

ABSORPTION OF MICROWAVES BY MOLECULES

A Thesis

Submitted to the Faculty of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree of

Master of Science

in Biomedical Engineering

in the Department of Electrical Engineering

University of Saskatchewan

by

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Saskatoon, Saskatchewan

October, 1968

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ACKNOWLEDGEMENTS

The author thanks Dr. S. J. Webb and Dr. A. D. Booth for their help and encouragement in the preparation of this thesis. I would also like to thank Arnold Krause for his constructive criticism and suggestions. I thank Charlie Kresse, Tom Brown and Orland Turriff for technical help and advice. I express my gratitude to Miss Irene Wohlgemuth and John Webb for their assistance.

I am grateful for financial assistance from the Defence Research Board, the National Research Council and for a Teaching Assistantship from the University of Saskatchewan.

UNIVERSITY OF SASKATCHEWAN

Electrical Engineering Abstract 68A107

"ABSORPTION OF MICROWAVES BY MOLECULES"

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A.D. Booth

M.Sc. Thesis presented to College of Graduate Studies
October 1968.

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.

This work was financed by the Defence Research Board under Grant No. 1801-09 and by the National Research Council under Grant No. A1616 and the University of Saskatchewan in the form of a Teaching Assistantship.

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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

ν 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.¹² 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.¹²

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

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

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

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:⁹

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

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

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 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

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

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

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

According to Bohr's postulate¹² 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:⁴

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

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 $D=10^{-3}B$.

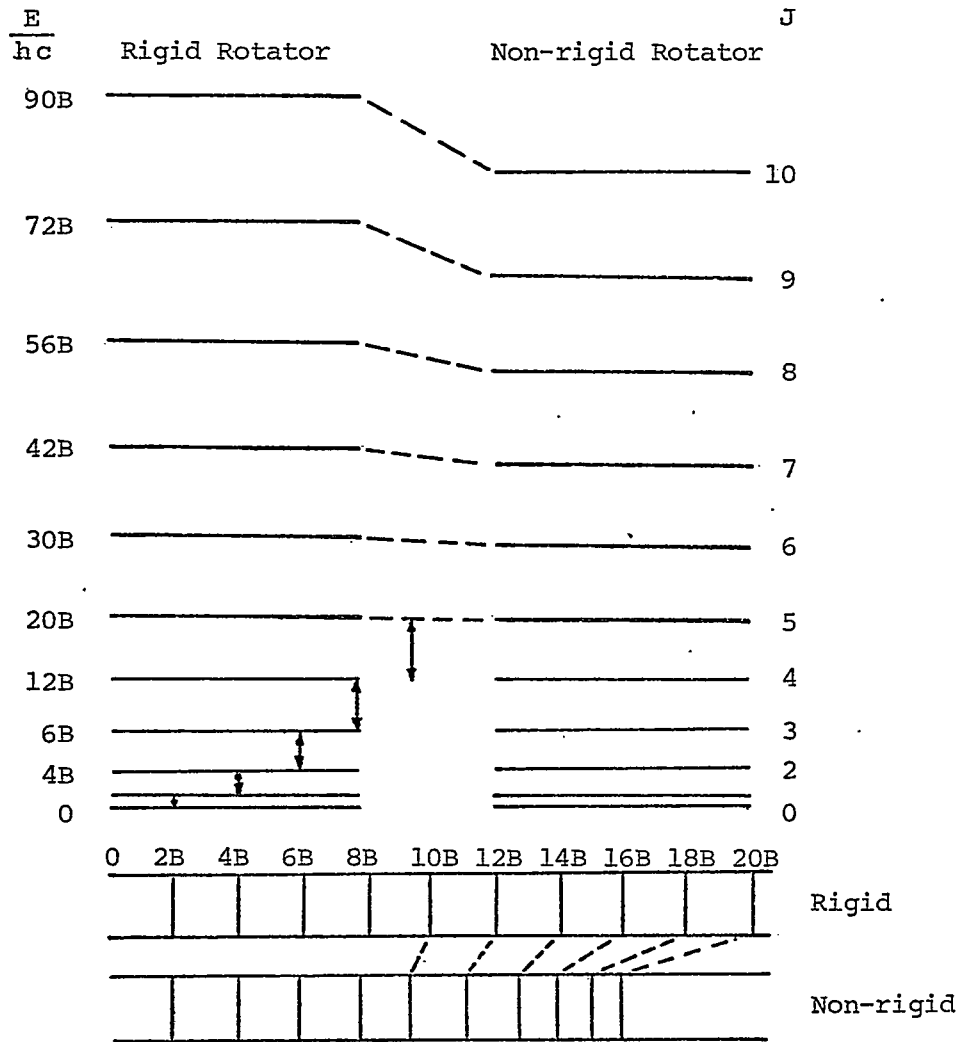


Figure 2.1

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

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

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 .

ξ 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.

α 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.^{6,4} 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.¹³

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.

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

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

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

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

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

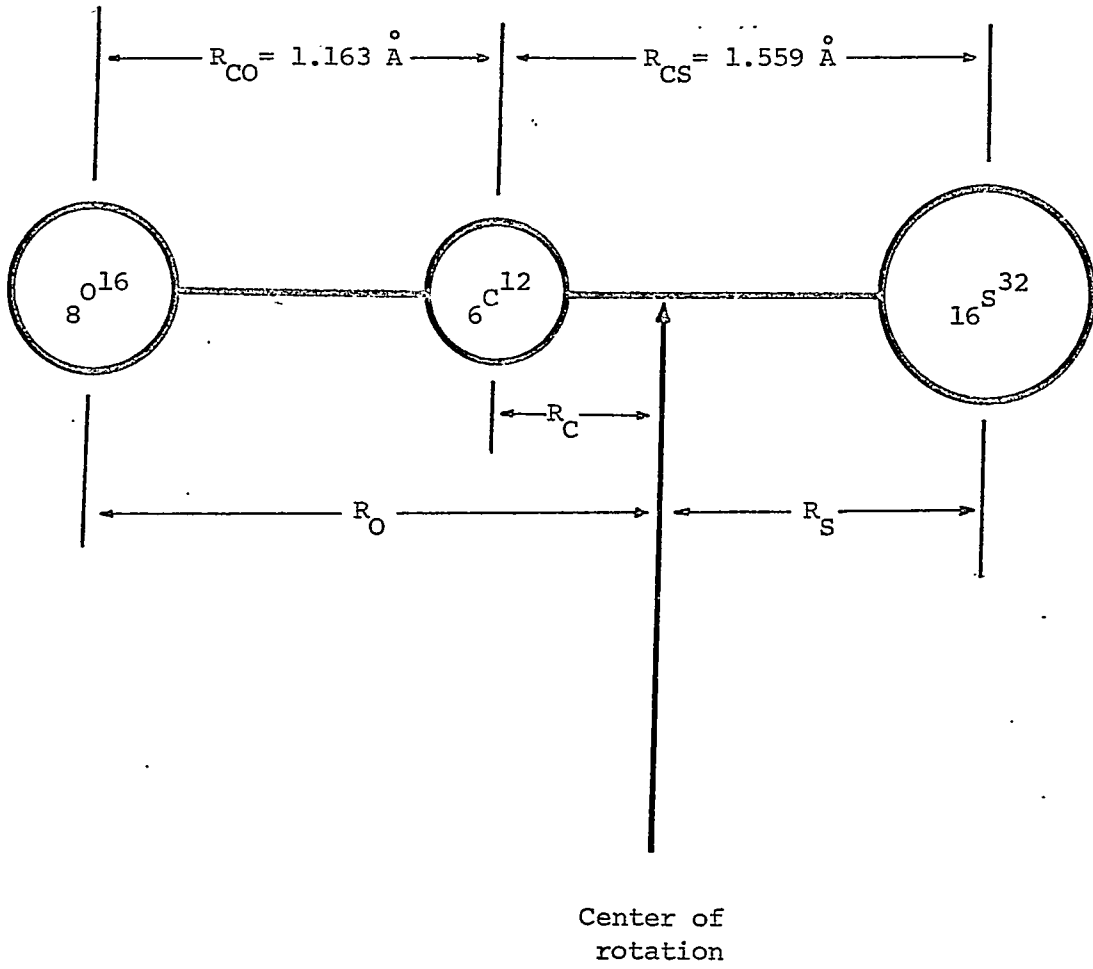
$$= 137.929 \times 10^{-40} \text{ gm.cm.}^2 \quad \text{amu.} = 1.6600 \times 10^{-24} \text{ gm.}$$

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.

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

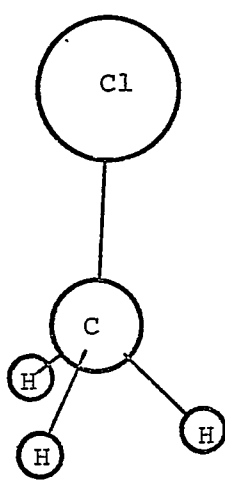
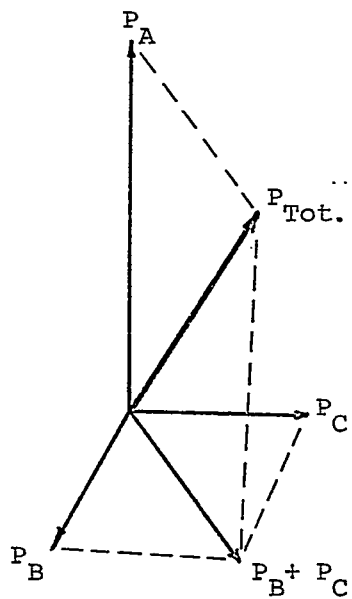
The angular momentum about the unique axis, A, is assumed to be quantized and is given the quantum number K.

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

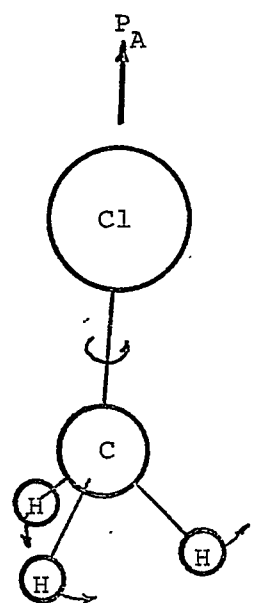
Since the moments of inertia about the B and C axes are equal, the vector sum of angular momentum is treated as a unit.

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:

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

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.

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

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

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

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.⁹ The center of rotation will be on the carbon-hydrogen axis and its location is determined from the following information:^{6,9,18}

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

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

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

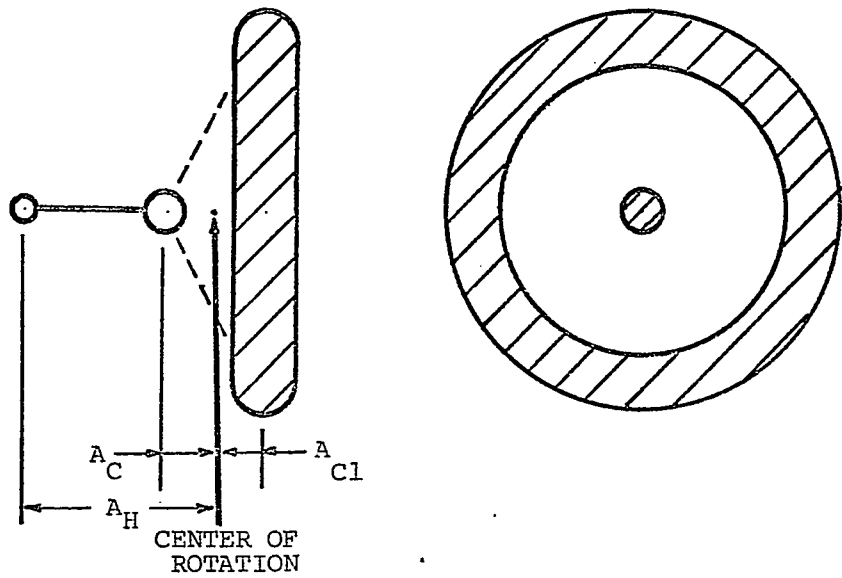
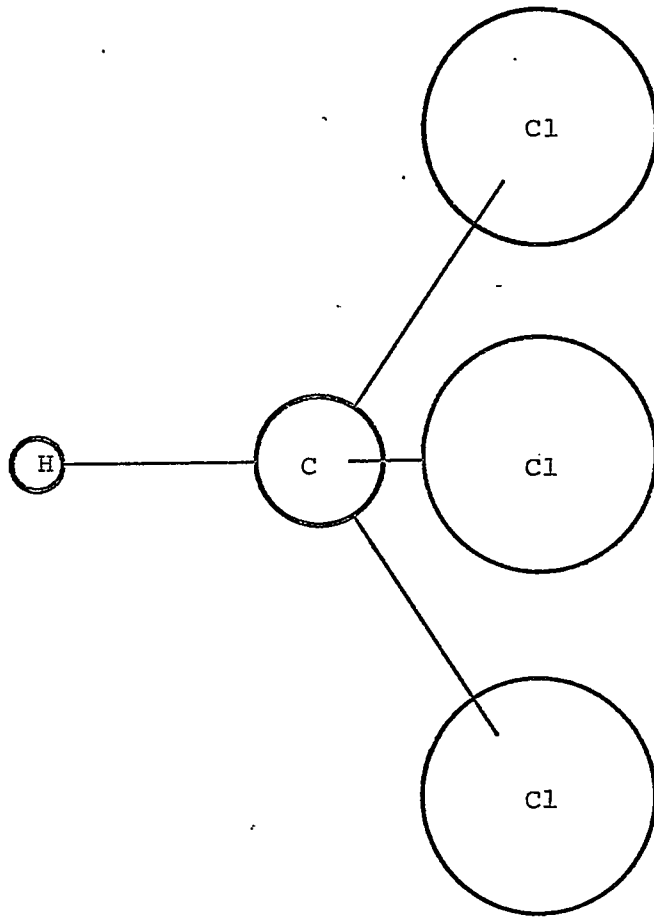
$$\theta_{H_C Cl} = 108.6^\circ$$

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

Element	Atomic Weight	Abundance
Cl ³⁵	34.97867	75.4%
Cl ³⁷	36.99750	24.0%
C ¹²	12.00386	98.891%
C ¹³	13.00756	1.108%
H ¹	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 $C^{12}H^{135}Cl_3$ and $C^{12}H^{137}Cl_2^{35}$

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.¹⁷

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 Barrow⁶, Gordy et al.⁹, and Townes and Schawlow²¹. 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 are⁹ as follows:

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

Formaldehyde, or H_2CO , 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.²⁰

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

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

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:²⁰

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

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

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 .^{9,21}

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

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:^{2,12,14}

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

Where μ_x is the electric dipole moment in the x direction

ψ_n and ψ_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:^{2,9,14}