

Molecular Spectroscopy : Study of the interaction of electromagnetic waves with matter.

Regions of the Spectrum

(i) Radiofrequency region :  $3 \times 10^6 - 3 \times 10^{10}$  Hz ; 10m - 1cm  
wavelengths.

Nuclear Magnetic resonance (NMR) and electron spin resonance (ESR) spectroscopy. The energy change involved — arising ~~from~~ from the reversal of spin of a nucleus or electron, is of the order 0.001 - 10 Joules/mole.

(ii) Microwave Region :  $3 \times 10^{10} - 3 \times 10^{12}$  Hz ; 1cm - 100  $\mu$ m  
wavelength

Rotational spectroscopy, separations between the rotational levels of molecules are of the order of hundreds of Joules per mole.

(iii) Infra-red region :  $3 \times 10^{12} - 3 \times 10^{14}$  Hz ; 100  $\mu$ m - 1  $\mu$ m  
wavelengths

Vibrational spectroscopy — one of the most valuable spectroscopic regions for the chemist. Separations between levels are some  $10^4$  joules/mole.

(iv) Visible and Ultra-violet regions :  $3 \times 10^{14} - 3 \times 10^{16}$  Hz ;  
1  $\mu$ m - 10 nm  
wavelength

Electronic spectroscopy. The separations between the energies of valence electrons are some hundreds to kilojoules per mole.

(V) X-ray region :  $3 \times 10^{16} - 3 \times 10^{20}$  Hz;  $10 \text{ nm} - 100 \text{ pm}$  ②  
wavelength.

Energy changes involving the inner electrons of an atom or a molecule, which may be of order ten thousand kilojoules.

(VI)  $\gamma$ -ray region :  $3 \times 10^{18} - 3 \times 10^{20}$  Hz;  $100 \text{ pm} - 1 \text{ pm}$   
Wave length.

Energy changes involve the rearrangement of nuclear particles, having energies of  $10^9 - 10^{11}$  Joules per gram atoms.

~~Other type of spectroscopy~~ One other type of spectroscopy

↳ Raman spectroscopy → this yields information similar to that obtained in the microwave and infra-red regions. Experimental method → observations are made in the visible region.

From the viewpoint of experimental methods and theoretical significance - molecular spectra <sup>fall</sup> into three groups;

(i) The far infra-red region (long wavelengths 20-150  $\mu$ )

(ii) The near (short wavelengths) infrared region

(iii) visible or ultra-violet region

A transition between two electronic levels of molecule → results in radiation that falls in the ~~near~~ visible or ultra-violet region.

With each electronic level are associated a number of vibrational energy levels → A transition between two vibrational levels results in a radiation in ~~near~~ <sup>infra</sup> ~~red~~ <sup>red</sup> region.

(iii) With each vibrational level is associated a set of rotational levels. A transition between two rotational energy levels results in a radiation that falls in far infra-red or microwave regions.

## Features of Rotational Spectra

(i) The bands which appear in far infra-red or microwave region at  $\lambda = 200 \times 10^4 \text{ \AA}$  or more are due to transitions of small energy changes, about  $0.005 \text{ eV}$ . Electrons and vibrational energy states will not be excited  $\rightarrow$  only transitions that are purely rotational will appear.

Only those molecules which have permanent electric dipole moment can give rise to pure rotational spectra.

Homonuclear diatomic molecules such as  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$  etc. do not exhibit pure rotational spectra.

Heteronuclear diatomic molecule such as  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$   $\rightarrow$  exhibit rotational spectra.

(ii) In practice, rotational spectra are observed in absorptions.

(ii) According to classical electrodynamics, a rotating molecule can lead to emission of radiation only if a changing dipole moment is associated with it.

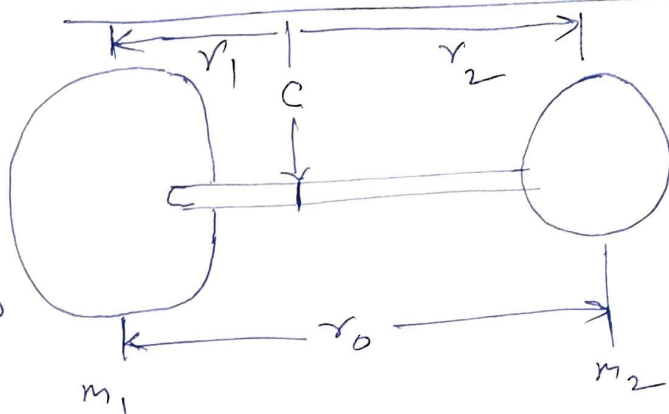
Rotational Spectra  $\rightarrow$  Rotational energy along with all other forms of molecular energy

is quantized  $\rightarrow$  this means that a molecule cannot have any arbitrary amount of rotational energy, but its energy is limited to certain definite values.

which depends on the shape and size of the molecule (4) concerned. The permitted energy values  $\rightarrow$  so-called rotational energy levels  $\rightarrow$  may be calculated for any molecule by solving the Schrödinger eq<sup>n</sup> for the system of the molecule.

### Diatom molecules: - The rigid Diatomic Molecule

Simplest of all linear molecules, masses  $m_1$  and  $m_2$  are joined by a rigid bar (the bond) whose length is



$$r_0 = r_1 + r_2 \quad \text{--- (1)}$$

The molecule rotates end-over-end about a point  $C$ , the centre of gravity: This is defined by the moment, or balancing eq<sup>n</sup>:

$$m_1 r_1 = m_2 r_2 \quad \text{--- (2)}$$

The moment of ~~inertia~~ inertia about  $C$  is defined (4);

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

$$= m_2 r_2 r_1 + m_1 r_1 r_2 \quad \text{--- (from eq (2))}$$

$$I = r_1 r_2 (m_1 + m_2) \quad \text{--- (3)}$$

but from eq<sup>n</sup> (1) & (2)

$$m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$$

$$\Rightarrow r_1 = \frac{m_2 r_0}{m_1 + m_2} \quad \text{and} \quad r_2 = \frac{m_1 r_0}{m_1 + m_2} \quad \text{--- (4)}$$

Replacing eq<sup>n</sup> (4) into (3)

$$I = \frac{m_1 m_2 r_0^2}{(m_1 + m_2)} = \mu r_0^2 \quad \text{--- (5)}$$

where  $\mu = \frac{m_1 m_2}{m_1 + m_2} \rightarrow$  reduced mass of the system. (5)

Eq<sup>n</sup> (5)  $\rightarrow$  moment of inertia in terms of the atomic masses and the bond length.

If the molecule is rotating with angular velocity  $\omega$ , classically it would have energy  $\frac{1}{2} I \omega^2$  and angular momentum

$$I \omega = J \frac{h}{2\pi}, \quad J = 0, 1, 2, \dots$$

The allowed rotational energies will be given

by 
$$E_r = \frac{1}{2} I \omega^2$$
$$= \frac{1}{2I} (I^2 \omega^2)$$
$$= \frac{J^2 h^2}{8\pi^2 I} \quad J = 0, 1, 2, \dots$$
 rotational quantum number

By the use of the Schrödinger eq<sup>n</sup> it may be also shown that the rotational energy levels allowed to the rigid diatomic molecules are given by the expressions:

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

where  $J = 0, 1, 2, \dots$  (6)

$h \rightarrow$  Planck's constant

$I \rightarrow$  moment of inertia

$J \rightarrow$  rotational quantum number, its restriction to integral values arises directly out of the sol<sup>n</sup> to the Schrödinger eq<sup>n</sup>.

from eq<sup>n</sup> (6)  $\nu = \frac{\Delta E}{h} \text{ Hz}$  or  $\bar{\nu} = \frac{\Delta E}{hc} \text{ cm}^{-1}$

In the rotational region spectra are usually discussed in terms of wavenumber

$$\epsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) \text{ cm}^{-1} \quad (J=0, 1, 2, \dots)$$
 (7)