ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

FINAL REPORT

PROJECT NO. A-265

DETERMINATION OF MOLECULAR CONSTANTS BY
MICROWAVE AND RADIO-FREQUENCY SPECTROSCOPY

By

T. L. WEATHERLY,
QUITMAN WILLIAMS, and
LORIMER CLAYTON, JR.

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

OCTOBER 1, 1953 to MAY 31, 1957

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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)


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# I. SUMMARY OF WORK PERFORMED

Research under this contract began on 1 October 1953. At that time the microwave spectrograph was still under construction and some expected delays were encountered in assembling all the necessary equipment for the investigation of molecules by this method. Therefore, a large part of the research time was devoted to radio-frequency spectroscopy during this early period. A large number of chlorine compounds were investigated for pure nuclear quadrupole resonance in the frequency region 20 to 45 Mc. Resonance absorption lines were found in 14 of these. These radio-frequency spectra provide evidence about chemical bond analysis that will be useful in the development of new theories.

Work on the microwave spectrum of nitrosyl bromide began in the summer of 1954, and since that time the larger part of the research time has been spent on microwave spectroscopy. This decision to emphasize microwave spectroscopy was influenced to some extent by the concentration of several other laboratories on the radio-frequency field.

The microwave spectra of nitrosyl bromide (NOBr) and nitryl chloride ($NO_2Cl$) have been investigated in the region 20,000 to 40,000 Mc. A complete analysis has been made of the $J = 2 \rightarrow 3$ transition for nitrosyl bromide and the $J = 2 \rightarrow 3$ and $J = 3 \rightarrow 4$ transitions for nitryl chloride. The Stark effect for both molecules has also been studied. Calculations from the spectra give the rotational constants, moments of inertia, internuclear distances, bond angles, quadrupole coupling constants, and dipole moments.

The Stark effect for the previously reported $J = 2 \rightarrow 3$ transition of chlorotrifluoromethane ($CClF_3$) has also been observed and preliminary calculations have been made. The work on this molecule has not yet been completed. A summary of the results on each molecule will be found in Chapter III, Section C.

In this report the radio-frequency and microwave work are discussed separately. In each case a brief introduction is followed by sections on experimental technique and results. The appendix contains a listing of all microwave spectral lines observed for nitrosyl bromide and nitryl chloride. A very useful computational procedure for quadrupole interactions which is not found in the literature is also included in the appendix.

## II.  RADIO-FREQUENCY SPECTROSCOPY

### A.  Introduction

Many molecular crystals containing nuclei with nonzero quadrupole moment exhibit narrow absorption lines in the radio-frequency region.  These lines result from transitions between molecular energy levels split by the interaction of the nuclear quadrupole moment with the electric field gradient at the nucleus (interaction of a nonspherical charge with a nonuniform field).  The electric field gradient is a symmetric tensor whose components are the second derivatives of the electric potential along space fixed axes; i. e.,

$$\begin{bmatrix} \dfrac{\partial^2 V}{\partial X^2} & \dfrac{\partial^2 V}{\partial X \partial Y} & \dfrac{\partial^2 V}{\partial X \partial Z} \\[2ex] \dfrac{\partial^2 V}{\partial Y \partial X} & \dfrac{\partial^2 V}{\partial Y^2} & \dfrac{\partial^2 V}{\partial Y \partial Z} \\[2ex] \dfrac{\partial^2 V}{\partial Z \partial X} & \dfrac{\partial^2 V}{\partial Z \partial Y} & \dfrac{\partial^2 V}{\partial Z^2} \end{bmatrix} .$$

By transformation to principal axes the number of independent components of this tensor may be reduced to three, namely

$$\begin{bmatrix} \dfrac{\partial^2 V}{\partial X^2} & 0 & 0 \\[2ex] 0 & \dfrac{\partial^2 V}{\partial Y^2} & 0 \\[2ex] 0 & 0 & \dfrac{\partial^2 V}{\partial Z^2} \end{bmatrix} .$$

All charges other than the nucleus itself contribute to the field gradient. If none of the charges penetrates the nucleus then the potential will satisfy Laplace's equation within the nucleus and we have

$$\frac{\partial^2 V}{\partial X^2} + \frac{\partial^2 V}{\partial Y^2} + \frac{\partial^2 V}{\partial Z^2} = 0 ,$$

reducing the number of independent components of the field gradient to two. Finally, if the Z-axis is a symmetry axis for the external charge distribution we have from the last equation

$$\frac{\partial^2 V}{\partial Z^2} = -\frac{1}{2}\frac{\partial^2 V}{\partial X^2} = -\frac{1}{2}\frac{\partial^2 V}{\partial Y^2}$$

and the field gradient has only one independent component. In such cases the quadrupole interaction energy has the form

$$E_Q = \frac{e\, Q\, \partial^2 V/\partial Z^2}{4\, I\, (2I - 1)} \left[ 3\, m_I^2 - I(I - 1) \right]$$

where

> Q is the nuclear quadrupole moment,
>
> e is the electronic charge,
>
> I is the nuclear spin, and
>
> $M_I$ is the Z-component of I.

The quantity $eQ\, \partial^2 V/\partial Z^2$, sometimes written $X_{ZZ}$, is called the quadrupole coupling constant. In the case of the chlorine compounds studied, the nuclear

spin is 3/2 and the above equation predicts two energy levels for each isotope of chlorine. The absorption lines resulting from transitions between these levels occur near 30 Mc.

The electron distribution near the nucleus makes the largest contribution to $\partial^2 V/\partial Z^2$. This electron distribution is influenced considerably by the type of chemical bond holding the atom in the molecule, and the resonance frequencies in the chlorine compounds studied exhibit this dependency on chemical bond type. Placement of neighboring atoms also has a small effect on the resonance frequency. The existence of three resonance frequencies for m-dichlorobenzene indicates three different environments for the chlorine nuclei of this molecule. While this dependence of resonance frequency on crystal structure gives some information about the crystal (number of nonequivalent sites), it complicates the problem of bond analysis. Detailed discussions of the correlation between quadrupole coupling constants and chemical bond type can be found in the literature in the papers of Townes and Daily[1], Livingston[2], and Goldstein[3] and in the recent book by Townes and Schawlow[4].

B. Experimental Technique

The circuit for the pure quadrupole spectrometer is of the type used by Dr. Ralph Livingston of Oak Ridge. It consists of an oscillator with its tank circuit inductance imbedded in the sample. Part of the tank circuit capacitance is that of a vibrating capacitor, a modified earphone driven by a step-down transformer and a Variac. This produces frequency modulation at 60 cps over a range of several megacycles. Another capacitance in the tank circuit can be varied manually through a 40 to 1 gear box to change the center frequency of the oscillator from 14 to 50 Mc.

If the frequency of the oscillator is swept over an absorption line, the absorption of energy by the sample causes a change in the oscillator plate current and a voltage pulse across a plate load resistance. This voltage pulse is amplified and applied to the vertical input of an oscilloscope which has a horizontal sweep of 60 cps. In this manner a visual presentation of the absorption line is obtained.

Frequency measurements are made with a Signal Corps B. C. 221 frequency meter. Its antenna is placed near the oscillator so that the signal from the frequency meter is mixed with that of the oscillator. A low audio frequency beat note appears on the oscilloscope as a brief disturbance with a width slightly greater than that of an absorption line. To determine the line frequency one adjusts the frequency meter until the disturbance is centered on the absorption line.

An alternative method of detecting the absorptions utilizing the Zeeman effect is also used. The application of a magnetic field to a crystal splits the nuclear quadrupole energy levels into several components. The splitting depends upon the orientation of the crystal in the field so that in a non-uniform crystal sample, such as a powder, the presence of a magnetic field removes any sharp absorption lines. A magnetic field which alternates between zero and a positive value at a frequency $f_1$ causes an absorption line to appear and disappear with a frequency $f_1$ when the oscillator is tuned to the absorption line frequency. Any signal developed across the plate load resistance is fed into a phase sensitive detector whose reference voltage is the same frequency as the magnetic field. The output of this detector is recorded using an Esterline Angus recording milliammeter while the oscillator is being tuned by

an electric motor. Any lines found this way are then displayed on the oscillo-scope so that their frequency can be measured as described above.

C. Results

Seventy-one chlorine compounds were investigated for nuclear quadrupole resonance between 20 and 45 Mc. Resonance absorption lines were detected for the 14 compounds listed in Table I. All measurements were made at liquid nitro-gen temperature.

TABLE I

QUADRUPOLE RESONANCES FOR $Cl^{35}$
AT LIQUID NITROGEN TEMPERATURE

| Compound | Frequency (Mc) |
|---|---|
| 1. 1,4-Dichloro-2-nitrobenzene $Cl_2C_6H_3NO_2$ | 35.921 37.874 |
| 2. 1,2-Dichloro-4-nitrobenzene $Cl_2C_6H_3NO_2$ | 36.488 37.055 |
| 3. 1-Chloro-2,4-dinitrobenzene $ClC_6H_3(NO_2)_2$ | 37.796 |
| 4. 4-Chloro-3,5-xylenol $ClC_6H_2(CH_3)_2OH$ | 34.348 34.415 |
| 5. Ethyl Trichlorosilane $C_2H_5SiCl_3$ | 18.756 18.842 18.865 |
| 6. Ethyl Chloroformate $ClCOOC_2H_5$ | 33.858 |
| 7. Ethyl Trichloroacetate $CCl_3COOC_2H_5$ | 40.200 40.339 |

(continued)

TABLE I (Concluded)

| Compound | Frequency |
|---|---|
| | (Mc) |
| 8.  1-Chloro-2-fluorobenzene | 36.294 |
| 9.  p-Chloroaniline $ClC_6H_4NH_2$ | 34.151 |
| 10.  1,2,3-Trichloropropane $CH_2ClCHClCH_2Cl$ | 34.581 34.776 |
| 11.  m-Dichlorobenzene $C_6H_4Cl_2$ | 34.80 34.871 35.027 |
| 12.  1-Chloro-3-nitrobenzene $ClC_6H_4NO_2$ | 35.457 |
| 13.  2,5-Dimethylbenzenesulfonyl Chloride $(CH_3)_2C_6H_3SO_2Cl$ | 32.265 |
| 14.  p-Toluenesulfonyl Chloride $CH_3C_6H_4SO_2Cl$ | 32.457 |

The two resonance frequencies observed for each of the compounds 1,4-dichloro-2-nitrobenzene and 1,2-dichloro-4-nitrobenzene, are presumably produced by chlorine atoms occupying different positions in the molecule. In the first molecule the nitro group occupies the ortho-position with respect to chlorine 1 and the meta-position with respect to chlorine 4. Comparison of the resonance frequencies of chlorobenzene, o-chloronitrobenzene, and m-chloronitrobenzene reported by Dean and Pound[5] shows that the presence of a nitro group in the ortho-position increases the resonance frequency by a larger amount than the nitro group in the meta-position. This would indicate

that the resonance at 37.874 Mc is produced by chlorine 1 and the resonance at 35.921 Mc by chlorine 4. Quantitative estimates of the resonance frequencies obtained by adding the frequency shifts produced by a nitro group and a chlorine atom are in reasonable agreement with the observed frequencies. Such estimates are complicated by the difference in crystal structure and by the temperature dependence of quadrupole resonance.

In 1,2-dichloro-4-nitrobenzene the nitro group occupies the meta-position with respect to chlorine 2 and the para-position with respect to chlorine 1. Quadrupole resonance has not been observed in p-nitrochlorobenzene and the frequency shift is difficult to estimate with accuracy because of the presence of the resonance effect described by Pauling[6]. For this reason the two resonances in this molecule are not identified.

The resonance frequency for 1-chloro-2,4-dinitrobenzene is higher than the value 34.622 Mc reported by Livingston[7] for monochlorobenzene. This increase in the $Cl^{35}$ resonance frequency produced when nitro groups replace hydrogen atoms in monochlorobenzene is also evident in the measurements of Dean and Pound.[8]

Two resonances were found for 4-chloro-3,5-xylenol at frequencies slightly lower than those for parachlorophenol[8] at this temperature. Thus the substitution of methyl groups for hydrogen at carbon atoms 3 and 5 decreases the resonance frequency. The existence of two resonance frequencies for 4-chloro-3,5-xylenol presumably results from two nonequivalent chlorine positions in the crystal lattice.

The three absorption lines found for ethyl trichlorosilane occur at relatively low frequencies, indicating a decrease in resonance frequency with

increased electronegativity difference. These frequencies are slightly lower than those reported by Livingston[9] for tetrachlorosilane. This frequency decrease is probably the result of increased ionic character of the remaining C-Cl bonds when one chlorine atom is replaced by an ethyl group.

Resonances in ethyl chloroformate and ethyl trichloroacetate were observed using Zeeman modulation and a phase-sensitive detector. Comparison of the structural formulas and resonance frequencies of these two molecules with trichloroacetyl chloride[10] further illustrates the effect of chemical bonding on nuclear quadrupole resonance. In Molecules 1 and 2 of Table II the chlorines on the left end have almost identical bonding to the carbon atom and their resonance frequencies are almost the same. In Molecules 2 and 3 the carbon trichloro groups $(CCl_3)$ have almost identical bonding and again the resonance frequencies are about the same. The existence of two resonances for the carbon trichloro group of ethyl trichloracetate and three for the same group in trichloroacetyl chloride is probably the result of a difference in crystal structure.

The resonance at 36.294 Mc for 1-chloro-2-fluorobenzene when compared with the resonance at 34.622 Mc for monochlorobenzene indicates that the highly electronegative fluorine withdraws electrons from the ring, thus increasing the chlorine resonance frequency. The substitution of an $NH_2$ group at the same position lowers the resonance frequency slightly as evident from the resonance at 34.151 Mc for p-chloroaniline.

The remaining resonances were reported and discussed by other investigators[2,8,11,12] at about the time our measurements were made.

As mentioned above, the positions of neighboring atoms have a small effect on resonance frequency. Therefore, in a solid whose structure is not completely

## TABLE II

### COMPARISON OF $Cl^{35}$ QUADRUPOLE RESONANCES IN RELATED COMPOUNDS

| Compound | Frequency (Mc) |
|---|---|
| 1. Ethyl chloroformate    $Cl - C - O - C_2H_5$ (with $\parallel$ $O$ below) | 33.858 |
| 2. Trichloroacetyl Chloride[†]   $Cl - C - CCl_3$ (with $\parallel$ $O$ below) | 33.721 <br> 40.132 <br> 40.473 <br> 40.613 |
| 3. Ethyl Trichloroacetate   $C_2H_5 - O - C - CCl_3$ (with $\parallel$ $O$ below) | 40.200 <br> 40.339 |

[†]Data from Livingson[9]

uniform the resonance will be broad with very little absorption at any one frequency. In such cases a resonance may not be detected at all. The chemicals used in these investigations were of commercial grade and it was not always possible to crystallize them uniformly. This is presumably one reason why only 14 resonances were found in 71 compounds investigated.

An unambigious interpretation of quadrupole couplings cannot be made in terms of chemical bond types. Quadrupole couplings do, however, provide additional evidence concerning bonds which will be increasingly valuable in the development of new theories.

## III. MICROWAVE SPECTROSCOPY

### A. Introduction

The internal energy of a molecule of a gas may be divided into three parts, electronic, vibrational, and rotational. The radiation emitted or absorbed when the molecule changes its rotational energy state falls in the microwave region of the spectrum. From the frequencies of these rotational spectral lines it is possible to determine the rotational constants and moments of inertia of the molecule. If measurements are made on all available isotopic species of the molecule it is sometimes possible to calculate all the internuclear distances, as in cases of nitryl chloride and nitrosyl bromide.

For a molecule containing a nucleus with electric quadrupole moment, the rotational lines will be split into components. The number of components is determined by the number of allowed orientations of the nucleus, which is in turn determined by the nuclear spin. This splitting results from an interaction between the nuclear quadrupole moment and the electric field gradient, the type of interaction described in Section II-A for solids. For a gas molecule the electric field gradient effective in causing splitting is the average gradient referred to space-fixed axes. This average field gradient along space-fixed axes can be calculated from the field gradient along molecule-fixed axes and the rotational state of the molecule. Therefore, it is possible to express the quadrupole splitting of the rotational lines in terms of the quadrupole coupling constants $eQ\partial^2V/\partial a^2$, $eQ\partial^2V/\partial b^2$, and $eQ\partial^2V/\partial c^2$, where the partial derivations are taken with respect to the principal axes of the molecule.

By measuring the quadrupole splitting of the rotational lines one can determine the quadrupole coupling constants. These constants are valuable to the

theoretical chemist in the analysis of chemical bonds. Quadrupole coupling determinations from the microwave spectrum of a gas are usually more useful for bond analysis than the information obtained from the radio-frequency spectrum of a solid. The microwave determination yields the magnitude and sign of the three diagonal elements of the quadrupole coupling tensor and these are free from the complicating effects of neighboring molecules.

When the molecules of a gas are subjected to an electric field, the rotational energy levels are split into component levels by the Stark effect. This splitting results from an interaction between the molecular dipole moment and the applied electric field. Since the applied field can be measured the dipole moment can be calculated from the spectrum. When both Stark effect and quadrupole splitting are present simultaneously, the spectrum is rather complex. A first order theory of the Stark effect for asymmetric-top molecules with quadrupole interaction has been worked out by Mizushima.[13]

The microwave spectra of nitrosyl bromide and nitryl chloride have been studied under this contract. For these molecules it has been possible to calculate rotational constants, moments of inertia, internuclear distances, quadrupole coupling constants, and dipole moments. The results of this work are discussed below.

B. Experimental Technique

The microwave spectrograph used in these investigations is similar to that described by Hughes and Wilson.[14] The absorption cell is a 20-foot section of X-band waveguide with a brass strip running lengthwise down the center of the guide. The plane of the strip is perpendicular to the E-field of the microwave energy. The Stark voltage is impressed between the center electrode and

the waveguide, thus producing an electric field in the region occupied by the gas. This voltage is an 85-kc square wave alternating between zero and an adjustable negative voltage.

As a result of the 85-kc electric field applied to the molecules, the microwave energy is amplitude modulated when the klystron frequency coincides with an absorption line. The output of the crystal detector mounted at the end of the absorption cell is fed into an HRO communications receiver tuned to receive an 85-kc c-w signal. Whenever the klystron frequency is swept over an absorption line, the output of the receiver is an audio frequency signal which can be displayed on an oscilloscope.

The output of the crystal detector can also be fed into an 85-kc phase-sensitive detector whose reference voltage is supplied by the Stark voltage generator. The signal from the phase-sensitive detector may be displayed on an oscilloscope if the klystron is being swept electrically, but greater sensitivity is obtained by tuning the klystron slowly with an electric motor and recording the lines with an Esterline Angus recording milliammeter. Absorptions due to transitions between Stark-split energy levels (Stark components) occur during that half of the cycle when the Stark voltage is not zero and absorptions due to transitions between the unsplit levels (main lines) occur when the Stark voltage is zero. Thus the 85-kc signal due to a Stark component is 180° out of phase with a main line signal, and a distinction can be made in the phase-sensitive detector so that the recording milliammeter deflects in one direction for Stark components and in the opposite direction for main lines. The recording of the $J = 2_1 \rightarrow 3_0$ transition of $NO_2Cl^{35}$ in Figure 6 shows the Stark components inverted.

Frequency measurements are made by the method described by Unterberger and Smith.[15] Standard frequencies in the microwave region are obtained by starting with a 5-Mc crystal controlled oscillator and multiplying the frequency with vacuum tube circuits until an output of 2160 Mc is obtained. This, along with 30, 90, 270, and 540 Mc is applied to a multiplier and mixer crystal mounted in the waveguide, thus producing standard frequencies 30 Mc apart in the microwave region. This one crystal also receives energy from the klystron so that a beatnote between the klystron frequency and one of the standard frequencies appears across the crystal. A calibrated HRO receiver is used to measure the frequency of the beatnote. An absorption type wavemeter is used to determine which standard frequency is beating with the klystron. Also, it is possible to turn off the 30-Mc markers, leaving standard frequency markers every 90 Mc apart in the microwave region. It is then easy to identify the standard frequencies with the absorption type wavemeter.

Since both nitrosyl bromide and nitryl chloride decomposed in the cell, it was found necessary to admit them continuously at one end of the 20-foot absorption cell while pumping from the other end. It was also found necessary to keep the cell cooled to dry ice temperature for both samples. Two methods were used to admit the samples to the cell at the proper pressures. In one method the sample is contained in a glass holder immersed in liquid nitrogen. Lowering the liquid nitrogen level below the sample increases the temperature of the top of the sample and thereby increases the vapor pressure. Reasonable control over the pressure can be maintained by raising or lowering the liquid nitrogen vessel the thickness of one or more standard 3 by 5 cards.

The second method was developed while working on nitryl chloride and has been tried only with this molecule. In this method a constriction is placed

between the sample and the cell. The sample is maintained at dry ice temperature, which produces a vapor pressure much too high to detect absorption lines, but on the cell side of the constriction the pressure is greatly reduced. This pressure can be controlled by raising or lowering the level of the dry ice and acetone solution which surrounds the sample. If the acetone extends several inches above the dry ice an appreciable temperature gradient exists near the surface of the acetone. This furnishes an excellent control over the temperature of the sample.

Figure 1 shows the constriction as it is used. It consists of a small glass tube drawn out to a fine capillary. A ring seal joins its larger end inside the vacuum line between the sample and the cell, and a bypass line with a stopcock is sealed around the ring seal to speed the removal of air from the sample holder. The small capillary extends through a ground glass joint which can be removed, leaving the capillary tube exposed so that it can be broken off in small pieces to adjust the pressure by a trial and error method. Once the size of the capillary was properly fixed it required no more attention and the pressure inside the cell was easily reproduced day after day.

C. Results

1. Nitrosyl Bromide

A detailed discussion of the work on nitrosyl bromide will be found in Technical Reports No. 1 and 2, OOR Project No. 1016. The molecular data obtained are summarized in the following section. The frequencies of all the observed spectral lines for this molecule are listed in Appendix II.

a. Summary of Results for Nitrosyl Bromide. An analysis of the $J = 2 - 3$ transition of nitrosyl bromide gives the rotational constants (A, B, and C) listed in Table III.
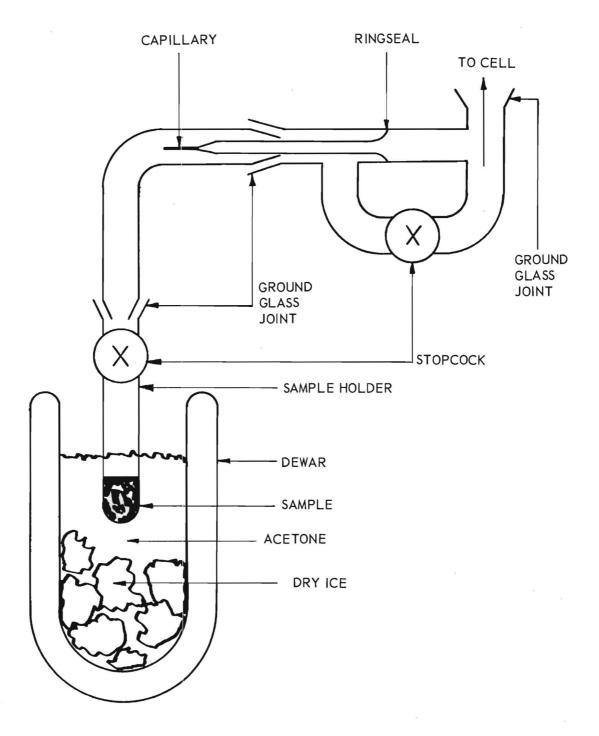
Figure 1.  Apparatus for Admitting Gas into the Cell at a Controlled
           Pressure.

## TABLE III

### MOLECULAR CONSTANTS OF NITROSYL BROMIDE

|  | $NOBr^{79}$ (Mc) | $NOBr^{81}$ (Mc) |
|---|---|---|
| A | 83,340 | 83,340 |
| B | 3,747.2 | 3,722.5 |
| C | 3,586.0 | 3,563.3 |
| $\chi_{aa}$ | 388 | 326 |
| $\chi_{bb}$ | -240 | -200 |
| $\chi_{cc}$ | -149 | -125 |

The structural parameters obtained from the above rotational constants are $d(N - O) = 1.15A$, $d(N - Br) = 2.14A$, $d(O - Br) = 2.81A$, and $\angle Br-N-O = 114°$. The N - O and N - Br distances are exactly the same as the electron diffraction results of Ketelaar and Palmer[16]; however, the O - Br distance is .04A shorter than their value.

The quadrupole couplings obtained from an analysis of the hyperfine structure of the rotational lines are given in Table III. An interpretation of the quadrupole coupling constants with regard to the N - Br bond indicates contributions from single bonded, double bonded, and ionic structures.

The Stark effect for nitrosyl bromide was investigated in an effort to determine the molecular dipole moment. Unfortunately the component of dipole moment along the principal axis b contributes practically nothing to the splitting of the hyperfine lines in an electric field and therefore cannot be determined. The component along principal axis a is found to be 1.76 Debye.

Since the writing of Technical Reports No. 1 and 2 some work has been done on the theory of the Stark effect of an asymmetric top with hyperfine structure which indicates that a higher order correction to Mizushima's theory may be needed. This work, when complete, may lead to a slight change in the dipole moment of the nitrosyl bromide molecule.

## 2. Chlorotrifluoromethane

The microwave spectrum of chlorotrifluoromethane has been investigated by Coles and Hughes[17]; however, the dipole moment of this molecule has not been measured. We have attempted to resolve the Stark components of the $J = 2 \rightarrow 3$ group in order to measure the dipole moment. This group consists of six strong lines and several weak ones, making the resolution and identification of Stark components very difficult. In spite of this some Stark components have been resolved. The weak field theory of Low and Townes[18] has been applied and found to be inadequate for this case. We are now in the process of applying the intermediate field theory. The latter theory is quite tedious to work out and requires the solution of fourth order secular determinants. Preliminary calculations indicate a dipole moment in the vicinity of 0.5 Debye. More precise frequency measurements must be made before an accurate dipole moment can be obtained.

## 3. Nitryl Chloride

Studies of the microwave spectrum of nitryl chloride were initiated in March, 1955, with the intent of resolving certain ambiguities in the structural-form determination afforded by the infrared spectrum.[19] Shortly after this work was begun, Millen and Sinnott[20] in England reported their determination of the rotational constants of $NO_2Cl^{35}$ from its $0_0 - 1_{-1}$, $1_{-1} - 2_{-2}$,

and $2_{-2} - 3_{-3}$ transitions, and mentioned observation of numerous other lines in the region from 8500 to 27,500 Mc. A Y-shaped planar molecular form was established conclusively by the absence of transitions involving energy levels antisymmetric in its identical oxygen nuclei.

Subsequent work here was directed toward accurate measurement of the frequencies of all observable lines in the spectra of $NO_2Cl^{35}$ and $NO_2Cl^{37}$ in the region 25,000 to 40,600 Mc, calculation of quadrupole coupling constants from the hyperfine structure, and determination of the approximate dipole moment of $NO_2Cl^{35}$ from the Stark effect.

It was noted in the course of these investigations that the spectrum of the molecule by itself affords only a very weak determination of the rotational constants; in fact, our transition frequencies as well as the lower-J transitions reported by Millen and Sinnott can be predicted accurately by sets of rotational constants in which the constant A varies by several hundred megacycles. For a stronger determination, it was found necessary to treat the molecule as a rigid planar rotor so that the relation $I_a + I_b - I_c = 0$ among the moments of inertia could be used as an additional restriction. The resulting rotational constants differ considerably from those proposed by Millen and Sinnott, but are understood to be in good agreement with revised values obtained by Dr. Sinnott in more recent unpublished work.[21]

Molecular dimensions have been calculated from the rotational constants obtained through the rigid-rotor treatment.

    a. Summary of Results for Nitryl Chloride. The molecular information derived from the microwave spectrum is summarized in Table IV.

## TABLE IV

## NITRYL CHLORIDE MICROWAVE DATA

Transitions Observed:

$2_{-2} - 3_{-3}$, $2_1 - 3_0$, $2_2 - 3_1$, $3_{-3} - 4_{-4}$, $3_0 - 4_{-1}$, $3_1 - 4_0$

| | $NO_2Cl^{35}$ | $NO_2Cl^{37}$ |
|---|---|---|
| A | 13250 Mc | 13250 Mc |
| B | 5173.8 | 5019.0 |
| C | 3721.1 | 3640.4 |
| $\chi_{aa}$ | -94.7 | -74.6 |
| $\chi_{bb}$ | 52.2 | 41.1 |
| $\chi_{cc}$ | 42.5 | 33.5 |

Rotational Constants Calculated from 2 - 3 Transitions, using $I_a + I_b - I_c = 0$

The six transitions listed were observed for both isotopic species; they lie in the region 25,000 to 37,100 Mc. In addition, the $4_{-4} - 5_{-5}$ transition of $NO_2Cl^{37}$ was observed at 40,600 Mc. A complete tabulation of the 65 lines measured is given in Appendix III.

The rotational constants shown were calculated from the 2 - 3 transitions using the relation $I_a + I_b - I_c = 0$. Fitting of the 2 - 3 transitions results in prediction errors of from 0.1 to 0.6 Mc for the 3 - 4 transitions and of about 0.25 Mc for the lower-J transitions reported by Millen and Sinnott. The prediction error for the single 4 - 5 transition observed is slightly in excess of 2 Mc. These small discrepancies cannot be removed by adjustment of

the rotational constants; certain regularities in their magnitudes suggest that they are due to centrifugal distortion of the molecular framework.

The molecular dimensions shown were calculated from the moments of inertia corresponding to the tabulated rotational constants.

The quadrupole coupling constants were calculated from the hyperfine structure of the 2 - 3 transitions, using a "maximum likelihood" fitting process to make efficient use of the experimental data. They predict the observed splittings of the 58 well-resolved lines in Appendix III with a standard deviation of 0.02 Mc.

Determination of the dipole moment of $NO_2Cl^{35}$ was undertaken by analysis of the Stark splitting of the $2_1 - 3_0$ transition. Except at small fields, the method of Mizushima proved to be only qualitatively correct for this transition because of the near-degeneracy of the $2_1$ and $2_2$ levels. The complete theory of the Stark effect in an asymmetric rotor with quadrupole interaction has not yet been worked out for the case of near-degeneracy; however, an approximate treatment of the shift of a single component by the method of Golden and Wilson[22] gave good agreement with experiment for a dipole moment of 0.53 Debye. This figure is close to one of 0.51 Debye obtained at small fields by application of the nondegenerate theory.

    b. Rotational Constants of Nitryl Chloride. To facilitate identification of the observed lines, a predicted spectrum was first compiled using estimated rotational constants, assuming a Y-shaped planar structure with internuclear distances comparable to those found in other compounds. The 2 - 3 transitions were observed at frequencies roughly 1000 Mc lower than those predicted. Before sufficient data had been gathered to permit an adjustment of

rotational constants, Millen and Sinnott reported the values A = 13,012 Mc, B = 5164.7 Mc, and C = 3730.5 Mc for $NO_2Cl^{35}$. A revised spectrum calculated from these constants was found to be in quite accurate agreement with experiment, permitting ready identification of the 3 - 4 transitions subsequently observed. An accurate prediction of the $NO_2Cl^{37}$ spectrum was also obtained by calculating molecular dimensions from the $NO_2Cl^{35}$ constants, substituting the nuclear mass for $Cl^{37}$, and calculating the rotational constants of the resulting structure.

The determination of rotational constants was re-examined after treatment of the hyperfine splitting had permitted precise evaluation of group-center frequencies for all 2 - 3 and 3 - 4 transitions. Use was made of the expressions given by Gordy, et al.[23] for low-J rotational energies as explicit functions of A, B, and C. These expressions lead to those in Table V for the frequencies of pertinent nitryl chloride transitions. Rotational constants can be obtained by substitution of observed group-center frequencies and simultaneous solution of appropriate sets of the equations.

It will be seen that not all of these relations impose independent restrictions upon the rotational constants; i.e., Relations 1 and 4 contain the same information, as do Relations 3 and 5. Nevertheless, the set is somewhat overdetermined, and the equation can be expected to be slightly inconsistent because of centrifugal distortion.

In order to effect solution of the equations in a manner which would clearly indicate the degree of inconsistency and the strength of the determination, a digital computer (Univac Scientific 1101) was employed to tabulate individually the independent restrictions obtained by substituting Relation 4 in Relations

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TABLE V

TRANSITION FREQUENCY RELATIONS

(1) $\nu(0_0 \to 1_{-1}) = B + C$

(2) $\nu(1_{-1} \to 2_{-2}) = 2A + B + C - 2\sqrt{(B-C)^2 + (A-C)(A-B)}$

(3) $\nu(2_{-2} \to 3_{-3}) = 3(B+C) - 2\left\{\left[4(B-C)^2 + (A-B)(A-C)\right]^{1/2} \right.$
$$\left. - \left[(B-C)^2 + (A-B)(A-C)\right]^{1/2}\right\}$$

(4) $\nu(2_1 \to 3_0) = 3(B+C)$

(5) $\nu(2_2 \to 3_1) = 3(B+C) + 2\left\{\left[4(B-C)^2 + (A-B)(A-C)\right]^{1/2}\right.$
$$\left. - \left[(B-C)^2 + (A-B)(A-C)\right]^{1/2}\right\}$$

(6) $\nu(3_0 \to 4_{-1}) = 6A + B + C - 2\left[4(B-C)^2 + 9(A-B)(A-C)\right]^{1/2}$

2, 6, and in the relation obtained by subtracting Relation 3 from 5. (Relation 2 was tabulated for $NO_2Cl^{35}$ only, using the frequencies published by Millen and Sinnott.) Some of the computer read-out sheets for $NO_2Cl^{35}$ are reproduced in Figures 2 through 4. The tables represent, in effect, "graphs" of B or C as a function of A. Simultaneous solution of any pair of relations is accomplished by a simple inspection of the tables to determine their "intersection", i.e., to find a value of A for which the corresponding values of B or C are the same in both tables.

It happens that in the region of interest the three relations plot as almost exactly parallel curves, so that the six transitions of Table V afford

$NO_2Cl^{35}$ ROTATIONAL CONSTANTS

$1_{-1}$ to $2_{-2}$ TRANSITION

(Continued)

| A | B | C | | A | B | C |
|---|---|---|---|---|---|---|
| | | | | 13260 | 5173.705 | 3721.195 |
| | | | | 13270 | 5174.115 | 3720.785 |
| | | | | 13280 | 5174.524 | 3720.376 |
| | | | | 13290 | 5174.934 | 3719.966 |
| 12800 | 5154.594 | 3740.306 | | 13300 | 5175.343 | 3719.557 |
| 12810 | 5155.015 | 3739.885 | | 13310 | 5175.752 | 3719.148 |
| 12820 | 5155.436 | 3739.464 | | 13320 | 5176.161 | 3718.739 |
| 12830 | 5155.856 | 3739.044 | | 13330 | 5176.569 | 3718.331 |
| 12840 | 5156.277 | 3738.623 | | 13340 | 5176.977 | 3717.923 |
| 12850 | 5156.697 | 3738.203 | | 13350 | 5177.385 | 3717.515 |
| 12860 | 5157.116 | 3737.784 | | 13360 | 5177.793 | 3717.107 |
| 12870 | 5157.536 | 3737.364 | | 13370 | 5178.201 | 3716.699 |
| 12880 | 5157.955 | 3736.945 | | 13380 | 5178.608 | 3716.292 |
| 12890 | 5158.374 | 3736.526 | | 13390 | 5179.015 | 3715.885 |
| 12900 | 5158.793 | 3736.107 | | 13400 | 5179.422 | 3715.478 |
| 12910 | 5159.211 | 3735.689 | | 13410 | 5179.829 | 3715.071 |
| 12920 | 5159.629 | 3735.271 | | 13420 | 5180.235 | 3714.665 |
| 12930 | 5160.047 | 3734.853 | | 13430 | 5180.641 | 3714.259 |
| 12940 | 5160.465 | 3734.435 | | 13440 | 5181.047 | 3713.853 |
| 12950 | 5160.882 | 3734.018 | | 13450 | 5181.453 | 3713.447 |
| 12960 | 5161.300 | 3733.600 | | 13460 | 5181.859 | 3713.041 |
| 12970 | 5161.717 | 3733.183 | | 13470 | 5182.264 | 3712.636 |
| 12980 | 5162.133 | 3732.767 | | 13480 | 5182.669 | 3712.231 |
| 12990 | 5162.550 | 3732.350 | | 13490 | 5183.074 | 3711.826 |
| 13000 | 5162.966 | 3731.934 | | 13500 | 5183.479 | 3711.421 |
| 13010 | 5163.382 | 3731.518 | | 13510 | 5183.883 | 3711.017 |
| 13020 | 5163.798 | 3731.102 | | 13520 | 5184.287 | 3710.613 |
| 13030 | 5164.213 | 3730.687 | | 13530 | 5184.691 | 3710.209 |
| 13040 | 5164.629 | 3730.271 | | 13540 | 5185.095 | 3709.805 |
| 13050 | 5165.044 | 3729.856 | | 13550 | 5185.499 | 3709.401 |
| 13060 | 5165.459 | 3729.441 | | 13560 | 5185.902 | 3708.998 |
| 13070 | 5165.873 | 3729.027 | | 13570 | 5186.305 | 3708.595 |
| 13080 | 5166.287 | 3728.613 | | 13580 | 5186.708 | 3708.192 |
| 13090 | 5166.702 | 3728.198 | | 13590 | 5187.111 | 3707.789 |
| 13100 | 5167.115 | 3727.785 | | 13600 | 5187.513 | 3707.387 |
| 13110 | 5167.529 | 3727.371 | | 13610 | 5187.915 | 3706.985 |
| 13120 | 5167.942 | 3726.958 | | 13620 | 5188.317 | 3706.583 |
| 13130 | 5168.356 | 3726.544 | | 13630 | 5188.719 | 3706.181 |
| 13140 | 5168.768 | 3726.132 | | 13640 | 5189.121 | 3705.779 |
| 13150 | 5169.181 | 3725.719 | | 13650 | 5189.522 | 3705.378 |
| 13160 | 5169.593 | 3725.307 | | 13660 | 5189.923 | 3704.977 |
| 13170 | 5170.006 | 3724.894 | | 13670 | 5190.324 | 3704.576 |
| 13180 | 5170.418 | 3724.482 | | 13680 | 5190.725 | 3704.175 |
| 13190 | 5170.829 | 3724.071 | | 13690 | 5191.125 | 3703.775 |
| 13200 | 5171.241 | 3723.659 | | 13700 | 5191.525 | 3703.375 |
| 13210 | 5171.652 | 3723.248 | | 13710 | 5191.925 | 3702.975 |
| 13220 | 5172.063 | 3722.837 | | 13720 | 5192.325 | 3702.575 |
| 13230 | 5172.474 | 3722.426 | | 13730 | 5192.725 | 3702.175 |
| 13240 | 5172.885 | 3722.015 | | 13740 | 5193.124 | 3701.776 |
| 13250 | 5173.295 | 3721.605 | | 13750 | 5193.524 | 3701.376 |

Figure 2. Two Computer Read-Out Sheets Tabulating the Restriction Upon the Rotational Constants of $NO_2Cl^{35}$ Imposed by the $1_{-1} \rightarrow 2_{-2}$ Transition Frequency, using (B+C) from the $2_1 \rightarrow 3_0$ Transition.

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NO$_2$CL$^{35}$ ROTATIONAL CONSTANTS

J 2 to 3 TRANSITIONS

(Continued)

| A | B | C | A | B | C |
|---|---|---|---|---|---|
| 12800 | 5155.516 | 3739.384 | 13260 | 5174.166 | 3720.734 |
| 12810 | 5155.927 | 3738.973 | 13270 | 5174.566 | 3720.334 |
| 12820 | 5156.337 | 3738.563 | 13280 | 5174.966 | 3719.934 |
| 12830 | 5156.747 | 3738.153 | 13290 | 5175.366 | 3719.534 |
| 12840 | 5157.157 | 3737.743 | 13300 | 5175.765 | 3719.135 |
| 12850 | 5157.567 | 3737.333 | 13310 | 5176.164 | 3718.736 |
| 12860 | 5157.977 | 3736.923 | 13320 | 5176.563 | 3718.337 |
| 12870 | 5158.386 | 3736.514 | 13330 | 5176.962 | 3717.938 |
| 12880 | 5158.795 | 3736.105 | 13340 | 5177.361 | 3717.539 |
| 12890 | 5159.203 | 3735.697 | 13350 | 5177.759 | 3717.141 |
| 12900 | 5159.612 | 3735.288 | 13360 | 5178.157 | 3716.743 |
| 12910 | 5160.020 | 3734.880 | 13370 | 5178.555 | 3716.345 |
| 12920 | 5160.428 | 3734.472 | 13380 | 5178.953 | 3715.947 |
| 12930 | 5160.836 | 3734.064 | 13390 | 5179.350 | 3715.550 |
| 12940 | 5161.244 | 3733.656 | 13400 | 5179.748 | 3715.152 |
| 12950 | 5161.651 | 3733.249 | 13410 | 5180.145 | 3714.755 |
| 12960 | 5162.058 | 3732.842 | 13420 | 5180.542 | 3714.358 |
| 12970 | 5162.465 | 3732.435 | 13430 | 5180.938 | 3713.962 |
| 12980 | 5162.872 | 3732.028 | 13440 | 5181.335 | 3713.565 |
| 12990 | 5163.278 | 3731.622 | 13450 | 5181.731 | 3713.169 |
| 13000 | 5163.684 | 3731.216 | 13460 | 5182.127 | 3712.773 |
| 13010 | 5164.090 | 3730.810 | 13470 | 5182.523 | 3712.377 |
| 13020 | 5164.496 | 3730.404 | 13480 | 5182.918 | 3711.982 |
| 13030 | 5164.902 | 3729.998 | 13490 | 5183.314 | 3711.586 |
| 13040 | 5165.307 | 3729.593 | 13500 | 5183.709 | 3711.191 |
| 13050 | 5165.712 | 3729.188 | 13510 | 5184.104 | 3710.796 |
| 13060 | 5166.117 | 3728.783 | 13520 | 5184.498 | 3710.402 |
| 13070 | 5166.521 | 3728.379 | 13530 | 5184.893 | 3710.007 |
| 13080 | 5166.926 | 3727.974 | 13540 | 5185.287 | 3709.613 |
| 13090 | 5167.330 | 3727.570 | 13550 | 5185.681 | 3709.219 |
| 13100 | 5167.734 | 3727.166 | 13560 | 5186.075 | 3708.825 |
| 13110 | 5168.137 | 3726.763 | 13570 | 5186.469 | 3708.431 |
| 13120 | 5168.541 | 3726.359 | 13580 | 5186.862 | 3708.038 |
| 13130 | 5168.944 | 3725.956 | 13590 | 5187.256 | 3707.644 |
| 13140 | 5169.347 | 3725.553 | 13600 | 5187.649 | 3707.251 |
| 13150 | 5169.750 | 3725.150 | 13610 | 5188.041 | 3706.859 |
| 13160 | 5170.152 | 3724.748 | 13620 | 5188.434 | 3706.466 |
| 13170 | 5170.555 | 3724.345 | 13630 | 5188.827 | 3706.073 |
| 13180 | 5170.957 | 3723.943 | 13640 | 5189.219 | 3705.681 |
| 13190 | 5171.359 | 3723.541 | 13650 | 5189.611 | 3705.289 |
| 13200 | 5171.761 | 3723.139 | 13660 | 5190.003 | 3704.897 |
| 13210 | 5172.162 | 3722.738 | 13670 | 5190.394 | 3704.506 |
| 13220 | 5172.563 | 3722.337 | 13680 | 5190.786 | 3704.114 |
| 13230 | 5172.964 | 3721.936 | 13690 | 5191.177 | 3703.723 |
| 13240 | 5173.365 | 3721.535 | 13700 | 5191.568 | 3703.332 |
| 13250 | 5173.765 | 3721.135 | 13710 | 5191.959 | 3702.941 |
|  |  |  | 13720 | 5192.349 | 3702.551 |
|  |  |  | 13730 | 5192.739 | 3702.161 |
|  |  |  | 13740 | 5193.130 | 3701.770 |
|  |  |  | 13750 | 5193.520 | 3701.380 |

Figure 3.  Two Computer Read-Out Sheets Tabulating the Restriction Upon the Rotational Constants of NO$_2$Cl$^{35}$ Imposed by the 2 $\longrightarrow$ 3 Transition Frequencies.

$NO_2Cl^{35}$ ROTATIONAL CONSTANTS $\quad$ $NO_2Cl^{35}$ ROTATIONAL CONSTANTS

$3_0$ to $4_{-1}$ $\quad$ TRANSITION $\qquad$ $3_0$ to $4_{-1}$ $\quad$ TRANSITION

| A | B | C | A | B | C |
|---|---|---|---|---|---|
| 12800 | 5155.788 | 3739.112 | 13300 | 5176.652 | 3718.248 |
| 12810 | 5156.212 | 3738.688 | 13310 | 5177.065 | 3717.835 |
| 12820 | 5156.635 | 3738.265 | 13320 | 5177.475 | 3717.425 |
| 12830 | 5157.057 | 3737.843 | 13330 | 5177.885 | 3717.015 |
| 12840 | 5157.481 | 3737.419 | 13340 | 5178.297 | 3716.603 |
| 12850 | 5157.902 | 3736.998 | 13350 | 5178.707 | 3716.193 |
| 12860 | 5158.324 | 3736.576 | 13360 | 5179.116 | 3715.784 |
| 12870 | 5158.747 | 3736.153 | 13370 | 5179.527 | 3715.373 |
| 12880 | 5159.168 | 3735.732 | 13380 | 5179.936 | 3714.964 |
| 12890 | 5159.589 | 3735.311 | 13390 | 5180.345 | 3714.555 |
| 12900 | 5160.011 | 3734.889 | 13400 | 5180.755 | 3714.145 |
| 12910 | 5160.431 | 3734.469 | 13410 | 5181.164 | 3713.736 |
| 12920 | 5160.851 | 3734.049 | 13420 | 5181.572 | 3713.328 |
| 12930 | 5161.271 | 3733.629 | 13430 | 5181.980 | 3712.920 |
| 12940 | 5161.692 | 3733.208 | 13440 | 5182.389 | 3712.511 |
| 12950 | 5162.112 | 3732.788 | 13450 | 5182.797 | 3712.103 |
| 12960 | 5162.530 | 3732.370 | 13460 | 5183.204 | 3711.696 |
| 12970 | 5162.951 | 3731.949 | 13470 | 5183.612 | 3711.288 |
| 12980 | 5163.370 | 3731.530 | 13480 | 5184.019 | 3710.881 |
| 12990 | 5163.788 | 3731.112 | 13490 | 5184.426 | 3710.474 |
| 13000 | 5164.207 | 3730.693 | 13500 | 5184.834 | 3710.066 |
| 13010 | 5164.625 | 3730.275 | 13510 | 5185.240 | 3709.660 |
| 13020 | 5165.043 | 3729.857 | 13520 | 5185.646 | 3709.254 |
| 13030 | 5165.462 | 3729.438 | 13530 | 5186.053 | 3708.847 |
| 13040 | 5165.879 | 3729.021 | 13540 | 5186.459 | 3708.441 |
| 13050 | 5166.296 | 3728.604 | 13550 | 5186.864 | 3708.036 |
| 13060 | 5166.714 | 3728.186 | 13560 | 5187.270 | 3707.630 |
| 13070 | 5167.130 | 3727.770 | 13570 | 5187.675 | 3707.225 |
| 13080 | 5167.547 | 3727.353 | 13580 | 5188.080 | 3706.820 |
| 13090 | 5167.964 | 3726.936 | 13590 | 5188.485 | 3706.415 |
| 13100 | 5168.380 | 3726.520 | 13600 | 5188.890 | 3706.010 |
| 13110 | 5168.795 | 3726.105 | 13610 | 5189.294 | 3705.606 |
| 13120 | 5169.212 | 3725.688 | 13620 | 5189.699 | 3705.201 |
| 13130 | 5169.627 | 3725.273 | 13630 | 5190.102 | 3704.798 |
| 13140 | 5170.042 | 3724.858 | 13640 | 5190.506 | 3704.394 |
| 13150 | 5170.457 | 3724.443 | 13650 | 5190.910 | 3703.990 |
| 13160 | 5170.872 | 3724.028 | 13660 | 5191.313 | 3703.587 |
| 13170 | 5171.286 | 3723.614 | 13670 | 5191.716 | 3703.184 |
| 13180 | 5171.700 | 3723.200 | 13680 | 5192.118 | 3702.782 |
| 13190 | 5172.115 | 3722.785 | 13690 | 5192.522 | 3702.378 |
| 13200 | 5172.527 | 3722.373 | 13700 | 5192.924 | 3701.976 |
| 13210 | 5172.941 | 3721.959 | 13710 | 5193.325 | 3701.575 |
| 13220 | 5173.355 | 3721.545 | 13720 | 5193.729 | 3701.171 |
| 13230 | 5173.767 | 3721.133 | 13730 | 5194.130 | 3700.770 |
| 13240 | 5174.180 | 3720.720 | 13740 | 5194.531 | 3700.369 |
| 13250 | 5174.594 | 3720.306 | 13750 | 5194.933 | 3699.967 |
| 13260 | 5175.005 | 3719.895 | | | |
| 13270 | 5175.417 | 3719.483 | | | |
| 13280 | 5175.830 | 3719.070 | | | |
| 13290 | 5176.241 | 3718.659 | | | |

Figure 4. Two Computer Read-Out Sheets Tabulating the Restriction Upon the Rotational Constants of $NO_2Cl^{35}$ Imposed by the $3_0 \rightarrow 4_{-1}$ Transition Frequency, using (B+C) from the $2_1 \rightarrow 3_0$ Transition.

only a very weak determination of the rotational constants. Small displacements of the curves by centrifugal distortion are sufficient to shift A by several hundred megacycles. Furthermore, since the frequencies of the $3_1 - 4_0$ and $3_{-3} - 4_{-4}$ transitions are predicted about equally well by any of the tabulated sets of constants, it is clear that they can impose no strong additional restriction. The transitions which would help matters are those which are absent because they involve levels antisymmetric in the oxygen atoms, and those which should be very weak because the molecule is nearly a prolate symmetric top.

If the molecule is treated as a rigid planar rotor, the relation $I_a + I_b - I_c = 0$ can be used as an additional constraint upon the rotational constants for a stronger determination. Figure 5 shows a tabulation of the restriction obtained by substitution of Relation 4 in the above relation. It will be seen that this table has a sharply defined intersection with each of the other tables at $A \doteq 13,250$ Mc. Rotational constants for the 2 - 3 intersection are listed in Table IV, along with those obtained in the same manner for $NO_2Cl^{37}$. The constants for $NO_2Cl^{35}$ are considerably different from those published by Millen and Sinnott, but it is understood that in more recent unpublished work Dr. Sinnott has obtained revised sets of rotational constants in which A is close to 13,240 Mc.[21]

Group-center transition frequencies calculated from these constants are included in Appendix III, and differences between observed and calculated frequencies are listed in Table VI. The differences, although small, are greater than possible experimental errors except for the fitted 2 - 3 transitions. It is not possible to fit all transitions simultaneously with any single set of

$NO_2Cl^{35}$ ROTATIONAL CONSTANTS

APPROXIMATE RELATION ASSUMING
PLANAR MOLECULE WITH ZERO
QUANTUM DEFECT

(Continued)

| A | B | C |
|---|---|---|
| 12800 | 5198.085 | 3696.815 |
| 12810 | 5197.530 | 3697.370 |
| 12820 | 5196.980 | 3697.920 |
| 12830 | 5196.425 | 3698.475 |
| 12840 | 5195.875 | 3699.025 |
| 12850 | 5195.325 | 3699.575 |
| 12860 | 5194.775 | 3700.125 |
| 12870 | 5194.225 | 3700.675 |
| 12880 | 5193.680 | 3701.220 |
| 12890 | 5193.130 | 3701.770 |
| 12900 | 5192.585 | 3702.315 |
| 12910 | 5192.035 | 3702.865 |
| 12920 | 5191.495 | 3703.405 |
| 12930 | 5190.950 | 3703.950 |
| 12940 | 5190.405 | 3704.495 |
| 12950 | 5189.865 | 3705.035 |
| 12960 | 5189.320 | 3705.580 |
| 12970 | 5188.780 | 3706.120 |
| 12980 | 5188.240 | 3706.660 |
| 12990 | 5187.700 | 3707.200 |
| 13000 | 5187.160 | 3707.740 |
| 13010 | 5186.625 | 3708.275 |
| 13020 | 5186.085 | 3708.815 |
| 13030 | 5185.550 | 3709.350 |
| 13040 | 5185.015 | 3709.885 |
| 13050 | 5184.480 | 3710.420 |
| 13060 | 5183.945 | 3710.955 |
| 13070 | 5183.415 | 3711.485 |
| 13080 | 5182.880 | 3712.020 |
| 13090 | 5182.345 | 3712.555 |
| 13100 | 5181.815 | 3713.085 |
| 13110 | 5181.285 | 3713.615 |
| 13120 | 5180.755 | 3714.145 |
| 13130 | 5180.225 | 3714.675 |
| 13140 | 5179.700 | 3715.200 |
| 13150 | 5179.170 | 3715.730 |
| 13160 | 5178.645 | 3716.255 |
| 13170 | 5178.120 | 3716.780 |
| 13180 | 5177.595 | 3717.305 |
| 13190 | 5177.070 | 3717.830 |
| 13200 | 5176.545 | 3718.355 |
| 13210 | 5176.020 | 3718.880 |
| 13220 | 5175.500 | 3719.400 |
| 13230 | 5174.975 | 3719.925 |
| 13240 | 5174.460 | 3720.440 |
| 13250 | 5173.935 | 3720.965 |
| 13260 | 5173.415 | 3721.485 |
| 13270 | 5172.900 | 3722.000 |
| 13280 | 5172.380 | 3722.520 |
| 13290 | 5171.865 | 3723.035 |
| 13300 | 5171.345 | 3723.555 |
| 13310 | 5170.830 | 3724.070 |
| 13320 | 5170.315 | 3724.585 |
| 13330 | 5169.800 | 3725.100 |
| 13340 | 5169.285 | 3725.615 |
| 13350 | 5168.775 | 3726.125 |
| 13360 | 5168.265 | 3726.635 |
| 13370 | 5167.750 | 3727.150 |
| 13380 | 5167.240 | 3727.660 |
| 13390 | 5166.730 | 3728.170 |
| 13400 | 5166.220 | 3728.680 |
| 13410 | 5165.710 | 3729.190 |
| 13420 | 5165.205 | 3729.695 |
| 13430 | 5164.695 | 3730.205 |
| 13440 | 5164.190 | 3730.710 |
| 13450 | 5163.685 | 3731.215 |
| 13460 | 5163.180 | 3731.720 |
| 13470 | 5162.675 | 3732.225 |
| 13480 | 5162.170 | 3732.730 |
| 13490 | 5161.665 | 3733.235 |
| 13500 | 5161.165 | 3733.735 |
| 13510 | 5160.665 | 3734.235 |
| 13520 | 5160.165 | 3734.735 |
| 13530 | 5159.660 | 3735.240 |
| 13540 | 5159.160 | 3735.740 |
| 13550 | 5158.660 | 3736.240 |
| 13560 | 5158.165 | 3736.735 |
| 13570 | 5157.665 | 3737.235 |
| 13580 | 5157.170 | 3737.730 |
| 13590 | 5156.670 | 3738.230 |
| 13600 | 5156.180 | 3738.720 |
| 13610 | 5155.680 | 3739.220 |
| 13620 | 5155.185 | 3739.715 |
| 13630 | 5154.695 | 3740.205 |
| 13640 | 5154.205 | 3740.695 |
| 13650 | 5153.710 | 3741.190 |
| 13660 | 5153.220 | 3741.680 |
| 13670 | 5152.725 | 3742.175 |
| 13680 | 5152.240 | 3742.660 |
| 13690 | 5151.750 | 3743.150 |
| 13700 | 5151.260 | 3743.640 |
| 13710 | 5150.770 | 3744.130 |
| 13720 | 5150.285 | 3744.615 |
| 13730 | 5149.795 | 3745.105 |
| 13740 | 5149.310 | 3745.590 |
| 13750 | 5148.825 | 3746.075 |

Figure 5. Two Computer Read-Out Sheets Tabulating the Restriction Upon the Rotational Constants of $NO_2Cl^{35}$ Imposed by the Relation $I_a+I_b-I_c=0$, using (B+C) from the $2_1 \rightarrow 3_0$ Transition.
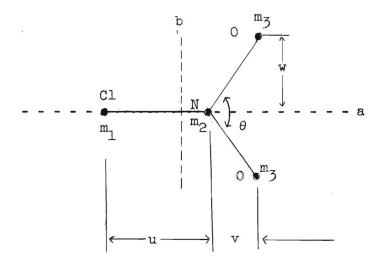
## TABLE VI

### DIFFERENCES BETWEEN OBSERVED AND CALCULATED GROUP-CENTER FREQUENCIES

| Transition | Group-Center Frequency Deviation (Measured Minus Calculated) | |
| --- | --- | --- |
| | $NO_2Cl^{35}$ (Mc) | $NO_2Cl^{37}$ (Mc) |
| $4_{-4} - 5_{-5}$ | | -2.22 |
| $3_1 - 4_0$ | 0.10 | 0.10 |
| $3_0 - 4_{-1}$ | -0.32 | -0.31 |
| $3_{-3} - 4_{-4}$ | -0.59 | -0.58 |
| $2_2 - 3_1$ | 0.00 | 0.01 |
| $2_1 - 3_0$ | -0.03 | -0.03 |
| $2_{-2} - 3_{-3}$ | 0.01 | 0.03 |
| $1_{-1} - 2_{-2}$ | 0.23[†] | |
| $0_0 - 1_{-1}$ | 0.23[†] | |

[†] Based on measured frequencies published by Millen and Sinnott.[20]

rotational constants, whether or not the condition $I_a + I_b - I_c = 0$ is imposed. A notable characteristic of the differences is their similarity for the two isotopes of chlorine. Centrifugal distortion is suggested as the cause, first by the slight relative displacements of the computer tabulations for different transitions, and more conclusively by the 0.23-Mc error in the prediction of the $0_0 - 1_{-1}$ transition frequency. The frequency of this transition must be precisely one-third that of the $2_1 - 3_0$ transition for any rigid rotor, regardless of its rotational constants.

c. **Molecular Dimensions of Nitryl Chloride.** For the structure



the moments of inertia are given by:

$$I_a = 2 m_3 w^2$$

$$I_b = 1/M \left\{ m_1 \left[ (m_2 + 2m_3) u^2 + 4m_3 uv + 2m_3 v^2 \right] + 2m_2 m_3 v^2 \right\}$$

$$I_c = I_a + I_b$$

where $M = m_1 + m_2 + 2m_3$.

The simplicity of the structure thus permits ready determination of the molecular dimensions from the rotational constants, using the relation $I_a = (1/A) \, 5.05531 \times 10^5$ Mc/amu-A$^2$ and the similar expression for $I_b$. The dimension $\underline{w}$ is given immediately by $I_a$. To find $\underline{u}$ and $\underline{v}$ one can solve simultaneously the equations for $MI_b$ for $NO_2Cl^{35}$ and $NO_2Cl^{37}$. Subtraction of the equations for the two isotopes gives a numerical value for the quantity

$$(m_2 + 2m_3) \, u^2 + 4m_3 \, uv + 2m_3 \, v^2$$

which can be substituted in the sum of the equations to find $\underline{v}^2$. Once $\underline{v}$ is known, the quadratic above can be solved for $\underline{u}$. Simple trigonometry then gives the N - O distance and the O-N-O angle.

The rotational constants listed in Table IV lead to the following molecular dimensions:

$$d(N - O) = 1.207 \text{ A}$$
$$d(N - Cl) = 1.830 \text{ A}$$
$$\angle (ONO) = 129.50° .$$

The figures shown in Table IV have been rounded in view of the approximation made in assuming molecular rigidity. The N - Cl distance is considerably larger than the sum of the single covalent bond radii, but is not so great as in nitrosyl chloride (NOCl), where the anomaly is attributed to ionic bond character.

d. Quadrupole Coupling Constants of Nitryl Chloride. The observable hyperfine splittings of nitryl chloride transitions are due to the chlorine nucleus; those due to the nitrogen nucleus are too small to resolve. Quadrupole couplings were calculated by first order theory from a fitting of the hyperfine structures of the 2 - 3 transitions, using the "maximum likelihood" procedure described in Appendix III.

Separate maximum likelihood fittings of the hyperfine components of each 2 - 3 transition were first performed, resulting in the estimates tabulated below without roundoff.

| | $2_{-2} - 3_{-3}$ Transition (Mc) | $2_1 - 3_0$ Transition (Mc) | $2_2 - 3_1$ Transition (Mc) |
|---|---|---|---|
| $\chi_{aa}^{35}$ | -94.81 | -94.64 | -95.07 |
| $\chi_{bb}^{35}$ | 52.35 | | 50.47 |
| $\chi_{cc}^{35}$ | 42.46 | | 44.60 |
| $\chi_{aa}^{37}$ | -74.38 | -74.68 | -74.77 |
| $\chi_{bb}^{37}$ | 40.67 | | 40.28 |
| $\chi_{cc}^{37}$ | 33.71 | | 34.49 |

The splitting of the $2_1 - 3_0$ transition is independent of $\chi_{bb}$ and $\chi_{cc}$. The lack of consistency between isotopic species in the magnitudes of the discrepancies suggests that they are due to the sensitivity of single-transition determinations to small frequency measurement errors rather than to possible higher order effects resulting from the proximity of the $2_1$ and $2_2$ rotational energy levels.

To make more efficient use of the data, simultaneous fittings of all the lines of all three transitions were next performed for each isotope. The resulting estimates are listed below, again without roundoff.

| | $NO_2Cl^{35}$ | $NO_2Cl^{37}$ |
|---|---|---|
| | (Mc) | (Mc) |
| $\chi_{aa}$ | -94.70 | -74.58 |
| $\chi_{bb}$ | 52.11 | 41.21 |
| $\chi_{cc}$ | 42.59 | 33.37 |

In an effort to refine the determination of $\chi_{bb}$ and $\chi_{cc}$, which are not so strongly constrained as $\chi_{aa}$, a final simultaneous fitting of all lines of all transitions of both isotopes was performed. In this calculation the measured ratio $\chi_{aa}^{35}/\chi_{aa}^{37} = 1.2697$ was used for the ratio $Q^{35}/Q^{37}$. The following coupling constants were obtained.

| | $NO_2Cl^{35}$ | $NO_2Cl^{37}$ |
|---|---|---|
| | (Mc) | (Mc) |
| $\chi_{aa}$ | -94.70 | -74.58 |
| $\chi_{bb}$ | 52.21 | 41.12 |
| $\chi_{cc}$ | 42.49 | 33.46 |

These values of $\chi_{bb}$ and $\chi_{cc}$ differ by only 0.1 Mc from those determined for each isotope separately. Values shown in Table III are rounded accordingly.

These coupling constants predict the observed quadrupole-interaction shifts of 58 well-resolved lines (including the higher-J transitions

subsequently observed) with a standard deviation of 0.02 Mc, confirming the adequacy of first order theory within the limits of experimental measurement capability.

From the couplings normal to the bond axis a 5- or 6-per-cent double bonding would be estimated according to the theory of Goldstein.[3] The large coupling constant along the bond indicates that the remaining single bond involves very little s-hybridization and very little ionic character.
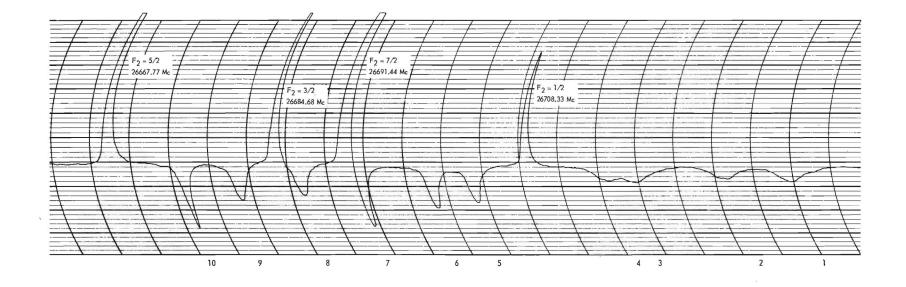
e. Stark Effect for Nitryl Chloride. Determination of the dipole moment of $NO_2Cl^{35}$ was undertaken by analysis of the Stark splitting of the $2_1$ - $3_0$ transition. In Figure 6, a recording made at an electric field intensity of 515 volts/cm, all ten Stark components of this transition are visible as downward deflections.

Splittings of the $2_1$ energy level were first calculated for several values of the quantity $\mu E$ (dipole moment times field intensity), using an IBM 650 computer to diagonalize the Hamiltonian matrices of Mizushima.[13] This procedure was not necessary for the $3_0$ level; there the average value of the molecular electric field gradient at the chlorine nucleus vanishes, so that there is no quadrupole interaction and the Stark energies are those for an ordinary asymmetric rotor.

Comparison of recordings with calculated Stark structures showed good qualitative agreement and indicated a dipole moment in the neighborhood of 0.5 Debye. Quantitatively, however, there was at higher field intensities a pronounced foreshortening in the observed shifts of those components which were displaced by more than about 30 Mc from their parent lines.

Of particular interest is Component No. 2 in Figure 6, for which $M = m_I + m_J = 7/2$. For this component the splitting of the $J = 2$ level is

Figure 6. The $J = 2_1 \longrightarrow 3_0$ Transition of $NO_2Cl^{35}$ Showing the Stark Components for an Electric Field of 515 Volts/cm. The $F_2$ Values are for the Lower State. The Values of F in the Upper State are not Identified as the $3_0$ Level is Degenerate in F.

obtained from a first degree secular equation. The displacement of the component from the $F_2 = 7/2$ line is found to be proportional to $E^2$, being in fact identical to the displacement for an asymmetric top without quadrupole interaction. The dashed line in Figure 7 shows this expected behavior, for comparison with the observed shifts.

The failure of the nondegenerate theory can be attributed primarily to the proximity of the $2_1$ and $2_2$ energy levels, whose separation is 178.89 Mc. The solid curve in Figure 7 shows the behavior predicted by the theory of Golden and Wilson[22] for an asymmetric top without quadrupole interaction in the case of near-degeneracy. The agreement with experiment is very good indeed, even though a nonvanishing influence of quadrupole interaction might be expected in a rigorous treatment of the degenerate case. Also neglected is a similar but considerably smaller effect resulting from the proximity of the $3_0$ and $3_1$ levels. The best-fitting dipole moment of 0.53 Debye compares favorably with a value of 0.51 Debye obtained from the nondegenerate theory at low field intensities.

Although Golden and Wilson pointed out that cases of near-degeneracy are almost inevitable for asymmetric-top molecules, no theory has been developed for the Stark splitting of close-spaced asymmetric-top energy levels in the presence of quadrupole interaction. The need for such a theory is clearly illustrated by the present analysis, where only transitions involving near-degenerate levels exhibit sufficiently large splitting for accurate measurement.

    f. Excited Vibrational States of Nitryl Chloride. In addition to the strong absorption lines listed in Appendix III, a number of weaker lines have been detected which are listed in Table VII. These weaker lines appear
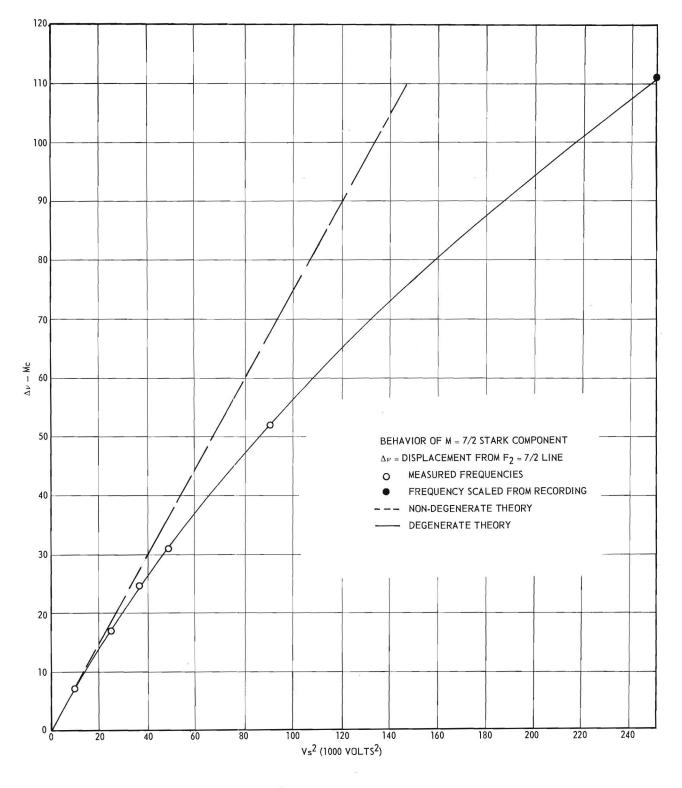
Figure 7. Behavior of M=7/2 Stark Component for $J=2_1 \rightarrow 3_0$ Transition of $NO_2Cl^{35}$.

## TABLE VII

## WEAK NITRYL CHLORIDE ABSORPTION LINE[†] FREQUENCIES

| $J_r$ | $NO_2Cl^{35}$ (Mc) | $NO_2Cl^{37}$ (Mc) |
|---|---|---|
| $3_1 \to 4_0$ | 36,740[††] (4 lines) | 35,689.5 |
| | | 35,686.9 |
| | | 35,681.7 |
| | | 35,679.0 |
| $3_0 \to 4_{-1}$ | 35,129.4 | 34,210[††] (4 lines) |
| | 35,126.2 | |
| | 35,120.0 | |
| | 35,116.8 | |
| $2_2 \to 3_1$[†††] | 27,145[††] | 26,375[††] |
| | 27,110[††] | 26,350[††] |
| $2_1 \to 3_0$[†††] | 26,450[††] | 25,750[††] |
| | 26,425[††] | 25,730[††] |

[†] These lines presumably result from rotational transitions in an excited vibration state.

[††] Measurements made with absorption wavemeter.

[†††] The two larger of the four lines are given here.

in groups of four, and the pattern of four lines is almost identical to that of one of the strong groups. A weak group corresponding to each strong group is observed with the exception of the $2_{-2} \to 3_{-3}$ and the $3_{-3} \to 4_{-4}$ transitions. The latter require very high Stark voltages for detection and their weaker counterparts might well be below the sensitivity of the spectrograph. Each weak group is found at a lower frequency than the corresponding strong group. Calculations show that they do not result from isotopic forms of nitryl

chloride containing $N^{15}$ or $O^{18}$. These facts seem to identify the weak groups as resulting from absorption by molecules in an excited vibration state. This interpretation, however, points up a slight inconsistency with published work of Ryason and Wilson[19] on the infrared spectrum of nitryl chloride.

The observed excited vibration lines are apparently the transitions $2_1 \rightarrow 3_0$, $2_2 \rightarrow 3_1$, $3_0 \rightarrow 4_{-1}$ and $3_1 \rightarrow 4_0$. Ryason and Wilson report the following assignment of fundamental vibration frequencies for nitryl chloride:

$$\nu_1(A_1) = 1293 \text{ cm}^{-1} \qquad \nu_4(B_1) = 1685 \text{ cm}^{-1}$$

$$\nu_2(A_1) = 794 \text{ cm}^{-1} \qquad \nu_5(B_1) = 367 \text{ cm}^{-1}$$

$$\nu_3(A_1) = 651 \text{ cm}^{-1} \qquad \nu_6(B_2) = 411 \text{ cm}^{-1}$$

Taking account of the restrictions placed on the total wave function by the presence of identical oxygen nuclei, the observed transitions are allowed only for a vibrational mode of species $A_1$ and $A_2$, i.e., $\nu_1$, $\nu_2$ and $\nu_3$. If these lines result from an excited $\nu_3$, for instance, then lines resulting from an excited $\nu_5$ vibration should be observable. A singly excited $\nu_5$ vibration should permit the transitions $2_0 \rightarrow 3_{-1}$ and $2_{-1} \rightarrow 3_{-2}$ which are not permitted in the ground state. A search was made for the $2_{-1} \rightarrow 3_{-2}$ transition but none was found.

Some additional measurements will be made in order to obtain a more positive identification of the weak groups before a definite conclusion is reached.

## IV. SCIENTIFIC TRAINING OF STUDENTS

Four graduate students have been employed under this contract while working on advanced degrees.

1. Mr. James H. Mauldin received his Master's Degree in June, 1955. Mr. Mauldin constructed the high voltage square wave generator used for Stark modulation of the microwave spectrograph and tested it by examining the Stark effect of carbonyl sulfide. His thesis is entitled "A High Voltage Square Wave Generator for Stark Modulation."

2. Mr. Donald F. Eagle received his Master's Degree in June, 1956. Mr. Eagle did the work on the Stark effect of nitrosyl bromide and is now working toward his Doctor of Philosophy in Physics. His Master's Thesis is entitled "Stark Effect and Nuclear Quadrupole Splitting in the Rotation Spectrum of Nitrosyl Bromide."

3. Mr. Lorimer Clayton, Jr. expects to complete his work for Doctor of Philosophy in Physics in December 1957. His work on nitryl chloride will be the subject of his thesis.

4. Mr. Edward L. Beeson is working toward his Doctor of Philosophy in Physics and will use his work on the Stark effect of chlorotrifluoromethane as a part of his research for that degree.

Respectfully submitted:

T. L. Weatherly
Project Co-director

Quitman Williams
Project Co-Director

Lorimer Clayton, Jr.
Research Physicist

Approved:

J. E. Boyd
Associate Director

## V.  PUBLICATIONS

"Pure Quadrupole Spectra of Some Nitrochlorobenzene," T. L. Weatherly and Quitman Williams: J. Chem. Phys. $\underline{21}$, 2073 (1953)(L).

"Nuclear Quadrupole Resonances in Some Chlorine Compounds," Quitman Williams and T. L. Weatherly: J. Chem. Phys. $\underline{22}$, 572 (1954)(L).

"Nuclear Quadrupole Resonance in Ethyl Chloroformate and Ethyl Trichloracetate," T. L. Weatherly and Quitman Williams: J. Chem. Phys. $\underline{22}$, 958 (1954)(L).

"The Microwave Spectrum of Nitrosyl Bromide," Quitman Williams and T. L. Weatherly: (Paper presented at the New York meeting of the American Physical Society, Jan. 27-29, 1955).

"The Microwave Spectrum and Molecular Constants of Nitrosyl Bromide," T. L. Weatherly and Quitman Williams: J. Chem. Phys. $\underline{25}$, 717 (1956); also Technical Report No. 1, OOR Project No. 1016, Engineering Experiment Station, Georgia Institute of Technology (1955).

"The Stark Effect in the Rotational Spectrum of Nitrosyl Bromide," Donald F. Eagle, T. L. Weatherly and Quitman Williams: Technical Report No. 2, OOR Project No. 1016, Engineering Experiment Station, Georgia Institute of Technology, 1956.

"Quadrupole Coupling Constants of Nitryl Chloride," Lorimer Clayton, Quitman Williams and T. L. Weatherly: Abstract, Bull. Am. Phys. Soc., $\underline{1}$, 341 (1956).

"A High Voltage Square Wave Generator for Stark Modulation," James H. Mauldin: Master's Thesis, Georgia Institute of Technology, 1955.

"Stark Effect and Nuclear Quadrupole Splitting in the Rotational Spectrum of Nitrosyl Bromide," Donald F. Eagle: Master's Thesis, Georgia Institute of Technology, 1956.

VI.  APPENDIXES

## APPENDIX I. COMPUTATIONAL PROCEDURES
## FOR QUADRUPOLE INTERACTION IN AN
## ASYMMETRIC-TOP MOLECULE

The first order theory of quadrupole hyperfine structure in asymmetric-top molecules has been worked out by Bragg and others, and is summarized quite effectively in the book by Townes and Schawlow.[4] The purpose of this appendix is to outline a number of algebraic manipulations which have proved convenient in the application of the theory to analysis of spectra.

### A. Quadrupole Interaction Energy

As is well known, the quadrupole interaction energy for any type of molecule can be expressed as

$$W_Q = \frac{e\, q_J\, Q}{2I(2I - 1)(2J - 1)J} \left[ \frac{3}{4} C(C + 1) - I(I + 1)J(J + 1) \right] \qquad (1)$$

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

$F = I + J,\ I + J - 1,\ \ldots\ldots\ |I - J|$

and  $q_J = \left( \frac{\partial^2 V}{\partial Z^2} \right)_{av}$

where $V$ is the potential at the nucleus in question resulting from all extranuclear charges, and $Z$ is the direction of $J$, fixed in space.

Of the several expressions which have been proposed for the evaluation of $q_J$ for an asymmetric-top molecule, the most convenient appears to be that of Bragg and Golden:

$$q_J = \frac{1}{(J+1)(2J+3)} \left\{ \frac{\partial^2 V}{\partial a^2} \left[ J(J+1) + E(\kappa) - (\kappa+1)\frac{\partial E(\kappa)}{\partial \kappa} \right] \right.$$

$$\left. + 2\frac{\partial^2 V}{\partial b^2}\frac{\partial E(\kappa)}{\partial \kappa} + \frac{\partial^2 V}{\partial c^2}\left[ J(J+1) - E(\kappa) + (\kappa-1)\frac{\partial E(\kappa)}{\partial \kappa} \right] \right\}$$

where $\underline{a}$, $\underline{b}$, and $\underline{c}$ are the directions of the principal axes, and $E(\kappa)$ is the tab-ulated rigid-rotor reduced energy for the level in question, a function of the asymmetry parameter $\kappa$.

In substituting this expression in Equation 1, one obtains as factors the "quadrupole couplings": $\chi_{aa} = e\frac{\partial^2 V}{\partial a^2}Q$, $\chi_{bb} = e\frac{\partial^2 V}{\partial b^2}Q$, and $\chi_{cc} = e\frac{\partial^2 V}{\partial c^2}Q$. Since V obeys Laplace's Equation, the relation

$$\chi_{aa} + \chi_{bb} + \chi_{cc} = 0$$

can be used to effect a simplification. Suitable factoring yields the simple expression:

$$W_Q = \left[ A(J,\tau)\chi_+ + B(J,\tau)\chi_- \right] f(I,J,F) \tag{2}$$

where $\chi_+ = \chi_{aa} + \chi_{cc}$

$\chi_- = \chi_{aa} - \chi_{cc}$

$$A(J,\tau) = 1 - \frac{3}{J(J+1)}\frac{\partial E(\kappa)}{\partial \kappa}$$

$$B(J,\tau) = \frac{1}{J(J+1)}\left[ E(\kappa) - k\frac{\partial E(\kappa)}{\partial \kappa} \right],$$

and $f(I,J,F)$ is the tabulated quantity known as Casimir's function:

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

It is sometimes more convenient to use an alternative form:

$$W_Q = \left[ C(J,\tau)\chi_{aa} + D(J,\tau)\chi_{cc} \right]\ f(I,J,F) \qquad (3)$$

where $C(J,\tau) = A(J,\tau) + B(J,\tau)$

$\qquad D(J,\tau) = A(J,\tau) - B(J,\tau).$

The coefficients $A(J,\tau)$ and $B(J,\tau)$ may be found in general by simple inter-polations in tables[†] of $E(\kappa)$; however, for low-J energy levels they can be ex-pressed as explicit functions of $\kappa$. These expressions as well as those for $C(J,\kappa)$ and $D(J,\tau)$ are given in Table A.I for the levels through $J = 3$.

## B. Spacings of Hyperfine Components

If the quadrupole interaction energy is written in the form

$$W_Q = G(J,\tau)f(IJF) \qquad (4)$$

where the factor $G(J,\tau)$ represents, for a given molecule, either of the brack-eted quantities in the last section, then the frequency of the hyperfine com-ponent $J,\tau,F \rightarrow J',\tau',F'$ is

$$\nu = \nu_0 + G(J',\tau')f(IJ'F') - G(J,\tau)f(IJF) \qquad (5)$$

where $\nu_0$ is the unperturbed "group-center" frequency for the transition $J_\tau \rightarrow J'_{\tau'}$.

------

[†]Tables of both $E(\kappa)$ and $f(I,J,F)$ may be found in the back of Townes and Schaw-low.[4]

TABLE A–1
CONSTANTS FOR EVALUATION OF QUADRUPOLE INTERACTION ENGERIES IN ASYMMETRIC–TOP MOLECULES

| $J_\tau$ | $A(J,\tau)$ | $B(J,\tau)$ | $C(J,\tau)$ | $D(J,\tau)$ |
|---|---|---|---|---|
| $0_0$ | $0$ | $0$ | $0$ | $0$ |
| $1_1$ | $-1/2$ | $1/2$ | $0$ | $-1$ |
| $1_0$ | $1$ | $0$ | $1$ | $1$ |
| $1_{-1}$ | $-1/2$ | $-1/2$ | $-1$ | $0$ |
| $2_2$ | $-\dfrac{\kappa}{\sqrt{\kappa^2+3}}$ | $\dfrac{1}{\sqrt{\kappa^2+3}}$ | $\dfrac{1-\kappa}{\sqrt{\kappa^2+3}}$ | $-\dfrac{1+\kappa}{\sqrt{\kappa^2+3}}$ |
| $2_1$ | $1/2$ | $1/2$ | $1$ | $0$ |
| $2_0$ | $-1$ | $0$ | $-1$ | $-1$ |
| $2_{-1}$ | $1/2$ | $-1/2$ | $0$ | $1$ |
| $2_{-2}$ | $\dfrac{\kappa}{\sqrt{\kappa^2+3}}$ | $\dfrac{-1}{\sqrt{\kappa^2+3}}$ | $\dfrac{\kappa-1}{\sqrt{\kappa^2+3}}$ | $\dfrac{1+\kappa}{\sqrt{\kappa^2+3}}$ |
| $3_3$ | $-\dfrac{1}{4}\left[1+\dfrac{8\kappa-6}{\sqrt{4\kappa^2-6\kappa+6}}\right]$ | $\dfrac{1}{4}\left[1-\dfrac{2\kappa-4}{\sqrt{4\kappa^2-6\kappa+6}}\right]$ | $-\dfrac{5}{2}\left[\dfrac{\kappa-1}{\sqrt{4\kappa^2-6\kappa+6}}\right]$ | $-\dfrac{1}{2}\left[1+\dfrac{3\kappa-1}{\sqrt{4\kappa^2-6\kappa+6}}\right]$ |
| $3_2$ | $\dfrac{1}{2}\left[1-\dfrac{\kappa}{\sqrt{\kappa^2+15}}\right]$ | $\dfrac{5}{2}\left[\dfrac{1}{\sqrt{\kappa^2+15}}\right]$ | $\dfrac{1}{2}\left[1+\dfrac{5-\kappa}{\sqrt{\kappa^2+15}}\right]$ | $\dfrac{1}{2}\left[1-\dfrac{5+\kappa}{\sqrt{\kappa^2+15}}\right]$ |
| $3_1$ | $-\dfrac{1}{4}\left[1+\dfrac{8\kappa+6}{\sqrt{4\kappa^2+6\kappa+6}}\right]$ | $-\dfrac{1}{4}\left[1-\dfrac{2\kappa+4}{\sqrt{4\kappa^2+6\kappa+6}}\right]$ | $-\dfrac{1}{2}\left[1+\dfrac{3\kappa+1}{\sqrt{4\kappa^2+6\kappa+6}}\right]$ | $-\dfrac{5}{2}\left[\dfrac{\kappa+1}{\sqrt{4\kappa^2+6\kappa+6}}\right]$ |
| $3_0$ | $0$ | $0$ | $0$ | $0$ |
| $3_{-1}$ | $-\dfrac{1}{4}\left[1-\dfrac{8\kappa-6}{\sqrt{4\kappa^2-6\kappa+6}}\right]$ | $\dfrac{1}{4}\left[1+\dfrac{2\kappa-4}{\sqrt{4\kappa^2-6\kappa+6}}\right]$ | $\dfrac{5}{2}\left[\dfrac{\kappa-1}{\sqrt{4\kappa^2-6\kappa+6}}\right]$ | $-\dfrac{1}{2}\left[1-\dfrac{3\kappa-1}{\sqrt{4\kappa^2-6\kappa+6}}\right]$ |
| $3_{-2}$ | $\dfrac{1}{2}\left[1+\dfrac{\kappa}{\sqrt{\kappa^2+15}}\right]$ | $-\dfrac{5}{2}\left[\dfrac{1}{\sqrt{\kappa^2+15}}\right]$ | $\dfrac{1}{2}\left[1-\dfrac{5-\kappa}{\sqrt{\kappa^2+15}}\right]$ | $\dfrac{1}{2}\left[1+\dfrac{5+\kappa}{\sqrt{\kappa^2+15}}\right]$ |
| $3_{-3}$ | $-\dfrac{1}{4}\left[1-\dfrac{8\kappa+6}{\sqrt{4\kappa^2+6\kappa+6}}\right]$ | $-\dfrac{1}{4}\left[1+\dfrac{2\kappa+4}{\sqrt{4\kappa^2+6\kappa+6}}\right]$ | $-\dfrac{1}{2}\left[1-\dfrac{3\kappa+1}{\sqrt{4\kappa^2+6\kappa+6}}\right]$ | $\dfrac{5}{2}\left[\dfrac{\kappa+1}{\sqrt{4\kappa^2+6\kappa+6}}\right]$ |

The frequency separation between two such hyperfine components of the same transition is therefore

$$
\begin{aligned}
\nu_1 - \nu_2 = G(J',\tau') &\left[ f(IJ'F'_1) - f(IJ'F'_2) \right] \\
- G(J,\tau) &\left[ f(IJF_1) - f(IJF_2) \right].
\end{aligned} \tag{6}
$$

As a preliminary step in the analysis of spectra, it is helpful to prepare a table of the numerical values of the coefficients of the G's for the spacings between all pairs of hyperfine components of each transition of interest. This can be done quite readily by reference to tables of Casimir's function, and it will generally be found that certain pairs of spacings are either equal or otherwise simply related regardless of the values of the molecular parameters $G(J,\tau)$ and $G(J',\tau')$. This result, a consequence of the simple rational-fraction form of $f(IJF)$, is useful in the identification of components. Furthermore, certain spacings can often be found from which numerical values of the G's can be determined immediately, thus leading quickly to first estimates of the quadrupole couplings.

Since the spacing relations determined in this manner depend only upon $I, J,$ and $J'$, and are independent of $\tau$ and the G's, one table suffices for several transitions and applies to any molecule with the same $I$.

C. Maximum Likelihood Calculation of Quadrupole Couplings

The process of calculating quadrupole couplings is one of successive refinement, closely connected with the determination of group-center frequencies and the calculation of rotational constants. A first estimate of group-center frequencies by taking intensity-weighted averages of hyperfine component

frequencies will generally permit calculation of the rotational constants and $\kappa$ with sufficient accuracy for making first estimates of quadrupole couplings as mentioned in Section B. These couplings in turn permit a more accurate determination of group-center frequencies, from which $\kappa$ can be obtained with sufficient accuracy for use in calculation of precise quadrupole couplings. Finally, the rotational constants can be revised if necessary, using precise group-center frequencies.

If appropriate transitions can be observed, various spacings can often be found such that each depends strongly upon a different coupling constant; in this case, a quick solution from the expressions for $G(J, \tau)$ is likely to be accurate. However, when spacings are small or when the experimental data are limited (as for nitryl chloride, where many energy levels are absent), the quadrupole coupling determination becomes quite sensitive to frequency-measurement errors. It is then important to make efficient use of all available data.

If several hyperfine components are involved, one usually has at his disposal an overdetermined set of equations in $\chi_{aa}$ and $\chi_{cc}$, slightly inconsistent because of frequency measurement errors. Some kind of "averaging" or data-smoothing procedure is clearly desirable so that advantage may be taken of this overdetermination to minimize the error in the solution for $\chi_{aa}$ and $\chi_{cc}$. In choosing such a procedure, however, one must take care to avoid improper weighting of individual frequency measurements.

It is usually reasonable to assume that the frequencies of all well-resolved lines are measured with equal probable error, and to exclude all ill-resolved lines from consideration. The so-called "maximum likelihood" statistical method then affords a convenient means of accomplishing smoothing while ensuring proper weighting of all constraints.

An arbitrary linear combination of some or all of the well-resolved components of a given transition can be expressed in the form

$$a_{i1}\nu_1 + a_{i2}\nu_2 + \ldots a_{in}\nu_n = c_i \chi_{aa} + d_i \chi_{cc} + \nu_o \sum_{j=1}^{n} a_{ij}$$

where for a particular choice of coefficients $a_{ij}$, the numerical values of $c_i$ and $d_i$ can be calculated from Equation 5, using

$$G(J,\tau) = C(J,\tau)\chi_{aa} + D(J,\tau)\chi_{cc}.$$

Now if the $a_{ij}$'s are chosen such that

$$\sum_{j=1}^{n} a_{ij} = 0 \tag{7}$$

only two unknowns, $\chi_{aa}$ and $\chi_{cc}$, remain. The maximum likelihood method involves reduction of an appropriately chosen set of such equations to the two equations below, which can then be solved for the couplings.

$$\sum_i c_i(a_{i1}\nu_1 + a_{i2}\nu_2 + \ldots a_{in}\nu_n) = \sum_i (c_i^2 \chi_{aa} + c_i d_i \chi_{cc}) \tag{8a}$$

$$\sum_i d_i(a_{i1}\nu_1 + a_{i2}\nu_2 + \ldots a_{in}\nu_n) = \sum_i (c_i d_i \chi_{aa} + d_i^2 \chi_{cc}) \tag{8b}$$

An "appropriately chosen" set is one for which the line-frequency coefficients
satisfy, in addition to Equation 7, the conditions:

$$\sum_j a_{ij} a_{kj} = \begin{cases} 1, & i = k \qquad\qquad (9a) \\ \\ 0, & i \neq k. \qquad\qquad (9b) \end{cases}$$

Condition 9a ensures that the probable error of each linear combination is the
same, while 9b makes the errors in different linear combinations statistically
independent (uncorrelated). Among n line frequencies, n different linear com-
binations can be chosen which satisfy condition 9, but only (n-1) can be found
which satisfy Equation 7 in addition. To make use of all constraints, one must
use a complete set of (n-1) such linear combinations. The choice is, of course,
not unique, but all sets so chosen lead to identical solutions.

The selection of a set of linear combinations to satisfy condition 9 amounts
to the construction of a coefficient matrix whose rows represent orthonormal vec-
tors, and this is a convenient way to handle the problem in practice. If the
first (n-1) rows of such a matrix are chosen to satisfy Equation 7, the last
row will represent a linear combination involving the group-center frequency $\nu_o$,
which must be regarded as a third unknown since its determination is not inde-
pendent of the quadrupole couplings. Consequently, the last row imposes no ad-
ditional constraint upon the couplings and should be dismissed from consideration.

For a strong determination of the quadrupole couplings, it is desirable to
perform a maximum likelihood fitting of the hyperfine structures of several
transitions simultaneously. To do so, it is only necessary to find appropriate
linear combinations of the components of the individual transitions as described

above, compute the corresponding $c_i$'s and $d_i$'s, and then include all such combinations for all transitions in the summations of Equations 8a and 8b.

Table AII

CALCULATED AND OBSERVED FREQUENCIES OF THE
$J = 2 \rightarrow 3$ TRANSITION OF NITROSYL BROMIDE

| Transition | | NOBr[79] | | | NOBr[81] | | |
|---|---|---|---|---|---|---|---|
| J | F | Calculated Frequency | Weighted Average[†] | Observed[††] Frequency | Calculated Frequency | Weighted Average[†] | Observed Frequency[††] |
| | | (Mc) | (Mc) | (Mc) | (Mc) | (Mc) | (Mc) |
| $2_{-1}-3_{-2}$ | 5/2-5/2 | 21,743.36 | | 21,742.93 | 21,606.47 | | 21,606.22 |
| | 1/2-3/2 | 21,745.67 | | 21,745.74 | 21,608.51 | | 21,608.49 |
| | 7/2-9/2 | 21,747.78 | | 21,747.91 | 21,610.24 | | 21,609.91 |
| | 3/2-5/2 | 21,769.93 | | 21,769.84 | 21,628.84 | | 21,628.84 |
| | 5/2-7/2 | 21,772.04 | | 21,771.95 | 21,630.58 | | 21,630.32 |
| $2_{-2}-3_{-3}$ | 5/2-7/2 | 21,994.15 } | 21,994.17 | 21,993.86 | 21,852.62 } | 21,852.64 | 21,852.23 |
| | 7/2-9/2 | 21,994.18 } | | | 21,852.65 } | | |
| | 3/2-5/2 | 22,018.19 } | 22,018.21 | 22,016.97 | 21,872.77 } | 21,872.78 | 21,871.10 |
| | 1/2-3/2 | 22,018.23 } | | | 21,872.80 } | | |
| $2_1-3_0$ | 7/2-9/2 | 21,972.00 } | | | 21,834.22 } | | |
| | 7/2-7/2 | 21,972.00 | | | 21,834.22 | | |
| | 7/2-5/2 | 21,972.00 } | 21,973.03 | 21,972.29 | 21,834.22 } | 21,834.70 | 21,835.19 |
| $2_2-3_1$ | 7/2-9/2 | 21,972.94 | | | 21,835.17 | | |
| | 7/2-7/2 | 21,973.00 | | | 21,835.22 | | |
| | 7/2-5/2 | 21,972.97 } | | | 21,835.20 } | | |
| $2_1-3_0$ | 3/2-3/2 | 21,994.74 } | | | 21,857.47 } | | |
| | 3/2-5/2 | 21,999.74 } | 22,000.21 | 22,001.07 | 21,857.47 } | 21,857.95 | 21,858.69 |
| $2_2-3_1$ | 3/2-3/2 | 22,000.64 } | | | 21,858.39 } | | |
| | 3/2-5/2 | 22,000.70 } | | | 21,858.44 } | | |

(continued)

Table AII (concluded)

CALCULATED AND OBSERVED FREQUENCIES OF THE
J = 2 → 3 TRANSITION OF NITROSYL BROMIDE

| Transition J | F | NOBr[79] Calculated Frequency (Mc) | Weighted Average[†] (Mc) | Observed[††] Frequency (Mc) | NOBr[81] Calculated Frequency (Mc) | Weighted Average[†] (Mc) | Observed Frequency[††] (Mc) |
|---|---|---|---|---|---|---|---|
| $2_1 - 3_0$ | 5/2-3/2 | 22,069.08 ⎫ | | | 21,915.59 ⎫ | | |
| | 5/2-5/2 | 22,069.08 ⎪ | | | 21,915.59 ⎪ | | |
| | 5/2-7/2 | 22,069.08 ⎬ | 22,069.56 | 22,069.77 | 21,915.59 ⎬ | 21,916.08 | 21,916.77 |
| $2_2 - 3_1$ | 5/2-3/2 | 22,069.97 ⎪ | | | 21,916.50 ⎪ | | |
| | 5/2-5/2 | 22,070.03 ⎪ | | | 21,916.54 ⎪ | | |
| | 5/2-7/2 | 22,070.05 ⎭ | | | 21,916.57 ⎭ | | |
| $2_0 - 3_{-1}$ | 7/2-9/2 | 22,230.43 | | 22,230.38 | 22,086.79 | | 22,086.65 |
| | 1/2-3/2 | 22,233.93 | | 22,233.60 | 22,089.69 | | 22,089.42 |
| | 5/2-7/2 | 22,254.69 | | 22,254.57 | 22,107.12 | | 22,106.69 |
| | 3/2-5/2 | 22,258.20 | | 22,258.34 | 22,110.03 | | 22,110.25 |

[†] The calculated relative intensitites were used for the weighting factors.

[††] The estimated errors of the observed frequencies are 0.25 Mc.

Table AIII

OBSERVED LINE FREQUENCIES
FOR THE $J = 3 \rightarrow 4$ AND $J = 4 \rightarrow 5$ TRANSITION OF NOBr[†]

| Transition | Frequency (Mc) |
|---|---|
| $J = 3 \rightarrow 4$ | 28 820.1 |
| | 28 823.9 |
| | 28 827.4 |
| | 28 829.4 |
| | 28 831.7 |
| | 29 007.1 |
| | 29 014.9 |
| | 29 122.8 |
| | 29 132.6 |
| | 29 154.0 |
| | 29 196.0 |
| | 29 266.4 |
| | 29 307.9 |
| | 29 320.0 |
| | 29 326.3 |
| | 29 330.4 |
| | 29 359.1 |
| | 29 463.3 |
| | 29 468.4 |
| | 29 504.3 |
| | 29 517.8 |
| | 29 618.2 |
| | 29 657.8 |
| | 29 664.0 |
| $J = 4 \rightarrow 5$ | 35 870 |
| | 36 030 |
| | 36 280 |
| | 36 420 |
| | 36 480 |
| | 36 630 |
| | 36 710 |
| | 36 810 |
| | 36 830 |
| | 37 100 |

[†] This table contains only the more intense lines for these transitions.

APPENDIX III

NO$_2$Cl  MICROWAVE SPECTRUM

$3_1 - 4_0$ Transition  Measured Group Center Frequency  = 37085.46 Mc.

NO$_2$Cl$^{35}$  Calculated Group Center Frequency  = 37085.36 Mc.

| $F_3$ | $F_4$ | Theoretical Relative Intensity | Measured Frequency (Mc) | Measured Group Center Frequency plus Calculated Quadrupole Interaction Shift | Calculated Frequency (Mc) |
|---|---|---|---|---|---|
| 5/2 | 5/2 | 2.30 | not reslvd. | 37093.56 | 37093.46 |
| 3/2 | 5/2 | 14.3 | 37092.52 | 37092.52 | 37092.42 |
| 9/2 | 11/2 | 33.3 | 37089.15 | 37089.13 | 37089.03 |
| 7/2 | 7/2 | 3.02 | not reslvd. | 37082.99 | 37082.89 |
| 5/2 | 7/2 | 19.1 | 37082.50 | 37082.51 | 37082.41 |
| 7/2 | 9/2 | 25.5 | 37079.11 | 37079.12 | 37079.02 |
| 9/2 | 9/2 | 2.31 | not reslvd. | 37078.08 | 37077.98 |

$3_0 - 4_{-1}$ Transition  Measured Group Center Frequency  = 35439.63 Mc.

NO$_2$Cl$^{35}$  Calculated Group Center Frequency  = 35439.95 Mc.

| $F_3$ | $F_4$ | Theoretical Relative Intensity | Measured Frequency (Mc) | Measured Group Center Frequency plus Calculated Quadrupole Interaction Shift | Calculated Frequency (Mc) |
|---|---|---|---|---|---|
| * | 5/2 | 16.7 | 35446.36 | 35446.32 | 35446.64 |
|  | 11/2 | 33.3 | 35443.08 | 35443.04 | 35443.36 |
|  | 7/2 | 22.2 | 35436.91 | 35436.95 | 35437.27 |
|  | 9/2 | 27.8 | 35433.63 | 35433.67 | 35433.99 |

* Level degenerate in F.

## $NO_2Cl$ MICROWAVE SPECTRUM

$3_{-3} - 4_{-4}$ Transition     Measured Group Center Frequency     = 33932.71 Mc.[*]

$NO_2Cl^{35}$     Calculated Group Center Frequency     = 33933.30 Mc.

| $F_3$ | $F_4$ | Theoretical Relative Intensity | Measured Frequency (Mc) | Measured Group Center Frequency plus Calculated Quadrupole Interaction Shift | Calculated Frequency (Mc) |
|------|------|------|------|------|------|
| 5/2 | 5/2 | 2.30 | 33953.0 | 33952.94 | 33953.53 |
| 7/2 | 7/2 | 3.02 | 33941.4 | 33941.52 | 33942.11 |
| 7/2 | 9/2 | 25.5 | 33933.83 | 33933.81 | 33934.40 |
| 9/2 | 11/2 | 33.3 | 33933.17 | 33933.16 | 33933.75 |
| 5/2 | 7/2 | 19.1 | 33930.97 | 33930.96 | 33931.55 |
| 3/2 | 5/2 | 14.3 | 33930.27 | 33930.31 | 33930.90 |
| 9/2 | 9/2 | 2.31 | 33911.19 | 33911.18 | 33911.77 |

[*]Obtained using the four principal lines only.

$2_2 - 3_1$ Transition     Measured Group Center Frequency     = 27382.92 Mc.[*]

$NO_2Cl^{35}$     Calculated Group Center Frequency     = 27382.92 Mc.

| $F_2$ | $F_3$ | Theoretical Relative Intensity | Measured Frequency (Mc) | Measured Group Center Frequency plus Calculated Quadrupole Interaction Shift | Calculated Frequency (Mc) |
|------|------|------|------|------|------|
| 1/2 | 3/2 | 10.0 | 27407.00 | 27406.99 | 27406.99 |
| 7/2 | 9/2 | 35.7 | 27389.88 | 27389.90 | 27389.91 |
| 7/2 | 7/2 | 4.08 | 27388.8 | 27388.86 | 27388.87 |
| 3/2 | 3/2 | 4.00 | 27383.8 | 27383.75 | 27383.75 |
| 3/2 | 5/2 | 16.0 | 27382.73 | 27382.71 | 27382.71 |
| 5/2 | 5/2 | 5.22 | 27366.1 | 27366.11 | 27366.11 |
| 5/2 | 7/2 | 24.5 | 27365.61 | 27365.63 | 27365.63 |

[*]Obtained using the four principal lines only.

## NO$_2$Cl  MICROWAVE SPECTRUM

$2_1 - 3_0$ Transition   Measured Group Center Frequency = 26684.67 Mc.

NO$_2$Cl$^{35}$     Calculated Group Center Frequency = 26684.70 Mc.

| $F_2$ | $F_3$ | Theoretical Relative Intensity | Measured Frequency (Mc) | Measured Group Center Frequency plus Calculated Quadrupole Interaction Shift | Calculated Frequency (Mc) |
|---|---|---|---|---|---|
| 1/2 | * | 10 | 26708.33 | 26708.35 | 26708.38 |
| 7/2 | * | 40 | 26691.44 | 26691.44 | 26691.46 |
| 3/2 | * | 20 | 26684.68 | 26684.67 | 26684.70 |
| 5/2 | * | 30 | 26667.77 | 26667.76 | 26667.79 |

*Level degenerate in F.

$2_{-2} - 3_{-3}$ Transition   Measured Group Center Frequency = 25986.49 Mc.

NO$_2$Cl$^{35}$     Calculated Group Center Frequency = 25986.48 Mc.

| $F_2$ | $F_3$ | Theoretical Relative Intensity | Measured Frequency (Mc) | Measured Group Center Frequency plus Calculated Quadrupole Interaction Shift | Calculated Frequency (Mc) |
|---|---|---|---|---|---|
| 3/2 | 3/2 | 4.00 | 26004.59 | 26004.60 | 26004.59 |
| 5/2 | 5/2 | 5.22 | 25998.57 | 25998.56 | 25998.55 |
| 5/2 | 7/2 | 24.5 | 25988.01 | 25988.00 | 25987.99 |
| 7/2 | 9/2 | 35.7 | 25987.43 | 25987.40 | 25987.39 |
| 3/2 | 5/2 | 16.0 | 25981.95 | 25981.96 | 25981.95 |
| 1/2 | 3/2 | 10.0 | 25981.33* | 25981.36 | 25981.35 |
| 7/2 | 7/2 | 4.08 | obscured* | 25964.76 | 25964.75 |

*Obscured by NO$_2$Cl$^{37}$ line, $2_1 - 3_0$ ; $F_2 = 5/2$

## NO$_2$Cl   MICROWAVE SPECTRUM

$4_{-4}$ - $5_{-5}$ Transition | Measured Group Center Frequency | = 40600.57 Mc.

NO$_2$Cl$^{37}$ | Calculated Group Center Frequency | = 40602.78 Mc.

| F$_4$ | F$_5$ | Theoretical Relative Intensity | Measured Frequency (Mc) | Measured Group Center Frequency plus Calculated Quadrupole Interaction Shift | Calculated Frequency (Mc) |
|---|---|---|---|---|---|
| 7/2 | 7/2 | 1.48 | not meas. | 40616.88 | 40619.09 |
| 9/2 | 9/2 | 1.96 | not meas. | 40605.99 | 40608.20 |
| 9/2 | 11/2 | 25.8 | 40601.22 | 40601.19 | 40603.41 |
| 11/2 | 13/2 | 31.8 | 40600.75 | 40600.77 | 40602.98 |
| 7/2 | 9/2 | 20.7 | 40599.89 | 40599.88 | 40602.09 |
| 5/2 | 7/2 | 16.7 | 40599.43 | 40599.46 | 40601.67 |
| 11/2 | 11/2 | 1.49 | not meas. | 40583.77 | 40585.99 |

$3_1$ - $4_0$ Transition | Measured Group Center Frequency | = 35990.35 Mc.

NO$_2$Cl$^{37}$ | Calculated Group Center Frequency | = 35990.25 Mc.

| F$_3$ | F$_4$ | Theoretical Relative Intensity | Measured Frequency (Mc) | Measured Group Center Frequency plus Calculated Quadrupole Interaction Shift | Calculated Frequency (Mc) |
|---|---|---|---|---|---|
| 5/2 | 5/2 | 2.30 | not reslvd. | 35996.65 | 35996.55 |
| 3/2 | 5/2 | 14.3 | 35995.90 | 35995.91 | 35995.80 |
| 9/2 | 11/2 | 33.3 | 35993.27 | 35993.24 | 25993.13 |
| 7/2 | 7/2 | 3.02 | not reslvd. | 35988.39 | 35988.29 |
| 5/2 | 7/2 | 19.1 | 35988.03 | 35988.04 | 35987.94 |
| 7/2 | 9/2 | 25.5 | 35985.36 | 35985.37 | 35985.27 |
| 9/2 | 9/2 | 2.31 | not reslvd. | 35984.63 | 35984.52 |

## NO$_2$Cl  MICROWAVE SPECTRUM

$3_0 - 4_{-1}$ Transition          Measured Group Center Frequency     = 34512.83 Mc.

NO$_2$Cl$^{37}$                    Calculated Group Center Frequency   = 34513.14 Mc.

| F$_3$ | F$_4$ | Theoretical Relative Intensity | Measured Frequency (Mc) | Measured Group Center Frequency plus Calculated Quadrupole Interaction Shift | Calculated Frequency (Mc) |
|---|---|---|---|---|---|
| * | 5/2 | 16.7 | 34518.11 | 34518.11 | 34518.42 |
| * | 11/2 | 33.3 | 34515.53 | 34515.52 | 34515.83 |
| * | 7/2 | 22.2 | 34510.72 | 34510.72 | 34511.03 |
| * | 9/2 | 27.8 | 34508.11 | 34508.13 | 34508.44 |

*Level degenerate in F.

$3_{-3} - 4_{-4}$ Transition        Measured Group Center Frequency     = 33158.89 Mc.

NO$_2$Cl$^{37}$                    Calculated Group Center Frequency   = 33159.47 Mc.

| F$_3$ | F$_4$ | Theoretical Relative Intensity | Measured Frequency (Mc) | Measured Group Center Frequency plus Calculated Quadrupole Interaction Shift | Calculated Frequency (Mc) |
|---|---|---|---|---|---|
| 5/2 | 5/2 | 2.30 | not meas. | 33174.91 | 33175.49 |
| 7/2 | 7/2 | 3.02 | not meas. | 33165.84 | 33166.43 |
| 7/2 | 9/2 | 25.5 | 33159.75 | 33159.74 | 33160.32 |
| 9/2 | 11/2 | 33.3 | 33159.29 | 33159.26 | 33159.84 |
| 5/2 | 7/2 | 19.1 | 33157.49 | 33157.49 | 33158.07 |
| 3/2 | 5/2 | 14.3 | 33156.97 | 33157.01 | 33157.60 |
| 9/2 | 9/2 | 2.31 | not meas. | 33141.84 | 33142.42 |

## $NO_2Cl$ MICROWAVE SPECTRUM

$2_2 - 3_1$ Transition      Measured Group Center Frequency    = 26600.74 Mc.[*]

$NO_2Cl^{37}$      Calculated Group Center Frequency    = 26600.73 Mc.

| $F_2$ | $F_3$ | Theoretical Relative Intensity | Measured Frequency (Mc) | Measured Group Center Frequency plus Calculated Quadrupole Interaction Shift | Calculated Frequency (Mc) |
|---|---|---|---|---|---|
| 1/2 | 3/2 | 10.0 | 26619.69 | 26619.68 | 26619.66 |
| 7/2 | 9/2 | 35.7 | 26606.22 | 26606.23 | 26606.22 |
| 7/2 | 7/2 | 4.08 | not reslvd. | 26605.48 | 26605.47 |
| 3/2 | 3/2 | 4.00 | 26601.4 | 26601.34 | 26601.33 |
| 3/2 | 5/2 | 16.0 | 26600.60 | 26600.59 | 26600.58 |
| 5/2 | 5/2 | 5.22 | 26587.5 | 26587.50 | 26587.49 |
| 5/2 | 7/2 | 24.5 | 26587.14 | 26587.15 | 26587.14 |

[*]Obtained using the four principal lines only.

$2_1 - 3_0$ Transition      Measured Group Center Frequency    = 25977.93 Mc.

$NO_2Cl^{37}$      Calculated Group Center Frequency    = 25977.96 Mc.

| $F_2$ | $F_3$ | Theoretical Relative Intensity | Measured Frequency (Mc) | Measured Group Center Frequency plus Calculated Quadrupole Interaction Shift | Calculated Frequency (Mc) |
|---|---|---|---|---|---|
| 1/2 | * | 10 | 25996.61 | 25996.57 | 25996.61 |
| 7/2 | * | 40 | 25983.23 | 25983.25 | 25983.29 |
| 3/2 | * | 20 | 25977.92 | 25977.93 | 25977.96 |
| 5/2 | * | 30 | 25964.60 | 25964.61 | 25964.64 |

[*]Level degenerate in F.

## $NO_2Cl$   MICROWAVE SPECTRUM

$2_{-2} - 3_{-3}$ Transition        Measured Group Center Frequency        = 25355.22 Mc.

$NO_2Cl^{37}$        Calculated Group Center Frequency        = 25355.19 Mc.

| $F_2$ | $F_3$ | Theoretical Relative Intensity | Measured Frequency (Mc) | Measured Group Center Frequency plus Calculated Quadrupole Interaction Shift | Calculated Frequency (Mc) |
|---|---|---|---|---|---|
| 3/2 | 3/2 | 4.00 | 25369.52 | 25369.53 | 25369.51 |
| 5/2 | 5/2 | 5.22 | 25364.68 | 25364.73 | 25364.71 |
| 5/2 | 7/2 | 24.5 | 25356.38 | 25356.38 | 25356.35 |
| 7/2 | 9/2 | 35.7 | 25355.97 | 25355.94 | 25355.92 |
| 3/2 | 5/2 | 16.0 | 25351.64 | 25351.64 | 25351.61 |
| 1/2 | 3/2 | 10.0 | 25351.20 | 25351.20 | 25351.18 |
| 7/2 | 7/2 | 4.08 | 25338.08 | 25338.05 | 25338.02 |

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