Microwave Spectroscopy - Microwave spectroscopy deals with the pure rotational motion of molecules and is also known as rotational spectroscopy

microwave region 100 μm (3×10^{12} Hz) to 1cm (3×10^{10} Hz).

The molecules must possess permanent dipole moment to have interaction with radiations in the microwave region.

When a molecule having dipole moment rotates, it generates an electric field which can interact with the electric component of the microwave radiation. During the interaction, energy can be absorbed or emitted and thus the rotation of the molecules gives rise to a spectrum.

If molecules are not having dipole moments, interaction is not possible and these molecules are said to be microwave inactive

Microwave inactive molecules – H_2, Cl_2 etc

Microwave active molecules – HCl, CH_3Cl

The microwave spectra obtained in most of the molecules are generally absorption spectra.

Difference between Infrared and Microwave Spectroscopy

The absorption spectrum in the microwave region is characteristic of the absorbing molecules as a whole, whereas spectrum in the infrared region is characteristic of the functional groups present in the absorbing molecule.

2. The resolution of the lines in the microwave spectrum is very much greater than that obtained by the infrared method.

3 In microwave spectroscopy, the substance must be in gaseous state. On the other hand, in the infrared spectrum the substance may be in the solid, liquid or gaseous state.

4. In microwave spectroscopy, the spectra observed are nearly always absorption spectra. But in the infrared spectroscopy the spectra observed may be absorption or emission spectra.

Rotational spectra of Diatomic molecules

The Rigid Diatomic Molecule

In order to interprete the pure rotational spectra consider a diatomic molecule. ~~in which~~ ~~Let m_1 and~~ Let m_1 and m_2 are the masses of atoms A and B which are joined by a rigid bar whose length is r.

$$r = r_1 + r_2 \quad \text{——— (1)}$$

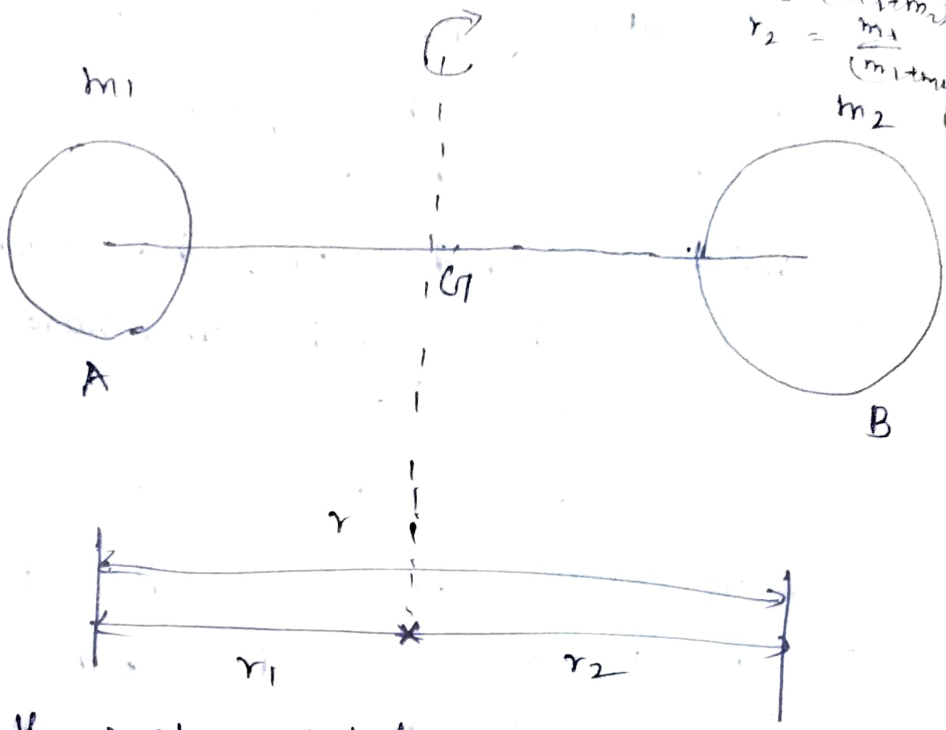
r_1 and r_2 are the distances of atoms A and B from the centre of gravity G of the molecule AB. The molecule rotates end - over - end about the centre of gravity. The moment of inertia about G is given by

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{——— (2)}$$

$m_1(r - r_2) = m_2 r_2$

$m_1 r = (m_1 + m_2) r_2$

$r_2 = \frac{m_1}{(m_1+m_2)} r$



As the system is balanced about its centre of gravity G,

$$m_1 r_1 = m_2 r_2 \quad \text{— ③}$$

Substituting eqn ③ in ②

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

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

$$I = r_1 r_2 (m_1 + m_2) \quad \text{— ④}$$

$m_1 r_1 = m_2 r_2$

$m_1 r_1 = m(r - r_2)$

$m_2 r_2 = m_2(r - r_1)$

$m_1 r_1 = m_2 (r - r_1)$

$m_1 r_1 = m_2 r - m_2 r_1$

$(m_1 + m_2) r_1 = m_2 r$

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

from eqn ① and ③ $r = r_1 + r_2 \Rightarrow r_1 = r - r_2$, $r_2 = r - r_1$

$m_1 r_1$ ~~$= m_2 r_2 = m_2 (r - r_1)$~~ — ~~⑤~~

~~Solving eqns ④ and ⑤~~

using the two equations $m_1 r_1 = m_2 r_2$ and $r = r_1 + r_2$

~~$m_1 r_1 = m_2 r_2 = m_2 (r + r_1)$~~ ⟵ ⑤

using eqn ④ and ⑤ we get

$$\left. \begin{aligned} r_1 &= \frac{m_2}{(m_1+m_2)} r \quad \text{and} \\ r_2 &= \frac{m_1}{(m_1+m_2)} r \end{aligned} \right\} \quad \text{— ⑥}$$

Substituting the value of eqn ⑥ in ②

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

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

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

$$I = \frac{m_1 m_2}{(m_1+m_2)} r^2 = \mu r^2 \quad — (7)$$

where $\mu = \frac{m_1 m_2}{(m_1+m_2)}$ is called the — (8) reduced mass of the diatomic molecule

The permitted energy values - the so called rotational energy levels may in principle be ~~called~~ calculated by solving the schrondinger's equation for the system represented by that molecule.

$E = h\nu$
$E = hc/\lambda$
$1/\lambda = \frac{E}{hc}$

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ Joules where } J = 0, 1, 2, \quad — (9)$$

where h = Planck's constant
I = Moment of Inertia
J = Rotational quantum number
it takes integral values from 0 upwards

In rotational region, spectra are generally expressed in terms of wave numbers,

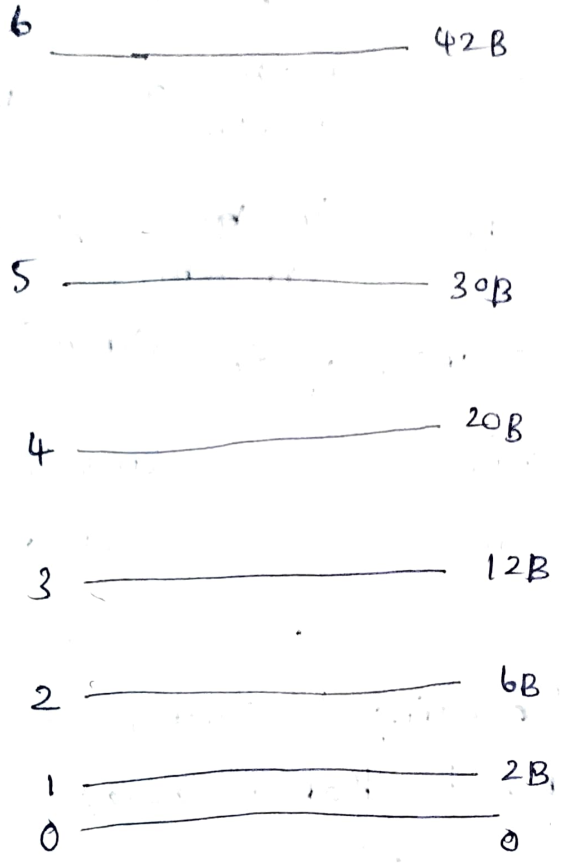
$$\epsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) \text{ cm}^{-1} \quad — (10)$$

where $B = \frac{h}{8\pi^2 Ic}$ cm^{-1} — ⑫

B is called the rotational constant

$\varepsilon_J = BJ(J+1)$ cm^{-1} — ⑬

Energy level diagram



From eqn ⑬ when $J = 0$

we have $\varepsilon_J = 0$ and we would say that the molecule is not rotating at all.

For $J = 1$ ~~$\varepsilon_J = B \cdot 1$~~ $\varepsilon_1 = B \cdot 1(1+1)$

$\varepsilon = 2B cm^{-1}$ — ⑭

From eqn ⑭ the rotating molecule has its lowest angular momentum. Similarly we can calculate the value of ε_J for $J = 2, 3, 4 \ldots$

There is no limit to the rotational energy of the molecule may have.

In practice of course, there comes a point at which the centrifugal force of a rapidly rotating diatomic molecule is greater than the strength of the bond, and the molecule is disrupted, but this point is not reached at normal temperatures.

Frequency of rotational spectral lines

We have to consider differences between the levels in order to discuss the spectrum. If a molecule in the ground state i.e $J = 0$ state absorbs incident radiation ~~then~~ and the absorbed energy raised it to the higher state say $J = 1$ state.

The absorbed energy will be

$$\bar{\nu}_J \cancel{\Delta E} = \varepsilon_{J=1} - \varepsilon_{J=0}$$

$$= B\{(1+1) - 0(0+1)\}$$

$$= 2B\,cm^{-1}$$

An absorption line will appear at $2B\,cm^{-1}$

If the molecule is raised from the $J = 1$ to the $J = 2$ level by the absorption of more energy:

$$\bar{\nu}_{J=1 \to J=2} = 6B - 2B = 4B\,cm^{-1}$$

It means that an absorption will appear at $4B\,cm^{-1}$

In general when the molecule is raised from J to $J+1$

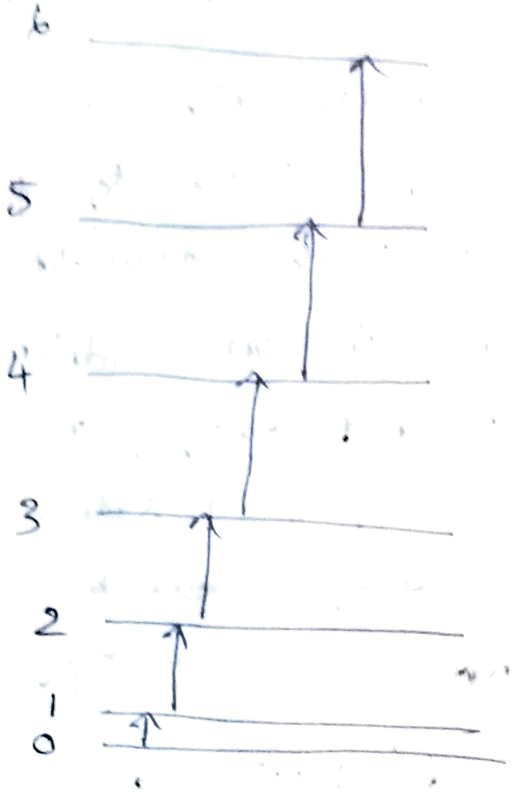
$$\bar{\nu}_{J \to J+1} = B\left[(J+1)(J+2) - J(J+1)\right]$$

$$= B\left[J^2 + 3J + 2 - J^2 - J\right]$$

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

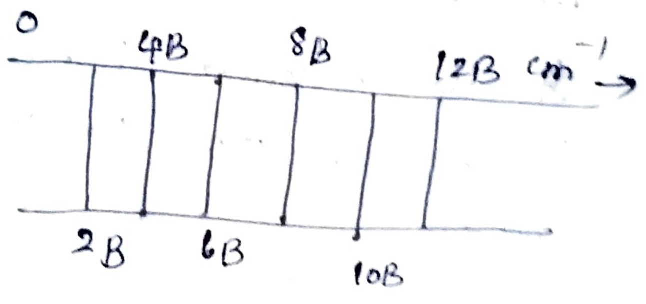
Thus a stepwise raising of the rotational energy results in an absorption spectrum consisting of lines at 2B, 4B, 6B ... cm⁻¹

Allowed rotational transitions of a rigid diatomic molecule



absorption spectrum

~~emission spectrum~~



emission spectrum

Selection rule for rotational spectrum

$\Delta J = \pm 1$

The transitions i.e., $J = 0 \rightarrow J = 2 \rightarrow J = 4$ are forbidden.

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