

DETERMINATION OF MOLECULAR CONSTANTS
BY MICROWAVE AND RADIO-FREQUENCY SPECTROSCOPY

by

THOMAS L. WEATHERLY

and others,

Project A-265

Contract No. DA-01-009-ORD-465

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia
1953-1957

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Technical Report.

No. 1. Weatherly, T. L. and Williams, Quitman.

Microwave Spectrum and Molecular Constants of Nitrosyl
Bromide. September 19, 1955.

No. 2. Eagle, D. F., Weatherly, T. L. and Williams, Quitman.

The Stark Effect in the Rotational Spectrum of Nitrosyl
Bromide. October 2, 1956.

Final Report.

Weatherly, T. L., Williams, Quitman and Clayton, Lorimer, Jr.

October 1, 1953--May 31, 1957.

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

SCHOOL OF PHYSICS



Status Report No. 1

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor:--

Georgia Tech Research Institute
Research Building
Georgia Institute of Technology
Atlanta, Georgia

Period:--

1 January 1956 to 31 March 1956

Project No. :--

OOR 1016

Contract No. :--

DA-01-009-ORD-465

Submitted by:--

T. L. Weatherly
Associate Professor

Joel Q. Williams
Associate Professor

Approved by:--

J. E. Boyd, Associate Director
Engineering Experiment Station

Status Report No. 1

Determination of Molecular Constants

of

Microwave and Radio Frequency Spectroscopy

Contract No. DA-01-009-ORD-465

Personnel: During the winter quarter ending 31 March, 1956 the co-directors, Joel Q. Williams and T. L. Weatherly, have devoted one-third time to research under this contract. Mr. Donald F. Eagle and Mr. Lorimer Clayton, Jr. have been employed as graduate assistants for one-third time and one-fifth time respectively. This is the same group that was employed under contract number DA-01-009-ORD-353.

Fiscal: Expenditures during the quarter were as follows:

Personal Services	\$ 1986.60
Overhead	1042.96
Supplies	168.35
Freight and Express	<u>4.57</u>
Total	\$ 3202.48

Research: Investigation of the microwave spectrum of nitril chloride (NO_2Cl) and nitrosyl bromide (NOBr) which began under contract DA-01-009-ORD-353 has continued in the quarter covered by this report. The rotational lines of nitril chloride have proved to be much narrower than the previously measured nitrosyl bromide lines, making more accurate frequency measurements possible. In order to take full advantage of this it was necessary to make some improvements in frequency measuring techniques. These improvements have been made by Mr. Clayton and the lines listed in Table I were measured to an accuracy of $\pm .05$ Mc/sec.

The paper "Microwave Spectrum and Molecular Constants of Nitrosyl Bromide" mentioned in Status Report No. 8 has been accepted for publication by the Journal of Chemical Physics. The Stark effect for the rotational lines of this molecule is still being investigated. The Stark component frequencies of the $2_{0-3_{-1}}$ transition of NOBr^{79} have been measured and compared with calculated values using the theory of Mizushima (Theory of the Stark Effect of Asymmetric Rotator with Hyperfine Structure, J. Chem. Phys. 21, 539, 1953). Theoretically one should be able to calculate the components of dipole moment along all three principal axes. Since the molecule is planar one component is zero. Of the remaining two, the component along the axis of intermediate inertia has very little effect on the spectrum and cannot be determined. The component along the axis of least inertia has been calculated from the observed spectrum and found to be 1.76 Debye. Using this value all the measured line frequencies are in good agreement with the calculated frequencies.

More detailed results on both of these molecules will be reported later.

Table I

Rotational Absorption Lines of Nitryl Chloride

J	F	Frequency (Mc/sec)	
		$\text{NO}_2\text{Cl}^{35}$	$\text{NO}_2\text{Cl}^{37}$
$2_2 - 3_1$	$1/2 - 3/2$	$27,407.00 + .05$	$26,619.69 + .05$
	$7/2 - 9/2$	$27,389.88 - .05$	$26,606.22 - .05$
	$7/2 - 7/2$	$27,388.82$	
	$3/2 - 3/2$	$27,383.83$	$26,601.39$
	$3/2 - 5/2$	$27,382.73$	$26,600.60$
	$5/2 - 5/2$	$27,366.10$	$26,587.4$
	$5/2 - 7/2$	$27,365.61$	$26,587.14$
$2_1 - 3_0$	$1/2 - 3/2$	$26,708.33$	$25,996.61$
	$7/2 - 9/2, 7/2$	$26,691.44$	$25,983.23$
	$3/2 - 5/2, 3/2$	$26,684.68$	$25,977.92$
	$5/2 - 7/2, 5/2$	$26,667.77$	$25,964.60$
$2_{-2} - 3_{-3}$	$3/2 - 3/2$	$26,004.59$	$25,369.52$
	$5/2 - 5/2$	$25,998.57$	$25,364.68$
	$5/2 - 7/2$	$25,998.01$	$25,356.38$
	$7/2 - 9/2$	$25,987.43$	$25,355.97$
	$3/2 - 5/2$	$25,981.95$	$25,351.64$
	$1/2 - 3/2$	$25,981.33$	$25,351.20$
	$7/2 - 7/2$		$25,338.08$

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

SCHOOL OF PHYSICS



Status Report No. 2

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor:--

Georgia Tech Research Institute
Research Building
Georgia Institute of Technology
Atlanta, Georgia

Period:--

1 April 1956 to 30 June 1956

Project No. :--

OCR 1016

Contract No. :--

DA-01-009-ORD-465

Submitted by:--

T. L. Weatherly
Associate Professor

Joel Q. Williams
Associate Professor

Approved by :--

J. E. Boyd, Associate Director
Engineering Experiment Station

Status Report No. 2

Determination of Molecular Constants

by

Microwave and Radio Frequency Spectroscopy

Contract No. DA-01-009-ORD-465

Personnel: During the quarter ending 30 June 1956, the co-directors, Joel Q. Williams and T. L. Weatherly have devoted one-third time to research under this contract. Mr. Lorimer Clayton worked 30% of full time as a graduate assistant.

Mr. Donald F. Eagle worked one-third time as a graduate assistant for the quarter. Mr. Eagle received his Master's Degree in June using as a basis for his thesis the work on the Stark effect of nitrosyl bromide. Beginning 1 July 1956, Mr. Edward L. Beeson will be employed as a graduate assistant for one-fourth time replacing Mr. Eagle.

Fiscal: Expenditures during the quarter were as follows:

Personal Services-----	\$ 2,122.14
Overhead-----	1,114.12
Supplies-----	640.42
Freight and Express-----	5.84
Travel-----	171.25
Total-----	\$ 4,053.77

Research: Analysis of the quadrupole splitting of the $J = 2 \rightarrow 3$ transition of nitryl chloride (NO_2Cl) has been completed. The following coupling constants for the chlorine nucleus have been calculated from the spectrum.

	$\text{NO}_2\text{Cl}^{35}$	$\text{NO}_2\text{Cl}^{37}$
$eQ \frac{\partial^2 V}{\partial a^2}$	-94.7 mc	-74.6 mc
$eQ \frac{\partial^2 V}{\partial b^2}$	52.2 mc	41.1 mc
$eQ \frac{\partial^2 V}{\partial c^2}$	42.5 mc	33.5 mc

These calculations provide a positive identification of the spectral lines of the $J = 2 \rightarrow 3$ group. Application of the asymmetric rotator theory to the spectrum so far measured does not lead to a unique determination of the three rotational constants. It is hoped that additional lines can be found which will lead to at least one more relation between these constants. A number of lines of the $J = 3 \rightarrow 4$ transition have been measured in this attempt.

Analysis of the Stark effect for nitrosyl bromide (NOBr) has been carried as far as it seems profitable, and a technical report on this work will be written during the next quarter.

A search has been made for rotational spectral lines of iodine bromide (IBr) but none were found. This experiment will be repeated, perhaps during the next quarter.

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA

SCHOOL OF PHYSICS

Status Report No. 3

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor:--

Georgia Tech Research Institute
Research Building
Georgia Institute of Technology
Atlanta, Georgia

Period:--

1 July 1956 to 30 September 1956

Project No. :--

OOR 1016

Contract No. :--

DA-01-009-ORD-465



Submitted by:--

T. L. Weatherly
Associate Professor

Joel Q. Williams
Associate Professor

Approved by :--
J. E. Boyd

J. E. Boyd, Associate Director
Engineering Experiment Station

Status Report No. 3

Determination of Molecular Constants

by

Microwave and Radio Frequency Spectroscopy

Contract No. DA-01-009-ORD-465

Personnel: During the summer quarter ending 30 September 1956, the co-directors Joel Q. Williams and T. L. Weatherly have devoted one half time to research under this contract. Mr. Lorimer Clayton worked approximately 30% of full time as a graduate assistant and Mr. Edward L. Beeson worked 25% of full time as a graduate assistant.

Fiscal: Expenditures during the quarter were as follows:

Personal Services-----	\$ 2738.47
Overhead-----	1437.69
Supplies-----	62.23
Freight and Express-----	5.25

Total-----\$ 4243.64

Research: Investigation of the microwave spectrum of NO_2Cl has continued. Tentative rotational constants have been calculated from the lines already observed. These are listed below.

	$\text{NO}_2\text{Cl}^{35}$	$\text{NO}_2\text{Cl}^{37}$
A	13,250 Mc	13,250 Mc
B	5,173.8 Mc	5,019.0 Mc
C	3,721.1 Mc	3,640.3 Mc

The structure of NO_2Cl calculated from the above constants is

d (N-O) = 1.21 A

d (N-Cl) = 1.81 A

$\angle \text{O N O} = 129.5^\circ$

Some trouble has been encountered in preparing a sample of sufficient purity for observing the weak lines of the spectrum. Methods of preparing NO_2Cl have been reexamined and a new sample will be prepared during the next quarter. It is hoped that additional weak lines of the spectrum can then be measured. The Stark effect of NO_2Cl will be investigated in order to determine its dipole moment.

Measured Stark splittings for the $J = 2_0 \rightarrow 3_{-1}$ transition of NOBr have been compared with splittings calculated from the theory of Mizushima. The results were inconclusive. The Stark splittings were then remeasured at four different field intensities and the required calculations made. The results of this analysis are discussed in Technical Report Number 2.

GEORGIA INSTITUTE OF TECHNOLOGY

ATLANTA, GEORGIA

SCHOOL OF PHYSICS

Status Report No. 4

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor:--

Georgia Tech Research Institute
Research Building
Georgia Institute of Technology
Atlanta, Georgia

Period:--

1 October 1956 to 31 December 1956

Project No. :--


OOR 1016

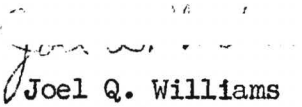
Contract No :--

DA-01-009-ORD-465

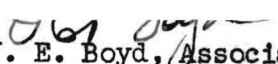


Submitted by:--


T. L. Weatherly
Associate Professor


Joel Q. Williams
Associate Professor

Approved by :--


J. E. Boyd, Associate Director
Engineering Experiment Station

Status Report No. 4

Determination of Molecular Constants

by

Microwave and Radio Frequency Spectroscopy

Contract No. DA-01-009-ORD-465

Personnel: During the quarter ending 31 December 1956 the co-directors, Joel Q. Williams and T. L. Weatherly have devoted one-third time to research under this contract. Mr. Lorimer Clayton worked approximately 30% of full time as a graduate assistant during the quarter. Mr. Edward L. Beeson, graduate assistant, worked 25% of full time for October and November only. He felt that he needed more time to devote to his graduate studies and other duties. However, it is anticipated that he will return to the project.

Fiscal: Expenditures during the quarter were as follows:

Personal Services-----	\$ 2,064.49
Overhead -----	1,083.86
Supplies -----	82.57
Travel -----	98.62
Total-----	<u>\$ 3,329.54</u>

Research: Investigation of the microwave spectrum and structure of nitryl chloride has continued during the last quarter. The structure of NO_2Cl reported in Status Report No. 3 contained one typographical error. The N-Cl distance is calculated to be 1.83 Å rather than 1.81 Å as reported. The complete structure is

$$\begin{aligned}d(\text{N} - \text{O}) &= 1.21 \text{ Å} \\d(\text{N}-\text{Cl}) &= 1.83 \text{ Å} \\\angle \text{ONO} &= 129.5^\circ\end{aligned}$$

The problem of getting a pure sample of NO_2Cl into the wave guide has been solved. This improvement of sample purity has made possible the observation of additional weak lines which are probably produced by rotational transitions for molecules in excited vibrational states.

The results for the quadrupole coupling constants, rotational constants and structure of NO_2Cl were reported at the Chicago meeting of the American Physical Society. During the five months period of extension for this research contract the above mentioned vibrational lines will be further investigated and an analysis of the Stark effect of NO_2Cl and CClF_3 will be attempted.

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GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA 13, GEORGIA

SCHOOL OF PHYSICS

Status Report No. 5

DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND RADIOFREQUENCY SPECTROSCOPY

Contractor :--

Georgia Tech Research Institute
Research Building
Georgia Institute of Technology
Atlanta, Georgia

Period :--

1 January 1957 to 31 ~~March~~ 1957

Project No. :--

OCR 1016

Contract No :--

DA-01-009-ORD-465



Submitted by :--

T. L. Weatherly
Associate Professor

Joel Q. Williams
Associate Professor

Approved by :--

J. E. Boyd, Associate Director
Engineering Experiment Station

Status Report No. 5

Determination of Molecular Constants

by

Microwave and Radio Frequency Spectroscopy

Contract No. DA-01-009-ORD-465

Personnel: During the quarter ending 31 March 1957 the co-directors, Joel Q. Williams and T. L. Weatherly, devoted approximately 24% time to research under this contract. Mr. Lorimer Clayton worked 23% of full time as a graduate assistant during the quarter. Mr. Edward Beeson, graduate student, devoted a very small amount of time to the study of the Stark effect of CClF_3 . It is anticipated that he will return to the project on 1 April at a 1/4 time rate.

Fiscal: Expenditures during the quarter were as follows:

Personal Services -----	1460.14
Overhead-----	766.58
Supplies-----	170.36
Travel-----	180.17
<hr/>	
Total-----	\$ 2577.25

Research: An investigation of the Stark effect of NO_2Cl is now in progress. Fifteen recordings of the $2_1 \rightarrow 3_0$ transition have been made at voltages between 90 and 500. The ten Stark components of this group of four lines have been clearly resolved and identified. Calculations based on the theory of Mizushima have been made with the aid of the IBM 650 computer for one Stark voltage. These calculations are in good qualitative agreement with the observed spectrum. Precise frequency measurements of the Stark components must be made before an accurate comparison with the theory can be made.

Work on the Stark effect of CClF_3 is also underway. Recordings have been made of the $J = 2 \rightarrow 3$ transition for several different Stark voltages. The theory of Low and Townes will be used to analyze the spectrum. The necessary matrix elements have been calculated for some of the observed Stark voltages in preparation to punching cards for the computer.

Technical Report No. 1



DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND
RADIO-FREQUENCY SPECTROSCOPY

Contractor: Georgia Tech Research Institute
Research Building
Georgia Institute of Technology

Department of Army Project No. 599-01-004

Ordnance Research and Development Project No. TB2-0001

OOR Project No. 1016

Contract No. DA-01-009-ORD-353

MICROWAVE SPECTRUM AND MOLECULAR CONSTANTS
OF NITROSYL BROMIDE

by

T. L. Weatherly and Quitman Williams

Submitted 19 September 1955

(ABSTRACT)

The microwave spectrum of NOBr has been studied in the region 20,000 to 40,000 Mc/sec and an analysis made of the $J = 2 \rightarrow 3$ transition. The following molecular constants were obtained.

	NOBr ⁷⁹	NOBr ⁸¹
Rotational Constants		
(Mc/sec)		
A	83,340	83,340
B	3,747.24	3,722.49
C	3,586.00	3,563.34
Asymmetry Parameter		
b	-.001012	-.000998
Quadrupole Coupling Components		
(Mc/sec)		
χ_{aa}	388.3	325.5
χ_{bb}	-239.5	-200.2
χ_{cc}	-148.8	-125.3

The structural parameters obtained from these are $d(\text{N-O}) = 1.15 \text{ \AA}$, $d(\text{N-Br}) = 2.14 \text{ \AA}$, $d(\text{O-Br}) = 2.81 \text{ \AA}$ and $\angle \text{Br-N-O} = 114^\circ$. The interatomic distances are compared with electron diffraction results and a brief interpretation of the quadrupole coupling in terms of chemical bonds is given.

Introduction

The internuclear distances and bond angle of nitrosyl bromide have been measured by electron diffraction. J. A. Ketelaar and K. J. Palmer¹ report the values $d(\text{N-Br}) = 2.14 \pm .02 \text{ \AA}$, $d(\text{N-O}) = 1.15 \pm .04 \text{ \AA}$, $d(\text{O-Br}) = 2.85 \pm .02 \text{ \AA}$, and $\angle \text{Br-N-O} = 117^\circ \pm 3^\circ$. The moments of inertia for NOBr^{81} calculated from this structure are $I_A = 9.39 \times 10^{-40} \text{ gm cm}^2$, $I_B = 230 \times 10^{-40} \text{ gm cm}^2$ and $I_C = 240 \times 10^{-40} \text{ gm cm}^2$ indicating that the molecule is an almost symmetric top. The rotational spectrum predicted on the basis of these moments consists of three groups of lines centered at approximately 21,400, 28,500, and 35,700 Mc/sec for the $J = 2 \rightarrow 3$, $3 \rightarrow 4$, and $4 \rightarrow 5$ transitions respectively. Similarly the predicted spectrum for NOBr^{79} in this region consists of three groups of lines which overlap the corresponding groups of NOBr^{81} . The observed lines fall into groups 400 to 700 Mc/sec higher in frequency than those predicted. This rough agreement between the observed and calculated spectra served as a preliminary identification of the J values involved in each transition. The observed spectrum is difficult to interpret due to the asymmetry of the molecule, the large quadrupole moments of the bromine nuclei, the presence of two isotopic species, and a complicated Stark effect. The present analysis is based primarily on the $J = 2 \rightarrow 3$ transition.

Experimental

The sample of NOBr was prepared by admitting gaseous NO and Br_2 in the ratio 2 to 1 to a 1000 cc flask until a final pressure of 1 atmosphere was obtained. The mixture was then frozen with liquid nitrogen and the excess NO was pumped off. The NOBr was given off the remaining solid as its temperature was increased. This sample was allowed to flow through an absorption cell cooled to dry ice temperature.

The absorption lines were observed on the oscilloscope of a Stark modulated microwave spectrograph. The absorption cell consisted of X-band waveguide 18 feet

long with a brass strip mounted in the center as first described by Hughes and Wilson². The Stark voltage was an 85 kc square wave of variable amplitude but zero-based so that one side of the square wave was held at ground potential. Frequencies were measured using a microwave frequency standard built by Scientific Associates of Atlanta, Georgia. It employs a 5 Mc/sec crystal controlled oscillator which may be zero-beat against the 5 or 10 Mc/sec signal from station WWV. The oscillator frequency is multiplied by vacuum tube circuits up to 2,160 Mc/sec and multiplied by a 1N26 silicon crystal to the microwave region. The frequency measurements were made in the manner described by Unterberger and Smith³ with the exception that they were made in pairs by first sweeping the klystron from low to high frequency and then reversing the sweep voltage. The average of the two measurements was taken as the line frequency.

Analysis of Data

The observed and computed line frequencies are listed in Table I. The value of F in this table is obtained by the addition of the rotational quantum number J and the spin $I = 3/2$ of the bromine nucleus. The small quadrupole interaction of the nitrogen nucleus was expected to produce splittings of less than 1 Mc/sec and has been neglected. The rotational spectrum of NOBr for the $J = 2 \rightarrow 3$ transition consists of five lines for each isotopic species as shown in Figure 1. Each of these lines is split into several components by the large bromine nuclear quadrupole interaction with the electric field gradient at the bromine nucleus giving the 28 lines of observable intensity listed in Table I.

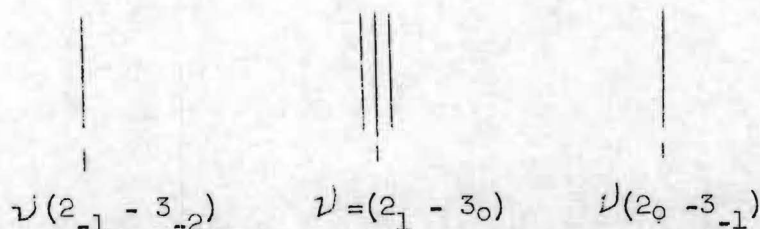


Figure 1. Pure rotational spectrum for the $J = 2 \rightarrow 3$ transition of NOBr⁷⁹.

Table I. Calculated and observed frequencies (Mc/sec) of the $J = 2 \rightarrow 3$ transition of NOBr. The estimated errors of the observed frequencies are 0.25 Mc/sec.

Transition J F		NOBr ⁷⁹			NOBr ⁸¹		
		Calculated freq.	Weighted average*	Observed freq.	Calculated freq.	Weighted average*	Observed freq.
$2_{-1}^{-3} - 2$	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		
$2_1^{-3} - 0$	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 intensities were used for the weighting factors.

The quadrupole splitting of the observed lines was calculated by the first-order theory of Bragg⁴. For the initial calculations the electron distribution near the bromine nucleus was assumed to be symmetric about the N-Br bond axis. This resulted in a predicted spectrum in fairly close agreement with that observed, and the coupling constants reported previously⁵. Later measurements revealed the splitting of the $2_{-1} \rightarrow 3_{-2}$ and $2_{\bar{0}} \rightarrow 3_{-1}$ lines shown in Table I and made possible a calculation of the diagonal components of the quadrupole coupling tensor with respect to the molecular principal axes. Bragg's theory was applied first by the use of his equation (8) and the tabulated line intensities of Cross, Hainer and King⁶ making a linear interpolation. Because of the coarseness of the table of line intensities a second calculation was made using Bragg's equation (10) and the expansion coefficients $S_{K\tau}$ computed for a rotator with asymmetry parameter $b = 10^{-3}$. The difference in the spectra calculated by the two methods was almost insignificant. The spectrum predicted by the latter method is recorded in Table I. The coupling constants computed from the observed spectrum are listed in Table II, where $\chi_{aa} = eQ (\partial^2 V / \partial a^2)$, $\chi_{bb} = eQ (\partial^2 V / \partial b^2)$, and $\chi_{cc} = eQ (\partial^2 V / \partial c^2)$.

Table II. Bromine Quadrupole Coupling Constant.

	Br ⁷⁹	Br ⁸¹
χ_{aa}	388.3 ± 2.9 Mc/sec	325.5 ± 2.9 Mc/sec
χ_{bb}	-239.5 ± 3.6	-200.2 ± 3.6
χ_{cc}	-148.8 ± 6.5	-125.3 ± 6.5

From the observed spectrum and the calculated quadrupole splittings the rotational spectrum without quadrupole splitting was determined. The rotational constants were then calculated by the theory of Wang⁷. According to this theory

the rotational energies of an asymmetric top molecule are given by

$$F(J_{\tau}) = (1/2) (B+C)J(J+1) + [A - 1/2 (B+C)] W_{\tau}, \quad (1)$$

where A, B, and C, are the rotational constants, and J is the rotational quantum number. The $2J + 1$ values of W_{τ} are obtained as solutions to algebraic equations in terms of the asymmetry parameter

$$b = - \frac{(B-C)}{2A-(B+C)}.$$

For NOBr b is approximately 10^{-3} and it is convenient to expand the values of W_{τ} in terms of b . The values of W_{τ} which are important to this analysis are:

for $J = 2$

$$W_{+1} = 4$$

$$W_0 = 1-3b$$

$$W_{-1} = 1 + 3b$$

for $J = 3$

$$W_0 = 4$$

$$W_{-1} = 1-6b - \frac{15}{8} b^2 + \frac{45}{32} b^3 + \dots$$

$$W_{-2} = 1+6b - \frac{15}{8} b^2 - \frac{45}{32} b^3 + \dots$$

These values of W_{τ} when substituted into equation (1) give for the frequency of the center line of Figure 1

$$\nu (2_{+1} - 3_0) = 3(B+C)$$

and for the frequency difference between the upper and lower lines

$$\nu (2_0 - 3_{-1}) - \nu (2_{-1} - 3_{-2}) = 3(B-C) \left[1 - \frac{15}{32} b^2 + \dots \right].$$

Since b^2 is approximately 10^{-6} this term and all higher order terms of the last equation may be neglected and approximate values of the rotational constants B and C may be determined from the three lines identified in Figure 1. The approximate values of B and C were then adjusted slightly to obtain the best fit of observed and calculated spectra. The resulting rotational constants are listed in Table III. The constant A in this table was determined from the relation $I_C = I_A + I_B$ for a planar molecule. Although this relationship is not entirely accurate for a vibrating molecule the error introduced should be small compared to the limits placed on this constant in Table III.

Table III. Rotational Constants for NOBr.

	NOBr ⁷⁹	NOBr ⁸¹
A	83,340 \pm 104 Mc/sec	83,340 \pm 117 Mc/sec
B	3,747.24 \pm .10	3,722.49 \pm .11
C	3,586.00 \pm .10	3,563.34 \pm .11
Asymmetry Parameter		
b	-.001012	-.000998

The rotational constants of two isotopic species of NOBr along with a knowledge of the general shape of the molecule provide more than enough data for computing the structure. In order to make use of all the data the structural parameters were calculated by two different methods which prove to be almost independent. The first has been described by J. Kraitchman⁸ and makes use of the moments of inertia I_A^{79} , I_B^{79} , I_A^{81} , and I_B^{81} , the factor of major importance being the difference $I_B^{81} - I_B^{79}$.

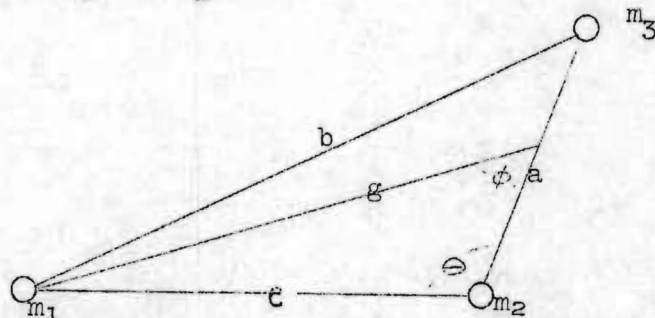


Figure 2. Parameters used in determining the molecular structure. The line g joins m_1 with the center of mass of m_2 and m_3 .

A second solution utilizing different data may be obtained by computing the momental dyadic in terms of a , b , c , and θ of Figure 2 and transforming to principal axes. From the secular determinant one obtains the equations

$$I_C = (m_2 m_3 a^2 + m_1 m_3 b^2 + m_1 m_2 c^2) / M$$

$$I_A I_B = m_1 m_2 m_3 a^2 c^2 \sin^2 \theta / M$$

where m_1 are the respective masses and M is the total mass. By applying the above equations to each isotopic species one gets for the structural constants of Figure 2

$$a^2 = \frac{m_1' MI_C - m_1 M' I_C'}{(m_1' - m_1)m_2 m_3}$$

$$g^2 = \frac{M'M(I_C' - I_C)}{(m_2 + m_3)^2 (m_1' - m_1)}$$

$$\sin^2 \phi = \frac{M I_A I_B}{m_1 m_2 m_3 a^2 g^2}$$

where a is the distance between atoms 2 and 3, g is the distance from 1 to the center of mass of 2 and 3, and ϕ is the angle between g and a . Isotopic substitution is made for atom 1 and the primed quantities refer to the molecule containing the heavier isotope. The bond distances and angle may be obtained from a , g , and ϕ by the laws of trigonometry. The values of a , b , c , and θ obtained by this method depend on I_A^{79} , I_B^{79} , I_C^{79} , and I_C^{81} with I_C^{79} and I_C^{81} having the greatest influence on the results.

Since the accuracy of the first method depends on a precise measurement of I_B^{79} and I_B^{81} and the accuracy of the second method depends on a precise measurement of I_C^{79} and I_C^{81} both methods were used for determining a , b , and c . The results of the two methods agreed to within .01 Å for all distances. The average values obtained by the two methods are recorded in Table IV.

Table IV. Structure of NOBr from microwave data.

$d(N-O) = 1.15 \pm .06$ Å
$d(N-Br) = 2.14 \pm .06$ Å
$d(Br-O) = 2.81 \pm .04$ Å
$\angle Br-N-O = 114^\circ$

Results

The observed lines in Table I varied in width from 1 to 3 Mc/sec. Calculated lines separated by less than 1 Mc/sec have been weighted according to their relative intensities and averaged. In most cases this weighted average agrees with the observed line to within less than .5 Mc/sec, the most notable exceptions being the $2_{-2} \rightarrow 3_{-3}$ transition in each molecule. These lines, unlike the others, require a very high Stark voltage for detection, and it seems likely that they were displaced to lower frequencies by incompletely separated Stark components.

The structural parameters listed in Table IV differ from the electron diffraction results only in the O-Br distance and the bond angle. Unfortunately the present analysis does not give structural constants as accurately as electron diffraction. The geometry of the molecule is such that a change in one distance can be compensated by proper adjustment of the two remaining distances with very little effect on the spectrum. However, if $d(\text{N-O}) = 1.15 \text{ \AA}$ and $d(\text{N-Br}) = 2.14 \text{ \AA}$ as measured by electron diffraction and calculated from the spectrum, then $d(\text{O-Br})$ must be less than 2.83 Å. Therefore it would seem that the electron diffraction measurement of this distance is a little large.

The ratio of the Br^{79} to Br^{81} quadrupole coupling components from Table II is $1.193 \pm .020$ for the components χ_{aa} and $1.196 \pm .040$ for the components χ_{bb} . These ratios are in good agreement with coupling constant ratios obtained from pure quadrupole resonance in solid bromine compounds.

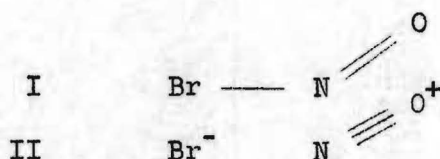
In order to increase the usefulness of the bromine quadrupole coupling tensor for analysis of the N-Br bond it has been transformed to a coordinate system with z axis oriented along the bond direction, x axis in the plane of the molecule and y axis perpendicular to this plane. Such a transformation requires the knowledge of the component χ_{ab} as well as the diagonal elements listed in Table II. Goldstein⁹ has pointed out that this off-diagonal element

may be computed if we assume that the xyz axes are principal axes of the quadrupole coupling tensor. Following this suggestion the value of χ_{xy} obtained from the tensor transformation was set equal to zero and the resulting equation solved for χ_{ab} . The transformation to xyz axes was then made in the usual way. The diagonal elements in Mc/sec with respect to this set of axes are

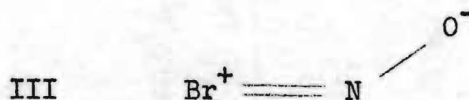
	NOBr ⁷⁹	NOBr ⁸¹
χ_{xx}	-290.2	-242.6
χ_{yy}	-148.8	-125.3
χ_{zz}	+439.0	+367.9

The asymmetry parameter $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$ is -0.322 for NOBr⁷⁹ and -0.319 for NOBr⁸¹.

Ketelaar and Palmer¹ have suggested for NOBr the two structures



each making a 50% contribution. The second of these was introduced to explain the large N-Br distance of 2.14 Å compared to a sum of covalent radii 1.84 Å. The large asymmetry parameter $\eta \approx -0.320$ suggests an appreciable contribution of a third structure,



The importance of this structure in bond formation is related to the quantity

$$\delta = \frac{\chi_{xx} - \chi_{yy}}{- (3/2) (\text{eqQ})_{\text{atomic}}}$$

defined by Goldstein⁹. This quantity is a measure of the number of electronic charges lost by the bromine in double bond formation. Assuming an $(\text{eqQ})_{\text{atomic}}$ for Br⁷⁹ of 769.6 Mc/sec¹⁰ the value of δ becomes 0.12 indicating roughly a

12% contribution of structure III. The individual contributions of structures I and II may be estimated from χ_{zz} by using the method of Townes and Dailey¹¹ assuming a pure p covalent bond in structure I. The resulting contributions are 49% for structure I and 39% for structure II. It should be emphasized that the above estimates of the percent contribution of each structure are very crude, and will undoubtedly require revision as more is learned concerning the relation of quadrupole coupling to chemical bonds.

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Technical Report No. 2



DETERMINATION OF MOLECULAR CONSTANTS BY MICROWAVE AND
RADIO-FREQUENCY SPECTROSCOPY

Contractor: Georgia Tech Research Institute
Research Building
Georgia Institute of Technology

Department of Army Project No. 5B99-01-004

Ordnance Research and Development Project No. TB2-0001

QOR Project No. 1016

Contract No. DA-01-009-ORD-465

THE STARK EFFECT IN THE ROTATIONAL SPECTRUM
OF NITROSYL BROMIDE

by

D. F. Eagle, T. L. Weatherly, and Quitman Williams

Submitted 2 October 1956

Abstract

The Stark effect of the $J_r = 2_0 \rightarrow 3_{-1}$, $F = 7/2 \rightarrow 9/2$ and $1/2 \rightarrow 3/2$ transitions of nitrosyl bromide has been analysed using the theory of Mizushima. The results of "weak field" and "stronger field" calculations are compared with the observed Stark splittings. The component of dipole moment along the principal axis of least inertia is found to be 1.76 Debye units. The component at right angles to the plane of the molecule is of course zero, and the third component is found to contribute so little to the Stark splitting of these transitions that it cannot be measured.

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Technical Report Number 2

The Stark Effect in the Rotational Spectrum of Nitrosyl Bromide

The geometric structure of nitrosyl bromide (NOBr) and its principal axes are illustrated in Figure 1.

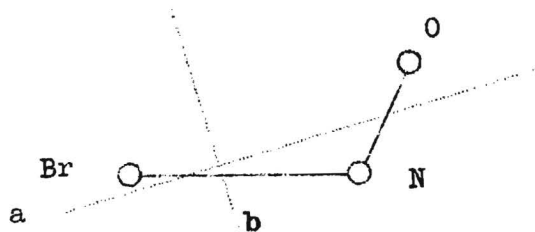


Figure 1

The distances are those determined from the analysis of the $J = 2 \rightarrow 3$ transition for NOBr⁷⁹ and NOBr⁸¹ discussed in Technical Report Number 1. The components of electric dipole moment will be designated μ_a , μ_b and μ_c , where μ_c is of course equal to zero.

The $J = 2 \rightarrow 3$ transition for NOBr⁷⁹ consists of five lines which overlap the corresponding five for NOBr⁸¹. Each of these is split into a number of components by the interaction of the bromide nuclear quadrupole moment with the electric field gradient resulting from the electrons and other nuclei.¹ As a result the $J = 2 \rightarrow 3$ transition consists of approximately thirty clearly observable lines making the resolution of Stark components very difficult.

All the observed lines of the $J = 2 \rightarrow 3$ transition were examined in order to find lines whose Stark components could be clearly resolved. The $J = 2_0 \rightarrow 3_{-1}$, $F = 7/2 \rightarrow 9/2$ and $F = 1/2 \rightarrow 3/2$ lines were finally chosen. These lines are separated by approximately three megacycles and split into a total of five Stark components in an electric field. Recordings were made of the lines at several different electric field intensities, and the Stark components were identified by noting their displacement with increasing field. Due to the presence of other lines the five Stark components of interest were seldom all visible on the same recording. However at field

¹The splitting produced by the quadrupole moment of the nitrogen nucleus is too small to be detected.

intensities between 370.1 volts/cm and 429.0 volts/cm all five could be clearly seen. A recording of the observed lines at 370.1 volts/cm is reproduced in Figure 2 and the observed splittings are given in Table I.

The theory for the Stark effect of an asymmetric top molecule with hyperfine structure due to nuclear quadrupole interaction has been worked out by Mizushima.² In the case of a weak electric field the Stark effect may be treated as a small perturbation on the system characterized by the indices $J \tau IFM$. The Stark energy is then calculated by second order perturbation theory and added to the rotational plus quadrupole energy. As the electric field increases and the Stark splitting approaches the quadrupole splitting in magnitude, the Stark effect ceases to be a small perturbation. In that case the Stark plus quadrupole energy may be computed from secular equations given by Mizushima for what he calls the "stronger field case."

In zero electric field the $F = 7/2 \rightarrow 9/2$ and $F = 1/2 \rightarrow 3/2$ hyperfine lines are separated from the theoretical position of the $J = 2_0 \rightarrow 3_{-1}$ pure rotational line by 10.9 Mc and 7.4 Mc respectively. The Stark splittings listed in Table I are of this same order of magnitude. Therefore at this field intensity Mizushima's stronger field theory should apply. In spite of this the first calculation was made according to the weak field theory in order to obtain an approximate value for the dipole moment before attempting to solve the secular equations required in the stronger field case. The results of both the weak field and stronger field calculations are given in Table I along with the observed splittings.

In both the weak and stronger field cases the contribution of μ_b to the Stark splitting was found to be negligible. In order to illustrate this the results of stronger field calculations assuming $\mu_b = 0$ and $\mu_b = .65$ are given in Table I. The best fit of calculated splittings to observed splittings for the weak field case was obtained with $\mu_a = 1.70$ Debye units. The stronger field case gives the best fit for $\mu_a = 1.76$ Debye units. As one would expect the results of the stronger field theory are in closer agreement with the observed Stark splittings than are the predictions of the weak field theory. However it is interesting to note that, if one adjusts the dipole moment for a best fit in each case separately, the results of the weak and stronger field theories do not differ a great deal.

In order to obtain a more complete check between calculated and observed line splittings, measurements were made at several dif-

²Theory of the Stark Effect of Asymmetric Rotator with Hyperfine Structure, Masataka Mizushima; J. Chem. Phys. 21, 539 (1953)

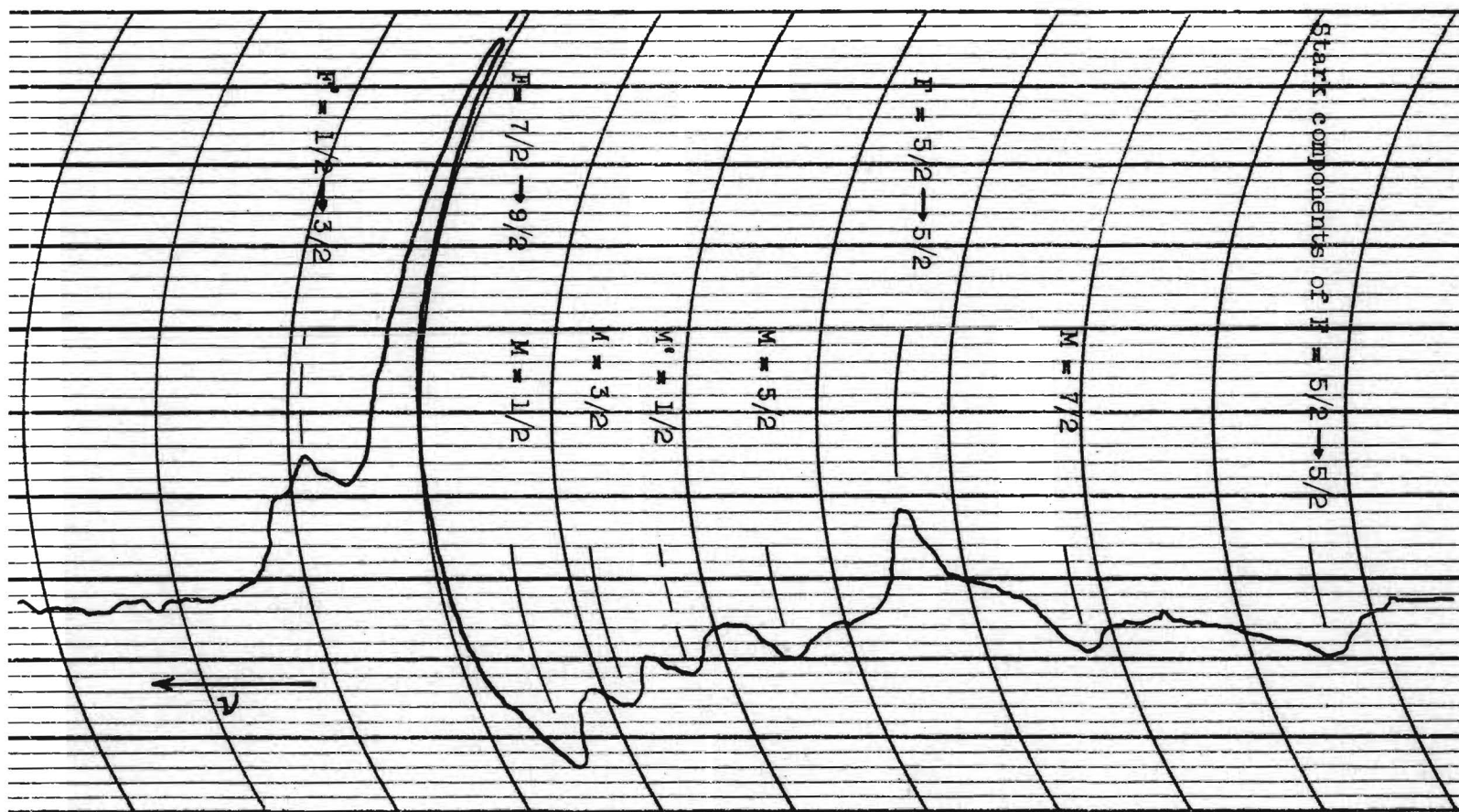


Figure 2. A recording of the observed lines and Stark components.

Table I. Calculated and observed values of the Stark splitting of the $J_{\pi} = 2_0 \rightarrow 3_{-1}$ transition of NOBr^{79} for an electric field of 370.1 volts/cm.

F	M	Calculated values (Mc)			Observed (Mc)
		Weak field $\mu_a = 1.70, \mu_b = 0$	Stronger field $\mu_a = 1.76, \mu_b = .65$	Stronger field $\mu_a = 1.76, \mu_b = 0$	
$7/2 \rightarrow 9/2$	$7/2$	18.53	19.90	19.88	19.3
	$5/2$	10.81	10.25	10.25	10.0
	$3/2$	5.80	4.98	4.97	5.0
	$1/2$	3.09	2.47	2.47	3.1
$1/2 \rightarrow 3/2$	$1/2$	10.81	9.48	9.48	9.7

Table II. Comparison of the observed and calculated Stark splitting using Mizushima's "Stronger field" approximation with $\mu_a = 1.76$ Debye and $\mu_b = 0$. The estimated error of the observed frequencies is 0.2 Mc. The quadrupole coupling constants used in all calculations are those reported in Technical Report No. 1: $\chi_{aa} = 388.3$ Mc, $\chi_{bb} = -239.5$ Mc, and $\chi_{cc} = -148.8$ Mc.

Field Intensity	F	M	Calc. (Mc)	Obs. (Mc)	Diff. (Mc)
370.1 v/cm	$7/2 \rightarrow 9/2$	$7/2$	19.88	19.3	-0.6
		$5/2$	10.25	10.0	-0.3
		$3/2$	4.97	5.0	0.
		$1/2$	2.47	3.1*	0.6*
	$1/2 \rightarrow 3/2$	$1/2$	9.48	9.7	0.2
380.6 v/cm	$7/2 \rightarrow 9/2$	$7/2$	21.03	20.7	-0.4
		$5/2$	10.77	10.8	0.
		$3/2$	5.22	5.3	+0.1
		$1/2$	2.60	3.0 *	+0.4 *
	$1/2 \rightarrow 3/2$	$1/2$	9.94	10.2	+0.3
407.6 v/cm	$7/2 \rightarrow 9/2$	$7/2$	24.13	23.4	-0.7
		$5/2$	12.16	12.3	+0.1
		$3/2$	5.88	5.8	-0.1
		$1/2$	2.94	3.3 *	+0.4 *
	$1/2 \rightarrow 3/2$	$1/2$	11.17	11.3	+0.1
429.0 v/cm	$7/2 \rightarrow 9/2$	$7/2$	26.74	25.8	-0.9
		$5/2$	13.29	13.2	-0.1
		$3/2$	6.43	6.5	+0.1
		$1/2$	3.23	3.6 *	+0.4 *
	$1/2 \rightarrow 3/2$	$1/2$	12.16	12.5	+0.3

*The $7/2 \rightarrow 9/2$ main line overlaps this Stark component.

ferent field intensities. The observed Stark splittings for each field intensity along with those calculated by Mizushima's stronger field theory using $\mu_a = 1.76$ Debye units are recorded in Table II. The tabulated differences in Table II deserve some comment. The absorption lines were observed by the use of a phase sensitive detector which produces a positive signal for the main absorption lines and a negative signal for Stark components. As a result a weak Stark component overlapping a strong main line will be displaced away from the main line. This effect has undoubtedly introduced some error into the observed splittings indicated with a star. The $F = 7/2 \rightarrow 9/2$, $M = 1/2$ Stark component overlaps the $F = 7/2 \rightarrow 9/2$ main line and the observed splitting is increased.

Discounting the starred measurements the most noticeable discrepancy between observed and calculated splittings occurs for the $F = 7/2 \rightarrow 9/2$, $M = 7/2$ Stark component. The difference in this case is consistently negative and apparently increases with field intensity. Although this difference is small it appears to be significant. The derivation of Mizushima's secular equations for the stronger field case involves some approximations³ which might account for the observed differences.

Both the weak and stronger field calculations involve a computation of Stark splitting by non-degenerate perturbation theory. Although this appears to be permissible for the $2_0 \rightarrow 3_{-1}$ transition one would be forced to take account of the near degeneracy of energy levels in order to compute the splitting of the $2_1 \rightarrow 3_0$ and $2_2 \rightarrow 3_1$ lines since the 2_1 and 2_2 levels almost coincide as do the 3_0 and 3_1 levels.

Unfortunately this analysis does not completely determine the dipole moment of NOBr since the component μ_b could not be measured. The calculated Stark splittings of all the lines of the $J = 2 \rightarrow 3$ group were examined in the hope of finding one sensitive to μ_b , but none were found. The value 1.76 Debye units for the component μ_a for the NOBr gas compares favorably with the reported value 1.87 Debye units for the total dipole moment of NOBr in a solution of carbon tetrachloride.⁴

³ Stark Effect and Nuclear Quadrupole Splitting in the Rotational Spectrum of Nitrosyl Bromide, Donald F. Eagle; Master's Thesis Georgia Institute of Technology 1956.

⁴ Tables of Electric Dipole Moments, compiled by L. G. Wesson (The Technology Press, Massachusetts Institute of Technology.)

ENGINEERING EXPERIMENT STATION
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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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DEPARTMENT OF THE ARMY NO. 5B99-01-004
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GEORGIA TECH RESEARCH INSTITUTE (CONTRACTOR)

OCTOBER 1, 1953 to MAY 31, 1957

ENGINEERING EXPERIMENT STATION
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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.,

$$\begin{bmatrix} \frac{\partial^2 V}{\partial X^2} & \frac{\partial^2 V}{\partial X \partial Y} & \frac{\partial^2 V}{\partial X \partial Z} \\ \frac{\partial^2 V}{\partial Y \partial X} & \frac{\partial^2 V}{\partial Y^2} & \frac{\partial^2 V}{\partial Y \partial Z} \\ \frac{\partial^2 V}{\partial Z \partial X} & \frac{\partial^2 V}{\partial Z \partial Y} & \frac{\partial^2 V}{\partial Z^2} \end{bmatrix} .$$

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

$$\begin{bmatrix} \frac{\partial^2 V}{\partial X^2} & 0 & 0 \\ 0 & \frac{\partial^2 V}{\partial Y^2} & 0 \\ 0 & 0 & \frac{\partial^2 V}{\partial Z^2} \end{bmatrix} .$$

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

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

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 χ_{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 Daily¹, Livingston², and Goldstein³ and in the recent book by Townes and Schawlow⁴.

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 oscilloscope 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 nitrogen temperature.

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

Compound	Frequency (Mc)
1. 1,4-Dichloro-2-nitrobenzene $\text{Cl}_2\text{C}_6\text{H}_3\text{NO}_2$	35.921 37.874
2. 1,2-Dichloro-4-nitrobenzene $\text{Cl}_2\text{C}_6\text{H}_3\text{NO}_2$	36.488 37.055
3. 1-Chloro-2,4-dinitrobenzene $\text{ClC}_6\text{H}_3(\text{NO}_2)_2$	37.796
4. 4-Chloro-3,5-xyleneol $\text{ClC}_6\text{H}_2(\text{CH}_3)_2\text{OH}$	34.348 34.415
5. Ethyl Trichlorosilane $\text{C}_2\text{H}_5\text{SiCl}_3$	18.756 18.842 18.865
6. Ethyl Chloroformate $\text{ClCOOC}_2\text{H}_5$	33.858
7. Ethyl Trichloroacetate $\text{CCl}_3\text{COOC}_2\text{H}_5$	40.200 40.339

(continued)

TABLE I (Concluded)

Compound	Frequency (Mc)
8. 1-Chloro-2-fluorobenzene	36.294
9. p-Chloroaniline $\text{ClC}_6\text{H}_4\text{NH}_2$	34.151
10. 1,2,3-Trichloropropane $\text{CH}_2\text{ClCHClCH}_2\text{Cl}$	34.581 34.776
11. m-Dichlorobenzene $\text{C}_6\text{H}_4\text{Cl}_2$	34.80 34.871 35.027
12. 1-Chloro-3-nitrobenzene $\text{ClC}_6\text{H}_4\text{NO}_2$	35.457
13. 2,5-Dimethylbenzenesulfonyl Chloride $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{SO}_2\text{Cl}$	32.265
14. p-Toluenesulfonyl Chloride $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	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 Pound⁵ 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 Pauling⁶. 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 Livingston⁷ for monochlorobenzene. This increase in the Cl³⁵ 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-xyleneol at frequencies slightly lower than those for parachlorophenol⁸ 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-xyleneol 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 Livingston⁹ 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 chloride¹⁰ 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 trichloroacetate 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	$\begin{array}{c} \text{Cl}-\text{C}-\text{O}-\text{C}_2\text{H}_5 \\ \\ \text{O} \end{array}$	33.858
2. Trichloroacetyl Chloride [†]	$\begin{array}{c} \text{Cl}-\text{C}-\text{CCl}_3 \\ \\ \text{O} \end{array}$	33.721 40.132 40.473 40.613
3. Ethyl Trichloroacetate	$\begin{array}{c} \text{C}_2\text{H}_5-\text{O}-\text{C}-\text{CCl}_3 \\ \\ \text{O} \end{array}$	40.200 40.339

[†]Data from Livingston⁹

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 unambiguous 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 $eQ\partial^2 V/\partial a^2$, $eQ\partial^2 V/\partial b^2$, and $eQ\partial^2 V/\partial c^2$, 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 $\text{NO}_2\text{Cl}^{35}$ 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.

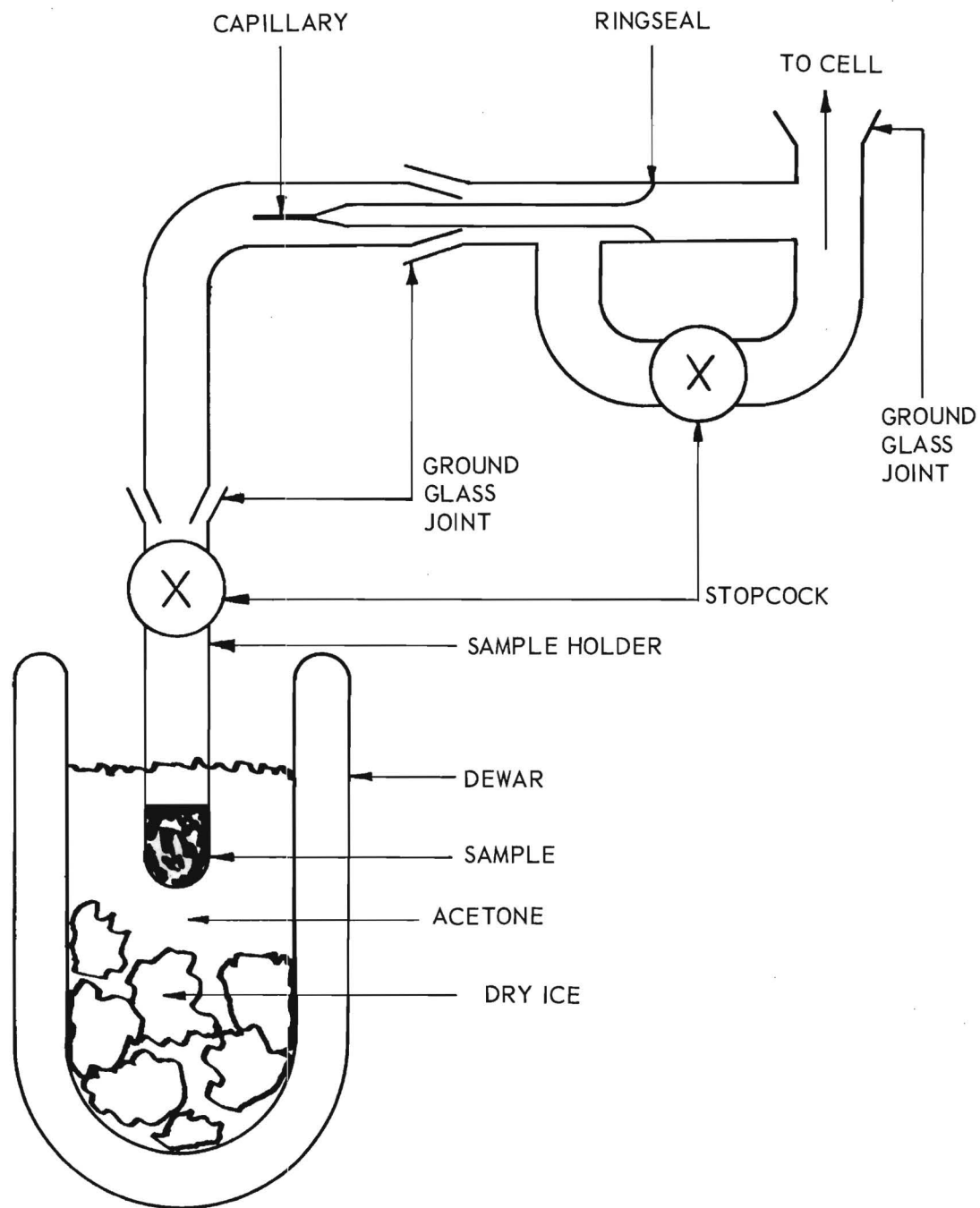


Figure 1. Apparatus for Admitting Gas into the Cell at a Controlled Pressure.

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
χ_{aa}	388	326
χ_{bb}	-240	-200
χ_{cc}	-149	-125

The structural parameters obtained from the above rotational constants are $d(\text{N} - \text{O}) = 1.15\text{\AA}$, $d(\text{N} - \text{Br}) = 2.14\text{\AA}$, $d(\text{O} - \text{Br}) = 2.81\text{\AA}$, and $\angle \text{Br-N-O} = 114^\circ$. The N - O and N - Br distances are exactly the same as the electron diffraction results of Ketelaar and Palmer¹⁶; however, the O - Br distance is .04\AA 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 Hughes¹⁷; 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 Townes¹⁸ 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 Sinnott²⁰ 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 anti-symmetric in its identical oxygen nuclei.

Subsequent work here was directed toward accurate measurement of the frequencies of all observable lines in the spectra of $\text{NO}_2\text{Cl}^{35}$ and $\text{NO}_2\text{Cl}^{37}$ 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 $\text{NO}_2\text{Cl}^{35}$ 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.

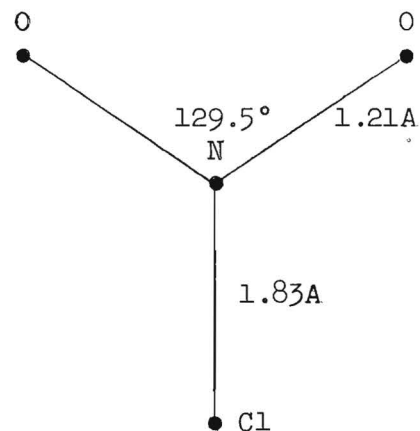
a. Summary of Results for Nitryl Chloride. The molecular information derived from the microwave spectrum is summarized in Table IV.

TABLE IV
NITRYL CHLORIDE MICROWAVE DATA

Transitions Observed:

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

	$\text{NO}_2\text{Cl}^{35}$	$\text{NO}_2\text{Cl}^{37}$
A	13250 Mc	13250 Mc
B	5173.8	5019.0
C	3721.1	3640.4
χ_{aa}	-94.7	-74.6
χ_{bb}	52.2	41.1
χ_{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 $\text{NO}_2\text{Cl}^{37}$ 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 $\text{NO}_2\text{Cl}^{35}$ 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 Wilson²² 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 $\text{NO}_2\text{Cl}^{35}$. 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 $\text{NO}_2\text{Cl}^{37}$ spectrum was also obtained by calculating molecular dimensions from the $\text{NO}_2\text{Cl}^{35}$ 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

TABLE V
TRANSITION FREQUENCY RELATIONS

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

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

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

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

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

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

2, 6, and in the relation obtained by subtracting Relation 3 from 5. (Relation 2 was tabulated for $\text{NO}_2\text{Cl}^{35}$ only, using the frequencies published by Millen and Sinnott.) Some of the computer read-out sheets for $\text{NO}_2\text{Cl}^{35}$ 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 Cl^{35} ROTATIONAL CONSTANTS 1_{-1} to 2_{-2} TRANSITION

(Continued)

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

Figure 2. Two Computer Read-Out Sheets Tabulating the Restriction Upon the Rotational Constants of NO Cl^{35} Imposed by the $1_{-1} \rightarrow 2_{-2}$ Transition Frequency, using (B+C) from the $2_{-1} \rightarrow 3_0$ Transition.

NO ₂ CL ³⁵ ROTATIONAL CONSTANTS			(Continued)		
J 2 to 3 TRANSITIONS			A	B	C
			13260	5174.166	3720.734
			13270	5174.566	3720.334
			13280	5174.966	3719.934
			13290	5175.366	3719.534
			13300	5175.765	3719.135
			13310	5176.164	3718.736
			13320	5176.563	3718.337
			13330	5176.962	3717.938
			13340	5177.361	3717.539
			13350	5177.759	3717.141
			13360	5178.157	3716.743
			13370	5178.555	3716.345
			13380	5178.953	3715.947
			13390	5179.350	3715.550
			13400	5179.748	3715.152
			13410	5180.145	3714.755
			13420	5180.542	3714.358
			13430	5180.938	3713.962
			13440	5181.335	3713.565
			13450	5181.731	3713.169
			13460	5182.127	3712.773
			13470	5182.523	3712.377
			13480	5182.918	3711.982
			13490	5183.314	3711.586
			13500	5183.709	3711.191
			13510	5184.104	3710.796
			13520	5184.498	3710.402
			13530	5184.893	3710.007
			13540	5185.287	3709.613
			13550	5185.681	3709.219
			13560	5186.075	3708.825
			13570	5186.469	3708.431
			13580	5186.862	3708.038
			13590	5187.256	3707.644
			13600	5187.649	3707.251
			13610	5188.041	3706.859
			13620	5188.434	3706.466
			13630	5188.827	3706.073
			13640	5189.219	3705.681
			13650	5189.611	3705.289
			13660	5190.003	3704.897
			13670	5190.394	3704.506
			13680	5190.786	3704.114
			13690	5191.177	3703.723
			13700	5191.568	3703.332
			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 NO₂Cl³⁵ Imposed by the 2 → 3 Transition Frequencies.

NO ₂ Cl ³⁵ ROTATIONAL CONSTANTS			NO ₂ Cl ³⁵ ROTATIONAL CONSTANTS		
3 ₀ to 4 ₋₁ TRANSITION			3 ₀ to 4 ₋₁ 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 NO₂Cl³⁵ Imposed by the 3₀ → 4₋₁ Transition Frequency, using (B+C) from the 2₁ → 3₀ 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 $A \approx 13,250$ Mc. Rotational constants for the 2 - 3 intersection are listed in Table IV, along with those obtained in the same manner for $\text{NO}_2\text{Cl}^{37}$. The constants for $\text{NO}_2\text{Cl}^{35}$ 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 Cl^{35} ROTATIONAL CONSTANTS			(Continued)		
APPROXIMATE RELATION ASSUMING PLANAR MOLECULE WITH ZERO QUANTUM DEFECT			A	B	C
A	B	C			
12800	5198.085	3696.815	13250	5173.935	3720.965
12810	5197.530	3697.370	13260	5173.415	3721.485
12820	5196.980	3697.920	13270	5172.900	3722.000
12830	5196.425	3698.475	13280	5172.380	3722.520
12840	5195.875	3699.025	13290	5171.865	3723.035
12850	5195.325	3699.575	13300	5171.345	3723.555
12860	5194.775	3700.125	13310	5170.830	3724.070
12870	5194.225	3700.675	13320	5170.315	3724.585
12880	5193.680	3701.220	13330	5169.800	3725.100
12890	5193.130	3701.770	13340	5169.285	3725.615
12900	5192.585	3702.315	13350	5168.775	3726.125
12910	5192.035	3702.865	13360	5168.265	3726.635
12920	5191.495	3703.405	13370	5167.750	3727.150
12930	5190.950	3703.950	13380	5167.240	3727.660
12940	5190.405	3704.495	13390	5166.730	3728.170
12950	5189.865	3705.035	13400	5166.220	3728.680
12960	5189.320	3705.580	13410	5165.710	3729.190
12970	5188.780	3706.120	13420	5165.205	3729.695
12980	5188.240	3706.660	13430	5164.695	3730.205
12990	5187.700	3707.200	13440	5164.190	3730.710
13000	5187.160	3707.740	13450	5163.685	3731.215
13010	5186.625	3708.275	13460	5163.180	3731.720
13020	5186.085	3708.815	13470	5162.675	3732.225
13030	5185.550	3709.350	13480	5162.170	3732.730
13040	5185.015	3709.885	13490	5161.665	3733.235
13050	5184.480	3710.420	13500	5161.165	3733.735
13060	5183.945	3710.955	13510	5160.665	3734.235
13070	5183.415	3711.485	13520	5160.165	3734.735
13080	5182.880	3712.020	13530	5159.660	3735.240
13090	5182.345	3712.555	13540	5159.160	3735.740
13100	5181.815	3713.085	13550	5158.660	3736.240
13110	5181.285	3713.615	13560	5158.165	3736.735
13120	5180.755	3714.145	13570	5157.665	3737.235
13130	5180.225	3714.675	13580	5157.170	3737.730
13140	5179.700	3715.200	13590	5156.670	3738.230
13150	5179.170	3715.730	13600	5156.180	3738.720
13160	5178.645	3716.255	13610	5155.680	3739.220
13170	5178.120	3716.780	13620	5155.185	3739.715
13180	5177.595	3717.305	13630	5154.695	3740.205
13190	5177.070	3717.830	13640	5154.205	3740.695
13200	5176.545	3718.355	13650	5153.710	3741.190
13210	5176.020	3718.880	13660	5153.220	3741.680
13220	5175.500	3719.400	13670	5152.725	3742.175
13230	5174.975	3719.925	13680	5152.240	3742.660
13240	5174.460	3720.440	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 $\text{NO}_2\text{Cl}^{35}$ Imposed by the Relation $I_a + I_b - I_c = 0$, using $(B+C)$ from the $2_1 \rightarrow 3_0$ Transition.

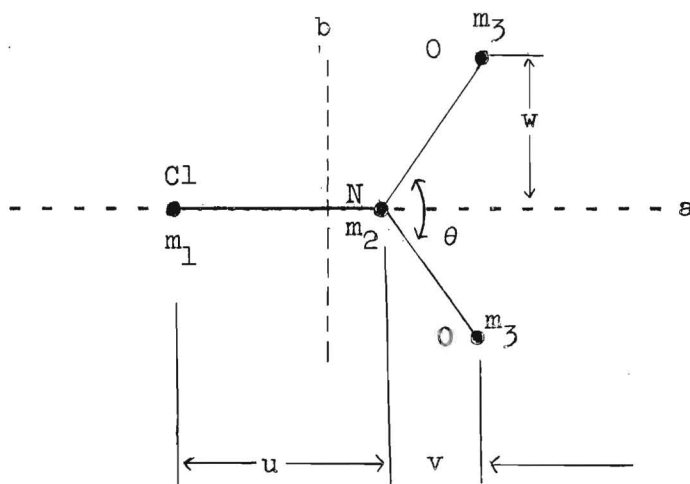
TABLE VI
DIFFERENCES BETWEEN OBSERVED AND
CALCULATED GROUP-CENTER FREQUENCIES

Transition	Group-Center Frequency Deviation (Measured Minus Calculated)	
	$\text{NO}_2\text{Cl}^{35}$ (Mc)	$\text{NO}_2\text{Cl}^{37}$ (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 $I_a = (1/A) 5.05531 \times 10^5 \text{ Mc/amu-A}^2$ and the similar expression for I_b . The dimension w is given immediately by I_a . To find u and v one can solve simultaneously the equations for MI_b for $\text{NO}_2\text{Cl}^{35}$ and $\text{NO}_2\text{Cl}^{37}$. 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:

$$d(N - O) = 1.207 \text{ A}$$

$$d(N - Cl) = 1.830 \text{ A}$$

$$\angle (ONO) = 129.50^\circ .$$

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.

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

The splitting of the $2_1 - 3_0$ transition is independent of χ_{bb} and χ_{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.

	$\text{NO}_2\text{Cl}^{35}$	$\text{NO}_2\text{Cl}^{37}$
	(Mc)	(Mc)
χ_{aa}	-94.70	-74.58
χ_{bb}	52.11	41.21
χ_{cc}	42.59	33.37

In an effort to refine the determination of χ_{bb} and χ_{cc} , which are not so strongly constrained as χ_{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.

	$\text{NO}_2\text{Cl}^{35}$	$\text{NO}_2\text{Cl}^{37}$
	(Mc)	(Mc)
χ_{aa}	-94.70	-74.58
χ_{bb}	52.21	41.12
χ_{cc}	42.49	33.46

These values of χ_{bb} and χ_{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 $\text{NO}_2\text{Cl}^{35}$ 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 μE (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

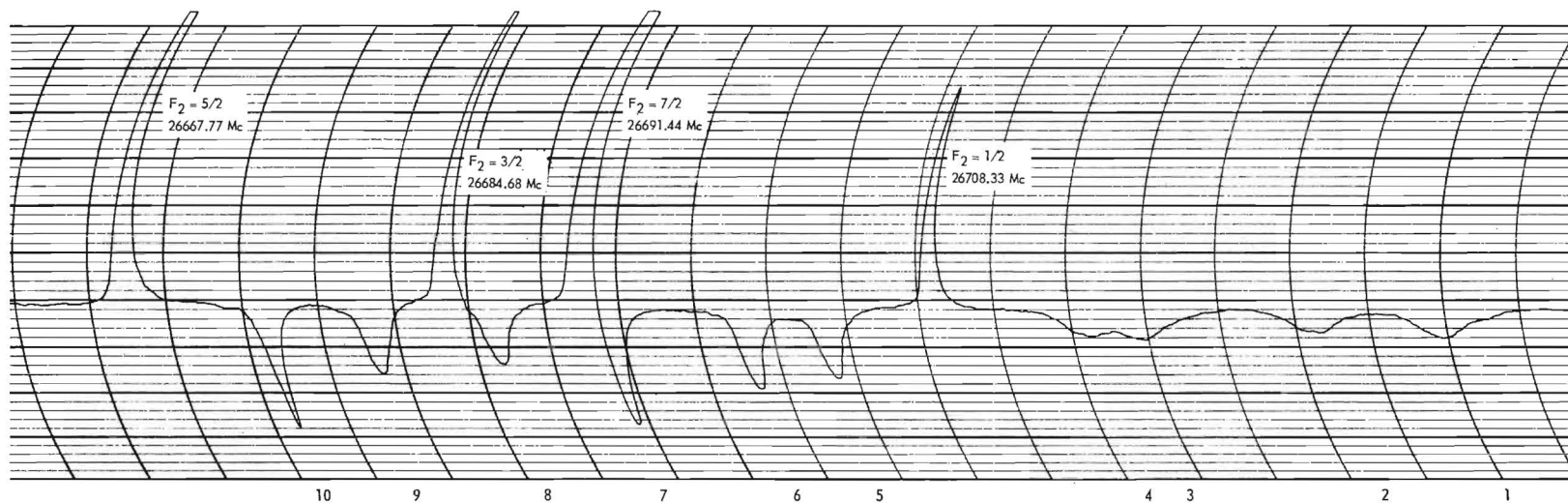


Figure 6. The $J = 2_1 \rightarrow 3_0$ Transition of $\text{NO}_2\text{Cl}^{35}$ Showing the Stark Components for an Electric Field of 515 Volts/cm. The F_2 Values are for the Lower State. The Values of F in the Upper State are not Identified as the 3_0 Level is Degenerate in F .

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 Wilson²² 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

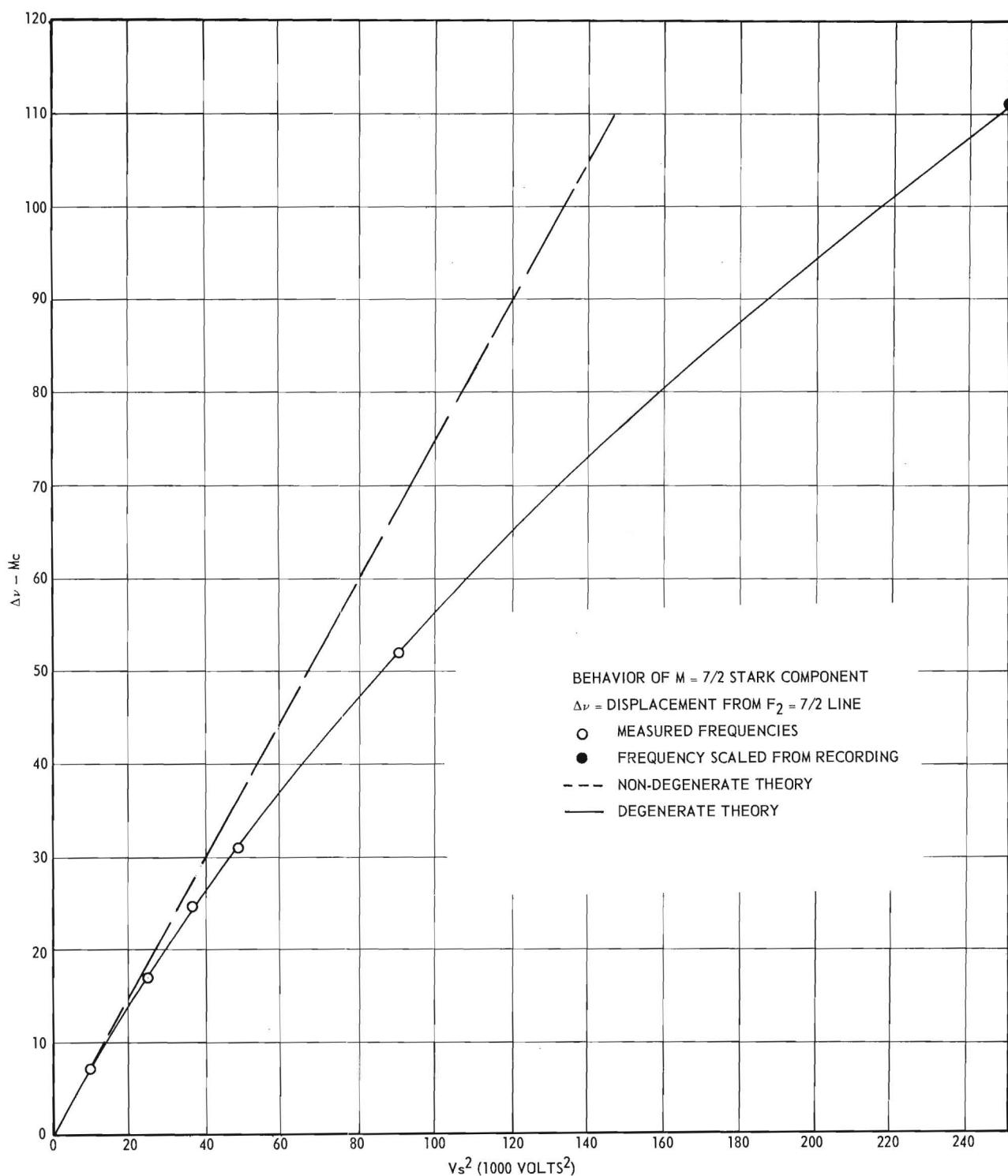


Figure 7. Behavior of $M=7/2$ Stark Component for $J=2_1 \rightarrow 3_0$ Transition of $\text{NO}_2\text{Cl}^{35}$.

TABLE VII
WEAK NITRYL CHLORIDE ABSORPTION LINE[†] FREQUENCIES

J_r	$\text{NO}_2\text{Cl}^{35}$ (Mc)	$\text{NO}_2\text{Cl}^{37}$ (Mc)
$3_1 \rightarrow 4_0$	36,740 ^{††} (4 lines)	35,689.5 35,686.9 35,681.7 35,679.0
$3_0 \rightarrow 4_{-1}$	35,129.4 35,126.2 35,120.0 35,116.8	34,210 ^{††} (4 lines)
$2_2 \rightarrow 3_1$ ^{†††}	27,145 ^{††} 27,110 ^{††}	26,375 ^{††} 26,350 ^{††}
$2_1 \rightarrow 3_0$ ^{†††}	26,450 ^{††} 26,425 ^{††}	25,750 ^{††} 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 $2_{-2} \rightarrow 3_{-3}$ and the $3_{-3} \rightarrow 4_{-4}$ 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 Wilson¹⁹ 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:

$\nu_1(A_1) = 1293 \text{ cm}^{-1}$	$\nu_4(B_1) = 1685 \text{ cm}^{-1}$
$\nu_2(A_1) = 794 \text{ cm}^{-1}$	$\nu_5(B_1) = 367 \text{ cm}^{-1}$
$\nu_3(A_1) = 651 \text{ cm}^{-1}$	$\nu_6(B_2) = 411 \text{ cm}^{-1}$

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., ν_1 , ν_2 and ν_3 . If these lines result from an excited ν_3 , for instance, then lines resulting from an excited ν_5 vibration should be observable. A singly excited ν_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:

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~~Quitman Williams~~
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Lorimer Clayton, Jr.
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V. PUBLICATIONS

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

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

"Nuclear Quadrupole Resonance in Ethyl Chloroformate and Ethyl Trichloroacetate," T. L. Weatherly and Quitman Williams: J. Chem. Phys. 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. 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., 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

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

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

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

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 extra-nuclear 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 a, b, and c are the directions of the principal axes, and $E(\kappa)$ is the tabulated rigid-rotor reduced energy for the level in question, a function of the asymmetry parameter κ .

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:

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

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

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

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

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

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:

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

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

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

The coefficients $A(J, \tau)$ and $B(J, \tau)$ may be found in general by simple interpolations in tables[†] of $E(\kappa)$; however, for low- J energy levels they can be expressed as explicit functions of κ . 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

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

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

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

where ν_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 Schawlow.⁴

TABLE A-1
CONSTANTS FOR EVALUATION OF QUADRUPOLE INTERACTION ENERGIES IN ASYMMETRIC-TOP MOLECULES

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

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

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

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 τ 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 κ 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 κ 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 χ_{aa} and χ_{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 χ_{aa} and χ_{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

$$a_{i1}v_1 + a_{i2}v_2 + \dots + a_{in}v_n = c_i\chi_{aa} + d_i\chi_{cc} + v_0 \sum_{j=1}^n a_{ij}$$

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

$$\sum_{j=1}^n a_{ij} = 0 \quad (7)$$

only two unknowns, χ_{aa} and χ_{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.

$$\sum_i c_i (a_{i1}v_1 + a_{i2}v_2 + \dots + a_{in}v_n) = \sum_i (c_i^2\chi_{aa} + c_i d_i\chi_{cc}) \quad (8a)$$

$$\sum_i d_i (a_{i1}v_1 + a_{i2}v_2 + \dots + a_{in}v_n) = \sum_i (c_i d_i\chi_{aa} + d_i^2\chi_{cc}) \quad (8b)$$

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

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

(9b)

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 combinations 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 vectors, 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 ν_0 , which must be regarded as a third unknown since its determination is not independent of the quadrupole couplings. Consequently, the last row imposes no additional 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.

APPENDIX II. NITROSYL BROMIDE LINE FREQUENCIES

Table AII

CALCULATED AND OBSERVED FREQUENCIES OF THE
J = 2 → 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	21,973.03	21,972.29	21,834.22	21,834.70	21,835.19
	7/2-7/2	21,972.00			21,834.22		
	7/2-5/2	21,972.00			21,834.22		
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	22,000.21	22,001.07	21,857.47	21,857.95	21,858.69
	3/2-5/2	21,999.74			21,857.47		
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
 $J = 2 \rightarrow 3$ TRANSITION OF NITROSYL BROMIDE

J	Transition	F	NOBr ⁷⁹			NOBr ⁸¹		
			Calculated Frequency	Weighted Average [†]	Observed ^{††} Frequency	Calculated Frequency	Weighted Average [†]	Observed ^{††} Frequency
			(Mc)	(Mc)	(Mc)	(Mc)	(Mc)	(Mc)
2_1	-3_0	5/2-3/2	22,069.08	22,069.56	22,069.77	21,915.59	21,916.08	21,916.77
		5/2-5/2	22,069.08			21,915.59		
		5/2-7/2	22,069.08			21,915.59		
2_2	-3_1	5/2-3/2	22,069.97	22,069.56	22,069.77	21,916.50	21,916.08	21,916.77
		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	22,230.38	22,086.79	22,086.79	22,086.65
		1/2-3/2	22,233.93			22,089.69		22,089.42
		5/2-7/2	22,254.69			22,107.12		22,106.69
		3/2-5/2	22,258.20			22,110.03		22,110.25

[†]The calculated relative intensities 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[†]

<u>Transition</u>	<u>Frequency</u> (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
$J = 4 \rightarrow 5$	29 517.8
	29 618.2
	29 657.8
	29 664.0
	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

NO₂Cl MICROWAVE SPECTRUM

$3_1 - 4_0$ Transition Measured Group Center Frequency = 37085.46 Mc.
 NO₂Cl³⁵ Calculated Group Center Frequency = 37085.36 Mc.

F_3	F_4	Theoretical Relative Intensity	Measured Frequency (Mc)	Measured Group Center Frequency plus Cal- culated 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.
 NO₂Cl³⁵ Calculated Group Center Frequency = 35439.95 Mc.

F_3	F_4	Theoretical Relative Intensity	Measured Frequency (Mc)	Measured Group Center Frequency plus Cal- culated 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.

NO₂Cl MICROWAVE SPECTRUM

3 ₋₃ - 4 ₋₄ Transition	Measured Group Center Frequency	= 33932.71 Mc.*
NO ₂ Cl ³⁵	Calculated Group Center Frequency	= 33933.30 Mc.

F ₃	F ₄	Theoretical Relative Intensity	Measured Frequency (Mc)	Measured Group Center Frequency plus Cal- culated 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 ₂ Cl ³⁵	Calculated Group Center Frequency	= 27382.92 Mc.

F ₂	F ₃	Theoretical Relative Intensity	Measured Frequency (Mc)	Measured Group Center Frequency plus Cal- culated 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_2Cl MICROWAVE SPECTRUM

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

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

F_2	F_3	Theoretical Relative Intensity	Measured Frequency (Mc)	Measured Group Center Frequency plus Cal- culated 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.

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

F_2	F_3	Theoretical Relative Intensity	Measured Frequency (Mc)	Measured Group Center Frequency plus Cal- culated 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 $\text{NO}_2\text{Cl}^{37}$ line, $2_1 - 3_0$; $F_2 = 5/2$

NO₂Cl MICROWAVE SPECTRUM

4₋₄ - 5₋₅ Transition Measured Group Center Frequency = 40600.57 Mc.

NO₂Cl³⁷ Calculated Group Center Frequency = 40602.78 Mc.

F ₄	F ₅	Theoretical Relative Intensity	Measured Frequency (Mc)	Measured Group Center Frequency plus Cal- culated 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

3₁ - 4₀ Transition Measured Group Center Frequency = 35990.35 Mc.

NO₂Cl³⁷ Calculated Group Center Frequency = 35990.25 Mc.

F ₃	F ₄	Theoretical Relative Intensity	Measured Frequency (Mc)	Measured Group Center Frequency plus Cal- culated 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	35993.13
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

NO₂Cl MICROWAVE SPECTRUM

3₀ - 4₋₁ Transition Measured Group Center Frequency = 34512.83 Mc.

NO₂Cl³⁷ Calculated Group Center Frequency = 34513.14 Mc.

F ₃	F ₄	Theoretical Relative Intensity	Measured Frequency (Mc)	Measured Group Center Frequency plus Cal- culated 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.

NO₂Cl³⁷ Calculated Group Center Frequency = 33159.47 Mc.

F ₃	F ₄	Theoretical Relative Intensity	Measured Frequency (Mc)	Measured Group Center Frequency plus Cal- culated 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.*
 $\text{NO}_2\text{Cl}^{37}$ Calculated Group Center Frequency = 26600.73 Mc.

F_2	F_3	Theoretical Relative Intensity	Measured Frequency (Mc)	Measured Group Center Frequency plus Cal- culated 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.
 $\text{NO}_2\text{Cl}^{37}$ Calculated Group Center Frequency = 25977.96 Mc.

F_2	F_3	Theoretical Relative Intensity	Measured Frequency (Mc)	Measured Group Center Frequency plus Cal- culated 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.

$\text{NO}_2\text{Cl}^{37}$ Calculated Group Center Frequency = 25355.19 Mc.

F_2	F_3	Theoretical Relative Intensity	Measured Frequency (Mc)	Measured Group Center Frequency plus Cal- culated 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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