MICROWAVE SPECTROSCOPY part-1

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- The microwave spectroscopy explores that part of the electromagnectic spectrum which is in range of $3x10^{23}$ to $3x10^{10}$ HZ
- The region lies between the far infrared and radiofrequency regions.
- Represents changes of absorbing molecule from one rotational level to another.

Condition for microwave spectroscopy

- Molecule must possess permanent dipole moment.
- Molecule having dipole moment rotate, it generates an electric field which interacts with the electric component of the microwave radiation.
- During the interaction ,energy can be absorbed or emitted and thus the rotation of molecules gives rise to a spectrum.

Difference between infrared and microwave spectroscopy

- Absorption spectrum in the microwave region is characteristic of the molecule as whole where as in the infrared region is characteristic of the functional groups present in the molecule.
- Resolution of the lines in the microwave spectrum is much greater than that obtained by infrared spectrum.

- In microwave spectroscopy the substance must be in gaseous state .But in infrared spectroscopy the substance may be in solid ,liquid or in gaseous states.
- In microwave spectroscopy the spectra observed are always absorption spectra but in infrared spectroscopy the spectra observed may be absoption or emission spectra.

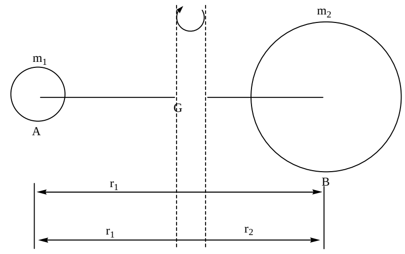
Theory of microwave spectroscopy

- Rotational energy along with all forms of molecular energy is quantised.
- It means the rotational energy levels calculated by solving schrodinger equation for the system represented by the molecule.

Diatomic molecule as a rigid rotator

- A rotating diatomic molecule whose nuclei are supposed to be separated by a definite mean distance treated as rigid rotator with free axis of rotation.
- A diatomic molecule in which masses m_1 and m_2 of atoms A and B are joined by a rigid bar whose length is r and given by-
- $R=r_1+r_2$ ---------(1)

- r_1 abd r_2 are the distance of atoms A and B from the centre of gravity G of AB molecule
- The moment of inertia $I=m_1r_1^2 + m2r_2^2$ --(2)



- As the system is balanced about its centre of gravity G, one may write

$m_1r_1=m_2r_2$ ---(3)

- On substituting equations, we obtain the following expression:

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

- ------(4)
- But from equartion (4) and (3), we have

$m_1r_1=m_2r_2=m_2(r-r_1)$

------(5)

- On solving equations (4) and (5), we get--

$$r_1=\frac{m_2}{m_2+m_2} r \text{ and } r_2=\frac{m_1}{m_1+m_2} r$$

- On putting these values of r_1 and r_2 in equation (2), we get

$$I=\frac{m_1m_2^2}{(m_1+m_2)^2} r^2 + \frac{m_1^2m_2}{(m_1+m_2)^2} r^2$$

$$= \frac{m_1m_2^2+ m_1^2m_2}{(m_1+m_2)^2} r^2$$

$$= \frac{m_1m_2(m_1+m_2)}{(m_1+m_2)^2} r2$$

$$I= \frac{m_1m_2}{m_1+m_2} r^2 = ur^2$$

- Here u is the reduced mass of the diatomic molecule and its value

$$u =\frac{m_1m_2}{m_1+m_2}$$

Equation (2.7) defines moment of inertia in terms of atomic masses d bond length.

A rotating molecule having a permanent dipole or magnetic moment generates an electric field which can interact with the electric component of the microwave region. If it is assumed that a diatomic molecule behaves like a rigid rotator, the rotational energy levels equation for the system represented by that molecule.

$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$ Joules where J= 0, 1, 2,
where h= Planck's constant,
I= Moment of Inertia,
J= Rotational quantum number; it takes integral values from zero upwards, and

$\frac{(J+1)h^2}{4\pi^2}$ = The square of the rotational angular momentum.

- In rotational region, spectra are generally expressed in terms waves numbers, so it becomes useful to consider energies in these its. Thus, one may write

$$\epsilon_J = \frac{E_J}{hc} = \frac{h^2}{8\pi^2 1hc} J(J+1)\ cm^{-1}$$

$$= \frac{h}{8\pi^2 Ic} (J+1)\ cm^{-1}$$

Here c is the velocity of light expressed in cm per second. It is common to write B for $h/8\pi^2Ic$ so that equation reads as

$c_J = J(J+1)B\ cm^{-1}$
Here B is called the rotational constant and may be expressed in cm^{-1},
$B = h/8\pi^2 Ic\ cm^{-1}$

- From the equation of velocity of light, we can show that allowed energy levels diagrammatically as the figure of moment of inertia. When J=0, equation becmes as

ϵ_J= BJ(J+1) cm-1 = B 0(0+1)=0

From the equation above it is evident that the molecule is not rotating at all. When J=1, equation becomes as
ϵ_J = B.1(1+1)=2B cm-1

From above equation it follows that a rotating molecule has its lowest angular momentum. Similarly, one can calculate the value of ϵ_J
For J=2,3,4……… The allowed rotational energy levels of a rigid diatomic molecule are shown below……