} \left\{ \frac{[(\phi_{Zg})_{J\tau J+1\tau'}]^2}{W_{J\tau}^0 - W_{J+1\tau'}^0} \right\} \right]. \quad (33)
 \end{aligned}$$

The W^0 are the unperturbed rotational energies of the asymmetric rotor, the ϕ_{Zg} are the matrix elements of the direction cosines of the angle between the direction of the external field, Z , and the component of dipole moment, g , and \mathcal{E} is the electric field strength. Line strengths are also proportional to the square of the direction cosine matrix elements, and a table of line strengths has been published (17) in which line strengths are given for different values of J, τ , and k . The published line strengths are not given for the value of k calculated for this molecule. The transition considered here is between low J numbers, so the wave functions are easy to calculate. Rather than interpolate in

the table of line strengths, the dipole moment matrix elements needed were calculated in order to get the best accuracy possible. The matrix elements were evaluated in terms of symmetric rotor wave functions. A high degree of accuracy is necessary in the calculations because the Stark effect of the transition depends upon both components μ_a and μ_c of the dipole moment. Calculations showed the Stark effect of the $J_r = 0_0 - 1_1$ transition is more strongly dependent upon μ_a than upon μ_c . Because several rotational transitions induced by interaction of radiation with μ_c were observed, and no transitions induced by interaction with μ_a were observed, it was ascertained that μ_a must be small compared to μ_c .

It was not possible to find Stark components that depend solely upon μ_a or μ_c . Because each Stark component depends upon both μ_a and μ_c , it was necessary to include the value of μ_a and μ_c in every calculation of Stark energy. Stark effect calculations were made for several different combinations of components of dipole moment and Stark voltage. The secular equations were solved by an IBM 650 computer. The calculated Stark spectrum consisted of five Stark components each of which has a positive displacement as the Stark voltage is increased. Only three components could be observed. Their displacements were large enough to clear the hyperfine structure, but only two of them were strong enough to be observed on a visual presentation of the spectrum at Stark voltages over 450 V. The third one was recorded and the Stark displacement was determined from the recordings for different voltages. A graph of the measured Stark effect is shown in Figure 8 on which the circles represent measured points. The calculated Stark effects were compared to

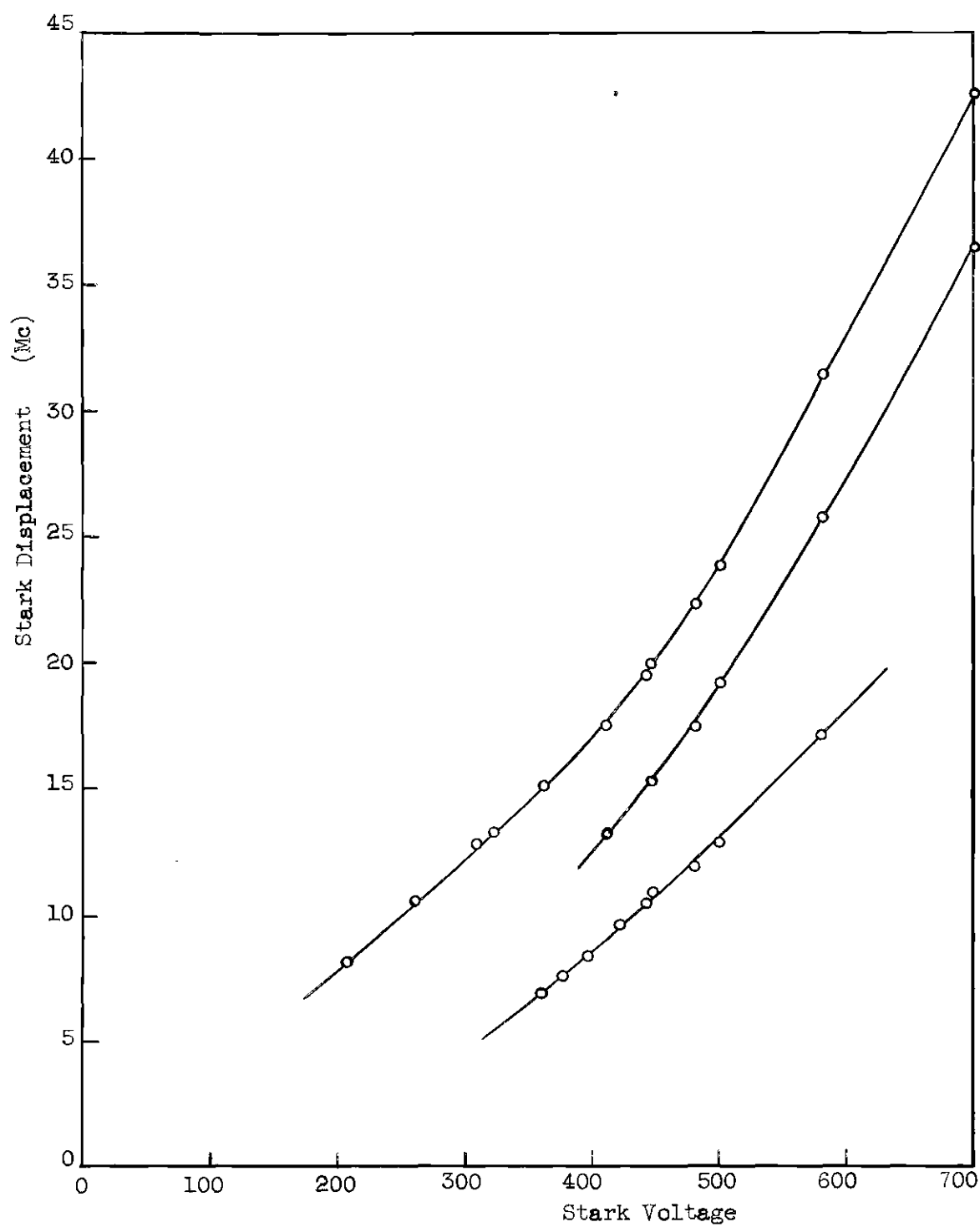


Figure 8. Observed Stark Effect of Chlorodifluoromethane.

the measured Stark spectrum and the components of dipole moment were refined until the calculated and measured Stark spectra were practically the same. The components of dipole moment were found to be $\mu_a = 0.12$ Debye and $\mu_c = 1.45$ Debye. The possible error is estimated to be ± 0.02 Debye for each component. The calculated and measured frequencies of the observed Stark components are shown below for a Stark voltage of 500 V (Stark field = 1073 V/cm).

Table 10. Stark Components for the $J_u = 0_0 - 1_1$ Transition of CHClF_2 at 1073 Volts/cm $^\tau$

Calculated Frequency (Mc)	Measured Frequency (Mc)	Calculated Displacement (Mc)	Measured Displacement (Mc)	Error (Mc)
15,119.85	15,119.88	23.89	23.92	-0.03
15,114.96	15,115.17	19.00	19.21	-0.21
15,109.37	15,109.01	13.41	13.05	+0.36

CHAPTER VI

THE STARK EFFECT OF CHLOROTRIFLUOROMETHANE

The chlorotrifluoromethane used in the experiment described here has the trade name "Freon-13". It was obtained from the Matheson Company, Incorporated, and is reported to have a purity of 99.0 per cent.

Coles and Hughes (7) made measurements of the spectrum of this symmetric top molecule from which they obtained the rotational constants, quadrupole coupling constants and molecular structure. They did not report the dipole moment. It was decided to undertake the evaluation of the dipole moment by measuring and analyzing the Stark effect. The Stark effect was measured for the $J = 2 - 3$ transition. Best results were obtained with the waveguide cooled to dry ice temperature and with the pressure at about 0.05 mm of mercury. The Stark spectrum for this transition is fairly complex. Only small Stark voltages were used in the measurements, because the Stark lines broaden as the voltage is increased.

The theory developed by Low and Townes (8) for the Stark effects of symmetric top molecules with nuclear quadrupole coupling was used in the work on "Freon-13". Low and Townes discuss three separate cases for the Stark effect.

A. Weak Field Case

In the weak field case the splitting of the rotational line due to the Stark effect is small compared to the splitting caused by the nuclear quadrupole interaction. The Stark energies can be found by

non-degenerate perturbation theory in which the Stark energy is treated as a small perturbation on the rotational plus quadrupole energy.

B. Strong Field Case

In the strong field case the Stark splitting of the rotational line is large compared to the quadrupole splitting, and the quadrupole interaction is treated as a small perturbation on the rotational plus Stark energies.

C. Intermediate Field Case

In the intermediate field case the effects of the quadrupole splitting and Stark splitting are comparable in magnitude. In order to determine the energies one must solve secular equations which diagonalize the matrix of $H_Q + H_E$ where H_Q is the quadrupole Hamiltonian, and H_E the Stark effect Hamiltonian.

Experiment showed that the observed Stark displacements were fairly small; therefore, an attempt was made to fit the Stark spectrum to the weak field theory. However, the results obtained from the theory were not consistent with observed data. The strong field theory was then tried, but the results were unsatisfactory even at higher voltages. Because of the disagreement of the simpler theories and the observed data, it was necessary to use the more complicated intermediate field theory.

In the intermediate field theory, it is necessary to compute matrix elements of the quadrupole Hamiltonian plus the Stark effect Hamiltonian and diagonalize the matrix in order to determine the energies. The matrix elements are computed from a set of wave functions

which can be functions of different sets of quantum numbers. One can use the set of quantum numbers J, K, I, F and M in which M is chosen with respect to a space-fixed frame of reference (the electric field) to represent the wave functions, or one can use the set of quantum numbers J, K, I, m_J , and m_I in which m_J and m_I are chosen with respect to the space-fixed frame of reference to represent the wave functions. Low and Townes chose the set $\psi(JKIFM)$. The secular equation obtained in this representation is

$$\left| \langle JKIFM | H_Q + H_E | JKIF'M' \rangle - w \delta_{FF'} \delta_{MM'} \right| = 0 \quad (34)$$

where \vec{J} is the angular momentum of the molecular framework and K is the component of \vec{J} along the molecular symmetry axis. The total angular momentum \vec{F} is the vector sum $\vec{J} + \vec{I}$, and M is the component of the total angular momentum along the direction of the applied electric field. The value of M is given by the relation $M = m_J + m_I$ where m_J and m_I are components of \vec{J} and \vec{I} respectively along the applied electric field, and w is the perturbation energy. The matrix of the secular equation is diagonal in M and therefore can be divided into submatrices of the first, second, and higher order. A submatrix exists for each allowed value of M . For a given value of M a secular equation can be written in the form:

$$\left| \langle JKIFM | H_Q + H_E | JKIF'M \rangle - w \delta_{FF'} \right| = 0. \quad (35)$$

In the JKIFM representation H_Q is diagonal in F , and the secular equation can be expressed as:

$$\left| \langle JKIFM | H_E | JKIF'M \rangle + \langle JKIFM | H_Q | JKIFM \rangle - w \delta_{FF'} \right| = 0. \quad (36)$$

In this determinant the rows and columns differ only in the value of F . The quantum number F takes on the values $J + I, J + I - 1, \dots, |J - I|$, and the quantum number M takes on the values $F, F - 1, \dots, -F$. When M has the value $J + I$, it is required that $F = J + I$ and the secular equation is first order. For $M = J + I - 1$, the values of F can be $J + I$ or $J + I - 1$, and the secular equation is second order. The highest degree of the secular equation is the smaller of the numbers $2J + 1$ or $2I + 1$.

The diagonal elements of the quadrupole Hamiltonian appearing in equation (36) are given by:

$$\langle JKIFM | H_Q | JKIFM \rangle = eqQ \left[\frac{3K^2}{J(J+1)} - 1 \right] f(IJF) \quad (37)$$

where

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

and

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

The function f is often called Casimir's function and has been tabulated in order to simplify calculations (21). The charge of the proton is represented by e , the nuclear quadrupole moment by Q and the second derivative of the electrostatic potential along the molecular axis by q .

In order to obtain the matrix elements of H_E it is necessary to expand the wave function $\psi(JKIFM)$ in terms of the wave functions $\psi(JKIm_Jm_I)$ as follows:

$$\psi(JKIFM) = \sum_{m_J} a_{Fm_J} \psi(JKIm_Jm_I) . \quad (38)$$

The coefficients a_{Fm_J} are the Clebsch-Gordan coefficients given by Condon and Shortley (22). For a particular M , the sum includes only those values of m_J for which $m_J + m_I = M$. For example, if $M = F - 1 = J + I - 1$, there are two possible ways in which M can be formed, i.e.:

$$M = m_J + m_I$$

where

$$m_J = J \text{ and } m_I = I - 1$$

or

$$m_J = J - 1 \text{ and } m_I = I.$$

Hence, in this case there are two possible wave functions which are formed by appropriate linear combinations of the different $\psi(JKIm_Jm_I)$ by using the linear coefficients a_1 and a_2 obtained from Condon and Shortley. The wave functions are:

$$\begin{aligned} \psi_1(JKIFM) &= a_1 \psi(J, K, I, m_J = J, m_I = I - 1) \\ &+ a_2 \psi(J, K, I, m_J = J - 1, m_I = I), \end{aligned} \quad (39)$$

$$\begin{aligned} \psi_2(JKIFM) &= -a_2 \psi(J, K, I, m_J = J, m_I = I - 1) \\ &+ a_1 \psi(J, K, I, m_J = J - 1, m_I = I). \end{aligned} \quad (40)$$

The matrix elements can then be found using the relation:

$$\langle JKIm_Jm_I | H_E | JKIm_Jm_I \rangle = - \frac{\mu E K m_J}{J(J+1)}. \quad (41)$$

The secular equations were written for values of $J = 3$, $K = 2$, with $M = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$, and for $J = 2$, $K = 2$, with $M = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$. These equations were divided by μEK in order to get the solutions for $\frac{W}{\mu EK}$ and thereby facilitate calculations for different values of dipole moment μ and Stark field E . The higher degree equations were solved by using an IBM 650 computer. Calculations were carried out for several combinations of dipole moment and Stark voltage.

There are no simple selection rules for the intermediate field Stark effect. It is necessary to determine the dipole moment matrix elements for the transitions in order to decide which transitions are allowed and to determine their relative intensities. The intensities of the transitions are proportional to the square of the dipole moment matrix elements.

In order to determine the dipole moment matrix elements, it is necessary to find the coefficients for the expansion of the wave functions $\Psi(JKLM)$ in terms of the $\Psi(JKlm_Jm_L)$ for each different energy. This is done by putting the root of the secular equation for the energy level whose wave function is to be determined into the matrix of the secular equation and multiplying the matrix on the right by a column matrix of the unknown coefficients. This gives a system of n linear equations in n unknowns for a secular equation of the n th degree. The equations are homogeneous and so do not have a unique solution. Orthogonal wave functions are desired, however, so only $n-1$ of the linear equations are needed, along with the normalizing condition that the sum of the squares of the coefficients must have the value unity, in order to

get a unique set of expansion coefficients for the wave function of the energy level. This gives the perturbed wave functions in terms of $\psi(\text{JKIFM})$. Then the expansions in terms of $\psi(\text{JKIm}_{Jm_I})$ are substituted for the $\psi(\text{JKIFM})$ to obtain the perturbed wave functions in terms of $\psi(\text{JKIm}_{Jm_I})$.

The Z component of the dipole moment matrix element for a transition $i \rightarrow j$ is given by

$$(\mu_Z) = \mu_Z \int \cos(zZ) \psi_i \psi_j^* dt \quad (42)$$

where μ_Z is the dipole moment along the symmetry axis of the symmetric top molecule and $\cos(zZ)$ represents the cosine of the angle between the molecular axis and the Z axis fixed in space.

The matrix elements of $\cos(zZ)$ for a symmetric top are given by Cross, Hainer, and King (17). Substitution of these into equation (42) gives

$$(\mu_g)_{\text{JKm}_J J' K' m'_J} = \mu \varnothing_{JJ'} \varnothing_{JKJ' K'} \varnothing_{Jm_J J' m'_J} \quad (43)$$

where μ is the molecular dipole moment. The \varnothing 's, which might be called factors of the direction cosine matrix, are each dependent on the rotational quantum numbers indicated by the subscripts. The \varnothing 's are also dependent on the particular component μ_g which is being evaluated and on the molecular axis along which the dipole moment μ lies. For the case of dipole moment along the molecular symmetry axis, which is considered here, and with $J' = J + 1$, one has

$$\varnothing_{JJ'} = \frac{1}{4(J+1)\sqrt{(2J+1)(2J+3)}} \quad (44)$$

$$\phi_{JKJ'K} = 2\sqrt{(J+1)^2 - K^2} \quad , \quad (45)$$

$$\phi_{Jm_JJ'm_J} = 2\sqrt{(J+1)^2 - m_J^2} \quad , \quad (46)$$

$$\mu = \mu_z \quad . \quad (47)$$

The space-fixed component of dipole moment is given by

$$(\mu_z)_{JKm_JJ+1Km_J} = \mu_z \frac{\sqrt{(J+1)^2 - K^2} \sqrt{(J+1)^2 - m_J^2}}{(J+1) \sqrt{(2J+1)(2J+3)}} \quad , \quad (48)$$

and the relative intensities are proportional to the squares of the dipole moment matrix elements which connect the states under consideration.

The squares of the dipole moment matrix elements divided by the square of the dipole moment were found for all Stark transitions. These quantities are proportional to the intensities of the Stark transitions and were used as relative intensities. Allowed Stark transitions are those for which the dipole moment matrix elements are non-zero. The predicted Stark effect indicated that various Stark lines tended to overlap and pass each other as the Stark voltage changed. Several of the allowed Stark transitions for a particular Stark voltage had frequencies which were close together. These frequencies were weighted with their relative intensities to find a weighted average which was used to predict the Stark spectrum for that voltage.

Many recordings of the CClF_3 spectrum were made using different Stark voltages. Stark displacements were measured with respect to the rotational lines $J = 2 - 3$, $K = 2$, $F = \frac{3}{2} - \frac{5}{2}$ and $\frac{3}{2} - \frac{3}{2}$ at a frequency of 20,013.68 Mc and $J = 2 - 3$, $K = 2$, $F = \frac{7}{2} - \frac{9}{2}$ and $\frac{7}{2} - \frac{7}{2}$ at a frequency of 20,019.17 Mc. The first frequency mentioned is the group center for the transition, but the second one is more intense and better resolved on recordings. Two of the Stark components were fairly easy to follow as the voltage was varied. Their average measured displacements are shown in Table 11 for different Stark voltages.

The Stark spectrum calculated from a dipole moment of 0.50 Debye and the average measured Stark spectrum were in good agreement for Stark voltages of 30 V and 50 V which correspond to electric fields of 64.4 V/cm and 107.3 V/cm respectively. The calculated Stark energies which were obtained as roots of the secular equations are identified by numbering the roots (1), (2), (3), etc., in increasing order. Table 11 gives a comparison of measured Stark components and calculated Stark components which are identified as just mentioned. This is for a dipole moment of 0.50 Debye and shows the best agreement obtained between calculated and measured Stark effects. The estimated possible error for the dipole moment is 0.05 Debye.

Table 11. Calculated and Measured Stark Components of Chlorotrifluoromethane

Stark Displacements are with Respect to Transition $J = 2 - 3$, $K = 2$, $F = 3/2 - 5/2$ and $3/2 - 3/2$ at 20,013.68 Mc for $\mu = 0.50$ Debye.

Stark Voltage	Stark Transition <u>M</u>	Predicted Stark Displacement (Mc)	Relative Intensity	Predicted Weighted Average Displacement (Mc)	Average Measured Displacement (Mc)
30	7/2 (1)-(1)	10.98	0.0529	10.96	11.06
	5/2 (2)-(1)	10.96	0.0548		
	3/2 (3)-(1)	10.94	0.0289		
	1/2 (4)-(1)	10.66	0.0001		
30	3/2 (3)-(2)	8.24	0.0524	8.14	8.13
	5/2 (2)-(2)	8.26	0.0449		
	3/2 (1)-(1)	7.29	0.0038		
	1/2 (4)-(2)	7.96	0.0424		
50	7/2 (1)-(1)	14.57	0.0794	14.88	14.84
	5/2 (2)-(1)	14.96	0.0440		
	3/2 (3)-(1)	15.93	0.0204		
50	5/2 (2)-(2)	10.46	0.0518	10.68	10.90
	3/2 (3)-(2)	11.43	0.0165		
	3/2 (1)-(1)	11.90	0.0001		

CHAPTER VII

THE STARK EFFECT OF NITROSYL CHLORIDE

The nitrosyl chloride used in the experiments described here was obtained from The Matheson Company, Incorporated, who describe it as having a purity of 93.0 per cent.

The microwave spectrum has been analyzed by Rogers (3), who estimated the electric dipole moment to be $\mu_a = 1.28$ Debye. He determined the rotational constants and quadrupole coupling coefficients by analysis of the microwave spectrum. Rogers did not report a determination of the molecular structure from the microwave spectrum. Electron diffraction studies by Ketelaar and Palmer (23) yielded the following values for interatomic distance and bond angle:

$$d(\text{N} - \text{Cl}) = 1.95 \pm .01 \text{ \AA}, \quad d(\text{N} - \text{O}) = 1.14 \pm .02 \text{ \AA},$$

$d(\text{O} - \text{Cl}) = 2.65 \pm .01 \text{ \AA}$, angle $\text{O} - \text{N} - \text{Cl} = 116^\circ \pm 2^\circ$. The rotational constants obtained by Rogers indicate that NOCl is approximately a prolate symmetric molecule.

An investigation of the Stark effect of the $J_r = 1_1 - 2_0$ transition showed that the Stark displacement of the strongest, most easily measured Stark component was not linear with respect to the square of the Stark voltage. This indicated the presence of near-degenerate rotational levels which one would expect for this molecule since it is almost a symmetric top.

Calculations using the theory of Mizushima (5) indicated that the large Stark component was, in reality, made up of several unresolved

smaller components. The intensities of the Stark components were determined as explained in Chapter VI. The average of the calculated frequencies of the quadrupole plus Stark lines weighted with their intensities coincided with the frequency of the Stark line without quadrupole splitting. Because of this, it was possible to neglect the quadrupole splitting and apply the theory of Golden and Wilson (6) for the Stark effect of the asymmetric rotor. The displacement of the Stark component as a function of Stark voltage squared is shown in Figure 9. Measured displacements are shown as circles. One can see that the displacement is not linear. The effects of near-degeneracy of energy levels were included in the calculations using the method described by Golden and Wilson.

Initial calculations were based on the value of dipole moment $\mu_a = 1.28$ Debye estimated by Rogers. This gave a curve indicating less Stark displacement than that observed for various Stark fields. From the experimental data and these calculations it was determined that a component of dipole moment, μ_a , of about 1.86 Debye would cause the calculated Stark effect to coincide with the measurements. In Figure 8 the circles represent measured points and the curve represents the theoretically predicted Stark effect for a dipole moment $\mu_a = 1.86$ Debye. The error in the dipole moment is estimated to be ± 0.02 Debye.

An attempt was made to determine μ_b . Calculations for the transition measured showed that μ_b has only a small effect on the Stark displacement; a value of $\mu_b = 1$ Debye causes a change in the Stark line frequency of less than 1 Mc for a Stark voltage of 400 V. This is a change of about 1 part in 200 of the Stark displacement at this voltage and is

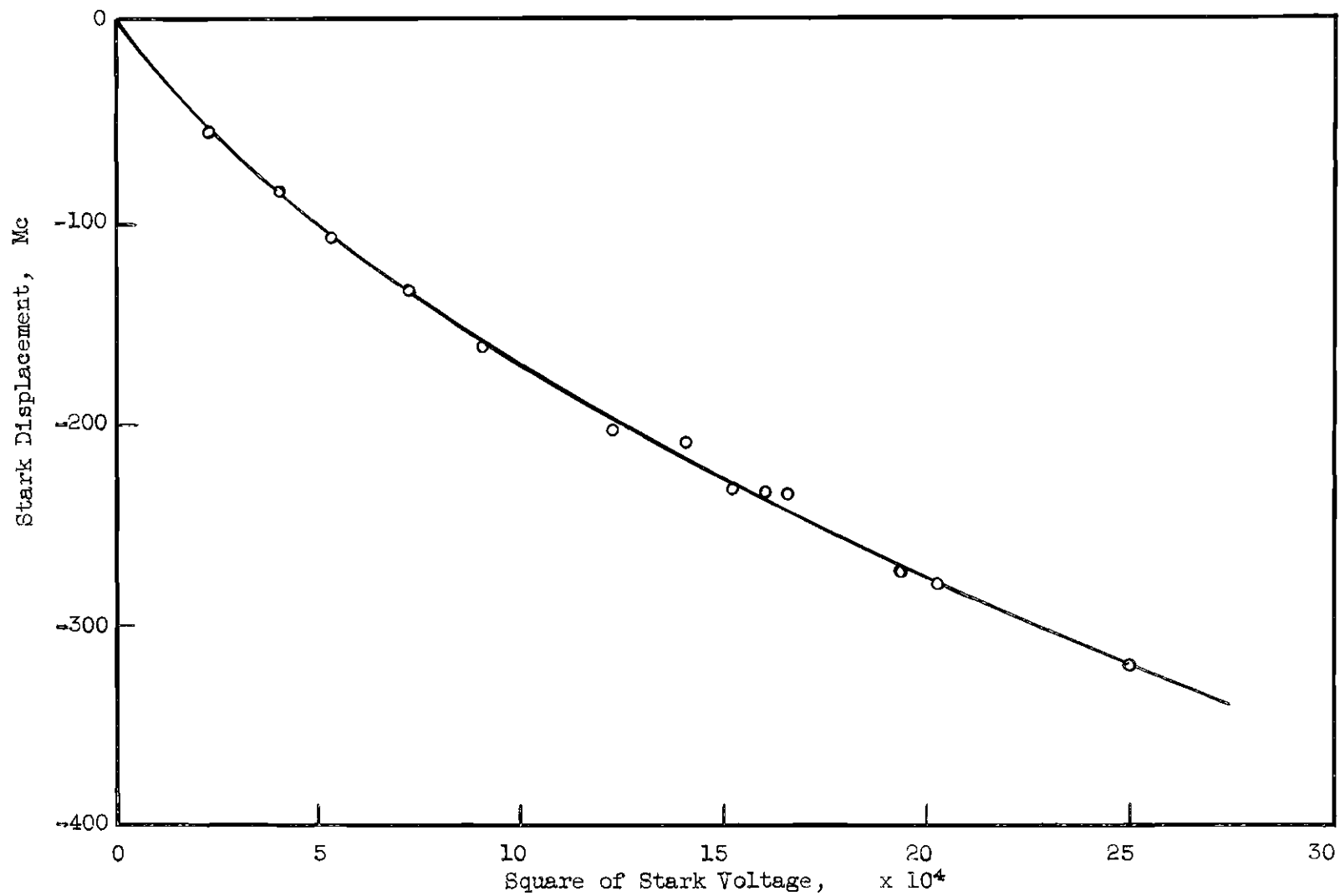


Figure 9. The Stark Effect of Nitrosyl Chloride.

too small to be measured accurately. An attempt was made to use another transition in an effort to determine μ_b , but none of the detectable transitions were sensitive to μ_b .

It is possible to explain how Rogers' estimate of the dipole moment is in error if we assume that the effects of near-degeneracy were ignored in making the estimate. It was noticed that the Stark displacement produced by a component of dipole moment $\mu_a = 1.28$ Debye in a non-degenerate calculation was practically the same as that caused by $\mu_a = 1.86$ Debye in the near-degenerate calculation for a Stark voltage of 500 V which produces a Stark field of 1,073 V/cm. Thus a calculation of μ_a based on this Stark field for the $J_T = 1_1 - 2_0$ transition would yield the value 1.28 Debye if the near-degenerate effects were not taken into consideration.

The agreement of the observed Stark effect with the predicted Stark effect indicates that the influence of the near-degeneracy of the energy levels must be considered if an accurate value for the dipole moment is to be obtained.

CHAPTER VIII

CONCLUSIONS

Asymmetric top molecules exhibit much more complex absorption spectra in the microwave region than symmetric top molecules. There are many unidentified transitions in the frequency range between 14,500 and 37,000 Mc which was investigated in the microwave spectrum of chlorodifluoromethane. Many of the unidentified absorption lines occur as strong pairs, and are believed to be caused by transitions between high J-number rotational energy levels. The quadrupole coupling coefficients are sensitive to small errors in the measurement of frequencies of the hyperfine structure, but the maximum likelihood method employed in calculating them gives the best possible results from the large number of measurements made. The coefficients obtained are believed to be accurate.

The structure of chlorodifluoromethane determined from the effective moments of inertia does not agree with the structure determined by electron diffraction. The disagreement may arise because of the effects of centrifugal distortion of the molecule or because of the effects of molecular vibrations. The transitions observed were believed to be for the ground vibrational state of the molecule, but the effects of centrifugal distortion were not evaluated. It is difficult to determine accurately the structure of a complex molecule unless the spectra of several isotopic species can be measured. The structure of chlorodifluoromethane can be more accurately evaluated by making measurements of the

spectra of other isotopic species than those utilized in the experiments described. Different species involving isotopes of carbon and/or hydrogen would be particularly useful. Species of chlorodifluoromethane involving different isotopes of fluorine would be undesirable, because the only symmetry of the molecule would be destroyed when both fluorine atoms were not of the same species, and the spectrum would be extremely complicated; in addition, all the fluorine isotopes except F^{19} are radioactive and have short half-lives. A great deal of confidence should not be placed in the structure determined from microwave spectroscopy until other isotopic species have been investigated and the information obtained has been applied to a refinement of the structural determination.

The measurement of the Stark effect of chlorodifluoromethane yielded components of the electric dipole moment which are accurately evaluated. It is doubtful if this determination could be improved appreciably by further investigations. The transition observed is the easiest one to use for an evaluation of dipole moment by analysis of the Stark effect. It is a transition between low-energy levels, so the effects of centrifugal distortion are negligible, and the Stark effect is easy to analyze because the Stark spectrum is the simplest one possible for the molecule and is well resolved.

The calculations of the Stark effect of chlorotrifluoromethane turned out to be more laborious than was anticipated. Further consideration of the problem leads to the conclusion that it would be easier to employ the $JKIm_Jm_I$ representation. The matrix elements of H_E could then

be calculated directly without the need of expanding the wave functions, and the matrix elements of H_Q in this representation have been tabulated by Kellogg et al. (24). The intensities would also be easier to determine. Therefore it is recommended that the $JKLm_Jm_L$ representation be used for calculating the intermediate field Stark effect of all symmetric top molecules.

At the time the experiments on chlorotrifluoromethane were carried out, measurements were made on the $J = 2 - 3$ transition, because that was the lowest- J transition that could be observed with the equipment available. The Stark components were weak and hard to measure and the Stark effect was very complicated for that transition. Better experimental results should be obtained with less labor by analyzing the Stark effect of the $J = 1 - 2$ transition which has a simpler, more easily analyzed Stark spectrum.

The experiments on nitrosyl chloride were performed in order to ascertain the importance of the effects of near-degeneracy of energy levels when evaluating dipole moments by analysis of the Stark spectrum. The analysis of the Stark effect of nitrosyl chloride indicates that in the case of a nearly-symmetric top it is absolutely necessary to take into account the effects of the near-degeneracy of the energy levels in order to arrive at a valid determination of electric dipole moment. The results of the investigation confirm the validity of the theory which includes the effects of near-degeneracy for the case of the nitrosyl chloride molecule. In this particular case it was permissible to neglect nuclear quadrupole interactions, and the theory of Golden and Wilson, which includes the effects of near-degeneracy, proved to be completely satisfactory.

It is interesting to make a comparison of the values of dipole moments determined by microwave spectroscopy and by other methods. Table 12 gives such a comparison for the molecules of this investigation.

The dipole moment $\mu = 1.29$ Debye given for CHClF_2 in Table 12 was listed in reference (25) and is evidently an estimate. Reference (25) lists the frequencies of several absorptions in the microwave spectrum of CHClF_2 , but none were identified, and it is hard to guess how the dipole moment was obtained without identifying transitions and measuring the Stark effect.

Dipole moments which have been determined from the Stark effect of different methane derivatives make an interesting comparison. The total dipole moment of CHClF_2 found from the components in Table 12 lies between the dipole moment $\mu = 1.2$ of CHCl_3 mentioned in reference (28) and the dipole moment $\mu = 1.64$ of CHF_3 mentioned in reference (29). The value of μ for CClF_3 in Table 12 compares with the value of $\mu = 0.45$ for CCl_3F found by temperature variation procedure, and the value $\mu = 0.53$ for CCl_3F found by optical procedure including the effects of infrared contributions to the molar polarization. The calculation of dipole moments by the temperature variation procedure usually gives results that differ only a few percent from dipole moments determined by analysis of the Stark effect (26). The dipole moment of NOCl which appears in Table 12 is similar in magnitude to the dipole moments calculated from the Stark effect, $\mu = 1.81$ for NOF mentioned in reference (26), and $\mu_a = 1.80$ for NOBr mentioned in reference (4).

Table 12. Dipole Moments Determined by Microwave Spectroscopy and by Other Methods

	Microwave Spectroscopy Debye Units	Other Methods Debye Units
CHClF ₂	$\mu_a = 0.12 \pm .01$ $\mu_c = 1.45 \pm .01$	$\mu_{\text{total}} = 1.29$ [†] 1.409 ^{††} 1.48 *
CClF ₃	$\mu = 0.50 \pm .05$	$\mu = 0.65$ * 0.45 ** 0.39 ^{††}
NOCl	$\mu_a = 1.86 \pm .02$	$\mu_{\text{total}} = 1.83 \pm .01$ ***

[†]See reference (25).

^{††}Obtained by temperature variation procedure (26).

*Determined by optical procedure using molar refraction (26).

**Determined by optical procedure including effects of infrared contributions to the molar polarization (26).

***Obtained for NOCl in solution (27).

CHAPTER IX

RECOMMENDATIONS

The effects of centrifugal distortion should be measured in the chlorodifluoromethane molecule. In order to do this it will be necessary to identify and measure some high- J number transitions. It is recommended that various species of the molecule in which different isotopes of carbon and hydrogen are substituted be investigated. Rotational constants of the different isotopic species of the molecule, when corrected for the effects of centrifugal distortion, should lead to a fairly easy and accurate determination of the positions of the hydrogen and carbon atoms in the molecule. The position of the fluorine atoms can be found easily and precisely when the positions of the other atoms are accurately known.

The Stark effect of chlorotrifluoromethane should be measured for a lower- J transition than that measured as described in Chapter VI in order to obtain more precise measurements. It is recommended that the $J = 1 - 2$ transition be investigated and the measurements be used to refine the value of dipole moment.

It should be ascertained whether or not the effects of near-degeneracy of energy levels have been considered in calculations of dipole moments of other nearly-symmetric tops by analysis of the Stark effect. The values of dipole moments of near-symmetric tops should be redetermined in those cases where near-degeneracy of rotational levels

has been ignored. Theoretical investigations for the Stark effect of asymmetric molecules in which near-degenerate effects and nuclear quadrupole interactions are both present are in progress in this laboratory (School of Physics, Georgia Institute of Technology) at present, and the results should be available in the near future.

APPENDIX

DERIVATION OF A RELATION INVOLVING MOMENTS OF INERTIA OF CHClF_2

Let the hydrogen, carbon, chlorine and fluorine atoms be designated by the subscripts 1, 2, 3, and 4, respectively. (See Figure 4.) Equations for the moments of inertia of $\text{CHCl}^{35}\text{F}_2$ in the principal axis system are

$$I_x = m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2 + 2m_4(y_4^2 + z_4^2), \quad (49)$$

$$I_y = m_1(x_1^2 + z_1^2) + m_2(x_2^2 + z_2^2) + m_3(x_3^2 + z_3^2) + 2m_4(x_4^2 + z_4^2), \quad (50)$$

$$I_z = m_1 x_1^2 + m_2 x_2^2 + m_3 x_3^2 + 2m_4(x_4^2 + y_4^2). \quad (51)$$

Adding equations (49) and (51) gives the equation

$$I_x + I_z = m_1(x_1^2 + z_1^2) + m_2(x_2^2 + z_2^2) + m_3(x_3^2 + z_3^2) + 2m_4(x_4^2 + 2y_4^2 + z_4^2). \quad (52)$$

Let \bar{x} and \bar{z} be coordinates of the center of mass of $\text{CHCl}^{37}\text{F}_2$ in the $\text{CHCl}^{35}\text{F}_2$ principal axis system. Let M be the mass of the $\text{CHCl}^{37}\text{F}_2$ molecule and Δm be the difference in mass between Cl^{35} and Cl^{37} . Equations for I'_y and $I'_x + I'_z$ can be written using coordinates of the principal axis system of $\text{CHCl}^{35}\text{F}_2$ by use of the parallel axis theorem as follows:

$$\begin{aligned}
I'_y &= m_1(x_1^2 + z_1^2) + m_2(x_2^2 + z_2^2) + (m_3 + \Delta m)(x_3^2 + z_3^2) \\
&\quad + 2m_4(x_4^2 + z_4^2) - M(\bar{x}^2 + \bar{z}^2).
\end{aligned}
\tag{53}$$

$$\begin{aligned}
I'_x + I'_z &= m_1(x_1^2 + z_1^2) + m_2(x_2^2 + z_2^2) + (m_3 + \Delta m)(x_3^2 + z_3^2) \\
&\quad + 2m_4(x_4^2 + 2y_4^2 + z_4^2) - M(\bar{x}^2 + \bar{z}^2).
\end{aligned}
\tag{54}$$

Subtract equation (50) from equation (53) to find

$$I'_y - I_y = \Delta m(x_3^2 + z_3^2) - M(\bar{x}^2 + \bar{z}^2). \tag{55}$$

Subtract equation (52) from equation (54) to find

$$(I'_x + I'_z) - (I_x + I_z) = \Delta m(x_3^2 + z_3^2) - M(\bar{x}^2 + \bar{z}^2). \tag{56}$$

The following equation is obtained from equations (55) and (56):

$$(I'_y - I_y) - (I'_x - I_x) - (I'_z - I_z) = 0. \tag{57}$$

A similar relation is true for any molecule in which the substituted atom lies in a molecular plane of symmetry.

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