THE MICROWAVE SPECTRA OF 2-CHLOROPROPANE AND 2-BROMOPROPANE

Thesis for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY Frederick Lee Tobiason 1963

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#### ABSTRACT

### THE MICROWAVE SPECTRA OF 2-CHLOROPROPANE AND 2-BROMOPROPANE

by Frederick Lee Tobiason

A presentation of the theory of rotational spectra with the perturbations caused by nuclear quadrupole and internal rotation interactions is given. The development centers around the asymmetric rotor with emphasis placed on the determination of molecular structure. Sections are included which describe the microwave spectrometer and the preparation of samples.

The microwave spectra of the isotopic species  $(CH_3)_2CHCl^{35}$ ,  $(CH_3)_2CHCl^{37}$ ,  $(CH_3)_2CDCl^{35}$ ,  $(CH_3)_2C^{13}HCl^{35}$ ,  $C^{13}H_3CHCl^{35}CH_3$ ,  $CH_2DCHCl^{35}CH_3$  (3 species), and  $CD_3CDCl^{35}CH_3$  have been examined, and from the rotational constants of the first eight species, a complete structure has been obtained by the substitution method. The parameters obtained are as follows: r(CC) = 1.522 A, r(CC1) = 1.798 A,  $r(CH_{sec}) = 1.091$  A,  $r(CH_{methyl}) = 1.092$  A;  $< CCC = 112^{\circ}42'$ ,  $< CCC1 = 109^{\circ}24'$ ,  $< CCH_{sec} = 109^{\circ}54'$ ,  $< CCH_{\alpha} = 110^{\circ}51'$ ,  $< CCH_{\beta}$ ,  $_{\gamma} = 109^{\circ}40'$ .

The quadrupole coupling parameters along the principal axes are  $\chi_{aa}$  = -61.49 Mc,  $\chi_{bb}$  = 34.81 Mc, and  $\chi_{cc}$  = 26.68 Mc.

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This leads to values of  $\chi_{bond}$  = -69.61 Mc if cylindrical charge distribution is assumed; and  $\chi_{bond}$  = -67.82 Mc and  $\eta_{bond}$  = 0.0275, assuming that the z axis and the CCl internuclear line coincide.

A study of the first excited torsional state transitions of  $(CH_3)_2CHCl^{35}$  and  $CD_3CDCl^{35}CH_3$  was made. A lower limit of 3400 cal/mole was set on the potential barrier hindering internal rotation by the frequency method, and an estimate of 3800 cal/mole was made by the intensity method.

The microwave spectra of the  $(CH_3)_2 CHBr^{79}$ , the  $(CH_3)_2 CHBr^{81}$ , and the  $(CH_3)_2 C^{13} HBr^{79}$  isotopic species of 2-bromopropane were assigned. Using the substitution method it was found that r(CBr) = 1.962 A.

The quadrupole coupling constants along the principal inertial axes are  $\chi_{aa} = 477.9 \text{ Mc}$ ,  $\chi_{bb} = -262.9 \text{ Mc}$ , and  $\chi_{cc} = -215.1 \text{ Mc}$  for bromine-79. This leads to values of  $\chi_{bond} = 525.7 \text{ Mc}$  if cylindrical charge distribution is assumed; and  $\chi_{bond} = 512.1 \text{ Mc}$  and  $\eta_{bond} = 0.0266$ , assuming that the z axis of the quadrupole tensor and the CBr internuclear line coincide.

## THE MICROWAVE SPECTRA OF 2-CHLOROPROPANE AND 2-BROMOPROPANE

By

Frederick Lee Tobiason

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

To my mother in memory of my father

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### I. HISTORICAL BACKGROUND

Active experimentation in microwave spectroscopy began only after the development of 1.25 centimeter radar equipment during World War II, even though the first experiments were carried out in 1933 by Cleeton and Williams (1). The radar equipment had been discarded for practical reasons and became readily available to universities at the end of the war.

Much of the early work in microwave spectroscopy was devoted to the development of a more sensitive instrument and to the theoretical and experimental study of the inversion spectrum of ammonia. One of the reasons why ammonia was studied was that its spectrum is very intense. High resolution spectroscopy was first demonstrated in the experiments carried out on ammonia by Bleaney and Penrose (2, 3) and by Coles and Good (4).

The most significant instrumental advance was the result of a suggestion by Hughes and Wilson (5) to apply a periodic electric field (Stark-field) to the microwave absorption cell. The resulting Stark-modulated spectrometer was much more sensitive than any instrument previously available. With the development of sensitive instruments, additional studies were carried out on symmetric tops and linear molecules.

These molecules were studied first because of the simplicity of their spectra.

The hyperfine structure that appeared in the ammonia spectrum was accounted for by the existence of a quadrupole moment in  $N^{14}$  (6). Under high resolution the complex hyperfine structure due to quadrupolar interactions provides a wealth of information concerning the electronic distribution about a nonspherical nucleus. From the treatment of Townes and Dailey (7) it is possible to obtain information about hybridization and ionic character of chemical bonds from quadrupole coupling constants.

Early theory predicted that the Stark effect would cause a shift and splitting of the frequencies of the absorption lines which would be proportional to the square of the electric field strength and to the square of the dipole moment in linear molecules (8). This was verified by means of measurements carried out on the Stark splittings of the OCS molecule (9), and the first of many dipole moments was determined by microwave spectroscopy.

In addition to the splittings caused by quadrupole interaction and the Stark effect, hyperfine structure may arise from internal rotations within the molecule. Potential barriers hindering internal rotation may be calculated from the measured hyperfine splittings. The first barrier determination by means of microwave spectroscopy was for methyl alcohol ( $CH_3OH$ ) (10). Later developments made by

Wilson's group at Harvard University (11, 12) produced a convenient method of analyzing barrier splittings. Now the most accurate method for determining small barrier potentials is by microwave spectroscopy.

The most important application of microwave spectroscopy is the determination of molecular structure. Internuclear distances and bond angles were first determined by varying these parameters until the computed moments of inertia reproduced the experimental moments of inertia obtained from the rotational constants for several isotopic species of the molecule. A better method suggested by Kraitchman (13) makes use of differences in the moments of inertia of two isotopically substituted molecules in order to determine the coordinates of the substituted atom. This method requires isotopic substitution of all the nonequivalent atoms in the molecule and is insensitive to atoms located near a principal axis or the center of mass of the molecule. A workable relationship between the substitution parameters and the equilibrium parameters has not been established, and consequently the effect of vibrations on the determined parameters has not been determined. Even with these limitations, the substitution method is one of the better methods for the determination of bond distances and bond angles in molecules.

#### II. THEORY OF ROTATIONAL SPECTRA

#### 2.1 Introduction

The microwave region of the electromagnetic spectrum includes wavelengths from 0.06-30 cm (frequencies from 500-1 kMc<sup>†</sup>), or between the far infrared and the radio frequency regions. In the microwave region one ordinarily observes pure rotational spectra (absorption transitions between rotational energy states with the same vibrational and electronic energies) with vibration, nuclear quadrupole, and internal rotation interactions as perturbations. Microwave spectra are usually studied in the ground vibrational and electronic states although the inversion spectrum of some molecules (such as ammonia) and low energy vibrational states contribute richly to the spectra.

Since the rotational transitions arise from properties of the angular momentum of rotating bodies, the theory will begin with a discussion of angular momentum and energy of rotation.

### 2.2 Angular Momentum and Rotational Energy

The Hamiltonian for a rigid asymmetric rotor is given by the expression

<sup>†</sup>One kMc = one kilomegacycle/second = one gigacycle/ second = 1000 megacycles (Mc)/second = 10<sup>9</sup> cycles/second.

$$H_{R} = \frac{\hbar^{2}}{2} \left( \frac{P_{a}^{2}}{I_{a}} + \frac{P_{b}^{2}}{I_{b}} + \frac{P_{c}^{2}}{I_{c}} \right)$$
(2-1)

where  $P_a$ ,  $P_b$ , and  $P_c$  are the components of angular momentum along the a, b, and c principal axes of the molecule respectively, and  $I_a \leq I_b \leq I_c$  are the principal moments of inertia about the principal axes. Expressions for the eigenvalues of  $H_R$  (the energy levels) cannot be obtained in closed form except for a few of the lowest energy levels.

In a general molecule-fixed Cartesian axis system, a solution to the matrix equations for the commutation relations for the components of angular momentum,

$$P_{\mathbf{x}}P_{\mathbf{y}} - P_{\mathbf{y}}P_{\mathbf{x}} = -iP_{\mathbf{z}},$$

$$P_{\mathbf{y}}P_{\mathbf{z}} - P_{\mathbf{z}}P_{\mathbf{y}} = -iP_{\mathbf{x}},$$
(2-2)
and 
$$P_{\mathbf{z}}P_{\mathbf{x}} - P_{\mathbf{x}}P_{\mathbf{z}} = -iP_{\mathbf{y}},$$

is

$$(P_{y})_{J,K;J,K+1} = -i(P_{x})_{J,K;J,K+1} = \frac{1}{2} [J(J+1) - K(K+1)]^{\frac{1}{2}},$$
(2-3)

$$(P_z)_{J,K;J,K} = K,$$
 (2-4)

$$(P_{y}^{2})_{J,K;J,K} = (P_{x}^{2})_{J,K;J,K} = \frac{1}{2} [J(J+1) - K^{2}], \qquad (2-5)$$

$$(P^{2})_{J,K;J,K} = P_{x}^{2} + P_{y}^{2} + P_{z}^{2} = J(J+1). \qquad (2-6)$$

The quantum number  $J = 0, 1, 2 \dots$  and the quantum number  $K = 0, \pm 1, \pm 2 \dots \pm J$ 

where  $J \ge K$ . The x, y, z axes used here do not refer to space-fixed axes, but to axes fixed in the rotating molecule. The x, y, z axes may be identified with the a, b, c axes in six ways, subject only to the restriction  $I_a \le I_b \le I_c$ .

The Hamiltonian may be written in terms of the rotational constants, A, B, C,

$$H_{R}(A,B,C) = h(AP_{a}^{2} + BP_{b}^{2} + CP_{c}^{2}),$$
 (2-7)

where

$$A = \frac{h}{8\pi^2 I_a}, B = \frac{h}{8\pi^2 I_b}, C = \frac{h}{8\pi^2 I_c}, and A \ge B \ge C.$$
 (2-8)

If a change of variables is made as proposed by Ray (14) using two scalar quantities  $\sigma$  and  $\rho$ ,

$$A' = \sigma A + \rho$$
  

$$B' = \sigma B + \rho$$
 (2-9)  

$$C' = \sigma C + \rho,$$

the Hamiltonian can be written as

$$H_{R}(A',B',C')/h = [(\sigma A + \rho)P_{a}^{2} + (\sigma B + \rho)P_{b}^{2} + (\sigma C + \rho)P_{c}^{2}], \quad (2-10)$$

or

$$H_{R}(A',B',C')/h = \sigma(AP_{a}^{2} + BP_{b}^{2} + CP_{c}^{2}) + \rho(P_{a}^{2} + P_{b}^{2} + P_{c}^{2}), \qquad (2-11)$$

which by (2-6) and (2-7) reduces to

$$H_{R}(A',B',C')/h = \sigma H_{R}(ABC) + \rho J(J+1).$$
 (2-12)

Ray's choice for  $\sigma$  and  $\rho$  were

$$\sigma = \frac{2}{A-C}, \ \rho = \frac{-(A+C)}{(A-C)},$$
 (2-13)

so that

$$\sigma A + \rho = 1,$$
 (2-14)

$$\sigma B + \rho = \frac{2B - A - C}{A - C} = \varkappa, \qquad (2 - 15)$$

and 
$$\sigma C + \rho = -1$$
. (2-16)

The dimensionless quantity  $\varkappa$  is called Ray's asymmetry parameter and is confined to  $-1 \le \varkappa \le 1$ . The limit of  $\varkappa = -1$ or B = C describes a prolate-symmetric rotor, while the limit  $\varkappa = +1$  or B = A defines an oblate-symmetric rotor. Kappa equal to zero is the most asymmetric case.

Together with equations (2-13) through (2-16), equation (2-11) leads to the usual form for the energy expression of an asymmetric top

$$\frac{W_R}{h} = \frac{A+C}{2} J(J+1) + \frac{A-C}{2} E_{\tau}^J(n) \qquad (2-17)$$

where the  $W_R$  are the eigenvalues of  $H_R(A,B,C)$ , the  $E_{\tau}^J(\kappa)$ are the eigenvalues of the matrix,

$$H_{R}(A',B',C')/h = P_{a}^{2} - P_{c}^{2} + \kappa P_{b}^{2},$$
 (2-18)

and the quantum number  $\tau = J$ , J-1, J-2, . . . -J. In this form

$$E_{\tau}^{J}(\kappa) = -E_{-\tau}^{J}(-\kappa).$$
 (2-19)

This approach was further developed by King, Hainer, and Cross (15) who evaluated the reduced energies  $E(\varkappa)$ , classified the energy levels according to symmetry, and listed the symmetry properties of the asymmetric rotor wave functions. Tables of  $E(\varkappa)$  have since been given for J = 0through 12 at intervals of 0.01 in  $\varkappa$  (16).

Once the energy for two levels is calculated, the frequency is obtained from the Bohr condition,

$$\frac{W_2 - W_1}{h} = \mathcal{Y}. \qquad (2-20)$$

Instead of labeling the energy levels with J and  $\tau$ as is done above, it is sometimes useful to label them with J, K<sub>-1</sub>, and K<sub>+1</sub>. The quantum numbers K<sub>-1</sub> and K<sub>+1</sub> are positive integers or zero and are related to the angular momentum about the a axis of the limiting prolate symmetric top and the c axis of the limiting oblate symmetric top. The relations between the sets of quantum numbers are  $\tau = K_{-1} - K_{+1}$  and  $K_{-1} + K_{+1} = J$  or J + 1.

The allowed rotational transitions are classified according to the change in J ( $\Delta J = -1$ , 0, and +1 label the P, Q, and R branches respectively) and as a, b, or c according to the direction of the component of the dipole moment responsible for the transition. The selection rules for a, b, and c-type transitions are

a type:	∆K <sub>-1</sub> = even	$\Delta K_{+1} = \text{odd},$
b type:	$\Delta K_{-1} = odd$	$\mathbf{AK}_{+1} = \text{odd},$
c type:	$\Delta K_{-1} = \text{odd}$	∆K <sub>+1</sub> = even.

The basic theory for the energy levels of a molecule outlined above is for a rigid rotator. However, the atoms in the molecule are forced away from an axis of rotation by a centrifugal force which is different for every energy level. The resulting small change in the moments of inertia will perturb the rigid rotator energy levels, causing a shift of the transition frequencies. Centrifugal distortion may have an enormous effect on the spectra of lighter asymmetric top molecules (e.g., hundreds of megacycles in HDS) since the transitions are usually between levels of very large rotational energy. In heavier molecules where the moments of inertia are large, the centrifugal distortion is usually small, and accurate rotational constants may be obtained by neglecting the complicated corrections which require six additional parameters. A centrifugal distortion theory for asymmetric rotators has been worked out by Kivelson and Wilson (17).

Experimental values of the rotational constants are determined from the measured frequencies of the rotational transitions. Experimental values of the moments of inertia may then be obtained by means of equations (2-8).

### 2.3 Moments of Inertia

For a rigid molecule, the moment of inertia I about any axis passing through the center of mass is given by

$$I = \sum_{i} m_{i} r_{i}^{2} \qquad (2-21)$$

where  $m_i$  is the mass of the i<sup>th</sup> atom and  $r_i$  is its perpendicular distance from the axis.

The rotational constants and the moments of inertia determined from microwave spectroscopy are called the effetive rotational constants and the effective moments of inertia. They are averaged over the vibrational state in a peculiar way and include terms coupling rotation and vibration. They are consequently not equal to either the equilibrium values or the average values of these quantities. The relationship between the rotational constants in a given vibrational state and the equilibrium values is

$$A_{v_1,v_2} = A_e - \sum_i \alpha_i (v_i + \frac{a_i}{2}).$$
 (2-22)

Here  $A_e$  is the equilibrium value of A, the  $\alpha_i$ 's are constants, and  $v_i$  is the quantum number of the i<sup>th</sup> vibrational mode with  $d_i$  its degeneracy. Hence, to determine the equilibrium values of the rotational constants it is necessary to know the rotational constants for each singly excited vibrational state in addition to the ground state.

The moments of inertia may be defined in terms of a momental ellipsoid. The locus of  $I^{-\frac{1}{2}}$  plotted along axes passing through the center of mass is defined as the momental ellipsoid. The center of the momental ellipsoid is at the center of mass of the molecule, and the principal axes of the ellipsoid are the principal axes referred to above

following equation (2-1). A molecule is classified as an asymmetric top molecule if all three moments of inertia are unequal, as a symmetric top molecule if two of the moments of inertia are equal, or as a linear molecule if one of the moments of inertia equals zero (18).

If the molecule has a plane of symmetry, then two of the principal axes must lie in the plane and the third must be perpendicular to it. The plane of symmetry is called the principal plane. This is true of the most common isotopic species of both 2-chloropropane and 2-bromopropane.

The moments of inertia are related to the rotational energies through the angular momentum,

$$\vec{P} = \vec{I}\vec{\omega}. \qquad (2-23)$$

Here  $\vec{P}$  is the angular momentum vector,  $\vec{\omega}$  is the angular velocity vector, and I is defined as the moment of inertia dyadic or moment of inertia tensor. An expression for I in dyadic notation is given by (19)

$$I = \sum_{i} m_{i} (r_{i}^{2} \vec{l} - \vec{r}_{i} \vec{r}_{i})$$
 (2-24)

where  $\vec{r}_i = x_i \vec{i} + y_i \vec{j} + z_i \vec{k}$  is the radius vector from the center of mass to the i<sup>th</sup> mass,  $m_i$ , and  $\vec{l}$  is the unit dyadic. In tensor form,

$$I = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix}$$
(2-25)

where the elements in terms of rectangular Cartesian coordinates measured from the center of mass are

$$I_{xx} = \sum_{i} m_{i} (y_{i}^{2} + z_{i}^{2}), \quad I_{xy} = I_{yz} = -\sum_{i} m_{i} x_{i} y_{i},$$

$$I_{yy} = \sum_{i} m_{i} (x_{i}^{2} + z_{i}^{2}), \quad I_{yz} = I_{zy} = -\sum_{i} m_{i} y_{i} z_{i}, \quad (2-26)$$

$$I_{zz} = \sum_{i} m_{i} (x_{i}^{2} + y_{i}^{2}), \quad I_{xz} = I_{zx} = -\sum_{i} m_{i} x_{i} z_{i}.$$

The diagonal elements are the moments of inertia and the off-diagonal elements are called the products of inertia.

In the calculations and in the discussion of an asymmetric top it is more convenient to use a planar dyadic P defined in a center of mass system by

$$\mathbf{P} = \sum_{i} \mathbf{m}_{i} \vec{\mathbf{r}}_{i} \vec{\mathbf{r}}_{i} \qquad (2-27)$$

where  $m_i$  and  $\vec{r}_i$  are defined as before. The planar dyadic P may also be written in tensor form (the second-moment tensor) as

$$\mathbf{P} = \begin{pmatrix} \boldsymbol{\Sigma}_{i}^{m_{i}} \mathbf{x}_{i}^{2} & \boldsymbol{\Sigma}_{i}^{m_{i}} \mathbf{x}_{i}^{y_{i}} & \boldsymbol{\Sigma}_{i}^{m_{i}} \mathbf{x}_{i}^{z_{i}} \\ \boldsymbol{\Sigma}_{i}^{m_{i}} \mathbf{x}_{i}^{y_{i}} & \boldsymbol{\Sigma}_{i}^{m_{i}} \mathbf{y}_{i}^{2} & \boldsymbol{\Sigma}_{i}^{m_{i}} \mathbf{y}_{i}^{z_{i}} \\ \boldsymbol{\Sigma}_{i}^{m_{i}} \mathbf{x}_{i}^{z_{i}} & \boldsymbol{\Sigma}_{i}^{m_{i}} \mathbf{y}_{i}^{z_{i}} & \boldsymbol{\Sigma}_{i}^{m_{i}} \mathbf{z}_{i}^{2} \end{pmatrix}. \quad (2-28)$$

The tensors I and P may be formally regarded as symmetric matrices and hence may be diagonalized by an orthogonal transformation. The diagonalization is equivalent to a rotation of the x, y, z axis system in terms of which the components of the two tensors were computed. An S matrix which diagonalizes the I matrix also diagonalizes the P matrix; the eigenvalues of I are the principal moments of inertia and those of P are the principal second moments. The orthogonal transformation is given by

$$\widetilde{SIS} = I_{abc}$$
 (2-29)  
 $\widetilde{SPS} = P_{abc}$ 

where the diagonal values of  $I_{abc}$ , the principal I's, and the diagonal values of  $P_{abc}$ , the principal P's, are related by the expressions

$$P_{aa} = (I_{b} + I_{c} - I_{a})/2,$$

$$P_{bb} = (I_{a} + I_{c} - I_{b})/2,$$
(2-30)
and 
$$P_{cc} = (I_{a} + I_{b} - I_{c})/2.$$

If the mass of the  $s^{th}$  atom of a molecule is increased by an amount  $\Delta m$  (as in isotopic substitution), then in general there will be a translation of the center of mass and a rotation of the principal axes with respect to the principal axis system of the original molecule.

The second moments of a molecule defined above in terms of an axis system whose origin is at the center of mass can be written in a translated axis system by making use of the parallel axis theorem. The two systems of axes are shown in Fig. 1. The origin of the x, y, z system is at the center of mass and x", y", z" are the parallel,



Fig. 1. Coordinate systems for a molecule in a center-ofmass axis system and a translated axis system.

translated axes. The result of the application of the parallel axis theorem is as follows:

$$P = P'' - \frac{(\sum_{i} m_{i} \vec{r}_{i}'')(\sum_{i} m_{i} \vec{r}_{i}'')}{\sum_{i} m_{i}}$$
(2-31)

where

$$P = \sum_{i} m_{i} \vec{r}_{i} \vec{r}_{i},$$

$$P'' = \sum_{i} m_{i} \vec{r}_{i} "\vec{r}_{i} ",$$

$$\vec{r}_{i} " = \mathbf{x}_{i} "\vec{i} + \mathbf{y}_{i} "\vec{j} + \mathbf{z}_{i} "\vec{k} = \vec{r}_{i} - \vec{r}_{o},$$

$$\vec{r}_{o} = \mathbf{x}_{o} \vec{i} + \mathbf{y}_{o} \vec{j} + \mathbf{z}_{o} \vec{k} = \text{the vector connecting}$$

$$\text{the origins of the two systems,}$$

$$\vec{r}_{i} = \mathbf{x}_{i} \vec{i} + \mathbf{y}_{i} \vec{j} + \mathbf{z}_{i} \vec{k},$$
and 
$$\sum_{i} m_{i} \vec{r}_{i} " = \vec{r}_{o} \sum_{i} m_{i}.$$

$$(2-32)$$

If mass  $m_s$  is increased by  $\Delta m$ , the second moments of this isotopic species can be calculated by means of an equation similar to equation (2-31) using coordinates in a center-of-mass axis system of the parent molecule. The moments of the substituted species will then be given with respect to its own center of mass and to axes parallel to the axes of the parent molecule. The second moment dyadic for the substituted molecule in this system is

$$\mathbf{P}' = \mathbf{P} + \Delta \mathbf{m} \vec{\mathbf{r}}_{s} \vec{\mathbf{r}}_{s} - \frac{(\Delta \mathbf{m} \vec{\mathbf{r}}_{s})(\Delta \mathbf{m} \vec{\mathbf{r}}_{s})}{\sum_{i} \mathbf{m}_{i} + \Delta \mathbf{m}} = \mathbf{P} + \mu \vec{\mathbf{r}}_{s} \vec{\mathbf{r}}_{s} \quad (2-33)$$

where

$$\mathcal{M} = \frac{\Delta \mathrm{m} \mathrm{M}}{\mathrm{M'}},$$

M = the molecular weight of the original species, M' = the molecular weight of the isotopic species,  $\Delta m = M' - M$ , and  $\vec{r}_s = x_s \vec{i} + y_s \vec{j} + z_s \vec{k}$ .

If the center-of-mass axis system of the parent molecule is in addition the principal axis system of the parent, the coordinates  $x_i$ ,  $y_i$ ,  $z_i$  are usually labeled  $a_i$ ,  $b_i$ ,  $c_i$ . The substitution coordinates  $x_s$ ,  $y_s$ ,  $z_s$  become the  $a_s$ ,  $b_s$ ,  $c_s$  coordinates of the substituted atom measured in the principal axis system of the parent molecule.

The P' matrix is

$$P' = \begin{pmatrix} P_{aa} + \mu a_{s}^{2} & \mu a_{s} b_{s} & \mu a_{s} c_{s} \\ \mu b_{s} a_{s} & P_{bb} + \mu b_{s}^{2} & \mu b_{s} c_{s} \\ \mu c_{s} a_{s} & \mu c_{s} b_{s} & P_{cc} + \mu c_{s}^{2} \end{pmatrix}.$$
(2-34)

If this matrix is diagonalized, the principal values of P'  $(P'_{aa}, P'_{bb}, P'_{cc})$  for the substituted molecule will be found. Kraitchman (13) has shown that

$$|a_{s}| = \{\mu^{-1} [(P'_{aa} - P_{aa})(1 + \frac{P'_{bb} - P_{bb}}{P_{bb} - P_{aa}})(1 + \frac{P'_{cc} - P_{cc}}{P_{cc} - P_{aa}})]\}^{\frac{1}{2}}.$$
(2-35)

Expressions for  $|b_s|$  and  $|c_s|$  may be obtained by cyclic permutation of the subscripts.

The moments of inertia for different isotopic species are obtained by analysis of the microwave spectra. The unprimed P's and the primed P's then can be calculated, and hence the coordinates for any substituted atom may be determined. If every nonequivalent site in the molecule is substituted, the coordinates of every atom can be computed. However, only the absolute values of the coordinates will be obtained so the signs must be determined from prior knowledge of the structure. Then by applying simple geometry to these coordinates, all the bond angles and bond distances of the molecule can be determined. More details on the use of Kraitchman's equations will be given in Chapter IV.

#### 2.4 Nuclear Electric Quadrupole Moments

The nonspherical distribution of charges in nuclei such as chlorine and bromine gives rise to the so-called quadrupole moment. These nuclei interact with the electrons and other nuclei in a molecule to produce a variation in the electrostatic energy of the system with nuclear orientation. Every nuclear orientation leads to a different coupling with the overall rotation of the molecule, and consequently to different interaction energies. Transitions between these perturbed energy levels give rise to quadrupole hyperfine structure.

The energy of interaction between a nucleus having a quadrupole moment and the electric field in the molecule depends on the value of the nuclear spin I, on the nuclear quadrupole moment Q, and on the tensor quantity  $\vec{\nabla}\vec{\nabla}V$ , where V is the electrostatic potential due to all charges external

to the nonspherical nucleus. This fundamental problem of nuclear quadrupole interaction with molecular rotation was first worked out for one quadrupolar nucleus by Casimir (20) and has been extended to asymmetric tops with one or two quadrupolar nuclei, including first and second order effects (21, 22, 23). The part of the quadrupole interaction energy dependent on rotational state is given by Casimir as

$$W_{Q} = eQ \left\langle \frac{\partial^{2}V}{\partial Z^{2}} \right\rangle_{av} \frac{(3/4)C(C+1) - I(I+1)J(J+1)}{2J(2J-1)I(2I-1)}$$
(2-36)

where

C = F(F+1) - I(I+1) - J(J+1), F = J+I, J+I-1, . . . |J-I| = the total angular momentum quantum number, J = the rotational angular momentum quantum number, I = the nuclear spin quantum number, Q = the quadrupole moment,

and  $\langle \frac{\partial^2 V}{\partial Z^2} \rangle_{av.}$  is the average gradient at the nucleus in a space-fixed direction. Classically,

$$\left\langle \frac{\partial^2 v}{\partial z^2} \right\rangle_{av.} = \left\langle \sum_{j} e \left[ \frac{3 \cos^2 \theta_j - 1}{\vec{r}_j^3} \right] \right\rangle_{av.}$$
 (2-37)

where  $\vec{r}_j$  is the radius vector from the nucleus to the i<sup>th</sup> electronic charge, and  $\theta_j$  is the angle  $\vec{r}_j$  makes with the space-fixed axis.

For an asymmetric top the quantity  $\langle \frac{\partial^2 \mathbf{v}}{\partial Z^2} \rangle_{av.}$ , as obtained by Bragg and Golden (22) using a first order

treatment, is expressed by

$$q_{J} \equiv \left\langle \frac{\partial^{2} v}{\partial Z^{2}} \right\rangle_{av} = \frac{2}{h(2J+3)(J+1)} \left[ q_{aa} \frac{\partial W_{R}}{\partial A} + q_{bb} \frac{\partial W_{R}}{\partial B} + q_{cc} \frac{\partial W_{R}}{\partial C} \right]$$
(2-38)

where

$$\frac{\partial W_{R}}{\partial A} = \frac{h}{2} \left[ J(J+1) + E(\kappa) - (\kappa+1) \frac{\partial E(\kappa)}{\partial \kappa} \right]$$

$$\frac{\partial W_{R}}{\partial B} = h \frac{\partial E(\kappa)}{\partial \kappa}$$
(2-39)

$$\frac{\partial \mathbf{w}_{\mathbf{R}}}{\partial \mathbf{C}} = \frac{h}{2} \left[ \mathbf{J}(\mathbf{J}+1) - \mathbf{E}(\mathbf{n}) + (\mathbf{n}-1) \frac{\partial \mathbf{E}(\mathbf{n})}{\partial \mathbf{n}} \right]$$

and  $q_{aa}$ ,  $q_{bb}$ , and  $q_{cc}$  are the field gradients  $\frac{\partial^2 v}{\partial a^2}$ ,  $\frac{\partial^2 v}{\partial b^2}$ ,  $\frac{\partial^2 v}{\partial c^2}$ , respectively, along the principal axes.

Since Laplace's equation  $(\nabla^2 V = 0)$  holds, only two of the three constants  $q_{aa}$ ,  $q_{bb}$ , and  $q_{cc}$  are independent. Writing equation (2-38) in terms of the so-called quadrupole coupling constants  $\chi_{aa} = eQq_{aa}$ ,  $\chi_{bb} = eQq_{bb}$ , and  $\chi_{cc} = eQq_{cc}$ and making use of Laplace's equation, one finds that

$$W_Q = Y(F) [\chi_{aa} f_1(J, n) + (\chi_{bb} - \chi_{cc}) f_2(J, n)].$$
 (2-40)

The function

$$f(I,J,F) = Y(F) = \frac{(3/4)C(C+1) - I(I+1)J(J+1)}{2(2J-1)I(2I-1)(2J+3)}$$
(2-41)

is known as Casimir's function and has been tabulated (16, 18). The functions  $f_1(J,\varkappa)$  and  $f_2(J,\varkappa)$  depend only upon the rotational quantum number J and the asymmetry parameter  $\varkappa$ , and can be derived from equation (2-38):

$$f_{1}(J, \kappa) = \frac{2}{J(J+1)} \left(\frac{\partial W_{R}}{\partial A} - \frac{\partial W_{R}}{\partial B}\right)$$

$$f_{2}(J, \kappa) = \frac{2}{J(J+1)} \left(\frac{\partial W_{R}}{\partial B} - \frac{\partial W_{R}}{\partial C}\right)$$
(2-42)

where the  $\frac{\partial W_R}{\partial A}$ , etc., are given by equations (2-39). We now define  $\frac{\partial^2 V}{\partial a^2} = q_m$ , and  $\frac{\partial^2 V}{\partial b^2} - \frac{\partial^2 V}{\partial c^2}/q_m = \eta$ . The first order perturbation correction then becomes

$$W_{O} = \alpha q_{m} + \beta q_{m} \eta \qquad (2-43)$$

where

$$\alpha = eQY(F) f_1(J, \kappa)$$
and  $\beta = eQY(F) f_2(J, \kappa).$ 

$$(2-44)$$

One obtains values of  $W_Q$  (where  $W_Q \ll W_R$ ) for every different value of F, and the total energy for the perturbed rotational level is  $W = W_R + W_Q$ . For I = 3/2 as in Cl<sup>35</sup>, Cl<sup>37</sup>, Br<sup>79</sup>, and Br<sup>81</sup>, there are four values of F for each J (except J = 0 or 1) and hence each rotational level is split into four levels by the perturbation.

The useful chemical interpretation of quadrupole coupling constants is obtained from these parameters in a molecule-oriented axis system. In this thesis the axis system is oriented approximately along the carbon-halogen bond, and corresponds to the principal axes of the quadrupole coupling tensor.

In general, only first order perturbation is used to fit the quadrupole spectra, and only the diagonal elements of the symmetric coupling constant tensor are obtained. Even so, once  $\chi_{aa}$ ,  $\chi_{bb}$ , and  $\chi_{cc}$  are determined, they may be transformed from the principal inertial axis system into the principal quadrupolar axis system. This could be done exactly if the off-diagonal elements could be determined from second order effects. However, by assuming a cylindrical charge distribution about one of the principal quadrupolar axes, or that a principal axis of the tensor and the carbonhalogen internuclear line coincide, the transformation may be carried out. Once the elements of this transformed tensor are known, they may be related to the ionic character of the bond and to the hybridization of the halogen bonding orbital (7). Further details are given on these transformations and interpretations in Chapter IV.

#### 2.5 Potential Barriers Hindering Internal Rotation

A perturbation which gives rise to additional hyperfine splittings in the rotational spectra is due to internal rotation (the rotation of one segment of a molecule with respect to the remainder). From an analysis of these splittings one can determine accurately the height of the potential barrier hindering the internal rotation. The availability of accurate values of the height of potential barriers hindering internal rotation has given much information concerning the influencing intramolecular forces even though the precise nature of the origin of potential barriers is still somewhat a theoretical mystery.
The problem of determining the effect on the rotational spectra of a symmetric rotor (a methyl group) attached to an asymmetric frame (the rest of the molecule) has been studied extensively by Wilson and his co-workers (11, 12). Coupling between the angular momenta of internal and overall rotation has been shown to be the most important mechanism producing barrier-dependent splittings in the rotational spectrum. In the principal axis method, as the theory developed by these workers is named, the top-frame coupling is treated by perturbation theory, and tables have been compiled giving the perturbation coefficients which are needed for an analysis of the spectra (24, 25).

In problems involving two equivalent symmetric rotors, such as in 2-chloropropane, the possibility arises for coupling between the tops as well as between the tops and the frame. The analysis of such spectra is much more complicated than the analysis of spectra in a one-top problem. The first theoretical approach to the two-top problem was by Swalen and Costain (26) in a study of acetone. The most extensive work however has been and is being pursued by Pierce and his co-workers (27, 28).

In the study of a two-top molecule such as  $CD_3CDClCH_3$ , the internal rotation can be treated as a one-top problem. This is because the tunneling of the heavier  $CD_3$  group is very much less than that of the  $CH_3$  group. The method for single top systems employed here is the one developed by

Herschbach (12). The model is that of a threefold symmetric rotor attached to an asymmetric frame. The potential barrier of the top is assumed to have a sinusoidal shape given by the first term in a Fourier series expansion of the periodic hindering potential. The expression for a top having threefold symmetry (Fig. 2) is

$$V(\alpha) = \frac{V_3}{2} (1 - \cos 3\alpha)$$
 (2-45)

where  $V_3$  is the barrier height, and  $\alpha$  is the angle of the top with respect to the frame.

If the barrier height is large, the internal motion will be small torsional oscillations in the three separate potential wells (Fig. 2). This is equivalent to a harmonic oscillator whose triply degenerate energy levels are depicted in the right-hand side of Fig. 3. As the barrier height is lowered, each torsional level v splits into two sublevels: a nondegenerate level,  $v_A$  (quantum number  $\sigma = 0$ ), and a doubly degenerate level,  $v_E$  ( $\sigma = \pm 1$ ). The splitting may be regarded as arising from tunneling through the potential barrier. The A and E classifications refer to the symmetry of transformations under the C<sub>3</sub> symmetry group.

The torsional energy levels are determined by the barrier height  $V_3$  and by a reduced moment of inertia rI $\alpha$ , where

$$\mathbf{r} = \mathbf{1} - \sum_{g} \frac{\lambda_{g}^{2} \mathbf{I}_{\alpha}}{\mathbf{I}_{g}}, \qquad (2-46)$$



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



Fig. 3. Energy level diagram

- $I_{\alpha}$  = the moment of inertia about the internal rotor symmetry axis,
- $\lambda_g$  = the direction cosine between the g principal axis and the internal top symmetry axis,
- and I = the moment of inertia for the entire molecule about the g principal axis.

Rotational spectra would not be affected by these torsional splittings if it were not for the coupling of angular momenta between the overall and the internal rotation. Because there is no dipole moment change with torsional motion, the A and E energy levels give separate rotational spectra. Since the coupling has different effects on the A and E sublevels of each torsional level v, the rotational transitions from a torsional state v occur as doublets instead of as a single line for a rigid rotator. The frequency separations of the doublets depend on the structural parameters and on the barrier height.

Molecules in torsional states with v > 0 have different moments of inertia which shift the energy levels from those of the ground state, and therefore shift the rotational spectra.

An effective Hamiltonian for each torsional state v is given by

$$H_{v\sigma} = H_{r} + hF \sum_{n} W_{v\sigma}^{(n)} \heartsuit^{n} \qquad (2-47)$$

where H<sub>r</sub> is the rigid rotator Hamiltonian,

$$F = \frac{h}{8\pi^{2} r I \alpha} \text{ or } F = \frac{505.531}{r I \alpha} \text{ in kilomegacycles}, (2-48)$$

$$\bigotimes = \sum P_{g} \lambda_{g} \frac{I_{\alpha}}{I_{g}} = \alpha P_{x} + \beta P_{y} + \gamma P_{z},$$

$$\alpha = \frac{\lambda_{x} I_{\alpha}}{I_{x}}, \quad \beta = \frac{\lambda_{y} I_{\alpha}}{I_{y}}, \quad \gamma = \frac{\lambda_{z} I_{\alpha}}{I_{z}};$$

$$P_{g} = the g arris component of the total angular$$

P<sub>g</sub> = the g-axis component of the total angular momentum,

and  $W_{v\sigma}^{(n)}$  = the n<sup>th</sup> order perturbation coefficient.

The  $W_{V\sigma}^{(n)}$  depend only on the ratio  $V_3/F$ , and have been tabulated (24) against a dimensionless parameter s through fourth order (n = 0 to 4) for the three lowest torsional levels v = 0, 1, 2. The parameter

$$s = 4.66139 (V_3/F)$$
 (2-49)

where F is in kMc and  $V_3$  is in cal/mole. The  $W_{v\sigma}^{(n)}$  differ in sign and magnitude for the A and E levels of a given torsional level v, and therefore the different rotational spectra arising from  $H_{vE}$  and  $H_{vA}$  allow the barrier height to be determined. The selection rule is  $\Delta \sigma = 0$  so that transitions between E levels ( $\mathcal{V}_E$ ) and between A levels ( $\mathcal{V}_A$ ) are observed.

In carrying out a calculation to second order,  ${}^{H}\!\!\!\!\!\!v\sigma$  becomes

$$H_{v\sigma} = H_r + hFW_v^{(1)} + hFW_v^{(2)} + hFW_v^{(2)}$$
 (2-50)

The odd order terms in ö vanish for the A levels, while those for the E levels can be treated as a perturbation. The energies for the A and E levels can be written as follows:

$$W_{vA} = W_{R} + \frac{\partial W_{R}}{\partial A} A_{vA}' + \frac{\partial W_{R}}{\partial B} B_{vA}' + \frac{\partial W_{R}}{\partial C} C_{vA}'$$
(2-51)

$$W_{vE} = W_R + \frac{\partial W_R}{\partial A} A'_{vE} + \frac{\partial W_R}{\partial B} B'_{vE} + \frac{\partial W_R}{\partial C} C'_{vE} + \Delta W^{(1)} \qquad (2-52)$$

where the partial derivatives of  $W_R$  are given by equation (2-39) and  $\Delta W^{(1)}$  represents the contribution from the term first order in  $\bigcirc$  and is negligible in asymmetric top cases where there are large separations between energy levels. The terms including  $A'_A$ ,  $A'_E$ , etc. are the second order contributions where  $A'_A$ ,  $A'_E$ , etc., are corrections to the effective rotational constants.

The difference in energy between the A and E levels (neglecting the first order term) is

$$W_{A} - W_{E} = \frac{\partial W_{R}}{\partial A} (A_{VA}^{\dagger} - A_{VE}^{\dagger}) + \frac{\partial W_{R}}{\partial B} (B_{VA}^{\dagger} - B_{VE}^{\dagger}) + \frac{\partial W_{R}}{\partial C} (C_{VA}^{\dagger} - C_{VE}^{\dagger})$$
(2-53)

where

$$A'_{vA} - A'_{vE} = F\alpha^{2} [W_{vA}^{(2)} - W_{vE}^{(2)}]$$
  

$$B'_{vA} - B'_{vE} = F\beta^{2} [W_{vA}^{(2)} - W_{vE}^{(2)}]$$

$$C'_{vA} - C'_{vE} = F\gamma^{2} [W_{vA}^{(2)} - W_{vE}^{(2)}].$$
(2-54)

In the first excited torsional state v = 1, substituting both v = 1 and the high barrier equation  $W_{1A}^{(2)} = -2W_{1E}^{(2)}$  in the above expressions, the equation can be rewritten as

$$W_{A} - W_{E} = \frac{3}{2} FW_{1A}^{(2)} \left[\alpha^{2} \frac{\partial W_{R}}{\partial A} + \beta^{2} \frac{\partial W_{R}}{\partial B} + \gamma^{2} \frac{\partial W_{R}}{\partial C}\right] \qquad (2-55)$$

and the difference in frequency of the A and E component is  $\mathcal{V}_{A} - \mathcal{V}_{E} = \frac{3FW_{1A}^{(2)}}{2h} \left[\alpha^{2} \Delta(\frac{\partial W_{R}}{\partial A} + \beta^{2} \Delta(\frac{\partial W_{R}}{\partial B} + \gamma^{2} \Delta(\frac{\partial W_{R}}{\partial C})\right] (2-56)$ 

where the differences in the partial derivative of  $W_R$  are between the two rigid rotator levels in question. These equations will be used in Chapter IV to set a lower limit on the potential barrier for  $CD_3CDCl^{35}CH_3$  as determined from the absence of splittings in the first excited torsional state rotational spectrum.

Use can be made of the foregoing equations and existing tables to evaluate the potential barrier hindering internal rotation by means of relative intensity measurements (29) of rotational transitions in the excited torsional state and in the ground state.

In the high barrier case, the motion of the top is essentially one of a simple harmonic oscillator, and the purely torsional energy is given by

$$E_{v\sigma} = hFW_{v\sigma}^{(0)}. \qquad (2-57)$$

The difference in energy between the ground and first excited torsional state is

$$E_{l\sigma} - E_{0\sigma} = hF(W_{l\sigma}^{(0)} - W_{0\sigma}^{(0)})$$
 (2-58)

which is equal to the torsional frequency multiplied by h. The torsional frequency may be determined from the relative intensities of the first excited torsional state and the ground state by use of the Boltzmann equation. The relative intensity R is given by

$$R = \frac{N_{v'}}{N_{v}} = \frac{g_{v'}}{g_{v}} \exp(\frac{-h \bigvee_{vv'}}{kT}) \qquad (2-59)$$

where  $N_{v'}$  and  $N_{v}$  are the populations of the upper and ground states,  $g_{v'}$  and  $g_{v}$  are the statistical weights, and  $\mathcal{N}_{vv'}$ is the torsional frequency of the top and is expressed by

$$\mathcal{V}_{\mathbf{v}\mathbf{v}'} = \frac{-\mathbf{k}\mathbf{T}}{\mathbf{h}} \,\ell\,\mathbf{n} \,\left(\mathbf{R}\,\frac{\mathbf{g}_{\mathbf{v}}}{\mathbf{g}_{\mathbf{v}'}}\right)\,. \tag{2-60}$$

After  $y_{vv'}$  is determined, it is used with expression (2-58) to compute  $(W_1^0 - W_0^0)$ . From the difference between these perturbation coefficients, s and hence  $V_3$  can be evaluated.

The difficulty of making intensity measurements in the microwave region lessens the accuracy of this method. Some of the difficulties are wave reflections in the waveguide, noise interference, interfering transitions, small splitting effects from internal rotation, and quadrupole components not completely resolved. The last two decrease the intensity from that of the unsplit transition. Even with these problems, one can obtain fairly accurate values if the intensity measurements are made a number of times under varied conditions.

#### III. STARK MODULATED MICROWAVE SPECTROMETER

#### 3.1 Introduction

The general microwave spectrometer consists of a source for generating the electromagnetic radiation, a sample absorption cell, a detection system, a means of displaying or recording the detected signal, and finally a method for measuring the frequency of the detected absorption signal. To improve the sensitivity of the instrument, a periodic Stark-field is applied by means of a square-wave generator or a sinusoidal generator. The periodic Stark-field modulates the absorption signal and provides a coherent AC signal for amplification and detection. In the Michigan State University instrument, a 100 kc square-wave Stark-field is applied.

A block diagram of the instrument in use at Michigan State University is shown in Fig. 4. The main components of this spectrometer will be described in the following sections.

#### 3.2 Klystron Oscillators

A schematic diagram for a typical klystron oscillator is shown in Fig. 5, and in Table I is a list of klystrons with their frequency range and operating voltages.



Fig. 4. Block diagram of microwave spectrometer



Fig. 5. A circuit schematic for a typical klystron oscillator.

X-138.2 - 12.4Varian Associates (a) $400^{0}$ $41$ X-1212.4 - 18.0Varian Associates50058X 962218.0 - 22.5EMI/US <sup>(b)</sup> 200011R 960222.5 - 26.0EMI/US200012R 951827.9 - 32.3EMI/US200013R 951627.9 - 32.3EMI/US200013R 951827.9 - 32.3EMI/US200013R 951827.9 - 32.3EMI/US200013R 951827.9 - 32.3EMI/US200013R 951827.9 - 37.5EMI/US200013R 951827.9 - 37.5EMI/US200013R 954632.0 - 27.330.0Raytheon <sup>(C)</sup> 18008 $(a)Varian Associates, 611 Hansen Way, Palo Alto, California.(alifornia.)$	Klystron	Frequency range (kMc)	Manufacturer	Beam voltage	Beam current in milliamperes (d)
X-1212.4 - 18.0Varian Associates50058R 962218.0 - 22.5EMI/US(b)200011R 960222.5 - 26.0EMI/US200012R 951827.9 - 32.3EMI/US200013R 954632.0 - 37.5EMI/US200013R 954632.0 - 37.5EMI/US200013R 954632.0 - 25.0Raytheon(c)18008 $2 K 33$ 22.0 - 25.0Raytheon(c)18008 $(a) Varian Associates, 611 Hansen Way, Palo Alto, California.(alifornia)$	X-13	8.2 - 12.4	Varian Associates <sup>(a)</sup>	40Di	41
R 9622 18.0 - 22.5 $EMI/US^{(b)}$ 2000 11 R 9602 22.5 - 26.0 $EMI/US$ 2000 12 R 9518 27.9 - 32.3 $EMI/US$ 2000 13 R 9546 32.0 - 37.5 $EMI/US$ 2000 13 2 K 33 22.0 - 25.0 Raytheon <sup>(c)</sup> 1800 8 QK 289 27.3 - 30.0 Raytheon (c) 2250 8 $(a)_{Varian Associates, 611 Hansen Way, Palo Alto, California.$	X-12	12.4 - 18.0	Varian Associates	500	58
R 9602 $22.5 - 26.0$ $EMI/US$ $2000$ $12$ R 9518 $27.9 - 32.3$ $EMI/US$ $2000$ $12$ R 9546 $32.0 - 37.5$ $EMI/US$ $2000$ $13$ R 9546 $32.0 - 37.5$ $EMI/US$ $2000$ $13$ $2 K 33$ $22.0 - 25.0$ $Raytheon^{(c)}$ $1800$ $8$ $QK 289$ $27.3 - 30.0$ Raytheon^{(c)} $2250$ $8$ $(a)Varian Associates, 611 Hansen Way, Palo Alto, California.$	R 9622	18.0 - 22.5	EMI /US <sup>(b)</sup>	2000	11.8
R 9518       27.9 - 32.3       EMI/US       2000       12         R 9546       32.0 - 37.5       EMI/US       2000       13         2 K 33       22.0 - 25.0       Raytheon <sup>(C)</sup> 1800       8         QK 289       27.3 - 30.0       Raytheon       2250       2550       8         (a)Varian Associates, 611 Hansen Way, Palo Alto, California.       (a)Ito, California.       2250       10	<b>R</b> 9602	22.5 - 26.0	EMI /US	2000	12.2
R 9546       32.0 - 37.5       EMI/US       2000       13         2 K 33       22.0 - 25.0       Raytheon <sup>(c)</sup> 1800       8         QK 289       27.3 - 30.0       Raytheon       2250       8         (a)Varian Associates, 611 Hansen Way, Palo Alto, California.	R 9518	27.9 - 32.3	EMI/US	2000	12.2
2 K 33 22.0 - 25.0 Raytheon <sup>(C)</sup> 1800 8 QK 289 27.3 - 30.0 Raytheon 2250 8 <sup>(a)</sup> Varian Associates, 611 Hansen Way, Palo Alto, California.	R 9546	32.0 - 37.5	EMI /US	2000	13.2
QK 289 27.3 - 30.0 Raytheon 2250 8 (a)Varian Associates, 611 Hansen Way, Palo Alto, California.	2 K 33	22.0 - 25.0	Raytheon <sup>(c)</sup>	1800	ω
<sup>(a)</sup> Varian Associates, 611 Hansen Way, Palo Alto, California.	QK 289	27.3 - 30.0	Raytheon	2250	ω
	(a) <sub>Vari</sub>	an Associates, 611	L Hansen Way, Palo Alto, C	California.	

List of Klystrons Now in Use at Michigan State University. Table I. (b)EMI/US Ltd., 13259 Sherman Way, North Hollywood, California.

(c)Raytheon Manufacturing Company, Waltham, Massachusetts.

 $^{
m (d)}$ Reflector voltages used are always between -50 and -400 volts.

An FXR Type Z815B<sup>†</sup> power supply is used to drive the klystrons. The power supply includes two ranges of beam voltage, 200-1800 volts and 1800-3600 volts, a reflector voltage of 0 to -1000 volts (relative to the beam voltage), 0 to -300 volts (relative to the beam voltage) applied to the grid, and 6.3V AC for the heater. In place of the heater voltage from the FXR, a separate, regulated DC filament supply is used for heating the cathode.

A beam voltage up to 2000 volts is applied between the anode and the cathode of the klystron tube, forcing electrons off the heated cathode. The electrons pass by the anode and through a cavity whose dimensions can be controlled by an external screw-type plunger. A bunching of the electrons is induced by an alternating electric field developed within the cavity. That is, those electrons in phase with the AC field are speeded up, and those out of phase are slowed down. After the electrons pass through the cavity they are repelled by the reflector plate which is at a high negative potential, and are returned through the cavity, giving up energy to the cavity in the form of pulses. Depending upon the voltages and dimensions of the cavity, a nearly monochromatic signal is directed from the outlet of the cavity into the absorption cell. The frequency of

<sup>&</sup>lt;sup>†</sup>Manufactured by Electronics and X-Ray Division, F.R. Machine Works, Inc., Woodside 77, New Jersey.

the klystron can be changed by changing the reflector voltage and/or the cavity size.

## 3.3 Waveguide Absorption Cells

Two sample cells are in operation at Michigan State University. Both are X-band waveguides<sup>†</sup> and are approximately ten feet long. One is made of brass with a silvered inside surface, and the other is made of copper. A cross-section of the brass waveguide is shown in Fig. 6.



Teflon Tape:  $0.062' \times 0.400''$  with 0.032'' groove 0.010'' deep Coin Silver Septum:  $0.032'' \times 0.796''$ Length of Waveguide: 10'

Fig. 6. Stark waveguide cross section.

The X-band waveguide will conduct electromagnetic radiation of a frequency from 8 kMc to beyond 40 kMc. A coin silver

<sup>&</sup>lt;sup>†</sup>The band type refers to the inside dimensions of the waveguide and the wavelengths which can be conducted through it.

septum for the Stark electrode, insulated on the top and bottom by grooved Teflon strips, runs the length of the rectangular waveguide. The sample cells are vacuum tight, sealed by means of mica windows and O-rings. Transition tapers are available for reducing the waveguide dimensions to K, P, or R band, enabling different klystrons and frequency meters to be connected. Table II gives a list of the different bands, the frequency range of each band, and the crystals used in the respective frequency regions.

Samples are introduced into the waveguide cell from the vacuum line shown in Fig. 7. The vapor in sample bulb A is solidified at  $-196^{\circ}$ C and the bulb is pumped on to insure removal of non-condensable material. Then the bulb is allowed to warm and a small amount of vapor is introduced into the cell. The relative pressure of the sample in the waveguide is determined by a thermocouple vacuum gauge, and the usual operating pressure is approximately  $10^{-2}$ mm of mercury. Any sample which is condensable at  $-196^{\circ}$ C may be returned from the waveguide to the sample bulb for future use.

### 3.4 Square-wave Generator

A modulating electric field may be put on the sample by using a sinusoidal wave or square-wave form. At Michigan State University a 100 kc square-wave generator designed by Hedrick (30) is used. The square-wave voltage has

Band	Frequency range (kMc)	Crystals
X	8.2 - 12.4	1N23
Р	12.4 - 18.0	1N23 1N78
К	18.0 - 26.5	1N26 1N78
R	26.5 - 40.0	1N26 1N53

Table II. Band Frequencies and Detectors Used.



a range in amplitude of 0-1250 volts on the Stark electrode; however, voltages over 1000 volts have a tendency to arc and burn the Teflon stripping. The square-wave generator can be operated from the zero-based voltage or from any positive or negative DC bias. A method for supplying an exact DC bias for the base line of the squarewave has been put into use. The bias voltage is measured accurately using a potentiometer bridge. This method allows precise measurement of the Stark voltage, and hence enables accurate determination of dipole moments.

The electric field is introduced onto the Stark electrode by means of a coaxial cable through a vacuumtight N-type coaxial connector which is connected to the electrode by a spring loaded contact which fits through a hole in the Teflon stripping. When the square-wave generator is on, the molecules are in the electric field during alternate 5-microsecond periods. This has the effect of turning on and off absorption lines 100,000 times per second. Since the Stark transitions occur when the field is on, the Stark spectra will be 180 degrees out of phase with the zero-field absorption lines.

#### 3.5 Detection

The most commonly used detector of microwave power is the silicon crystal rectifier. A small wafer of silicon with a tungsten whisker contact imbedded in a metal

cartridge composes the rectifier where one electrode is formed by the metal cartridge and the other by a pin contact. The crystal diode rectifies the AC microwave power, producing a signal which contains both AC and DC components. These components are separated in a 100 kilocycle tuned preamplifier. The DC signal which is proportional to the microwave power input is sent directly to the power meter, while the AC signal which contains the modulated absorption signal is sent to the phase-sensitive detector. The phase-sensitive detector whose phase reference is the 100 kilocycle square-wave selectively amplifies signals that are in phase and 180 degrees out of phase. The signal is sent to the oscilloscope or recorder. On the oscilloscope a plot of frequency versus microwave absorption is formed by sweeping the klystron repeller voltage and the x axis of the oscilloscope simultaneously with a sawtooth voltage. On both the recorder and the oscilloscope, the zero-field transitions and the Stark-field transitions are recorded in opposite directions. This is due to the action of the phase-sensitive detector and the 180 degree phase difference between the two signals. A trace of a recording is shown in Fig. 8.

#### 3.6 Frequency Measurement

An approximate measurement of the frequency of a transition may be made by means of a frequency meter. The frequency meter contains a cavity whose dimensions can be



changed by a micrometer plunger. When the microwave radiation is passing through the cavity, some of the energy will be absorbed if the cavity dimensions are set properly. This small absorption of energy by the frequency meter can be displayed on one trace of the dual-beam oscilloscope. The frequency meters are generally calibrated by the manufacturer, and charts are provided giving vernier scale readings on the plunger versus frequency of absorption. Frequency meter readings can be in error by 10-20 Mc unless the calibration is exceedingly accurate. A list of the frequency meters in use at Michigan State University is given in Table III.

For more accurate measurements, use is made of the instruments shown in Fig. 9. The fundamental standard frequency source is a Manson Laboratories RD-140 high-stability, one-megacycle oscillator, which varies in frequency only 1 part in 10<sup>8</sup> per day. This crystal-controlled oscillator is standardized to better than 1 part in 10<sup>7</sup> by beating its tenth harmonic against the 10 Mc carrier of radio station WWV from the National Bureau of Standards. This procedure is carried out by connecting a short antenna to a 1 Mc output which is rich in harmonics. A receiver tuned to 10 Mc then receives and mixes the tenth harmonic and the signal from WWV. If the tenth harmonic of the oscillator and the WWV signal are comparable in intensity and frequency, then the background noise will pulsate.

Manufacturer	Model	Frequency range (kMc)
Narda <sup>(a)</sup>	810	8.2 - 12.4
Narda	809	12.4 - 18.0
<b>DeMornay-</b> Bonardi <sup>(b)</sup>	DB <b>E-7</b> 15-2	18.0 - 26.5
<b>DeMornay-B</b> onardi	DBD-715-2	26.0 - 39.0

Table III. Frequency Meters in Use at Michigan State University.

(a) The Narda Microwave Corporation, 118-160 Herricks Road, Mineola, New York.

(b)DeMornay-Bonardi Corporation, 780 S. Arroyo Parkway, Pasadena, California.





When the 1 Mc oscillator is adjusted so that the pulsating signal is less than once every two seconds, the two signals differ in frequency by less than one cycle per second (1 part in  $10^7$ ). Another way of checking the frequency of the 1 Mc oscillator is to put the output of the receiver on the y axis of an oscilloscope set for slow sweep time. The frequency of the wave-form appearing on the face of the oscilloscope will represent the difference in frequency between the WWV signal and the tenth harmonic of the standard oscillator. By adjusting the oscillator crystal to reduce the frequency of this wave-form to zero, the oscillator is set to exactly one megacycle.

The 1 Mc output from the crystal oscillator is connected to the input of a Gertsch AM-1A VHF interpolator where the signal is amplified and selectively multiplied by any number between 19 and 38. The output of the multiplier is mixed with the output of a stable 1-2 Mc low-frequency oscillator (LFO), and the added frequencies are used to control the frequency of a 20-40 Mc oscillator. To determine the frequency of the LFO, a Lissajous figure is displayed on a second oscilloscope by sending the LFO signal to the x axis of the oscilloscope and the 1 Mc standard frequency signal to the y axis. Only under rational ratios of x/ywill a figure appear, and from the shape of the figure the LFO frequency can be set to better than  $\pm 1$  cps.

The output signal from the Gertsch AM-1A is of some frequency between 20 and 40 Mc plus harmonics. The output signal and the 1 Mc standard signal are connected to the Gertsch FM-4A microwave frequency multiplier. This instrument contains a 500-1000 Mc variable-tuned oscillator which may be locked to a frequency which is  $\pm$  10 megacycles from a harmonic in the signal from the AM-1A interpolator. Thus generated frequencies in the range of 500-1000 Mc known to one part in 10<sup>7</sup> are available at the output of the FM-4A microwave multiplier.

The mathematical representation for a generated standard frequency is given by

$$V_{\rm s} = [m(K+)]_{\rm LFO} \pm 10] \, {\rm N} \, {\rm Mc}$$
 (3-4)

where

m, K, and N are integers,
K = 19-38 Mc,
m = 1, 2 . . .,
N = 1, 2 . . .,

and

$$\mathcal{V}_{LFO} = 1-2 \text{ Mc},$$
  
K+  $\mathcal{V}_{LFO} = 20-40 \text{ Mc}.$ 

The output from the FM-4A is sent through a coaxial cable to a crystal diode which is rectifying the microwave signal. The two signals mix on this crystal and the sums and differences between the microwave signal, the standard generated signal, and the harmonics of both go back through the coaxial cable to a low-pass filter which allows only the first few harmonics of the smallest difference frequency to pass to a receiver. When the receiver is tuned to the difference signal, a sound can be heard through the speakers, or the beat signal seen on the oscilloscope. This beating sound arises from the effect of the sawtooth voltage on the klystron electrode. That is, since the klystron frequency is varied with the sawtooth voltage, its frequency will correspond to the generated standard frequency only once during each sawtooth sweep. The frequency of the receiver,  $\mathcal{V}_{\rm rec}$ , the standard frequency,  $\mathcal{V}_{\rm s}$ , and the frequency of the microwave radiation,  $\mathcal{V}_{\rm mic}$ , are related as follows:

$$\mathcal{V}_{rec} = \left| n \mathcal{V}_{s} - \mathcal{V}_{mic} \right| \qquad (3-2)$$

or

$$\mathcal{Y}_{mic} = n \mathcal{Y}_{s} \pm \mathcal{Y}_{rec}$$
 (3-3)

where n is an integer. To determine the exact frequency of an absorption line, the frequency difference signal which appears as a marker on the oscilloscope face is moved to coincide with the center of the absorption line, and the receiver reading is then added or subtracted to the standard frequency, depending upon whether it is a high frequency marker (marker moves to a higher frequency as receiver is turned to a higher frequency) or a low frequency marker (marker moves to a lower frequency as receiver dial moves to a higher frequency).

Frequency differences may be read off a Hallicrafters SX-62-A<sup>†</sup> receiver to  $\pm$  0.2 Mc, and measurements to  $\pm$  0.02 Mc may be made with a Collins<sup>‡</sup> receiver which can be read to 1 kc. Because of a time delay between the 100 kc signal and the beat marker reaching the scope, measurements must be made while sweeping both directions to average out time delay, and hence frequency discrepancies.

If, for an example, the absorption line and hence microwave frequency was 21,750.50 Mc, and if a high frequency marker is desired, the Gertsch AM-1A frequency may be set at 29.000000 Mc and the  $V_{\rm LFO}$  at 0.200000 Mc, and the Gertsch FM-4A locked in at 749.2000 Mc. This will generate a frequency of 21,726.80 Mc, which is 29 × 749.2000 Mc, and the difference, 23.70 Mc, is the frequency at which the receiver will be set when the marker is right on the center of the absorption line.

The Micro-Now<sup>\*</sup> frequency multiplier can take the place of all components shown in Fig. 9. Using a 5 Mc base frequency which can be tuned to WWV, this instrument

<sup>†</sup>The Hallicrafters Company, 4401 W. Fifth Avenue, Chicago 24, Illinois.

<sup>‡</sup>Collins Radio Company, Cedar Rapids, Iowa.

<sup>\*</sup>Micro-Now Instrument Company, 6340 North Tripp Avenue, Chicago 46, Illinois.

multiplies it to 25, 50, 150, and 450 Mc. These signals and their harmonics are sent to the mixer crystal in place of the output from the Gertsch FM-4A. All other principles are the same, except that in using the Micro-Now many more markers appear over a short range of microwave frequency.

#### IV. DETERMINATION OF THE MOLECULAR STRUCTURE OF 2-CHLOROPROPANE

#### 4.1 Introduction

The microwave study of 2-chloropropane was undertaken at Michigan State University as part of a continuing study of some halogenated hydrocarbons. The aim of this study was to determine accurate structural parameters and quadrupole coupling constants for 2-chloropropane and to compare them with those of methyl chloride (31), ethyl chloride (32), and cyclopropyl chloride (33). As part of the study an attempt was made to determine the potential barrier hindering internal rotation of the two methyl groups.

The only previous determinations of the molecular structure of 2-chloropropane were by electron diffraction (34, 35). In 1939 Beach and Stevenson (34) reported the following parameters:

> $r(CC1) = 1.75 \pm 0.02 \text{ A}$ < CCC1 = 109 ± 3° < CCC = 110 ± 3°.

Then in 1954 Yamaka (35) reported

 $r(CC1) = 1.76 \pm 0.02 \text{ A}$  $r(CC) = 1.55 \pm 0.02 \text{ A}$  $< CCC \approx < CCC1 = 109.5 \pm 1.5^{\circ}.$  By means of pure quadrupole resonance spectroscopy on the solid, Livingston (36) reported |eQq| = 64.14 Mc at 20<sup>o</sup> Kelvin, and Scrocco, Bucci, and Maestro (37) reported 64.1 Mc at  $80^{\circ}$ K.

The potential barrier hindering internal rotation of either of the two methyl groups in 2-chloropropane as determined by the thermodynamic method was reported to be 2200 cal/mole (38).

## 4.2 Preparation of Isotopic Species

Since in the determination of molecular structure using Kraitchman's method (13) every nonequivalent atomic site must be isotopically substituted, at least eight different species of 2-chloropropane were needed for this study.

In most of the syntheses semi-micro vacuum line techniques were used. The purity of the final products was checked by infrared spectroscopy.

The species of 2-chloropropane studied were  $(CH_3)_2 CHCl^{35}$ (in the ground and the first excited torsional states),  $(CH_3)_2 CHCl^{37}$  in natural abundance,  $(CH_3)_2 C^{13}HCl^{35}$ ,  $C^{13}H_3 CHCl^{35} CH_3$ ,  $(CH_3)_2 CDCl^{35}$ ,  $CH_2 DCHCl^{35} CH_3$  (three species: trans [ $\alpha$ ], gauche<sub>1</sub> [ $\beta$ ], gauche<sub>2</sub> [ $\gamma$ ]),<sup>†</sup> and  $CD_3 CDCl^{35} CH_3$ in the ground and two excited torsional states.

<sup>&</sup>lt;sup>†</sup><u>Trans</u> and <u>gauche</u> refer to the relative positions of deuterium with respect to the adjacent CC bond. Fig. 10 illustrates the positions of the  $\alpha$ ,  $\beta$ , and  $\gamma$  hydrogen atoms.



Fig. 10. A model of a 2-chloropropane molecule depicting the positions of the  $\alpha,~\beta,$  and  $\gamma$  hydrogen atoms.

$$(CH_3)_2$$
CHCl<sup>35</sup> and  $(CH_3)_2$ CHCl<sup>37</sup>

The  $(CH_3)_2CHCl^{35}$  and  $(CH_3)_2CHCl^{37}$  spectra were examined using a white label sample of 2-chloropropane obtained from the Eastman Kodak Company. The  $Cl^{37}$  species is present in natural abundance to the extent of 24.6%.

## $(CH_3)_2C^{13}HC1$

The preparation of  $(CH_3)_2C^{13}HC1^{35}$  was begun using a modification of the method developed by Cox, Turner, and Warne (39) for the preparation of  $Na(OOC^{13}CH_3)$ . The starting material was 2.44 grams of 19% C<sup>13</sup> enriched potassium cyanide<sup>†</sup> which was dissolved in 6 ml of water and added to 6.22 grams of methyl iodide in a small flask fitted with a long, narrow neck and a standard taper ground joint. The flask was sealed off in vacuo and shaken until the mixture became homogeneous. The flask was cracked open and the contents were distilled into a flask containing carbonatefree sodium hydroxide (100% in excess). This flask was evacuated, sealed, and heated for four hours at 80°C to convert the methyl cyanide to sodium acetate. The mixture was removed from the second flask and acidified with sulfuric acid; silver sulfate was added, and the acetic acid- $C^{13}$ (91% yield) was removed by steam distillation. The acetic acid was converted to barium acetate (89% yield) with an

<sup>&</sup>lt;sup>†</sup>Purchased from the Oak Ridge National Laboratory, Oak Ridge, Tennessee.

equivalent amount of barium hydroxide. After drying in vacuo over P205, the barium acetate was pyrolysed in vacuum at 500°C (40, 41), yielding 0.8 cc of acetone. The acetone was purified by bulb-to-bulb distillation, and was dried over magnesium sulfate. A lithium aluminum hydride reduction was carried out on the acetone in diethylene glycol-diethyl ether (42) using 2-phenoxyethanol as the substituting alcohol. The 2-propanol was distilled from the reaction mixture and was converted to 2-chloropropane by reacting it with phosphorus pentachloride. The chlorination was completed by letting (CH3)2CHOH react with PC15 at the lowest possible temperature. A small flask containing 2 grams of PCl<sub>5</sub> was attached to the vacuum line and evacuated. The  $(CH_3)_2CHOH$  (0.3 cc) was distilled into the reaction bulb. The liquid air dewar was then removed from the reaction bulb to allow the bulb to warm. As the alcohol started to move down the sides of the flask onto the PCl<sub>5</sub>, the liquid air was applied again to cool the reaction flask. Upon warming slowly, the reaction occurred instantaneously and the reaction products were trapped at -196°C as they left the reaction mixture. The volatile components were removed by distillation at -78°C. The 2-chloropropane was distilled at -10°C into a bulb containing potassium carbonate to remove any acidic by-products. The  $CO_2$  formed was removed at  $-78^{\circ}C$  and the 2-chloropropane (0.2 cc) was distilled into the sample bulb.

The infrared spectrum showed no impurities. The equations for the overall preparation are as follows:

$$\begin{array}{rcl} \mathrm{CH}_{3}\mathrm{I} &+ \mathrm{KC}^{13}\mathrm{N} &\xrightarrow{\mathrm{H}_{2}\mathrm{O}} &\mathrm{CH}_{3}\mathrm{C}^{13}\mathrm{N} &+ \mathrm{KI} \\ \mathrm{CH}_{3}\mathrm{C}^{13}\mathrm{N} &+ \begin{array}{c} 1 \\ 2 \end{array}) & \begin{array}{c} \frac{\mathrm{NaOH}}{\mathrm{H}_{2}\mathrm{SO}_{4}} &\mathrm{CH}_{3}\mathrm{C}^{13}\mathrm{OOH} & \begin{array}{c} \frac{\mathrm{Ba}(\mathrm{OH})_{2}}{2} & (\mathrm{CH}_{3}\mathrm{C}^{13}\mathrm{OO})_{2}\mathrm{Ba} \\ \mathrm{(CH}_{3}\mathrm{C}^{13}\mathrm{OO})_{2}\mathrm{Ba} & \begin{array}{c} \frac{\mathrm{500^{\circ}C}}{\mathrm{vacuum}} & (\mathrm{CH}_{3})_{2}\mathrm{c}^{13}\mathrm{O} &+ \mathrm{Ba}\mathrm{C}^{13}\mathrm{O}_{3} \\ \mathrm{4(CH}_{3})_{2}\mathrm{c}^{13}\mathrm{O} &+ \mathrm{LiA1H}_{4} & \begin{array}{c} \frac{(\mathrm{diethylene}\ \mathrm{glycol}-}{\mathrm{diethyl\ ether})} &\mathrm{LiA1} & [\mathrm{OH}(\mathrm{c}^{13}\mathrm{H}_{3})_{2}]_{4} \\ \mathrm{LiA1} & [\mathrm{OH}(\mathrm{c}^{13}\mathrm{H}_{3})_{2}]_{4} &+ \begin{array}{c} \mathrm{4HO}_{-}(\mathrm{CH}_{2})_{2}\mathrm{-O}_{-}\mathrm{O} &\longrightarrow \\ & & & & & & & & \\ \mathrm{4(CH}_{3})_{2}\mathrm{c}^{13}\mathrm{HOH} &+ \begin{array}{c} \mathrm{LiA1} & [\mathrm{O}_{-}(\mathrm{CH}_{2})_{2}\mathrm{-O}_{-}\mathrm{O} & - & & \\ & & & & & & & \\ \mathrm{CH}_{3})_{2}\mathrm{c}^{13}\mathrm{HOH} &+ \begin{array}{c} \mathrm{POL}_{5} & - & & & & \\ \end{array} \right) & \left(\mathrm{CH}_{3})_{2}\mathrm{c}^{13}\mathrm{HOI} &+ \begin{array}{c} \mathrm{POCl}_{3} &+ \operatorname{HO1}_{*} \end{array}\right) \end{array}$$

# C<sup>13</sup>H<sub>3</sub>CHClCH<sub>3</sub>

A sample of propionic acid containing 15%  $CH_3CH_2C^{13}OOH^{\dagger}$ was reduced by lithium aluminum hydride in diethylene glycol-diethyl ether, using 2-phenoxyethanol to release the n-propyl alcohol. The alcohol was pumped from the reaction mixture and trapped in liquid air (42). The n-propyl alcohol was allowed to react with phosphorus pentachloride using the same technique as described in the preparation of  $(CH_3)_2C^{13}HCl$ . The resulting 1-chloropropane

<sup>&</sup>lt;sup>†</sup>The sample was obtained from Mr. Roy Foley of Kedzie Chemical Laboratory, Michigan State University.

was rearranged over anhydrous AlCl<sub>3</sub> (43) to yield 2-chloropropane. The overall reactions are as follows:

$$4CH_{3}CH_{2}C^{13}OOH + 3LiAlH_{4} \xrightarrow{(diethylene glycol-)}{diethyl ether}$$

$$(CH_{3}CH_{2}C^{13}H_{2}O)_{4}LiAl + 2LiAlO_{2} + 4H_{2}$$

$$\operatorname{Lial(OH}_{2}\operatorname{C}^{13}\operatorname{CH}_{2}\operatorname{CH}_{3})_{4} + 4\operatorname{HO}_{(CH}_{2})_{2} - O - \varphi \longrightarrow$$
$$\operatorname{4CH}_{3}\operatorname{CH}_{2}\operatorname{C}^{13}\operatorname{H}_{2}\operatorname{OH} + \operatorname{Lial}[O - (CH}_{2})_{2} - O - \varphi]_{4}$$

$$CH_3CH_2C^{13}H_2OH + PC1_5 \longrightarrow CH_3CH_2C^{13}H_2C1 + POC1_3 + HC1$$

$$CH_3CH_2C^{13}H_2CI \xrightarrow{A1Cl_3} C^{13}H_3CHClCH_3 + HCl + AlCl_3 (polymer).$$

## $(CH_3)_2CDC1$

Approximately 0.003 moles of 2-deuteropropene<sup>†</sup> and a slight excess of hydrogen chloride were allowed to react over anhydrous aluminum chloride at -78°C to form 2-chloropropane. The resulting product was purified by distillation. The reaction is

 $CH_2 = CD-CH_3 + HC1 \xrightarrow{A1Cl_3} (CH_3)_2CDC1.$ 

## CH<sub>2</sub>DCHClCH<sub>3</sub>

This compound was prepared in two steps. Deuterium chloride was prepared by a reaction of 98%  $D_2O$  with

<sup>&</sup>lt;sup>†</sup>The sample was a commercial preparation from Merck Chemicals, and was obtained from Dr M.T. Rogers of Kedzie Chemical Laboratory, Michigan State University.
phosphorus trichloride. The deuterium chloride was reacted with propene at  $-78^{\circ}$ C over anhydrous aluminum chloride. The compound was purified by bulb-to-bulb distillation. The use of AlCl<sub>3</sub> in this reaction caused deuterium exchange, giving other deuterated species and also  $(CH_3)_2$ CHCl. The reaction steps are given by:

$$3D_2O + PCl_3 \longrightarrow 3DCl + D_3PO_3$$
  
 $CH_2 = CHCH_3 + DCl \xrightarrow{AlCl_3} CH_2DCHClCH_3$ 

#### CD<sub>3</sub>CDC1CH<sub>3</sub>

A sample of deuterated 2-propanol (CD<sub>3</sub>CDOHCH<sub>3</sub>)<sup>†</sup> with small impurities of tetramethylsilane and carbontetrachloride was obtained.

To purify the sample, vacuum line distillations were used but were not wholly successful. Since these two impurities would not interfere with either the chlorination or the rotational spectra, a direct reaction was carried out using phosphorus pentachloride as previously described. The reaction is

 $CD_3CDOHCH_3 + PCl_5 \longrightarrow CD_3CDC1CH_3 + POCl_3 + HCl_1$ 

# 4.3 Preliminary Calculation of Transition Frequencies

The first step in the preliminary calculations of transition frequencies is to assume a structural model for

<sup>&</sup>lt;sup>†</sup>The sample was obtained from Mr. Chester Orzech of the Kedzie Chemical Laboratory, Michigan State University.

the molecule. The following values for the molecular parameters were assumed:

all 
$$r(CH) = 1.09 \text{ A}$$
  
 $r(CC) = 1.53 \text{ A}$   
 $r(CC1) = 1.785 \text{ A}$   
 $< CCC = 110^{\circ}$   
all other angles = 109.5°.

A general right-handed Cartesian coordinate system with the z axis perpendicular to the plane of symmetry was located in the molecule. Spherical polar coordinates were then determined for every atom. Punched paper tape containing the polar coordinates and atomic masses in a systematic form was prepared for input into the "MISTIC" digital computer at Michigan State University. The structure program (44) which was stored in the computer then acted upon the input data in a sequential manner to compute first the general rectangular Cartesian coordinates (x", y", and z") and then the second moment tensor in the general coordinate system. Next, the center-of-mass coordinates and the second moments in the center-of-mass coordinate system. were computed using equation (2-31).

The second-moment matrix in the center-of-mass axis system with the z axis perpendicular to the plane of symmetry is

$$P = \begin{pmatrix} P_{xx} & P_{xy} & 0 \\ P_{xy} & P_{yy} & 0 \\ 0 & 0 & P_{zz} \end{pmatrix}.$$
 (4-1)

The principal P's may be found by diagonalizing this matrix as shown by equation (2-29), where

$$s = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$
(4-2)

The angle  $\theta$  is between the a and x axes, and is given by the expression

$$\tan 2\theta = \frac{2P_{xy}}{P_{yy} - P_{xx}} . \qquad (4-3)$$

After the principal P's are determined, the principal moments of inertia are computed from expressions obtained from equation (2-30),

$$I_{a} = P_{bb} + P_{cc},$$
  

$$I_{b} = P_{aa} + P_{cc},$$
  

$$I_{c} = P_{aa} + P_{bb},$$
  
(4-4)

and the rotational constants are obtained by use of equation (2-8). The asymmetric top rigid rotator energy levels can now be computed from equation (2-17). Kappa is given by equation (2-15), and the  $E(\kappa)$ 's are determined by fourth

order interpolation from the  $E(\varkappa)$  table in Townes and Schawlow (16, Appendix IV). The transition  $\mathcal{V}$  is determined from equation (2-20).

The class or type of transition looked for is governed by the direction of the dipole moment with respect to the principal axes. In asymmetric tops, the dipole moment seldom lies along a principal axis. In the case of 2-chloropropane, where the z axis is perpendicular to the plane of symmetry,  $P_{zz}$  would remain the same in the similarity transformation. Then by examining the transformation of  $P_{xx}$ and  $P_{yy}$  by using equations (4-4) along with the corresponding equations in the x, y, z axes system, one can deduce that the axes correspondence is  $x \rightarrow a$ ,  $y \rightarrow c$ , and  $z \rightarrow b$ . Since the a axis is roughly parallel to the CCl bond and since the dipole moment of the molecule is probably nearly parallel to the CCl internuclear line, a-type transitions should be observed. Figure 11 shows a projection of 2-chloropropane in the ac plane of symmetry.

Before examining the rotational spectra, the hyperfine splittings due to the chlorine quadrupole moment must be estimated. Preliminary calculations are made by assuming that the quadrupole coupling constant along the CCl bond  $(eQq_{zz} = \chi_{zz})$  is equal to that determined experimentally for a compound such as methyl chloride or ethyl chloride, and then transforming this quantity into the principal axis system of 2-chloropropane. Assuming a cylindrically symmetric





charge distribution about the CCl bond, for which  $-\frac{1}{2}\chi_{zz} = \chi_{yy} = \chi_{xx}$ , the quadrupole tensor is written as

$$\chi_{\text{bond}} = \begin{pmatrix} \chi_{zz} & 0 & 0 \\ 0 & \chi_{yy} & 0 \\ 0 & 0 & \chi_{xx} \end{pmatrix}. \quad (4-5)$$

This tensor is transformed by use of the following expression:

$$\chi_{abc} = \widetilde{s} \chi_{bond} s \qquad (4-6)$$

where S is given by equation (4-2) with  $\theta = \theta_z$ , the angle between the a axis and the CCl internuclear line.

For 2-chloropropane with an ac plane of symmetry,  $\chi_{yy}$  is unchanged in the transformation and equals  $\chi_{bb}$ , while  $\chi_{aa}$  and  $\chi_{cc}$  are given by

$$\chi_{aa} = \chi_{zz} \cos^{2}\theta_{z} + \chi_{xx} \sin^{2}\theta_{z}$$

$$\chi_{cc} = \chi_{zz} \sin^{2}\theta_{z} + \chi_{xx} \cos^{2}\theta_{z}.$$
(4-7)

Once the quadrupole coupling constants  $(\chi_{aa}, \chi_{bb}, \chi_{cc})$ are computed, use is made of equation (2-43) to calculate the corrections to the energy levels due to the quadrupole coupling. After these energies are computed, the hyperfine structure is constructed as shown in Table IV for the  $2_{20} \rightarrow$  $3_{21}$  transition. The selection rules governing these transitions are  $\Delta J = 0, \pm 1; \Delta F = 0, \pm 1;$  and  $\Delta I = 0$ . The frequency of an observed hyperfine component is equal to

		F		
	Compu	tation of $\mathcal{V}_{\mathbf{Q}}$	2	
F =	J + 3/2	J + 1/2	J - 1/2	J - 3/2
$\frac{W_{Q}}{h}$ (3 <sub>21</sub> )	0.63Mc	-1.26Mc	-0.38Mc	l.51Mc
$\frac{W_{Q}}{h}$ (2 <sub>20</sub> )	-4.14	10.34	0	-14.47
$\mathcal{V}_{Q} = \frac{\Delta W_{Q}(M_{C})}{h}$	4.77	-11.60	-0.38	15.98
<b>Rel</b> ative intensity <sup>a</sup>	35.7	24.5	16.0	10.0

Table IV. Computation of Hyperfine Splittings for the  $2_{20} \rightarrow 3_{21}$  Transition in 2-Chloropropane Using the  $\Delta F = 1$  Components.



<sup>a</sup>Reference 16, Appendix I.

$$\mathcal{V}_{o} = \mathcal{V}_{R} + \mathcal{V}_{Q} \tag{4-7}$$

where  $\mathcal{V}_Q$  and  $\mathcal{V}_R$  are given by the Bohr frequency condition.

The calculated hyperfine pattern in Table IV may be compared to the observed pattern in Fig. 12.

## 4.4 Examination of the Microwave Spectra

The spectra of all the species were examined at Dry Ice temperature using the conventional Hughes-Wilson spectrometer described in Chapter III.

The  $0_{00} \rightarrow 1_{01}$  transition was predicted to be below the range of our klystrons, so a search was made for the  $J = 1 \rightarrow 2$  transitions predicted to fall in the 12.4-17.5 kMc region. Unfortunately, the crystal detector mount used at that time was not a good one for this region and consequently the signal to noise ratio and resolution were poor. It therefore seemed best to look for the  $J = 2 \rightarrow 3$  transitions predicted to lie in the 20-25 kMc region. Recordings were made over much of this region, and transitions having the hyperfine structure with the expected intensity pattern and the approximate splittings were measured. An assignment was assumed correct when five transitions could be computed with the rigid rotator expression. For final fits of the rotational constants to the experimentally observed frequencies, use was made of the expression

$$\mathcal{V}_{o} - \mathcal{V}_{c} = \Delta(\frac{\partial W_{R}}{\partial A})(A_{o} - A_{c}) + \Delta(\frac{\partial W_{R}}{\partial B})(B_{o} - B_{c}) + \Delta(\frac{\partial W_{R}}{\partial C})(C_{o} - C_{c})$$
(4-8)





where the subscript "o" stands for "observed" and the subscript "c" stands for "calculated." The partial derivatives of the rigid rotator energy with respect to the rotational constants A, B, and C are given by equation (2-39).

With a correct assignment assured, an experimental evaluation of the quadrupole coupling parameters was made using differences in equation (2-43) for low J transitions. The frequency difference of the hyperfine components within a transition are given by

$$\delta(\Delta \mathcal{V}) = \delta(\Delta \alpha) q_{\rm m} + \delta(\Delta \beta) q_{\rm m} \eta. \qquad (4-9)$$

The constants  $\delta(\Delta \alpha)$  and  $\delta(\Delta \beta)$  were computed using the observed rotational constants, and  $q_m$  and  $q_m\eta$  were fit by least squares. The standard deviations of the parameters  $q_m$  and  $q_m\eta$  were used in conjunction with Snedecor's F tests for the equality of variance to set the experimental error within a 95% confidence interval. Once the quadrupole coupling parameters are determined accurately, a reverse procedure to that shown in Table IV will give more precise rigid rotator frequencies  $(\mathcal{Y}_{\mathbf{R}} = \mathcal{Y}_{\mathbf{0}} - \mathcal{Y}_{\mathbf{Q}})$ . With more precise rigid rotator frequencies, the rotational constants A, B, and C can be redetermined using a least squares fit on equation (4-8). Transitions were included that had high dependence on all three rotational constants. The asymmetry ( $\kappa = -.34$  to -.47) is sufficient to allow an accurate determination of the least moment of inertia. Centrifugal distortion, which seemed to be small,

was not taken into account. The standard deviation of the parameters  $\delta A$ ,  $\delta B$ , and  $\delta C$  determined by the least squares analysis were used with the F tests for the equality of variances to estimate the error within a 95% confidence interval.<sup>†</sup>

The quadrupole coupling constants for the other isotopic species were obtained by transforming  $\chi_{aa}$ ,  $\chi_{bb}$ , and  $\chi_{cc}$  from the  $(CH_3)_2CHCl^{35}$  principal axis system into the principal axis system of the substituted species, with the exception of  $(CH_3)_2CHCl^{37}$  where in addition use was made of the nuclear quadrupole moment ratio,  $Q(Cl^{35})/Q(Cl^{37}) = 1.2688$ , (16), to find the  $Cl^{37}$  coupling constants. These transformed coupling constants fit the hyperfine splittings within the experimental error.

In Appendices I and II the measured frequencies of the hyperfine components for the various isotopic species are listed. The frequencies in most cases were measured to  $\pm$  0.02 Mc, although with weaker transitions as in the CH<sub>2</sub>D sample which was a mixture of three species, measurements of  $\pm$  0.05 Mc were not uncommon.

The hypothetical unsplit frequencies ( $\mathcal{V}_{\mathbf{R}}$ 's) for transitions in  $(CH_3)_2CHCl^{35}$  (ground and first excited torsional states) and various isotopic species are given in Table V.

A comparison of the calculated and the observed frequencies of the hyperfine components for selected transitions from  $(CH_3)_2CHC1^{35}$  is shown in Table VI.

<sup>&</sup>lt;sup>†</sup>This error analysis assumes a random error which is not strictly true here because of centrifugal distortion.

Table V. H	ypothetical Un	split Frequenc	ies (Mc) in 2-Chl	Loropropane.	
Transition	$(CH_3)_2$ CHCI $^{35}$	$(CH_3)_2^{CHCl}$	$(CH_3)_2 C^{13}HCI^{35} C^{1}$	<sup>13</sup> H <sub>3</sub> CHCI <sup>35</sup> CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CDCI <sup>35</sup>
$1_{11} \rightarrow 2_{12}$	14193.54	13898.83			14075.17
$1_{01} \stackrel{1}{\rightarrow} 2_{02}$	15229.64	14908.71			15044.26
1 <sub>10</sub> → 2 <sub>11</sub>	16920.10	16505.91			16611.82
$2_{12} \rightarrow 3_{13}$	21105.42	20681.51	21058.97	20748.20	
$2_{02} \xrightarrow{3_{03}}$	22134.22	21715.56	22084.23	21749.69	21913.75
$221 \rightarrow 322$	23335.18	22803.52	23267.63		23015.17
<b>220 → 32</b> 1	24535.96	23891.16	24451.17	24221.03	24116.32
$2_{11} \rightarrow 3_{12}$	25144.47	24549.42	25062.64	24786.83	
$3_{21} \div 4_{22}$			33263.37	32958.63	
<sup>3</sup> 22 → <sup>4</sup> 23	30855.22	30173.23	30769.42	30379.80	
5 <sub>05</sub> → 5 <sub>24</sub>	23820.25	23645.74			22382.95
$6_{15} \div 6_{16}$	25251.36	24457.45	25061.48	25092.66	23576.88

Transition	$CH_2 DCHCl ^{35}CH_3(\alpha)$	CH2DCHCl <sup>35</sup> CH <sub>3</sub> (B)	$cH_2$ DCHCl <sup>35</sup> CH <sub>3</sub> ( $\gamma$ )	$(CH_3)_2 CHCl^{35}(v=1)$
$1_{11} \rightarrow 2_{12}$	13871.56			14172.24
$1_{01} \xrightarrow{2}_{02}$	14901.13	14604.13	14895.50	15206.70
$1_{10} \stackrel{1}{_{\sim}} 2_{11}$	16752.54	16190.10	16533.85	16893.23
$2_{12} \rightarrow 3_{13}$	20578.83	20246.20	20678.96	21073.68
$2_{02} \xrightarrow{3}_{03}$	21505.31	21256.88	21642.44	22101.87
$2_{21} \xrightarrow{3}_{22}$	22968.11	22349.55		23298.90
$^220 \rightarrow 3_{21}$	24430.71	23441.95	24020.58	24495.87
$^{2}$ 11 $\rightarrow$ $^{3}$ 12	24823.32	24073.68	24564.88	25104.98
$3_{21} \xrightarrow{4} 4_{22}$	33240.50	31890.16	32666.19	
$3_{22} \rightarrow 4_{23}$	30298.78	29566.16	30185.01	
6 <sub>15</sub> → 6 <sub>16</sub>	25617.57	24132.43	24143.36	

Table V.--Continued

Transition	F → F'	Observed Frequency	Calculated Frequency
$1_{11} \rightarrow 2_{12}$	$5/2 \rightarrow 7/2 \\ 3/2 \rightarrow 5/2 \\ 1/2 \rightarrow 3/2 \\ 5/2 \rightarrow 5/2 \\ 3/2 \rightarrow 3/2 \\ 1/2 \rightarrow 1/2$	14197.18 14181.84 14202.20 14190.49 14186.96 <sup>a</sup> 14208.94	14197.18 14181.81 14202.22 14190.50 14186.57 14208.90
1 <sub>01</sub> → 2 <sub>02</sub>	$5/2 \rightarrow 7/2 \\ 3/2 \rightarrow 5/2 \\ 1/2 \rightarrow 3/2 \\ 5/2 \rightarrow 5/2 \\ 3/2 \rightarrow 3/2 \\ 1/2 \rightarrow 1/2$	15230.70 15231.64 15214.27 15216.24 15241.94 15228.70	15230.70 15231.60 15214.27 15216.23 15241.94 15228.74
1 <sub>10</sub> → 2 <sub>11</sub>	$5/2 \rightarrow 7/2 \\ 3/2 \rightarrow 5/2 \\ 1/2 \rightarrow 3/2 \\ 5/2 \rightarrow 5/2 \\ 3/2 \rightarrow 3/2 \\ 1/2 \rightarrow 1/2$	16923.94 16908.53 16926.80 16915.19 16914.71 16935.51	16923.84 16908.47 16926.70 16915.15 16914.68 16935.39
$2_{12} \rightarrow 3_{13}$	$7/2 \rightarrow 9/2 \\ 1/2 \rightarrow 3/2 \\ 5/2 \rightarrow 7/2 \\ 3/2 \rightarrow 5/2 \end{cases}$	21106.94 21103.34	21106.98 21107.01 21103.37 21103.40
$2_{02} \rightarrow 3_{03}$	$7/9 \rightarrow 9/2$ $5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$ $1/2 \rightarrow 3/2$	22134.57 22135.60 22131.55 22130.50	22134.64 22135.63 22131.58 22130.60
2 <sub>21</sub> → 3 <sub>22</sub>	$7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$ $1/2 \rightarrow 3/2$	23339.55 23324.20 23335.15 23350.60	23339.55 23324.18 23324.16 23350.53
$2_{20} \rightarrow 3_{21}$	$7/2 \rightarrow 9/2 5/2 \rightarrow 7/2 3/2 \rightarrow 5/2 1/2 \rightarrow 3/2$	24540.77 24524.35 24535.57 24551.92	24540.80 24524.45 24535.66 24552.02

Table VI. Calculated and Observed Frequencies (Mc) for the Hyperfine Components in (CH<sub>3</sub>)<sub>2</sub>CHCl<sup>35</sup>

Transition	F → F'	Observed Frequency	Calculated Frequency
4 <sub>04</sub> → 4 <sub>23</sub>	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	20516.14 20523.00 20520.51 20513.65	20516.04 20522.92 20520.51 20513.62
5 <sub>05</sub> → 5 <sub>24</sub>	$\begin{array}{r} 13/2 \rightarrow 13/2 \\ 11/2 \rightarrow 11/2 \\ 9/2 \rightarrow 9/2 \\ 7/2 \rightarrow 7/2 \end{array}$	23818.64 23821.61 23822.69 23817.66	23818.81 23821.59 23822.68 23817.72

Table VI.--Continued

<sup>a</sup>Interfering transition.

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## 4.5 Molecular Structure

In this study every nonequivalent atomic site in 2-chloropropane was isotopically substituted. This allows the coordinates of every atom to be determined by the use of Kraitchman's equations (2-35).

The experimental rotational constants and the moments of inertia are given in Table VII. The principal second moments are given in Table VIII.

For an atom substituted in the plane of symmetry (the ac plane in this case),  $P_{bb}$  and  $P_{bb}$  should be the same for a rigid molecule. The changes observed in  $P_{bb}$  upon isotopic substitution can be attributed to changes in the zero-point vibrations. The largest change in  $P_{bb}$  usually occurs upon deuterium substitution. In 2-chloropropane the largest change occurs in the  $C^{13}$  substitution where  $\Delta P_{bb} = 0.0065$  amu  $A^2$ . By comparing second moments of molecules having a similar plane of symmetry, it is found that in propane  $\Delta P_{aa} = 0.0054$ amu  $A^2$  for  $C^{13}$  substitution, and  $\Delta P_{aa}$  for deuterium substitution is 0.0001 (45). The change in  $P_{aa}$  for dimethyl sulfide and dimethyl silane in substituting  $S^{34}$  and  $Si^{30}$  is 0.0005 and -0.0012 amu  $A^2$  respectively (27, 28).

Since Kraitchman's equations are derived for a rigid molecule, the coordinates for an atom substituted in an ac plane of symmetry are given by

$$\begin{vmatrix} a_{s} \end{vmatrix} = \left\{ \mathcal{L}^{-1} \left[ \Delta P_{aa} \left( 1 + \frac{\Delta^{P} cc}{P_{cc} - P_{aa}} \right) \right] \right\}^{\frac{1}{2}}$$
$$\begin{vmatrix} b_{s} \end{vmatrix} = 0 \tag{4-10}$$

A D

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ents of Inertia	Mc) and Mome	<b>Constants</b> (	Rotational	VII.	Table
	ents of Inerti	Mc) and Moments of Inerti	Constants (Mc) and Moments of Inerti	Rotational Constants (Mc) and Moments of Inerti 2-Chloroprane	VII. Rotational Constants (Mc) and Moments of Inerti 2-Chloropane

Species	A	Bb	υ	La	Ib	Ic
$(CH_3)_2 CHCl^{35}$	8068.09 ± 0.05	4570.82	3207.57	62.6580	110.5997	157.6056
$(CH_3)_2$ CHCI <sup>37</sup>	8067.62 ± 0.1	4452.33	3148.82	62.6617	113.5430	160.5461
$(CH_3)_2 CDCl^{35}$	7793.09 ± 0.1	4470 <b>.</b> 01	3201.70	64.8691	113.0938	157.8947
$(cH_3)_2 c^{13}HcI^{35}$	8048.41 ± 0.3	4553.49	3202.40	62.8113	111.0205	157.8599
с <sup>1 3</sup> н <sub>3</sub> снс1 <sup>35</sup> сн <sub>3</sub>	$7872.19 \pm 0.3$	4513.08	3148.72	64.2174	112.0146	160.5515
$CH_2 DCHCL^{35} CH_3(\alpha)^{c}$	7512.61 ± 0.4	4548.26	3107.78	67.2856	111.1486	162.6659
$CH_2DCHCL^{35}CH_3(\beta)$	7876 <b>.4</b> 6 ± 0.3	4370.13	3079.69	64.1825	115.6788	164.1500
$cH_2 D C H c I^{35} c H_3(\gamma)$	$7693.18 \pm 0.7$	4461.66	3148.87	65.7116	113.3056	160.5438
		Ľ	6			

<sup>a</sup>Conversion factor 5.05531 ×  $10^{3}$  Mc-amu A<sup>2</sup>.

<sup>b</sup>The error estimated for the B and C rotational constants is  $\pm$  0.02 Mc. <sup>C</sup>Position of deuterium with respect to the CC bond.

Species	P <sub>aa</sub>	P <sub>bb</sub>	P <sub>cc</sub>
(CH <sub>3</sub> ) <sub>2</sub> CHCl <sup>35</sup>	102.7736	54.8319	7.8261
(CH <sub>3</sub> ) <sub>2</sub> CHCl <sup>37</sup>	105.7137	54.8324	7.8293
(CH <sub>3</sub> ) <sub>2</sub> CDCl <sup>35</sup>	103.0597	54.8350	10.0341
(CH <sub>3</sub> ) <sub>2</sub> C <sup>13</sup> HCl <sup>35</sup>	103.0346	54.8254	7.9859
с <sup>13</sup> н <sub>3</sub> снс1 <sup>35</sup> сн <sub>3</sub>	104.1744	56.3771	7.8402
$CH_2DCHCl^{35}CH_3(\alpha)^a$	103.2644	59.4015	7.8841
CH <sub>2</sub> DCHCl <sup>35</sup> CH <sub>3</sub> (B)	107.82313	56.3269	7.8556
$\operatorname{CH}_2\operatorname{DCHCl}^{35}\operatorname{CH}_3(\gamma)$	104.0690	56.4749	9.2367

Table VIII. Second Moments (amu  $A^2$ ) for 2-Chloropropane.

<sup>a</sup>Position of D with respect to the CC bond.

$$\left|c_{s}\right| = \left\{ \mu^{-1} \left[\Delta P_{cc} \left(1 + \frac{\Delta P_{aa}}{P_{aa} - P_{cc}}\right)\right]\right\}^{\frac{1}{2}}.$$

These expressions are obtained from the full Kraitchman equations (equation 2-35) by setting  $\Delta P_{bb} = 0$ . Since the experimental  $\Delta P_{bb}$  is not zero a question arises as to whether equations (2-35) or (4-10) should be used. The difference between the coordinates calculated in the two ways is found to be less than 0.0001 A which has a negligible effect on the computed bond distances and bond angles. When atoms are substituted near a principal axis or the center of mass, the coordinates computed from Kraitchman's equations tend to be small (46). In such cases the atom may be located by using the conditions that in the principal axis system  $\sum m_i \vec{r}_i = 0$  (center-of-mass condition) and  $\sum m_i a_i c_i = 0$  (product of inertia vanishes).

Table IX gives the coordinates determined from the experimental rotational constants after a direct application of Kraitchman's equations. Table X shows the change in the coordinates when the c coordinates of the heavy atoms lying near a principal axis have been corrected by setting  $\sum m_i c_i$  and  $\sum m_i a_i c_i$  equal to zero. The corresponding structures for these sets of coordinates and an average structure are given in Table XI.

Recent calculations of the vibrational effects on structure determination indicate that bond lengths between heavy atoms may shorten by as much as 0.0001 A upon isotopic

Atom	а	Ъ	с
C1	1.2286 A	0	0.0409 A
C (center)	-0.5128	0	-0.4021
C (end)	-1.1695	± 1.2666 A	0.1222
H (secondary)	-0.5303	0	-1.4929
Η (α)	-0.6664	± 2.1546	-0.2588
Н (В)	-2.2184	± 1.2891	-0.1796
Н (ү)	-1.1136	± 1.2833	1.2203
	$\sum_{i^{m}i^{a}i} = -0$ $\sum_{i^{m}i^{a}i^{c}i} = -0$ $\sum_{i^{m}i^{a}i^{c}i} = -0$	0.1473 amu A 0.3902 amu A 0.0118 amu A <sup>2</sup>	

a

Table IX. Experimental Coordinates of Atoms in the (CH<sub>3</sub>)<sub>2</sub>CHCl<sup>35</sup> Principal Axis System.

	c Coor	dinate
Atom	Kraitchman's Equations	Assuming ∑m <sub>i</sub> c <sub>i</sub> = 0 ∑m <sub>i</sub> a <sub>i</sub> c <sub>i</sub> = 0
Cl	0.0409 A	0.0462 A
C (center)	-0.4021	-0.4021
C (end)	0.1222	0.1308

Table X. Comparison of the Heavy Atom Coordinates Determined by Kraitchman's Equations or by Assuming  $\sum m_i c_i = 0$  and  $\sum m_i a_i c_i = 0$ .

	I <sup>a</sup>	IIp	IIIc
r(CCl)	1.7968 A	1.7982 A	1.798 ± 0.005 A
r(CC)	1.5200	1.5230	$1.522 \pm 0.002$
r(CH <sub>sec</sub> )	1.0909	1.0909	1.091 ± 0.005
r(CH <sub>methyl</sub> )	1.0920	1.0920	1.092 ± 0.01
<000	112 <sup>0</sup> 53'	112 <sup>0</sup> 32'	112 <sup>0</sup> 42' ± 25'
<0001	109 <sup>0</sup> 30'	109 <sup>0</sup> 17'	109 <sup>0</sup> 24' ± 21'
<cch<sub>sec</cch<sub>	109°45'	110 <sup>0</sup> 3'	109 <sup>0</sup> 54' ± 30'
<c1ch<sub>sec</c1ch<sub>	105 <sup>0</sup> 12'	105 <sup>0</sup> 21'	105 <sup>0</sup> 16' ± 30'
$< CCH_{\alpha}^{d}$	111 <sup>0</sup> 3'	110 <sup>0</sup> 39'	110 <sup>0</sup> 51' ± 30'
$< CCH_{\beta}$ and $\gamma$	109 <sup>0</sup> 38'	109 <sup>0</sup> 42'	109 <sup>0</sup> 40' ± 30'
$< H_{\alpha} CH_{\beta}$ = $< H_{\beta} CH_{\gamma}$	109 <sup>0</sup> 6'	109 <sup>0</sup> 4'	109 <sup>0</sup> 5' ± 30'
$<$ H $_{\alpha}$ CH $_{\gamma}$	108 <sup>0</sup> 16'	108 <sup>0</sup> 40'	108 <sup>0</sup> 27' ± 30'
I <sub>a</sub>	62.3516 amu	A <sup>2</sup> 62.4219 amu A	2
I <sub>b</sub>	110.2004	110.2707	
I <sub>c</sub>	156.9412	156.9412	

Table XI. Structural Parameters for 2-Chloropropane.

<sup>a</sup>Taken directly from coordinates determined by Kraitchman's equations.

<sup>b</sup>Correcting the coordinates of the heavy atoms with  $\Sigma_{im_ic_i} = 0$  and  $\Sigma_{im_ia_ic_i} = 0$ .

<sup>C</sup>Average structure.

 ${}^d\!H_{\alpha}$  is trans and  ${}^H\!_{\beta}$  and  ${}_{\gamma}$  are gauche with respect to the CC bond.

substitution, and 0.003 A between a heavy atom and hydrogen upon deuterium substitution (47, 48).

Calculations made by reducing the bond lengths of heavy atoms that are attached to the atom substituted indicate that such reductions could have a great effect on structure determination as computed from Kraitchman's equations. The procedure is to first assume a structure for the molecule (here use was made of the determined coordinates for 2-chloropropane), and to compute the rotational constants. Then the rotational constants are computed for the isotopic species where each of the heavy atoms is isotopically substituted without changing the bond distances. These rotational constants will allow computation of a reference set of heavy atom coordinates. Now the previous step is repeated with the bond lengths to heavy atoms from the atom isotopically substituted reduced by a consistent amount. Table XII gives the rotational constants computed for different shortenings of bond lengths. Table XIII shows the coordinates as calculated from Kraitchman's equations, and Table XIV gives the corresponding structural parameters for a series of changes in the bond lengths. Examination of these tables shows that if small changes occur in the bond lengths upon isotopic substitution, there may be a considerable error in some of the structural parameters deduced by means of Kraitchman's equations. The only coordinates that are greatly changed here are those of the central carbon atom where a larger

	Reduc	ction of Bond Len	ngth upon Isotop	oic Substitution.	
Set		( CH <sub>3</sub> ) <sub>2</sub> CHCl <sup>35</sup>	$(CH_3)_2$ CHCl $^{37}$	$(cH_3)_2 c^{13}Hc1^{35}$	с <sup>13</sup> н <sub>3</sub> снс1 <sup>35</sup> сн <sub>3</sub>
Original <sup>a</sup>	<b>∀</b> ≘O	8110.86 4614.84 3242.37	8110.33 4495.32 3183.00	8089.48 4596.76 3236.85	7912.84 4556.17 3182.42
0.00005 <sup>b</sup>	C B A		8110.33 4495.49 3183.08	8089.94 4597.01 3237.04	7913.06 4556.21 3182.48
0.0001	C B A		8110.34 4495.67 3183.17	8090.40 4597.26 3237.22	7913.17 4556.23 3182.50
0.0005	C B A		8110.38 4497.04 3183.85	8094.06 4599.23 3238.72	7914.51 4556.48 3182.82

Change of Rotational Constants (Mc) in 2-Chloropropane Due to Table XII.

<sup>b</sup>Reduction of bond lengths in angstroms to atom substituted. <sup>a</sup>No bonds reduced in length when the atom was substituted.

Coordinate	Set	Cl	C (middle)	C (end)
Original <sup>a</sup>	a	1.2219 A	-0.5176 A	-1.1663 A
	b	0	0	1.2659
	c	0.0466	-0.4084	0.1329
0.00005 <sup>b</sup>	a	1.2210	-0.5119	-1.1660
	b	0	0	1.2652
	c	0.0463	-0.4082	0.1330
0.0001	a	1.2201	-0.5064	-1.1658
	b	0	0	1.2649
	c	0.0462	-0.4077	0.1325
0.0005	a	1.2129	-0.4590	-1.1636
	b	0	0	1.2605
	c	0.0443	-0.4054	0.1306

Table XIII. Coordinates Calculated from Kraitchman's Equations for Small Reductions in Bond Lengths upon Isotopic Substitution.

<sup>a</sup>No bonds reduced in length when the atom was substituted.

<sup>b</sup>Reduction of bond lengths in angstroms to atom substituted.

				·	
	Bond Reduction				
Parameter	0 <sup>a</sup>	0.00005 A <sup>b</sup>	0.0001 A	0.0005 A	
r(CC1)	1.7980 A	1.7915 A	1.7852 A	1.7313 A	
r(CC)	1.5220	1.5236	1.5253	1.5403	
<(CCC)	112034'	112017'	112 <sup>0</sup> 3'	109 <sup>0</sup> 50'	
<(CCC1)	108 <sup>0</sup> 48'	108 <sup>0</sup> 59'	109 <sup>0</sup> 9'	110 <sup>0</sup> 34'	

Table XIV. Changes in the Structural Parameters of 2-Chloropropane for the Corresponding Coordinates in Table XIII.

<sup>a</sup>No bond lengths reduced when the atom was substituted.

<sup>b</sup>Reduction of bond lengths in angstroms to atom substituted. change is expected since three bonds are affected. It is interesting that the  $\Delta P_{\rm bb}$  (for center  $C^{13}$  substitution) calculated assuming a 0.0001 A bond reduction reproduced the experimental difference (Table XV). This illustrates one of the problems in using substitution parameters (i.e., vibrational effects), and indicates the need to take vibration into account in order to obtain extremely precise structural parameters.

#### 4.6 Discussion of the Structure

The parameters shown in Table XI are quite different from those first determined by electron diffraction. Many comparisons of bond distances obtained by recent electron diffraction and microwave spectroscopy show that it was not uncommon for the early workers in electron diffraction to underestimate the uncertainties in their numbers. Comparing the present structural parameters of 2-chloropropane with those of related molecules that were determined by the substitution method one observes that the CCl bond distance of 1.798 A is 0.01 A longer than the bond distance in ethyl chloride which, in turn, is 0.007 A longer than the bond distance in methyl chloride; but it is 0.0005 A shorter than the CCl bond distance in tertiary butyl chloride (49). Uncertainties in the CCl bond distance may be large for two reasons; first, the proximity of the chlorine atom to the c principal axis (0.0462 A), and, second, the vibrational effects. The errors estimated for the parameters in Table XI

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ropane	gths 1
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2-Ch]	E Bond
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nu A <sup>2</sup>	ductic
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Table	

Set	( CH <sub>3</sub> ) 2 CHCI <sup>35</sup>	$(CH_3)_2$ CHCI <sup>37</sup>	$(CH_3)_2 C^{13}HCI^{35}$	с <sup>1 3</sup> н <sub>3</sub> снс1 <sup>35</sup> сн <sub>3</sub>
Original <sup>a</sup>	54.3485	54.3485	54.3484	55.8916
0.00005 <sup>b</sup>		54.3485	54.3450	55.8897
0.0001		54.3485	54.3418	55.8890
0.0005		54.3485	54.3153	55.8786

<sup>a</sup>No bond lengths reduced when the atom was substituted.

<sup>b</sup>Reduction of bond lengths in angstroms to atom substituted.

are based in part on how the zero-point vibrational effects affect bond length change upon isotopic substitution.

The CC bond distance of 1.522 A can be compared with 1.526 A in propane (45), 1.526 A in ethane (50), 1.520 A in ethyl chloride (32), and 1.530 A in tertiary butyl chloride (49). These distances are all between carbon atoms of approximately the same hybridization. An example of the effect of change in hybridization on a CC bond distance is the value of 1.501 A obtained for the CC single bond in propylene (52). The CCC angle in 2-chloropropane is  $112^{\circ}42'$ , the CCCl angle is nearly tetrahedral, and the CCH<sub>sec</sub> angle is  $109^{\circ}54'$ . This set of angles cannot be explained in terms of a simple hybridization calculation. The small ClCH<sub>sec</sub> angle of  $105^{\circ}16'$  is comparable with the XCH angle in ethyl chloride and in ethyl bromide (51).

Upon examining the methyl group parameters, an unsymmetrical methyl group is evident. The  $H_{\beta}CH_{\gamma}$  triangle seems to be in a plane parallel to the plane of symmetry. A complete study of the unsymmetrical nature of the methyl group was not attempted since the hydrogen coordinates may be uncertain because of the small c coordinates and the large vibrational effects upon deuterium substitution. However, there is no question that the equilibrium configuration of the methyl groups is staggered with respect to the CCl bond. Figure 13 shows a projection of 2-chloropropane in the ab plane.



Table XVI shows a comparison of the structural parameters of 2-chloropropane with those of related molecules.

#### 4.7 Quadrupole Analysis

The parameters  $\textbf{q}_m$  and  $\textbf{q}_m \boldsymbol{\eta}$  were determined as described in section 4.3. The parent species [(CH<sub>3</sub>)<sub>2</sub>CHCl<sup>35</sup>] was fit by least squares and the values for  $\boldsymbol{q}_m$  and  $\boldsymbol{q}_m\boldsymbol{\eta}$  are given within a 95% confidence interval. Since only a-type transitions were observed,  $\boldsymbol{q}_m \boldsymbol{\eta}$  was less sensitive to the hyperfine splittings than  $q_m$ . The quadrupole coupling constants  $\chi_{aa}$ ,  $\chi_{
m bb}$ , and  $\chi_{
m cc}$  were determined from the values of q<sub>m</sub> and  $q_{m}\eta$  and the relation  $\chi_{aa} + \chi_{bb} + \chi_{cc} = 0$ . The values for the parent species are  $\chi_{aa}$  = -61.49 ± 0.11 Mc,  $\chi_{bb}$  = 34.81  $\pm$  0.25 Mc, and  $\chi_{cc}$  = 26.68  $\pm$  0.25 Mc. The quantities  $\boldsymbol{q}_m,\;\boldsymbol{q}_m\boldsymbol{\eta},\;\text{and }\boldsymbol{\eta}$  given in Table XVII represent the diagonal values of the quadrupole coupling tensor in the principal axis system of the molecule. The off-diagonal elements could not be determined since second order effects were negligible. Consequently, when the quadrupole coupling constant tensor is diagonalized to find the charge distribution along the CCl bond at the chlorine nucleus, it must be transformed using either of two assumptions.

If it is assumed that the principal axis (the z axis) of the quadrupole tensor and the CCl internuclear line coincide, the tensor can be diagonalized because the off-diagonal elements are zero in the principal axis system and the required

Molecule	r(CC)	r(CCl)	<000	<ccx< th=""></ccx<>
(CH <sub>3</sub> ) <sub>3</sub> CCl <sup>a</sup>	1.530 A	1.803 A	110°56'	107059'
(CH3)2CHClb	1.522	1.798	112042'	109 <sup>0</sup> 24'
Сн <sub>3</sub> сн <sub>2</sub> с1 <sup>с</sup>	1.520	1.788		111°2'
CH3C1d		1.781		
(CH <sub>3</sub> ) <sub>3</sub> CH <sup>e</sup>	1.525		111 <sup>0</sup> 9'	
$(CH_3)_2CH_2^f$	1.526		112 <sup>0</sup> 24'	109 <sup>0</sup> 32'

Table XVI. Comparison of the Molecular Parameters of 2-Chloropropane with Those of Similar Molecules.

<sup>a</sup>Reference 50.

<sup>b</sup>This thesis.

<sup>c</sup>Reference 32.

<sup>d</sup>Reference 31.

<sup>e</sup>Reference 49.

fReference 45.

<u>P</u> 1	rincipal Inerti	al Axis System	<u>n</u>
Isotopic Species	eQq <sub>m</sub> (Mc)	eQq <sub>m</sub> ŋ(Mc)	η
(CH <sub>3</sub> ) <sub>2</sub> CHCl <sup>35</sup>	-61.49 ± 0.11	8.13 ± 0.49	$-0.1322 \pm 0.0082$
(CH <sub>3</sub> ) <sub>2</sub> CHCl <sup>37</sup>	-48.46	6.40	-0.1322
$(CH_3)_2 CDCL^{35}$	-61.89	7.64	-0.1234
(CH <sub>3</sub> ) <sub>2</sub> C <sup>13</sup> HCl <sup>35</sup>	-61.56	7.96	-0.1294
с <sup>13</sup> н <sub>3</sub> снс1 <sup>35</sup> сн <sub>3</sub>	-61.37	8.15	-0.1328
$CH_2DCHCl^{35}CH_{3(\alpha)}$	-61.53	7.92	-0.1288
CH <sub>2</sub> DCHCl <sup>35</sup> CH <sub>3(β)</sub>	-61.65	7.80	-0.1264
CH <sub>2</sub> DCHC1 <sup>35</sup> CH <sub>3(y)</sub>	-60.61	8.80	-0.1453
CD <sub>3</sub> CDC1 <sup>35</sup> CH <sub>3</sub>	-60.22	6.94	-0.1152

Table	XVII.	Quadrupole	Coupling	Constants	for
		2-Chloropro	opane.		

	CCl Bond Axis Syst	tem
	1 <sup>b</sup>	2 <sup>c</sup>
$\chi_{zz}$ (Mc)	-67.82 ± 0.12	$-69.61 \pm 0.50$
η <sub>bond</sub> d	$0.028 \pm 0.003$	0
$\theta_z^e$	14026'	16 <sup>0</sup> 12' ± 30'
I	23%	22%

 $a_{\eta} = (\chi_{bb} - \chi_{co})/\chi_{aa}.$ 

<sup>b</sup>Assuming the z axis of quadrupole tensor and the CCl internuclear line coincide.

<sup>c</sup>Assuming cylindrical charge distribution.

 $d_{\eta_{\text{bond}}} = (\chi_{xx} - \chi_{yy}) / \chi_{zz}.$ 

<sup>e</sup>Angle between the a and z axes.

transformation angle may be obtained from the structure. The relationships for this transformation are given by

$$\chi_{zz} = \frac{\chi_{aa} \cos^2\theta_z - \chi_{cc} \sin^2\theta_z}{\cos^2\theta_z - \sin^2\theta_z}$$
(4-11)

$$\chi_{\mathbf{x}\mathbf{x}} = \frac{\chi_{aa} \sin^2 \theta_z - \chi_{cc} \cos^2 \theta_z}{\sin^2 \theta_z - \cos^2 \theta_z}$$
(4-12)

where  $\theta_z$  is the angle between the a axis and the z axis and is determined from the geometry of the molecule. In 2-chloropropane where there is an ac plane of symmetry,  $\chi_{yy} = \chi_{bb}$ . The parameters computed using this assumption are listed at the bottom of Table XVII under column 1. The significance of the non-zero value for  $\eta$  is not clear. It has been interpreted in terms of double bond character, but could possibly arise from the assumption used to obtain  $\chi_{zz}$ .

Secondly, if the charge distribution about the CCl bond is considered to be cylindrically symmetric,

$$\chi_{zz} = -2\chi_{xx} = -2\chi_{yy} = -2\chi_{bb}, \qquad (4-13)$$

and  $\boldsymbol{\theta}_{\mathbf{Z}}$  may be determined from the relation

$$\chi_{aa} = \chi_{zz} \left( \frac{3 \cos^2 \theta_z - 1}{2} \right).$$
 (4-14)

The values determined using this assumption are listed in Table XVII under column 2.

The magnitude of the quadrupole coupling constants in the bond direction has been shown to be related to the ionic character of the bond (6, 53, 54, 55). The ionic character is given by the relationship

$$I = (1 - s^{2} + d^{2} - II) - q_{zz}/q_{at}$$
 (4-15)

where  $s^2$  and  $d^2$  are the s and the d character of the chlorine atomic orbital involved in the CCl bond, II is related to the double-bond character of the CCl bond, and  $eQq_{at} =$ -109.74 Mc is the quadrupole coupling constant of atomic chlorine. By assuming that  $s^2 = 0.15$  and that  $d^2$  and II are negligible, the ionic character in the CCl bond is found to be 22-23%. This is greater than in ethyl chloride and smaller than in tertiary butyl chloride, which is the expected order based on the inductive effect of methyl group addition.

Table XVIII is a comparison of the quadrupole coupling constants and the bond distances of a sequence of chlorinated compounds. The consistent increase in the CCl bond distance and decrease in the quadrupole coupling constant is noted. This can be explained qualitatively by considering inductive effects from the electropositive methyl group and competition for the electrons between the chlorine and carbon atoms in multihalogenated compounds (56). As the electropositive methyl group is added, the electrons will be pulled away from the chlorine, thus tending to increase the bond length and to decrease  $\left< \frac{\partial^2 V}{\partial Z^2} \right>_{av.}$  (equation 2-37).

Molecule	r(CC1)	eQq <sub>zz</sub> (Mc) <sup>a</sup>	$eQq_{zz}(Mc)^b$	eQq <sub>zz</sub> (Mc)	<sup>c</sup> Ref.
(CH <sub>3</sub> ) <sub>3</sub> CCl	1.803	62.3	66.9	66.9	50
(CH3)2CHC1	1.798	64.1	69.12	67.82	this thesis
CH <sub>3</sub> CH <sub>2</sub> Cl	1.788	66.0	71.24	68.80	32
CH <sub>3</sub> C1	1.781	68.40	74.74	74.74	31
С <sub>3</sub> н <sub>5</sub> С1			73.45		59
CH <sub>2</sub> C1 <sub>2</sub>	1.775	72.47	79.66	78.40	60
ссі <sub>з</sub> н	1.758	76.98	80.39	80.39 <sup>d</sup>	61
cc1 <sub>4</sub>	1.766 <sup>e</sup>	81.85	86 <sup>f</sup>	86 <sup>f</sup>	62
SiH <sub>3</sub> CH <sub>2</sub> Cl	1.788		72	68.70	63
SiH <sub>3</sub> Cl	2.050		40	40	64
SiF <sub>3</sub> Cl	1.989		43	43	65

Table XVIII. Comparison of Absolute Values of the Quadrupole Coupling Constants and Bond Lengths in Halogenated Hydrocarbons.

<sup>a</sup>Solid at 20<sup>0</sup> (References 57 and 58).

<sup>b</sup>Assuming cylindrical symmetric charge distribution.

<sup>C</sup>Assuming that the z axis of the quadrupole tensor and the CCl internuclear line coincide.

<sup>d</sup>Reference 66.

<sup>e</sup>Determined by electron diffraction.

<sup>f</sup>Estimated from the solid value.
In multichlorinated compounds the chlorine atoms compete for the carbon atom electrons, causing a decrease in ionic character of the CCl bonds, reducing the CCl bond length, and increasing  $\langle \frac{\partial^2 V}{\partial Z^2} \rangle_{av}$ .

One may note that the change in  $\chi_{zz}$  going from  $CH_3CL$ to CH<sub>3</sub>CH<sub>2</sub>Cl is only 2.4 Mc in the solid state<sup>†</sup> and only 3.50 Mc in the gas phase assuming cylindrical charge distribution, but is 5.94 Mc when the z axis and CCl internuclear line are assumed to coincide. It would seem that if one is to compare coupling constants, the assumption of cylindrical symmetry should be used unless the principal coupling constants could be determined exactly. One argument for this is from the recent work on ethyl bromide where  $\chi_{zz}$ , determined by using cylindrical charge distribution, was within 1% of  $\chi_{zz}$  obtained from the fully known coupling tensor. In comparing molecules of approximately the same hybridization,<sup>‡</sup> the X bonds may be directly correlated to bond distances. Figure 14 shows a plot of  $\chi_{ extsf{zz}}$  (gas values) versus r(CCl). The plot of  $\chi_{zz}$  (determined from the coupling tensor transformation) versus r(CCl) shows a significant

 $^{\dagger}\chi_{zz}$  for nuclei of spin I = 3/2, obtained from nuclear quadrupole resonance on the solid, represent only average values which are essentially those of a symmetrical charge distribution. For these values,  $\eta$  is assumed equal to zero.

<sup>&</sup>lt;sup>‡</sup>It is known that there must be a change in hybridization for compounds such as methylene chloride having angles HCH = 112° and ClCCl = 112°, which cannot be explained by the usual hybridization theory.



break in the curve between ethyl chloride and methyl chloride which would suggest an abrupt change in chemical properties. Based on the r(CCl) versus  $\chi_{zz}$  plot along with known inductive effects of methyl group addition, one might expect that the longer straight chain chlorinated hydrocarbons (such as n-propyl chloride) would have CCl bond lengths (based on substitution parameters) that fall between those of ethyl chloride and isopropyl chloride.

If one examines the change in going from 2-chloropropane to cyclopropyl chloride (essentially closing the ring), the large increase in  $\chi_{bond}$  may be due to loss of an effective methyl group and to a partial change in hybridization  $(sp^3 \rightarrow sp^2)$ , both which increase the quadrupole coupling constant (56).

### 4.8 Internal Rotation

The first excited torsional state of  $(CH_3)_2CHCl^{35}$ , and the ground (0, 0 state), the  $CD_3$  (1, 0 state), and the  $CH_3$  (0, 1 state) torsional states of  $CD_3CDCl^{35}CH_3$  were examined. The attempt to determine the potential barrier hindering internal rotation was carried out using  $CD_3CDCl^{35}CH_3$  since it could be treated as a one-top problem (section 2.5).

Assignments were made based on the relative intensity of torsional state transitions compared to ground state transitions and on the hyperfine splitting. Computation of the Boltzmann factor using reasonable estimates of the torsional energy indicated that the intensity ratio of the (1,0)/(0,1) state should be 1.5. Observed ratios were 1.3 to 1.7.

The measured hyperfine components for  $CD_3CDCl^{35}CH_3$ in the (0, 0), (1, 0), and (0, 1) torsional states are given in Appendix III. The hypothetical unsplit frequencies are listed in Table XIX. Table XX lists the rotational constants for the  $CD_3CDCl^{35}CH_3$  species and for  $(CH_3)_2CHCl^{35}$  in the first excited torsional state.

By applying the methods given in section 2.5, a lower limit was put on the height of the barrier hindering internal rotation of the methyl group in  $\text{CD}_3\text{CDCl}^{35}\text{CH}_3$ . The calculation is based on the observation of no splitting in the  $12_{49} \rightarrow$  $12_{48}$  transition in the (0, 1) torsional state. Parameters used in the internal rotation calculation are listed in Table XXI. Splittings greater than 0.5 Mc would have been detectable, and since no splitting was observed, the potential barrier must be greater than 3400 cal/mole.

An estimate of the potential barrier hindering internal rotation of the methyl group was made from relative intensity measurements as described in section 2.5. The potential barriers determined by this method are listed in Table XXII and range from 3577 to 3920 cal/mole. The intensity ratios are not very accurate ( $\pm$  6%) and can be regarded only as an estimate. The study of the internal rotation problem in 2-chloropropane is being continued in this laboratory.

Transition	(0,0) state	(1,0) state	(0,1) state
$2_{12} \rightarrow 3_{13}$	19270.60		
$2_{02} \rightarrow 3_{03}$	20103.08		
$2_{21} \rightarrow 3_{22}$	21273.32	21244.7	
$2_{20} \rightarrow 3_{21}$	22443.14		
$3_{22} \rightarrow 4_{23}$	28107.19		
$3_{30} \rightarrow 4_{31}$	29200.28		
$3_{12} \rightarrow 4_{13}$	29955.59	29915.78	29919.09
$3_{21} \rightarrow 4_{22}$	30502.42	30458.86	30474.40
$4_{14} \rightarrow 5_{15}$	31450.97	31413.26	31407.45
$4_{04} \rightarrow 5_{05}$	31720.64	31683.16	31673.76
$4_{23} \rightarrow 5_{24}$	34738.20	34693.61	
$4_{13} \rightarrow 5_{14}$	36516.85	36470.39	36466.88
9 <sub>28</sub> → 9 <sub>27</sub>	29004.63	28947.00	
$12_{49} \rightarrow 12_{48}$	23496.43	23423.06	23574.63

Table XIX. Hypothetical Unsplit Frequencies (Mc) for  $CD_3CDC1^{35}CH_3$  in v = 0 and v = 1 Torsional States.

Tabl	e XX.	Rotational Co 2-Chloropropa	onstants (Mc) and Mom ane Species Used in I	lents of Inertia (amu internal Rotation Stu	t A <sup>2</sup> ) <sup>a</sup> of Idy.
			Torsional	. State vv'	
	cD3CD	CI <sup>35</sup> CH <sub>3</sub> (0,0)	cD <sub>3</sub> cDC1 <sup>35</sup> CH <sub>3</sub> (1,0)	сD <sub>3</sub> сDC1 <sup>35</sup> СН <sub>3</sub> (0,1)	$(CH_3)_2 CHCl^{35}(v=1)$
A A	686	9.21 ± 0.7	6861.67 ± 0.7	6851.55 ± 1.2	8060.24 ± 2.0
В	415	2.48 ± 0.06	4146.49 ± 0.06	4148.51 ± 0.09	4563.43 ± 0.09
U	293	<b>8.53 ± 0.06</b>	2935.11 ± 0.06	2934.37 ± 0.09	3202.87 ± 0.09
п а	7	3.5937	73.6746	73.7834	62.7191
$\mathbf{I}_{\mathrm{b}}$	12	1.7418	121.9178	121.8584	110.7787
пс	17	2.0353	172.2358	172.2792	157.8369
				C L	

<sup>a</sup>Conversion factor used: 5.05531  $\times$  10<sup>5</sup> Mc-amu A<sup>2</sup>.

	CD <sub>3</sub> CDC1CH <sub>3</sub> (0,1) state	CD <sub>3</sub> CDC1CH <sub>3</sub> (1,0) state	(CH <sub>3</sub> ) <sub>2</sub> CHCl (v = 1) state
A	6851.55 Mc	6861.67 Mc	8060.24 Mc
В	4148.51	4146.49	4563.43
С	2934.37	2935.11	3202.87
I <sub>a</sub>	73.78345 amu A <sup>2</sup>	73.67463 amu	A <sup>2</sup> 62.71910 amu A <sup>2</sup>
I <sub>b</sub>	121.85845	121.91781	110.77873
I <sub>c</sub>	172.27923	172.23579	157.83688
$I_{\alpha}$	3.161	6.317	3.161
λ <sub>a</sub> a	-0.33250	0.52402	-0.43124
λ <sub>b</sub>	0.87059	0.78270	0.83176
$^{\lambda}c$	-0.36270	0.33594	0.34960
r	0.973195	0.940582	0.968472
$rI_{\alpha}$	3.0763	5.9418	3.0613
F	164.3324 kMc	84.9375 kMc	165.1339 kMc
<sub>α</sub> 2	0.000203		
β <sup>2</sup>	0.000510		
<sub>Y</sub> 2	0.000044		

Table XXI. Parameters Used in the Calculation of the Potential Barrier Hindering Internal Rotation of the Methyl Group in 2-Chloropropane.

<sup>a</sup>Determined from ground state.

.

Species	] I i	Relative ntensity Ratio	F (kMc)	S	V (cal/mole)
(CH <sub>3</sub> ) <sub>2</sub> CHCl <sup>35</sup>	(v=1)	0.32	165.1339	110.4	3920 ± 500
CD <sub>3</sub> CDC1 <sup>35</sup> CH <sub>3</sub>	(0,1)	0.17	164.3324	105.2	3709
CD <sub>3</sub> CDC1 <sup>35</sup> CH <sub>3</sub>	(1,0)	0.28	84.9375	196.3	3577
CD <sub>3</sub> CDC1 <sup>35</sup> CH <sub>3</sub>	(0,1)			97.0	3421 <sup>a</sup>

Table XXII. Height of Potential Barrier Hindering Internal Rotation in 2-Chloropropane.

<sup>a</sup>Lower limit to barrier height determined by no observable splitting in (0,1) first excited torsional state. A comparison of potential barriers hindering internal rotation of the methyl group of compounds similar to 2-chloropropane is in Table XXIII. The parameters in this series of related one-top and two-top molecules indicate that the barrier will increase or remain nearly the same with the addition of one more methyl group. Therefore, finding a potential barrier for 2-chloropropane greater than the 2200 cal/ mole reported in reference 38 is not at all unreasonable.

Molecule	V <sub>3</sub> (cal/mole)	CXC	Method	Reference
(CH <sub>3</sub> ) <sub>2</sub> CHCl	3800	112°42'	Ia	this thesis
CH3CH2CI	3685		. <b>F</b> p	32
(CH <sub>3</sub> ) <sub>3</sub> CH	3900		I	67
(CH <sub>3</sub> ) <sub>3</sub> CF	4300	112 <sup>0</sup> 42'	I	67
сн <sub>3</sub> сно	1150		F	68
(CH <sub>3</sub> ) <sub>2</sub> CO	760	116 <sup>0</sup> 14'	F	26
CH3SIH3	1700		F	69
(CH <sub>3</sub> ) <sub>2</sub> SiH <sub>2</sub>	1665	110 <sup>0</sup> 59'	F	70
сн <sub>з</sub> он	1070		F	10
(CH <sub>3</sub> ) <sub>2</sub> 0	2720	111 <sup>0</sup> 37 '	F	71
сн <sub>з</sub> sн	1270		F	72
(CH <sub>3</sub> ) <sub>2</sub> S	2132	98 <sup>0</sup> 52 '	F	27

Table XXIII. A Comparison of the Height of Potential Barriers Hindering Internal Rotation in Related Molecules.

<sup>a</sup>From intensity measurements.

<sup>b</sup>From frequency measurements.

## V. THE MICROWAVE SPECTRUM OF 2-BROMOPROPANE

## 5.1 Introduction

A study of 2-bromopropane by microwave spectroscopy should provide important information for the comparison of the structures of small halogenated hydrocarbons. The structure of methyl bromide is well-known (73), and that of ethyl bromide has just been completed (51). These together with cyclopropyl bromide and tertiary butyl bromide would make available for possible interpretation a series of monobromo hydrocarbons similar to the monochloro series.

The only previous work done on 2-bromopropane was by electron diffraction in 1939 (34). The following parameters were reported:

> $r(CBr) = 1.91 \pm 0.03 \text{ A}$ < CCC = 109.5° ± 3° < CCBr = 109.5° ± 3° r(CH) = 1.09 A assumed r(CC) = 1.54 A assumed.

# 5.2 Preparation of Isotopic Samples

The present investigation was confined to an attempt to determine the quadrupole coupling constants and the geometry of the CCBrC skeleton. Consequently only  $(CH_3)_2 CHBr^{79}$ ,  $(CH_3)_2 CHBr^{81}$ ,  $(CH_3)_2 C^{13} HBr$ , and  $C^{13} H_3 CHBr CH_3$  were investigated.

The (CH<sub>3</sub>)<sub>2</sub>CHBr was obtained from the Eastman Kodak Company and used without further purification. The sample contains 50.52% bromine-79 and 49.48% bromine-81 in natural abundance.

For the preparation of  $(CH_3)_2C^{1.3}HBr$ , the 19% labeled isopropyl alcohol remaining from the  $(CH_3)_2C^{1.3}HCl$  synthesis was used. A slight excess of pure phosphorus tribromide was dropped on the labeled alcohol (0.2 cc) in vacuo while the reaction mixture was stirred in a flask surrounded by an ice bath. A cold finger was used over the reaction. The evolved products were trapped as they escaped and were purified by vacuum line distillations. The infrared spectrum of the final product showed small impurities in addition to the 2-bromopropane. The yield was approximately 0.1 cc.

The  $C^{1.3}H_3CHBrCH_3$  species was prepared using the enriched n-propyl alcohol left from the  $C^{1.3}HCHClCH_3$  synthesis. The n-propyl alcohol (0.2 cc) was distilled into a flask set up for magnetic stirring. Phosphorus tribromide was slowly dropped on the alcohol, and the reaction mixture was refluxed on a trichloroethylene-Dry Ice cold finger. The volatile products were trapped as they left the reaction mixture and as the vessel warmed after completion of the reaction. The n-propyl bromide was separated by vacuum line distillations. The product was converted to 2-bromopropane by rearrangement over anhydrous aluminum bromide. The infrared spectrum indicated impurities to be present, but there was insufficient sample to risk separation by vapor phase chromatography.

The mass spectrum of this sample indicated that the sample was enriched in  $C^{13}H_3CHBrCH_3$  by 17%. The reaction steps are  $3CH_3CH_2C^{13}H_2OH + PBr_3 \longrightarrow 3CH_3CH_2C^{13}H_2Br + H_3PO_3 + (HBr)$  $CH_3CH_2C^{13}H_2Br \xrightarrow{A1Br_3} C^{13}H_3CHBrCH_3 + HBr + A1Br_3$  (polymer).

# 5.3 Prediction of the Transition Frequencies

By using the experimental parameters from 2-chloropropane with the CBr distance and quadrupole coupling constants determined in ethyl bromide (74), a good estimation of the transition frequencies for 2-bromopropane were obtained.

The parameters used for the initial computations were

$$r(CC) = 1.522 \text{ A}$$
  
 $r(CH) = 1.093 \text{ A}$   
 $r(CBr) = 1.94 \text{ A}$   
 $< CCC = 113^{\circ}$   
 $< BrCH = 104.26^{\circ}.$ 

The quadrupole coupling constants used were  $\chi_{zz}$  = 537.5 Mc for the Br<sup>79</sup> species and  $\chi_{zz}$  = 450.9 Mc for the Br<sup>81</sup> species.

The preliminary calculations were made by the same method as those for 2-chloropropane in Chapter IV. A projection of 2-bromopropane at its ac plane of symmetry is shown in Fig. 15.



### 5.4 Examination of the Rotational Spectra

Based on the first order quadrupole interaction calculation, most of the transitions selected for study would appear as two "doublets" showing equal splittings. The Br<sup>79</sup> and the Br<sup>81</sup> species have transitions of equal intensity separated by approximately 100 Mc. The transitions were easy to assign, but the second order quadrupole effects are apparently great enough to cause an asymmetric splitting of the doublet pairs, the splitting being larger than predicted in one pair and being smaller in the other. The first order quadrupole coupling constants are based on transitions where the splittings in the doublets appeared to be equal.

The measured hyperfine components are listed in Appendix IV. In determining the hypothetical unsplit frequencies, the approximate first order coupling constants were used to find  $\mathcal{V}_R$ . The average value of the  $\mathcal{V}_R$ 's were taken to find the  $\mathcal{V}_R$  to be used in the rigid rotator expression. The computed hypothetical unsplit frequencies are listed in Table XXIV.

The rotational constants were obtained by fitting the rigid rotator energy expression by least squares. The least moment of inertia was not as accurately determined as the other two moments of inertia since the transitions with any significant A dependence were of high J, and consequently the centrifugal distortion effects would cause a deviation from the rigid rotator expression. Also the  $U_R$ 's are not determined as accurately as possible since the second order

Table XXIV.	Hypothetic	al Unsplit Fr	equencies (M	c) <sup>a</sup> for 2-Bro	nopropane.	
	(CH <sub>3</sub> ) <sub>2</sub>	CHBr <sup>79</sup>	(CH <sub>3</sub> ) <sub>2</sub>	CHBr <sup>81</sup>	(CH <sub>3</sub> ) <sub>2</sub> C	13 <sub>HBr</sub> 79
Transition	Observed	Calculated	Observed	Calculated	Observed	Calculated
$2_{12} \rightarrow 3_{13}$	14673.52	14673.69				
$202 \rightarrow 303$	15428.30	15428.30				
313 → 414	19509.04	19509.00	19378.79	19378.66	19397.02	19396.85
3 <sub>03</sub> → 4 <sub>04</sub>	20340.52	20340.73	20205.22	20205.14	20221.00	20220.97
$3_{22} \xrightarrow{4} 4_{23}$	20810.36	20810.63	20660.89	20661.01		
$3_{12} \stackrel{1}{\rightarrow} 4_{13}$	21981.07	21981.02	21816.34	21816.26	21829.44	21829.46
<sup>4</sup> 04 <sup>→</sup> 505	25099.21	25099.16	24938.14	24937.88		
5 <sub>15</sub> → 6 <sub>16</sub>	29057.52	29057.91	28867.50	28867.92	28895.16	28875.33
5 <sub>05</sub> → 6 <sub>06</sub>	29729.92	29730.41	29544.39	29544.51	29569.06	29569.09
$5_{14} \rightarrow 6_{15}$	32636.16	32636.20	32400.76	32400.67	32420.41	32420.40
5 <sub>23</sub> → 6 <sub>24</sub>	32582.36	32582.79	32323.20	32323.64		
<sup>5</sup> 24 → 625	31039.38	31039.45	30820.60	30820.50		

<sup>a</sup>Estimated from first order quadrupole splittings.

quadrupole effects have not been taken into account. The rotational constants, the moments of inertia, and the second moments for the isotopic species studied are listed in Table XXV.

#### 5.5 Molecular Structure

The coordinates of the center carbon atom and the bromine atom may be computed using Kraitchman's equations, and the constants determined from the three isotopic species studied. The coordinate calculations are based on differences, and therefore errors due to centrifugal distortion and second order quadrupole effects will tend to cancel. This is because the rotational constants are determined by the same method using for the most part the same transitions. The computed coordinates are

	a	<u>b</u>	<u>c</u>
C <sub>middle</sub>	-1.0752 A	0	-0.4029 A
Br	0.8428	0	0.0124

The CBr bond distance based on these coordinates is 1.962 A. The c coordinate for the bromine atom is no doubt too small (46). A change of 0.03 A in this coordinate will increase the CBr distance by 0.006 A. If the A rotational constant in the parent species were in error by one megacycle more than the A constant in the other two species, the CBr distance could be changed by  $\pm$  0.006 A.

	(CH <sub>3</sub> ) <sub>2</sub> CHBr <sup>79</sup>	(CH <sub>3</sub> ) <sub>2</sub> CHBr <sup>81</sup>	(CH <sub>3</sub> ) <sub>2</sub> C <sup>13</sup> HBr <sup>79</sup>
A	8036.64 ± 5	8036.32 ± 5	8016.99 ± 5
В	$2917.67 \pm 0.07$	$2894.40 \pm 0.07$	$2895.74 \pm 0.07$
C	2295.38 ± 0.07	$2280.92 \pm 0.07$	$2283.50 \pm 0.07$
I	62.9033	62.9058	63.0575
Ib	173.2653	174.6583	174.5775
I <sub>c</sub>	220.2385	221.6347	221.3843
Paa	165.3002	166.6936	166.4522
P <sub>bb</sub>	54.9383	54.9411	54.9322
P <sub>cc</sub>	7.9650	7.9647	8.1254

Table XXV. Rotational Constants (Mc), Moments of Inertia (amu A<sup>2</sup>),<sup>a</sup> and Second Moments (amu A<sup>2</sup>)<sup>b</sup> for 2-Bromopropane.

<sup>a</sup>Conversion factor:  $5.05531 \times 10^5$  Mc-amu A<sup>2</sup>.

<sup>b</sup>Computed from equation 2-30.

The CBr distance in 2-bromopropane is 0.012 A longer than in ethyl bromide (51) which in turn is 0.011 A longer than in methyl bromide (73). The CBr internuclear line makes an angle of  $12^{\circ}14'$  with the a inertial axis.

The calculated rotational constants for  $(CH_3)_2 CHBr^{79}$ were only 60 Mc higher than those determined experimentally. This is approximately the difference one finds between the experimental rotational constants and those determined from substitution coordinates. This would indicate that the initially assumed parameters are very nearly the correct ones.

Work is continuing in this laboratory to determine the rotational constants for  $C^{13}H_3CHBr^{79}CH_3$  so that a more complete structural analysis can be made. The spectra for this species is complicated by the probable presence of n-propyl bromide and perhaps from new second order effects brought about by the loss of the symmetry in the molecule. An analysis of these second order effects which is very lengthy is not yet complete.

# 5.6 Quadrupole Analysis

The first order quadrupole coupling tensor was obtained from transitions that appear as doublets of equal splitting such as the  $5_{14} \rightarrow 6_{15}$  and  $3_{22} \rightarrow 4_{23}$ . The first order coupling constants for bromine-79 and bromine-81 in the principal inertial axis system are listed in Table XXVI.

	(CH <sub>3</sub> ) <sub>2</sub> CHBr <sup>79</sup>	(CH <sub>3</sub> ) <sub>2</sub> CHBr <sup>81</sup>	
eQq <sub>m</sub>	$477.9 \pm 3 Mc$	$400.4 \pm 3 Mc$	
eQq <sub>m</sub> ŋ	$-47.8 \pm 6 Mc$	$-40.7 \pm 6 Mc$	
η	-0.100 ± 0.01	$-0.102 \pm 0.01$	
Xaa	$477.9 \pm 3 Mc$	$400.4 \pm 3 Mc$	
Хрр	$-262.9 \pm 4$	$-220.5 \pm 4$	
Xcc	$-215.1 \pm 4$	$-179.8 \pm 4$	

Table XXVI. Quadrupole Coupling Constants in 2-Bromopropane.

In CBr Bond Axis System

	$(CH_3)_2 CHBr^{79}$		$(CH_3)_2 CHBr^{81}$	
	1 <sup>a</sup>	2 <sup>b</sup>	3 <sup>a</sup>	4 <sup>b</sup>
$\chi_{zz}$	512.1±3 Mc	525.7±8 Mc	429.0±3 Mc	441.0±8 Mc
η <sub>bond</sub> c	0.027±0.006	0	0.028±0.006	0
$\theta_z^{d}$	12 <sup>0</sup> 14'	14 <sup>0</sup> 15'±1 <sup>0</sup>	12 <sup>0</sup> 14'	14°20'±1°
I	19%	17%	18%	16%

<sup>a</sup>Assuming that the z axis of the quadrupole tensor and the CBr internuclear line coincide.

<sup>b</sup>Assuming cylindrical charge distribution.

$$c_{\eta_{\text{bond}}} = \left(\chi_{xx} - \chi_{yy}\right) / \chi_{zz}.$$

 ${}^{d}\theta_{z}$  is the angle between the a and the z axes.

The quadrupole coupling constants are computed in a molecular axis system by assuming a cylindrical charge distribution about the CBr bond, or that the z principal axis of the quadrupole tensor and the CBr internuclear line coincide. The results from these calculations are listed at the bottom of Table XXVI. If the off-diagonal element  $\chi_{\rm ac}$  can be determined from the second order calculations, it will be possible to diagonalize the quadrupole tensor which will allow a check as to which of the foregoing assumptions is the more valid.

The ionicity may be computed from equation (4-15) where  $eQq_{at}$  for  $Br^{79}$  is 769.8 Mc, and  $eQq_{at}$  for  $Br^{81}$  is 643.1 Mc (16). The ionic character of the CBr bond is less than that of the CCl bond in 2-chloropropane. This is the expected trend based on the electronegativities of the halogens.

A comparison of quadrupole coupling constants and bond lengths for a series of bromides is given in Table XXVII. The trend in coupling constants and bond lengths is similar to that for the chlorine analogues. It would be interesting to have an accurate parameter for the CBr distance and coupling constant for tertiary butyl bromide. One might be able to give a reasonable estimate for the bond length and coupling constant by an analogy between the listed series in Table XXVII and the similar chlorine series.

Table XXVII.	A Comparison of Quadrupole Coupling Constants of 2-Bromopropane with Those of
	Similar Compounds.

	r(CBr) A	$\chi_{zz}^{a(M_{c})}$	$\chi_{zz}^{b}(Mc)$
CH <sub>3</sub> Br <sup>79</sup>	1.939 <sup>c</sup>	577.3 <sup>d</sup>	577.3
CH <sub>3</sub> CH <sub>2</sub> Br <sup>79e</sup>	1.950	547.1	541.0
$(CH_3)_2 CHBr^{79f}$	1.962	525.7	512.1

<sup>a</sup>Assuming cylindrical charge distribution.

<sup>b</sup>Assuming that the z axis of the quadrupole tensor and the CBr internuclear line coincide.

> <sup>c</sup>Reference 73. <sup>d</sup>Reference 75. <sup>e</sup>Reference 51. f<sub>This thesis.</sub>

#### VI. SUMMARY

The microwave spectra for a number of isotopic species of 2-chloropropane and 2-bromopropane have been examined and their rotational transitions assigned. From an analysis of the hyperfine splittings due to the chlorine and bromine nuclear quadrupole moments the first order quadrupole coupling constants were obtained.

The ground state rotational constants for a sufficient number of isotopic species of 2-chloropropane were obtained enabling a complete determination of the molecular structure by the substitution method. The important bond distances and bond angles were determined to be r(CC) = 1.522 A,  $r(CC1) = 1.798 \text{ A}, < CCC = 112^{\circ}42', < CCC1 = 109^{\circ}24'.$  An estimate of the vibration effects on the atom coordinates as determined by Kraitchman's equations was made by assuming small reductions in the bond lengths upon isotopic substitution. It was clearly illustrated that the zero-point changes in the vibrational energy upon isotopic substitution can have a significant effect on the bond distances and bond angles computed by the substitution method. A study of CH<sub>3</sub>CHClCH<sub>3</sub> and CD<sub>3</sub>CDClCH<sub>3</sub> in the first excited torsional state allowed an estimation of the height of the potential barrier hindering internal rotation of the methyl group.

Using the rotational constants obtained from the three species of 2-bromopropane analyzed, the CBr bond distance was determined by the substitution method. The computed bond length is r(CBr) = 1.962 A.

The quadrupole coupling constants obtained for both 2-chloropropane and 2-bromopropane fill important places in the methyl to tertiary butyl halide series. In both series a regular increase in bond length and ionic character and a corresponding decrease in the quadrupole coupling constant This trend is discussed in terms of the inducis observed. tive effects of methyl group addition. The two assumptions for transforming the quadrupole coupling tensor from the principal inertial axis system to the carbon-halogen axis system are considered in terms of which is the "best" one to use when making comparisons. It is argued that when comparing coupling constants between symmetric and asymmetric top molecules, the constants obtained by employing a cylindrical symmetric charge distribution should be taken as the "best" of the two values.

Meası	ıred Hyperfine	Components (Mc)	for Isotopic Sp	ecies of 2-Chloropropane
Transition	$(CH_3)_2$ CHCI <sup>35</sup>	(СН <sub>3</sub> ) <sub>2</sub> СНСІ <sup>37</sup>	$(CH_3)_2 C^{13}HCI^{35}$	$c^{13}H_{3}CHCI^{35}CH_{3}(CH_{3})_{2}CDCI^{35}$
$\frac{1}{11} \stackrel{-}{_{\rightarrow}} 2_{12}$				
$\frac{5/2}{3/2} \neq \frac{7/2}{5/2}$	14197.18 14181.84	13901.71 13889.58		14078.82 14063.36
$\frac{1/2}{5/2} \pm \frac{3/2}{5/2}$	14202.20 14190.49			14083.89 14072.02
$\frac{3/2}{1/2} \rightarrow \frac{3/2}{1/2}$	14186.96 <sup>a</sup> 14208.94			14068.26
<sup>1</sup> 01 → 202				
5/2 - 7/2	15230.70	14909.62		15045.37
3/2 + 5/2 1/2 + 3/2	15231.64 15214.27	14910.20 14896.53		15046.20
5/2 - 5/2	15216.24	14898.10		15030.71
$\frac{3/2}{1/2} \rightarrow \frac{3/2}{1/2}$	15241.94 15228.70	14918.40 14908.07		15056.66
$\frac{1}{10} \stackrel{-}{\rightarrow} \frac{2}{11}$				
$5/2 \rightarrow 7/2$	16923.94	16508.94		16615.68
$\frac{3/2}{1/2} \neq \frac{5/2}{3/2}$	16908.53 16926.80	16496.79 16511.21		16600.18 16618.64
5/2 + 5/2	16915.19			درآ 6606.59
$\frac{3}{1}/2 - \frac{3}{1}/2$	16935.51			16627.23

APPENDIX I

Transition	(CH <sub>3</sub> ) <sub>2</sub> CHCI <sup>35</sup>	(CH <sub>3</sub> ) <sub>2</sub> CHCl <sup>37</sup>	$(CH_3)_2 C^{13}HCl^{35}$	с <sup>1 3</sup> н <sub>3</sub> снс1 <sup>35</sup> сн <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CDCl <sup>35</sup>
$\frac{2_{12}}{2_{12}} = \frac{3_{13}}{2_{13}}$					
1/2 + 3/2	21106.94	20682./2	21060.50	20/49./I	
$5/2 \pm 7/2$ $3/2 \pm 5/2$	21103.34	20679.88	21056.87	20746.14	
$2_{02} - 3_{03}$					
$\frac{7}{5} \frac{1}{2} \rightarrow \frac{9}{2}$	22134.57 22135 60	{21716.25	22084.59 22085 57	21750.05 21751 04	21914.13 21013 76
$3/2 \pm 5/2$ $1/2 \pm 3/2$	22131.55 22130.50	٤ 21712,98	22080.59 22080.59	21746.98b 21746.35 <sup>b</sup>	21910.05 21910.05
$\frac{2}{21} \rightarrow \frac{3}{22}$					
$\frac{7}{5} \frac{1}{2} \neq \frac{9}{2}$	23339.55 2339.55	22807.03 <sup>b</sup> 22794 80	23272。00 <sup>b</sup> 23256_67		23019.56 23014 12
$\frac{3}{2} - \frac{5}{2}$	23335.15 23350.60 23350.60	22803.58			23015.17 23030.66
$\frac{220}{220} \rightarrow \frac{321}{221}$					
7/2 - 9/2	24540.77	23894.89	24455.95	24225.79	24121.01
5/2 + 7/2 $3/2 + 5/2$	24524.35 24535.57	23882.06 23890.88	24439.54 24450.92	24209.140 24220.41 <sup>b</sup>	24104.72 24115.98
$1/2 \rightarrow 3/2$	24551.92				

Transition	(CH <sub>3</sub> ) <sub>2</sub> CHCI <sup>35</sup>	$(CH_3)_2$ CHCI $^{37}$	$(cH_3)_2 c^{13}Hc1^{35}$	с <sup>1 3</sup> н <sub>3</sub> снс1 <sup>35</sup> сн <sub>3</sub>	$(CH_3)_2 CDCI^{35}$
$\frac{2_{11}}{3_{12}} \rightarrow \frac{3_{12}}{3_{12}}$					
$\frac{7}{2} - \frac{9}{2}$	25145.95	24550.62	25064.24	24788.40	
$\begin{array}{c} 5/2 \\ 5/2 \\ 7/2 \\ 7/2 \\ 5/2 \\$	25142.50 25142.04 25133.88 25148.30	٤ 24547.74	25060.72	24784.93	
$3_{22} - 4_{23}$					
$\begin{array}{c} 9/2 \rightarrow 11/2 \\ 7/2 \rightarrow 9/2 \\ 7/2 \rightarrow 9/2 \\ 7/2 \end{array}$	30847.38 30851.46	30174.93 30170.28	30771.58 30765.64	30381.97 30376.02	
3/2 - 5/2	30859.45	30176.56	30773.65	30384.05	
<sup>3</sup> 03 → 404					
$\begin{array}{c} 9/2 \ -11/2 \\ 7/2 \ -9/2 \\ 3/2 \ -5/2 \\ 3/2 \ -5/2 \end{array}$	28580.50 28581.07 28579.34 28578.74	28076.58 28077.03 {28075.61	28061.13 28061.70	28061.13 28061.70 28059.93 28059.33	
$3_{21} \rightarrow 4_{22}$					
$\begin{array}{c} 9/2 & \rightarrow 11/2 \\ 7/2 & \rightarrow 9/2 \\ 5/2 & \rightarrow 7/2 \\ 3/2 & \rightarrow 5/2 \end{array}$			33265.81 33259.21 33261.39 33267.91	32961.04 32954.54 32956.53 32963.20	

Transition	( CH <sub>3</sub> ) <sub>2</sub> CHCl <sup>35</sup>	$(CH_3)_2$ CHCI $^{37}$	$(CH_3)_2 C^{13}HCI^{35}$	с <sup>13</sup> н <sub>3</sub> снс1 <sup>35</sup> сн <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CDCl <sup>35</sup>
505 → 524					
$13/2 \rightarrow 13/2$	23818.64	23644.57 <sup>b</sup>			22381.35
$\begin{array}{c} 11/2 \rightarrow 11/2 \\ 9/2 \rightarrow 9/2 \\ 7/2 \rightarrow 7/2 \end{array}$	23822.69 23822.69	23041.02 23646.67			22384.32
7/1 - 7/1	7301/100	23043.11			22380.32
$6_{16} \rightarrow 6_{15}$					
unresolved	25251.36	24457.45	25061.48	25092.66	23576.88
5 <sub>15</sub> → 5 <sub>14</sub>					
$\frac{13}{2} - \frac{13}{2}$	19172.52		19017.17 <sup>b</sup>		
$\frac{11}{2} - \frac{11}{2}$	19171.66		19016.48		
6 <sub>24</sub> → 6 <sub>25</sub>					
$15/2 \rightarrow 15/2$	13308.12	12405.63			
$\frac{13/2}{11/2} \rightarrow \frac{13/2}{11/2}$	13305.56 13306.16	12403.68			
9/2 - 9/2	13308.72				

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Transition	$(CH_3)_2 CHCI^{35}$	$(CH_3)_2$ CHCI <sup>37</sup>	(CH <sub>3</sub> ) <sub>2</sub> C <sup>13</sup> HCl <sup>35</sup>	с <sup>1 3</sup> н <sub>3</sub> снс1 <sup>35</sup> сн <sub>3</sub>	$(CH_3)_2 CDCL^{35}$
<sup>4</sup> 04 → <sup>4</sup> 23					
$\frac{13/2}{11/2} \rightarrow \frac{13/2}{11/2}$	20516.14 20523.00				
$\frac{9/2}{7/2} \rightarrow \frac{9/2}{1/2}$	20520.51 20513.65				
$3_{13} \rightarrow 3_{12}$					
$\begin{array}{c} 9/2 \rightarrow 9/2 \\ 7/2 \rightarrow 7/2 \\ 5/2 \rightarrow 5/2 \end{array}$	8129.56 8127.63 8128.63				
<sup>4</sup> 14 → 413					
$\frac{11/2}{5/2} \xrightarrow{1} \frac{11/2}{5/2}$	13290.23				
$\frac{9/2}{7/2} \div \frac{9/2}{7/2} $	13288.98				

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<sup>a</sup>Interfering transition.

<sup>b</sup>Measured from a recording trace.

: (Mc) for Isotopic Species of 2-Chloropropane	$(CH_3)_2 CHCl^{35}(v=1)$	14175.93 14160.50	15207.73 15208.69 15191.32 15193.31 15218.92	16897.14 <sup>a</sup> 16881.66
vic Species of 2-Ch	$CH_2DCHCI^{35}CH_3(\gamma)$		14896.52 14897.52 14880.33 14882.32	16537.59 16522.52
ents (Mc) for Isotop	сн <sub>2</sub> рснс1 <sup>35</sup> сн <sub>3</sub> (в)		14605.21 14606.05 14603.35	16193.91 16190.11
ed Hyperfine Components (	$CH_2DCHCL^{35}CH_3(\alpha)$	13875.21 13859.96	14902.13 14903.28 1485.75 14901.09	16756.36 16741.12
Measured Hyperfine	Transition	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \frac{1}{01} \xrightarrow{1} 202 \\ 5/2 \xrightarrow{1} 7/2 \\ 3/2 \xrightarrow{1} 5/2 \\ 3/2 \xrightarrow{1} 3/2 \\ 1/2 \xrightarrow{1} 1/2 \\ 1/2 \xrightarrow{1} 1/2 $	$\frac{1}{5/2} \stackrel{1}{\rightarrow} \frac{2}{11} \stackrel{1}{} \frac{1}{5/2} \stackrel{1}{\rightarrow} \frac{2}{5/2} \stackrel{1}{} \frac{3}{2} \stackrel{2}{} \stackrel{1}{} \frac{3}{} \stackrel{2}{} \stackrel{1}{} \stackrel{1}{} \stackrel{2}{} \stackrel{1}{} \stackrel{1}{} \stackrel{1}{} \stackrel{2}{} \stackrel{1}{} \stackrel{1}} \stackrel{1}{} \stackrel{1}} \stackrel{1}} \stackrel{1}{} \stackrel{1}{2$

APPENDIX II

Transition	$CH_2DCHC1^{35}CH_3(\alpha)$	CH2DCHCl <sup>35</sup> CH <sub>3</sub> (B)	$CH_2DCHC1^{35}CH_3(\gamma)$	(CH <sub>3</sub> ) <sub>2</sub> CHCl <sup>35</sup> (v=1)
$2_{12} \xrightarrow{3}_{13}$				
$7/2 \rightarrow 9/2$	20580.31	20247.71	20680.38	21075.23
$\frac{5}{2} \neq \frac{3}{2}$ $\frac{5}{2} \neq \frac{3}{2}$	20576.81	20244.13	20677.02	21071.58
$2_{02} \stackrel{\rightarrow}{\rightarrow} 3_{03}$				
7/2 + 9/2 5/2 + 7/2 3/2 + 5/2 1 - 3/2	21505.61 21506.74	21257.28 21258.18	21642.72 21643.84	22102.24 22103.19 22099.11
$\frac{2}{2} 1 \rightarrow \frac{3}{2} 2$				07.0077
$7/2 \pm 9/2$ $5/2 \pm 7/2$ $3/2 \pm 5/2$ $1/2 \pm 3/2$	22972.50 22956.88 22968.39	22353.93 22338.56 22349.48		23303.25 23287.95
$2_{20} \stackrel{7}{\rightarrow} 3_{21}$				
$7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$	24435.51 24419.04 24430.23	23446.64 23430.56 23441.45	24025.27 24020.25	24500.63 24495.9
$1/2 \rightarrow 3/2$				

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Transition	$CH_2DCHCI^{35}CH_3(\alpha)$	CH <sub>2</sub> DCHCI <sup>35</sup> CH <sub>3</sub> (B)	$CH_2 DCHCI ^{35} CH_3(\gamma)$	(CH3)2CHCl <sup>35</sup> (v=1)
$\frac{2_{11} - 3_{12}}{7/2} - \frac{9/2}{2}$	24824.77	24075.28	24566.45	25106.43
$\begin{array}{c} 1 \\ 5 \\ 5 \\ 7 \\ 7 \\ 7 \\ 7 \\ 7 \\ 7 \\ 7 \\ 7$	24821.32	24071.74 24077.4	24563.00 24568.6	25103.31 25108.50
$\frac{3_{22}}{9/2} - \frac{4_{23}}{11/2}$ $\frac{9/2}{7/2} - \frac{9/2}{9/2}$ $\frac{3/2}{3/2} - \frac{5/2}{5/2}$	30299.92 30294.03 30296.08 30302.00	29568.34 29562.38 29564.40 29570.46	30186.29 30181.06 30183.06 30188.46	
$\frac{3_{12}}{9/2} \xrightarrow{4_{13}} \frac{4_{13}}{11/2}$ $\frac{9/2}{5/2} \xrightarrow{7/2} \frac{9/2}{7/2}$ $\frac{3/2}{3/2} \xrightarrow{5/2}$	32429.53 32428.98 32427.76	31645.29 31644.36 31643.43	32243.68 32242.70 32241.77	
$\frac{3_{21}}{9/2} \xrightarrow{4_{22}}{11/2}$ $\frac{9/2}{5/2} \xrightarrow{9/2}{3/2} \xrightarrow{5/2}{5/2}$	33242.99 33236.44 33238.39 33244.93	31892.58 31885.98 31888.20 31894.76	32668.63 32662.13 32664.07 32670.38	

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Transition	$CH_2 DCHCl ^{35}CH_3(\alpha)$	сн <sub>2</sub> Dснс1 <sup>35</sup> сн <sub>3</sub> (в)	$CH_2DCHCI^{35}CH_3(\gamma)$	$(CH_3)_2CHCl^{35}(v=1)$
6 <sub>16</sub> → 6 <sub>15</sub> unresolved	25617.57	24132.43	24143.36	
$\frac{5_{15} - 5_{14}}{13/2 - 13/2}$ $\frac{13/2 - 13/2}{11/2 - 11/2}$	19767.72			
$\frac{624 \rightarrow 625}{15/2 \rightarrow 15/2}$ $\frac{15/2 \rightarrow 15/2}{11/2 \rightarrow 11/2}$				13274.46 13271.84 13272.49
4 <u>04</u> → 505 unresolved			34124.90	

<sup>a</sup>Interfering transition.

Transition	(0,0) State	(1,0) State	(0,1) State
$\frac{2_{12} \rightarrow 3_{13}}{2_{12}}$			
$7/2 \rightarrow 9/2$	19272.04		
$5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$	19268.63		
$2_{02} \rightarrow 3_{03}$			
$7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$ $1/2 \rightarrow 3/2$	20103.43 20104.44 20100.48 20099.36	21249.1 21234.2 21244.8	
$2_{21} \rightarrow 3_{22}$			
$\frac{7/2}{5/2} \rightarrow \frac{9/2}{5/2}$	21277.68		
$3/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$	21202.54 21273.29		
$\frac{1}{2} \rightarrow 3$	21200.25		
$\frac{20}{20}$ $\frac{3}{21}$			
$7/2 \rightarrow 9/2$	22447.84		
$3/2 \rightarrow 5/2$	22442.70		
$1/2 \rightarrow 3/2$	22458.82		
$\frac{3_{22}}{2} \rightarrow 4_{23}$			
$9/2 \rightarrow 11/2$	28109.32		
$7/2 \rightarrow 9/2$	28103.42		
$\frac{3}{2} \rightarrow \frac{5}{2}$	28111.29		
$3_{30} \rightarrow 4_{31}$			
$\frac{1}{9/2} \rightarrow 11/2$	29204.91		
$7/2 \rightarrow 9/2$	29190.62		
$5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$	29197.75 29212.49		
,, -			

Measured Hyperfine Transitions (Mc) for  ${\rm CD}_3{\rm CDCl}^{35}{\rm CH}_3$  in vv' Torsional States

<b>Tr</b> ansition	(0,0) State	(1,0) State	(0,1) State
$3_{12} \rightarrow 4_{13}$		******	
$9/2 \rightarrow 11/2$ 7/2 → 9/2 }	29956.19 29955.39	29916.37 29915.58	29919.70 29918.87
$5/2 \rightarrow 7/2$	29954.35	29914.56	29917.86
$3_{21} \rightarrow 4_{22}$			
$9/2 \rightarrow 11/2$ $7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$	30504.84 30498.43 30500.41 30506.74	30461.21 30454.92 30456.87 30463.21	30476.89 30470.42 30472.36 30478.70
$4_{14} \rightarrow 5_{15}$			
$\frac{11/2 \rightarrow 13/2}{11/2}$	31451.20	31413.47	31407.05
$9/2 \rightarrow 11/2 = 7/2 \rightarrow 9/2 = 5/2 \rightarrow 7/2$	31450.39	31412.69	
$4_{04} \rightarrow 5_{05}$			
$11/2 \rightarrow 13/2$	31720.83	31683.40	31673.98
$5/2 \rightarrow 11/2$ $7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$	31720.10	31682.59	31673.21
4 <sub>23</sub> → 5 <sub>24</sub>			
$11/2 \rightarrow 13/2$	34739.27	34694.78	
$ \frac{3}{2} \rightarrow \frac{7}{2} \\ \frac{9}{2} \rightarrow \frac{11}{2} \\ \frac{7}{2} \rightarrow \frac{9}{2} $	34736.75	34692.07	
$\frac{4_{13} \rightarrow 5_{14}}{5_{14}}$			
$11/2 \rightarrow 13/2$	36517.04	36470.64	36467.11
$9/2 \rightarrow 11/2$ $7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$	36516.32	36469.80	36466.32

APPENDIX III--Continued

Transition	(0,0) State	(1,0) State	(0,1) State
8 <sub>08</sub> → 8 <sub>27</sub>			
$17/2 \rightarrow 17/2$	31830.22		
$13/2 \rightarrow 13/2$ $19/2 \rightarrow 19/2$ $13/2 \rightarrow 13/2$	31828.68		
$9_{28} \rightarrow 9_{27}$			
unresolved	29004.63	28947.36	
$12_{310} \rightarrow 12_{39}$			
unresolved	35985.64	35911.31	
$10_{28} \rightarrow 10_{29}$			
unresolved	34107.55		
$12_{49} \rightarrow 12_{48}$			
$27/2 \rightarrow 27/2$	23497.42	23424.02	23575.49
$21/2 \rightarrow 21/2  25/2 \rightarrow 25/2  23/2 \rightarrow 23/2  3/2 \rightarrow 23/2 $	23495.13	23423.06	23573.33

APPENDIX III--Continued
Transition	(CH <sub>3</sub> ) <sub>2</sub> CHBr <sup>79</sup>	(CH <sub>3</sub> ) <sub>2</sub> CHBr <sup>81</sup>	(CH <sub>3</sub> ) <sub>2</sub> C <sup>13</sup> HBr <sup>79</sup>
$\frac{2_{12} \rightarrow 3_{13}}{2_{12}}$			
$7/2 \rightarrow 9/2$	14661.26		
$5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$	14690.24		
$2_{02} \rightarrow 3_{03}$			
$7/2 \rightarrow 9/2 5/2 \rightarrow 7/2 3/2 \rightarrow 5/2 1/2 \rightarrow 3/2$	15423.41 15421.42 15451.13 15453.61		
$\frac{3_{13} \rightarrow 4_{14}}{4_{14}}$			
9/2 → 11/27/2 → 9/25/2 → 7/23/2 → 5/2	19502.12 19513.96 19519.21 19508.34	19372.88 19382.95 19387.29 19578.22	19390.33 19402.07 19407.32 19395.82
3 <sub>03</sub> → 4 <sub>04</sub>			
$ \frac{9/2 \rightarrow 11/2}{7/2 \rightarrow 9/2} \\ \frac{5/2 \rightarrow 7/2}{3/2 \rightarrow 5/2} $	20338.02 20335.52 20349.70 20352.03	20203.06 20201.09 20212.96 20214.75	20218.45 20216.03 20230.21
$\frac{3_{22}}{22} \rightarrow 4_{23}$			
$9/2 \rightarrow 11/2$ $7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$	20793.08 20840.74 20823.76	20646.46 20686.28 20672.24 20632.44	
$3_{12} \rightarrow 4_{13}$			
$9/2 \rightarrow 11/2$ $7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$	21974.30 21985.23 21992.49 21980.78	21810.76 21819.87 21825.92 21816.14	21822.63 21833.66 21840.99 21828.99

Measured Hyperfine Components (Mc) for Isotopic Species of 2-Bromopropane

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Transition	(CH <sub>3</sub> ) <sub>2</sub> CHBr <sup>79</sup>	$(CH_3)_2 CHBr^{81}$	(CH <sub>3</sub> ) <sub>2</sub> C <sup>13</sup> HBr <sup>79</sup>
$4_{04} \rightarrow 5_{05}$			
$\begin{array}{r} 11/2 \rightarrow 13/2 \\ 9/2 \rightarrow 11/2 \\ 7/2 \rightarrow 9/2 \\ 5/2 \rightarrow 7/2 \end{array}$	25097.49 25095.57 25103.64 25106.44	24936.69 24935.04 24941.91 24944.17	
$5_{15} \rightarrow 6_{16}$			
$13/2 \rightarrow 15/2$ $11/2 \rightarrow 13/2$ $9/2 \rightarrow 11/2$ $7/2 \rightarrow 9/2$	29054.57 29057.24 29061.24 29058.35	28865.38 28867.62 28870.85 38868.46	28892.57 28895.21 28898.26 28896.40
$5_{05} \rightarrow 6_{06}$			
$\begin{array}{r} 13/2 \rightarrow 15/2 \\ 11/2 \rightarrow 13/2 \\ 9/2 \rightarrow 11/2 \\ 7/2 \rightarrow 9/2 \end{array}$	29729.13 29726.98 29732.56 29734.45	29543.68 29541.95 29546.56 29548.24	29568.21 29566.12 29571.77 29573.60
$5_{14} \rightarrow 6_{15}$			
$13/2 \rightarrow 15/2$ $11/2 \rightarrow 13/2$ $9/2 \rightarrow 11/2$ $7/2 \rightarrow 9/2$	32633.64 32635.70 32640.29 32638.17	32398.66 32400.37 32404.19 32402.44	32417.85 32419.96 32424.62 32422.37
5 <sub>23</sub> → 6 <sub>24</sub>			
$13/2 \rightarrow 15/2$	32675.17	32328.85	32353.40
$ \begin{array}{c} 11/2 \rightarrow 13/2 \\ 9/2 \rightarrow 11/2 \end{array} \} $	32590.13	32317.23	
5 <sub>24</sub> → 6 <sub>25</sub>			
$13/2 \rightarrow 15/2$	31046.23	30826.28	
$11/2 \rightarrow 13/2$ $9/2 \rightarrow 11/2$	31033.13	30815.29	

APPENDIX IV--Continued

## REFERENCES

- 1. C. E. Cleeton and N. H. Williams, Phys. Rev. <u>45</u>, 234 (1934).
- 2. B. Bleaney and R. P. Penrose, Nature 157, 339 (1946).
- 3. B. Bleaney and R. P. Penrose, Phys. Rev. 70, 775 (1946).
- 4. D. K. Coles and W. E. Good, Phys. Rev. 70, 979 (1946).
- 5. R. H. Hughes and E. B. Wilson, Jr., Phys. Rev. <u>71</u>, 562 (1947).
- B. P. Dailey, R. L. Kylh, M. W. P. Strandberg, J. H. Van Vleck, and E. B. Wilson, Jr., Phys. Rev. <u>70</u>, 984 (1946).
- 7. C. H. Townes and B. P. Dailey, J. Chem. Phys. <u>17</u>, 782 (1949).
- 8. Peter Debye, <u>Polar</u> <u>Molecules</u>, Chemical Catalog Co., New York (1929).
- 9. T. W. Dakins, W. E. Good, and D. K. Coles, Phys. Rev. <u>70</u>, 560 (1946).
- 10. D. G. Burkhard and D. M. Dennison, Phys. Rev. <u>84</u>, 408 (1951).
- R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., J. Chem. Phys. <u>26</u>, 1695 (1957).
- 12. D. R. Herschbach, J. Chem. Phys. 31, 91 (1959).
- 13. J. Kraitchman, Am. J. Phys. <u>21</u>, 17 (1953).
- 14. B. S. Ray, Zeits F. Physik 78, 74 (1932).
- G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. <u>11</u>, 27 (1943).
- C. H. Townes and A. L. Schawlow, <u>Microwave</u> <u>Spectroscopy</u>, McGraw-Hill, New York, 1955.

- 17. D. Kivelson and E. B. Wilson, Jr., J. Chem. Phys. <u>20</u>, 1575; Phys. Rev. <u>87</u>, 214A (1952).
- W. Gordy, W. V. Smith, and R. F. Trambarulo, <u>Microwave</u> <u>Spectroscopy</u>, John Wiley & Sons, New York, 1953.
- H. Goldstein, <u>Classical Mechanics</u>, Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1950, p. 149.
- 20. H. B. G. Casimir, <u>On the Interaction between Atomic</u> <u>Nuclei and Electrons</u>, Teylers Tweede Genootschap, E. F. Bohn, Haarlem, 1936.
- 21. J. K. Bragg, Phys. Rev. 74, 533 (1948).
- 22. J. K. Bragg and S. Golden, Phys. Rev. 75, 735 (1949).
- 23. G. Knight and B. T. Feld, Phys. Rev. 74, 354 (1948).
- 24. D. R. Herschbach, <u>Tables</u> for the <u>Internal Rotation</u> <u>Prob-</u> <u>lem</u>, Dept. of Chemistry, Harvard University, Cambridge, Mass., 1951, J. Chem. Phys. 27, 975 (1957).
- R. W. Kilb, <u>Tables</u> of <u>Degenerate</u> <u>Mathieu</u> <u>Functions</u>, Dept. of Chemistry, <u>Harvard University</u>, <u>Cambridge</u>, Mass., 1951.
- 26. J. D. Swalen and C. C. Costain, J. Chem. Phys. <u>31</u>, 1562 (1959).
- 27. L. Pierce, J. Chem. Phys. 34, 498 (1961).
- 28. L. Pierce and M. Hayashi, J. Chem. Phys. <u>35</u>, 479 (1961).
- 29. H. Minden and B. P. Dailey, Phys. Rev. 82, 338A (1951).
- 30. L. C. Hedrick, Rev. Sci. Instr. 20, 781 (1949).
- 31. S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes, and J. Kraitchman, J. Chem. Phys. <u>20</u>, 1112 (1952) and Phys. Rev. <u>82</u>, 327A (1952).
- R. H. Schwendeman and G. D. Jacobs, J. Chem. Phys. <u>36</u>, 1245 (1962).
- 33. R. H. Schwendeman and G. D. Jacobs (unpublished work).
- 34. J. Y. Beach and D. P. Stevenson, J. Am. Chem. Soc. <u>61</u>, 2643 (1939).

- 35. Mashio Yamaka, Bull. Chem. Soc., Japan, 27, 170 (1954).
- 36. R. Livingston, J. Chem. Phys. 20, 1170 (1952).
- 37. E. Scrocco, P. Bucci, and M. Maestro, J. Chim. Phys. <u>56</u>, 623 (1959).
- 38. K. E. Howlett, J. Chem. Soc., 1784 (1955).
- 39. J. D. Cox, H. S. Turner, and R. J. Warne, J. Chem. Soc., 3167 (1950).
- 40. M. J. Coon, J. Biol. Chem. <u>187</u>, 71 (1950).
- 41. M. J. Coon and S. Gurin, J. Biol. Chem. 180, 1159 (1949).
- 42. S. Heimel and A. S. Gordon, J. Am. Chem. Soc. <u>73</u>, 2942 (1951).
- 43. T. I. Crowell and G. L. Jones, Jr., J. Am. Chem. Soc. <u>73</u>, 3506 (1951).
- 44. R. H. Schwendeman, J. Mol. Spec. <u>6</u>, 301 (1961).
- 45. D. R. Lide, Jr., J. Chem. Phys. <u>33</u>, 1514 (1960).
- 46. V. W. Laurie, J. Chem. Phys. 34, 291 (1961).
- 47. V. W. Laurie and D. R. Herschbach, J. Chem. Phys. <u>37</u>, 1668 (1962).
- 48. D. R. Herschbach and V. W. Laurie, J. Chem. Phys. <u>37</u>, 1687 (1962).
- 49. D. R. Lide, Jr., and May Jen, NBS report 7711, Sept. 1962 (in press).
- 50. D. R. Lide, Jr., J. Chem. Phys. <u>33</u>, 1519 (1960).
- 51. Cyprian Flanagan and L. Pierce, J. Chem. Phys. (to be published).
- 52. D. R. Lide, Jr., and Daniel Christensen, J. Chem. Phys. <u>35</u>, 1374 (1961).
- 53. B. P. Dailey and C. H. Townes, J. Chem. Phys. <u>23</u>, 118 (1955).
- 54. B. P. Dailey, J. Chem. Phys. <u>33</u>, 1641 (1960).

- 55. T. P. Das and E. L. Hahn, <u>Nuclear Quadrupole Resonance</u> Spectroscopy, Academic Press, Inc., New York, 1958.
- 56. H. O. Hooper and P. J. Bray, J. Chem. Phys. <u>33</u>, 334 (1960).
- 57. R. Livingston, J. Chem. Phys. 19, 1434 (1951).
- 58. R. Livingston, J. Phys. Chem. 57, 496 (1953).
- 59. G. D. Jacobs, Thesis, Michigan State University, 1961.
- 60. W. H. Flygare and W. D. Gwinn, J. Chem. Phys. <u>36</u>, 787 (1962).
- 61. May Jen and D. R. Lide, Jr., J. Chem. Phys. <u>36</u>, 2525 (1962).
- 62. L. S. Bartell, L. O. Brockway, and R. H. Schwendeman, J. Chem. Phys. <u>23</u>, 1854 (1955).
- 63. R. H. Schwendeman and G. D. Jacobs, J. Chem. Phys. <u>36</u>, 1251 (1962).
- 64. B. P. Dailey, J. M. Mays, and C. H. Townes, Phys. Rev. <u>76</u>, 1362, 472A (1949).
- 65. J. Sheridan and W. Gordy, J. Chem. Phys. 19, 965 (1951).
- 66. W. Gordy, J. W. Simmons, and A. G. Smith, Phys. Rev. <u>74</u>, 243 (1947).
- 67. D. R. Lide, Jr., and D. E. Mann, J. Chem. Phys. <u>29</u>, 914 (1958).
- 68. R. W. Kilb, Thesis, Harvard University, 1956.
- 69. R. W. Kilb and L. Pierce, J. Chem. Phys. 27, 108 (1957).
- 70. L. Pierce, J. Chem. Phys. 31, 547 (1959).
- 71. P. H. Kasai and R. J. Meyers, J. Chem. Phys. <u>30</u>, 1096 (1959).
- 72. T. Kojima and T. Nishikawa, J. Phys. Soc., Japan, <u>12</u>, 680 (1957).
- 73. J. A. Kraitchman and B. P. Dailey, J. Chem. Phys. <u>22</u>, 1477 (1954).

- 74. R. S. Wagner, B. P. Dailey, and N. Solimene, J. Chem. Phys. <u>26</u>, 1593 (1957).
- 75. J. W. Simmons and W. E. Anderson, Phys. Rev. <u>80</u>, 338 (1950).

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