A COMPREHENSIVE MODEL FOR THE ROTATIONAL SPECTRA OF PROPYNE
CH\textsubscript{3}CCH IN THE GROUND AND V\textsubscript{1}\textsubscript{0}=1,2,3,4,5 VIBRATIONAL STATES

DISSERTATION

Presented to the Graduate Council of the
North Texas State University in Partial
Fulfillment of the Requirements

For the Degree of

DOCTOR OF PHILOSOPHY

By

Won Myung Rhee, B.S., M.S.

Denton, Texas

December, 1986
Won Myung, Rhee. A Comprehensive Model for the Rotational Spectra of Propyne CH\textsubscript{3}CCH in the Ground and \(v_{10}=1,2,3,4\) and 5 Vibrational States. Doctor of Philosophy (Physics), December, 1986, 104 pp., 14 tables, 6 illustrations, bibliography, 60 titles.

The energy states of \(C\textsubscript{3}V\) symmetric top polyatomic molecules were studied. Both classical and quantum mechanical methods have been used to introduce the energy states of polyatomic molecules. Also, it is shown that the vibration-rotation spectra of polyatomic molecules in the ground and excited vibrational states can be predicted by group theory.

A comprehensive model for predicting rotational frequency components in various \(v_{10}\) vibrational levels of propyne was developed by using perturbation theory and those results were compared with other formulas for \(C\textsubscript{3}V\) symmetric top molecules. The \(v_{10}=1,2,3\) and ground rotational spectra of propyne in the frequency range 17-70 GHz have been reassigned by using the derived comprehensive model. The \(v_{10}=3\) and \(v_{10}=4\) rotational spectra of propyne have been investigated in the 70 GHz, and 17 to 52 GHz regions, respectively, and these spectral components assigned using the comprehensive model. Molecular constants for these vibrationally excited states have been determined from more than 100 observed rotational transitions.
From these experimentally observed components and a model based upon first principles for $C_{3v}$ symmetry molecules, rotational constants have been expressed in a form which enables one to predict rotational components for vibrational levels for propyne up to $v_{10} = 5$. This comprehensive model also appears to be useful in predicting rotational components in more highly excited vibrational levels but data were not available for comparison with the theory.

Several techniques of assignment of rotational spectra for each excited vibrational state are discussed. To get good agreement between theory and experiment, an additional term $0.762(J+1)$ needed to be added to $K_l=1$ states in $v_{10}=3$. No satisfactory theoretical explanation of this term has been found.

Experimentally measured frequencies for rotational components for $J \rightarrow (J+1) = +1$ ($0 \leq J \leq 3$) in each vibration $v_{10} = n$ ($0 \leq n \leq 4$) are presented and compared with those calculated using the results of basic perturbation theory.

The $v_9 = 2$ rotational spectrum of the propyne molecule was introduced in Appendix A to compare the rotational spectra of the same molecule in different vibrational levels $v_9$ and $v_{10}$. 
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>List</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATION</td>
<td>viii</td>
</tr>
<tr>
<td>Chapter</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>Rigid Rotor</td>
<td></td>
</tr>
<tr>
<td>Distortable Rotor</td>
<td></td>
</tr>
<tr>
<td>The Effects of Vibration</td>
<td></td>
</tr>
<tr>
<td>II. HAMILTONIAN FOR TREATING THE VIBRATION-ROTATION INTERACTION OF POLYATOMIC MOLECULES</td>
<td>20</td>
</tr>
<tr>
<td>Derivation of Hamiltonian</td>
<td></td>
</tr>
<tr>
<td>Power Series of the Hamiltonian</td>
<td></td>
</tr>
<tr>
<td>Twice Contact Transformation</td>
<td></td>
</tr>
<tr>
<td>Non-zero Matrix Element of the Twice Transformed Hamiltonian for Molecules of C(_{3v}) Symmetry</td>
<td></td>
</tr>
<tr>
<td>III. DERIVATION OF A COMPREHENSIVE MODEL</td>
<td>33</td>
</tr>
<tr>
<td>Perturbation Theory</td>
<td></td>
</tr>
<tr>
<td>Accidental Degeneracy</td>
<td></td>
</tr>
<tr>
<td>IV. EXPERIMENTAL APPARATUS</td>
<td>45</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS--Continued

V. ANALYSIS OF EXPERIMENTAL RESULTS  . . . . . . . . . . . . . . 55

The Ground State Spectrum
The $v_{10}=1$ State Spectrum
The $v_{10}=2$ State Spectrum
The $v_{10}=3$ State Spectrum
The $v_{10}=4$ State Spectrum
The General Form of the Rotational Constants
The $v_{10}=5$ State Spectrum

VI. CONCLUSIONS  . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 75

APPENDICES  . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 78

A. The $v_{\rho}=2$ Rotational Spectra of Propyne
B. The Linear Molecule and Symmetric Top Molecules as a Rigid Rotor
C. Distortable Rotor For Prolate Symmetric Top Molecules
D. Rotational Energy of Symmetric Top Molecules in the Excited Vibrational State
E. Accidental Degeneracy
F. Program To Assign $v_{10}=n$ Rotational Constants
G. Program To Calculate $v_{10}=n$ Rotational Transition Frequencies

REFERENCES  . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 99
LIST OF TABLES

Table

I. Classes of Molecules ................. 3

II. Diagonal Matrix Element of the Twice Transformed Hamiltonian $H^+$ ................. 31

III. Non-Diagonal Matrix Element of the Twice Transformed Hamiltonian $H^+$ ................. 32

IV. The Comprehensive Model of Propyne and $C_{3v}$ Symmetry Molecules ................. 44

V. Rotational Transition Frequencies for CH$_3$CCH in the Ground State ................. 56

VI. Rotational Transition Frequencies for CH$_3$CCH in the $v_{10} = 1$ Excited Vibrational State ................. 59

VII. Rotational Transition Frequencies for CH$_3$CCH in the $v_{10} = 2$ Excited Vibrational State ................. 62

VIII. Rotational Transition Frequencies for CH$_3$CCH in the $v_{10} = 3$ Excited Vibrational State ................. 66

IX. Rotational Transition Frequencies for CH$_3$CCH in the $v_{10} = 4$ Excited Vibrational State ................. 69
LIST OF TABLES-- Continued

Table

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>X.</td>
<td>Rotational Constants for CH$<em>3$CCH in the $v</em>{10}$ Vibrational States</td>
<td>71</td>
</tr>
<tr>
<td>XI.</td>
<td>General Forms of Rotational Constants</td>
<td>72</td>
</tr>
<tr>
<td>XII.</td>
<td>Rotational Transition Frequencies for CH$<em>3$CCH in the $v</em>{10}= 5$ Excited Vibrational State</td>
<td>73</td>
</tr>
<tr>
<td>XIII.</td>
<td>Rotational Constants for Propyne in the $v_9= 2$ State</td>
<td>79</td>
</tr>
<tr>
<td>XIV.</td>
<td>Rotational Transition Frequencies for CH$_3$CCH in the $v_9= 2$ Excited Vibrational State</td>
<td>80</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>The Symmetric Top Molecule, Propyne</td>
<td>6</td>
</tr>
<tr>
<td>2.</td>
<td>Symmetric Top with Space-fixed (XYZ) and Molecule-fixed axes (xyz)</td>
<td>8</td>
</tr>
<tr>
<td>3.</td>
<td>Vibrational Modes of a Triatomic Linear Molecule</td>
<td>17</td>
</tr>
<tr>
<td>4.</td>
<td>Coriolis Force in a Linear XYZ Triatomic Molecule</td>
<td>17</td>
</tr>
<tr>
<td>5.</td>
<td>Spectrometer for Measuring Rotational Spectrum of Propyne</td>
<td>46</td>
</tr>
<tr>
<td>6.</td>
<td>A Typical Chart Recorder Scan of Rotational Components of Propyne</td>
<td>51</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

D. M. Dennison\(^1\) and H. H. Nielsen\(^2\) laid the early foundations for the theory of vibration-rotation energy of polyatomic molecules in 1931 and 1951, respectively. From 1950 to 1965 many scientists, Nielsen\(^3\), Anderson et al.\(^4\), Goldsmith et al.\(^5\), three papers by G. Amat et al.\(^6,7,8\), S. Maes\(^9\), and Grenier Besson\(^10\) made major contributions to set up the vibration-rotation energy and frequency formula for polyatomic molecules. In 1965, Tarragon\(^11\) developed a theory and applied it to some polyatomic molecules which have C\(_{\text{3v}}\) symmetry. Also she made specific rotational energy and frequency formulas for C\(_{\text{3v}}\) symmetric top molecules in the ground state and vibrationally excited states \(v_1 = 1, 2\) and 3. These main contributions by Nielsen, Amat and Nielsen, and Tarrago are examined with varying degrees of detail in the following chapter.

Although a number of papers have appeared for specific cases of C\(_{\text{3v}}\) symmetry molecules, no one has set up a general form for the vibration-rotation energy and frequency formula for polyatomic molecules which have the same symmetry. Therefore, all the energy and frequency formulas which have appeared in the literature before appear in different forms.
This work has four major objectives.

1. Derivation of a comprehensive model for vibration-rotation energy and frequency for polyatomic molecules which have $C_{3v}$ symmetry.

2. Reassignment of all the structural patterns of the propyne molecule using the comprehensive model and then make a comparison between the comprehensive model and previous models and formulas.

3. To set up the general forms of rotational constants for the propyne molecule.

4. To make additional measurements of rotational spectra of the propyne molecule in the $v_{10} = 3$ and $v_{10} = 4$ states.

Generally, polyatomic molecules can be classified into four different categories depending upon their symmetry. The four classifications are designated as linear molecule, symmetric top molecule, spherical top molecule and asymmetric top molecule, whose classification depends upon the principal moments of inertia of each molecule. Table I gives a summary of these classification. Also, Table I shows two different symmetric top molecules; prolate top and oblate top. A prolate symmetric top is one in which the two equal moments of inertia are greater than the other moment of inertia. An oblate symmetric top is one in which the
<table>
<thead>
<tr>
<th>Classes</th>
<th>Principal Moment of Inertia ( (I_x, I_y, I_z) )</th>
<th>Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>( I_x = I_y = I_z = 0 )</td>
<td>Acetylene</td>
</tr>
<tr>
<td>Symmetric Top</td>
<td>( I_x = I_y \neq I_z )</td>
<td>( \text{CH}_3\text{CCH} )</td>
</tr>
<tr>
<td>Prolate Top</td>
<td>( I_x = I_y &gt; I_z )</td>
<td>( \text{CH}_3\text{Cl} )</td>
</tr>
<tr>
<td>Oblate Top</td>
<td>( I_x = I_y &lt; I_z )</td>
<td>( \text{BCl}_3 )</td>
</tr>
<tr>
<td>Spherical Top</td>
<td>( I_x = I_y = I_z )</td>
<td>Methane</td>
</tr>
<tr>
<td>Asymmetric Top</td>
<td>( I_x \neq I_y \neq I_z )</td>
<td>Formaldehyde</td>
</tr>
</tbody>
</table>

Assumed \( z \) as symmetry axis.
degenerate moment of inertia is less than the other one. By this definition propyne is a prolate symmetric top molecule. Most of the symmetric top molecules observed in the microwave region are prolate.

Group theory is a powerful tool in dealing with the symmetry of molecules. It is useful to recall that there are 32 point groups in a crystal whose symmetry elements are rotation, inversion, reflection, plane of symmetry and center of symmetry. Also, recall that a point group means that there is always one point in the group that is unaffected by all the group symmetry operations: rotations, reflections, and inversions. An important point group of symmetric top molecules is the group of molecules that has $C_{3V}$ symmetry. The propyne molecule in this study has $C_{3V}$ symmetry and an explanation of that property follows.

$C_{nv}$ - consists of $C_n$ and $\sigma_v$ and any other elements to have closure(E).

* closure: the "product" of any two elements in the set must also belong to the set, i.e., the set is closed.

$C_n$ - Rotations are labeled by $C_n$ where the rotations are $2\pi/n$ about an axis through the origin. The axis of highest $n$ is called principle axis.

* $C_3$ is a $2\pi/3$ rotation.

$\sigma_v$ - reflection in a vertical plane that contains the principle axis. (mirror image)
Figure 1 shows a diagram of symmetric top molecule CH$_3$-CCH (commonly called propyne and methyl acetylene) showing bond lengths and bond angle. These structural parameters are taken from a paper by Duncan et al.\textsuperscript{15} and by Dubrulle et al.\textsuperscript{16}. Propyne is a molecule of interest to many areas of science, especially for astrophysics. Its existence has been confirmed in the atmosphere of Titan which is the seventh moon of Saturn as well as in the Taurus dark clouds.\textsuperscript{17}

It is the rotational motion of molecules that is primarily responsible for the spectra observed in microwave spectroscopy.\textsuperscript{18} There are several ways to get the formula for the rotational spectra of molecules. The simplest method to calculate the rotational energy of polyatomic molecules is by using the rigid rotor assumption.\textsuperscript{19}

1. Rigid Rotor

A. linear molecules - The rotational energy for linear polyatomic molecule in the rigid rotor assumption is given by\textsuperscript{20} (see Appendix B)

$$E_r(J,K) = \hbar BJ(J+1) \quad (l = 1)$$

B. Symmetric top molecule - Figure 2 shows a symmetric top molecule along with a space-fixed coordinate system XYZ. The
FIGURE 1. The Symmetric Top Molecule, PROPYNE.
coordinate system which rotates with the molecule is labeled xyz. The rotational energy of the rigid rotor is given in terms of the principal moments of inertia $I_x$, $I_y$, and $I_z$.

Classically, the pure rotational energy is

$$E_r = \frac{p_x^2}{2I_x} + \frac{p_y^2}{2I_y} + \frac{p_z^2}{2I_z} \quad (1-2)$$

where $P_x = I_x \omega_x$, $P_y = I_y \omega_y$, $P_z = I_z \omega_z$

The center of mass is assumed as origin of the principal axis.

For the Quantum Mechanical approach, $P_x$, $P_y$, $P_z$ and $E_r$ become operators

$$H_r = \frac{P_x^2}{2I_x} + \frac{P_y^2}{2I_y} + \frac{P_z^2}{2I_z} \quad (1-3)$$

and

$$P^2 = P_x^2 + P_y^2 + P_z^2 \quad (1-4)$$

$P$ : total angular momentum operator
Fig. 2. Symmetric Top with Space-fixed (XYZ) and Molecule-fixed (xyz) axes.
In a symmetric top, one of the principal axes of inertia must lie along the molecular axis of symmetry. Here \( z \) is chosen as the symmetric axis of the top. For the prolate symmetric top molecule, the Hamiltonian operator of Eq. (1.3) can be expressed as

\[
H_r = \frac{p_x^2}{2I_x} + \frac{p_z^2}{2I_z} \left( \frac{1}{I_z} - \frac{1}{I_x} \right)
\]  

Eigenvalues for the angular momentum operators and energy operator for the symmetric top rotor are

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

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

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

where

\[
J = 0, 1, 2, 3, \ldots
\]  

\[
K = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm J
\]  

\[
M = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm J
\]

By equations (1-4), (1-5), (1-6) and (1-7), the final form of the rotational energy of a symmetric top molecule with
rigid rotor assumption is given by \(^{23}\) (see Appendix B for details)

\[ E_r(J,K) = \hbar [BJ(J+1) + (A-B)K^2] \quad (1-12) \]

where \(J\) is the total angular momentum quantum number, \(K\) is the quantum number for the projection of the total angular momentum along the symmetry axis, \(M\) is the quantum number for the projection of the total angular momentum along the \(Z\) space-fixed axis (see Figure 2). The rotational constants used in Eqs. (1-1) and (1-7) are defined by

\[ B = \frac{\hbar}{8\pi^2 I_x (=I_y)} \quad (1-13) \]

\[ A = \frac{\hbar}{8\pi^2 I_z} \quad (1-14) \]

It is necessary that any permanent dipole moment must lie along the symmetry axis in a symmetric top molecule. All matrix elements of this dipole moment resolved along a space-fixed axis vanish except those between states corresponding to \(J \rightarrow J\) or \(J+1, K \rightarrow K^{24}\). The selection rules for the absorption spectra \(^{25}\) are

\[ \Delta J = +1, \Delta K = 0 \quad (1-15) \]
Application of these rules to the rotational energy formulas for linear and symmetric top molecules gives the formula for the absorption frequencies.

\[ \nu_r = 2B(J+1) \]  \hspace{1cm} (1-16)

Under the rigid rotor assumption, linear and symmetric top molecules have the same absorption rotational spectra formula.

2. Distortable rotor

When the prolate top molecule propyne is rotating about its center of mass, bond lengths and bond angle are changing. These distortions are due to the centrifugal forces at play in the molecule. Centrifugal stretching is treated as a perturbation on the eigenstates of a rigid rotor. A complete procedure for derivation of rotational energy of a distortable prolate symmetric top molecule is in Appendix C. The expression for the rotational energy of the distortable symmetric top molecule to the first order perturbation treatment is

\[ E_r(J,K) = \hbar \left[ BJ(J+1) + (A-B)K^2 - D_J J^2 (J+1)^2 \right. \\
\left. - D_K J^2 (J+1)^2 - D_K K^4 \right] \]  \hspace{1cm} (1-17)
With the selection rules for absorption spectra, this energy equation gives the rotational frequency as

\[ \nu_R(J,K) = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 \quad (1-18) \]

If one includes higher order centrifugal distortion effects to the sixth power in the angular momentum components \( P_6 \) to the rotational energy, the following result is obtained.\(^{27}\)

\[ E_R(J,K) = h [BJ(J+1)+(A-B)K^2-D_JJ^2(J+1)^2 \]
\[ -D_{JK}J(J+1)K^2-D_KK^2+H_JJ^3(J+1)^3 \quad (1-19) \]
\[ +H_JJ^2(J+1)^2K^2+H_KJ^3(J+1)K^4+H_KK^6] \]

By applying the same absorption selection rules and considering the centrifugal distortion to sextic order, the rotational frequency formula for the symmetric top molecule becomes

\[ \nu_R(J,K) = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 \]
\[ +H_J(J+1)^3[(J+2)^3-J^3]+4H_{JK}K^2(J+1)^3 \]
\[ +2H_{KJ}(J+1)K^4 \]
3. The effects of vibration

Only pure rotational frequencies and energy states of linear and symmetric top molecules both under the rigid and distortable rotor assumption were discussed so far. But other major departures from those assumptions occur for molecules in excited vibrational states. The effects of vibration of molecule on the rotational spectra are as follows.

A. Changing the rotational constants

For symmetric top molecules in excited vibrational states, the effective rotational constants differ from those of the ground state. One obvious reason for that is the principal moments of inertia of a molecule are altered by the vibration of molecules. If a symmetric top molecule bends, the moment of inertia about an axis perpendicular to the symmetry axis will decrease and the rotational constant B will increase. If a symmetric top molecule stretches, the moment of inertia about an axis perpendicular to the symmetry axis will increase and B will decrease. This is opposite to the behavior of the rotational constant A in prolate symmetric top molecules. In 1980, Claude Meyer et al. expressed the rotational constants in excited vibrational states as
\( B_v = B_0 - \alpha v - \gamma v^2 \) \hspace{1cm} (1-21)

\( A_v = A_0 - \beta v - \delta v^2 \) \hspace{1cm} (1-22)

Where \( B_v \) and \( A_v \) are the rotational constants in the excited vibrational states, \( B_0 \) and \( A_0 \) are the rotational constants in the ground state, and \( \alpha, \gamma, \beta \) and \( \delta \) are called constants of anharmonicity.

From equation (1-18), the rotational frequency of either a prolate or oblate symmetric top can be expressed by

\[
\nu_r(J,K) = 2B_v(J+1) - 4D^V_J(J+1)^3 - 2D^V_{JK}(J+1)K^2
\]

(1-23)

The new values of all the rotational constants in excited vibrational states are expected to have systematic variation with the vibrational quantum number.
B. Degenerate Coriolis splittings (\( \ell \)-type doubling)

The best approach to consider the effect of a degenerate vibrational mode on the rotational spectrum of a symmetric top molecule is to begin by considering a simple triatomic linear molecule. A linear molecule with \( n \) atoms has \((3n-5)\) modes of vibrations,\(^2\) however, not all of these modes have different frequencies. The bending modes are always doubly degenerate, i.e., there are two bending modes of vibration both of which have the same frequency. So, a non-symmetric triatomic linear molecule has two nondegenerate parallel modes \( v_1 \) and \( v_3 \) and a doubly degenerate bending mode \( v_2 \). Figure 3 illustrates these three vibrational modes of triatomic linear molecule.\(^3\) Two parallel modes correspond to the stretching vibrations of the two bonds XY and YZ. The bending modes \( v_2 \) is doubly degenerate because the molecule is free to bend in two orthogonal planes. It is obvious that these stretching and bending modes cause a change in the averaged or effective molecular parameters; bond lengths and bond angles. This leads to a slight change in the moment of inertia and a consequent altering of the rotational spectra.

In addition to these effects, there are other effects of interaction of rotation with the degenerate bending vibrational modes. If \( z \) is chosen along the molecular axis,
the degenerate vibrations of the non-rotating molecules can be considered as orthogonal bending motions of the molecule in the xz and yz planes. In the rotating molecule this degeneracy is lifted by the interaction between vibration and rotation. This interaction is due to the Coriolis force in the vibrating-rotating molecules. It has a value $F = 2mv \times \omega$, where $\omega$ is angular velocity of rotation of the molecule and $v$ is the linear velocity of the vibrating atom.

A Coriolis force occurs in all cases of the rotating and vibrating polyatomic molecule. Figure 4 shows the effect of Coriolis forces on a rotating linear triatomic molecule.

If the molecule is rotating about the x axis, then bending in the xz plane is not quite equivalent to bending in yz plane. This non-equivalency is only because of a Coriolis force in the vibrating-rotating molecule. The direction of the bending in the xz plane and that of the angular momentum $J$ of the molecule is perpendicular to each other, so this vibrational mode is excited by the Coriolis force. But the bending in the yz plane and angular velocity $\omega$ have the same direction, so this mode is not changed by the Coriolis force. Therefore, the effective moment of inertia about each axis of rotation is different for the two cases cited above. As result of this vibration-rotation interaction, the two degenerate energy levels are slightly split; this splitting is called $l$-type doubling.
Fig. 3. Vibrational Modes of a Triatomic Linear Molecule. (Bending mode $V_2$ is doubly degenerate)

Fig. 4. Coriolis Force in a Linear XYZ Molecule.

Curved Arrow: Direction of Rotation.
Solid Arrow: Normal Motion of the Vibrational Mode.
Dashed Arrow: Coriolis Force.
For symmetric top molecules such as CH₃CCH which have a linear group along the symmetry axis, there are degenerate bending vibrational modes which give rise to $\ell$-type doubling of the rotational levels similar to that described for linear molecules. There is a component of this vibrational angular momentum along the figure axis which adds to, or subtracts from, the pure rotational angular momentum about the symmetry axis. This component has the value $\zeta \hbar$ and with the Coriolis interaction term we can write

\[ p = \zeta \hbar \]  \hspace{1cm} (1-24)

\[ \ell = v, v-2, - - - -, -v \] \hspace{1cm} (1-25)

Where $\zeta$ is the Coriolis coupling constant and $v$ is the vibrational quantum number. When the vibrating motions are perpendicular to the symmetric axis, $\zeta = 1$ and the vibrational component along $z$ (symmetric axis) is $\ell \hbar$, just as in the linear molecules. In the symmetric top, however, this component along the symmetry axis, in general, will be less than $\ell \hbar$, or $0 < \zeta < 1$.

By considering the $\ell$-type doubling contribution to the rotational energy of the symmetric top molecule, the new rotational energy of symmetric top molecules in the excited vibrational states has a form (see Appendix D for derivation)
\[ E(J,K,l) = h[B_v J(J+1) + (A-B) K^2 - 2\ell \ell K \Lambda_V] \] (1-28)

This gives a splitting in the energy levels of \( 4\ell \ell K \Lambda_A \) between the levels with \( K \ell \) positive and those with \( K \ell \) negative. These splittings by \( \ell \)-type doubling are easily detected in propyne when this molecule is excited to \( v_{10}=1 \) and \( v_{10}=3 \) vibrational states.

The basic frequency and energy equations and symmetry properties for the propyne molecule have been outlined in this chapter. Further details will be given as the need arises.

The reminder of this paper is divided into five chapters. Theory of vibration-rotation interaction in the symmetric top molecule is discussed in Chapter II. Derivation of the comprehensive model developed from perturbation theory is found in Chapter III. The experimental equipment and procedure used in this study are presented in Chapter IV. The measurements made in this work and data analysis using the comprehensive model are presented in Chapter V. Conclusions and a brief summary of the entire work are given in Chapter VI.
CHAPTER II

HAMILTONIAN FOR TREATING THE VIBRATION-ROTATION INTERACTION OF POLYATOMIC MOLECULES

Derivation of Hamiltonian

The Hamiltonian for a rotating vibrating polyatomic molecule was discussed first by E. B. Wilson and J. B. Howard.\textsuperscript{35} To derive the exact Hamiltonian, Wilson and Howard derived the classical Hamiltonian and then used the method of Podolsky\textsuperscript{36} to obtain the quantum mechanical Hamiltonian. J. E. Wollrab\textsuperscript{37} also explained this process well by expressing the kinetic energy in terms of angular momentum. An equivalent but more useful Hamiltonian was formulated in 1940 by B. T. Darling and D. M. Dennison.\textsuperscript{38} In 1951 H. H. Nielsen\textsuperscript{2} developed a useful Hamiltonian for calculating the vibration-rotation energies of molecules. The Hamiltonian, as expressed by Darling and Dennison is

\[ H = \frac{1}{2} \left[ \sum_{\alpha} \frac{1}{\mu_\alpha} \left( p_\alpha - p_\alpha^* \right)^2 \right] + \frac{1}{2} \sum_{\alpha, \beta} \frac{1}{\mu_{\alpha, \beta}} \left( p_{\alpha, \beta} - p_{\alpha, \beta}^* \right)^2 + V \]  \hspace{1cm} (2-1)
Where $\alpha$ and $\beta$ range over $x, y$ and $z$ which are the principal axes of inertia of the molecule. $P_\alpha$ and $p_\alpha$ are components of the total and internal angular momentum, respectively, $p_{\alpha \sigma}$ is momentum conjugate to the normal coordinate $Q_{\alpha \sigma}$ and $V$ is the potential function of the molecular force field. The equation for $p_{\alpha \sigma}^*$ is given as

$$p_{\alpha \sigma}^* = - i \hbar \frac{\partial}{\partial Q_{\alpha \sigma}}$$  \hspace{1cm} (2-2)

A complete procedure to derive the Hamiltonian and matrix elements of the Hamiltonian for the vibrating rotating symmetric top molecule is not the main topic of this dissertation, so this chapter introduces only the steps to get the matrix elements of the Hamiltonian for a symmetric top molecule that can be used to derive a comprehensive model for propyne. For completeness, a summary is now given for the details needed to derive the comprehensive model.

The inertial parameters in eq.(2-1) are given by

$$\mu_{\alpha \alpha} = (I_{\beta \beta}^\prime I_{\gamma \gamma}^\prime - I_{\beta \gamma}^\prime) u \hspace{1cm} (2-3)$$

$$\mu_{\alpha \beta} = (I_{\gamma \gamma}^\prime I_{\alpha \beta} + I_{\alpha \gamma}^\prime I_{\gamma \beta}) u \hspace{1cm} (2-4)$$
\[ \mu = \begin{vmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & I_{zz} \end{vmatrix} \] (2-5)

and

\[ I'_{\alpha\beta} = I^e_{\alpha\beta} + \sum_{A'_{\sigma'}} A'_{\alpha\sigma'} Q_{A'_{\sigma'}} + \sum_{A'_{\sigma'}} A'_{\beta A'_{\sigma'}} \cdot A'_{\sigma' A'_{\sigma'}} + Q_{A'_{\sigma'}} Q_{A'_{\sigma'}} (2-6) \]

\[ I'_{\alpha\beta} = I^e_{\alpha\beta} - \sum_{A'_{\sigma'}} A'_{\alpha A'_{\sigma'}} - \sum_{A'_{\sigma'}} A'_{\beta A'_{\sigma'}} \cdot A'_{\sigma' A'_{\sigma'}} - Q_{A'_{\sigma'}} Q_{A'_{\sigma'}} (2-7) \]

Where \( I^e_{\alpha\alpha} \) and \( I^e_{\alpha\beta} \) are the equilibrium values of the moments and products of inertia, respectively. By introducing the Coriolis coupling coefficient we have

\[ P_{\alpha} = \sum_{A'_{\sigma'}} \sum_{A'_{\sigma'}} \zeta_{\alpha} Q_{A'_{\sigma'}} P_{A'_{\sigma'}} (2-8) \]

and equation (2-1) becomes

\[ H = \frac{1}{2} \sum_{\alpha\beta} \left\{ \left( P_{\alpha} - p_{\alpha} \right) \mu_{\alpha\beta} \left( p_{\beta} - p_{\beta} \right) \right\} (2-9) \]

\[ + \mu \left[ \mathcal{P}_{\alpha} \mu_{\alpha\beta} \left( p_{\beta} \right) \right] \]

\[ + \frac{1}{2} \sum_{\alpha\sigma'} \left\{ \left( \mathcal{P}_{\alpha} \right)^{\alpha\sigma'} u_{\alpha\sigma'} + \left( \mathcal{P}_{\alpha} \right)^{\alpha\sigma'} \left( \mathcal{P}_{\alpha} \right)^{\alpha\sigma'} \right\} + v \]

Also, rearranging Equation (2-9) by the power of \( P_{\alpha}, P_{\beta} \), the following result is obtained.
\[ H = \frac{1}{2} \sum_{\alpha, \beta} \{ \mu_\alpha \beta P_\alpha P_\beta - (p_\alpha \mu_\alpha + \mu_\beta P_\beta) P_\beta \} \]  

\[ + \frac{1}{2} \sum_{\sigma, \tau} p_\sigma^* p_\tau + U + V \]  

with replacements

\[ U = \frac{1}{2} \mu \sum_{\alpha, \beta} \left[ P_\alpha \mu_\beta \mu^{-1/2} \left( P_\beta \mu^{-1/2} \right) \right] \]  

\[ - \frac{1}{8} \mu \sum_{\sigma, \tau} \left[ P_\sigma^* \mu - \frac{3}{4} \left( P_\sigma^* \mu \right)^2 \right] \]  

It is not possible to find directly the eigenvalues of the Hamiltonian operator in Eq. (2-10). The general procedure to get the solution of the Hamiltonian for vibrating rotating polyatomic molecule is as follows:

**Power Series Generation of the Hamiltonian**

1. Expand the Hamiltonian in a power series to the fourth order with respect to normal coordinates to get

\[ H = H_0 + \lambda H_1 + \lambda^2 H_2 + \lambda^3 H_3 + \lambda^4 H_4 \]  

According to the customary notation, \( \lambda \) is a parameter of smallness equal to unity, which denotes the order of magnitude of the different terms in \( H \). By detailed calculation, comparison and substitution, each term of the
Hamiltonian can be shown to have the following forms. In these equations, $\lambda_\alpha$ is a force constant of the harmonic potential given by $V = \frac{1}{2} \sum_{\alpha \sigma} \lambda_\alpha Q^2_{\alpha \sigma}$ and $q_{\alpha \sigma}$ is a dimensionless normal coordinate and $p_{\alpha \sigma}$ is its conjugate momentum which is defined by $q_{\alpha \sigma} = \left( \frac{\lambda_\alpha}{\hbar} \right)^{1/2} Q_{\alpha \sigma}$, $p_{\alpha \sigma} = -i\hbar \frac{\partial}{\partial q_{\alpha \sigma}}$. The final results for $H$ are in the following form.

\[
H_0 = \frac{1}{2} \sum_{\alpha \sigma} \sum_{\beta \sigma'} \left\{ \frac{P_{\alpha \sigma}^2}{\hbar^2} + \hbar \lambda_\alpha \left( \frac{p_{\beta \sigma}}{\hbar^2} + q_{\beta \sigma}^2 \right) \right\}
\]

\[
H_1 = \frac{1}{2} \sum_{\alpha \sigma} \sum_{\alpha \beta} \left\{ \frac{\Omega_{\alpha \sigma \beta}}{\hbar} \left( \frac{\hbar^2}{\lambda_\alpha} \right)^{1/2} q_{\alpha \sigma} p_{\beta \sigma} - \frac{\hbar \lambda_\alpha}{\hbar^2} q_{\alpha \sigma} p_{\beta \sigma} \right\} + V_1 \tag{2-13}
\]

\[
H_2 = \frac{1}{2} \sum_{\alpha \sigma \omega \omega'} \sum_{\alpha \beta} \left\{ \frac{\Omega_{\alpha \sigma \omega \omega'}}{\hbar^2} \left( \frac{\hbar^2}{\lambda_\alpha} \right)^{1/2} \left[ P_{\alpha \sigma} q_{\omega \omega'} + q_{\omega \omega'} P_{\alpha \sigma} \right] - \frac{\hbar}{\hbar^2} q_{\omega \omega'} \right\} + V_2
\]

\[
H_3 = \frac{1}{2} \sum_{\alpha \sigma \omega \omega'} \sum_{\alpha \beta} \left\{ \frac{\Omega_{\alpha \sigma \omega \omega'}}{\hbar^2} \left( \frac{\hbar^2}{\lambda_\alpha} \right)^{1/2} \left[ P_{\alpha \sigma} q_{\omega \omega'} + q_{\omega \omega'} P_{\alpha \sigma} \right] - \frac{\hbar}{\hbar^2} q_{\omega \omega'} \right\} + V_3
\]
Twice Contact Transformation

2. Perform the first contact transformation in order to partially diagonalize the Hamiltonian matrix. W. H. Shaffer, H. H. Nielsen and L. H. Thomas in 1939 and Van Vleck and Kemble first formulated such a contact transformation $T$ to remove the off-diagonal element of the first order terms in $\lambda$. $T$ may be expanded in terms of a Hermitian matrix $S^z$ as

$$T = e^{i\lambda S^z} = \hat{1} + i\lambda \hat{S} - \frac{\lambda^2}{2} \hat{S}^2 + \cdots \quad (2-14)$$

$\hat{1}$: unit matrix

$$H' = THT = H_0' + \lambda H_1' + \lambda^2 H_2' + \lambda^3 H_3' + \cdots \quad (2-15)$$

$$H_0' = H_0$$

Where the $S$ function is chosen such that the first two terms, $H_0' + \lambda H_1'$, in the expansion of $H'$ are diagonal with respect to the quantum number $v$.

3. Group the terms of the same true order of magnitude in $\lambda$, which means that one expands the transformed Hamiltonian and arranges the terms in order of powers of $\lambda$ as
\[ H' = h'_0 + \lambda h'_1 + \lambda^2 h'_2 + \lambda^3 h'_3 + \lambda^4 h'_4 + \cdots \] 

(2-16)

By comparing Eq.(2-15) and Eq.(2-16)

\[ h'_0 = h'_o = H_0 \]

\[ h'_1 = H_1 + [i S, H_0] \] 

(2-17)

\[ h'_2 = H_2 + [i S, h'_1] + [i S, H_0] \]

\[ h'_3 = H_3 + [i S, h'_2] + [i S, h'_1] \]

These equations can be expressed by a combination of the vibrational operators \( p_{\infty} \) and \( q_{\infty} \) and of rotational operators \( P_\alpha, P_\beta, P_\gamma \).

4. Perform the second contact transformation\(^{51}\) using

\[ \Upsilon = e^{i \lambda^2 S} = I + i \lambda^2 S - \frac{\lambda^3}{2} S^2 + \cdots \] 

(2-18)

then

\[ H^+ = \Upsilon H \Upsilon = H_0^+ + \lambda H_1^+ + \lambda^2 H_2^+ + \cdots \] 

(2-19)

in such a manner that \( H_0^+ + \lambda H_1^+ + \lambda^2 H_2^+ \) will be diagonal with respect to the vibrational quantum number \( v \). In general, these operators will not be diagonal in \( \kappa_\sigma \) or \( K \), where \( \kappa_\sigma \) corresponds to the vibrational angular momentum associated...
with the $s$-th vibrational mode and $K$ is the rotational quantum number corresponding to the projection of the total angular momentum about the symmetry axis.

5. Group the terms, taking into account the true order of magnitude of the terms in powers of $\lambda$. The twice transformed Hamiltonian $H$ then can be expressed as

$$H^+ = h_0^+ + \lambda h_1^+ + \lambda^2 h_2^+ + - - - \quad (2-20)$$

By comparing the equations (2-17), (2-19), (2-20), the expressions for the operators $H_n^+, h_n^+$ are as follows

$$H_0^+ = h_0$$
$$H_1^+ = h_1'$$
$$H_2^+ = h_2' + i [S, h_0'] \quad (2-21)$$
$$H_3^+ = h_3' + i [S, h_1']$$
$$H_4^+ = h_4' + i [S, h_2'] - \frac{1}{2} \{S, [S, h_0']\}$$

The regrouped components of the twice transformed Hamiltonian are

$$h_0^+ = h_0'$$
$$h_1^+ = h_1'$$
$$h_2^+ = h_2' + [i S, h_0']$$
\[
\begin{align*}
    h_3^+ &= h_3^{'} + [iS,h_1^{'}] + [iS,h_0'] \\
    h_4^+ &= h_4^{'} + [iS,h_2^{'''}] + [iS,h_1']
\end{align*}
\]
where
\[
h_2^{'''} = h_2^{'} + [iS,h_0'] = \frac{1}{2}(h_2^{'} + h_2^{''})
\]

The explicit expression\(^4^7\) for regrouped components of the doubly transformed Hamiltonian in terms of the vibrational rotational operators are not presented in this work. Even though the operators \( h_3^+, h_4^+ \) will have terms that are off-diagonal in \( v \), these terms will contribute to the energy in an order higher than the fourth and do not need to be considered for the fourth order correction to the energy. Furthermore, all of the operators are diagonal in \( J \) and \( M \) so that only matrix elements of the form

\[
\langle J,M,v_1,v_2,\cdots,v_s,\cdots | h_0^++h_1^++h_2^++h_3^++h_4^+ | J,M,v_1,v_2,\cdots,v_s,\cdots \rangle \quad (2-23)
\]

need to be calculated. For axially symmetric top molecules such as \( \text{CH}_3\text{CCH} \), the only off-diagonal terms which are of consequences to fourth order of approximation arise from \( h_2 \) and are off-diagonal in \( K \) and \( I \) only.

6. Solve the secular equation; the eigenvalues are obtained by arranging the matrix elements into submatrices of the general energy matrix and solving the secular equation. This
equation is very complicated and lengthy to solve for the polyatomic molecule. Symbolically the procedure is to solve the following equation

\[
\text{det } \begin{vmatrix} J, K, M, \ldots, V_s, \xi_s, M_s, \ldots \end{vmatrix} h^+_0 + h^+_1 + h^+_2 + h^+_3 + h^+_4 \]

\[
J, K', M, \ldots, V, \xi'_s, M'_s \ldots)
\]

\[
-\delta_{KK'} - \delta_{ss} - \delta_{MM'} - E_{V,R} = 0 \quad (2.24)
\]

Non-Zero Matrix Elements of the Twice Transformed Hamiltonian for Molecules of C\(_{3v}\) Symmetry

When calculating the energies of molecules with special symmetry, there are basically two approaches which can be used. The first approach is to solve the secular equation of the general Hamiltonian matrix. This is the exact method. The second approach which has been followed here is an approximation method by the perturbation theory when matrix elements are calculated. Matrix elements for molecules of \(C_{3v}\) symmetry will have the form

\[
\langle J, K, M, V_n, V_t, \xi_t \ldots | H^+ | J, K+\Delta K, M, V_n+\Delta V_n, V_t+\Delta V_t, \xi_t+\Delta \xi_t \rangle \quad (2.25)
\]
where \( n \) and \( r \) are the quantum numbers corresponding to a non-degenerate normal vibration and a degenerate normal vibration, respectively. Unless accidental resonances occur only those elements with \( \Delta n \) and \( \Delta r \) equal to zero need to be considered. In any case, the matrix elements of Eq. (2-25) for symmetric top molecules which have \( C_3V \) symmetry are non-vanishing only if \( n, s, t \)

\[
- \Delta K + \frac{t}{2} \Delta \Lambda_t = 3p
\]  

(2-26)

where \( p \) is an arbitrary integer.

It is not necessary to present all of the details of the derivation of the matrix elements because in 1975, A. Bauer, G. Tarrago and A Remy published a paper giving all the matrix elements of the Hamiltonian for molecules of \( C_3V \) symmetry. All these diagonal and non-diagonal elements are expressed in terms of all molecular constants and parameters. Also, these matrix elements are written by using the zeroth order functions \( |v,j,k,l> \) as basis and including all the contributions originating with twice contact transformed Hamiltonian to the fifth order. For convenience, Table II and Table III show the diagonal and non-diagonal matrix elements which can be used for the vibration-rotation energy calculation by using the perturbation theory in Chapter III.
TABLE II. Diagonal Matrix Elements of \( H^+ \)

\[
\langle v, J, K, \ell | H^+ | v, J, K, \ell \rangle = E_v + (X_0 + X_1 v) \ell^2 \\
+ (B_0 + B_1 v + B_2 v^2 + B_3 \ell^2) J (J+1) \\
+ \left[ (A_0 - B_0) + (A_1 - B_1) v + (A_2 - B_2) v^2 + (A_3 - B_3) \ell^2 \right] K^2 \\
- 2 \{ (A_0 \ell^2) v + (A_1 \ell^2) v^2 + (A_2 \ell^2) \ell^2 \} K \ell \\
- (D_J^0 + D_J^1 v) J^2 (J+1)^2 \\
- (D_J^0 + D_J^1 v) J (J+1) K^2 \\
- (D_K^0 + D_K^1 v) K^4 \\
+ (n_J + n_J^1 v) J (J+1) K \ell \\
+ (n_K + n_K^1 v) K^3 \ell \\
+ n_J J^2 (J+1)^2 K \ell + n_{JK} J (J+1) K^3 \ell + n_{KK} K^5 \ell \\
+ H_J^0 (J+1)^3 + H_{JK} J^2 (J+1)^2 K^2 + H_{KK} J (J+1) K^4 + H_K^6.
\]
TABLE III. Non-Diagonal Matrix Elements of $H^+$

\[
\begin{align*}
\langle v, J, K, \ell | H^+ | v, J, K \pm 2, \ell \pm 2 \rangle &= \left[ q_0 + f_{22}^J + f_{22}^J (J+1) + f_{22}^K (K^2) \right] a_{2,JK}^{\pm,\ell} + v \ell \\
\langle v, J, K, \ell | H^+ | v, J, K \pm 1, \ell \mp 2 \rangle &= \left[ q_{12} + f_{12}^J (J+1) + f_{12}^K (K^2) \right] (2K \pm 1) + d_{12} (\ell \pm 1) a_{1,JK}^{\pm,\ell} + v \ell \\
\langle v, J, K, \ell | H^+ | v, J, K \pm 2, \ell \pm 0 \rangle &= f_{24}^{a_2,JK} b_{4,\ell}^{\pm,\ell} + v \ell \\
\langle v, J, K, \ell | H^+ | v, J, K \pm 3, \ell \rangle &= \left[ q_3 + f_{3J} (J+1) + f_{3K} (K^2) \right] (2K \pm 3) + d_3 \ell a_{3,JK}^{\pm,\ell} + v \ell \\
\langle v, J, K, \ell | H^+ | v, J, K \pm 6, \ell \rangle &= q_6^{b_6,\ell} a_{6,JK}^{\pm,\ell} + v \ell \\
\langle v, J, K, \ell | H^+ | v, J, K \pm 1, \ell \pm 4 \rangle &= f_{14} (2K \pm 1) a_{1,JK}^{\pm,\ell} + v \ell \\
\langle v, J, K, \ell | H^+ | v, J, K \pm 4, \ell \mp 2 \rangle &= f_{42}^{a_4,JK} b_{4,\ell}^{\pm,\ell} + v \ell \\
\langle v, J, K, \ell | H^+ | v, J, K \pm 6, \ell \rangle &= f_6^{a_6,JK} b_{6,\ell}^{\pm,\ell} + v \ell \\
\end{align*}
\]

where

\[
\begin{align*}
a_{n,JK}^{\pm,\ell} &= \frac{1}{\sqrt{2}} \sum_{n=1}^{\infty} \left[ J(J+1) - (\pm n-1) (K \pm n) \right]^{\ell/2} \\
b_{2n,\ell}^{\pm,\ell} &= \frac{1}{\sqrt{2}} \sum_{n=1}^{\infty} \left[ v+\ell+1 \pm (2n-1) \right] \left[ v-\ell+1 \mp (2n-1) \right]^{\ell/2}
\end{align*}
\]
CHAPTER III

DERIVATION OF A COMPREHENSIVE MODEL

Bauer et. al.\textsuperscript{50} have published a paper with diagonal and non-diagonal matrix elements of the Hamiltonian for a C\textsubscript{3v} symmetry polyatomic molecule. The origin of that work was from the formulation by Nielsen et. al.\textsuperscript{2,6,7,8} of the vibrational energy up to the fourth order in vibration and the sixth order in rotation. Tarrago\textsuperscript{11} has produced a paper along similar lines. In this chapter a similar model will be derived from fundamental concepts.

To obtain the rotation-vibration energy, a perturbation treatment is applied to the Hamiltonian to effect its solution for finite vibration-rotation interaction. Similar work has been done by Amat, Nielsen, Tarrago\textsuperscript{39} and used in several other papers\textsuperscript{51,52,53,54,55}; but each time the resulting energy equation has a different form and does not predict results for vibrations greater than \(v_{10}=4\). Since these formulas do not predict the energy or frequency for \(v_{10}=5\) and higher excited vibrational states of the propyne molecule, a general model has been developed to do so.

In this chapter, a comprehensive model which can be used for any vibrational state of a C\textsubscript{3v} symmetry molecule by
substituting the proper \( v \) and \( \lambda \) into a general energy equation is derived. The derivation is as follows.

**Perturbation Theory**

The Hamiltonian is subdivided in perturbation treatment as

\[
H = H^0 + H^1
\]

(3-1)

Where \( H^0 \) is an unperturbed Hamiltonian whose eigenfunctions are known and \( H^1 \) is a perturbed Hamiltonian which is significantly smaller than the zeroth order terms of \( H^0 \) in the absence of near degeneracies. The basis functions are the product of \( \psi_r \psi_v \) where \( \psi_r \) is the basis function of the rotational part of \( H^0 \) and \( \psi_v \) is an orthonormal function of the molecular normal coordinate. \( H^0 \) is diagonal in the vibrational quantum numbers, although it need not be diagonal in all of the rotational quantum numbers. \( H^1 \) is generally not diagonal in either the rotational or vibrational quantum numbers. As was seen in Chapter II some off-diagonal terms are partially diagonalized by performing two contact transformations on \( H \).

There are two assumptions in the perturbation theory. One begins with the perturbed Hamiltonian \( H^1 \) in some sense being small compared to the unperturbed Hamiltonian \( H^0 \), i.e.,
The other assumption in the perturbation approach is that the eigenstates and eigenenergies of the total Hamiltonian \( H \), do not differ appreciably from those of the unperturbed Hamiltonian \( H^0 \).

The complete energy calculation is then

\[
H^0 \phi_n^0 = E_n^0 \phi_n^0 \quad (3-3)
\]

\[
E_n^0 = \langle \phi_n^0 | H^0 | \phi_n^0 \rangle = H_{nn}^0 \quad (3-4)
\]

Where \( \phi_n^0 \) and \( E_n^0 \) are, respectively, the eigenstates and eigenvalues of the unperturbed Hamiltonian. Also, by some calculation and comparison of eigenstates and eigenenergies\(^{5,7} \), the first order energy correction from perturbation theory has a form

\[
E_1^1 = H_{nn}^1 \quad (3-5)
\]

and the second order energy correction has the form

\[
E_2^n = \sum_{i \neq n} \frac{|H_{ni}^1|^2}{E_n^0 - E_i^0} \quad (3-6)
\]
The total energy has a form given by

\[ E_n = E_n^0 + E_n^1 + E_n^2 \]  

(3-7)

As can be seen from equations (3-4), (3-5) and (3-6), the unperturbed energy and the first order energy correction are calculated from the diagonal matrix elements of the Hamiltonian. The second order energy correction is obtained from the non-diagonal matrix elements of the Hamiltonian.

In order to apply this perturbation theory to our vibration-rotation energy calculation by using Bauer's diagonal and non-diagonal matrix elements of the doubly transformed Hamiltonian \( H^+ \), some observations must be made.

The unperturbed Hamiltonian \( H^0 \) in the perturbation theory above is not the same as \( H_0 \) given in Eq.(2-12), the power series expression of the Hamiltonian. Also, the value of \( H^1 \) is not same as \( H_1 \). Because the twice contact transformed Hamiltonian \( H^+ \) contains both unperturbed and perturbed terms, rotation-vibration energy can be calculated by considering diagonal contributions and non-diagonal contributions of \( H^+ \). ie,

\[ E_{v_R} = E_{Diag.} + E_{Non-Diag.} \]  

(3-8)
The diagonal contribution to energy is given by:

\[ E_{\text{Diag}} = \langle \nu, J, K, \ell | H^+ | \nu, J, K, \ell \rangle \quad (3-9) \]

Then using Table IX with some new notations,

\[ E_{\text{Diag}}(\nu, J, K, \ell) = E_{\nu} + X_{\ell, \ell} \ell^2 + B_{\nu} J(J+1) + \gamma_{\ell, \ell} \ell^2 J(J+1) \quad (3-10) \]

\[ + (A-B)_{\nu} K^2 + (A_{3}-B_{3}) \ell^2 K^2 - 2(A_{4})_{\nu} K \ell \]

\[ - 2(A_{4})_{3} K \ell^3 - D_{J} J^2 (J+1)^2 - D_{JK} J(J+1) K^2 - D_{K} K^2 \]

\[ + \eta_{J} J(J+1) K \ell + \eta_{K} K \ell^2 + \eta_{JJ} J^2 (J+1)^2 K \ell \]

\[ + \eta_{JK} J(J+1) K \ell^2 + \eta_{KK} K \ell^3 + H_{J} J^3 (J+1)^3 \]

\[ + H_{JK} J^2 (J+1)^2 K^2 + H_{KK} J(J+1) K^4 + H_{K} K^6 \]

where \( B_{\nu}, A_{\nu} \): Rotational constants.
\( X_{\ell, \ell} \): Anharmonic constant.
\( \xi \): Coriolis coupling constant.
\( D_{J}, D_{JK}, D_{K} \): First order centrifugal distortion constants.
\( H_{J}, H_{JK}, H_{KK}, H_{K} \): Higher order centrifugal distortion constant
\( B_{3} = \gamma_{\ell, \ell} \)
\( \eta_{J}, \eta_{JJ}, \eta_{JK}, \eta_{K} \): Higher order diagonal matrix elements.
The non-diagonal contributions to energy is given by:

\[ E_{N.D} = \sum_{i \neq n} \frac{H_{n i}^+ H_{i n}^+}{E_n - E_i} \]  \hspace{1cm} (3-11)

Where

\[ |n| = |v, J, K, \ell| \]

\[ |i| = |v, J, K \pm 1, \ell \mp 2| \]

\[ |v, J, K \pm 2, \ell \pm 2| \]

\[ |v, J, K \pm 2, \ell \pm 4| \]

and where the quantum numbers \( v, J, K \) and \( \ell \) are the standard set for vibration, rotation and Coriolis interaction.

In the energy expressions all the diagonal matrix elements and three major non-diagonal matrix elements of the following type were considered: \( \langle v, J, K, \ell \mid H^+ \mid v, J, K \pm 1, \ell \mp 2 \rangle \), \( \langle v, J, K, \ell \mid H^+ \mid v, J, K \pm 2, \ell \pm 2 \rangle \) and \( \langle v, J, K, \ell \mid H^+ \mid v, J, K \pm 2, \ell \pm 4 \rangle \) which gives some contribution to the energy in the highly excited vibrational state, i.e., \( v_{10} = 4 \) and higher. All these non-diagonal elements are diagonalized about \( v \) and \( \ell \).

The quantity \( q \) is the coefficient of \( \langle K, \ell \mid H^+ \mid K \pm 2, \ell \pm 2 \rangle \), and \( q_{12} \) and \( d_{12} \) are the coefficients of \( \langle K, \ell \mid H^+ \mid K \pm 1, \ell \mp 2 \rangle \), \( f_{24} \) is the coefficient of \( \langle K, \ell \mid H^+ \mid K \pm 2, \ell \pm 4 \rangle \). The coefficients \( f_{12}, f_{22} \) and \( f_{24} \), in the low excited vibrational states, were small and ignored but were considered with \( f_{24} = 0.007 \) for the \( v_{10} = 4 \) and higher vibrations.
These non-diagonal contributions in terms of vibration rotation quantum numbers and rotational constants are given by:

\[ E_{N,D} = \frac{[q_{12}(2K+1)+d_{12}(\ell-1)]^2(a_1^+b_2^-)^2}{H^{+}_{vJK\ell}-H^{+}_{vJK+1\ell-2}} + \frac{[q_{12}(2K-1)+d_{12}(\ell+1)]^2(a_1^-b_2^+)^2}{H^{+}_{vJK\ell}-H^{+}_{vJK-1\ell+2}} 
+ \frac{(q\sqrt{a_2^+b_2^-})^2}{H^{+}_{vJK\ell}-H^{+}_{vJK+2\ell+2}} + \frac{(q\sqrt{a_2^-b_2^+})^2}{H^{+}_{vJK\ell}-H^{+}_{vJK-2\ell-2}} + \frac{(f_{24}a_2^+b_4^-)^2}{H^{+}_{vJK\ell}-H^{+}_{vJK+2\ell-4}} + \frac{(f_{24}a_2^-b_4^+)^2}{H^{+}_{vJK\ell}-H^{+}_{vJK-2\ell+4}} \]  

(3-12)

where \( H^{+}_{vJK} = [vJK \mid H^{+} \mid vJK] \) etc. . .

\[ a_1^+ = [J(J+1)-K(K\pm1)]^{1/2} \]

\[ a_2^+ = [J(J+1)-K(K\pm1)]^{1/2} [J(J+1)-(K\pm1)(K\pm2)]^{1/2} \]  

(3-13)

\[ b_1^+ = [(v+\ell+1\pm1)(v-\ell+1\mp1)]^{1/2} \]

\[ b_2^+ = [(v+\ell+1\pm1)(v-\ell+1\mp1)(v+\ell+1\mp3)(v-\ell+1\mp3)]^{1/2} \]

To calculate the energy difference which appears in the denominator of \( E_{N,D} \) some small terms ,ie, \( A_3, B_3 = \gamma_{20}(A\zeta), D_{JK}, D_{K}, D_J, J^J, J^J, J^J, K^J, K^J, H_J, H_{JK}, H_{KJ}, H_K \) were ignored, since these terms are very small compared to \( A_V, B_V, X_{\ell,2} \).
Therefore, the energy difference terms are simplified to

\[
H^*_{VJK' - H^*_{VJK, l-2}} = 8X_{l_2} (K-l)^2 - 2(A-B)(2K+1) + 2\zeta (2K-l+2)
\]

By the same procedure,

\[
H^*_{VJK' - H^*_{VJK, l+2}} = 8X_{l_2} (K+l)^2 + 2(A-B)(2K-1) - 2\zeta (2K+l-2)
\]

Finally, the rotational-vibrational energy for C_3v symmetry molecules is given by

\[
E(v, J, K, \ell) = E_{\text{Diag.}} + E_{\text{N.D.}}
\]

By using the selection rule for absorption spectra

\[
\Delta J = +1 , \quad \Delta K = 0 , \quad \Delta v = 0 , \quad \Delta \ell = 0
\]

one can get the frequency

\[
\nu(v, J, K, \ell) = \frac{E(v, J, K, \ell) - E(v, J+1, K, \ell)}{h}
\]
Hence, the rotational frequency becomes

\[(v, J, K, \ell) = A_1 + A_2 + A_3 + A_4\] (3-18)

Where

\[
A_1 = \left\{ \begin{array}{l}
2B_v(J+1) + 2Y_{2,2} + 2(J+1) - 4D_j(J+1)^3 - 2D_JK^2(J+1) \\
+ 2n_JK^3(J+1) + 4n_JK^6(J+1)^3 + 2n_JK^3L(J+1) \\
+ H_{J(J+1)}^3[(J+2)^3 - 3J^2] + 2H_{JKK}K^2(J+1)^3 + 2H_{JKK}K^4(J+1)
\end{array} \right.
\]

\[
A_2 = \left\{ \begin{array}{l}
\frac{(v-l)(v+l+2)(J+1)[(J+1)^2-(K+1)^2]g^2_v}{x_{l,2}(l+1) + (A-B)(K+1) - A\xi(K+l+2)} + \frac{(v-l)(v+l+2)(J+1)[(J+1)^2 - \xi(l+1)]}{x_{l,2}(l+1) + (A-B)(K+1) - A\xi}
\end{array} \right\}
\]

\[
A_3 = \left\{ \begin{array}{l}
\frac{2(v-l)(v+l+2)[g_{12}(2K+1) + d_{12}(l+1)]^2}{4x_{l,2}(l+1) - (A-B)(2K+1) - 2A\xi(2K-l+2)} - \frac{2(v-l)(v+l+2)(J+1)}{4x_{l,2}(l+1) - (A-B)}
\end{array} \right\}
\]

\[
A_4 = \left\{ \begin{array}{l}
\frac{\xi_{24}^2(v-l)(v+l+2)(v+l+4)(v-l-2)}{8x_{l,2}(l+2) - 4(A-B)(K-l) - 4A\xi(2K-l-4)} \right] C_1^- + \frac{\xi_{24}^2(v-l)(v-l-2)}{8x_{l,2}(l+2) - 4(A-B)} \right] C_1^+
\]

Where

\[
\left[ (J+1)(J+2) - K(K+1) \right] \left[ (J+1)(J+2) - (K+2)(K+3) \right] - (J+1) - K(K+1) \right) \right] \equiv C_1^+
\]

\[
\left[ (J+1) - (K+1)(K+2) \right] \equiv C_1^-
\]
Accidental Degeneracy

Some quantum number sets had to have special attention. Any combinations of quantum numbers which make \( K^l = 1 \) or \( K^l = -2 \) cause accidental degeneracies. Accidental degeneracy makes the energies in the denominators of the \( E_{ND} \) terms same, and \( E_{ND} \) appears to be infinity. To avoid these undesired cases, direct diagonalization was employed to solve the secular equation for these special quantum number sets. In this general model, quadrupole interaction, proton-proton interaction, spin-rotation interaction etc..., which appear not to be important for the propyne molecule from our experimental results, were ignored.

The direct diagonalization method used is given by:

\[
H_{d\psi} d = E_{d\psi} d; \text{diagonal}
\]

\[
H\psi = \lambda\psi
\]

\[
(\hat{\mathbf{\hat{H}}} - \lambda\mathbf{\hat{1}})\psi = 0
\]

\[
| \hat{\mathbf{\hat{H}}} - \lambda\mathbf{\hat{1}} | = 0
\]

By using the Table III in Chapter II, the determinant has a form:

\[
\begin{align*}
\begin{vmatrix}
  v, J, K, \ell & v, J, K + 2, \ell + 2 & v, J, K - 2, \ell - 2 \\
  v, J, K, \ell & E - \lambda & q_v a_2^+ b_2^+ & q_v a_2^- b_2^- \\
  v, J, K + 2, \ell + 2 & q_v a_2^+ b_2^+ & E - \lambda & 0 \\
  v, J, K - 2, \ell - 2 & q_v a_2^- b_2^- & 0 & E - \lambda
\end{vmatrix}
\end{align*}
\]

= 0
No interactions between \((K+2, \ell+2)\) and \((K-2, \ell-2)\) were assumed.

\[
(E-\lambda)(E-\lambda)^2 - (q_v a_2^+ b_2^+)^2 - (E-\lambda)(q_v a_2^- b_2^-)^2 = 0
\]

\[
\lambda = E
\]

\[
\lambda = E \pm q_v \left[ (a_2^+ b_2^+)^2 + (a_2^- b_2^-)^2 \right] \nu
\]

\[
\lambda = E \pm q_v \left[ \left( J(J+1)-K(K+1) \right) \left( J(J+1)-(K+1)(K+2) \right) (v+\ell+2) 
+ \left( J(J+1)-K(K-1) \right) \left( J(J+1)-(K-1)(K-2) \right) (v+\ell) (v+\ell+2) \right] \nu
\]

when

\[
v=1, \ K\ell=1 \ \{ \begin{array}{ll} K=-1 & \ell=-1 \\ K=1 & \ell=1 \end{array}
\]

\[
\lambda = E \pm q_v (J+1)(\nu+1)
\]  \hspace{1cm} (3-19)

Applying the absorption selection rule \(\Delta J=+1\) to Eq. (3-19)

\[
\Delta \nu = \pm 2q_v (J+1)(\nu+1) \quad \text{if } K\ell=1
\]  \hspace{1cm} (3-20)

By the same procedure (see Appendix E), \(A_4\) becomes

\[
\Delta \nu = \pm 2f_{24} (J+1) \nu (\nu+2) \quad \text{if } K\ell=-2
\]  \hspace{1cm} (3-21)

Finally, a comprehensive model for the rotational frequency of \(C_{3v}\) symmetry molecules has been obtained by using the perturbation theory and partial diagonalization method. The final form which gives the frequency of a transition \(J \to J+1\) for any vibrational levels of the propyne molecule in low \(J\) transitions is given in Table IV.
TABLE IV. The Frequency Formula for the Comprehensive Model of Propyne and Other $C_3V$ Symmetry Molecules.

\[
\begin{align*}
\nu(J,K,l) &= 2(J+1)[B_v + \gamma \ell^2 - D_{JK} K^2 + \eta_{JK} K^2 \ell^2 + \eta_{JK} K^2 \ell^3] \\
- 4D_{JK} (J+1)^3 + 4\eta_{JK} K \ell (J+1)^3 \\
- \frac{\{v - \ell'\} (v + \ell' + 2) (J+1) [J+1]^2 - (K+1)^2} {X \ell' \ell (K+1) - (A-B_v) (K+1) - A^2 (K+1)^2} q_0^2 \\
+ \frac{\{v + \ell'\} (v + \ell' + 2) (J+1) [J+1]^2 - (K-1)^2} {X \ell' \ell (K-1) - (A-B_v) (K-1) - A^2 (K-1)^2} q_0^2 \\
+ \frac{2(v + \ell') (V - \ell' + 2) (J+1) [q_{12} (2K+1) + d_{12} (\ell - 1)^2]} {4X \ell' \ell (\ell - 1) - (A-B_v) (2K+1) - 2A^2 (2K-\ell + 1) - 2A^2 (-2K + \ell + 2)} \\
- \frac{2(v - \ell') (V + \ell' + 2) (J+1) [q_{12} (2K-1) + d_{12} (\ell + 1)^2]} {4X \ell' \ell (\ell + 1) - (A-B_v) (2K-1) + 2A^2 (2K + \ell - 2)} \\
+ \frac{12 \ell_4^2 (v - \ell') (V + \ell' + 2) (v + \ell' + 4) (v - \ell' - 2)} {8X \ell' \ell (\ell - 2) - 4(A-B_v) (K-1) - 4A^2 (2K-\ell - 2)} \delta_{J+1} (J+1) \delta_{K(K+1)} \\
+ \frac{12 \ell_4^2 (v + \ell') (V - \ell' + 2) (v - \ell' - 4) (v + \ell' + 2)} {8X \ell' \ell (\ell + 2) - 4(A-B_v) (K+1) - 4A^2 (2K + \ell + 4)} \delta_{J+1} (J+1) \delta_{K(K+1)}
\end{align*}
\]
CHAPTER IV

EXPERIMENTAL APPARATUS

A microwave spectrometer suitable for measuring the rotational spectrum of CH$_3$CCH in this work was available in our laboratory. This spectrometer is similar to those described by E. A. Rinehart et al$^{58}$, J. A. Roberts$^{59}$, and I. C. Story et al$^{60}$. A block diagram of the spectrometer is shown in Figure 5.

In a typical spectroscopic experiment, radiation is supplied from a source and guided through an absorption cell to be detected and displayed in some fashion. This whole procedure can be divided into five areas of instrumentation according to the function of each. The categories chosen here for discussion are listed below.

1. Radiation Source

2. Absorption Cell

3. Detection and Display

4. Sample Gas Handling

5. Generation of Standard Frequency
Figure 5. Spectrometer for Measuring Rotational Spectra.
Microwave Sources

Four klystrons were used in this experiment as radiation source. A Varian X-12 and OKI 20V10 klystrons were used to generate radiation in the 17 GHz region; an OKI 24V11 was used to generate radiation in the 26 GHz region; an OKI 35V10 was used to generate radiation in the 34 GHz region as fundamental frequencies. All of these klystrons provide a stable, tunable source of monochromatic microwave radiation. The detailed construction of the klystron is out of the scope of this work and is given elsewhere in standard microwave electronic books. In some cases it was necessary to generate harmonics to reach the higher frequency transitions. A crossed waveguide multiplier was used to provide radiation in the 52 GHz and 68 GHz regions by producing the second harmonics of the OKI 24V11 and 35V10 klystrons, respectively.

There are two different adjustments of a reflex klystron to produce appropriate radiation. Coarse frequency adjustment of the klystron was achieved by mechanically altering the size of the klystron's resonant cavity by means of a flexible diaphragm and a connected screw assembly. Fine frequency adjustment was then achieved by the fine adjustment of the repeller voltage. It is also possible to sweep a range of frequencies by sweeping the repeller of the
klystron with a voltage ramp available from the sweep of the oscilloscope used for signal display. The frequency response of a klystron can be measured by applying a control voltage to its repeller and measuring the frequency shift. A typical value of klystron sensitivity indicates that one volt change in the repeller voltage will result in one MHz change in the output frequency of the klystron, approximately. Each klystron is highly individual in this respect. About ten megahertz frequency shift was achieved by using the voltage signal from the time base of an oscilloscope. The exact range was measured by applying the ramp voltage and directly observing the frequency shift of the klystron relative to the frequency markers which were generated when the klystron frequency was swept relative to a fixed standard reference source.

Absorption Cell

A K-band rectangular copper absorption cell which has a silver coated inside wall to produce better conduction was used. A thirty meter absorption cell was used for the strong signals found in the ground, \( v_{10} = 1 \) and \( v_{10} = 2 \) vibrational states. To detect the weaker signals in the higher excited vibrational states, i.e., \( v_{10} = 3, 4 \), the absorption cell was lengthened to 60 meter, thus giving improved sensitivity and better signal-to-noise ratio.
The ends of the absorption cell were vacuum sealed with Teflon windows to allow changing the transition sections and detectors without altering the pressure in the absorption cell. Breaking the conduction path of the radiation in this manner gives rise to reflections which greatly enhance the standing wave pattern of the system. Various methods are employed to reduce this effect. One technique is to employ approximate quarter wavelength gaps at the end sections, much like the effect of a quarter wavelength plate in optics. This effect has been discussed in some detail by I. R. Dagg et al.68.

Detection and Display

Crystal diodes were used for primary detection. Germanium 1N26 diodes were used to detect the frequency from the ten gigahertz to forty gigahertz region. Germanium 1N53 diodes were used for frequencies above forty gigahertz.

A dual-trace Hickok Electric oscilloscope (Model 1805A) provided visual display for the absorption. Strong signals in the low vibrational states were detected directly on the video, but weak signals in highly excited vibrational states were detected only by using a slow scan sweep with display on the chart recorder and by optimizing the gain and fine tuning of all parts of the equipment. In any case, the
spectral line profiles were displayed on a dual-trace recorder manufactured by Rika-Denki (Model B201) with one pen producing the frequency markers and another pen producing the appropriate derivative of the spectral line profile. Figure 6 shows one typical example of the line profile and standard frequency markers.

Sample Gas Handling System

Both gas handling and high vacuum capabilities were required for the apparatus. The absorption cell was evacuated by using a Van Waters and Rogers HV-1 oil vapor diffusion pump, cold-trapped with liquid nitrogen to remove the pressure of the gas molecules in the absorption cell. This was fore-pumped by a Welch Duo-Seal 1405 mechanical pump.

Once the apparatus had been evacuated, high purity propyne (99.6 percent) gas was admitted to the absorption cell from a sample tank which had been pumped to remove residual air and water vapor before admission of the sample gas.

The peak line intensity of the absorption spectrum was found to be very sensitive to the pressure of gas in the cell. So, it was necessary to keep the appropriate low pressure to get the maximum intensity of each line. The gas
Fig. 6. A typical chart recorder scan of rotational spectra ($v_0=1,2$). B.G. is the background display.
pressure in the absorption cell was measured by MKS Baraton Type 170M-27D pressure meter with accuracy to 0.0001 torr. A gas pressure of about 20-30 mtorr of propyne was observed to produce maximum peak absorption in this work.

Generation of Standard Frequency

In order to measure the rotational absorption frequency which is displayed on the chart recorder, a well known frequency interval must be recorded along with the absorption profile. A method used in this work for accurate measurement is to heterodyne the microwave frequency with a precisely known standard frequency which lies within the range of an available interpolation receiver. A Well-Gardner BC-348 Q radio receiver was used. The setting in the receiver was 1.5 MHz, so that as the klystron frequency was swept through the range of interest, markers appeared at 1.5 MHz above and 1.5 MHz below the center line frequency, giving a total marker spread of 3 MHz. These signals are beat notes between the fundamental of the klystron and appropriate harmonics of the fixed standard.

All frequencies are ultimately related to the frequency of a Hewlett-Packard 105B quartz oscillator which provides a signal of 100 KHz that is good to one part in 10^10. A General Radio 1112A, 1112B reference is phase locked to the
quartz oscillator and thus produces a highly stable 1 GHz comb of signals. The beat notes are produced when this signal, a signal of less than 100 MHz, and the fundamental of the klystron are combined in a mixer multiplier unit.

A beat note will be produced if

\[ f_k \pm m \times 1 \text{GHz} \pm n \times f_v = f_R \]  \hspace{1cm} (4-1)

where \( f_k \) is the klystron frequency, \( f_R \) is radio receiver setting (1.5 MHz in this work), and \( m \) and \( n \) are integers.

The value of \( m \) can be easily determined by the use of a wavemeter\(^6\). The fundamental klystron's frequency can be obtained roughly by reading the wavemeter with accuracy of about 10 MHz. To determine \( n \), a Tektronic 191 variable oscillator was used. The output frequency of the variable oscillator is measured with a Hewlett-Packard model 5383A counter which has accuracy to 1 part in 10\(^9\). By assuming a value of \( n \) and setting the variable oscillator at

\[ f_v' = \frac{n f_v}{n'} \]  \hspace{1cm} (4-2)

for \( n' \) an integer, marker will be produced if the choice of \( n \) is correct. The center frequency of the absorption profile is easily determined by a method of interpolation.\(^7\)
The greatest experimental difficulty in this experiment arises from the weak intensity of \( v_{10} = 4 \) absorptions. If the variation of the population of energy states in accordance with the Boltzmann distribution is considered, the \( v_{10} = 4 \) transitions will be less than one percent as intense as the ground state transitions. Moreover, the \( v_{10} = 4 \) transitions are even weaker since a number of degeneracies have been removed with respect to the quantum number producing further redistribution of the spectral line intensity. So, some weak components could not be detected.

All of the experimental frequency measurements of the propyne molecule in the 17-70 GHz region from the ground to \( v_{10} = 4 \) vibrational state are tabulated and discussed in Chapter V.
CHAPTER V

ANALYSIS OF EXPERIMENTAL RESULTS

A. The Ground State Spectrum

To assign the microwave spectra of propyne in the ground state, Dubrulle et al derived the quartic equation:

\[ v(J,K) = 2B_0 (J+1) - 2D_{JK}(J+1)K^2 - 4D_J(J+1)^3 \]

\[ + 4H_{JKK}(J+1)^3K^2 + 2H_{JJK}(J+1)K^4 + H_J(J+1)^3[(J+2)^3 - J^3] \]

From our comprehensive model one can get the same formula by substituting \( v=0 \) and \( \kappa=0 \). We have ignored the sextic order centrifugal distortion constants to assign our ground state rotational spectra, since the contributions of these terms to the frequencies is less than the experimental error in the low \( J \) transitions studied.

Our measurements were made using the video spectrometer described in Chapter IV. The ground state lines were exceptionally strong and therefore easily measured with experimental accuracy within \( \pm 60 \text{kHz} \). As a test of the model, the result of Ware and Roberts, the calculated values by Dubrulle et. al., and those from our comprehensive model are given in Table V for comparison.
### TABLE V. Rotational Transition Frequencies for CH$_3$CCH in the Ground State

<table>
<thead>
<tr>
<th>J</th>
<th>K</th>
<th>$\nu_{\text{exp}}$ (MHz)</th>
<th>$\nu_{\text{calc}}$ (MHz)</th>
<th>$\nu_{\text{calc}}$ (MHz)</th>
<th>($\nu_a\cdot\nu_b$) (MHz)</th>
<th>($\nu_a\cdot\nu_c$) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>17 091.718</td>
<td>17 091.743</td>
<td>17 091.743</td>
<td>-0.025</td>
<td>-0.025</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>34 183.349</td>
<td>34 183.415</td>
<td>34 183.415</td>
<td>-0.066</td>
<td>-0.066</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>34 182.727</td>
<td>34 182.761</td>
<td>34 182.761</td>
<td>-0.034</td>
<td>-0.034</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>51 274.947</td>
<td>51 274.947</td>
<td>51 274.947</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>51 273.980</td>
<td>51 273.967</td>
<td>51 273.967</td>
<td>+0.013</td>
<td>+0.013</td>
</tr>
<tr>
<td>2</td>
<td>±2</td>
<td>51 271.000</td>
<td>51 271.026</td>
<td>51 271.025</td>
<td>-0.026</td>
<td>-0.025</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>68 366.298</td>
<td>68 366.270</td>
<td>68 366.269</td>
<td>+0.028</td>
<td>+0.029</td>
</tr>
<tr>
<td>3</td>
<td>±1</td>
<td>68 364.990</td>
<td>68 364.962</td>
<td>68 364.962</td>
<td>+0.028</td>
<td>+0.028</td>
</tr>
<tr>
<td>3</td>
<td>±2</td>
<td>68 360.976</td>
<td>68 361.042</td>
<td>68 361.040</td>
<td>-0.066</td>
<td>-0.064</td>
</tr>
<tr>
<td>3</td>
<td>±3</td>
<td>68 354.498</td>
<td>68 354.509</td>
<td>68 354.503</td>
<td>-0.011</td>
<td>-0.005</td>
</tr>
</tbody>
</table>

- a Roberts and Ware (72)
- b Dubrulle et. al (16)
- c Our Comprehensive Model
As can be seen from the table, the two calculated values are nearly the same. There are only 1-2 kHz difference even with the ignorance of sextic order centrifugal distortion constants. Both calculational values were obtained by using the same constants set which was derived from the data of Ware and Roberts\textsuperscript{72}.

B. The \( v_{10} = 1 \) Spectrum

Nielsen\textsuperscript{3} was the first to calculate the rotational transition frequencies for symmetric top molecules in an excited \( v_{10} = 1 \) state. In 1951 Anderson et. al.\textsuperscript{4} reported calculations on the \( v_{10} = 1 \) bending mode of trifluoromethyl acetylene. Also, they reported some deviation of their experimental values from their calculated values as high as 200 kHz, which is outside the range of their experimental error. In 1962 Grenier-Besson and Amat\textsuperscript{73} derived a frequency formula for trifluoromethyl acetylene in the \( v_{10} = 1 \) state and obtained a superior assignment. The formula used by Grenier-Besson and Amat is given below.

Grenier-Besson and Amat's formula is given by:

\[
\nu(J,K,I) = 23^* (J+1) - 2D_J (J+1) (K^2-1)^2 - 4D_J (J+1)^3 + 2r^*(J+1)(K^2-1) \\
\pm 4\gamma_v (J+1) \quad \text{if } K=1
\]
\[
- \frac{4q_v^2(J+1)^3}{[B_v-A_v+(\alpha \zeta)_v](K\ell-1)} \quad \text{if } K\ell \neq 1
\]

\[
B^* = B_v - D_{JK} + \eta J^+ \frac{12r^2}{B_v - A_v - 2(\alpha \zeta)_v}
\]

\[
\rho^* = \eta J^- 2D_{JK}^+ \frac{2q_v^2}{B_v - A_v + (\alpha \zeta)_v} + \frac{8r^2}{B_v - A_v - 2(\alpha \zeta)_v}
\]

From our comprehensive model one can obtain the \(v_{1o}=1\) rotational frequency formula by putting \(v=1\) and \(\ell=1\) to get

\[
u(J,K,\ell) = 2(J+1)(B_v + \gamma_{\ell K}^2 - D_{JK}K^2 + \eta_{JK}K^2 + \eta_{JK}K^2) (5-3)
\]

\[-4D_J(J+1)^3 + 4\eta_{JJK}(J+1)^3 + v_{\text{non diagonal}}\]

The observed frequencies of Ware and Roberts, the calculated values using Amat's formula and those using our comprehensive model are tabulated in Table VI. Close agreement between the two calculated values again can be seen from the table.
### TABLE VI. Rotational Transition Frequencies for CH₃CCH in the \( v_{10} = 1 \) excited Vibrational State

<table>
<thead>
<tr>
<th>J</th>
<th>K</th>
<th>L</th>
<th>( \nu_{\exp}^a ) (MHz)</th>
<th>( \nu_{\text{calc}}^b ) (MHz)</th>
<th>( \nu_{\text{calc}}^c ) (MHz)</th>
<th>(( \nu^a - \nu^b )) (MHz)</th>
<th>(( \nu^a - \nu^c )) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>±1</td>
<td>17 139.588</td>
<td>17 139.632</td>
<td>17 139.610</td>
<td>-0.044</td>
<td>-0.022</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>34 246.269</td>
<td>34 246.321</td>
<td>34 246.268</td>
<td>-0.052</td>
<td>+0.001</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>±1</td>
<td>34 277.184</td>
<td>34 277.202</td>
<td>34 277.164</td>
<td>-0.018</td>
<td>+0.020</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>±1</td>
<td>34 279.161</td>
<td>34 279.142</td>
<td>34 279.080</td>
<td>+0.019</td>
<td>+0.081</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>34 313.523</td>
<td>34 313.421</td>
<td>34 313.369</td>
<td>+0.102</td>
<td>+0.154</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>51 369.214</td>
<td>51 369.300</td>
<td>51 369.221</td>
<td>-0.086</td>
<td>-0.007</td>
</tr>
<tr>
<td>2</td>
<td>±2</td>
<td>±1</td>
<td>51 410.612</td>
<td>51 410.671</td>
<td>51 410.625</td>
<td>-0.059</td>
<td>-0.013</td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>±1</td>
<td>51 415.471</td>
<td>51 415.560</td>
<td>51 415.481</td>
<td>-0.089</td>
<td>-0.010</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>±1</td>
<td>51 418.341</td>
<td>51 418.409</td>
<td>51 418.270</td>
<td>-0.068</td>
<td>+0.071</td>
</tr>
<tr>
<td>2</td>
<td>±2</td>
<td>±1</td>
<td>51 418.915</td>
<td>51 418.876</td>
<td>51 418.856</td>
<td>+0.039</td>
<td>+0.059</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>51 469.901</td>
<td>51 469.850</td>
<td>51 469.872</td>
<td>+0.051</td>
<td>+0.029</td>
</tr>
</tbody>
</table>

- a Roberts and Ware (72)
- b Grenier-Besson and Amat (73)
- c Our Comprehensive Model
C. The $v_{10} = 2$ Spectrum

In 1971, Bauer used a frequency formula, given below, for the $v_8=2$ state to assign the rotational spectrum of Acetonitrile\(^{74}\).

\[\nu(J,K,0) = 2(J+1)B - 4(J+1)^3 - 2(J+1)K^2D_{JK} + \frac{16(J+1)\lambda(J+1)^2 + (2\mu - \lambda)}{\mu^2K^2 - \lambda^2} + \frac{K^2 - \lambda}{(q')^2} + 32(J+1)4K^2(q'_{12})^2(\pi - 2\rho) + 2\rho q'_{12}d_{12}\] + \pi(q_{12} - d_{12})^2 / (4c^2K^2 - \pi^2)

and

\[\nu(J,K,\pm 2) = 2(J+1)(B + 4\lambda_{12} - 4(J+1)^3D_{J} - 2(J+1)K^2D_{JK} + \frac{2(J+1)K\lambda_{J} + 4(J+1)[4(J+1)^2 - (K\ell - 2)^2]}{\mu(K\ell - 4) + 2\lambda}\] + \frac{-16(J+1)[(K\ell + 1) + d_{12}]^2}{\rho(K\ell - 2)} - \pi, \text{ for } K\ell \neq -2 \] + \left\{\begin{array}{l}
16(J+1)[(J+1)^2 - 1](q')^2, \text{ for } K\ell = 4 \\
0 \end{array}\right.

+ \left\{\begin{array}{l}
+16(J+1)\ell_{24}^+ \\
-16(J+1)\ell_{24}^- \end{array}\right. \frac{-2[d_{12}^1 - q'_{12}]^2}{\pi}, \text{ for } K\ell = -2
This theory of Bauer predicts weak splittings in the \( K_1=-2 \) and \( K_2=4 \). We could not detect these predicted splittings in the propyne molecule, although the resolution of the spectrometer allows it. If these splittings in Bauer's formula are ignored and \( v=2 \) and \( t=0, \pm 2 \) are put into our comprehensive model, with the notation \( \lambda, \mu, \pi, \rho \) as given below, the formulas become identical and good agreement is found with observed experimental frequencies.

\[
\begin{align*}
\lambda &= A - B - 2A \xi + x_{22} \\
\mu &= A - B + A \xi \\
\pi &= A - B + 4A \xi + 4x_{22} \\
\rho &= A - B + 2A \xi
\end{align*}
\]

The contributions of the constants \( f_{12}, f_{22}, f_{24} \) to the frequency were found to be ignorable in the \( v_1=2 \) spectrum. Table VII shows the comparison between the observed values and those calculated from Bauer's formula and our comprehensive model. Assignment of Bauer's new data, shared with this laboratory by private communication, has also been made by the comprehensive model.
TABLE VII. Rotational Transition Frequencies for CH$_3$CCH 

in the $v_{10}$ ~ 2 Excited Vibrational State $^{3}$

<table>
<thead>
<tr>
<th>J</th>
<th>K</th>
<th>$\ell$</th>
<th>a(1) $\nu_{exp}$ (MHz)</th>
<th>a(2) $\nu_{exp}$ (MHz)</th>
<th>b $\nu_{cal}$ (MHz)</th>
<th>c $\nu_{cal}$ (MHz)</th>
<th>($\nu_{a}$-$\nu_{b}$) (MHz)</th>
<th>($\nu_{a}$-$\nu_{c}$) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>17 187.337</td>
<td>17 187.367</td>
<td>17 187.367</td>
<td>17 187.367</td>
<td>-0.030</td>
<td>-0.030</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>±2</td>
<td>17 186.451</td>
<td>17 186.386</td>
<td>17 186.386</td>
<td>17 186.386</td>
<td>+0.065</td>
<td>+0.065</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>±2</td>
<td>34 369.481</td>
<td>34 369.446</td>
<td>34 369.446</td>
<td>34 369.446</td>
<td>+0.035</td>
<td>+0.035</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>±2</td>
<td>34 373.015</td>
<td>34 373.036</td>
<td>34 373.036</td>
<td>34 373.036</td>
<td>-0.021</td>
<td>-0.021</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>0</td>
<td>34 373.759</td>
<td>34 373.833</td>
<td>34 373.833</td>
<td>34 373.833</td>
<td>-0.074</td>
<td>-0.074</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>±2</td>
<td>34 374.513</td>
<td>34 374.573</td>
<td>34 374.573</td>
<td>34 374.573</td>
<td>-0.060</td>
<td>-0.060</td>
</tr>
<tr>
<td>2</td>
<td>±2</td>
<td>±2</td>
<td>51 547.171</td>
<td>51 547.234</td>
<td>51 547.234</td>
<td>51 547.234</td>
<td>-0.063</td>
<td>-0.063</td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>±2</td>
<td>51 553.774</td>
<td>51 553.632</td>
<td>51 553.632</td>
<td>51 553.632</td>
<td>+0.142</td>
<td>+0.142</td>
</tr>
<tr>
<td>2</td>
<td>±2</td>
<td>0</td>
<td>51 556.785</td>
<td>51 556.833</td>
<td>51 556.833</td>
<td>51 556.833</td>
<td>+0.048</td>
<td>+0.048</td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>±2</td>
<td>51 560.432</td>
<td>51 560.213</td>
<td>51 560.213</td>
<td>51 560.213</td>
<td>+0.219</td>
<td>+0.219</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>±2</td>
<td>51 560.432</td>
<td>51 560.296</td>
<td>51 560.296</td>
<td>51 560.296</td>
<td>+0.136</td>
<td>+0.136</td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>0</td>
<td>51 561.503</td>
<td>51 561.457</td>
<td>51 561.457</td>
<td>51 561.457</td>
<td>+0.046</td>
<td>+0.046</td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>±2</td>
<td>51 561.503</td>
<td>51 561.565</td>
<td>51 561.565</td>
<td>51 561.565</td>
<td>-0.062</td>
<td>-0.062</td>
</tr>
<tr>
<td>2</td>
<td>±2</td>
<td>±2</td>
<td>51 563.305</td>
<td>51 562.351</td>
<td>51 562.351</td>
<td>51 562.351</td>
<td>+0.954</td>
<td>+0.954</td>
</tr>
</tbody>
</table>

a(1) Roberts and Ware (75)  
a(2) Bauer Experimental Results  
b Bauer Equations (74)  
c Comprehensive Model
<table>
<thead>
<tr>
<th>J K l'</th>
<th>a(1) $\nu_{\text{exp}}$ (MHz)</th>
<th>a(2) $\nu_{\text{exp}}$ (MHz)</th>
<th>b $\nu_{\text{cal}}$ (MHz)</th>
<th>c $\nu_{\text{cal}}$ (MHz)</th>
<th>$(\nu_{a} - \nu_{b})$ (MHz)</th>
<th>$(\nu_{a} - \nu_{c})$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 ±6 0</td>
<td>120 226.202</td>
<td>120 225.648</td>
<td>120 225.648</td>
<td>+0.554</td>
<td>+0.554</td>
<td></td>
</tr>
<tr>
<td>6 ±5 0</td>
<td>120 251.276</td>
<td>120 251.418</td>
<td>120 251.418</td>
<td>-0.142</td>
<td>-0.142</td>
<td></td>
</tr>
<tr>
<td>6 ±2 ±2</td>
<td>120 270.668</td>
<td>120 270.678</td>
<td>120 270.678</td>
<td>-0.010</td>
<td>-0.010</td>
<td></td>
</tr>
<tr>
<td>6 ±4 0</td>
<td>120 273.313</td>
<td>120 273.207</td>
<td>120 273.207</td>
<td>+0.106</td>
<td>+0.106</td>
<td></td>
</tr>
<tr>
<td>6 ±1 ±2</td>
<td>120 281.806</td>
<td>120 281.782</td>
<td>120 281.782</td>
<td>+0.024</td>
<td>+0.024</td>
<td></td>
</tr>
<tr>
<td>6 ±3 0</td>
<td>120 294.410</td>
<td>120 293.730</td>
<td>120 293.730</td>
<td>+0.680</td>
<td>+0.680</td>
<td></td>
</tr>
<tr>
<td>6 ±4 ±2</td>
<td>120 299.840</td>
<td>120 299.386</td>
<td>120 299.386</td>
<td>+0.454</td>
<td>+0.454</td>
<td></td>
</tr>
<tr>
<td>6 ±0 0</td>
<td>120 303.104</td>
<td>120 302.540</td>
<td>120 302.540</td>
<td>+0.564</td>
<td>+0.564</td>
<td></td>
</tr>
<tr>
<td>6 ±3 ±2</td>
<td>120 308.110</td>
<td>120 307.180</td>
<td>120 307.180</td>
<td>+0.930</td>
<td>+0.930</td>
<td></td>
</tr>
<tr>
<td>6 ±2 ±2</td>
<td>120 310.850</td>
<td>120 310.673</td>
<td>120 310.673</td>
<td>+0.177</td>
<td>+0.177</td>
<td></td>
</tr>
</tbody>
</table>

a(1) Roberts and Ware (75)
a(2) Bauer Experimental Results
b Bauer Equations (74)
c Comprehensive Model
D. The $v_{10} = 3$ Spectrum

Bauer, Godon and Maes\textsuperscript{70} have given a frequency expression, as shown below, for $v_8 = 3$ to assign the microwave spectra of methyl isocyanide.

$$f = 2 B_0 (J+1) + 2 \gamma_{v0} (J+1) - 4 D_J^v (J+1)^3 - 2 D_{JK}^v (J+1) K^2 + 2 \eta_J (J+1) K^2$$

$$f = 2 B_0 (J+1) + 2 \gamma_{v0} (J+1) - 4 D_J^v (J+1)^3 - 2 D_{JK}^v (J+1) K^2 + 2 \eta_J (J+1) K^2$$

$$= \frac{22 a_{12}^2 (2K^2 + 1)}{\rho (J+1)} + \frac{24 |a_{12}(2K^2 - 1) + 2 a_{12}|^2}{\rho (2K^2 + 1) - 2\pi (J+1)}$$

$$= \frac{12 (a_v^2 + a_v^j f_{22}^j [3 (J+1)^2 - K^2 (K^2 + 2)] [3 (J+1)^2 - K^2 (K^2 + 2)] [3 (J+1)^2 - K^2 (K^2 + 2)] (J+1)}{\rho (K^2 - 1) + 2\lambda}$$

$$= \frac{16 (a_v^2 + a_v^j f_{22}^j [3 (J+1)^2 - K^2 (K^2 - 2)] [3 (J+1)^2 - K^2 (K^2 - 2)] [3 (J+1)^2 - K^2 (K^2 - 2)] (J+1)}{\rho (K^2 - 1)}$$

$$= \frac{12 (a_v^2 + a_v^j f_{22}^j [3 (J+1)^2 - K^2 (K^2 - 2)] [3 (J+1)^2 - K^2 (K^2 - 2)] [3 (J+1)^2 - K^2 (K^2 - 2)] (J+1)}{\rho (K^2 - 1) + 2\lambda}$$

$$= \frac{16 (a_v^2 + a_v^j f_{22}^j [3 (J+1)^2 - K^2 (K^2 - 2)] [3 (J+1)^2 - K^2 (K^2 - 2)] [3 (J+1)^2 - K^2 (K^2 - 2)] (J+1)}{\rho (K^2 - 1)}$$

An identical formula can be obtained from our comprehensive model by putting $v = 3$, $l = 1$ and $j = \pm 3$ in our model and substituting $\lambda, K, \pi, \rho$ as linear combinations of $A, B, \gamma, \eta_{JK}$ with $\eta_{JJ}$ and $\eta_{JK}$ chosen zero. Table VIII shows large differences between the two calculational values when the terms $\eta_{JJ}$ and $\eta_{JK}$ are included. The comprehensive model,
which contains both \( \eta_{JJ} \) and \( \eta_{JK} \) is therefore seen to be superior to the Bauer formula.

The constant set in the \( v_{10}=2 \) vibrational state was used as a trial constant set to obtain approximate constants for the \( v_{10}=3 \) level. Good agreement with the experimental data for all measurements was not found. Systematic departures between observed values and calculated values were studied to determine additional procedures to be used for refining the calculations. Inclusion of the higher order diagonal terms \( \eta_{JJ}, \eta_{JK} \) removed systematic bias and gave satisfactory convergence values for \( \eta_{JJ}=0.00123 \) and \( \eta_{JK}=0.0022 \) which were obtained from the experimental data. The \( \ell \)-type doubling constant \( q_{\ell}=4.1778 \) was obtained from the data set of \( K_{\ell}=1 \) quantum states. Prakash and Roberts previously published the rotational spectra of propyne in the 17-52 GHz region for the \( v_{10}=3 \) vibrational state. This work has been extended with new observations of the rotational components of propyne for the \( J=4-3 \) transition and good agreement has been found between these data and the comprehensive model.

E. The \( v_{10}=4 \) Spectrum

In 1977, Bauer and Godon published a paper on the microwave spectra of methyl isocyanide in the \( v_6=4 \) state. To assign their observed rotational frequencies, they used
<table>
<thead>
<tr>
<th>J</th>
<th>K</th>
<th>L</th>
<th>( \nu_{\text{exp}} ) (MHz)</th>
<th>( \nu_{\text{calc}} ) (MHz)</th>
<th>( \nu_{\text{calc}} ) (MHz)</th>
<th>( \nu_{\text{a,b}} ) (MHz)</th>
<th>( \nu_{\text{a,c}} ) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>\pm 1</td>
<td>17 233.364</td>
<td>17 233.614</td>
<td>17 233.614</td>
<td>-0.250</td>
<td>-0.250</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>\pm 3</td>
<td>17 232.133</td>
<td>17 232.223</td>
<td>17 232.223</td>
<td>-0.090</td>
<td>-0.090</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>34 402.395</td>
<td>34 402.252</td>
<td>34 402.280</td>
<td>+0.163</td>
<td>+0.115</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>34 536.117</td>
<td>34 535.922</td>
<td>34 535.970</td>
<td>+0.195</td>
<td>+0.147</td>
</tr>
<tr>
<td>1</td>
<td>\pm 1</td>
<td>1</td>
<td>34 465.500</td>
<td>34 465.284</td>
<td>34 465.236</td>
<td>+0.216</td>
<td>+0.264</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>\pm 1</td>
<td>34 467.064</td>
<td>34 466.960</td>
<td>34 466.960</td>
<td>+0.104</td>
<td>+0.104</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>\pm 3</td>
<td>34 464.785</td>
<td>34 464.426</td>
<td>34 464.426</td>
<td>+0.359</td>
<td>+0.359</td>
</tr>
<tr>
<td>1</td>
<td>\pm 1</td>
<td>\pm 3</td>
<td>34 459.794</td>
<td>34 459.836</td>
<td>34 459.691</td>
<td>-0.042</td>
<td>+0.103</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>51 602.897</td>
<td>51 603.095</td>
<td>51 603.241</td>
<td>-0.198</td>
<td>-0.344</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>51 803.539</td>
<td>51 803.630</td>
<td>51 803.776</td>
<td>-0.091</td>
<td>-0.237</td>
</tr>
<tr>
<td>2</td>
<td>\mp 2</td>
<td>\pm 1</td>
<td>51 692.472</td>
<td>51 692.833</td>
<td>51 692.451</td>
<td>-0.361</td>
<td>+0.011</td>
</tr>
<tr>
<td>2</td>
<td>\pm 1</td>
<td>\pm 1</td>
<td>51 697.101</td>
<td>51 697.433</td>
<td>51 697.287</td>
<td>-0.332</td>
<td>-0.186</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>\pm 1</td>
<td>51 699.596</td>
<td>51 699.768</td>
<td>51 699.768</td>
<td>-0.172</td>
<td>-0.172</td>
</tr>
<tr>
<td>2</td>
<td>\pm 2</td>
<td>\pm 1</td>
<td>51 699.596</td>
<td>51 699.556</td>
<td>51 699.928</td>
<td>+0.040</td>
<td>-0.332</td>
</tr>
<tr>
<td>2</td>
<td>\pm 2</td>
<td>\pm 3</td>
<td>51 680.330</td>
<td>51 680.926</td>
<td>51 679.812</td>
<td>-0.596</td>
<td>+0.518</td>
</tr>
<tr>
<td>2</td>
<td>\pm 1</td>
<td>\pm 3</td>
<td>51 689.317</td>
<td>51 689.823</td>
<td>51 689.385</td>
<td>-0.506</td>
<td>-0.068</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>\pm 3</td>
<td>51 696.730</td>
<td>51 696.586</td>
<td>51 696.586</td>
<td>+0.144</td>
<td>+0.144</td>
</tr>
<tr>
<td>2</td>
<td>\pm 1</td>
<td>\pm 3</td>
<td>51 701.139</td>
<td>51 702.211</td>
<td>51 702.649</td>
<td>+0.928</td>
<td>+0.490</td>
</tr>
<tr>
<td>2</td>
<td>\pm 2</td>
<td>\pm 3</td>
<td>51 701.340</td>
<td>51 700.161</td>
<td>51 701.275</td>
<td>+1.179</td>
<td>+0.065</td>
</tr>
</tbody>
</table>

**Note:**
- a(1) Roberts and Prakash (77)
- a(2) New Data this Work
- b Bauer, Godon and Maes (76)
- c Our Comprehensive Model
<table>
<thead>
<tr>
<th>J</th>
<th>K</th>
<th>L</th>
<th>(a^{(1)}) (\nu_{\text{exp}}) (MHz)</th>
<th>(a^{(2)}) (\nu_{\text{exp}}) (MHz)</th>
<th>(b) (\nu_{\text{calc}}) (MHz)</th>
<th>(c) (\nu_{\text{calc}}) (MHz)</th>
<th>((\nu^{a}\nu^{b})) (MHz)</th>
<th>((\nu^{a}\nu^{c})) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-1</td>
<td>-1</td>
<td>68 803.104</td>
<td>68 803.656</td>
<td>68 803.988</td>
<td>-0.552</td>
<td>-0.884</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>69 071.372</td>
<td>69 071.035</td>
<td>69 071.368</td>
<td>+0.337</td>
<td>+0.004</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(\pm 2)</td>
<td>(\pm 1)</td>
<td>68 921.857</td>
<td>68 922.900</td>
<td>68 922.130</td>
<td>-1.043</td>
<td>-0.273</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(\pm 1)</td>
<td>(\pm 1)</td>
<td>68 928.316</td>
<td>68 928.991</td>
<td>68 928.659</td>
<td>-0.675</td>
<td>-0.343</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>(\pm 1)</td>
<td>68 931.430</td>
<td>68 931.769</td>
<td>68 931.769</td>
<td>-0.339</td>
<td>-0.339</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(\pm 2)</td>
<td>(\pm 1)</td>
<td>68 933.910</td>
<td>68 933.045</td>
<td>68 933.815</td>
<td>+0.865</td>
<td>+0.095</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>(\pm 3)</td>
<td>68 935.699</td>
<td>68 934.149</td>
<td>68 935.569</td>
<td>+1.550</td>
<td>+0.130</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(\pm 1)</td>
<td>(\pm 3)</td>
<td>68 928.316</td>
<td>68 928.684</td>
<td>68 928.684</td>
<td>-0.368</td>
<td>-0.368</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(\pm 2)</td>
<td>(\pm 3)</td>
<td>68 937.175</td>
<td>68 936.100</td>
<td>68 937.097</td>
<td>+1.075</td>
<td>+0.078</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(\pm 3)</td>
<td>(\pm 3)</td>
<td>68 940.947</td>
<td>68 936.707</td>
<td>68 940.966</td>
<td>+4.240</td>
<td>-0.019</td>
<td></td>
</tr>
</tbody>
</table>

\(a^{(1)}\) Roberts and Prakash (77)
\(a^{(2)}\) New Data this Work
\(b\) Bauer, Godon and Maes (74)
\(c\) Our Comprehensive Model
an analytical formulation giving the frequency of an excited
degenerate state \( v_s = 4 \), which has been obtained by Tarrago
and shared by private communication with them.

There are three differences between Bauer et. al.'s
formula and our comprehensive model. First, they added one
more non-diagonal Hamiltonian matrix element to their energy
and frequency derivation than our comprehensive model; the
element \( \langle K, \ell | \hat{H}^+ | K, \ell + 6 \rangle \) whose coefficient is \( g_6 \). Secondly,
they ignored higher order diagonal terms \( \eta_{JJ} \), \( \eta_{JK} \), which is
the major reason why there is a large difference between the
two calculated values in Table IX. The values given for \( \eta_{JJ} = 0.003 \) and \( \eta_{JK} = 0.006 \) presented in the summary table were
obtained from the observed frequency values. Also, to get a
better fit, \( f_{24} = 0.007 \) was assigned in this highly excited
vibrational state.\(^7\) The weak intensity due to the low
population in this state caused problems to detect all
frequencies in the 17-52 GHz region. The weak signals
produced larger experimental errors than were encountered in
the ground, \( v_{10} = 1, 2 \) and 3 components.

F. The General Form of the Rotational Constants

All the rotational constants of the propyne molecule from
the ground state to \( v_{10} = 4 \) state are shown in Table X. From
these constants, derived from experimentally observed
<table>
<thead>
<tr>
<th>J</th>
<th>K</th>
<th>L</th>
<th>$\nu_{\text{exp}}$ (MHz)</th>
<th>$\nu_{\text{cal}}$ (MHz)</th>
<th>$\nu_{\text{cal}}$ (MHz)</th>
<th>$(\nu_{a} - \nu_{b})$ (MHz)</th>
<th>$(\nu_{a} - \nu_{c})$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>17 278.585</td>
<td>17 278.585</td>
<td>17 278.585</td>
<td>+0.021</td>
<td>+0.021</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>±2</td>
<td>17 278.278</td>
<td>17 278.257</td>
<td>17 278.257</td>
<td>+0.179</td>
<td>+0.179</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>±4</td>
<td>17 277.010</td>
<td>17 276.831</td>
<td>17 276.831</td>
<td>+0.179</td>
<td>+0.179</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>34 556.808</td>
<td>34 556.955</td>
<td>34 556.955</td>
<td>-0.147</td>
<td>-0.147</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>±2</td>
<td>34 556.808</td>
<td>34 556.617</td>
<td>34 556.617</td>
<td>+0.191</td>
<td>+0.191</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>±2</td>
<td>34 556.808</td>
<td>34 556.264</td>
<td>34 556.504</td>
<td>+0.544</td>
<td>+0.304</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>±2</td>
<td>34 553.348</td>
<td>34 553.648</td>
<td>34 553.408</td>
<td>-0.300</td>
<td>-0.060</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>±4</td>
<td>34 553.348</td>
<td>34 553.609</td>
<td>34 553.609</td>
<td>-0.261</td>
<td>-0.261</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>±4</td>
<td>34 547.324</td>
<td>34 547.776</td>
<td>34 547.296</td>
<td>-0.428</td>
<td>+0.052</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>±4</td>
<td>34 558.234</td>
<td>34 558.381</td>
<td>34 558.861</td>
<td>-0.147</td>
<td>-0.627</td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>0</td>
<td>51 833.821</td>
<td>51 833.318</td>
<td>51 833.318</td>
<td>+0.503</td>
<td>+0.503</td>
</tr>
<tr>
<td>2</td>
<td>+1</td>
<td>-2</td>
<td>51 870.727</td>
<td>51 872.357</td>
<td>51 870.629</td>
<td>-1.630</td>
<td>+0.098</td>
</tr>
<tr>
<td>2</td>
<td>±2</td>
<td>±2</td>
<td>51 836.464</td>
<td>51 835.316</td>
<td>51 837.188</td>
<td>+1.148</td>
<td>-0.724</td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>±4</td>
<td>51 838.729</td>
<td>51 837.428</td>
<td>51 838.868</td>
<td>+1.301</td>
<td>-0.139</td>
</tr>
<tr>
<td>2</td>
<td>±2</td>
<td>±4</td>
<td>51 848.731</td>
<td>51 844.643</td>
<td>51 848.387</td>
<td>+4.088</td>
<td>+0.344</td>
</tr>
</tbody>
</table>

a Roberts and Rhee. (79)
b Bauer and Godon. (78)
c Our Comprehensive Model.
frequencies, we can predict the general tendency and derive
a general power series to predict the constants for any
vibrational level. Sufficient information was obtained for
the following constants to predict the trend and express
each constant in a power series form. The other constants,
f_{12}, f_{22}, f_{24}, \eta_{JJ}, \eta_{JK} etc... could not be so expressed
with the data available. Table XI gives the general form of
all rotational constants of the propyne molecule for which
sufficient data could be obtained to express them in a power
series form.

The constant set predicted for \( v_{10} = 5 \) from the general
form is reported in Table X.

G. The \( v_{10} = 5 \) Spectrum

By putting the predicted constants set and \( v=5, \ell=\pm1, \)
\( \ell=\pm3, \ell=\pm5 \) into the comprehensive model, one can predict the
rotational spectra of propyne in the \( v_{10} = 5 \) state. Those
predicted calculational frequencies are shown in Table XII.

Due to the weak intensity and low population, we could
not detect experimental data with our conventional video
spectrometer for the frequency range accessible to us.
Hopefully, we can obtain the observed frequencies in this
high vibrational state by increasing the sensitivity of the
detection system and by obtaining microwave oscillators
### TABLE X. All Rotational Constants for CH$_3$CCH in the $V_{10}$ Vibrational States.

<table>
<thead>
<tr>
<th></th>
<th>$V_{10}=1$</th>
<th>$V_{10}=2$</th>
<th>$V_{10}=3$</th>
<th>$V_{10}=4$</th>
<th>$V_{10}=5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_v$</td>
<td>8 545.87712</td>
<td>8 569.9919</td>
<td>8 593.9546</td>
<td>8 617.624</td>
<td>8 640.616</td>
</tr>
<tr>
<td>$D_J$</td>
<td>0.00292</td>
<td>0.00302</td>
<td>0.00312</td>
<td>0.00323</td>
<td>0.00334</td>
</tr>
<tr>
<td>$D_JK$</td>
<td>0.163423</td>
<td>0.16387</td>
<td>0.16432</td>
<td>0.16476</td>
<td>0.16521</td>
</tr>
<tr>
<td>$\eta_J$</td>
<td>0.3335</td>
<td>0.33441</td>
<td>0.33532</td>
<td>0.33623</td>
<td>0.33714</td>
</tr>
<tr>
<td>$\eta_{JJ}$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.00023</td>
<td>0.003</td>
</tr>
<tr>
<td>$\eta_{JK}$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0022</td>
<td>0.006</td>
</tr>
<tr>
<td>$A_v$</td>
<td>158 853</td>
<td>156 346</td>
<td>153 942</td>
<td>151 639</td>
<td>149 439</td>
</tr>
<tr>
<td>$\delta$</td>
<td>1.0</td>
<td>0.905</td>
<td>0.889</td>
<td>0.875</td>
<td>0.86</td>
</tr>
<tr>
<td>$\gamma''_{II}$</td>
<td>0.1798</td>
<td>-0.2164</td>
<td>-0.2221</td>
<td>-0.21</td>
<td>-0.1932</td>
</tr>
<tr>
<td>$q_v$</td>
<td>4.1938</td>
<td>4.1858</td>
<td>4.1778</td>
<td>4.1698</td>
<td>4.1698</td>
</tr>
<tr>
<td>$q_{12}$</td>
<td>-12</td>
<td>-33.681</td>
<td>-37.64</td>
<td>-39.5</td>
<td>-54.88</td>
</tr>
<tr>
<td>$d_{12}$</td>
<td>78.33</td>
<td>112.11</td>
<td>135</td>
<td>147</td>
<td>148.1</td>
</tr>
<tr>
<td>$x_{II}$</td>
<td>149 759</td>
<td>147 834</td>
<td>148 989</td>
<td>153 224</td>
<td>160 539</td>
</tr>
<tr>
<td>$f_{12}$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$f_{22}$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$f_{24}$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
TABLE XI. General Forms of Rotational Constants for CH₃CCH Molecule.

\[ B_v = 8545.87712 + 24.2046v - 0.11687v^2 + 0.0372304v^3 - 0.0101258v^4 \]
\[ A_v = 158853 - 2557.52v + 51v^2 \]
\[ \gamma_{\ell \ell} = -0.0092 - 0.106967v + 0.02855v^2 - 0.00218333v^3 \]
\[ D_{JK} = 0.163423 + 0.0004462v \]
\[ D_J = 0.00292 + 0.0000959991v + 0.00000200048v^2 \]
\[ n_J = 0.3335 + 0.00091058v \]
\[ q_v = 4.2018 - 0.00800018v \]
\[ q_{12} = 43.026 - 76.9062v + 24.484v^2 - 2.60383v^3 \]
\[ d_{12} = 33.6602 + 50.1149v - 5.44498v^2 \]
\[ x_{\ell \ell} = 154764 - 6545.12v + 1540.02v^2 \]
\[ \zeta = 1 - 0.193064v + 0.141912v^2 - 0.0523312v^3 + 0.00908289v^4 - 0.000599968v^5 \]
TABLE XII. Calculated Rotational Transition Frequencies for CH₃CCH in the v₁₀ = 5 Excited Vibrational State.

<table>
<thead>
<tr>
<th>J</th>
<th>K</th>
<th>ℓ</th>
<th>V_{cal} (MHz)</th>
<th>J</th>
<th>K</th>
<th>ℓ</th>
<th>V_{cal} (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>±1</td>
<td>17 320.008</td>
<td>2</td>
<td>-1</td>
<td>-1</td>
<td>51 810.713</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>±3</td>
<td>17 319.546</td>
<td>2</td>
<td>+1</td>
<td>+1</td>
<td>52 110.362</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>±5</td>
<td>17 318.574</td>
<td>2</td>
<td>+2</td>
<td>+1</td>
<td>51 951.313</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>34 540.548</td>
<td>2</td>
<td>+1</td>
<td>±1</td>
<td>51 956.199</td>
</tr>
<tr>
<td>1</td>
<td>+1</td>
<td>+1</td>
<td>34 740.314</td>
<td>2</td>
<td>0</td>
<td>±1</td>
<td>51 958.506</td>
</tr>
<tr>
<td>1</td>
<td>+1</td>
<td>-1</td>
<td>34 638.016</td>
<td>2</td>
<td>±2</td>
<td>±1</td>
<td>51 960.574</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>±1</td>
<td>34 639.636</td>
<td>2</td>
<td>+2</td>
<td>±3</td>
<td>51 941.457</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>±3</td>
<td>34 634.620</td>
<td>2</td>
<td>+1</td>
<td>±3</td>
<td>51 951.337</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>±3</td>
<td>34 639.052</td>
<td>2</td>
<td>0</td>
<td>±3</td>
<td>51 958.482</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>±5</td>
<td>34 642.257</td>
<td>2</td>
<td>±1</td>
<td>±3</td>
<td>51 963.804</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>±5</td>
<td>34 630.248</td>
<td>2</td>
<td>±2</td>
<td>±3</td>
<td>51 964.433</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>±5</td>
<td>34 637.080</td>
<td>2</td>
<td>+2</td>
<td>±5</td>
<td>51 930.092</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>±5</td>
<td>34 642.599</td>
<td>2</td>
<td>+1</td>
<td>±5</td>
<td>51 944.307</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>0</td>
<td>±5</td>
<td>51 955.453</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>±1</td>
<td>±5</td>
<td>51 964.627</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>±2</td>
<td>±5</td>
<td>51 972.968</td>
</tr>
</tbody>
</table>
which will give us access to the 70-125 GHz frequency range as fundamentals.
CHAPTER VI

CONCLUSIONS

Some of the problems of the pure rotational spectrum of a vibrating-rotating polyatomic molecule has been investigated. Both classical and quantum mechanical approaches have been presented to explain the physical significance of some of the gross features of the rotational spectra of linear and symmetric top molecules. Vibrational effects to the rotational spectra have been studied in the excited doubly degenerate vibrational states. The general quantum mechanical Hamiltonian for vibrating-rotating polyatomic molecule of arbitrary symmetry has been discussed. A complete procedure to get the solution of the fourth order series expansion of this Hamiltonian through the use of successive contact transformations has been outlined. By using Bauer's Hamiltonian matrix elements which are derived for the $C_{3v}$ symmetry molecules, a comprehensive model for predicting the rotational spectra of polyatomic molecules of $C_{3v}$ symmetry has been developed from basic perturbation theory. As test of this model, comparisons between this model and other formulas have been made and very good agreement between the comprehensive model and other models, when suitable modifications have been made in the non-general formulas, has been found.
A total of 86 rotational transitions for the ground, \( v_{10} = 1, v_{10} = 2, v_{10} = 3 \) and \( v_{10} = 4 \) vibrational states of propyne molecule have been reassigned by using the comprehensive model. Of these 86 lines, the transition of \( J = 3 \rightarrow 4 \) in \( v_{10} = 3 \) and all the lines in the \( v_{10} = 4 \) vibrational states were measured here for the first time. Also, a total of 34 rotational constants for structure of the propyne molecule have been derived for the first time from the microwave data of the ground state to \( v_{10} = 4 \) vibrational state which were measured as part of this work.

For the first time general forms of the 11 different rotational constants of the propyne molecule have been achieved by analyzing the 88 rotational constants which were obtained from the observed spectra of the ground state, \( v_{10} = 1, 2, 3 \) and \( 4 \) vibrational states. These general forms of the rotational constants of the propyne molecule allowed us to predict the rotational constants of the \( v_{10} = 5 \) vibrational state of this molecule. From these constants, rotational spectra of the propyne molecule in the \( v_{10} = 5 \) state can be predicted.

Some exceptional phenomena have been detected in the \( v_{10} = 3 \) rotational spectrum of propyne molecule. It has been shown that the observed spectra in the \( K = \pm 1 \) and \( \ell = \pm 1 \) states diverge systematically from the calculational values. The divergence increase with \( J \) according to
\[ \nu(J, \pm 1, \pm 1) = 0.762 (J+1) + \nu_a(J, \pm 1, \pm 1) \]

where \( \nu_a(J, \pm 1, \pm 1) \) is the frequency predicted by the model.

This departure may be caused by the ignorance of the terms \( f_{12}(J+1) \) and \( f_{22}(J+1) \) in the non-diagonal matrix elements of the Hamiltonian for the rotational energy calculation. Similar exceptional phenomena were reported in the \( v_\nu = 1 \) vibrational state.\(^2\) No satisfactory theoretical explanations as to why this exception arises for this special quantum number set has been found.

This study of the microwave rotational spectra of highly excited vibrational states has been greatly complicated by the low intensity of some of these transitions. This problem could be partially solved by increasing the sensitivity of the detection system and by obtaining the microwave oscillators which will give us access to the 70-125 GHz frequency range as fundamentals.
APPENDIX A

THE $v_9=2$ ROTATIONAL SPECTRA OF PROPYNE

In order to test the comprehensive model for other than the $v_{10}$ vibrations, an experimental test was run on the $v_9$ spectrum of propyne. Some rotational components in the $v_9=2$ vibrational state of propyne have been observed in the frequency range 17-72 GHz region. Molecular constants for this vibrationally excited state have been determined from more than 11 observed rotational transitions. See Table XIII below for a list of these constants. Good agreement between the experimental frequencies and the calculated frequencies obtained from a constant set for the $v_9=2$ spectrum has been found.

Some transitions in $v_9=2$ state are overlapped by the strong lines of $v_9=1$ state at 34 223.401 and 51 334.949 MHz. (See Fig. 6) This overlap made it impossible to assign some components precisely. The rotational components of the propyne molecule which were obtained in the $v_9=2$ state are given in the Table XIV.
Table XIII. Rotational Constants for Propyne in the \( v_\nu = 2 \) State

\( v_\nu = 2 \)

\[
\begin{align*}
B_v &= 8\,556.1996 \text{ MHz} \\
D_J &= 0.00296 \text{ MHz} \\
\eta_J &= 0.4687 \text{ MHz} \\
\eta_{JJ} &= 0.0 \text{ MHz} \\
X_{22} &= 150\,000 \text{ MHz} \\
d_{12} &= 0.0 \\
\gamma_{12} &= 0.0
\end{align*}
\]

\[
\begin{align*}
A_v &= 137\,392 \text{ MHz} \\
D_{JK} &= 0.1672 \text{ MHz} \\
\eta_{JK} &= 0.0 \text{ MHz} \\
q_v &= 2.2613 \text{ MHz} \\
q_{12} &= -10 \text{ MHz} \\
\xi &= 0.94 \\
f_{12} &= f_{22} = f_{24} = 0.0
\end{align*}
\]
Table XIV.
Summary of Experimental and Theoretical Data for Some Rotational Components in the $v_z=2$ Vibrational Level of Propyne

<table>
<thead>
<tr>
<th>$J$</th>
<th>$K$</th>
<th>$\ell$</th>
<th>$\nu_{\text{exp}}$ (MHz)</th>
<th>$\nu_{\text{cal}}$ (MHz)</th>
<th>$(\nu_{\text{exp}}-\nu_{\text{calc}})$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>17 112.387</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>17 112.285</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>0</td>
<td>34 223.992</td>
<td>34 222.992</td>
<td>[1]</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>34 224.672</td>
<td>34 220.070</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>±2</td>
<td>34 224.508</td>
<td>34 224.508</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>±2</td>
<td>34 227.592</td>
<td>34 227.492</td>
<td>+0.100</td>
</tr>
<tr>
<td>2</td>
<td>±2</td>
<td>0</td>
<td>51 332.922</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>0</td>
<td>51 335.750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>51 336.781</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>±2</td>
<td>±2</td>
<td>51 322.344</td>
<td>51 321.328</td>
<td>+1.016</td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>±2</td>
<td>51 330.025</td>
<td>51 329.961</td>
<td>+0.064</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>±2</td>
<td>51 336.617</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>±2</td>
<td>51 340.980</td>
<td>51 341.094</td>
<td>-0.114</td>
</tr>
<tr>
<td>2</td>
<td>±2</td>
<td>±2</td>
<td>51 343.854</td>
<td>51 343.742</td>
<td>+0.112</td>
</tr>
<tr>
<td>3</td>
<td>±3</td>
<td>0</td>
<td>58 436.781</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>±2</td>
<td>+0</td>
<td>68 443.453</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>±1</td>
<td>0</td>
<td>68 447.100</td>
<td>68 447.234</td>
<td>-0.134</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>68 448.875</td>
<td>68 448.594</td>
<td>+0.281</td>
</tr>
<tr>
<td>3</td>
<td>±3</td>
<td>±2</td>
<td>68 413.953</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>±2</td>
<td>±2</td>
<td>68 427.917</td>
<td>68 428.156</td>
<td>-0.239</td>
</tr>
<tr>
<td>3</td>
<td>±1</td>
<td>±2</td>
<td>68 439.672</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>±2</td>
<td>68 448.633</td>
<td>68 448.547</td>
<td>+0.086</td>
</tr>
<tr>
<td>3</td>
<td>±1</td>
<td>±2</td>
<td>68 454.518</td>
<td>68 454.516</td>
<td>+0.002</td>
</tr>
<tr>
<td>3</td>
<td>±2</td>
<td>±2</td>
<td>68 457.956</td>
<td>68 458.047</td>
<td>-0.091</td>
</tr>
<tr>
<td>3</td>
<td>±3</td>
<td>±2</td>
<td>68 458.812</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) These lines are overlapped by the very strong lines of the $v_g=1$ at 34 223.401 and 51 334.949 MHz.
APPENDIX B

THE LINEAR MOLECULE AND SYMMETRIC TOP
MOLECULES AS A RIGID ROTOR

Classically the angular momentum and energy of rotation of a rigid body is represented by

\[ E_r = \frac{1}{2} \mathbf{r} \cdot \mathbf{p} \]  
\[ \mathbf{p} = \mathbf{i} \mathbf{r} \]  

(B 1)

(B 2)

By choosing \( x, y, z \) as body fixed principal axis and the \( P \)'s and \( I \)'s as the corresponding angular momenta and moments of inertia respectively, Eq. (B 1) becomes

\[ E_r = \frac{1}{2} \left( \frac{p_x^2}{I_x} + \frac{p_y^2}{I_y} + \frac{p_z^2}{I_z} \right) \]  

(B 3)

For the quantum mechanical treatment, \( E_r \) and the \( P \)'s are replaced by the Hamiltonian operator and corresponding angular momentum operators. The quantum mechanical expression for a rigid rotor is given by

\[ \hat{H}_r = \frac{1}{2} \left( \frac{\hat{p}_x^2}{I_x} + \frac{\hat{p}_y^2}{I_y} + \frac{\hat{p}_z^2}{I_z} \right) \]  

(B 4)
where \( \hat{H}_r \), \( \hat{P} \)'s are appropriate operators

The total angular momentum squared, \( P^2 \), is given by

\[
P^2 = P_x^2 + P_y^2 + P_z^2
\]  \( \text{(B 5)} \)

For a linear molecule, with \( z \) assumed as the molecular axis, \( I_x = I_y \), \( I_z = 0 \),

Eq. (B 4) becomes

\[
H_r = \frac{1}{2I_x} (P_x^2 + P_y^2)
\]  \( \text{(B 6)} \)

\[
H_r = \frac{1}{2I_x} P_z^2
\]  \( \text{(B 7)} \)

By using the matrix elements for \( P_z \) and \( H_r \) from Eqs. (1-6), (1-7) and the definitions of rotational constants from Eq. (1-13), the energy of rotation for a linear molecule under the rigid rotor assumption is easily shown to be

\[
E_r = \hbar BJ(J+1)
\]  \( \text{(B 8)} \)

For a prolate symmetric top molecule, \( z \) assumed as the symmetry axis and \( I_x = I_y > I_z \). From Eqs. (B 4) and (B 5)

\[
H_r = \frac{P_x^2}{2I_x} + \frac{P_z^2}{2} \left( \frac{1}{I_z} - \frac{1}{I_x} \right)
\]  \( \text{(B 9)} \)
By using the same eigenvalue equations (1-6), (1-7) and the definitions of rotational constants from Eqs. (1-13), (1-14), the rotational energy for a prolate symmetric top molecule with the rigid rotor assumption is shown to be

\[ E_r(J,K) = \hbar \left[ BJ(J+1) + (A-B)K^2 \right] \]  

(B10)
APPENDIX C

DISTORTABLE ROTOR FOR PROLATE
SYMMETRIC TOP MOLECULES

Centrifugal stretching is treated as a perturbation on the eigenstates of the rigid rotor. If \( H_r \) represents the Hamiltonian of the rigid rotor and \( H_d \) represents that of the distortional energy, the total rotational Hamiltonian is

\[
H = H_r + H_d
\]  

(C 1)

Reference 10 has shown that the centrifugal distortional Hamiltonian has the form

\[
H_d = \frac{\hbar^4}{4} \sum_{x, y, \delta} \frac{\partial \delta}{\partial x} \frac{\partial \delta}{\partial y} \frac{\partial \delta}{\partial \delta} P_x P_y P_\delta
\]  

(C 2)

where \( x, \beta, \gamma, \delta \) represent the principal coordinate axes of the moments of inertia and where each must be summed over all three coordinate axes.

The first order perturbation treatment \( H^1_d \) has the form

\[
H^1_d = \frac{1}{4} \sum \tau^\prime \alpha \beta \gamma \delta \frac{\partial^2 \tau}{\partial \alpha \partial \beta} \frac{\partial^2 \tau}{\partial \beta \partial \gamma}
\]  

(C 3)
\[
\hat{H}_d = \frac{1}{4}(\tau_{xxx} p_x^4 + \tau_{yyy} p_y^4 + \tau_{zzz} p_z^4 + \tau_{xxyy})
\]

\[
+ \tau_{xxzz} (p_x^2 p_z^2 + p_y^2 p_z^2)
\]

\[
+ \tau_{yyzz} (p_x^2 p_z^2 + p_y^2 p_z^2)
\]

Where \(x, y, z\) represent the principal axes and \(z\) represents the symmetry axis of the top.

The definition of the coefficients in the distortional Hamiltonian is given by

\[
\tau_{xxxx} = \frac{\hbar}{2} \tau_{yyyy} = \frac{\hbar}{2} \tau_{zzzz} = \tau_{xxzz} = \tau_{yyzz} = \tau_{xyxy} = \tau_{xxyy}
\]

\[
\tau_{xxzz} = \tau_{yyzz} = \tau_{xyxy} = \tau_{xxyy} = \tau_{xxxx} - 2\tau_{xyxy}
\]

For a symmetric top molecule

\[
\tau_{xxxx} = \tau_{yyyy} = \tau_{zzzz}
\]

\[
\tau_{xxzz} = \tau_{yyzz} = \tau_{xyxy} = \tau_{xxyy} = \tau_{xxxx} - 2\tau_{xyxy}
\]

A general definition of the distortion coefficients has been designated in the literature as

\[
D_J = -\frac{\hbar^4}{4} \tau_{xxxx}
\]

\[
D_{JK} = -2D_J - \frac{\hbar^4}{2} (\tau_{xxzz} + 2\tau_{zzzz})
\]

\[
D_K = -D_J - D_{JK} - \frac{\hbar^4}{4} \tau_{zzzz}
\]
The first order energy correction in the perturbation due to the centrifugal distortion is

\[ E_d^1 = \langle J, K | H_d^1 | J, K \rangle \]  \hspace{1cm} (C 7)

By manipulating and rearranging the coefficients and using the definitions for \( D_j, D_{JK}, D_K \), in the Eqs.(C 3),(C 4),(C 5),(C 6) and (C 7), the resulting expression has the form

\[ E_d^1 = -h[D_j J^2 (J+1)^2 + D_{JK} J (J+1) K^2 + D_K K^4] \]  \hspace{1cm} (C 8)

Addition of \( E_d^1 \) to the rigid rotor values of Eq.(B10) gives the usual expression for the rotational energy of the non-rigid prolate symmetric top molecule with centrifugal distortion in the following form.

\[ E_d^1(J,K) = h[B J(J+1) + (A-B) K^2 - D J^2 (J+1)^2 J - D_{JK} J (J+1) K^2 + D_K K^4] \]  \hspace{1cm} (C 9)
The first attempts to identify the splittings caused by the Coriolis interaction in the rotational spectra was by Teller\textsuperscript{33}, and Johnston and Dennison\textsuperscript{24}.

They approached the problem along the following lines. If $P_x, P_y, \text{ and } P_z$ represent the over-all angular momentum about principal axis including that caused by pure rotation of the molecule and that caused by vibration, the pure rotational Hamiltonian can be expressed as

$$H = \frac{(P_x - P_x)^2}{2I_x} + \frac{(P_y - P_y)^2}{2I_y} + \frac{(P_z - P_z)^2}{2I_z} \quad (D \ 1)$$

where $P_x, P_y, P_z$ represent the components of the angular momentum which arise from the degenerate vibrational motions.

For a prolate symmetric top in a doubly degenerate vibrational mode with the symmetry axis taken as the $z$ axis

$$I_x = I_y = I_b, \quad I_z = I_a \quad (D \ 2)$$

and

$$P_x = P_y = 0. \quad (D \ 3)$$
Eq. (D 1) can be rewritten by using the Eqs. (D 2) and (D 3) as follows

\[ H = \frac{p^2}{2I_b} - \frac{p_z^2}{2I_b} + \frac{(p_z^2 - p_z)^2}{2I_a} \]  
\[ = \frac{p^2}{2I_b} + \frac{1}{2} \left( \frac{1}{I_a} - \frac{1}{I_b} \right) p_z^2 - \frac{p_z p_T}{I_a} \]  

In the last expression the term \( p_z^2 / 2I_a \) was neglected, which represents pure vibrational energy and which does not change with the rotational state.

By making some substitutions

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

and

\[ p_z = K \hbar \]
\[ p_T = \ell \hbar \]

The final form of the rotational energy of a symmetric top molecule in the doubly degenerate vibrational state can be expressed as

\[ E(J,K,T) = \hbar \left[ B J(J+1) + (A_v - B_v) K^2 - 2\ell \zeta K \right] \]  

Where \( A_v, B_v \) : rotational constants in the excited vibrational state

\( \zeta \) : Coriolis coupling constant.
Quantum number sets $K\lambda=-2$ cause accidental degeneracies which make the energy difference in $E_{ND}$ of Eq. (3-11) zero. To remove this undesired case, a direct diagonalization method was employed for these special quantum sets. This procedure is given schematically as follows.

\[ H_d \psi_d = E \psi_d \quad d: \text{diagonal}. \]

\[ \hat{H} \psi = \lambda \psi \]

\[ |\hat{H} - \lambda \mathbf{1}| = 0 \]

To solve this secular equation, Table III was used.

\[
\begin{array}{c|ccc}
V, J, K, \ell & V, J, K+2, \ell-4 & V, J, K-2, \ell+4 \\
\hline
V, J, K, \ell & E-\lambda & f_{24} a_2^+ b_4^- & f_{24} a_2^- b_4^+ \\
V, J, K+2, \ell-4 & f_{24} a_2^+ b_4^- & E-\lambda & 0 \\
V, J, K-2, \ell+4 & f_{24} a_2^- b_4^+ & 0 & E-\lambda \\
\end{array}
\]

No interactions between $(K+2, \ell-4)$ and $(K-2, \ell+4)$ were assumed.
\[(E-\lambda) [(E-\lambda)^2 - (f_{24} a_2^+ b_4^-)^2] - (E-\lambda) (f_{24} a_2^- b_4^+)^2 = 0\]

\[\lambda = E\]

\[\lambda = E \pm f_{24} \left[ (a_2^+ b_4^-)^2 + (a_2^- b_4^+)^2 \right]^{1/2}\]

From the Table III

\[a_2^\pm = [J(J+1) - K(K \pm 1)]^{1/2} [J(J+1) - (K+1) (K \pm 2)]^{1/2}\]

\[b_4^\pm = [(v + \ell + 1 \pm 1) (v - \ell + 1 \pm 1) (v + \ell + 1 \pm 3) (v - \ell + 1 \pm 3)]^{1/2}\]

\[\lambda \text{ becomes}\]

\[\lambda = E \pm f_{24} \left\{ [(J(J+1) - K(K+1)) [J(J+1) - (K+1)(K+2)]
\begin{align*}
& (v + \ell) (v - \ell + 2) (v + \ell - 2) (v + \ell + 2) + [(J(J+1) - K(K-1)]
\end{align*}
\right.\]

\[[(J+1)J - (K-1)(K-2)] (v + \ell + 2) (v - \ell) (v + \ell + 4) (v - \ell - 2)]^{1/2}\]

if \(K \ell = -2\) then \(K=1, \ell=-2\) and \(K=-1, \ell=2\). (see Table IV)

(D 6) becomes

\[\lambda = E \pm f_{24} J(J+1) v(v+2)\]

Applying the selection rules for absorption spectra,

\[v = \pm 2 f_{24} J(J+1) v(v+2) \quad \text{if } K \ell = -2\]
APPENDIX F

PROGRAM TO ASSIGN \( v_{10} = n \) ROTATIONAL CONSTANTS

The computer program developed for calculations in this work is recorded here for convenience.

This program can be used to assign any rotational constants in any vibrational states of propyne by putting the proper \( v \) and the observed frequency values. This program is an example to determine \( q_{12}, d_{12} \) and \( x^\lambda \) for the \( v_{10} = 4 \) rotational components of propyne. The machine language of this program is FORTRAN IV.

```c
--- PROGRAM -----

DOUBLE PRECISION V, B1, G, D1, D2, D3, Q, Q1, A, Z
DOUBLE PRECISION SN1, SN2, SN3, F1, F2, F3
DOUBLE PRECISION F5, S1, D6, D7, D8, D9, S3, S4, S6, S7, S8, S5

DIMENSION VAL(45), EXPVAL(26)

DATA EXPVAL/

91

v=4.0
TOL=0.2
NUM=15
```
\[
\begin{align*}
B1 &= 8545.87712D0 + 24.2046D0 \times V - 11687D0 \times V^2 \\
B1 &= B1 + 0.0372304D0 \times V^2 - 0.011258D0 \times V^3 \\
G &= -0.0992 - 1.06967D0 \times V + 0.02855D0 \times V^2 - 0.0021833D0 \times V^3 \\
D1 &= 1.63423D0 + V \times 4.462D - 4 \\
SN1 &= 0.3335D0 + V \times 9.1058D - 4 \\
SN2 &= 0.0 \\
SN3 &= 0.0 \\
D2 &= 0.0292D0 + V \times 9.59991D - 5 + V^2 \times 2.00048D - 6 \\
Q &= 4.2018D0 - 8.00018D - 3 \times V \\
A &= 158853.0D - 2557.52D0 \times V + 51 \times V^2 \\
Z &= 1 - 1.178665D0 \times V + 1.11914D0 \times V^2 - 3.13322D - 2 \times V^3 + 3.083 \\
F1 &= 0.0 \\
F2 &= 0.0 \\
F3 &= 0.007
\end{align*}
\]

WRITE(6,11)
FORMAT(1X,'Q1',25X,'D3',25X,'X1',35X,'FREQ')

DO 900 IQ=1,150,1
Q1=IQ
901 Q1=-Q1

DO 800 ID=1,1200,1
D3=ID

DO 700 IX=140000,175000,100
X1=IX

IND=0

DO 600 IL=1,5,2
L=IL-1
601 L=-L

DO 500 IJ=1,3
J=IJ-1

DO 400 IK=1,IJ
K=IK-1
401 K=-K

\[
\begin{align*}
F5 &= 4 \times (J+1) \times (Q+2 \times F2 \times (J+1)^2) \\
S1 &= 2 \times (J+1) \times (B1+G \times L^2 - D1 \times K^2 + SN1 \times K^L + SN3 \times K^3 \times L) \\
S1 &= S1 - 4 \times D2 \times (J+1)^3 + 4 \times SN2 \times K^L \times (J+1)^3
\end{align*}
\]
\[D6 = 4 \times X1 \times (L-1) - (A-B1) \times (2 \times K+1) - 2 \times A \times Z \times (2 \times K-L+2)\]
\[D7 = 4 \times X1 \times (L+1) + (A-B1) \times (2 \times K-1) - 2 \times A \times Z \times (-2 \times K+L+2)\]
\[D8 = X1 \times (L+1) + (A-B1) \times (K+1) - A \times Z \times (K+L+2)\]
\[D9 = X1 \times (L-1) + (A-B1) \times (K-1) - A \times Z \times (K+L-2)\]

\[C2 = (V+L) \times (V-L+2) \times (J+1)\]
\[C3 = (V-L) \times (V+L+2) \times (J+1)\]

\[S3 = C3 \times Q**2 \times ((J+1)**2 - (K+1)**2) / D8\]

\[\text{IF (}(D8 \text{.EQ.0.0).AND.}(V \text{.EQ.1.0}) ) \text{ S3=-F5}\]
\[\text{IF (}(D8 \text{.EQ.0.0).AND.}(V \text{.EQ.3.0}) ) \text{ S3=-2*F5}\]

\[S4 = C2 \times Q**2 \times ((J+1)**2 - (K-1)**2) / D9\]

\[\text{IF (}(D9 \text{.EQ.0.0).AND.}(V \text{.EQ.1.0}) ) \text{ S4=F5}\]
\[\text{IF (}(D9 \text{.EQ.0.0).AND.}(V \text{.EQ.3.0}) ) \text{ S4=2*F5}\]

\[S6 = 2 \times C2 \times (Q1 \times (2 \times K+1) + D3 \times (L-1)) \times **2 / D6\]
\[S7 = 2 \times C3 \times (Q1 \times (2 \times K-1) + D3 \times (L+1)) \times **2 / D7\]
\[S5 = S4 - S3\]
\[S8 = S6 - S7\]

\[\text{IND=IND+1}\]
\[\text{VAL(IND)=S1+S5+S8}\]

\[\text{IF (}(K \text{.LT.0}) \text{ GOTO 401}\]
\[\text{CONTINUE}\]
\[\text{400 CONTINUE}\]

\[\text{IF (}(L \text{.LT.0}) \text{ GOTO 601}\]
\[\text{CONTINUE}\]
\[\text{600 CONTINUE}\]

\[\text{NFREQ}=0\]
\[\text{DO 300 II}=1,45\]
\[\text{DO 200 JJ}=1,26\]
\[\text{IF (}(\text{VAL(II)-TOL}) \text{.GT.EXPVAL(JJ)} \text{ GOTO 200}\]
\[\text{IF (}(\text{VAL(II)+TOL}) \text{.LT.EXPVAL(JJ)} \text{ GOTO 300}\]
\[\text{NFREQ=NFREQ+1}\]
\[\text{GOTO 300}\]
\[\text{200 CONTINUE}\]
\[\text{300 CONTINUE}\]
IF (NFREQ.GE.NUM) WRITE(6,1) Q1,D3,X1,NFREQ
FORMAT(/3(F12.4,2X),I5)

700 CONTINUE

800 CONTINUE

900 IF (Q1.LT.0.0) GOTO 901
    CONTINUE
    STOP
    END
APPENDIX G

PROGRAM TO CALCULATE $v_t = n$ ROTATIONAL TRANSITION FREQUENCIES

This program can be used to calculate rotational transition frequencies for any excited vibrational states of any $C_{3v}$ molecule for which rotational constants have been derived. This program is an example for calculation of rotational spectra of molecule in any excited vibrational states by changing $v$ and $L$.

C  -------- COMPREHENSIVE MODEL FOR C  --------

C

$B_1 = R \cdot G = \gamma \cdot D_1 = D_{JK}, D_2 = D_J, Q = q \cdot Q_1 = q_{12}, D_3 = d_{12}, Z = i$

SN1 = $\eta_{J}$, SN2 = $\eta_{J}^{\prime}$, SN3 = $\eta_{J}^{\prime \prime}$, F1 = f_{12}, F2 = f_{22}, F3 = f_{24}

REAL L
REAL J
REAL K

V=2
L=0

DOUBLE PRECISION B1, G, D1, SN1, SN2, SN3, D2, Q, Q1, D3, A, Z
DOUBLE PRECISION X1, F1, F2, F3, T0, T1, T2, T3, D9, SN1, S1
DOUBLE PRECISION T4, T5, S2, S2, T6, T7, T8, T9, S3, S4
DOUBLE PRECISION S5, F9

C  ------ COEFFICIENTS ------

B1=8545.87712D0+24.2046D0*V-.11687D0*V**2
B1=B1+.0372304D0*V**3-.0101258D0*V**4
G=-.0992-.106967D0*V+.02855D0*V**2-.00218333D0*V**3
D1=.163423D0+V*4.462D-4
D2=.00292D0+V*9.59991D-5+V**2*2.00048D-6
SN1=.3335D0+V*9.1058D-4
SN2=0.0
SN3=0.0

95
\[ Q = 4.2018D0 - 8.00018D - 3*V \]
\[ Q1 = 43.026D0 - 76.9062D0*V + 24.484D0*V**2 - 2.60383D0*V**3 \]
\[ D3 = 33.6602D0 + 50.1149D0*V - 5.4498D0*V**2 \]
\[ A = 15883.5D0 - 2557.52D0*V + 51*v**2 \]
\[ Z = -1.17865D0*V + 1.11914D0*V**2 - 3.13322D0*V**3 + 3.0832D - 3*V \]
\[ X1 = 154764.0D0 - 6545.12D0*V + 1540.02D0*V**2 \]
\[ F1 = 0.0 \]
\[ F2 = 0.0 \]
\[ F3 = 0.0 \]

\[
\begin{align*}
& \text{DO 750 } JJ=1,4 \\
& \quad \quad \quad \quad J=JJ-1 \\
& \quad \quad \quad \quad JK=2*J+1 \\
& \text{DO 740 } KK=1,JK \\
& \quad \quad \quad \quad K=KK-(J+1)
\end{align*}
\]

\[
\begin{align*}
& \text{C DIAGONAL TERMS} \\
& \quad T0 = 2*(J+1)*(B1+G*L**2-D1*K**2+SN1*K*T) \\
& \quad T1 = 4*D2*(J+1)**2+4*SN2*K*L*(J+1)**3 \\
& \quad D9 = T0 + T1 \\
& \text{C NON-DIAGONAL TERMS} \\
& \quad 1ST TERM \\
& \quad T2 = (V-L)*(V+L+2)*(J+1)*((J+1)**2-(K+1)**2)*Q**2 \\
& \quad T3 = X1*(L+1)+(A-B1)*(K+1)-A*Z*(K+L+2) \\
& \quad IF (L.EQ.-1 .AND. K.EQ.-1) \text{ GOTO 350} \\
& \quad SM1 = -T2/T3 \\
& \quad IF (V.EQ.3 .AND. L.EQ.1 .AND. K.EQ.1) \text{ GOTO 390} \\
& \quad S1 = SM1 \\
& \text{GOTO 410} \\
& \text{350 } S1 = -2*Q*(J+1)*(V+1) \\
& \text{GOTO 410} \\
& \text{390 } S1 = .762*(J+1)+SM1
\end{align*}
\]

\[
\begin{align*}
& \text{C 2ND TERM} \\
& \quad T4 = (V-L)*(V-L+2)*(J+1)*((J+1)**2-(K-1)**2)*Q**2 \\
& \quad T5 = X1*(L-1)+(A-B1)*(K-1)-A*Z*((K-L-2) \\
& \quad IF (L.EQ.1 .AND. K.EQ.1) \text{ GOTO 480}
\end{align*}
\]
SM2 = T4/T5
IF (V.EQ.3 .AND. L.EQ.-1 .AND. K.EQ.-1) GOTO 520
S2 = SM2
GOTO 540

480 S2 = 2*Q*(J+1)*(V+1)
GOTO 540
520 S2 = .762*(J+1) + SM2

C ------ 3RD TERM ------
540 T6 = 2*(V+L)*(V-L+2)*(J+1)*(Q1*(2*K+1)+D3*(L-1))*2
T7 = 4*X1*(L-1)-(A-B1)*(2*K+1)-2*A*Z*(2*K-L+2)
S3 = T6/T7

C ------ 4TH TERM ------
T8 = 2*(V-L)*(V+L+2)*(J+1)*(Q1*(2*K-1)+D3*(L+1))*2
T9 = 4*X1*(L+1)-(A-B1)*(2*K-1)+2*A*Z*(-2*K+L+2)
S4 = T8/T9

C ------ 5TH TERM ------
IF (L.EQ.2 .AND. K.EQ.-1) GOTO 660
IF (L.EQ.-2 .AND. K.EQ.1) GOTO 680
S5 = 0
GOTO 730
660 S5 = 2*F3*V*(V+2)*(J+1)
GOTO 730
680 S5 = -2*F3*V*(V+2)*(J+1)

C ------ FREQUENCY(F9) ------
730 F9 = D9 + S1 + S2 + S3 + S4 + S5
J8 = J + 1
J7 = J
K7 = K
L7 = L

732 WRITE (6,735) K7, L7, J7, J8, F9
735 FORMAT (':K=', I2, ', L=', I2, ', J=', I2, ', TO J=', I2, ', F=', F12.5
740 CONTINUE

WRITE(6,745)
745 FORMAT('0'
750   CONTINUE
    STOP
    END
)

REFERENCES


20. Ref. 18, p. 117.


22. Ref. 18, p. 136.

23. Ref. 18, p. 137.

24. Ref. 12, p. 27.


27. Ref. 18, Chapter 8.


29. Ref. 18, p. 121.


32. Ref. 30, p. 31.


37. Ref. 12, p. 399.


40. Ref. 21, Chapter 9.

41. Ref. 39, Chapter II.

43. Ref. 12, p. 411.


46. Ref. 39, p. 16.

47. Ref. 39, p. 38, 45, 50, 51.


49. Ref. 39, Chapter VI.


57. Ref. 56, pp. 551-553.


64. Radar Circuit Analysis, A. F. Manual 52-8, Chapter 11.


69. Ref. 30, pp. 468-470.

70. J. M. Ware, Dissertation Appendix E (North Texas State University, 1985).
71. Ref. 16.


