SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF PHYSICS

UNIT – I - Spectroscopy – SPHA5303

UNIT-1 – Microwave Spectroscopy

- Using electromagnetic radiation as a probe to obtain information about atoms and molecules that are too small to see.

- Electromagnetic radiation is propagated at the speed of light through a vacuum as an oscillating wave.

Two oscillators will strongly interact when their energies are <u>equal.</u>

$$E_1 = E_2 \qquad \lambda_1 = \lambda_2 \qquad \upsilon_1 = \upsilon_2$$

If the energies are different, they will <u>not</u> strongly interact!
We can use electromagnetic radiation to probe atoms and molecules to find what energies they contain.

Electromagnetic relationships:
$\lambda\upsilon = c$
$E = h\upsilon$
$E = hc/\lambda$
λ = wave length
υ = frequency
c = speed of light
E = kinetic energy
h = Planck's constant

	<u>Freq. (Hz)</u>	<u>Wavelength (m)</u>
Radio waves	$10^4 - 10^{12}$	$3 \times 10^4 - 3 \times 10^{-4}$
Infrared (heat)	$10^{11} - 3.8 \times 10^{14}$	$3 \times 10^{-3} - 8 \times 10^{-7}$
Visible light	$3.8 \times 10^{14} - 7.5 \times 10^{14}$	$8 \times 10^{-7} - 4 \times 10^{-7}$
Ultraviolet	$7.5 \times 10^{14} - 3 \times 10^{17}$	$4 \times 10^{-7} - 10^{-9}$
X rays	$3 \times 10^{17} - 3 \times 10^{19}$	$10^{-9} - 10^{-11}$
Gamma rays	$> 3 \times 10^{19}$	$< 10^{-11}$

Regions of Electromagnetic Radiation   The interaction of radiation with matter

		Change of Orientation	Change of Configuration	Change of Electron Distribution		Change of Nuclear Configuration
Change of Spin						
n.m.r.	e.s.r.	Microwave	Infra-red	Visible and ultra-violet	X-ray	γ-ray

|							
	10^{-2}	1	100	10^{4}	cm^{-1}	10^{6} wavenumber 10^{8}	
10 m	100 cm	1 cm	100 μm	1 μm		10 nm wavelength 100 pm	
3×10^{8}	3×10^{8}	3×10^{10}	3×10^{12}	3×10^{14}	Hz	3×10^{18} frequency 3×10^{18}	
10^{-3}	10^{-1}	10	10^{3}	10^{5}	joules/mole	10^{7} energy 10^{8}	

Moment of Inertia

- **Moment of inertia (I)**, also called **mass moment of inertia** or the **angular mass**, is a measure of an object's resistance to changes in its rotation rate. It is the rotational analog of mass.
- The moment of **inertia** of an object about a given axis describes how difficult it is to change its angular motion about that axis.

Molecules can be classified into five main groups depending on their moments of inertia

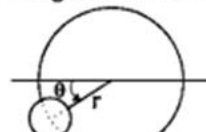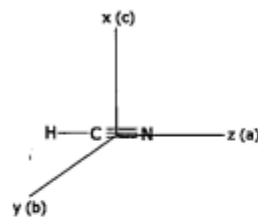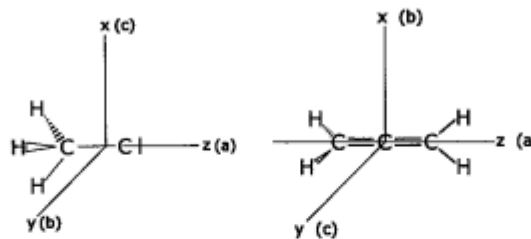|		
1.	$I_C = I_B , I_A = 0$	Linear molecules
2.	$I_C = I_B = I_A$	Spherical top
3.	$I_C = I_B > I_A$	Prolate symmetric top
4.	$I_C > I_B = I_A$	Oblate symmetric top
5.	$I_C > I_B > I_A$	Asymmetric top
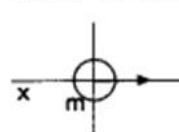
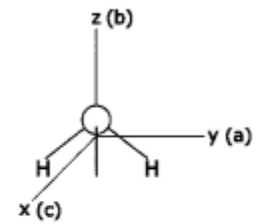Figure 6.1: Linear and circular motion of a particle of mass m.

$I_C = I_B, I_A = 0$
Linear Molecule

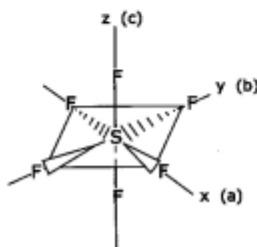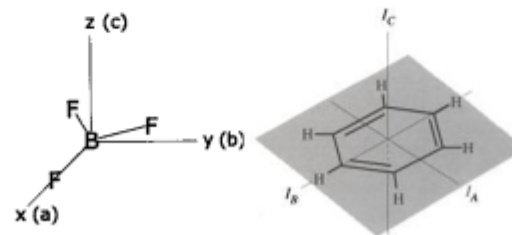$I_C = I_B > I_A$
Prolate symmetric top

$I_C > I_B > I_A$
Asymmetric top

$I_C = I_B = I_A$
Spherical Top

$I_C > I_B = I_A$
Oblate symmetric top

7

Molecular Rotations

- Rotational transitions are of little use to the spectroscopist. Rotational levels are quantized, and absorption of IR by gases yields line spectra.
- However, in liquids or solids, these lines broaden into a continuum due to molecular collisions and other interactions.

$$L \approx I\omega_{rot} = Ma_0^2 \omega_{rot} \qquad I \approx Ma_0^2$$

$$Ma_0^2\omega_{rot} = \hbar \qquad \Rightarrow E_{rot} = \hbar\omega_{rot} \approx \frac{\hbar^2}{Ma_0^2} \approx \left(\frac{m_e}{M}\right) E_{el}$$

Vibrational-Rotational Transitions

- In general, a molecule which is an excited vibrational state will have rotational energy and can lose energy in a transition which alters both the vibrational and rotational energy content of the molecule.
- The total energy content of the molecule is given by the **sum** of the vibrational and rotational energies. For a molecule in a specific vibrational and rotational state, denoted by the pair of quantum numbers (**v, J**), we can write its energy as: $E(v, J) = E_{vib}(v) + E_{rot}(J)$
- The energies of these three transitions form a very distinctive pattern. If we consider the lower vibrational state to be the initial state, then we can label the absorption lines as follows.
- Transitions for which the **J** quantum number decreases by 1 are called **P-branch transitions**, those which increase by 1 are called **R-branch transitions** and those which are unchanged are called **Q-branch transitions**.

Molecular Vibrations

- In order to predict equilibrium stable-isotope fractionations, it is necessary to know the characteristic frequencies of molecular vibrations. It is also necessary to know how much each vibrational frequency in a molecule changes when a heavy isotope is substituted for a light one. Vibrational frequencies for isotopically substituted molecules are not always known, so it is often necessary to use some type of force-field model to predict them.
- Molecular vibrations are also important in understanding infrared absorption and the mechanisms and kinetics of chemical reactions. Frequencies are most commonly measured with infrared or Raman spectroscopy. Rotational-vibrational spectroscopy, isotope substitution, and many forms of force-field modeling are used to determine characteristic atomic motions.

Vibrational Motion

- Subdivided into so-called normal modes of vibration which rapidly increase with the number of atoms in the molecule. Each of these normal vibrational modes contributes RT to the average molar energy of the substance and is a primary reason why heat capacities increase with molecular complexity.
- If there are X_{vib} modes of vibration, then the vibrational energy contributes $X_{vib}(RT)$ to the average molar energy of the substance.

❖ **Homonuclear diatomic molecules (such as H_2, O_2, N_2 , Cl_2) – have zero dipole (non polar) -- have zero change of dipole during the rotation – hence <u>NO</u> interaction with radiation -- hence <u>homonuclear diatomic molecules are microwave inactive</u>**

❖ **Heteronuclear diatomic molecules (such as HCl, HF, CO) – have permanent dipolemoment (polar compound) -- change of dipole occurs during the rotation – hence interaction with radiation takes place – Therefore, <u>heteronuclear diatomic molecules are microwave active.</u>**

Molecular rotations
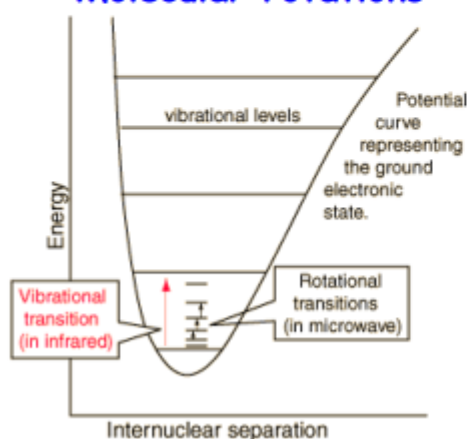
A diatomic molecule can rotate around a vertical axis. The rotational energy is quantized.
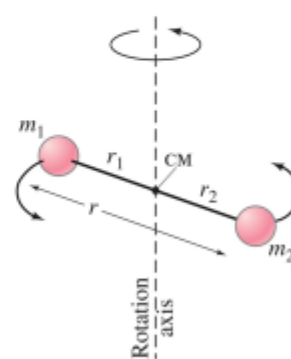
- A diatomic molecule may be thought of as two atoms held together with a massless, rigid rod (*rigid rotator model*).
- Consider a diatomic molecule with different atoms of mass m_1 and m_2, whose distance from the center of mass are r_1 and r_2 respectively.
- The moment of inertia of the system about the center of mass is:

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

Rotational levels

- The classical expression for energy of rotation is : In the harmonic oscillator model, the energy was all potential energy. In the rigid rotor, it's all kinetic energy:

- where J is the rotational quantum number

Assume a rigid (not elastic) bond $r_0 = r_1 + r_2$

For rotation about center of gravity, C :

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

$$r_1 = \frac{m_2 r_0}{m_1 + m_2} \qquad r_2 = \frac{m_1 r_0}{m_1 + m_2}$$

$$E_r = \frac{I\omega^2}{2} = \frac{L^2}{2I} \quad where\ L = angular\ momentum$$

$$L^2 \rightarrow \left(\frac{h}{2\pi}\right)^2 J(J+1)$$

$$E(J) = \frac{1}{2I}\left(\frac{h}{2\pi}\right)^2 J(J+1) = h c B_v J(J+1)$$

$$B_v = \frac{h}{8\pi^2 c I} \quad the\ rotational\ constant$$

Moment of inertia about C:

$$I_c = m_1 r_1^2 + m_2 r_2^2 = m_2 r_2 r_1 + m_1 r_1 r_2 = r_1 r_2 (m_1 + m_2)$$

$$\Rightarrow I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2 \qquad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

μ = reduced mass,

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

$$= m_1 r_1 \left[\frac{m_2 r_2}{m_1}\right] + m_2 r_2 \left[\frac{m_1 r_1}{m_2}\right]$$

$$= r_1 r_2 [m_1 + m_2]$$

$$= \left[\frac{m_1 r_0}{m_1 + m_2}\right]\left[\frac{m_2 r_0}{m_1 + m_2}\right][m_1 + m_2]$$

$$= \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

Quantization of Rotational Energy

Molecular rotational energy is *quantized*

By solving Schrödinger equation for rotational motion

rotational energy level is given by

Rotational energy of level J

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

Rotational energy level in *wavenumbers* (cm^{-1})

$$E_J = \frac{h}{8\pi^2 I c}$$

Where J is the rotational quantum number, having the values 0, 1, 2....Note that J = 0 is the lowest level, and the molecule is not rotating in this level.   Now the rotational frequency is the same as the frequency of the microwave radiation need to cause the rotation: $\nu\,/\,Hz = \Delta\,E/h$ $\bar{\nu}/cm^{-1} = \dfrac{\Delta E}{hc}$

or in energy units: , where c is in cms^{-1}.

So $J(J+1)$ cm^{-1} = BJ(J+1)   cm^{-1}

B is called the rotational constant for a given molecule. Its units are cm^{-1}, since J is just a quantum number (label).

Energy of rotational energy levels: (Not equally spaced)

J level		Energy
J = 6		42B
J = 5	——————————	30B
J = 4	——————————	20B
J = 3	——————————	12B
J = 2	══════════	6B
J = 1	══════════	2B
J = 0	══════════	0B

ROTATIONAL SPECTRUM

Selection Rule   :   Apart from **Specific rule- DJ= ±1**, Gross rule- the molecule should have a **permanent electric dipole moment, m** . Thus, **homonuclear diatomic molecules do not have a pure rotational spectrum. Heteronuclear diatomic molecules do have rotational spectra**

$\Delta j = \pm 1$

$\Delta j = +1\;(absorption)$

$\Delta j = -1\;(emission)$

Appearance of rotational spectrum We can calculate the energy corresponding to rotational transitions Δ E=EJ' −EJ   for $\Delta J = J_{final} - J_{initial} = +1$

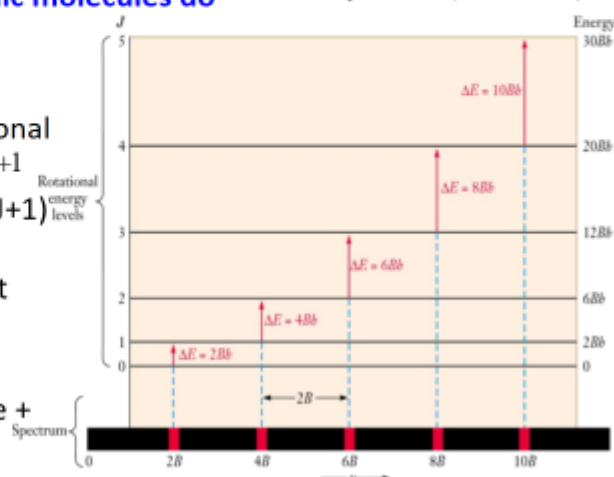Or generally: J → J + 1 $\bar{\nu}$ = B(J+1)(J+2) - BJ(J+1)

= **2B(J+1) cm^{-1}**

Microwave absorption lines should appear at

J = 0   → J = 1 : $\bar{\nu}$ = 2B - 0 = 2B cm^{-1}

J = 1   → J = 2 :   =   = 4B cm^{-1}

Note that the selection rule is ΔJ = ±1, where + applies to absorption and - to emission.

Find r(C—O) $I = \dfrac{h}{8\pi^2 Bc} = \dfrac{2.7992774 \times 10^{-46}}{B}$ kgm²

$$= \mu r^2 \qquad r = \sqrt{\dfrac{I}{\mu}}$$

B = 1.921175 cm^{-1} ; μ = 1.1386378 x 10^{-26} kg

r(C—O) = 1.131 x 10^{-10} m = 0.1131 nm.

C-O bondlength is 0.1131 nm.

Intensity depends upon two factors:

1.Greater initial state population gives stronger spectral lines.This population depends upon temperature, T.

k = Boltzmann's constant, 1.380658 x 10^{-23} J K^{-1}

$(k = R/N)$ $\dfrac{N_J}{N_0} \propto \exp\left(-\dfrac{E_J}{kT}\right) - \exp\left(-\dfrac{hc\,\bar{v}}{kT}\right)$

We conclude that the population is smaller for higher J states.

$$\dfrac{N_J}{N_0} \propto e\left(-\dfrac{1.52034\bar{v}}{T}\right) \qquad \dfrac{hc}{k} = 1.52034 \text{ cmK}$$

Relative Intensities of rotation spectral lines

Now we understand the locations (positions) of lines in the microwave spectrum, we can see which lines are strongest.
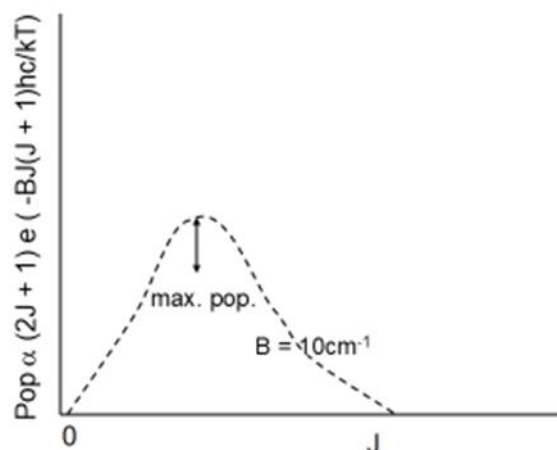
J _____↑_____ BJ(J+1)

J=0 _____ 0

2.Intensity also depends on degeneracy of initial state.

(degeneracy = existence of 2 or more energy states having exactly the same energy) Each level J is (2J+1) degenerate ⇒ **population is greater for higher J states.**

To summarize: Total relative population at energy $E_J \propto$ (2J+1) exp (-E_J / kT) maximum population occurs at nearest integral J value to

Plot of population of rotational energy levels versus value of J.

The Non-Rigid Rotor

If the shape of the molecule is allowed to distort upon rotation
Then the restriction of the rigid rotor is lifted. It may be
expected that as the rotational energy increases the molecule
will have it's bond lengthened because of the centrifugal
distortion. This will lead to an effective decrease in the
rotational energy since the longer bond will lead to a decrease
in the rotational energy. We can refine the theory by adding
 a correction term, containing the centrifugal distortion
constant, D, which corrects for the fact that the bond is not rigi

$$F(J) = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2$$

Here, *D* is the centrifugal distortion constant.

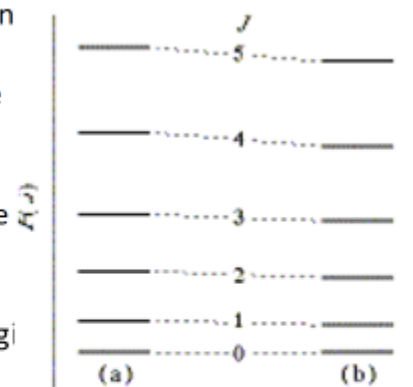For the $J \to J+1$ transitions, the absorption frequency is given by

$$\tilde{\nu} = F(J+1) - F(J) = 2\tilde{B}(J+1) - 4\tilde{D}(J+1)^3 \qquad J = 0, 1, 2, .$$

$$D = \frac{h^3}{32\pi^4 I^2 r^2 kc} cm^{-1} = \frac{4B^3}{\nu_{vib}^2}$$

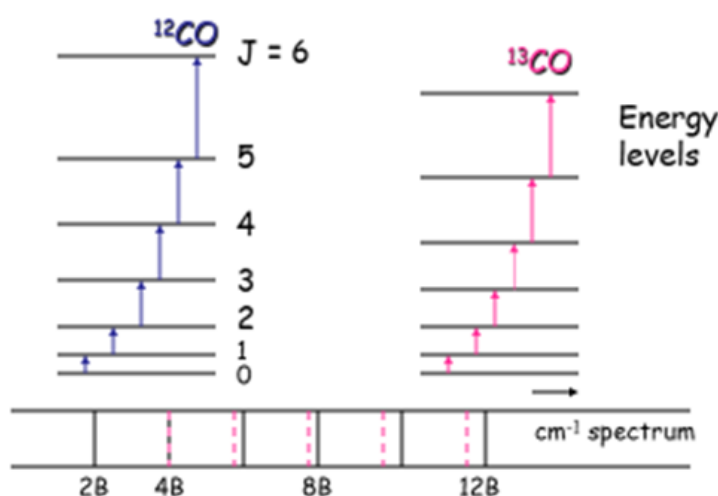where $\tilde{\nu}_{vib}$ is bond stretch wavenumber.

i) can find J values of lines in a spectrum - fitting 3 lines gives 3 unknowns: J, B, D.
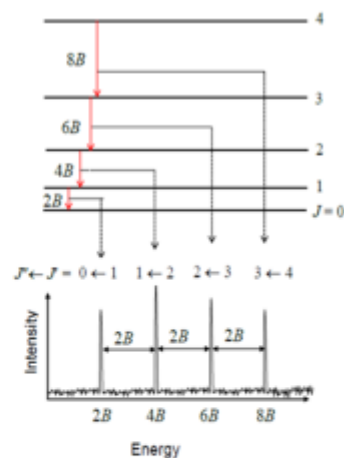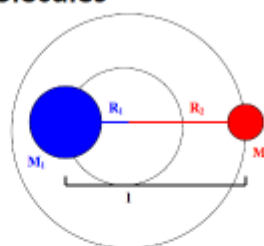ii) We can estimate $\tilde{\nu}_{vib}$ from the small correction term. D.

Effect of isotopes

From $^{12}C^{16}O \to$ $^{13}C^{16}O$, mass increases, B decreases ($\propto$ 1/I), so energy levels lower.

9

Linear Molecules

- Linear molecules(Rigid rotors)
- Bond length directly calculated
- $I_a = I_b, I_c = 0 \quad I = R^2 u = \dfrac{(M_1 M_2)}{(M_1 + M_2)} R^2$
- Selection Rule $\Delta J = J' - J'' = \pm 1$
- $v_{J' \leftrightarrow J''} = E(J') - E(J'') = 2B(J'' + 1)$
  - Where $J'' = Lower\ level$
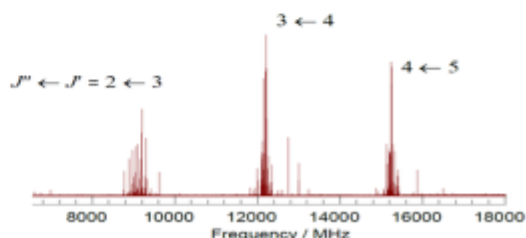   - $J' = Upper\ Level$

Symmetric Tops (Rotors)

- Two rotational axes same, one different
- Oblate $I_a \neq I_b = I_c$ (Benzene, XeF_4)
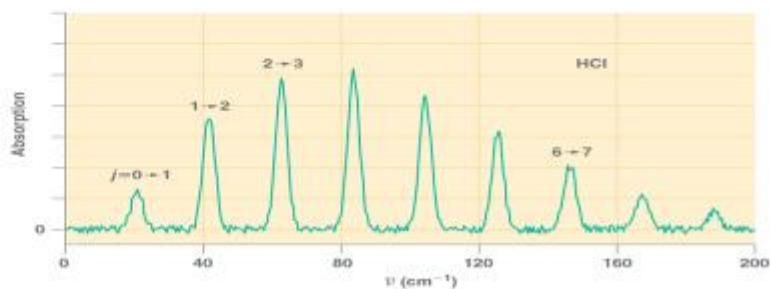- Prolate $I_a = I_b \neq I_c$ (CH_3Cl, NH_3)

Hyperfine Splitting

- Coupling of Nuclear spin and molecular rotation.
  - If J > I, 2I+1 levels
  - If J < I, 2J+1 levels.
  CF_3I, Splitting due to ^{127}I

- Gas samples
  - As a diluted analyte in a non-MW reactive gas such as Neon
- Solids
  - Laser abatement
  - Vaporization
- Liquids
  - Vaporization
  - Supersonic Expansion

Microwave Spectrometer

SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF PHYSICS

UNIT – II - Spectroscopy – SPHA5303

UNIT-2 – Vibrational Spectroscopy

Definition of Infrared Spectroscopy

- The absorption of light, as it passes through a medium, varies linearly with the distance the light travels and with concentration of the absorbing medium. Where a is the absorbance, the Greek lower-case letter epsilon is a characteristic constant for each material at a given wavelength (known as the extinction coefficient or absorption coefficient), c is concentration, and l is the length of the light path, the absorption of light may be expressed by the simple equation a= epsilon times c times l.

- Infrared spectroscopy is the measurement of the wavelength and intensity of the absorption of mid-infrared light by a sample. Mid-infrared is energetic enough to excite molecular vibrations to higher energy levels.

- The wavelength of infrared absorption bands is characteristic of specific types of chemical bonds, and infrared spectroscopy finds its greatest utility for identification of organic and organometallic molecules. The high selectivity of the method makes the estimation of an analyte in a complex matrix possible.

Theory of Infrared Absorption Spectroscopy

- For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electrical field of the radiation (remember that electromagnetic radiation consists of an oscillating electrical field and an oscillating magnetic field, perpendicular to each other) interacts with fluctuations in the dipole moment of the molecule.

- If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration.

Infrared radiation λ = 2.5 to 17 μm, υ = 4000 to 600 cm^{-1}
These frequencies match the frequencies of covalent bond stretching and bending vibrations. Infrared spectroscopy can be used to find out about covalent bonds in molecules. **IR is used to tell: what type of bonds are present and structural information.**

Vibration

- Infrared radiation is largely thermal energy.
- It induces stronger **molecular vibrations** in covalent bonds, which can be viewed as springs holding together two masses, or atoms.
- **Specific** bonds respond to (absorb) **specific** frequencies

VIBRATIONAL MODES

- Covalent bonds can vibrate in several modes, including **stretching, rocking, and scissoring**.
- The most useful bands in an infrared spectrum correspond to stretching frequencies, and those will be the ones we'll focus on.
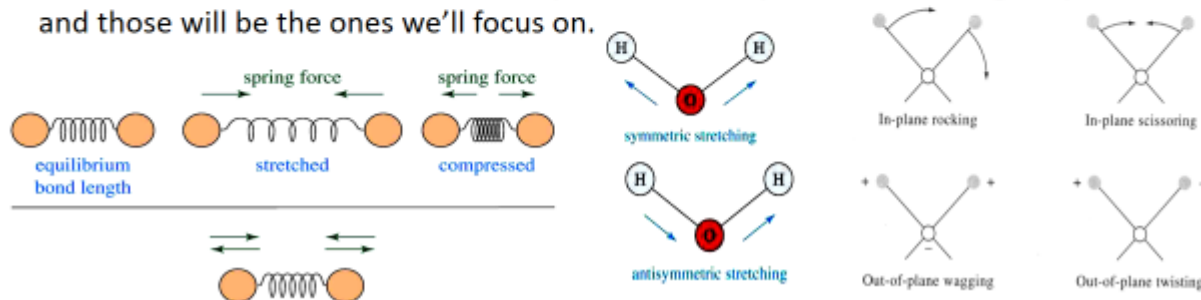

IR SPECTRUM IN ABSORPTION AND TRANSMISSION MODE

The IR spectrum is basically a plot of transmitted (or absorbed) frequencies vs. intensity of the transmission (or absorption). Frequencies appear in the *x*-axis in units of inverse centimeters (wavenumbers), and intensities are plotted on the *y*-axis in percentage units.

INFORMATION OBTAINED FROM IR SPECTRA

- IR is most useful in providing information about the presence or absence of specific **functional groups**.
- IR can provide a **molecular fingerprint** that can be used when comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.
- IR **does not** provide detailed information or proof of molecular formula or structure. It provides information on molecular fragments, specifically functional groups.
- Therefore it is very limited in scope, and must be used in conjunction with other techniques to provide a more complete picture of the molecular structure.
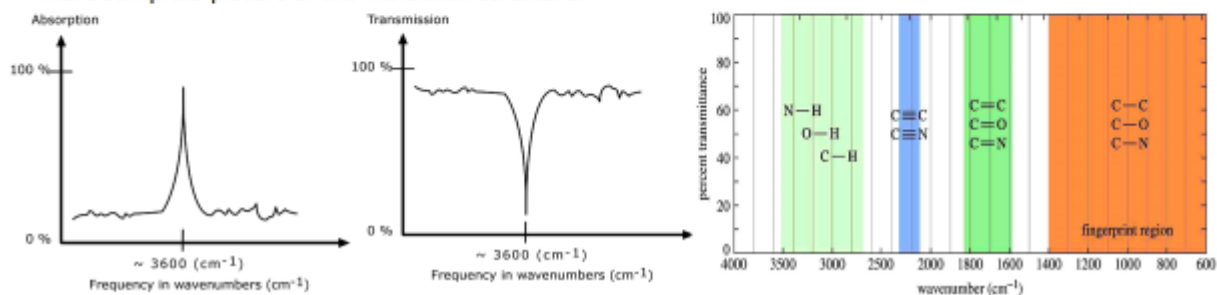
IR SPECTRUM OF ALKENES

Besides the presence of C-H bonds, alkenes also show sharp, medium bands corresponding to the **C=C bond stretching vibration** at about **1600-1700 cm⁻¹**. Some alkenes might also show a band for the =C-H bond stretch, appearing around **3080 cm⁻¹** as shown below. However, this band could be obscured by the broader bands appearing around 3000 cm⁻¹ (see next slide)
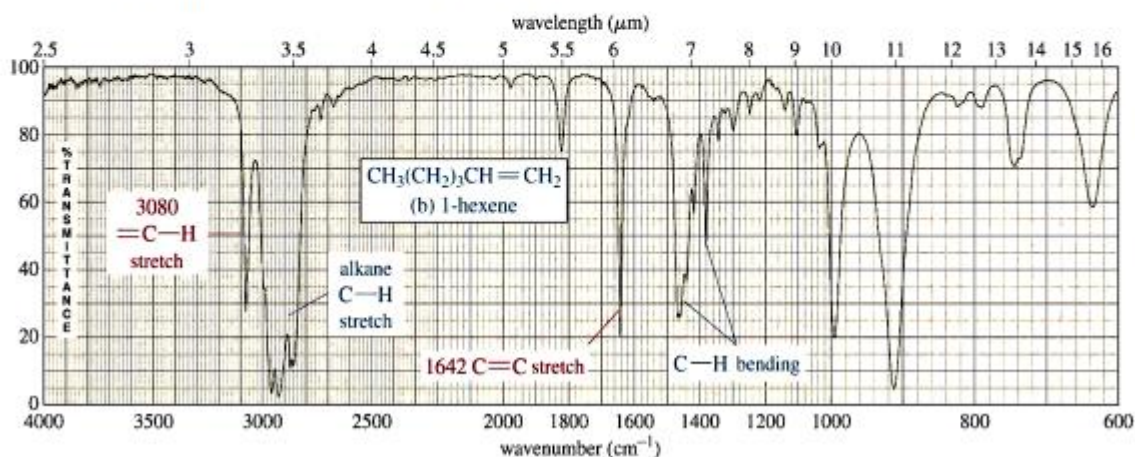
Mechanical Model of Stretching Vibrations

1.Simple harmonic oscillator.

Hooke' s Law (restoring force of a spring is proportional to the displacement)   **F = -ky**
Where: F = Force, k = Force Constant (stiffness of spring), y = Displacement
Natural oscillation frequency of a mechanical oscillator depends on:
  a) mass of the object   b)   force constant of the spring (bond)
The oscillation frequency is independent of the amount of energy imparted to the spring.

• Frequency of absorption of radiation can be predicted with a modified Hooke's Law.

$$\bar{v} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$ Where: n = wavenumber of the abs. peak (cm⁻¹), c = speed of light (3 x 10¹⁰ cm/s), k = force constant, m = reduced mass of the atoms

$$\mu = \frac{M_x \bullet M_y}{M_x + M_y}$$ Where: M_x = mass of atom x in kg,
 M_y = mass of atom y in kg

• Force constants are expressed in N/m (N = kg•m/s²)
Range from 3 x 10² to 8 x 10² N/m for single bonds
  - 500 N/m is a good average force constant for single bonds when predicting k.
  - $k = n(500\ N/m)$ for multiple bonds where n is the bond order
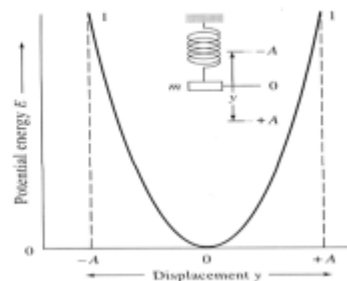
Anharmonic oscillators

Bonds act as anharmonic oscillators because as atoms get close, they repel one another, and at some point a stretched bond will break.
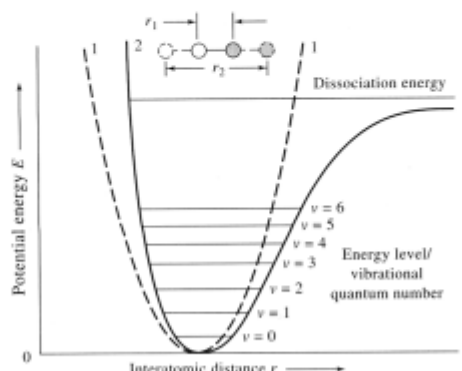
2.6 Type A, B and C bands in Asymmetric Rotor Molecules

Classification of Vibrational Bands of Asymmetric Rotor:

➢ Asymmetric Rotor Molecules have less symmetry.
➢ 3 M of I are different ($I_A \neq I_B \neq I_C$).
➢ Vibrations with dipole moment changes parallel to A, B and C axes are called A, B, and C bands
➢ Each band type has a distinct shape based on the relative intensities of the P-, Q- and R-branch lines in the vibrational band.
➢ A-type, B-type and C-type bands are produced when the transition dipole moment aligns with the a-axis, b-axis and c-axis respectively.
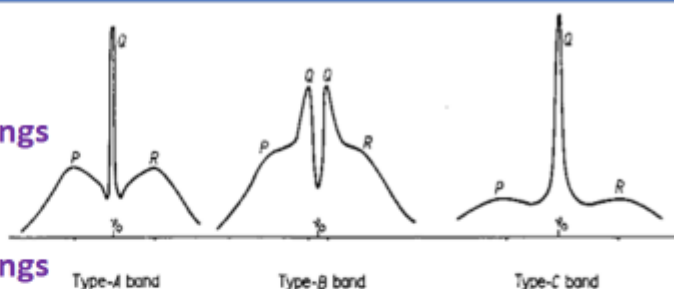
A and C bands have

- broad
- more or less symmetric wings
- a sharp central peak

B band has

- more or less symmetric wings
- no central peak

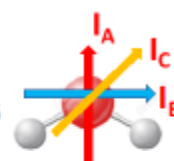Type-A band   Type-B band   Type-C band

- ➢ All these bands are dependent on the relative values of the M of I.
- ➢ For Planar molecules,
  - $I_C > I_A$
  - So central peak of the C band is relatively strong compared with the central peak of the A band.
- ➢ If the dipole moment change is not exactly parallel to any of the a, b, or c axes, a mixed contour results.

Asymmetric Top Molecule:

Most of the molecules belong to this category. H_2O – Water
- ➢ Have 3 different dipole moments during the rotation about A, B
- ➢ Have 3 different M of I. $I_A \neq I_B \neq I_C$
- ➢ So rotational and vibrational spectrum is complicated.
- ➢ No simple general eqn for $E_{J,v}$ and $\tilde{v}_{J,v}$ can be derived for this molecule.
- ➢ So it may be treated by approximate methods. (good for small molecules)
- ➢ The prolate ($I_A < I_B = I_C$) and the oblate ($I_A > I_B = I_C$) symmetric rotors represent the two extreme limits of an asymmetric rotor.
- ➢ Consider a molecule some what intermediate to the extreme cases.

Its energy levels can be evaluated by the use of perturbation theory by writing the rotational Hamiltonian (H) as,

$$H_{rot} = H_{Prolate} + H'_{Prolate} \quad\quad OR \quad\quad H_{rot} = H_{Oblate} + H'_{Oblate}$$

H'_P = Hamiltonian Deviation from prolate ($I_A < I_B = I_C$) to asymmetric ($I_A \neq I_B \neq I_C$)
H'_O = Hamiltonian Deviation from oblate ($I_A > I_B = I_C$) to asymmetric ($I_A \neq I_B \neq I_C$)

- ➢ The energy is obtained by the usual perturbation technique using prolate or oblate rotor wave function as basic functions.
- ➢ The two correlations (prolate or oblate) must correlate with the two limiting cases.
- ➢ The quantum number K for asymmetry is

$$K_{asymmetry} = \frac{2B - A - C}{A - C} = \text{Asymmetric parameter}$$

- ➢ Limiting values for $K_{asymmetry}$ are -1 for prolate and $+1$ for oblate.
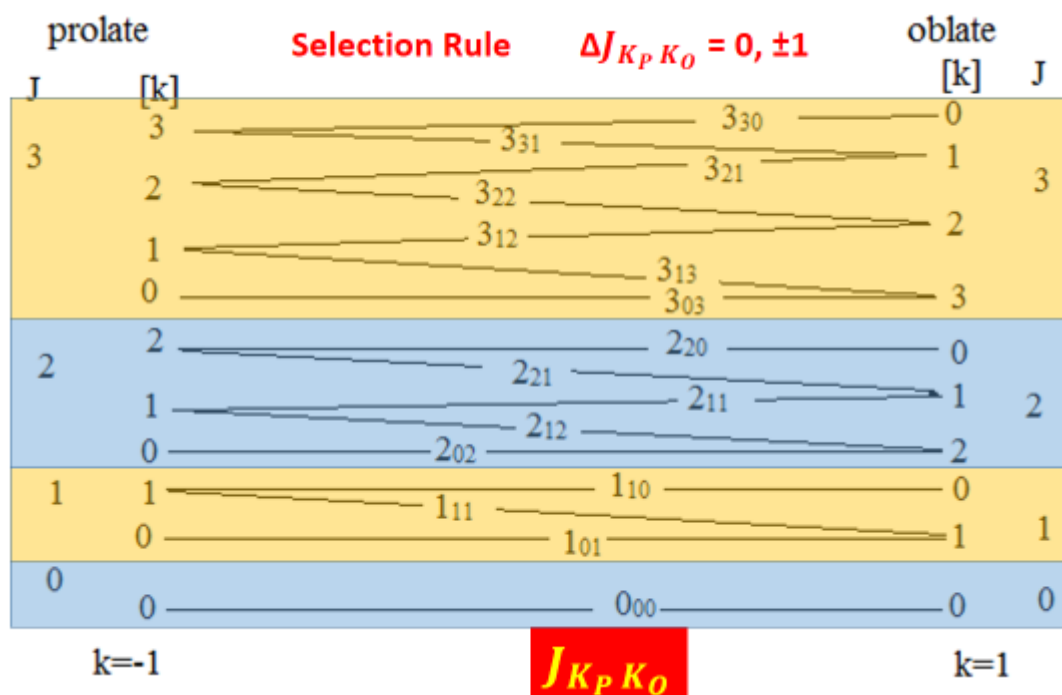- ➢ Energy levels are labelled with total angular momentum quantum number $J_{K_P K_O}$

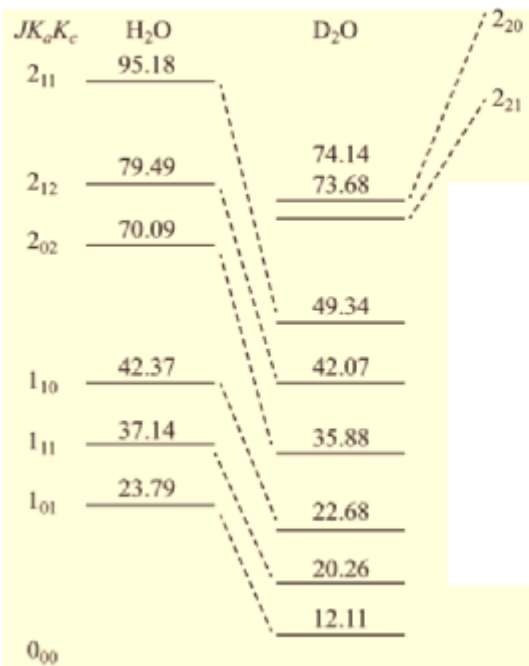$$\tilde{v}_{J,K} = B\,J(J+1) + (A - B)\,K^2 \qquad cm^{-1}$$

$$A = \frac{h}{8\Pi^2 I_A c} \qquad\qquad B = \frac{h}{8\Pi^2 I_B c} \qquad \text{are rotational constants}$$

$J = 0, 1, 2, 3, ----$

$K = 0, \pm 1, \pm 2, ., \pm J$ are quantum numbers

All states with K > 0 are doubly degenerate

Slide 1

JK_aK_c — H$_2$O — D$_2$O

2_{11} 95.18

2_{20}

2_{21}

2_{12} 79.49 — 74.14 / 73.68

2_{02} 70.09

49.34

1_{10} 42.37 — 42.07

1_{11} 37.14 — 35.88

1_{01} 23.79 — 22.68

20.26

12.11

0_{00}

Selection Rule

For A-type Band:
$\Delta J = 0, \pm 1$ $\qquad \Delta K_P = 0, (\pm 2)$
$\qquad\qquad\qquad \Delta K_O = \pm 1, (\pm 3)$

For B-type Band:
$\Delta J = 0, \pm 1$ $\qquad \Delta K_P = \pm 1, (\pm 3, \pm 5, \ldots)$
$\qquad\qquad\qquad \Delta K_O = \pm 1, (\pm 3, \pm 5, \ldots)$

For C-type Band:
$\Delta J = 0, \pm 1$ $\qquad \Delta K_P = \pm 1, (\pm 3, \pm 5, \ldots)$
$\qquad\qquad\qquad \Delta K_O = 0, (\pm 2, \pm 4, \ldots)$

( ) – Weak Transitions

Slide 2

JK_aK_c — H$_2$O — **A'#Band**

2_{11} 95.18

2_{12} 79.49

2_{02} 70.09

1_{10} 42.37

1_{11} 37.14

1_{01} 23.79

0_{00}

2_{12} to 2_{11}

1_{10} to 2_{11}

1_{11} to 2_{12}

1_{01} to 2_{02}
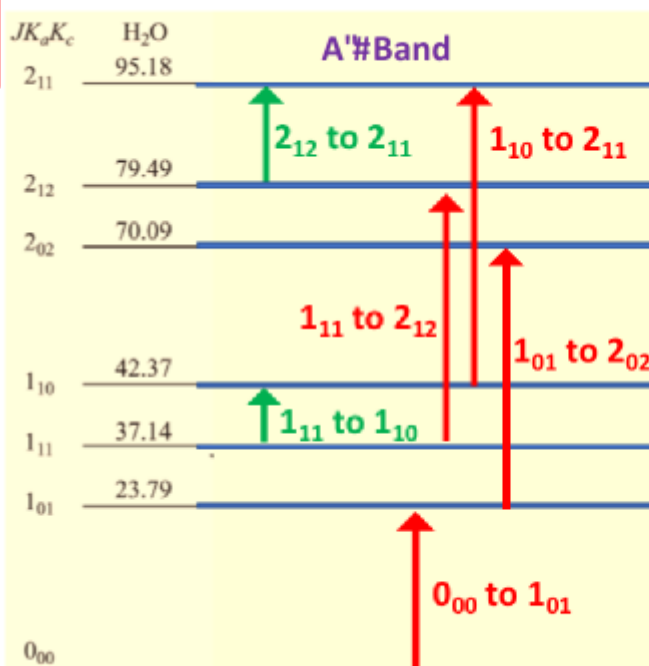
1_{11} to 1_{10}
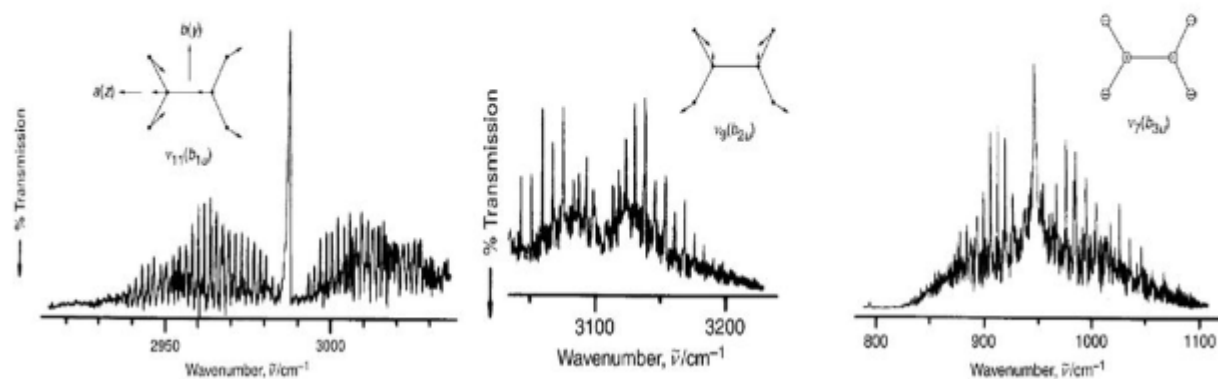
0_{00} to 1_{01}

**Selection Rule
for A-type Band:**
$\Delta J = 0, \pm 1$
$\Delta K_P = 0, (\pm 2)$
$\Delta K_O = \pm 1, (\pm 3)$

$\Delta J = 0$ $\quad \Delta K_P = 0$ $\quad \Delta K_O = \pm 1$
$(\Delta J_{K_P K_O})_A = 1_{11}$ to 1_{10}
$\qquad\qquad\qquad 2_{12}$ to 2_{11}

$\Delta J = \pm 1$ $\quad \Delta K_P = 0$ $\quad \Delta K_O = \pm 1$
$(\Delta J_{K_P K_O})_A = 0_{00}$ to 1_{01}
$\qquad\qquad\qquad 1_{01}$ to 2_{02}
$\qquad\qquad\qquad 1_{11}$ to 2_{12}
$\qquad\qquad\qquad 1_{10}$ to 2_{11}

IR spectrum of asymmetric rotor – Ethylene
with type A, B and C bands

IR spectrum of asymmetric rotor – Fluorobenzene
with type A, B and C bands
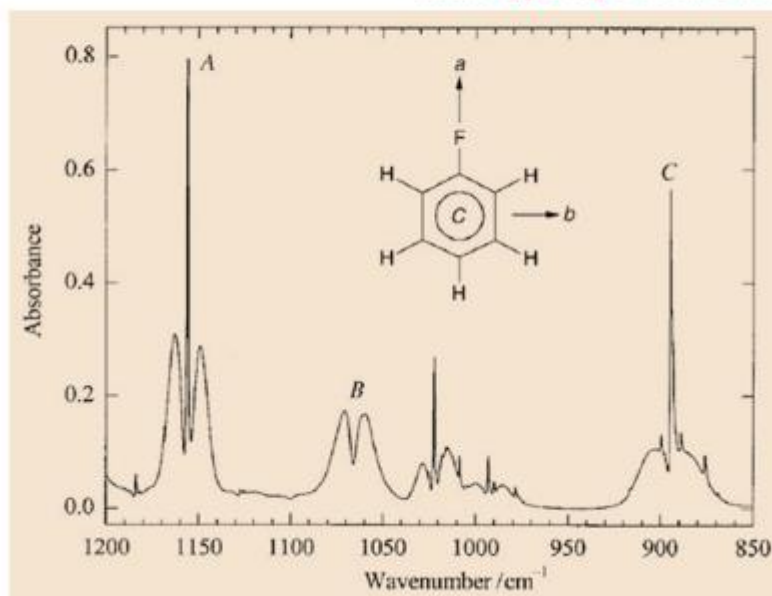
Coriolis Interaction:

It describes Ro-Vibration energy structure for a single vib mode of a molecule

➢ Actually, more number of vibrational modes and corresponding rotational energy levels are possible for a single polyatomic molecule.
➢ At some instance, rotational energy levels belonging to different vibrational states may be nearly the same.
➢ This induces a coupling effect between the energy levels of the 2 vib states.
➢ So these energy levels are shifted from their normal energy levels.
➢ Observed position of spectral lines (involving these levels) are affected.
➢ The most commonly observed type of coupling is **Coriolis resonance.**

Types of interaction:

▪ A-type band interacting with a B-type band gives rise to c-type Coriolis band.
▪ B-type band interacting with a C-type band gives rise to a-type Coriolis band.
▪ C-type band interacting with a A-type band gives rise to b-type Coriolis band

IR Spectrometer

Sources - inert solids that heat electrically to 1500 – 2200 K.

● Emit *blackbody radiation* produced by atomic and molecular oscillations excited in the solid by thermal energy.

The inert solid "glows" when heated.

Common sources:

1. Nernst glower -constructed of a rod of a rare earth oxide (lanthanide) with platinum leads.
2. Globar -Silicon carbide rod with water cooled contacts to prevent arcing.
3. Incandescent wire -tightly wound wire heated electrically. Longer life but lower intensity.
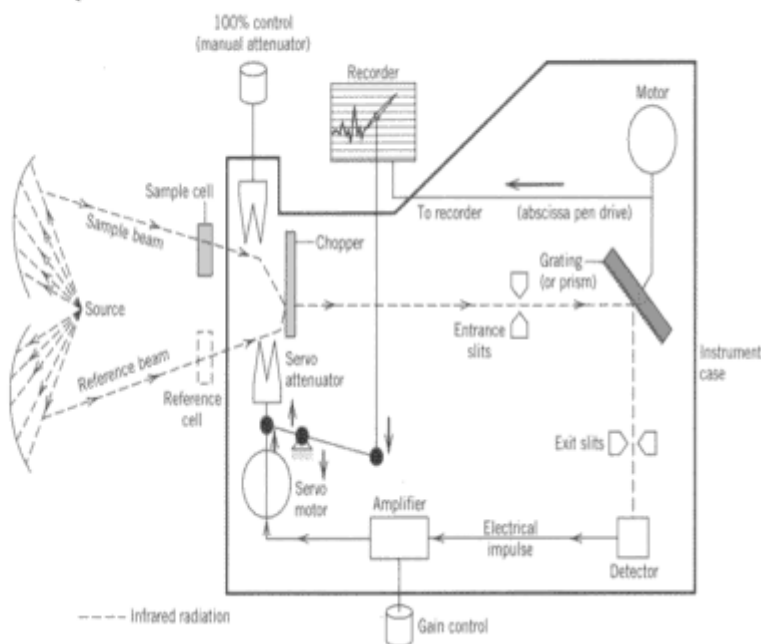
Detectors – measure minute changes in temperature.

1. Thermal transducer

Constructed of a bimetal junction, which has a temperature dependant potential (V). (similar to a thermocouple)

Have a slow response time, so they are not well suited to FT-IR.

2. Pyroelectric transducer

Constructed of crystalline wafers of triglycine sulfate (TGS) that have a strong temperature dependent polarization.

Have a fast response time and are well suited for FT-IR.

3. Photoconducting transducer

Constructed of a semiconducting material (lead sulfide, mercury/cadmium telluride, or indium antimonide) deposited on a glass surface and sealed in an evacuated envelope to protect the semiconducting material from the environment.

Absorption of radiation promotes nonconducting valence electrons to a conducting state, thus decreasing the resistance (W) of the semiconductor.

Fast response time, but require cooling by liquid N_2.

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DEPARTMENT OF PHYSICS

UNIT – III - Spectroscopy – SPHA5303

Raman Spectroscopy

- When radiation passes through a transparent medium, the species present scatter a fraction of the beam in all directions.

- In 1928, the Indian physicist C. V. Raman discovered that the visible wavelength of a small fraction of the radiation scattered by certain molecules differs from that of the incident beam and furthermore that the shifts in wavelength depend upon the chemical structure of the molecules responsible for the scattering.

- The theory of Raman scattering shows that the phenomenon results from the same type of quantized vibrational changes that are associated with infrared absorption. Thus, the difference in wavelength between the incident and scattered visible radiation corresponds to wavelengths in the mid-infrared region.

- The Raman scattering spectrum and infrared absorption spectrum for a given species often resemble one another quite closely.
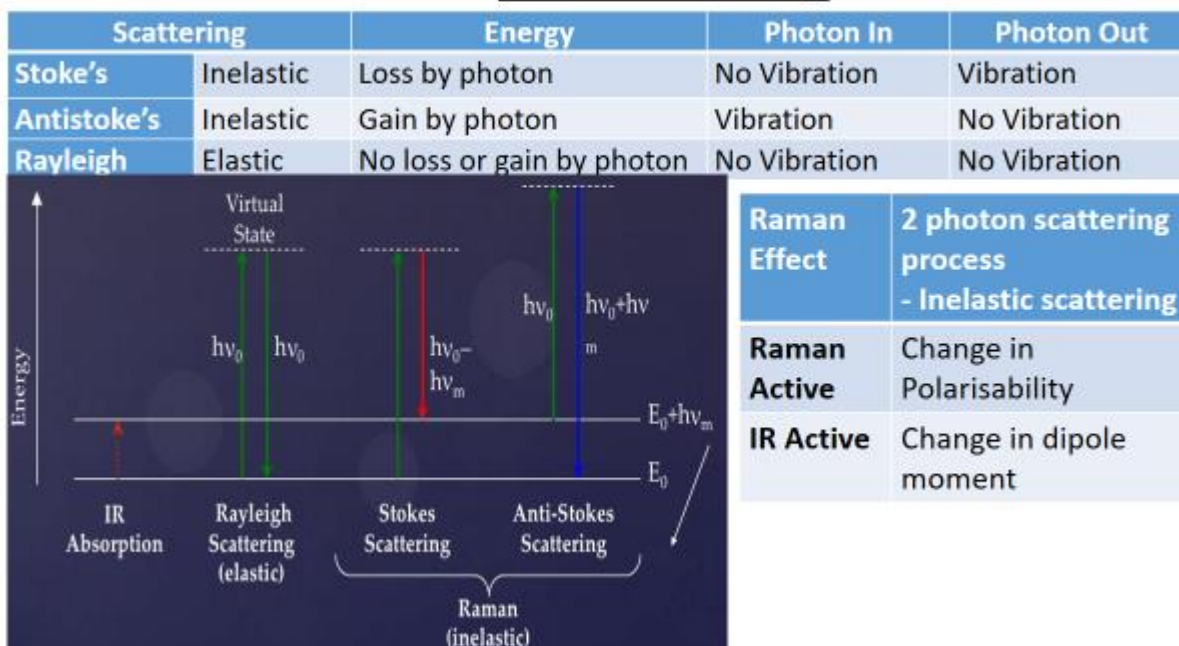
THEORY OF RAMAN SPECTROSCOPY

Raman spectra are acquired by irradiating a sample with a powerful laser source of visible or near-infrared monochromatic radiation. During irradiation, the spectrum of the scattered radiation is measured at some angle (often 90 deg) with a suitable spectrometer. At the very most, the intensities of Raman lines are 0.001 % of the intensity of the source; as a consequence, their detection and measurement are somewhat more difficult than are infrared spectra.

Excitation of Raman Spectra

A Raman spectrum can be obtained by irradiating a sample of carbon tetrachloride (Fig 18-2) with an intense beam of an argon ion laser having a wavelength of 488.0 nm (20492 cm^{-1}). The emitted radiation is of three types:

1. **Stokes** scattering

2. **Anti-stokes** scattering

3. **Rayleigh** scattering

Raman Scattering

Scattering		Energy	Photon In	Photon Out
Stoke's	Inelastic	Loss by photon	No Vibration	Vibration
Antistoke's	Inelastic	Gain by photon	Vibration	No Vibration
Rayleigh	Elastic	No loss or gain by photon	No Vibration	No Vibration

Raman Effect	2 photon scattering process - Inelastic scattering
Raman Active	Change in Polarisability
IR Active	Change in dipole moment

Mutual Exclusion Principle

- In a molecule with a center of symmetry it is seen that vibrations that are Raman active are IR inactive and vice-versa. Also In molecules having inversion center, none of the normal modes of vibrations will be both Raman and IR active. This is known as "mutual exclusion principle".

- Carbondioxide has an inversion center or center of symmetry. The following are its normal modes of vibrations. The IR and Raman active modes are indicated below each type of vibration.

Symmetric Stretch	Asymmetric Stretch	In –Plane Bending	Out Of–Plane Bending
O—c—O	O—c—O	O—c—O	O—c—O
IR Inactive	IR Active	IR Active	IR Active
Raman Active	Raman Inactive	Raman Inactive	Raman Inactive

- In molecules with different elements of symmetry, certain bands may be active in IR, Raman, both or neither.

- For a complex molecule that has no symmetry except identity element, all of the normal modes are active in both IR and Raman.

- In general the strong bands in the IR spectrum of a compound correspond to weak bands in the Raman and vice versa. This complimentary nature is due to the electrical characteristic of the vibration.
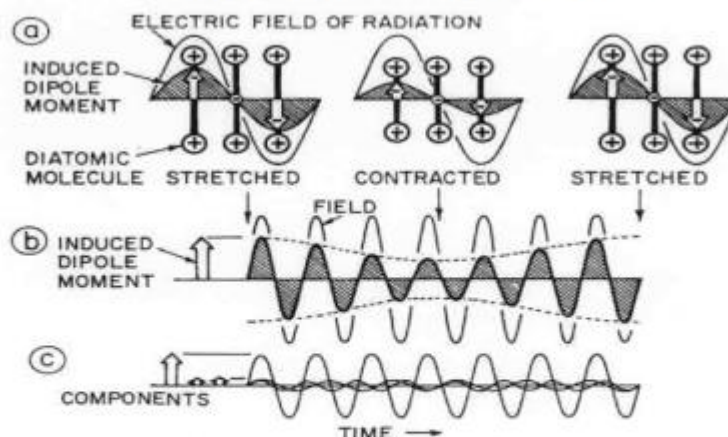
Classical Theory of Raman Effect

FIG. 1.32. Classical theory for the origin of the Raman effect. In (a) we see a diatomic molecule where "+" represents protons and "−" represents the center of gravity of the electrons. The electrons are displaced by the external field of the photon and an induced dipole moment is generated which changes when the bond length changes during the molecular vibration. The induced dipole moment is plotted in (b) as an amplitude modulated wave with steady amplitude components shown in (c) from which scattered radiation is generated.

3.3. – Quantum theory of Raman effect

According to the Quantum theory,

- Radiation consisting of a stream of particles (photons) having energy ($h\nu$)
- These photons are colliding with molecules, then scattered.
- If the collision is perfectly elastic, $\nu_{scattered} = \nu_{inc.\ photon}$ **Rayleigh lines**
- If the collision is inelastic, $\nu_{scattered} \neq \nu_{inc.\ photon}$ **Raman lines**

The molecule can gain or lose some amount of energy.

   ΔE = Difference in energy between 2 of its allowed states

   ΔE = Difference in vibrational energy between 2 of its allowed states

   ΔE = Difference in rotational energy between 2 of its allowed states

   ΔE = Difference in vib.-rational energy between 2 of its allowed states

   $\Delta E = h\nu_{in} - h\nu_{scattered}$ Raman Shift = $\Delta\nu = (\nu_{in} - h\nu_{scattered})$

If molecule gains energy, $E_{scattered} = h\nu - \Delta E$ $\nu_{scattered} = \nu - \dfrac{\Delta E}{h}$

If molecule loses energy, $E_{scattered} = h\nu + \Delta E$ $\nu_{scattered} = \nu + \dfrac{\Delta E}{h}$

Classically,
- **Raman lines (Stokes and Anti-Stokes) should have same Intensity.**
- **But experimentally (Intensity)$_{Stokes}$ > (Intensity)$_{Anti-Stokes}$**

Quantum Mechanically,
- **This is because such transitions are more probable and more intense.**
- **Here excited photon is reaching a new level called "Virtual Level".**
- **Energy is not presented in this virtual level since excited photon wont stay in this virtual level.**
- **Excited photon immediately returns to lower stationary level after emitting the photon.**
- **So Fluorescence effect (transition between stable states) differs from Raman effect.**
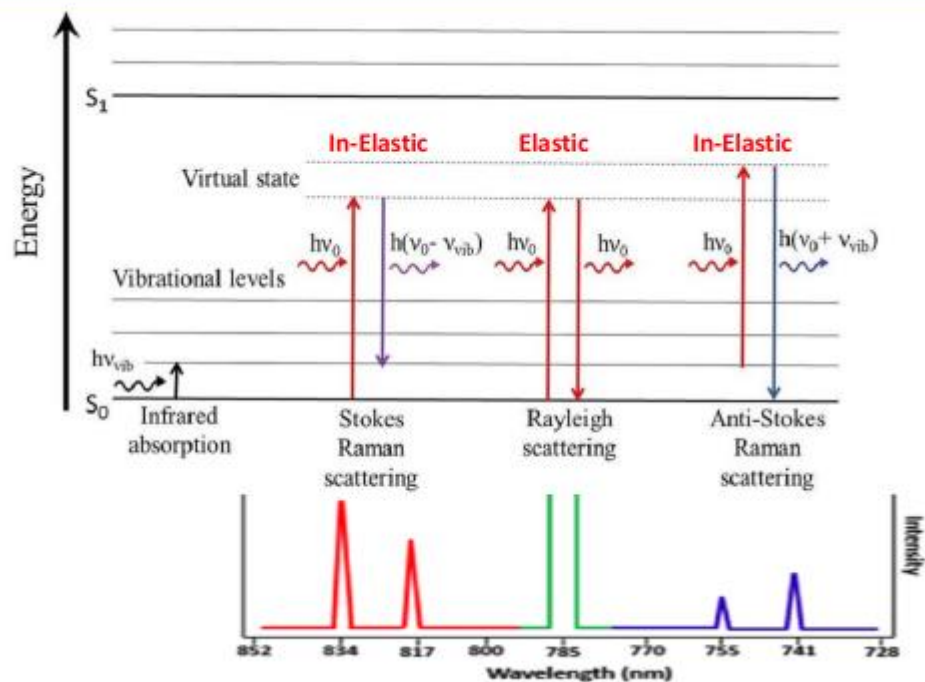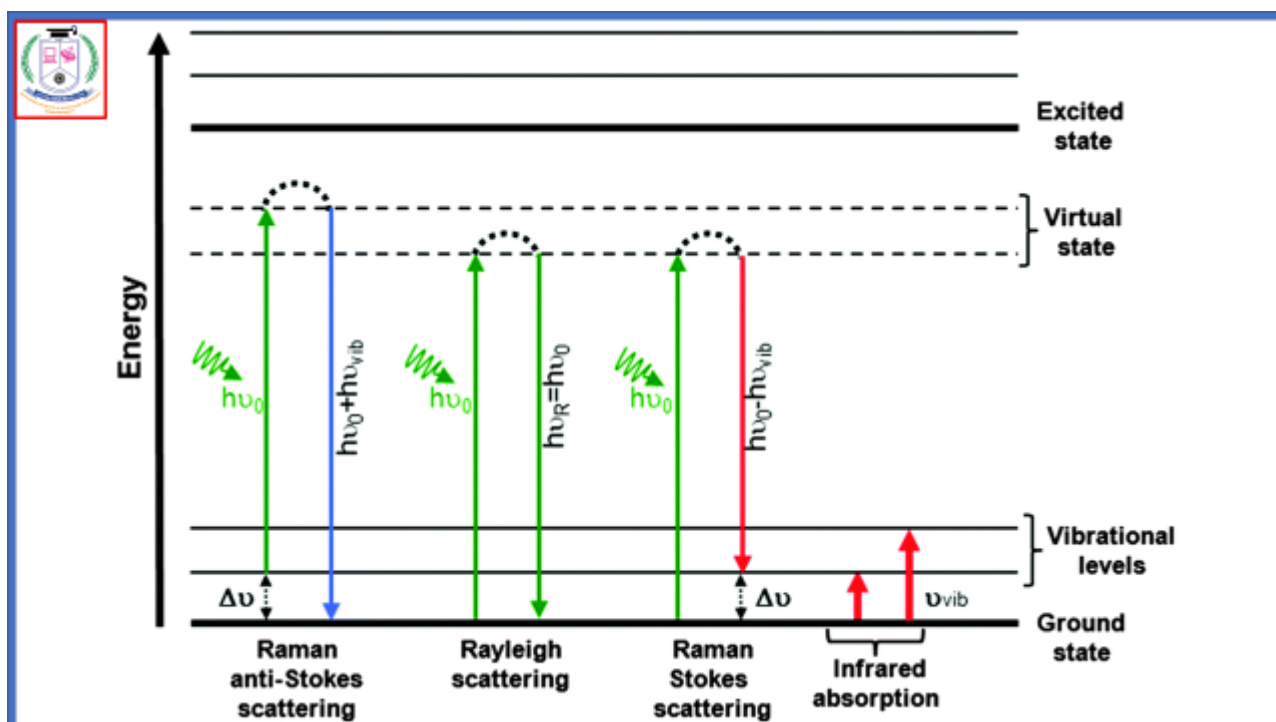
5

Probability of Energy Transition in Raman Effect: Polarizability

When an electromagnetic radiation (light) is incident on a molecule [molecule is placed in an electric field], electrons and nuclei are displaced.

- An induced dipole moment (μ) is produced in the molecule due the displacement of electrons and nuclei
- Now molecule is said to be **polarized**.

$$\mu \propto E$$
$$\mu = \alpha E$$

E is the strength of the electric field
α is the polarizability of the molecule

H Atom

H₂ Molecule

E

E

Bond Axis is //ᵃˡ to E

x is small displacement produced by oscillating dipole from equilibrium position

Change in polarizability of the oscillating dipole is, $\alpha = \alpha_0 + \beta_{vib/rot}\left(\frac{x}{A}\right)$

α_0 – Equilibrium polarizability

$\beta_{vib/rot}$ – Rate of change of polarizability with the vibration/rotation.

x – Displacement of oscillating dipole from equilibrium position

A – Vibrational/Rotational amplitude

Here the displacement is along the x-axis.

induced dipole moment along the x-axis is, $\mu_x = \alpha_{xx} E_x$

α_{xx} – Polarizability along x-axis when E acts in the same direction (x-axis)

$\alpha_{xx} = (\alpha_0)_{xx} + \beta_{XX}\left(\frac{x}{A}\right)$

Transition probability along x-axis is $P(x) = \int \varphi_f^* \, \mu_x \, \varphi_i \, d\tau$

$\varphi_i \; and \; \varphi_f$ – Wavefunction of oscillating dipole at the initial and final states.

$P(x) = \int \varphi_f^* \, \alpha_{xx} E_x \, \varphi_i \, d\tau \qquad = E_x \int \varphi_f^* \, [(\alpha_0)_{xx} + \beta_{XX}(\frac{x}{A})] \, \varphi_i \, d\tau$

$P(x) = E_x (\alpha_0)_{xx} \int \varphi_f^* \, \varphi_i \, d\tau \; + \; (\frac{E_x}{A}) (\beta_{XX}) \int \varphi_f^* \, x \, \varphi_i \, d\tau$

$P(x) = E_x (\alpha_0)_{xx} \int \varphi_f^* \, \varphi_i \, d\tau \; + \; (\frac{E_x}{A}) (\beta_{XX}) \int \varphi_f^* \, x \, \varphi_i \, d\tau \qquad \boxed{\int \varphi_1^* \, \varphi_1 \, d\tau = 1, \int \varphi_2^* \, \varphi_1 \, d\tau = 0}$

(1). When $\varphi_i = \varphi_f$ (Polarizability Ellipsoid)$_{initial}$ = (Polarizability Ellipsoid)$_{final}$ = Spherical

Vibration/Rotation does not alter the polarizability of the molecule, $\beta_{vib/rot} = 0$

$P(x) = E_x (\alpha_0)_{xx} \int \varphi_i^* \, \varphi_i \, d\tau = E_x (\alpha_0)_{xx}$ It gives probability of **Rayleigh scattering.**

(2). When $\varphi_i \neq \varphi_f$ (Polarizability Ellipsoid)$_{initial}$ ≠ (Polarizability Ellipsoid)$_{final}$ ≠ Spherical

Vibration/Rotation alters the polarizability of the molecule, $\beta_{vib/rot} \neq 0$

$P(x) = 0 + (\frac{E_x}{A}) (\beta_{XX}) \int \varphi_f^* \, x \, \varphi_i \, d\tau \qquad$ It gives probability of **Raman scattering.**

If Vibration/Rotation doesn't alter the polarizability of molecule, $\beta_{vib/rot} = 0$

$P(x) = 0 + 0 \qquad\qquad\qquad$ **No Raman scattering.**

- **Molecule whether homonuclear or not (having permanent dipole or not) the Polarization ellipsoid will not be spherical.**
- **Polarization ellipsoid should change its dimensions during the molecular vibration/rotation.**
- **These molecules exhibit both vibrational and rotational Raman spectra**

Raman Spectrometers

Raman spectrometers were similar in design and used the same type of components as the classical ultraviolet/visible dispersing instruments. Most employed double grating systems to minimize the spurious radiation reaching the transducer. Photomultipliers served as transducers. Now Raman spectrometers being marketed are either Fourier transform instruments equipped with cooled germanium transducers or multichannel instruments based upon charge-coupled devices.
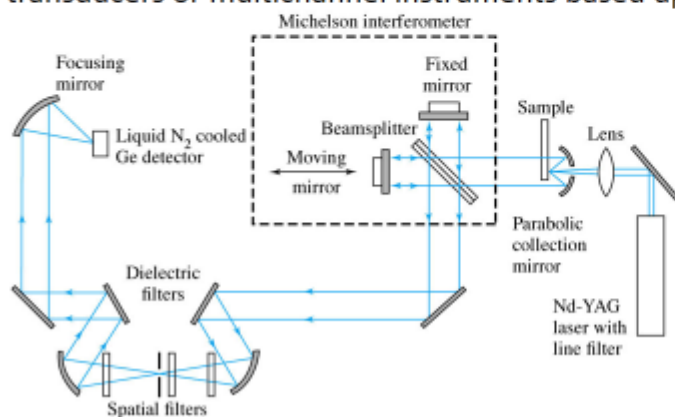
APPLICATIONS OF RAMAN SPECTROSCOPY

Raman Spectra of Inorganic Species

The Raman technique is often superior to infrared for spectroscopy investigating inorganic systems because aqueous solutions can be employed. In addition, the vibrational energies of metal-ligand bonds are generally in the range of 100 to 700 cm^{-1}, a region of the infrared that is experimentally difficult to study. These vibrations are frequently Raman active, however, and peaks with Δv values in this range are readily observed. Raman studies are potentially useful sources of information concerning the composition, structure, and stability of coordination compounds.

Raman Spectra of Organic Species

Raman spectra are similar to infrared spectra in that they have regions that are useful for functional group detection and fingerprint regions that permit the identification of specific compounds. Raman spectra yield more information about certain types of organic compounds than do their infrared counterparts.

Biological Applications of Raman Spectroscopy

Raman spectroscopy has been applied widely for the study of biological systems. The advantages of his technique include the small sample requirement, the minimal sensitivity toward interference by water, the spectral detail, and the conformational and environmental sensitivity.

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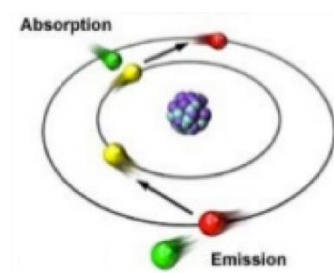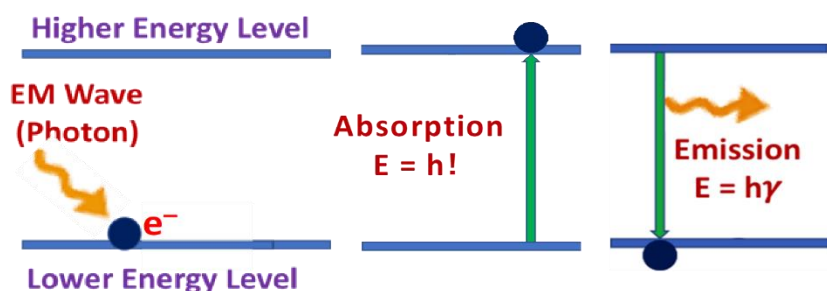**DEPARTMENT OF PHYSICS**

UNIT – IV - Spectroscopy – SPHA5303

Introduction

- ➢ **EM wave interacts with molecules leads excitation of electron.**
- ➢ **This interaction creates transition between electronic energy levels in the molecules gives a UV-Visible (Electronic) spectrum.**
- ➢ **UV frequency = 10^{14} to 10^{16} Hz**
- ➢ **UV Wavenumber = 10^4 to 10^6 cm^{-1}**

Higher Energy Level

EM Wave (Photon)

Absorption
E = h!

Emission
E = hγ

e⁻

Lower Energy Level

Absorption

Emission

4.1 – Intensity of Vib.-Electronic Spectra (Franck-Condon Principle)

According to Morse theory, vibrational energy of diatomic anharmonic molecule in a particular electronic state is

$$V(x) = E = D_e [1 – \exp(– ax^2)]$$

here

$$D_e = D_o + \frac{1}{2} h\omega_e = D_o + \frac{1}{2} \varpi_e$$

D_o – dissociation energy at zero point level (v = 0)
D_e – dissociation energy at equilibrium distance (r_e)
$x = r – r_{eq}$

a – constant characteristic of inter nuclear bond in a specific electronic state

Morse curve represents the energy when one atom is considered fixed on the r = 0 axis and the other is allowed to oscillate between the limits of the curve.
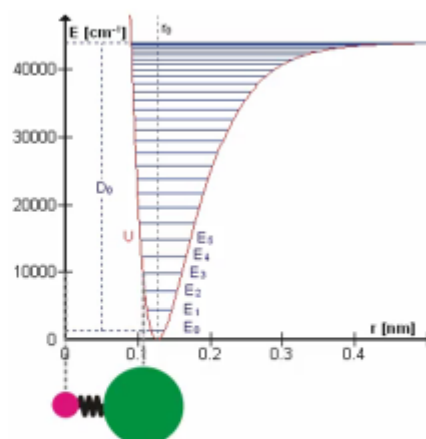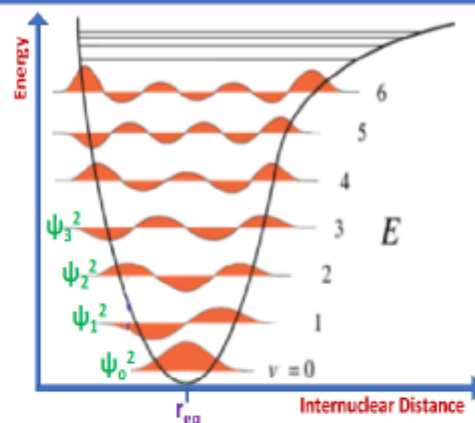
According to Classical theory, oscillating atom would spend most of its time on the curve at the turning point of its motion

According to Quantum theory,

- For v = 0, atom is most likely to be found at the center of its motion (at r_{eq}).
- For v = 1, 2,..., atom is most likely to be found near extreme limits
- For v = high, classical and quantum pictures merge.

$$\Psi^2 = \int \Psi^*_{Vib}\ \Psi_{vib}\ dr = \text{Probability}$$

Franck-Condon Principle states that, an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.

This is due to the fact that,

- Nuclei are much more massive than electrons.
- Electronic transition takes place faster than the nuclei can respond.

When a molecule is undergoing an electronic transition from lower (E_0) to excited (E_1) electronic state,

- Molecules in the lower and excited states are **stable.**
- Molecules are **oscillating (vibrating)** in both E_0 and E_1 electronic states.
- Excited state is also explained by **Morse curve.**
- Position of r_{eq} in the lower and excited states are **same or slightly different.**
- Electronic transition occurs **vertically.**

Case – 1:

E$_1$ has same r$_{eq}$ as E$_0$

- Vertical transition from v''=0 level will be most likely to occur into v'= 0.
- So intensity due to (0,0) transition is maximum.

➤ Vertical transition from v''=0 level will be less likely to occur into v'= 1, 2, 3, ……..
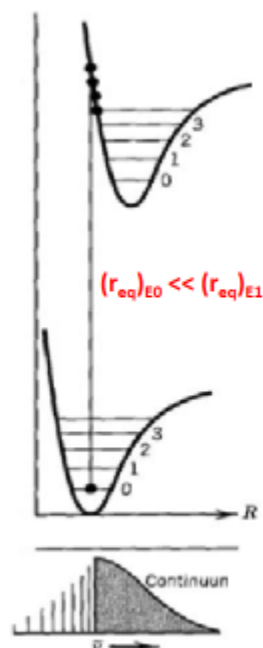➤ So intensity due to (1,0), (2,0), --- transitions are gradually decreasing from (0,0).
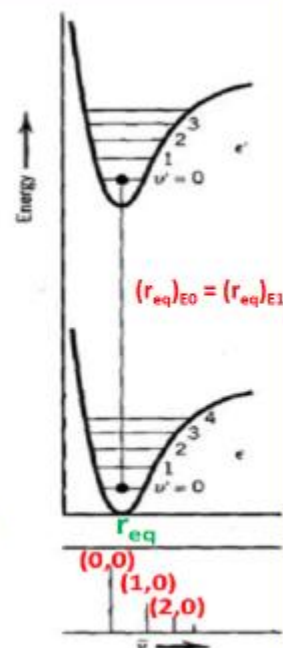
Case – 2:

E$_1$ has a slightly smaller r$_{eq}$ than E$_0$

Case – 3:

E$_1$ has a slightly greater r$_{eq}$ than E$_0$

- Vertical transition from v''=0 level will be most likely to occur into v'=2.
- So intensity due to (2,0) transition is maximum.

➤ Vertical transition from v''=0 level will be less likely to occur into v'=0,1, 3, 4, ……..
➤ So intensity due to (0,0), (1,0), (3,0), (4,0), --- transitions are gradually decreasing from (2,0).
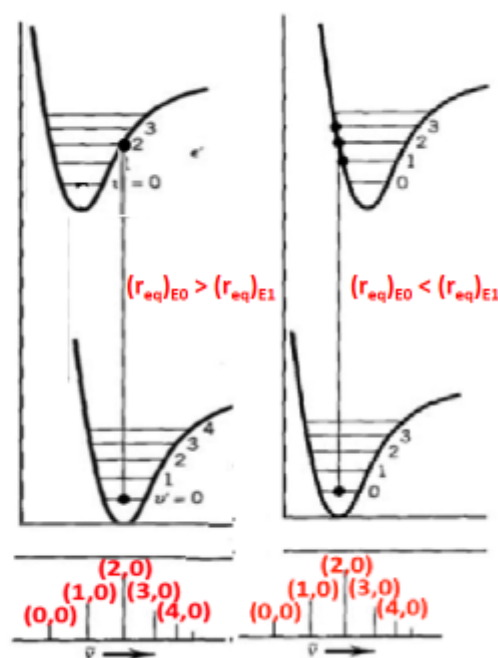
Case – 4:

   E_1 has a considerably greater r_{eq} than E_0

- Vertical transition from v''=0 level will be most likely to occur into v'=7.
- So intensity due to (7,0) (near dissociation) transition is maximum.

➤ Vertical transition from v''=0 level will be less likely to occur into v'=0,1, 2, 3, 4, 5, 6, 8, 9, ...
➤ So intensity due to (0,0), (1,0), (3,0), (4,0), --- transitions are gradually decreasing from (7,0).

➤ If v' increases, distance between spectral lines decreases.
➤ If v' > dissociation level, molecule will dissociate without vibration. So transitions are not quantized. This spectrum is called **Continuum.**

$(r_{eq})_{E0} \ll (r_{eq})_{E1}$

Case – 1:
E_1 has same r_{eq} as E_0
Case – 2:
E_1 has a slightly smaller r_{eq} than E_0
Case – 3:
E_1 has a slightly greater r_{eq} than E_0
Case – 4:
E_1 has a considerably greater r_{eq} than E_0
Most probable transition = Strongest spectral line (v', v'')
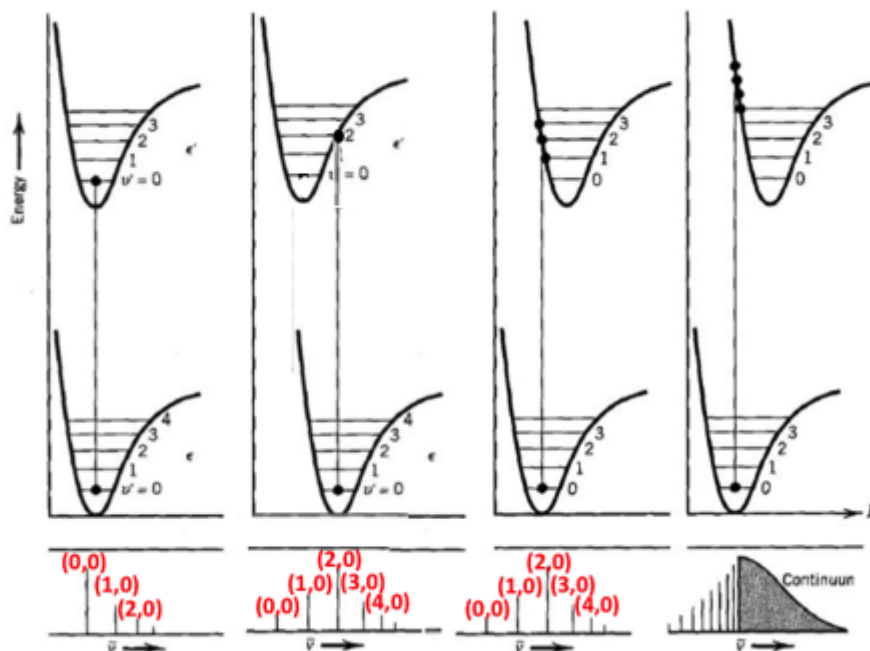
4.3. Rotational Fine Structure of Electronic-Vibration Transitions (Fortrat Diagram)

Electronic spectrum of a diatomic molecule

- Consists of 2 or more series of convergent lines correspond to vibrational coarse structure on each electronic transition.
- These lines are broad and diffuse (scatter).
- With more resolution, each line appears as a combination of more very close lines (ie Rotational Fine Structure).

Rotational energy of diatomic molecule is

$$\mathcal{E}_{Rot} = \left(\frac{h}{8\pi^2 I c}\right) J(J+1) = B\, J(J+1) \quad cm^{-1}$$

By using Born-Oppenheimer approximation, $\quad \mathcal{E}_{Total} = \mathcal{E}_{El} + \mathcal{E}_{Vib} + \mathcal{E}_{Rot} \quad cm^{-1}$

$$\Delta\mathcal{E}_{Total} = \Delta(\mathcal{E}_{El} + \mathcal{E}_{Vib}) + \Delta\mathcal{E}_{Rot}$$
$$= \tilde{v}_{(v',v'')} + \Delta[B\, J(J+1)] \quad cm^{-1}$$

$\tilde{v}_{(v',v'')}$ = Wavenumber of an Electronic-Vibrational transition from v'' to v'.

Selection Rule for J depends upon the type of electronic transition of molecule. $\quad \Delta J = 0$ and ± 1

- For both lower and upper electronic states not have the electronic angular momentum about the internuclear axis,
  $$\Delta J = \pm 1 \quad \text{So P and R branches will appear.}$$
- For either lower state or the upper state or both have electronic angular momentum about the internuclear axis,
  $$\Delta J = 0 \quad \text{So Q branch will appear.}$$
  $$\tilde{v}_{(Spectrum)} = \tilde{v}_{(v',v'')} + [B'\, J'(J'+1)] - [B''\, J''(J''+1)] \quad cm^{-1}$$

When an electron is excited,

- A bond is created between the nuclei.
- Bond in upper state is weaker than in lower state.
- $(r_{eq})_{upper} > (r_{eq})_{lower}$
- $(M \text{ of } I)_{upper} > (M \text{ of } I)_{lower}$
- $(B)_{upper} < (B)_{lower}$ $\quad$ So B' < B''

(a) For R branch, $\Delta J = +1$ $(J' - J'') = +1$ $J' = J'' + 1$

$$\tilde{\nu}_R = \tilde{\nu}_{(v',v'')} + B'\,(J''+1)\,(J''+2) - B''\,J''(J''+1)$$
$$\tilde{\nu}_R = \tilde{\nu}_{(v',v'')} + (B' + B'')(J''+1) + (B' - B'')(J''+1)^2$$

(b) For P branch, $\Delta J = -1$ $(J' - J'') = -1$ $J'' = J' + 1$

$$\tilde{\nu}_P = \tilde{\nu}_{(v',v'')} - (B' + B'')(J'+1) + (B' - B'')(J'+1)^2$$

These two eqns can be combined into the eqn,

$$\tilde{\nu}_{P,\,R} = \tilde{\nu}_{(v',v'')} + (B' + B'')m + (B' - B'')m^2 \quad cm^{-1}$$
$$m = -(J'+1) = (J''+1) = \pm1, \pm2,\ldots$$

$(-m) \longrightarrow$ P branch
$(+m) \longrightarrow$ R branch

Here $m \neq 0$,   So **no band origin occurs in P and R branches**

(c) For Q branch, $\Delta J = 0$ $J' = J'' \neq 0$

$$\tilde{\nu}_Q = \tilde{\nu}_{(v',v'')} + (B' - B'')(J'') + (B' - B'')(J'')^2 \qquad cm^{-1}$$

Here $J' = J'' \neq 0$,   So **no band origin occurs in Q branch**
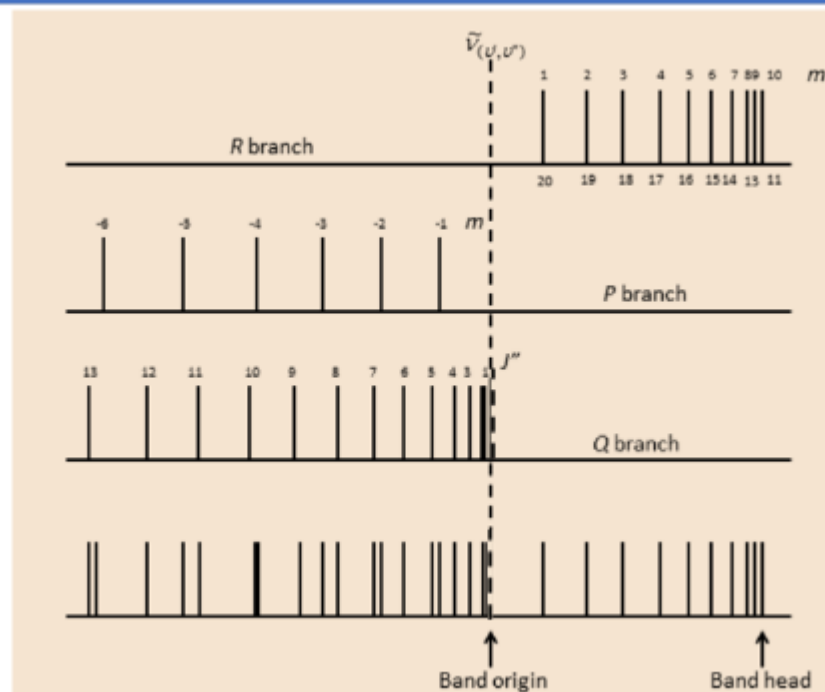
Predissociation – Dissociation occurs before the dissociation limit.

➢ It is found for molecules where excited potential curves of a bound state (Morse curve)and an unbound state (Continuous curve) cross each other.

➢ A lesser amount of energy lifts the molecule in a state where the electrons can rearrange to an unbound state (internal conversion).

➢ In the spectral range that corresponds to these energies, a blurred zone appears. Beyond this zone, there are again discrete lines.
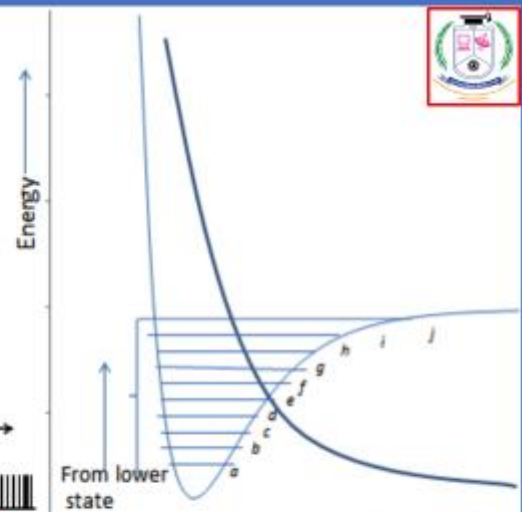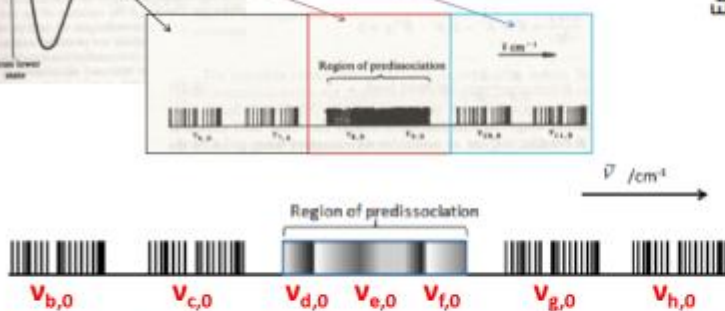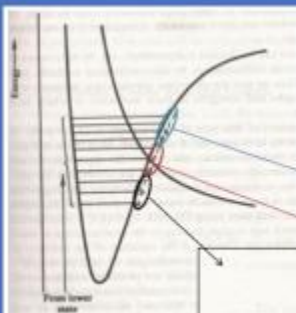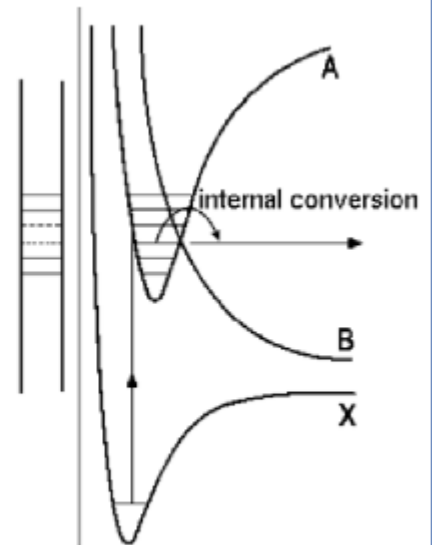
➢ During the transition from some lower state vibrational level to the upper state vibrational level (a, b, c),

▪ Normal Vib-Electronic spectrum occurs with rotational fine structure.

- During the transition from some lower state vibrational level to the upper state vibrational level (d, e, f),
  - Molecule will "cross over" on to the continuous curve (Transition from Morse curve to Continuous curve) (internal conversion).
  - So molecule dissociates without any absorption or emission of energy .
  - This cross over is faster than time taken by molecule to rotate (10^{-10} sec).
  - Predissociation occur before the molecule rotates.
  - So all rotational fine structure will be destroyed but vibrational structure is not destroyed.
  - If cross over is faster than vibration time (10^{-13} sec), continuum occur.
- During the transition from some lower state vibrational level to the upper state vibrational level (g, h, …),
  - Molecule spends more time at extreme ends and less time in the middle.
  - Molecule spends very less time at the cross over point.
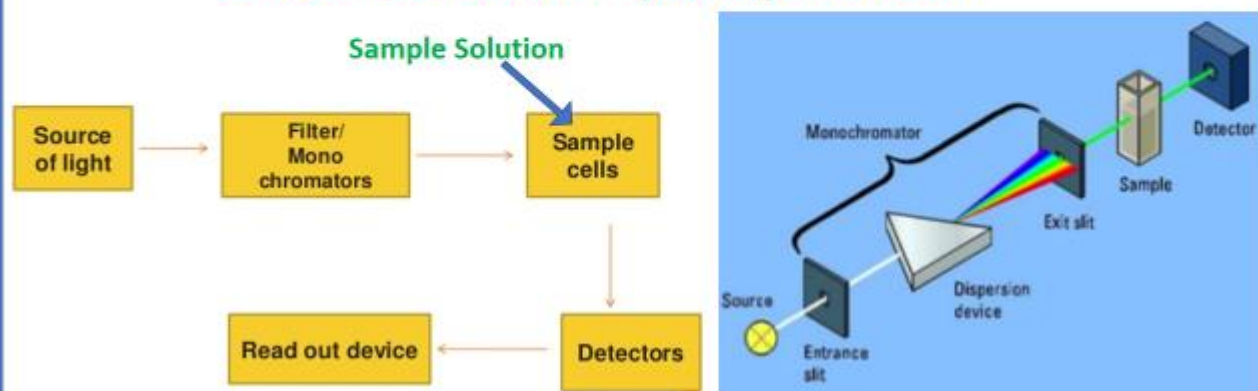 - Normal Vib-Electronic spectrum occurs with rotational fine structure.

4.7. UV-Visible Spectrophotometer

A UV-Vis spectrophotometer is used to determine the absorption of light from a sample and can be used as a detector.
- Single-Beam UV / Vis Spectrophotometer
- Dual-Beam UV / Vis Spectrophotometer.

Single-Beam UV / Vis Spectrophotometer

Io is the intensity of incident light

It is the intensity of transmitted light

| Standard solution | Adjust to get 100% of transmittance |
| Unknown solution | T % of transmittance is noted with different λ |

Merit:
- Simple in construction
- Easy to operate
- Economical

Demerits:
- Fluctuation due to radiation source is more
- Quick scanning is not possible

Dual-Beam UV / Vis Spectrophotometer

Chopper (Beam Slitter)   Is a device containing a circular disc.
- (1/3) of the disc is opaque
- (1/3) of the disc is transparent
- (1/3) of the disc is mirror

Chopper splits the monochromatic beam of the light into 2 beams of equal intensities.
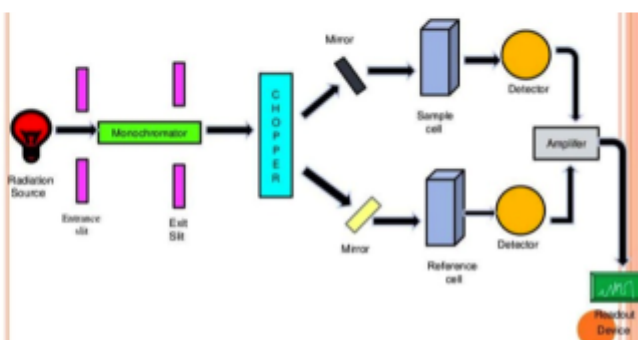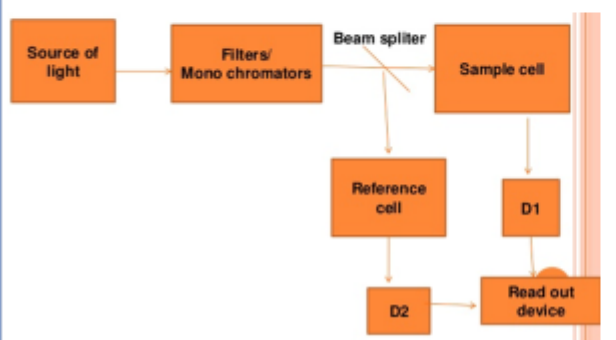
Merit:

- Quick scanning is possible
- Scanning over a wide λ region is possible.
- Fluctuation due to radiation source is minimum
- $I_{unknown} / I_{standard}$ = measurement is possible directly with different λ
- Adjustment to get 100% of transmittance is not required

Demerit:

- Construction is complicated
- More expensive.

SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF PHYSICS

UNIT – V - Spectroscopy – SPHA5303

Unit – 5   Nuclear Spectroscopy

Introduction

Nucleus =   Proton   +   Neutron

M_p = 1 amu = 1.67×10^{-27} Kg   No mass

Charge = 1.6×10^{-19} C   No charge

Spin of proton = ½   Spin of neutron = ½

Total mass of nucleus   = $M_p + M_n$

Total charge of nucleus   = +P

Total spin of nucleus   = Spin of proton + Spin of neutron = ½ + ½ = 1

For ^{1}H nucleus,   For ^{2}H nucleus,   For ^{4}He nucleus,

P = 1, n = 0   P = 1, n = 1   P = 2, n = 2

Total mass = 1   Total mass = 2   Total mass = 4

Total spin = ½   Total spin = 1   Total spin = 0

Spin of p //al to spin of n (Spin of p //al to spin of n) & (Spin of p ⊥r to spin of n)

If p = Even, n = Even,

     Mass = p+n = Even,   Nuclear spin = 0, ^{4}He, ^{12}C, ^{16}O, …

If p = Odd, n = Odd,

     Mass = p+n = Even,   Nuclear spin = 1, 2,… ^{2}H = 1, ^{10}B = 3, …

If p = Even/Odd, n = Odd/Even,

     Mass = p+n = Odd,   Nuclear spin = ½, 3/2,… ^{1}H = ½, ^{17}O = 5/2, …

Nuclear spin quantum number = I = 0, ½, 1, 3/2, ….

Angular momentum of nucleus is

     L = I, (I − 1), (I − 2), …, 0, …, −(I − 2), −(I − 1), −I   for I = 0, 1, 2, …

     L = I, (I − 1), (I − 2), …, ½, − ½, …, −(I − 2), −(I − 1), −I   for I = ½, 3/2, …

Magnetic Moment   Non-Magnetic

Odd Mass Numbers   Even Mass Numbers
Hydrogen-1   Carbon-12
                    Oxygen-16

Angular
Momentum
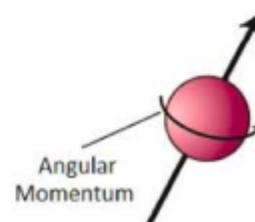
5.1. Interaction between Spin and Magnetic Field

- Electrons are moving around the nucleus in an circular orbits.
- Electric current is circulating in the opposite direction of motion of electron. So magnetic dipoles are produced.
- From classical electrodynamics, a rotating electrically charged particle creates a magnetic dipole.
- Spinning particle (electron) behaves as a tiny bar magnet placed along the spin axis.
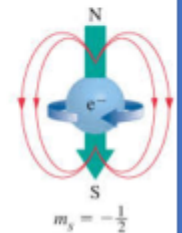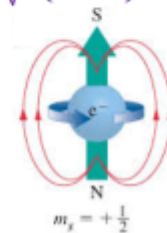- Magnetic moment of spinning electron is

$$\mu_e = \frac{e}{2m_e} L \qquad = \frac{eh}{4\pi m_e}\sqrt{S(S+1)} \qquad \text{since } L = \frac{h}{2\pi}\sqrt{S(S+1)}$$

- Magnetic moment of spinning nucleus is

$$\mu_n = \frac{e}{2m_p} L \qquad = \frac{eh}{4\pi m_p}\sqrt{I(I+1)} \qquad \text{since } L = \frac{h}{2\pi}\sqrt{I(I+1)}$$

Magnetic moment due to the electron's orbital motion

e – Charge of an electron = 1.6×10^{-19} C
m_e – Mass of an electron = 9.11×10^{-31} Kg
S – Spin quantum number of an electron
L – Angular momentum of an electron
m_p – Mass of proton = 1.67×10^{-27} Kg
I – Spin quantum number of nucleus

$m_s = +\frac{1}{2}$, $m_s = -\frac{1}{2}$

If electrons and nuclei are not a point charges, then

$$\mu_e = \frac{G\,eh}{4\pi m_e}\sqrt{S(S+1)} \qquad\qquad \mu_n = \frac{G\,eh}{4\pi m_p}\sqrt{I(I+1)}$$

G is the numerical factor

G = ±g = Lande splitting factor

    Electron G-factor depends on quantum state of an electron

    Nuclear G-factor calculated from expt only

G = –g   for electron

G = +g   for nucleus

Bohr Magneton $\beta_e = \dfrac{eh}{4\pi m_e} = 9.273 \times 10^{-24}$ (J/T)

Nuclear Magneton $\beta_n = \dfrac{eh}{4\pi m_p} = 5.05 \times 10^{-27}$ (J/T)

Magnetic moment of spinning electron and nucleus are

$$\mu_e = -\,g_e\,\beta_e\,\sqrt{S(S+1)} \qquad\qquad \mu_n = g_n\,\beta_n\,\sqrt{I(I+1)}$$
$$\mu_e = -\,g_e\,\beta_e\,L_e \qquad\qquad\qquad \mu_n = g_n\,\beta_n\,L_n$$

Consider Nuclear spin quantum number = I = ½

Angular momentum of nucleus

L_n = I, (I − 1), (I − 2), …, ½, − ½, …, −(I − 2), −(I − 1), −I   for I = ½, 3/2, …

L_n = − ½ and + ½

Magnetic moment of spinning nucleus in the absence of an external magnetic field (B_o) is $\mu_n = g_n \beta_n L_n$

Magnetic moment of spinning nucleus in the presence of an external magnetic field (B_o) is $(\mu_n)_{ext} = \mu_n B_o = g_n \beta_n L_n B_o$

For L_n = − ½, $(\mu_n)_{ext}$ = − ½ $g_n \beta_n B_o$

For L_n = + ½, $(\mu_n)_{ext}$ = + ½ $g_n \beta_n B_o$

Separation bet neighboring energy levels is

ΔE = [+ ½ $g_n \beta_n B_o$] − [− ½ $g_n \beta_n B_o$]

ΔE = [$g_n \beta_n B_o$] J

Frequency is

ν = ($\Delta E/h$) = ($g_n \beta_n B_o$)/h   Hz
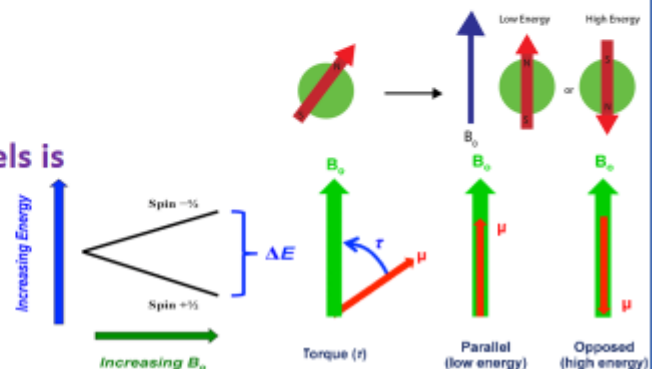
5.2a. Population of Energy Levels

Classical theory states that, at a temp TK, the ratio of the population of energy levels is $\frac{N_{upper}}{N_{lower}} = \exp\left(\frac{-\Delta E}{KT}\right)$

For ^1H, Nuclear spin quantum number = I = ½

    Angular momentum of nucleus = L_n = − ½ and + ½

    For L_n = − ½, $(\mu_n)_{ext}$ = − ½ $g_n \beta_n B_o$

    For L_n = + ½, $(\mu_n)_{ext}$ = + ½ $g_n \beta_n B_o$

For Nuclei, $(\Delta E)_n$ = [$g_n \beta_n B_o$] = 66.24 x 10^{-27} J

For Electron, $(\Delta E)_e$ = [$g_e \beta_e B_o$] = 43.56 x 10^{-24} J

    At room temp (T = 300 K), K = 1.38 x 10^{-23} J/K

For Nuclei, $\frac{N_{upper}}{N_{lower}} = \exp\left(\frac{-\Delta E}{KT}\right)$ = exp (− 0.16 x 10^{-4}) = 0.9999984 ≈ 1

For Electron, $\frac{N_{upper}}{N_{lower}} = \exp\left(\frac{-\Delta E}{KT}\right)$ = exp (− 0.1052 x 10^{-1}) = 0.989535 ≈ 1

$\frac{N_{upper}}{N_{lower}}$ ≈ 1 for both nuclei and electron

So spins are almost equally distributed between 2 energy levels.

g_n = 5.585

β_n = 5.05 x 10^{-27} (J/T)

B_o = 2.3487 Tesla

g_e = 2
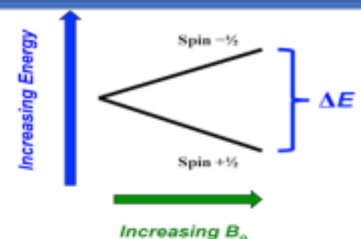
β_e = 9.273 x 10^{-24} (J/T)

5.2b. Larmor Precession

Precession

If the axis of rotation of a body is itself rotating about a second axis, then the body is said to be precessing about the second axis.

Nuclear spin quantum number = I

Angular momentum of nucleus = $L = \dfrac{h}{2\pi}\sqrt{I(I+1)}$
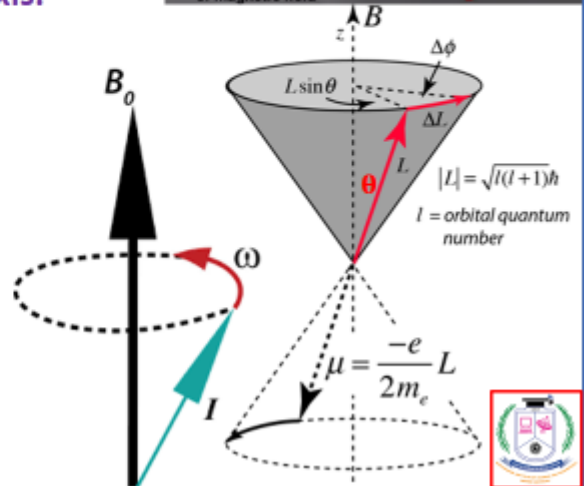
Magnetic moment of spinning nucleus is

$\mu_n = \dfrac{e}{2m_p} L = \dfrac{eh}{4\pi m_p}\sqrt{I(I+1)} = g_n\,\beta_n\,\sqrt{I(I+1)}$

g_n is the g-factor for nucleus

β_n is the Nuclear Magneton $= \dfrac{eh}{4\pi m_p}$

ω = Angular velocity
B = External applied magnetic field

nucleus in the absence of magnetic field

$|L| = \sqrt{l(l+1)}\hbar$
l = orbital quantum number

$\mu = \dfrac{-e}{2m_e} L$

When a nucleus of magnetic moment μ_n is placed in a magnetic field B, it experiences a torque $\quad \tau = \mu_n \times B = \mu_n\, B\, \sin\theta \quad$ -------(1)

$\qquad \tau = \dfrac{dL}{dt}$ = Rate of change of angular momentum

- This Torque rotates the magnetic moment around the magnetic field.
- Spinning/orbiting magnetic moment tends to precess around the applied external magnetic field called **Larmor Precession.**
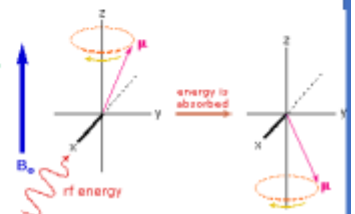- Nucleus tends to precess around the magnetic field with a frequency called **Larmor Frequency (ν).**

Angular velocity = $\omega = \dfrac{d\phi}{dt} = \dfrac{1}{dt}\dfrac{\Delta L}{L\sin\theta} = \dfrac{\tau}{L\sin\theta} = \dfrac{\mu_n B \sin\theta}{L\sin\theta} = \dfrac{\mu_n B}{L} = \dfrac{e}{2\,m_p} B$

WKT, $\omega = 2\pi\,\nu$

Larmor Frequency = $\nu = \dfrac{\omega}{2\pi} = \dfrac{\mu_n B}{2\pi L} = \dfrac{g_n\,\beta_n\,\sqrt{I(I+1)}\,B}{2\pi\dfrac{h}{2\pi}\sqrt{I(I+1)}} = \dfrac{g_n\,\beta_n\,B}{h}$

This is the frequency separation bet energy levels.

So particle (nucleus) spins interact with EM radiation.

If $\nu_{EM} = \nu_{precess}$,
- Resonance occurs.
- EM radiation can interact coherently with particle (nucleus).
- Energy can be exchanged.
- So transitions occur.

If $\nu_{EM} \neq \nu_{precess}$,
- No resonance occurs.
- EM radiation can't interact coherently with particle (nucleus).
- Energy can't be exchanged.
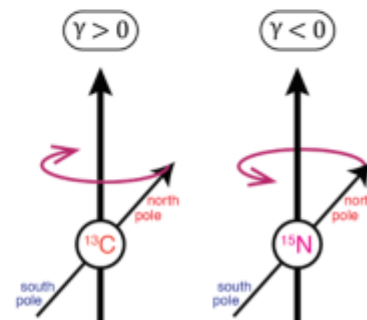- So no transitions occur.

NMR – Spinning particle is nucleus

ESR   – Spinning particle is electron

γ = gyromagnetic ratio = $\dfrac{\mu}{L}$ = $\dfrac{magnetic\ moment}{angular\ momentum}$

If γ = +ive, direction of precess is clockwise

If γ = −ive, direction of precess is anti-clockwise

5.3. Chemical Shift

Consider an atom is placed in an external magnetic field B.
Surrounding electron cloud tends to circulate around the nucleus.
So small magnetic field is induced to oppose the external magnetic field B (Lenz law) (diamagnetic property).

$B_{induced} \propto B_{applied}$
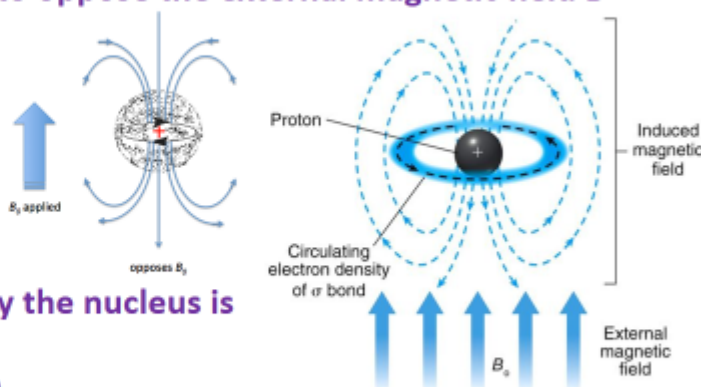
$B_{induced} = \sigma\ B_{applied}$

σ is shielding factor

$\sigma = 10^{-5}$ for protons

$\sigma < 10^{-3}$ for other nuclei

Total magnetic field experienced by the nucleus is

$B_{effective} = B_{applied} - B_{induced}$

$= (B - \sigma B) = B (1 - \sigma)$

Thus the nucleus can be said to be shielded from the applied field by diamagnetic electronic circulation.

Shielding Effect: When a proton is present inside the magnetic field, more applied magnetic field is required to cause excitation.
- Proton is attached to the electropositive atom.

Deshielding Effect: When a proton is present outside the magnetic field, less applied magnetic field is required to cause excitation.
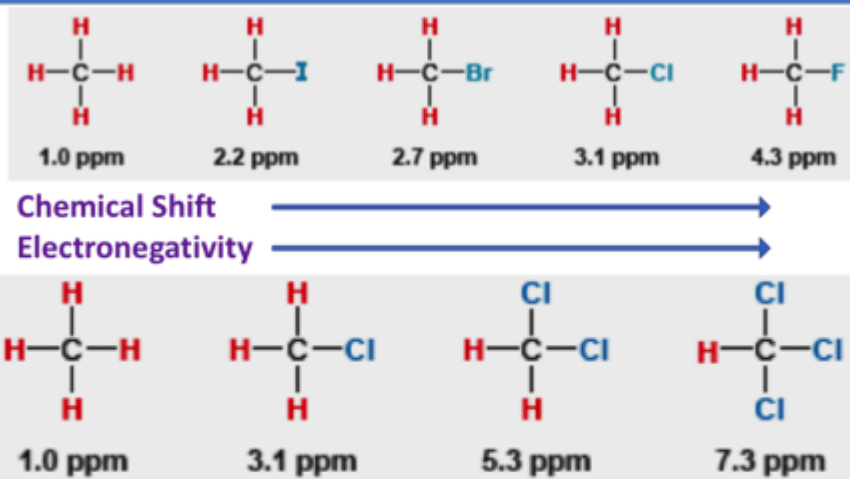- Proton is attached to the electronegative atom.

Chemical Shift: Shift in the position of the NMR region resulting from the shielding and deshielding by electrons.
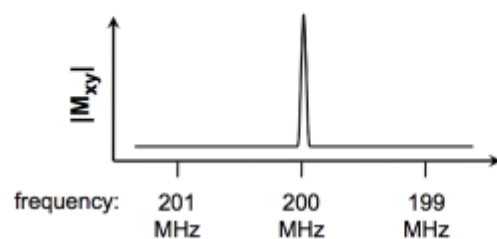- Chemical shift is measured in PPM – Parts Per Million.

Shielding effect Deshielding effect
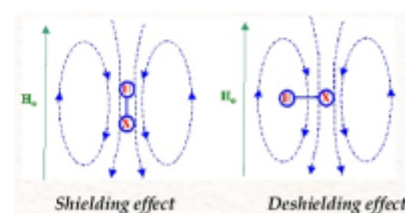
- Chemical shift (δ) is the difference in resonant frequencies of two nuclei due to differences in their local molecular environments
- Measures in parts per million (ppm)
- Frequency shift (in Hz) scales with B_o

$$\delta = \frac{\text{(shift in Hz from TMS)}}{\text{(spectrometer frequency in MHz)}}$$
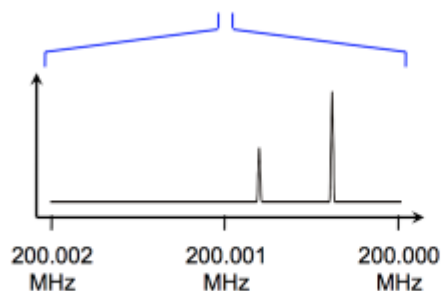
Chemical Shift →
Electronegativity →

| 1.0 ppm | 2.2 ppm | 2.7 ppm | 3.1 ppm | 4.3 ppm |

| 1.0 ppm | 3.1 ppm | 5.3 ppm | 7.3 ppm |

An NMR Spectrum

No surprise: NMR spectrum of CH_3OH shows the presence of ^1H nuclei at Larmor frequency.

frequency: 201 MHz   200 MHz   199 MHz

but what if we look closer??
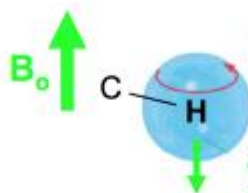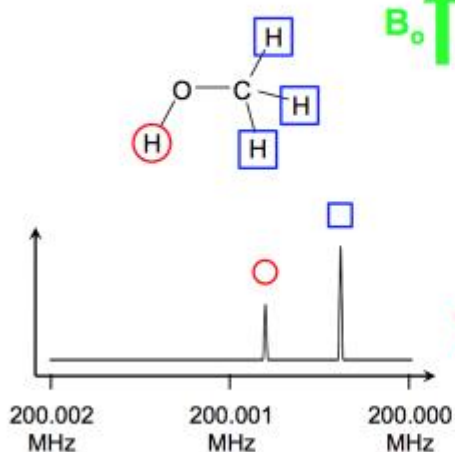
Not all ^1H nuclei wobble at the exact same frequency;

Differences in frequency reflect differences in magnetic environment.

200.002 MHz   200.001 MHz   200.000 MHz

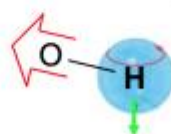## "Shielding" Influences Proton Frequency

NMR spectrum of CH_3OH:

B_o

C—H

Magnetic field induces circulation of e⁻ cloud.

Circulation generates an *opposing* magnetic field.

So, magnetic field and frequency are *lower* than one might expect.

O—H

Electron-withdrawing oxygen means
- Smaller e⁻ cloud on H
- Less opposing magnetic field
- **Higher frequency**

| 200.002 MHz | 200.001 MHz | 200.000 MHz |

Chemical Shift: A Proportional Horizontal Axis

Problem: Differences in frequency depend on spectrometer field strength, vary from instrument to instrument.

Solution: Define an absolute scale independent of spectrometer frequency, called "chemical shift".

$$\text{chemical shift, ppm } \delta = \frac{\text{shift downfield from TMS (in Hz)}}{\text{spectrometer frequency (in MHz)}}$$

frequency

200.002	200.001	200.000	MHz
2000	1000	0	Hz (*diff.*)
10	5	0	ppm

Frequency defined as $\delta = 0$ ppm

H_3C—Si—C—H
(with CH_3 groups)

tetramethylsilane (TMS)

9