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QUADRUPOLE HYPERFINE STRUCTURE IN THE  
ROTATIONAL SPECTRUM OF  $\text{CFCl}_3$  AND  $\text{CHCl}_3$

A THESIS

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QUADRUPOLE HYPERFINE STRUCTURE IN THE  
ROTATIONAL SPECTRUM OF  $\text{CFCl}_3$  AND  $\text{CHCl}_3$

Approved:

Chairman \_\_\_\_\_  
\_\_\_\_\_

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## TABLE OF CONTENTS

|   | Page |
|---|------|
| ACKNOWLEDGMENTS . . . . .   | ii   |
| LIST OF TABLES. . . . .   | iv   |
| LIST OF ILLUSTRATIONS . . . . .   | v    |
| Chapter   |      |
| I. INTRODUCTION . . . . .   | 1    |
| II. ANGULAR MOMENTUM ALGEBRA . . . . .  | 7    |
| The Rotation Operator. . . . .  | 7    |
| Vector Coupling Coefficients . . . . .  | 13   |
| The Wigner 3-nj Symbols. . . . .  | 14   |
| Irreducible Tensor Operators . . . . .  | 16   |
| The Quadrupole Interaction Hamiltonian . . . . .                                    | 18   |
| Matrix Elements of the Hamiltonian . . . . .  | 20   |
| III. THE STATE FUNCTION . . . . .   | 30   |
| The Resultant Nuclear Spin Eigenvector . . . . .                                    | 30   |
| The Total Angular Momentum Eigenvector . . . . .                                    | 44   |
| Relative Intensities of the Hyperfine Lines. . . . .                                | 54   |
| IV. QUADRUPOLE HYPERFINE STRUCTURE IN $\text{CFCl}_3$ AND $\text{CHCl}_3$ . . . . . | 59   |
| The Calculated Spectra . . . . .  | 60   |
| The Observed Spectra . . . . .  | 68   |
| V. CONCLUSIONS AND RECOMMENDATIONS. . . . .   | 85   |
| APPENDIX. . . . .   | 89   |
| LITERATURE CITED. . . . .   | 97   |
| VITA. . . . .   | 100  |

## LIST OF TABLES

| Table |  | Page |
|-------|--|------|
| 1.    | The Permutation Group on Three Objects . . . . .                                 | 32   |
| 2.    | The Genealogical Coefficients. . . . .   | 39   |
| 3.    | The Reduction Coefficients . . . . .   | 43   |
| 4.    | Splittings and Relative Intensities of the Strongest<br>Hyperfine Lines. . . . . | 62   |
| 5.    | Rotational Constant of $\text{CFCl}_3$ from Various Transitions. . . .           | 78   |
| 6.    | Rotational Constant of $\text{CHCl}_3$ from Various Transitions. . . .           | 84   |

## LIST OF ILLUSTRATIONS

| Figure  | Page |
|---|------|
| 1. $J = 1 \rightarrow 2, K = 1$ Theoretical Hyperfine Spectrum. . . . .   | 66   |
| 2. $J = 2 \rightarrow 3, K = 1$ and 2 Theoretical Hyperfine Spectrum. . . .   | 67   |
| 3. $J = 1 \rightarrow 2$ Transition in $\text{CFCl}_3$ at $-78^\circ\text{C}$ , $50\mu$ Hg, $20\text{v/cm}$ . . .   | 71   |
| 4. $J = 2 \rightarrow 3$ Transition in $\text{CFCl}_3$ at $-78^\circ\text{C}$ , $15\mu$ Hg, $200\text{v/cm}$ . . .  | 75   |
| 5. $J = 3 \rightarrow 4$ Transition in $\text{CFCl}_3$ at $-78^\circ\text{C}$ , $10\mu$ Hg, $150\text{v/cm}$ . . .  | 76   |
| 6. $J = 4 \rightarrow 5$ Transition in $\text{CFCl}_3$ at $-78^\circ\text{C}$ , $10\mu$ Hg, $300\text{v/cm}$ . . .  | 77   |
| 7. $J = 1 \rightarrow 2$ Transition in $\text{CHCl}_3$ at $-78^\circ\text{C}$ , $10\mu$ Hg, $20\text{v/cm}$ . . .   | 80   |
| 8. $J = 2 \rightarrow 3$ Transition in $\text{CHCl}_3$ at $-78^\circ\text{C}$ , $5\mu$ Hg, $300\text{v/cm}$ . . .   | 81   |
| 9. $J = 3 \rightarrow 4$ Transition in $\text{CHCl}_3$ at $-78^\circ\text{C}$ , $3\mu$ Hg, $200\text{v/cm}$ . . .   | 82   |
| 10. $J = 4 \rightarrow 5$ Transition in $\text{CHCl}_3$ at $-78^\circ\text{C}$ , $15\mu$ Hg, $160\text{v/cm}$ . . . | 83   |

## CHAPTER I

## INTRODUCTION

The effect of a nuclear electric quadrupole moment on the spectrum of an atom has been treated in detail by Casimir (1), and the hyperfine structure in the rotational spectrum of a molecule containing a single quadrupolar nucleus can be treated in an almost identical manner (2). The case of a molecule containing two quadrupolar nuclei was treated by Bardeen and Townes (3). The occurrence of three identical nuclei coupled to a molecule by electric quadrupole interaction is uncommon except in symmetric tops containing three halogens such as  $\text{CHBr}_3$  or  $\text{CHCl}_3$ . Previous attempts at analyzing the quadrupole splitting in the rotational spectra of such molecules have led to contradictory results.

Bersohn (4)(5) derived expressions for the splitting due to two or more quadrupolar nuclei in a molecule by using the algebra of irreducible tensor operators developed by Racah (6)(7)(8) for treating atomic spectra. Mizushima and Ito (9) used Bersohn's work to calculate the effect of the quadrupole interaction on the  $J = 0 \rightarrow 1$  rotational transition in  $\text{CHBr}_3$ . Kojima et al. (10) attempted to measure this transition, but the spectrum they reported was later shown to be of spurious origin (11). P. N. Wolfe (12)(13) compared the  $J = 2 \rightarrow 3$  rotational spectrum in  $\text{CHCl}_3$  with Bersohn's theory and obtained the value  $-80.39 \text{ Mc/sec}$  for the quadrupole coupling constant of the chlorine nuclei. By improving the resolution and sensitivity of the conventional Stark modulated spectrometer, Long (14)(15)



was able to measure the  $J = 1 \rightarrow 2$  transition in  $\text{CHCl}_3$ . He obtained  $-102.5$  Mc/sec for the quadrupole coupling constant. Long also obtained the value  $-110.8$  Mc/sec for the quadrupole coupling constant in  $\text{CFCl}_3$ . From measurements conducted in the solid state, Livingston (16) had obtained absolute values of  $76.98$  Mc/sec and  $79.63$  Mc/sec respectively for these constants. One would expect better agreement than this between the values obtained in the gaseous and solid states (17).

In addition to the discrepancy in the quadrupole coupling constants Long found that in the case of both  $\text{CHCl}_3$  and  $\text{CFCl}_3$  it was necessary to assign values to the centrifugal distortion coefficients which were much larger than the theoretical values in order to account for the observed spectra. He found that the centrifugal distortion coefficient  $D_J$  was negative and changed with  $J$ . Previous investigations had yielded only positive, constant values for  $D_J$  in molecules of this type. Long suggested that either the assumption that the electronic charge was symmetric about the C - Cl bond was erroneous or the quadrupole interaction theory was incorrect. Subsequently Johnson (18) examined the centrifugal distortion in symmetric top molecules, including those having C - Cl bonds. He found good agreement between the theoretical and measured centrifugal distortion coefficients with only two exceptions,  $\text{CHCl}_3$  and  $\text{CFCl}_3$ . These were the only molecules examined having three quadrupolar nuclei.

Favero and Mirri (19) then investigated the spectra of  $\text{CHCl}_3$  and  $\text{CFCl}_3$  in various transitions from  $J = 15$  to  $J = 29$  (at these frequencies the splitting due to the quadrupole interaction is quite small and can be neglected). They obtained values for the centrifugal distortion coefficients which were in good agreement with the theoretical values. These

authors concluded that the anomalous behavior reported by Long was due to the very complicated hyperfine pattern which occurs for low values of  $J$ .

Weatherly (20) calculated the quadrupole hyperfine splitting for  $\text{CFCl}_3$  using a method which differed from Bersohn's. His calculation yielded  $-81.5$  Mc/sec for the quadrupole coupling constant. The calculation also indicated that the centrifugal distortion coefficients would be near the theoretical values. Weatherly's approach does not utilize the permutation symmetry of the function representing the resultant spin of the three identical nuclei and requires the diagonalization of matrices which in some cases are twenty by twenty in size. In this study no calculation of the relative intensity of the various hyperfine lines was made. Weatherly was able to conclude that Bersohn's theory did not take into account all of the effects of the Pauli exclusion principle.

Svidzinskii (21) has discussed the problem of calculating the hyperfine structure in the rotational spectra of molecules due to multiple interactions of various types and has shown how to use the symmetry properties of the molecule to maximum advantage in simplifying the resulting matrices. Svidzinskii's work is an extension of Bersohn's, although Svidzinskii does include a discussion of the appropriate state functions to use when identical nuclei are involved. Unfortunately Svidzinskii's paper contains a host of typographical errors. Furthermore an erroneously defined permutation operator leads to a mistake which is compounded through the paper.\*

In this study the method suggested by Svidzinskii is corrected and

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\* A letter communicating these results to Dr. Svidzinskii in the USSR was returned marked "Addressee Unknown."

used to compute the complete rotational hyperfine structure pattern in symmetric top molecules containing three identical quadrupolar nuclei of spin  $3/2$ . The matrix elements derived by Bersohn are shown to be incomplete, and the calculation of relative intensities as derived by Wolfe and used by Wolfe and Long is shown to be erroneous. A comparison of the computed spectra with the observed spectra for  $\text{CFCl}_3$  and  $\text{CHCl}_3$  leads to values of the quadrupole coupling constants of  $-79.9 \pm .6$  Mc/sec and  $-77.9 \pm .5$  Mc/sec respectively. The centrifugal distortion coefficients of Favero and Mirri are found to be sufficient to account for the observed spectra when combined with the predicted quadrupole splitting.

Chapter II contains a summary of those aspects of the quantum theory of angular momentum which are needed in order to compute the quadrupole spectrum. The derivation of the quadrupole Hamiltonian is also included in this chapter. While all of this material may be found in various references, there are so many different conventions concerning choices of phase and normalization that it seemed advisable to include this summary in order to establish a consistent notation and to make the thesis self contained.

Chapter III deals with the construction of the proper state function for a molecule containing three identical nuclei. Part of the material on nuclear spin functions duplicates Bersohn's results, but the use of projection operators (suggested by Svidzinskii) is a more general approach and will be easier to extend to cases involving nuclear spins other than  $3/2$ . Using the results from Chapter II, the matrix elements for the quadrupole interaction are computed. The chapter concludes with a discussion of the relative intensities of the hyperfine lines.

For the  $J = 1 \rightarrow 2$ ,  $|K| = 1$  case the matrices of Chapter III yield 194 lines spread over a frequency range of 96 megacycles/sec. In some cases the separation between lines is about one tenth of a megacycle/sec. The effects of pressure broadening, finite spectrometer resolution, and the rapid decrease of line strengths with decreasing frequency make it impossible to compare individual lines in the observed spectrum with the computed lines except in the case of a few of the strongest lines. An estimate of the combined effects of pressure broadening and poor resolution was made by assuming a Van Vleck - Weisskopf line shape and summing intensities with the aid of a computer program developed by Nave (22) for this purpose. The computed line spectra, pressure broadened spectra, and the experimentally observed spectra are presented in Chapter IV. The quadrupole coupling constants were computed by comparing the observed and theoretical separation of the strongest lines in the  $J = 1 \rightarrow 2$  spectra.

After quadrupole splitting and centrifugal distortion effects have been taken into account it is then possible to compute the rotational constant B. The rotational constant for  $\text{CFCl}_3$  was found to be  $2465.82 \pm .02$  Mc/sec. The rotational constant for  $\text{CHCl}_3$  was found to be  $3302.07 \pm .03$  Mc/sec. These values are for the most abundant symmetric top species and are believed to be more accurate than any previously reported values. No attempt was made to measure the spectra of various isotopic species of these molecules and thereby correct the reported values (23)(24) of the bond distances and angles. It is suggested that this be done since the quadrupole splitting can now be assigned correctly. Other suggestions and a summary of the results obtained are presented in Chapter V.

The matrix elements for the cases  $J = 1, 2,$  and  $3$  are tabulated in an Appendix. The quadrupole hyperfine structure of any symmetric top molecule containing three identical quadrupolar nuclei of spin  $3/2$  may be computed by substituting the proper bond angle into these matrices and diagonalizing.

## CHAPTER II

## ANGULAR MOMENTUM ALGEBRA

The theory of rotation groups in quantum mechanics has been developed mainly by Wigner (25) and Racah (6)(7)(8). This theory, concerned with the applications of irreducible tensor operators and Wigner 3-nj symbols, has become an integral part of modern atomic and nuclear physics. Biersohn (4) was one of the first to utilize the theory in a problem involving the rotational motion of molecules. Those parts of the theory which are needed for the present problem are summarized in this chapter; details may be found in the book by Edmonds (26).

The Rotation Operator

In quantum mechanics the commutation relations (cyclic in xyz) for the angular momentum operators,

$$[J_x, J_y] = iJ_z$$

give rise to sets of  $2j + 1$  eigenvectors  $u(jm)$  which satisfy the equations

$$(J_x^2 + J_y^2 + J_z^2) u(jm) = j(j + 1) u(jm)$$

and

$$J_z u(jm) = m u(jm) .$$

In these equations  $j$  is a positive integer or half-integer and  $m$  ranges

from  $-j$  to  $+j$  in integral steps. An eigenvector  $u(jm)$  describes a physical system having a squared angular momentum of  $j(j+1)$ . The component of the angular momentum along the  $z$  axis is given by  $m$ . For integral values of  $j$  the angular momentum operators may be represented by differential operators and the eigenvectors may be represented by spherical harmonic functions. For half-integral values of  $j$  no such single-valued and continuous representation is possible. Since the exact form of the eigenvectors is seldom needed we shall continue to use the symbols  $u(jm)$  for integral or half-integral values of  $j$ .

The behavior of the angular momentum eigenvectors under a rotation of the coordinate axes is of interest. Consider the coordinate system  $x'y'z'$  which is obtained from the coordinate system  $x y z$  by performing the following rotations in the order given:

- (1) a rotation by  $\phi$  ( $0 \leq \phi < 360^\circ$ ) about the  $z$  axis which carries the system  $x y z$  into the system  $x_1y_1z_1$ ,
- (2) a rotation by  $\phi$  ( $0 \leq \phi < 180^\circ$ ) about the  $y_1$  axis which carries the system  $x_1y_1z_1$  into the system  $x_2y_2z_2$ ,
- (3) a rotation by  $\gamma$  ( $0 \leq \gamma < 360^\circ$ ) about the  $z_2$  axis which carries the system  $x_2y_2z_2$  into the system  $x'y'z'$ .

All rotations are to be carried out in a right-handed sense. We will regard the initial  $x y z$  system as being fixed in space and the  $x'y'z'$  system as being oriented so that the  $z'$  axis coincides with the symmetry axis of a symmetric top molecule. For a molecule such as  $\text{CHCl}_3$  we number the identical nuclei 1, 2, and 3 and specify that the  $y'$  axis passes through nucleus 1. We further specify that the positive direction of the  $z'$  axis is the direction of motion of a right-handed screw in a rota-

tion that would carry nucleus 1 into nucleus 2. The angles  $\phi$  and  $\theta$  are the usual polar coordinates of the  $z'$  axis and  $\gamma$  measures the rotation about this axis.

Observe that rotations (2) and (3) are defined with respect to rotated axes. When calculating the matrix elements of the rotation operator it is more convenient to define all rotations with respect to a set of axes which remains fixed in space. This may be done by carrying out the above rotations in reverse order (27), thus:

- (1') rotate about the z axis by  $\gamma$ ,
- (2') rotate about the y axis by  $\theta$ ,
- (3') rotate about the z axis by  $\phi$ .

The rotations (1'), (2'), and (3') produce the same relative orientation between the x y z coordinate system and the  $x'y'z'$  coordinate system as the rotations (1), (2), and (3). The first description does have the advantage that it makes the meaning of the angle  $\gamma$  easier to see.

The operator corresponding to the rotations (1'), (2'), and (3') is (28)

$$D(\phi, \theta, \gamma) = \exp(i\phi J_z) \exp(i\theta J_y) \exp(i\gamma J_z).$$

The effect of this operator on an eigenvector  $u(jm)$  may be expressed by a linear unitary transformation,

$$D(\phi, \theta, \gamma) u(jm) = \sum_{m'=-j}^{m'=j} D_{m' m}^{(j)}(\phi, \theta, \gamma) u(jm') \quad (1)$$



where

$$D_{m'm}^{(j)}(\phi, \theta, \gamma) = (u(jm'), D(\phi, \theta, \gamma) u(jm)).$$

The notation  $(a, b)$  is used to represent the scalar product of the vectors  $a$  and  $b$ . Analytic expressions for the matrix elements of the rotation operator are given by Edmonds (29). Since the vectors  $u(jm)$  are eigenvectors of  $J_z$  it is easy to see that the matrix elements will be functions of the form

$$D_{m'm}^{(j)}(\phi, \theta, \gamma) = e^{im'\phi} d_{m'm}^{(j)}(\theta) e^{im\gamma} \quad (2)$$

where  $d_{m'm}^{(j)}$  is some function of  $\theta$ .

When  $j$  is an integer and  $m$  is zero the functions in equation 2 are spherical harmonics. When dealing with irreducible tensor operators certain annoying factors may be eliminated by defining the spherical harmonic functions by

$$C_m^{(\ell)}(\phi, \theta) = (-1)^{m'} D_{m'0}^{(\ell)}(\phi, \theta, \gamma). \quad (3)$$

Since there are so many conventions in use for the phase and normalization of spherical harmonic functions, the functions in equation 3 will be listed here for the case  $\ell = 2$ :

$$C_2^{(2)}(\phi, \theta) = \frac{\sqrt{6}}{4} e^{i2\phi} \sin^2\theta, \quad (4a)$$

$$C_1^{(2)}(\phi, \theta) = \frac{-\sqrt{6}}{2} e^{i\phi} \sin \theta \cos \theta, \quad (4b)$$

$$C_0^{(2)}(\phi, \theta) = \frac{1}{2} (3\cos^2\theta - 1). \quad (4c)$$

The functions for negative values of  $m$  may be obtained from the identity

$$C_{-m}^{(\ell)}(\phi, \theta) = (-1)^m C_m^{(\ell)*}(\phi, \theta).$$

If  $j$  is an integer and both  $m$  and  $m'$  are zero the functions in equation 2 are Legendre polynomials  $P_\ell(\cos \theta)$ . These polynomials are related to the spherical harmonics in the following way. Consider two vectors  $\vec{r}_1$  and  $\vec{r}_2$  which have polar coordinates  $\phi_1, \theta_1$  and  $\phi_2, \theta_2$  respectively, and let the angle between the two vectors be  $\theta$ . Then we have

$$C_0^{(\ell)}(\theta) = P_\ell(\cos \theta) = \sum_{m=-\ell}^{\ell} (-1)^m C_m^{(\ell)}(\phi_1, \theta_1) C_{-m}^{(\ell)}(\phi_2, \theta_2). \quad (5)$$

If the magnitude of  $\vec{r}_2$  is less than the magnitude of  $\vec{r}_1$  then the quantity

$\frac{1}{|\vec{r}_1 - \vec{r}_2|}$  may be expanded as

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{\ell=0}^{\infty} (r_1)^{-(\ell+1)} (r_2)^\ell P_\ell(\cos \theta). \quad (6)$$

This result will be needed when deriving the Hamiltonian for the electric

quadrupole interaction of a nucleus.

One final property of the matrix elements of the rotation operator which we shall need subsequently may be derived by the successive application of equations (4.2.4), (4.2.5), and (4.2.6) in Edmonds' book (26). This relationship is

$$d_{m m}^{(j)}(180^\circ - \theta) = (-1)^{j-m} d_{m -m}^{(j)}(\theta). \quad (7)$$

The angular momentum of a symmetric top molecule can be described by a function which is proportional to the matrix elements of the rotation operator,

$$u(\text{JMK}) = \left( \frac{2J + 1}{8\pi^2} \right)^{\frac{1}{2}} D_{\text{MK}}^{(\text{J})}(\phi, \theta, \gamma). \quad (8)$$

$J(J + 1)$  is the square of the total angular momentum,  $M$  is its projection on the fixed  $z$  axis, and  $K$  is its projection on the  $z'$  axis fixed in the molecule.  $J$  is an integer and  $K$  ranges from  $-J$  to  $+J$  as does  $M$ . The rotational energy of the molecule is (30)

$$E_{\text{JK}} = J(J + 1)Bh + K^2(C - B)h$$

where  $C$  is the rotational constant about the  $z'$  axis,  $B$  is the rotational constant about any axis through the center of mass perpendicular to the  $z'$  axis, and  $h$  is Planck's constant. The energy is seen to be degenerate with

respect to the sign of  $K$ . When constructing the state function of a symmetric top molecule having rotational energy  $E_{JK}$  one must use the functions in equation 8 with both positive and negative values of  $K$ , as will be seen in Chapter III.

### Vector Coupling Coefficients

Interactions which couple two or more angular momenta are frequently encountered; for example, the coupling of the nuclear spins to the angular momentum of the molecular framework by the electric quadrupole interaction. In such cases  $m$  is no longer a good quantum number for the individual systems. However, the total angular momentum of the system will be conserved and it is desirable to have a representation in terms of the total angular momentum. Consider two interacting systems having angular momenta  $j_1$  and  $j_2$ . An eigenvector which describes the total angular momentum may be written in the form

$$u(j_1, j_2, jm) = \sum_{m_1, m_2} (j_1 m_1 j_2 m_2 | j_1 j_2 jm) u(j_1 m_1) u(j_2 m_2). \quad (9)$$

The quantities  $(j_1 m_1 j_2 m_2 | j_1 j_2 jm)$  are called vector coupling coefficients (31). They are functions of the quantum numbers displayed in them and vanish unless  $m = m_1 + m_2$  and unless  $j$  lies in the range from  $|j_1 - j_2|$  to  $j_1 + j_2$ . The order in which the vectors are coupled is important. If we let  $u(j_2, j_1, jm)$  be the vector obtained by coupling in the reverse order from equation 9 (i.e. the roles of  $j_1$  and  $j_2$  are interchanged), then these two vectors are related by

$$u(j_2, j_1, j_m) = (-1)^{j_1+j_2-j} u(j_1, j_2, j_m) \quad (10)$$

### The Wigner 3-j Symbols

Certain symmetries of the vector coupling coefficients may be exhibited in a clearer fashion by defining a 3-j symbol (32):

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1-j_2-m_3}}{(2j_3+1)^{\frac{1}{2}}} (j_1 m_1 j_2 m_2 | j_1 j_2 j_3 - m_3) .$$

In particular the 3-j symbol is unchanged under an even permutation of its columns and changes by  $(-1)^{j_1+j_2+j_3}$  under an odd permutation. The same factor is obtained if one replaces each  $m$  by  $-m$ . For typographical convenience we shall use the equivalent notation  $X(j_1 j_2 j_3; m_1 m_2 m_3)$  for the 3-j symbol. The orthogonality of the 3-j symbols is expressed by (33)

$$\sum_{m_1, m_2} X(j_1 j_2 j_3; m_1 m_2 m_3) X(j_1 j_2 j_3'; m_1 m_2 m_3') = \frac{\delta_{j_3 j_3'} \delta_{m_3 m_3'}}{(2j_3+1)} . \quad (11)$$

Now let us consider the coupling of three angular momentum eigenvectors  $u(j_1 m_1)$ ,  $u(j_2 m_2)$ , and  $u(j_3 m_3)$  to obtain an eigenvector  $u(j m)$ .

Here are two of the possible alternative coupling schemes:

- (1) Couple  $u(j_1 m_1)$  to  $u(j_2 m_2)$  to obtain a vector  $u(j_{12} m_{12})$ .  
Couple this vector to  $u(j_3 m_3)$  to obtain  $u(j m)$ . Denote this result by  $u(j_{12}, j_3, j m)$ .

- (2) Couple  $u(j_2 m_2)$  to  $u(j_3 m_3)$  to obtain a vector  $u(j_{23} m_{23})$ . Couple  $u(j_1 m_1)$  to this vector to obtain  $u(j m)$ . Denote this result by  $u(j_1, j_{23}, j m)$ .

In both cases there are several possible values of the intermediate momenta  $j_{12}$  or  $j_{23}$  which lead to the same final value of  $j$ . The vectors with the same  $j$  obtained from different intermediate momenta are orthogonal. The two coupling schemes are connected by a unitary transformation

$$u(j_1, j_{23}, j m) = \sum_{j_{12}} (j_1, j_{23} | j_{12}, j_3)^{(j)} u(j_{12}, j_3, j m).$$

The coefficients in this expansion are related to Wigner's 6-j symbols,

$$\left\{ \begin{array}{ccc} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{array} \right\} = \frac{(-1)^{j_1+j_2+j_3+j} (j_1, j_{23} | j_{12}, j_3)^{(j)}}{[(2j_{12} + 1)(2j_{23} + 1)]^{\frac{1}{2}}}. \quad (12)$$

In modern usage the 6-j symbol is distinguished from the 3-j symbol by the use of curly brackets in place of parentheses. For typographical convenience we shall resort to an older notation and write  $W(j_1 j_2 j_{12} : j_3 j j_{23})$  for the 6-j symbol. The reader is cautioned that this usage of the  $W$  symbol differs by a phase factor from some of the  $W$  symbols used in earlier literature. As defined in equation 12 the 6-j symbol is invariant under any permutation of its columns and under the interchange of upper and lower entries in any two columns (34). Recoupling transformations between four, five, or six angular momentum eigenvectors involve 9-j, 12-j, or 15-j symbols. These will not be needed.

Values of the 3-j and 6-j symbols have been tabulated by Rotenberg et al. (35) and expressed as powers of prime numbers. This tabulation not only eliminates the tedious numerical calculations which usually accompany problems of the type treated here but also makes possible a substantial simplification in expressions involving more than one 3-j or 6-j symbol by allowing one to cancel prime factors.

### Irreducible Tensor Operators

It is frequently the case that even though the complete state function of a system is not known, that part which describes the angular momentum of the system is known and appears as an angular momentum eigenvector multiplying the remainder of the state function. When we have an operator whose angular dependence is known it is then possible to separate the evaluation of matrix elements of the operator into two parts, one involving the angular momentum and the other involving the other coordinates which describe the system. That part of the matrix element involving the angular momentum is proportional to a 3-nj symbol. This is the basis of Racah's algebra of irreducible tensor operators.

An irreducible tensor operator of rank  $k$  (where  $k$  is an integer) is defined as a set of  $2k + 1$  operators which transform under rotations like the eigenvectors of the angular momentum operators. The spherical harmonic functions are examples of such quantities. If  $A_q^{(k)}$  is a component of an irreducible tensor operator then the matrix elements of this component between states of sharp angular momentum are

$$(u(n' j' m'), A_q^{(k)} u(n j m)) = (-1)^{j' - m'} X(j' k j; -m' q m) (n' j' \| A \| n j) \quad (13)$$

where  $n$  represents all other quantum numbers which describe the state. The quantity  $(n' j' \| A \| n j)$  is called the reduced matrix element. It represents that part of the matrix element which is independent of spatial orientation, that is, independent of the quantum numbers  $m'$ ,  $q$ , and  $m$ . The reduced matrix element has the same value for all components of the irreducible tensor operator (36).

The scalar product of two irreducible tensor operators is defined by

$$A \cdot B = \sum_q (-1)^q A_q^{(k)} B_{-q}^{(k)} .$$

Given two irreducible tensor operators of the same rank  $k$  which act on the angular momentum eigenvectors  $u(j_1 m_1)$  and  $u(j_2 m_2)$  respectively, the matrix element of the scalar product of these two operators in a representation in which  $j_1$  is coupled to  $j_2$  to obtain an angular momentum  $j$  is

$$\begin{aligned} & (u(n_1' j_1', n_2' j_2', jm), A \cdot B u(n_1 j_1, n_2 j_2, jm)) = & (14) \\ & (-1)^{j_1 + j_2' + j} W(j j_2' j_1' : k j_1 j_2) (n_1' j_1' \| A \| n_1 j_1) (n_2' j_2' \| B \| n_2 j_2) . \end{aligned}$$

Another relationship which will prove useful concerns the reduced matrix element of an operator  $B$  acting on an eigenvector  $u(j_1 m_1)$  in a scheme in which  $u(j_1 m_1)$  is coupled to  $u(j_2 m_2)$ . This relationship is

$$\begin{aligned} & (n_1' j_1', n_2 j_2, j \| B \| n_1 j_1, n_2 j_2, j) = (-1)^{j_1' + j_2 + j + k} & (15) \\ & [(2j + 1)(2j' + 1)]^{\frac{1}{2}} W(j_1' j' j_2 : j j_1 k) (n_1' j_1' \| B \| n_1 j_1) \end{aligned}$$



In our problem A will represent some derivative of a molecular electric field and B the corresponding nuclear electric multipole moment (37).

### The Quadrupole Interaction Hamiltonian

The potential  $V(\vec{r})$  at a point  $\vec{r}$  external to a charge distribution whose density is  $\rho(\vec{r}')$  can be expressed by means of the spherical harmonics in a series of the form

$$V(\vec{r}) = \sum_{\ell, m} Q_m^{(\ell)} C_m^{(\ell)*} (\phi, \theta)(r)^{-(\ell+1)}. \quad (16)$$

The coefficients  $Q_m^{(\ell)}$  are called multipole moments of the charge distribution and are given by

$$Q_m^{(\ell)} = \int \rho(\vec{r}') (r')^\ell C_m^{(\ell)} (\phi', \theta') dv'$$

Similarly if we consider the potential  $V(\vec{r}')$  at some point inside a region of space due to a charge distribution  $\rho(\vec{r})$  external to this region we have

$$V(\vec{r}') = \sum_{\ell, m} q_m^{(\ell)} C_m^{(\ell)*} (\phi', \theta') (r')^\ell \quad (17)$$

where

$$q_m^{(\ell)} = \int \rho(\vec{r}) C_m^{(\ell)} (\phi, \theta)(r)^{-(\ell+1)} dv.$$

The coefficients  $q_m^{(\ell)}$  are proportional to various derivatives of the potential (38).

In view of the above relations the multipole moment operators in quantum mechanics are defined by

$$Q_m^{(\ell)} = e C_m^{(\ell)} (\phi', \theta')(r')^\ell$$

where  $e$  is the electronic or protonic charge as required. A similar definition applies for the operator which gives the derivatives of the potential. These operators are obviously irreducible tensor operators since they transform under rotations like the spherical harmonics.

The electrostatic potential energy of a nucleus due to the surrounding electrons in a molecule is given by

$$W = - \int \bar{U}_m \bar{U}_n e^2 \sum_{i,j} \frac{1}{|\vec{r}_{ei} - \vec{r}_{pj}|} U_m U_n dv_m dv_n .$$

$U_m$  and  $U_n$  are the state functions of the molecular electrons and the nucleus respectively,  $\vec{r}_{ei}$  is the position vector of the  $i^{\text{th}}$  electron in a space fixed frame,  $\vec{r}_{pj}$  is the position vector of the  $j^{\text{th}}$  proton in a space fixed frame, and the integral is evaluated over the coordinates of all electrons and protons. Upon applying equations 5 and 6 this becomes

$$W = - \int \bar{U}_m \bar{U}_n e^2 \sum_{i,j} \sum_{\ell,m} [(r_{ei})^{-(\ell+1)} (r_{pj})^\ell (-1)^m C_m^{(\ell)} (\phi_{ei}, \theta_{ei}) C_{-m}^{(\ell)} (\phi_{pj}, \theta_{pj})] U_m U_n dv_m dv_n .$$

The term with  $\ell = 0$  is isotropic and hence makes no contribution to the rotational energy. This would be the only non-vanishing term if the nuclear charge were spherically symmetric. The term with  $\ell = 1$  is zero since nuclei are presumed not to have electric dipole moments (39). We are interested here in the effect on the rotational motion of a molecule produced by the terms with  $\ell = 2$ . Thus we see that the Hamiltonian operator for the quadrupole interaction energy is a scalar product of two irreducible tensor operators,

$$H = A \cdot B = \sum_m (-1)^m A_m^{(2)} B_{-m}^{(2)} .$$

The operator

$$A_m^{(2)} = -e \sum_i (r_{ei})^{-3} C_m^{(2)}(\phi_{ei}, \theta_{ei}) \quad (18)$$

gives the derivatives of the potential due to the electrons, and the operator

$$B_m^{(2)} = e \sum_j (r_{pj})^2 C_m^{(2)}(\phi_{pj}, \theta_{pj}) \quad (19)$$

gives the components of the quadrupole moment of the nucleus.

#### Matrix Elements of the Hamiltonian

Svidzinskii has shown that when identical nuclei are located in equivalent positions in a molecule the total interaction energy of the identical nuclei can be expressed in terms of the interaction energy of one of them (40). We shall use nucleus 1 for obtaining the interaction

energy. Consider a coupling scheme in which the spins of the three quadrupolar nuclei are coupled to obtain a resultant spin I according to

$$\vec{J}_2 + \vec{J}_3 = \vec{I}, \quad \vec{J}_1 + \vec{I} = \vec{F}.$$

The resultant nuclear spin will be coupled to the angular momentum of the molecular framework according to

$$\vec{J} + \vec{I} = \vec{F}.$$

The matrix elements of the quadrupole interaction Hamiltonian of nucleus 1 are given by equation 14:

$$(u(vJK'I'F), A \cdot B u(vJKIF)) = (-1)^{J+I'+F} W(FI'J:2JI) \quad (20)$$

$$(vJK' \| A \| vJK)(I' \| B \| I).$$

The quantum number  $v$  represents the vibrational state of the molecule (see Chapter III). Our notation indicates that we assume that the quadrupole interaction energy is diagonal in  $J$ . This is reasonable because the quadrupole interaction energy is small compared to the rotational energy of the molecule.

The reduced matrix element  $(vJK' \| A \| vJK)$  can be related to the derivatives of the electrostatic potential in the coordinate frame attached to the molecule. This may be seen by considering the matrix element of  $A_0^{(2)}$  between the molecular wave functions. According to equation 13 this

matrix element is

$$(u(vJM'K'), A_0^{(2)} u(vJMK)) = (-1)^{J-M'} X(J2J; -M'0M)(vJK' || A || vJK). \quad (21)$$

This same matrix element may be evaluated in a different fashion by the use of the spherical harmonic addition theorem. Using equations 18, 4c, and 5 we have

$$\begin{aligned} A_0^{(2)} &= -e \sum_i (r_{ei})^{-3} \frac{1}{2} (3\cos^2\theta_{ei} - 1) \\ &= -e \sum_i (r_{ei})^{-3} \sum_m (-1)^m C_m^{(2)}(\phi_a, \theta_a) C_{-m}^{(2)}(\phi'_{ei}, \theta'_{ei}) \end{aligned}$$

where  $\phi_a$  and  $\theta_a$  are the polar coordinates of the fixed z axis with respect to the molecular reference frame and  $\phi'_{ei}$  and  $\theta'_{ei}$  are the polar coordinates of the  $i^{\text{th}}$  electron in this same frame. Now the molecular wave function may be written as a product of a function  $U_e$  describing the distribution of the electrons with respect to the molecular axes and a function  $u(JMK)$  describing the rotational motion of the molecule as a whole. Thus equation 21 may be written in the equivalent form

$$\begin{aligned} \int \bar{U}_m A_0^{(2)} U_m dv_m &= - \int \bar{U}_e u(JM'K') e \sum_i (r_{ei})^{-3} \sum_m [(-1)^m \\ &C_m^{(2)}(\phi_a, \theta_a) C_{-m}^{(2)}(\phi'_{ei}, \theta'_{ei})] U_e u(JMK) dv_e dy \sin \theta d\theta d\phi. \end{aligned} \quad (22)$$

Consideration of the definition of  $\phi_a$  and  $\theta_a$  as given above and the defini-

tion of the angles  $\gamma$ ,  $\theta$ , and  $\phi$  as given on page 8 shows that

$$\phi_a = 180^\circ - \gamma, \quad \theta_a = \theta.$$

Hence we may write equation 22 as

$$\int \bar{U}_m A_0^{(2)} U_m dv_m = \sum_m [q_{-m}^{(2)} \int \bar{u}(JM'K') (-1)^m C_m^{(2)}(180^\circ - \gamma, \theta) u(JMK) \quad (23)$$

$$d\gamma \sin \theta d\theta d\phi]$$

where

$$q_{-m}^{(2)} = - \int \bar{U}_e e \sum_i (r_{ei})^{-3} C_{-m}^{(2)}(\phi'_{ei}, \theta'_{ei}) U_e dv_e.$$

The rotational functions in the integral on the right hand side of equation 23 are the symmetric top functions in equation 8. The value of the integral is (41)

$$(-1)^{K'-M'} (2J+1) X(J2J; -M'0M) X(J2J; -K'-mK).$$

A comparison of equations 21 and 23 now gives

$$(-1)^{J-M'} X(J2J; -M'0M) (\langle vJK' || A || vJK \rangle) = (-1)^{K'-M'} (2J+1) X(J2J; -M'0M)$$

$$\sum_m q_{-m}^{(2)} X(J2J; -K'-mK).$$

Thus the reduced matrix element  $\langle vJK' || A || vJK \rangle$  is given by

$$(\nu JK' \| A \| \nu JK) = (-1)^{J+K'} (2J+1) \sum_m q_{-m}^{(2)} X(J2J; -K' - mK).$$

The summation on  $m$  is superfluous since from the properties of the 3-j symbol only the term with  $-K' - m + K = 0$  does not vanish. Replacing  $-m$  by  $K' - K$  then gives

$$(\nu JK' \| A \| \nu JK) = (-1)^{J+K'} (2J+1) X(J2J; -K'(K'-K)K) q_{K'-K}^{(2)}. \quad (24)$$

Next we consider the meaning of the quantities  $q_m^{(2)}$ . Substituting the spherical harmonic functions 4a, 4b, and 4c into equation 17 gives, for the  $l = 2$  terms,

$$\begin{aligned} r'^2 & \left[ q_{-2}^{(2)} \frac{\sqrt{6}}{4} e^{i2\phi'} \sin^2\theta' + q_{-1}^{(2)} \frac{\sqrt{6}}{2} e^{i\phi'} \sin\theta' \cos\theta' \right. \\ & + q_0^{(2)} \frac{1}{2} (3\cos^2\theta' - 1) - q_1^{(2)} \frac{\sqrt{6}}{2} e^{-i\phi'} \sin\theta' \cos\theta' \\ & \left. + q_2^{(2)} \frac{\sqrt{6}}{4} e^{-i2\phi'} \sin^2\theta' \right], \end{aligned}$$

where  $\phi'$  and  $\theta'$  are measured with respect to the molecular axes. Now the potential at a nucleus may also be expanded in a Taylor's series about the nucleus as an origin. The second-order terms in this expansion are

$$\begin{aligned} & \frac{x'^2}{2} \frac{\partial^2 V}{\partial x'^2} + \frac{y'^2}{2} \frac{\partial^2 V}{\partial y'^2} + \frac{z'^2}{2} \frac{\partial^2 V}{\partial z'^2} + x'y' \frac{\partial^2 V}{\partial x' \partial y'} \\ & + x'z' \frac{\partial^2 V}{\partial x' \partial z'} + y'z' \frac{\partial^2 V}{\partial y' \partial z'}. \end{aligned}$$

By using identities such as  $x' = r' \sin \theta' \cos \phi'$  we may compare the coefficients of similar terms in the two expansions for the potential. This leads to the identities

$$q_0^{(2)} = \frac{1}{2} \frac{\partial^2 V}{\partial z'^2}$$

and

$$q_2^{(2)} = q_{-2}^{(2)} = \frac{\sqrt{6}}{12} \left( \frac{\partial^2 V}{\partial x'^2} - \frac{\partial^2 V}{\partial y'^2} \right)$$

All other terms are zero for reasons to be mentioned in the next paragraph.

For the particular case of a molecule such as  $\text{CHCl}_3$  we assume that the electrostatic potential at a Cl nucleus is symmetric about the C - Cl bond axis. We also assume that the potential satisfies Laplace's equation at the nucleus, that is, that none of the electrons penetrate the region where the nucleus is located. In the case of nucleus 1 the C - Cl bond lies in the  $y'z'$  plane (see page 9). Let the angle between the bond axis and the  $z'$  axis be  $\beta$  ( $\beta \leq 90^\circ$ ). Call the second derivative of the potential with respect to the bond axis  $\frac{\partial^2 V}{\partial c^2}$ . Under the above assumptions the only non-zero derivatives of the potential in the molecular coordinate frame are found to be

$$\frac{\partial^2 V}{\partial z'^2} = \frac{3\cos^2\beta - 1}{2} \frac{\partial^2 V}{\partial c^2}$$

and

$$\frac{\partial^2 V}{\partial x'^2} - \frac{\partial^2 V}{\partial y'^2} = \frac{-3\sin^2\beta}{2} \frac{\partial^2 V}{\partial c^2}.$$



More complicated expressions are obtained in the case of nuclei 2 and 3 but fortunately these are not needed.

The angle  $\alpha$  between two C - Cl bond axes is called the bond angle. Since this is the angle customarily used in specifying the shape of the molecule the  $q_m^{(2)}$ 's will be expressed in terms of this angle. The geometry of the molecule yields the relation

$$\cos \alpha = \frac{3\cos^2\beta - 1}{2} .$$

It is also customary to represent  $\frac{\partial^2 V}{\partial c^2}$  by the symbol  $q$  with no superscripts. Adopting this notation gives finally

$$q_0^{(2)} = \frac{q \cos \alpha}{2}$$

and

$$q_2^{(2)} = q_{-2}^{(2)} = q \frac{\sqrt{6}}{12} (\cos \alpha - 1).$$

Referring to equation 24 we see that the reduced matrix elements of the operator A have the values

$$(vJK||A||vJK) = (-1)^{J+K} (2J + 1) X(J2J;-KCK) \frac{q \cos \alpha}{2} ,$$

$$(vJ-1||A||vJ1) = (-1)^{J-1} (2J + 1) X(J2J;1-21) \frac{q\sqrt{6}}{12} (\cos \alpha - 1),$$

and

$$(vJ1||A||vJ-1) = (-1)^{J+1} (2J + 1) X(J2J;-12-1) q \frac{\sqrt{6}}{12} (\cos \alpha - 1).$$

The last two of the above expressions are equal to one another by the symmetry properties of the 3-j symbol. Using explicit formulas for the 3-j symbol we obtain finally

$$(\nu_{JK} \| A \| \nu_{JK}) = \frac{(2J+1) [3K^2 - J(J+1)] q \cos \alpha}{\sqrt{(2J+3)(2J+2)(2J+1)(2J)(2J-1)}}, \quad (25a)$$

and

$$\begin{aligned} (\nu_{J1} \| A \| \nu_{J-1}) &= \frac{(2J+1)J(J+1) q (\cos \alpha - 1)}{\sqrt{(2J+3)(2J+2)(2J+1)(2J)(2J-1)}} \quad (25b) \\ &= (\nu_{J-1} \| A \| \nu_{J1}). \end{aligned}$$

These expressions are valid only for nucleus 1 since the derivatives of the potential in the molecular frame were evaluated only for that case.

In equations 25a and 25b we have considered only the reduced matrix elements of the operator A between states with the same value of K or between states of  $K = 1$  with states of  $K' = -1$ . From equation 24 and the remarks preceding it we see that there could be matrix elements between any two states for which  $K - K' = 2$  (since  $q_2^{(2)}$  is not zero) or  $K - K' = -2$  (since  $q_{-2}^{(2)}$  is not zero). We do not need to consider these more general cases since in Chapter III it will be seen that the wave functions corresponding to a particular value of the rotational energy contain K and -K. The only values for which  $K - (-K) = 2$  or  $K - (-K) = -2$  occur when  $|K| = 1$ . It is not necessary to consider the matrix elements of the quadrupole interaction between states corresponding to different rotational energies because the energy gap between these states is large compared to the quad-

rupole interaction energy.

The reduced matrix element  $(I' \| B \| I)$  is evaluated by the use of equation 15 which gives

$$(j_1, L, I' \| B \| j_1, L, I) = (-1)^{j_1+L+I+2} [(2I+1)(2I'+1)]^{\frac{1}{2}}$$

$$W(j_1 I' L; I j_1 2)(j_1 \| B \| j_1).$$

The reduced matrix element  $(j_1 \| B \| j_1)$  is proportional to the nuclear quadrupole moment. The nucleus is presumed to be in rapid rotation about the spin axis. On the average there will be cylindrical symmetry of the nuclear charge about this axis so that not all components of the quadrupole moment tensor are independent of one another. The term conventionally referred to as "the quadrupole moment" (42) is defined by

$$eQ = \int \bar{U}_n e \sum_j (3z_{pj}^2 - r_{pj}^2) U_n dv_n$$

when the nucleus is in a state having the maximum projection of its angular momentum along the z axis. From equations 4c and 19 we see that

$$e \sum_j (3z_{pj}^2 - r_{pj}^2) = 2e \sum_j (r_{pj})^2 C_0^{(2)}(\phi_{pj}, \theta_{pj}) = 2 B_0^{(2)}$$

Using equation 13 gives

$$eQ = (u(j_1 j_1), 2 B_0^{(2)} u(j_1 j_1)) = 2 X(j_1 2 j_1; -j_1 0 j_1)(j_1 \| B \| j_1)$$

or

$$(j_1 \| B \| j_1) = \frac{eQ}{2X(j_1^2 j_1; -j_1^0 j_1)} .$$

For  $j_1 = 3/2$  this result becomes

$$(3/2 \| B \| 3/2) = \sqrt{5} eQ . \quad (26)$$

Combining equations 20, 25, and 26 it now appears that we could compute the matrix elements of the quadrupole interaction energy of nucleus 1 in the prescribed coupling scheme. However, the correct state function for the symmetric top molecule involves linear combinations of angular momentum eigenvectors with different values of  $K$ . Hence the matrix elements used in the first order perturbation theory will contain more than one term of the type in equation 20. The construction of the proper state function is the subject of Chapter III.

At this point we see that the dependence of the rotational energy of a molecule on the electrostatic quadrupole coupling of the nucleus will be expressed as a multiple of  $eQq$  where  $eQ$  is the quadrupole moment of the nucleus and  $q$  is the second derivative of the electrostatic potential along the bond axis. No attempt will be made to evaluate  $eQ$  or  $q$  separately which is a complex and independent problem.

## CHAPTER III

## THE STATE FUNCTION

In order to calculate the correction to the rotational energy of a molecule due to the nuclear electric quadrupole interaction by means of first order perturbation theory we must know the rotational dependence of the state function of the system. According to the Pauli exclusion principle the state function must change sign under the exchange of two identical nuclei with half-integral spins. If the nuclei have integral spins the state function must remain unchanged. The restriction imposed by the Pauli exclusion principle affects the choice of the angular momentum eigenvectors used in constructing the state function. Since the permutation symmetry of the total angular momentum eigenvector depends upon the behavior of the nuclear spin eigenvector, the eigenvector representing the resultant nuclear spin will be considered first.

The Resultant Nuclear Spin Eigenvector

For molecules such as  $\text{CHCl}_3$  which contain identical nuclei at equivalent positions, the quadrupole interaction Hamiltonian does not change when identical nuclei are permuted. If we use, as basis vectors for this problem, linear combinations of the resultant spin eigenvectors which are also the basis vectors for an irreducible representation of the group of permutations of three objects, then there will be no matrix elements of the Hamiltonian between basis vectors of different representations (43).

The matrices representing the elements of the group of permutations of three objects are shown in Table 1 (44). This group has three irreducible representations: totally symmetric,  $A^{(1)}$ ; antisymmetric,  $A^{(2)}$ ; and the two dimensional representation E. Using these matrices we can construct a projection operator which, when applied to an angular momentum eigenvector representing the coupled spins of three identical nuclei, gives an eigenvector that belongs to the  $k^{\text{th}}$  row (if there is more than one row) of one of the irreducible representations. In order to construct this operator we shall review the manner in which a matrix representation is constructed.

Generally one starts from any set of linearly independent functions  $U_i$  and applies to each function all of the operators  $O_R$  corresponding to the elements of the group. The resulting function can be expressed as a linear combination of these same functions,

$$O_R U_i = \sum_{j=1}^n R_{ji} U_j . \quad (27)$$

The quantities  $R_{ji}$  form the elements of a matrix representation of the operator  $O_R$  where  $j$  numbers the row of the matrix and  $i$  numbers the column (45). It may be possible to construct more than one irreducible representation by using different functions as the basis vectors. In this case the above equation is written as (46)

$$O_R U_i^{(v)} = \sum_{j=1}^n R_{ji}^{(v)} U_j^{(v)} . \quad (28)$$

TABLE 1. The Permutation Group on Three Objects

| REPRESENTATION | GROUP ELEMENTS                                 |   |   |   |   |  |
|----------------|--|---|---|---|---|--|
|                | (0)  | (123)   | (132)   | (23)  | (31)  | (12)   |
| $A^{(1)}$      | 1  | 1   | 1   | 1   | 1   | 1  |
| $A^{(2)}$      | 1  | 1   | 1   | -1  | -1  | -1   |
| E              | $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ | $\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$ | $\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$ | $\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$ | $\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$ | $\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$ |

Now multiply equation 28 by  $R_{kk}^{(w)*}$  and sum over all elements of the group:

$$\sum_R R_{kk}^{(w)*} O_R U_i^{(v)} = \sum_j U_j^{(v)} \sum_R R_{kk}^{(w)*} R_{ji}^{(v)} .$$

The coefficients  $R_{ji}^{(v)}$  satisfy the following equation (47):

$$\sum_R R_{kk}^{(w)*} R_{ji}^{(v)} = \frac{g}{n_w} \delta_{jk} \delta_{ik} \delta_{vw} ,$$

where  $g$  is the order of the group and  $n_w$  is the dimension of the  $w^{\text{th}}$  representation. Therefore we have

$$\sum_R R_{kk}^{(w)*} O_R U_i^{(v)} = \frac{g}{n_w} U_k^{(v)} \delta_{ik} \delta_{vw} .$$

The operator

$$P_k^{(w)} = \frac{n_w}{g} \sum_R R_{kk}^{(w)*} O_R \quad (29)$$

is called a projection operator (48). Consider any function which can be expressed in terms of the basis functions

$$U = \sum_v \sum_{i=1}^{n_v} a_i^{(v)} U_i^{(v)}$$

where the  $a_i^{(v)}$  are constants. Applying the projection operator to  $U$  gives



$$P_k^{(w)} U = \frac{n_w}{g} \sum_v \sum_{i=1}^{n_v} a_i^{(v)} \sum_R R_{kk}^{(w)*} O_R U_i^{(v)} = a_k^{(w)} U_k^{(w)}, \quad (30)$$

that is, it gives a function which belongs to the  $k^{\text{th}}$  row of the  $w^{\text{th}}$  irreducible representation.

Recall that the eigenvector representing the resultant nuclear spin  $I$  is to be obtained by coupling the spin of nucleus 2 to nucleus 3 to obtain an intermediate momentum  $L$ , then coupling the spin of nucleus 1 to  $L$  to obtain  $I$ . Let us abbreviate the resultant vector by the symbol  $u(LI)$ . We seek a projection operator which can be applied to this vector to give a vector which belongs to the  $k^{\text{th}}$  row of one of the irreducible representations of the permutation group of three objects. Generally the vector obtained is not of unit norm, hence we write

$$P_k^{(w)} u(LI) = N^{\frac{1}{2}} u(w_k I)$$

where  $u(w_k I)$  is a vector normalized to one. The symbol  $w$  represents either  $E$ ,  $A^{(1)}$ , or  $A^{(2)}$ . This equation may be written

$$P_k^{(w)} u(LI) = N^{\frac{1}{2}} u(w_k I) = \sum_L (u(L'I), P_k^{(w)} u(LI)) u(L'I). \quad (31)$$

The normalizing factor is obtained by realizing that a second application of the projection operator does not lead to a new result. This may be seen by applying  $P_k^{(w)}$  to the function  $U_k^{(w)}$  in equation 30. A second application of  $P_k^{(w)}$  in equation 31 gives

$$N^{\frac{1}{2}} u(w_k I) = \sum_{L', L''} (u(L' I), P_k^{(w)} u(L' I)) (u(L' I), P_k^{(w)} u(LI)) u(L'' I). \quad (32)$$

Equating the summations on the right hand sides of equations 31 and 32 and taking the scalar product with  $u(LI)$  gives

$$(u(LI), P_k^{(w)} u(LI)) = \sum_{L'} (u(LI), P_k^{(w)} u(L' I)) (u(L' I), P_k^{(w)} u(LI)).$$

Taking the scalar product of  $N^{\frac{1}{2}} u(w_k I)$  with itself in equation 31 gives

$$N = \sum_{L'} (u(LI), P_k^{(w)} u(L' I)) (u(L' I), P_k^{(w)} u(LI)).$$

Upon comparing these last two results we see that the normalization factor is

$$N = (u(LI), P_k^{(w)} u(LI)).$$

The normalized eigenvectors we seek are therefore given by

$$u(w_k I) = \sum_{L'} \frac{(u(L' I), P_k^{(w)} u(LI))}{[(u(LI), P_k^{(w)} u(LI))]^{\frac{1}{2}}} u(L' I). \quad (33)$$

Thus we need to know the matrix elements of the projection operator. From equation 29 we see that these matrix elements will be given in terms of

the matrix elements of the operator  $O_R$  by

$$(u(L'I), P_k^{(w)} u(LI)) = \frac{n_w}{g} \sum_R R_{kk}^{(w)*} (u(L'I), O_R u(LI)).$$

In our case  $O_R$  is an operator which permutes the spin coordinates among the identical nuclei. In order to understand this statement we shall write the vectors  $u(LI)$  in an expanded form. For the sake of clarity assign nucleus 1 a spin of A, nucleus 2 a spin of B, and nucleus 3 a spin of C. Write the vector  $u(LI)$  as

$$u(1A \times (2B \times 3C)L, I) . \quad (34)$$

Now define a permutation operator  $S(123)$  which assigns the spin of nucleus 1 to nucleus 2, the spin of nucleus 2 to nucleus 3, and the spin of nucleus 3 to nucleus 1. The effect of the operator  $S(123)$  on the vector in equation 34 is given by

$$S(123) u(1A \times (2B \times 3C)L, I) = u(2A \times (3B \times 1C)L, I) . \quad (35)$$

This operator rotates the spin coordinates of the nuclei by  $120^\circ$  counterclockwise as seen from the positive  $z'$  axis (see page 9) while the nuclei are considered to remain fixed in space. Later on we shall have occasion to deal with operators which permute the spatial coordinates of the nuclei, carrying the spins with them. The combined operation of rotating the nuclei by  $120^\circ$  clockwise and permuting the spins  $120^\circ$  counterclockwise is

seen to leave the configuration of the system unchanged except for permuting the numbers on the identical nuclei.

Making use of the 6-j symbol as defined by equation 12, we may expand the right hand side of equation 35 as

$$u(2A \times (3B \times 1C)L, I) = \sum_{L'} (-1)^{A+B+C+I} [(2L+1)(2L'+1)]^{\frac{1}{2}} \\ W(ABL':CIL) u((2A \times 3B)L' \times 1C, I) .$$

Using equation 10 we can rearrange the coupling in the vectors under the summation sign. We now have

$$S(123) u(1A \times (2B \times 3C)L, I) = \sum_{L'} (-1)^{A+B+2C+L'} [(2L+1)(2L'+1)]^{\frac{1}{2}} \\ W(ABL':CIL) u(1C \times (2A \times 3B)L', I) .$$

However the letters A, B, and C were used only for clarity. In fact all of the nuclear spins are identical and equal to  $3/2$  for the nuclei of interest here. Recalling that vectors obtained with different values of L are orthonormal gives, for the matrix elements of the permutation operator,

$$(u(L'I), S(123)u(LI)) = (-1)^{L'} [(2L+1)(2L'+1)]^{\frac{1}{2}} W\left(\frac{3}{2} \frac{3}{2} L': \frac{3}{2} II\right). \quad (36)$$

Matrix elements of the other permutation operators are obtained in a similar fashion. They are given by

$$\begin{aligned}
(u(L'I), S(132)u(LI)) &= (-1)^{L-L'} (u(L'I), S(123)u(LI)), \\
(u(L'I), S(23)u(LI)) &= (-1)^{3-L} \delta_{L'L}, \\
(u(L'I), S(31)u(LI)) &= -(-1)^{L'} (u(L'I), S(123)u(LI)), \\
(u(L'I), S(12)u(LI)) &= -(-1)^{L-2L'} (u(L'I), S(123)u(LI)), \\
(u(L'I), S(0)u(LI)) &= \delta_{L'L},
\end{aligned}$$

where  $S(0)$  represents the identity (no permutation). The expression in equation 36 differs from the corresponding matrix element given by Svidzinskii (49) by a factor which, in the notation used here, amounts to replacing  $(-1)^{L'}$  by  $(-1)^L$ .

Thus matrix elements of the projection operator are given by

$$(u(L'I), P_k^{(w)} u(LI)) = \frac{n_w}{g} \sum_R R_{kk}^{(w)*} (u(L'I), S(R)u(LI)) \quad (37)$$

where  $R$  represents (123), (132), etc. We now have all of the information necessary to calculate the expansion coefficients in equation 33. These coefficients are called genealogical coefficients (50) and are listed in Table 2. The notation in equation 33 indicates that these coefficients depend upon the choice of an initial intermediate momentum  $L$ . When the genealogical coefficients are computed one discovers that only the phases of the coefficients depend upon the choice of  $L$ . For the one dimensional representations  $A^{(1)}$  and  $A^{(2)}$  the choice of phases is immaterial. For the two dimensional representation  $E$  one must choose either both upper signs

TABLE 2. The Genealogical Coefficients

| w | A <sup>(1)</sup>       |                       |     | A <sup>(2)</sup>      | E <sub>1</sub> |                         |         |         | E <sub>2</sub> |                          |                          |         |
|---|------------------------|-----------------------|-----|-----------------------|----------------|-------------------------|---------|---------|----------------|--------------------------|--------------------------|---------|
| L | I                      |                       |     | I                     | I              |                         |         |         | I              |                          |                          |         |
|   | 3/2                    | 5/2                   | 9/2 | 3/2                   | 1/2            | 3/2                     | 5/2     | 7/2     | 1/2            | 3/2                      | 5/2                      | 7/2     |
| 0 |                        |                       |     | $-\sqrt{\frac{1}{6}}$ |                | $\pm\sqrt{\frac{5}{6}}$ |         |         |                |                          |                          |         |
| 1 | $-\sqrt{\frac{7}{10}}$ | $\sqrt{\frac{8}{15}}$ |     |                       |                |                         |         |         | $\pm 1$        | $\mp\sqrt{\frac{3}{10}}$ | $\mp\sqrt{\frac{7}{15}}$ |         |
| 2 |                        |                       |     | $\sqrt{\frac{5}{6}}$  | $\pm 1$        | $\pm\sqrt{\frac{1}{6}}$ | $\pm 1$ | $\pm 1$ |                |                          |                          |         |
| 3 | $\sqrt{\frac{3}{10}}$  | $\sqrt{\frac{7}{15}}$ | 1   |                       |                |                         |         |         |                | $\mp\sqrt{\frac{7}{10}}$ | $\mp\sqrt{\frac{8}{15}}$ | $\mp 1$ |

or both lower signs for the  $E_1$  and  $E_2$  coefficients under a given value of  $I$ . This does not affect the choice of signs under any other value of  $I$ .

As a simple illustration of this last remark consider the effect of the operator  $S(123)$  on the vectors with  $L = 2$ ,  $I = 7/2$ , and  $L = 3$ ,  $I = 7/2$ . Using equation 36 to calculate the matrix elements we have

$$S(123) u(2 \ 7/2) = -\frac{1}{2} u(2 \ 7/2) - \frac{\sqrt{3}}{2} u(3 \ 7/2) ,$$

$$S(123) u(3 \ 7/2) = \frac{\sqrt{3}}{2} u(2 \ 7/2) - \frac{1}{2} u(3 \ 7/2) .$$

Now let the basis vector for  $E_1$  be  $u(2 \ 7/2)$  and the basis vector for  $E_2$  be  $-u(3 \ 7/2)$ . Referring to the definition of a matrix representation given in equation 27 we see that this choice of basis vectors gives

$$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

for the matrix representation of the operator  $S(123)$  which corresponds to the matrix listed under  $(123)$  in Table 1. Choosing  $-u(2 \ 7/2)$  and  $+u(3 \ 7/2)$  for the basis vectors for  $E_1$  and  $E_2$  leads to the same result.

In the table of genealogical coefficients published by Svidzinskii (51) the phases have been omitted and the representations  $E_1$  and  $E_2$  have been erroneously assigned. Using the procedure described in the preceding paragraph it was found that no choice of phases would lead to the

correct matrix representation for each operator when the matrix elements were computed using Svidzinskii's equation (2.13). This may be the source of the error in Svidzinskii's table.

When the nuclear spin vectors in equation 33 are used, equation 20 becomes

$$\begin{aligned} (u(vJK'w_k I'F), A \cdot B u(vJKw_k IF)) &= (-1)^{J+I'+F} W(FI'J:2JI) \\ & (vJK' \|A\| vJK) (w_k I' \|B\| w_k I) . \end{aligned}$$

We shall abbreviate the genealogical coefficients by  $G(w_k, L', I)$ . Then the reduced matrix element for B may be written

$$(w_k I' \|B\| w_k I) = \sum_{L', L''} G(w_k, L' I') (L' I' \|B\| L'' I) G(w_k, L'', I) .$$

The reduced matrix element  $(L' I' \|B\| L'' I)$  is evaluated by the use of equation 15. Since B refers only to nucleus 1 this element vanishes unless  $L' = L''$ . We then have for the interaction energy of nucleus 1

$$\begin{aligned} (u(vJK'w_k I'F), A \cdot B u(vJKw_k IF)) &= (-1)^{J+I'+F} W(FI'J:2JI) \quad (38) \\ (vJK' \|A\| vJK) [(2I+1)(2I'+1)]^{\frac{1}{2}} (j \|B\| j) & \sum_{L'} [G(w_k, L', I') \\ (-1)^{j+L'+I} W(jI'L':Ij2) G(w_k, L', I)] & . \end{aligned}$$

Since the nuclei are identical and are located in equivalent posi-



tions in the molecule, the matrix elements of the total electric quadrupole interaction energy are obtained by multiplying equation 38 by three (52). When this is done we collect those terms which involve only nuclear spin quantum numbers and define a nuclear reduction coefficient by

$$C(w_k, I', I) = 3 (-1)^{I'+I} [(2I+1)(2I'+1)]^{\frac{1}{2}} \sum_{L'} [(-1)^{L'} G(w_k, L', I')] W(jI'L':Ij2) G(w_k, L', I) \quad (39)$$

Note that the reduction coefficient is symmetric in  $I$  and  $I'$  by the symmetry properties of the 6- $j$  symbol. These coefficients will depend upon the choice of phases in the genealogical coefficients. If one uses all of the upper signs or all of the lower signs in Table 2 one obtains the reduction coefficients shown in Table 3. The reverse choice of signs under some value of  $I$  in the table of genealogical coefficients changes the sign of the reduction coefficient wherever that value of  $I$  appears. When the quadrupole interaction matrix is computed this would change the sign of all matrix elements in a row and column corresponding to that value of  $I$  (except for the diagonal element) and hence would make no change in the eigenvalues of the matrix. Thus the relative phase of the genealogical coefficients must be observed but the choice of an absolute phase is unimportant.

The reduction coefficients in Table 3 differ by a sign at several points from those published by Svidzinskii (53). The coefficients for the  $E_1$  and  $E_2$  representations are reversed. The exact expressions given here give rise to a simplification in the matrix elements which is not possible

Table 3. The Reduction Coefficients

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|  |   |
|--|---|
| $C(A^{(1)}, \frac{3}{2}, \frac{3}{2}) = \frac{3}{5}$           | $C(E_1, \frac{5}{2}, \frac{5}{2}) = \frac{3\sqrt{21}}{35}$  |
| $C(A^{(1)}, \frac{3}{2}, \frac{5}{2}) = \frac{4\sqrt{6}}{5}$   | $C(E_1, \frac{5}{2}, \frac{7}{2}) = \frac{36\sqrt{7}}{35}$  |
| $C(A^{(1)}, \frac{5}{2}, \frac{5}{2}) = \frac{-\sqrt{21}}{10}$ | $C(E_1, \frac{7}{2}, \frac{7}{2}) = \frac{3\sqrt{42}}{7}$   |
| $C(A^{(1)}, \frac{5}{2}, \frac{9}{2}) = \frac{-3}{2}$          | $C(E_2, \frac{1}{2}, \frac{3}{2}) = \frac{-3\sqrt{3}}{5}$   |
| $C(A^{(1)}, \frac{9}{2}, \frac{9}{2}) = \frac{-\sqrt{33}}{2}$  | $C(E_2, \frac{3}{2}, \frac{3}{2}) = \frac{3}{5}$            |
| $C(A^{(2)}, \frac{3}{2}, \frac{3}{2}) = -1$                    | $C(E_2, \frac{1}{2}, \frac{5}{2}) = \frac{\sqrt{42}}{10}$   |
| $C(E_1, \frac{1}{2}, \frac{3}{2}) = \frac{-\sqrt{3}}{5}$       | $C(E_2, \frac{3}{2}, \frac{5}{2}) = \frac{-9}{5}$           |
| $C(E_1, \frac{3}{2}, \frac{3}{2}) = \frac{11}{5}$              | $C(E_2, \frac{3}{2}, \frac{7}{2}) = \frac{6\sqrt{3}}{5}$    |
| $C(E_1, \frac{1}{2}, \frac{5}{2}) = \frac{-3\sqrt{42}}{10}$    | $C(E_2, \frac{5}{2}, \frac{5}{2}) = \frac{-\sqrt{21}}{35}$  |
| $C(E_1, \frac{3}{2}, \frac{5}{2}) = \frac{-3}{5}$              | $C(E_2, \frac{5}{2}, \frac{7}{2}) = \frac{-12\sqrt{7}}{35}$ |
| $C(E_1, \frac{3}{2}, \frac{7}{2}) = \frac{2\sqrt{3}}{5}$       | $C(E_2, \frac{7}{2}, \frac{7}{2}) = \frac{-\sqrt{42}}{7}$   |

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when Svidzinskii's decimal fractions are used.

### The Total Angular Momentum Eigenvector

The total angular momentum eigenvector is constructed by coupling the angular momentum  $J$  of the molecular framework to the vector representing the resultant nuclear spin  $I$  which was obtained in the previous section. We know in detail how the nuclear spin function behaves when the spin coordinates are permuted. In order that the total angular momentum eigenvector have the proper symmetry we must know what operations on the function  $u(JMK)$  of equation 8 correspond to interchanging the spatial coordinates of the nuclei.

First consider the operation which interchanges the positions of nuclei 2 and 3 (see page 8). This interchange can be accomplished by rotating the molecule about the  $y'$  axis (which passes through nucleus 1) by  $180^\circ$  and then reflecting all of the nuclei in the  $x'y'$  plane. However, we must describe this process in terms of rotations carried out in the space fixed frame since none of the angles  $\phi$ ,  $\theta$ , or  $\gamma$  which appear in equation 8 describe a rotation about the molecular  $y'$  axis. In terms of rotations about space fixed axes the rotations:

- (1) rotate about the  $z$  axis by  $180^\circ - \gamma$ ,
- (2) rotate about the  $y$  axis by  $180^\circ - \theta$ ,
- (3) rotate about the  $z$  axis by  $180^\circ + \phi$ ,

produce an orientation of the molecule which differs from the orientation described by the rotations (1'), (2'), and (3') in Chapter II by an amount corresponding to a rotation by  $180^\circ$  about the  $y'$  axis. The effect of reflection in the  $x'y'$  plane on the rotational function can be taken into

account by realizing that reflection is equivalent to an inversion of coordinates about the origin followed by a rotation by  $180^\circ$  about the  $z'$  axis. This rotation must be expressed in step (1) above. With these comments in mind we now have, for the operation which interchanges nuclei 2 and 3:

- (1') rotate about the  $z$  axis by  $360^\circ - \gamma$ ,
- (2') rotate about the  $y$  axis by  $180^\circ - \theta$ ,
- (3') rotate about the  $z$  axis by  $180^\circ + \phi$ ,
- (4') invert the coordinates about the origin.

Actually the process of inversion could be performed at any point since rotations and inversions commute. The process of interchanging the spatial coordinates of nuclei 2 and 3 will be represented by an operator  $R(23)$  and its effect on the symmetric top angular momentum eigenvectors is given by

$$\begin{aligned} R(23) D_{MK}^{(J)}(\phi, \theta, \gamma) &= e^{iM(180^\circ + \phi)} d_{MK}^{(J)}(180^\circ - \theta) e^{iK(360^\circ - \gamma)} \\ &= (-1)^M e^{iM\phi} (-1)^{J-M} d_{M-K}^{(J)}(\theta) e^{-iK\gamma} \\ &= (-1)^J D_{M-K}^{(J)}(\phi, \theta, \gamma) \end{aligned}$$

where we have used equation 7.

The complete state function of the molecule also contains a term which describes the vibrational motion of the molecule and this vibrational function is affected by the inversion operation. In order to understand the meaning of this vibrational term consider first a planar symmetric top such as  $\text{BF}_3$ . The boron atom can execute vibrations perpendicular to the

plane of the three fluorine atoms which would be along the direction of the  $z'$  axis as we have defined it. The functions describing this motion are characterized by a vibrational quantum number  $v$ . The lowest vibrational energy corresponds to  $v = 0$  with higher integral values of  $v = 1, 2, \dots$  corresponding to successively higher energy levels. The potential energy for this vibrational motion is approximately parabolic with the minimum occurring at  $z' = 0$ . If this potential is distorted by adding a "hill" about  $z' = 0$  then the vibrational function still has the same symmetry with respect to inversion about the origin as in the undistorted case, but as the height of the hill is increased the energy levels approach each other in pairs. The best illustration of this effect is found in  $\text{NH}_3$  for which the energy difference between two vibrational modes corresponds to a frequency lying in the microwave region. In a molecule such as  $\text{CHCl}_3$  the hill is so high that the two lowest vibrational levels have the same energy even though they are described by different functions. This degeneracy must also be taken into account when obtaining the quadrupole hyperfine levels. The effect of the inversion of coordinates on the vibrational function is to multiply this function by  $(-1)^v$  where  $v$  is 0 or 1 for the ground state which is the only state that will be considered here (54).

Thus when the spatial coordinates of nuclei 2 and 3 are exchanged the effect of this exchange on the rotational - vibrational state of the molecule is given by

$$R(23) u(vJMK) = (-1)^{I+v} u(vJM-K) .$$

Nuclei 1 and 3 or 1 and 2 may be exchanged by the same process as described

above with an additional rotation of  $120^\circ$  or  $240^\circ$  added to step (1'). This additional rotation multiplies the state function by  $e^{iK 120^\circ}$  or  $e^{iK 240^\circ}$  respectively.

We can now construct a state function which exhibits the proper behavior when the spatial and spin coordinates of nuclei 2 and 3 are exchanged. Nuclear spin functions of species  $A^{(1)}$  remain unchanged when the spins of nuclei 2 and 3 are exchanged. Hence a normalized function which exhibits the proper behavior is

$$u(E_{JK}A^{(1)}_{IF}) = \frac{1}{\sqrt{2}} [u(vJKA^{(1)}_{IF}) + (-1)^{J+v+2j} u(vJ-KA^{(1)}_{IF})] .$$

The factor  $(-1)^{2j}$  where  $j$  is the nuclear spin makes this function change sign when nuclei 2 and 3 are exchanged if  $j$  is half-integral and remain unchanged if  $j$  is integral.

The nuclear spin functions of species  $A^{(2)}$  change sign when the spins of nuclei 2 and 3 are exchanged. A wave function having the proper symmetry in this case is given by

$$u(E_{JK}A^{(2)}_{IF}) = \frac{1}{\sqrt{2}} [u(vJKA^{(2)}_{IF}) - (-1)^{J+v+2j} u(vJ-KA^{(2)}_{IF})] .$$

The case of nuclear spin functions of species E is only slightly more difficult. Observe from Table 1 that functions belonging to the second row of E remain unchanged under the operation of permuting the spins of nuclei 2 and 3 (i.e. they behave like  $A^{(1)}$  functions in this

case) while functions belonging to the first row change sign (behave like  $A^{(2)}$  functions). Then it will be seen that the proper wave function in this case is of the form

$$u(E_{JK}EIF) = \frac{1}{2} [u(vJKE_2IF) + (-1)^{J+v+2j} u(vJ-KE_2IF)] + \\ \frac{1}{2} [u(vJKE_1IF) - (-1)^{J+v+2j} u(vJ-KE_1IF)] .$$

Now let us consider whether or not these functions behave properly when any other two nuclei are exchanged, say 1 and 3. This is best done by considering the integral or half-integral spin cases separately although the outcome is the same. For the  $A^{(1)}$  case let us assume that  $j$  is half-integral and try a function of the same form as before but with the addition of unknown phase factors  $X$  and  $Y$  as follows:

$$u(E_{JK}A^{(1)}IF) = \frac{1}{\sqrt{2}} [X u(vJKA^{(1)}IF) + (-1)^{J+v} Y u(vJ-KA^{(1)}IF)] .$$

Applying S(13) and R(13) gives

$$\frac{1}{\sqrt{2}} e^{iK 120^\circ} [(-1)^{J+v} X u(vJ-KA^{(1)}IF) + Y u(vJKA^{(1)}IF)] .$$

Requiring that this function be minus the original function leads to the equations:

$$e^{iK 120^\circ} X + Y = 0 ,$$

$$X + e^{iK 120^\circ} Y = 0 .$$

These equations have non-trivial solutions for the phase factors X and Y if and only if the determinant of the coefficients is zero. This leads to the condition

$$e^{iK 240^\circ} = 1 .$$

Thus it is seen that wave functions exhibiting the proper symmetry are possible only if K is zero or a multiple of three. When this is the case we have

$$X = -Y .$$

For the case of integral spins we require that the result of applying the operators S(13) and R(13) be equal to the original function. This leads to the result

$$X = Y$$

with the same restrictions on K as before. Letting  $X = 1$  we obtain the same phase factors as are already given by the factor  $(-1)^{2j}$ . Identical results are obtained in the case of nuclear spin eigenvectors of species  $A^{(z)}$ .



The nuclear spin states of species E present a more complicated problem which can nevertheless be solved by the same approach. We shall try a function of the form used before. Assume that  $j$  is half-integral, and use an abbreviated notation for the rotational-vibrational eigenvectors:

$$u(E_{JK}^{EIF}) = \frac{1}{2} X [u(KE_2) - (-1)^{J+v} u(-KE_2)] + \frac{1}{2} Y [u(KE_1) + (-1)^{J+v} u(-KE_1)] .$$

Applying S(13) and R(13) gives

$$\begin{aligned} & \frac{1}{2} X e^{iK 120^\circ} (-1)^{J+v} \left[ \frac{\sqrt{3}}{2} u(-KE_1) - \frac{1}{2} u(-KE_2) \right] \\ & - \frac{1}{2} X e^{iK 120^\circ} \left[ \frac{\sqrt{3}}{2} u(KE_1) - \frac{1}{2} u(KE_2) \right] \\ & + \frac{1}{2} Y e^{iK 120^\circ} (-1)^{J+v} \left[ \frac{1}{2} u(-KE_1) + \frac{\sqrt{3}}{2} u(-KE_2) \right] \\ & + \frac{1}{2} Y e^{iK 120^\circ} \left[ \frac{1}{2} u(KE_1) + \frac{\sqrt{3}}{2} u(KE_2) \right] . \end{aligned}$$

Requiring that this function be equal to minus the original function gives the equations:

$$\left( \frac{e^{iK 120^\circ}}{2} + 1 \right) X + \frac{\sqrt{3}}{2} e^{iK 120^\circ} Y = 0$$

$$\frac{-\sqrt{3}}{2} e^{iK 120^\circ} X + \left( \frac{e^{iK 120^\circ}}{2} + 1 \right) Y = 0 .$$

The requirement that the determinant of the coefficients vanish leads to the equation

$$e^{iK 240^\circ} + e^{iK 120^\circ} + 1 = 0$$

which is satisfied for any integral value of  $K$  not equal to zero or a multiple of three. The solution for the phase factors is

$$Y = e^{i 90^\circ} X .$$

Letting  $X = 1$  gives  $Y = i$ . An identical result is obtained for the case of integral  $j$ .

Summarizing, we see that for  $K$  equal to zero or a multiple of three the state functions are

$$u(E_{JK} A^{(1,2)} IF) = \frac{1}{\sqrt{2}} [u(vJKA^{(1,2)} IF) \pm (-1)^{J+v+2j} u(vJ-KA^{(1,2)} IF)] , \quad (40)$$

where the upper sign is chosen for  $A^{(1)}$  and the lower for  $A^{(2)}$ . For  $K$  not zero or a multiple of three the state functions are

$$\begin{aligned} u(E_{JK} EIF) &= \frac{1}{2} [u(vJKE_2 IF) + (-1)^{J+v+2j} u(vJ-KE_2 IF)] \\ &+ i \frac{1}{2} [u(vJKE_1 IF) - (-1)^{J+v+2j} u(vJ-KE_1 IF)] . \end{aligned} \quad (41)$$

We have seen in Chapter II that the reduced matrix elements of the operator  $A$  link either states with the same value of  $K$  or states of  $K = 1$  with states of  $K = -1$ . Therefore when  $K$  is zero or a multiple of three the matrix elements of the quadrupole interaction are

$$(u(E_{JK}^{(1,2)} I' F), A \cdot B u(E_{JK}^{(1,2)} I F)) = (-1)^{J+F+j} W(FI' J: 2JI) \quad (42)$$

$$(vJK \| A \| vJK) (j \| B \| j) C(A^{(1,2)}, I', I),$$

since  $(vJ-K \| A \| vJ-K) = (vJK \| A \| vJK)$  from the symmetry properties of the 3- $j$  symbol. There will be matrix elements of this type for both  $v = 0$  and  $v = 1$ . When  $K$  is a multiple of three the matrix elements are the same in both cases. When  $K$  is zero equation 42 must be used with caution since  $u(JMK) = u(JM-K)$  in this case and some of the wave functions in equation 40 vanish for particular values of  $J$  and  $v$ . In fact, if  $j$  is half-integral the wave functions containing nuclear spin functions of species  $A^{(1)}$  vanish whenever  $J + v$  is even and wave functions containing nuclear spin functions of species  $A^{(2)}$  vanish whenever  $J + v$  is odd.

When  $K$  is not a multiple of three the matrix elements of the quadrupole interaction are

$$\begin{aligned} & (u(E_{JK}^{(1,2)} I' F), A \cdot B u(E_{JK}^{(1,2)} I F)) = (-1)^{J+F+j} W(FI' J: 2JI) \\ & \frac{1}{4} [ (vJK \| A \| vJK) (E_2 I' \| B \| E_2 I) + (-1)^{J+v+2j} (vJK \| A \| vJ-K) (E_2 I' \| B \| E_2 I) \\ & + (-1)^{J+v+2j} (vJ-K \| A \| vJK) (E_2 I' \| B \| E_2 I) + (vJ-K \| A \| vJ-K) (E_2 I' \| B \| E_2 I) \end{aligned}$$

$$\begin{aligned}
& + (v_{JK}||A||v_{JK})(E_1 I' ||B||E_1 I) - (-1)^{J+v+2j} (v_{JK}||A||v_{J-K})(E_1 I' ||B||E_1 I) \\
& - (-1)^{J+v+2j} (v_{J-K}||A||v_{JK})(E_1 I' ||B||E_1 I) + (v_{J-K}||A||Av_{JK})(E_1 I' ||B||E_1 I) \}.
\end{aligned}$$

The matrix elements linking  $K$  and  $-K$  are non-zero only when  $|K| = 1$ . We have also seen that  $(v_{J-1}||A||v_{J1}) = (v_{J1}||A||v_{J-1})$ . Using the appropriate reduction coefficient to evaluate the reduced matrix elements of  $B$  we have

$$(u(E_{JK}EI'F), A \cdot B u(E_{JK}EIF)) = (-1)^{J+F+j} w(FI'J:2JI)(j||B||j) \quad (43)$$

$$[C(+, I', I)(v_{JK}||A||v_{JK}) + (-1)^{J+v+2j} C(-, I', I)(v_{J-K}||A||v_{JK})],$$

where

$$C(+, I', I) = \frac{1}{2} [C(E_2, I', I) + C(E_1, I', I)] \quad (44a)$$

and

$$C(-, I', I) = \frac{1}{2} [C(E_2, I', I) - C(E_1, I', I)] . \quad (44b)$$

Since the last reduced matrix element in equation 43 is non-zero only when  $|K| = 1$ , the appearance of the factor  $(-1)^v$  gives different matrix elements for  $v = 0$  and  $v = 1$  in this case.

The process of classifying the nuclear spin functions according to their permutation symmetry allows a considerable simplification of the quadrupole interaction matrix elements by permitting only certain values of  $I$  to occur for a given  $K$ . Bersohn (4) realized that this would be the case but he did not evaluate the reduced matrix elements  $(v_{JK}||A||v_{JK})$  in terms of the derivatives of the potential as we have done and therefore

seems not to have considered the possibility of these matrix elements linking states of  $K = 1$  with states of  $K = -1$ . Neither did he consider the overall permutation symmetry of the system as Svidzinskii has done. Therefore he computed separate expressions for the interaction energy of each nucleus instead of multiplying the interaction energy of one nucleus by three. For every case except  $|K| = 1$  Bersohn's expressions for the quadrupole interaction energy reduce to the ones given here. The term  $(\nu_{J-1} \| A \| \nu_{J1})$  missing from his matrix elements is the source of the errors made by Wolfe (12) and Long (14) in computing the hyperfine pattern and assigning the lines.

#### Relative Intensities of the Hyperfine Lines

The relative intensity of a rotational transition in a molecule is proportional to the square of the matrix element of the dipole moment operator between the initial and final states (55). When the matrices of the quadrupole interaction are diagonalized the state function corresponding to a hyperfine level is given by

$$u(E_{JK}^T) = \sum_I B_{TI} u(E_{JK}^{wIFM_F})$$

where the quantities  $B_{TI}$  are the matrix elements of the diagonalizing transformation. The index T is used to distinguish states corresponding to different eigenvalues. The vectors  $u(E_{JK}^{wIFM_F})$  are those given in equations 40 and 41. The quantum number  $M_F$  was omitted there since the quadrupole interaction is independent of the orientation of the molecule. The total intensity of a line is obtained by summing over all possible values of  $M_F$ ,

thus,

$$\begin{aligned}
 N &= \sum_{M_F^i M_F^f} [(u(E_{JK}^i), d_m^{(1)} u(E_{JK}^f))]^2 \quad (45) \\
 &= \sum_{M_F^i M_F^f} \left[ \sum_I B_{TI}^i B_{TI}^f (u(E_{JK}^i w_{IF}^i M_F^i), d_m^{(1)} u(E_{JK}^f w_{IF}^f M_F^f)) \right]^2
 \end{aligned}$$

where  $i$  and  $f$  refer to initial and final states. The operator  $d_m^{(1)}$  is a component of the dipole moment operator in a space fixed coordinate frame. For polarized electric fields such as are used in microwave spectroscopy we choose the  $z$  axis to be the direction of polarization. Then we need only evaluate the component  $d_0^{(1)}$ . The first step in evaluating equation 45 is to use equation 13 to obtain

$$\begin{aligned}
 (u(E_{JK}^i w_{IF}^i M_F^i), d_0^{(1)} u(E_{JK}^f w_{IF}^f M_F^f)) &= (-1)^{F^i - M_F^i} X(F^i 1 F^f; -M_F^i 0 M_F^f) \\
 &\quad (E_{JK}^i w_{IF}^i || d || E_{JK}^f w_{IF}^f).
 \end{aligned}$$

Now according to the orthogonality properties of the 3-j symbols given in equation 11 we have

$$\sum_{M_F^i M_F^f} X(F^i 1 F^f; -M_F^i 0 M_F^f)^2 = \sum_{M_F^i M_F^f} X(F^f 1 F^i; -M_F^f 0 M_F^i)^2 = \frac{1}{3}$$

where we have used the symmetry properties of the 3-j symbol. The relative intensity now becomes

$$N = \frac{1}{3} \left[ \sum_I B_{TI}^i B_{T'I}^f (E_{JK}^{i \text{wIF}^i} \| d \| E_{JK}^{f \text{wIF}^f}) \right]^2 .$$

Since we are computing the relative intensities the constant factor of  $1/3$  will be omitted hereafter.

The reduced matrix element of the dipole moment operator is evaluated by the use of equation 15 which gives

$$(E_{JK}^{i \text{wIF}^i} \| d \| E_{JK}^{f \text{wIF}^f}) = (-1)^{J^i + I + F^f + 1} [(2F^i + 1)(2F^f + 1)]^{\frac{1}{2}} \\ W(J^i F^i I : F^f J^f 1) (v^i J^i K^i \| d \| v^f J^f K^f) .$$

This last reduced matrix element is evaluated by a procedure identical to that used in Chapter II to evaluate  $(vJK' \| A \| vJK)$ . Instead of equation 24 we obtain in this case

$$(v^i J^i K^i \| d \| v^f J^f K^f) = (-1)^{J^i + K^i} [(2J^i + 1)(2J^f + 1)]^{\frac{1}{2}} \quad (46)$$

$$X(J^i 1 J^f ; -K^i m K^f) q_m^{(1)}$$

where  $q_m^{(1)}$  represents a component of the dipole moment in the molecular reference frame. For a symmetric top molecule such as  $\text{CHCl}_3$  this dipole moment lies exclusively along the  $z'$  axis. Hence the only non-vanishing component is  $q_0^{(1)}$  and this component will be designated by the symbol  $d$ . Setting  $m = 0$  in equation 46 makes this expression vanish unless  $K^i = K^f$

which is a well known selection rule. In this case the 3-j symbol also vanishes unless  $J^f = J^i$ ,  $J^f = J^i - 1$ , or  $J^f = J^i + 1$ . We shall be interested only in the absorption process  $J^f = J^i + 1$ . When these results are used to compute the matrix elements of the dipole moment operator between the state functions given in equations 40 and 41 it is found that these matrix elements vanish unless  $v$  differs by one in the initial and final states.

Letting  $J^i = J$ ,  $J^f = J + 1$ , and substituting an explicit formula for the 3-j symbol in equation 46 we have

$$(\nu^i_{JK} \| d \| \nu^f_{J+1K})^2 = \left( \frac{(J+1)^2 - K^2}{3(J+1)} \right) d^2 .$$

The relative intensities are now given by

$$N = \left( \frac{(J+1)^2 - K^2}{3(J+1)} \right) d^2 (2F^i + 1)(2F^f + 1) \left[ \sum_I B_{TI} B_{T'I} \right. \quad (47)$$

$$\left. (-1)^{J^i + I + F^f + 1} W(J^i F^i I; F^f J^f 1) \right]^2$$

The factor  $(-1)^{J^i + I + F^f + 1}$  does not appear in a similar expression derived by Wolfe (56). This has an appreciable effect on the computed intensities of the hyperfine lines arising from levels associated with more than one value of  $I$ .

For the case  $J = 3$ ,  $|K| = 2$  the reduced matrix element  $(\nu_{JK} \| A \| \nu_{JK})$  vanishes so that all of the quadrupole hyperfine levels are degenerate.



The intensities of the lines involving these levels were computed by using  $B_{TI} = 1$  for each value of  $I$ , calculating the intensities corresponding to different values of  $I$  separately, and adding all of the intensities corresponding to the same frequency.

On the basis of the calculation leading to equation 47 one would expect that the most intense lines in a given hyperfine transition would be those associated with the smallest values of  $K$ . This conclusion is false for the following reasons: (1) In the conventional Stark modulated spectrometer lines corresponding to  $K = 0$  may not be observed under normal operating conditions since these levels have a weak Stark effect. (2) For the non-zero values of  $K$  the quantum numbers  $v = 0$  and  $v = 1$  give rise to exactly the same matrix elements in every case except  $|K| = 1$ . The expression for the intensities must be multiplied by 2 to account for the degeneracy in  $v$  in these cases. Thus the most intense line in a rotational transition will be associated with  $|K| = 2$  (except of course for the  $J = 0 \rightarrow 1$  and  $1 \rightarrow 2$  transitions). Since Wolfe was not aware that the degeneracy in  $v$  was removed in the  $|K| = 1$  case the intensities he assigned to these levels are too strong by a factor of 2. Long used Wolfe's formula for the relative intensities and therefore he assumed that the strongest lines he observed in each transition were  $|K| = 1$  lines. This assignment, coupled with erroneous values for the quadrupole coupling constants, is the source of the apparent anomaly in the centrifugal distortion coefficients.

## CHAPTER IV

QUADRUPOLE HYPERFINE STRUCTURE IN  $\text{CFCl}_3$  AND  $\text{CHCl}_3$ 

When the matrix elements of equation 43 are computed and the eigenvalues obtained, they yield one hundred ninety-four hyperfine lines for the  $J = 1 \rightarrow 2$ ,  $|K| = 1$  transition. For a quadrupole coupling constant of  $-80$  Mc/sec the separation between some lines is less than  $0.1$  Mc/sec. For higher  $J$  transitions the number of hyperfine lines increases while the separation between some of the strongest lines decreases. In spite of the improvements made by Long (14) the spectrometer used to investigate these lines does not have the sensitivity and resolution necessary to detect all of the lines. The effect of pressure broadening makes it unlikely that complete resolution can ever be obtained with the conventional microwave spectrometer. The effect of poor resolution is to cause a shift in the apparent absorption frequency of a line due to the presence of one or more nearby lines. This effect can be minimized by working at low pressures, but then the relative absorption becomes so weak that only the strongest lines can be detected. Maximum effort was devoted to measuring the frequency of the strongest lines in several transitions at low pressure rather than to measuring numerous lines in a single transition at high pressure, since it was found that pressure broadening effects made a detailed comparison of observed and computed lines impossible.

The Calculated Spectra

Examination of equation 43 and the reduction coefficients in Table 3 shows that when  $F = J + 7/2$ ,  $|K| = 1$ , we have but two matrix elements, one for  $v = 0$  and the other for  $v = 1$ . Since these levels are associated with the largest possible values of  $F$  they give rise to the strongest  $|K| = 1$  lines. When  $F = J + 5/2$  we have a two by two matrix for each of the cases  $v = 0$  and  $v = 1$ . One of the eigenvalues of each matrix is identical to the single matrix element for  $F = J + 7/2$ , which increases the intensity of the lines arising from these levels. The next most intense  $|K| = 1$  lines arise from transitions between the second eigenvalue of one of these matrices and the second eigenvalue of the corresponding matrix for the rotational state  $J + 1$  for which  $F = (J + 1) + 5/2$ . For other values of  $K$  which are not zero or multiples of three there is a similar result. The matrix obtained for  $F = J + 7/2$  is one by one. The matrix obtained for  $F = J + 5/2$  is two by two and one of the eigenvalues is identical to the  $J + 7/2$  eigenvalue. There does not seem to be any obvious symmetry relation of the 6-j symbols which would lead one to expect this result but it was observed to occur for values of  $J$  from 1 through 5 and probably occurs in all cases.

In the case  $|K| = 1$  the coefficients  $C(+, I', I)$  and  $C(-, I', I)$  defined in equations 44a and 44b are such that  $C(-, I', I) = -2C(+, I', I)$  when  $I = I' = 7/2$ ,  $I = I' = 5/2$ , and  $I = 7/2, I' = 5/2$ . This makes the dependence on  $\cos \alpha$  the same for all of these matrix elements. The angular dependence can be factored out and the eigenvalues and eigenvectors obtained for an arbitrary value of  $\cos \alpha$ . These values of  $I$  give rise to the strongest hyperfine lines. Exact expressions for the frequency and relative intensity

of the strongest lines in the  $J = 1 \rightarrow 2$ ,  $J = 2 \rightarrow 3$ , and  $J = 3 \rightarrow 4$  transitions are shown in Table 4. The frequency of the three most intense lines in the  $J = 4 \rightarrow 5$  spectrum are also shown, but the relative intensities were not computed since the 6-j symbols of Rotenberg et al. (35) do not extend beyond entries greater than 8, and the F values involved in these cases are  $17/2$ . All matrix elements for  $|K| = 1$  and 2,  $J = 1, 2$ , and 3 are given in the Appendix. The complete hyperfine structure pattern for the  $J = 1 \rightarrow 2$  and  $2 \rightarrow 3$  transitions may be found by substituting the proper bond angle into these matrices and diagonalizing. There seems to be little point in computing the detailed spectrum for higher J values since there are so many hyperfine lines that adequate resolution appears hopeless at present. It is possible to obtain an expression for the strongest ( $|K| = 2$ ) hyperfine component in a given transition. This component corresponds to a frequency shift of

$$\frac{-3 (J^2 + 19J + 30) eQq \cos \alpha}{(2J + 2)(2J + 3)(2J + 4)(2J + 5)} \quad (48)$$

for a transition from J to J + 1. This formula must be applied with some caution since the actual peak in an absorption may not correspond to this frequency shift for reasons to be discussed below.

Townes and Schawlow (57) have discussed the shapes and widths of spectral lines. Their results may be summarized by saying that over a sufficiently narrow frequency range the shape of most lines observed in microwave spectroscopy can be represented by the formula

$$N = \frac{D p^2}{(f - f_0) - (kp)^2} \quad (49)$$

Table 4. Splittings and Relative Intensities of the Strongest Hyperfine Lines

| Transition  | Splitting                                | Relative Intensity |
|---|--|--------------------|
| $J = 1 \rightarrow 2,  K  = 1$<br>$v = 0 \rightarrow 1$ | $\frac{eQq}{280} (6 - 23 \cos \alpha)$   | $\frac{11}{5}$     |
| "   | $\frac{eQq}{280} (6 + 47 \cos \alpha)$   | $\frac{7}{10}$     |
| "   | $\frac{-eQq}{140} (32 - 41 \cos \alpha)$ | $\frac{3}{10}$     |
| $J = 1 \rightarrow 2,  K  = 1$<br>$v = 1 \rightarrow 0$ | $\frac{-eQq}{280} (6 + 11 \cos \alpha)$  | $\frac{11}{5}$     |
| "   | $\frac{eQq}{280} (59 \cos \alpha - 6)$   | $\frac{7}{10}$     |
| "   | $\frac{eQq}{140} (32 - 23 \cos \alpha)$  | $\frac{3}{10}$     |
| $J = 2 \rightarrow 3,  K  = 1$<br>$v = 0 \rightarrow 1$ | $\frac{-eQq}{336} (4 + 5 \cos \alpha)$   | $\frac{208}{63}$   |
| "   | $\frac{eQq}{84} (4 \cos \alpha - 1)$     | $\frac{64}{49}$    |
| $J = 2 \rightarrow 3,  K  = 1$<br>$v = 1 \rightarrow 0$ | $\frac{eQq}{336} (4 - 13 \cos \alpha)$   | $\frac{208}{63}$   |
| "   | $\frac{eQq}{84} (2 \cos \alpha + 1)$     | $\frac{64}{49}$    |

Table 4. Splittings and Relative Intensities of the Strongest Hyperfine Lines (Continued)

| Transition  | Splitting                                 | Relative Intensity |
|---|---|--------------------|
| $J = 2 \rightarrow 3,  K  = 2$                          | $\frac{-eQq}{14} \cos \alpha$             | $\frac{44}{9}$     |
| $J = 2 \rightarrow 3,  K  = 2$                          | $\frac{35}{196} eQq \cos \alpha$          | $\frac{20}{9}$     |
| $J = 3 \rightarrow 4,  K  = 1$<br>$v = 0 \rightarrow 1$ | $\frac{eQq}{2640} (20 - 59 \cos \alpha)$  | $\frac{25}{6}$     |
| "   | $\frac{eQq}{2640} (20 + 7 \cos \alpha)$   | $\frac{1155}{648}$ |
| $J = 3 \rightarrow 4,  K  = 1$<br>$v = 1 \rightarrow 0$ | $\frac{-eQq}{2640} (20 + 19 \cos \alpha)$ | $\frac{25}{6}$     |
| "   | $\frac{eQq}{2640} (47 \cos \alpha - 20)$  | $\frac{1155}{648}$ |
| $J = 3 \rightarrow 4,  K  = 2$                          | $-2 \frac{eQq}{55} \cos \alpha$           | $\frac{1735}{234}$ |
| "   | $7 \frac{eQq}{110} \cos \alpha$           | $\frac{903}{234}$  |
| $J = 3 \rightarrow 4,  K  = 3$                          | $-31 \frac{eQq}{80} \cos \alpha$          | $\frac{7}{6}$      |
| "   | $-31 \frac{eQq}{88} \cos \alpha$          | $\frac{7}{45}$     |
| $J = 4 \rightarrow 5,  K  = 1$<br>$v = 0 \rightarrow 1$ | $\frac{eQq}{5720} (23 \cos \alpha - 30)$  |                    |

Table 4. Splittings and Relative Intensities of the Strongest Hyperfine Lines (Concluded)

| Transition  | Splitting                                | Relative Intensity |
|---|--|--------------------|
| $J = 4 \rightarrow 5,  K  = 1$<br>$v = 1 \rightarrow 0$ | $\frac{eQq}{5720} (30 - 83 \cos \alpha)$ |                    |
| $J = 4 \rightarrow 5,  K  = 2$                          | $\frac{-61 eQq}{2860} \cos \alpha$       |                    |

$N$  is the intensity at the frequency  $f$  of a line whose unperturbed frequency is  $f_0$ .  $D$  is a constant which contains the square of the dipole moment matrix element, and  $k$  is a constant related to the mean time between collisions of the molecules. The pressure of the gas is given by  $p$ .

A bond angle of  $111^\circ$  and a quadrupole coupling constant of  $-80$  Mc/sec (approximately the values for  $\text{CFCl}_3$  or  $\text{CHCl}_3$ ) were substituted into the matrix elements listed in the Appendix and the eigenvalues and intensities were obtained with the aid of a computer. These intensities were substituted for  $D$  in equation 49 and the total intensity was computed for a pressure of 25 microns at intervals of 0.2 Mc/sec. The value 12.3 was chosen for  $k$  since this gave a line width at half maximum of about 0.5 Mc/sec for the strongest lines in the  $J = 1 \rightarrow 2$  spectrum, and this is approximately the width observed. The line spectra and computed pressure broadened spectra are shown in Figures 1 and 2 for a frequency range of 20 Mc/sec.

Examination of these figures suggests that even though there are several lines near the strongest lines in the  $J = 1 \rightarrow 2$  spectrum, these two lines are so much stronger than any of their neighbors that the peak in the absorption ought to occur at the actual frequency of these lines. Each of the pair of second strongest lines (whose separation is equal to the separation of the strongest pair of lines) has a very weak neighbor which does not shift the absorption peak very much. Some other lines are relatively isolated but may not be strong enough to be observed. Other stronger peaks can not be precisely identified with any single line. For example the large peak near  $-7$  Mc/sec is actually due to three separate lines.

In the  $J = 2 \rightarrow 3$  spectrum one of the strongest  $|K| = 1$  lines and



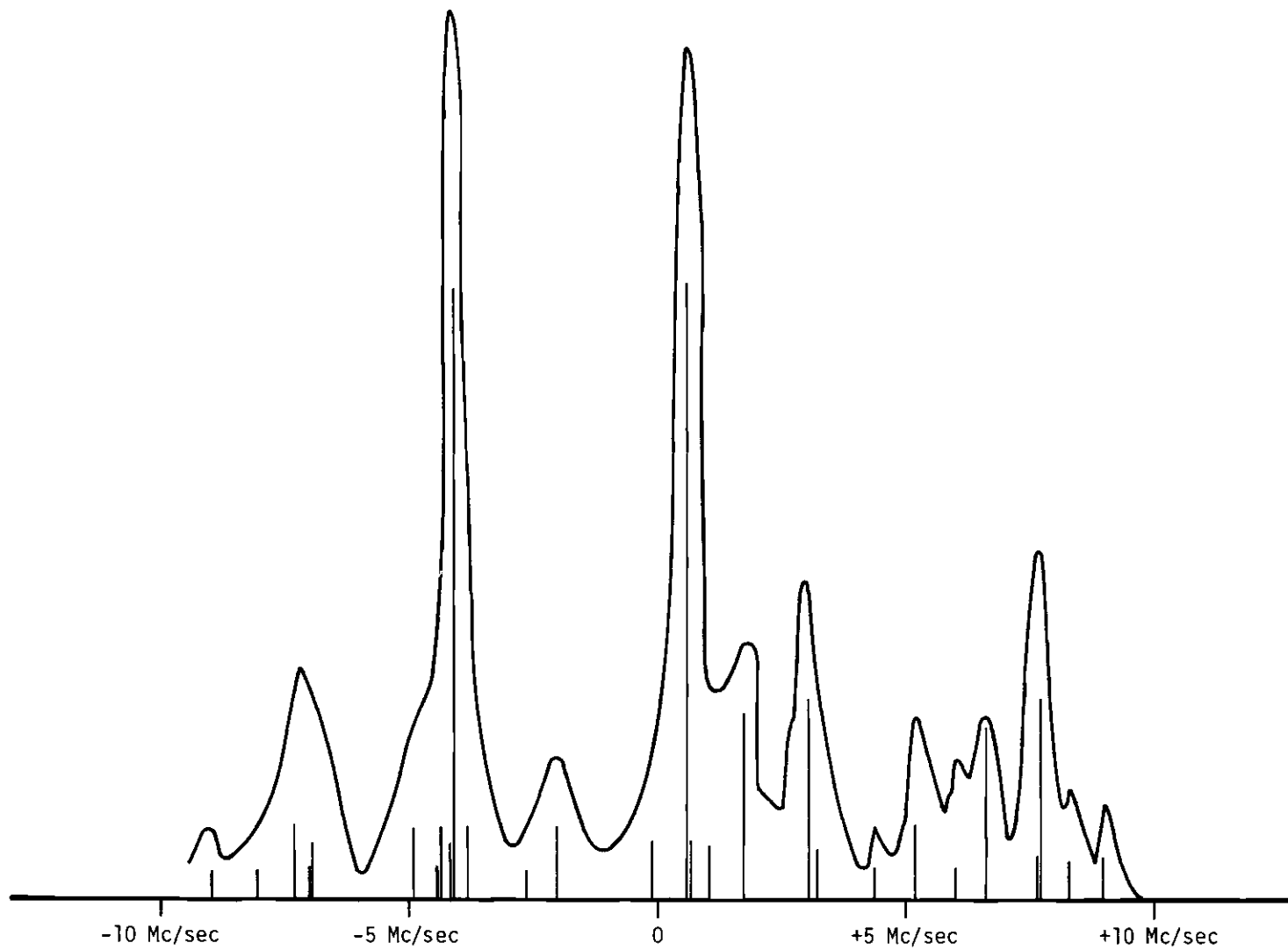


Figure 1.  $J = 1 \rightarrow 2, K = 1$  Theoretical Hyperfine Spectrum.

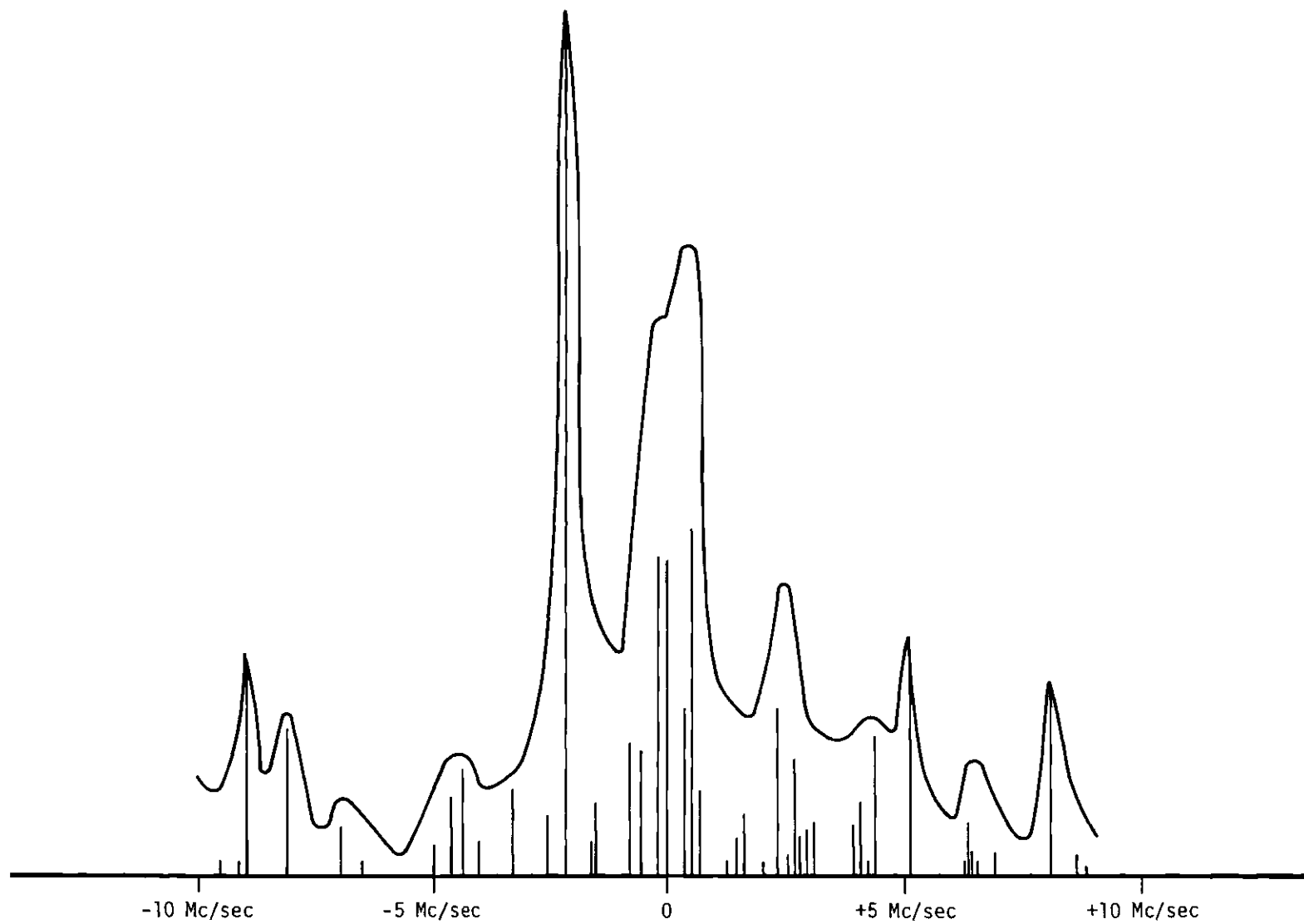


Figure 2.  $J = 2 \rightarrow 3$ ,  $K = 1$  and  $2$  Theoretical Hyperfine Spectrum.

the strongest  $|K| = 2$  line nearly overlap ( $-2.06$  Mc/sec and  $-2.05$  Mc/sec respectively). On the basis of a relative intensity calculation alone this should give a line nearly three times as strong as the next strongest line. When broadening is taken into account we see that three other moderately strong lines combine to give a peak nearly as intense. At higher pressures the broadening is sufficient to make the peak intensity due to the three moderate lines greater than the intensity due to the two strong lines near  $-2$  Mc/sec. At low pressures the peak at approximately  $0.5$  Mc/sec might coincide with the line there, and there appears to be some hope of detecting the line near  $-0.25$  Mc/sec. The third most prominent feature is composed of two lines near  $+2.5$  Mc/sec. The lines near  $-9$ ,  $+5$ , and  $+8$  Mc/sec are relatively isolated but are perhaps too weak to be measured accurately.

#### The Observed Spectra

The spectrometer used to obtain the spectra of  $\text{CFCl}_3$  and  $\text{CHCl}_3$  was the one described in detail by Long (14). The phase sensitive detector used in this type of spectrometer causes the deflection due to a Stark component of an absorption line to be in the opposite direction from the deflection due to the absorption line itself. Thus when a Stark component of one line coincides with the absorption frequency of another both will be lost. With so many hyperfine lines present the Stark pattern is expected to be complicated. Considerable variation in the recorded spectra was observed when the Stark field was varied. Most measurements were made at Stark fields of  $200$  volts/cm or less since this is sufficient to remove most Stark components from the center of the pattern without producing

appreciable second order Stark effects (58). The highest frequency line in the pair of second most intense  $|K| = 1$  lines in the  $J = 1 \rightarrow 2$  transition was not observed unless the Stark field was less than 40 volts/cm.

When centrifugal distortion effects are included the frequency of a rotational transition from  $J$  to  $J + 1$  is given in terms of the centrifugal distortion coefficients  $D_{JK}$  and  $D_J$  as (59)

$$f = 2(J + 1)(B - D_{JK}K^2) - 4D_J(J + 1)^3 + f_q, \quad (50)$$

where  $f_q$  is the frequency shift produced by the quadrupole interaction. The splitting between any two lines having the same value of  $K$  in the same transition will be independent of centrifugal distortion effects and may be used to determine the quadrupole coupling constant. The splitting between the two most intense  $|K| = 1$  lines in the  $J = 1 \rightarrow 2$  transition was used for this purpose. From Table 4 it may be seen that the splitting between these two lines is given by

$$\Delta f_q = - 3 \frac{eQq}{70} (1 - \cos \alpha). \quad (51)$$

The measured spectra are shown in Figures 3 through 10. The errors assigned to the measured frequencies are probable errors obtained by dividing the mean deviation by the square root of the number of independent measurements (60). Because of the long time constants associated with the detection circuit the peak in an absorption does not occur in the same position when the klystron is swept upward in frequency as it does when the

klystron is swept downward. Equal numbers of runs were made sweeping in both directions, and one upward and downward run together were counted as a single independent measurement in determining the probable error. Since the splitting between the two most intense lines in the  $J = 1 \rightarrow 2$  spectrum is independent of the sweep direction each run was counted as an independent measurement in determining the probable error in this number.

The  $J = 1 \rightarrow 2$  transition in  $\text{CFCl}_3$  is shown in Figure 3. Note the general qualitative agreement between Figure 3 and the predicted spectrum in Figure 1. Some of the deflections in Figure 3 are caused by noise rather than by absorption lines. The presence of noise also causes a random variation in the peak of a true absorption. The frequencies shown in Figure 3 and the other figures represent averages of a large number of runs over the absorption lines. It is not possible to make a reliable comparison of the results of a single run with the predicted spectrum.

The separation between the two strong lines labelled A and B in Figure 3 was found to be  $4.65 \pm .02$  Mc/sec. The Cl - C - Cl bond angle in this molecule is  $111 \pm .3^\circ$  (23), and therefore  $\cos \alpha$  is  $-0.358 \pm .005$ . Using equation 51 and combining the maximum probable errors in  $\Delta f_q$  and  $\cos \alpha$  gives  $-79.9 \pm .6$  Mc/sec for the quadrupole coupling constant. The probable error of  $\pm .6$  Mc/sec is somewhat conservative. There is a procedure for computing the probable error which allows for the possibility that independent errors may cancel one another (61) but the improvement over the range given here is slight.

From Table 4 we see that one of the strongest  $|K| = 1$  lines corresponds to a frequency shift of

A =  $9859.26 \pm .03$  Mc/sec

B =  $9863.91 \pm .03$  Mc/sec

C =  $9865.01 \pm .09$  Mc/sec

D =  $9866.47 \pm .05$  Mc/sec

E =  $9869.82 \pm .09$  Mc/sec

F =  $9871.12 \pm .05$  Mc/sec

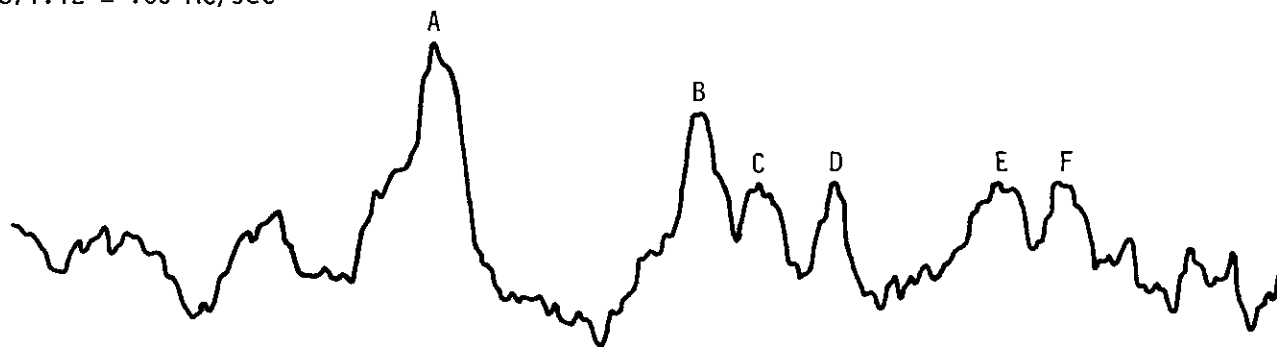


Figure 3.  $J = 1 \rightarrow 2$  Transition in  $\text{CFCl}_3$  at  $-78^\circ\text{C}$ ,  $50\mu\text{ Hg}$ ,  $20\text{v/cm}$ .

$$f_q = \frac{eQq}{280} (6 - 23 \cos \alpha) . \quad (52)$$

Using the probable error in  $eQq$  and  $\cos \alpha$  gives a frequency shift of  $-4.06 \pm .06$  Mc/sec. The probable error in this number is too large since the error in  $\cos \alpha$  has been weighted too heavily. A better estimate of the error is obtained by substituting equation 51 into equation 52 to obtain

$$f_q = - \Delta f_q \frac{(6 - 23 \cos \alpha)}{120 (1 - \cos \alpha)} . \quad (53)$$

Using the maximum and minimum possible values for  $\Delta f_q$  and  $\cos \alpha$  gives  $-4.06 \pm .03$  Mc/sec. This is the predicted splitting of the line labelled A in Figure 3. Therefore in the absence of quadrupole splitting we would observe the  $J = 1 \rightarrow 2$  absorption in  $\text{CFCl}_3$  at  $9863.32 \pm .06$  Mc/sec.

The pair of second strongest lines in the  $J = 1 \rightarrow 2$  transition corresponds to frequency shifts of

$$f_q = \frac{eQq}{280} (6 + 47 \cos \alpha) \quad (54)$$

and

$$f_q = \frac{-eQq}{280} (6 - 59 \cos \alpha) . \quad (55)$$

These correspond to frequencies of  $3.09 \pm .07$  Mc/sec and  $7.74 \pm .09$  Mc/sec respectively. Therefore we would expect lines at  $9866.41 \pm .13$  Mc/sec and  $9871.06 \pm .15$  Mc/sec and these correspond to the lines labelled D and F

Figure 3. The lines labelled C and E correspond to two lines having a relative intensity of about 0.6 arising from an  $F = 5/2 \rightarrow 7/2$  transition for which an exact expression cannot be given. For a bond angle of  $111^\circ$  the computer gave  $-0.0833 eQq$  and  $-0.0222 eQq$  for the frequency shift of these lines. These would correspond to frequency shifts of  $6.66 \pm .05$  Mc/sec and  $1.77 \pm .02$  Mc/sec, or frequencies of  $9865.09 \pm .08$  Mc/sec and  $9870.0 \pm .1$  Mc/sec which overlap the observed frequencies.

Favero and Mirri (19) obtained  $0.46$  kc/sec for  $D_J$  which gives a frequency shift of  $-0.01$  Mc/sec for the  $J = 1 \rightarrow 2$  transition.  $D_{JK}$  was not given by Favero and Mirri but theoretically it is about  $-.5$  kc/sec (62). Using an observed frequency of  $9859.26 \pm .03$  Mc/sec, a frequency shift of  $-4.06 \pm .03$  Mc/sec due to the quadrupole interaction, and a frequency shift of  $-0.01$  Mc/sec due to centrifugal distortion, equation 50 gives

$$B - D_{JK} = 2465.825 \pm .015 \text{ Mc/sec}$$

for the  $J = 1 \rightarrow 2$ ,  $|K| = 1$  transition. Due to the assumed smallness of  $D_{JK}$  this value must be nearly equal to the rotational constant. Using this value for  $B$  we could now calculate the frequencies of the higher  $J$  lines in the spectrum. Since the probable error would be multiplied by  $2(J + 1)$  this calculation does not afford a very meaningful check on the consistency of the theory. Instead we shall compute the value of  $B$  separately from each transition and compare the results.

In the  $J = 2 \rightarrow 3$  transition we have seen that the strongest  $|K| = 2$  line overlaps one of the pair of strong  $|K| = 1$  lines. From Table 4 the frequency shift of the  $|K| = 2$  line is



$$f_q = \frac{-eQq}{14} \cos \alpha \quad (56)$$

which gives  $-2.04 \pm .03$  Mc/sec. Assuming that line A in Figure 4 corresponds to this transition we have  $14,794.86 \pm .06$  Mc/sec as the frequency in the absence of quadrupole coupling. The second member of the pair of strong  $|K| = 1$  lines is shifted by

$$f_q = \frac{-eQq}{336} (4 + 5 \cos \alpha) \quad (57)$$

or  $+0.525 \pm .005$  Mc/sec. The predicted line at  $14,795.38 \pm .06$  Mc/sec agrees with the observed line within the limits of the probable error. The prominence labelled B in Figure 4 corresponds to a similar prominence in Figure 2 which arises from a  $|K| = 1$ ,  $F = 9/2 \rightarrow 11/2$  transition nearly superimposed on a  $|K| = 2$ ,  $F = 7/2$  transition (recall the degeneracy in the upper state). An average of these two shifts is  $-0.25$  Mc/sec which gives a predicted frequency of  $14,794.61 \pm .08$  Mc/sec.

The  $J = 3 \rightarrow 4$  and  $4 \rightarrow 5$  transitions in  $\text{CFCl}_3$  are shown in Figures 5 and 6 along with the measured frequency of the strongest line in each transition. These frequencies differ somewhat from those reported by Long (63). The spectra shown here were obtained at lower pressures than Long used in order to obtain better resolution.

Equation 50 can be written in the form

$$\frac{f - f_q}{2(J + 1)} = B - D_{JK} K^2 - 2D_J (J + 1)^2 \quad (58)$$

A =  $14792.82 \pm .03$  Mc/sec

B =  $14794.72 \pm .05$  Mc/sec

C =  $14795.44 \pm .05$  Mc/sec

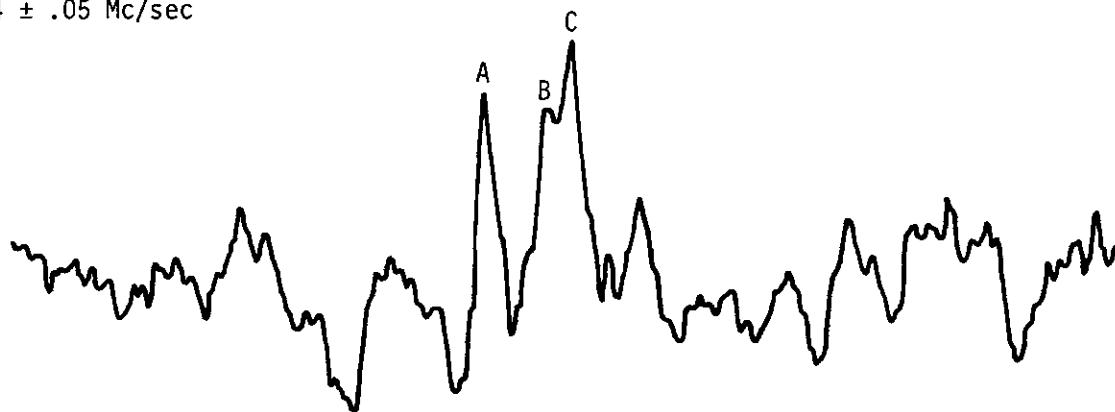


Figure 4.  $J = 2 \rightarrow 3$  Transition in  $\text{CFCl}_3$  at  $-78^\circ\text{C}$ ,  $15\mu\text{ Hg}$ ,  $200\text{v/cm}$ .

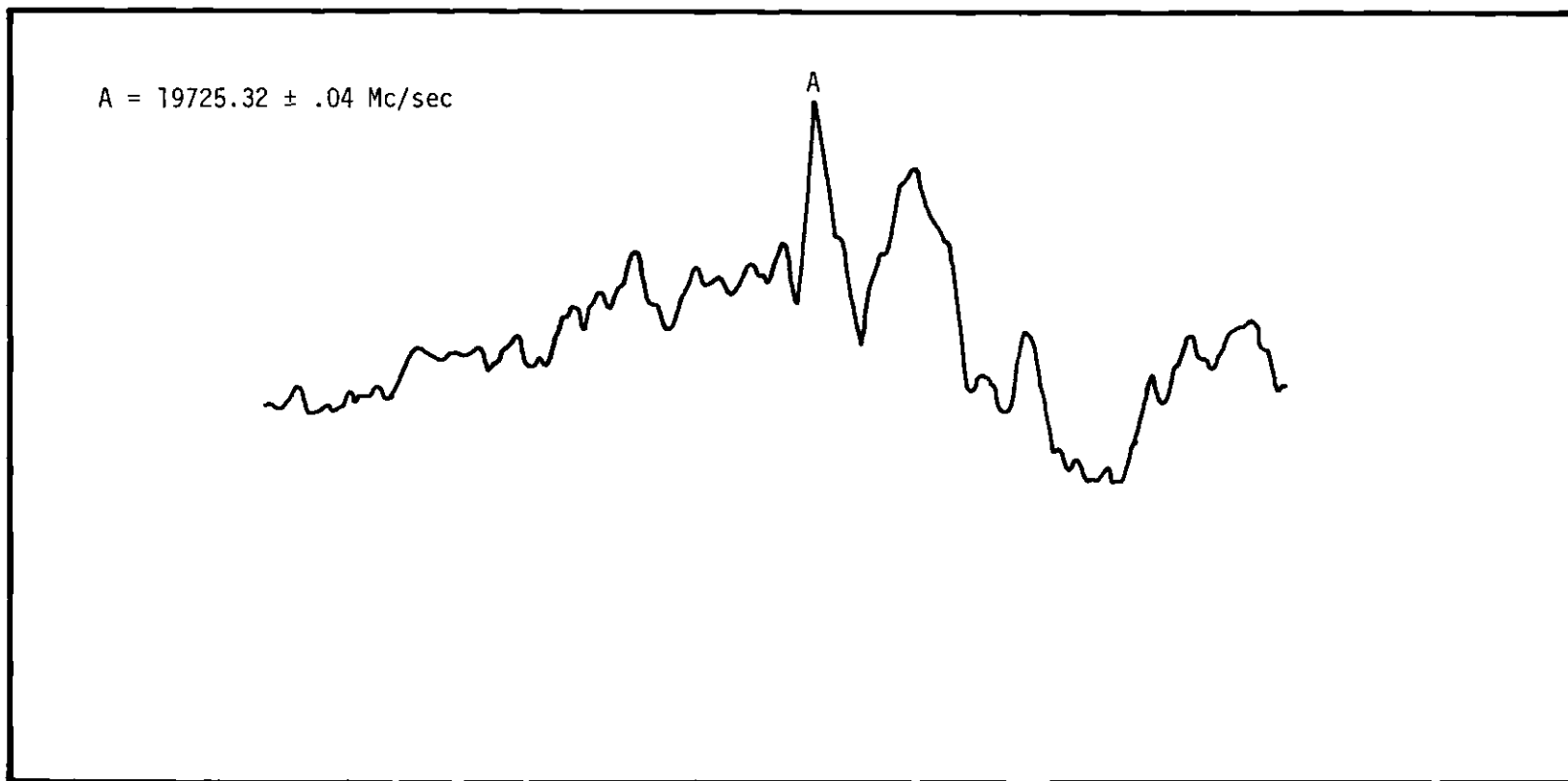


Figure 5.  $J = 3 \rightarrow 4$  Transition in  $\text{CFCl}_3$  at  $-78^\circ\text{C}$ ,  $10\mu\text{ Hg}$ ,  $150\text{v/cm}$ .

$A = 24657.44 \pm .02 \text{ Mc/sec}$



Figure 6.  $J = 4 \rightarrow 5$  Transition in  $\text{CFCl}_3$  at  $-78^\circ\text{C}$ ,  $10\mu\text{ Hg}$ ,  $300\text{v/cm}$ .

where  $f$  is the measured frequency of a line and  $f_q$  is the theoretical quadrupole frequency shift of this line. Long pointed out (64) that if centrifugal distortion effects were small the quantity  $(f - f_q)/2(J + 1)$  ought to be nearly constant for various transitions. This quantity has been computed and tabulated in Table 5 and compared with the values obtained by Long. The effect of the coefficient  $D_J$  (which was not available to Long) has also been included in the table. The variation in the quantity  $B - D_{JK} K^2 - 2D_J(J + 1)^2$  obtained by Long led him to conclude that  $D_J$  was large, negative, and changed with frequency. From Table 5 it is seen that the effect of centrifugal distortion is actually quite small.

Table 5. Rotational Constant of  $\text{CFCl}_3$  from Various Transitions

| Transition            | $B - D_{JK} K^2 - 2D_J(J + 1)^2$ |                       | $2D_J(J + 1)^2$ | $B - D_{JK} K^2$   |
|-----------------------|----------------------------------|-----------------------|-----------------|--------------------|
|                       | Long (64)                        | Present Investigation |                 |                    |
| $J = 1 \rightarrow 2$ | $2465.39 \pm .01$                | $2465.83 \pm .015$    | .004            | $2465.83 \pm .01$  |
| $J = 2 \rightarrow 3$ | $2465.63 \pm .01$                | $2465.81 \pm .01$     | .008            | $2465.82 \pm .01$  |
| $J = 3 \rightarrow 4$ | $2465.72 \pm .00$                | $2465.79 \pm .006$    | .015            | $2465.81 \pm .006$ |
| $J = 4 \rightarrow 5$ | $2465.76 \pm .00$                | $2465.80 \pm .003$    | .023            | $2465.82 \pm .003$ |

All units are megacycles/sec.

The cause of the variation obtained by Long is due to the erroneous computation of the hyperfine structure and the subsequent erroneous assignment of the lines.

The variation in the quantity  $B - D_{JK} K^2$  shown in the last column of Table 5 may be due to the shifting in the peak of an absorption line due to the presence of a nearby line. On the basis of these data a conservative estimate of the rotational constant of  $\text{CFCl}_3$  is  $2465.82 \pm .02$  Mc/sec if we assume that the magnitude of  $D_{JK}$  is less than .5 kc/sec.

The  $J = 1 \rightarrow 2$  transition in  $\text{CHCl}_3$  is shown in Figure 7. Again note the general agreement with Figure 1. The splitting between the two strong lines is  $4.55 \pm .02$  Mc/sec. The Cl - C - Cl bond angle is  $111.3 \pm .2^\circ$  (24) and therefore  $\cos \alpha$  is  $-0.363 \pm .003$ . These values give  $-77.9 \pm .5$  Mc/sec for the quadrupole coupling constant. Equation 53 then gives the shift of the low frequency line as  $-3.99 \pm .03$  Mc/sec. Hence the unperturbed line would occur at  $13,208.29 \pm .08$  Mc/sec. Equations 54 and 55 predict the second strongest pair of lines to fall at  $13,211.37 \pm .12$  Mc/sec and  $13,215.92 \pm .13$  Mc/sec which is within the allowed error. Note that the lines arising from the  $F = 5/2 \rightarrow 7/2$  transition do not appear as they did in the case of  $\text{CFCl}_3$ . This may be due to interfering Stark components.

The  $J = 2 \rightarrow 3$  transition in  $\text{CHCl}_3$  is shown in Figure 8. Using equation 56 we predict that the unperturbed line would fall at  $19,812.23 \pm .07$  Mc/sec. Equation 57 predicts a strong line at  $19,812.73 \pm .07$  Mc/sec which is observed. The  $J = 3 \rightarrow 4$  and  $4 \rightarrow 5$  transitions are shown in Figures 9 and 10. When these data are combined with the centrifugal distortion coefficients of Favero and Mirri we obtain the values for the rotational constant shown in Table 6. On the basis of this table a conservative estimate of the rotational constant of  $\text{CHCl}_3$  is  $3302.07 \pm .03$  Mc/sec.

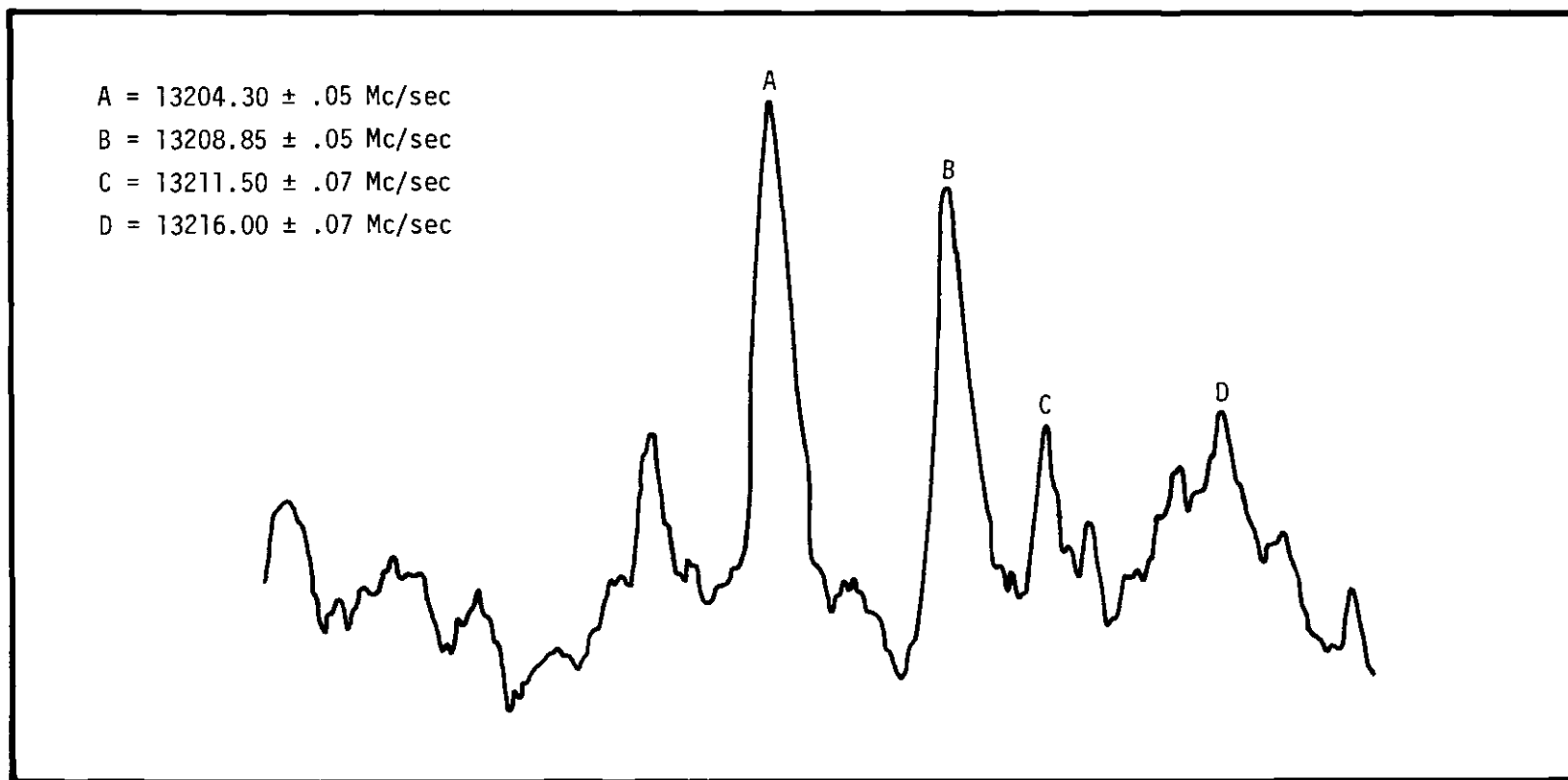


Figure 7.  $J = 1 \rightarrow 2$  Transition in  $\text{CHCl}_3$  at  $-78^\circ\text{C}$ ,  $10\mu\text{ Hg}$ ,  $20\text{v/cm}$ .

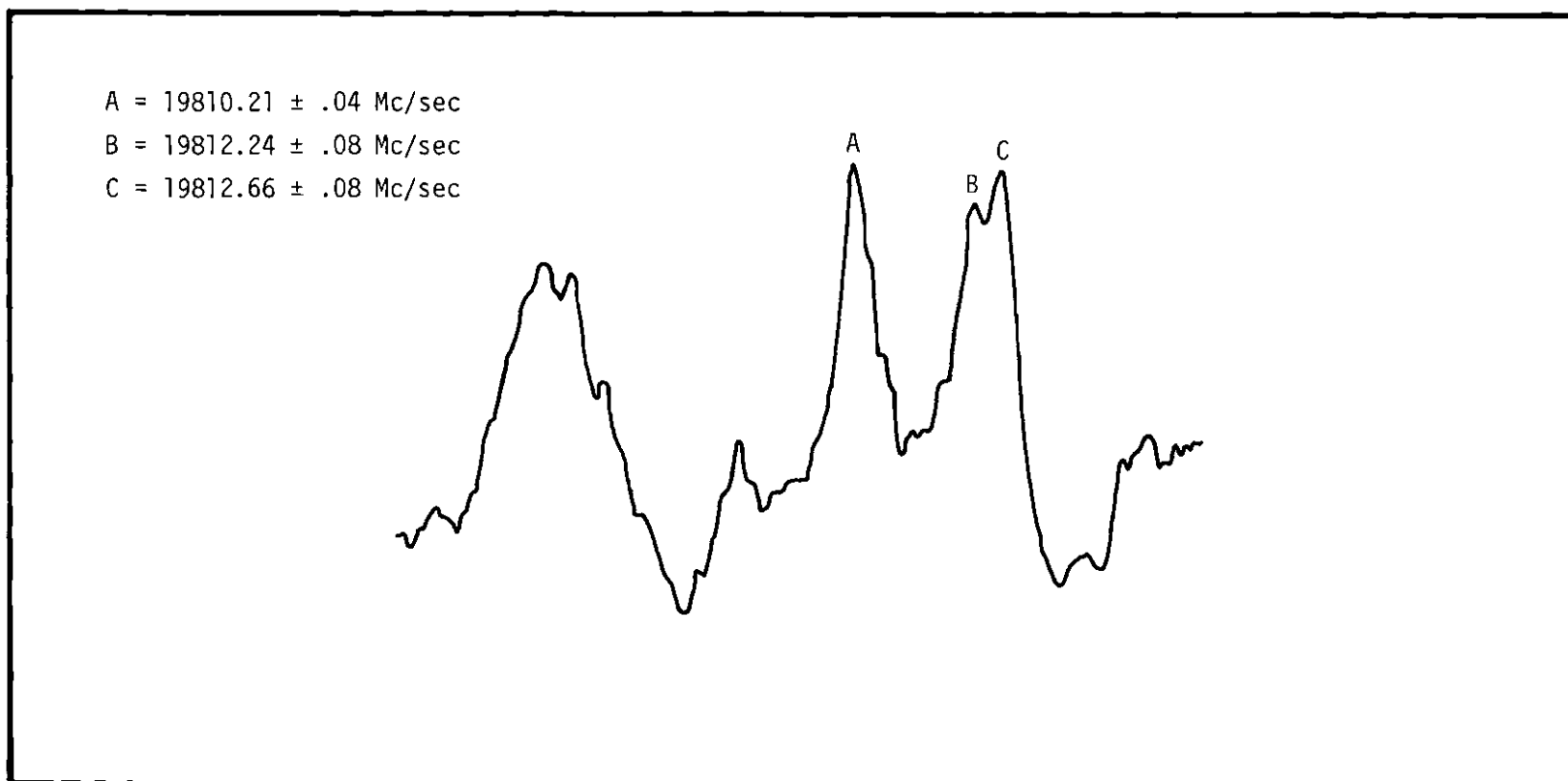


Figure 8.  $J = 2 \rightarrow 3$  Transition in  $\text{CHCl}_3$  at  $-78^\circ\text{C}$ ,  $5\mu\text{ Hg}$ ,  $300\text{v/cm}$ .



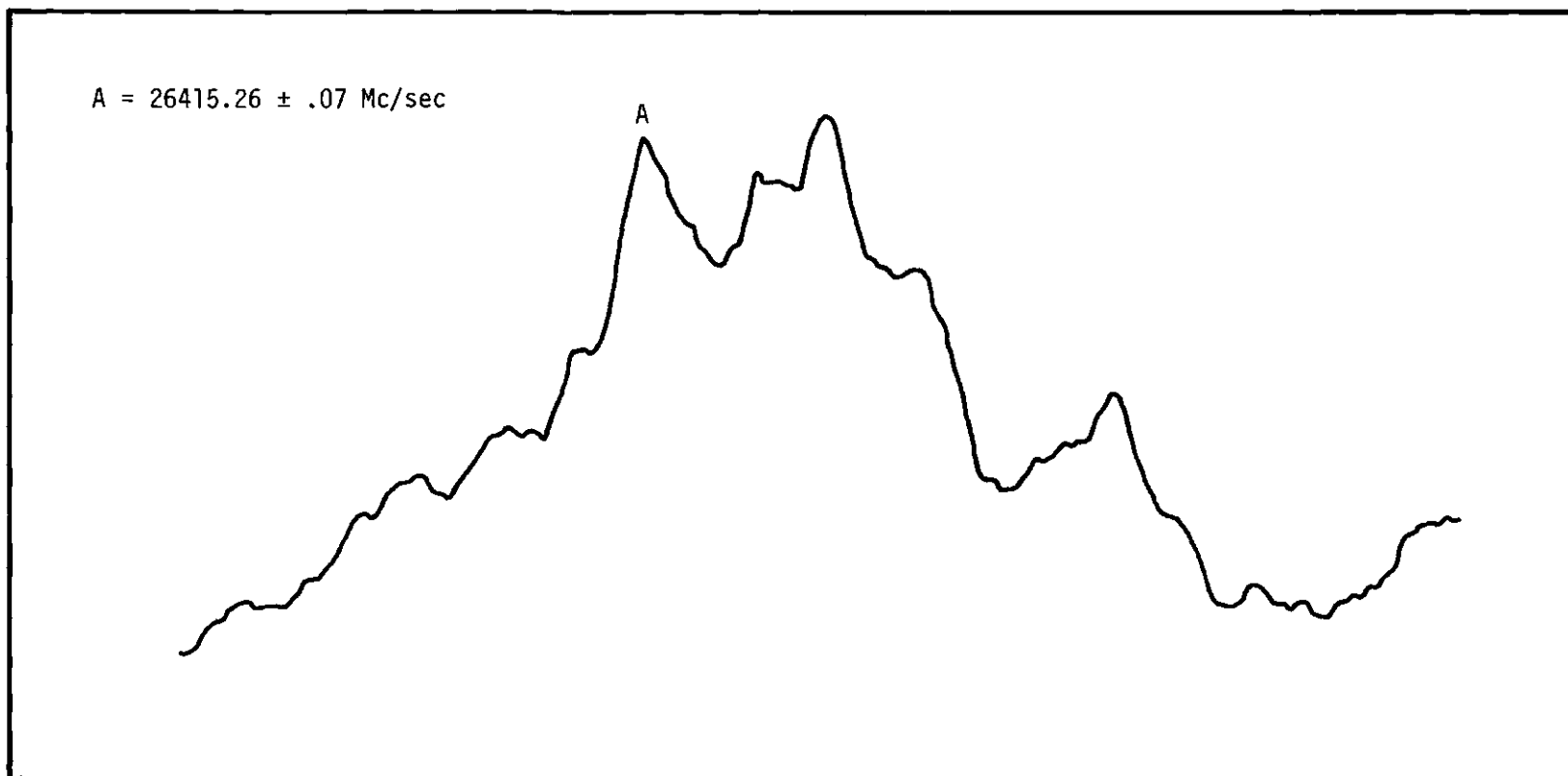


Figure 9.  $J = 3 \rightarrow 4$  Transition in  $\text{CHCl}_3$  at  $-78^\circ\text{C}$ ,  $3\mu\text{ Hg}$ ,  $200\text{v/cm}$ .

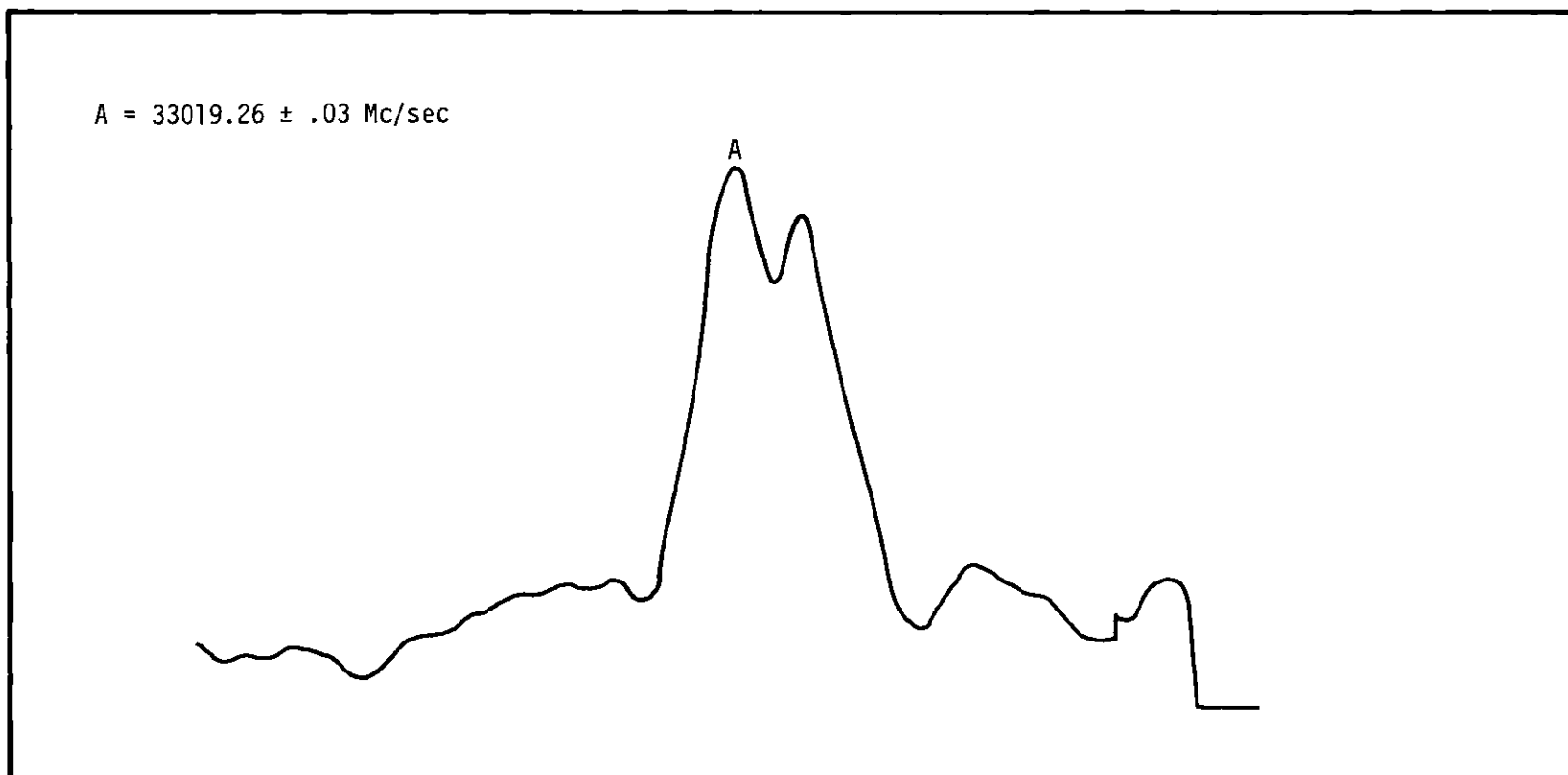


Figure 10.  $J = 4 \rightarrow 5$  Transition in  $\text{CHCl}_3$  at  $-78^\circ\text{C}$ ,  $15\mu\text{ Hg}$ ,  $160\text{v/cm}$ .

Table 6. Rotational Constant of  $\text{CHCl}_3$  from Various Transitions

| Transition                         | $B - D_{JK} K^2 - 2D_J(J+1)^2$ | $2D_J(J+1)^2$ | $D_{JK} K^2$ | B                 |
|------------------------------------|--------------------------------|---------------|--------------|-------------------|
| $J = 1 \rightarrow 2$<br>$ K  = 1$ | $3302.07 \pm .02$              | .01           | .00          | $3302.08 \pm .02$ |
| $J = 2 \rightarrow 3$<br>$ K  = 2$ | $3302.04 \pm .02$              | .03           | -.01         | $3302.06 \pm .02$ |
| $J = 3 \rightarrow 4$<br>$ K  = 2$ | $3302.04 \pm .02$              | .05           | -.01         | $3302.08 \pm .02$ |
| $J = 4 \rightarrow 5$<br>$ K  = 2$ | $3301.99 \pm .01$              | .08           | -.01         | $3302.06 \pm .01$ |

All units are megacycles/sec.

## CHAPTER V

## CONCLUSIONS AND RECOMMENDATIONS

Bersohn (4) was among the first to realize that Racah's algebra of irreducible tensor operators (6)(7)(8) could readily be extended to problems involving the rotational motion of molecules. In the course of this work Bersohn derived general expressions for the matrix elements of the quadrupole interaction energy in a molecule containing three identical quadrupolar nuclei. P. N. Wolfe (12)(13) succeeded in resolving the quadrupole hyperfine structure in the  $J = 2 \rightarrow 3$  transition of  $\text{CHCl}_3$  and attempted to evaluate the quadrupole coupling constant by using Bersohn's theory. This attempt was complicated by the fact that it was not possible to assign the  $|K| = 1$  and  $|K| = 2$  lines unambiguously in the absence of any knowledge of the magnitude of the centrifugal distortion coefficients. Long (14)(15) was able to observe the  $J = 1 \rightarrow 2$  transition in  $\text{CHCl}_3$  and  $\text{CFCl}_3$  as well and was thereby able to make a better comparison with Bersohn's theory. These results indicated that either the theory was in error or there was an anomaly in the centrifugal distortion coefficients. By measuring higher  $J$  transitions Favero and Mirri (19) showed that the centrifugal distortion coefficients were in good agreement with the theoretical values.

In this study the terms in the electric quadrupole interaction Hamiltonian which involve the electric field gradient operator have been evaluated in detail. Bersohn did not do this. When the requirements of

the Pauli exclusion principle are imposed on the state function of the molecule and this state function is used to calculate the electric field gradient, terms are obtained which were not included in the calculations used by Wolfe and Long. These additional terms arise only in the  $|K| = 1$  case. Some simplification over Bersohn's results has been obtained by making greater use of the symmetry properties of the molecule as suggested by Svidzinskii (21).

For the case  $|K| = 1, J = 1 \rightarrow 2$  the calculation predicts that the two strongest lines are of equal intensity and are shifted from the unperturbed frequency by

$$\frac{eQq}{280} (6 - 23 \cos \alpha)$$

and

$$\frac{-eQq}{280} (6 + 11 \cos \alpha)$$

respectively. The quadrupole coupling constant  $eQq$  may be evaluated by measuring the splitting between these two lines. This splitting is given by

$$\Delta f_q = -3 \frac{eQq}{70} (1 - \cos \alpha) .$$

For higher  $J$  transitions the most intense line is a  $|K| = 2$  line. The frequency shift produced by the quadrupole interaction in a rotational transition from  $J$  to  $J + 1$  is given by

$$f_q = \frac{-3 (J^2 + 19J + 30) eQq \cos \alpha}{(2J + 2)(2J + 3)(2J + 4)(2J + 5)} .$$

It may be the case however that other lines in the hyperfine pattern overlap one another to such an extent that they produce absorptions which are more intense than this line.

A detailed comparison of the theoretical spectrum with the observed spectrum has not been possible due to the limited resolution of the spectrometer. Nevertheless there is a sound basis for believing that the calculation of the quadrupole hyperfine structure presented here is correct. The magnitude of the quadrupole coupling energy obtained for  $\text{CFCl}_3$  and  $\text{CHCl}_3$  is very close to that obtained in solid state measurements. Of course the same thing might be said for the value obtained by Wolfe (12) for  $\text{CHCl}_3$ . However Long (14) used the same theory that Wolfe used and obtained a different value for the quadrupole coupling constant by measuring a different transition. The overall qualitative agreement between the predicted and observed  $J = 1 \rightarrow 2$  and  $2 \rightarrow 3$  spectra is encouraging. While many of the predicted lines were too weak to be observed, at least there were no lines observed where none was predicted. Finally, when the theoretical frequency shifts are combined with the measured frequencies of the various transitions they give rise to values of the rotational constant B which are more consistent with one another than the values obtained using Bersohn's calculations.

When the predicted and observed spectra are compared they give  $-79.9 \pm .6$  Mc/sec for the quadrupole coupling constant in  $\text{CFCl}_3^{35}$  and the quantity  $B - D_{JK} K^2$  is found to be  $2465.82 \pm .02$  Mc/sec. If  $D_{JK}$  is less than .5 kc/sec as centrifugal distortion theory predicts then this number must be

very close to the value of the rotational constant.

For  $\text{CHCl}_3^{35}$  the quadrupole coupling constant is found to be  $-77.9 \pm .5$  Mc/sec and the rotational constant B is  $3302.07 \pm .03$  Mc/sec.

The size of the quadrupole coupling constant depends upon the value of the bond angle  $\alpha$ . The values used in this investigation are those given by Loubser (23) and Jen and Lide (24). These values may not be correct since these investigators did not resolve the quadrupole hyperfine structure. The calculation presented here should be extended to the asymmetric top case and used in connection with the spectra of various isotopic species of these molecules in order to obtain the bond distances and angles more precisely.

It is possible to use the wave functions presented in this thesis to obtain simultaneously the effects of quadrupole interactions and external applied electric fields. This allows one to treat the Stark effect in the presence of hyperfine structure. Such a program has already been undertaken (22).

## APPENDIX

The matrix elements of the quadrupole interaction Hamiltonian for a molecule containing three identical quadrupolar nuclei of spin  $3/2$  are given here for the cases  $J = 1, 2,$  and  $3$ ;  $|K| = 1$  and  $2$ . A detailed spectrum for the  $J = 1 \rightarrow 2$  and  $2 \rightarrow 3$  transitions in such a molecule may be obtained by substituting the appropriate bond angle  $\alpha$  into these matrix elements and diagonalizing over the resultant nuclear spin  $I$ . The matrix elements  $B_{TI}$  of the diagonalizing transformation may then be substituted into equation 47 to obtain the intensities of the transitions. A factor of  $eQq$  has been omitted from every element shown here.

$J = 1, |K| = 1$

| F   | I   | I'  | $v = 0$                                     | $v = 1$                                   |
|-----|-----|-----|---|---|
| 9/2 | 7/2 | 7/2 | $\frac{(3 \cos \alpha - 2)}{40}$            | $\frac{(2 - \cos \alpha)}{40}$            |
| 7/2 | 7/2 | 7/2 | $\frac{(2 - 3 \cos \alpha)}{14}$            | $\frac{(\cos \alpha - 2)}{14}$            |
|     | 5/2 | 5/2 | $\frac{(2 - 3 \cos \alpha)}{280}$           | $\frac{(\cos \alpha - 2)}{280}$           |
|     | 7/2 | 5/2 | $\frac{3\sqrt{6} (3 \cos \alpha - 2)}{140}$ | $\frac{3\sqrt{6} (2 - \cos \alpha)}{140}$ |
| 5/2 | 7/2 | 7/2 | $\frac{3(3 \cos \alpha - 2)}{56}$           | $\frac{3(2 - \cos \alpha)}{56}$           |
|     | 5/2 | 5/2 | $\frac{2(3 \cos \alpha - 2)}{175}$          | $\frac{2(2 - \cos \alpha)}{175}$          |
|     | 3/2 | 3/2 | $\frac{(11 \cos \alpha - 4)}{200}$          | $\frac{(4 + 3 \cos \alpha)}{200}$         |



J = 1, |K| = 1 (continued)

| F   | I   | I'  | v = 0  | v = 1  |
|-----|-----|-----|--|--|
| 5/2 | 7/2 | 5/2 | $\frac{9\sqrt{10} (2 - 3 \cos \alpha)}{350}$ | $\frac{9\sqrt{10} (\cos \alpha - 2)}{350}$   |
|     | 7/2 | 3/2 | $\frac{\sqrt{15} (1 + \cos \alpha)}{50}$     | $\frac{\sqrt{15} (3 \cos \alpha - 1)}{50}$   |
|     | 5/2 | 3/2 | $\frac{3\sqrt{6} (1 + \cos \alpha)}{200}$    | $\frac{3\sqrt{6} (3 \cos \alpha - 1)}{200}$  |
| 3/2 | 5/2 | 5/2 | $\frac{(2 - 3 \cos \alpha)}{100}$            | $\frac{(\cos \alpha - 2)}{100}$              |
|     | 3/2 | 3/2 | $\frac{(4 - 11 \cos \alpha)}{50}$            | $\frac{-(4 + 3 \cos \alpha)}{50}$            |
|     | 1/2 | 1/2 | 0  | 0  |
|     | 5/2 | 3/2 | $\frac{-3\sqrt{21} (1 + \cos \alpha)}{200}$  | $\frac{3\sqrt{21} (1 - 3 \cos \alpha)}{200}$ |
|     | 5/2 | 1/2 | $\frac{3\sqrt{35} (3 \cos \alpha - 2)}{200}$ | $\frac{3\sqrt{35} (2 - \cos \alpha)}{200}$   |
|     | 3/2 | 1/2 | $\frac{-\sqrt{15} (1 + \cos \alpha)}{200}$   | $\frac{\sqrt{15} (1 - 3 \cos \alpha)}{200}$  |
| 1/2 | 3/2 | 3/2 | $\frac{(11 \cos \alpha - 4)}{40}$            | $\frac{(4 + 3 \cos \alpha)}{40}$             |
|     | 1/2 | 1/2 | 0  | 0  |
|     | 3/2 | 1/2 | $\frac{\sqrt{6} (1 + \cos \alpha)}{40}$      | $\frac{\sqrt{6} (3 \cos \alpha - 1)}{40}$    |

J = 2, |K| = 1

| F    | I   | I'  | v = 0                            | v = 1                          |
|------|-----|-----|----------------------------------|--------------------------------|
| 11/2 | 7/2 | 7/2 | $\frac{(2 - 3 \cos \alpha)}{28}$ | $\frac{(\cos \alpha - 2)}{28}$ |

$J = 2, |K| = 1$  (continued)

| F   | I   | I'  | $v = 0$                                     | $v = 1$                                     |
|-----|-----|-----|---|---|
| 9/2 | 7/2 | 7/2 | $\frac{19(3 \cos \alpha - 2)}{392}$         | $\frac{19(2 - \cos \alpha)}{392}$           |
| 9/2 | 5/2 | 5/2 | $\frac{(3 \cos \alpha - 2)}{196}$           | $\frac{(2 - \cos \alpha)}{196}$             |
|     | 7/2 | 5/2 | $\frac{\sqrt{33}(2 - 3 \cos \alpha)}{98}$   | $\frac{\sqrt{33}(\cos \alpha - 2)}{98}$     |
| 7/2 | 7/2 | 7/2 | $\frac{2(3 \cos \alpha - 2)}{49}$           | $\frac{2(2 - \cos \alpha)}{49}$             |
|     | 5/2 | 5/2 | $\frac{17(2 - 3 \cos \alpha)}{1960}$        | $\frac{17(\cos \alpha - 2)}{1960}$          |
|     | 3/2 | 3/2 | $\frac{(4 - 11 \cos \alpha)}{140}$          | $\frac{-(4 + 3 \cos \alpha)}{140}$          |
|     | 7/2 | 5/2 | $\frac{\sqrt{6}(3 \cos \alpha - 2)}{196}$   | $\frac{\sqrt{6}(2 - \cos \alpha)}{196}$     |
|     | 7/2 | 3/2 | $\frac{-3\sqrt{14}(1 + \cos \alpha)}{196}$  | $\frac{3\sqrt{14}(1 - 3 \cos \alpha)}{196}$ |
|     | 5/2 | 3/2 | $\frac{-9\sqrt{21}(1 + \cos \alpha)}{980}$  | $\frac{9\sqrt{21}(1 - 3 \cos \alpha)}{980}$ |
| 5/2 | 7/2 | 7/2 | $\frac{5(2 - 3 \cos \alpha)}{392}$          | $\frac{5(\cos \alpha - 2)}{392}$            |
|     | 5/2 | 5/2 | $\frac{(2 - 3 \cos \alpha)}{196}$           | $\frac{(\cos \alpha - 2)}{196}$             |
|     | 3/2 | 3/2 | $\frac{(11 \cos \alpha - 4)}{56}$           | $\frac{(4 + 3 \cos \alpha)}{56}$            |
|     | 1/2 | 1/2 | 0   | 0   |
|     | 7/2 | 5/2 | $\frac{17\sqrt{3}(3 \cos \alpha - 2)}{490}$ | $\frac{17\sqrt{3}(2 - \cos \alpha)}{490}$   |
|     | 7/2 | 3/2 | $\frac{-9\sqrt{7}(1 + \cos \alpha)}{490}$   | $\frac{9\sqrt{7}(1 - 3 \cos \alpha)}{490}$  |
|     | 7/2 | 1/2 | 0   | 0   |

J = 2, |K| = 1 (continued)

| F   | I   | I'  | v = 0                                       | v = 1  |
|-----|-----|-----|---|--|
|     | 5/2 | 3/2 | $\frac{\sqrt{21} (1 + \cos \alpha)}{196}$   | $\frac{\sqrt{21} (3 \cos \alpha - 1)}{196}$  |
| 5/2 | 5/2 | 1/2 | $\frac{\sqrt{2} (2 - 3 \cos \alpha)}{20}$   | $\frac{\sqrt{2} (\cos \alpha - 2)}{20}$      |
|     | 3/2 | 1/2 | $\frac{\sqrt{42} (1 + \cos \alpha)}{280}$   | $\frac{\sqrt{42} (3 \cos \alpha - 1)}{280}$  |
| 3/2 | 7/2 | 7/2 | $\frac{15(2 - 3 \cos \alpha)}{196}$         | $\frac{15(\cos \alpha - 2)}{196}$            |
|     | 5/2 | 5/2 | $\frac{(3 \cos \alpha - 2)}{196}$           | $\frac{(2 - \cos \alpha)}{196}$              |
|     | 3/2 | 3/2 | 0   | 0  |
|     | 1/2 | 1/2 | 0   | 0  |
|     | 7/2 | 5/2 | $\frac{9\sqrt{3} (3 \cos \alpha - 2)}{245}$ | $\frac{9\sqrt{3} (2 - \cos \alpha)}{245}$    |
|     | 7/2 | 3/2 | $-\frac{\sqrt{3} (1 + \cos \alpha)}{70}$    | $\frac{\sqrt{3} (1 - 3 \cos \alpha)}{70}$    |
|     | 7/2 | 1/2 | 0   | 0  |
|     | 5/2 | 3/2 | $\frac{3(1 + \cos \alpha)}{56}$             | $\frac{3(3 \cos \alpha - 1)}{56}$            |
|     | 5/2 | 1/2 | $\frac{\sqrt{3} (2 - 3 \cos \alpha)}{40}$   | $\frac{\sqrt{3} (\cos \alpha - 2)}{40}$      |
|     | 3/2 | 1/2 | $-\frac{\sqrt{3} (1 + \cos \alpha)}{40}$    | $\frac{\sqrt{3} (1 - 3 \cos \alpha)}{40}$    |
| 1/2 | 5/2 | 5/2 | $\frac{(3 \cos \alpha - 2)}{70}$            | $\frac{(2 - \cos \alpha)}{70}$               |
|     | 3/2 | 3/2 | $\frac{(4 - 11 \cos \alpha)}{40}$           | $\frac{-(4 + 3 \cos \alpha)}{40}$            |
|     | 5/2 | 3/2 | $\frac{-3\sqrt{14} (1 + \cos \alpha)}{280}$ | $\frac{3\sqrt{14} (1 + 3 \cos \alpha)}{280}$ |

$$J = 2, |K| = 2$$

| F    | I   | I'  |                                       | F   | I   | I'  |  |
|------|-----|-----|---------------------------------------|-----|-----|-----|--|
| 11/2 | 7/2 | 7/2 | $\frac{\cos \alpha}{14}$              |     |     |     |  |
| 9/2  | 7/2 | 7/2 | $\frac{-19 \cos \alpha}{196}$         | 5/2 | 5/2 | 3/2 | $-\frac{\sqrt{21} \cos \alpha}{49}$    |
|      | 5/2 | 5/2 | $\frac{-\cos \alpha}{98}$             |     | 5/2 | 1/2 | $\frac{\sqrt{2} \cos \alpha}{10}$      |
|      | 7/2 | 5/2 | $\frac{\sqrt{33} \cos \alpha}{49}$    |     | 3/2 | 1/2 | $-\frac{\sqrt{42} \cos \alpha}{70}$    |
| 7/2  | 7/2 | 7/2 | $\frac{-4 \cos \alpha}{49}$           | 3/2 | 7/2 | 7/2 | $\frac{15 \cos \alpha}{98}$            |
|      | 5/2 | 5/2 | $\frac{17 \cos \alpha}{980}$          |     | 5/2 | 5/2 | $\frac{-\cos \alpha}{98}$              |
|      | 3/2 | 3/2 | $\frac{\cos \alpha}{10}$              |     | 3/2 | 3/2 | 0                                      |
|      | 7/2 | 5/2 | $\frac{-\sqrt{6} \cos \alpha}{98}$    |     | 7/2 | 5/2 | $-\frac{18 \sqrt{3} \cos \alpha}{245}$ |
|      | 7/2 | 3/2 | $\frac{3\sqrt{14} \cos \alpha}{49}$   |     | 7/2 | 3/2 | $\frac{2\sqrt{3} \cos \alpha}{35}$     |
|      | 5/2 | 3/2 | $\frac{9\sqrt{21} \cos \alpha}{245}$  |     | 7/2 | 1/2 | 0                                      |
| 5/2  | 7/2 | 7/2 | $\frac{5 \cos \alpha}{196}$           |     | 5/2 | 3/2 | $\frac{-3 \cos \alpha}{14}$            |
|      | 5/2 | 5/2 | $\frac{\cos \alpha}{98}$              |     | 5/2 | 1/2 | $\frac{\sqrt{3} \cos \alpha}{20}$      |
|      | 3/2 | 3/2 | $\frac{-\cos \alpha}{4}$              |     | 3/2 | 1/2 | $\frac{\sqrt{3} \cos \alpha}{10}$      |
|      | 1/2 | 1/2 | 0                                     | 1/2 | 5/2 | 5/2 | $\frac{-\cos \alpha}{35}$              |
|      | 7/2 | 5/2 | $\frac{-17\sqrt{3} \cos \alpha}{245}$ |     | 3/2 | 3/2 | $\frac{7 \cos \alpha}{20}$             |
|      | 7/2 | 3/2 | $\frac{18\sqrt{7} \cos \alpha}{245}$  |     | 5/2 | 3/2 | $\frac{-3\sqrt{14} \cos \alpha}{70}$   |
|      | 7/2 | 1/2 | 0                                     |     |     |     |  |

$$J = 3, |K| = 1$$

| F    | I   | I'  | v = 0  | v = 1   |
|------|-----|-----|--|---|
| 13/2 | 7/2 | 7/2 | $\frac{(\cos \alpha - 4)}{48}$               | $\frac{(4 - 7 \cos \alpha)}{48}$              |
| 11/2 | 7/2 | 7/2 | $\frac{(4 - \cos \alpha)}{56}$               | $\frac{(7 \cos \alpha - 4)}{56}$              |
|      | 5/2 | 5/2 | $\frac{(4 - \cos \alpha)}{336}$              | $\frac{(7 \cos \alpha - 4)}{336}$             |
|      | 7/2 | 5/2 | $\frac{\sqrt{26} (\cos \alpha - 4)}{168}$    | $\frac{\sqrt{26} (4 - 7 \cos \alpha)}{168}$   |
| 9/2  | 7/2 | 7/2 | $\frac{41(4 - \cos \alpha)}{1680}$           | $\frac{41(7 \cos \alpha - 4)}{1680}$          |
|      | 5/2 | 5/2 | $\frac{(\cos \alpha - 4)}{280}$              | $\frac{(4 - 7 \cos \alpha)}{280}$             |
|      | 3/2 | 3/2 | $\frac{-(8 + 13 \cos \alpha)}{240}$          | $\frac{(8 - 29 \cos \alpha)}{240}$            |
|      | 7/2 | 5/2 | $\frac{\sqrt{3} (\cos \alpha - 4)}{420}$     | $\frac{\sqrt{3} (4 - 7 \cos \alpha)}{420}$    |
|      | 7/2 | 3/2 | $\frac{\sqrt{462} (1 - 4 \cos \alpha)}{420}$ | $-\frac{\sqrt{462} (1 + 2 \cos \alpha)}{420}$ |
|      | 5/2 | 3/2 | $\frac{\sqrt{154} (1 - 4 \cos \alpha)}{280}$ | $-\frac{\sqrt{154} (1 + 2 \cos \alpha)}{280}$ |
| 7/2  | 7/2 | 7/2 | $\frac{(4 - \cos \alpha)}{84}$               | $\frac{(7 \cos \alpha - 4)}{84}$              |
|      | 5/2 | 5/2 | $\frac{(\cos \alpha - 4)}{280}$              | $\frac{(4 - 7 \cos \alpha)}{280}$             |
|      | 3/2 | 3/2 | $\frac{(8 + 13 \cos \alpha)}{120}$           | $\frac{(29 \cos \alpha - 8)}{120}$            |
|      | 1/2 | 1/2 | 0  | 0   |
| 7/2  | 7/2 | 5/2 | $\frac{\sqrt{66} (4 - \cos \alpha)}{420}$    | $\frac{\sqrt{66} (7 \cos \alpha - 4)}{420}$   |
|      | 7/2 | 3/2 | $\frac{\sqrt{462} (1 - 4 \cos \alpha)}{420}$ | $-\frac{\sqrt{462} (1 + 2 \cos \alpha)}{420}$ |

$J = 3, |K| = 1$  (continued)

| F   | I   | I'  | v = 0   | v = 1   |
|-----|-----|-----|---|---|
|     | 7/2 | 1/2 | 0   | 0   |
|     | 5/2 | 3/2 | $\frac{\sqrt{7} (4 \cos \alpha - 1)}{280}$      | $\frac{\sqrt{7} (1 + 2 \cos \alpha)}{280}$      |
|     | 5/2 | 1/2 | $\frac{\sqrt{7} (\cos \alpha - 4)}{80}$         | $\frac{\sqrt{7} (4 - 7 \cos \alpha)}{80}$       |
|     | 3/2 | 1/2 | $\frac{(4 \cos \alpha - 1)}{40}$                | $\frac{(1 + 2 \cos \alpha)}{40}$                |
| 5/2 | 7/2 | 7/2 | $\frac{(\cos \alpha - 4)}{112}$                 | $\frac{(4 - 7 \cos \alpha)}{112}$               |
|     | 5/2 | 5/2 | $\frac{(\cos \alpha - 4)}{4200}$                | $\frac{(4 - 7 \cos \alpha)}{4200}$              |
|     | 3/2 | 3/2 | $\frac{(8 + 13 \cos \alpha)}{400}$              | $\frac{(29 \cos \alpha - 8)}{400}$              |
|     | 1/2 | 1/2 | 0   | 0   |
|     | 7/2 | 5/2 | $\frac{29 \sqrt{5} (4 - \cos \alpha)}{2100}$    | $\frac{29 \sqrt{5} (7 \cos \alpha - 4)}{2100}$  |
|     | 7/2 | 3/2 | $\frac{3 \sqrt{70} (1 - 4 \cos \alpha)}{700}$   | $\frac{-3 \sqrt{70} (2 \cos \alpha + 1)}{700}$  |
|     | 7/2 | 1/2 | 0   | 0   |
|     | 5/2 | 3/2 | $\frac{17 \sqrt{14} (4 \cos \alpha - 1)}{1400}$ | $\frac{17 \sqrt{14} (1 + 2 \cos \alpha)}{1400}$ |
|     | 5/2 | 1/2 | $\frac{\sqrt{210} (\cos \alpha - 4)}{600}$      | $\frac{\sqrt{210} (4 - 7 \cos \alpha)}{600}$    |
|     | 3/2 | 1/2 | $\frac{\sqrt{15} (1 - 4 \cos \alpha)}{100}$     | $\frac{-\sqrt{15} (1 + 2 \cos \alpha)}{100}$    |
| 3/2 | 7/2 | 7/2 | $\frac{5 (\cos \alpha - 4)}{168}$               | $\frac{5 (4 - 7 \cos \alpha)}{168}$             |
|     | 5/2 | 5/2 | $\frac{11 (4 - \cos \alpha)}{2800}$             | $\frac{11 (7 \cos \alpha - 4)}{2800}$           |

J = 3, |K| = 1 (continued)

| F   | I   | I'  | v = 0                                       | v = 1   |
|-----|-----|-----|---|---|
|     | 3/2 | 3/2 | $-\frac{(8 + 13 \cos \alpha)}{100}$         | $\frac{(8 - 29 \cos \alpha)}{100}$            |
|     | 7/2 | 5/2 | $\frac{13\sqrt{10}(4 - \cos \alpha)}{1400}$ | $\frac{13\sqrt{10}(7 \cos \alpha - 4)}{1400}$ |
|     | 7/2 | 3/2 | $\frac{\sqrt{35}(1 - 4 \cos \alpha)}{350}$  | $-\frac{\sqrt{35}(1 + 2 \cos \alpha)}{350}$   |
|     | 5/2 | 3/2 | $\frac{9\sqrt{14}(4 \cos \alpha - 1)}{700}$ | $\frac{9\sqrt{14}(1 + 2 \cos \alpha)}{700}$   |
| 1/2 | 7/2 | 7/2 | $\frac{5(\cos \alpha - 4)}{112}$            | $\frac{5(4 - 7 \cos \alpha)}{112}$            |
|     | 5/2 | 5/2 | $\frac{(4 - \cos \alpha)}{140}$             | $\frac{(7 \cos \alpha - 4)}{140}$             |
|     | 7/2 | 5/2 | $\frac{\sqrt{6}(4 - \cos \alpha)}{140}$     | $\frac{\sqrt{6}(7 \cos \alpha - 4)}{140}$     |

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J = 3, |K| = 2 - All matrix elements are zero.

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\*The abbreviations used in this section follow the Style Manual published by the American Institute of Physics (Second Edition, 1959).



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## VITA

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In September, 1965 Mr. Wolf was appointed Assistant Professor of Physics at Davidson College. He was married to the former Cary Bruns Hunt in 1956 and has three children.