Rotation Of Molecules

- Spectroscopy in the microwave region is concerned with the study of rotating molecules
- Rotation of 3D body may be quite complex
- Rotational components about three mutually perpendicular directions through the centre of gravity - the principal axis of rotation.
- Three principal moments of inertia I_A, I_B, and I_C

Classification of molecules

(i) Linear molecules:

- ✓ Atoms are arranged in a straight line.
- ✓ e.g. HCl or OCS

The three directions of rotation may be taken as :

(a) about the bond axis,

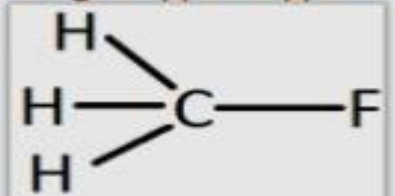
(b) end-over-end rotation in the plane of the paper,

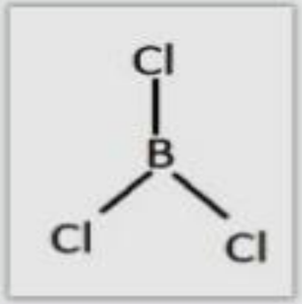
(c) end-over-end rotation at right angles to the plane. Here

(ii) Symmetric top: Consider a molecule such as methyl fluoride, three hydrogen atoms are bonded tetrahedrally to the carbon

The moment of inertia about the C-F bond axis is now not negligible, however, because it involves the rotation of three comparatively massive hydrogen atoms of this axis

Symmetric tops: $I_B = I_C \neq I_A \quad I_A \neq 0$



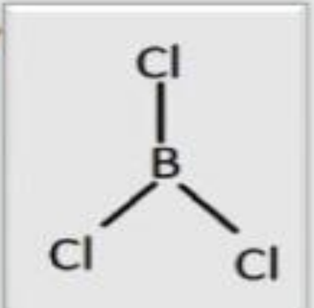


Cont

Two subdivisions of this class

- Methyl fluoride above, $I_B=I\text{-}_C>I_A$, then the molecule is called *prolate* symmetric top
- If $I_B=I_C<I_A$, it is referred to as *oblate*

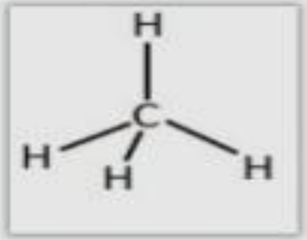
An example of the layer type is boron trichloride, which, as shown, is planar and sy



$$I_A = 2I_B = 2I_C$$

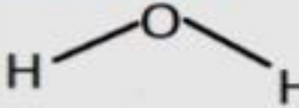
(iii) Spherical top: when a molecule has all three moments of inertia identical, it is called spherical tops.

e.g, CH_4



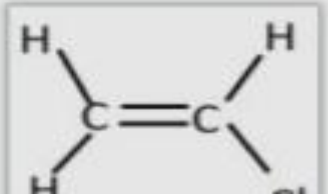
$$I_A = I_B = I_C.$$

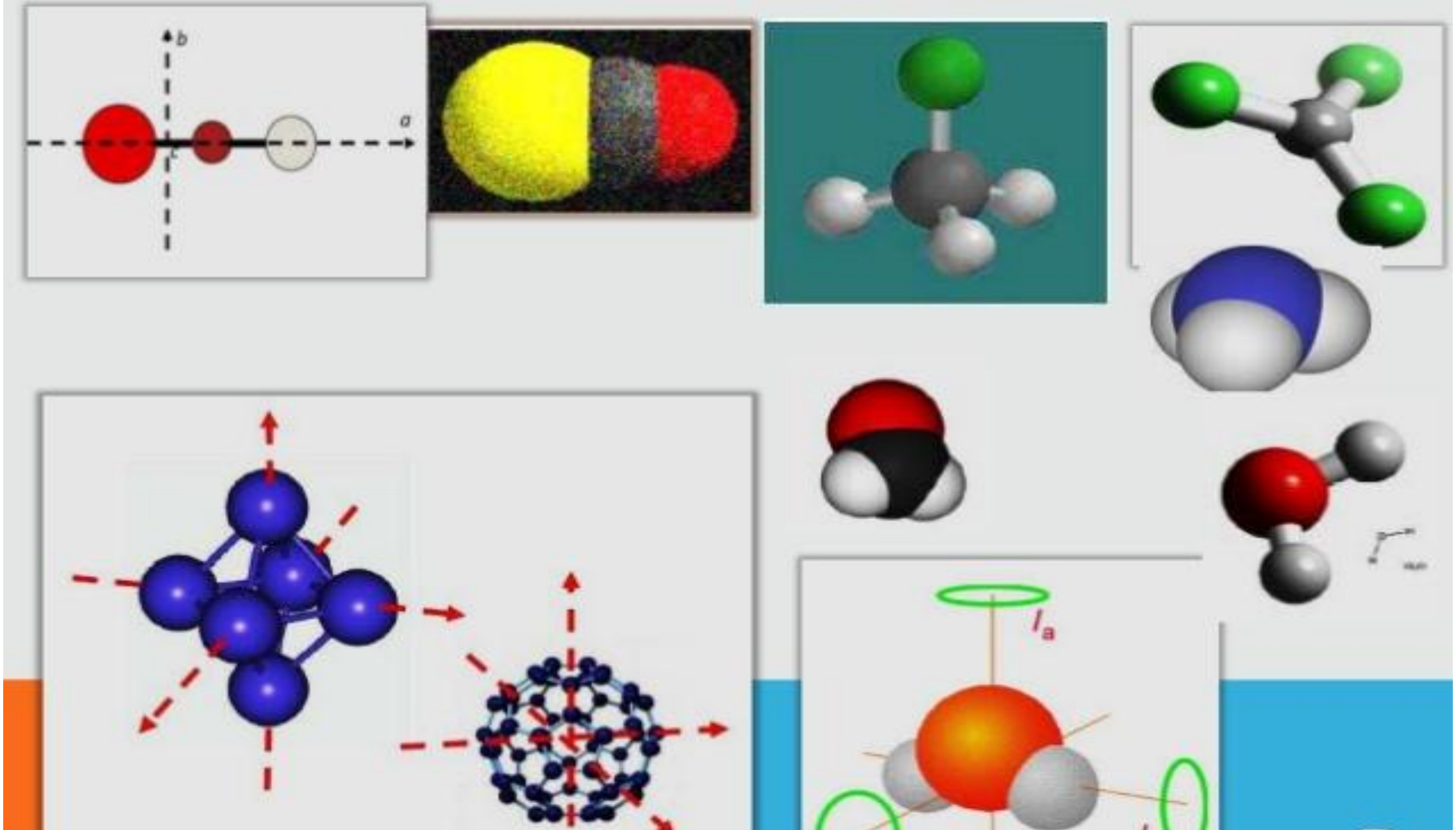
(iv) Asymmetric top: These molecules, to which the majority of substance belong, have all three moments of inertia different:



$$I_A \neq I_B \neq I_C$$

Simple example are H_2O and $CH_2{=}CHCl$




b
a
I_a

Rotational Spectra:Molecular Requirements

- Spectroscopy in the microwave region is concerned with the study of rotating molecules.
- Only molecules that have a permanent dipole moment can absorb or emit electromagnetic radiation in such transitions.
- In the rotation of HCl, fluctuation seen to be exactly similar to the fluctuating electric field of radiation.
- Thus interaction can occur, energy can be absorbed or emitted and the ***rotation gives rise to a spectrum.***

WHICH TYPE OF MOLECULE DOESN'T SHOW ROTATIONAL SPECTRUM AND WHY……???

- In homonuclear molecules like N_2 & O_2 , no change occur in dipole moment during the rotation.
- Linear diatomic molecules are rotationally inactive for rotation about the bond axis.

i. The moment of inertia is very small (zero) about the bond axis.
ii. No change in dipole occurs when it is rotating about bond axis.

- Homonuclear molecules, however show rotational Raman spectra (which is arises due to the polarisability of the molecules.)

Techniques And Instrumentation

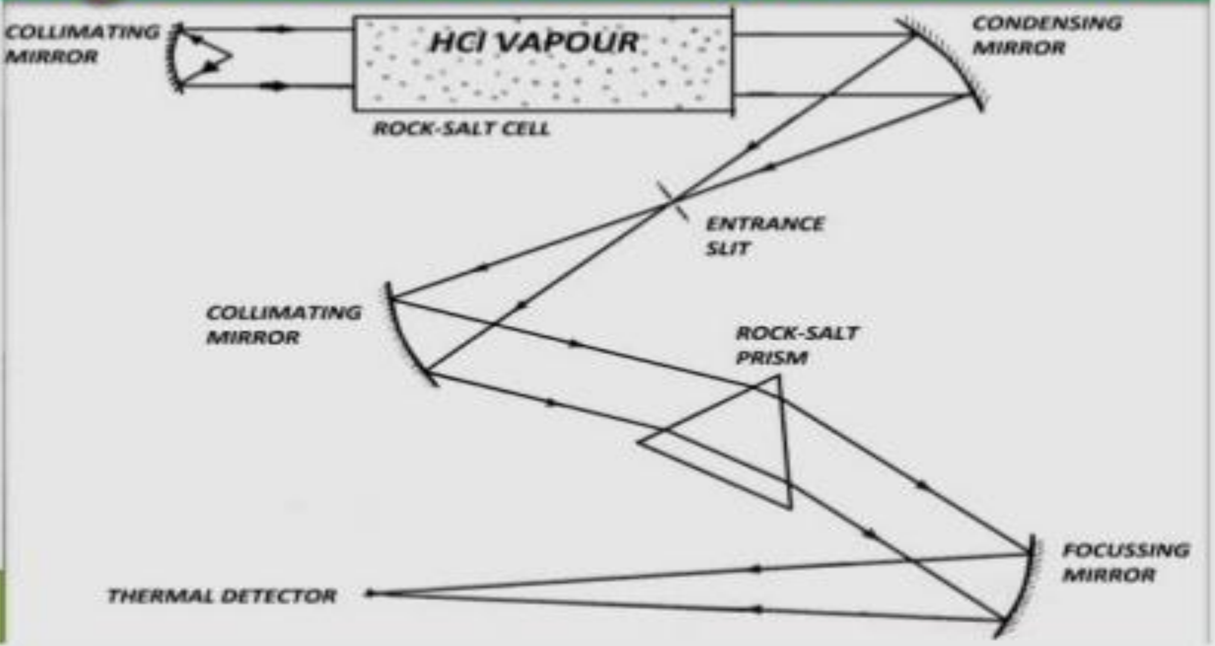
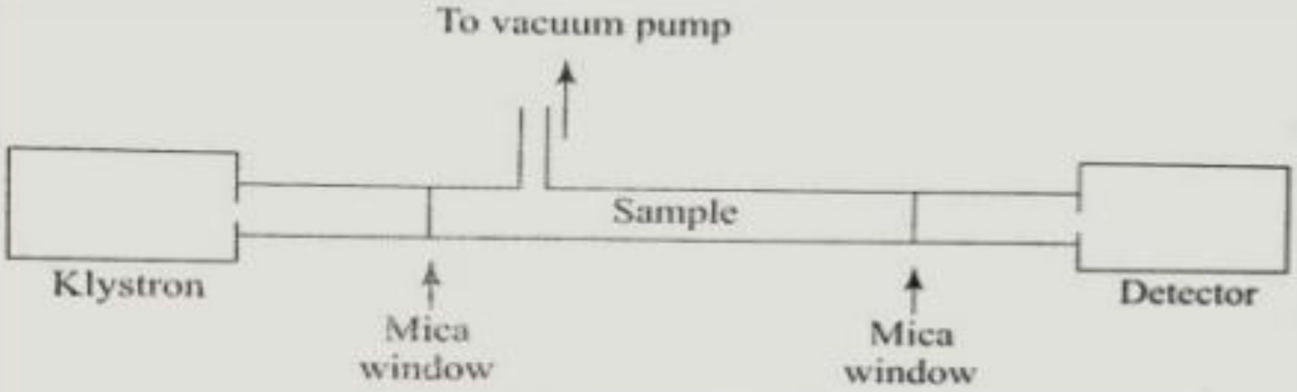


Fig.1

The basic requirements for observing pure rotational spectra in absorption are a source of continuous radiation in the proper infrared region, a dispersive device and a detector.

- Radiation from the source is taken, which passes through the HCl vapour
- The transmitted beam falls on a condensing mirror
- The collimated beam passes through a rock-salt prism and is brought to a focus at the thermal detector by means of a focusing mirror



Schematic diagram of a microwave spectrometer.

I. **Source and monochromator:** Klystron valve is monochromatic source, emits radiation over only a vey narrow freq. range.

II. **Beam direction:** Achieved by use of waveguides (rectangular) inside which radiation is confined.

III. **Sample and sample space**

Molecule As A Rigid Rotator: Diatomic Molecule

The simplest model of a rotating molecule is that of a rigid rotator

By the definition of Centre of mass, we have

$$M_1 r_1 = M_2 r_2$$

Also $$r_1 + r_2 = r$$

From these two equation, we have

$$r_1 = \frac{M_2}{M_1 + M_2} r \quad \text{and} \quad r_1 = \frac{M_1}{M_1 + M_2} r$$

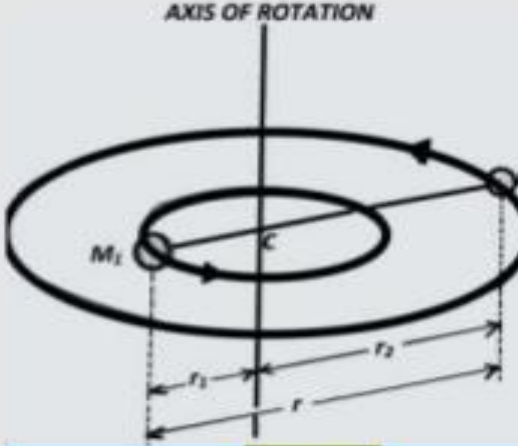


Fig.2

Now, the moment of inertia of the molecule about the axis of rotation is given by

$$I = M_1 r_1^2 + M_2 r_2^2$$

$$= \frac{M_1 M_2}{M_1 + M_2} r^2$$

But $\frac{M_1 M_2}{M_1 + M_2}$ is the reduced mass μ of the molecule. Then

$$I = \mu r^2$$

Thus the diatomic molecule is equivalent to a single point mass μ at a fixed distance r from the axis of rotation. Such a system is called a ***rigid rotator***.

Schrodinger equation for a rigid rotator, which is

$$\boxed{\Delta^2\psi + \frac{8\pi^2\mu}{h^2}E\psi = 0}$$

The potential energy term V has been taken zero because r is fixed.

In spherical polar coordinate system

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\psi}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2\mu}{h^2}E\psi = 0 \quad \text{----------- (i)}$$

Using separable variable method

$$\psi(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

On solving by separable variable method, we have two equations

$$\frac{d^2\Phi}{d\phi^2} = -M^2\Phi \qquad \text{------------ (ii)}$$

And,

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left(\frac{8\pi^2 IE}{h^2}-\frac{M^2}{\sin^2\theta}\right)\Theta = 0 \qquad \text{------------ (iii)}$$

The solution of the Φ-equation

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{iM\phi} \qquad \text{------------ (iv)}$$

On solving Θ-eq.

This eq. is identical to the associated Legendre's differential equation, provided

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

Or,

$$\boxed{E_J = \frac{h^2}{8\pi^2 I} J(J+1)} \quad \text{-----------} \ (v)$$

In this expression, h is Planck's constant and I is moment of inertia, either I_B or I_C, since both are equal.

The quantity J, which takes integral values from zero upwards, is called the Rotational Quantum Number.

Spectrum Of Rigid Rotator

In the rotational region, spectra are usually discussed in terms of wave numbers.

$$\varepsilon = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1)\ cm^{-1} \quad (J=0, 1, 2, \ldots) \quad \text{(vi)}$$

Where c is velocity of light, Is here expressed in cm s^{-1} .

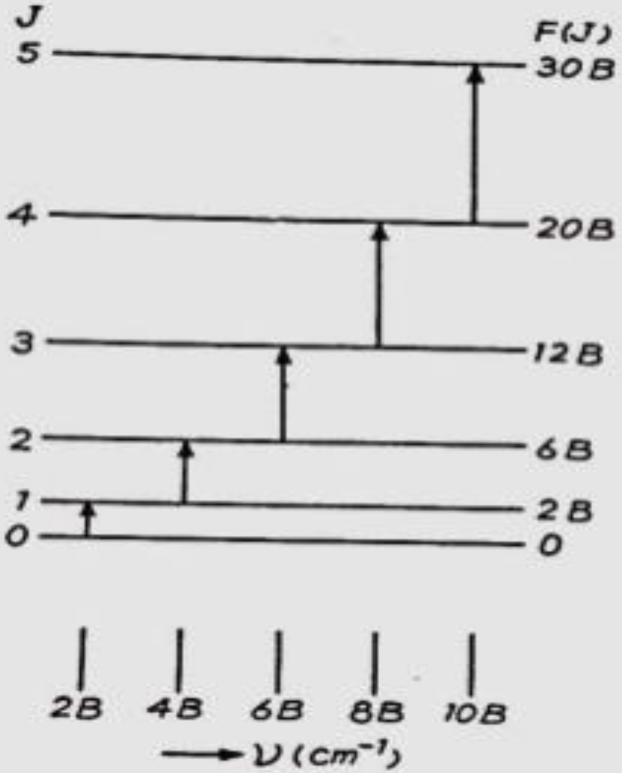
$$\boxed{\varepsilon = BJ(J+1)\ cm^{-1}} \quad \text{(vii)}$$

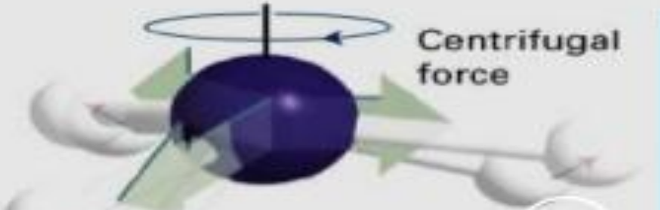
Where B, *the rotational constant*, is given by

$$\boxed{B = \frac{h}{8\pi^2 I} cm^{-1}}$$

From eq.(vii) allowed energy levels

- For J = 0, ε is zero-molecule is not rotating
- For J=1, the rotational energy is ε_1= 2B and a rotating molecule has its *lowest angular momentum*
- For increasing J values, ε_J may have no limit to the rotational energy





If we imagine the molecule to be in the the ground state, in which no radiation occurs

To raise the molecule to J= 1 state energy absorbed will be

$$\varepsilon_{J1} - \varepsilon_{J0} = 2B - 0 = 2B\ cm^{-1}$$

$$\bar{\nu}_{J=0\rightarrow J=1} = 2Bcm^{-1}$$

Further for J=1 to J=2

$$\bar{\nu}_{J-1\ \rightarrow J-2} = 4Bcm^{-1}$$

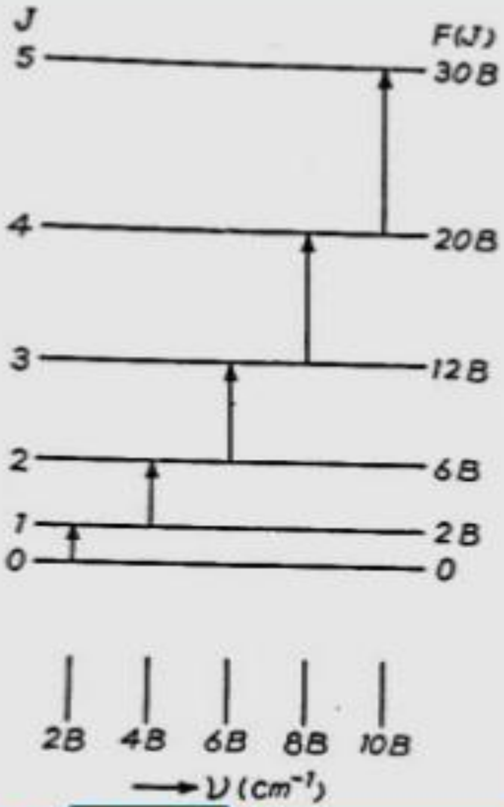


Fig.3.1

In general,

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

Or,

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

Thus a step wise raising of the rotational energy results in an absorption spectrum consisting of lines at 2B, 4B, 6B, … cm-1.

we need only consider transition in which J changes by one unit - all other transitions being *spectroscopically forbidden*, such a result, it is called a **selection rule**,

Selection rule: ΔJ= ±1

level, while it is moving in gaseous state.

⑪ Determination of bond length of rigid diatomic molecules—HCl

On absorbing microwave radiation, HCl-molecule undergo **rotational motion** involving transitions from lower energy level to higher level. From the transition, it gives equally spaced spectral lines with a gap of '2B' where the first line appears. The moment of inertia and the bond length is calculated from these spectral lines.

For example, in the calculation of the bond length of HCl. The first line is observed at 20.7 cm^{-1} in its microwave spectra.

$$\Rightarrow \quad 2B = 20 \cdot 7\,cm^{-1} \Rightarrow \boxed{B = 10 \cdot 35\,cm^{-1}}$$

But
$$B = \frac{h}{8\pi^2 IC} \Rightarrow \boxed{I = \frac{h}{8\pi^2 BC}}$$

$$\Rightarrow \quad \frac{6 \cdot 625 \times 10^{-27}}{8 \times (3 \cdot 14)^2 \times 10 \cdot 35 \times 3 \times 10^{10}} = 2 \cdot 705 \times 10^{-40}\ gm.cm^2.$$

$$\text{Reduced mass of HCl, } U_{HCl} = \frac{m_1 m_2}{m_1 + m_2} \times \frac{1}{N} = \frac{1 \times 35 \cdot 5}{1 + 35 \cdot 5} \times \frac{1}{6 \cdot 023 \times 10^{23}}$$

$$m_1 + m_2 \quad N \quad 1+35\cdot5 \quad 6\cdot023\times10^{23}$$

$$\Rightarrow \qquad U_{HCl} = 1\cdot614\times10^{-24} \text{ gm/molecule.}$$

$$I = ur^2 \Rightarrow r^2 = \frac{I}{u} \boxed{\Rightarrow r = \sqrt{\frac{I}{u}}}$$

$$\Rightarrow \qquad r = \sqrt{\frac{2\cdot705\times10^{-40}}{1\cdot614\times10^{-24}}} = \sqrt{1\cdot71\times10^{-16}}$$

$$= 1\cdot31\times10^{-8}\,\text{cm} = 1\cdot31\,\text{A}^\circ$$

$\therefore$ The bond length of HCl $= 1\cdot31\,\text{A}^\circ$