One therefore concludes that this primary radiation has an absorption mean free path of about 70 g/cm^2.

Types of secondary radiation which might exhibit this large absorption at these high energies are π-mesons, protons, and neutrons. Neutrons can be eliminated from consideration because of the evidence that nuclear interactions causing electron showers (observed in a cloud chamber) large enough to be bursts are largely (81 percent) caused by ionizing particles.[24] Thus, it seems that the burst-producing radiation (other than μ-mesons and air showers) must consist of very high energy protons (primary or secondary) and/or of π-mesons produced by them.

The probability that secondary radiation generated in the atmosphere produces a large portion of these bursts is small, since this would lead to an absorption mean free path longer than the collision mean free path. On the other hand, the probability that secondary radiation generated in the lead and iron absorber produces a large portion of the bursts is large, since the absorption mean free paths for lead and iron are about twice the collision mean free paths. This increased probability may be due to the possibility that several π-mesons can interact simultaneously in the burst-producing region of the absorber and produce a burst in the ionization chamber which is several times larger than a burst produced by one π-meson alone. This means that the average energy of the successive collisions may not be attenuated as fast in the absorber as it is in the atmosphere. The increased probability may also be due to the absence of the decay of π-mesons in lead and iron.

The author is much indebted to his sponsor Professor Marcel Schein who suggested this project and supported it with many valuable discussions and suggestions. The kindness of Dr. M. A. Tuve of the Carnegie Institution of Washington, D. C., for allowing the University of Chicago to continue to use the Carnegie Model "C" ionization chamber is deeply appreciated. Thanks are due the Climax Molybdenum Company for its hospitality and cooperation.

PHYSICAL REVIEW VOLUME 83, NUMBER 2 JULY 15, 1951

The Microwave Absorption Spectrum of Nitrosyl Chloride NOCl*

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(Received April 2, 1951)

The absorption spectrum of nitrosyl chloride has been studied in the region between 21,000 and 23,000 mc/sec. Eight groups of closely spaced absorption lines have been observed; thirty-one individual lines have been resolved. The main features of the observed spectrum can be satisfactorily explained in terms of the rotational transition $J=1\rightarrow2$ for molecules in the ground and lowest excited vibrational state; the observed hyperfine-structure is satisfactorily explained in terms of nuclear quadrupole interactions involving the chlorine nuclei. The rotational constants for molecules in the ground vibrational state are: for NOCl^{35}, $A=2.845$, $B=0.19141$, and $C=0.17934$ cm^{-1}; for NOCl^{37}, $A=2.854$, $B=0.18682$, and $C=0.17534$ cm^{-1}. Values for the quadrupole interaction terms are given. The ratio Q^{35}/Q^{37} obtained in this study was 1.34 ±0.08.

ELECTRON diffraction studies[1] of nitrosyl chloride have yielded the following values for interatomic distance and bond angle: $d(\mathrm{N-Cl})=1.95\pm0.01\times10^{-8}$ cm; $d(\mathrm{N-O})=1.14\pm0.02\times10^{-8}$ cm; $d(\mathrm{O-Cl})=2.65\pm0.01\times10^{-8}$ cm; angle $\mathrm{ONCl}=116°\pm2°$. From these values and from the known masses of the nitrogen, oxygen, and chlorine atoms, it is possible to calculate approximate values for the principal moments of inertia of the NOCl molecule. These calculated values are: $I_A=8.82\times10^{-40}$ g·cm^2, $I_B=149\times10^{-40}$ g·cm^2, $I_C=158\times10^{-40}$ g·cm^2; and the corresponding rotational constants are: $A=3.17$ cm^{-1}, $B=0.188$ cm^{-1}, $C=0.177$ cm^{-1}. These values indicate that NOCl is, to a close approximation, a *prolate symmetric molecule.*

Treating NOCl as a symmetric molecule for which the centrifugal stretching can be neglected and assuming the dipole moment to lie principally along the unique axis, one would expect the frequencies in the rotational spectrum to be given by the expression

$$\nu=(B+C)(J+1),$$

which predicts absorption lines in the vicinity of 0.366 cm^{-1}, 0.732 cm^{-1}, and 1.09 cm^{-1} for lower J values of 0, 1, and 2, respectively. The predicted 0.732-cm^{-1} line falls in a spectral region for which microwave oscillator tubes are readily available. Therefore, the microwave absorption spectrum of NOCl was studied in this region in the hope of observing absorption lines associated with the transition $J=1$ to $J=2$.

In the study of the absorption spectrum, the re-

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* This research has been made possible through support and sponsorship extended by the Geophysical Research Directorate of the Air Force Cambridge Research Laboratories under contract with the Ohio State University Research Foundation. It is published for technical information only and does not represent recommendation or conclusions of the sponsoring agency.

[1] J. A. A. Ketelaar and K. J. Palmer, J. Am. Chem. Soc. 59, 2629 (1939).

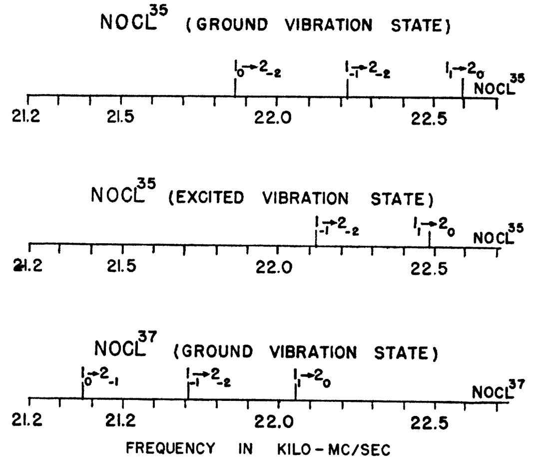

FIG. 1. Observed spectrum of nitrosyl chloride. $J=1\rightarrow 2$.

cording Stark-effect-modulation spectrograph developed in this laboratory[2] was used. The frequencies of absorption lines were measured by means of a frequency meter of the type described in an earlier report.[3]

The observed absorption spectrum in the region studied consists of 8 groups of closely spaced lines, 31 of which have been resolved. The large number of lines involved in the $J=1$ to $J=2$ transition may be attributed in part to the fact that NOCl is not an exactly symmetric molecule, in part to the fact that some of the molecules are in an excited vibrational state, and in part to a hyperfine structure produced by isotopic effects and by interactions between nuclear electric quadrupole moments and the electric field due to the other changes in the molecule.

The effects due to the slight asymmetry will be considered first. Wang[4] has obtained the following expression for the rotational energy levels of an asymmetric molecule:

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

where τ is an index assigned to run from $+J$ for the highest level to $-J$ for the lowest level and may therefore have $2J+1$ values. The values of the corresponding W_τ for various low J values can be determined from expressions obtained by Nielsen[5] and by Randall, Dennison, *et al.*,[6] which give W_τ in terms of an asymmetry parameter $b=\tfrac{1}{2}(C-B)/[A-\tfrac{1}{2}(B+C)]$. For $J=1$ and 2, the expressions for W_τ are

$$\begin{aligned} J=1 \quad & W_\tau=0, \quad W_\tau^2-2W_\tau+(1-b^2)=0. \\ J=2 \quad & W_\tau-1+3b=0, \quad W_\tau-1-3b=0, \qquad (2) \\ & W_\tau-4=0, \quad W_\tau^2-4W_\tau-12b^2=0. \end{aligned}$$

Use of electron diffraction data to obtain b and the application of certain selection rules indicate in order of increasing frequency the following possible transitions in the region studied: $1_0\rightarrow 2_{-1}$, $1_{-1}\rightarrow 2_{-2}$, and $1_{+1}\rightarrow 2_0$ These three spectral "lines" should have frequency separations of several hundred mc/sec and should actually consist of three groups of closely spaced hyperfine-structure components.

As there are two abundant isotopes of chlorine, three groups of lines are to be expected for $NOCl^{35}$ and three groups for $NOCl^{37}$. The absorption lines due to $NOCl^{37}$ should appear at lower frequencies and, in view of the smaller isotopic abundance of Cl^{37}, should be less intense than the corresponding lines due to $NOCl^{35}$. The groups of lines actually observed are shown schematically in Fig. 1.

In addition to the six groups of lines predicted, two other groups of weak lines were observed. It is believed that these additional lines are due to $NOCl^{35}$ molecules in an excited vibrational state. One bit of evidence for this tentative assignment is the observed variation in line intensity with temperature. Whereas the six groups of lines attributed to molecules in the ground vibrational state became more intense as the temperature was lowered from room temperature to dry ice temperature, the intensity of the remaining two sets of lines showed no increase as the temperature was lowered to this temperature range; this behavior is to be expected for transitions between low rotational levels in an excited vibrational energy state of low frequency since the relative populations of the lowest rotational levels are increasing and the total population of the vibrational state is decreasing.[7] If this interpretation is correct, a third group of weak lines due to $NOCl^{35}$ and three groups of even weaker lines due to $NOCl^{37}$ in excited vibrational states should exist in the region. These lines have not yet been observed.

Each of the rotational transitions mentioned thus far is further complicated by nuclear quadrupole effects. The observed hyperfine structures of several of the rotational lines are shown in the spectrograms reproduced in Fig. 2. The observed hyperfine structure patterns showed marked similarity to the patterns to be expected for the $J=1\rightarrow 2$ transition for a symmetric molecule containing a nucleus of spin $I=\tfrac{3}{2}$ on the axis of symmetry;[8] this similarity was found useful in making the initial identifications and tentative assignments under the assumption that the chlorine nuclei are responsible for the observed splitting.[9]

However, in making an analysis of the observed

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[2] W. J. Pietenpol and J. D. Rogers, "A recording Stark-effect-modulation spectrograph for the microwave region," Symposium on Molecular Structure (Ohio State University, June, 1949).

[3] Rogers, Cox, and Braunschweiger, Rev. Sci. Instr. **21**, 1014 (1950).

[4] C. S. Wang, Phys. Rev. **34**, 243 (1929).

[5] H. H. Nielsen, Phys. Rev. **38**, 1432 (1931).

[6] Randall, Dennison, Ginsburg, and Weber, Phys. Rev. **52**, 160 (1937).

[7] Assuming that the vibrational state involved is $\nu_2=290$ cm^{-1}, the low frequency state proposed by C. M. Beeson and D. M. Yost [J. Chem. Phys. **7**, 44 (1939)], one would expect a net decrease of approximately 25 percent in the population of the $J=1$ level as the temperature was decreased from room temperature to dry ice temperature. The population of the $J=1$ level in the ground level increases by approximately 60 percent for this same temperature change.

[8] D. K. Coles and W. E. Good, Phys. Rev. **74**, 533 (1948).

[9] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).

patterns, the theory of Knight and Feld[10] was employed. This theory was developed to account for nuclear quadrupole coupling effects in a slightly asymmetric molecule; the application of this theory to the spectrum of nitrosyl chloride is similar to its application to vinyl chloride, $C_2H_3Cl^{35}$, by Knight and Feld.[11]

A list of the observed absorption lines and their assignments is given in Table I. The validity of the assignments was tested by calculations of quadrupole coupling coefficients by applying the theory to various sets of lines. For example, three independently determined values for the coupling term $eQ\partial^2V/\partial Z'^2$ for $NOCl^{35}$ were -50.1 ± 0.7 mc/sec, -48.3 ± 1.0 mc/sec, and -50.0 ± 0.8 mc/sec; for $NOCl^{37}$ the corresponding terms were -36.1 ± 0.9 mc/sec, -37.9 ± 4.3 mc/sec, and -35.7 ± 1.5 mc/sec. It is believed that the consistency is sufficiently good to validate the assignments listed in Table I and to support the assumption that the chlorine nuclei are responsible for the observed hyperfine-structure.

TABLE I. Microwave absorption of $NOCl^{35}$.

Transitions		Observed frequency mc/sec
J	F	
$1_0\rightarrow2_{-1}$	$3/2\rightarrow5/2$	21857.42 ± 0.10
	$3/2\quad3/2$	21860.70 ± 0.10
	$5/2\quad5/2$	21864.59 ± 0.15
	$5/2\quad7/2$	21869.38 ± 0.08
	$1/2\quad3/2$	21873.93 ± 0.10
	$1/2\quad1/2$	21879.07 ± 0.10
$1_{-1}\rightarrow2_{-2}$	$5/2\rightarrow5/2$ $1/2\quad3/2$	22215.08 ± 0.10
	$3/2\quad5/2$ $5/2\quad7/2$	22227.37 ± 0.03
	$3/2\quad3/2$	22236.45 ± 0.08
$1_1\rightarrow2_0$	$3/2\rightarrow5/2$	22580.47 ± 0.03
	$3/2\quad3/2$ $5/2\quad5/2$	22585.47 ± 0.13
	$5/2\quad7/2$ $1/2\quad3/2$	22592.95 ± 0.07
	$1/2\quad1/2$	22601.72 ± 0.14
Excited vibrational state lines		
$1_{-1}\rightarrow2_{-2}$	$1/2\rightarrow3/2$ $5/2\quad5/2$	22106.31 ± 0.20
	$3/2\quad5/2$ $5/2\quad7/2$	22118.93 ± 0.07
	$3/2\quad3/2$	22126.81 ± 0.20
$1_1\rightarrow2_0$	$3/2\rightarrow5/2$	$22471.6\ \pm0.3$
	$3/2\quad3/2$ $5/2\quad5/2$	$22476.2\ \pm0.3$
	$5/2\quad7/2$ $1/2\quad3/2$	$22483.7\ \pm0.3$
Microwave absorption of $NOCl^{37}$		
$1_0\rightarrow2_{-1}$	$3/2\rightarrow5/2$	21362.64 ± 0.30
	$3/2\quad3/2$	$21364.7\ \pm0.6$
	$5/2\quad5/2$	21367.47 ± 0.20
	$5/2\quad7/2$	21371.53 ± 0.15
$1_{-1}\rightarrow2_{-2}$	$5/2\rightarrow5/2$ $1/2\quad3/2$	21703.77 ± 0.08
	$3/2\quad5/2$ $5/2\quad7/2$	21713.25 ± 0.11
	$3/2\quad3/2$	21719.68 ± 0.20
$1_1\rightarrow2_0$	$3/2\rightarrow5/2$	22052.07 ± 0.10
	$3/2\quad3/2$ $5/2\quad5/2$	22056.03 ± 0.10
	$5/2\quad7/2$	22062.26 ± 0.10
	$1/2\quad3/2$	22068.11 ± 0.18
	$1/2\quad1/2$	22071.33 ± 0.16

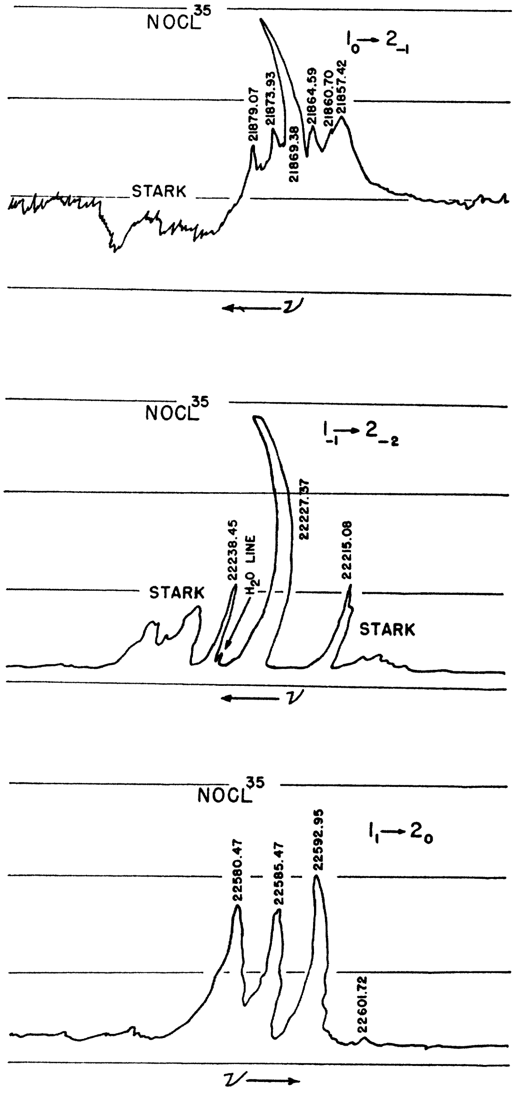

FIG. 2. Observed hyperfine structure patterns of nitrosyl chloride.

In Table II are given the average values obtained for the interaction terms $eQ\partial^2V/\partial x'^2$, $eQ\partial^2V/\partial y'^2$, and $eQ\partial^2V/\partial z'^2$, where the primes indicate a molecule-fixed coordinate system with x', y', and z' corresponding to the principal axes of inertia. Although there are some rather large uncertainties in the values of the quadrupole coupling terms for $NOCl^{37}$, it is interesting to note that the ratio of the interaction terms for $NOCl^{35}$ to those for $NOCl^{37}$ is close to 1.3, the ratio for Q^{35}/Q^{37} obtained

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[10] G. Knight and B. T. Feld, Phys. Rev. **74**, 354 (1948).

[11] G. Knight and B. T. Feld, M.I.T. Technical Report, No. 123, (1949) (unpublished).

TABLE II. Quadrupole interaction terms.

Molecule		Term	
	$eQ\partial^2V/\partial x'^2$ mc/sec	$eQ\partial^2V/\partial y'^2$ mc/sec	$eQ\partial V/\partial z'^2$ mc/sec
$NOCl^{35}$	29.9±1.0	19.6±2.0	−49.5±1.0
$NOCl^{37}$	23±5	14±9	−37±6

TABLE III. Rotational constants.

Molecule	A	B	C
$NOCl^{35}$	2.845 cm^{-1}	0.19141 ±0.00001 cm^{-1}	0.17934 ±0.00001 cm^{-1}
$NOCl^{37}$	2.854 cm^{-1}	0.18682 ±0.00001 cm^{-1}	0.17534 ±0.00001 cm^{-1}

in studies of symmetric and linear molecules.[12] The value of this ratio obtained from the "best" data on corresponding lines of NOCl is $Q^{35}/Q^{37}=1.34\pm0.08$; it should be noted that this value is based on the assumption that similar fields exist at the chlorine nuclei in the two isotopic molecules.

After the effects due to nuclear quadrupole interactions had been determined, it was possible to obtain values for the rotational constants A, B, and C by using the frequencies due to rotational energy changes in connection with Eqs. (1) and (2). From (1) and (2) it is possible to obtain simple expressions for some of the low term values in terms of the rotational constants; the term values of interest here are $F(1_1)$, $F(2_0)$, $F(1_0)$ and $F(2_{-1})$, where it may be shown that

$$F(1_1)=A+B,\quad F(2_0)=A+4B+C \tag{3}$$

and

$$F(1_0)=A+C,\quad F(2_{-1})=A+B+4C. \tag{4}$$

The values of B and C given in Table III are obtained from a series of careful measurements of the intense hyperfine-structure components $F=5/2\rightarrow7/2$ of the transitions $J_\tau=1_1\rightarrow2_0$ and $J_\tau=1_0\rightarrow2_{-1}$ used in connection with (3) and (4).

The value of the rotational constant A is not directly obtainable from these measurements. Darling and Dennison[13] have shown that a relation between the moments of inertia exists such that $\Delta=I_C-I_A-I_B$, where Δ is a quantity independent of the anharmonic portion of the potential energy which may be calculated if the normal frequencies are known. These are, however, known very incompletely, and it seems impracticable to estimate a value for Δ. It may quite safely be assumed, however, that in the normal state, Δ will be small compared with I_A, I_B, or I_C, and that no great error is introduced by assuming the molecule to be a rigid rotator, in which case $\Delta=0$.

The values of the rotational constant A given in Table III are obtained from the equation

$$C^{-1}=A^{-1}+B^{-1}, \tag{5}$$

which follows from the relation

$$I_C=I_A+I_B \tag{5'}$$

which exists between the moments of inertia of a planar rigid rotator. The value obtained for A is of the same order of magnitude as the value obtained from electron diffraction data but, since Δ is unknown, may be subject to significant uncertainties. For these reasons, no limits can be set on the uncertainty in the values for the rotational constant A.

The values obtained for the rotational constants B and C are considerably more precise than the values obtained from electron diffraction data. The values for the asymmetry parameters are $b=-0.002271$ for $NOCl^{35}$ and $b=-0.002147$ for $NOCl^{37}$. These values indicate that NOCl is slightly more asymmetric than would be estimated from electron diffraction results, which give a value $b=-0.0018$.

Well-resolved Stark patterns were obtained for several of the absorption lines. From these Stark patterns and from the theory of Golden and Wilson,[14] it was possible to obtain an estimate of the component μ_A of the molecular dipole moment parallel to the axis of least moment of inertia. This component $\mu_A=1.28$ ±0.04 Debye units.

The writers wish to express their appreciation to Professor H. H. Nielsen for his advice and encouragement and for his criticism of the manuscript.

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[12] For a list of these ratios, see Geschwind, Gunther-Mohr, and Townes, Phys. Rev. **81**, 288 (1951).

[13] B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940).

[14] S. Golden and E. B. Wilson, J. Chem. Phys. **16**, 669 (1948).