

ABSORPTION OF MICROWAVES BY MOLECULES

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by

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Saskatoon, Saskatchewan

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UNIVERSITY OF SASKATCHEWAN

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"ABSORPTION OF MICROWAVES BY MOLECULES"

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ABSTRACT

This thesis describes the construction of microwave spectrometers with a frequency range of 10 percent in the 4mm. and 2mm. regions.

Rotational absorption lines were observed in carbonyl sulfide, formaldehyde and chloroform. Variations in line width were observed with changes in temperature and pressure. Changes in absorption intensity were observed for changes in temperature, pressure, microwave power, microwave frequency and absorbing material.

The rate of proliferation of the bacterial cells *Escherichia coli* was observed during irradiation with various microwave frequencies. An interaction was observed between the microwave field and the cell materials and this interaction appeared to be frequency dependent.

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## 1. INTRODUCTION

### 1.1 Purpose of Absorption Spectroscopy

Absorption spectroscopy is one of the many methods used to gain information about the structure of molecules and atoms. The technique is based on the idea that these exist in discrete energy configurations and that transitions from one energy level to another occur in several ways one of which is a result of excitation due to absorption of electromagnetic radiation. A given molecule or atom will absorb only certain frequencies of electromagnetic radiation which are determined by the energy differences between levels involved in possible transitions. Energy change and frequency absorbed in a transition are related by the following equation:

$$h\nu = E_1 - E_2$$

where:  $h$  is Planck's constant

$\nu$  is the frequency of radiation

$E_1$  and  $E_2$  are the energy levels of a molecule or atom before and after the transition.

Experimental spectroscopic data can be used to quantitatively determine size, shape, flexibility, electronic arrangement and nuclear arrangement of molecules. In the study of molecules, absorption spectroscopy is preferable because the high excitation required to obtain emission spectra will often destroy the molecule. Electronic transitions occur as a result of absorption of visible and ultraviolet light and thus will give information about possible changes in the molecular orbitals of electrons. The vibrational energy transitions produce spectra in the infrared region allowing information to be obtained about the bending and stretching energies associated with the interatomic bonds

of a molecule. Transitions in the energy levels associated with the rotation of atoms or chemical groups absorb in the high microwave region and thus may be used to indicate possible changes in the energy of total molecular rotation. Energy levels associated with electron spin resonance (E.S.R.) lead to absorption in the microwave region but these energies depend on electronic interaction with an applied magnetic field. A similar phenomenon, nuclear magnetic resonance (N.M.R.) gives rise to spectra in the very high frequency of V.H.F. radio region and is dependent on nuclear interaction with an environmental magnetic field. A more thorough discussion of the fields of absorption spectroscopy may be found in Appendix A.

Electron spin resonance and nuclear magnetic resonance have been little used in biological investigations but ultraviolet and infrared spectroscopy have been employed extensively particularly in biochemical and microbiological research. This project was designed to ascertain the value of microwave spectroscopy in these fields. The absorption of microwaves was expected to cause low energy transitions in the bending and twisting modes of large functional groups and thus provide information about the role of these energies in biological processes.

## 1.2 Project History and Aims

Preliminary tests were carried out by Dr. S. J. Webb and Prof. A. Wacker as early as 1962. They constructed an absorption cell using waveguide horns to direct the microwaves through it. The horns were spaced about two and one-half feet apart with the result that a large portion of the microwave power did not reach the detector. In addition, the use of a harmonic generator introduced a conversion loss of more than twenty decibels while diminished output power due to klystron

ageing made detection difficult. The problem of low signal strength was partially resolved by using a waveguide absorption cell and the signal strength was improved greatly by discarding the harmonic generator, using the lower frequencies generated directly by the klystron.

The aim of this project, therefore, was to improve the construction of the spectrometer, observe the spectra of some simple molecules and observe any interaction between these microwaves and biological materials.

2. THEORY OF ROTATIONAL TRANSITION SPECTRA

2.1 Rotational Energy Levels

2.1.1 Linear molecules

Rotating molecules can best be described by a mixture of classical and quantum mechanics. The basic equation in wave mechanics is that of Schrödinger. This is the first equation appearing below in one dimensional form.<sup>12</sup> The second equation is the time independent Schrödinger equation in spherical co-ordinates which applies to a rotating mass with a fixed pivot, ignoring translation of the center of mass.<sup>12</sup>

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}$$

$$-\frac{\hbar^2}{2m} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) \right\} + V(r)\psi = E\psi$$

where:  $\hbar$  is Planck's constant divided by  $2\pi$

$m$  is the mass of the rotating particle

$r$  is the radius; the distance from the particle to the pivot

$E$  is the total energy of the particle (excluding rest energy)

$V$  is the potential energy of the mass, a function of  $r$

$\Psi(x,t)$  is the wave function of the particle

$$\Psi(r,\phi,\theta,t) = \psi(r,\phi,\theta) \Phi(t)$$

$$\Phi(t) = e^{-iEt/\hbar}$$

$\psi(r,\phi,\theta)$  is the time independent wave function.

If the radius of the rotating mass is constant, then there will be no

vibrational stretching energy, some of the terms in the second equation become zero and the constant stretching energy may be subtracted to obtain an equation involving rotational energy only.

$$\frac{1}{\sin^2 \theta} \cdot \frac{\partial^2 \psi}{\partial \theta^2} + \frac{1}{\sin \theta} \cdot \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \psi}{\partial \theta} + \frac{8\pi^2 m r^2 E_{\text{rot}}}{h^2} \psi = 0$$

where:  $h$  is Planck's constant.

Physically significant solutions of this equation are possible for only certain values of energy. With each energy there is a corresponding wave function. Solutions are as follows:<sup>9</sup>

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

$$\psi_J = N_{JM} e^{iM\theta} P_J^M(\cos \theta)$$

where:  $J$  is the rotational quantum number.

$N_{JM}$  is a normalizing factor to make the all space integral of the probability density,  $\psi \cdot \psi^*$ , unity.

$P_J^M$  is the associated Legendre function.

$M$  is the magnetic quantum number and takes  $2J+1$  integral values as the angular momentum vector takes  $2J+1$  directions.

The remainder of this discussion will use the classical approach although only the energy solution of the above equation will be used. Linear molecules may be studied as a single mass rotating about the molecular center of mass. The classical moment of inertia is:

$$I_A = I_B = \sum_i m_i r_i^2$$

$$I_C = 0$$

where:  $m_i$  is the mass of each particle or atom in the molecule

$r_i$  is the radius of each atom from the center of mass

Rotation about C axis corresponds to electronic transitions.

The center of mass is defined such that

$$0 = m_1 x_1 + m_2 x_2 + m_3 x_3 \dots$$

where the center of mass is at the origin. Classically, energy and momentum are related by the equation:

$$E = \frac{P^2}{2I} = \frac{1}{2} I \omega^2$$

so that

$$P = \frac{h}{2\pi} \sqrt{J(J+1)} \quad J = 1, 2, 3, \dots$$

The total angular momentum,  $P$ , is quantized and the directional component of  $P$  is also quantized.

$$P_Z = \frac{h}{2\pi} M \quad M = -J, -(J-1), \dots, J, \dots, J-1, J$$

Since the rotational angular momentum can take  $2J + 1$  different directions, rotational energy levels are  $2J + 1$  degenerate. This degeneracy may be removed by applying a magnetic field and so  $M$  is called the magnetic quantum number. Selection rules are derived from Schrodinger's equation, and the probability density,  $\psi \cdot \psi^*$ . Selection rules for rotational

transitions are:

$$\Delta J = \pm 1 \quad \text{and} \quad \Delta M = 0, \pm 1$$

Energy levels can be determined by spectroscopy because it is possible to equate energy change to the frequency of the photon which would cause a transition involving that energy change. Energy levels are expressed in terms of the frequency required to cause a transition from the zero rotational energy, (or ground state), to that energy level even though that transition may be spectroscopically prohibited. The frequency of an electromagnetic wave is found by measuring the wavelength and dividing it into the speed of light. Since the speed of light cannot be measured as accurately as wavelength, spectroscopists specify energy and energy change in terms of wavelength. The most common unit is  $\text{cm}^{-1}$ , or reciprocal wavelength, which when multiplied by the speed of light, gives the frequency.

$$E = h\nu \quad \nu = \frac{c}{\lambda} \quad E = \frac{hc}{\lambda} \quad \frac{E}{hc} = \lambda^{-1} = \bar{\nu} \quad \nu = c\bar{\nu}$$

Thus

$$\frac{E_J}{hc} = \bar{\nu}_J = \frac{h}{8\pi^2 Ic} J(J+1)$$

One of the constants which appears in all expressions of rotational energy is frequently substituted as follows:

$$\frac{E_J}{hc} = \bar{\nu}_J = BJ(J+1)\text{cm}^{-1} \quad B = \frac{h}{8\pi^2 cI}$$



According to Bohr's postulate<sup>12</sup> the frequency of absorption in the transition  $\Delta J = +1$  will be as follows:

$$E_{J_{\text{upper}}} - E_{J_{\text{lower}}} = h\nu$$

and

$$\begin{aligned} \bar{\nu} &= B(J+1)(J+2) - B(J)(J+1) \\ &= 2B(J+1) \end{aligned}$$

where  $J$  is the quantum number of the lower energy level.

Thus for a rigid rotor we would expect absorption at frequencies  $2B$ ,  $4B$ ,  $6B$ ,  $8B$ , ... Energy levels and possible transitions are shown on the next page.

So far the discussion has considered molecules as rigid rotors where the internuclear distance is constant. Real molecules are non-rigid. The potential energy of the bond increases as the bond is stretched from its equilibrium position. The potential energy curve for stretching and compression is illustrated in Appendix A. Centrifugal force tends to stretch the inter-atomic bond and increase the moment of inertia of the molecule, this decreases the rotational energy of the molecule for a given quantum number. When the Schrodinger wave equation is applied to a non-rigid rotor, the energy levels are found to be:<sup>4</sup>

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2$$

THE CHANGE IN ROTATIONAL ENERGY LEVELS AND ROTATIONAL SPECTRUM  
 WHEN PASSING FROM A RIGID TO A NON-RIGID DIATOMIC MOLECULE.  
 LEVELS ON THE RIGHT CALCULATED USING  $D=10^{-3}B$ .

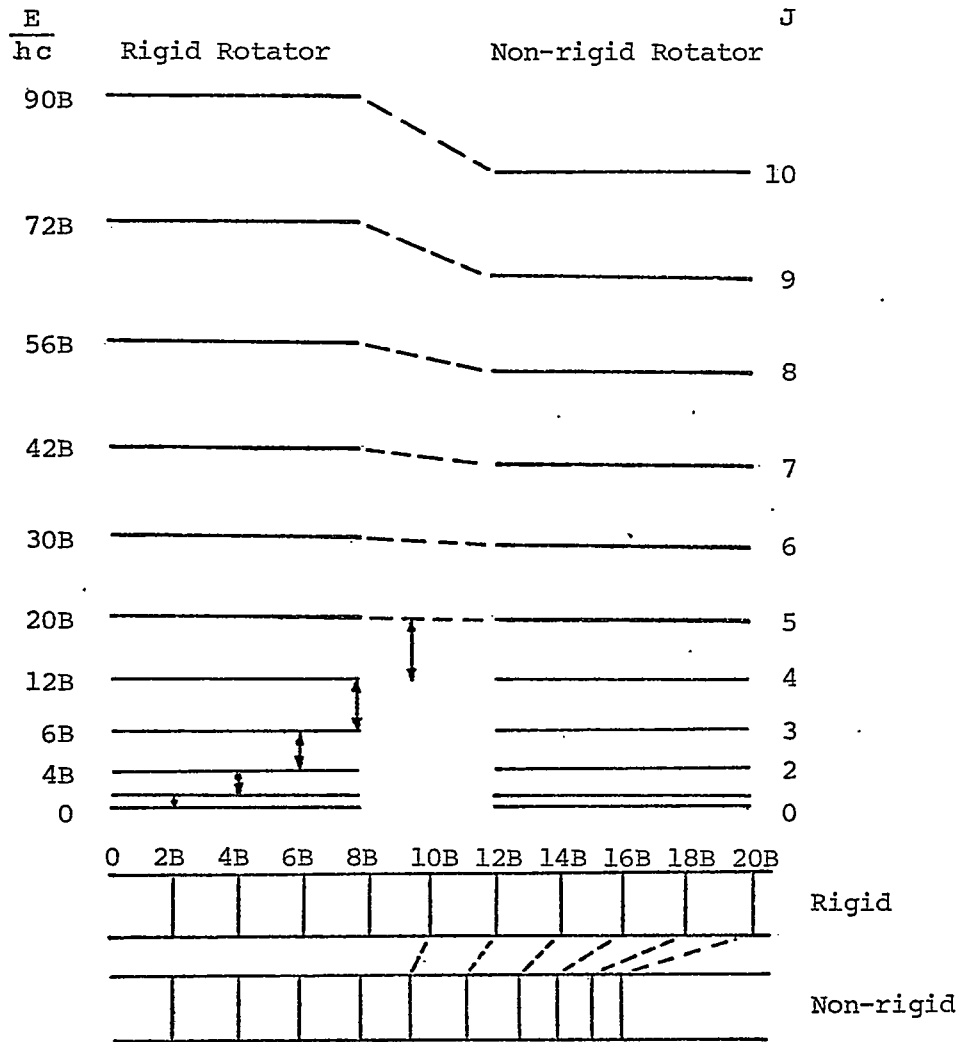


Figure 2.1

$$\frac{E_J}{hc} = BJ(J + 1) - DJ^2(J + 1)^2$$

$$\frac{E_{J_{\text{upper}}}}{hc} - \frac{E_{J_{\text{lower}}}}{hc} = 2B(J + 1) - 4D(J + 1)^3$$

where:  $k$  is the force constant of the inter-atomic bond of a diatomic molecule.

$r$  is the inter-nuclear distance of the diatomic molecule.

The small centrifugal distortion correction term,  $D$ , is based on the simple harmonic oscillator model. More terms are required to describe the real molecule but they are extremely small and the first two terms are generally adequate to describe a spectral line. The term  $D$  may be expressed in terms of  $B$  and  $w$ :

$$D = \frac{4B^3}{w^2} \quad \text{for diatomic molecules}$$

and

$$D = 4B^3 \cdot \frac{\xi_1^2}{\omega_1^2} + \frac{\xi_3^2}{\omega_3^2} \quad \text{for triatomic linear molecules.}$$

where:  $w$  is the vibrational frequency of an inter-atomic bond .

$\xi$  is a weighting factor.

In addition to centrifugal stretching of non-rigid rotors, vibrational motion can increase the average moment of inertia. During simple harmonic vibration the time average of the radius will be the same as the equilibrium radius, however, the time average of the radius squared will be larger than the square of the equilibrium

radius

$$\frac{\int_0^T r dt}{T} = \frac{\int_0^{2\pi} (r_0 + \delta r \cos \theta) d\theta}{2\pi} = r_0$$

$$\begin{aligned} \frac{\int_0^T r^2 dt}{T} &= \frac{\int_0^{2\pi} (r_0^2 + 2r_0 \delta r \cos \theta + \delta r^2 \cos^2 \theta) d\theta}{2\pi} \\ &= r_0^2 + \frac{\delta r^2}{2} \end{aligned}$$

The moment of inertia, which is directly proportional to the radius squared, will increase as the vibrational quantum number increases. Thus,  $B_v$  is slightly dependent on the vibrational quantum number,  $v$ .

$$B_v = B_e - \alpha(v + 1/2)$$

$$B_0 = B_e - \alpha(0 + 1/2)$$

where:  $B_0$  is the value of  $B$  for vibrational quantum number 0

$B_e$  is the extrapolated value for the equilibrium inter-nuclear distance.

$\alpha$  is a small positive constant.

Carbonyl sulfide or OCS is a linear triatomic molecule which is often used in microwave spectroscopy. It has a relatively strong permanent dipole moment of 0.71 Debye and has a high coefficient of absorption. The molecule is linear and all three atoms have zero nuclear spin, therefore the spectrum is very simple and has no nuclear effect hyperfine structure. The center of rotation of the molecule is between the sulfur and carbon atoms and its position can be determined,

enabling calculation of the moment of inertia. The inter-atomic distances given here were determined using microwave spectroscopy.<sup>6,4</sup> The carbon-oxygen distance is an average of two values. The isotopic weights of the most abundant form,  $O^{16}C^{12}S^{32}$ , will be used.<sup>13</sup>

$R_{CO}$	$1.163 \pm 0.001 \text{ \AA}$	A.Wt. Carbon	12.00386
$R_{CS}$	$1.559 \pm 0.001 \text{ \AA}$	Oxygen	16.00000
		Sulfure	32.98085

$$(R_{CS} - R_C)(A.Wt. Sulfur) = (R_{CO} + R_C)(A.Wt. Oxygen) + R_C(A.Wt. Carbon)$$

$$(1.559 - R_C)(31.981) = (1.163 + R_C)(16.000) + R_C(12.004)$$

$$R_C(59.985) = 31.250$$

$$R_C = .5210 \text{ \AA} \quad R_O = 1.684 \text{ \AA} \quad R_S = 1.038 \text{ \AA}$$

The moment of inertia about the linear axis will be zero and the moment of inertia about each of the other two axes will be the same.

$$I_A = 0, \quad I_B = I_C$$

$$I_B = \sum_i m_i r_i^2$$

$$= (16.000)(1.684)^2 + (1.2004)(0.521)^2 + (31.981)(1.038)^2$$

$$= 45.374 \quad 3.259 \quad 34.458$$

$$= 83.090 \text{ amu. \AA}^2 \quad \text{where: } \text{\AA} = 10^{-8} \text{ cm.}$$

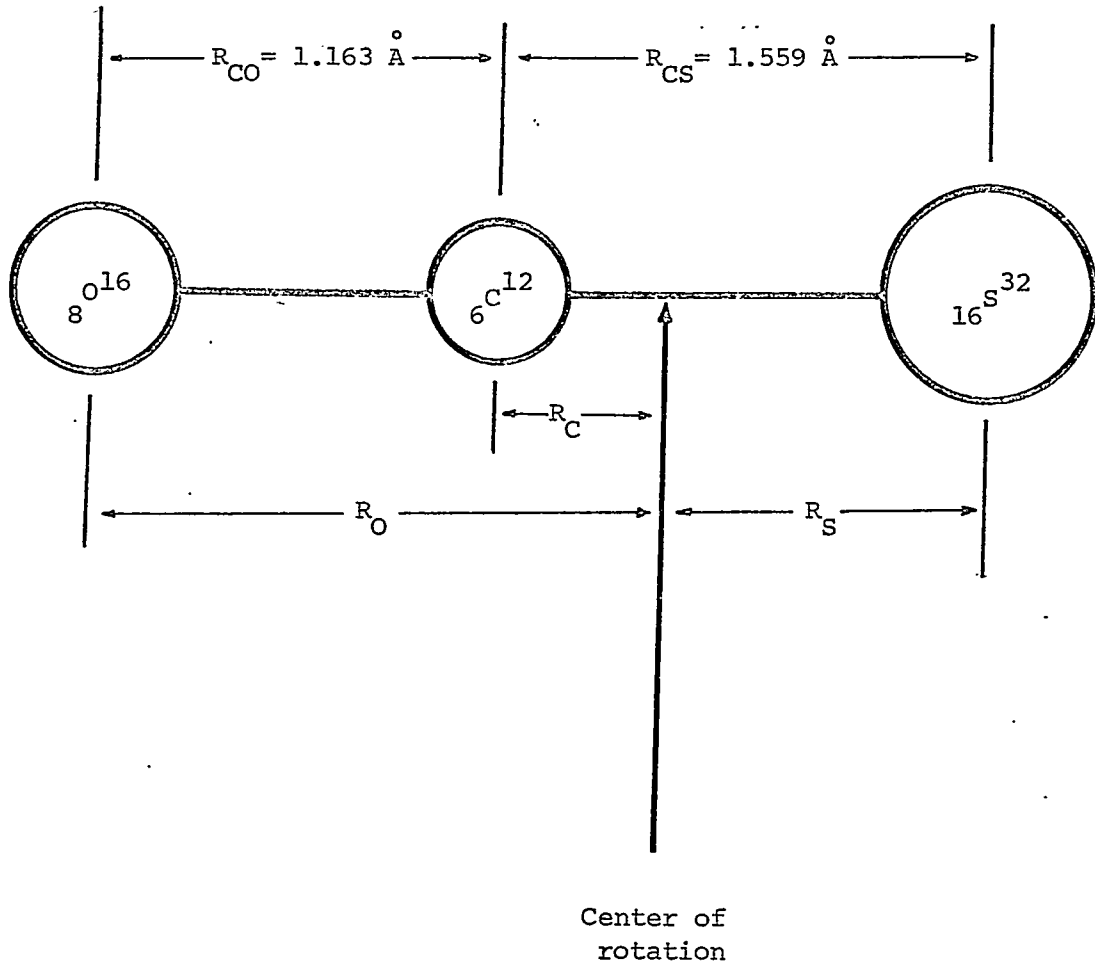
$$= 137.929 \times 10^{-40} \text{ gm.cm.}^2 \quad \text{amu.} = 1.6600 \times 10^{-24} \text{ gm.}$$

The rotational constant may be calculated from the moment of inertia

$$B = \frac{h}{8\pi^2 cI}$$

STRUCTURE OF THE CARBONYL SULFIDE MOLECULE

Figure 2.2



$$B = \frac{6.6238 \times 10^{-27} \text{ sec.gm. cm.}^2/\text{sec.}^2}{8\pi^2 (2.9979 \times 10^{10}) (137.929 \times 10^{-40}) \text{ gm.cm.}^3/\text{sec.}}$$

$$B = 0.20288 \text{ cm.}^{-1} = 6,082.2 \text{ Mc}$$

where:  $h = 6.6238 \times 10^{-27}$  joule.sec.

$c = 2.99790 \times 10^{10}$  cm./sec.

If  $O^{16}C^{12}S^{32}$  were a rigid rotor it would display spectra at wave numbers  $2B, 4B, 6B, \dots$  and the frequencies of E-M absorption would be:

Transition $J \rightarrow J + 1$	Wave Number ↓	Frequency GHz
$0 \rightarrow 1$	0.4058	12.164
$1 \rightarrow 2$	0.8115	24.329
$2 \rightarrow 3$	1.2173	36.493
$3 \rightarrow 4$	1.6231	48.657
$4 \rightarrow 5$	2.0288	60.822
$5 \rightarrow 6$	2.4346	72.986
$11 \rightarrow 12$	4.8692	145.972

Since OCS is not a rigid molecule and deviates from the rigid rotor approximation, observed spectra will differ slightly from those listed above and the centrifugal stretching factor, D, introduced previously, will be required to explain the experimental results.

About 4% of all OCS will be of the form  $O^{16}C^{12}S^{34}$  which has a rotational constant of  $B = 5,932.8$  GHz.

### 2.1.2 Symmetric top molecules

Symmetric top rotors display relatively simple spectra although they are slightly more complex than linear rotors. The moment of inertia about each axis is finite and two moments of inertia are equal. The total rotational energy can be expressed as the sum of the rotational energies about each axis.

$$I_A = I_B \neq I_C \qquad I_A = 0$$
$$E_{\text{Rot.}} = \frac{P_A^2}{2I_A} + \frac{P_B^2}{2I_B} + \frac{P_C^2}{2I_C}$$

The total angular momentum is the vector sum of the angular momenta about the three axes. This sum is quantized as in linear molecules and is given the quantum number J.

$$P_J^2 = P_A^2 + P_B^2 + P_C^2$$
$$P_J = \sqrt{J(J+1)} \frac{h}{2\pi}$$
$$J = 0, 1, 2, \dots$$

The angular momentum about the unique axis, A, is assumed to be quantized and is given the quantum number K.

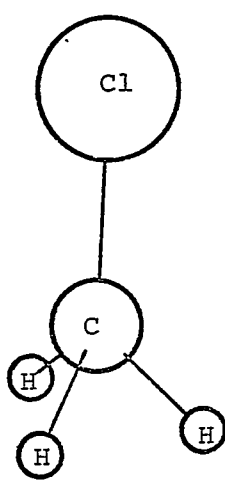
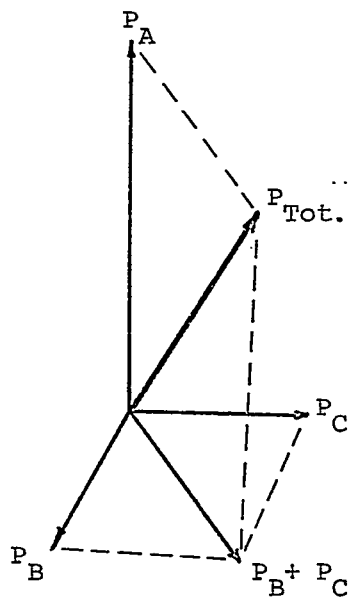
$$P_A = K \frac{h}{2\pi}$$
$$K = 0, \pm 1, \pm 2, \pm 3, \dots, \pm J$$

Since the moments of inertia about the B and C axes are equal, the vector sum of angular momentum is treated as a unit.

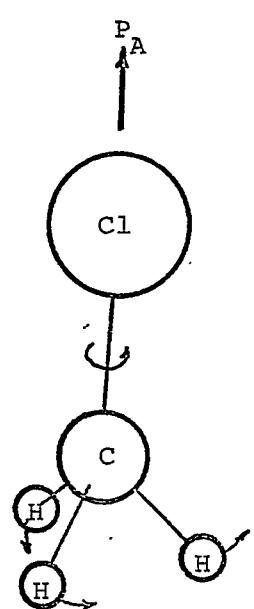


ANGULAR MOMENTUM VECTORS OF A SYMMETRIC TOP MOLECULE

Figure 2.3



$K = 0$



$K > 0$

$$\begin{aligned}
 P_B^2 + P_C^2 &= P_T^2 - P_A^2 \\
 &= J(J + 1) \left(\frac{h}{2\pi}\right)^2 - K^2 \left(\frac{h}{2\pi}\right)^2
 \end{aligned}$$

Thus the rotational energy of the molecule may be expressed:

$$\begin{aligned}
 E_{JK} &= K^2 \frac{h^2}{8\pi^2 I_A} + J(J + 1) \frac{h^2}{8\pi^2 I_B} - K^2 \frac{h^2}{8\pi^2 I_B} \text{ erg} \\
 \bar{\nu}_{JK} &= \frac{h}{8\pi^2 c I_B} (J)(J + 1) + \left(\frac{h}{8\pi^2 I_A} - \frac{h}{8\pi^2 c I_B}\right) K^2 \text{ cm}^{-1} \\
 &= B J(J + 1) + (A - B) K^2
 \end{aligned}$$

Where A and B are rotational constants similar to that for a linear molecule. Since rotation about the unique axis can lead to no change in the direction of the permanent dipole moment, changes in K quantum number are spectroscopically forbidden. The selection rules for rotational transitions are:

$$\Delta J = \pm 1$$

$$\Delta K = 0$$

and the spectrum will be independent of K for a rigid rotor. The rotational spectrum would be described as follows:

$$\begin{aligned}
 \bar{\nu}_{J \rightarrow J+1} &= 2B(J + 1) \text{ cm}^{-1} \\
 K &\rightarrow K
 \end{aligned}$$

A real molecule is not actually rigid, consequently, there will be some deformation due to centrifugal force. To correct for this, small constants are introduced,  $D_K$ , for distortion due to rotation about the unique axis,  $D_J$ , for stretching due to total molecular

rotation and  $D_{JK}$  for interaction between the two motions.

$$\frac{E_{JK}}{hc} = B J(J+1) + (A-B)K^2 - (D_J J^2 (J+1)^2) - (D_{JK} J(J+1)K^2) - D_K K^4 \text{ cm}^{-1}$$

$$\bar{\nu}_{J \rightarrow J+1, K \rightarrow K} = 2B(J+1) - 4D_J (J+1)^3 - 2D_{JK} K^2 (J+1) \text{ cm}^{-1}$$

All constants are positive except  $D_{JK}$  which may be negative or positive depending on the shape of the molecule.<sup>9</sup>

Methyl tri-chloride, or chloroform, is a symmetric top molecule. The permanent dipole moment lies along the carbon-hydrogen unique axis and has a strength of 1.87 Debye.<sup>9</sup> The center of rotation will be on the carbon-hydrogen axis and its location is determined from the following information:<sup>6,9,18</sup>

$$R_{CH} = 1.073 \pm 0.001 \text{ \AA}$$

$$\theta_{Cl_C Cl} = 110.4^\circ \pm 0.05^\circ$$

$$R_{CCl} = 1.767 \pm 0.001 \text{ \AA}$$

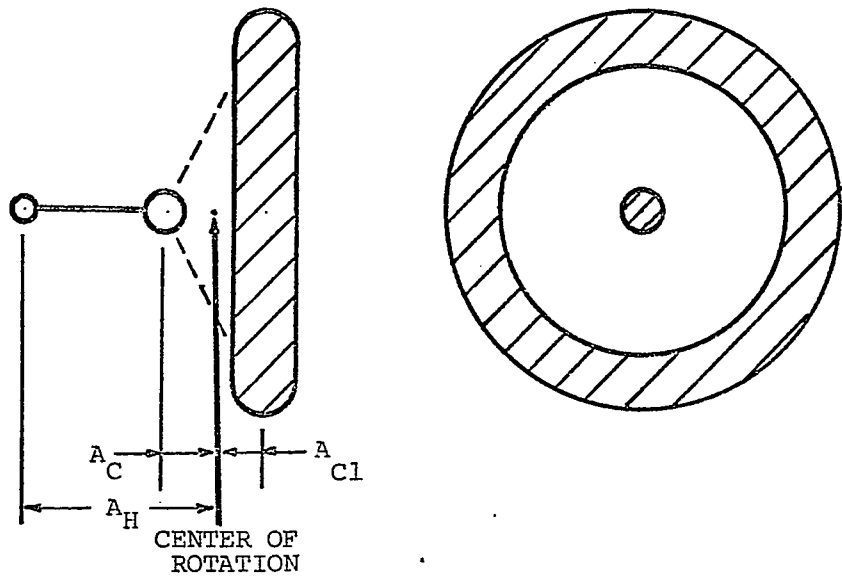
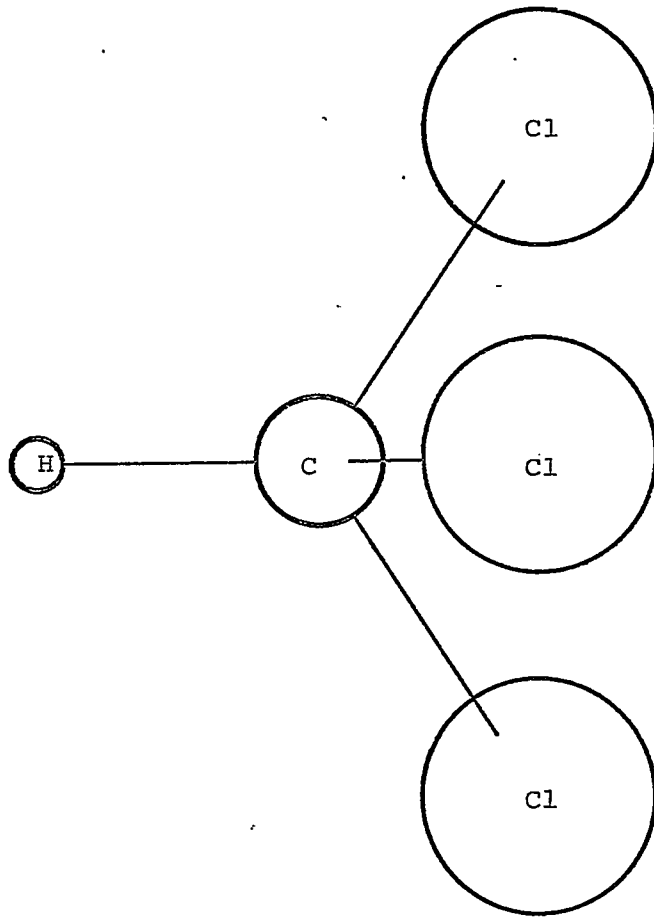
$$\theta_{H_C Cl} = 108.6^\circ$$

Isotopic weights and abundances of the elements involved were obtained from the HANDBOOK OF CHEMISTRY AND PHYSICS.<sup>13</sup>

Element	Atomic Weight	Abundance
Cl <sup>35</sup>	34.97867	75.4%
Cl <sup>37</sup>	36.99750	24.0%
C <sup>12</sup>	12.00386	98.891%
C <sup>13</sup>	13.00756	1.108%
H <sup>1</sup>	1.00813	99.98%

STRUCTURE OF THE CHLOROFORM MOLECULE

Figure 2.4



$$A_H = A_C - 1.073$$

$$A_{Cl} = 1.767 \cos (180^\circ - 108.6^\circ) + A_C$$

$$A_H (\text{A.Wt. Hydrogen}) + A_C (\text{A.Wt. Carbon}) + A_{Cl} (3) (\text{A.Wt. Chlorine}) = 0$$

The most common forms of chloroform are  $C^{12}H^{1}Cl_3^{35}$  and  $C^{12}H^{1}Cl_2^{37}Cl^{35}$

which will appear in almost equal proportions if the natural isotopic ratio of chlorine is present. The heavier isotope will make the second form a slightly asymmetric top. This form can be treated as a symmetric top as the deviation is small.

$$0 = (A_C - 1.073) (1.008) + A_C (12.004) + (104.937) (A_C + (1.767) (.31786))$$

$$0 = 58.939 - 1.082 + A_C (12.004 + 1.008 + 104.937)$$

$$0 = 57.857 + A_C (117.949)$$

$$A_C = 0.49052 \text{ \AA} \quad A_H = -1.563 \text{ \AA} \quad A_{Cl} = 0.0711 \text{ \AA}$$

When the center of rotation is known the moments of inertia may be calculated:

$$\begin{aligned} I_A &= 3 (\text{A.Wt. Chlorine}) (1.767 \sin 108.6^\circ)^2 \\ &= 104.936 (1.675)^2 \\ &= 294.41 \text{ amu \AA}^2 \quad \text{amu} = 1.6600 \times 10^{-24} \text{ gm.} \\ &= 488.72 \times 10^{-40} \text{ gm.cm.}^2 \quad \text{\AA} = 10^{-8} \text{ cm.} \end{aligned}$$

In calculation of the moment of inertia  $I_B$  or  $I_C$ , the three chlorine atoms will have no definite radius from the axis of rotation if there is any rotation about the A axis. During rotation about the A axis the time average of the chlorine atom positions will be in the shape of a ring, radius  $1.767 \sin 108.6^\circ$ . This average position will be used during the calculation of  $I_B$ .

$$I_B = A.Wt._C (A_C)^2 + A.Wt._H (A_H)^2 + \frac{3A.Wt._{Cl}}{2\pi} \int_0^{2\pi} [A_{Cl}^2 + (\sin \theta \cdot 1.767 \sin 108.6^\circ)^2] d\theta$$

$$I_B = 12.004(0.491)^2 + 1.008(1.565)^2 + 3Wt._{Cl} (A_{Cl})^2$$

$$+ \frac{104.936}{2\pi} (1.767)^2 (0.94777)^2 \int_0^{2\pi} \sin^2 \theta d\theta$$

$$I_B = 2.894 + 2.469 + 104.936(0.0711)^2 + \frac{52.468}{\pi} (2.807) \left[ \frac{\theta}{2} - \frac{\sin 2\theta}{4} \right]_0^{2\pi}$$

$$= 5.363 + 104.937(0.00508) + \frac{52.468}{\pi} (2.805) (\pi)$$

$$= 5.363 + 0.531 + 147.170$$

$$= 153.064 \text{ amu } \text{Å}^2$$

$$= 254.086 \times 10^{-40} \text{ gm.cm.}^2$$

The rotational constants for chloroform  $C^{12}H^1Cl_3^{35}$  are calculated as follows:

$$A = \frac{h}{8\pi^2 c I_A} = 0.05729 \text{ cm.}^{-1}$$

$$B = \frac{h}{8\pi^2 c I_B} = 0.11002 \text{ cm.}^{-1}$$

If the chloroform molecule were a rigid rotor, it would display spectra at wave numbers 2B, 4B, 6B, 8B, ... and the frequencies of electromagnetic absorption would be:

TRANSITION J→J+1 K→K	WAVE NUMBER $\bar{\nu}$	FREQUENCY GHZ
0→1	0.22003	6.596
-	-	-
9→10	2.2003	65.962
10→11	2.42033	72.559
11→12	2.6404	79.155

Chloroform is not a rigid molecule and absorption frequencies will deviate very slightly from those calculated. The spectra will have fine structure as the molecule will stretch a different amount with each different quantum No., K. This stretching will change the rotational constant B. Chlorine has a nuclear spin of 5/2 and has an electric quadrupole moment. The nuclear spin of the chlorine atoms will interact slightly with the molecular rotational spin and cause slight changes in the rotational energy with different orientations of the two spins. These hyperfine splitting effects are small and the spectra cannot be resolved in a gas pressure of greater than 0.1 mm. of mercury.<sup>17</sup>

The isotopic combination  $C^{12}H^1Cl^{37}Cl_2^{35}$  will have slightly different spectra than the previous form because the moment of inertia will be larger. The spectral deviation of this second form can be calculated quite accurately from the following considerations. Ninety-six percent of the contribution to the moment of inertia comes from the chlorine atoms and their total weight would be increased by 1.94% with the substitution of the next heavier isotope of chlorine. Thus the spectra of  $C^{12}H^1Cl^{37}Cl_2^{35}$  will be 1.86% lower in frequency than that of  $C^{12}H^1Cl_3^{35}$ . At the frequency of the experimental equipment, 72 GHz, this would amount to 1.35 GHz.

### 2.1.3 Asymmetric top molecules

Asymmetric top rotors display very complex spectra in which the absorption frequencies are not in arithmetic multiples. The moments of inertia about three molecular axes are unequal and the total rotational energy, as in classical mechanics, is the sum of the rotational energies about each axis.

$$I_A \neq I_B \neq I_C$$

$$E_{\text{Rot.}} = \frac{P_A^2}{2I_A} + \frac{P_B^2}{2I_B} + \frac{P_C^2}{2I_C}$$

The total angular momentum is quantized as in linear and symmetric top molecules but no component of this momentum is quantized as in symmetric molecules. The energy levels are discussed at length by Barrow<sup>6</sup>, Gordy et al.<sup>9</sup>, and Townes and Schawlow<sup>21</sup>. The energy levels of the asymmetric top rotor are correlated with those of a symmetric rotor. It should be noted that while a selection rule  $\Delta K = 0$  exists for symmetric rotors, there is no equivalent rule for asymmetric rotors, thus many more transitions are allowed spectroscopically. Some energy levels for asymmetric rotors are<sup>9</sup> as follows:

$J_K$ (k=-1) $K$ (k=+1)	Energy
0 <sub>00</sub>	0
1 <sub>10</sub>	A+B
1 <sub>11</sub>	A+C
1 <sub>01</sub>	B+C
2 <sub>20</sub>	$2A+2B+2C+2\sqrt{(B-C)^2 + (A-C)(A-B)}$
2 <sub>21</sub>	4A+B+C
2 <sub>11</sub>	A+4B+C
2 <sub>12</sub>	A+B+4C
2 <sub>02</sub>	$2A+2B+2C-2\sqrt{(B-C)^2 + (A-C)(A-B)}$

Formaldehyde, or H<sub>2</sub>CO, is an asymmetric top molecule. By combining the most abundant atomic isotopes of carbon, hydrogen and oxygen we can



see that over 98% of formaldehyde will be in the form  $\text{H}_2^{12}\text{C}^{16}\text{O}$ . As previously shown, rotational constants A, B, and C can be determined from the atomic weights and the following inter-atomic bond angles and distances.<sup>20</sup>

$$R_{\text{CH}} = 1.12 \pm 0.01 \text{ \AA} \qquad \theta_{\text{HCH}} = 118^\circ \pm 2^\circ$$

$$R_{\text{CO}} = 1.21 \pm 0.01 \text{ \AA}$$

These distances are not highly accurate and the rotational constants calculated from them will not be as accurate as those obtained from spectroscopy. Rotational constants determined from spectroscopy are:<sup>20</sup>

$$A = 282.106 \text{ GHz} \qquad B = 38.834 \text{ GHz} \qquad C = 34.004 \text{ GHz}$$

$$= 9.4100 \text{ cm.}^{-1} \qquad = 1.2955 \text{ cm.}^{-1} \qquad = 1.1343 \text{ cm.}^{-1}$$

Thus some of the lower frequency transition spectra will occur as follows:

TRANSITION	WAVE NUMBER	FREQUENCY
$0_{00} \ 1_{01}$	B+C	72.828
$0_{00} \ 1_{11}$	A+C	316.110
$0_{00} \ 1_{10}$	A+B	320.940
$1_{11} \ 2_{12}$	B+3C	140.836
$1_{10} \ 2_{11}$	3B+C	150.496
$2_{12} \ 2_{11}$	3B-3C	14.520

## 2.2 Factors Affecting Intensity of Absorption

### 2.2.1 Population of energy states

The intensity of an absorption line will be directly dependent on the number of molecules in the lower energy state of the transition

being observed. In microwave spectroscopy transitions occur between a given vibrational and rotational state to the same vibrational state and a different rotational state. Vibrational energies are high compared to  $kT$  at room temperature and according to the Boltzmann distribution, most molecular species will have 99% of the population in the ground vibrational state. Temperature variations will have little effect on the intensities of rotational transitions involving the ground vibrational state. Rotational energies are of the same order of magnitude as  $kT$  at room temperature. Thus the molecular population will be scattered through the rotational energy levels and the number in each energy position will be determined by Boltzmann distribution. Each rotational energy level is degenerate and has  $2J+1$  positions. The population of each level varies widely with temperature.

The population of the rotational and vibrational states may be expressed mathematically.

$$N_r = N_0 (2J+1) e^{-E_r/kT} = N_0 (2J+1) e^{-hBJ(J+1)/kT}$$

$$N_0 = \frac{N}{\sum_J (2J+1) e^{-E_r/kT}}$$

Where  $N_r$  is the number of molecules in a given rotational state and  $N_0$  is the number in the ground state and  $N$  is the total number of molecules in the given volume. These equations neglect degeneracies due to the internal quantum number  $K$ .<sup>9,21</sup>

$$N_v = N_0 g_v e^{-E_v/kT}$$

Where  $g_v$  is the number of degeneracies of a particular vibrational state,  $E_v$  is the energy of that state and  $N_0$  is the number of

molecules in the vibrational ground state. This is given by:

$$N_0 = \frac{N}{\sum_v g_v e^{-E_v/kT}} \approx N$$

Thus the number of molecules in a given rotational and vibrational state can be expressed as:

$$N_{JV} = N \left(\frac{N_V}{N}\right) \left(\frac{N_J}{N}\right) = N F_V F_J$$

Where F represents the fraction of the population in a given vibrational or rotational state.

### 2.2.2 Electromagnetic interaction

The probability of interaction of electromagnetic radiation with an atom or molecule is related to the transition moment which is defined as:<sup>2,12,14</sup>

$$\mu_{x_{nm}} = \int \psi_n \psi_m^* \mu_x d\tau$$

Where  $\mu_x$  is the electric dipole moment in the x direction

$\psi_n$  and  $\psi_m$  are the wave functions of the two states involved in the transition.

The transition moments in the other two directions are similarly defined. The integral is over all space of the wave functions. The transition moment is zero for all transitions except  $J \rightarrow J \pm 1$  and  $M \rightarrow M$  or  $M \pm 1$ .

The Einstein coefficient of absorption, or the transition probability for absorption is  $B_{n \rightarrow m}$ . The coefficient for induced emission is equal to that for absorption. At microwave frequencies there is very little spontaneous emission the coef. of emission equals that of absorption. For isotropic radiation the Einstein coefficient is:<sup>2,9,14</sup>

$$B_{n \rightarrow m} = \frac{8\pi^3}{3h} (\mu_{x_{nm}}^2 + \mu_{y_{nm}}^2 + \mu_{z_{nm}}^2)$$

The Einstein coefficient for polarized radiation is:

$$B_{n \rightarrow m} = \frac{8\pi^2}{h} \left( \begin{array}{c} 2 \\ z_{nm} \end{array} \right)$$

The radiation in microwave spectroscopy is plane polarized in the z direction so that only that component of transition moment will interact with the field. For plane polarized microwave radiation only transitions with  $M \rightarrow M$  are possible.<sup>9</sup> Transitions with  $M \rightarrow M \pm 1$  are possible when some component of the microwave radiation is circularly polarized. Thus there are molecules in  $2J+1$  positions at the J level which will absorb and there are mol. in  $2J+1$  positions at the J+1 level which can emit radiation. The number of absorbing and emitting molecules will differ slightly due to Boltzman distribution.

$$N_J = N_0 (2J+1) e^{-hBJ(J+1)/kT}$$

$$N_{J+1} = N_0 (2J+1) e^{-hB(J+1)(J+2)/kT}$$

$$N_J - N_{J+1} = N_J \left( 1 - \frac{N_{J+1}}{N_J} \right) = N_J \left( 1 - e^{-hv/kT} \right) \approx N_J \frac{h 2B(J+1)}{kT}$$

Since  $hv = h2B(J+1) \ll kT$  at room temperature.

Thus the probability that a net absorption occurs in unit time and volume would be:

$$B_{J \rightarrow J+1} N_J \frac{h 2B(J+1)}{kT} \rho$$

Where  $\rho$  is the radiation density or energy per unit volume. If each absorption requires energy  $hv$  then the change in energy density per second would be:

$$\frac{\delta \rho}{\delta t} = -h2B(J+1)\rho N_J \frac{h\nu}{kT} B_{J \rightarrow J+1}$$

$$\text{and } \frac{\delta \rho}{\delta x} = \frac{-h\nu}{c} \rho N_J \frac{-h\nu}{kT} B_{J \rightarrow J+1}$$

since the energy travels at the speed of light and  $\delta x = c\delta t$ .

The absorption coefficient is defined as  $\frac{-1}{P} \left( \frac{dP}{dx} \right)$  and can be expressed as  $\frac{-1}{\rho} \left( \frac{d\rho}{dx} \right)$  since energy density is directly proportional to the power transmitted. The absorption coefficient is then:

$$\alpha_{J \rightarrow J+1} = \frac{h^2 \nu^2}{ckT} N_J B_{J \rightarrow J+1}$$

$$\alpha_{J \rightarrow J+1} = \frac{8\pi^3 \nu^2 N_J}{ckT} \mu_{J \rightarrow J+1}^2$$

### 2.2.3 Line broadening

In the previous section we developed the absorption coefficient for a rotational transition. This absorption may be spread over a relatively wide range of frequency and the absorption coefficient at a particular frequency is a function of the shape of the absorption peak. To account for this, a factor,  $S$ , is introduced.

$$\alpha_\nu = \frac{8\pi^3 \nu^2 N_J}{ckT} \mu_{J \rightarrow J+1}^2 S(\nu, \nu_0)$$

The line shape function derived by Van - Vleck and Weisskopf is given by Gordy et al.<sup>9</sup> and Townes and Schawlow<sup>21</sup> as:

$$S(\nu, \nu_0) = \frac{\nu}{\pi \nu_0} \left[ \frac{\Delta \nu}{(\nu_0 - \nu)^2 + \Delta \nu^2} + \frac{\Delta \nu}{(\nu_0 + \nu)^2 + \Delta \nu^2} \right]$$

where  $\nu_0$  is the resonant peak frequency

$$\Delta \nu = \frac{1}{2\pi\tau}$$

$\tau$  is the mean time between collisions

$2\Delta\nu$  is the line width between half power points.

In microwave spectroscopy where sharp lines are observed  $\nu \approx \nu_0$ , the second term is small compared to the first and the equation reduces to:

$$S(\nu, \nu_0) = \frac{1}{\pi} \left[ \frac{\Delta\nu}{(\nu_0 - \nu)^2 + \Delta\nu^2} \right]$$

At resonance  $\nu = \nu_0$  and the previous equation becomes:

$$S(\nu_0) = \frac{1}{\pi\Delta\nu}$$

and the absorption coefficient resonance is:

$$\alpha_{\nu_0} = \frac{8\pi^2 \nu^2 N_J \mu^2}{ckT\Delta\nu} z_{J \rightarrow J+1}$$

#### 2.2.4 Saturation effect

In thermal equilibrium there will be slightly more molecules to undergo absorption than there are to undergo emission, as outlined in section 2.2.2. During absorption of radiation there will be a net increase in the number of molecules in the  $J+1$  state, tending to make the populations of the upper and lower states of the transition equal. Boltzman distribution is regained by energy transfers during molecular collisions. Since collisions occur at a finite rate, thermal equilibrium Boltzman distribution will be maintained only for low radiation power. When the populations become more equal the rate of emission approaches that of absorption and the attenuation constant will decrease. Experiments show that the measured peak absorption fell rapidly once the power present per molecule rose above a certain value.

## 2.3 Factors Affecting Line Width

### 2.3.1 Pressure of gaseous sample

The factor which has the most effect on the width of a microwave spectral line is the pressure of the gaseous sample. Gas molecules collide with other gas molecules and with the sides of the container and the collision rate is proportional to the total pressure of the gas sample. Energy transfers occur with collisions and the lifetime of any energy state is defined as the mean time between interactions. The collision frequency in a gas can be expressed as:<sup>29</sup>

$$f = 4\sqrt{\pi} r^2 \left(\frac{RT}{M}\right)^{1/2} \frac{N}{V}$$
$$= 4\sqrt{\pi} r^2 \frac{1}{(\text{MRT})^{1/2}} P$$

$$\tau = \frac{(\text{MRT})^{1/2}}{P 4\sqrt{\pi} r^2}$$

where  $f$  is the collision frequency per molecule

$\tau$  is the average time between collision

$r$  is the molecular radius

$M$  is the molecular weight

$V$  = gas volume

$P$  = gas pressure

$PV = NRT$  is universal gas law.

The uncertainty principle has been stated by Heizenberg as:<sup>12</sup> "A

measurement of the energy of a particle (or any system) performed during

a time interval  $\Delta T$  must be uncertain by the amount  $\Delta E$ , where the

relation between the two quantities is:

$$\Delta E \cdot \Delta T \geq \frac{h}{2\pi} \quad "$$

This may be expressed in terms of a spectral frequency to show that the width of an energy level, and hence the width of a spectral line, is proportional to the pressure of a gas sample if the temperature is constant.

$$\Delta h\nu \cdot \tau \geq \frac{h}{2\pi}$$

$$\Delta\nu \geq \frac{1}{2\pi\tau}$$

$$\tau \propto \frac{1}{P}$$

### 2.3.2 Doppler effect

If the temperature is finite, the gas molecules in an absorption cell will have translational kinetic energy. In terms of the waveguide and source reference frame the radiation absorbed by a molecule approaching the source will be lower frequency than that absorbed by a stationary molecule. Similarly a molecule moving away from the source will absorb a higher radiation frequency.

At room temperature the frequency difference of half power points of the Doppler broadened line would be about 100 kc for the 72 GHz line of OCS. An equation describing Doppler broadening is given by Ingram<sup>8</sup> as:

$$\text{Line width} = 2\Delta\nu = 7.2 \times 10^{-7} \left(\frac{T}{M}\right)^{1/2} \nu_0$$

where M is the molecular weight

T is the absolute temperature in °K.

### 2.3.3 Modulation rate

When sinusoidal modulation is employed in a spectrometer two extra absorption lines will appear on either side of the real line. These lines are separated from the real line by the modulation frequency.



Square wave modulation produces similar results. This effect occurs for both modulation of the source and Stark Zeeman modulation of the absorption line. This effect is generally not noticeable unless the gas pressure is very low and the collision broadening is small.

#### 2.3.4 Power saturation broadening

The power density enters into the line shape factor and Townes<sup>21</sup> has revised the expression to the following:

$$S = \frac{\Delta\nu}{(\nu - \nu_0)^2 + \Delta\nu^2 + B_{J \rightarrow J+1} P/c\pi^2}$$

where P is the average incident power per unit area. Increased input power not only lowers the absorption peak but increases the line width.

#### 2.4 Stark and Zeeman Effects

The application of an electric or magnetic field will change the energy levels of an atom or molecule. The presence of a field will remove the degeneracy found in rotational energy levels.

Stark effect in rotational spectra is studied by placing the molecules in an electric field. The angular momentum of the molecule will be quantized in the field direction in  $2J+1$  directions having  $J+1$  angles with the field direction.

If the molecule has a component of electric dipole in the direction of the angular momentum J, then first order Stark effect is observed. Energy splittings are given by Gordy<sup>9</sup> as:

$$\Delta E = \frac{|\vec{E}| \mu K M_J}{J(J+1)} \quad J=0, K=0 \quad \text{and} \quad \Delta E = 0 \quad J=0$$

where  $\mu$  is the dipole moment

$\vec{E}$  is the electric field vector.

Splitting is directly proportional to field strength and to an approximation is inversely dependent on  $J^2$ . Each energy level is split into  $2J+1$  sub levels and often less than 100 volts is required to separate these levels by 3 or 5 MHz when  $J$  is small.

If the molecule has no component of dipole moment in the direction of the angular momentum vector, then second order Stark effect is observed. This occurs in linear molecules and in symmetric top molecules when  $K=0$ . The field perturbs the rotating electric dipole and causes slight changes in the energy of rotation. The magnitude perturbation is dependent on the acute angle the angular momentum vector makes with the field direction. The molecules will have angular momentum vectors making  $J+1$  angles with the field, thus the energy level is split into  $J+1$  sub levels corresponding to  $M=0; M=\pm 1, \dots M=\pm J$ . The energy level splittings for second order effect are given by Gordy<sup>9</sup> and Barrow<sup>6</sup> as:

$$\Delta E = \frac{\mu^2 |\vec{E}|^2}{2hB} \cdot \frac{J(J+1) - 3M_J^2}{J(J+1)(2J-1)(2J+3)} \quad J=0 \quad K=0$$

$$\Delta E = - \frac{\mu^2 |\vec{E}|^2}{6hB} \quad J=0$$

The splitting is proportional to  $E^2$  and approximately proportional to  $J^{-2}$ . The stark splitting for the  $J=1 \rightarrow 2$  rotational line of OCS is approximately 3MHz for an applied field of 1000 volts/cm.

Zeeman effect is of little use in microwave spectroscopy as magnetic fields of many thousand gauss are needed to cause splittings of a line width. The same splitting can be achieved with Stark effect using a voltage of several hundred volts. Zeeman effect refers to the interaction

of molecular magnetic moment and an external magnetic field. The energy splitting is given as follows:<sup>9</sup>

$$\Delta E = g_J B_I M_J \vec{H}$$

where  $g_J$  is the gyromagnetic ratio, a function of the rotational state

$B_I$  is a nuclear magneton

$\vec{H}$  is the magnetic field strength.

Thus the energy levels are split into  $2J+1$  levels by application of a magnetic field. For an example, a field of more than 100,000 gauss is required to cause a splitting of 3MHz in the  $J=1 \rightarrow 2$  line of OCS. The splitting due to Zeeman effect is generally less than the splitting due to interaction of different nuclear spins with the total molecular spin.

Zeeman effect can be studied with a solenoidal coil about the waveguide or a field perpendicular to the microwave magnetic vector. Stark effect can be studied by an insertion of an electrode in the waveguide (See Appendix C). These effects may be used to modulate a spectral line allowing use of a narrow band amplifier in detection.

### 3. MICROWAVE SPECTROMETERS

#### 3.1 Simple Spectrometer

The simple spectrometer consists of a radiation source, an absorption cell and a detection system. A spectral line is observed as a decrease in the detected signal at a particular frequency. A simple spectrometer in the microwave region can be constructed with a klystron source, a waveguide absorption cell and a point contact crystal diode detector. The optimum length of waveguide absorption cell depends on the type of detection and the loss in the waveguide. An unbiased detector as used in these experiments has a square law characteristic for low powers and Gordy<sup>9</sup> gives the optimum waveguide length as:

$$L_{opt.} = \alpha^{-1}$$

where  $\alpha$  is the attenuation coefficient of the waveguide.

The attenuation coefficients of the waveguides used in these experiments include the effective path of the wave and are as follows:<sup>22,9</sup>

WAVEGUIDE SIZE	OPERATING FREQUENCY GHZ	ATTENUATION CONST. Nepers per Foot
2mm.	140	0.4
4mm.	70	0.1

Accordingly the optimum waveguide lengths would be 2.5 feet and 10 feet respectively. One foot and 2 foot absorption cells were used in these experiments. The materials tested in these spectrometers reacted with the waveguide material, increasing the attenuation constant and partially justifying the shorter length.

### 3.2 Balanced Spectrometer

To obtain an output only when an absorption is present, balanced spectrometer can be used. Balancing may be done by subtracting two microwave signals or the outputs from two detectors. The microwave signal balancing can be done by using a 4 port hybrid "T" to equally divide the signal into two shorted branches of equal length. The returning signals are coupled to the fourth port of the hybrid "T"<sup>10,26,27</sup> and the unbalanced signal will be observed by a detector in that arm. If a sample gas is admitted to one of the branches then an absorption line will appear as an unbalanced signal. If the power absorbed by the gas is  $P$ , the unbalanced power will be:<sup>9</sup>

$$\Delta P' \approx \Delta P \left( \frac{\Delta P}{4P} \right) \quad \Delta P \ll P$$

The unbalanced power is less than the absorbed power, thus this spectrometer is less sensitive than the simple spectrometer. This spectrometer requires both phase and amplitude balancing. This is difficult at short wavelengths if the frequency is being swept.

A balanced spectrometer may also be constructed by dividing the microwave in two arms of approximately equal length, each with a detector at each end. If the differential voltage between the detectors is observed the absorption line of a gas in one of these arms will produce an output. This spectrometer requires amplitude balancing only and is not particularly frequency dependent. This type of spectrometer was used by Costain and Forsythe<sup>25</sup> in experiments with ammonia. Balanced spectrometers, if they are well balanced, do not give an output for klystron discontinuities and waveguide reflections. This is an advantage in the search of absorption lines.

















































































































































