

# Chapter 11

A molecule is made up two or more atoms joined by a net attractive force between them.

A molecule emits and absorbs energy in the same way an atom does.

Molecules can store kinetic energy of rotation, and vibration.

The vibration-rotation spectra give information on the strength of the bond, the length of the bond etc..

The bonding mechanisms are

- \* **Ionic** bonding is formed by attraction of two oppositely charged ions such as  $\text{Na}^+\text{Cl}^-$  to form  $\text{NaCl}$  molecule.
- \* **Covalent** bonding is formed by the sharing of valence electrons of the atoms such as  $\text{H}_2$ ,  $\text{O}_2$  molecules
- \* **Hydrogen** bonding is formed by a hydrogen atom and two negatively charged ions such as  $(\text{HF}_2)^-$  ionic molecule.
- \* **Van der Waals** bonding is a weak electrostatic bond between atoms that do not form ionic or covalent bonding.

There are three types in which the attractive forces are due to

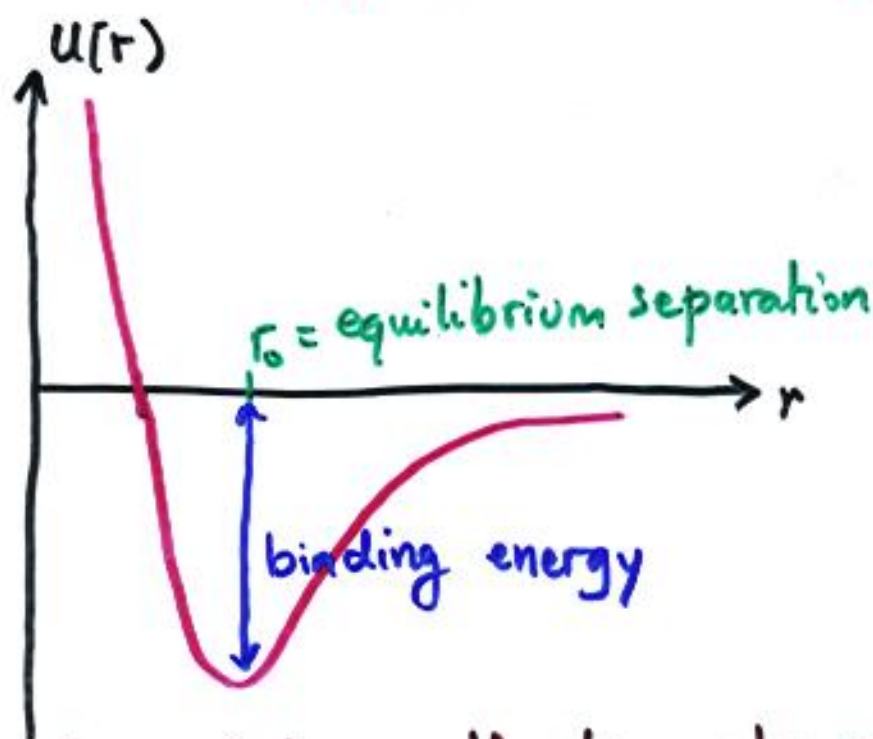
- Dipole-Dipole occurs between two atoms having permanent electric dipole moment. (HCl and H<sub>2</sub>O)

- Dipole-Induced dipole occurs between a polar molecule having a permanent dipole which induces a dipole moment in a non-polar molecule.

- Dispersion or London occurs between two non-polar molecules.

In these three cases the forces  $F \propto \frac{C}{r^7}$

The total potential energy of the molecule varies as follows



at  $r_0$  the net force between the two atoms is zero and the molecule is stable.



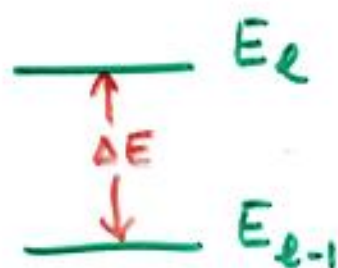
Molecules can store rotational energy as well as vibrational energy.

$$E_{\text{rot}} = \frac{\hbar^2}{2 I_{\text{cm}}} l(l+1) \quad l = 0, 1, 2, \dots$$

$l$ : rotational quantum number.

$$I_{\text{cm}} = \mu R_0^2$$

↑ reduced mass     ↑ bond length



$$\Delta E = \frac{\hbar^2}{I_{\text{cm}}} l$$

↑ quantum number of the higher energy state.

Photons should be observed at the frequencies

$$\omega_0 = \frac{\Delta E}{\hbar} = \frac{\hbar}{I_{\text{cm}}}, \quad 2\omega_0, \quad 3\omega_0, \dots$$

transitions:  $0 \rightarrow 1$       $1 \rightarrow 2$       $2 \rightarrow 3 \dots$

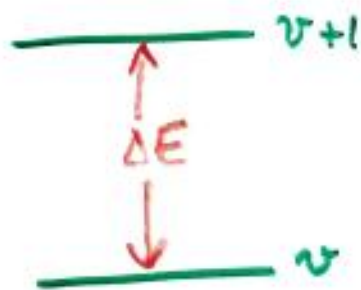
$$E_{\text{vib}} = \left(v + \frac{1}{2}\right) \hbar \omega \quad v = 0, 1, 2, \dots$$

$v$ : vibrational quantum number.

$\omega$ : frequency of vibration and related to the force constant by:

$$k = \mu \omega^2$$

↑ a measure of the bond strength     ↑ reduced mass =  $\frac{m_1 m_2}{m_1 + m_2}$



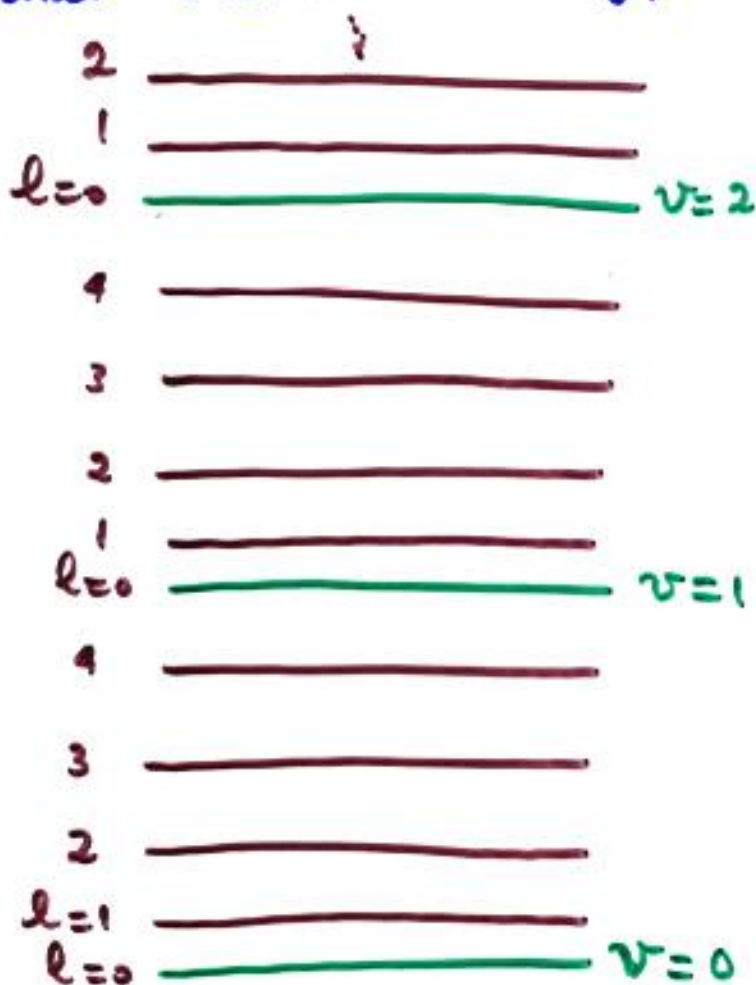
$\Delta E = \hbar\omega$  does not change as the levels are equally spaced.

$v=0 \Rightarrow E_{vib} = \frac{1}{2}\hbar\omega$  is called the zero-point energy.

In general, an excited molecule will rotate AND vibrate at the same time

$$\Rightarrow E_{rot-vib} = \frac{\hbar^2}{2I_{cm}} l(l+1) + (v + \frac{1}{2})\hbar\omega$$

The rotational-vibrational energy levels are as follows:



Each level is indexed by  $l$  and  $v$ !

For example: level  $v=0, l=1$  is different from level  $v=1, l=1$ , etc...

Optical transitions are subject to selection rules:

$$\left. \begin{array}{l} \Delta l = \pm 1 \\ \Delta v = \pm 1 \end{array} \right\} \text{simultaneously.}$$

$\Rightarrow$  Pure vibrational transition cannot occur!

↳ rotational " " " " !

In order to have a transition, say to higher level, the absorbed photon energy is:

$$\Delta E = \hbar\omega + \frac{\hbar^2}{2I_{cm}} 2(l+1) \quad \Delta l = +1$$

$$\Delta E = \hbar\omega - \frac{\hbar^2}{I_{cm}} l \quad \Delta l = -1$$

example

transition  
 $v=0, l=1$

$\rightarrow v=1, l=2$

example

transition

$v=0, l=3$

$v=1, l=2$