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Microwave Spectroscopy

→ Rotational Spectra:

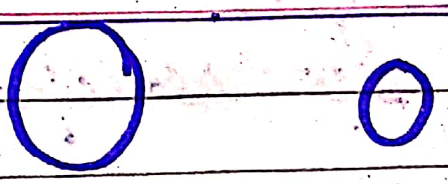
Rotational energy is quantized this means that a molecule cannot have any arbitrary amount of rotational energy but its energy is limited to attain definite value depending upon the shape and size of the molecule concerned. The permitted energy value- so called rotational energy levels- may be calculated for the molecule by solving Schrodinger Equation for the system represented by that molecule.

DIATOMIC MOLECULES

⇒ Rotational Spectrum of Rigid diatomic molecule:

It is applicable for the simplest of all linear molecules.

A diatomic molecule has two atoms with mass m_1 & m_2 respectively, which are joined by a rigid bar (the bond whose length is r_0)



$r_0 = r_1 + r_2$

$r_2 = r_0 - r_1 \longrightarrow ①$

C = centre of gravity (towards heavier ato

r_0 = total distance b/w m_1 & m_2

r_1 = distance of body "m_1" from centre of gra

r_2 = distance of body "m_2" from centre of gra

The molecule rotates end over end about point **"C"** the centre of gravity.

According to law of moment

$m_1 r_1 = m_2 r_2$

$m_1 r_1 = m_2 (r_0 - r_1)$ (by putting value of r_2)

$m_1 r_1 = m_2 r_0 - m_2 r_1$

$m_1 r_1 + m_2 r_1 = m_2 r_0$

$r_1 (m_1 + m_2) = m_2 r_0$

$$r_1 = \frac{m_2 r_0}{m_1 + m_2}$$

Similarly $r_2 = \dfrac{m_1 r_0}{m_1 + m_2}$

The moment of inertia about poin "C" is given as

moment of Inertia = $m_1 r_1 \times$ distance from C

$= m_1 r_1 \times r_1 = m_1 r_1^2$

$$I = m_1 r_1^2 + m_2 r_2^2$$

$$I = m_1 r_1 . r_1 + m_2 r_2 . r_2$$

$$I = r_1 r_2 (m_2 + m_1)$$

Substitute the value of r_1 and r_2 from eq ③ & eq ④ in eq ⑤

$$I = \left(\frac{m_2 r_0}{m_1 + m_2}\right) . \left(\frac{m_1 r_0}{\cancel{m_1 + m_2}}\right) (\cancel{m_1 + m_2})$$

we get

$$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) r_0^2$$

r_0 = inter nuclear distance b/w two atoms or bond length.

μ = reduced mass (mass of two atoms reduced in one mass, the mass of atoms does not decrease but no. of atoms decreased so called reduced mass)

moment of inertia of diatomic molecule is

$$I = \mu r_0^2$$

By using Schrodinger wave Equation it may be shown that rotational energy level allowed to rigid molecule is given by expression

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

E_J = rotational energy of J^{th} level (its units are joule)

h = Plank's constant

I = moment of inertia which may be I_A, I_B & I_C.

$I_A = 0$ for linear molecule so it is neglected

While $I_B = I_C$

J = rotational quantum number

$J = 0, 1, 2, 3 \cdots$ (Its values are integral no.)

The eq ⑦ expresses the allowed energies in joules. We, However, interested in difference b/w these energies or more particularly in corresponding frequency so

$$\Delta E = h\upsilon \Rightarrow \upsilon = \Delta E / h \text{ (Hertz)}$$

In rotational spectroscopy, spectra are usually discussed in terms of wave number so it is useful to consider energy in these units (ie. $\bar{\upsilon}$ un

$$\bar{\upsilon} = \frac{\upsilon}{c} = \frac{\Delta E}{hc} \text{ units } (cm^{-1})$$

Divide eq ⑦ by hc we get (for converting units i

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

but $\epsilon_J = \frac{E_J}{hc}$ Therefore

$$\epsilon_J = \frac{h}{8\pi^2 I_C} J(J+1) \text{ units } cm^{-1}$$

c = velocity of light (cm/s)

for a given system

$$\frac{h}{8\pi^2 I_C} = \text{constant}$$

Suppose $I = I_B$

$$\frac{h}{8\pi^2 I_B C} = B \text{ (rotational constant)}$$

In this case we consider as I_B (but I_B & I_C a equal) because in case of I_C it becomes ambig

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Here we can use I_c for rotational constant "C" but notation "B" is conventional.

The above expression can be written as

$$\epsilon_J = BJ(J+1) \quad cm^{-1}$$

The relation expresses the rotational energy of rigid diatomic molecule.

Calculation of rotational energy of Energy levels:

We know that

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$J = 0, 1, 2, 3 \ldots$

For J=0 $\epsilon_J = \epsilon_0$

$\epsilon_0 = B(0)(0+1) = 0B$

So we can say that molecule is not rotating in this energy level or all molecules in J=0 energy level are at rest.

For J=1 $\epsilon_J = \epsilon_1$

$\epsilon_1 = B(1)(1+1) = 2B$

For J=2 $\epsilon_J = \epsilon_2$

$\epsilon_2 = B(2)(2+1) = 6B$

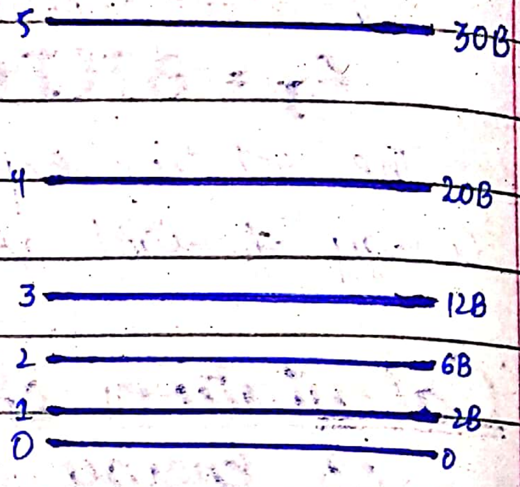
For J=3 $\epsilon_J = \epsilon_3$

$\epsilon_3 = B(3)(3+1) = 12B$

For J=4 $\epsilon_J = \epsilon_4$

$\epsilon_4 = B(4)(4+1) = 20B$

The figure given below show allowed rotational energy levels in rigid diatomic molecule-



We may continue to calculate ϵ_J with increasing J value because in principle ther is no limit to the rotational energy of the m

Differences b/w Energy Levels:

Now consider the differences b/w energy levels in order to discuss spectrum

If we imagine that the molecule is in J=0 state (ground rotational state) we ca let incident radiation be absorbed to ra it to the J=1 state. Plainly the energy absorbed will be

$$\Delta\epsilon = \epsilon_{J=1} - \epsilon_{J=0}$$

$$\Delta\epsilon = 2B - 0B$$

$$\Delta\epsilon = 2B$$

or $$\bar{\nu}_{J=0\rightarrow J=1} = 2B \text{ cm}^{-1}$$

In other words an absorption line will appear at $2B\ cm^{-1}$

If now the molecule is raised from $J=1$ to $J=2$ level by the absorption of more energy. We say

$$\bar{\upsilon}_{J=1\rightarrow J=2} = \epsilon_{J=2} - \epsilon_{J=1}$$
$$= 6B - 2B = 4B\ cm^{-1}$$

Similarly energy differenie b/w 2nd and 3rd energy level is

$$\epsilon_{J=3} - \epsilon_{J=2} = 12B - 6B = 6B\ cm^{-1}$$

In general raise of molecules from the states J to state $J+1$ we would have

$$\epsilon_{J+1} - \epsilon_J = B(J+1)(J+1+1) - BJ(J+1)$$
$$= B(J^2+3J+2) - BJ^2 - BJ$$
$$= \cancel{BJ^2} + 3BJ + 2B - \cancel{BJ^2} - BJ$$
$$= 2BJ + 2B$$

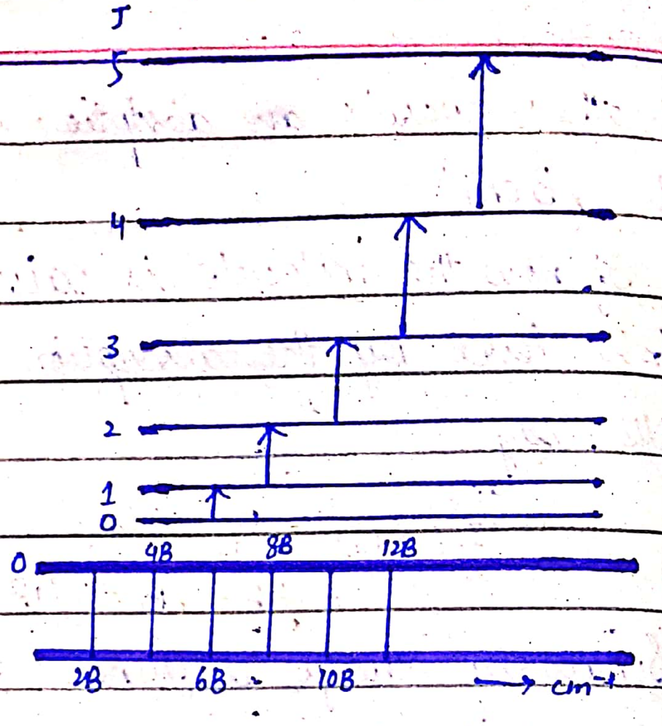
$$\epsilon_{J+1} - \epsilon_J = 2B(J+1)\ cm^{-1}$$

This is general formula for determination of energy difference b/w rotational energy levels of rigid diatomic molecule.

We can also write it for transition in Spectroscopy.

$$\bar{\upsilon}_{J\rightarrow J+1} = 2B(J+1)$$

$\bar{\upsilon}$ = energy difference b/w two energy levels (adjecent)



The stepwise raising of rotational energy result in an absorption spectrum consisting of lines at 2B, 4B, 6B, ... cm⁻¹

$$\bar{\nu}_{J\to J+1} = 2B(J+1)\ cm^{-1}$$

$$\nu_{J+1\to J+2} = 4B(J+1)\ cm^{-1}$$

$$\nu_{J+2\to J+3} = 6B\ cm^{-1}$$

While a similar lowering would result i

an identical emission spectrum.

All the lines in the spectrum of rigid di

molecule are equally spaced and difference b

them is 2B.

Transition b/w Energy levels:

We know that transition ca

occur from a particular level only to

its immediate neighbour either above o

below (We have not, for instance, considere the sequence of transitions $J=0 \rightarrow J=2 \rightarrow J=4$)

According to **Selection Rule** we only consider transition in which J changes by one unit, all other transitions being spectroscopically forbidden. We may formulate it for rigid diatomic rotator as

Selection Rule $\Delta J = \pm 1$

Here

(+1) mean transition from lower energy level to Higher Energy level
(−1) means transition from Higher energy level to lower Energy level

In **Homonuclear molecules**, dipole moment doesnot change during rotation and no rotation spectrum will be observed.

for example N_2 and O_2

While in **Heteronuclear molecules**, there is change in dipole moment and a clear rotational spectrum will observed for example HCl and CO.

Rotation about the bond axis In rigid diatomic molecule was rejected due to two reasons ($I_A = 0$)

① The moment of inertia about the bond is very small so the energy level would be extremely spaced this mean that a molecule requires a greater energy to be raised from $J=0$ to $J=1$ state and such a transition doesnot occur under normal conditions. Thus rotation of diatomic and all linear molecules in the $J=0$ state

② If such a transition occur, there would be no dipole change and spectrum is not obtained.

Thats why rotation about bond axis is rejected.

Advantages / Application of Rotational Spectra:

With the help of rotational spectrum we can determine moment of Inertia and hence the bond length.

Example: Rotational Spectrum of Carbon Monooxide

Gilliam et al.† have measured the first line in the rotation spectrum of CO at $3.84235 cm^{-1} = 2B = \bar{\nu}_{J=0 \rightarrow J=1}$

The value of **B** is calculated as

$$B = \frac{3.84235}{2} = 1.92118\ cm^{-1}$$

While B is rotational constant whose value is $B = \frac{h}{8\pi^2 I_c}$

The value of **I** is calculated as

$$I_{co} = \frac{h}{8\pi^2 Bc} = \frac{6.625\times10^{-34}\ Js}{8(3.14)^2(1.92118\,cm^{-1})(3\times10^{10}\,cms^{-1})}$$

$$I_{co} = 14.5695\times10^{-47}\ kg\,m^2$$

We express B in cm^{-1} units and c in cms^{-1}

Determination of Reduced mass:

We know that $I = \mu r_0^2$

The relative atomic weight H = 1.0080 C = 12.000 O = 15.9994 and absolute mass of Hydrogen atom = 1.67343×10^{-27} kg that of carbon & O atom is 19.92168 and 26.56136×10^{-27} kg respectively. So reduced mass is calculated as

$$\mu = \frac{19.92168 \times 26.56136\times10^{-54}}{46.48303\times10^{-27}}$$

$$\mu = 11.38365\times10^{-27}\ kg$$

Determination of Bond Length:

We know that $I = \mu r^2$

$$r^2 = \frac{I}{\mu} = 1.2799\times10^{-22}\ m^2$$

$$r_{co} = 0.1131\ nm \text{ or } 1.131\ A°$$

So In short words we can say that with the help of rotational spectrum we can calculate moment of Inertia (I), reduced mass (μ), bond length (r) of molecule

The Intensities of Rotational Spectral Lines:

The intensity of rotational spectra depends upon two factors

(i) Transition Probability

(ii) Total Population of energy level from which transition occur to next one

(1) Transition Probability:

"The degree of probability of a molecule in one state changing to another state is called Transition Probability."

For considering intensities of spectral lines we must know about the relative probabilities of transition between the various energy levels. Transitions are of two types.

- Forbidden Transition
- Allowed Transition

i) Forbidden Transition:

Transition in which J changes by more than one unit are called forbidden Transitions

example $\Delta J = \pm 2, \pm 3$ e.t.c

Transition probability for all these changes is zero.

(iii) Allowed Transitions: "The transitions in which J changes by one unit above or below is called Allowed Transitions"

$$\Delta J = \pm 1$$

Probability of all changes with $\Delta J = \pm 1$ is almost the same. That why intensity of all spectral lines should be same. So we need not to consider this factor.

Therefore, Difference in the intensities of Spectral lines is only due to population of energy levels.

For example: Intrinsic probability of a single molecule in moving from $J=0$ to $J=1$ state is the same as that of single molecule moving from $J=1$ to $J=2$

2. Population:

Intensity of spectral lines are directly proportional to the initial no. of molecules in each level.

For example: In a normal gas sample that will be initially different number of molecules in each level and therefore different total number of molecules will carry out transition b/w the various levels.

Thats why intensities of spectral lines $\propto$ no. of molecules in each level

Factors: Total population of energy lev
depends upon two factors

i- Boltzmann factor
ii- Degeneracy of Energy level.

i- Boltzmann Factor: The first factor governing the population of the level is the Boltzmannfactor.

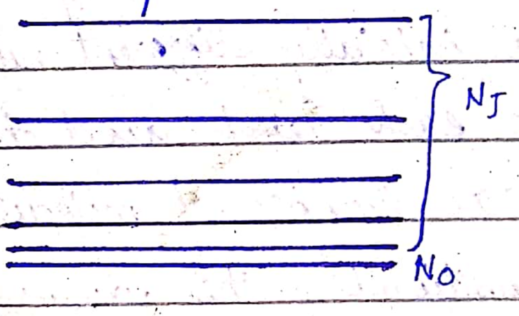
We know that rotational energy in the lowest energy level ($J=0$) is zero. If N_0 molecule in this state present than the number of molecules in any higher state is given by

$$\frac{N_J}{N_0} = e^{-E_J/KT} \longrightarrow ①$$

N_J = no. of molecules in J^{th} level

e.g: if $J=1$ it means
if $J=2$

N_0 = No. of molecules in $J=0$ level.
K = boltzmann constant
E_J = Energy with respect to N_J/Energy of J
T = Temprature.



Since we know that

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

In terms of $\bar{\nu}$

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

while $B = \frac{h}{8\pi^2 Ic}$ so

$$\frac{E_J}{hc} = BJ(J+1)$$

$$E_J = Bhc\,J(J+1) \longrightarrow ②$$

Substituting value of E_J from eq ② in eq ① we get

$$\frac{N_J}{N_0} = e^{-\frac{BhcJ(J+1)}{KT}} \longrightarrow ③$$

The value of "B" always remain between 1 — 1. c is velocity of light in cm/s.

A very simple calculation shows that how **N_J varies with J**.

For example taking a typical value of $B = 2cm^{-1}$ and temprature $= 300k$ the relative population in **J=1** state is given as

$K = 1.38 \times 10^{-23}$ J dgree^{-1} molecule^{-1}

$$\frac{N_1}{N_0} = e^{\left(-\frac{2 \times 6.63 \times 10^{-34} \times 3 \times 10^{10} \times 1 \times 2}{1.38 \times 10^{-23} \times 300}\right)}$$

$$\frac{N_1}{N_0} = e^{-0.0192}$$

$$\frac{N_1}{N_0} = 0.98$$

$$N_1 = 0.98 N_0$$

$$N_1 = \frac{0198}{100} N_0$$

$$N_1 = 98\% \text{ of } N_0$$

It means that approximately population of $J=1$ level is 98% of the population of $J=0$ level.

Similarly for $J=2$

$$\frac{N_2}{N_0} = e^{\left(-\frac{2\times 6.63\times 10^{-34}\times 3\times 10^{10}\times 2(2+1)}{1.38\times 10^{-23}\times 300}\right)}$$

$$\frac{N_2}{N_0} = e^{-0.0192\times 3}$$

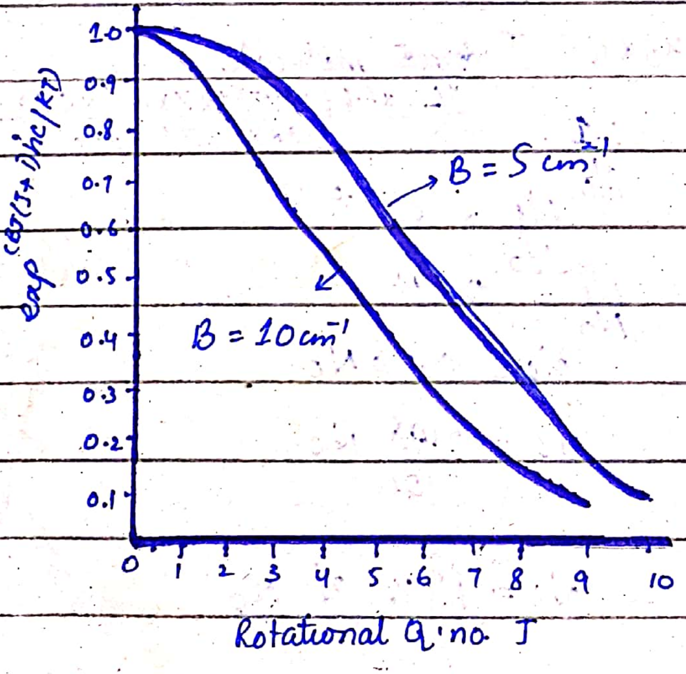
$$\frac{N_2}{N_0} = 0.944$$

$$N_2 = 0.94N_0$$

$$N_2 = \frac{0.944N_0}{100}$$

$$N_2 = 94\% \text{ of } N_0$$

Population of $J=2$ level is 89% of population of $J=0$. It means that population is exponantially (rapidly increases) by increasing the value of J and with larger B. Graphs can be plotted which show these results also.



ii- Degeneracy of Energy level:-

In any energy level there are sublevels whose energies are equal exactly. this is called degeneracy of energy levels.

The general formula is:

$$\text{Degeneracy} = 2J+1$$

for example	Degeneracy
for $J=0$	$2(0)+1 = 1$
$J=1$	$2(1)+1 = 3$
$J=2$	$2(2)+1 = 5$
$J=3$	$2(3)+1 = 7$

$$\text{Degeneracy} \propto \text{value of } J$$

Both these factors (Boltzmann and degeneracy) are opposite to each other.

Effect of Isotopic substitution on Rotational Spectrum of Rigid diatomic molecule:

Isotopic substitution: "Replacement of a particular atom in a molecule by its isotope is called isotopic substitution".

The resulting Isotopic molecule is chemically identical with original molecule. Isotopic molecule is identical in every aspect with original molecule except for atomic mass.

In particular there is not appreciable in the internuclear distance (bond length) due to isotopic substitution.

For rigid diatomic molecule.

We know that

$$\bar{\nu} = 2B(J+1) \quad \because B = \frac{h}{8\pi^2 Ic}$$

while $I = \mu r^2$

I depends upon reduced mass. There is, however, a change in total mass and hence in the moment of inertia and B value of the molecule so energy difference b/w energy levels of molecules also chang

$$\boxed{\text{Isotopic substitution} \propto \text{reduced mass} \propto \text{moment of inertia} \propto \frac{1}{B} \propto \frac{1}{\text{Energ b/w}}}$$

Example: Considering Carbon mono oxide a an example we see that on going from $^{12}C^{16}O$ (normal molecule) to $^{13}C^{16}O$ (isotopic molecule) there is increase in mass and decrease in the B value. This change will be reflected in the rotational energy levels of the molecule. Fig (a) shows much exaggerated, the relative lowering of ^{13}C levels with respect to those of ^{12}C.

The separation b/w rotational energy levels of an isotopically substituted molecul

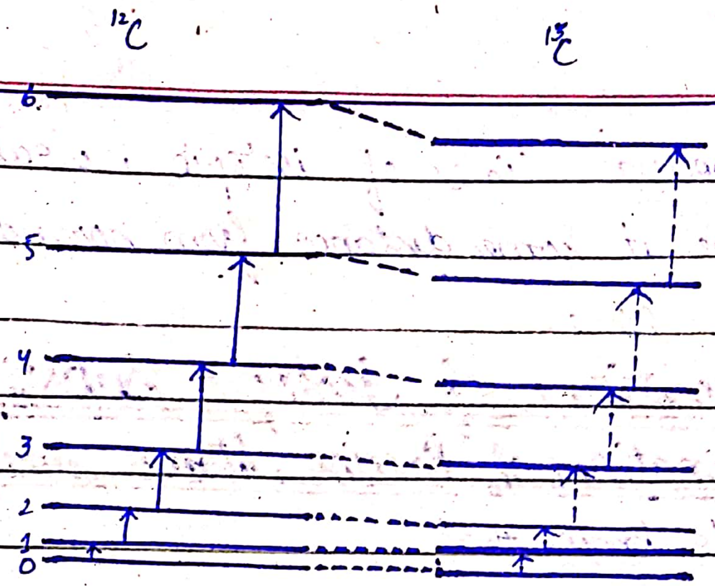
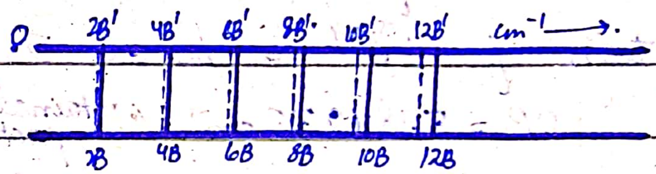


Fig (a)

(heavier) $2B'$ will be less than that for original molecule ($2B$).



Transition of Isotopic molecule are shown by dotted line, while solid lines for normal molecule

We know that

$\frac{B}{B'}$ = for normal molecule rotational constant / for isotopic molecule

$$\frac{B}{B'} = \frac{h}{8\pi^2 Ic} \times \frac{8\pi^2 I'c}{h}$$

$$\frac{B}{B'} = \frac{I'}{I} = \frac{\mu' \cancel{r^2}}{\mu \cancel{r^2}}$$

(As Bondlength (r) is same for normal and isotopically substituted molecule so r is cancelled out)

$$\frac{B}{B'} = \frac{\mu'}{\mu}$$

Comparing B and B' we come to know that

$$B > B'$$

The spectral lines of isotopic molecul must be at some distance from normal spectral line.

Application of Isotopic Substitu

① Determination of Precise Atomic weigh

We know that

$$\frac{B}{B'} = \frac{I'}{I} = \frac{\mu' r^2}{\mu r^2} = \frac{\mu'}{\mu}$$

Gilliam et al found the first rotational absorption of ${}^{12}\mathrm{C}\,{}^{15.994}\mathrm{O}$ to be at 3.84235cm

$$2B = 3.84235\ \mathrm{cm}^{-1} \quad \text{(obtained from spectrum)}$$

The value of B determined from spectru

$$B = 1.92118\ \mathrm{cm}^{-1}$$

While that of ${}^{13}\mathrm{C}\,{}^{15.9994}\mathrm{O}$ was at 3.61337cm

$$2B' = 3.61337\ \mathrm{cm}^{-1} \quad \text{(Obtained from spectrum)}$$

The value of B is given below

$$B' = 1.83669\ \mathrm{cm}^{-1}$$

So $$\frac{B}{B'} = \frac{\mu'}{\mu}$$

The value of μ' for ${}^{13}\mathrm{C}\,{}^{15.9994}\mathrm{O} = \dfrac{m' \times 15.9994}{(m'+15.9994)\,6.022\times 1}$

$$\mu \text{ for } {}^{12}\mathrm{C}\,{}^{15.9994}\mathrm{O} = \frac{12 \times 15.9994}{6.022\times 10^{23}(12+15.9994)}$$

So

$$\frac{\mu'}{\mu} = \frac{m' \times \cancel{15.9994} \times 6.02\times 10^{23}\ (12+15.9994)}{(m+15.9994) \times \cancel{6.02\times 10^{23}}\ (12\times \cancel{15.9994})}$$

$$\frac{\mu'}{\mu} = \frac{m'}{(m'+15.9994)} \times \frac{(12+15.9994)}{12}$$

$$\frac{\mu'}{\mu} = \frac{m'(12+15.9994)}{(m'+15.9994)\times 12} = \frac{363.9922}{347.9928}$$

$$\frac{\mu'}{\mu} = 1.046$$

Atomic weight of ^{13}C = m' = 13.0007

(error is 0.05%.)

The better result is obtained from this method than other methods for determination of atomic mass so as Mass Spectroscopy.

② Relative abundance of naturally occuring isotope:

We can easily determine the relative abundance of naturally occuring isotope. Example: Relative abundance of naturally occuring $^{13}C\,^{15.9994}O$ is about 1% of ordinary Carbon monoxide.

The order of relative abundance of naturally occuring Isotope of Carbon monoxide is $^{12}C\,^{15.994}O > {}^{13}C\,^{15.994}O > {}^{14}C\,^{15.9994}O$ (very very less)

Thus microwave studies can give directly an ultimate of the relative abundance of naturally occuring isotopes by comparison of absorption intensities of spectral lines.

Rotational spectrum of Hydrogen Flouride is given by:

Rotational spectrum of HF

J	$\bar{\nu}_{obs}$ (cm^{-1})	$\bar{\nu}_{calc}$ (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})	B $= \frac{1}{2}\Delta\bar{\nu}$	r (nm)
0	41.08	41.11	41.11	20.56	0.0929
1	82.19	82.18	40.96	20.48	0.0931
2	123.15	123.14	40.85	20.43	0.0932
3	164.00	163.94	40.62	20.31	0.0935
4	204.62	204.55	40.31	20.16	0.0938
5	244.93	244.89	40.08	20.04	0.0941
6	285.01	284.93	39.64	19.82	0.0946
7	324.65	324.61	39.28	19.64	0.0951
8	363.93	363.89	38.89	19.45	0.0955
9	402.82	402.70	38.31	19.16	0.0963
10	441.13	441.00	37.81	18.91	0.0969
11	478.94	478.74			

Rotational Spectrum of "NON RIGID" Rotator:

Non Rigid Rotator: "A molecule in which the internuclear distance b/w bonded atoms increases and decreases due to elasticity of bond is called Non-Rigid Rotator.

Infact all real molecules are non rigid atoms and our assumption about a bond to be rigid is only an approximation.

Spectrum of Non-Rigid Rotator:

The Schrodinger wave Equation may be set up for a non-rigid molecule and the rotational energy levels are found to be $E_J = \frac{h^2}{8\pi^2 Ic} J(J+1) - \frac{h^3}{32\pi^4 I^2 r^2 Kc} J^2(J+1)^2$ in cm⁻¹

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^3}{32\pi^4 I^2 r^2 K} J^2(J+1)^2 \text{ in Joules.}$$

for a given molecule $B = \frac{h}{8\pi^2 Ic}$
"B" is rotational constant.

and $\frac{h^3}{32\pi^4 I^2 r^2 Kc} = D$ = centrifugal distortion constant

So above expression can be written as

$$E_J = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1} \longrightarrow ①$$

For non rigid rotator we assume that non-rigid rotator show simple Harmonic motion. Eq ① applies for a simple Harmonic force field only; if the force field is anharmonic then expression becomes.

$$E_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 \ldots \text{cm}^{-1}$$

Where H and K are small constant and depend upon the geometry of the molecule. They are neglegible as compared to D.

Relationship b/w B and D:

We can make a relationship b/w B and D. The value of B is given below

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

Taking cube of above expression and mutiply with 4 -

$$4(B)^3 = 4\left(\frac{h}{8\pi^2 Ic}\right)^3$$

$$4B^3 = \frac{4h^3}{8\times8\times8\,\pi^6 I^3 c^3}$$

We know that $K = 4\pi^2\bar{\omega}^2 c^2 \mu$

$$\bar{\omega}^2 = \frac{K}{4\pi^2 c^2 \mu}$$

and $I = \mu r^2$

Divide eq ② with $\bar{\omega}^2$

$$\frac{4B^3}{\bar{\omega}^2} = \frac{\cancel{4}h^3}{8\times8\times8\,\pi^{6} I^2 \cdot I c^{3}} \cdot \frac{4\pi^2 c^2 \mu}{K}$$

$$= \frac{h^3}{32\pi^4 I^2 \mu r^2 \cdot c} \cdot \frac{\mu}{K}$$

$$\frac{4B^3}{\bar{\omega}^2} = \frac{h^2}{32\pi^4 I^2 r^2 Kc}$$

we know that $D = \frac{h^2}{32\pi^4 I^2 r^2 Kc}$

So substitute eq ③ with D we get

$$\boxed{\frac{4B^3}{\bar{\omega}^2} = D}$$ The expression shows relationship of B & D.

Such type of calculation is called Back calculation.

$\bar{\omega}$ = Vibrational frequency of bond

These frequencies are in the order of 10^{-3}

and the value of B remain $1-10\,cm^{-1}$.

$$D = \frac{(10)^3}{(10^3)^2} = 10^{3-6} = 10^{-3}\,cm^{-1}$$ (Here we 4

The value of D is approximately $10^{-3}\ cm^{-1}$ is less than value of B so in expression

$$\epsilon_J = BJ(J+1) - DJ^2(J+1)^2$$

The correction term $DJ^2(J+1)^2$ is almost negligible for small J values.

$$\epsilon_J = BJ(J+1) \text{ for rigid rotator}$$

Then above expression is same as we use for rigid rotator.

While for larger J values (10 or larger than 10) term $DJ^2(J+1)^2$ may become appreciable, therefore, not neglected.

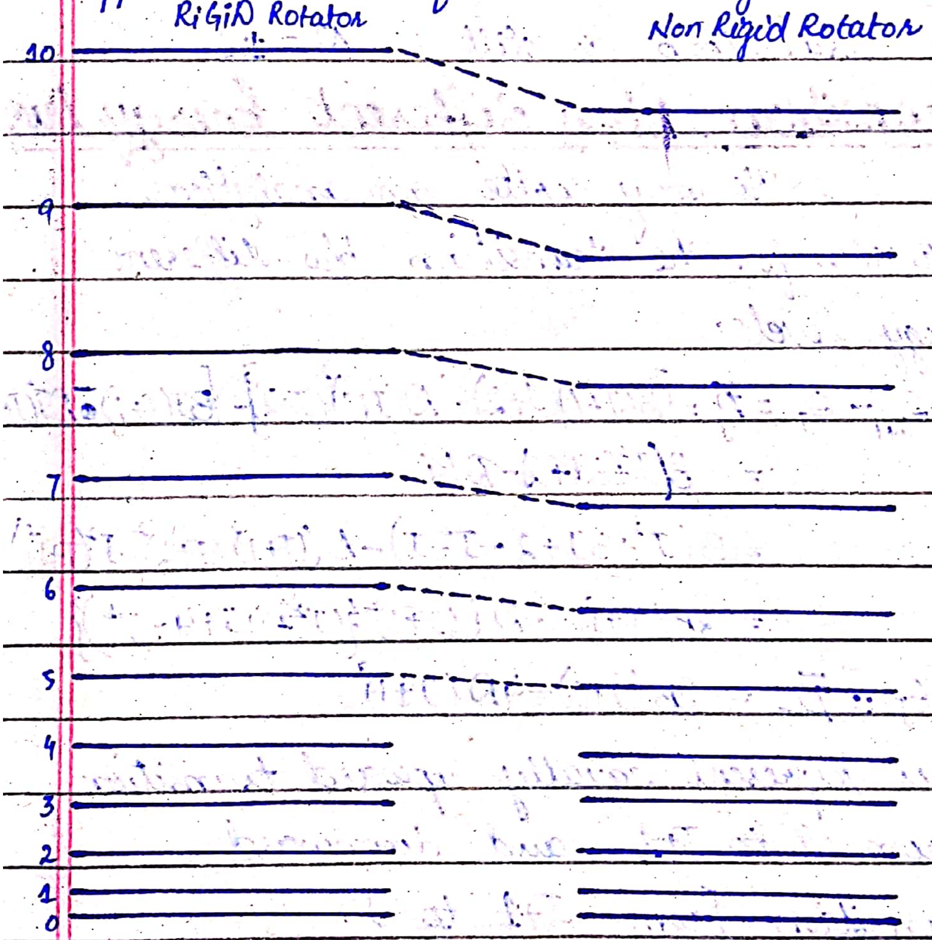
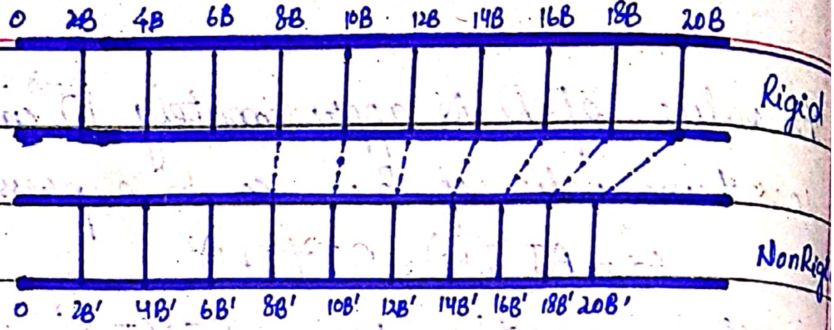


Figure shows lowering of rotational levels



when passing from the rigid rotator to the non-rigid rotator diatomic molecule. Th spectra are also calculated and compared wi dashed line connecting corresponding energy levels and transition of rigid and no rigid molecule.

It should be noted that selection rul for transition is still $\Delta J = \pm 1$

Transition b/w different Energy l

We may write an analytical expression for the transition b/w different energy levels.

$$\epsilon_{J+1} - \epsilon_J = \bar{\nu}_J = [B(J+1)(J+2) - D(J+1)^2(J+2)^2] - [BJ(J+1) - D$$

$$= \cancel{B[J^2+3J+2]-D[J}$$

$$= B(J^2+3J+2-J^2-J) - D((J+1)^2(J+2)^2 - J^2(J$$

$$= 2B(J+1) - D((J+1)^2\{(\cancel{J^2}+4J+4-\cancel{J^2})\}$$

$$\epsilon_J = \bar{\nu}_J = 2B(J+1) - 4D(J+1)^3$$

This represent equally upward transition from J to J+1 and downward transition from J+1 to J.

Conclusion: Thus we see analytically, the spectrum of the elastic rotator (non-rigid) is similar to that of the rigid molecule except that each line is slightly displaced to low frequency and displacement increases with $(J+1)^3$.

Application / Significance of value of D:

Knowledge of D give three important useful information.

① Assignment of J-values to the spectral line:

It allow us to determine the J value of line in an observed spectrum. If we have measured a few isolated transition we can not easily determined that from which J value these transitions arise. The equation ④ provided, three consecutive lines have been measured, give unique value for B, D and J and from these values we can calculate wave number. e-g: for HF molecule the equation obtained is

$$\epsilon_J = 41.22(J+1) - 8.52\times10^{-3}(J+1)^3$$

By putting wave number here we can obtain the value of J.

② Determination of value of force constan or strength of Bond:

for example: the force constant for H-F is given as

$$K = 4\pi^2 c^2 \bar{\omega}^2 \mu = 960\ Nm^{-1}$$

The value of force constant (K) is very great that indicates HF is a relatively strong bond.

③ Determination of Vibrational frequency of diatomic molecule:

By the knowledge of D, we can determine, rather inaccurately the vibrational frequency of diatomic molecule

Example: For H-F, the value of vibratio frequency ($\bar{\omega}^2$) as

$$\sqrt{\bar{\omega}^2} = \frac{4B^3}{D} = \sqrt{(16.33 \times 10^{16}\ cm^{-1})^2}$$

$$\bar{\omega}_{calculated} \simeq 4050\ cm^{-1}$$

$$\bar{\omega}_{observed} \cong 4138.3\ cm^{-1}$$

There is 2% inaccuracy in this calculation partly due to the **assumption of Simple Harmonic motion** and partly due to **very small and relatively inaccurate value of D.**

POLYATOMIC MOLECULES

The molecules in polyatomic range may be

ⓐ Linear molecules
ⓑ Non-Linear molecules
  (i) Symmetric Top molecules
  (ii) Spherical Top molecules
  (iii) Asymmetric Top molecules

(a) **Linear Molecules:** Example of linear polyatomic molecules are OCS (carboxy sulphide), $HC \equiv CCl$ (Chloroacetylene). All the atoms lie on a straight line, since this type give rise to particularly simple spectra in the microwave region.

The conditions for Linear polyatomic molecules are $I_B = I_C$, $I_A = 0$

The energy levels are given by expression

$$\epsilon_J = BJ(J+1) - DJ^2(J+1)^2 + \dots \text{cm}^{-1}$$

The spectrum will show 2B separation modified by the distortion constant. Infact whole of the discussion on diatomic molecules applies equally to all linear molecules. However three important points are given below:

① The moment of inertia for the end over end rotation of a polyatomic linear molecule is considerably greater than that of the diatomic molecule, the B value will be much smaller and the spectral lines more closely spaced. The B values for diatomic molecule are approximately $10\ cm^{-1}$. B value for triatomic values can be $1\ cm^{-1}$ or less and for larger molecules smaller still.

② The molecules having dipole moment exhibit a rotational spectrum. Thus "OCS" will be "microwave active" and "OCO" is "microwave inactive". It should be noted that isotopic substitution does not lead to a dipole moment. Since the bond lengths and atomic charges are unaltered by the substitution. Thus "$^{16}OC^{18}O$" is microwave inactive.

③ A non-cyclic polyatomic molecule containing N-atoms has altogether (N-1) individual bond lengths to be determined. Thus in the triatomic molecule for example OCS

No: of atoms "N" = 3

Bond length = N-1 = 3-1

= 2

thus in OCS, there is the CO distance, r_{co} and the CS distance, r_{cs}. On the otherhand, there is only one moment of Inertia for end over end rotation of OCS and only this one value can be determined from spectrum. Table ~~for~~ shows data for this molecule

J → J+1	$\bar{\nu}_{obv}$ (cm⁻¹)	$\Delta\bar{\nu}$	B (cm⁻¹)
0 → 1	...	2×0.4055	0.2027
1 → 2	0.8109		
2 → 3	1.2163	0.4054	0.2027
3 → 4	1.6217	0.4054	0.2027
4 → 5	0.0271	0.4054	0.2027

From table we observed no appreciable centrifugal force and taking value of B as 0.2027 cm⁻¹ we calculate

$$I_B = \frac{h}{8\pi^2 BC} = 137.95\times10^{-47}\ \text{kgm}^2$$

From this one observation it is impossible to deduce the two unknown r_{co} and r_{cs}. The difficulty can be overcome if we study a molecule with different atomic masses but the same bond length i.e: an isotopically substituted molecule. Since this will have a different moment of inertia.

Let us consider the rotation of **OCS**

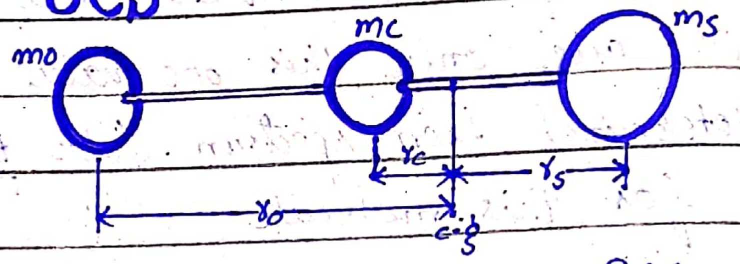


Figure shows the molecule OCS where

r_o = distance of oxygen from C.G

r_c = distance of carbon atom from C.G

r_s = distance of sulphur atom from C.G

C.G = Centre of gravity

m_o = mass of oxygen atom

m_s = mass of sulphur atom

m_c = mass of carbon atom

r_{co} = Bond length or internuclear distance b/w carbon and Oxygen

r_{cs} = Bond length or internuclear distance b/w Carbon and Sulphur.

According to Law of moment

$$m_o r_o + m_c r_c = m_s r_s \longrightarrow ①$$

moment of Inertia is given by

$$I = m_o r_o^2 + m_c r_c^2 + m_s r_s^2 \longrightarrow ②$$

from figure we know that

$r = r_{co} + r_c$

and $r_s = r_{cs} - r_c$

Substituting eq no ③ in eq no ① and simplifying.

$$m_o(r_{co}+r_c) + m_c r_c = m_s(r_{cs}-r_c)$$

$$m_o r_{co} + m_o r_c + m_c r_c = m_s r_{cs} - m_s r_c$$

$$m_o r_c + m_c r_c + m_s r_c = m_s r_{cs} - m_o r_{co}$$

$$(m_o + m_c + m_s) r_c = m_s r_{cs} - m_o r_{co}$$

But $m_o + m_c + m_s = M$ (total mass of molecule)

$$M r_c = m_s r_{cs} - m_o r_{co} \rightarrow ④$$

Substituting eq no. ③ in eq no. ② we get

$$I = m_o(r_{co}+r_c)^2 + m_c r_c^2 + m_s(r_{cs}-r_c)^2$$

$$I = m_o r_{co}^2 + m_o r_c^2 + 2m_o r_{co} r_c + m_c r_c^2 + m_s r_{cs}^2 - m_s r_c^2 - 2m_s r_{cs} r_c$$

$$I = (m_o+m_c+m_s) r_c^2 + m_o r_{co}^2 + m_s r_{cs}^2 + 2r_c(m_o r_{co} - m_s r_{cs})$$

while $m_o + m_c + m_s = M$

$$I = M r_c^2 + m_o r_{co}^2 + m_s r_{cs}^2 + 2r_c(m_o r_{co} - m_s r_{cs}) \rightarrow ⑤$$

Substituting value of r_c from eq no ④ into eq no. ⑤

$$I = \frac{M(m_s r_{cs} - m_o r_{co})^2}{M^2} + m_o r_{co}^2 + m_s r_{cs}^2 + \frac{2(m_s r_{cs} - m_o r_{co})}{M}(m_o r_{co} - m_s r_{cs}) \times$$

$$I = \frac{(m_s r_{cs} - m_o r_{co})^2}{M} + m_o r_{co}^2 + m_s r_{cs}^2 - \frac{2(m_s r_{cs} - m_o r_{co})^2}{M}$$

$$\boxed{I = m_o r_{co}^2 - m_s r_{cs}^2 - \frac{(m_s r_{cs} - m_o r_{co})^2}{M}} \rightarrow ⑥$$

For isotopically substituted molecule ^{18}OCS

the above eq becomes

$$I' = m'_O r_{CO}^2 + m_S r_{CS}^2 - \frac{(m'_O r_{CO} - m_S r_{CS})^2}{M'}$$

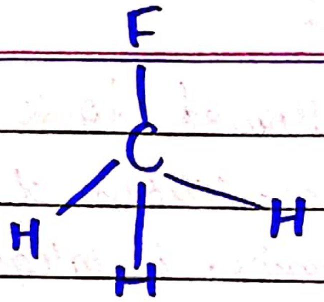
By isotopic substitution bond length does not change but moment of inertia change (I'), which is helpful to determine bond length. Microwave studies have led to very precise determination of many bond length in such molecules. If polyatomic molecule is linear than discussion of their spectrum is same as for diatomic molecule.

Symmetric Top Molecule:

The rotational energy level of symmetric top molecules are more complicated than those of linear molecules because of their symmetry, their pure rotational spectra are still relatively simple.

Example: Best example of symmetric top molecules is **methyl flouride**

The condition for symmetric top molecule is given next.



$I_B = I_C \neq I_A \qquad I_A \neq 0$

There are now two directions of rotation in the molecule might absorb or emit energy.

① Rotation along main symmetry axis (C-F bond axis in this case)

② Rotation perpendicular to main symmetry axis.

Thus we need two quantum numbers to describe the degree of rotation. One for I_A, one for I_B or I_C because $I_B = I_C$. ~~are~~ We choose a quantum number **J** to represent the total angular momenta about different axis.

It is then conventional to use K

K = represent the angular momentum about the axis (about C-F bond in this case)

We can determine quantum number J, one quantum number is **K** then other can be easily determined.

Let us consider values are

which are allowed to K and J. Both must, by the conditions of quantum ~~numbers~~ mechanics, be integral or zero. The total angular momentum is

$$J = 0, 1, 2, 3 \cdots\cdots \infty$$

When we fix J values then value of K is restricted or more limited. The rotational energy can be divided into several ways b/w motion about the main symmetry axis and motion perpendicular to the axis.

Let us consider $J = 3$

Case I: If all rotation is about the top axis (C–F bond axis) then

$K = J$ So value of K is $K = 3$

Case II: If motion perpendicular to axis increases accordingly then $K \neq J$

The value of $K = 2, 1, 0$

In these cases maximum value of K ~~never~~ is 3. K may be equal to J. But value of K never greater than J since J is quantum number represent total angular momentum & K is the part of J.

Additionally we can imagine

positive and negative values of K corresponding to clockwise and anticlockwise rotation about the symmetry axis. so value of ~~J~~ K will be

$$K = 3, 2, 1, 0, -1, -2, -3$$

In general for a total angular momentum J, K can take value

$$K = J, J-1, J-2 \cdots 0 \cdots -(J-1), -J$$

So number of values of K is given as

$$\text{No. of values of } K = (2J+1)$$

For example:

When value of $J=3$ then value of $K=7$ it means In $J=3$ rotational energy level, there are 7 sublevels according to value of K

Similarly $J=4$ then $K=9$

Transition occur b/w K sublevels of one J^th^ to the same K sublevel of next J rotational energy level.

Rigid Symmetric Top Molecules:

If we consider the case of rigid symmetric top molecules i.e. one in which the bonds are supposed not to stretch under centrifugal forces. Then schrödinger wave equation may give the allowed energy levels for rotation as

$$\epsilon_{J,K} = \frac{E_{J,K}}{hc} = BJ(J+1) + (A-B)K^2 \; cm^{-1} \quad ①$$

We know that

rotational constant $B = \frac{h}{8\pi^2 I_B c}$

and $A = \frac{h}{8\pi^2 I_A c}$

The energy depends on K^2 so it is immaterial whether the top spins clockwise or anticlockwise; the energy is the same for a given angular momentum. For all $K > 0$ therefore the rotational energy level are doubly degenerate.

Selection rule: The selection rule for this molecule is

$$\Delta J = \pm 1 \;, \quad \Delta K = 0$$

These selection rules help to determine energy difference b/w energy levels.

On applying these rules to eq we get the spectrum.

$$\epsilon_{J+1,K} - \epsilon_{J,K} = \bar{\nu}_{J,K} = [B(J+1)(J+2) + \cancel{(A-B)K^2}] - [BJ(J+1) + \cancel{(A-B)K^2}]$$

$$\epsilon_{J+1,K} - \epsilon_{J,K} = 2B(J+1) \quad cm^{-1}$$

Thus the spectrum is independent of K and hence rotational changes about the symmetry axis do not give rise to a rotational spectrum, because rotation about symmetry axis does not change the dipole moment.

Eq no. ② shows that the spectrum is same for a linear molecule and only one moment of inertia for end over end rotation can be determined. the equation apply to rigid molecule.

A real molecule has elastic bond and spectrum become more complicated.

Applications:-

1. The microwave spectra of such molecules give very precise estimates of their bond length.
2. The bond angle of these molecules can be determined from their microwave spectra.

Spherical Top Molecules:

Spherical top show no microwave spectra.

Asymmetric Top Molecules:

These molecules having three different moments of inertia, also have much more complicated rotational energy levels and spectra. No simple general expressions can be derived for them and they are usually treated by approximation method much computat being required before agreement b/w ~~derived~~ observed and calculated spectra is achieved

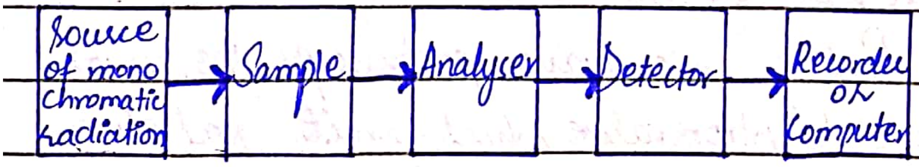
Application: Such methods have been very successful for small molecules and much accurate bond length and bond angle data have been derived.

Representative data for some linear, symmetric top, Asymmetric top molecules are calculated in the table. The table illustrates the great precision which has been achieved.

Molecule	Type	Bond Length (nm)	Bond Angle (°)
NaCl	Diatomic	0.23606 ± 0.00001	—
COS	Linear	0.1164 ± 0.0001 (CO) 0.1559 ± 0.0001 (CS)	—
HCN	Linear	0.106317 ± 0.000005 (CH) 0.115535 ± 0.000006 (CN)	—
NH_3	Sym. Top	0.1008 ± 0.0004	107.3 ± 0.2
$CHCl_3$	Sym. Top	0.10959 ± 0.00005 (CH) 0.17812 ± 0.00005 (CCl)	108.0 ± 0.2 (HCH)
H_2O	Asym. top	0.09584 ± 0.00005	104.5 ± 0.3
O_3	Asym. top	0.1278 ± 0.0002	116.8 ± 0.5

Techniques And Instrumentation of MW Spectroscopy:

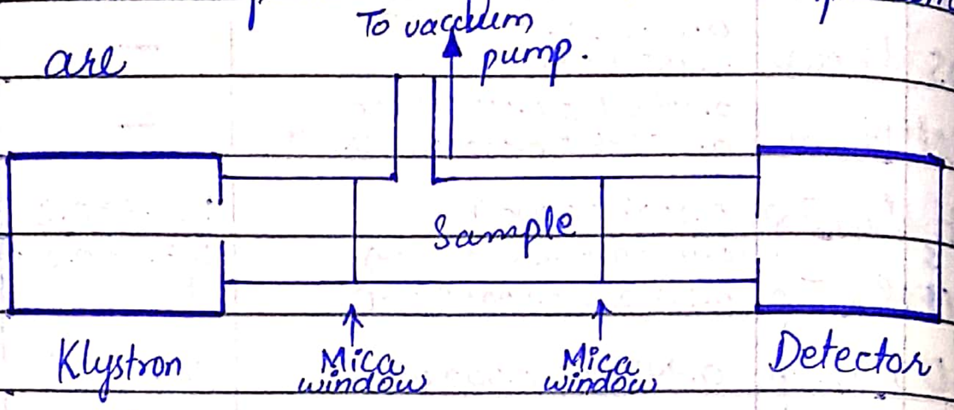
Microwave spectroscopy is used rarely as a routine analysis tool. Now it is largely surprised by other method. While General Schematic diagram of Absorption spectrometer is



All parts of microwave spectrometer are involved in scanning process.

Microwave Spectrometer

The components of Microwave spectromet are



i. Source and Monochromator
ii. Beam Direction
iii. Sample and Sample Space
iv. Detector

1. **Source & Monochromator:** Sources are different for different branches of spectrosco Generally the source are of two types (i) White light source (ii) Klystron valve
When light souce contain a wide range o frequency from which only desired frequency is selected by monochromator.

But in microwave spectroscopy the usual source is Klystron valve which emit radiation of very low/narrow range frequency therefore it acts as the monochromator thats why we have no need to use separate monochromator. The actual emission frequency of source is variable electronically and so a limited range of frequency using simple Klystron without monochromator in microwave spectro~~scopy~~meter all parts are involved in scanning process.

Klystron valve have one disadvantage that the total energy radiated is very small of the order of millimeters only. However This is all concentrated into a very narrow range of frequencies and the electric field generated at these frequencies is more intence then might be expected from radiative power- This problem can be solved by using sharply tuned detector which is sufficiently sensitive to detect.

② Beam direction or Wave Guide:

"These are actually hollow tubes of rectangular cross section made up of Cu or Silver "Ag" inside which the radiation is confined"

The tubing may be gently tapered or bent to focus or direct the radiation to concentrate and fall on the detector.

Vacuum Pump// Atmospheric absorption is considerable, so the whole system must be efficiently evacuated. For this purpose vacuum pump is used to remove the air from whole apparatus.

③ Sample and Sample Space:

Norma gaseous sample is used and is retained in a piece of evacuated waveguide by a very thin mica window. Very small pressures is sufficient to obtain a spectru The mica window allow the radiation to pass through it and doesnot allow sample to pass through it. Many substances which (solid or Liquid) have sufficiently high vapour pressure t allow them to be studied by this technique which are latter converted into gaseous phase due to their high vapour pressure.

④ Detector and Recorder:

Detectors are of two types.

(i) Radioreciever (ii) Simple crystal detecto

Radioreciever can be used as detector i MW spectrometer. Radioreciever should be tuned

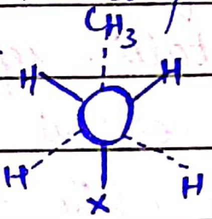
However Simple crystal detector is found to be a more sensitive and easier to use. This detector detects the radiation focussed o it by the waveguide. The signal it gives, is amplified for display or for permanent record on paper. So simple crystal detect is mostly used now-a-days.

Application of Microwave Spectroscopy

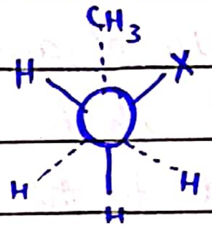
① Microwave spectra is one of the best methods in measuring dipole moments. The rotational energy level in a molecule is an electric field depend on the dipole moment of the molecule and the stark effect

② Among the interesting application of microwave spectroscopy is the study of rotational isomerism

Example: Consider the molecule of n-propyl chloride $CH_3CH_2CH_2-Cl$. Two rotational isomers of this compound are trans and gauche confirmation:



(Trans)



(Gauche)

Spectrum shows sharp rotational lines of trans isomer and somewhat broad lines of the gauche isomer. So it can predict different conformational isomers provided they have different moment of inertia.

③ Microwave techniques have made pure rotational transition in heavier molecule readily accessible

④ Microwave spectroscopy has led to major advances in the study of internel rotation.

For-example: For internel rotations of methyl group in sample molecule, some of the pure rotational transition are fal into doublets usually with spacing of a few megahertz. From this splitting the barrier height can be determined to a accuracy of better then 5%. Some of thes accurate barrier heights are

Molecule	**Bond**	**Barrier Height**
CH_3-CH_3	C–C	11.5
CH_3-CCl_3	C–C C–Cl	11.3 15.4

⑤ One of the most useful extension of the Microwave technique is the inclusio in the cell of a metallic septum by means of which an electric field can be applied to the gas while the spectrum is being scanned.

⑥ Microwave spectroscopy tells us about rigi rotator and non-rigid rotator. A treatment that assumes the molecular dimensions are independent of molecular vibrations and undisturbed by molecular rotation is known as rigid rotator approximation. While a modification that occur as a result of the centrifugal distortion the rotation produces. Such treatment is said to be deal with the non rigid rotator.

⑦ Rotational spectra can ~~deal~~ ~~with~~ provide accuate information abaut structure and shapes of molecules.

⑧ With the help of Microwave Spectroscopy we can determine spectral transition frequencies by applying selection rule.

⑨ Microwave spectroscopy is a highly sensitive and specific analytical tool

⑩ Microwave spectroscopy is also quantitative since the intensity of a spectrum observed under given conditions is directly ~~proportional~~ dependent, On the amount of substances present. Thus mixture can be readily analysed.

⑪ Microwave spectroscopy can readily be distinguish the pressure of isotopes in a sample.

⑫ Microwave analysis used in the chemical examination in intesstellar space. Microwaves has extended the analysis of the detection of simple stable molecules in space.

⑬ By Microwaves spectroscopy, the emission of Microwaves by molecules and comparing the relative intensities of rotational transitions particularly in the spectrum of ammonia, accurate estima can be made of the temprature of intessteller molecule

⑭ Microweave spectroscopy has become ver familiar in recent years in Kitchen in the shape of the Microwave Oven. Its mode of operation depends entirely upon absorptio by the food of the microwave radiation in which it is bathed.

⑮ Microwave Spectra of linear, symmetric Top and Asymmetricto p molecules give very precise estimate of Their bond angles.

For example:

Molecule	Type	Bond Angle
NH_3	Symmetric Top	107.3 ± 0.2
CH_3Cl	Symmetric Top	108.0 ± 0.2
H_2O	Asymmetric Top	104.5 ± 0.3
O_3	Asymmetric Top	116.0 ± 0.5

⑯ Microwave Spectroscopy tells us that whether a molecule is microwave active (having permanent dipole) and microwave inactive (having no permanent dipole

⑰ Microwave Spectroscopy tells us about the width and intensity of spectral line or spectral transition.

⑱ Microwave Spectroscopy give information about transition probability, degree of probability of a system and population of energy state.

⑲ Microwave Spectroscopy ~~tells us about~~ helps to determine path length of sample e.g. If 50% of electromagnetic radiation is absorbed by a sample of 1cm pathlength then only 75% of radiation will be absorb by the sample of path length 2cm.

⑳ Microwave spectroscopy tells us about principle axis of rotation in different molecules.

㉑ With Microwave analysis we can ~~to~~ use the measure spacing b/w adjacent rotational level to deduce a value of the rotational constant B of the molecule.

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

Example: Rotational spectrum of CO. Gilliam et al † have measured the first line (J=0) in the rotational spectrum of Carbon monoxide as

$$3.84235 = 2B = \bar{\nu}_{0\to1}$$

The value of B can be calculated as

$B = \frac{3.84235\ cm^{-1}}{2} = 1.92118\ cm^{-1}$ for CO

(22) The resolving power of the arrangement of Microwave spectrometer is 10^5 times greater than that of best infrared grating spectrometer

(23) Microwave spectroscopy help to determine bond length of molecules.

For example $I = \mu r^2$ or $r^2 = \frac{I}{\mu}$

Bond Length of NaCl = 0.23606 ± 0.00001

" " " NH_3 = 0.1008 ± 0.0004

(24) Microwave spectroscopy help to deter degeneracy of energy level by formula

Degeneracy = 2J + 1

For example:

Value of J	Degeneracy
J = 0	2(0) + 1 = 1
J = 1	2(1) + 1 = 3
J = 2	2(2) + 1 = 5

(25) Microwave spectroscopy is helpful in determination of precise atomic weight of isotopically substituted molecules.

For example: Atomic weight of ^{13}C-m is 13.0001 in $^{13}CO^{16}$

(26) Microwave spectroscopy can give directly an estimate of relative abundance

of naturally occuring isotopes and comparison of absorption intensities.
For example: The order of relative abundance of naturally occuring isotope of Carbonmonoxide is

$$^{12}CO^{15.9994} > {}^{13}CO^{15.9994} > {}^{14}CO^{15.9994}$$

(27) Determination of vibrational frequency of diatomic molecules is done by microwave Spectroscopy.

<u>For example:</u> For Hydrogen Flouride
The value of vibrational frequency is

$$\bar{\omega}_{\text{calculated}} \approx 4050\ cm^{-1}$$

(28) Microwave spectroscopy determine value of force constant or strength of bond.

For example: The force constant of H-F is given below

$$K = 4\pi^2 c^2 \bar{\omega}^2 \mu = 960\ Nm^{-1}$$

The value of force constant (K) is very great which indicates that H-F is a relatively strong bond.

(29) Microwave Spectroscopy determine energy difference b/w different energy levels. The general formula for rigid diatomic molecule is $\epsilon_{J+1} - \epsilon_J = 2B(J+1)$ units cm^{-1}