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STUDIES IN MICROWAVE SPECTROSCOPY:

$^{14}_N^{16}O^{17}$, METHYL VINYL KETONE, AND
A SPECTROMETER FOR UNSTABLE MOLECULES

by

Peter D. Foster

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ABSTRACT

Some 150 hyperfine transitions belonging to the 8_{08}^{17} and 9_{19}^{10,10} rotational transitions of ^14N^16O^17O have been observed in the microwave region. The new coupling constants which have been determined are the odd-electron expectation values on oxygen. They are

\[ |\gamma(0)|^2 = 0.71 \times 10^{24} \text{ cm}^{-3}, \]
\[ \langle \frac{3f^2_a - 1}{r^3} \rangle = -4.71 \times 10^{24} \text{ cm}^{-3}, \]

and
\[ \langle \frac{f_b - if_c}{r^3} \rangle = 5.04 \times 10^{24} \text{ cm}^{-3}. \]

The conformation and barrier to internal rotation in methyl vinyl ketone have been determined. The most stable configuration is with the double bonds trans to each other, and \( V_3 = 1250 \text{ cal/mole}. \)

A new fast-flow, high-frequency video microwave spectrometer has been constructed to search for new unstable molecules. As yet no new chemical species have been identified.
ACKNOWLEDGEMENT

My sincere thanks to Dr. R. F. Curl for his continuing guidance during the past three years.

The generous support of a National Defense Education Act Fellowship during my entire graduate career is gratefully acknowledged.

The last two sections of Chapter I have appeared, in essence, as a publication co-authored with Drs. V. M Rao and R. F. Curl, Jr.

To my wife Judy, I shall always be grateful.
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INTRODUCTION

Three rather different studies in microwave spectroscopy are presented in this thesis, all utilizing the excellent resolution obtainable from quantum measurements in the microwave region.

Chapter I presents a study of the microwave spectrum of methyl vinyl ketone (3-butene-2-one), a molecule with a conjugated bond system. The barrier to internal rotation of the methyl group and the steric configuration of the heavy atom skeleton of the molecule have been determined. The results of most previous work on C=C—C=C systems have indicated that the most stable configuration is with the double bonds trans to each other, and all atoms except for two methyl hydrogens in a plane. Because of the different nature of the conjugated system (C=C—C=O) in methyl vinyl ketone, it was hoped that some other steric isomer might be observed.

Chapter II presents a study of the very complex rotational hyperfine spectrum of the molecule $^{14}\text{N}^{16}\text{O}^{17}\text{O}$, a stable free radical with two nuclear spins. The purpose of the study is to determine the Fermi and dipole-dipole coupling constants of the $^{17}\text{O}$ nucleus with the odd electron. These constants are related to the character of the odd electron orbital in the vicinity of the oxygen nucleus. The combined results of this work and previous determinations of the dipole moment and spin-rotation
and $^{14}$N Fermi, dipole-dipole and quadrupole coupling constants may be used as a severe test of any proposed wave mechanical description of chemical bonding in nitrogen dioxide.

Chapter III presents the results, to date, of the use of a new microwave spectrometer for the study of simple unstable molecules. It is hoped to gain some information about the physical properties of the intermediates in chemical reactions. A fast-flow, high-frequency, video spectrometer with a free space absorption cell has been constructed, but as yet no new chemical species have been identified.
CHAPTER I
MICROWAVE SPECTRUM OF
METHYL VINYL KETONE

INTERNAL ROTATION

The presence in a non-rigid molecule of a functional group
with an axis of 3-fold or higher symmetry allows the possibility
of an internal torsional motion which may be treated as a special
case of rotation-vibration coupling. This type of motion is
generally referred to as internal rotation. If the barrier to
this motion is sufficiently low, the interaction of torsion
and overall rotation in a molecule is noticed in the rotational
spectrum of the molecule. In the case of a molecule with a
3-fold symmetric group the triple degeneracy of the rotational
energy levels associated with a particular vibrational state
is partially removed and rotational transitions appear as
doublets. One component of the doublet belongs to the non-
degenerate A representation and the other belongs to the
doubly-degenerate E representation of the C₃ symmetry group.
The spacing of these doublets is dependent on the magnitude of
rotation-vibration coupling, and hence on the barrier to
internal rotation.

The theoretical treatment of internal rotation has re-
ceived much attention¹ and is adequate for most molecules.
The model for the calculation is a rigid top rotating against
a rigid frame, with the symmetry axis of the top taken as the
axis of internal rotation. The origin of potential barriers is not clearly understood. The only requirement that can be placed on the potential function hindering internal rotation is that it be periodic in the relative angle $\alpha$ between the two parts of the molecule. In the case of a 3-fold barrier the hindering potential $V(\alpha)$ can be expressed as a cosine series expansion in $3\alpha$, such as

$$V(\alpha) = \frac{V_3}{2} (1 - \cos 3\alpha) + \frac{V_6}{2} (1 - \cos 6\alpha) + \ldots$$

(1)

It is customary to take the potential function simply as

$$V(\alpha) = \frac{V_3}{2} (1 - \cos 3\alpha).$$

The Hamiltonian for this system may be written as

$$H = \frac{\lambda^2}{2} \sum_{g} P_{g}^{2}/I_{g} + \frac{\lambda^2}{2} (P - P)^{2}/rI_{\alpha} + V(\alpha)$$

(2)

where

$$P = \sum_{g} \lambda_{g} I_{g} / I_{g},$$

$g = x, y, z$ refers to principal axes of inertia fixed in the framework part.

$P_{g}$ = components of the total angular momentum along the principal axis.

$P$ = angular momentum of the internal top along its symmetry axis.

$I_{g}$ = principal moments of inertia of the entire molecule.

$rI_{\alpha}$ = moment of inertia of the top about its symmetry axis.

$\lambda_{g}$ = direction cosines of the top axis.

$rI_{\alpha}$ = reduced moment of inertia of the top, where

$$r = 1 - \sum_{g} \lambda_{g}^{2} I_{g} / I_{g}$$
The terms
\[ p^2 \frac{\hbar^2}{2RI\alpha} + V_3/2(1-\cos 3\alpha) \]

lead to Mathieu's equation. The boundary conditions of invariance under \( \alpha \to \alpha + 2\pi \) is satisfied by solutions periodic in \( 2\pi/3 \) (A species) and those periodic in \( 2\pi \) (E species).

Herschbach's\(^3\) treatment of the high barrier case is applicable to methyl vinyl ketone. Briefly, the basis for a matrix representation is taken to be the Mathieu eigenfunction of (3) times the usual symmetric rotor eigenfunctions. A perturbation expansion in \( \tilde{P} \) is performed. Since \( \tilde{P}^2 \) is quadratic in the \( P_g \), the second order terms may be combined with the rigid rotor terms from the asymmetric rotor part of the Hamiltonian. In the case of methyl vinyl ketone both the A and E series lines fit rigid rotor spectra. Higher order terms in the expansion are negligible.

Barriers to internal rotation of methyl groups in numerous molecules have been determined\(^1\). Attempts to correlate and predict methyl barriers have generally failed\(^4\). However, methyl vinyl ketone belongs to a series of substituted acetone molecules in which the barrier to internal rotation is insensitive to the substituent group. The parent molecule, acetone itself, does not conform to the series.

**CONFORMATION**

It is not practical to undertake a complete structural determination of a molecule as complex as methyl vinyl ketone
by microwave methods. However, the steric configuration of the heavy atom skeleton of the molecule is readily determined by making reasonable estimates of the bond lengths and angles in the various possible isomers and calculating the moments of inertia of each isomer. The rotational constants determined from the spectrum of a particular rotamer will, in nearly every case, agree with only one of the possible steric configurations.

SPECTRUM AND INTERPRETATION

Methyl vinyl ketone was obtained from Matheson Coleman & Bell, and was used without further purification. The region 7-33 Gc/sec was observed with a conventional 100 Kc/sec Stark modulation spectrometer. Frequencies were measured to ± 0.3 Mc/sec. All lines were observed at dry-ice temperature.

The spectrum appeared as widely-spaced singlet and doublet lines. Assigned lines are listed in Table I. The lines at 7219.9 and 11886.9 Mc/sec have single Stark lobes to high and were assigned as the $0_{00} \rightarrow 1_{01}$ and $0_{00} \rightarrow 1_{11}$ transitions. The line at 15769.0 Mc/sec has a fast lobe to low and a slower one to high frequency and was assigned as the $1_{10} \rightarrow 2_{11}$ transition. These three lines were sufficient to determine the location of the entire spectrum. The $1 \rightarrow 2$, $2 \rightarrow 2$ and $2 \rightarrow 3$ assignments were confirmed by their Stark effects.
**TABLE I**

Rotational assignment of methyl vinyl ketone.

<table>
<thead>
<tr>
<th>Transition</th>
<th>( v_A^{(\text{obs})} ) (Mc/sec)</th>
<th>( v_A^{(\text{calc})} - v_A^{(\text{obs})} ) (Mc/sec)</th>
<th>( (v_A - v_E)^{\text{obs}} ) (Mc/sec)</th>
<th>( (v_A - v_E)^{\text{calc}} ) (Mc/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>00-101</td>
<td>7 219.9</td>
<td>-0.1</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>00-111</td>
<td>11 886.9</td>
<td>-0.1</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>11-212</td>
<td>13 110.4</td>
<td>0.0</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>10-202</td>
<td>14 194.1</td>
<td>-0.2</td>
<td>0.0</td>
<td>0.6</td>
</tr>
<tr>
<td>10-211</td>
<td>15 709.0</td>
<td>-0.2</td>
<td>0.9</td>
<td>1.0</td>
</tr>
<tr>
<td>10-212</td>
<td>17 777.5</td>
<td>-0.1</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>212-221</td>
<td>17 988.5</td>
<td>-0.1</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>212-303</td>
<td>17 144.4</td>
<td>-0.4</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>212-313</td>
<td>19 524.0</td>
<td>0.1</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>202-303</td>
<td>20 727.8</td>
<td>-0.2</td>
<td>0.0</td>
<td>0.6</td>
</tr>
<tr>
<td>303-312</td>
<td>10 326.6</td>
<td>-0.6</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>413-422</td>
<td>13 163.3</td>
<td>-0.2</td>
<td>0.0</td>
<td>-0.1</td>
</tr>
<tr>
<td>404-413</td>
<td>14 473.6</td>
<td>-0.2</td>
<td>3.0</td>
<td>2.8</td>
</tr>
<tr>
<td>404-505</td>
<td>32 617.1</td>
<td>-0.1</td>
<td></td>
<td>1.7</td>
</tr>
<tr>
<td>514-523</td>
<td>14 139.5</td>
<td>0.1</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>505-514</td>
<td>19 894.7</td>
<td>-0.4</td>
<td>4.4</td>
<td>4.2</td>
</tr>
<tr>
<td>625-624</td>
<td>11 554.4</td>
<td>0.0</td>
<td>4.5</td>
<td>4.6</td>
</tr>
<tr>
<td>615-624</td>
<td>16 606.4</td>
<td>0.2</td>
<td>2.5</td>
<td>2.6</td>
</tr>
<tr>
<td>624-633</td>
<td>20 891.3</td>
<td>0.4</td>
<td>-1.6</td>
<td>-1.7</td>
</tr>
<tr>
<td>726-725</td>
<td>17 611.6</td>
<td>0.1</td>
<td>6.5</td>
<td>6.4</td>
</tr>
<tr>
<td>716-725</td>
<td>20 714.9</td>
<td>0.6</td>
<td>4.4</td>
<td>4.6</td>
</tr>
</tbody>
</table>

*The E component of this transition was not measured.*
The closely-spaced doublets were due to transitions between rotational energy levels which were split by torsional vibration of the methyl group. To a good approximation, both the A series and the E series lines fit rigid-rotor assignments with $A_A > A_E$, $B_A > B_E$, and $C_A = C_E$. Components of the doublets were assigned to symmetry species A or E by using these facts.

Rotational constants were obtained by least-square fitting the A series lines to a rigid-rotor energy level pattern. Rotational constants, moments of inertia and the estimated standard deviation, $S$, are given in Table II.

$$S = [(v_{obs} - v_{calc})^2/(N_{obs} - N_{par})]^{1/2}$$

where $N_{par}$ is the number of adjustable parameters. For a molecule as heavy as methyl vinyl ketone little centrifugal distortion is expected for $J < 10$. The values of $v_{A} - v_{A_{calc}}$ probably reflect the uncertainty in measurement. The observed moments of inertia are consistent with a structure in which the two double bonds are trans. Little further structural information can be derived from the moments of inertia since there are three pieces of information in the moments of inertia and twenty-four structural parameters.

The spectrum in the region $0 \rightarrow 2$ appeared with single lines without any resolution with the exception of the transition $1_{10} \rightarrow 2_{11}$. This showed that the barrier due to internal rotation is high. As no lines were assigned in the excited states, the high $J$ lines ($J > 2$) of the ground state were studied. The splittings observed for the lines are listed in
Table I.

The treatment of internal rotation used was the same as that used by Kilb, Lin and Wilson on acetaldehyde.

TABLE II
Rotational Constants and Moments of Inertia of the A Lines

\begin{align*}
A &= 8941.45 \pm 0.06 \text{ Mc/sec} \\
B &= 4274.48 \pm 0.02 \\
C &= 2945.32 \pm 0.02 \\
S &= 0.29 \text{ Mc/sec} \\
I_a &= 56.521 \text{ u} \cdot \text{A}^2 \\
I_b &= 118.231 \\
I_c &= 171.586 \\
I_a + I_b - I_c &= I_\alpha - \Delta = 3.166 \text{ u} \cdot \text{A}^2
\end{align*}

\[ \text{Conversion factor: } 5.05377 \times 10^5 \text{ u} \cdot \text{A}^2 \text{ Mc/sec (C}^2 = 12.00000) \]

The methyl group axis is oriented almost parallel to the b-axis of the molecule. This makes \( \lambda_a \) quite small and therefore the coefficient of \( P_a \) in \( \Phi \) is quite small. The coefficient of \( P_b \) in \( \Phi \) is small because \( I_\alpha/I_b \) is small. As a result the perturbation expansion of Herschbach converges rapidly and the internal rotation splittings are small. Only the terms in
Herschbach's expansions giving rise to change in the rotational constants \( \Delta A = A_A - A_E \) and \( \Delta B = B_A - B_E \) are important. Then \( \Delta A = \alpha^2 F \Delta \eta \) and \( \Delta B = \beta^2 F \Delta \eta \); where \( F = \frac{\mu^2}{2rI_\alpha} \), \( \alpha = \lambda_a I_\alpha / I_a \), \( \beta = \lambda_b I_\alpha / I_b \), and \( \Delta \eta \) is the difference (A minus E) of coefficients in the \( \phi \) expansion. Thus the quantities \( \Delta \eta \) and \( \lambda_a \) may be determined from \( \Delta A \) and \( \Delta B \).

The observed non-zero internal-rotation splittings were least-square fit to the parameters \( \Delta A \) and \( \Delta B \). The calculated internal rotation parameters are given in Table III. The splittings, \( \nu_A - \nu_E \) were calculated for all lines from the relation \( \nu_A - \nu_E = \frac{\partial \nu}{\partial A} \Delta A + \frac{\partial \nu}{\partial B} \Delta B \). The comparisons of \( (\nu_A - \nu_E)^{\text{calc}} \) with \( (\nu_A - \nu_E)^{\text{obs}} \) are given in Table I. As is often the case the uncertainty in the barrier primarily arises from the uncertainty in the assumed value of \( I_\alpha \).

**TABLE III**

**Internal Rotation Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta A )</td>
<td>0.096 ( \pm ) 0.030 Mc/( \text{sec} )</td>
</tr>
<tr>
<td>( \Delta B )</td>
<td>0.349 ( \pm ) 0.006 Mc/( \text{sec} )</td>
</tr>
<tr>
<td>( s )</td>
<td>35.2 ( \pm ) 0.2( ^a )</td>
</tr>
<tr>
<td>( \lambda_b )</td>
<td>0.968 ( \pm ) 0.010</td>
</tr>
<tr>
<td>( F )</td>
<td>1.65 ( \times ) 10^5 Mc/( \text{sec} )</td>
</tr>
<tr>
<td>( V_3 )</td>
<td>1250 ( \pm ) 20 cal/mole</td>
</tr>
<tr>
<td>( I_\alpha )</td>
<td>3.164 u ( \cdot ) ( ^a )</td>
</tr>
</tbody>
</table>

\( ^a V_3 = 9/4 \) Fs
\( ^b \) Assumed
The electric dipole moment was determined from Stark effect measurements on the $^0_{0011}$, $^1_{1121}$, $^1_{0102}$, and $^1_{0121}$ transitions. The components $\mu_a^2$ and $\mu_b^2$ were obtained by least-square fitting the observed Stark coefficients, $\frac{\Delta v}{E^2}$, with weighting to give a constant relative error. The observed Stark coefficients and the dipole moment are given in Table IV. Rogers$^6$ gives $\mu = 2.98D$ by dielectric measurements.

DISCUSSION

This work shows that the most stable configuration of the molecule is that with the conjugated system in a trans configuration. No evidence was found to indicate the presence of the cis configuration. It would be dangerous to conclude that no other configuration exists from this negative evidence, but it would be surprising if another configuration were present in large concentrations. The structure is analogous to the results of Lide for 2-fluorobutadiene$^7$ and isoprene$^8$.

The barrier to internal rotation, 1250 cal/mole, is very close to that in other similar molecules$^1$ (CH$_3$CHO 1150 cal/mole, CH$_3$CIF 1080, CH$_3$COCl 1350, and CH$_3$COCN 1270).

The discrepancy between the dielectric value and the microwave value of .18D is somewhat larger than is usually found. Often such measurements agree within 0.1D. Because of the sign ambiguities resulting on taking the square roots of $\mu_a^2$ and $\mu_b^2$, there are two possible orientations of $\mu$. One has $\mu$ directed almost along the C = O bond.
CHAPTER II
MICROWAVE SPECTRUM OF $^{14}_N^{16}O^{17}O$

BACKGROUND

Nitrogen dioxide is a stable free radical. The study of the microwave spectrum of a free radical differs from the study of a molecule with no net electron spin. The usual pattern of energy levels associated with an asymmetric rotor is complicated by the removal of the degeneracy with respect to orientation of electron spin. In the case of $^{14}_N^{16}O^{17}O$, there are also two nuclei with spin angular momenta. Coupling of the nuclear spins with the electron spin removes the degeneracy with respect to alignment of the nuclear spins. A typical rotational level is split into 36 hyperfine levels (see Figure 1). The study of $^{14}_N^{16}O^{17}O$ is unique in that it is the first polyatomic molecule with an electron spin and two nuclear spins whose rotational hyperfine spectrum has been assigned.

There has been extensive work on the microwave spectrum of nitrogen dioxide$^9-16$. Analysis of the hyperfine structure of $^{14}_N^{16}O_2$, $^{15}_N^{16}O_2$, and $^{14}_N^{16}O^{18}O$ proceeded over a period of 15 years in several laboratories. The assignment was reported by Bird et al. in 1964. They give a detailed account of the steps leading to the assignment. The chief problems were a lack of prior knowledge of the magnitude of the hyperfine coupling constants, and the difficulty
in settling on a unique mathematical solution to the problem
with the limited amount of data obtainable. The dipole
moment of nitrogen dioxide determined by the Stark effect
of an $^8_0 8^{-7,17}$ transition was reported by Hodgeson, Sibert,
and Curl in 1963 $^{17}$.

Bird et al. also discussed the magnetic coupling
constants ($(0)_I$, $(aa)_I$, etc.) in terms of a simplified
electronic structure. The symmetry of the odd electron
orbital was determined and the percentage $2sN$ and $2pN$
character of the odd electron was estimated.

The study of $^{14}_N, ^{16}_0, ^{17}_0$ was undertaken primarily to
obtain similar information about the behavior of the odd
electron in the vicinity of the oxygen atom. The know-
ledge of the dipole-dipole and Fermi coupling constants
for the $^{17}_0$ nucleus would then, when combined with the
previous work by Bird et al. $^{14}$ and Hodgeson, Sibert, and
Curl$^{17}$ represent a rather complete characterization of
the ground electronic state of the molecule. Previous
to this work, this much information on the ground electronic
state of any bent triatomic molecule had not been available.
The combined data on nitrogen dioxide should serve as a
severe test of any complete wave-mechanical description
of chemical bonding in the molecule.

The new information is not available from the study
of $^{16}_0$ or $^{18}_0$ containing isotopes since they have no
nuclear spin.
The microwave spectrum of $^{14}_N^{16}_0^{17}_0$ was first observed by Hodgeson. The lines he measured are given in Appendix III. In addition, he developed most of the computational methods necessary to analyze a rotating asymmetric molecule with an electron spin and two nuclear spins. There was also available to this author an unpublished spectrum of the $8_{08}^{-7}_{17}$ region with approximate frequency markers, also obtained by Hodgeson. It is noteworthy that Dr. Hodgeson also contributed greatly to the analysis of the hyperfine spectra of $^{14}_N^{16}_0^{2} , ^{15}_N^{16}_0^{2}$, and $^{14}_N^{16}_0^{18}_0$. He was not able to continue the study of $^{14}_N^{16}_0^{17}_0$ in the time available to him.

This work presents an extensive study of the regions of the $8_{08}^{-7}_{17}$ and $9_{19}^{-10}_{0,10}$ rotational transitions of $^{14}_N^{16}_0^{17}_0$. The observed spectrum is shown in Figure 2. Nearly all of the observed lines have been assigned to $^{14}_N^{16}_0^{17}_0$ and the $^{17}_0$ magnetic coupling constants have been well determined.

THEORY

Nitrogen dioxide is one of the few chemical species whose ground electronic state exhibits a net electron spin angular momentum ($\mathbf{S}$). Other molecules of this type whose hyperfine microwave spectra have been investigated are OH, SO, O$_2$, NO and $^{18}$ClO$_2$. The application of the tensor coupling method to the analysis of the hyperfine
structure of free radicals was first made by Curl and co-workers on C10$_2$ $^{22}$. The method is appropriate for a molecule with any degree of asymmetry. It was subsequently used in the final analysis of the spectra of the NO$_2$ isomers previously mentioned $^{14,16}$. A straightforward extension of their equations was used in calculating the new matrix elements appropriate to the $^{14}$N$^{16}$O$^{17}$O Hamiltonian.

In the species $^{14}$N$^{16}$O$^{17}$O there are, in addition to electron spin, nuclear spins associated with the $^{17}$O ($I_1 = 5/2$) and $^{14}$N ($I_2 = 1$) nuclei. In the absence of coupling between spin and mechanical angular momenta (N) the molecule would have the usual pattern of energy levels associated with an asymmetric rotor. However, the interaction of rotation with electron spin removes the $2S+1$ (two) fold degeneracy with respect to orientation of electron spin. Furthermore, the interaction of nuclear spin with electron spin and the interaction of the nuclear quadrupoles with their field environments remove the $2I_1+1$ (six) fold degeneracy with respect to alignment of the $^{17}$O nuclear spin and the $2I_2+1$ (three) fold degeneracy with respect to alignment of the $^{14}$N nucleus. The resulting hyperfine levels for a typical rotational energy level are indicated in Figure 1.

The calculation of the hyperfine splitting of a rotational energy level is carried out in three steps.
First, an effective Hamiltonian is derived. Next, a coupling scheme for the angular momenta is chosen. This is equivalent to choosing a set of basis functions for computing the Hamiltonian matrix. Lastly, the matrix elements are calculated and Hamiltonian matrix is diagonalized.

The Hamiltonian for a system with rotational, electronic and nuclear spin states has been discussed by several authors. Curl and Kinsey\textsuperscript{23} have given the operators in spherical tensor notation which is appropriate for the tensor coupling method used here. The Hamiltonian has the form

\[ H = H_0 + H_{sr} + H_{dd}(1) + H_f(1) + H_q(1) + H_{dd}(2) + H_f(2) + H_q(2). \]  \hspace{1cm} (4)

$H_0$ is the asymmetric rotor Hamiltonian. $H_{sr}$ is the operator describing the interaction of electron spin and mechanical rotation. $H_{dd} + H_f$ describes the interaction of the nuclear and electron magnetic dipoles. $H_q$ is the nuclear quadrupole term. The nuclear interactions are written separately for the $^{17}$O and $^{14}$N nuclei.

The explicit form of the Hamiltonian is central to the solution of this problem, and it is presented here for completeness. It is discussed in detail by a number of authors\textsuperscript{23-25}.

$H_0$ is the Hamiltonian of a rigid asymmetric rotor and is given by
\[ H_0 = A N_a^2 + B N_b^2 + C N_c^2 \]  \hspace{1cm} (5)

where A, B, and C are the rotational constants for a rigid molecule. \( N_a, N_b, \) and \( N_c \) are the operators associated with overall rotation about the principal axes of the molecule. The eigenvalues of \( H_0 \) are known\(^2\text{6}\).

The \( H_{sr} \) term has been derived by Van Vleck\(^2\text{7}\). The notation of Curl and Kinsey\(^2\text{3}\) is used here. There are significant first and second order contributions. The first order effect is the direct interaction of rotation and electron spin magnetic dipoles. The second order effect arises from two sources.

\[ H_{sr(a)} = -2(AN_a L_a + BN_b L_b + CN_c L_c), \]  \hspace{1cm} (6)

where \( L \) is the total orbital angular momentum. This occurs because the rotational energy of the molecule is \( AN_a^2 + BN_b^2 + CN_c^2 \), where \( N = N - L \). The other second order term is

\[ H_{sr(b)} = \sum_{s,j} h_{sj} \cdot S_j, \]  \hspace{1cm} (7)

where \( h_{sj} \) is the spin-orbit coupling operator for electron \( j \). The second order terms are off-diagonal in electronic energy. After a Van Vleck transformation\(^2\text{8}\), the ground electronic state is associated with a Hamiltonian which has the same form as the first order term. The effective spin-rotation Hamiltonian is then

\[ H_{sr(\text{eff})} = A N_a S_a + B N_b S_b + C N_c S_c \]  \hspace{1cm} (8)

The interaction between electron spin and nuclear spin is the result of the two terms \( H_{dd} + H_f \). There is
the classical energy of interaction between two dipoles,

\[ H_{dd} = g_I g_S \mu_N \mu_B \left[ \frac{S^I}{r^3} - \frac{3 (I^I \cdot r) (S^I \cdot r)}{r^5} \right] \]  \hspace{1cm} (9)

where \( g_I \) is the nuclear g factor, \( g_S \) is the electron g factor, \( \mu_N \) is the nuclear magneton, \( \mu_B \) is the Bohr magneton, and \( \mathbf{r} \) is the radius vector of the electron with respect to the nucleus. The other term, \( H_f \), may be thought of as arising as a correction to \( H_{dd} \) because the classical expression is derived assuming a finite distance between the interacting dipoles. This is not correct for the case of an electron in an s orbital. There is a non-zero probability that the electron will be at the nucleus (\( \mathbf{r} = 0 \)). The correction term is called the Fermi, or contact term, and has the form

\[ H_f = -\frac{8\pi}{3} g_I g_S \mu_N \mu_B |\Psi(0)|^2 (\mathbf{r} \cdot \mathbf{s}) \]  \hspace{1cm} (10)

with \( \mu_n > 0 \) and \( \mu_B > 0 \).

\( H_q \) arises from the interaction of the nuclear electric quadrupole moment and the gradient of the electric field at the nucleus. It has the form

\[ \frac{-eQ}{2I(2I-1)} \left[ \frac{\partial^2 V}{\partial a^2} I_a^2 + \frac{\partial^2 V}{\partial b^2} I_b^2 + \frac{\partial^2 V}{\partial c^2} I_c^2 \right] \]  \hspace{1cm} (11)

where \( e \) is the electronic charge, \( Q \) is the quadrupole moment of the nucleus, and \( V \) is the potential field at the nucleus due to electrons.

The terms \( H_{sr} \), \( H_{dd} \), \( H_f \), and \( H_q \) in (4) are referred to as the hyperfine Hamiltonian. The form of the terms presented here is for a molecule with \( C_{2v} \) symmetry. For the
molecule $^{14}_N^{16}_O^{17}_O$ the symmetry is slightly broken. The justification for this approximation is that, within experimental error, the observed hyperfine spectrum can be analyzed using (4). This was also the case in Cl$^{35}_1^{16}_O^{17}_O^{22}(b)$. The coupling constants which may be determined from the spectrum of $^{14}_N^{16}_O^{17}_O$ are listed in Table V. The notation of Curl and Kinsey is used.

**TABLE V**

Hyperfine Coupling Constants and the Hyperfine Hamiltonian$^a,c$

$$H_{sr} = A_{s} S_{a} S_{a} + B_{s} S_{b} S_{b} + C_{s} S_{c} S_{c}$$

$$H_{dd} = (aa)_{I} I_{a} S_{a} + (bb)_{I} I_{b} S_{b} + (cc)_{I} I_{c} S_{c}$$

$$(aa)_{I} + (bb)_{I} + (cc)_{I} = 0$$

$$(aa)_{I} = -g_{a} g_{I} \mu_{B} \Upsilon_{N} \left\langle \frac{1-3}{3} a \right\rangle$$

$$(bb)_{I} = -g_{b} g_{I} \mu_{B} \Upsilon_{N} \left\langle \frac{1-3}{3} b \right\rangle$$

$$(cc)_{I} = -g_{c} g_{I} \mu_{B} \Upsilon_{N} \left\langle \frac{1-3}{3} c \right\rangle$$

$$H_{f} = (0)_{I} (I^{*} S)$$

$$(0)_{I} = -(8\pi/3) g_{I} \mu_{B} \Upsilon_{N} |\Upsilon(0)|^2 ; \mu_B > 0, \mu_N > 0$$

$$H_{q} = (aa)_{Q} I_{a}^2 + (bb)_{Q} I_{b}^2 + (cc)_{Q} I_{c}^2$$

$$(aa)_{Q} + (bb)_{Q} + (cc)_{Q} = 0$$

$$(aa)_{Q} = \frac{-eQ}{2I(2I-1)} \frac{3}{8a^2}$$
TABLE V (continued)

Hyperfine Coupling Constants and the Hyperfine Hamiltonian\(^a, c\)

\[
\begin{align*}
(bb)_Q &= \frac{-eQ}{2I(2I-1)} \frac{\delta^2 V}{\delta b^2} \\
(cc)_Q &= \frac{-eQ}{2I(2I-1)} \frac{\delta^2 V}{\delta c^2}
\end{align*}
\]

\(^a\) The notation of Curl and Kinsey is used.

\(^b\) The spin-rotation coupling constants depend on the electronic structure of the molecule, including excited states. See Reference (23).

\(^c\) The subscript I and subscript Q parameters may be determined for \(^{14}\)N and \(^{17}\)O.

\(^d\) The \(\hat{a}_a\), \(\hat{a}_b\), \(\hat{a}_c\) are unit vector components from the nucleus to odd electron.

The choice of a set of basis functions is complicated by the presence of two nuclear spins. Let us first consider a molecule such as \(^{14}\)N\(^{16}\)O\(_2\) with one nuclear spin. If the rotational, electronic, and spin wave functions are combined in a manner which makes the complete wave function an eigenfunction of the total angular momentum \(F\), then the Hamiltonian matrix will be block diagonal in \(F\) (since [HF-FH] = 0). \(F\) is the resultant of \(N\), \(S\) and \(I\). There are three possible schemes for forming \(F\). They are:

1. J scheme \(N + S = J; J + I = F\)
2. G scheme \(I + S = G; G + N = F\)
3. E scheme \(N + I = E; E + S = F\).
The scheme to be chosen depends on which term in the Hamiltonian makes the dominant contribution to the magnitude of the hyperfine splittings. With the choice of coupling scheme is implied a prescription for writing the basis function. For the \( J \) scheme the basis is, in Dirac notation,

\[ |N \, T \, S \, J \, I \, F \, M_F \rangle . \]

The symbols imply the eigenvectors of the set of operators \( N^2, S^2, J^2, I^2, F^2 \), and \( F_z \). Experimentally, it is found that the \( J \) scheme is appropriate for all the observed transitions of \( ^{14}N^{16}O_2 \).

In \( ^{14}N^{16}O^{17}O \) the spin-rotation interaction is also the dominant term in the hyperfine Hamiltonian. But the presence of spin angular momentum associated with \( ^{17}O \) (which we now call \( I_1 \)) leaves an ambiguity in the coupling scheme which may be described as

- \( F_1 \) scheme \( N + S = J; \quad J + I_1 = E_1; \quad E_1 + I_2 = E \)
- \( F_2 \) scheme \( N + S = J; \quad J + I_2 = E_2; \quad E_2 + I_1 = E \).

The choice of \( F_1 \) or \( F_2 \) coupling is nearly arbitrary since the magnitudes of the hyperfine parameters related to nucleus 1 and nucleus 2 are expected to be similar. The \( F_1 \) scheme is chosen for convenience in calculating the second order spin-rotation dipole-dipole interaction, which is found to be important for the \( ^{17}O \) nucleus. This interaction is discussed below. The basis function associated with the \( F_1 \) scheme is
\[
|N \uparrow S J I_1 F_1 I_2 F M_F >
\]
where \(\uparrow\) is the asymmetric rotor quantum number. The fact that there is no clear basis for choosing between the \(F_1\) and the \(F_2\) coupling schemes suggests that there will be strong mixing of the two schemes. It then is to be expected that transitions will occur in which \(\Delta N = \Delta F \neq \Delta F_1\).

The calculation of the Hamiltonian matrix elements is carried out using the tensor coupling method. This method has been successfully applied in analyzing the hyperfine spectra of \(^{35}\text{Cl}\)\text{\(^{16}\text{O}_2\)}, \(^{37}\text{Cl}\)\text{\(^{16}\text{O}_2\)}, \(^{35}\text{Cl}\)\text{\(^{16}\text{O}^{18}\text{O}\)}, \(^{14}\text{N}\)\text{\(^{16}\text{O}_2\)}, \(^{15}\text{N}\)\text{\(^{16}\text{O}_2\)}, and \(^{14}\text{N}\)\text{\(^{16}\text{O}^{18}\text{O}\)}. Original developments in the application of the theory of tensors to the coupling of angular momenta were made by Racah\(^29\) and Wigner\(^30\). Edmonds\(^31\) has given an extended treatment of this topic. The first application of the method to the treatment of hyperfine structure in molecules is found in the works of Curl and Kinsey\(^22(c)\), \(^23\). Their paper on the calculation of matrix elements of the hyperfine Hamiltonian is a primary reference for this work. A brief discussion of the method is given below.

The operators in the Hamiltonian are expressed as spherical tensor operators. Curl and Kinsey\(^23\) have done this for all the operators of interest here, and have also given some useful relations between spherical and Cartesian tensors. The matrix elements of the hyperfine Hamiltonian
are calculated in the uncoupled scheme and the elements in the coupled scheme are obtained by the use of vector recoupling coefficients.

Any interaction term in the $^{14}{\text{N}}_{16}{\text{O}}_{17}$ Hamiltonian can be expressed as

$$\left\{\left[T(k_1) \times U(k_2)\right]_{k_{12}} \times Y(k_3)\right\}_{k_{123}} \times Z(k_4) = X(k)$$

(12)

By this is meant that a tensor of rank $k$, $T(k_1)$, couples with a tensor of rank $k_2$, $U(k_2)$, to give a resultant of rank $k_{12}$. $Y(k_3)$ then couples with

$$\left[T(k_1) \times U(k_2)\right]_{k_{12}}$$

to give a resultant tensor of rank $k_{123}$. The tensor $X(k)$ is the resultant of coupling of $Z(k_4)$ with the resultant of rank $k_{123}$.

In the $F_1$ coupling scheme $T(k_1)$ is related to the operator $N^2$, $U(k_2)$ to $S^2$, $Y(k_3)$ to $I_1^2$, $Z(k_4)$ to $I_2^2$ and $X(k)$ to $F^2$.

The equation (13) relating the matrix elements in the uncoupled scheme to those in the coupled scheme is obtained directly by another iteration of equation (2) of reference (23) using equation 7.1.5 of Edmonds' book$^{31}$. 

$$<N'T'SJ'I_1F_1'I_2F'||X(k)||NS'SJ'I_1F_1'I_2F>$$

$$= [(2F+1)(2F'+1)(2k+1)(2F_1+1)(2F_1'+1)]$$

$$\left(2k_{123}+1\right)(2J+1)(2J'+1)(2k_{12}+1)^{1/2}.$$ 

(continued on next page)
\[
\begin{align*}
\left\{ \begin{array}{c} F'_1 \\
I_2 \\
F' \\
\end{array} \right\} & \left\{ \begin{array}{c} F_1 \\
I_2 \\
F \\
\end{array} \right\} \left\{ \begin{array}{c} k_{123} \\
k_4 \\
k \\
\end{array} \right\} \left\{ \begin{array}{c} J' \\
I_1 \\
F \\
\end{array} \right\} \left\{ \begin{array}{c} J \\
I_1 \\
F \\
\end{array} \right\} k_3 \left\{ \begin{array}{c} N' \\
S \\
F \\
\end{array} \right\} \left\{ \begin{array}{c} N \\
S \\
F \\
\end{array} \right\} k_1 \\
\left\{ \begin{array}{c} J' \\
I_1 \\
F \\
\end{array} \right\} \left\{ \begin{array}{c} J \\
I_1 \\
F \\
\end{array} \right\} k_{123} \left\{ \begin{array}{c} F'_1 \\
F' \\
F \\
\end{array} \right\} \left\{ \begin{array}{c} I_2 \\
I_2 \\
I_2 \\
\end{array} \right\} \right\} 
\end{align*}
\]

(13)

This expression was first obtained by Hodgeson\textsuperscript{16}. The terms in curly brackets are Wigner 9j symbols. Edmonds\textsuperscript{31} has given useful relations for evaluating the 9j symbols. In particular, if any of the \( k \)'s are zero the 9j reduces to the product of a 6j symbol and a simple function of elements of the 9j. The double line implies that the quantity is a reduced matrix element. They are related to the actual matrix elements by Wigner 3j symbol. For example,

\[
<F' || X(k) || F> = (-1)^{M'_F - F'_F} <F'M_F || X(k; Q)|| F_M_F> 
\]

(14)

\[
\left( \begin{array}{c} F' \\
-1 \\
M'_F \\
Q \\
M_F \\
\end{array} \right) 
\]

where

\( X(k, Q) \) is the \( Q \)th element of the rank \( k \) spherical tensor.

The Hamiltonian matrix is nearly block diagonal in the rotational quantum number \( N \). The matrix elements off-diagonal in \( N \) can be reduced to fourth order in the energy by application of a Van Vleck perturbation\textsuperscript{28}. When this is done, the matrix elements associated with block \( N \) have the form \((F_1\) coupling scheme)
\[
\frac{\langle N_{TJF} | H_1 | N_{TJ} F_1 F \rangle}{E(N_{TJF}) - E(N'' TJ'' F''_1 F)} + \sum_{N'' \neq N, J', F_1''} \frac{\langle N_{TJF} | H_1 | N'' TJ'' F''_1 F \rangle - \langle N'' TJ'' F''_1 F | H_1 | N_{TJ} F_1 F \rangle}{E(N_{TJF}) - E(N'' TJ'' F''_1 F)}
\]

(15)

where \( H \) is the total Hamiltonian, \( H_0 \) is the asymmetric rotor Hamiltonian, and \( H_1 \) is the hyperfine Hamiltonian. The energy is expected to be correct to second order in \( H_1/\Delta E \).

The first two terms in (15) are diagonal in \( N_T \). The matrix elements, diagonal in \( N_T \), associated with nucleus 1 are the same as those previously used for the work on \( \text{ClO}_2 \)\(^{22}\) and \( \text{NO}_2 \)\(^{14}\). Nucleus 2 matrix elements diagonal in \( N_T \) were first calculated by Hodgson\(^{16}\), and are given in Appendix I.

Terms in the summation are all much smaller than the first two terms in (15) because of the large energy denominator. It can be shown for the parameters obtained for \( \text{N}_1\text{O}_2\)\(^{170}\) that only a few terms in the summation over \( N'', J'', F_1'' \) contribute significantly to the hyperfine spectrum within the accuracy of our measurements. These "correction" matrix elements are of the type \( \Delta N = \pm 1, \Delta K = 0 \). The calculation of these matrix elements may be simplified by ignoring the slight asymmetry of the molecule and using the Wang symmetric top basis\(^{32}\),
\[ |N_{-1} \gamma J F_{1} F \rangle, \text{ where} \]
\[ |N_{-1} \gamma \rangle = \frac{1}{\sqrt{2}} \left[ |N_{-1} \rangle + (-1)^{\gamma} |N-K_{-1} \rangle \right]. \]

A further simplification of (15) is made by recognizing that
\[ E(NTJ_{1} F_{1} F) = E(N \tau J_{1} F_{1} F) = E(NT) - E(N \tau) \]
(16)
\[ E(NTJ_{1} F_{1} F) - E(N \tau J_{1} F_{1} F) = E(NT) - E(N \tau) \]
When \( H_{1} \) is written as \( H_{f}(1)+H_{dd}(1)+H_{q}(1)+H_{f}(2)+H_{dd}(2)+H_{q}(2) \),
with the number 1 terms related to the \( ^{170} \) nucleus, the
significant contributions to the summation in (15) are;
\[ E_{+} = \frac{\langle N+1K_{-1} \gamma J F_{1} F | H_{sr} | N_{-1} \gamma J F_{1} F \rangle^{2}}{E(NT) - E(N+1 \tau)} \]
\[ E_{-} = \frac{\langle N_{-1} \gamma J F_{1} F | H_{sr} | N-1K_{-1} \gamma J F_{1} F \rangle^{2}}{E(NT) - E(N-1 \tau)} \]
\[ e_{+} = \]
\[ 2\frac{\langle N_{-1} \gamma J_{+} F_{1} F | H_{sr} | N+1K_{-1} \gamma J_{+} F_{1} F \rangle \langle N+1K_{-1} \gamma J_{+} F_{1} F | H_{dd}(1) | N_{-1} \gamma J_{+} F_{1} F \rangle}{E(NT) - E(N+1 \tau)} \]
\[ e_{-} = e_{+} \text{ with } N \text{ replaced by } N-1 \text{ and } J_{+} \text{ replaced by } J_{-}, \text{ and} \]
\[ e_{\pm} = \]
\[ \frac{\langle N_{-1} \gamma J_{+} F_{1} F | H_{sr} | N+1K_{-1} \gamma J_{+} F_{1} F \rangle \langle N+1K_{-1} \gamma J_{+} F_{1} F | H_{dd}(1) | N_{-1} \gamma J_{+} F_{1} F \rangle}{E(NT) - E(N+1 \tau)} + \]
\[ \frac{\langle N_{-1} \gamma J_{+} F_{1} F | H_{dd}(1) | N-1K_{-1} \gamma J_{+} F_{1} F \rangle \langle N-1K_{-1} \gamma J_{+} F_{1} F | H_{sr} | N_{-1} \gamma J_{+} F_{1} F \rangle}{E(NT) - E(N-1 \tau)} \]
where \( J_{+} = N+S \) and \( J_{-} = N-S \). The matrix elements off-
diagonal in \( N \) are given in Appendix II. For the molecule
\( \text{ClO}_{2}^{22(b)} \) it was also necessary to include all but the \( e_{\pm} \)
term in fitting the hyperfine spectrum.
<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_o$</td>
<td>$9 \times 10^5$ Mc/sec</td>
</tr>
<tr>
<td>$E_{sr}$</td>
<td>200</td>
</tr>
<tr>
<td>$E_f(2)$</td>
<td>70</td>
</tr>
<tr>
<td>$E_f(1)$</td>
<td>35</td>
</tr>
<tr>
<td>$E_{dd}(1)$</td>
<td>10</td>
</tr>
<tr>
<td>$E_{+,E_-}$</td>
<td>10</td>
</tr>
<tr>
<td>$E_{dd}(2)$</td>
<td>5</td>
</tr>
<tr>
<td>$E_{q}(2)$</td>
<td>2</td>
</tr>
<tr>
<td>$e_{+,e_-}$</td>
<td>1</td>
</tr>
<tr>
<td>$e_\pm$</td>
<td>0.5</td>
</tr>
<tr>
<td>$E_{q}(1)$</td>
<td>0</td>
</tr>
</tbody>
</table>

- The hyperfine quantities are intended to represent average values, and may not be correct for any particular hyperfine level.
The magnitude of the contribution from each term in (15) is indicated in Table VI for the 7_{17} rotational level, which is typical of the two rotational transitions studied here.

In the $F_\parallel$ coupling scheme the hyperfine Hamiltonian matrix of dimension 36x36 associated with a rotational level $N$ (for $N\geq4$) factors into 9 subblocks. They are of dimension 1x1, 3x3, 5x5, 6x6, 6x6, 5x5, 3x3, and 1x1 for $F$ equal to $N+4$, $N+3$, $N+2$, $N+1$, $N$, $N-1$, $N-2$, $N-3$, and $N-4$ respectively.

The computation of matrix elements and diagonalization of the Hamiltonian matrix were carried out on the Rice University Computer. In the assignment of intermediate quantum numbers to the calculated eigenvalues, a complication occurs in $^{14}\text{N}_2^{16}\text{O}_{17}^{17}$ which does not exist for the NO$_2$ isomers with only one nuclear spin. In the case of the larger subblocks of the Hamiltonian matrix it is not clear which values of the intermediate quantum numbers $J$ and $F_\parallel$ correlate with the eigenvalues obtained after diagonalization. This is equivalent to saying that the off-diagonal elements in the matrix are large enough to cause a significant mixing of coupling schemes. The intermediate angular momenta are no longer constants of the motion and the quantum numbers $J$ and $F_\parallel$ have no meaning. To distinguish eigenvalues in the same F subblock of the Hamiltonian a number, $\lambda$, is assigned to the eigenvalues,
with \( \lambda = 1 \) for the lowest, etc. The pseudoquantum number \( \lambda \) always uniquely distinguishes the eigenvalues in a subblock \( F \), since states with the same symmetry may not cross.

Many of the matrix element calculations were programmed by Hodgeson\textsuperscript{16}. Programs to compute \( 6j \) and \( 9j \) symbols were written by Mr. E. E. Sibert. A spectrum plotting routine was written by Mr. Neal Rachlin. The line intensities are plotted against frequency to provide a useful means of comparing observed and calculated spectra.

**EXPERIMENTAL**

A 50 cc-atm sample of oxygen containing 55.45\(^{17}\)\(_{0}\) was obtained from Yeda Research and Development Co., Rheovoth, Israel. \(^{14}\)\(_{N}\)\(^{16}\)\(_{0}\)\(^{17}\)\(_{0}\) is prepared by the reaction

\[
2 ~ ^{14}\, ^{N}\, ^{16}\, ^{0}\, ^{17}\, ^{0} + ^{17}\, ^{0}_{2} \rightarrow 2 ~ ^{14}\, ^{N}\, ^{16}\, ^{0}\, ^{17}\, ^{0}.
\]

The reaction is rapid and complete. The equilibrium

\[
2 \, ^{N}_{2} \, ^{0}_{4} \leftrightarrow ^{N}_{2} \, ^{0}_{4}
\]

is present. Spectral measurements were made at dry-ice temperature, where the equilibrium strongly favors \( ^{N}_{2} \, ^{0}_{4} \). It was necessary to renew the sample at about five minute intervals because of chemical reaction with the waveguide.

A conventional 100 kc/sec Stark-modulated spectrometer was used. The klystron was mechanically driven at approximately 7 Mc/sec/min. The output of the phase
sensitive detector was displayed on a strip chart recorder. Frequency measurements were made by calibrating the fundamental of a Gertsch model FM-4 microwave frequency multiplier with a Hewlett-Packard model 5253A 100-500 Mc/sec frequency counter, and beating the output of the Gertsch with the klystron radiation. The beat note was detected on a 0-35 Mc/sec radio receiver. Markers corresponding to the beat note were spaced at approximately 2 Mc/sec intervals on the recorder tracing. Line frequencies were measured by linear interpolation between markers. Frequency measurements are believed accurate to ± 0.3 Mc/sec.

The signal to noise ratio of the strongest line is approximately 20 at the maximum sensitivity of the spectrometer. The spectrometer is not suitable for making reliable relative intensity measurements of widely spaced lines. However, the crude, strong line-weak line, intensity comparisons which could be made were very useful in seeking an initial assignment.

**SPECTRUM AND INTERPRETATION**

The rotational constants of $^{14}_N^{16}_O^{17}_O$ were calculated by the use of Kraitchman's equations from the rotational constants and $r_s$ structure of $^{14}_N^{16}_O^2$. They are $A = 237617$, $B = 12608.87$ and $C = 11950.51$ Mc/sec. Using these rotational constants, the rigid rotor spectrum of
$^{14}\text{N}^{16}\text{O}^{17}\text{O}$ was predicted. The $^{8}_{08} - ^{7}_{17}$ transition lies at 19.91 and the $^{9}_{19} - ^{10}_{0,10}$ at 34.46 Kmc/sec. There is known to be a slight shift ($\simeq 20$ Mc/sec) of both of these lines due to centrifugal distortion.

In the region 19.4-20.4 Kmc/sec some 130 lines have been observed and in the region 34.2-34.6 Kmc/sec some 60 lines have been observed. In general, the $^{8}_{08} - ^{7}_{17}$ region appears to be a mass of very closely spaced lines, with only one prominent feature. A line stronger than any other by about a factor of two appears at 20153.6 Mc/sec. The $^{9}_{19} - ^{10}_{0,10}$ region appears to have an approximate center of symmetry at about 34.46 Kmc/sec. This suggests that J scheme coupling is fairly pure for this transition, and that the two subbands correspond to N+S and N−S levels. The observed spectrum is plotted in Figure 2, and the assigned lines are given in Table VII.

The assignment of the lines was greatly simplified by the availability of the spin-rotation coupling constants for $^{14}\text{N}^{16}\text{O}^{2}$ and $^{14}\text{N}^{16}\text{O}^{18}\text{O}$, and the Fermi, dipole-dipole and quadrupole coupling constants for the $^{14}\text{N}$ nucleus. Additionally, the quadrupole moment of the $^{17}\text{O}$ nucleus is known to be nearly zero, forcing the $^{17}\text{O}$ quadrupole coupling constants to be small. There are then only three parameters for which good initial estimates are not available. They are the Fermi and dipole-dipole coupling.
constants of the $^{170}$ nucleus.

An initial assignment of the $^{808-717}$ transitions was made using the lines measured by Hodgeson. The predicted $^{808-717}$ spectrum is such that for nearly all reasonable values of the $^{170}$ coupling constants, the $F \ 12\rightarrow 11$, $\lambda \ 1\rightarrow 1$ transition is stronger than any other line by a factor of $\approx 2$. The observed spectrum also has a similar line at about the same frequency. Hodgeson correctly assigned the $F \ 12\rightarrow 11$, $\lambda \ 1\rightarrow 1$ transition as the line he measured at 20154.1 Mc/sec. An analysis of the relative location of $F \ 10\rightarrow 9\lambda \ 1\rightarrow 2$, $F \ 11\rightarrow 10\lambda \ 2\rightarrow 3$ and $F \ 11\rightarrow 10\lambda \ 1\rightarrow 2$ transitions with large changes in the $^{170}$ coupling constants revealed that they were likely to be the lines measured by Hodgeson at 20113.2, 20181.8, and 20219.3 Mc/sec respectively. A least squares fit on the unknown $^{170}$ parameters using these four lines yielded a spectrum which accounted for most of the lines observed by Hodgeson. With good starting values for all the hyperfine parameters available the assignment shown in Table VII was made.

The method used in refining the new $^{170}$ coupling constants to best fit the observed spectrum is somewhat indirect. In spite of the fact that there are many more observations ($\approx 150$) than there are parameters to be determined (15), it is not possible to find a unique mathematical solution. The linear combination $\approx 2A_s - C_s$ is
essentially undetermined from our data and this is reflected as a large uncertainty in these parameters when a full least square analysis is performed.

In view of the fact that the subscript $s$ parameters are known for $^{14}\text{N}^{16}\text{O}_2$ and $^{14}\text{N}^{16}\text{O}^{18}\text{O}$, a way to refine our data would be the usual least square technique\textsuperscript{35}, but with the subscript $s$ parameters fixed. This method has certain disadvantages in that errors in the values taken for $A_s$, $B_s$, and $C_s$ will cause errors in the determination of other hyperfine parameters. There was available to this author a diagnostic technique for determining the sources of poor convergence in a least square fit. The method is due to R. F. Curl\textsuperscript{36}. A brief description is given in Appendix IV.
<table>
<thead>
<tr>
<th>$F' \rightarrow F$</th>
<th>$\lambda' \rightarrow \lambda$</th>
<th>$\nu_{\text{obs}}$ (Mc/sec)</th>
<th>$\nu_{\text{calc}} - \nu_{\text{obs}}$ (Mc/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12→11</td>
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TABLE VII (continued)

HYPERFINE ASSIGNMENT OF $^{14}_N^{16}O^{17}_O$

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**TABLE VII (continued)**

**HYPERFINE ASSIGNMENT OF **\(^{14}N\)\(^{16}O\)\(^{17}O\)**

\(^{8}O^{8}^{8}\)\(^{7}^{1}^{17}^{17}\)

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**TABLE VII (continued)**

HYPERFINE ASSIGNMENT OF $^{14}_{N}16_{O}17_{O}$

$^{08-7}_{17}$

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### TABLE VII (continued)

**HYPERFINE ASSIGNMENT OF $^{14}_N^{16}O^{17}O_{9,19}^{10,0,10}$**

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<td>+0.3</td>
</tr>
<tr>
<td>7→8</td>
<td>2→1</td>
<td>34 322.6</td>
<td>-0.1</td>
</tr>
<tr>
<td>2→1</td>
<td></td>
<td>34 372.7</td>
<td>+0.3</td>
</tr>
<tr>
<td>2→2</td>
<td></td>
<td>34 414.6</td>
<td>+0.2</td>
</tr>
<tr>
<td>4→3</td>
<td></td>
<td>34 423.3</td>
<td>-0.1</td>
</tr>
<tr>
<td>5→4</td>
<td></td>
<td>34 465.2</td>
<td>-0.2</td>
</tr>
<tr>
<td>3→3</td>
<td></td>
<td>34 509.0</td>
<td>0.0</td>
</tr>
<tr>
<td>4→4</td>
<td></td>
<td>34 520.9</td>
<td>+0.1</td>
</tr>
<tr>
<td>5→5</td>
<td></td>
<td>34 554.8</td>
<td>0.0</td>
</tr>
<tr>
<td>3→4</td>
<td></td>
<td>34 606.9</td>
<td>-0.2</td>
</tr>
<tr>
<td>6→7</td>
<td>1→1</td>
<td>34 377.9</td>
<td>+0.5</td>
</tr>
<tr>
<td>3→2</td>
<td></td>
<td>34 461.2</td>
<td>+0.1</td>
</tr>
<tr>
<td>2→2</td>
<td></td>
<td>34 542.8</td>
<td>-0.3</td>
</tr>
</tbody>
</table>
TABLE VII (continued)

HYPERFINE ASSIGNMENT OF $^{14}_N^{16}O^{17}_0$

$9_{19}^{19}-10_{0,10}$

<table>
<thead>
<tr>
<th>$F' \rightarrow F$</th>
<th>$\lambda' \rightarrow \lambda$</th>
<th>$\nu_{obs}$ (Mc/sec)</th>
<th>$\nu_{calc} - \nu_{obs}$ (Mc/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 → 3</td>
<td></td>
<td>34 547.5</td>
<td>0.0</td>
</tr>
<tr>
<td>5 → 6</td>
<td>1 → 1</td>
<td>34 566.3</td>
<td>-0.3</td>
</tr>
</tbody>
</table>
The diagnostic method is extremely helpful in the analysis of the data reported here. The eigenvector corresponding to the smallest eigenvalue of the system of normal equations associated with our data is concerned primarily with $A_8$ and $C_8$, with $B_8$ to a lesser extent, and to a very slight extent with the remainder of the hyperfine parameters.

We therefore have very good estimates of the subscript $I$ and $Q$ hyperfine parameters determined by our data without carrying out a full least squares analysis. The final parameters obtained are given in Table VIII, along with the most precise values of the $^{14}N$ coupling constants available from work on other isomers of nitrogen dioxide. The uncertainties quoted $\sigma_{est}$ were obtained from the mean standard deviations ($S$) and the variances ($B_{ii}^{-1}$) in the parameters: $\sigma_{est} = S(B_{ii}^{-1})^{1/2}$.

The errors (calc-obs) in the assigned lines were obtained using the parameters in column two of Table VIII. Calculated frequencies were corrected by a constant term which accounts for centrifugal distortion and small errors in the rotational constants.
\[\text{TABLE VIII}\]

<table>
<thead>
<tr>
<th></th>
<th>Lees, et al.\textsuperscript{a}</th>
<th>This Work</th>
<th>Combined \textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>14\textsubscript{N}16\textsubscript{O}\textsubscript{2} Basis</td>
<td>14\textsubscript{N}16\textsubscript{O}17\textsubscript{O}</td>
<td>14\textsubscript{N}16\textsubscript{O}2 Basis</td>
<td></td>
</tr>
<tr>
<td>\textit{(Weighted)}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A_s) \textsuperscript{b}</td>
<td>5401.74±0.07 \text{Mc/sec}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B_s) \textsuperscript{b}</td>
<td>7.65±0.02</td>
<td>7.65±0.02</td>
<td></td>
</tr>
<tr>
<td>(C_s) \textsuperscript{b}</td>
<td>-95.24±0.07</td>
<td>-95.24±0.02</td>
<td></td>
</tr>
<tr>
<td>((0)I_1^{17\text{O}}) \textsuperscript{c}</td>
<td>-63.76±0.03</td>
<td>-63.76±0.03</td>
<td></td>
</tr>
<tr>
<td>((aa)I_1^{17\text{O}}) \textsuperscript{c}</td>
<td>50.48±0.08</td>
<td>50.48±0.08</td>
<td></td>
</tr>
<tr>
<td>((cc)I_1^{17\text{O}}) \textsuperscript{c}</td>
<td>55.85±0.10</td>
<td>55.85±0.10</td>
<td></td>
</tr>
<tr>
<td>((0)I_1^{14\text{N}})</td>
<td>147.27±0.03</td>
<td>147.28±0.05</td>
<td>147.27±0.03</td>
</tr>
<tr>
<td>((aa)I_1^{14\text{N}})</td>
<td>-22.23±0.07</td>
<td>-21.93±0.14</td>
<td>-22.23±0.07</td>
</tr>
<tr>
<td>((cc)I_1^{14\text{N}})</td>
<td>-17.60±0.08</td>
<td>-17.00±0.24</td>
<td>-17.60±0.08</td>
</tr>
<tr>
<td>((aa)Q_1^{17\text{O}}) \textsuperscript{c}</td>
<td>-0.202±0.014</td>
<td>-0.202±0.014</td>
<td></td>
</tr>
<tr>
<td>((cc)Q_1^{17\text{O}}) \textsuperscript{c}</td>
<td>-0.009±0.016</td>
<td>-0.009±0.016</td>
<td></td>
</tr>
<tr>
<td>((aa)Q_1^{14\text{N}})</td>
<td>0.36±0.06</td>
<td>0.41±0.08</td>
<td>0.36±0.06</td>
</tr>
<tr>
<td>((cc)Q_1^{14\text{N}})</td>
<td>1.30±0.05</td>
<td>1.33±0.15</td>
<td>1.30±0.05</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reference (37).

\textsuperscript{b} \(A_s\), \(B_s\), and \(C_s\) are poorly determined by our data. See text.

\textsuperscript{c} Not determined from previous work.

\textsuperscript{d} Spin-rotation and \(14\text{N}\) coupling constants taken from Reference (37), \(17\text{O}\) coupling constants from this work. No adjustment of \(17\text{O}\) parameters was made to correct for the slight asymmetry of \(14\text{N}16\text{O}17\text{O}\).
DISCUSSION OF THE MAGNETIC COUPLING CONSTANTS

A complete interpretation of the hyperfine coupling constants in nitrogen dioxide must await more exact quantum mechanical calculations than are available at present. However, it is possible to make some comments about the general nature of the odd electron orbital in the vicinity of the oxygen nucleus.

The molecular symmetry of NO₂ corresponds to that of the C₂ᵥ point group. Hijikata, Lin, and Baird have analyzed the data from microwave and electron spin resonance spectra of NO₂ and concluded that the odd electron orbital has the symmetry of the a₁ (fully symmetric) representation. Bird et al. have interpreted their values of (0)₁₁₁₁¹⁴N, (aa)₁₁₁₁¹⁴N and (cc)₁₁₁₁¹⁴N as indicating that the odd electron orbital has 9-10% 2s character and between 26 and 52% 2p character on the nitrogen atom, directed along the axis of symmetry.

The Fermi constant (0)₁₁₁₁¹⁷O can be interpreted in terms of the 2s character of the odd electron on oxygen. To estimate the 2s character we need only the magnitude of |Υ(0)|² for an idealized 100% 2s oxygen electron. This may be obtained approximately from a Hartree-Fock 2s atomic oxygen orbital. This approach was also used by Miller, Townes, and Kotani in interpreting the Fermi constant of ¹⁶O¹⁷O. Their value of
$(0)_{I}^{(17)}$ is -56 Mc/sec and is comparable to our value of -63.76 Mc/sec. Both indicate that the odd electron has
2-3% 2s character on the oxygen atom.

To estimate the 2p character of the odd-electron
orbital on oxygen, calculation of the oxygen dipole-
dipole constants for an idealized 100% 2p oxygen orbital
is needed. The value of \( \frac{1}{r^3} \) = 29$x$10$^24$ cm$^{-3}$, based
on a pure 2p in atomic oxygen, is used here. Our value of
\( (cc)_{I}^{(17)} \) indicates approximately 45% 2p character on
oxygen.

In view of the extensive data now available on the
hyperfine coupling constants in nitrogen dioxide, a LCAO-MO
can be estimated for the odd electron. A 2s 2p approxi-
mation similar to that made by Fischer-Hjalmars on O$_3$
is used. To facilitate comparison with her calculations we
adopt the basis

\[
\Psi(4a_1) = \frac{C_1}{\sqrt{2}}[2s(0_1)+2s(0_2)] + C_2 2s(N) + \frac{C_3}{\sqrt{2}}[(2p_b(0_1)+2p_b(0_2)]
+ C_4 2p_b(N) + \frac{C_5}{\sqrt{2}}[(2p_a(0_1)-2p_a(0_2)],
\]

where a and b refer to the inertial axes of the molecule.

From the estimates discussed above, we obtain $C_1^2 = .06$,
$C_2^2 = .09$, $C_3^2 = .88$, $C_4^2 = .45$ and $C_5^2 = .03$. For the
$4a_1$ orbital of ozone, by a LCAO-SCF-MO calculation, Fischer-
Hjalmars obtains

$C_1^2 = .0061; C_2^2 = .0275, C_3^2 = .920, C_4^2 = .218, and C_5^2 = .054.$
Curl has constructed a set of LCAO-MO orbitals assuming sp² hybridization and equivalence of 1-electron Coulomb integrals, and used them to discuss the hyperfine coupling constants in ClO₂. The coefficients of his 4a₁ orbital may be placed on our basis by assuming a bond angle of 120°. Then

\[ C_1^2 = 0, \quad C_2^2 = 0.17, \quad C_3^2 = 0.38, \quad C_4^2 = 0.33, \quad \text{and} \quad C_3^2 = 0.13. \]

This simplified orbital appears to give less good agreement with the observed coupling constants than does the orbital of Fischer-Hjalmars.
CHAPTER III
A MICROWAVE SPECTROMETER FOR SIMPLE UNSTABLE MOLECULES

PURPOSE
Perhaps the most challenging area of chemical research today is the study of the chemical and physical properties of unstable, or reactive molecules. Short-lived species appear to play an important role as intermediates in many chemical reactions. Of the varied methods which are being used to study these molecules, microwave spectroscopy has certain advantages. Among these are high resolution and very accurate measurement of small energy differences. The fundamental information which can be obtained from rotational spectra are molecular structural parameters. Many reactive species have a net electron spin or net orbital angular momentum. The microwave spectra of these molecules can yield a wealth of information, similar to that described in Chapter II, about molecular electronic structure and chemical bonding. It appears that a microwave spectrometer especially suited for the study of unstable molecules would be a valuable research tool.
**BASIC DESIGN REQUIREMENTS**

The application of microwave spectroscopy to the study of unstable molecules is by no means an idea which has originated in our laboratory. It is difficult to estimate how much effort has been extended in searching for the rotational spectra of reactive molecules. A conservative estimate would be 50 man-years. The totality of relatively unstable molecules which have assigned microwave spectra comprises a lamentably short list. They are OH, SO, SH, S\(_2\)O, CS, AlF, SeH, TeH, CN, and SiF\(_2\)\(^{18,19,42-48}\). And for many of these molecules, much has been left undone. A discussion of the specific methods used in the production and detection of the spectra of each of these molecules will not be presented here. There is ample description in the references cited. Spectrometer design appears to have been as varied as the molecules studied, and in every case much trial and error manipulation of the apparatus was necessary to produce the molecule in detectable concentrations. This is a result of a general uncertainty about the chemical properties (e.g., reaction mechanisms and rates) of reactive molecules. A conclusion to be drawn from the studies mentioned above is that the production and detection, by microwave methods, of unstable molecules requires a major effort, and the chances for success are usually not well established.

In the light of these facts, several features which
it would be desirable to include in the design and construction of a versatile microwave spectrometer for the study of unstable molecules may be outlined.

First, from the very nature of the problem, a fast flow system is indicated. Reactive molecules are not in equilibrium with their environment, and must be continuously generated and passed through the absorption cell. (An alternative procedure would be a rapid-scan microwave spectrometer and generate unstable molecules by high energy pulsation of stable molecules. Such an instrument is under construction at the University of California). Physically, in addition to a fast pumping device, a fast flow of low density gas requires that the absorption cell and exhaust system have a large cross-sectional area.

Secondly, it is generally true that reactive molecules tend to recombine at metal surfaces at a much higher rate than at a non-metallic surface, such as glass or teflon. Thus, it is desirable that the portion of the spectrometer from the inlet system through the absorption cell be devoid of metallic surfaces. This, and the above requirement of rapid flow, precludes the use of Stark modulation to improve the sensitivity of the spectrometer. The Stark field must be set up by electrodes in close proximity to the sample.

Thirdly, the loss in sensitivity in a video spectrometer
as opposed to a Stark-modulation spectrometer, can be partially regained by increasing the operating frequency. Since absorption intensity in the microwave region increases approximately as the square of frequency, operation at millimeter wavelengths can give 100 times the sensitivity of a video spectrometer operating in the conventional centimeter region. If the molecule of interest is a free radical, Zeeman modulation may be applied to further increase sensitivity. The magnetic field strength required is moderate and may be easily produced by an external solenoid. The necessity to operate at high frequencies is not a severe limitation in terms the type of rotational spectra which may be observed. In general, the transitions of primary interest are the low J transitions. For simple molecules with small moments of inertia these transitions are usually in the millimeter region.

Lastly, in view of the existing uncertainty in the optimum methods of producing unstable molecules, a versatile molecule generating system should be constructed so that various molecular dissociation processes and chemical reaction may be tried. Flowing a stable molecule through a microwave resonant cavity, or a high temperature zone are generally reliable ways of dissociating stable species into reactive intermediates. Excited molecules may also be reacted in situ with suitable cold molecules to produce
unstable species.

A spectrometer having the general features described above has been constructed. It is now being tested.

**FUNDAMENTALS OF CONSTRUCTION**

The basic design of our spectrometer is not original. A similar apparatus has been used by Kewley et al.\(^{44(b)}\) to obtain the spectra of CS and SO. Improvements on their system have been suggested by Dr. K. V. L. N. Sastry\(^{49}\).

Methods of achieving a fast flow vacuum system are well known and the details will not be reported here. We believe molecules with half lives on the order of milliseconds can be detected in our spectrometer.

Because of the requirements of rapid throughput from the molecule source to the exhaust system, and the necessity to eliminate metal-sample reactions, our absorption cell is a 4" diameter glass tube, with teflon windows to permit the passage of the microwave beam. Overall length of the absorption cell is approximately 24". This may readily be varied if desirable.

The inlet for reactive species is directly into the absorption cell with minimal constrictions. We have readily available a 125 watt microwave generator and resonant cavity, high temperature furnaces, and an induction heater. All are easily connected to the inlet.
flow system for production of reactive species by molecular
dissociation processes. Secondary reactants may be intro-
duced at several points.

The requirement of high frequency operation presents
some special problems in radiation sources and microwave
hardware which are not encountered in the conventional micro-
wave region.

The teflon windows on the absorption cell are actually
converging lenses. High-frequency radiation from a source
whose dimensions are on the order of millimeters is
brought up to the dimensions of the absorption cell by an
S-band horn antenna, collimated by the first lens, passed
through the absorption cell, and then refocussed by the
second lens and passed through an S-band receiving horn
to the detector.

Initial attempts at obtaining reliable mm-wave sources
were concerned with the harmonic generation technique in-
troduced by King and Gordy. This method consists essentially
of inserting a non-linear crystal rectifier into a low
frequency microwave beam and taking the harmonic output as
a source of high-frequency radiation. Since the dimensions
of the rectifying element must be small in comparison to
the radiation wavelength, the construction and manipulation
of the harmonic generator are exacting. The rectifier contact
is formed by electrolytically sharpening a fine tungsten wire
(≈ .002" diameter) and lightly touching the wire to the surface of small chip of a semiconductor, such as boron-doped silicon. Detection of the high frequency radiation is similar in principle, but the detector is somewhat simpler in construction because of the absence of the fundamental frequency.

The excellent results obtained by Gordy and co-workers\textsuperscript{19,50,51} using this technique on both stable and unstable molecules are well known. However, we have found the harmonic generation technique to be extremely tedious at best. The chief problems are difficulty in identifying the principal harmonic number of the radiation from a particular rectifier contact, and a general instability of the point contacts, especially at the detector.

Recently we have obtained a klystron which oscillates in the 95-105 Kmc/sec region. It can conservatively be estimated that one day of searching with this klystron is equivalent to weeks of work using the harmonic generation technique. While harmonic generation is in principal very versatile in terms of range of output frequency, for the reasons cited above, high-frequency klystrons seem to be the most economical sources for mm-wave spectroscopy.

In the brief period that the instrument described above has been operating usefully as a spectrometer, assigned transitions belonging to the stable molecules OCS and SO$_2$
have been readily observed. Initial attempts to observe
the $S\Omega$ transition at 99299.9 Mc/sec$^9$ by passing $SO_2$ through
a microwave discharge have been unsuccessful. This is not
surprising in light of the major effort which is usually
involved in seeking the optimum conditions for production
of a reactive molecule in any particular experimental arrange-
ment. Initial failures are certainly not to be taken as
conclusive in the attempt to find new reactive species.

**PROSPECTIVE MOLECULES**

The extensive compilation by Herzberg$^{52}$ is a useful
list of reactive diatomic molecules which are known to
exist. However, the tabulated data were obtained by visible
and ultraviolet spectroscopy. It is unfortunate that present
microwave spectrometers do not approach the sensitivity ob-
tainable in optical spectroscopy.

The recent work of Carrington and Levy$^{53}$ on the gas
phase electron spin resonance spectra of $ClO$, $BrO$, and $NS$
indicate that these molecules may have detectable microwave
spectra. The ground electronic state of $ClO$ is a $^2\pi_{3/2}$ and
the $J 3/2-5/2$ transition should lie at about 96.3 Kmc/sec
(for $^{35}Cl$)$^{54}$. $^{79}BrO$ has a similar electronic structure and
the $J 5/2-7/2$ transition should occur at approximately
94.5 Kmc/sec$^{54}$. $^{14}_N^{32}S$ has a $^2\pi_{3/2}$ ground state. The $J 1/2-3/2$
transition is at 70 Kmc/sec and the $J 3/2-5/2$ is at 166 Kmc/sec$^{55}$.  

The molecule $S_2$ exists as the predominant species in low pressure sulfur vapor at about $500^\circ C$. It may be possible to obtain sufficient concentrations of $S_2$ by flowing sulfur vapor through a hot tube furnace. The transitions are magnetic dipole ($^3\Sigma$ ground state) as in oxygen. While the transitions are expected to be weaker than those in oxygen, they may be observable, since $^{16}O^{17}O$ was studied with a sample $\approx 1\%$ enriched in $^{17}O$.

There are many other species which may have detectable microwave spectra. While searching for these new species is difficult and uncertain, the new information which may be gained is of great value.
APPENDIX I

Nucleus 2 Matrix Elements Diagonal in Nτ

\[ <N^\tau S^\tau I^\tau_1 F^\tau_1 I^\tau_2 F^\tau_1 | H_f(2) | N^\tau S^\tau I^\tau_1 F^\tau_1 I^\tau_2 F^\tau_1> \]

\[ = (-1)^{N+S+2J^\tau_1 +I^\tau_1 +2F^\tau_1 +I^\tau_2 +F^\tau_1} \]

\[ 1/4 [ (2F^\tau_1 +1)(2F^\tau_1 +1)(2J^\tau_1 +1)(2J^\tau_1 +1)(2S)(2S+1)(2I^\tau_2) \]
\[ (2I^\tau_2 +1)(2I^\tau_2 +2) ]^{\frac{1}{2}} \]

\[ \cdot \left\{ \begin{array}{ccc}
F^\tau_1 & F^\tau_1 & 1 \\
I^\tau_2 & I^\tau_2 & F
\end{array} \right\} \cdot \left\{ \begin{array}{ccc}
J^\tau_1 & J^\tau_1 & 1 \\
F^\tau_1 & F^\tau_1 & I
\end{array} \right\} \cdot \left\{ \begin{array}{ccc}
S & S & N
\end{array} \right\} \]

\[ <N^\tau S^\tau I^\tau_1 F^\tau_1 I^\tau_2 F^\tau_1 | H_{dd}(2) | N^\tau S^\tau I^\tau_1 F^\tau_1 I^\tau_2 F^\tau_1>^a \]

\[ = (-1)^{J^\tau_1 +I^\tau_1 +2F^\tau_1 +I^\tau_2 +F^\tau_1} \sum I^\tau_2 \]

\[ 1/8 \left[ \frac{30(2F^\tau_1 +1)(2F^\tau_1 +1)(2J^\tau_1 +1)(2J^\tau_1 +1)(2I^\tau_2 +1)(2I^\tau_2 +1)}{(2N-1)(2N+3)(2N+1)} \right] \]

\[ \times (2S)(2S+1)(2S+2)(2N)(2N+2) \]

\[ \cdot \left\{ \begin{array}{ccc}
F^\tau_1 & F^\tau_1 & 1 \\
I^\tau_2 & I^\tau_2 & F
\end{array} \right\} \cdot \left\{ \begin{array}{ccc}
J^\tau_1 & J^\tau_1 & 1 \\
F^\tau_1 & F^\tau_1 & I
\end{array} \right\} \cdot \left\{ \begin{array}{ccc}
N & N & 2
\end{array} \right\} \]
\[
\langle NTSJ'_{I_1} F_1 I_2 F | H_q (2) | NTSJI_{I_1} F_1 I_2 F \rangle
\]

\[
= (-1)^{N+S+J+J'+I_1+2F_1+I+F} \sum_{Q_2} \frac{(2F_1+1)(2F_1'+1)(2J+1)(2J'+1)(2I_2+1)(2I_2+2)(2I_2+3)}{(2N-1)(2N+3)(2N+1) \times (2I_2)(2I_2-1)(2N)(2N+2)}^{1/4}
\]

\[
\cdot \left\{ \begin{align*}
N & N 2 \\
J' & J 2
\end{align*} \right\} \cdot \left\{ \begin{align*}
F_1 & F_1 2 \\
F_1 & F_1 1
\end{align*} \right\} \cdot \left\{ \begin{align*}
I_2 & I_2 F
\end{align*} \right\}
\]

\[\text{2 The } \sum \text{'s are defined in Appendix I, reference (23). They are functions of the coupling constants, } N, \text{ and the rotational constants of the molecule.}\]
APPENDIX II

$H_{sr}$ and $H_{dd}(1)$ Matrix Elements Off-Diagonal in $N\tau$

\[ <N+1K_{-1}^{Y}SJ_{1}^{I_{1}}F_{1}^{I_{2}}F|H_{sr}|NK_{-1}^{Y}SJ_{1}^{I_{1}}F_{1}^{I_{2}}F> \]

\[ = \frac{-3K[(N+1)^2-K^2]^k}{4(N+1)} \{(aa)_s + (-1)^{N-1K} \frac{N_{J_{1}}^{k}}{6(N+1)(2(cc)_s + (aa)_s)} \} \]

\[ <N+1K_{-1}^{Y}SJ_{1}^{I_{1}}F_{1}^{I_{2}}F|H_{dd}(1)|NK_{-1}^{Y}SJ_{1}^{I_{1}}F_{1}^{I_{2}}F> \]

\[ = [J(J-1) + I_1(I_1+1) - F(F+1)] 3K[(N+1)^2-K^2]^k \]

\[ \{(aa)_{I_1} + (-1)^{N_{J_{1}}^{k}} \frac{N_{J_{1}}^{k}}{6(N+1)(2(cc)_{I_1} + (aa)_{I_1})} \} \]

\[ = \frac{2(2N+1)(2N+3)(N+1)}{2(2N+1)(2N+3)(N+1)} \]

\[ <N+1K_{-1}^{Y}SJ_{1}^{I_{1}}F_{1}^{I_{2}}F|H_{dd}(1)|NK_{-1}^{Y}SJ_{1}^{I_{1}}F_{1}^{I_{2}}F> \]

\[ = (-1)^{J_{-}^{I_{1}}+F} \frac{5I_1(I_1+1)(2I_1+1)(2J_{-1})^k}{6(N+2)(N)} \]

\[ \left\{ \begin{array}{c} J_{-1} J_+ 1 \\ I_1 I_1 F_1 \end{array} \right\} \left\{ \begin{array}{c} N+1 N 2 \\ S S 1 \end{array} \right\} \]
\[<N-1K_{-1}^{S}J_{-}I_{1}F_{1}I_{2}F|H_{dd}(1)|NK_{-1}^{S}J_{+}I_{1}F_{1}I_{2}F>\]

\[= (-1)^{J_{-}+I_{1}+F_{1}+F_{2}}[N^{2}-K^{2}]^{\frac{1}{2}}K\{(aa)_{I_{1}}(-1)^{N-1}\frac{I_{1}}{6}N(2(cc)_{I_{1}}+(aa)_{I_{1}})\}
\]

\[
\begin{bmatrix}
5I_{1}(I_{1}+1)(2I_{1}+2)(2J_{-}+1) \\
6(n-1)(n+1)
\end{bmatrix}
\]

\[
\begin{bmatrix}
J_{-} & J_{+} & 1 \\
I_{1} & I_{1} & F_{1}
\end{bmatrix}
\begin{bmatrix}
N-1 & N & 2 \\
S & S & 1 \\
J_{-} & J_{+} & 1
\end{bmatrix}
\]

\[a\] See reference (22), Appendix.
APPENDIX III
Spectrum of $^{14}_N^16O^{17}_0$ Observed by Hodgeson

19  741.9 Mc/sec
19  801.1
19  853.7
19  860.2
19  881.9
19  885.7
19  901.6
19  913.4
19  918.5
19  938.2
19  960.5
20  014.4
20  113.2
20  154.1
20  181.8
20  219.3
20  266.8

a Appeared as closely spaced doublet or triplet of lines. The frequency given is that of the strongest member.
APPENDIX IV

Diagnostic Least Squares

In the usual method of least squares on a nonlinear system, the equations of condition may be written as

\[ Ax = a \]  \hspace{1cm} (A1)

where \( A \) is the matrix of derivatives, \( x \) is a vector of parameter changes to be determined and \( a \) is the vector of initial differences between observation and calculation. Then

\[ x = B^{-1}b, \]  \hspace{1cm} (A2)

where \( B = AA \) and \( b = Ax \). If one then iterates with

\[ x(1) = x(0) + B^{-1}b, \quad a(1) = obs - calc(1), \quad \text{and } A(1), \]

convergence of the system reduces the sum of the squares of the residuals to a minimum.

In the diagnostic method an orthogonal transformation \( 0 \) is found which diagonalizes \( B \). Then

\[ OBO^* = \lambda_i \]  \hspace{1cm} (A3)

where the \( \lambda_i \) are the eigenvalues of \( B \). Equation (A2) becomes

\[ y_i = \frac{c_i}{\lambda_i} \]  \hspace{1cm} (A4)

where \( y = 0x \) and \( c = Ob \). The \( y_i \) are eigenvectors of \( B \).

\* \( \lambda_i \) should not be confused with the hyperfine energy level index \( \lambda \).
and are orthogonal. It is then possible to carry out the least squares process in a stepwise fashion.

The smallest eigenvalue of $B$ will be associated with the most poorly determined eigenvector. If the eigenvalues of $B$ are arranged in decreasing order, then the parameter changes ($\delta y_1$) associated with the largest eigenvalue ($\lambda_1$) can be used to calculate $c_2$ (i.e., $0b$), and the process repeated for $\lambda_2$. It should be emphasized that the process is a full least squares if carried to completion, but if terminated because of the presence of a small eigenvalue $\lambda_s$ no least squares fit is obtained. However, by knowing $x_s$ (i.e., $\delta y_s$) some information has been gained about which particular linear combination of parameters is poorly determined by the data.
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