MICROWAVE ABSORPTION STUDIES OF ACETONE, CHLOROFORM,
AND HYDROGEN CYANIDE VAPORS

Dissertation

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By

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1951

Approved by:

[Signature]
Adviser
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MICROWAVE ABSORPTION STUDIES OF ACETONE, CHLOROFORM, AND HYDROGEN CYANIDE VAPORS

I. Introduction

Microwave spectroscopy had its beginning at the University of Michigan in 1933 where Cleeton and Williams\(^1\) investigated the

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absorption of ammonia in the 1.25 cm. region. Very little work was done in the field until after the second World War when microwave instruments and techniques developed for radar became available for pure research. Since that time interest in this field of spectroscopy has grown rapidly. At the present time microwave spectroscopy is being carried on at many of our leading universities, and hundreds of papers have been published on this subject.

The microwave region of the electromagnetic spectrum extends in wavelength from approximately 2 mm. to 50 cm. One of the great advantages of this type of spectroscopy is that spectral lines separated in frequency by less than 1 mc./sec. can be resolved, making possible the measurement of very small energy differences between quantized states. Microwave spectroscopy is therefore an ideal tool for studying the hyperfine structure of spectral lines. From this hyperfine structure it is possible to determine nuclear spins and nuclear quadrupole couplings.
By far the largest number of spectral lines in the microwave region are produced by transitions between rotational energy levels of molecules; however, investigation of this new region of the spectrum has led to the discovery of new types of spectral lines as well. The most notable example of this is the inversion spectrum of ammonia.

This dissertation will discuss the rotational spectrum of acetone and chloroform, and pure $J$-type doubling transitions in hydrogen cyanide. The latter is a new type of transition which was not observed until the advent of microwave spectroscopy and will be the principal topic of the dissertation. The experimental method will be discussed in the following section. Sections III, IV, and V deal with the individual molecules; in each case a discussion of the observed spectrum and a theoretical explanation are given. Experimental details of interest primarily to members of this laboratory are given in Appendix II.
II. The Experimental Method

All the spectral lines reported in this dissertation were observed with a Stark modulated microwave spectograph. A discussion of the Stark effect for linear and symmetric top molecules is given in Appendix I. In order to understand the principle of this type of modulation one need only know that a rotational energy level of a molecule is split into several closely spaced levels by placing this molecule in an electric field. Consequently a spectral line arising from a transition involving this energy level is split into a number of weaker components by the application of an electric field. This phenomenon has been used as a means of modulation in the spectrograph described below.

A block diagram of the microwave spectrograph used in this laboratory is shown in Figure 1. The apparatus actually used in the observation of a spectral line occupies the lower half of this diagram. The source of microwave radiation is the klystron "B". The motor produces a mechanical deformation of the klystron cavity slowly changing its frequency. When this frequency corresponds to that of a spectral line of the gas contained in the cell, an absorption of the microwave energy detected by the crystal "X₂" takes place. The 6kc square wave applied to the Stark electrode produces an electric field which is practically uniform throughout the waveguide absorption cell for one half the cycle and is zero for the other half. The spectral line therefore exists as a single line for one half the cycle and is split
FIGURE 1. THE SPECTROGRAPH
into a weaker line plus a number of Stark components during the other half cycle. This produces a 6kc modulation of the microwave energy detected by the crystal "X2". The narrow band amplifier selects this 6kc component of the crystal signal and, after amplification and rectification, applies it to the recorder. Therefore, as the klystron frequency is varied continuously through a region of the spectrum containing absorption lines of the gas in "cell B", the recorder will trace out these spectral lines and their Stark components. The use of this type of modulation and a narrow band amplifier increases the signal to noise ratio of the spectrograph in a manner inversely proportional to the band pass.

The method of frequency measurement employed here is that of Rogers, Cox, and Braunschweiger\(^2\). This method involves the use of a second spectrograph as shown in Figure 1. The klystron "A", which is the microwave energy source for this second spectrograph, is frequency modulated by the application of a 60 cycle/sec. sawtooth voltage to its repeller. The amplitude of this sawtooth voltage is adjusted to obtain a 60 cycle/sec. sweep of frequency over a range of about 20 mc/sec.

The midpoint of this frequency interval can be varied by mechanical tuning of the klystron.
By applying the sawtooth modulation voltage to the horizontal deflection plates of a cathode ray oscilloscope and the output of the detecting crystal "X₁" to the vertical plates, a plot of signal reaching "X₁" versus frequency is obtained. If this frequency interval contains a spectral line of the gas in "cell A", this line will appear on the oscilloscope as a sharp decrease in signal reaching "X₁". While this type of spectrograph is not as sensitive as the one described previously, it is sufficiently sensitive for the detection of the inversion lines of ammonia.

By filling "cell A" with ammonia one can use the carefully measured inversion lines of this molecule as frequency standards for the measurement of the frequency of "klystron B". In order to do this a small amount of power is coupled off each waveguide and applied to the crystal mixer "X₃". The resulting beat frequencies are detected by a communications receiver the output of which is displayed on the oscilloscope along with the ammonia line. The display of two signals on the screen of a single beam cathode ray oscilloscope has been accomplished by the use of an electronic switch as shown in Figure 1. Whenever one of the beat frequencies from the crystal "X₃" corresponds to \( f_R \), the frequency to which the receiver is tuned, a "pip" appears on the scope. If this "pip" coincides with the ammonia line on the screen of the oscilloscope, the unknown frequency \( f_B \) can be obtained from the relation

\[
f_R = \pm M(f_A - f_B)
\]

where \( f_A \) is the ammonia line frequency.
If \( f_R \), as given by the preceding equation, is outside the frequency range of the receiver, then the output of a harmonic generator operated from a 30 mc/sec. oscillator is applied to the crystal mixer "X3" as shown in Figure 1. The frequency \( f_B \) is then obtained from the relation

\[
f_R = \pm m(f_A - f_B) \pm nf_C
\]

where \( f_C \) is the exact frequency of the 30 mc/sec. crystal controlled oscillator. The integers "m" and "n" can be obtained by making a rough determination of the frequency \( f_B \) using a calibrated wavemeter.

By this method one can determine the frequencies of observed spectral lines to within about 0.1 mc/sec.. This method was used for the frequency determination of the lines reported in the following sections. The particular ammonia line used as a standard in each case is given in the Appendix.
III. The Microwave Spectrum of Acetone Vapor

The microwave spectrum of acetone has been observed in this laboratory for the frequency range 18,000 mc/sec. to 30,000 mc/sec. The observed spectrum consists of four strong lines, tracings of which are found in Figures 2, 3, 4, and 5. The relative intensities of these lines are indicated roughly by their heights as plotted in Figure 7. The lines show no Stark effect indicating that the number of Stark components was so large that the individual intensities were very small. The 17 lines in the region 22,000 mc/sec. to 25,000 mc/sec. reported by Bak3 were not observed. These lines must therefore be very much weaker than the four reported here.

An attempt has been made to interpret this spectrum as originating from transitions between rotational levels of an asymmetric top. The acetone molecule is a very complicated asymmetric top, and the inter-nuclear distances and bond angles are not very accurately known. It was therefore realized from the beginning that, unless this proved to be an unusual case, interpretation of the spectrum would be very difficult.

Figure 2. The acetone spectral line at 26,661.5 mc/sec
Figure 3. The acetone spectral line at 28,340.0 mc/sec
Figure 4. The acetone spectral line at 28,622.3 mc/sec
Figure 5. The acetone spectral line at 30,070 mc/sec
The Asymmetric Rotator

The problem of the rotator has been discussed by many authors. The treatment given here will be that of translating the classical rotator problem into quantum mechanics and solving it by the method of King, Hainer, and Cross.\(^4\)

\[4. \text{G. W. King, R. M. Hainer, Paul C. Cross, J. Chem. Phy. 11, 27 (1943).}\]

The quantum mechanical Hamiltonian for the rotator is identical in form to the classical expression

\[\mathcal{H} = \frac{1}{2} \left[ \frac{P_a^2}{I_a} + \frac{P_b^2}{I_b} + \frac{P_c^2}{I_c} \right], \quad (1)\]

where \(P_a, P_b, P_c\) are the components of total angular momentum directed along the body fixed principal axes of inertia. The classical relations

\[P_a^2 + P_b^2 + P_c^2 = P^2 = \text{const.}\]

and the Poisson brackets

\[\left[ P_\alpha, P_\beta \right] = P_\gamma\]

translate into quantum mechanics as

\[\frac{P_a^2}{I_a} + \frac{P_b^2}{I_b} + \frac{P_c^2}{I_c} = P^2 \quad (2)\]

and the commutation relation

\[P_\alpha P_\beta - P_\beta P_\alpha = -\hbar P_\gamma, \quad (3)\]
where $\hbar$ is Planck's constant $\hbar$ divided by $2\pi$.

In equation (2) suppose that $I_a \leq I_b \leq I_c$, and let

$$a = \frac{\hbar^2}{2I_a}, \quad b = \frac{\hbar^2}{2I_b}, \quad c = \frac{\hbar^2}{2I_c}.$$ 

The constants $a$, $b$, and $c$ as defined here are those used by King, Hainer, and Cross. They are not the rotational constants ordinarily encountered in molecular spectroscopy, defined as,

$$A = \frac{\hbar}{8} I_a, \quad B = \frac{\hbar}{8} I_b, \quad C = \frac{\hbar}{8} I_c.$$ 

One should note that if $a \neq b \neq c$ the rotator is an asymmetric top; if $a = b$ it is an oblate symmetric top, and if $b = c$ it is a prolate symmetric top.

In view of this definition of $a$, $b$, and $c$ the Hamiltonian will become,

$$H = \frac{1}{\hbar^2} \left( a P_a^2 + b P_b^2 + c P_c^2 \right). \quad (4)$$

In this expression $P_a$, $P_b$, and $P_c$ may be any set of angular momentum operators which satisfy the commutation relations (3). If $a$, $b$, and $c$ is a right handed coordinate system, there are three ways of identifying $P_a$, $P_b$, and $P_c$ with $P_x$, $P_y$, and $P_z$.

The commutation relations (3) for $P_x$, $P_y$, and $P_z$ are,

$$P_x P_y - P_y P_x = -i\hbar P_z,$$

$$P_y P_z - P_z P_y = -i\hbar P_x,$$ 

and $$P_z P_x - P_x P_z = -i\hbar P_y.$$ 

(5)
The non-vanishing matrix elements of the angular momentum operators are

\[
(J, K | P_j | J, K \pm 1) = \mp i (J, K | P_{\pm} | J, K \pm 1) = \\
1/2 \hbar \left[ J(J + 1) - K(K + 1) \right]^{1/2}
\]

and

\[
(J, K | P_z | J, K) = \hbar K,
\]

where \( K \) assumes the integral values \(-J\) to \(+J\). These are the angular momentum matrices of a symmetric top for which the quantum number \( J \) defines the square of the total angular momentum as \( P^2 = \hbar^2 J(J + 1) \), and the quantum number \( K \) specifies the component of \( P \) along the molecular symmetry axis \( z \) as \( P_z = \hbar K \). This solution is the one which diagonalizes \( P_z \) and \( P^2 \) and corresponds to the wave functions chosen by Wang,\(^5\) Mulliken,\(^6\) and Van Vleck.\(^7\) The non-vanishing matrix elements of the squares of the angular momenta will be

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\[
(J, K | P_j^2 | J, K) = (J, K | P_{\pm}^2 | J, K) = 1/2 \hbar^2 \left[ J(J + 1) - K^2 \right],
\]

\[
(J, K | P_z^2 | J, K \pm 2) = -(J, K | P_z^2 | J, K \pm 2) = \\
1/4 \hbar^2 \left[ \left[ J(J + 1) - K(K + 1) \right] \left[ J(J + 1) - (K \pm 1)(K \pm 2) \right] \right]^{1/2}
\]

\[
(J, K | P_z^2 | J, K) = \hbar^2 K^2,
\]

\[
(J, K | P_z^2 | J, K) = \hbar^2 J(J + 1)
\]
Calculation of the energies of the rotator is greatly facilitated by a change of variable, the purpose of which will become obvious later. According to equation (4) the energy of a rotator with rotational constants $a$, $b$, and $c$ is

$$ E(a, b, c) = \frac{1}{\hbar^2} (a P_a^2 + b P_b^2 + c P_c^2) \quad (7) $$

If the rotational constants $a$, $b$, $c$ are replaced by $(\sigma a + \rho)$, $(\sigma b + \rho)$, and $(\sigma c + \rho)$, where $\sigma$ and $\rho$ are scalar factors, then the energy becomes,

$$ E(\sigma a, \sigma b, \sigma c) = \frac{1}{\hbar^2} \left[ (\sigma a + \rho)P_a^2 + (\sigma b + \rho)P_b^2 + (\sigma c + \rho)P_c^2 \right] $$

or, $E(\sigma a, \sigma b, \sigma c) = \frac{1}{\hbar^2} \left[ (\sigma a + \rho)P_a^2 + (\sigma b + \rho)P_b^2 + (\sigma c + \rho)P_c^2 \right] .

With the aid of equations (2), (6a) and (7) this last equation is seen to be,

$$ E(\sigma a + \rho, \sigma b + \rho, \sigma c + \rho) = \sigma E(a, b, c) + \rho J(J + 1). \quad (8) $$

One may now define

$$ \sigma = \frac{2}{a - c} $$

$$ \rho = -\frac{a + c}{a - c} ; $$
then

\[ \sigma a + \sigma = \frac{2a}{a - c} - \frac{a + c}{a - c} = 1 , \]

\[ \sigma b + \sigma = \frac{2b}{a - c} - \frac{a + c}{a - c} = \frac{2b - a - c}{a - c} = \kappa , \]

\[ \sigma c + \sigma = \frac{2c}{a - c} - \frac{a + c}{a - c} = -1 , \quad (9) \]

and the parameter $\kappa$ takes values $-1 \leq \kappa \leq 1$. The parameter $\kappa$ expresses the degree of asymmetry of the rotator. For an oblate symmetric top $b = a$, and equation (9) gives $\kappa = 1$. For a prolate symmetric top $b = c$, and $\kappa = -1$. In the case of the most asymmetric top, where $b$ is the arithmetical average of $a$ and $c$, the parameter $\kappa = 0$.

After substitution of the relations (9) into equation (8) this equation becomes,

\[ E (\kappa) = (1, \kappa, -1) = \frac{2}{a - c} E (a b c) - \frac{a + c}{a - c} J(J + 1) \]

Solving this equation for $E (a b c)$ one gets,

\[ E (a b c) = 1/2 (a - c) E (\kappa) + 1/2 (a + c) J(J + 1) \]

or

\[ E (a b c) = 1/2 (a - c) E (\kappa) + 1/2 (a + c) J(J + 1) . \quad (10) \]

This equation expresses the energies of a rotator with rotational constants $(a, b, c)$ in terms of the quantities $E (\kappa)$. The quantities $E (\kappa)$ are numerically equal to the energies in ergs.
of a rotator with rotational constants \((1, \kappa, -1)\); however, they are dimensionless. The energy \(E_{\kappa}^J(a, b, c)\) has therefore the same dimensions as \(a\), \(b\), and \(c\).

It is possible to solve for the quantities \(E_{\kappa}^J(\kappa)\) once and for all, and afterward to be able to compute the energies of any rotator with the same asymmetry parameter \(\kappa\) simply by addition and multiplication. Since it is possible to show that \(E_{\kappa}^J(\kappa) = -E_{\kappa}^{-J}(\kappa)\) one need be concerned only with values of \(\kappa\) between \(-1\) and \(0\) instead of the complete range \(-1\) to \(+1\).

The Hamiltonian \((4)\) for \((a, b, c)\) equal to \((1, \kappa, -1)\) is

\[
H(\kappa) = \frac{1}{\kappa^2} (a^2 + \kappa \frac{P_b^2}{P_c^2} - \frac{P_a^2}{P_c^2}).
\]

With the matrix elements \((6)\) one can compute the energy matrix which will have elements

\[
(J, K | H(\kappa) | J, K),
\]

and

\[
(J, K | H(\kappa) | J, K \pm 2).
\]

This matrix is diagonal in \(J\) and splits up into submatrices, one for each value of \(J\). Each submatrix will have \(2J + 1\) rows and columns. When the submatrices are diagonalized the energies will appear as the diagonal elements. These diagonal elements are the roots of the secular determinant

\[
\left| (J, K | H(\kappa) | J, K') - \lambda J_{KK}' \right| = 0.
\]

The secular determinant may be factored into two submatrices by
arranging rows and columns so that elements of even \( J \) stand together
and elements of odd \( J \) stand together. These two submatrices may
again be factored by introducing the wave functions \( (1/2)^{1/2} \left[ \psi(J) \pm \psi(-J) \right] \)
in the place of \( \psi(J) \) and \( \psi(-J) \). The values of \( H^J_c(\kappa) \) are then
found by solving for the roots of the resulting four determinants.
For high \( J \) values one cannot find an exact solution for these roots.
King, Hainer and Cross\(^4\) have been able to express them in terms of a
continued fraction. As mentioned earlier there are three ways of
identifying a right-handed system \( a \ b \ c \) with \( x \ y \ z \), and the convergence
of the continued fraction will be affected by this identification.

King, Hainer and Cross\(^4\) have tabulated values of \( H^J_c(\kappa) \) for
\( J = 0 \) to \( J = 10 \) and for values of \( \kappa \) throughout the range \( \kappa = -1 \)
to \( \kappa = 0 \) at intervals of 0.1. The energies up to \( J = 10 \) of any
asymmetric rotator can be approximated by the use of this table and
equation (10).

The selection rules of the asymmetric rotator can be determined
from the symmetry classification of the rotational eigenfunction \( \psi_r \).

\( \psi_r \) is a function of the orientation of the principal axes \( a, b, c \)
with respect to a fixed coordinate system. Because of the symmetry
of the momental ellipsoid, an orientation which differs from a given
one by a rotation through 180° about one of the axes must have the
same probability and therefore the same \( |\psi_r|^2 \). This means that
\( \psi_r \) must remain unchanged or only change in sign for rotation of
180° about the axes \( a, b, c \). These rotations of 180° about \( a, b, c \)
will be designated by \( c^2_a, c^2_b, c^2_c \). The rotational levels of an
asymmetric top may be distinguished by their behavior (+ or −) with respect to the three operations $C^a_2$, $C^b_2$, $C^c_2$. Since any one of these operations is equivalent to the other two carried out in succession, the behavior of the levels will be completely specified by the rotations $C^c_2$ and $C^a_2$. There are four different species of levels described by ++, +−, −+, −−, where the first sign refers to the behavior with respect to $C^c_2$ and the second to the behavior with respect to $C^a_2$. It will be remembered that for a particular value of $J$ the secular determinant for $E (\kappa)$ separates into four submatrices. The four different species of levels correspond to the roots of the determinants of the four submatrices.

It has been shown by Dennison\(^8\) that the highest level $J_{+j}$ for a given $J$ is + with respect to $C^c_2$, the two next highest −, the two next are +, and so on. The lowest level $J_{-j}$ is + with respect to $C^a_2$, the two next higher −, the two next +, and so on. This behavior is connected with the fact that as $b \rightarrow a$ the symmetry of $\psi$ with respect to the operation $C^c_2$ must correspond to that of an oblate symmetric top and as $b \rightarrow c$ it must correspond to that of a prolate symmetric top.

For an asymmetric molecule with a permanent dipole moment the

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\(^8\) D. M. Dennison, Rev. Mod. Phys. 3, 280 (1931).
selection rule for $J$ is $^9 \triangle J = 0, \pm 1$. If the molecule has no


symmetry, the permanent dipole moment will in general not coincide
with or be perpendicular to any of the principal axes. In this case,
the only restriction is that levels of the same symmetry do not

\[ + + \leftrightarrow + + \rightarrow + , \quad + - \leftrightarrow + - \rightarrow + , \quad - + \leftrightarrow + + \rightarrow . \]

If the dipole moment lies in the axis of least moment of inertia
(a axis) only the transitions

\[ + + \rightarrow + - \quad \text{and} \quad + - \rightarrow + - \]

can take place. If the dipole moment lies along the axis of inter-
mediate moment of inertia (b axis), only the transitions

\[ + + \rightarrow + - \quad \text{and} \quad + - \rightarrow + + \]

can take place. If the dipole moment lies along the axis of largest
moment of inertia (c axis) only the transitions

\[ + + \leftrightarrow + - \quad \text{and} \quad - + \leftrightarrow + - \]

can take place. An example of level classification and allowed
transitions is given in Figure 6. The transitions indicated are
those for the case of the dipole moment lying along the axis of
intermediate moment of inertia. These energy levels have not been
drawn to scale.
With the aid of these selection rules and the energy levels calculated by use of the tables of King, Hainer, and Cross, the spectrum of an asymmetric top molecule can be predicted. This spectrum ordinarily contains a great many lines and, unless the molecule is very nearly symmetric, interpretation of the spectrum is extremely difficult.

The acetone molecule is assumed to have the structure shown below.

The interatomic distances and angles have been assumed to be:

- C — C \(1.573\) Å
- C — O \(1.225\) Å
- C — H \(1.0936\) Å
- \(<\text{C}=\text{C}=\text{O}\) 123°
- \(<\text{H}-\text{C}-\text{H}\) 112° 12'
No infrared data on bond distances and angles are available for this particular molecule. The above distances and angles are those given by Herzberg\textsuperscript{10} for similar bonds in other molecules. The orientation of the CH\textsubscript{3} group is not known. For the purpose of the calculation of the rotational constants it will be assumed that its center of mass lies on the line connecting the carbon atoms and that the total mass of this group is concentrated at this center of mass.

With the assumptions made above the rotational constants are

\[
\begin{align*}
    a &= 10.662 \text{ mc/sec.} \\
    b &= 8.823 \text{ mc/sec.} \\
    c &= 4.554 \text{ mc/sec.}
\end{align*}
\]

and the asymmetry parameter \( \kappa = 0.3978 \). The number of significant figures retained above is by no means justified. Available data on bond distances show as much as a 5\% variation. For this reason it was considered unnecessary to make the interpolation for \( \kappa = 0.3978 \), and \( \kappa \) has been rounded off to 0.4 in order that the tables of King, Hainer, and Cross\textsuperscript{4} could be read directly.
The predicted spectrum for values of $J$ up to $J = 6$ showed 23 lines in the region observed. The predicted and observed lines are listed below and plotted in Figure 7.

<table>
<thead>
<tr>
<th>Predicted $m_c$</th>
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<td>26,661.5</td>
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<tr>
<td>21,052</td>
<td>28,206</td>
<td>28,340.0</td>
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<tr>
<td>21,354</td>
<td>29,378</td>
<td>28,622.3</td>
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<tr>
<td>22,005</td>
<td>30,350</td>
<td>30,070</td>
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<tr>
<td>25,415</td>
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</tbody>
</table>

There is no obvious agreement between the predicted and observed lines for these low $J$-values. Moreover the level populations and transition probabilities for an asymmetric molecule of this size are such that one can expect relatively intense lines for $J$-values as high as $J = 30$. Obviously the number of lines predicted would be very large. While it is possible to calculate the energy levels up
FIGURE 7. THE SPECTRUM OF ACETONE

PREDICTED SPECTRUM

OBSERVED SPECTRUM
to such high values of \( J \), the errors involved because of inexact molecular constants (distances and angles) and approximations concerning the molecular model become excessive. Since the spectral lines depend on small differences between levels which are very in-exactly known, it becomes impossible to make accurate predictions. Therefore there is little hope of identifying the four observed lines for acetone. The fact that no Stark components were observed indicates that the \( J \)-values are high, as mentioned earlier. All these lines were observed to increase in intensity when the absorption cell was cooled with dry ice. This indicates that the \( J \)-values are probably less than 35.

While these lines have given us no information about the molecule itself, the absorption spectrum of such a widely used substance as acetone is of some value. For instance, these strong spectral lines would serve as a means of identifying acetone. The lines can also be used as frequency standards for the calibration of a wavemeter.
IV. The Microwave Spectrum of Chloroform

The microwave spectrum of chloroform has been investigated by Smith and Unterberger. These observers reported a line 21 mc/sec. wide centered at a frequency of 26,417 mc/sec. A further investigation of this spectrum was undertaken with the dual purpose of obtaining a more exact value of the rotational constant and of analyzing the hyperfine structure of this line due to the chlorine quadrupole interactions.

The observations of Smith and Unterberger were made at a pressure of 0.1 mm of Hg. By reducing the pressure to about 0.01 mm a line 4 mc/sec. wide centered at 26,416.6 mc/sec. was recorded. The intensity of this line was increased by cooling the absorption cell with dry ice; the observed line appears in Figure 8. An attempt to resolve the hyperfine structure of this line by further reducing the pressure was unsuccessful. When the pressure was reduced to 0.001 mm of Hg, the intensity of the line was reduced with little effect on the line width as shown in Figure 9. Upon still further reduction of pressure the line disappeared completely.

The spectrum of a symmetric top molecule such as chloroform can be easily obtained by a slight modification of the equations of the last section.
Figure 8. The chloroform line at a pressure of 0.01 mm of Hg.
Figure 9. The chloroform line at a pressure of 0.001 mm of Hg.
The Symmetric Rotator

The Hamiltonian for a symmetric rotator can be obtained from equation (4) by setting \( a = b \).

\[
H = \frac{1}{\hbar^2} \left( b P_a^2 + b P_b^2 + c P_c^2 \right)
\]

If one now makes the identification

\[
P_a = P_x, \quad P_b = P_y, \quad P_c = P_z
\]

this Hamiltonian becomes

\[
H = \frac{1}{\hbar^2} \left[ b(P_x^2 + P_y^2) + c P_z^2 \right] \tag{12}
\]

With the aid of the matrix elements (6) one can easily compute the energy matrix

\[
(J,K \mid H \mid J,K) = b \left[ J(J+1) - K^2 \right] + c K^2
\]

This matrix is diagonal in both \( J \) and \( K \) and the energies of the symmetric top are the diagonal elements.

\[
E(J,K) = b J(J+1) + (c - b) K^2 \tag{13}
\]

If the dipole moment of the symmetric top lies along the symmetry axis as is the usual case, the selection rules are

\[
\Delta J = 0, \pm 1, \quad \Delta K = 0.
\]
The absorption frequencies are easily obtained by subtraction as,

\[ \nu = E(J + 1) - E(J) = b(J + 1)(J + 2) - b J(J + 1) \]

or

\[ \nu = 2b(J + 1) \]  \hspace{1cm} (14)

The rotational spectrum of a symmetric top is therefore very simple when one neglects centrifugal stretching as has been done here.

The chloroform molecule has the structure shown below.

![Chloroform molecule diagram]

The interatomic distances and angles are the following:

\[ \begin{align*}
&\text{C} \quad \text{-} \text{Cl} \quad 1.77 \pm 0.02 \ \text{Å} \\
&\text{C} \quad \text{-} \text{H} \quad 1.09 \ \text{Å} \\
&\angle \text{Cl} - \text{C} - \text{Cl} \quad 112^\circ \pm 2^\circ
\end{align*} \]

The C — Cl distance and the Cl — C — Cl angle have been obtained from electron diffraction data. \(^\text{12}\) The C — H distance is that given

---

by Herzberg. The rotational constant \( b \), for \( \text{CHCl}_3^{35} \), calculated from these data is

\[
b_{\text{cal.}} = 3.250 \pm 75 \text{ mc/sec.}
\]

If the spectral line at 26,416.6 mc/sec. is identified as the \( J = 3 \) to \( J = 4 \) transition, the resulting value of \( b \) is 3,302.07 \( \pm \) 0.02 mc/sec. Therefore the measured value of \( b \) falls within the limits of the calculated value. The measured value of \( b \) corresponds to a moment of inertia

\[
I_b = 254.1 \times 10^{-40} \text{ gm. cm.}^2
\]

The value of the rotational constant obtained from this measurement,

\[
b_{\text{obs.}} = 3,302.07 \pm 0.02 \text{ mc/sec.}
\]

should be considerably more accurate than that reported by Smith and Unterberger since the spectral line from which it is derived is only one-fifth as broad as the line used in their calculations.

The width of this spectral line can be attributed to the fact that it consists of a number of components spread over a region four megacycles wide. The existence of these components is a result of the interaction of the quadrupole moments of the chlorine nuclei with the electric field gradient. The change in energy due
to this type of interaction has been given by Coles and Good\textsuperscript{13} for

\begin{equation}
W = eQ \frac{3J^2}{2J^2} \left[ \frac{3K^2}{J(J+1)} - 1 \right] \left[ \frac{(3/4)C(C + 1) - I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)} \right]
\end{equation}

where

\begin{itemize}
\item \(C = F(F + 1) - I(I+1) - J(J+1)\)
\item \(e = \) electronic charge
\item \(Q = \) quadrupole moment of the nucleus
\item \(V = \) electrostatic potential produced by all
\begin{itemize}
\item charges in the molecule except those inside
\item a small sphere surrounding the nucleus
\end{itemize}
\item \(z = \) coordinate along the molecular axis of
\item symmetry
\item \(I = \) nuclear spin
\item \(F = \) total angular momentum quantum number
\item obtained by vector addition of \(J\) and \(I\).
\end{itemize}

In equation (15) \(F\) takes integral values between \(|J-I|\) and
\(|J+I|\), and the product \(eQ \frac{3J^2}{2J^2}\) is called the quadrupole coupling. By substituting the allowed values of \(F\) into this equation one can calculate the splitting of the energy levels in terms of the quadrupole coupling. With the aid of the selection rules
\[ \Delta J = 0, \pm 1, \quad \Delta K = 0, \quad \Delta F = 0, \pm 1 \] (16)

one can then determine the hyperfine structure of the spectral line.

The hyperfine structure for a symmetric top molecule with two quadrupoles on the molecular axis has been given by Bardeen and Townes. In the present case however, there are three quadrupole moments all off the symmetry axis. Although this problem has not been solved, it is reasonable to suspect that the hyperfine structure produced in such a case could broaden this spectral line to the observed width of four megacycles per second.

V. The Microwave Absorption Spectrum of Hydrogen Cyanide

The rotational spectra of HCN and DCN have been investigated by Gordy.\(^\text{15}\) This observer reports a line for HCN at 88,601 mc/sec. and a line for DCN at 72,414 mc/sec. These spectral lines originate from transitions between the rotational levels \(J = 0\) to \(J = 1\) and are therefore the lowest-frequency lines in the rotational spectrum of each molecule.

While looking for rotational spectral lines of the dimer \((\text{HCN})_2\) in the region 16,000 mc/sec. to 36,000 mc/sec., Shulman and Townes\(^\text{16}\) discovered several new spectral lines. These lines had too great an intensity to be attributed to rotational transitions in a dimer which was less than 1 per cent abundant, and they obviously did not belong to the rotational spectrum of HCN since the lowest frequency line in that spectrum is at 88,601 mc/sec. The lines were interpreted by Townes as originating from transitions between levels split by \(\ell\)-type doubling according to the theory of Nielsen and Shaffer.\(^\text{17, 18}\) Further


investigations of \( J \)-type doubling transitions have been made in this laboratory. These investigations have resulted in the observations of three such lines for HCN and three for DCN. The observed lines appear in Figures 10 through 17. The tuning of the klystron source was considerably more uniform in the case of HCN, \( J = 10 \), and DCN, \( J = 11 \). For this reason these two lines have been chosen as examples of Stark effect and line structure for this type of transition. Two tracings of each line are given, one for a relatively high pressure, Figures 12 and 13, and the other for a low pressure, Figures 14 and 15. A comparison of the line widths demonstrates the pressure broadening of a spectral line. These lines will be referred to later when Stark effect and line structure are discussed.

A discussion of the theory of \( J \)-type doubling will be given on the following pages.

\( J \)-Type Doubling in Linear XYZ Molecules

A linear triatomic molecule has \( 3N-5 \), or four, normal modes of vibration. Of these, two are parallel modes and two are perpendicular as shown in Figure 18. When both the modes \( \nu_{21} \) and \( \nu_{22} \) are excited simultaneously, angular momentum about the axis of the molecule results. The magnitude of this angular momentum is given by,\(^{19}\)

\[\text{19.} \quad \text{Wave H. Shaffer, Rev. Mod. Phy. 16, 245 (1944).}\]
Figure 10. The spectral line for HCN, \( J=9 \)
Figure 11. The spectral line for DON, J = 10
Figure 12. The HCN, $J=10$, line at a relatively high pressure.
Figure 13 The DCN, J=11, line at a relatively high pressure.
Figure 14. The HCN, $j=10$, line at a low pressure
Figure 15. The DGN, \( J=11 \), line at a low pressure
Figure 16. The spectral line for HCN, $J=11$
Figure 17. The spectral line for DCN, $J=12$
\[
L_z = \pm \hat{l}_2 \xi
\]  

(17)

in which

\[
\hat{l}_2 = \nu_2, \nu_2-2, \nu_2-4, \ldots, 1, \text{ or } 0,
\]

where \(\nu_2\) is the quantum number associated with the mode of vibration \(\nu_2\).

The energy of the rotating vibrating molecule, to the degree of approximation ordinarily considered, is a function of \(\hat{l}_2^2\) and is therefore doubly-degenerate being independent of the sign of \(\hat{l}_2\). There are, however, terms in the Hamiltonian of a linear molecule which will remove this degeneracy. These terms can be attributed to the action of Coriolis forces on nuclei which are vibrating in a rotating coordinate system. Their effect is to split each rotational energy level into two levels. This phenomenon has been given the name \(\ell\)-type doubling.

A treatment of \(\ell\)-type doubling in polyatomic molecules has been given by Nielsen.\(^{18}\) In this article, the procedure has been to choose from the general Hamiltonian of an \(N\)-atomic molecule just those terms which are capable of removing the \(\ell\)-degeneracy and to solve the resulting perturbation problem. These terms will be corrections to the rotational constants due to vibration.

The Hamiltonian for an \(N\)-atomic molecule has been given to
FIGURE 18. MODES OF VIBRATION OF A LINEAR XYZ MOLECULE
second order of approximation by Nielsen\textsuperscript{20}. The terms of this


Hamiltonian of interest in this problem are:

\begin{align*}
H^{(0)} &= \frac{\hbar}{2} \sum_{S \sigma} \lambda^1_s \left[ (p_{s \sigma} - \mu^s_a)^2 + q_{s \sigma}^2 \right] + \frac{1}{2} \left\{ \frac{p_x}{I_{xx}} + \frac{p_y}{I_{yy}} + \frac{p_z}{I_{zz}} \right\} \\
H^{(1)} &= \sum_{\alpha} \sum_{S \sigma} \frac{1}{2} \sum_{S \sigma} \left[ \left( \frac{\lambda^1_s}{\lambda^s_a} \right)^{1/4} q_{s \sigma} \right] \left( p_{s \sigma} \right) \left( P_{s \sigma} \right) \\
H^{(2)} &= \sum_{\alpha} (\alpha S \sigma) \left[ A^{(\alpha V)}_{s s's' \sigma} \right] \left( P_{s \sigma} \right) \left( P_{s \sigma} \right) \\
&= \sum_{\alpha \beta \gamma} \left[ A^{(\alpha \beta \gamma)}_{s s's' \sigma} \right] \left( p_{s \sigma} \right) \left( P_{s \sigma} \right) \left( P_{s \sigma} \right) \left( P_{s \sigma} \right)
\end{align*}

where $\alpha, \beta, \gamma$ are summed over xyz.

The symbols appearing in equation (18) are identified as follows:

\begin{align*}
\sum_{\alpha \beta \gamma} \text{ Coriolis coupling factors given by} \\
\sum_{\alpha \beta \gamma} \left( 1_{\alpha \beta \gamma} \right) \left( 1_{\alpha \beta \gamma} \right) \left( 1_{\alpha \beta \gamma} \right) \left( 1_{\alpha \beta \gamma} \right)
\end{align*}

where $l_{\alpha \beta \gamma}$ are direction cosines relating to the normal coordinates $q_{s \sigma}$. 
\[ \lambda_5 = 4 \pi^2 e^2 \omega_s^2 \]

\( q_{s\sigma} \) normal coordinates

\[ p_{s\sigma} = -i\hbar \frac{\partial}{\partial q_{s\sigma}} \]  \( p_{s\sigma} \) momentum conjugate to \( q_{s\sigma} \)

\( P_{\alpha} \) angular momentum operator for the \( \alpha \)-axis

\( I_{\omega\alpha} \) moment of inertia about the \( \alpha \)-axis

\[ a_{s\sigma}(\omega, \phi) = 2 \sum_{i} M_i (\phi^{(s)}_{\omega\sigma} \lambda_{\omega\sigma} + \phi^{(s')}_{\omega\sigma} \lambda_{\omega\sigma'}) \]

\[ A_{s\sigma, s'\sigma'}(\omega, \phi) = \sum_{s''} \langle s'' | \phi^{(s)}_{s\sigma} \rangle \langle \phi^{(s')}_{s'\sigma'} | s'' \rangle \]

\[ A_{s\sigma, s'\sigma'}^{(\omega, \phi)} = \left\{ \sum_{i} M_i (\phi^{(s)}_{\omega\sigma} \lambda_{\omega\sigma} \phi^{(s')}_{s'\sigma'} - \phi^{(s)}_{\omega\sigma} \lambda_{\omega\sigma'} \phi^{(s')}_{s'\sigma}) \right\} \]

The relations between the normal coordinates and \( x_i y_i z_i \) are:

\[ N_1^{1/2} \int x_i = \sum_{s} (N_i^{1/2} \lambda_s \phi^{(s)}_{\omega\sigma} q_{s\sigma} \lambda_s^{1/2} \phi^{(s)}_{\omega\sigma} \phi^{(s)}_{\omega\sigma} \lambda_{\omega\sigma}) \]

where \( N_i \) are the nuclear masses and \( x_i y_i z_i \) are body fixed coordinates.

The second order energy correction can be more easily obtained if one performs a contact transformation on the Hamiltonian (18) chosen in such a way that the resulting first order Hamiltonian will be equal to zero. The transformed Hamiltonian will then be:
\[ H^{(0)} = H^{(0)} \]
\[ H^{(1)} = 0 \]
\[ H^{(2)} = \ldots - \sum_{\sigma} \sum_{\sigma'} \sum_{\sigma''} \left( \frac{\hbar}{2} \lambda^{1/4}_s \lambda^{1/4}_{s'} (I_s^{\sigma}\, I_{s'}^{\sigma'})^2 \right) \]
\[ \times \left\{ \left[ \sum_{\sigma} (a^{(\sigma)}_{s\sigma} a^{(\sigma)}_{s'\sigma'}) / (I_s^{\sigma}_s) \right] - 2 \sum_{s\sigma s'\sigma''} \sum_{s''\sigma''} \left[ \sum_{s'\sigma''} \sum_{s''\sigma''} (a^{(\sigma)}_{s\sigma} a^{(\sigma)}_{s'\sigma''})\lambda^{1/4}_s \lambda^{1/4}_{s'} / (\lambda_s - \lambda_{s''}) \right] \right\} \]
\[ \sum_{\sigma\sigma'} \sum_{\sigma''} \sum_{\sigma'''} \left[ \sum_{s\sigma} \sum_{s'\sigma'} \sum_{s''\sigma''} \left[ \sum_{s''\sigma''} \sum_{s'''\sigma'''} \left( a^{(\sigma)}_{s\sigma} a^{(\sigma)}_{s'\sigma'} a^{(\sigma)}_{s''\sigma''} a^{(\sigma)}_{s'''\sigma'''} / (I_{s''}^{\sigma''}) \right) \right] \right\} \]
\[ \times \left\{ \left[ \sum_{\sigma} (a^{(\sigma)}_{s\sigma} a^{(\sigma)}_{s'\sigma'}) / (I_s^{\sigma}_s) \right] - 2 \sum_{s\sigma s'\sigma''} \sum_{s''\sigma''} \left[ \sum_{s'\sigma''} \sum_{s''\sigma''} (a^{(\sigma)}_{s\sigma} a^{(\sigma)}_{s'\sigma''})\lambda^{1/4}_s \lambda^{1/4}_{s'} / (\lambda_s - \lambda_{s''}) \right] \right\} \]
\[ \times \left\{ \left[ \sum_{\sigma} (a^{(\sigma)}_{s\sigma} a^{(\sigma)}_{s'\sigma'}) / (I_s^{\sigma}_s) \right] - 2 \sum_{s\sigma s'\sigma''} \sum_{s''\sigma''} \left[ \sum_{s'\sigma''} \sum_{s''\sigma''} (a^{(\sigma)}_{s\sigma} a^{(\sigma)}_{s'\sigma''})\lambda^{1/4}_s \lambda^{1/4}_{s'} / (\lambda_s - \lambda_{s''}) \right] \right\} \]
\[ \times \left\{ \left[ \sum_{\sigma} (a^{(\sigma)}_{s\sigma} a^{(\sigma)}_{s'\sigma'}) / (I_s^{\sigma}_s) \right] - 2 \sum_{s\sigma s'\sigma''} \sum_{s''\sigma''} \left[ \sum_{s'\sigma''} \sum_{s''\sigma''} (a^{(\sigma)}_{s\sigma} a^{(\sigma)}_{s'\sigma''})\lambda^{1/4}_s \lambda^{1/4}_{s'} / (\lambda_s - \lambda_{s''}) \right] \right\} \]
\[ \times \left\{ \left[ \sum_{\sigma} (a^{(\sigma)}_{s\sigma} a^{(\sigma)}_{s'\sigma'}) / (I_s^{\sigma}_s) \right] - 2 \sum_{s\sigma s'\sigma''} \sum_{s''\sigma''} \left[ \sum_{s'\sigma''} \sum_{s''\sigma''} (a^{(\sigma)}_{s\sigma} a^{(\sigma)}_{s'\sigma''})\lambda^{1/4}_s \lambda^{1/4}_{s'} / (\lambda_s - \lambda_{s''}) \right] \right\} \]

The terms in \( H^{(2)} \) do not ordinarily contribute to the energy in second order unless \( s = s' \) and \( \sigma = \sigma' \). An exception is the case of an axially symmetric molecule with twofold degenerate frequencies. In such a case two coordinates, \( q_s \) and \( q_{s1} \), are associated with the frequency \( \omega_s \). Taking advantage of the simple relations existing
between the $A_{s\sigma s'\sigma'}^{(\omega \sigma)}$, the $a_{s\sigma}^{(\omega \sigma)}$, and the $\gamma_{s s'}^{(\omega)}$, for an axially symmetric molecule, the Hamiltonian becomes:

$$H(0)' = \hbar/2 \sum_{s\sigma} \chi_{s_{\sigma}}^{1/2} \left[ (p_{s\sigma}/\hbar)^2 + q_{s\sigma}^2 \right] + 1/2 \left( p_{x}^2 + p_{y}^2 \right) / I_{xx} + p_{z}^2 / I_{zz},$$

$$H(1)' = 0,$$

$$H(2)' = \sum_{\sigma} \sum_{s} \left( B_{s} / 4\omega_{s} \right) \left\{ \left[ (A_{s1s1} - A_{s2s2}) - (\alpha_{s1})^2 \right.ight.$$

$$\left. - (\alpha_{s2})^2 + (\alpha_{s1s2})^2 - (\alpha_{s1s2})^2 / I_{xx} \right) \left( e^{+i\chi_{s} r_{s}} \right)^2$$

$$+ 2 \sum_{s'} \left( \gamma_{s s'} \right)^2 \left[ \lambda_{s} / (\lambda_{s} - \lambda_{s'}) \right]$$

$$\left. \chi_{s} \left( e^{+i\chi_{s}} \right)^2 \left[ r_{s}^2 + \left( p_{r_{s}} \pm ip_{x} / r_{s} \right) / \hbar \right] \right\} / I_{xx},$$

where $q_{s1}$ and $q_{s2}$ have been replaced by $r_{s} \cos \chi_{s}$ and $r_{s} \sin \chi_{s}$ and the conjugate momenta $p_{s1}$ and $p_{s2}$ by their equivalents in $r_{s}$ and $\chi_{s}$. This is the portion of the Hamiltonian of an axially symmetric molecule which will contribute to $\ell$-type doubling as given by Nielsen.\textsuperscript{18} (Two typographical errors have been corrected; $e^{2i\chi_{s}}$ in Nielsen's equation has been replaced by $(e^{\pm i\chi_{s}})^2$, and $p_{x} / r_{s}$ has been replaced by $ip_{x} / r_{s}$). For a linear triatomic molecule, $A_{s1s1}^{(\omega \sigma)} - A_{s2s2}^{(\omega \sigma)} = -1$, $a_{s\sigma}^{(\omega \sigma)} = 0$, and the Hamiltonian can be further simplified to
\[ H(0)' = \frac{\mathcal{H}}{2} \sum_{f} \lambda_f^{1/2} \left[ (\mathbf{p}_{s_{\sigma}} - i\mathbf{p})^2 + \mathbf{q}_{s_{\sigma}}^2 \right] + \frac{1}{2} (\mathbf{p}_x^2 + \mathbf{p}_y^2) / \hbar \]

\[ H(1)' = 0, \]

\[ H(2)' = \sum_r e^{i\mathbf{q}} / 4 \omega_2 \left\{ -\left( \mathbf{r}_2 e^{i\mathbf{q}} \right)^2 + 2 \sum_{s'} \left( \mathbf{p}_{s'_s} \right)^2 \right\} \]

\[ \chi \left[ \frac{\lambda_2}{(\lambda_2 - \lambda_{s'})} \right] \]

\[ \chi (e^{i\mathbf{q}})^2 \left[ \mathbf{r}_2^2 + \left( (\mathbf{p}_{s'_s} + \mathbf{i} \mathbf{p}_{s'_s} / r_2 ) / \hbar \right)^2 \right] \]

\[ \chi (\mathbf{p}_x + \mathbf{i} \mathbf{p}_y)^2 / \hbar \]

(21)

A detailed analysis of the effect of the perturbing term \( H(2)' \) on the energy of a linear triatomic molecule will now be given. The treatment will depart from that given by Nielsen\(^{18} \) in order to take into account certain small terms of the energy matrix which were neglected in his solution of this problem.

In equation (21) the quantities \( e^{i\mathbf{q}} \) and \( e^{i\mathbf{q}} (\mathbf{p}_{s'_s} + \mathbf{i} \mathbf{p}_{s'_s} / r_2 ) \) are readily recognized as \( q_{21} + iq_{22} \), and \( p_{21} + ip_{22} \), respectively. These are the coordinates and conjugate momenta of a twofold-degenerate harmonic oscillator whose matrix elements have been evaluated many times and are given by Nielsen\(^{18} \) as

\[
\begin{align*}
(v_2, l_2 | e^{i\mathbf{q}} r_2 | v_{2-1}, l_2 + 1) &= (v_{2-1}, l_2 + 1 | e^{i\mathbf{q}} r_2 | v_2, l_2) = \\
&= \left[ (v_2 - l_2) / 2 \right]^{1/2}, \\
(v_2, l_2 | e^{i\mathbf{q}} r_2 | v_{2-1}, l_2 - 1) &= (v_{2-1}, l_2 - 1 | e^{-i\mathbf{q}} r_2 | v_2, l_2) = \\
&= \left[ (v_2 + l_2) / 2 \right]^{1/2},
\end{align*}
\]
The matrix elements of the angular momentum operators \( \hat{P} \) and \( \hat{X} \), when given in a form consistent with the problem at hand, are

\[
(J, \ell_2 \mid \hat{P}_x \mid J, \ell_2 \pm 1) = \mp i (J, \ell_2 \mid \hat{P}_y \mid J, \ell_2 \pm 1) = \hat{\kappa}/2
\]

\[
\chi [(J \mp \ell_2 + 1/2)^2]^{1/2}
\]  

These are the matrix elements of a symmetric rotator in which \( K \) has been replaced by \( \ell_2 \) (since for a linear molecule \( K \) is equal to \( \ell_2 \)). The matrix elements of \( \hat{P}_x \pm i \hat{P}_y \) are therefore

\[
(J, \ell_2 \mid \hat{P}_x \pm i \hat{P}_y \mid J, \ell_2 \pm 1) = \hat{\kappa} [(J \mp \ell_2)(J \pm \ell_2 + 1)]^{1/2}
\]  

The matrix elements of the quantities appearing in \( H^{(2)} \) are obtained by matrix multiplication of those given in equations (22) and (23). These are

\[
(v_2, \ell_2 \mid (e^{\pm iX_2} r_2)^2 \mid v_2, \ell_2 \pm 2) = - [(v_2 \mp \ell_2)(v_2 \pm \ell_2 + 2)]^{1/2},
\]

\[
(v_2, \ell_2 \mid (e^{\pm iX_2} r_2)^2 \mid v_2 + 2, \ell_2 \pm 2) = 1/2 [v_2 \pm \ell_2 + 2]
\]

\[
\chi (v_2 \mp \ell_2 + 4)]^{1/2}.
\]
\[(v_2, l_2 | (e^{\pm i\lambda_2} r_2)^2 | v_2, -2, l_2 \pm 2) = 1/2 \left[(v_2 \pm l_2) \right]^{1/2}, \tag{24} \]

\[(v_2, l_2 | \left[ e^{\pm i\lambda_2} ((p_x \pm i p_x / r_2)/\hbar) \right]^2 | v_2, -2, l_2 \pm 2) = -1/2 \left[(v_2 \mp l_2) (v_2 \mp l_2 + 2) \right]^{1/2}, \tag{25} \]

When the matrix elements (24), (25), (26) are combined according to equation (21) one has for the matrix elements of $H(2)^t$ the following:

\[(v_2, J, l_2 | H(2)^t | v_2, J, l_2 \pm 2) = \hbar c R^2 / 2 \omega_2 \left\{ 1 + 4 \sum_{x} (j_{2x}^x)^2 \right\}
\times \left\{ \lambda_2 / (\lambda_2 - \lambda_2) \right\} \times \left\{ \left[ j(J+1) - l_2 (l_2 \mp 1) \right] \times \left[ j(J+1) - (l_2 \mp 1) (l_2 \mp 2) \right] \left[ (v_2 \mp l_2) (v_2 \mp l_2 + 2) \right] \right\}^{1/2}, \tag{27} \]

\[(v_2, J, l_2 | H(2)^t | v_2 + 2, J, l_2 \pm 2) = \hbar c R^2 / 4 \omega_2 \left\{ \sqrt{j(J+1)} \right\}
\times \left[ j(J+1) - (l_2 \mp 1) (l_2 \mp 2) \right] \times \left[ (v_2 \mp l_2 + 2) (v_2 \mp l_2 + 4) \right]^{1/2}. \tag{28} \]
\[
(v_2, J, \ell_2 | H^{(2)}_f | v_2 -2, J, \ell_2 \pm 2) = \frac{\hbar c B}{\omega_0}
\]
\[
x \left[ 3(J+1) - \ell_2 (\ell_2 \pm 1) \right]
\]
\[
x \left[ 3(J+1) - (\ell_2 \pm 1)(\ell_2 \pm 2) \right]
\]
\[
x \left[ v_2 \mp \ell_2 (v_2 \mp \ell_2 -2) \right]^{1/2},
\]
(29)

where $\hbar^2 I_{xx}^{e}$ has been replaced by $2hcB_e$. Recalling that

\[
H' = H^{(0)}' + H^{(1)} + H^{(2)'},
\]
where $H^{(0)}'$ = $H^{(0)}$ and $H^{(1)'} = 0$, the energy matrix can be found by adding the matrix elements of $H^{(0)}$ and $H^{(2)'}. This matrix will be diagonal in $J$ and will split into submatrices, one for each value of $J$. These submatrices have the form

\[
\begin{array}{c|cccccccc}
 v_2 & 0 & 1 & 2 & 3 \\
 \ell_2 & 0 & -1 & +1 & -2 & 0 & +2 & -3 & -1 & +1 & +3 \\
\hline
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-1 & 0 & E_{11} & a_1 & 0 & 0 & 0 & X_2 & 0 & X_3 & 0 \\
1 & 0 & a_1 & E_{11} & 0 & 0 & 0 & 0 & X_2 & 0 & X_3 \\
-2 & X_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
2 & 0 & 0 & b_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
+2 & X_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-3 & 0 & X_2 & 0 & 0 & 0 & 0 & E_{33} & c_1 & 0 & 0 \\
-1 & 0 & 0 & X_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
+3 & 0 & X_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{array}
\]

(30)
The symbols appearing here are defined as follows:

\[ \hat{H}_{1} = (v_2, l_2 | H(0) | v_2, l_2) = (v_2, l_2 | H(0) | v_2, l_2), \]

\[ a_1 = \hbar c B_{e}^{2} / \omega_2 \left\{ 1 + 4 \sum_s \left[ \int \frac{\lambda}{2s^2} \lambda^2 / \lambda^2 \right] \right\} \sqrt{(J + 1)}, \]

\[ b_1 = \hbar c B_{e}^{2} / \omega_2 \left\{ 1 + 4 \sum_s \left[ \int \frac{\lambda}{2s^2} \lambda^2 / \lambda^2 \right] \right\} \left\{ \sqrt{(J + 1) - 2} \right\} \sqrt{J(J + 1)2}^{1/2}, \]

\[ c_1 = \hbar c B_{e}^{2} / \omega_2 \left\{ 1 + 4 \sum_s \left[ \int \frac{\lambda}{2s^2} \lambda^2 / \lambda^2 \right] \right\} \sqrt{J(J + 1) - 6} \sqrt{J(J + 1) - 2} \sqrt{J(J + 1)2}^{1/2}, \]

\[ c_2 = 2 \hbar c B_{e}^{2} / \omega_2 \left\{ 1 + 4 \sum_s \left[ \int \frac{\lambda}{2s^2} \lambda^2 / \lambda^2 \right] \right\} \sqrt{(J + 1)}, \]

\[ x_1 = \hbar c B_{e}^{2} / 2 \omega_2 \left\{ \sqrt{(J + 1) - 2} \right\} \sqrt{J(J + 1)2}^{1/2}, \]

\[ x_2 = \hbar c B_{e}^{2} / 2 \omega_2 \left\{ \sqrt{(J + 1) - 6} \right\} \sqrt{J(J + 1) - 2} \sqrt{6} \sqrt{J(J + 1)2}^{1/2}, \]

\[ x_3 = \hbar c B_{e}^{2} / 2 \omega_2 \sqrt{J(J + 1)2}^{1/2}. \]

(31)

In order to find the energies one must diagonalize the above matrix.

In microwave spectroscopy at ordinary temperatures there will be very few molecules in the first excited vibrational state and a negligible number in the states \( V_2 = 2 \) and higher. For this reason the corrections to \( H_1 \) due to the off diagonal elements are the only ones of interest. By looking at the matrix (30) one can see that only the state \( V_2 = 3 \) interacts with the state \( V_2 = 1 \) directly.
The state $V_2 = 5$ can interact with $V_2 = 1$ only through its effect on state $V_2 = 3$. For this reason all states higher than $V_2 = 3$ can be neglected without introducing an appreciable error. Since states of even $V_2$ do not interact with states of odd $V_2$, the even ones may be dropped from the matrix. When this has been done, the energy matrix takes the form

$$
\begin{array}{c|cccccc}
V_2 & 1 & +1 & +3 & -1 & -1 & +1 \\
\hline
V_2 & -1 & a_1 & X_2 & 0 & X_3 & 0 \\
+1 & a_1 & E_{11} & 0 & X_3 & 0 & X_2 \\
-3 & X_2 & 0 & E_{33} & c_1 & 0 & 0 \\
-1 & 0 & X_3 & c_1 & E_{31} & c_2 & 0 \\
3 & +1 & X_3 & 0 & 0 & c_2 & E_{31} & c_1 \\
+3 & 0 & X_2 & 0 & 0 & c_1 & E_{33} & c_1 \\
\end{array}
$$

(32)

If this matrix is diagonalized, the diagonal elements will be the roots of the secular determinant,
The expansion of this determinant is more readily accomplished by making the combinations of rows and columns indicated below.

\[
\begin{array}{c|ccc|ccc}
\vspace{1em} & 1 & -1 & -3 & 1 & 3 & 3 \\
\hline
v_2 \ l_2 & 1 & 3 & 1 & 3 & 3 & 3 \\
\hline
1 & 0 & 0 & 0 & X_2 & X_3 & 0 & 0 \vspace{1em} & E_{11} - \epsilon & a_1 & X_2 & 0 & X_3 & 0 \\
1 & 0 & 0 & 0 & X_2 & X_3 & 0 & 0 \\
2 & 0 & 0 & 0 & X_2 & c_1 & E_{33} - \epsilon & c_2 \vspace{1em} & E_{11} - \epsilon & X_2 & c_1 & c_2 & 0 \\
3 & 0 & 0 & 0 & X_2 & c_1 & E_{33} - \epsilon \vspace{1em} & 0 & 0 & 0 & 0 & 0 \\
\end{array}
\]

This is equivalent to introducing new wave functions

\[
(1/2)^{1/2} \left[ \psi(+l_2) \pm \psi(-l_2) \right] \text{ in place of } \psi(+l_2) \text{ and } \psi(-l_2).
\]

The effect of the elements $X_2$ and $X_3$ on the energy $E_{11}$ will be very small. If one neglects these elements entirely, the determinant
factors into the product of two minors, the roots of which give the energies for $V_2 = 1$ as

$$\varepsilon = E_{11} + a_1$$

and

$$\varepsilon = E_{11} - a_1.$$  \hfill (35)

The state of the molecule described by $V_2 = L_2 = 1$, and $J = J$, has been split into two states separated in energy by an amount

$$\Delta E = 2a_1$$

and in frequency by

$$\Delta \nu = \frac{\Delta E}{\hbar} = 2a_1 \left/ \hbar = 2cE_e^2 / \omega_2 \left\{ 1 + 4 \sum_{L'} (\langle \mathcal{X}_{2s1} \rangle^2 \lambda_{L'}/(\lambda_{s1} - \lambda_2)) \right\} J(J+1).$$

This equation may be written

$$\Delta \nu = q J(J + 1),$$  \hfill (36)

where $q$ is a constant for a particular molecule. It is defined by

$$q = 2c E_e^2 / \omega_2 \left\{ 1 + 4 \sum_{L'} (\langle \mathcal{X}_{2s1} \rangle^2 \lambda_2 / (\lambda_{s1} - \lambda_2)) \right\} J(J+1).$$  \hfill (37)

where $q$ is in cycles/sec., $E_e$ is in cm.$^{-1}$, $\omega_2$ is in cm.$^{-1}$, and $c$ is the velocity of light in cm./sec.. The energy level diagram for a linear $XYZ$ molecule in the state $V_2 = 1$ is shown in Figure 19. No attempt has been made to draw this diagram to scale, and only three rotational levels are shown.

It is of interest to note that $L_2$ is no longer a "good quantum number" in this degree of approximation, since the energy matrix is
not diagonal in \( l_2 \), and no definite value of \( l_2 \) is associated with
the new energy states. The eigenfunctions for the upper and lower
levels are

\[
\psi_+ = (1/2)^{1/2} \left[ \psi (+l_2) + \psi (-l_2) \right]
\]

and

\[
\psi_- = (1/2)^{1/2} \left[ \psi (+l_2) - \psi (-l_2) \right].
\]

Therefore each state is an equal mixture of the states \( \psi (+l_2) \) and
\( \psi (-l_2) \). The expectation value for \( L_z \) is zero for both states:

\[
L_z = \int \psi_+ \frac{\mathbf{L_z}}{\mathbf{L_z}} \psi_+ \, dv = 0,
\]

\[
L_z = \int \psi_- \frac{\mathbf{L_z}}{\mathbf{L_z}} \psi_- \, dv = 0.
\]

In order to compute \( q \) from equation (37) one must have explicit
definitions of the Coriolis coupling factors \( \gamma_{2k} \). These have been
given by A. H. Nielsen\(^{21} \) for the linear XYZ molecule as

\[\gamma_{21} = - \left[ M_1 M_3 / \sigma \, 1^e \right]^{1/2} \left( x_1^0 - x_3^0 \right) \cos \gamma \left[ M_2 / \sigma \, 1^e \right]^{1/2} \sin \gamma \]

and

\[\gamma_{23} = \left[ M_1 M_3 / \sigma \, 1^e \right]^{1/2} \left( x_1^0 - x_3^0 \right) \sin \gamma \left[ M_2 / \sigma \, 1^e \right]^{1/2} \cos \gamma , \]

where \( M_2 \) is the central atom, \( \sigma = M_1 + M_3 \), \( \Sigma = M_1 + M_2 + M_3 \), \( x_1^0 \)
are the equilibrium values of the coordinates, and

\[\tan 2 \gamma = 2k_4 / (k_1 - k_3) .\]
FIGURE 19. THE ENERGY LEVEL DIAGRAM FOR A LINEAR XYZ MOLECULE
The constants $k_i$ are defined as follows:

\[
k_1 = \frac{\left[ k_1(M_3/\sigma^2) + k_2(M_1/\sigma) \right]}{\mu_1},
\]
\[
k_3 = \frac{(k_1 - k_2)}{\mu_3},
\]
\[
k_4 = \left[ -k_1(M_3/\sigma) + k_2(M_1/\sigma) \right] \left( \frac{\mu_1 \mu_3}{\mu_1 + \mu_3} \right)^{1/2},
\]

where

\[
\mu_1 = \frac{M_1M_2}{M_1 + M_3} \quad \text{and} \quad \mu_3 = \frac{M_2 \sigma}{\sum}.
\]

The $k_i$ above are the valence force constants.

Using these equations and appropriate values of the masses, force constants, and fundamental frequencies, the q-value can be easily calculated, and the spectrum predicted by use of equation (36). The lines appearing in Figures 10 through 17 have been identified by comparison with the predicted spectrum. The line frequencies, associated J-values, measured q-values, and calculated q-values are recorded in Table I.
TABLE I

$\lambda$-type doubling constants for HCN and DCN

<table>
<thead>
<tr>
<th>J</th>
<th>$\Delta \nu$ mc./sec.</th>
<th>$q = \frac{\Delta \nu}{J(J+1)}$ mc./sec.</th>
<th>$\Delta q$ mc./sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>20,181.39 ± 0.15</td>
<td>224.238 ± 0.0015</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>24,660.40 ± 0.10</td>
<td>224.185 ± 0.0010</td>
<td>-0.053</td>
</tr>
<tr>
<td>11</td>
<td>29,585.12 ± 0.020</td>
<td>224.130 ± 0.0020</td>
<td>-0.055</td>
</tr>
</tbody>
</table>

Calculated $q = 226.2$ mc./sec.

| DCN |                        |                               |                  |
| 10  | 20,454.58 ± 0.015      | 185.951 ± 0.0015              | -0.048           |
| 11  | 24,539.20 ± 0.010      | 185.903 ± 0.0010              | -0.053           |
| 12  | 28,992.55 ± 0.020      | 185.850 ± 0.0020              |                  |

Calculated $q = 183.6$ mc./sec.

The measured $q$-value is 0.9% lower than the calculated value for HCN, and 1.2% higher for DCN. More interesting, however, is the decrease of $q$ with increasing $J$. This effect is present for both molecules and was not expected on the basis of equation (37).
It is conceivable that this variation of $q$ with $J$ is an effect of the off-diagonal elements $x_2$ and $x_3$ in the determinant (34) which have been neglected up to this point. When this determinant is expanded to include these elements, one obtains

$$
(E_{11} + a_1 - \epsilon) \left[ (E_{33} - \epsilon)(E_{31} + c_2 - \epsilon) - c_1 \right] (E_{11} + a_1 - \epsilon)
$$

$$
- (E_{11} + a_1 - \epsilon) \left[ (E_{33} - \epsilon)(E_{31} + c_2 - \epsilon) - c_1 \right] \left\{ x_3 \left[ x_2 c_1 + x_3 (E_{33} - \epsilon) \right] + x_2 \left[ x_3 c_1 + x_2 (E_{31} - c_2 - \epsilon) \right] \right\}
$$

$$
+ (E_{11} - a_1 - \epsilon) \left[ (E_{33} - \epsilon)(E_{31} - c_2 - \epsilon) - c_1 \right] \left\{ x_3 \left[ x_2 c_1 - x_3 (E_{33} - \epsilon) \right] + x_2 \left[ x_3 c_1 - x_2 (E_{31} - c_2  - \epsilon) \right] \right\}
$$

This equation factors into

$$
(E_{11} + a_1 - \epsilon) \left[ (E_{33} - \epsilon)(E_{31} - c_1 - \epsilon) - c_1 \right] - x_3 \left[ x_2 c_1 + x_3 (E_{33} - \epsilon) \right] - x_2 \left[ x_3 c_1 + x_2 (E_{31} - c_2 - \epsilon) \right] = 0
$$

(38)

and

$$
(E_{11} + a_1 - \epsilon) \left[ (E_{33} - \epsilon)(E_{31} + c_1 - \epsilon) - c_1 \right] + x_3 \left[ x_2 c_1 - x_3 (E_{33} - \epsilon) \right] + x_2 \left[ x_3 c_1 - x_2 (E_{31} + c_2 - \epsilon) \right] = 0.
$$

(39)
One must now find the roots of these equations which represent the energies for the state \( V_2 = 1 \). For these roots

\[ \epsilon \approx E_1 \]

and therefore

\[ E_{33} = \epsilon \approx E_3 - E_1 \gg c_1, c_2, X_2, \text{ or } X_3 \]

and

\[ E_{31} = \epsilon \approx E_3 - E_1 \gg c_1, c_2, X_2, \text{ or } X_3, \]

where \( E_3 \) and \( E_1 \) are the vibrational energies only. With the above approximations, equations (39) can now be written

\[
(\Xi_{11} - \epsilon - E_3)(E_3 - E_1)(E_3 - E_1) - (X_2^2 + X_3^2)(E_3 - E_1) = 0
\]

and

\[
(\Xi_{11} + \epsilon - E_3)(E_3 - E_1)(E_3 - E_1) - (X_2^2 + X_3^2)(E_3 - E_1) = 0,
\]

from which one gets

\[ E_{11} - \epsilon = (X_2^2 + X_3^2)/(E_3 - E_1) \]

and

\[ E_{11} + \epsilon = (X_2^2 + X_3^2)/(E_3 - E_1), \]

and finally

\[ \epsilon = \Xi_{11} - \epsilon = (X_2^2 + X_3^2)/(E_3 - E_1), \]

\[ \epsilon = \Xi_{11} + \epsilon = (X_2^2 + X_3^2)/(E_3 - E_1). \]

Therefore the effect of the off-diagonal elements is to depress both levels slightly without changing the spacing between them. The magnitude of the term \((X_2^2 + X_3^2)/(E_3 - E_1)\) for HCN, \( J = 10 \), is
approximately 2.1 mc./sec., and is consequently of little importance.
The explanation for the variation of \( q \) with \( J \) must be found elsewhere. It appears that this variation must be produced by terms of the general Hamiltonian of a linear molecule which were not included in the Hamiltonian (18).

It has been shown that \( \ell \)-type doubling is produced by the action of Coriolis forces on nuclei vibrating in a rotating coordinate system. These nuclei are subject to apparent centrifugal forces as well as Coriolis forces. These centrifugal forces tend to stretch the molecule, and this effect has been neglected in the derivation of \( \ell \)-type doubling given here. In order to take it into account one would have to revise the Hamiltonian (18) to include this effect and solve the perturbation problem again. One can see the effect of centrifugal stretching, however, by examining the expression for \( q \), given by the equation (37) as

\[
q = \frac{2c_2}{\omega_2} \left\{ 1 - 4 \sum_{\lambda} \left( \sum_{\lambda'} \lambda' \right)^2 \left( \frac{\lambda_2}{(\lambda_5 - \lambda_2)} \right) \right\}.
\]

If the molecule rotates, it will be stretched by centrifugal forces, and the moment of inertia will increase. The rotational constant will therefore decrease and \( q \), being proportional to \( B^2 \), will decrease, and hence might produce the observed effect. Ordinarily, the effect of centrifugal stretching is not included in the rotational constant. The rotational energy is usually written

\[
F_\nu(J) = B_\nu J(J + 1) - D_\nu J^2(J + 1)^2,
\]

where \( D_\nu \) is the centrifugal stretching coefficient. This equation
could just as well be written

\[ F_v^\prime(J) = B^\prime_v J(J + 1), \quad (42) \]

where

\[ B^\prime_v = B_v - D_v J(J + 1). \]

If now one replaces \( B_e \) by \( B^\prime_v \) in the expression for \( q \), the result is

\[ q = 2c \frac{B_{vJ}^2}{\omega_2} \left\{ 1 - 4 \sum_{s'} \left( \frac{\sigma_j(x)}{2s'} \right)^2 \lambda_{s'}/(\lambda_{s'} - \lambda_2) \right\}. \]

Assuming that the only effect of centrifugal stretching is to decrease the rotational constant, the derivatives of \( q \) with respect to \( J \) will be

\[ \frac{dq}{dJ} = \frac{dB_{vJ}}{2B_{vJ}} q = -\frac{2q}{B_{vJ}} D_v \left( 2J + 1 \right). \]

Therefore, for a change \( \Delta J \) in \( J \), one obtains a change in \( q \) of

\[ \Delta q = -\frac{2q}{B_{vJ}} D_v \left( 2J + 1 \right) \Delta J. \quad (43) \]

Taking the value of \( D_v \) determined in infrared spectroscopy\(^{22}\), \( \Delta q \) can be calculated. For HCN, \( J = 10 \), equation (43) predicts a \( \Delta q \) of

-0.021 mc. for \( \Delta J = 1 \). This is about one-half the observed change.

It is not surprising that the above calculation gave only one-half the required variation of \( q \), since only the effect of centrifugal stretching on \( B_e \) was considered. There will be an effect on the other quantities in the expression for \( q \) as well. No attempt has been made to compute corrections for all the quantities appearing in \( q \) because

this approach to the problem is not really justified, since the effects are not all independent. To explain this variation of $q$ one must compute the effect of centrifugal stretching terms in the Hamiltonian on this splitting. This is a fourth-order perturbation problem and is somewhat beyond the scope of the present work. The centrifugal stretching argument given here is merely a rough approximation which shows that this effect is large enough to warrant consideration.

The experimental results of the problem have shown that the $\ell$-type doubling $q$ value is a constant to second order of approximation as predicted by Nielsen. They show in addition that there is a decrease of $q$ with increasing $J$ in higher orders of approximation. In view of the above argument the most likely explanation of this variation is that it is an effect of centrifugal stretching.

The spectral lines in Figures 12 and 13 were observed at a relatively high pressure in order to make the Stark components visible. Each of these figures shows a strong main spectral line with unresolved Stark components spread out to its left. All attempts to resolve these Stark components were unsuccessful.

The Stark effect for this type of transition has not been predicted theoretically. If one considers the molecule a symmetric top with $K = \ell_2 = 1$, then the change in energy of a rotational level due to Stark effect can be calculated from equation (6) in the Appendix. However, when the selection rule $\Delta J = 0$ is added to
those of a symmetric top, namely $\Delta K = 0$ and $\Delta M = 0$, it is evident that $W_{\text{JEM}}$ does not change during a transition. Therefore the resulting line frequency is unaffected by the application of an electric field, and no Stark effect should be observed. There is a possibility of explaining the observed Stark effect by treating the molecule as an asymmetric top and using the theory of Golden and Wilson\textsuperscript{23}.


The appearance of a single sharp spectral line in Figure 14 gives one some information about transition probabilities for the case $\Delta J = 0$. Since the $^1\text{H}^{14}$ nucleus has a spin of one and a quadrupole moment, each rotational energy level of HCN is split into three levels corresponding to the three possible values of $F$. By analysis of the hyperfine structure of the rotational transition $J = 0$ to $J = 1$, Gordy\textsuperscript{15} has determined the quadrupole coupling of $^1\text{H}^{14}$ in the HCN molecule to be $4.58 \text{ mc/sec}$. When this value of $eQ \frac{2}{J+1}$ is substituted into equation (15) one finds the energy level for $J = 10$ to be split up as shown in Figure 20(a). Using the selection rule $\Delta F = 0, \pm 1$ the spectrum in Figure 20(b) is predicted. In this figure the central line corresponds to the selection rule $\Delta F = 0$, and the two lines on either side correspond to $\Delta F = \pm 1$. By reducing pressure to a minimum, it has been possible to decrease the width of the line for HCN, $J = 10$ to less
than one mc/sec. If the four outer lines were present at all, they were extremely weak. Therefore one might conclude that for this type of transition, in which $\Delta J = 0$, the changes of $F, \Delta F = \pm 1$, are exceedingly rare.

Although no intensity measurements were made, the line intensities can be estimated by comparing them with lines of known intensity. By comparison with the $N_2O$ line, the intensities of the HCN lines can be estimated to be about $5 \times 10^{-6}$ nepers/cm.

In conclusion it should be mentioned that the decrease of the $f$-type doubling constant with increasing $J$ reported here does not agree with the observations of Shulman and Townes. These observers found an increase of $q$ with increasing $J$. However, it has since been discovered that their frequency measurements were in error, and thus their work does not constitute a serious contradiction to the results reported here.
FIGURE 20. QUADRUPOLE SPLITTING OF THE HCN, J=10 SPECTRAL LINE
IV. Summary

An investigation of the acetone spectrum in the frequency region 18,000 to 30,000 mc/sec. has revealed the existence of four strong lines which have not been previously reported. These four spectral lines are assumed to originate from transitions between rotational levels of the acetone molecule; however, specific assignments have not been possible since the internuclear distances and angles are not accurately known.

The observation of a chloroform spectral line at 26,416.6 mc/sec. has resulted in a more exact determination of the rotational constant of that molecule than any previously reported. The width of this line indicates that it possesses a hyperfine structure due to interactions of the quadrupole moments of the Cl\(^{35}\) nuclei with the electric field gradient. Resolution of this hyperfine structure has not been accomplished and will undoubtedly be very difficult since the line is extremely weak.

The theory of \(J\)-type doubling developed by Nielsen has received additional confirmation by the observation of pure \(J\)-type doubling transitions in HCN and DCN. The measured \(q\) values for the six lines observed are in agreement with those predicted theoretically. These measured \(q\) values show a slight decrease with increasing \(J\) which is probably the result of a fourth order centrifugal stretching perturbation.
Appendix I

The Stark Effect

According to equation (6d) the square of the total angular
momentum for any rigid rotator is

\[
P^2 = J(J + 1) \hbar^2,
\]

(1')

where \( J \) is the total quantum number and takes the values \( 0, 1, 2, \ldots \).

If \( Z \) is a space fixed axis then the component of \( P \) along this
axis is given by

\[
P_Z = M \hbar,
\]

(2')

where \( M \) is the magnetic quantum number and takes the values
\( 0, \pm 1, \pm 2, \ldots \). For a symmetric top molecule with body fixed
symmetry axis \( z \)

\[
P_z = K \hbar,
\]

(3')

where \( K \) is the axial quantum number and, like \( M \), takes values
\( 0, \pm 1, \pm 2, \ldots \).

If no external field is present, the Hamiltonian for a symmetric
top molecule is

\[
H_{\text{sym}} = (P_x^2 + P_y^2)/2I_x + P_z^2/2I_z
\]

(4')

and the energy found by use of the matrix elements (6) is

\[
E(J, K) = J(J+1) \hbar^2/2I_x + K^2\hbar^2/2 (1/I_x - 1/I_z).
\]

(5')

The energy is therefore a function of \( K^2 \) and is independent of the
sign of \( K \). For each value of \( J \) there are \( K + 1 \) energy levels
corresponding to the allowed values of \( K \). The Hamiltonian for a
linear molecule is

\[ H_{\text{linear}} = \frac{p^2}{2I} \]  

and the energy is

\[ E(J) = J(J + 1) \frac{\hbar^2}{2I}. \]

Therefore for a rigid linear molecule there is one energy level corresponding to each value of \( J \). It should be noted that the energy does not depend on the quantum number \( M \) for either molecule if there is no external field.

When a molecule is placed in an electric field the molecular dipole moment interacts with this field, and each rotational energy level is split into sublevels corresponding to the \( 2J + 1 \) allowed values of \( M \). The magnitude of this interaction has been calculated by R. de Kronig.²⁴ For a symmetric top molecule with an electric dipole moment \( \mu \) in an electric field \( E \), the change in energy of the \( J,K \) level is

\[
W_{J,K} = -\frac{E\mu\mu}{J(J + 1)} + \frac{E^2\mu^2}{2B} \left\{ \frac{3K^2}{J(J + 1)} - 1 \right\} \left\{ \frac{3M^2}{J(J + 1)} - 1 \right\} - \frac{M^2\hbar^2}{3J(J + 1)}
\]

with

\[ W_{000} = -\frac{1}{6} \frac{E^2\mu^2}{B}. \]
where \( B \) is the rotational constant. The corresponding equations for a linear molecule are

\[
W_{JM} = \frac{\mu^2 B^2}{2B(2J - 1)(2J + 3)} \left[ 1 - \frac{M^2}{J(J + 1)} \right],
\]

and

\[
W_{00} = -\frac{1}{6} \frac{\mu^2 B^2}{B}. \tag{910}
\]

When the external field is parallel to the electric vector of the radiation, the selection rule for \( M \) is

\( \Delta M = 0. \)

Using this selection rule and the additional symmetric top selection rules

\( \Delta J = 0, \pm 1; \text{ and } \Delta K = 0, \)

one can predict the splitting of a spectral line produced by the electric field.
Appendix II

Experimental data relating to the particular molecules are given below.

Acetone

Sample— Commercial C. P. acetone.
Pressure— A pressure of about $10^{-3}$ mm of Hg was used with a continuous flow of sample through the wave guide. Pressure was regulated by cooling the sample in liquid air.
Temperature— Room temperature.
Frequency Standard— The NH$_3$ 10,10 line was used as a standard for all the lines except the one at 30,070 mc. This frequency was measured with a calibrated wavemeter.

Chloroform

Sample— Commercial C. P. chloroform.
Pressure— $10^{-2}$ mm of Hg at constant flow.
Temperature— Dry ice was applied to the waveguide absorption cell over approximately two-thirds of its length.
Frequency Standard— The NH$_3$ 8,8 line.

DCN and HCN

Samples— The HCN was prepared by mixing small quantities of HCN and H$_2$S$_6$. The gas evolved was frozen out in a liquid air trap. In the preparation of DCN, a solution of 50% H$_2$SO$_4$ and 50% D$_2$O was used.
Pressure— About $10^{-3}$ mm of Hg, controlled by cooling the sample.
Temperature— Room temperature.
Frequency Standard— The following NH$_3$ lines$^{25}$ were used as frequency standards:

<table>
<thead>
<tr>
<th>J</th>
<th>DCN</th>
<th>HCN</th>
<th>NH$_3$</th>
<th>Line</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10</td>
<td>9</td>
<td>7,5</td>
<td>20,804.80 mc.</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>10</td>
<td>5,5</td>
<td>24,532.94 mc.</td>
</tr>
<tr>
<td>12</td>
<td>11</td>
<td>11</td>
<td>10,10</td>
<td>28,604.73 mc.</td>
</tr>
</tbody>
</table>

AUTOBIOGRAPHY

I, Thomas Levi Weatherly, was born in Greenville, Mississippi, January 14, 1924. I received my secondary school education in the public schools of Little Rock, Arkansas and Memphis, Tennessee. I attended The University of Tennessee from September 1941 until April 1945 at which time I joined the United States Air Forces where I served until December 1945. I entered The Ohio State University in January of 1946 and received the Degree Bachelor of Science in 1947. I held an appointment of Graduate Assistant with the Physics Department from 1947 to 1950 and the position of Research Fellow during 1950-51 while completing the requirements for the Degree Doctor of Philosophy.