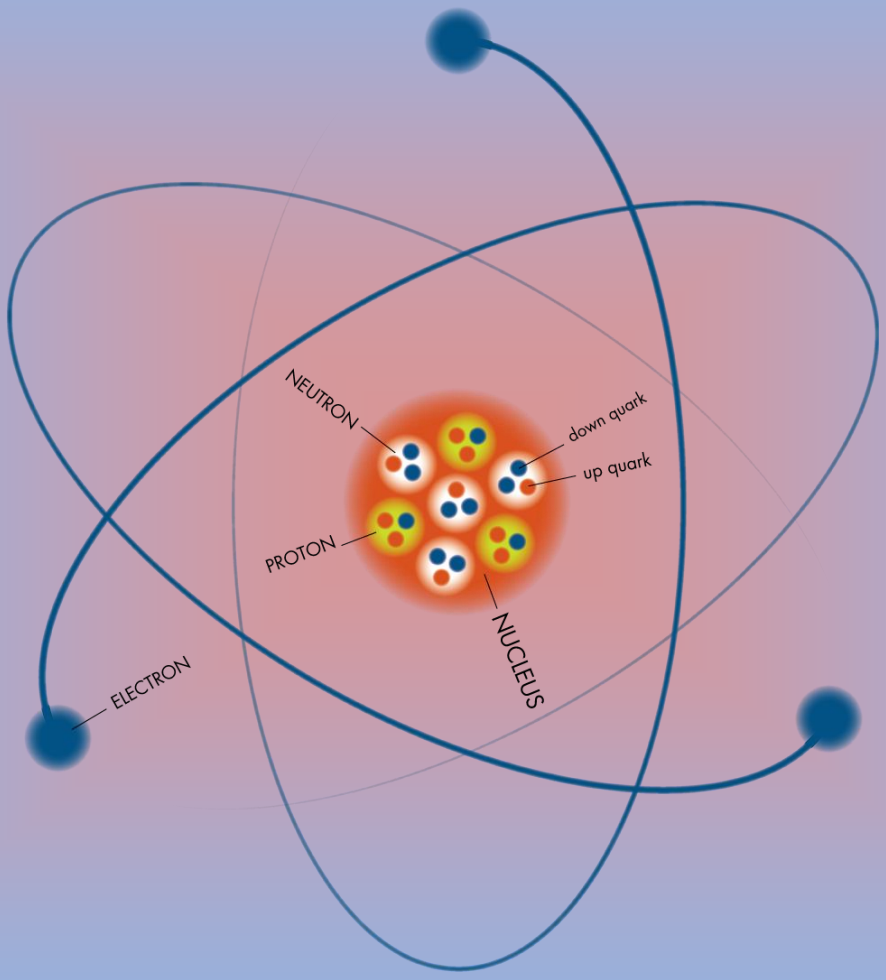
KARNATAKA STATE OPEN UNIVERSITY

Mukthagangothri, Mysore – 570 006

M.Sc. PHYSICS

(FIRST SEMESTER)



Course- MP 1.3

ATOMIC & MOLECULAR PHYSICS

M.Sc. PHYSICS

FIRST SEMESTER

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ATOMIC & MOLECULAR PHYSICS

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PRELUDE

Atomic and Molecular Physics is the study of structure of atoms and molecules, their energy states and also the interactions with other particles. It is one of the fast growing fields of Physics. Much advancement has happened since the first attempt to explain the structure of atoms at the beginning of last century. With the advent of Quantum Mechanics many fields in Physics gained considerable momentum. Spectroscopy, which is the study of interaction between matter and radiation, is one such field.

This course tries to throw light on some very important concepts of spectroscopic techniques. It consists of four blocks.

In the first block, a comprehensive discussion on the fundamentals of Molecular spectra is given. Here, different types of spectra of diatomic molecules, vibrational and rotational structures of the molecules can be understood in detail.

The second block deals with the very basics of the formation of matter i.e., Chemical bonds. While reading this block, the students can get clear picture about some basic questions like- why chemical bonds are formed? What are the types of bonds that exist in nature?

The third block talks about the LASERs. Lasers are one of the revolutionary discoveries of last century. It finds applications in many fields of science and technology like medicinal field, defense armory etc. In this block, a complete detail about the fundamental concepts of Lasers is revealed.

The last block unveils information about many of the advanced techniques of Laser spectroscopy in detail. Also, the main application of Lasers in the field of communication i.e., Optical fibers are discussed comprehensively.

Unit 1: Rotation, vibration and rotation-vibration spectra of diatomic molecules, selection rules, determination of rotational constants

Structure:

1.0 Objective:

After studying this unit you are going to understand

- The fundamentals of Rotational spectra, Vibrational spectra and Vibrational-Rotational spectra in detail.

1.1 Introduction:

There are three categories in the spectra of substances:

a) Continuous spectra:-

These are produced by the bodies heated to incandescent. This spectrum cannot be resolved into lines.

b) Line spectra :-

These are produced by atoms. The lines extend over a range of several hundred angstroms. These lines show further structure known as fine and hyperfine structures.

c) ***Band Spectra (OR) Molecular Spectra***:

These are produced by molecules and derive their names from the fact that in the visible region under low spectroscopic resolution, they appear as continuous band, bands of color. The band usually has a sharp edge at one end called 'band head' or 'band edge'. At the band head the intensity falls suddenly to zero, while it fades off slowly towards the other end.

Further, the molecular spectra are divided into three spectral ranges corresponding to different types of transitions between molecular energy states as:

(i) Electronic Spectra:-

- ❖ This spectra is observed in the visible and UV regions
- ❖ It is observed both in emission and absorption
- ❖ It is due to transitions between electronic states.
- ❖ Each spectrum consists of quite a large number of bands. Each individual band has a sharp edge, called band head, where intensity falls suddenly to zero and from this edge the intensity gradually decreases to the other side of the band.
- ❖ It is observed for heteronuclear as well as homonuclear molecules.

(ii) Vibrational – Rotational spectra :-

❖ These spectra are observed in absorption in the near infrared region.

❖ This spectrum arises due to the transitions between two rotational levels associated with same electronic level. The lines of the band result from transitions between rotational levels of one Vibrational level and rotational levels of the other.

❖ This spectrum is observed only for heteronuclear molecules. Like HCl, CO, etc Homonuclear molecules like H_2, N_2 etc do not produce Vibrational - rotational spectra.

(iii) Pure Rotational Spectra:-

❖ These spectra are observed in absorption in the far infrared (or) microwave region.

❖ This arises from transitions between two rotational levels associated with one and the same Vibrational level of a given electronic state.

❖ This spectrum is observed only for heteronuclear molecules.

Like atomic spectra, Molecular spectra are obtained by transitions between energy states of the molecules.

Note:

i. Rotational states are separated by quite small energy intervals $\left(\approx 10^{-3} eV\right)$ hence their spectra are in the micro wave region.

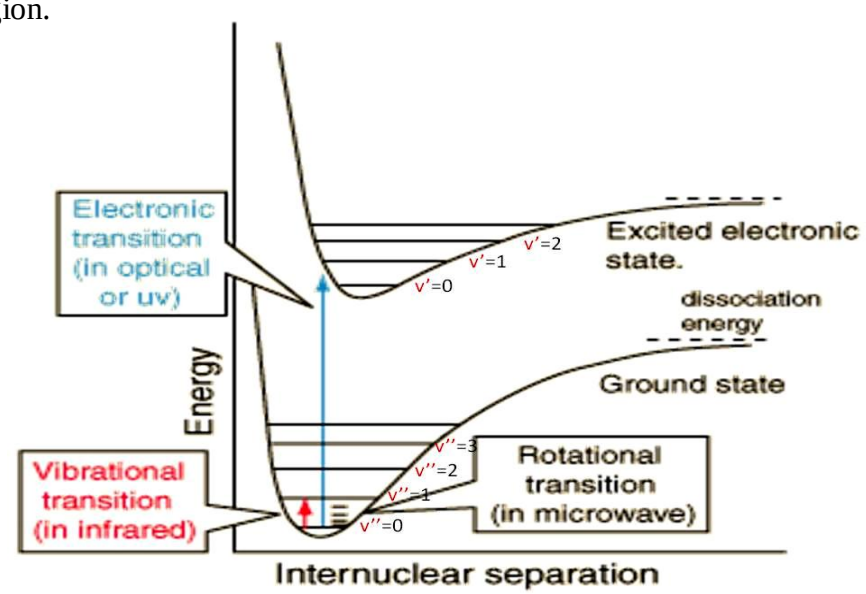


Fig (1)

ii. Vibrational states are separated by somewhat larger energy intervals $\left(\approx 10^{-1} eV\right)$ and the spectra falls in the near infrared region

iii. The electronic states have higher energy separation $\left(\approx 10 eV\right)$ and the corresponding spectra falls in the visible and UV regions.

Thus the total energy of the molecule (E) is the sum of Electronic energy (E_e), vibration energy (E_v) and rotational energy (E_r)

$$\boxed{E = E_e + E_v + E_r}$$

I. "Rotational Spectra"

Salient Features of Rotational Spectra:

1) Pure rotational spectra arise from transitions between rotational energy states and are observed in microwave (or) far infra red region of the electromagnetic spectrum.

2) Only molecules having permanent electric dipole can give rise to rotational spectra. It means homonuclear diatomic molecules such as H_2, O_2, N_2; symmetric linear molecules such as CO_2 and spherical top polyatomic molecules such as CH_4 do not exhibit rotational spectra.

3) In practice pure rotational spectra are observed in absorption. For heteronuclear diatomic molecules such as HCl, HBr etc., the rotational spectra consist of a series of absorption maxima which are very nearly equidistant on wave number scales.

1.2 Basic requirement for rotational spectra:

The very basic requirement for the rotational spectra is that the molecules must have a permanent dipole moment.

This is because, according to classical electrodynamics, a rotating molecule can lead to emission of radiation provided a changing dipole moment is associated with the molecule.

Hence all hetero nuclear diatomic molecules, whose centers of positive and negative charges do not coincide, have a permanent dipole moment. A rotating molecule can absorb infra red radiation and thereby increase the rotation, only if a permanent dipole is present. Such a

molecule interacts with the electric field of the incident radiation to absorb rotational energy and produce the absorption spectrum.

1.3 Rigid Rotator Model:- Explanation of Rotational Spectra of a diatomic molecule:

In this model, it is assumed that atoms of a diatomic molecule are held rigidly at fixed distances from each other. i.e., inter nuclear distance is assumed to be fixed at the equilibrium value.

Let m_1 and m_2 be the masses of the atoms separated by a distance *R*. Let r_1 and r_2 be their respective distances from the center of mass *C* (fig 2). The system is capable of rotating about an axis passing through its centre of mass and normal to inter nuclear axis.

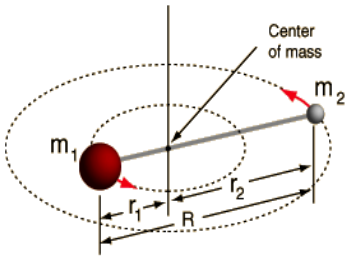


Fig (2)

The moment of inertia ***I*** about an axis passing through the Centre of mass ***C*** is

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \ldots\ldots(1)$$

By the definition,

$$m_1 r_1 = m_2 r_2 \quad \ldots\ldots(2)$$

and; $$R = r_1 + r_2 \quad \ldots\ldots(3)$$

Thus, putting equation (3) in equation (2) and simplifying, we get

$$r_1 = \frac{m_2}{m_1 + m_2} R \; ; \; r_2 = \frac{m_1}{m_1 + m_2} R \quad \ldots\ldots(4)$$

Substituting the values of r_1 and r_2 in (1) and simplifying, we get

$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) R^2 \quad \ldots\ldots(5)$$

but $\frac{m_1 m_2}{m_1 + m_2}$ is called the reduced mass and is denoted by μ

$$\therefore I = \mu R^2 \quad \ldots\ldots(6)$$

The Classical angular momentum ***L*** of the System is given by

$$L = I\omega_r \quad \ldots\ldots(7)$$

where ω_r is the angular velocity of rotation. Also, the rotational kinetic energy

$$E = \frac{I\omega_r^2}{2}$$

i.e., $$E = \frac{L^2}{2I} \quad \ldots\ldots(8)$$

Writing the Schrödinger wave equation for system we get

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}[E - V(r)]\psi = 0 \quad \ldots\ldots(9)$$

Where $\psi = \psi_{r\theta\phi} = R(r)\Theta(\theta)\Phi(\phi) = R(r)Y_{JM}(\theta,\phi)$ is the wave function.

Writing the equation (9) in spherical polar co-ordinates we get

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial\psi}{\partial\psi}\right) + \frac{1}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\psi}{d\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2\mu}{h^2}[E - V(r)]\psi = o \quad \ldots\ldots(10)$$

but in spherical polar co-ordinates, we write L^2 as

$$L^2 = \frac{-h^2}{4\pi^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \quad \ldots\ldots(11)$$

So, the 2nd and 3rd terms of equation (10) can be written as

$$\frac{1}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} = -\frac{4\pi^2L^2}{h^2r^2}\psi \quad \ldots\ldots(12)$$

Put equation (12) in equation (10)

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial\psi}{\partial r}\right) - \frac{4\pi^2L^2}{h^2r^2}\Psi + \frac{8\pi^2\mu}{h^2}[E - V(r)]\psi = o \quad \ldots\ldots(13)$$

Since we are assuming rigid rotator model, no change in potential energy is observed.

The potential energy V(r) is a constant, which for convenience can be taken as zero.

Also since inter nuclear distance *r* is constant; the derivative with respect to *r* in equation (13) can be dropped. Thus we finally have,

$$-\frac{4\pi^2 L^2}{h^2 r^2}\psi + \frac{8\pi^2 \mu}{h^2} E\psi = O$$

$$\Rightarrow L^2\psi = 2\mu r^2 E\psi \quad \ldots\ldots(14)$$

Thus our wave function contains only the spherical part i.e., $Y_{JM}(\theta,\phi)$.Also

$$Y_{JM}(\theta,\phi) = \sqrt{\frac{(2J+1)(J-M)!}{4\pi(J+M)!}}\,(-1)^M P_J^M(\cos\theta)e^{iM\phi} \quad \ldots\ldots(15)$$

Where J = magnitude of angular momentum

M = z – component of angular momentum

$P_J^M(\cos\theta)$ = Legendre's polynomial

We have the Eigen values relations for

L^2 and L_z as

$$L^2 Y_{JM}(\theta,\phi) = \frac{h^2}{4\pi^2} J(J+1) Y_{JM}(\theta,\phi) \quad \ldots\ldots(16)$$

and $L_z Y_{JM}(\theta,\phi) = \frac{Mh}{2\pi} Y_{JM}(\theta,\phi)$

Where J = 0, 1, 2… is called rotational quantum member

and

M = -J to +J = $0, \pm1, \pm2 \ldots\ldots \pm J = (2J+1)$*values*

Put equation (16) in equation (14)

$$\frac{h^2}{4\pi^2} J(J+1) = 2\mu r^2 E$$

$$\Rightarrow \boxed{E = \frac{h^2 J(J+1)}{8\pi^2 \mu r^2} = \frac{h^2 J(J+1)}{8\pi^2 I}} \quad \ldots\ldots(17)$$

The rotational energy levels are given by equation (17). The degeneracy of each level is equal to (2J+1). This number (2J+1) is also called "***statistical weight***".

According to equation (17), we have a series of discrete energy levels whose energy increases with increasing value of J.

Usually spectroscopic transitions are measured in wave number. Thus, the equation (17) is written in terms of wave number F (J) as

$$F(J)=\frac{E}{hc}=\frac{h}{8\pi^2 Ic}J(J+1) \quad \ldots\ldots(18)$$

Let us put, $\frac{h}{8\pi^2 Ic}=B$, known as rotational constant.

Then

$$F(J) = B\,J\,(J+1) \quad \ldots\ldots(19)$$

Substituting J=0, 1, 2 …… we get

F (J) = 0, 2B, 6B, 12B, 20B …….

Thus we have series of discrete energy levels whose spacing increase with increasing value of J. (as in fig 3)

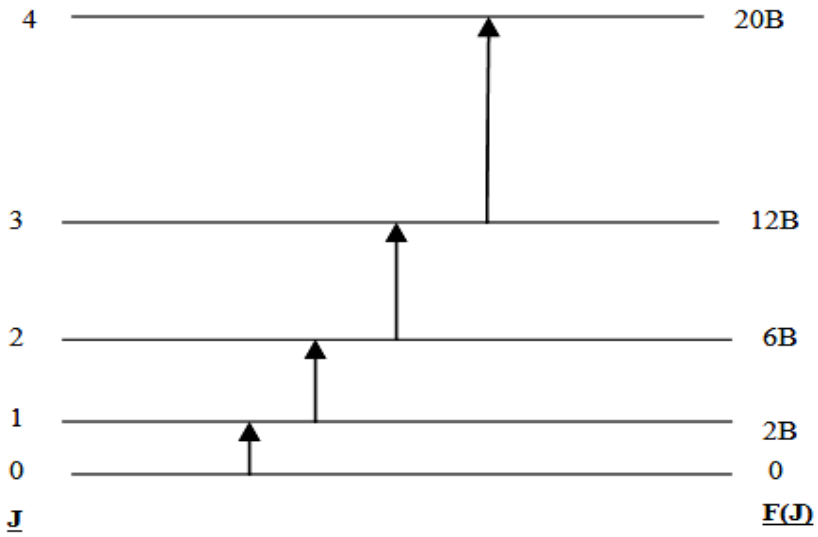


Fig (3)

When a transition takes place between an upper level J' and a lower level J'' the wave number of the emitted or absorbed radiation is given by

$$\bar{\nu} = F(J') - F(J'')$$

$$\bar{\nu} = BJ'(J'+1) - BJ''(J''+1) \quad \ldots\ldots(20)$$

Selection rules:-

Pure rotational transitions may be observed in the microwave or far-infrared regions, which are electric dipole transitions. A study of the matrix element of the dipole moment shows

that the rotational transitions can only occur such that J changes by unity. Thus the allowed selection rule is:

$$\boxed{\Delta J = \pm 1}$$

Since we have chosen $J' > J''$ we have

$J' = J'' + 1$

Thus

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

$\bar{\nu} = 2B(J''+1)$

For the sake of simplicity, we may write J for J'' so that

$$\boxed{\bar{\nu} = 2B(J+1)} \qquad \text{...}(21)$$

Where J = 0, 1, 2 …… and thus,

$\bar{\nu}$ = 2B, 4B, 6B, 8B ……….

Thus, the spectrum of simple rigid rotator consists of a series of equally spaced spectral lines with constant separation 2B.

Note:

In obtaining the rotational energy, we have ignored the rotation about the symmetry axis i.e., bond axis. There are two main reasons for this

a) The mass of an atom is located almost entirely in the nucleus whose radius is only 10^{-4} times the radius of the atom itself, therefore the main contribution to the moment of inertia of diatomic molecules about the symmetry comes from electrons. But, the mass of electron is very small compared to the total molecular mass and is concentrated in a region whose radius is about half the bond distance. The moment of inertia about the symmetry axis is thus very small and hence the value of B is large.

According to equation (18), the energy levels are therefore widely spaced. To raise the molecule from J = 0 state to J = 1 state requires large energy and such transition do not occur under normal spectroscopic conditions.

b) The molecule will be in J = 0 state for rotation about symmetry axis and they may be said to be not rotating. In such transitions, if occur, there is no dipole change and hence no rotational spectrum.

Also, according to rigid rotator model, the rotator does not experience any torques.

***Limitation of Rigid rotator model*:**

In liquids, solids and even dense gases, where intermolecular interactions come into play, the predictions of this theory fail.

1.4 Intensity of Rotational Levels:

The population of J^{th} level relative to the lowest level, under thermal equilibrium is given according to Boltzmann distribution law as

$$N_J = N_o(2J+1)e^{-\left(\frac{E_J}{kT}\right)} \quad \text{.....(22)}$$

Where

N_J = population of J^{th} level

N_o = population of J = 0 level (ground state)

(2J+1) = degeneracy of each level

E_J = energy of J^{th} level= F(J)*ch* = BJ(J+1)ch.

E_J = Bch J (J+1)

k = Boltzmann constant

T = temperature in Kelvin

So, equation (1) becomes

$$N_J = N_o(2J+1)e^{-\left(\frac{BchJ(J+1)}{kT}\right)} \quad \text{.....(23)}$$

gives the intensity of J^{th} level

Note: *Which rotational level has the maximum intensity ??*

Ans: The value of ***J*** for which the energy level has highest intensity is given by

$$\frac{dN_J}{dJ} = O$$

Substituting the value of N_J from equation (2) and differentiating we get

$$\left[\frac{2KT-(2J+1)^2 Bch}{KT}\right]e^{-\left(\frac{BchJ(J+1)}{kT}\right)}=O$$

$$(2J+1)^2=\frac{2kT}{ch}$$

$$\boxed{J_{\max}=\sqrt{\frac{kT}{2Bch}}-\frac{1}{2}}\qquad\qquad(24)$$

1.5 Isotope effect on Rotational Spectrum:

We have the rotational constant

$$B=\frac{h}{8\pi^2\mu r^2 c}$$

Where $\mu =$reduced mass,

But the value of reduced mass is different for different isotopes of the same molecule. Since the mass effects are negligible compared to electronic effects in the determination of equilibrium internuclear separation, this separation is the same in two isotopic molecules. Only the reduced masses are different.

Let B_i be the rotational constant for heavier isotope then

$$B_i < B$$

and so $F_i(J) < F(J)$

Thus, the separations of levels for the heavier isotope will be smaller than those of the corresponding levels of lighter isotope (see fig (4)). Hence spectral lines will also be closer.

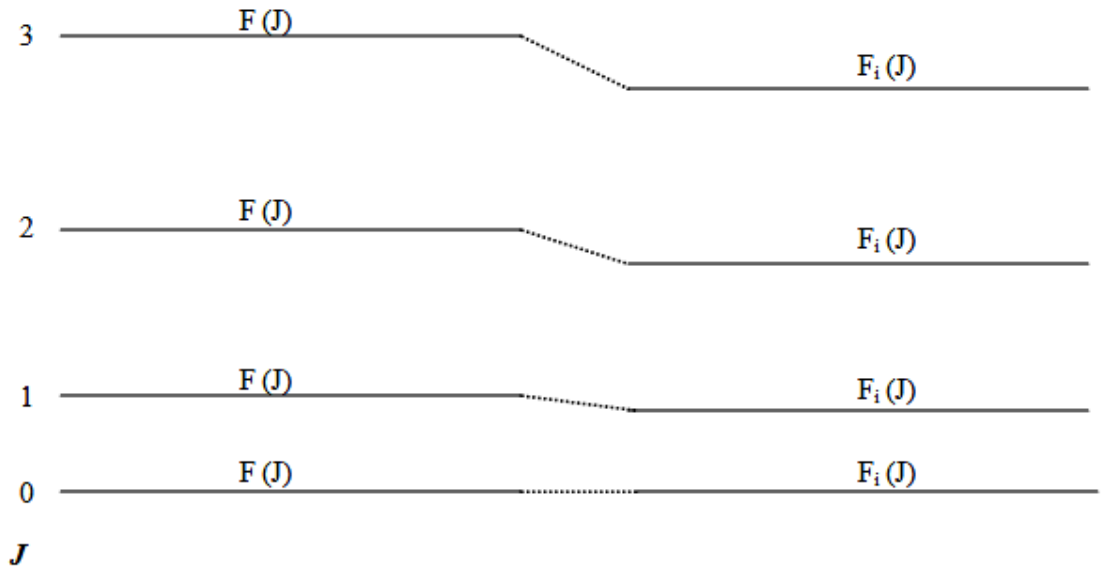


Fig (4)

1.6 Non – Rigid Rotator:

In practice, the rotational spectral lines are 'not' exactly equidistant as predicted by the Rigid Rotator model; the separations decrease slightly with increasing values of ***J***. This is due to the fact that the molecules are 'not' exactly rigid. They also stretch while in rotation. Taking this into account, the rotational terms come out to be

$$F(J) = BJ(J+1) - DJ^2(J+1)^2$$

Where D = Centrifugal distortion constant, which is much smaller than B.

Also $D = \frac{4B^2}{\omega}$; ω = angular frequency

Due to the centrifugal term, the increase in spacing between successive rotational levels with increasing values of J becomes slightly less rapid (see fig (2))

The corresponding wave numbers of the rotational lines are now

$$\bar{\nu} = F(J+1) - F(J) = 2B(J+1) - 4D(J+1)^3$$

This shows that the separations between lines decrease slightly with increasing '***J***' as shown in figure (5) below-

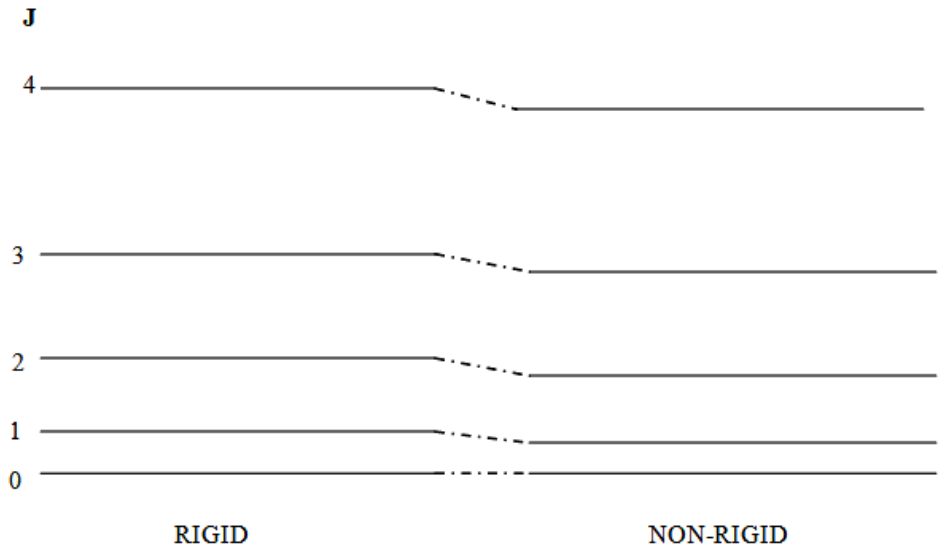


Fig (5)

II. "Vibrational Spectra"

This spectrum arises from transitions between Vibrational energy states associated with the same electronic state of the molecule. Also, these spectra are observed in near infrared region of the electromagnetic spectrum.

This spectrum is observed only for molecules having permanent dipole moments.

In practice, this spectrum is observed in absorption.

1.7 Simple Harmonic Oscillator Approximation:

The simplest model about the form of vibrations is to treat the molecule as a harmonic oscillator.

In this model it is assumed that atoms of diatomic molecule are vibrating along the direction of the bond.

The potential energy function under whose influence the nuclei vibrate is given by

$$V(r) = \frac{1}{2}k(r - r_e)^2 = \frac{1}{2}kx^2$$

Where k = force constant

r_e = equilibrium internuclear distance

x = displacement of the oscillator from the equilibrium position.

So, the one- dimensional Schrödinger wave equation describing this motion is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}[E - V(r)]\psi = O$$

Where μ = reduced mass of the oscillator (diatomic molecule)

But $V(r) = \frac{1}{2}kx^2$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}\left[E - \frac{1}{2}kx^2\right]\psi = O \quad \ldots\ldots(1)$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu E}{h^2}\psi - \frac{4\pi^2\mu k}{h^2}x^2\psi = O \quad \ldots\ldots(2)$$

Let us take $\frac{8\pi^2\mu E}{h^2} = \alpha$

and $\frac{\sqrt{4\pi^2\mu k}}{h^2} = \beta$

Then equation (2) becomes

$$\frac{d^2\psi}{dx^2} + \left(\alpha - \beta^2x^2\right)\psi = O \quad \ldots\ldots(3)$$

Let us introduce a dimensionless independent variable

$$\xi = \sqrt{\beta}x$$

$$\Rightarrow \frac{d^2}{dx^2} = \beta\frac{d^2}{d\xi^2}$$

Writing equation (3) in terms of the variable ξ, we have

$$\beta\frac{d^2\psi}{d\xi^2} + \left(\alpha - \frac{\beta^2\xi^2}{\beta}\right)\psi = O$$

(or)

$$\frac{d^2\psi}{d\xi^2} + \left(\frac{\alpha}{\beta} - \xi^2\right)\psi = O \quad \ldots\ldots(4)$$

A solution to above equation can be given by

$$\psi(\xi) = CU(\xi)e^{-\left(\xi^2/2\right)} \quad \ldots\ldots(5)$$

Substituting equation (5) in equation (4) we get

$$\frac{d^2U}{d\xi^2} - 2\xi\frac{dU}{d\xi} + \left(\frac{\alpha}{\beta} - 1\right)U = O$$

If we replace $\left(\frac{\alpha}{\beta} - 1\right)$ by $2v$, then this equation becomes Hermite differential equation and so we may put $H_v(\xi)$ in place of $U(\xi)$

Then,

$$\frac{d^2H_V(\xi)}{d\xi^2} - 2\xi\frac{dH_V(\xi)}{d\xi} + 2vH_V(\xi) = O \quad \ldots\ldots(6)$$

Also equation (5) can be written as

$$\psi(\xi) = CH_V(\xi)e^{\frac{-\xi^2}{2}}$$

These solutions are acceptable only for

$v = 0,1,2,\ldots\ldots\ldots$

The restriction on the values of 'v' gives a corresponding restriction on the values of energy E.

We have

$$\frac{\alpha}{\beta} - 1 = 2v$$

$$\Rightarrow \frac{\alpha}{\beta} = 2v + 1$$

$$\frac{8\pi^2\frac{\mu E}{h^2}}{\frac{2\pi}{h}\sqrt{\mu k}} = 2v + 1$$

$$\Rightarrow E = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\left(v + \frac{1}{2}\right)$$

$But\ \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \nu_{osc}$ = Classical frequency of oscillator.

$$\therefore E = h\nu_{osc}(v+\frac{1}{2}) \quad \text{.....(7)}$$

This gives the allowed energies for the diatomic molecule (harmonic oscillator)

'v' is called the vibration quantum number which can take only integral values i.e., $v = 0, 1, 2$ …….

Note:

A special feature of the quantum mechanical oscillator is "the existence of zero point energy" (minimum vibrational energy that the molecule may have at OK temperature and is a consequence of uncertainty principle).

Spectrum Analysis:

Let us analyze the expected spectrum of such a harmonic oscillator.

The vibrational terms (energies in wave number unit i.e., cm^{-1}) are represented here by G (v) and are given by

$$G(v) = \frac{E}{hc} = \frac{\nu_{osc}}{c}(v+\frac{1}{2}) \quad \text{.....(8)}$$

Where ν_{osc} is the classical frequency in wave number unit and is known as vibrational constant and is designated by $\overline{\omega}$

Thus,

$$G(v) = \overline{\omega}(v+\frac{1}{2}) \quad \text{.....(9)}$$

Substituting

$v = 0, 1, 2\ldots$ we have

$$G(v) = \frac{1}{2}\overline{\omega}, \frac{3}{2}\overline{\omega}, \frac{5}{2}\overline{\omega}.....$$

Thus we obtain a series of equispaced discrete vibrational levels having the common separation $\overline{\omega}$ as shown in fig (6)

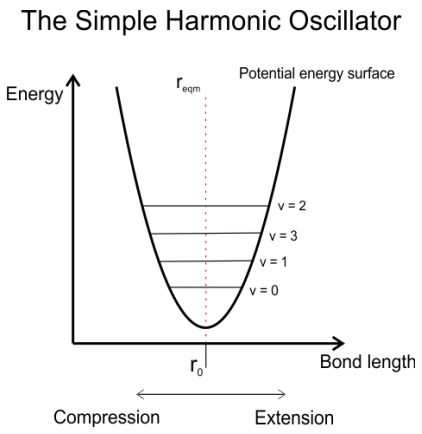


Fig (6)

Quantum mechanically, the emission of radiation takes place as a result of transition of the oscillator from a higher state to a lower state. Similarly absorption takes place by the reverse process (i.e., transition from lower state to higher state).

The wave number of emitted or absorbed radiation is given by

$$\bar{\nu} = G(v') - G(v'') \quad \text{.....(10)}$$

Where v' and v'' are the vibrational quantum numbers of the upper and lower vibrational states.

The transition moment for a transition between lower and upper vibrational states with wave functions $\psi_{v''}\xi\psi_{v'}$ of the harmonic oscillator is given by

$$R_{21} = \int \psi^*_{v'} M \psi_{v''} dx \quad \text{.....(11)}$$

Where $x = r - r_e$

M= electric dipole moment

For homonuclear molecules, M is zero and is non zero for heteronuclear diatomic molecules and varies with $r - r_e$. The variation in M can be expressed as

$$M = M_e + \left(\frac{dM}{dx}\right)_e x + \frac{1}{2!}\left(\frac{d^2M}{dx^2}\right)_e x^2 + \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \rightarrow (12)$$

Putting equation (12) in equation (11)

$$R_{21} = M_e \int \psi^*_{v'} \psi_{v''} dx + \left(\frac{dM}{dx}\right)_e \int \psi^*_{v'} x \psi_{v''} dx + \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \rightarrow (13)$$

The first term in equation (13) is zero as M_e is constant and simple harmonic oscillator wave functions are orthogonal.

The second term is non–zero iff v' and v'' differ by one. This constitutes the vibrational selection rule.

Selection Rule:

The vibrational transition can only occur when the molecule has a permanent dipole moment and $\boxed{\Delta v = \pm 1}$

which gives $v' = v'' + 1$

We know, the spacing between the vibrational levels is considerably larger than the spacing between the rotational levels of a molecule.

Hence, most of the molecules in a sample exist in v = 0 state i.e., zero - point energy states (except in case of very heavy molecules which have smaller vibrational spacings)

Thus the main vibrational transition in absorption is $v''=O \rightarrow v'=1$.The spectral band corresponding to this transition is called "fundamental band". The absorbed wave number corresponding to this transition is

$$\nu = G(v') - G(v'')$$

$$= \overline{\omega}(v'+\frac{1}{2}) - \overline{\omega}(v''+\frac{1}{2})$$

$$= \frac{3}{2}\overline{\omega} - \frac{1}{2}\overline{\omega} \quad \text{(because, } v'=1, v''=0\text{)}$$

$$\boxed{\nu = \overline{\omega}}$$

Thus, the frequency of radiated light is equal to frequency ($\overline{\omega}$) of the oscillator. Since the spacing between the energy levels is *equal*, the vibrational spectrum is expected to consist of a single band at $\overline{\omega}$.

1.8 Molecule as Anharmonic Oscillator:

The vibrational absorption spectrum of a diatomic molecule is dominated by $\Delta v = \pm 1$ transitions called "fundamental transitions".

But sometimes $\Delta v = \pm 2 \pm 3.....$ transitions are also observed in the spectrum. These are called "overtones". Usually, it is observed that first overtone $(\Delta v = \pm 2)$ is stronger than the second overtone $(\Delta v = \pm 3)$ which in turn is more intense than third overtone $(\Delta v = \pm 4)$ and so on.

The observation of the overtone indicates that the selection rule $(\Delta v = \pm 1)$ is not strictly obeyed. This in turn is attributed to the fact that the dipole moment of the molecule is not strictly linear with respect to inter nuclear displacement. $(x = r - r_e)$. This is expressed as "electrical anharmonicity" of the molecule.

Also, for actual molecule, the potential energy curve is not strictly parabolic (except near minimum). That is, potential energy function V(r) is not harmonic and hence can be

expressed in Taylor's series expansion. This is expressed as "mechanical anharmonicity" of the molecule.

$$V(r) = V(o) + \frac{\partial V(r)}{\partial r} + \frac{1}{2!}\left(\frac{\partial^2 V(r)}{\partial r^2}\right)_{r=r_e}(r - r_e)^2 + \frac{1}{3!}\left(\frac{\partial^2 V(r)}{\partial r^2}\right)_{r=r_e}(r - r_e)^3$$

The energy at $x = o$, i.e., V (o) can be taken as zero. The first derivative term is also absent because the slope is zero at the minimum in V (r). Therefore

$$V(r) = \frac{1}{2!}\left(\frac{\partial^2 V(r)}{\partial r^2}\right)(r - r_e)^2 + \frac{1}{3!}\left(\frac{\partial^3 V(r)}{\partial r^3}\right)_{r=r_e}(r - r_e)^3$$

$$= f(r - r_e)^2 - g(r - r_e)^3$$

$$V(r) = fx^2 - gx^3$$

where, $f = \frac{k}{2}$; $g << f$. On substituting this value of V (r) in the Schrödinger equation and solving by perturbation method, it is found that the Eigen values of the anharmonic oscillator are given by

$$E(v) = hc\overline{\omega}_e(V + \frac{1}{2}) - hc\overline{\omega}_e x_e(v + \frac{1}{2})^2 + hc\overline{\omega}_e y_e(v + \frac{1}{2})^3 \text{.....(14)}$$

Where $\overline{\omega}_e$ is called the oscillating frequency. The anharmonic correction terms $\overline{\omega}_e x_e$ and $\overline{\omega}_e y_e$ are related to the coefficients *f* and *g*. Further $\overline{\omega}_e >> \overline{\omega}_e x_e >> \overline{\omega}_e y_e$

$\overline{\omega}_e y_e$ is generally negligible in comparison with $\overline{\omega}_e x_e$

Thus, equation (14) can be written as

$$E(v) = hc\overline{\omega}_e(v + \frac{1}{2}) - hc\overline{\omega}_e x_e(v + \frac{1}{2})^2 \text{.....(15)}$$

The vibrational tern G (v) is obtained by dividing equation (15) by *ch*

$$G(v) = \frac{E(v)}{hc}) = \overline{\omega}_e(v + \frac{1}{2}) - \overline{\omega}_e x_e(v + \frac{1}{2})^2 \text{.....(16)}$$

The quantity $\overline{\omega}_e$ is the wave number spacing of energy levels that would occur if the potential curve were a parabola. But the equation (16) shows that the energy levels of the anharmonic oscillator are not equidistant but their reparation decreases slowly with increasing values of 'v'.

1.9 Potential Energy Functions:

A potential energy curve is a graphical representation of the potential energy $V(r)$ versus bond length (or) the change in potential energy of the molecule as a function of the distortion of the bond of the molecule from its equilibrium distance.

One of the most popular approximations for $V(r)$ is due to P.M.Morse (fig 7). The Morse function is an empirical potential that has the general appearance of anharmonic potential for a real molecule. It is given by

$$V(r) = D_e\left[1 - e^{-a(r-r_e)}\right]^2 \quad \text{.....(17)}$$

Where D_e = the dissociation energy and

a = constant for a given molecular electronic state

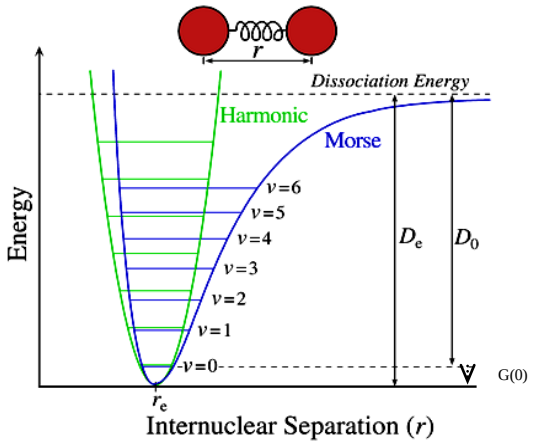


Fig (7)

The above function has the following features

(i) V(r) goes to zero at r = r_e

(ii) V(r) approaches D_e for larger ' r ' values

(iii) V(r) becomes very large as ***r*** tends to zero

When the molecule receives energy more than that corresponding to the uppermost vibrational level, it dissociates into atoms and excess energy appears as kinetic energy of these atoms. Hence a continuum joins the upper most level. The sign of x_e is usually positive, as a result of anharmonic correction, the vibrational energy levels become closer and closer as 'v' increases.

Also from harmonic oscillator approximation we had $G(v) = \overline{\omega}(v + \frac{1}{2})$

Comparing this with equation we have

$$\overline{\omega} = \overline{\omega}_e\left[1 - x_e(v + \frac{1}{2})\right] \quad \text{.....(18)}$$

Thus, anharmonic oscillator behaves like the harmonic oscillator but with frequency that decreases with increasing 'v'.

$\overline{\omega} = \overline{\omega}_e$, provided $v = -\frac{1}{2}$ (a hypothetical case)

Thus $\overline{\omega}_e$ is defined as the hypothetical equilibrium oscillation frequency of the anharmonic oscillator. The zero point energy is obtained by substituting $v = o$ in equation (16)

$$G(o) = \frac{\overline{\omega}_e}{2} - \frac{\overline{\omega}_e x_e}{4} \quad \text{.....(19)}$$

Which differs slightly from the one obtained for harmonic oscillator.

1.10 Wave number for the transition between vibrational levels:

The wave number for the transition between vibrational levels (neglecting y_e term) v' and v'' (where v' is the upper level and v'' is the lower level) is given by

$$\overline{\nu} = G(v') - G(v'')$$

We know from equation (16)

$$G(v) = (v + \frac{1}{2})\overline{\omega}_e - (v + \frac{1}{2})^2 \overline{\omega}_e x_e$$

$$\therefore \overline{\nu} = \left[\left(v' + \frac{1}{2} \right) \overline{\omega}_e - \left(v' + \frac{1}{2} \right)^2 \overline{\omega}_e x_e \right] - \left[(v'' + \frac{1}{2})\overline{\omega}_e - (v'' + \frac{1}{2})^2 \overline{\omega}_e x_e \right]$$

Simplifying we get

$$\overline{\nu} = (v' - v'')\overline{\omega}_e - \left[v'(v'+1) - v''(v''+1) \right] \overline{\omega}_e x_e \quad \text{.....(20)}$$

This gives the wave number for the transition between any two vibration levels.

Selection rules for anharmonic oscillator:

The selection rules for anharmonic oscillator are $\Delta v = \pm 1, \pm 2, \pm 3, ...$

1.11 Expressions for Fundamental band and overtones:

At normal temperature, before absorption of energy, majority of the molecules are in $v''=0$ state. Thus for $v''=0$ and $v'=1,2,3,.....$ we have

a) ***fundamental band***:-

Put $v''=o, v'=1$ in equation (20) and simplify

$$\bar{v}_{o\to 1}=(1-2x_e)\bar{\omega}_e$$

b) *First overtone*:-

Put $v''=o, v'=2$ in equation (20) and simplify

$$\bar{v}_{o\to 2}=(1-3x_e)2\bar{\omega}_e$$

c) *Second overtone*:-

Put $v''=o, v'=3$ in equation (20) and simplify

$$\bar{v}_{o\to 3}=3(1-4x_e)\bar{\omega}_e$$

If the wave numbers for two transitions are known, then x_e, $\bar{\omega}_e$ and $\bar{\omega}_e x_e$ can be determined.

At about absolute zero, molecules have no rotational energy but are merely vibrating with zero point energy. Now the energy required to separate the stable molecule initially in the v=0 level into unexcited atoms is known as 'dissociation energy'(D_o).

The term values relative to G (o) can be given from equation (16) i.e.,

$$G_o(v)=G(v)-G(o)$$

$$=(\bar{\omega}_e-\bar{\omega}_e x_e)v-(\bar{\omega}_e x_e)v^2$$

$$G_o(v)=\bar{\omega}_o v-\bar{\omega}_o x_o v^2 \quad \text{.....(21)}$$

where

$$\left.\begin{aligned}\bar{\omega}_o&=\bar{\omega}_e-\bar{\omega}_e x_e\\ \bar{\omega}_o x_o&=\bar{\omega}_e x_e\end{aligned}\right\} \quad \text{..... ..... (21 a)}$$

The separation between successive terms (or) first difference is

$$\Delta G(v+\frac{1}{2})=G_o(v+1)-G_o(v)$$

$$=\bar{\omega}_o-\bar{\omega}_o x_o-2\bar{\omega}_o x_o v,$$

$$\Delta G(v+\frac{1}{2})=\bar{\omega}_e-2\bar{\omega}_e x_e-2\bar{\omega}_e x_e v \quad \text{.....(22)}$$

The second difference is

$$\Delta^2 G_{v+1} = \Delta G(v+\frac{3}{2}) - \Delta G(v+\frac{1}{2})$$
$$= [G_o(v+2) - G_o(v+1)] - [G_o(v+1) - G_o(v)]$$
$$= -2\overline{\omega}_o x_o$$
$$\boxed{\Delta^2 G_{v+1} = -2\overline{\omega}_e x_e} \quad \text{.....(23)}$$

Now,

The dissociation energy D_0 is given by

$$D_o = [G_o(1) - G_o(o)] + [G_o(2) - G_o(1)] + ...$$

From figure (3)

$$D_e = D_o + G(o)$$
$$\boxed{D_e = D_o + \frac{\overline{\omega}_e}{2} - \frac{\overline{\omega}_e x_e}{4}}$$

When the anharmonic oscillator receives more energy than D_e, the molecule dissociates. Also above D_e there is no discrete vibrational level.

Thus D_e must be the maximum value of G (v)

i.e., $\boxed{D_e = G(v)}$ .....(24)

<u>To find the maximum value of V (=Vm):-</u>

The maximum value of v can be obtained by differentiating equation (16) with respect to v and equating it to zero. i.e.,

$$\frac{d[G(v)]_{v=v_m}}{dv} = o$$
$$\frac{d}{dv}\left[\overline{\omega}_e(v_m+\frac{1}{2}) - \overline{\omega}_e x_e(v_m+\frac{1}{2})^2\right] = o$$
$$\overline{\omega}_e - 2\overline{\omega}_e x_e(v_m+\frac{1}{2}) = o$$
$$\boxed{v_m = \frac{1}{2x_e} - \frac{1}{2}} \quad \text{.....(25)}$$

***<u>To find 'De'</u>*:-**

Substituting the value of V_m from equation (25) in equation (16) we get

$$G(v)_{\max} = \frac{\overline{\omega}_e}{4x_e}$$

From equation (21)

$$\boxed{D_e = G(v) = \frac{\overline{\omega}_e}{4x_e}} \quad \text{.....(26)}$$

III. "Vibrational – Rotational Spectra"

This spectrum arises due to the transition between rotational states of one vibrational level and rotational states of another vibrational level. Also the spectrum is observed in infrared region.

The near infra-red spectra of molecules consist of "bands", each band being composed of close lines arranged in a particular manner. In the series of lines which are not equidistant, a line is missing at the centre of the band. This missing line is known as null line" or 'zero-gap'. Further, the lines show a poor tendency of convergence towards the high wave number side and the band is said to be degraded towards the low-wave number side.

1.12 Molecule as Vibrating Rotator:

Let us consider the case in which diatomic molecule is simultaneously executing both vibrational and rotational motion. If we neglect the interaction between vibration and rotation, the total term value T is given by the sum of rotational term values F (J) and vibrational term values G (v) that is

$$T = G(v) + F(J) = \overline{\omega}_e(v + \frac{1}{2}) - \overline{\omega}_e x_e(v + \frac{1}{2})^2 + BJ(J+1) \text{.....(27)}$$

(Neglecting the centrifugal distortion 'D')

From the shape of the potential curve $[Fig(7)]$ we can find that as 'v' increases, the equilibrium internuclear separation r_e and hence the moment of inertia of the molecule increases so that the rotational constant B decreases.

Thus, B, which determines the spacings between the rotational levels, is different for different vibrational states. Therefore, the rotational constant associated with a vibrational state 'v' is written as B_v and not simply B.

Also, in a given vibrational state, the internuclear distance and hence the rotational constant changes during the vibration. Therefore, we must use a mean value for the rotational constant in a given vibrational state, namely.

$$B_r = \frac{h}{8\pi^2 \mu c}\left\langle \frac{1}{r^2} \right\rangle$$

Where, $\left\langle \frac{1}{r^2} \right\rangle$ is the mean value of $\frac{1}{r^2}$ in the vibrational state v during the vibration.

Quantum mechanical calculation shows that

$$B_v = B_e - \alpha_e (v + \frac{1}{2})$$

Where α_e is a constant depending upon the shape of the potential curve ($\alpha_e << B_e$) and B_e is the rotational constant corresponding to the separation r_e at the minimum of the potential curve.

Thus, the term values of a vibrating rotator in the presence of interaction between rotational and vibrational motion of the molecule can be written as

$$T = G(v) + F(V, J) = \overline{\omega}_e (V + \frac{1}{2}) - \overline{\omega}_e x_e (v + \frac{1}{2})^2 + B_v J(J+1) \text{.....(28)}$$

The value of B_v decreases slightly with increasing value of 'v'. The spacing between the rotational levels associated with v=1 are, for example slightly smaller than those between the levels associated with v=0 (as in fig 8)

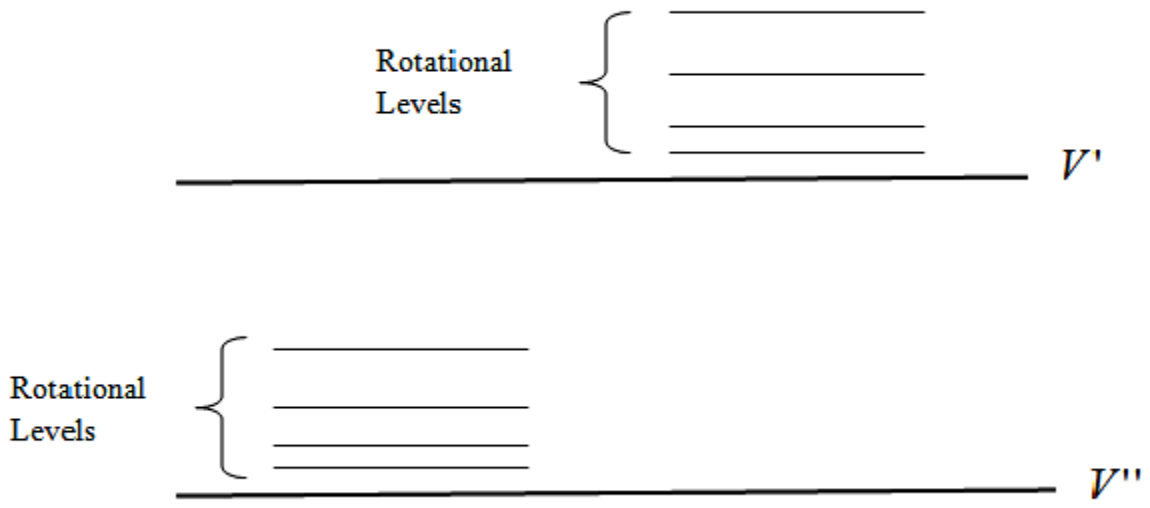


Fig (8)

The selection rules for the vibrating rotator are the same as for those systems individually, that is

$$\Delta v = \pm 1, \pm 2, ...$$
$$\Delta J = \pm 1$$

For the main absorption, we have $\Delta v = +1$ and the most probable transition is

$v'' = o \rightarrow v' = 1$

As for J, both the transitions $(\Delta J = \pm 1)$ are possible in absorption, because the two ***J*** levels involved now belong to different vibrational states.

For a given vibrational transition, the rotational transitions $\Delta J = +1$ give one set of lines called 'R – branch'.

While the rotational transitions $\Delta J = -1$ give the other set of lines called the 'P – branch'. All there lines together form a vibration – rotation band.

The wave- numbers of the branch – lines of a particular band v' and v'' are given by

$$\bar{\nu} = \left[G(v') + F(v', J')\right] - \left[G(v'') + F(v'', J'')\right]$$
$$= G(v') - G(v'') + B_v' J'(J'+1) - B_v'' J''(J''+1)$$
$$\bar{\nu} = \bar{\nu}_o + B_v' J'(J'+1) - B_v'' J''(J''+1) \quad \text{.....(29)}$$

Where $\bar{\nu}_o = G(v') - G(v'')$, is the wave number of the pure vibrational transition (for which $J' = J'' = O$) which is not allowed ($\Delta J \neq O$) and corresponds to missing line in the band. $\bar{\nu}_o$ Is known as the wave number of the "band –origin''

R – branch: $(\Delta J = +1)$

Here ($J' = J''+1$)

Substituting this in equation (29) and simplifying we get

$$\bar{\nu}_R = \bar{\nu}_o + 2B_v^{'} + (3B_v^{'} - B_v^{''})J'' + (B_v^{'} - B_v^{''})J^{''2} \quad \text{.....(30)}$$

Where J'', the lower rotational quantum number can take the values 0, 1, 2, …….

If we neglect vibration – rotation interaction, then ,

$B_v^{'} = B_v^{''} = B$, so that

$$\bar{\nu}_R = \bar{\nu}_o + 2B + 2BJ^{''}$$

$$\boxed{\bar{\nu}_R = \bar{\nu}_o + 2B(J^{''} + 1)} \quad \text{.....(31)}$$

Where J''= 0, 1, 2……

P- branch $(\Delta J = -1)$

Here $(J' = J''-1)$

Substituting this in equation (29) and simplifying we get

$$\bar{\nu}_p = \bar{\nu}_o - (B_v^{'} + B_v^{''})J^{''} + (B_v^{'} - B_v^{''})J^{''2} \quad \text{.....(32)}$$

If we neglect vibration – rotation interaction, then

$B_v^{'} = B_v^{''} = B$, so that

$$\boxed{\bar{\nu}_p = \bar{\nu}_o + 2BJ^{''}} \quad \text{.....(33)}$$

Where J''= 0,1,2,.....

The equations (30) and (32) can be combined in a single expression

$$\boxed{\bar{\nu} = \bar{\nu}_o + (B_v^{'} + B_v^{''})m + (B_v^{'} - B_v^{''})m^2} \quad \text{.....(34)}$$

Where,

m= J''+1 = 1, 2, 3 …… for lines R(0), R(1), R(2)……..

m= - J'' = -1, -2, -3…… for lines P(0), P(1), P(2)……..

and m = 0 corresponds to the zero gap.

Further, for vibration – rotation bands, both the involved vibrational levels belong to the same electronic state. Hence, the rotational constant for upper vibrational state $B_v^{'}$, is always smaller than that for the lower vibrational state $B_v^{''}(\text{since } r_v^{'} > r_v^{''})$

In other words ($B_v^{'} - B_v^{''}$) is always negative. Hence, as the above equation (34) shows, the line – spacing decreases as 'm' takes on increasing positive values.

This means, *the tendency of head formation* is always seen in the R –branch. Conversely, the *degradation* of band is always observed in the P- branch

This may be expressed as *''rotation – vibration brands are always degraded towards the lower wave – number side, that is, toward the red''.*

1.13 Let Us Sum up:

- While studying Rotational spectra, the Rigid Rotator Model is discussed in detail wherein we derived the expressions for energy of the rigid rotator, rotational constant
- Vibrational spectra is explained considering the simple harmonic oscillator potential
- Vibrational –rotational spectra is discussed in detail.

1.14 Solved problems:

1) The moment of inertia of the CO molecule is $1.45X10^{-46}$ kg-m^2 .Calculate the energy and the angular velocity in the lowest rotational energy level of the CO molecule ($h = 6.63X10^{-34} Js$)

.

Solution: The energy of a rotating diatomic molecule is given by

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

For the lowest rotational energy level J= 1

$$\therefore E = \frac{h^2}{4\pi^2 I}$$

$$E = \frac{(6.63\text{X}10^{-34})^2}{4\text{X}(3.14)^2\,\text{X}(1.45\text{X}10^{-46})}$$

$$E = 7.686\text{X}10^{-23}\,J$$

The angular velocity is

$$\omega = \sqrt{\frac{2E}{I}} = \sqrt{\frac{2\text{X}7.686\text{X}10^{-23}}{1.45\text{X}10^{-46}}} = 1.03X10^{12}s^{-1}$$

2) The J= $0 \rightarrow 1$ transition in HCl occurs at $20.68\,cm^{-1}$. Considering molecule to be a rigid rotator, calculate the wavelength of the transition $J = 14 \rightarrow 15$.

Solution: The wave number of the radiation absorbed in a rotational transition from J to J + 1 is

$$\bar{\nu} = 2B(J+1)$$

Where J refers to lower state

For the transition $J = 0 \rightarrow$ we have

$$\bar{\nu} = 2B, = 20.68$$

$$\therefore B = 10.34cm^{-1}$$

Now for the transition $J = 14 \rightarrow 15$

$$\bar{\nu} = 2B(J+1)$$

$$\bar{\nu} = 2B(14+1)$$

$$\bar{\nu} = 20.68\text{X}15$$

$$\bar{\nu} = 310.2cm^{-1}$$

The corresponding wavelength is

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{310.2} = 32\text{X}10^{-4}cm$$

(or)

$$\lambda = 32\mu m$$

3) The force constant of the bond in CO molecule is $1870\,Nm^{-1}$. Find the energy of the lowest vibrational level. The reduced mass of CO molecule is $1.14X10^{-26}$ kg.

(given $h = 6.63\text{X}10^{-34} Js, 1eV = 1.6\text{X}10^{-19} J$)

Solution: The frequency of vibration is

$$v_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\text{X}3.14}\sqrt{\frac{1870}{1.14\text{X}10^{26}}}$$

$$v_{osc} = 6.45\text{X}10^{13} s^{-1}$$

The vibrational energy of a diatomic molecule is

$$E_{v} = hv_{osc}(v + \frac{1}{2})$$

For lowest level $v = o$

$$\therefore E = \frac{1}{2}hv_{osc} = \frac{1}{2}(6.63\text{X}10^{-34})(6.45\text{X}10^{13})$$

$$E = 21.4\text{X}10^{-21} J$$

1.15 Questions for self study:

1) Obtain an expression for the rotational energy levels of a diatomic molecule.

2) Write down the expression for the energy of a rigid rotator model of a diatomic molecule and predict the pure rotational spectrum of the molecule

3) Discuss and explain briefly the principal features of the pure rotational band spectrum of a diatomic molecule. Show in a diagram the allowed rotational energy levels in terms of rotational constant.

4) Find the vibrational energy of a diatomic molecule when the potential energy is given by $V(r) = \frac{1}{2}k(r - r_e)^2$, where k is constant.

5) Explain how the study of vibrational spectrum of a diatomic molecule enables us to determine anharmonicity constant and equilibrium frequency of vibration.

6) What are P and R- branches in the vibration – rotation spectra? Explain their origin.

1.16 References:-

1. Introduction to Atomic and molecular spectroscopy by Vimal Kumar Jain.
2. Atomic and Molecular Spectra: Laser by Raj Kumar.

UNIT 2: Electronic spectra: Born-Oppenheimer approximation, (i) vibrational structure of electronic transition, progressions and sequences of vibrational bands,

Structure:

2.0 Objective:

- To understand Born-Oppenheimer approximation
- To analyse vibrational structure of electronic transitions

2.1 Introduction:

The Born-Oppenheimer Approximation is the assumption that the electronic motion and the nuclear motion in molecules can be separated.

The forces on both electrons and nuclei due to their electric charge are same in magnitude, and so the changes which occur in their momenta as a result of these forces must also be the same. One might, therefore, assume that the actual momenta of the electrons and nuclei were of similar magnitude. In this case, since the nuclei are so much more massive than the electrons, they must accordingly have much smaller velocities. Thus it is plausible that on the typical time-scale of the nuclear motion, the electrons will very rapidly relax to the ground-state configuration, so that in solving the time-independent Schrödinger equation, we can **assume *that the nuclei are stationary and hence, first solve the electronic ground-state, and calculate the energy of the system in that configuration and finally, solve for the nuclear motion*.** This separation of electronic and nuclear motion is known as the Born-Oppenheimer approximation.

Further in this unit, we study the classification of Electronic states which helps in the study of vibrational structure of Electronic transitions.

2.2 Born- Oppenheimer Approximation:

An isolated molecule in space consists of electrons, nuclei which are all in motion. Nuclei will be in vibrational motion with respect to each other and the molecule as a whole will have rotational and translational motion. Apart from this, electrons will have the energy corresponding to their electronic states. When we look at the molecule as a whole, there might be influence of motion of nucleus on the motion of electrons. Thus, when one writes the Hamiltonian of the atom, he should consider the contribution of all kinds of motion/energy associated with the molecule.

The total Hamiltonian for the molecule is given by

$$H = T_N + T_e + V_{ee}(r) + V_{NN}(R) + V_{eN}(r, R) \quad \text{.....(1)}$$

Where,

T_N = kinetic energy operator of all the nuclei

T_e = kinetic energy operator of all the electrons

$V_{ee}(r)$ =potential energy operator for electron-electron interaction

$V_{NN}(R)$ = potential energy operator for nuclear-nuclear interaction

$V_{eN}(r,R)$ = potential energy operator for electron-nuclear interaction

r = electronic coordinate; and

R= internuclear distance.

If we could solve for the eigenvalues and eigenfunctions of this Hamiltonian, we could predict any property we wished of a given system. But the problem cannot be solved exactly. So, approximation methods are used to solve the problem to the best possible level.

The eigenvalues and eigenfunctions of this Hamiltonian will be given by solution of the time-independent Schrodinger equation i.e.,

$$H\psi(r,R) = E\psi(r,R) \quad \text{.....(2)}$$

$\psi(r,R)$ is an eigenfunction of H with eigenvalue E.

Clearly, an exact solution of equation (2) is not possible and approximations must be made. Born-Oppenheimer approximation is one such approximation.

According to this approximation, the total wavefunction of the molecule can be split into two wavefunctions, one corresponding to electronic and other to the nuclear part. i.e., we can write

$$\psi(r,R) = \phi(r,R)\chi(R) \quad \text{.....(3)}$$

where $\chi(R)$ is the nuclear wavefunction,

$\phi(r,R)$ is the electronic wavefunction.

This approximation is based on the fact that "*nuclei are several thousand times heavier than electrons.*" In a dynamical sense, the electrons can be regarded as particles that follow the nuclear motion adiabatically, meaning that they are 'dragged' along with the nuclei without requiring a finite relaxation time. This, of course, is an approximation.

Another consequence of the mass difference between electrons and nuclei is that 'the nuclear components of the wavefunction are spatially more localized than electronic component of the wavefunction.' Hence it can be assumed that the nuclei occupy nearly fixed position in the atom.

Substituting equation (3) in equation (2) and using the approximation that nuclear wavefunction $\chi(R)$ is more localized than the electronic wavefunction $\phi(r,R)$ yields,

$$\frac{[T_e + V_{ee}(r) + V_{eN}(r,R)]}{\phi(r,R)}\phi(r,R) = E - \frac{T_N + V_{NN}(R)}{\chi(R)}\chi(R) \quad \text{.....(4)}$$

From this equation (4), it is clear that the left side can only be a function of **R** alone. Let this function be denoted by $\varepsilon(R)$. Thus,

$$\frac{[T_e + V_{ee}(r) + V_{eN}(r,R)]}{\phi(r,R)}\phi(r,R) = \varepsilon(R) \quad \text{.....(5)}$$

$$[T_e + V_{ee}(r) + V_{eN}(r,R)]\,\phi(r,R) = \varepsilon(R)\,\phi(r,R) \quad \text{.....(6)}$$

Equation (6) is an electronic eigenvalue equation for an electronic Hamiltonian

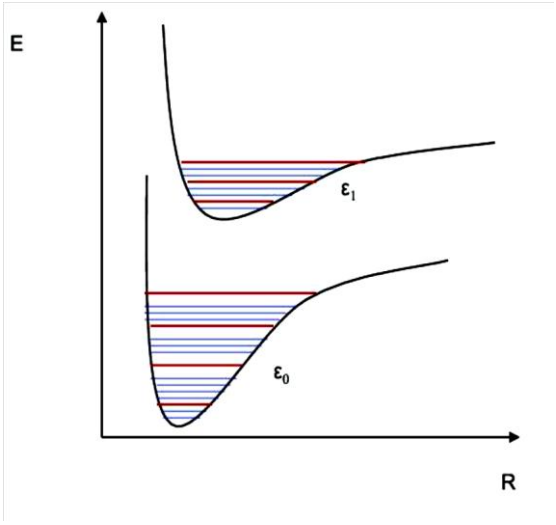
$$H_e(R) = [T_e + V_{ee}(r) + V_{eN}(r,R)] \quad \text{.....(7)}$$

which will yield a set of normalized eigenfunctions $\phi_n(r,R)$ and eigenvalues $\varepsilon_n(R)$, which depend on the nuclear positions ,R. For each solution, there will be a nuclear eigenvalue equation

$$[T_N + V_{NN}(R) + \varepsilon_n(R)]\,\chi(R) = \text{E}\,\chi(R) \quad \text{.....(8)}$$

Each eigenvalue, $\varepsilon_n(R)$, will give rise to an electronic surface, and these surfaces are known as Born-Oppenheimer surfaces.

Thus, the full internuclear potential for each electronic surface is given by $V_{NN}(R) + \varepsilon_n(R)$. On each Born-Oppenheimer surface, the nuclear eigenvalue problem can be solved, which yields a set of levels (rotational and vibrational in the nuclear motion), which is illustrated in the figure below



The Born-Oppenheimer surfaces on which the nuclear dynamics is described by a time-dependent Schrödinger equation for the time-dependent nuclear wavefunction X(R, t)

$$[T_N + V_{NN}(R) + \varepsilon_n(R)]\ X(R, t) = i\hbar \frac{\partial}{\partial t} X(R,t) \quad \text{……………………………………….(9)}$$

will evolve.

The physical interpretation of equation (9) is that the electrons respond instantaneously to the nuclear motion. Therefore, it is sufficient to obtain a set of instantaneous electronic eigenvalues and eigenfunctions at each nuclear configuration, R. [hence the parameter dependence of $\phi_n(r, R)$ and $\varepsilon_n(R)$ on R]

The eigenvalues in turn give a family of (uncoupled) potential surfaces on which the nuclear wavefunction evolves.

Thus, the total wavefunction can be written as

$$\psi(r, R) = \phi(r, R)\chi(R)$$

using Born-Oppenheimer approximation. This implies, the total energy E is

$$E = E_E + E_N \quad \text{…………………………………………………………….……….(10)}$$

Also, in a first approximation,

$$\chi(R) = \chi_v \chi_r \quad \text{…………………………………………………………………..…….(11)}$$

Where, χ_v = vibrational wavefunction,

χ_r = rotational wavefunction.

Hence the total energy E of the molecule apart from the translational energy may be given by,

$$E = E_e + E_v + E_r \quad \text{……………………………………………………………………..…………..(12)}$$

Where E_e is the energy of stable electronic state corresponding to minimum value of V.

The total energy in terms of wave numbers is

$$T = \frac{E}{hc} = \frac{E_e}{hc} + \frac{E_v}{hc} + \frac{E_r}{hc} = T_e + G(v) + F(J) \quad \text{……………………………………(13)}$$

The electrons move faster than the nuclei; thus the nuclei feel the potential energy of the averaged electronic distribution. This forms the basis of Born-Oppenheimer approximation.

However, the approximation can breakdown if electronic energy spacings are not large compared to vibrational spacings.

This breakdown results in a situation where,

(i) Time scales of nuclear and electronic motions are not separable

(ii) It is not possible to separate nuclear and electronic energies.

2.3 Classification of Electronic States:

In all the diatomic molecules, the electrons experience a strong electrostatic field of nuclei and move under the influence of the electric field which is cylindrically symmetric about the bond axis. The orbital angular momentum **L** precesses very rapidly about the direction of electrostatic field. But, the axial component of **L** is a constant of motion (fig 1). The axial component is characterized by the magnetic quantum number $\mathbf{M}_{L,}$ where M_L can take values from $-$ L to + L. that is., $\mathbf{M}_{L=}$ L, L-1, ……-L. Since internuclear field is also electrical in nature, the energy is not exchanged by the interchange of $M_L \leftrightarrow -M_L$. We denote the absolute value of $\mathbf{M}_L$ by the symbol Λ where

$\Lambda = |M_L| = 0, 1, 2\ldots\ldots\ldots\ldots$ L ……(14)

The symbols for different states are written as follows:

Λ	0	1	2	3	4…….
Symbol of state	Σ	Π	Δ	Φ	Γ, ……..

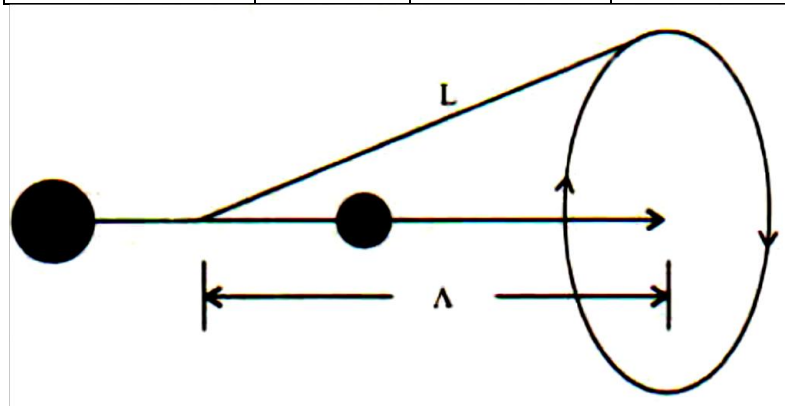


Fig (1) Vector diagram showing the coupling of L about the electric field along the internuclear axis.

We know that all states are ***doubly degenerate*** except $\sum$ state because of $M_L \leftrightarrow -M_L$ symmetry. (i.e., ± 1, ± 2, ± 3 etc.) The individual electronic spins add up vectorially to produce spin quantum number (S). It may be integral or half integral. This depends on whether there are even or odd number of electrons (remember electrons are Fermions i.e., they are spin half particles). If **S** is the total spin, then multiplicity is given by 2S+1. This multiplicity is designated by a superscript.

Thus, the term symbol for a state is written as $^{2S+1}\Lambda$. For $\Lambda > 0$, the orbital motion of the electrons produces a magnetic field along the bond axis and **S** precesses about the magnetic field direction (as shown in Fig 2). If M_S denote the quantized components of **S,** about the magnetic field direction, then their eigenvalues are given by $\hbar M_S$. Also, the quantum number M_S can take values S, S-1, S-2, ……-S = 2S+1 values (it is also represented by the symbol $\sum$).* For the electronic state $\sum$ (Λ =0), there is no resultant magnetic field and therefore, M_S is not defined. This state has only one component, whatever the multiplicity is. Spin-orbit coupling can lift the degeneracy of $^{2S+1}\Lambda$ state. In diatomic molecules, if the coupling between **L** and **S** is weak, we use the symbol Ω to designate the z – component of total angular momentum (spin plus orbital). The quantum number Ω is usually written as a subscript to the term symbol. So, the revised term symbol is $^{2S+1}\Lambda_\Omega$ with $\Omega = \Lambda + S, \Lambda + S-1 \ldots \Lambda - S$.

(*readers not to get confused with $\sum$ =0 state which was used earlier)

If we consider the Δ state (which is a triplet state) as an example, it is split by spin – orbit coupling into three doubly degenerate levels.

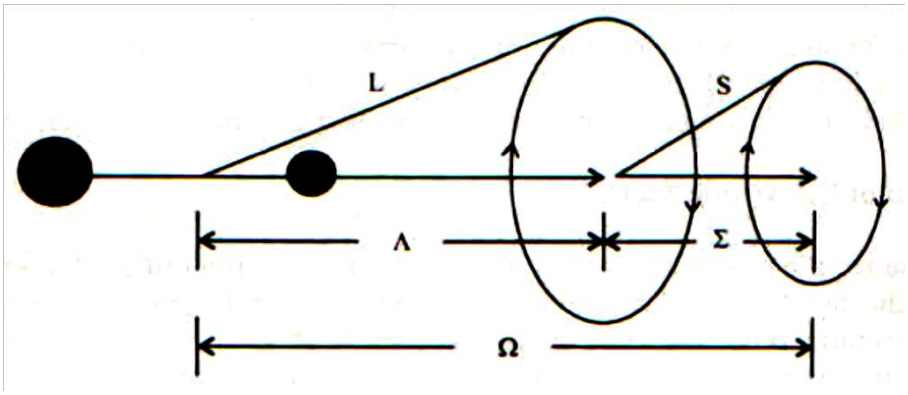


Fig (2) Vector addition of $\Lambda + \sum$ producing the total electronic angular momentum Ω

While classifying the molecular electronic states, symmetry properties of electronic functions must be considered besides quantum numbers $\sum, \Lambda$ and Ω. We define a reflection operator σ which when operated on a wavefunction twice in succession on electronic wavefunction gives back the original wavefunction, i.e.,

$$\sigma^2 \psi_e = (+1)\psi_e \quad \text{..... (15)}$$

Thus, the eigenvalue of σ^2 is 1. So, the two eigenvalues of σ operator are +1 and -1. If $\psi_e{}^+$ and $\psi_e{}^-$ represent the eigenfunction of σ with eigenvalues +1 and -1, respectively, then,

$$\sigma\psi_e{}^+ = (+1)\psi_e{}^+ \quad \text{.....(16)}$$

$$\sigma\psi_e{}^- = (-1)\psi_e{}^- \quad \text{..... (17)}$$

The function $\psi_e{}^+$ remains unchanged, whereas $\psi_e{}^-$ changes sign under reflection operation. This means, the even wavefunctions remain unchanged whereas the odd wavefunctions change their sign when σ operator acts on them. The electronic states which are doubly degenerate ($\Lambda > 0$), may be distinguished as + or -, for example, Δ^+, Δ^- etc. The electronic state $\sum$ is not degenerate but can still be classified as $\sum^+$ or $\sum^-$. Homonuclear diatomic molecules have inversion symmetry through the midpoint of the bond i.e., by considering midpoint as the origin of the cartesian coordinate system and by operating the inversion operator $(x_i, y_i, z_i) \rightarrow (-x_i, -y_i, -z_i)$ twice on the electronic wavefunction we get the same electronic wavefunction. Thus,

$$i^2 \psi_e = (+1)\psi_e \quad \text{..... (18)}$$

Thus, the eigenvalues of the inversion operator ***i*** are +1 and -1. The wavefunction either remains unchanged or changes sign under inversion.

If the wavefunction remains unchanged when operated by the inversion operator, it is called '***even or gerade (g)'***. On the other hand if wavefunction changes its sign upon inversion, it is called '***odd or ungerade (u)'***. The symbols ***g*** and ***u*** are written as subscripts to the term values. For example Δ_g, Δ_u etc.

While considering diatomic molecules we are concerned with cases in which S, $\sum, \Lambda$ and Ω adequately represent the quantized electronic angular momentum. In an isolated molecule, however, the total angular momentum is due to vectorial coupling of nuclear angular momentum **I**, electronic spin angular momentum **S** and electronic orbital angular momentum **L**. There are two very important cases of coupling that occurs generally. They are described as Hund's cases (a) and (b).

Hund's case (a):

In this case, we assume the interaction between nuclear rotation and electronic angular momentum to be weak. The spin orbit coupling is also considered to be weak. So, **L** and **S** precess independently about the bond axis in such diatomic molecules. The projections of **L** and **S**, i.e., Λ and $\sum$, respectively, add together to give Ω along the bond direction (fig 3).

In this case,

$$\mathbf{J=R+}\Omega \text{ ……..……... (19)}$$

With a quantum number $J= R+\Omega$

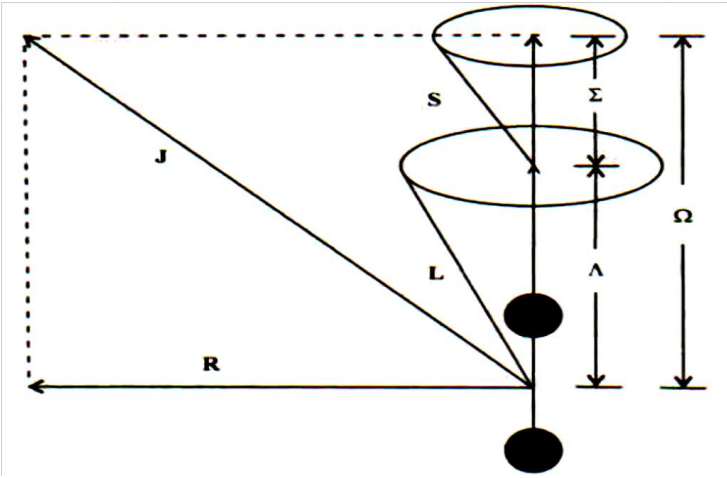


Fig (3) Schematic diagram for angular momentum coupling in Hund's case (a)

Hund's case (b):

In this case, the coupling between **S** and Λ is assumed to be very weak. **S** couples to the nuclear rotational axis. Here magnetic field is weak and **S** does not precess about the

bond axis, but remains fixed in space. Λ is added vectorially to **I** giving a resultant angular momentum **N**, which is given by,

N=R+ Λ **……..……** (20)

And then **N** combines with **S** to give total angular momentum **J**, (as in fig 4), that is

J=N+S…… (21)

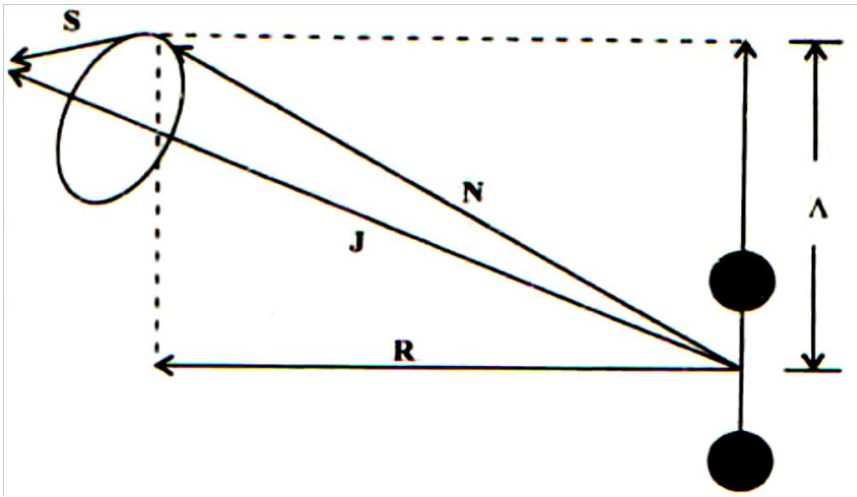


Fig (4) Schematic diagram for angular momentum coupling in Hund's case (b)

2.4 Vibrational Structure of Electronic Transitions:

The total energy E and term value T of the molecule are given by equations (12) and (13) respectively.

For a transition from the upper electronic state E' to lower electronic state E'', the wave number of spectral line is given by

$$\bar{\nu} = T' - T'' = (T_e' - T_e'') + [G'(v) - G''(v)] + [F'(J) - F''(J)] \quad \text{(22)}$$

The vibrational and rotational constants for the upper and lower states are different as they are associated with different electronic levels.

Substituting,

$\bar{\nu}_e = T_e' - T_e''$; $\bar{\nu}_v = G'(v) - G''(v)$ and $\bar{\nu}_r = F'(J) - F''(J)$

in equation (22) , we get

$$\bar{\nu} = \bar{\nu}_e + \bar{\nu}_v + \bar{\nu}_r \quad \text{(23)}$$

For a given electronic transition, $\bar{\nu}_e$ is a constant, as it corresponds to the energy difference (in terms of wavenumbers) between the upper and lower electronic states. Let us consider the case where the rotational structure is ignored. i.e., $\bar{\nu}_r$ =0. Then equation (23) becomes,

$$\bar{\nu} = \bar{\nu}_e + \bar{\nu}_v = \bar{\nu}_e + G'(v) - G''(v) \quad \text{..... (24)}$$

$$\bar{\nu} = \bar{\nu}_e + \left[\left(v'+\frac{1}{2}\right)\bar{\omega}_e' - \left(v'+\frac{1}{2}\right)^2 \bar{\omega}_e' x_e'\right] - \left[(v''+\frac{1}{2})\bar{\omega}_e'' - (v''+\frac{1}{2})^2 \bar{\omega}_e'' x_e''\right] \quad \text{..... (25)}$$

Since $\bar{\nu}_r$ =0, the spectral location corresponds to $J = 0 \rightarrow J = 0$ rotational transitions. Also, for an electronic transition, there is no restriction on the change in the vibrational quantum number $\bar{\nu}_o$. i.e.,

$$\boxed{\Delta v = unrestricted}$$

For $v = 0 \rightarrow v = 0$ transition, equation (25) becomes,

$$\bar{\nu}_{00} = \bar{\nu}_e + G'(0) - G''(0)$$

$$\bar{\nu}_{00} = \bar{\nu}_e + \left(\frac{\bar{\omega}_e'}{2} - \frac{\bar{\omega}_e' x_e'}{4}\right) - \left(\frac{\bar{\omega}_e''}{2} - \frac{\bar{\omega}_e'' x_e''}{4}\right) \quad \text{..... (26)}$$

$\bar{\nu}_{00}$ is the wavenumber of (v', v''), that is , (0,0) band which is often one of the most intense band in the system. Generally for any transition $v' \rightarrow v''$, we have,

$$\bar{\nu} = \bar{\nu}_e + \left(\frac{\bar{\omega}_e'}{2} - \frac{\bar{\omega}_e' x_e'}{4}\right) - \left(\frac{\bar{\omega}_e''}{2} - \frac{\bar{\omega}_e'' x_e''}{4}\right) + \left[\left(\bar{\omega}_e' - \bar{\omega}_e' x_e'\right)v' - \left(\bar{\omega}_e' x_e'\right)v'^2\right]$$
$$+ \left[\left(\bar{\omega}_e'' - \bar{\omega}_e'' x_e''\right)v'' - \left(\bar{\omega}_e'' x_e''\right)v''^2\right] \quad \text{.....(27)}$$

But,

$$** \ \bar{\omega}_0 = \bar{\omega}_e - \bar{\omega}_e x_e; \quad \bar{\omega}_0 x_0 = \bar{\omega}_e x_e \quad \text{.....(28)}$$

Substituting equations (26) and (28) in equation (27), we can write the vibrational levels measured relative to the $v = 0$ level in each state as:

$$\bar{\nu} = \bar{\nu}_{00} + [\bar{\omega}_0' v' - \bar{\omega}_0' x_0' v'^2] - [\bar{\omega}_0'' v'' - \bar{\omega}_0'' x_0'' v''^2]$$

(** from equation (21a) of previous chapter)

$$\bar{\nu} = \bar{\nu}_{00} + G_0'(v') - G_0''(v'') \quad \text{..... (29)}$$

where,

$G_0'(v') = [\bar{\omega}_0' v' - \bar{\omega}_0' x_0' v'^2]$; and

$G_0''(v'') = [\bar{\omega}_0'' v'' - \bar{\omega}_0'' x_0'' v''^2]$

The figure (5) below shows a set of vibrational energy levels associated with two electronic states between which electronic transitions are allowed. If the vibrational transitions accompany an electronic transition, then such transitions are called 'vibronic transitions.' Further, the vibronic transitions may be divided into progressions and sequences.

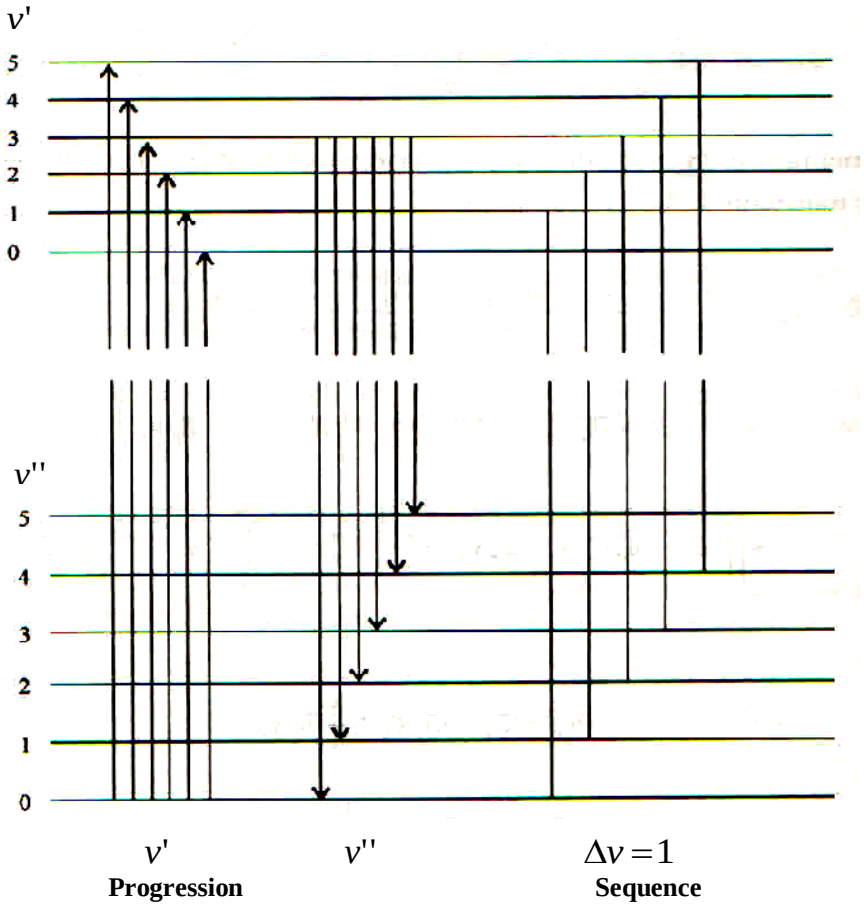


Fig (5) Vibrational Progression and Sequence in the Electronic spectrum of a diatomic molecule

Progression:

"A progression involves a series of vibronic transitions with a common lower or upper level".

For example, the v'' progression members all have $v'=3$ level common and $v'=0$ progression members all have $v''=0$ level common (v'= 0, 1, 2, ...) . Also, a v'' progression extends towards the lower wavenumber as v'' increases and terminates in a continuum where the lower electronic state dissociates whereas, a v' progression extends towards higher wavenumber as v' increases and terminates in a continuum where the upper electronic state dissociates.

Sequence:

A group of transitions with the same value of ' Δv 'is referred to as a ***sequence***.

Because of population requirements long sequences are observed mostly in emission.

We can see from the diagram that the progressions and sequences are not mutually exclusive. Each member of a sequence is also a member of two progressions. The members of the progression are generally widely spaced with approximate separation of $\overline{\omega}_e''$ in emission and $\overline{\omega}_e'$ in absorption.

Since $\overline{\omega}_e''$ and $\overline{\omega}_e'$ have slightly different values for the combining states, the members of the sequence are generally closely spaced with approximate separation equal to $\overline{\omega}_e'' - \overline{\omega}_e'$. The bands in each sequence are found to be grouped together and overlap each other partially in the spectrum.

2.5 Deslandres Table:

In order to analyze the components of vibrational electronic transitions, the wavenumber of each of the (v', v'') band heads (rather vibronic band origins) are arranged in what is known as 'Deslandres table'.

Here we consider a hypothetical $J=0 \rightarrow J=0$ transition between two states as the band origin. Also, here we neglect the rotational effects and consider only vibrational analysis. A band head measurement has to be used and a constant head-origin is assumed for all bands. These are arranged in such a way that the difference in the frequencies (or wavenumbers) in adjacent columns is approximately constant and varies uniformly. Similarly, the difference in the wavenumbers of adjacent rows is approximately constant and varies uniformly. The columns in

the table are labeled with the vibrational quantum number v'' of the lower electronic state and rows with the quantum number v' of the upper state. Each wavenumber in the table can then be identified as the transition between v' value of the row it occupies and v'' value of the column. The difference between the rows of the Deslandres table gives the spacing of the vibrational levels in the upper electronic state whereas the difference between the values in the column gives vibrational spacing in the lower electronic state.

i) For upper state:

The first difference $\Delta G'\left(1/2\right)$ value is obtained by subtracting $v' = 0$ value from $v' = 1$ value vertically below it in the table. On application of this to table, several values of $\Delta G'\left(1/2\right)$ would result. An arithmetic mean of the resulting $\Delta G'\left(1/2\right)$ value would be regarded as $\Delta G'\left(1/2\right)$ .i.e.,

$$\Delta G'\left(1/2\right) = G_0'(1) - G_0'(0) = \overline{\omega}_e' - 2\overline{\omega}_e' x_e' \quad \text{..... (30)}$$

By a similar procedure, the value of $\Delta G'\left(3/2\right)$ and $\Delta G'\left(5/2\right)$ etc would be found as follows:

$\Delta G'\left(3/2\right) = G_0'(2) - G_0'(1) = \overline{\omega}_e' - 4\overline{\omega}_e' x_e'$; and

$\Delta G'\left(5/2\right) = G_0'(3) - G_0'(2) = \overline{\omega}_e' - 6\overline{\omega}_e' x_e'$ etc.

The second difference of successive vibrational quanta is the same and gives the vibrational constant $\omega_e' x_e'$ (anharmonicity constant) for upper state:

$$\Delta^2 G' = 2\overline{\omega}_e' x_e' \quad \text{..... (31)}$$

ii) For lower state:

Now, the value of $\Delta G''\left(1/2\right)$ would be obtained by subtracting adjacent horizontal numbers in the $v'' = 1$ column from the ones in $v'' = 0$ column. An arithmetic mean of the resulting $\Delta G''\left(1/2\right)$ value would then be regarded as $\Delta G''\left(1/2\right)$ values. i.e.,

$$\Delta G''\left(1/2\right) = G_0''(1) - G_0''(0) = \overline{\omega}_e'' - 2\overline{\omega}_e'' x_e''$$

Similarly,

$\Delta G''\left(3/2\right) = G_0''(2) - G_0''(1) = \overline{\omega}_e'' - 4\overline{\omega}_e'' x_e''$; and

$\Delta G''\left(5/2\right) = G_0''(3) - G_0''(2) = \overline{\omega}_e'' - 6\overline{\omega}_e'' x_e''$

The arithmetic mean value is obtained from the values which do not deviate much.

Again, the second difference gives-

$$\boxed{\Delta^2 G'' = 2\omega_e'' x_e''} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (32)$$

where, $\overline{\omega}_e'' x_e''$ is the vibrational constant for the lower electronic state.

Finally, the value of $\overline{\omega}_e$ for both the states can be determined as follows:

$$\boxed{\begin{aligned} \overline{\omega}_e' &= \Delta G'\left(\tfrac{1}{2}\right) + 2\overline{\omega}_e' x_e' \\ \overline{\omega}_e'' &= \Delta G''\left(\tfrac{1}{2}\right) + 2\overline{\omega}_e'' x_e'' \end{aligned}} \ldots\ldots\ldots\ldots\ldots\ldots (33)$$

v' \ v''	0	1	2	**First Difference**
0	$\overline{\nu}_{00} + G_0'(0) - G_0''(0)$	$\overline{\nu}_{00} + G_0'(0) - G_0''(1)$	$\overline{\nu}_{00} + G_0'(0) - G_0''(2)$	
				$\Delta G'\left(\tfrac{1}{2}\right)$
1	$\overline{\nu}_{00} + G_0'(1) - G_0''(0)$	$\overline{\nu}_{00} + G_0'(1) - G_0''(1)$	$\overline{\nu}_{00} + G_0'(1) - G_0''(2)$	
				$\Delta G'\left(\tfrac{3}{2}\right)$
2	$\overline{\nu}_{00} + G_0'(2) - G_0''(0)$	$\overline{\nu}_{00} + G_0'(2) - G_0''(1)$	$\overline{\nu}_{00} + G_0'(2) - G_0''(2)$	
	$\Delta G''\left(\tfrac{1}{2}\right)$	$\Delta G''\left(\tfrac{3}{2}\right)$		

2.6 Let us sum up:

- The vitality of Born- Oppenheimer approximation in arriving at the energy equation has been studied.

- Also, by learning the classification of Electronic states and Hund's rule the vibrational Structure of Electronic Transitions can be understood by compressive study of the concepts like Progression and Sequence
- Deslandres table is discussed in detail, with the help of which, we could find the values of vibrational constants.

2.7 Questions for self study:

1. Explain how Born-Oppenheimer approximation can be used to find the expression for energy.
2. Arrive at the expression for vibrational constant using Deslandres table.

2.8 References:

1. Introduction to Atomic and Molecular Spectroscopy by V.K. Jain
2. Atomic and Molecular Spectra: Laser by Raj Kumar

Unit 3: Intensity distribution in vibrational structure, Franck-Condon factor

Structure:

3.0 Objective:

After studying this unit you are going to understand,

- Intensity distribution in vibrational structure
- Franck-Condon factor

3.1 Introduction:

The distribution of intensity among the bands of an electronic band-system varies greatly from one molecule to another, and also from one band-system to another of the same molecule.

The different types of intensity distributions are explained by Franck-Condon principle which states that "***An electronic transition in a molecule takes place, so much rapidly than vibrational transition so that the internuclear distance can be regarded as fixed and velocity is nearly the same before and after transition***".

3.2 Intensity Distribution in the Vibrational Structure:

Let us examine absorption transitions between two electronic states in a diatomic molecule. Here, we shall represent the electronic states by the potential curves. The shapes of potential curves are different for different electronic states. Let r_e'' correspond to the minimum of potential curve of ground state and r_e' correspond to the minimum of potential curve of excited states. Depending on relative value of r_e'' as compared to r_e' we can have four types of discussions.

(a) when $r_e'' < r_e'$:

Consider the potential curve for ground state as shown in fig (1) below

Let us consider a transition CG taking place from the minimum of ground state level to the excited state. Firstly, the time taken by the electronic transition is much smaller than vibrational transition; nuclei will not change their position during electronic transition. This means ***r*** remains fixed. But, the transitions are considered to be between points, which lie on the same vertical; such transitions are called '***vertical transitions***'.

Secondly, *the velocity at the minimum of ground state is zero*, which means in the excited

state it should end up at positions where the velocity is again zero. Such points are called 'turning points'.

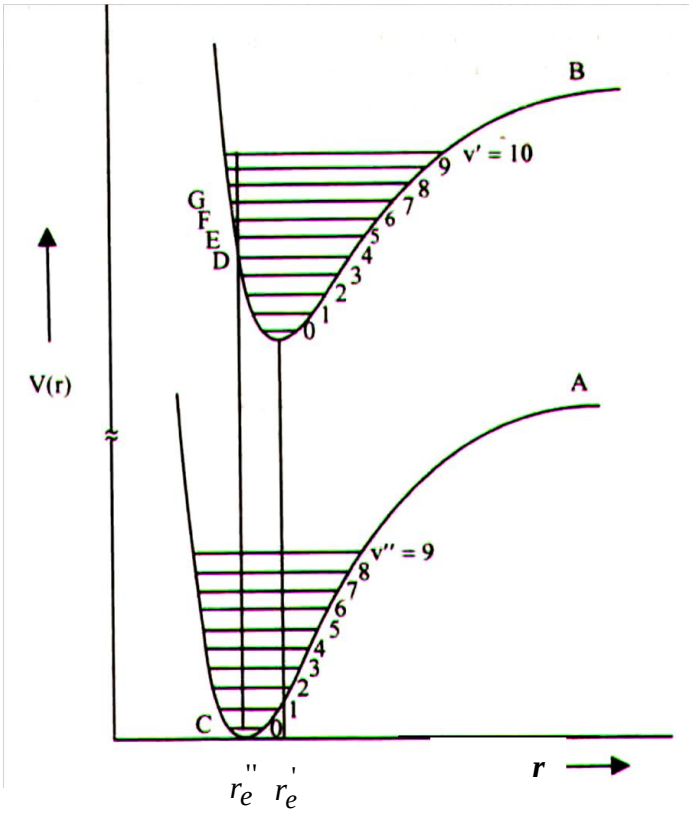


Fig (1) Illustration of the Franck –Condon Principle for $r_e'' < r_e'$

At these turning points of the potential curve, the energy is totally potential which infers that the velocity (and hence the kinetic energy) is zero at these points. The vertical transitions from ground state may end up in the excited state at D, E, F, G etc. However, only D is considered a turning point while E, F and G are not, as they have certain velocities (which is evident from the above diagram). Hence, the transition from C to D which is $(v''=0) \rightarrow (v'=4)$, is the most probable transition and hence the most intense. The other transitions $0 \rightarrow 1$, $0 \rightarrow 2$, $0 \rightarrow 3$, $0 \rightarrow 5$ etc. do happen, but are less probable and are less in intensity. Thus, in this case, the intensity of vibrational transition first increases, reaches a maximum and then decreases.

The below fig (2) shows intensity distribution of vibrational transitions for $r_e'' < r_e'$. We can observe that transition from C to G which is 0 to 4 (v'' to v'') is the most probable and it will be most intense.

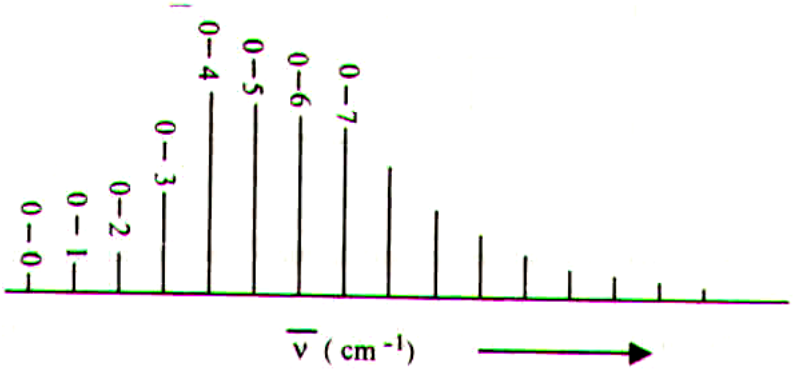


Fig (2) Intensity of vibrational transitions for $r_e'' < r_e'$

(b)when $r_e'' = r_e'$**:**

Let us consider a transition from the minimum of potential curve of ground state as shown in fig (3).

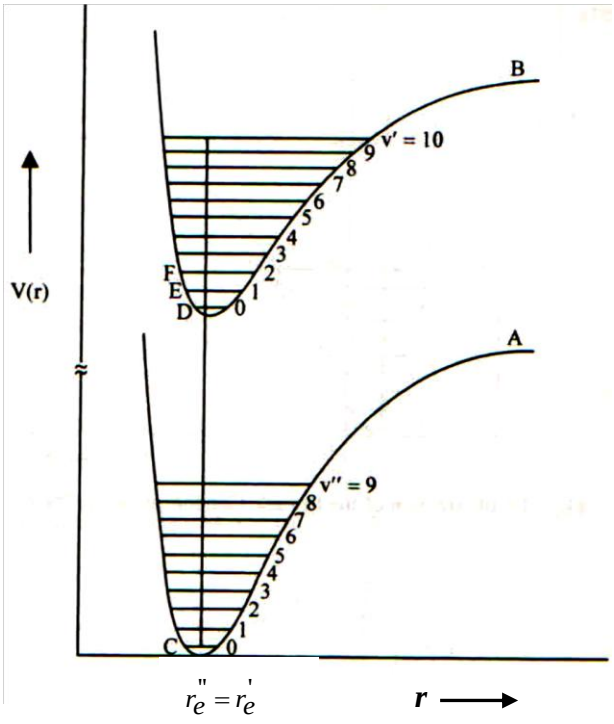


Fig (3) Illustration of the Franck Condon principle for $r_e'' = r_e'$

Since $r_e'' = r_e'$, the transition CD is a vertical transition with no change in ***r.*** Further, velocity is also same before and after the transition. Other vertical transitions from C to higher excited states

E, F etc. i.e., CE, CF etc all satisfy the condition ***r* = *constant***. However, the velocities (hence the kinetic energy) are not zero and in fact it goes on increasing as we move from D to E to F etc. This velocity increase during the transition from C to E, C to F makes the transition less probable. Therefore, the most probable and intense transition would be $0 \rightarrow 0$ and the intensity of $0 \rightarrow 1$, $0 \rightarrow 2$ etc. transitions goes on decreasing.

Thus, in this case vibrational transition is maximum for $0 \rightarrow 0$ i.e., most intense transition would be $0 \rightarrow 0$ and for other transition it decreases as shown in fig (4)

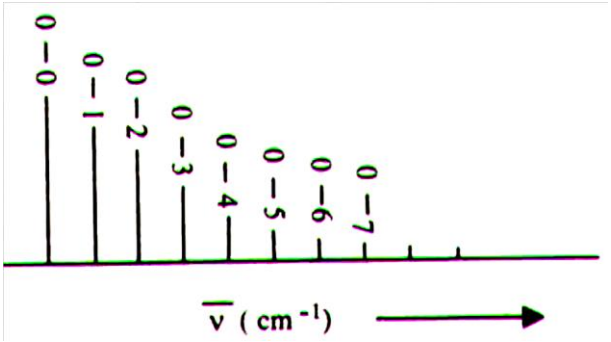


Fig (4): intensity distributions of vibrational transitions for $r_e'' = r_e'$

(c) when $r_e'' << r_e'$

Here, the transition takes place from the lowest vibrational state of the electronic ground state to higher vibrational state of the excited state as shown in fig (5).

In this case, both the conditions that "***r*** should be the same and velocity should not change" are satisfied only for very high values of v' (it can be observed in fig (5) where v'=9). Also, the vertical transitions for higher v' values take place but are associated with change in velocity.

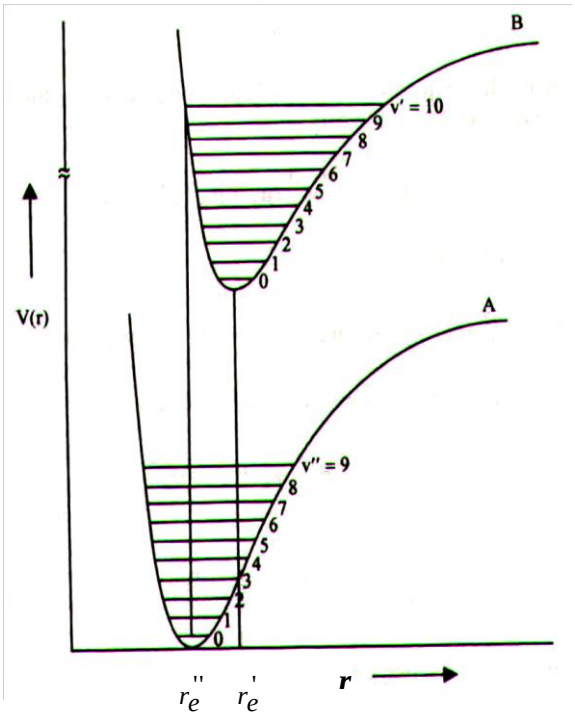


Fig (5) Illustration of the Franck Condon principle for $r_e'' << r_e'$

Hence the intensity of transition decreases. As the value of v' is very high, we are very near to the continuum of the upper state. As a result of this, we get an intensity distribution that looks like a continuum as shown in fig (6)

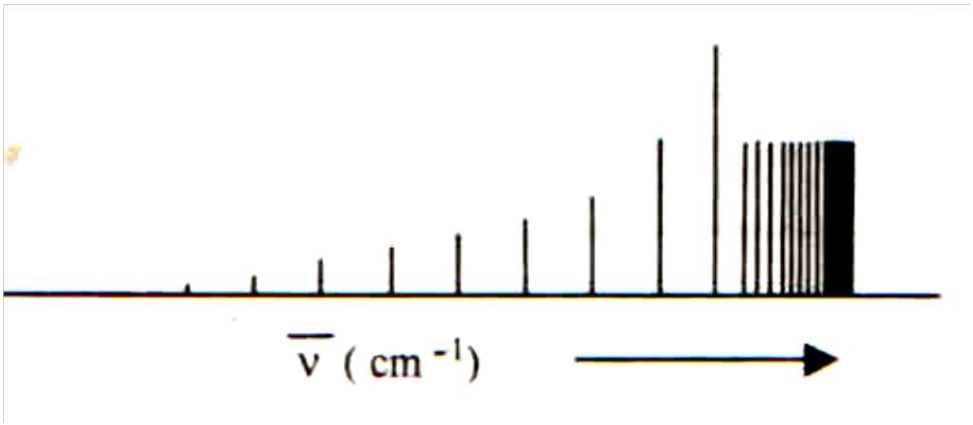


Fig (6): intensity distributions of vibrational transitions for $r_e'' << r_e'$

(d) when $r_e'' >> r_e'$:

For $r_e'' >> r_e'$ intensity distribution is same as that of case (a)

3.3 Franck –Condon factor:

Condon treated the intensities of vibronic transitions quantum mechanically. The intensity of vibronic transition between two states is proportional to the square of the transition moment R which is given as,

$$R = \int \psi'^{*} \mu \psi'' d\tau \quad \text{..... (1)}$$

Where μ is the electric dipole moment operator. The wave functions ψ' and ψ'' characterize upper and lower electronic states respectively. Neglecting the rotation and assuming that Born-Oppenheimer approximation holds good we have

$$\psi = \psi_e \psi_v \quad \text{..... (2)}$$

Assume that electric dipole moment μ can be separated into components μ_e due to electron and μ_N due to nuclei, then

$$R = \int \psi'^{*}_e \psi'^{*}_v (\mu_e + \mu_N) \psi''_e \psi''_v d\tau$$

Let $d\tau = d\tau_e d\tau_N$, so that

$$R = \int \psi'^{*}_e \psi'^{*}_v (\mu_e + \mu_N) \psi''_e \psi''_v d\tau_e d\tau_N \quad \text{..... (3)}$$

Where $d\tau_e$ and $d\tau_N$ are respectively the volume elements of the space of the electronic and nuclear coordinates respectively.

We can replace $d\tau_N$ by *dr* because the vibrational nuclear wavefunctions ψ_v depend only on the internuclear distance ***r***. So that,

$$R = \int \psi'^{*}_e \psi'^{*}_v \mu_e \psi''_e \psi''_v d\tau_e dr + \int \psi'^{*}_e \psi'^{*}_v \mu_N \psi''_e \psi''_v d\tau_e dr \quad \text{.....(4)}$$

The nuclear dipole moment μ_N is independent of the coordinates of the electrons (because it depends only on ***r***). Therefore, the second integral in the equation (4) can be written as

$$\int \left\{ \int \psi'^{*}_e \psi''_e d\tau_e \right\} \psi'^{*}_v \mu_N \psi''_v dr$$

Because of orthogonally of electronic wave functions

We have $\int \psi'^{*}_{e} \psi''_{e} d\tau_e = 0$. Hence,

$$R = \int \psi'^{*}_{e} \psi'^{*}_{v} \mu_e \psi''_{e} \psi''_{v} d\tau_e dr$$

Generally, the electronic wavefunction ψ_e varies very slowly with the internuclear distance ***r***, so that the last expression may be factorized to give

$$R = \int \psi'^{*}_{e} \mu_e \psi''_{e} d\tau_e \int \psi'^{*}_{v} \psi''_{v} dr$$

The term $\int \psi'^{*}_{e} \mu_e \psi''_{e} d\tau_e$ is the electronic transition moment R_e. Thus, we can write

$$R = R_e \int \psi'^{*}_{v} \psi''_{v} dr$$

Actually ψ_e and hence R_e depends to some extent on ***r.*** But, the variation of R_e is very slow and hence R_e may be approximated by an average value $\overline{R}_e$. We can write

$$\boxed{R = \overline{R}_e \int \psi'^{*}_{v} \psi''_{v} dr} \quad \text{..... (5)}$$

The average electronic transition moment $\overline{R}_e$, governs the intensity of the band-system as a whole. The relative intensities of the various bands of the system mainly depend on the square of the 'overlap' integral $\int \psi'^{*}_{v} \psi''_{v} dr$, which is the integral over the product of the vibrational wavefunctions of the two combining electronic states. This square of the overlap integral is called 'Franck-Condon' factor (q) i.e.,

$$\boxed{q = \left\{ \int \psi'^{*}_{v} \psi''_{v} dr \right\}^2} \quad \text{..... (6)}$$

The amount of overlap and the value of the Franck-Condon factor, depends on the relative positions of the maxima and the nodes of the vibrational wavefunction ψ_v in each of the two combining electronic states, and consequently upon the relative shapes and positions of the corresponding potential energy curves are such that the 'best overlapping' of the eigen function occurs for $(v''=0) \rightarrow (v'=2)$ levels. Thus, $(v''=0) \rightarrow (v'=2)$ is the most probable transition giving maximum intensity to the corresponding band fig (7).

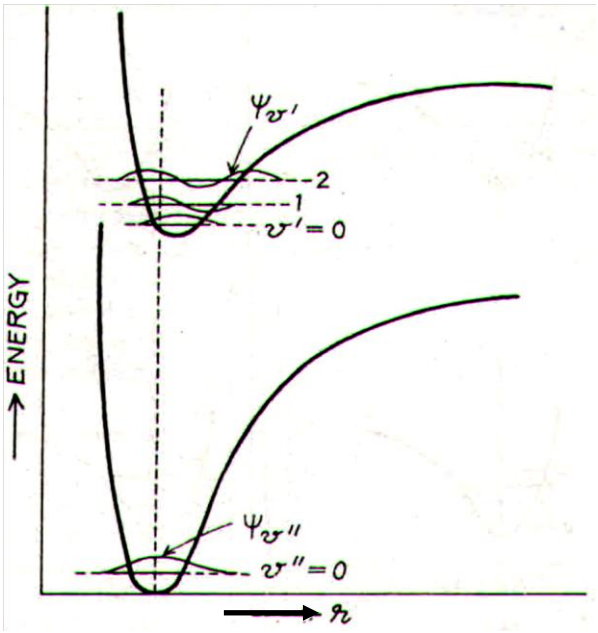


Fig (7)

In general, "*a vibrational transition will have a large Franck-Condon factor iff one of the two turning points of a level of one electronic state lies at approximately the same internuclear distance as one of the two turning points of a level of the other electronic state. But in case of* $v = 0$ *level the middle point of the level must be substituted rather than the turning point*".

3.4 Let us sum up:

Intensity Distribution in the Vibrational Structure and the Franck-Condon factor are discussed comprehensively in this unit.

3.5 Questions for self-study:

1. Explain the intensity distribution in the vibrational Structure in an electronic transition with the help of potential curves
2. What do you mean by Franck-Condon factor? Derive an expression for it.

3.6 References:-

1. Introduction to Atomic and molecular spectroscopy by Vimal Kumar Jain.
2. Atomic and Molecular Spectra: Laser by Raj Kumar.

UNIT 4: Franck-Condon principle, (ii) rotational structure of electronic transition, band head formation.

Structure:

4.0 Objectives:

- To understand Rotational structure of electronic transition in detail**.**
- To explain the formation of band heads in band spectra.

4.1 Introduction:

The characteristic time for an electronic transition is near to 10^{-16} seconds, whereas for a nuclear vibration the time has much larger value than the above which is nearly 10^{-13} seconds. Therefore, it can be assumed that during an electronic transition, nuclei remain fixed or stationary. Based on this assumption Franck explained the intensity distribution.

Franck-Condon principle states that ***"An electronic transition in a molecule takes place, so much rapidly than vibrational transition. This means in a vibronic transition (the vibrational transitions accompanying an electronic transition are called vibronic transitions), the internuclear distance can be regarded as fixed and velocity is nearly the same before and after transition."***

4.2 Rotational structure of electronic transition:

Rotational spectra are observable for the molecules that have permanent electric dipole moment. These can absorb electromagnetic radiation and can exhibit rotational spectra.

The possible changes in the rotational state for any given vibrational transition is given as

$$\bar{\nu} = \bar{\nu}_0 + \bar{\nu}_r$$

$$\bar{\nu} = \bar{\nu}_0 + F'(J') - F''(J'') \quad \text{.....(1)}$$

where $\bar{\nu}_0 = \bar{\nu}_e + \bar{\nu}_v$ is constant for a specific vibrational transition and is called the band origin or zero line. $\bar{\nu}_r$ depends on the different values of the rotational quantum number in the upper and lower state, respectively. $F'(J')$ and $F''(J'')$ are the rotational terms of upper and lower state respectively. $F'(J')$ and $F''(J'')$ are rotational terms of upper and lower state respectively.

For non-rigid vibrating oscillator we have,

$$F_v(J) = B_v J(J+1) - D_v J^2 (J+1)^2$$

Where $B_v = B_e - \alpha(v+\frac{1}{2})$

$D_v = D_e - \beta(v+\frac{1}{2})$

is the dissociation energy and it is a constant for a given molecular electronic state and B_e corresponds to the value of B for which $r = r_e$

The equation (1) becomes

$$\bar{\nu} = \bar{\nu}_0 + \left[B_v' J'(J'+1) - D_v' J'^2\right] - \left[B_v'' J''(J''+1) - D_v'' J''^2 (J''+1)^2\right] \text{.....,.....} (2)$$

The selection rules for the rotational transitions are

$$\boxed{\Delta J = J' - J'' = 0, \pm 1}$$

$\Delta J = 0$ is forbidden if both the electronic states have $\Lambda = 0$. For allowed transitions we have three series of lines or branches. These three branches are designated as $R(\Delta J = 1)$, $Q(\Delta J = 0)$ and $P(\Delta J = -1)$ branches.

For R-branch $(\Delta J = 1)$:

Put $J'' = J, J' = J+1$ in equation (2)

$$\bar{\nu}_R = \bar{\nu}_0 + \left[B_v'(J+1)(J+2) - D_v'(J+1)^2(J+2)^2\right] - \left[B_v'' J(J+1) - D_v'' J^2(J+1)^2\right] \text{.....} (3)$$

By neglecting the small term in D_v, equation (3) becomes

$$\bar{\nu}_R = \bar{\nu}_0 + 2B_v' + (3B_v' - B_v'')J + (B_v' - B_v'')J^2 = R(J) \text{.....} (4)$$

For Q branch $(\Delta J = 0)$:

Put $J'' = J, J' = J$ in equation (2)

$$\bar{\nu}_Q = \bar{\nu}_0 + \left[B_v' J(J+1) - D_v'(J^2(J+1)^2)\right] - \left[B_v'' J(J+1) - D_v'' J^2(J+1)^2\right]$$

By neglecting the small term in D_v we get

$$\bar{\nu}_Q = \bar{\nu}_0 + \left(B_v' - B_v''\right)J + (B_v' - B_v'')J^2 = Q(J) \text{.....} (5)$$

For P branch $(\Delta J = -1)$***:***

Put $J'' = J, J' = J - 1$ in equation (2)

$$\bar{\nu}_P = \bar{\nu}_0 + \left[B_v'(J-1)J - D_v'(J-1)^2 J^2 \right] - \left[B_v'' J(J+1) - D_v'' J^2 (J+1)^2 \right]$$

By neglecting the small term in D_v

$$\bar{\nu}_P = \bar{\nu}_0 - (B_v' + B_v'')J + (B_v' - B_v'')J^2 = P(J) \quad \text{.....(6)}$$

We can represent P and R branches by a single expression using equations (4) and (6).

$$\boxed{\bar{\nu}_{PR} = \bar{\nu}_0 + (B_v' + B_v'')m + (B_v' - B_v'')m^2} \quad \text{.....(7)}$$

where m=-J for P- branch with J = 1, 2, ……

and m=J+1 for R- branch with J=0, 1, 2,……

and Q-branch can also be represented by

$$\boxed{\bar{\nu}_Q = \bar{\nu}_0 + (B_v' - B_v'')q + (B_v' - B_v'')q^2} \quad \text{.....(8)}$$

where $q = J$ for J=1, 2,……..

In the absence of Q branch, there is only one series of lines in which the separation between lines changes regularly. Fig (5) shows all the three branches on an energy level diagram for $^1\Pi - ^1\Sigma$ transition.

For singlet Π-state, the possible values of J are $\Lambda, \Lambda+1, \Lambda+2, \ldots\ldots\ldots$ = 1, 2, 3,…..respectively. Similarly, for singlet Σ-state, the possible values of J are $\Lambda, \Lambda+1, \Lambda+2, \ldots\ldots\ldots$ = 0, 1, 2,…..respectively. As a result of this the lowest level of upper state corresponds to J=1 while for the lower state it is J=0. The first lines in the R, Q and P branches are those having J=0, 1 and 2, respectively. The P-branch starts from J=2, and there is no transition corresponding to J= 0 and 1. Substituting these values of J in equation (6) shows that there are missing lines at $\bar{\nu} = \bar{\nu}_0$ and $\bar{\nu} = \bar{\nu}_0 - 2B_v''$.

Similarly, the first line of Q-branch (corresponding to J=1) lies at [equation (5)]

$$\bar{\nu} = \bar{\nu}_0 + 2\left(B_v' - B_v''\right)$$

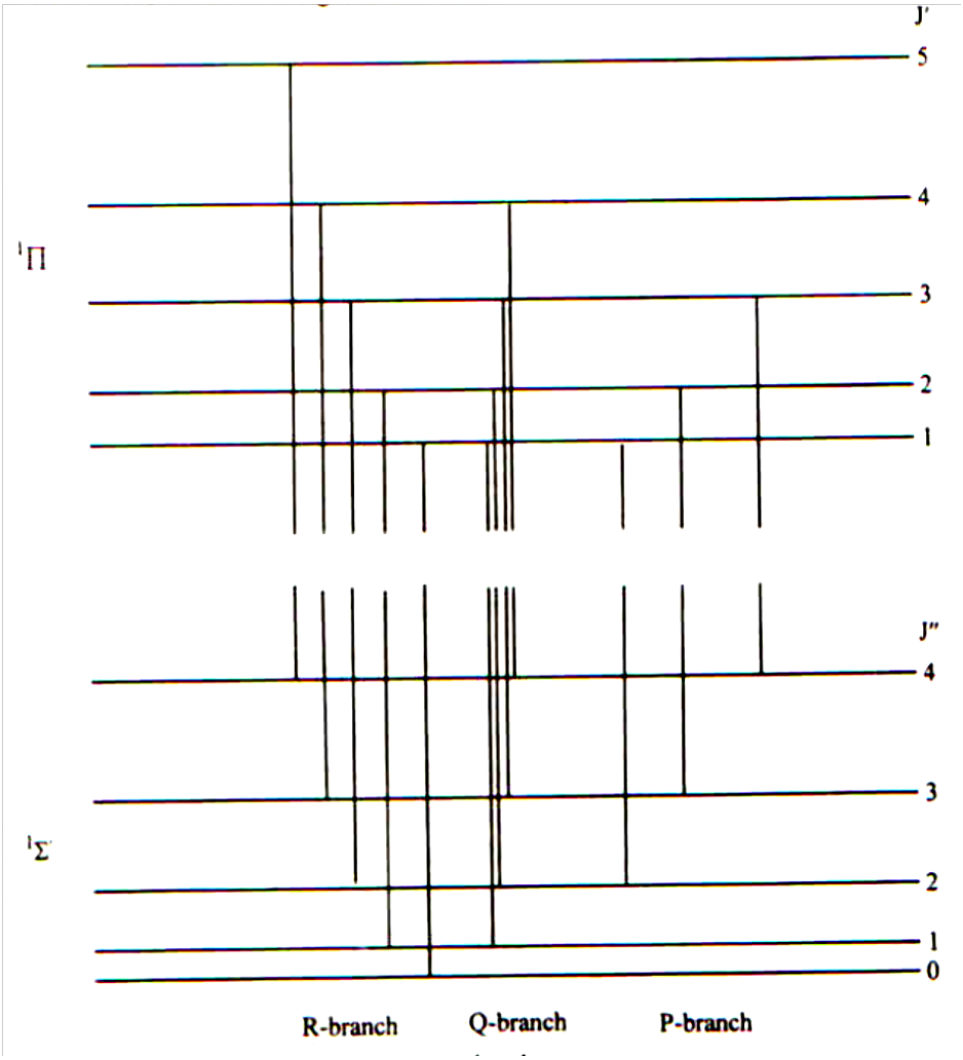


Fig (5) Rotational fine structure of $^1\Pi - ^1\sum$ vibronic transition in a diatomic molecule for which $r_e' > r_e''$.

4.3 Formation of band heads:

Since B_v' and B_v'' are not very different, Q-branch starts in the neighborhood of $\bar{\nu}_0$ and therefore gap at $\bar{\nu} = \bar{\nu}_0$ is not so apparent. P and R branches are represented by equations (4) and (6).

Plots of J against frequency of the rotational lines are called Fortrat diagram (fig below). Due to the quadratic term in equation (7), one of the two branches turns back, thus forming a band head.

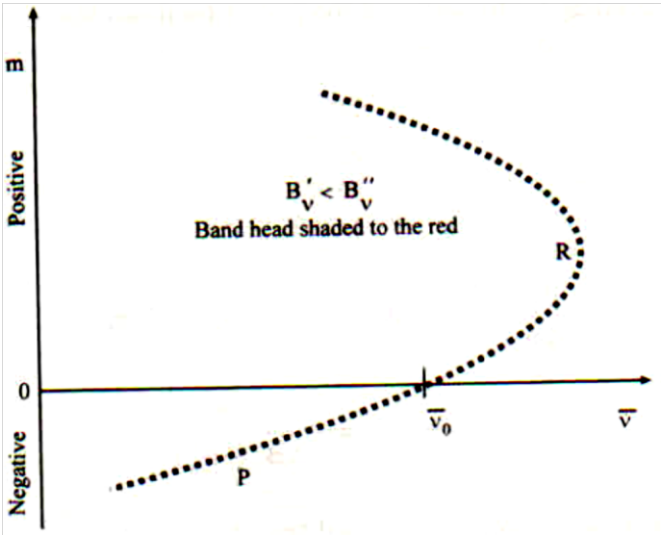


Fig (6) Fortrat parabola

Case (i) ($B_v' < B_v''$):

a) ***For R-branch (m = J+1):*** Since the linear and quadratic terms in equation (7) have opposite signs, the separation between lines goes on decreasing as *J* value increases. For a certain value of J, ***the quadratic term contribution exceeds the linear term contribution*** and the lines of the R-branch turn back towards lower value of $\bar{\nu}$ or higher value of wavelength as J value is further increased.

Therefore, in this case the band head lies on the short wavelength side of the zero line and the band is shaded towards the red (i.e., towards the larger wavelength). $B_v' < B_v''$ indicates that inter nuclear distance in vibrational state of upper electronic state is greater than that of vibrational state of the lower electronic state.

b) ***For P- branch (m = J):*** Here, both the linear and quadratic terms in equation (7) have same negative sign. Therefore, $\bar{\nu}_P$ decreases as the value of J increases. Also, for P=branch the spacing between lines increases at longer wave length side and no band head is formed.

c) ***For Q –branch (q = J):*** In this branch, both linear and quadratic terms of equation (8) have negative sign, As a result of this, the Q-branch extends to lower wave number side of $\bar{\nu}_0$ as the J value increases.

If $B_v'-B_v''$ is very small, lines in Q branch are not separately resolved for small value of J. Hence a single broad line may appear at $\bar{\nu}_0$ which is shaded towards the red.

Case (ii): ($B_v' > B_v''$):

$B_v' > B_v''$ indicates that inter nuclear distance in upper electronic state is smaller than that of lower electronic state and the coefficient $B_v'-B_v''$ is positive.

a) For R-branch: Here both the linear and quadratic terms of equation (7) have positive contribution. Thus $\bar{\nu}_R$ goes on increasing as the value of J increases. The separation between lines goes on increasing on the shorter wavelength side.

b) For P-branch: The linear term gives negative contribution to $\bar{\nu}_P$ while quadratic term gives positive contribution for a J value. For small J, the linear term is prominent and therefore, $\bar{\nu}_P$ shifts towards lower wave number side. However for large J, the contribution of quadratic term to $\bar{\nu}_P$ becomes important and a competition between linear and quadratic terms sets in. As a result of this competition, the spacing between the lines decreases while $\bar{\nu}_P$ also decreases. After a particular value of J, $\bar{\nu}_P$ stops decreasing and starts increasing. Thus, in this case the band head lies on the longer wavelength side which means the band will be shaded towards violet.(shorter wavelength side)

c) *In Q-branch:* both the linear and quadratic terms have positive contribution and therefore, the spacing between the lines go on increasing with J towards higher side of $\bar{\nu}_o$. If $B_v'-B_v''$ is small, the band head in P and R lies at a great distance from the zero line. If $B_v' \approx B_v''$, the head in P and R branch may lie at such a large distance from the band origin that it is not observed, since for the corresponding *m* values, the intensity of lines may have

decreased to zero. For Q – branch the linear term is small for $B_v' \approx B_v''$ and Q-branch parabola intersects at abscissa axis at about right angle.

A large difference in $B_v'$and B_v''causes the spreading out of the Q branch components and there by prevents the sharp Q –branch. The bands having a Q-branch often show two heads either in P and Q branch ($B_v' >> B_v''$) shaded towards violet or in R and Q branch ($B_v' >> B_v''$) shaded towards red.

The *m* value corresponding to the vertex of the Fortrat parabola, i.e., the band head is obtained by setting

$$\frac{d\bar{\nu}}{dm} = 0 \quad \text{.....(9)}$$

$$\Rightarrow \frac{d\bar{\nu}}{dm} = \frac{d\bar{\nu}_o}{dm} + (B_v' + B_v'') + 2(B_v' - B_v'')m = 0$$

$$\frac{d\bar{\nu}_0}{dm} = 0 \text{ as } \bar{\nu}_0 \text{ is constant}$$

$$\Rightarrow \boxed{m_{vertex} = -\frac{B_v' + B_v''}{2(B_v' - B_v'')}} \quad \text{.....(10)}$$

Usually m_{vertex} is not an integral number. The actual head then lies at the nearest whole numbered value of m.

(i) ***For R branch m=J+1,***

$\therefore$ Equation (10) becomes

$$(J+1)_{vertex} = -\frac{B_v' + B_v''}{2(B_v' - B_v'')}$$

$$J_{vertex} = \frac{B_v'' - 3B_v'}{2(B_v' - B_v'')} \quad \text{.....(11)}$$

(ii***) For P-branch m= -J,***

From equation (10)

$$(-J)_{vertex} = -\frac{B_v' + B_v''}{2(B_v' - B_v'')}$$

$$J_{vertex} = \frac{B_v' + B_v''}{2(B_v' - B_v'')} \quad \text{.....(12)}$$

(iii) ***For Q branch m=J,***

From equation (10)

$$J_{vertex} = \frac{B_v' + B_v''}{2(B_v' - B_v'')} \quad \text{.....(13)}$$

Substituting the value of m_{ventex} from equation (10) in equation (7)

$$\bar{\nu}_{vertex} - \bar{\nu}_0 = -\frac{(B_v' + B_v'')^2}{4(B_v' - B_v'')} \quad \text{.....(14)}$$

If $\bar{\nu}_{vertex} - \bar{\nu}_0$ is positive ($B_v' < B_v''$), the band shades to red. On the other hand if $\bar{\nu}_{vertex} - \bar{\nu}_0$ is negative $B_v' > B_v''$, the band shades towards violet.

4.4 Let us sum up:

- We have discussed the application of Franck – Condon principle to the rotational structure of electronic transition. The formation of band heads in P, Q and R branches of Rotational electronic spectra is discussed in detail.

4.5 Solved problems:

1. Wave number of the various rotational branches of the 4-11 band of the fourth positive group of co molecule (in cm^{-1}) are as follows.

R (o) = 48338.37	Q (1) = 48355.00	P (2) = 48328.58
R (1) = 48340.94	Q (2) = 48333.95	P (3) = 48324.14
R (2) = 48342.87	Q (3) = 48322.64	
R (3) = 48345.16		

Calculate the rotational constant of lower and upper state.

Solution: From combination relations obtained from equations (4), (5) and (6)

1) R (0) - Q (1) $= 2B_v'' = (48338.37 - 48335.0)cm^{-1} = 3.37cm^{-1}$

$$B_v'' = 1.685 cm^{-1}$$

2) R (1) - Q (2) $= 4B_v'' = (48340.94 - 48339.95) cm^{-1} = 6.99 cm^{-1}$

$$B_v'' = 1.7475 cm^{-1}$$

3) R (2) - Q (3) $= 6B_v'' = (48342.87 - 48332.64) cm^{-1} = 10.23 cm^{-1}$

$$B_v'' = 1.705 cm^{-1}$$

4) Q (1) - P (2) $= 4B_v'' = (48335.0 - 48328.58) cm^{-1} = 6.42 cm^{-1}$

$$B_v'' = 1.605 cm^{-1}$$

5) Q (2) - P (3) $= 6B_v'' = (48333.95 - 48324.58) cm^{-1} = 9.81 cm^{-1}$

$$B_v'' = 1.671 cm^{-1}$$

Average value is, $B_v'' 1.671 cm^{-1}$

From

1) R (2) - Q (2) $= 6B_v' = (48342.87 - 48333.95) cm^{-1} = 8.92 cm^{-1}$

$$B_v' = 1.487 cm^{-1}$$

2) R (3) - Q (3) $= (48345.16 - 48332.64) cm^{-1} = 12.52 cm^{-1} = 8B_v'$

$$B_v' = 1.56 cm^{-1}$$

3) Q (2) - P (2) $= 4B_v' = (48333.95 - 48328.58) cm^{-1} = 5.37 cm^{-1}$

$$B_v' = 1.3425 cm^{-1}$$

4) Q (3) - P (3) $= 6B_v' = (48332.64 - 48324.14) cm^{-1} = 8.50 cm^{-1}$

$$B_v' = 1.4166 cm^{-1}$$

The average value is $B_v' \approx 1.459 cm^{-1}$

2) The rotational constants by analyzing the band spectrum of molecule are obtained as $B_v' = 1.7527 cm^{-1}$ and $B_v'' = 1.6326 cm^{-1}$. The band origin is found to be at $19378 cm^{-1}$, estimate the position of the band head.

Solution: We have,

$$J_{vertex} = \frac{B_v' + B_b''}{2(B_v' - B_v'')} = \frac{1.7527 + 1.6326}{2(1.7527 - 1.6326)} \approx 14$$

The frequency at the vertex is

$$\bar{\nu}_{vertex} = \bar{\nu}_o - \frac{(B_v' + B_v'')^2}{4(B_v' - B_v'')}$$

$$= 19378 cm^{-1} - \frac{(1.7527 + 1.6326)^2}{4(1.7527 - 1.6326)}$$

$$= (19378 - 23.86) cm^{-1}$$

$$\bar{\nu}_{vertex} = 19354.1 cm^{-1}$$

4.6 Questions for self study:

1) Explain Rotational structure of electronic transition along with energy level diagram.
2) Explain the formation band head in rotational band spectra.

4.7 References:

1. Introduction to Atomic and Molecular Spectroscopy by V.K. Jain

2. Atomic and Molecular Spectra: Laser by Raj Kumar

Unit -5: The chemical bond: Parameters of molecular structure: bond energies, bond lengths and bond angles.

Structure:

5.0 Objectives:

After studying this unit we will come to know

- Why there are chemicals around us? What makes atoms to combine to form molecules?
- Types of chemical bonds
- The concept of molecular structure and its parameters
- Bond length, bond energy and bond angles and their variation.

5.1 Introduction:

All atoms consist of a central nucleus surrounded by one or more orbital electrons. Nucleus contains protons which are positively charged and neutrons which are electrically neutral. The number of positive charge in the nucleus is exactly balanced by an equal number of electrons orbiting around it. Most of the mass of the atom is counteracted at the nucleus as the electronic mass is very small compared to the protonic or neutronic mass.

Different models and theories exist to describe the nature of these orbits. The 103 or so elements at present known are all built up from these three fundamental particles in a simple way.

Because the nucleus is well inside the atom and electrically shielded by electrons, they won't contribute to the chemical behavior of the atom. Hence all the chemical properties of any material do not depend on the nucleus. It is the electrons, that too the electrons orbiting in the outermost orbits which give a specific chemical property to an element which in turn results in its electrical optical and spectroscopic properties. Hence, it is very important to know how electrons one distributed around the nucleus and how they behave under different conditions to understand the property of elements.

One exemption has to be mentioned here, that is when we are looking at the spectroscopic properties of an element, even inner orbital electrons contribute.

5.2 Build –up of Elements:

a. Characterizing an electron.

We shall observe an electron in two situations. First, the electron is "free" where it can possess any amount of energy. In this case the electron is characterized by the wave vector associated with its motion. Another is the electron being "bound", more precisely an

electron which is bound to an atom and orbiting the nucleus of the atom in one of the non radiating stationary orbits. In this case an electron is characterized by a set of four numbers known as four quantum numbers. These four quantum numbers describe the state of a bound electron in an atom which are almost necessary to calculate the energy, angular momentum etc for the electron in that orbit. These four quantum numbers are

i. **Principal quantum number (n)**

This can take integral values i.e., 1,2,3 …. and this describes, to which shell the electron belongs?

ii. **Azimuthal quantum number (ℓ)**

This can take values from zero to $n-1$, [*i.e.* if $n=5$, $\ell=0,1,2,3,4$]. This describes, to which sub shell of a given shell the electron belongs?

iii. **Magnetic quantum number (m)**

Magnetic quantum number can take values from $-\ell$ to ℓ of given azimuthal quantum number. [i.e., if ℓ=3, m can take values -3, -2, -1, 0, +1, +2, +3]. This describes how the orbit of the electron in a given sub shell is oriented

iv. **Spin quantum number (m_s)**

As the electron is a fermion, it has a half integral spin i.e., .½ ħ. This might have two orientation $\pm\frac{1}{2}\hbar$. This is denoted by spin quantum number S.

b.<u>Pauli exclusion principle:</u>

Since, electrons are fermions when they interact with each other their combined wave functions of those two electrons have to be ant symmetric. This forbiddens any two electrons to occupy same state. This is known as Pauli Exclusion Principle.

Pauli Exclusion Principle states that no two electrons in one atom can have same state or all four quantum numbers same. Based on this one can calculate the maximum number of electrons which can be contained in each energy level by permutating the four quantum numbers. For example, if $n=3$, the energy level corresponds to 'M shell'. Then there can be three sub shells with ℓ=0, 1,2 which are denoted by 3s, 3p and 3d respectively. Further m can take values 0 in 3s orbit, -1,0,+1 in 3p and -2, -1, 0, +1, +2 in 3d orbits respectively. m_s, the spin quantum number can take $\pm$½ value in every orbital, making the total number of electrons that can be accommodated in $n=3$ level as (1+3+5)2 =18 electrons.

c. ***Hunds Rule:***

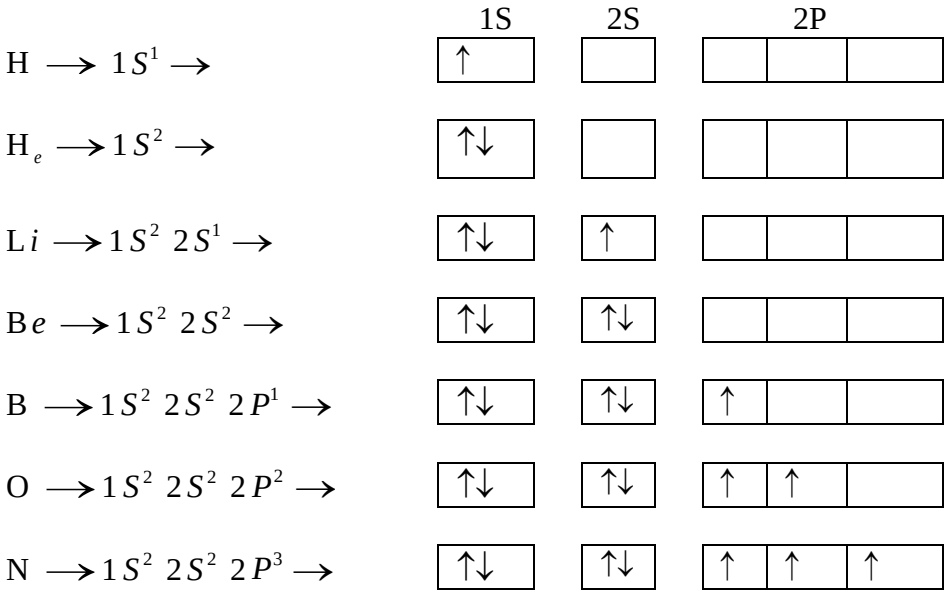
It is the fundamental nature of every object in this universe that it always tries to occupy the lowest resistant configuration or in other words, everything in this universe tries to attain lowest possible energies. This applies to atoms also. When an atom is in ground state, all its electrons tend to attain the lowest possible energy levels.

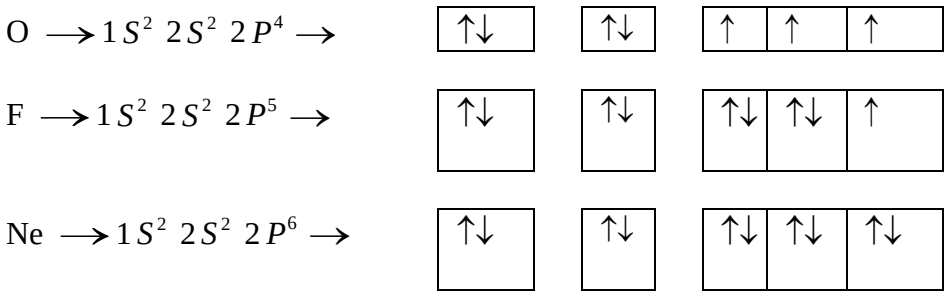
In the simplest element hydrogen, which has one electron, the electron occupies the level with ($n = 0,\ m = 0,\ m_s = +½$ or - ½)

Next, the helium atom has two electrons. Then the states of those two electrons are described by $n = 0,\ \ell = 0,\ m = 0,\ m_s = +½$ and ($n = 0,\ \ell = 0,\ m = 0,\ m_s = +½$). This can be put in a more compact form by Hunds rule.

Quantum No.	**K-shell**		**L-shell**					
n	1 (1s)		2 (2s)		2 (2p)			
l	0		0		1			
m	0		0		-1	0	+1	
m_s	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$

This goes on and on. Based on this, using Hunds rule one can write the electronic configuration of different dements as,





From above table or from Hunds rule one can conclude that 'by maintaining the electron distribution around the nucleus in a specific way, the atom tries to attain the lowest energy possible'. Then the following question arises-

Is this the only way to minimize the energy? Are there no other ways for an atom to decrease its energy even further?

The answer is yes. This can be achieved by means of combination of different atoms to form a cluster which we may call a molecule.

5.3 The Chemical Bond:

Why do we have molecules? Why two or more atoms react to form a molecule?

As we specified previously, every atom tries to attain a minimum / lowest energy level. A molecule will only be formed if it is more stable and has energy lower than individual atoms. i.e., a molecule will be formed if the electronic structure of atoms in molecule is more stable than that of isolated atoms.

To understand what is happening in terms of electronic structure, let us consider first thegroup-18 elements of periodic table. These comprise of the noble gases, helium, neon, argon, krypton, xenon and radon which are noted for their chemical inertness. Atoms of noble gases do not normally interact with any other atoms. The lack of reactivity is because the atoms already have a low energy and it cannot be lowered further by forming compounds. This lowest energy of noble gases is associated with their having completely filled outer shell. This is well known as noble gas electronic configuration and it is exceptionally stable arrangement of electrons.

Normally, electrons in the outermost shell of an atom are involved in forming bonds and by forming bonds each atom acquire a stable electronic configuration and that are why they form molecules. Because the noble gas electronic configuration is the most stable arrangement of electrons, most of the molecules attain this electronic configuration and there

are some exceptions as transition elements which attain less stable electronic configuration than this.

When a chemical bond is formed between two atoms, both the atoms attain an energy which is less than their energy in their isolated states. If one atom tries to go far from the other, the only way that can happen is by absorbing energy. If one does not provide sufficient energy, the atoms can not go for from each other; even if they try, an attractive force develops between them which keep them together. Hence one can also define chemical bond as the attraction between the atoms engaged in the chemical bond.

In this sense, one can define the strength of a chemical bond in terms of the force of attraction between two atoms held together by the bond. More attractive force between the atoms means the bond is stronger and it takes more energy to break the bond. In general, strong chemical bonding is associated with the sharing or transfer of electrons between the participating atoms. There are also some kinds of bonds which result because of dipole – dipole interactions. London dispersion force etc., which are considered to be weak bonds as the amount of force with which two atoms are bound to each is very less compared to other kinds of bonds.

5.4 Types of Bonds:

Atoms may attain a stable electronic configuration in three different ways; by wring electrons, by gaining electrons or by sharing electrons. Based on this observation, elements are divided into three groups.

i. Electropositive elements: These have more tendencies to give up electrons.
ii. Electropositive elements: These elements have more tendencies to accept the electrons.
iii. Elements which have little tendency either to lose or gain electrons.

Depending on the type of combination of elements during the formation of chemical bond, they are divided into three groups.

i. Electropositive + Electronegative = Ionic bond
ii. Electronegative + Electronegative = Covalent bond
iii. Electropositive + Electropositive = Metallic bond

Ionic bonding involves complete transfer of one or more electrons from one atom to another. Covalent bonding involves the sharing of a pair of electrons between two atoms and in metallic bonding the valence electrons are free to move throughout the whole crystal.

The above mentioned bonds are idealized or just extreme representation. In general any chemical bond might have the characteristics of two or all types of bonds.

5.5 Molecular Structure:

Before we start discussing about molecular structure, let us understand what a molecule is? One can define a molecule as a group of two or more number of atoms held together by chemical bonds which as a whole electrically neutral.

A molecule might contain only one type of elements like O_2 , N_2, H_2 gases or it might contain more than one element like water (H_2O) ,methane (CH_4) etc. Atoms or complexes connected by non covalent bonds like hydrogen bonds or ionic bonds are not considered as single molecule since they do not possess a fixed boundary at atomic dimension i.e., they are extended or have a spread throughout the material of interest.

a. Molecular Size: Most of the molecules have their size in nanometer scale. One can argue that DNA, few polymer molecules can be very large, comparable to a micrometer. But they are not considered as single molecules as they are formed by repetition few binding blocks which are usually called as monomers.

Molecular size varies widely with hydrogen molecule being the smallest molecule with average separation between the two nuclei of hydrogen equal to 0.74 A^O and mesoporous silica which has been produced with the average separation between two extreme atoms being around $1000A^O$.

b. Molecular Formula: Molecular formula gives the composition of molecular material in the terms of its elemental members as integral ratio. i.e., for example molecular formula of methane is $C_2\ H_6$ which says in one molecule of methane, there are two carbon atoms and six hydrogen atoms or in any amount of methane if the carbon content is two parts then hydrogen content is six parts. All most all sugars have a common empirical molecular formula $C_{n6}\ H_{n12}\ O_{n6}$ with n being any integer. This tells us that the ratio of carbon, hydrogen and oxygen in sugar is 1: 2: 1.

The molecular formula reflects exact number of atoms that make the molecule. However different isomers might have same molecular formula but they might be altogether different molecules. Hence molecular formula can not provide all the information required to know a molecule.

c. Molecular Geometry: In the beginning of the discussion of molecules we specified that the molecules are formed by a number of atoms through chemical bonds. A molecule may contain a large number of chemical bonds oriented in different directions. Hence a molecule can be regarded as a geometrical object with fixed equilibrium geometry. Knowing about the molecule means knowing the lengths of every bond in the molecule and the orientation of every bond with respect to another bond. All these together are known as 'molecular geometry'. Hence molecular geometry describes the geometrical structures of any molecule.

But knowing the geometrical structure of a molecule is not enough as it does not provide all the information about the molecule like bond strength of every individual bond, and the amount of energy to be supplied to break that bond. These informations are also needed to know the stability of molecule and weak bonds where chemical reactions can readily take place and many more. Hence complete information about a molecule can be obtained only when we know its geometrical and physical structures.

5.6 Parameters Of Molecular Structure:

Molecular structure of any chemical or compound provides complete information about the molecule and its property. It includes the molecular geometry which provides the information about the lengths of different bonds involved in the molecule, the angle between any two adjacent bonds, the position of every atom in the molecule with respect to any reference. It also includes the physical structure / parameters of the individual bonds like the bond energy, the elasticity of bonds which in turn helps one to calculate the rotational, vibrational constants of the molecule.

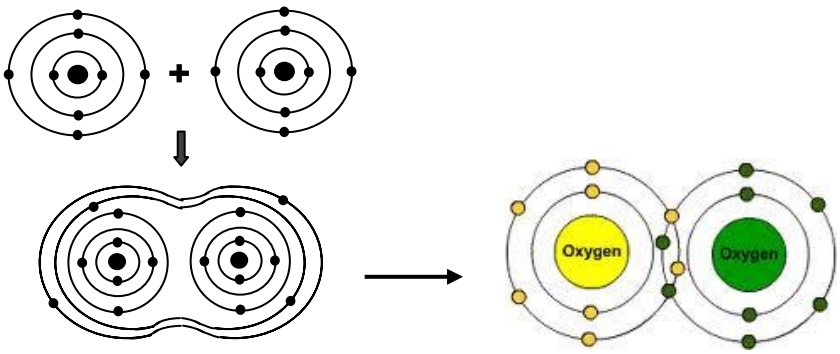
In this section we shall have a discussion of both geometrical structure of the molecule and its physical properties.

a. Bond length:

What happens when a chemical bond is formed? The answer is within the answer to another question why a chemical bond forms? We have already discussed in the beginning of

this unit why a chemical bond forms. An atom with unfilled outer shell is not energetically most stable; it always tries to attain most stable state that is lowest energy state which corresponds to completely filled outer shell electronic configurations. This results in a chemical bond.

For example consider two oxygen atoms. The electronic configuration of oxygen is $1S^2\ 2S^2\ 2P^4$ to have the completely filled noble gas electronic configuration; each oxygen atom needs two more electrons. They can not capture two electrons from somewhere and fill their shell as that leads to a doubly ionized oxygen anion which is energetically very unstable. If two such oxygen atoms come very near, near means the separation of atoms being of atomic dimensional order, then electron of one atom feels the presence of the other atom, this leads to interaction.



Because of the interaction, few orbits of outermost electronic shell overlap making two electrons from each atom revolve around both the nuclei. This can also be represented as sharing of electrons between those two oxygen atoms leading to a chemical bond. This creates an attractive force between the atoms, and the atoms are pulled near to each other. This can not continue resulting in the overlap of inner orbits as they are already completely filled. If oxygen atoms go further near, an opposition force develops to push them apart to avoid the overlap of inner atomic orbitals.

This maintains an average distance between the oxygen atoms in oxygen molecule. The similar phenomena takes place in most of the molecules resulting in maintenance of distance between two atoms involved in the chemical bond. This average distance is known as bond length. For oxygen it is about $1.2074\,A^O$. The radius of oxygen atom is $0.66\,A^O$ Note that the bond length is less than the sum of the radius of involved atoms.

When a chemical bond is formed, depending on the number of electrons participating in the chemical bond we also treat them as single, double and triple bonds. A single bond is

the one in which one pair of electrons are involved. A double bond is the bond in which two pairs (i.e., 4) of electrons are involved. Similarly in triple bond, three pairs of electrons are involved.

The chemical bond length increases as the size of participating atoms increase and it deceases as the number of participating electrons increase.

The following table provides a brief idea of bond lengths of different chemical bonds:

Bond	Bond length (pm)	Bond	Bond length (pm)
H-H	74.14	H-F	91.7
H-C	110	H-Cl	127
H-N	100	H-I	161
H-O	127		
H-Br	141.4		

If one atom is electronegative and another is electro positive, then the formation of chemical bond readily takes place and the bond length decrease as either electro-negativity or electro-positivity increases. Even if both the atoms are electronegative / electropositive then also chemical bond forms and the bond length decreases as electro negativity / electro-positivity increases.

The following table shows how bond length changes as the number of participating electrons change.

Bond	No. of electrons Involved	Bond length (pm)	Bond	No. of electrons Involved	Bond length (pm)
C-C	2	154	*C-N*	2	147
C = C	4	134	*C=N*	4	128
C ≡ C	6	120	*C ≡ C*	6	116
N-N	2	145	*C-O*	2	143
N=N	4	123	*C=O*	4	123
N ≡ N	6	109.8	*C ≡ O*	6	113

From above table, one can observe that bond lengths of C-C > C-N > C-O. This is because the electro negativity increases from C to N and to O.

b. Bond Energies:

As we have specified earlier, everything in this nature takes place for a reason. Not a philosophical one but a physical reason (i.e., minimizing the energy). Even chemical bonds form to minimize the energy. Thus the energy of two atoms engaged in a chemical bond must be less than their energy when they are isolated from each other. This difference in energy arises because of the formation of chemical bond. Hence this energy is known as bond energy.

Thus the bond energy of a chemical bond can be defined as the amount of energy decreased or released when a chemical bond is formed from individual atoms. In other words, it can also be defined in the reverse way as the amount of energy to be applied to a chemical bond to break it to form neutral atoms.

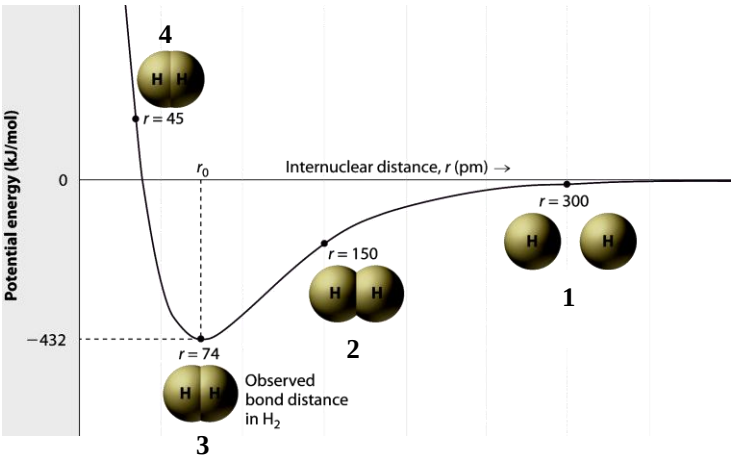
Bond energy is a measure of the strength of the chemical bond. Higher the bond energy, stronger will be the bond. Normally bond energies are measured per mole as the individual bond energies are too small. Hence in this context one can also define the bond energy as the heat required to be supplied to break one mole of molecules to individual atoms or the heat released when individual atoms form one mole of molecule.

Bond energy is directly correlated with bond length. Lesser the bond length, higher will be the expected bond energy. When we say less here, one should consider it relatively i.e., when a bond forms the bond length will be always less than the sum of the radii of participating atoms. Let us call this difference as ΔL

$\Delta L = R_A + R_B - L_{AB}$ where R_A and R_B are the radius of two atoms A and B respectively L_{AB} is their bond length. Higher the value of ΔL, lesser will be the value of L_{AB}. In terms of bond energy, higher the value of ΔL, higher will be the bond energy and hence stronger will be the bond.

For example, the covalent radius of boron is estimated to be 83 pm and the bond length of B-B bond in $B_2 Cl_4$ is 175 pm with ΔL being negative. This indicates the bond is very weak. In other case, the metallic radius of rhenium is 137.5 pm and Re - Re bond length in $Re_2 Cl_8$ is 224 pm making $\Delta L \cong 31$ pm. This indicates the bond between Re and Re in $Re_2 Cl_8$ is very strong.

Bond energy can also be understood based on potential energy curve for a molecule. In the case of hydrogen a schematic potential energy diagram is given below with four different cases



Case 1): The two hydrogen atoms are well separated so that there is no interaction between them and the interaction energy is zero.

Case 2): The two hydrogen atoms are comparably very near resulting in attractive interaction.

Case 3): The interaction potential energy is minimum resulting in most stable configuration at a distance of about 74 pm resulting in average bond length.

Case 4): If atoms go even further, to avoid further overlapping of atomic orbitals and to maintain the stability of the molecule, a repulsive force develops between the atoms.

Because of attractive force in the case of (2) and repulsive force at case (4), molecule attains a stable, minimum energy configuration at case (3) with average separation of 74 pm. When this takes place, an average energy of 432 KJ/mol will be released. This is known as bond energy. Now if we want to take hydrogen from case (3) to case (1) i.e., if we want to break the bond to form individual atoms, energy of 432 KJ/mol has to be supplied.

Bond energies are very closely associated with electronegativity / electropositivity of participating atoms. As the electronegativity / electropositivity decreases down the group, the bond energies also decrease. This can be observed in the following table.

Bond	**Bond Energy (KJ /mol)**	**Bond**	**(KJ /mol) Bond Energy**
H – F	135	C - F	116
H - l	103	C - Cl	81
H – Br	87.5	C - Br	68
H – I	71	C - I	51
Li – F	1030	Na – F	910
Li - Cl	834	Na - Cl	788

Li – I	7305	Na – Br Na - I	732 682
K – F K- Cl K – Br K – I	808 701 671		

Bond energies also increase as the number of electrons participating in the bond increases. This can be observed based on the values given in the table below.

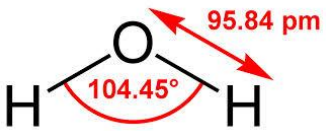
Bond	**Bond Energy (KJ /mol)**	**Bond**	**Bond Energy (KJ /mol)**
C – C	347	C – O	358
C = C	614	C = O	745
C ≡ *C*	839	C ≡ O	1070

Bond energy varies slightly depending on the environment i.e., the bond energy of the bond between carbon and oxygen is different in different molecules. This is shown in the table below

Bond	**(KJ /mol) Bond Energy**
C = O (CO_2)	192
C = O (aldehyde)	177
C = O (Ketone)	178
C = O (ester)	179
C = O (amide)	179
C = O (halide)	177

C. Bond Angles:

Bond angles play a very important role in determining molecular geometry. This gives the information about the orientation of one chemical bond with respect to another. The bond angle is defined as the angle between two bonds when three atoms bond together with two chemical bonds. In the case of water two hydrogen atoms are attached with one oxygen atom.



The angle between one O-H bond and another O-H bond is known as the bond angle. For water it is determined to be 104.45^o

Along with the bond angle normally one can also specify another angle associated with molecular geometry. That is torsional angle. For four atoms bonded to form a chain, the torsional angle is the angle between the plane formed by the first three atoms and the plane formed by last three atoms.

Bond angles and hence the molecular geometry is determined by quantum mechanical behavior of the electrons to form chemical bonds, atomic orbitals overlap through orbital hybridization. Depending on the orientation of atomic orbitals which participate in chemical bonding, the bonds orient. This leads to bond angle and hence a three dimensional geometry of the molecule.

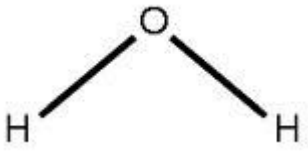
Some examples for bond angles are given below

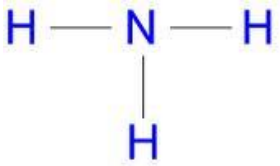
i) BF_3 $AlCl_3$ are planar, symmetric molecules. Hence their bond angle will be 120^o

ii) CO_2 $BeCl_2$ are also symmetric molecules in which four electrons participate in chemical bonding. Hence they are linear and their bond angle is 180^o

iii) CH_4 is the most simple hydrocarbon which is again symmetric. In this case the bond angle can be shown to be 109.5^o

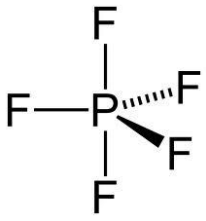
iv) In case of ammonia (NH_3) , water (H_2O) the bonds are not symmetric as in each bond only one pair of electrons participate and the remaining electrons are left over.





In these cases the bond angle cannot be determined using just geometry. It has been experimentally determined that the bond angles are 107^o for ammonia and 104.45^o for water

v) Phosphorus fluoride, PF_5 is a molecule which has the shape of trigonal bi pyramid with angles 120^o and 90^o.



5.7 Summary:

In this unit we have learnt

- Why chemical bonds are formed and when are they formed?
- Types of bonds
- Meaning of molecular structure
- Parameters of molecular structure
- Bond length, bond angle and bond energies

5.8 Questions for Self Study:

1) What is a chemical bond? Give a brief description of formation of chemical bonds
2) What is molecular structure?
3) Describe the parameters of molecular structure.
4) Write a note on bond length, its dependency and its variation
5) Write a note of bond energy, its dependency and its variation
6) Write a brief note on bond angle with examples.

5.9 References:

* Solid state physics – S.O. Pillai, New age International

* Concise Inorganic Chemistry – J.D. Lee, Wiley India Publication

Unit-6: Ionic bonds, ionic lattice energies and crystal lattice geometry

Structure

6.0 Objectives:

After studying this unit you are able to

- Explain the formation of ionic bond
- Identify properties of ionic compounds
- Evaluate the lattice energy of ionic compounds

6.1 Introduction:

According to the law of nature, the most stable state of a system is one which having minimum energy. Two or more atoms combines together to form a molecule because molecules posses less energy compare to the total energy of the individual atoms present in the molecule. Dalton attributed that the chemical combination is nothing but interaction between individual atoms. However this statement did not provide any indication about the manner in which the atoms attached themselves each other in a molecule. Franckland form is observation suggested that each element was characterized by a saturation capacity or valency and it is defined as the number of atoms of hydrogen with which one atom of a given element could combine. Kekule, extend this view and pointed out that valency is a fundamental and invariable property of an element. However the existence of compounds, such as PCl_3 and PCl_5; similarly $FeCl_2$ and $FeCl_3$, made it clear that valency of an element is not fixed. Rapid developments came when J.J.Thomson discovered the electron in 1897. He suggested that the chemical properties of the elements were somehow dependent on their electronic configuration. Inspired from J.J.Thomson discovery, Kossel investigated that the some elements, immediately following noble gases have tendency to lose one or more electron to form positively charged ions with noble gas electron configuration. Such elements are called electro-positive elements. Some elements, immediately preceding noble gases have tendency to gain one or more electrons to form negatively charged ions with noble gas configuration. Such elements are called electro-negative elements. When electro positive and electronegative elements are brought together, one or more electrons are transferred from electro-positive elements to electro-negative elements so that resulting charged ions has a stable configuration of the nearest noble gases. And the oppositely charged ions are held together by strong electrostatic force of attraction between them and resulting molecules are called ionic compounds or electrovalent compounds. In this unit we will learn more about formation, nature and properties of electrovalent bond.

6.2 Ionic bond or electrovalent bond:

A chemical bond is only some short of inter-atomic, inter-molecular, or inter-ionic attraction which holds the two constituents together. *When atoms with large electronegativity differences are brought together, electrons are transferred from low electronegativity (electro-positive) atoms to those of high electronegativity (electro-negative) atoms resulting in formation of opposite charged ions and there is a strong electrostatic force of attraction between oppositely charged ions. This electrostatic force binds the oppositely charged ions together is called electrovalent or ionic bond.*

Ionic bond can also defined as "A chemical bond formed due to the electrostatic attraction between stable ions formed by the complete transfer of electrons from one atom to another" it is important to remember that the electron lost or gain to form a ions between two atoms is always from the outermost shell.

An ion is an atom or group of atoms which is charged due to the loss or gain of one or more electrons. The atom which loses electron, it will contract (i.e., reduced in size), gets positive charge and called cation. On the other hand atom which gains electron will expand (i.e., increase in size), gets negative charge and called anion. For example in formation of sodium chloride molecule, an electron is transferred from sodium atom to chlorine atom. The resulting Na+ and Cl- ions possessing configurations of neon and argon respectively combine to form an electrovalent compound as shown below

Formation of ionic bond with other elements is shown in fig. 1.

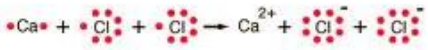


Fig. 1: Formation of ionic compounds

The anions formed in ionic compounds always achieve an inert gas configuration, whereas the cations formed may achieve any of the following configurations

a) Inert gas configuration (ns^2 or ns^2p^6)

b) Pseudo-inert gas configuration ($ns^2p^6d^{10}$)

c) Inert pair configuration [i.e., 18 + 2 electrons configuration] ($(n-1)s^2p^6d^{10}ns^2$)

d) $ns^2p^6d^x$ configuration where the sum of (2 + 6 + x) should be nine to seventeen

6.3 Conditions for the formation of ionic compound:

The formation of ionic compound C^+A^- is occur through the following steps,

i) Atom C give up an electron by absorbing energy equal to its ionization energy or ionization potential $(IP)_C$ and is converted in to cation C^+. Thus,

$$C + \text{Energy absorbed } [= (IP)_C] \rightarrow C^+ + e^-$$

ii) In the second step the atom A picks up the electron released from C and converted in to anion A^- by releasing energy equal to its electron affinity. i.e,

$$A + e^- \rightarrow A^- + \text{Energy released } [= -(EA)_A]$$

iii) In the final step cation C^+ and anion A^- combine together due to the electrostatic force of attraction and form a stable ionic crystal C^+A^-. Heat of formation of C^+A^- compound is equal to,

$-\frac{e^2}{r_{c+} + r_{a-}}$ is released. Here 'e' is the charges on C^+ and A^-, and r_{c+} and r_{a-} are the ionic radii of C^+ and A^- respectively. Thus,

$$C^+ + A^- \rightarrow C+A- + \text{energy released } \left(-\frac{e^2}{r_{c+} + r_{a-}}\right)$$

Thus the overall energy change, E_{ionc} in the formation of the ionic crystal C^+A^- is given by,

$$E_{ionic} = (IP)_C - (EA)_A - \left(-\frac{e^2}{r_{c+} + r_{a-}}\right)$$

The bonded ions C^+ and A^- are more stable than the free atoms C and A, therefore E_{ionic} is negative. Hence the value of $\left(-\frac{e^2}{r_{c+} + r_{a-}}\right)$ is always higher then $[(IP)_C - (EA)_A]$ i.e.,

$$\left(\frac{e^2}{r_{c+} + r_{a-}}\right) >> [(IP)_C - (EA)_A]$$

Therefore for the formation of a stable ionic compound C^+A^- (or ionic bond) the following conditions must be satisfied by C and A.

a) Atom C should have high tendency to lose electron. i.e, $(IP)_C$ should be low. Hence C should have electro-positive elements such as an alkali metal or alkaline earth metal.

b) Atom A should have high tendency to accept electron. i.e., $(EA)_A$ should be high. Hence atom A should be electro-negative elements such as halogens or elements of group VI A group elements.

6.4 properties of ionic compounds:

Some of the properties of ionic compounds are mentioned below:

a) Ionic compounds are soluble in polar solvents with high permitivities (dielectric constants). The energy of interaction of two oppositely charged ions is shown below

$$E = \frac{q^+ q^-}{4\pi r \varepsilon_0}$$

where q^+ and q^- are the charges, r is the distance of separation and ε_0 is the permittivity of the medium. For example, the permittivity of water is 7.25×10^{-10} $C^2m^{-1}J^{-1}$ giving relative permittivity of $82\varepsilon_0$ for water and that of liquid ammonia, equal to 2.2×10^{-10} $C^2m^{-1}J^{-1}$ corresponding to relative permittivity of $25\varepsilon_0$. Since the permittivity of water is more, the attraction between ions gets dissolved in water. But, the attractions between the solvent molecules and the ions are not strong enough to overcome the attractions holding the crystal together in organic solvents and hence, ionic compounds are insoluble in organic solvents.

b) Ionic compounds exhibit a very low conductance in solid state while they conduct quite well in molten state. This conductivity is due to the presence of ions that are free to move under the influence of an electric field. In the solid, the ions are bound strongly in the lattice and are not free to migrate and carry electrical current.

c) Ionic compounds generally have high melting points since ionic bonds usually are quite strong to break and the ionic bonds are omnidirectional. The high melting point of NaCl results from the strong electrostatic attractions between the Na^+ and Cl^- ions, and from the lattice structure.

d) Ionic compounds usually are hard but brittle.

6.5 Lattice Energy:

Each ion pair C^+A^- resulting from free atom C and A has a strong residual electric field, hence it will attract other ions pair and thus a large number of such ion pairs will arrange themselves in the most stable way within ionic crystal and cluster will formed and is called crystal lattice. In this process energy will be released. Thus the strength of attractive forces that operate between oppositely charged ions in the crystal is measured by a property called 'lattice energy. Hence *the decrease in energy that takes place in the process of bringing the ions from an infinite distance to their equilibrium position in the stable lattice is called lattice energy and is denoted by U.*

In other words the lattice energy of an ionic crystal C^+A^- may be defined as *the energy released when the correct number of gaseous cations C^+ and anions A^- are brought together from an infinite distance to form one gram mole of the solid crystal.*

a $C^{n+}(g)$ + b A^{n-} (g) $\rightarrow$ $C_aA_b(s)$ + Energy released (lattice energy U) in the case U is negative.

The lattice energy, U, is also the amount of energy required for complete separation of ions in one mole of a compound. i.e.,

$C_aA_b(s)$ + Energy given (lattice energy U) $\rightarrow$ a $C^{n+}(g)$ + b A^{n-} (g)

In this case U is positive and could be expressed in terms of kJ/mol. This quantity cannot be directly determined by experimentally, but it can be determined using Hess Law in the form of Born-Haber cycle. It can also be calculated from the electrostatic consideration of its crystal structure. For the reverse process, i.e., in the first case the energy released is called as the energy of crystallization, E_{cryst} . In other words, $U = - E_{cryst}$.

a $C^{n+}(g)$ + b A^{n-} (g) $\rightarrow$ $C_aA_b(s)$; E_{cryst} kJ/mol

The values of lattice energies (kJ/mol)for some ionic solids are shown in Table 1.

Table 1. Lattice energies of compounds of alkali and alkaline earth metal ions

Solid	U, kJ/mol	Solid	U, kJ/mol	Solid	U, kJ/mol	Solid	U, kJ/mol
LiF	1036	LiCl	853	LiBr	807	LiI	757
NaF	923	NaCl	786	NaBr	747	NaI	704
KF	821	KCl	715	KBr	682	KI	649
MgF_2	2957	$MgCl_2$	2526	$MgBr_2$	2440	MgI_2	2327

The lattice energy of a crystal depends on following factors, they are

i) Type of crystal structures,
ii) Charge on the ions and size of the ions.

The melting points of ionic solids are directly related to their lattice energies.

6.6 Theoretical calculation of lattice energy:

The theoretical treatment of the ionic lattice energy was proposed by Born and Lande. The derivation for lattice energy, known as Born-Lande equation is as follows:

The lattice energy of an ionic crystal is determined by coulombic interaction between all ions. (i.e., attractive forces between the oppositely charged ions and repulsive forces results from the interpenetration of outermost electron clouds while close packing).

Consider the formation an ionic pair, C^+A^- wherein the ions are separated by a distance, r. When the ions are approaches each other, at initial the attractive forces acting between them is directly proportional to the product of the charges carried by the cation and anion and inversely proportional to the distance of their separation. Thus the electrostatic energy of attraction is obtained from Coulomb's law shown below:

$$E = \frac{q^+ q^-}{4\pi r \varepsilon_0} \text{ ---------- (1)}$$

The energy is negative and becomes increases as the distance of separation between ions decreases. The variation of potential energy with distance of separation between a cation and an anion for an ionic compound like NaCl is shown in Fig.2.

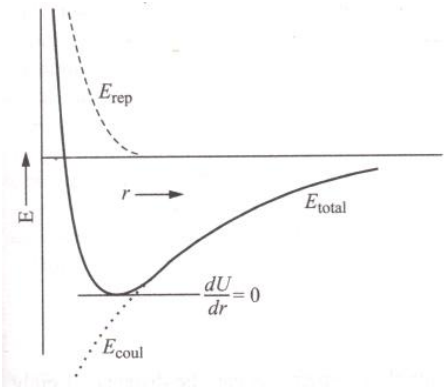


Figure 2: Energy curves for an ion pair

Since, it is common to express Z^+ and Z^- as multiples of the electronic charge,e =1.6×10^{-9} coulomb, the equation (1) is rewritten as

$$E = -\frac{q^+ q^- e^2}{4\pi r \varepsilon_0} \text{ ---------- (2)}$$

In an ionic crystal the force on any one ion will be determined not only by the oppositely charged ions which are directly surrounding it but also by the other ions (both positive and negative) at greater distance. Thus in ionic crystal not only two separate ions are to be considered but the whole crystal must be considered. Thus there will be more interactions than the simple one in an ion pair. The positive ions experience both attraction and repulsion from ions of opposite charge and ions of the same charge.

For example, let us consider the NaCl crystal, *r* be the distance between Na^+ and Cl^- ions. The nearest neighbors of Na^+ are 6 Cl^- ions at a distance $\sqrt{1}r$, 12 Na^+ ions at a distance $\sqrt{2}r$, 8 Cl^- at $\sqrt{3}r$, 6 Na^+ at $\sqrt{4}r$, 24 Na^+ at $\sqrt{5}r$, and so on. Thus, the energy due to one ion is

$$E = -\frac{q+q-e2}{4\pi\varepsilon_0 r}\left[\frac{6}{\sqrt{1}}+\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}+\frac{6}{\sqrt{4}}+\frac{2}{\sqrt{5}}+-----\right]\text{----------(3)}$$

where z^+ and z^- are the charges of the ions (=1 for NaCl); e is the charge of an electron (= $1.6022\text{x}10^{-19}$ C); $4\pi\varepsilon_o = 1.11265\text{x}10^{-10}$ $C^2/(J\ m)$ and the series shown in the bracket is called the Madelung constant, M. The above discussion is valid only for the sodium chloride (rock salt) structure type. This is a geometrical factor, depending on the arrangement of ions in the solid. The Madelung constant depends on the structure type, and its values for some structural types are given in Table 2.

Table 2. Madelung constants for some common crystal lattices

Solid	M	Anions : Cations	Type
NaCl	1.747558	6 : 6	Rock salt
CsCl	1.76267	8 : 8	CsCl type
CaF_2	2.51939	8 : 4	Fluorite
TiO_2	2.408	6 : 3	Rutile
Al_2O_3	4.1719	6 : 4	Corundum
ZnS	1.63806	4: 4	Zinc blende
ZnS	1.64132	4: 4	Wurtzite

As evident from the above Table, the value of A is evaluated only by the geometry of the lattice and is independent of ionic charge and radius.

Considering the Madelung constant, the energy of a pair of ions in the crystal is given by

$$E = \frac{-Aq^+q^-e^2}{4\pi r\varepsilon_0} \text{ ---------- (4)}$$

We know that unless there is repulsion energy to balance the attractive coulombic energy, no stable lattice can form. The repulsive energy is negligible at large distances but increases very rapidly as the ions approach each other closely. Born suggested that this repulsive energy could be expressed as follows:

$$E_R = \frac{B}{r^n} \text{ ---------- (5)}$$

where B is a constant and n is the Born exponent. This n is the number related to the electronic configurations of the ions involved. The values of n for inert gases and some common ionic solids are recorded in Table 3.

Table 3. Born exponent values for some ions and compounds

Element/ion	N	Ionic solid	N
He	5	LiF	5.9
Ne	7	LiCl	8.0
Ar, Cu^+	9	LiBr	8.7
Kr, Ag^+	10	NaCl	9.1
Xe, Au^+	12	NaBr	9.5

The total energy for a mole of the crystal lattice containing an Avogadro's number, N of ions is

$$U = E_C + E_R = -\frac{ANq^+q^-e^2}{4\pi\varepsilon_0 r} + \frac{NB}{r^n} \text{ ---------- (6)}$$

At the minimum in the curve,

$$\frac{dU}{dr} = 0 \text{ ---------- (7)}$$

This corresponds to the equilibrium situation. Therefore,

$$\frac{dU}{dr} = 0 = -\frac{ANq^+q^-e^2}{4\pi\varepsilon_0 r} - \frac{nNB}{r^n} \text{ ---------- (8)}$$

Since, the energy at the minimum is fixed, we can denote U_0 and r_0 to refer this energy and the equilibrium distance. From equation 8, we get

$$B = -\frac{ANq^+q^-e^2r^{n-1}}{4\pi\varepsilon_0 r} \text{ ---------- (9)}$$

$$U_0 = \frac{ANq^+q^-e^2}{4\pi\varepsilon_0 r_0}\left[1-\frac{1}{n}\right] \text{ ---------- (10)}$$

Equation 10 is known as the Born-Lande equation for the lattice energy of an ionic compound. Using this equation and the following data, the lattice energy of NaCl is calculated.

For NaCl: A=1.74756 ; N=6.022X10^{23} ions per mole (Avogadro's number), q^+= +1 for Na^+; q^- = -1 for Cl^-; $r_0 = r_{Na^+} + r_{Cl^-}$ = 2.814x10^{-10} m ; ε_0 = 8.854188x10^{-19} C

$N = n_{Na^+} + n_{Cl^-}/2 = [7+9]/2 = 8$; π = 3.14159

By substituting these values in equation 10, we get U_0 = -755 kJ/mol which is close to the experimental value of about -770 kJ/mol.

In the absence of knowledge of crystal structure, the appropriate Madulung constant, a reasonable estimation of the lattice energy can be obtained from the equation suggested by Kapustinskii as shown below:

$U_0 = [120{,}200\ \gamma q^+ q^-/(r_c + r_a)]\ [1-(34.5/r_c + r_a)]$ ---------- (11)

where γ is the number of ions per molecule of the compound (for example, 2 for NaCl, 3 for $CaCl_2$ and 5 for Al_2O_3), r_c and r_a are the radii of the cation and anion in pm, and q^+ and q^- are their charges. For NaCl, γ=2 and $r_c + r_a$ =281 pm. Substituting these values in equation 11, we get a lattice energy of -750 kJ/mol which is about 98% of the experimental value.

Born-Lande equation is modified for improving the repulsion. This is known as Born-Mayer equation and the same is shown below:

$$U_0 = \frac{ANq^+q^-e^2}{4\pi\varepsilon_0 r_0}\ [1-(0.345/r_0)] \quad \text{---------- (12)}$$

where $r_0 = r_c + r_a$.

6.7 Applications of lattice energy:

With the help of the lattice energy it is possible to estimate electron affinites, proton affintities and heats of formation. More applications are listed below.

1) In the discussion of the special properties of fluorine in relation to other halogens.
2) In the account of stabilities of metal hydrides, polyhalides and peroxides and superoxides.
3) In the derivation of crystal field stabilisation energies.
4) In the discussion of characterisation of high oxidation states of metals as fluorides and of their low oxidation states as iodides.

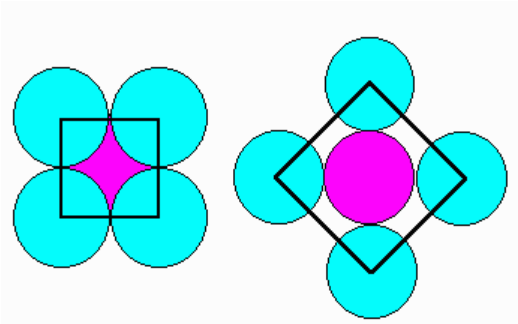
6.8 Relation between lattice energy and solubility of ionic solids:

The magnitude of lattice energy of an ionc solid gives an idea about its solubility in different solvents. For a solid to dissolve in a solvent the strong forces of attraction between its ions (lattice energy) must be overcome by the ion-solvent interactions. The salvation of ions is referred to in terms of salvation which is always negative i.e., in the process of salvation energy is released. The amount of salvation energy depends on the nature of the solvent. In case of non-polar (covalent) solvents, the salvation energy is small and hence is not sufficient to overcome the lattice energy of the solid. Consequently the solid does not dissolve in non-polar solvent. The salvation energy increases if the solvent has high dipole movement/ or high polarity. As a general rule for a solid to be able to dissolve in a particular solvent its

salvation energy must be greater than its lattice energy so that the latter may be overcome by the former.

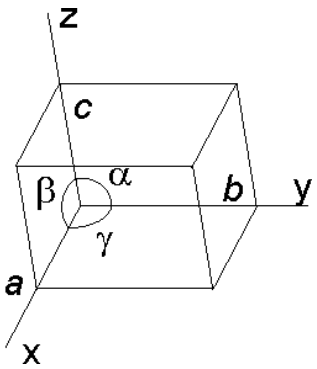
6.9 Crystal lattice or unit cell:

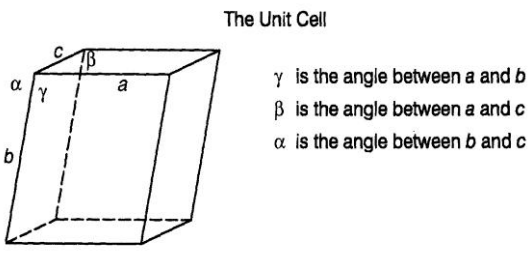
The reason for crystals form is the attraction between the atoms (ions). Because atoms (ions) attract one another it is often favorable to have many neighbors. Also because the atoms attract one another, there is a tendency to squeeze out as much empty space as possible and the empty spaces between the atoms are interstitial sites.



Crystal lattice is the periodic and systematic arrangement of atoms that are found in crystals. The crystal lattice can be considered as the points of intersection between straight lines in a three-dimensional network. The physical properties of crystals like cleavage, electronic band structure and optical transparency are predominantly governed by the crystal lattice. A unit cell is the smallest component of the crystal lattice and describes the arrangement of atoms in a crystal. The unit cell is characterized by its lattice parameters which consist of the length of the cell edges and the angles between them.

In a crystal the atoms are arranged in a regular repeating pattern. The smallest repeating unit is called the unit cell. Each unit cell is defined in terms of *lattice points***,** which is the points in space about which the particles are free to vibrate in a crystal. The entire crystal structure can be reconstructed from knowledge of the unit cell. The unit cell is characterized by three lengths and three angles. The quantities *a* and *b* are the lengths of the sides of the base of the cell and γ is the angle between these two sides. The quantity *c* is the height of the unit cell. The angles α and β are the angles between the base and the vertical sides of the unit cell.





The volume of the unit cell is readily calculated from knowledge of *a*, *b*, *c*, α, β, and γ.

The unit cells are classified into seven crystal systems namely

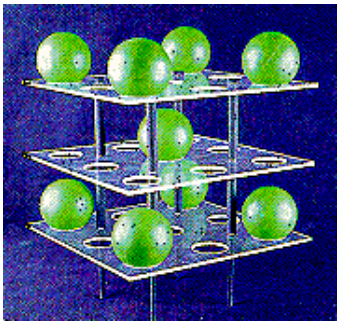
I) Cubic unit cell- there are three types of cubic unit cells which are simple cubic, body-centered cubic and face-centered cubic unit cell.

a) Simple cubic lattices- is the simplest unit cell and has 8 particles centered at the eight corners of the cubic cell.

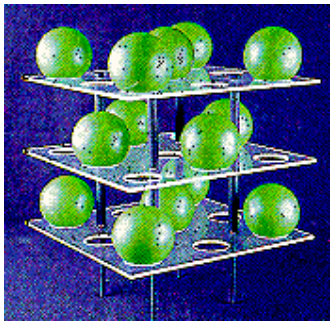
b) Body-centered cubic - there are eight particles on the eight corners of the unit cell (like in cubic-centered cell). In addition, there is a ninth particle in the center of the cubic unit cell.

c) Face-centered cubic unit cell- its structure has an additional structural particle at the center of each face.),

Simple cubic



Body-centered cubic



Face-centered cubic

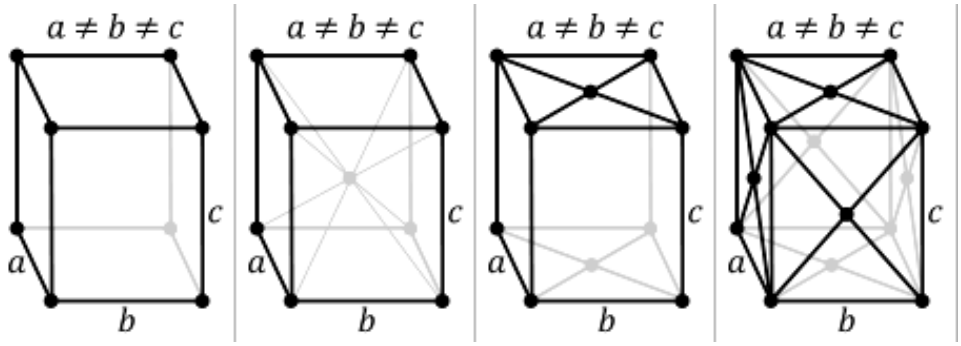
II) Orthorhombic- The Orthorhombic lattice has four types of unit cells.

a) The primitive cell (P) has fractional lattice points at each corner for a total of one lattice point per cell.

b) The base centered unit cell (C) has fractional lattice points at the cell corners and in the face-centered location of the basal planes for a total of two lattice points per cell.

c) The face-centered unit cell (F) has partial lattice points at the cell corners and at the center of each face for a total of four lattice points per cell, and

d) The body-centered orthorhombic cell (I) has partial lattice points at the cell corners and a lattice point in the body center of the cell for a total of two lattice points per cell.



Primitive **Body-centered** **Base-centered** **Face-centered**

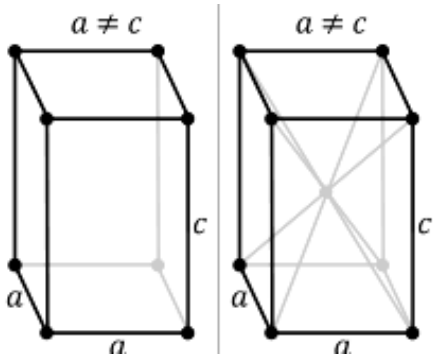
For each of these cells: a , b, c, have distinct values and a = b = g = 90^0

III) Tetragonal- Tetragonal unit cell is result from stretching a cubic unit cell along one of its lattice axis, therefore the cube becomes a rectangular prism with a square base. There are two types of tetragonal unit cell,

a) The simple tetragonal- which can be obtained from stretching the simple-cubic unit cell and

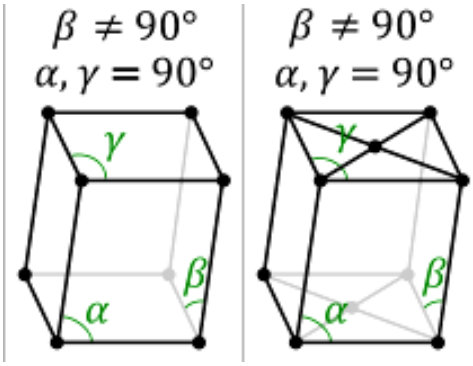
b) The centered tetragonal- which can be obtained from stretching either the face-centered or the body-centered cubic unit cell.

It is important to note that stretching of face-centered cubic would result in face-centered tetragonal, but face-centered tetragonal is equival to body-centered tetragonal.



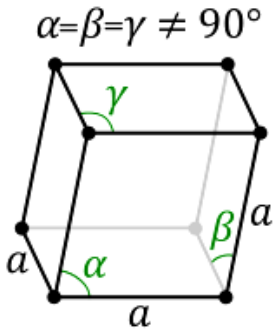
Primitive **Body-centered**

IV) Monoclinic unit cell- The monoclinic unit cell is described by vectors of unequal length, (as in the orthorhombic unit cell). Both form a rectangular prism with a parallelogram as their base. Therefore two pairs of vectors are perpendicular, while the third one makes an angle other than 90°. There are two monoclinic unit cells are exist, they are the primitive monoclinic and the centered monoclinic lattices with a rectangular and rhombic lattice, respectively.



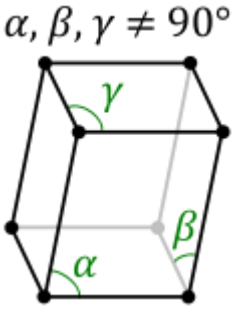
Primitive (P) **Base-centered (C)**

V) Rhombohedral unit cell- A Rhomohedral system is described by three non equal length vectors and also no two of which are orthogonal. The rhombohedral system can be explained as the cubic system stretched along a body diagonal. i.e., $a = b = c$; and $\alpha = \beta = \gamma \neq 90°$. There is only one rhombohedral type of unit cell.



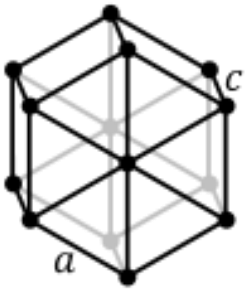
Rhombohedral

VI) Triclinic unit cell - Trigonal unit cell and Rhombohedral unit cell system are often confused with each other. The triclinic unit cell system is described by vectors of unequal length, as in the Rhombohedral unit cell system. In addition none of these three vectors are orthogonal to another. The triclinic unit cell is the least symmetric among all other unit cell system.



Triclinic

VII) Hexagonal unit cell- The hexagonal closest-packed structure is consists of a hexagonal unit cell, which has a diamond shaped or hexagonal base with sides of equal length ($a = b$). The base is perpendicular to the longest side (length c)) of the unit cell. An atom is centered on each corner of the unit cell and an atom is also centered inside the unit cell.



Hexagonal

The above information is outlined in Table 3

Table 3. Classification of space lattices by crystal system

Crystal system	Axial lengths and interaxial angles	Space lattice
Cubic	Three equal axes at right angles $a = b = c, \alpha = \beta = \gamma = 90°$	Simple cubic Body-centered cubic Face-centered cubic
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \alpha = \beta = \gamma = 90°$	Simple tetragonal Body-centered tetragonal
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \alpha = \beta = \gamma = 90°$	Simple orthorhombic Body-centered orthorhombic Base-centered orthorhombic Face-centered orthorhombic
Rhombohedral	Three equal axes, equally inclined $a = b = c, \alpha = \beta = \gamma \neq 90°$	Simple rhombohedral
Hexagonal	Two equal axes at 120°, third axis at right angles $a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	Simple hexagonal
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \alpha = \gamma = 90° \neq \beta$	Simple monoclinic Base-centered monoclinic
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	Simple triclinic

6.10 Packing Efficiency or Close packing:

In crystals structure, atoms are considered as hard spheres and in many crystals the atoms are pack together as tightly as possible. They will achieve this by forming a ***close-packed*** structure. In whatever way the constituent particles (atoms, molecules or ions) are packed, there is always some free space in the form of voids. Packing efficiency is the percentage of total space filled by the particles. The packing efficiency of a crystal structure provides information about how much of the available space is being occupied by atoms. It is usually represented by a percentage or volume fraction. The packing efficiency is given by the following equation

$$\frac{(number\ of\ atoms\ per\ cell) * (volume\ of\ one\ atom)}{volume\ of\ unit\ cell}$$

The two most efficient packing arrangements are the hexagonal closest-packed structure (hcp; Fig 5) and the cubic closest-packed structure (ccp; Fig 6). Consider the most efficient way of packing together equal-sized spheres and stacking close-packed atomic planes in three dimensions. For example, if plane A lies beneath plane B, there are two possible ways of placing an additional atom on top of layer B. If an additional layer was placed directly over plane A, this would give rise to the following series

...**ABABABAB**....

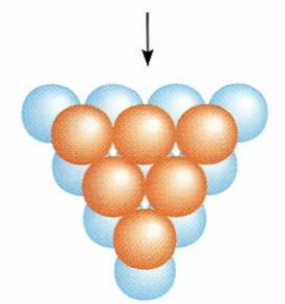


Fig. 5. Hexagonal closest-packed arrangement

This type of crystal structure is known as **hexagonal close packing (hcp)**.

In the hexagonal closest-packed structure, $a = b = 2r$ and $c = 4(2/3)^{1/2}\ r$, where r is the atomic radius of the atom. The sides of the unit cell are perpendicular to the base, thus $\alpha = \beta = 90^{o}$. The base has a diamond (hexagonal) shape corresponding with $\gamma = 120^{o}$.

However, if all the three planes are staggered relative to each other and that the sequence is repeated, then the following sequence arises

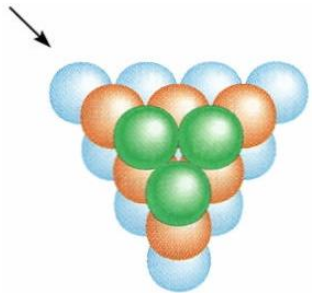


Fig. 6. Cubic close packing arrangement

ABCABCABC...,this type of crystal structure is known as cubic close packing (ccp). Both hcp and ccp are shown in Fig. 7 and Fig. 8.

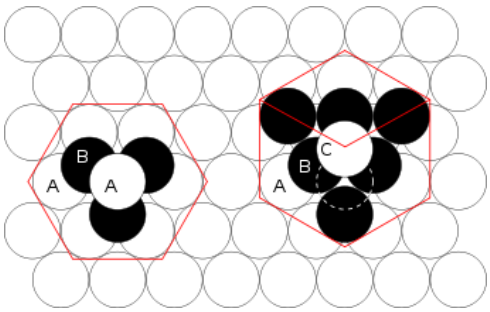


Fig. 7: Left panel-hcp packing and right panel – ccp packing

Ionic compounds are exists in various forms like salts, oxides, hydroxides, sulphates etc…., these compounds are held together by the electrostatic force of attraction between the positive and negative ions. Actually there will be repulsion if ions of same charges are adjacent and

attraction will occurs when positive ions are surrounded by negative ions and vice versa. The attractive forces between the opposite charge ions is maximum when each ion is surrounded by the greatest possible number of oppositely charged ions. The number of ions surrounded by particular ion is referred as coordination number and both positive and negative ions have the same coordination number when there are equal numbers of both positive and negative ions present in a compound, for example like in NaCl. But the coordination numbers for positive and negative ions are different numbers if both positive and negative ions present in a compound are not equal, for example like in $CaCl_2$.

6.11 summary of the unit:

Ionic bonds form when a metal reacts with a non-metal. Metals form positive ions by losing one or more electrons and non-metals form negative ions by gaining those electrons. The number of positive charges must equal the number of negative charges so that the compound has no charge overall. Ionic bonds are the *electrostatic* forces of attraction between oppositely charged ions. The oppositely charged ions are arranged in a regular way to form giant ionic *lattices*. Ionic *compounds* often form crystals as a result. The amount of energy required to separate a mole of the solid (s) into a gas (g) of its ions is called lattice energy denoted by symbol U. It separates the ions in a salt so that there is no interaction between the positive and negative ions. After the separation, the ions must be in a gaseous sate and the lattice energies are always positive. The same amount of energy is released when the ions are condensed from a gaseous state to a solid state. The released energy is called energy of crystallization (E_{cryst}).

In the ionic model, the bonding is described as the electrostatic interaction between charged spheres, whose sizes are given by the ionic radius. For determining an ionic radius, it is necessary to split up the internuclear separation into a contribution from the anion and a contribution from the cation. This is done by assuming the value of the radius of one ion, and then calculating the radii of other ions from this basis. the ionic radius of a given ion changes with coordination number: As the coordination number increases, the ions must get further away from the central ion in order to accommodate more of them, and hence the interionic separation increases, and the short ranged repulsion decreases, and the electron cloud on the central ion can expand, and hence the central ion increases in size. In an ionic structure each cation tends to surround itself with anions the number that can be grouped around it will depend on the relative size of the cations and anions. The Coordination Number (CN) is

defined as the number of anions that can fit around a cation. This number increases as the radius ratio increases. The number of anions that can 'fit' around a cation is related to the relative size difference between the ions, and this size difference can be described using the radius ratio, which is given by As the size (ionic radius r) of a cation increases, more anions of a particular size can pack around it. Thus, knowing the size of the ions, we should be able to predict a priori which type of crystal packing will be observed. We can account for the relative size of both ions by using the ratio of the ionic radii $\rho = \frac{r^+}{r^-}$. Anions are often larger than cations and therefore touch each other while close packing. Small cations then fit in the holes created between anions. The structures of many metals can be described as close packed arrays of spherical atoms. There are two alternative ways to maximize the packing efficiency of equally sized spheres. Cubic Close Packing (CCP) and Hexagonal Close Packing (HCP). Cubic close packing leads to a structure with a face centered cubic unit cell. This structure represents the simplest of all structures

6.12 Key words

Electrovalent bond; Lattice Energy; Crystal lattice; Unit cell; Packing efficiency.

6.13 Questions for self understanding

1) What is Electrovalent bond? Give five examples.

2) What are essential difference between an electrovalent bond and a covalent bond? Give two examples.

3) What elements are most likely to form ionic compounds?

4) Briefly discuss the conditions required for formation of ionic compounds.

5) What are the properties of ionc compounds?

6) What is Lattice Energy?

7) How theoretically calculate lattice energy of ionic compound?

8) Discuss relationship between lattice energy and solubility of ionic compounds.

9) What is unit cell?

10) Write a note on different types of crystal lattice?

11) What is close packing structure? Explain in brief.

6.14 References for further study

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Unit-7: The simplest covalent bonds: the hydrogen molecule ion and the hydrogen molecule

Structure

7.0 Objectives:

After studying this unit you are able to

- Explain the covalent bond formation
- Identify the properties of covalent compounds
- Explain the formation of hydrogen molecule ion
- Explain the formation of hydrogen molecule

7.1 Introduction:

Atoms having unpaired electrons tend to combine with other atoms with also have unpaired electrons. In this way unpaired electrons from both atoms are paired up. And the atoms involved in this pairing process attain a stable electronic arrangement. Two electrons shared between two atoms constitute a bond between them. The number of bonds formed by an atom is usually ame as the number of unpaired electrons in the ground state. However in some cases the atom may form more bonds than the number of unpaired electrons in the ground state. This happens by excitation of the atom i.e., electrons which were paired in the ground sate are unpaired and promoted into suitable empty orbital of higher energy. This increases the number of unpaired electrons and hence the number of bonds formed also increase. The shape of the molecule is primarily determined by the directions in which the orbitals involved in the bond formation are oriented. Electrons in the valence shell of the original atom which are paired are called lone pair.

In many cases the usual valency formula does not give a true representation of molecule or ion.

7.2 Covalent bond:

In 1919 Lewis suggested that there are atoms which attain inert gas configuration i.e., $1s^2$ or ns^2p^6 configuration by sharing one or more electron pairs with similar or dissimilar atoms. Each atom contributes one electron to the electron pair and has equal claim on the shared electron pair. Langmuir called the -electron pair bond a covalent bond. Thus the concept of covalent bond is known as Lewis Langmuir concept.

Therefore covalent bond is defined as *a chemical bond formed between two or more atoms in a molecule by sharing two electrons for each bond pair from each atom*.

A covalent bond is expressed in the formula by placing a bar (-) between the atoms bonded together. A covalent bond is non – polar and non – ionized because it is not formed by

transfer of electrons from one atom to the other and thus the molecule having the covalent bond does not acquire ions. For this reason covalent bond is also called non-polar bond.

7.3 Types of Covalent bond:

Covalent bond may be single covalent bond, double covalent bond or triple covalent bond. Double and triple covalent bonds are called multiple covalent bonds.

Single covalent bonds are formed by the sharing of only one electron pair between the bonded atoms e.g., H-H, Cl-Cl, F-F, ETC…

Double and triple covalent bonds are formed when the atoms bonded together by sharing two or three electron pairs respectively e.g., N≡N, O=O, HC≡CH, $H_2C=CH_2$, etc…

7.4 Polar and non-polar covalent bonds:

In a covalent bond between two similar atoms (A and A) the shared electron pair between them will be shared equally by both the atoms and hence the covalent bond will have no ionic character. Such type of bond is regarded as true covalent bond.

But a covalent bond formed either between two unlike atoms (A and B) or between two like atoms having different neighbors (e.g., C-atoms in $H_2C\text{-}CCl_3$ molecule), the shared bonded electron pair will not be equally distributed among both the atoms. This is because if atom A has a stronger attraction for electron pair (i.e., has greater electronegativity) than atom B, the shared electron pair will be attracted towards A and away from B. This type of permanent displacement of electron pair towards A in the covalent bond will develop a fraction of negative charge δ^- on atom A and a fraction of positive charge δ^+ on atom B. Therefore the molecule AB will be depicted is $A^{\delta-}$- $B^{\delta+}$ and the bond between A and B has some ionic character and is called called polar covalent bond.

The bond between the two like atoms (e.g., in H_2, Cl_2 etc molecules) is called a non-polar or homo-polar covalent bond or simply covalent bond. Actually covalent bonds also have slight ionic character e.g., the bond H-H in H_2 molecule also has about 2% ionic character which arises from the small contributions of the ionic resonance structures to the total structure of H_2 molecule.

In general when in a molecule AB the electronegativity of atom A = X_A is equal to that of B = X_B this will possible in a molecules having two identical atoms (eg H_2 Cl_2 molecules) then the bond A-B will be pure covalent. When $xA \neq x_B$ then the covalent bond formed between them will have some ionic character. The amount of ionic character will primarily depend on

the value of (X_A~X_B). Thus if $X_A > X_B$ the bond will be ionic and represented as A^- - B^+ and if $X_A < X_B$ then also it will be ionic and represented as A^+ - B^- but when $X_A = X_B$ then it is represented as A x B or A-B and the bond is purely covalent bond.

7.5 Characteristics of Covalent compound:

1. Covalent compounds are formed by the sharing of electrons between the atoms. Parts of their crystal lattice are molecules which are held by weak Van der Waals forces.
2. These are generally soluble in organic solvents.
3. Unlike electrovalent compounds which are solids these may be solids, liquids or gases. Their melting and boiling points are low.
4. These are generally soft easily fusible and volatile.
5. The covalent bond is directional and there is a possibility of position isomerism and stero isomerism amongst these compounds.

7.6 The overlap of atomic orbitals:

The following points are significant

1. The atoms which involve in forming a molecule are completely retain their identities in the resulting molecule.
2. The formation of a covalent bond is due to overlap of atomic orbitals. If the two atoms each having one unpaired electron come together and overlap, the spins of the two electrons get mutually neutralized resulting in the formation of a covalent bond which is localized between the two atoms. If the electrons present in the AO's have parallel spins no bond formation will occur ie no molecule will be formed.
3. If the AO's possess more than one unpaired electrons then more than one bond can be formed. Thus in N_2 molecule has three unpaired electrons hence there are three bonds in nitrogen molecule (N≡N).

1. Electrons which are already paired in the valence shell cannot participate in bond formation. However, they can participate only if they become unpaired without using much energy. It is known that the energy is released when a covalent bond is formed. If this energy exceed the energy needed to unpair the electron (by shifting it to the vacant orbital of slightly higher energy of the same main energy level) then more bonds are formed.

Thus N atom ($2s^2$, $2p_x1$, $2p_y^1$, $2p_z^1$) shares its three unpaired 2p-electrons with fluorine atom to form NF_3 but cannot form NF_5 since the second main energy level does not possess any other orbital which may accommodate one of the 2s electrons after promotion. On the other hand P($3s_2$, $2p_x^1$, $2p_y^1$, $2p_z^1$, $3d^0$) can form PF_5 since in the third main energy level 3d orbital is also available to accommodate one of the 3s electrons giving five unpaired electrons P ($3s^1$,$3p_x^1$,$3p_y^1$, $3p_z^1$, $3d^1$).

5. The strength of the covalent bond is directly related to the extent to which the two AO's can overlap in space. Maximum bonding orbitals overlap leads to more bonding electrons are concentrated between the nuclei, this minimize the nuclear repulsion and maximize the attractive forces between themselves. Hence the greater the overlap between the AO's the greater is the strength of the resulting covalent bond.

The extent of overlap of two AO's the represented by wave function ψ_A and ψ_B is expressed quantitatively by the overlap integral S which is given by

$$S = \int \psi_A \psi_B dr$$

When S is positive (i.e., S >0) there is a build-up of electron charge (ie electron density) between the nuclei of the two combining atoms and a bond can be formed. When S is negative ie S<0 there is a reduction in the electron density between the nuclei so that the repulsion between them is increased and they tend to move apart. When the overlap is zero (ie S=0) there is no net interaction (i.e., neither attraction nor repulsion) between the combining atoms.

For example if the radius of an s orbital is equal to 1 unit, then the length of a lobe of p orbital will be equal to $\sqrt{3}$ and the relative magnitudes or strength of the p and s orbitals would be in the ratio of $\sqrt{3}$:1. The bond strength is taken equal to the product of the magnitude of the bond orbitals of the two atoms forming the bond. Thus the strength of the s-s bond (i.e., bond formed by the overlap of s orbitals) is equal to 1 x 1 = 1 that of s-p bond equal to 1 x $\sqrt{3}$ = 1.732 and that of p-p bond equal to $\sqrt{3}$ x $\sqrt{3}$ = 3.

The relative bond strengths are as follows

s-s: 1 x 1 = 1, s-p: 1 x $\sqrt{3}$ = 1.732, p-p: $\sqrt{3}$ x $\sqrt{3}$ = 3

This shows that p orbitals can overlap with s or p orbitals more effectively than two s orbitals.

7.7 Overlap of atomic orbitals – sigma (σ) and pi (π) bonds:

Different types of overlap are possible depending on the type of atomic orbitals involved in bond formation. As a result of these overlap the covalent bond formed may be called as either a σ-covalent bond or a π -covalent bond.

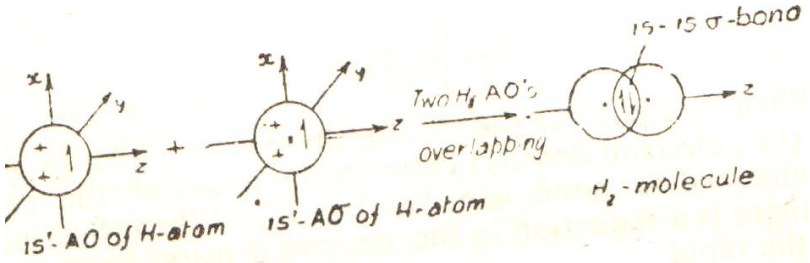
i) σ-bond

A covalent bond formed between two atoms by end to end or head to head overlap of atomic orbitals along their axes is called a σ-bond. All σ- bonds have axial symmetry. σ-bond is a strong bond, because maximum overlap of two orbitals along their axes.

If z-axis is the molecular axis,σ-bond is given by s-s, s-p_z and p_z-p_z overlaps. These σ-bonds are called (s-s)σ, (s-p_z)σ and (p_z-p_z)σ bonds respectively.

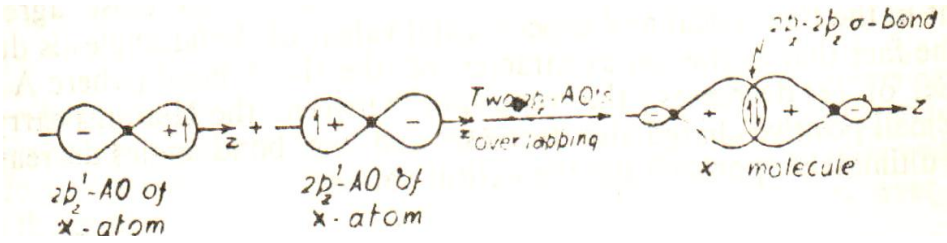
i) s-s overlap and structure of H_2 molecule

1s AO's of the two H atoms in a H_2 molecule overlap with each other and give a covalent bond between the



ii) p_z-p_z overlap and structure of X_2 molecule (X=F, Cl, Br, I)

The bond in X_2 molecule can be ascribed to the overlap of $2p_s$ AO's and is linearly directed ($X \rightarrow 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$) as shown in below figure.

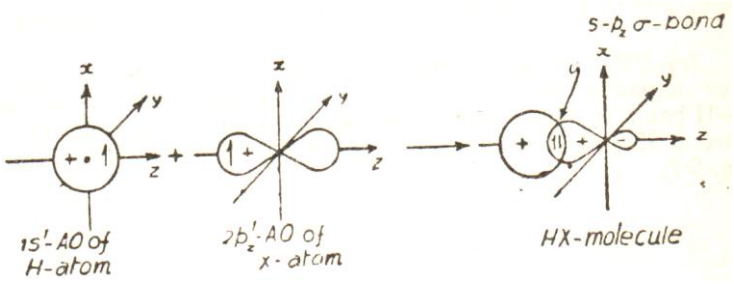


iii) s-p_z overlap

This type of overlap can be exemplified by considering the formation of HX (where X is F Cl Br or I) H_2O and NH_3 molecules.

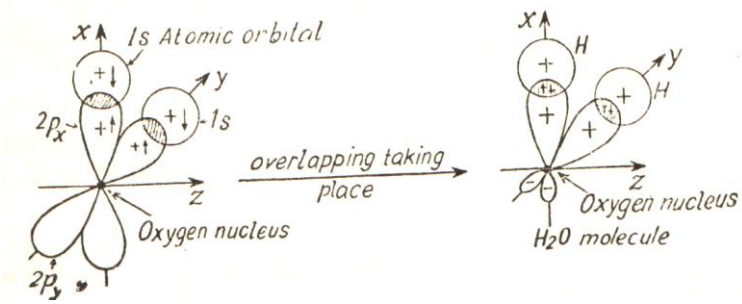
a) HX molecule (X is F, Cl, Br or I)

This molecule is also formed by the overlap of 1s – AO of H atom with $2p_z$ AO of X atom. Both the AO's are singly occupied



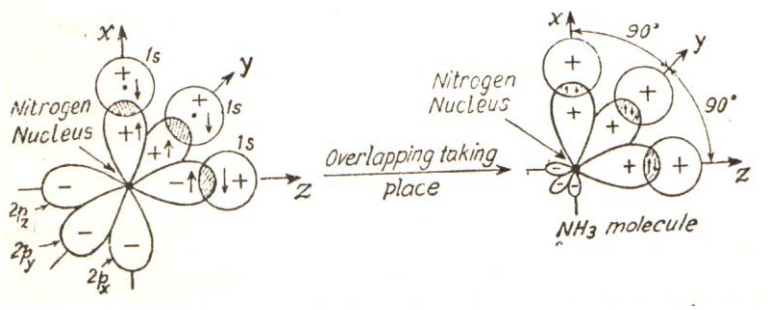
b) *Water Molecule (H_2O)*

O-atom with its valence shell configuration $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^2$ has two unpaired p electrons. These two AO's namely $2p_y$ and $2p_z$ overlap with two 1s orbitals of two H atoms and thus two s-p,σ-bonds are formed. Now since $2p_y$ and $2p_x$ AO's are at right angles to each other an angular structure with two O-H bonds inclined at 90^0 to each other would be expected, but the actual H-O-H angle, experimentally found in H_2O molecule is 105^0. The increase in the bond angle is due to the mutual electrostatic repulsion between the two H atoms which have fractional positive charge on them. This fractional positive charge is caused by the fact that the bond O-H is not purely covalent but has some ionic character. The experimental bond angles in other related molecules is H_2S = 92.2^0 H_2Se = 91.0^0 and H_2Te = 90^0, approach closely the expected theoretical value (i.e., 90^0). This close agreement in the theoretical and experimental value of bond angles is due to the fact that as the ionic character of the H-A bond where A is O, Se or Te decreases the repulsion between the H atoms carrying small positive charge also decreases and the bond angles decrease and ultimately approach the theoretical va



c) NH_3 molecule

There are three unpaired 2p orbital electrons in N ($2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$). Thus it is expected to form three N-H bonds in NH_3 molecule perpendicular to each other (i.e., inclined at 90^0) which would give a pyramidal shape to NH_3 molecule



The related molecules PH_3, AsH_3 and SbH_3 also have similar structure. The experimental H-N-H bond angle in NH_3 is 108^0 which is greater than the theoretical value of 90^0. The greater value of experimental bond angle is attributed to the mutual repulsion between the two H atoms. Bond angle of the related molecules (PH_3 = 93^0, AsH_3 = 92^0 and SbH_3 = 91^0) approach 90^0 due to the reason that as the repulsion between the two H atoms in these molecules on proceeding from $PH_3 \rightarrow SbH_3$ diminishes the bond angle H-A-H where A is P, As or Sb approaches 90^0.

ii) π-bond

A covalent bond formed between two atoms by the overlap of atomic orbitals along a line perpendicular to the molecular axis (side to side or lateral overlap) is called a π-bond.

If z axis is assumed to be the molecular axis π-bond is given by p_x-p_x and p_y-p_y over laps.

P_z and p_y orbitals which on overlapping respectively with p_x and p_y orbitals give π-bonds are referred to p_π-orbitals.

1) O_2 molecule

O-atom has $2s^2$, $2p_x^1$, $2p_y^2$, $2p_z^1$ configuration. Evidently $2p_z$ AO (singly occupied) of one O-atom will overlap with $2p_z$ AO of the other O-atom to give a p_z-p_z, σ- bond and the two $2p_x$ AOs singly occupied of both the O-atoms will overlap along a line perpendicular to z axis (molecular axis) to give another type of covalent bond known as π-bond. It is a p_x-p_x, π-bond Thus O_2 molecule has two covalent bonds, one is p_z-p_z σ-bond and the other is p_x-p_x π-bond.

2) N_2 molecule

N atom has $2s^2$, $2p_x^1$, $2p_{y1}$, $2p_z^1$ configuration. N_2 molecule has three covalent bonds one is σ- bond (2pz-2pz) and two π-bonds ($2p_x$-$2p_x$ and $2p_y$-$2p_y$)

7.8 Difference between σ-bonds and π-bonds:

1. σ-bond is formed by the overlap of orbitals by end to end overlap (along bond axes) while π-bond results from side to side overlapping of the orbitals.

2. Since the extent of overlapping of orbitals along the bond axes is always greater than the extent of overlapping at an angle 90^0, σ- bond is stronger than π-bond.

3. Electron cloud of a σ-bond is symmetrical about the line joining the two nuclei while that of a π-bond is unsymmetrical.

4. There can be free rotation of the atoms round the σ- bond. Such type of rotation is not possible round the π-bond since the electron clouds overlap above and below the plane of atoms.

5. σ-bond determines the direction of the bond and the extent of the internuclear distance. π-bond has no primary effect on the direction of the bond but shortens the internuclear distance

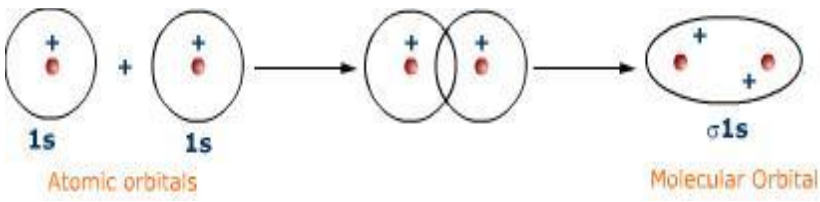
7.9 The hydrogen molecule ion:

The hydrogen molecule ion consists of an electron orbiting about two protons, and is the simplest imaginable molecule. Let us investigate whether or not this molecule possesses a bound state: *i.e.*, whether or not it possesses a ground-state whose energy is less than that of a hydrogen atom and a free proton. According to the variation principle, it is deduce that the H_2^+ion has a bound state if we can find *any* trial wave-function for which the total Hamiltonian of the system has an expectation value less than that of a hydrogen atom and a free proton.

7.10 Hydrogen molecule:

Hydrogen is the simplest atom. It has only 1 proton in the nucleus and 1 electron moving around it. The hydrogen molecule is also the simplest molecule it consists of 2 hydrogen atoms bound together.

Two independent hydrogen atoms get close enough, stick together by overlapping of s-orbitlas and form a molecule. In this case, the electrons that previously orbited in each of the atoms start to move around both nuclei. These electrons are responsible for the chemical bond between the two atoms. The two bonding electrons in this case outweigh the electrostatic repulsion between the 2 positive nuclei, so that a stable molecule is formed.



7.11 Summary of the unit:

Atoms having unpaired electrons tend to combine with other atoms with also have unpaired electrons. In this way unpaired electrons from both atoms are paired up. And the atoms involved in this pairing process attain a stable electronic arrangement. Two electrons shared between two atoms constitute a bond between them. The number of bonds formed by an atom is usually same as the number of unpaired electrons in the ground state. However in some cases the atom may form more bonds than the number of unpaired electrons in the ground state. This happens by excitation of the atom i.e., electrons which were paired in the ground sate are unpaired and promoted into suitable empty orbital of higher energy. This increases the number of unpaired electrons and hence the number of bonds formed also increase. The shape of the molecule is primarily determined by the directions in which the orbitals involved in the bond formation are oriented.

7.12 key words:

Covalent bond; Valence bond theory; σ-bond; π-bond.

7.13 Questions for self understanding:

1) What is Covalent bond?
2) Explain different types of Covalent bond?
3) What type of atoms are preferably form covalent bonds?
4) What are the Characteristics of Covalent compounds?
5) Discuss overlaping of atomic orbitals.
5) What are the necessary conditions for overlapping of atomic orbitals?
6) What are sigma and pi bonds?
7) What are the difference between σ-bonds and π-bonds?

7.14 References for further study:

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Unit-8: Atomic and molecular orbitals, electron dot structures, and the octet rule, Molecular geometry; hybridization, Bond polarity, Multiple bonds, Multicenter bonds, Metallic bonding.

Structure:

8.0 Objectives:

After studying this unit you are able to

- Predict the shape of the molecules using Valence bond theory
- Explain the octet rule and its importance
- Explain the concept of hybridization and characteristics of different hybrid orbitals

8.1 Introduction:

As you know, electrons are always moving. They spin very quickly around the nucleus of an atom. As the electrons zip around, they can move in any direction, as long as they stay in their shell**.** Electrons are constantly spinning in those atomic shells or orbitals, are specific distances from the nucleus. Chemical bonding is one of the most basic fundamentals of chemistry that explains other concepts such as molecules and reactions. Without it, scientists wouldn't be able to explain why atoms are attracted to each other or how products are formed after a chemical reaction has taken place. To understand the concept of bonding, one must first know the basics behind atomic structure.

All the atoms, except those of inert gases, participate readily in the formation of chemical bonding. It is necessary to understand the formation and nature of chemical bonds to arrive at the structures of molecules; study the interactions between them; and to understand the chemical reactivity. A chemical bond is formed by an atom to get more stability. Every atom tries to get more stability by lowering its potential energy. This can be achieved by making a bond. A chemical bond may be formed either by *sharing of electrons or by transfer of electrons* between atoms i.e., by *reorganization* of electrons between atoms.

8.2 Atomic orbitals:

An atomic orbital is a mathematical function that describes the wave-like behavior of either one electron or a pair of electrons in an atom. This function can be used to calculate the probability of finding any electron of an atom in any specific region around the atom's nucleus. The term may also refer to the physical region where the electron can be calculated to be, as defined by the particular mathematical form of the orbital.

Atomic orbitals can also be defined as the regions of space around the nucleus of an atom where an electron is likely to be found. Atomic orbitals allow atoms to make chemical bonds. The most commonly filled orbitals are *s, p, d,* and *f. s* orbitals have no angular nodes and are spherical. *P* orbitals have a single angular node across the nucleus and are shaped like dumbbells. *D* and *f* have two and three angular nodes, respectively. Only two electrons will

be found in any orbital space as defined by the Pauli Exclusion Principle. Once a shell of orbitals is completely filled, a new set of orbitals (*2s, 2p,* and so on) is available. *2p* would have one angular node, like *1p,* but also one radial node.

8.3 Molecular orbitals:

When two isolated atomic orbitals (A.Os) of two atoms having similar energy and symmetry combine linearly with each other by linear combination of atomic orbital (LCAO) method, two M.Os are obtained.

If both the atoms are of the same element that is called homo-nuclear diatomic molecule or ion (e.g. H_2, H_2^+, H_2^-, N_2, O_2, O_2^+, O_2^- etc). If both the atoms are of the different elements that is called hetero-nuclear diatomic molecular or ion (e.g. CO,NO, HF, CN^-, NO^+, NO^- etc)

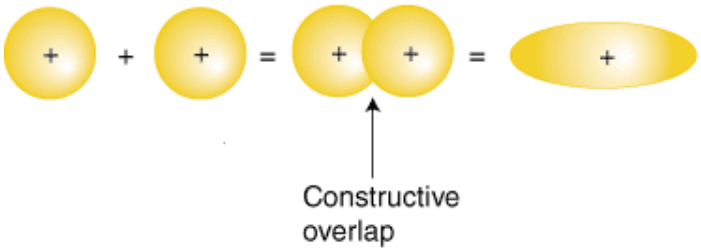
When three A.Os of similar energy and symmetry are combining with one another, three M.Os are obtained. Therefore the number of M.Os obtained is always equal to number of A.Os combining together.

8.4 Linear combination of Atomic Orbital (LCAO):

The molecular orbitals are obtained by the methods of LCAO. Suppose two atoms A and B form AB molecule. Their A.Os are represented by ψ_A and ψ_B respectively. There are two ways of their combination.

(a) *Additive overlap*

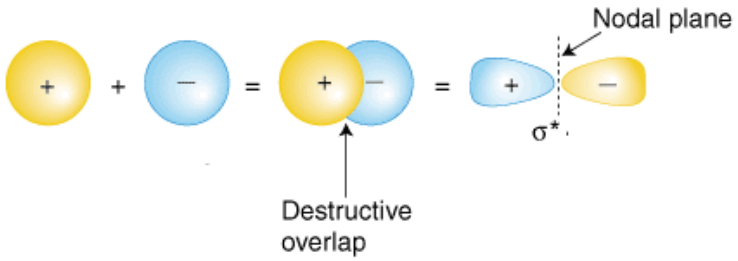
It is also called as positive overlap or ++ overlap. In this type of linear combination, the positive lobe (i.e.the lobe having +sign) of ψ_A overlaps with the positive lobe of ψ_B thus a molecular orbital is formed. This molecular orbital has lower energy than that of atomic orbitals of atoms A and B due to attraction between the nuclei of A and B. Such type of molecular orbital are known as bonding molecular orbital (BMO) and represented by ψ_b or σ_b



(b) *Subtraction overıap*

It is also known as negative overlap or +- overlap. In this type a molecular orbital is formed by linear combination the positive lobe of ψ_A overlapping with the negative lobe of ψ_B. This molecular orbital has higher energy than that of two atomic orbitals of atoms A and B due to

repulsion between the nuclei. Such type of molecular orbitals are known as anti-bonding molecular orbitals (ABMO) and represented as ψ_a or ψ^* or σ^*

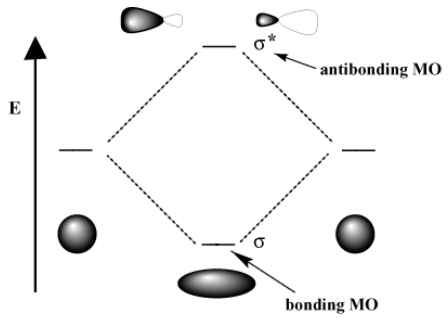


The formation of BMO and ABMO by the linear combination of ψ_A and ψ_B may be represented as:

$$\psi_b = \psi_A + \psi_B \text{ (++ overlap or constructive over lap)}$$

$$\psi_a = \psi_A - \psi_B \text{ (+- overlap destructive over lap)}$$

The relative order of the energy of ψ_A, ψ_B, ψ_b and ψ^* is shown in below figure



8.5 Conditions for the combination of atomic orbitals:

Any pair of atomic orbitals, one from each atom will combine to form two molecular orbitals [one bonding and one anti-bonding]. The combinations of AOs are subject to the following conditions.

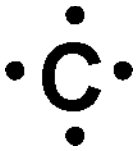
i) The combining orbitals have comparable magnitude of energies. According to this a homonuclear diatomic molecule will not be formed by the combination of 1s-orbital of one atom with 2s-orbital of another atom. Similarly 2s-orbital of one atom will not combine 2p-orbital of another atom because 1s and 2s and 2p-orbitals have very different energies. This is however possible in a heteronulcear diatomic molecule.

ii) The orbitals must overlap as much as possible. The greater the overlap of atomic orbitals, the greater is the build-up of charge between the nuclei.

iii) The orbital must have the same symmetry with respect to the molecular axis. According to this, z-axis is generally taken as the molecular (i.e., inter-nuclear) axis and x- and y-axes will be perpendicular to the molecular axis.

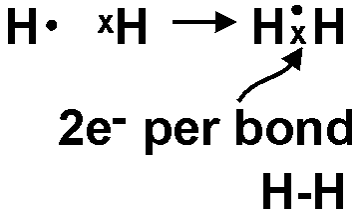
8.6 Electron dot structure:

It is a pictorial representation of the valence electron configuration around an atom. Valence electrons are represented by dots placed around the chemical symbol as shown in below figure

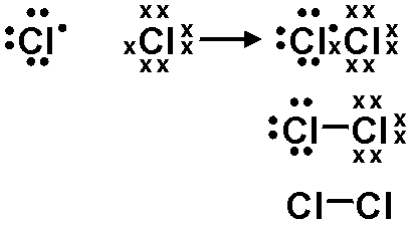


Electrons are placed up to two on each side of the elemental symbol for a maximum of eight, which is the number of electrons in a filled s and p shell. We place a single electron on each side before pairing them up (this is related to Hund's rule). Period one (hydrogen and helium) represents an exception where only a maximum of two electrons are placed on one side of the element.

For example i) H_2 molecule



i) Cl_2 molecule

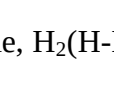
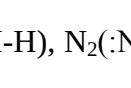


8.7 The Octet Rule:

It is found that when two atoms form covalent bonds, they attain an inert configuration with an octet electrons i.e., ns^2np^2-configuration is attained. This is known as octet rule.

In most of the cases, through the covalent linkage formation each of the combining species attains the octet i.e., $ns^2\ np^6$ configuration. If the species already bears the octet configuration, it will not display any tendency to form covalent linkage. In the case of hydrogen the inert

gas configuration of helium i.e., ns^2 is attained. This is very often referred to as the rule of duplet. There are a lot of molecules in which the rule of octet and duplet have been satisfied.

For example, H_2(H-H), N_2(:N≡N:), O_2(), CO_2(), H_2O(H-  -H), :NH_3, CCl_4, etc.

Deviation from the octet Rule

There are number of molecules in which the combining species or atoms have less than eight electrons (and they are called incomplete octet) or more than eight electrons (and they are called expansion of octet) in the covalently bonded molecules.

Incomplete Octet

In the molecules such as $BeCl_2$, BBl_3 and NO (:N=O) the central atoms i.e., Be, B and N bear four six and seven electrons respectively. It is important to note that other atoms except the central ones in the above compounds maintain the octet rule. A large number of compounds formed by Be (quartet), M (sextet) where M = B Al, Ga are known to form incomplete octets. Therefore these compounds are referred as electron deficient compounds and they are characterized by a tendency to receive back a lone pair electron to attain the octet. Hence the electron deficient compounds are called Lewis acids.

Expansion of Octet

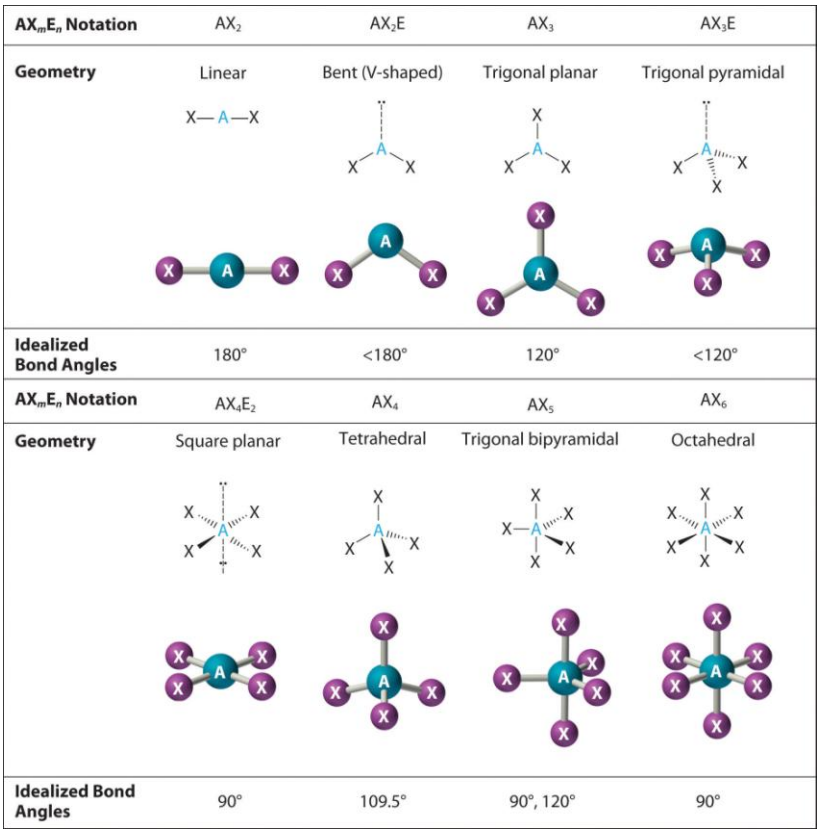
In the compounds like PCl_5 ClF_3, SF_6, SiF_6^{2-} etc…, the central elements P, Cl, S and Si are bearing ten, twelve and twelve electrons respectively and display the expansion of octet Similarly in OsF_8 there are sixteen electrons around Os. Here also except the central atoms all other atoms satisfy the octet rule.

8.8 Molecular geometry:

The specific three dimensional arrangement of atoms in molecules is referred to as molecular geometry. Molecular geometry can also be defined as the positions of the atomic nuclei in a molecule. Molecular geometry is associated with the specific orientation of bonding atoms. A careful analysis of electron distributions in orbitals will usually result in correct molecular geometry determinations. In addition, the simple writing of Lewis diagrams can also provide important clues for the determination of molecular geometry

Electron pairs around a central atom arrange themselves so that they can be as far apart as possible from each other**.** The valence shell is the outermost electron-occupied shell of an atom that holds the electrons involved in bonding. In a covalent bond, a pair of electrons is

shared between two atoms. In a polyatomic molecule, several atoms are bonded to a central atom using two or more electron pairs. The repulsion between negatively charged electron pairs in bonds or as lone pairs causes them to spread apart as much as possible. No of bonding electrons on the central atom and the poosible molecular geometry is listed in below table



8.9 Hybridization:

Consider a methane molecule (CH_4). In methane carbon atom forms 4 covalent bonds with 4 hydrogen atoms. The electronic configuration of carbon is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$ i.e., there are only two unpaired electrons hence its valency should be two. The only way obtain tetravalence is to excite the atom, then its configuration becomes $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$. In this configuration also there is one difficulty that three of the electrons have 'p' orbitals and the fourth one has 's' orbital. Therefore three bonds should be of one kind and the fourth one should be of a different kind. Also the mutual angles as calculated for p-p bonds and s-p bonds are 90^0 and $125^0$14' respectively. But all the C-H bonds angle in methane is equivalent and is equal to $109^0$28'. To solve these problems we mix the s and p orbitals and redistribution of energy takes place in such a way that all the four orbitals become equvilent. This phenomenon is known as hybridization. Therefore *mixing of pure atomic orbitals to give equal number of*

hybrid orbitals is referred to as hybridization. Since, in this hybridization there are one s and three p orbitals hence it is called as sp^3 hybridisation. The orbitals are known as sp^3 hybrid orbitals.

The energy of the hybrid orbitals is higher than the atomic orbitals in excited state but when hybrid orbitals are overlapped by the orbitals of the surrounding atom (i.e., bond formation takes place) the energy decreases too much and the bond becomes stable.

8.10 Hybridization rules:

The following are the rules for hybridization of atomic orbitals.

1. The orbitals of only similar energies belonging to the same atom or ion can be mixed to form hybrid orbitals. Dissimilar energies orbitals may bring hybrids but the exact nature cannot be defined.
2. Hybridization is a process of mixing orbitals of single atom or ion not like molecular orbital formation.
3. During hybridization we mix a certain number of orbitals as per requirement.
4. The number of atomic orbitals mixed together always equal to the number of hybrid orbitals obtained.
5. All the hybrid orbitals are similar but they are not necessarily identical in shape. They must differ from one another mainly in orientation shape.
6. Once an orbital has been used to build a hybrid orbital is no longer available to hold electrons in its pure form.

8.11 Types of Hybridization:

Different types of hybridization are known which are given in the following Table

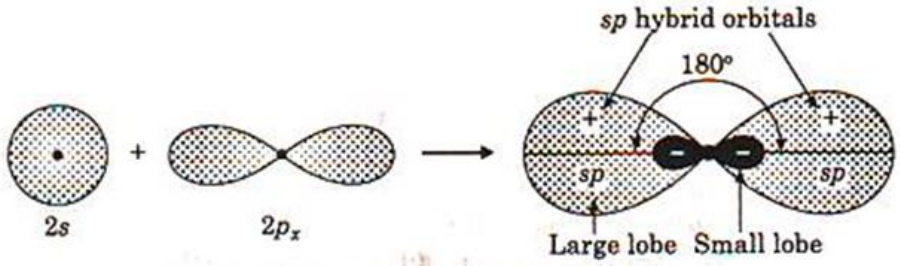
Hybridisation

Type of hybridisation	No. of hybrid orbitals obtained	Bond angle	Relative bond strength*	Structure	Examples
sp	2	180°	1.93	Linear	$BeCl_2$, CO_2, C_2H_2, $HgCl_2$, CN^-, N_3^-, $[Ag(NH_3)_2]^+$,
sp^2	3	120°	1.99	Plane triangle	SO_3, BF_3, $AlCl_3$, CO_3^{2-}
sp^3	4	109°28′	2.00	Tetrahedral	CH_4, C_2H_6, SO_4^{2-}, ClO_4^-
sp^2d	4	90°	2.69	Square planar	$[Ni(CN)_4]^{2-}$
sp^3d	5	120° and 90°	Varies	Trigonal bipyramidal	PCl_5, PF_5
sp^3d^2	6	90°	2.93	Octahedral	SF_6, $[Fe(CN)_6]^{4-}$
sp^3d^3	7	72° and 90°	–	Pentagonal bipyramidal	IF_7

*For s and p orbitals its values are 1.00 and 1.73 respectively.

a. sp-hybridisation

Formation for hybrid orbitals by mixing up of one 's' atomic orbital and one 'p' atomic orbital is called sp-hybridisation. In this type of hybridisation one 's' and one 'p' atomic orbital (if x-axis is the molecular axis then it is p_x orbital) of the valence shell of central atom of the given molecule or ion combine form two 'sp' hybrid orbitals as described in below figure.



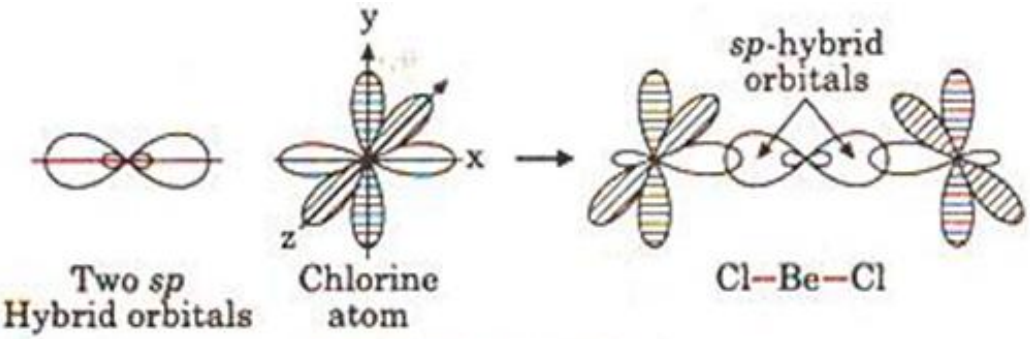
Formation of two *sp*-hybrid orbitals.

Characteristics of sp hybrid orbitals

1. Two sp hybrid orbitals [sp (1) and sp (2)] are completely equivalent and symmetrical.
2. These are stronger than pure s and pure p orbital from which it is formed after hybridisation. [Its relative power of overlapping is 1.93 with respect to s orbital].
3. These hybrid orbitals are collinear i.e., angle between the hybrid orbitals is 180^0.
4. It is oval shaped. In sp hybrid orbital one lobe is bigger while other is smaller. The bigger lobe is very large with respect to p orbital hence it has higher degree of overlapping. Thus it forms stronger bond.

Example: Formation of $BeCl_2$ molecule. In this molecule Be is the central atom whose electronic configuration is $1s^2\ 2s^2$. It does not have any unpaired electron therefore Be should not form compounds of the type $BeCl_2$. In order to explain formation $BeCl_2$, it is assumed that Be comes in excited state in which its electronic configuration becomes 1s2, $2s^1 2p_x^1$ now it has two unpaired electrons therefore $BeCl_2$ can be formed.If $BeCl_2$ is formed under this condition then the two bonds Be-Cl will be of different nature due to different type of overlapping ie s-p and p-p overlapping.. But both these bonds are identical (ie equal strength and bond length). It is explained by hybridisation. Therefore one 2s and one $2p_x$ orbitals of Be combine to form two identical sp hybrid orbitals with one electron each. These orbitals have higher energy than excited Be atom. Now these half filled sp hybrid orbitals overlap with two half filled 'p' orbitals of two chlorine atoms ($1s^2,2s^2,2p^6,3s^2,3p_x^2,3p_y^2,3p_z^1$) to form

two Be-Cl bonds by sp-p overlap. Thus hybridisation in $BeCl_2$ explains that two Be-Cl bonds are of equal strength with bond angle 180^0. Therefore $BeCl_2$ is a linear molecule.

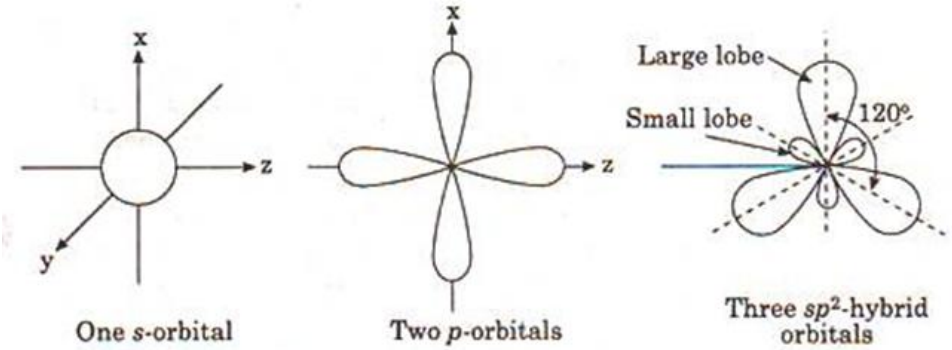


Formation of $BeCl_2$ molecule.

Other examples of sp hybridization molecules are CO, CO_2, C_2H_2, HCN, CN N_3^-, N_2 etc…,

b. sp^2 – Hybridisation

Formation for hybrid orbitals by mixing up of one 's' atomic orbital and two 'p' atomic orbital is called sp^2-hybridisation. In this type of hybridisation one 's' and two 'p' orbitals of the valence shell of central atom of the given molecule (or ion) combine to form three sp^2 hybrid orbitals as described as follows.



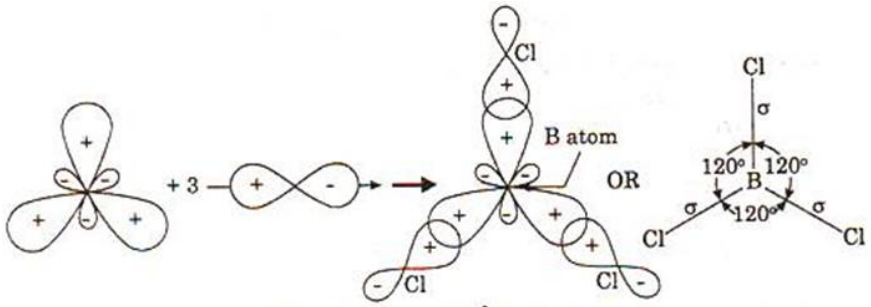
Formation of three sp^2 hybrid orbitals.

Characteristics of sp^2 hybrid orbitals:

1. Three sp^2 hybrid orbitals $sp^2(1)$ $sp^2(2)$ and $sp^2(3)$ are completely equivalent and symmetrical.
2. These are stronger than pure s and p orbitals from which it is formed after hybridisation. [Its relative power of overlapping is 1.99 with respect to s orbital].
3. These hybrid orbitals are planner with bond angle 120^0.

4. Since in this case contribution of p-orbitals is more hence it is *less oval* than sp-hybrid orbital. As usual in this case also one hybrid orbital is bigger while other one is smaller and it forms stronger bond.

Example: The formation of BCl_3 molecule. In this case B is the central atom whose electronic configuration is $1s^2$, $2s^2$, $2p^1$. It has only one unpaired electron therefore B-Cl can easily be formed but formation of BCl_3 compound is not. In order to explain the formation of BCl_3 it is assumed that B atom comes in excited state in which its electronic configuration becomes $1s^2$, $2s^1$, $2p_x^1$, $2p_y^1$. In this state B has three unpaired electrons hence formation of BCl_3 become possible. Suppose BCl_3 is formed under above mentioned condition, one B-Cl bond must be differs from other two B-Cl bonds. This is because of different type of orbitals overlapping [i.e., s-p and p-p overlapping]. But all the three bonds in BCl_3 molecule are identical [ie equal strength and bond length]. It can be explained only by hybridization as follows: one 2s and two 2p orbitals of B atom combine to form three identical sp^2 hybrid orbitals with one electron each. These orbitals have higher energy than excited B atom. Then the half filled sp^2 hybrid orbitals overlap with three half filled p orbitals of three chlorine atoms ($1s^2$, $2s^2$, $2p^6$, $3p_x^2$, $3p_y^2$, $3p_z^1$) to form three B-Cl bonds by sp^2-p overlap. Thus hybridisation in BCl_3 explains that three B-Cl bonds are of equal strength with bond angle 120^0, it is a planar molecule.

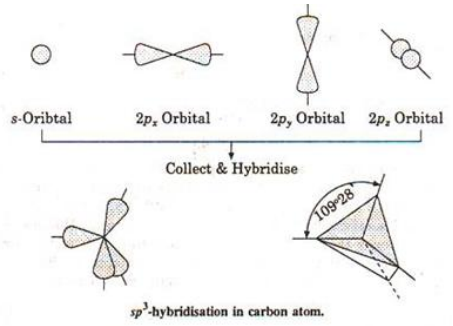


Formation of BCl_3 by sp^2-hybridisation.

Other examples are CO_3^-, CH_3^+, C_2H_4, SO_3 etc…

c. Sp^3 hybridization

Formation for hybrid orbitals by mixing up of one ‘s’ atomic orbital and three ‘p’ atomic orbital is called sp^3-hybridisation. In this type of hybridization one s and 3p orbitals of the valence shell of central atom of the given molecule (or ion) combine to form 4 sp3 hybrid orbitals as follows:



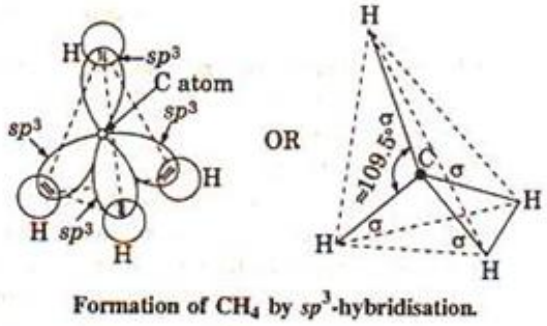
sp^3-hybridisation in carbon atom.

Characteristics of sp^3 hybrid orbitals:

1. All the four sp^3 hybrid orbitals $sp^3(1)$, $sp^3(2)$, $sp^3(3)$ and $sp^3(4)$ are equivalent and symmetrical.
2. sp^3 hybrid orbitals are directed towards the four corners of a regular tetrahedron and the angle between each pair of them is 109^0 28' or 109^0 5'
3. Their relative power of overlapping is 2.00 therefore sp^3 hybrid orbitals are stronger than sp and sp^2 hybrid orbitals.
4. In sp^3 hybridisation, the contribution of p orbitals is 75% it is still more than that of sp^2 hybridisation. Hence its shape is almost same as that of the parent p orbitals expect that the bigger lobe in sp^3 hybrid orbital is somewhat more spread and shorter in length than that in the pure p orbitals.

Example: the formation of CH_4 molecule.

In this molecule C atom is the central atom whose electronic configuration is $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$. It has only two unpaired electrons therefore CH_2 molecule should be formed. But CH_4 molecule is well known stable compound. In order to explain formation of CH_4 it is assumed that C atom comes in excited state $1s^2$, $2s^1$, $2px^1$, $2p_y^1$, $2p_z^1$ in this state it has four unpaired electrons. Therefore CH_4 molecule can be formed. However if CH_4 molecule is formed in this manner then one C-H bond differs from rest of the three C-H bonds due to different types of overlapping [ie s-s and s-p overlapping]. The four bonds in CH_4 molecule are identical [i.e, of equal strength and bond length]. It is explained only on the basis of hybridization as follows: one 2s and three 2p orbitals of C atom combine to form four identical sp^3 hybrid orbitals with one electron each. These orbitals have higher energy than excited C atom. Then these half filled sp^3 hybrid orbitals overlap with four half filled s orbitals of four hydrogen atoms ($1s^1$) and form four C-H bonds by sp^3-s overlapping. Thus the four C-H bonds CH_4 are equal strength with bond angle 109^0 28' and it has tetrahedral geometry.



Formation of CH_4 by sp^3-hybridisation.

Other examples of sp^3 hybrid molecules are C_2H_6, CCl_4, SiH_4, NH^+_4, SO_4^{2-}, ClO^-_4 etc

8.12 Bond polarity:

Bond polarity is a chemistry term that can be defined as a covalent bond between two atoms in which the electrons shaping the bond are unevenly distributed. As a result, the molecule then has a slight electrical dipole instant where one end is somewhat positive and the other is slightly negative

When two atoms of different elements are linked by a covalent bond, the shared electrons are not attracted equally by the two nuclei of bonding atoms. Due to unequal distribution of electron cloud, one end of the molecule acquires partial positive charge and the other end acquires equal partial negative charge. The polarity of bond gives partial ionic character. The percentage of partial ionic character depends upon the difference of E.N. of two atoms join with each other through a covalent bond

For example;

1. **HCl molecule:**

E.N. of H = 2.1

E.N of Cl = 3.0

Due to difference of E.N., the ability Cl^-atom to attract shared pair of electron is greater than that of H-atom. Therefore, covalent bond in HCl has ionic character. In HCl, covalent bond is 17% to 18% ionic.

1. HF molecule:

E.N. of H = 2.1

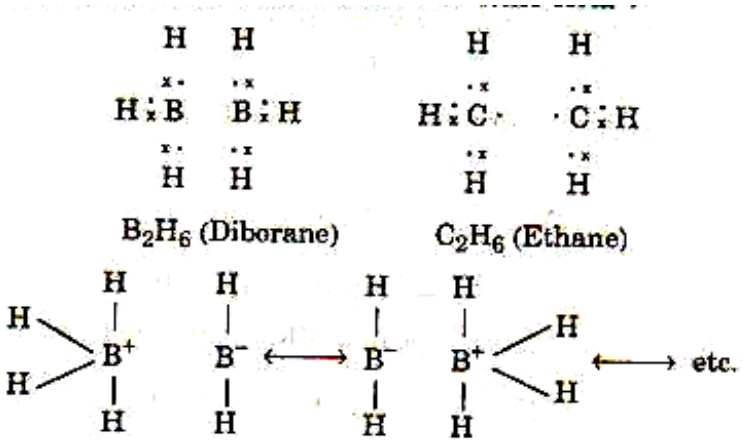
E.N. of F = 4.0

In this example difference of E.N. is greater as compare to HCl. Therefore, ionic character of HF is 64%. Ionic character of covalent compound affects properties of these compounds. For example viscosity, M.P., B.P. of compounds having ionic character are higher than that of non-polar compounds.

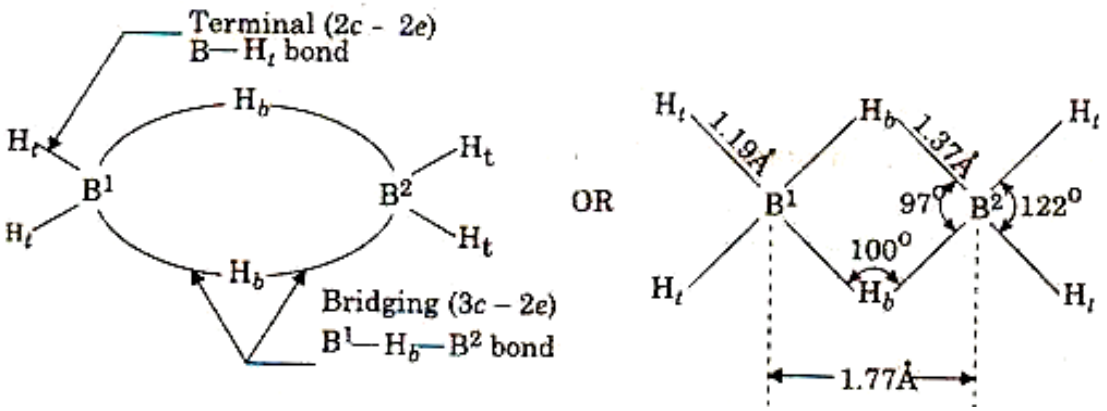
8.13 Multicenter bond:

A bond formed between three, and sometimes more atoms that contains only a single pair of electrons is called multicenter bond. The structure of boranes can be explained by considering them to be electron-deficient compounds containing multicentre bonds.

The structure of the diborane is of great interest. The diborane is an electron deficient compound i.e. there are not enough valency electrons to form the expected number of covalent bonds. The following structures were proposed for diboranes the ethane like structure of diborane and the ionic form



These structures have lack of experimental support, hence treated as incorrect one. $B_2H_4^-$ anion is isoelectronic with C_2H_4 but these two are not isostructural, because $B_2H_4^-$ anion has a cloud of electron density above and below the B-H plane as in C_2H_4. The neutral B_2H_6 molecule could then be formally produced by embedding a proton in the electronic cloud above and below the plane of $B_2H_4^{2-}$ ion. Although this structure was not accepted but this bonding model is currently accepted as the three centre-two electron 3c-2e bond.



Electron diffraction and spectral studies supports the hydrogen bridge structure in which one hydrogen atom forma bridge between two atoms, while the terminal hydrogen atoms form

normal covalent bonds with boron atoms. This structure may be represented in above figure. In this structure four hydrogen atoms (two each on the left and right hand side) are known as terminal hydrogen (H_t) and two other hydrogen atoms are known as bridging hydrogens (H_b). The two boron atoms and four terminal hydrogen atoms lie on the same plane while two bridging hydrogen atoms lie on a plane perpendicular to this plane. Different parameters are as given below:

The bridge structure of diborane is supported by the following facts;

i) Electron diffraction measurement confirms that four terminal hydrogen atoms are coplanar and two bridge hydrogen atoms occupy the plane above and below the plane.

ii) Vibrational spectral (Raman and infrared) studies show two intence band at 2101cm-1 and 2523cm-1 B-H bonds. This indicates that all the B-H bonds are not identical.

iii) Nuclear magnetic resonance studies show three main regions of absorption which are due to boron atoms, terminal hydrogen atoms and bridge hydrogen atoms. These studies again support the presence of bridging structure.

iv) The specific heat of diborane is found to be 54.4 kJ while for ethane is 12.5 kJ. This indicates that there is hindrance of rotation in diborane molecule that is due to bridge structure.

v) Diborane on methylation gives $B_2H_2(CH_3)_4$ indicating that four hydrogen atoms are of different nature than the rest of two hydrogen atoms, i.e, bridge hydrogen atoms.

8.14 Metallic bond:

The three-fourth of the known elements is metals. But much less theoretical work has been done to understand the bonding between the same or different metal atoms. This is because metals combine with each other to form products of indefinite composition called bertholides. The metallic bond is not ionic because ionic bond is formed between elements of different electronegativity. And it is not covalent bond because there are insufficient numbers of valency electrons on metal to form electron pair bonds with 8 to 20 neighboring metal atoms. *Metallic bonding is a force of attraction operating in a metal that holds the atoms together in a metallic structure. In metallic bonding, metal atoms form a close-packed, regular arrangement. The atoms lose their outer-shell electrons to become positive ions while the outer electrons become a 'sea' of mobile electrons surrounding a lattice of positive ions.* Thus Metals are made up of positive ions packed together in one of the three following arrangement,

i) Cubic close-packed (also called face-centred cubic).

ii) Hexagonal close-packed.

iii) Body-centered cubic.

The cohesive force in metals is very large and three conventional bonding types (ionic, covalent and coordinate) are unable to explain characteristic properties of the metals such as, metallic luster, high melting and boiling points, hardness, malleability, ductility, high density, thermal and electrical conductivity etc….. There may be new type of cohesive force in metals might exist and called metallic bond.

8.15 General properties of metals:

All metals have following characteristic physical properties

a) They are exceptionally good conductor of heat and electricity.

All metals are exceptionally good conductor of heat and electricity. Electric conductions is due to the movement of electrons. This is in contrast to the movement of ions in the aqueous solution of ionic compounds. In the solid state ionic compounds are poor conductor and there is an enormous difference in the conductivity between metals and ionic compounds.

b) They have characteristic metallic luster, bright, shiny and highly reflective.

All metals except copper and gold are silvery in color. Smooth metal surface have a lustrous shiny appearance. The shininess is special and appears in all angles. This is in contrast to the shininess of few non-metals like sulphur, iodine, which appears shininess when viewed at low angles

c) They are malleable and ductile.

The most important mechanical properties of metals are malleability and ductility. This shows that there is not much resistance for deformation of the structure. i.e., a larger cohesive force holds the structure together.

d) They readily forms alloys

8.16 Metals and metallic bond:

Metal are those materials which generally hard, and are characterized by high electrical and thermal conductivity, malleability, ductility, bright luster and good tensile strength. Basically 3 models have been proposed to account for the nature of bonding in metals. They are.

i) The electron sea model or free electron model

ii) Valence bond model

iii) The band model/molecular orbital approach

i) The electron sea model or free electron model:

This theory is called as electron pool or gas theory of boning in metals. This is the first theory of metallic bonding. Drude at the beginning of the 20th century made a guess about electronic structure and proposed electron theory for matels. This electron theory was further modified by Lorentz few years later, and hence this theory also known as ‘’Drude-Lorentz theory’’ of metals. The basic assumption of this theory is that, a metal crystal consists of positive metal ions (kernel) and whose valence electrons are free to move between the ions as if they constituted electron gas. The crystal is then visualized to be held together by electrostatic forces of attraction between the positively charged ions and negatively charged ions electron gas or Electron Sea as shown in the Fig 1.

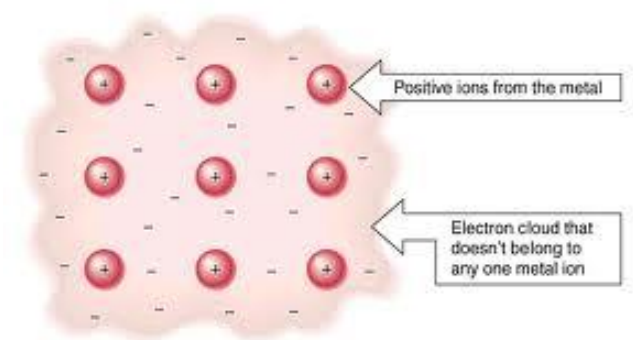


Figure 1: characterization of metallic state

Further, it is also assumed that the electrons are free to move throughout the entire crystal. *Thus the force of attraction, which binds a metal atom kernel to a number of electrons within its sphere of influence, is known as metallic bond.* The theory in its original form assumes that the classical kinetic theory of gases is applicable to the electron gas, mutual repulsion between electrons was ignored and the electrons were expected to have velocities which are temperature dependent according to a Maxwell-Boltzmann distribution law.

This free electron sea model was able to explain most of the metallic properties.

1. *High electrical conductivity* of metals is due to the presence of free mobile electrons. These electrons move readily in electric fields and hence conduct the electricity throughout the metal from one end to another.

2. *High thermal conductivity* is also because the presence of free mobile electrons. If one part of metal is heated, the electrons present in that part gain large amount of kinetic energy, and these electrons are free to move rapidly in the metal crystal from one end to another and convey the heat i.e., they conduct the heat to the other part of the crystal.

3. *Bright metallic luster* it is also explained once again due to the presence of free mobile electrons. When a light radiation impinges on the surface of the metal, the electrical component of the light waves sets the electron present on the surface into to and fro oscillations. These oscillating electrons emit radiations in the form of light. Thus when the light falls on the metal surface it appears as, light is being reflected and hence exhibits typical metallic luster.

ii) Valence bond model

The valence bond theory considers all possible interactions between the immediate neighboring atoms in the metallic crystal. Metals do not have sufficient number of valency electron to form covalent bonds with as many as 8 or 12 nearest neighbor atoms. Consequently it is assumed that a large number of resonance structures are possible.

Consider lithium, a simple metal which has a body-centered cubic structure, with eight nearest neighbors at a slightly greater distance. A lithium atom has one electron in its outer shell, and may be shared with one of its neighbors, to form a normal two-electron bond. The atom could equally well be bounded to any of its other eight neighbors and hence different arrangements are possible, as shown in fig 2. 2a and 2b are two examples.

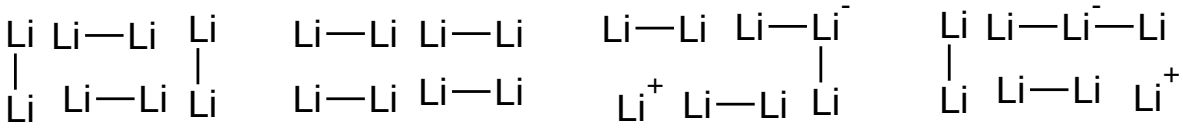


Figure 2: Representations of some different bonding possibilities in

On the other hand, lithium atom may form two bonds if it ionizes, and it can then form many structure similar to those in figures 2c and 2d. Hence Pauling suggested that the true structure is a mixture of all the many possible bonding forms. The more possible structures there are, the lower the energy. This means that the cohesive force which holds the structure together is large, and in metallic lithium the cohesive energy is three times greater than in Li_2 molecule. The cohesive energy increases from group 1 to 2 to 13, and this explained by the atoms being able to form an increased number of bonds, and give an even larger number of possible structures. The presence of ions could explain the electrical conduction, but the theory does not explain the conduction of heat in solids, or the luster, or the retention of metallic properties in the liquid state or in solution.

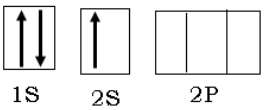
iii) The band model/molecular orbital approach

According to molecular orbital theory metallic bonding results the delocalization of the electron orbitals over all the atoms of a metal structure.

When two atomic orbitals combine, they form two molecular orbitals, a bonding molecular orbital with lower energy and a non bonding molecular orbital of higher energy compare to parent atomic orbitals. Similarly when three atomic orbitals are combines, three molecular orbitals, a bonding M.O. of lower energy, a non bonding M.O. of the same energy and a antibonding M.O. of higher energy compared to parent atomic orbitals. In general, combinations of N atomic orbitals yields N molecular orbitals of which N/2 are bonding M.Os, and remaining N/2 are anti bonding M.Os molecules. The larger the number of atomic orbitals overlaps, the energy separation between the various M.Os will be exceedingly small and this leads to the overlap of energy band.

For example, consider the lithium atom

The electronic configuration of lithium atom is



The Li_2 molecule exists in the vapour state, and bonding occurs using the 2s atomic orbital. There are three empty 2p orbitals in the valence shell, and *the presence of empty atomic orbitals (AOs) is a prerequisite for metallic properties*. (carbon in its excited state, nitrogen, oxygen, fluorine, and neon all lack empty AOs in the valence shell and are all non metals.)

The valence shell has more AOs than electrons, so even if the electrons are all used to form normal two- electron bonds, the atom cannot attain a noble gas structure. Hence compounds of this type are considered as 'electron deficient'.

According to the molecular orbital description of a Li_2 molecule, it has six electrons, arranged in molecular orbitals (MOs) as $\sigma\ 1s^2$, $\sigma^*\ 1s^2\ \sigma\ 2s^2$. Bonding occurs because the $\sigma\ 2s^2$ bonding MO is full and the corresponding anti bonding orbital is empty. Ignoring any other inner electrons, the 2s AOs on each of the 2 Li atoms combine to give two MOs, one bonding and one antibonding MO as shown in Fig 3a.

If three Li atoms joined to form Li_3, three 2s AOs would combine to form 3 MOs- one bonding, one non- bonding and other one is anti bonding. The energy of a non-bonding MO is lie in between the bonding and anti bonding orbitals. The three valence electrons from 3

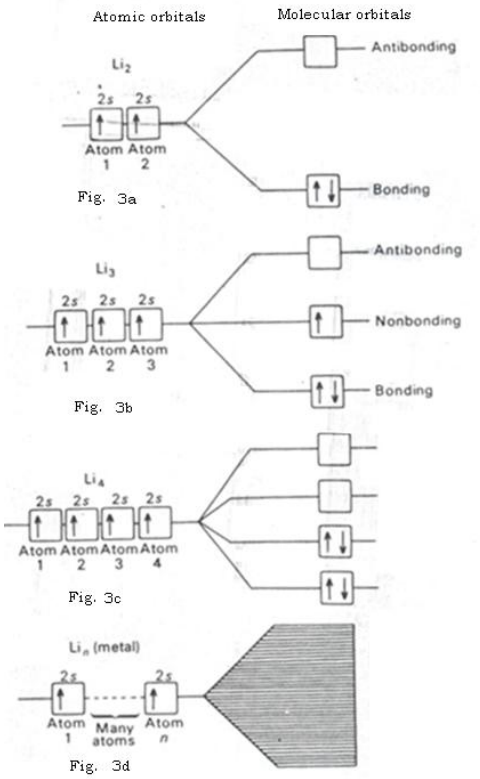
atoms would occupy the bonding MO (two electrons) and the non- bonding MO (one electron) as shown in Fig 3b.

In Li_4, the four AOs would form 4 MOs – two bonding, – and two anti bonding. The presence of two non bonding MOs between the bonding and anti bonding orbitals reduce the energy gap between the orbitals. The 4 valence electrons would occupy the two lowest energy MOs, which are both bonding orbitals, as shown in Fig.3c

As the number of electrons in the cluster increases , the spacing between the energy levels of the various orbitals decreases further , and when there are a large number of atoms, the energy levels of the orbitals are so close together that they almost form a continuum and appear as band as shown in Fig 3d.

The number of MOs must by definition be equal to the number of constituents AOs. Since there is only one valence electron per atom in Li , and a MO can hold two electrons, means that only half of the MOs in the 2s valence bands are filled i.e., the bonding MOs . Hence it requires only a minute amount of energy to perturb an electron to an unoccupied MO.

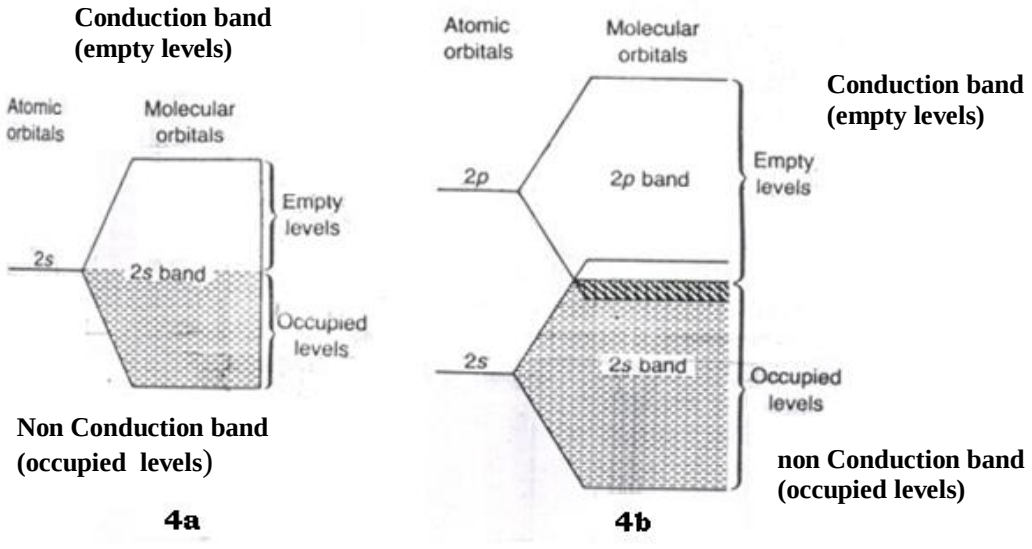
The MOs extend in three dimensions overall the atoms in the crystals, and hence electrons have a high degree of mobility. The mobile electrons account for the high thermal and electrical conduction of metals.



If one end of a piece of metal is heated , electrons at that end gain energy and move to an un occupied MO where they can travel rapidly to any other part of the metal, which in turn becomes hot. In a similar manner, electrical conduction takes place through a minor perturbation in energy promoting an electron to unfilled level, where it can move readily. In the absence of an electric field, equal numbers of electrons will move in all directions. If a positive electrode is placed at one end, and a negative electrode at the other, then electron will move towards the anode much more readily than in the opposite direction; hence an electric current flows.

Conduction occurs because the MOs extend over the whole crystal, and because there is effectively no energy gap between the filled and unfilled MOs. The absence of an energy gap in lithium is because only half the MOs in the valence band are filled with electrons (figure 4a).

In beryllium there are two valence electrons, so the valence electrons would just fill the 2s valence band of MOs. In an isolated beryllium atom, the 2s and 2p atomic orbitals differ in energy by 160 KJ/mole. As the 2s AOs forms a band of MOs similarly the 2p AOs form a 2p band of MOs. The upper part of the 2s band overlap with the lower part of the 2p band (fig. 4b). Because of this overlap of the bands, some of the 2p band is occupied and some of the 2s band is empty. Hence it is easy to perturb electrons to an unoccupied level in the conduction band where they can move throughout the crystal. Hence beryllium behaves as a metal.



The electronic energy bands were electrons can move are called the permitted bands. These bands are also known as Brillouin zones. Two Brillouin zones are separated from each other by empty bands are called forbidden zones or forbidden energy gap represented by Eg. The width of Brillouin zone depends on the overlapping of the electron zones. The level bellow

which all energy levels are filled is termed as Fermi level. It may fall within a band or with the gap between bands.
The energy gap of some inorganic materials is given below.

Element/compound	Band gap(ev)
Diamond ,C	6.0
Pb	0
White Sn(<13^{o}C)	0
Grey Sn (>13^{o}C)	0.1
Ge	0.7
LiF	11
LiCl	9.5
NaCl	8.5
CdS	2.5
CdSe	1.8
Pbs	0.37

The difference between the metals (conductors), semiconductors and insulators can be made on the basis of the energy gap, example is shown in the fig . 5a-c

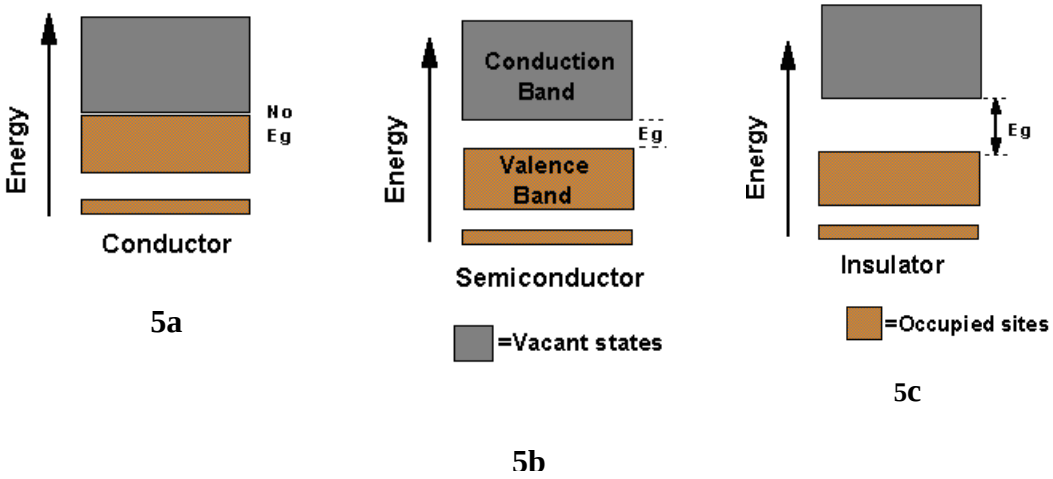


Figure 5a-c: Pictorial representation of conductor, semiconductor and insulator

On the basis of band theory on can explain behavior of solids as metals, insulators and semiconductors.

8.17 Metals (conductors):

Metals are those materials in which plenty of electrons are available for conduction. However, in terms of band theory, the conduction band of the metal is partially filled and contains large number of electrons. As the bands are overlapping (fig. 5a) band gap is practically nil and hence exhibit electrical and thermal conductivity.

8.18 Insulators (Non conductors):

Insulators are those materials in which the energy gap between conduction band and valence band is very large (fig 5b). Hence energy required for the promotion of an electron from the completely filled valence shell band to the empty conduction band is relatively very high and is therefore normally not available. Therefore, such materials are known as insulators.

8.19 Semiconductors:

In this type of materials the electrical properties are lie in between good conductors and insulators. Further, the energy gap of semiconductor lies in between that of insulator and conductor (fig 5c) these materials in their extremely pure form they will conduct the electricity and such semiconductors are known as 'intrinsic semiconductors'. Eg: Germanium, Silicon etc. Intrinsic semiconductors have filled valence band (non conduction band) and empty conduction band. The energy gap between them so small that, even at room temperature the electrons from the filled valence band can jump to the vacant conduction band and hence exhibit low thermal conductivity. Further, as the temperature is increased, the width of the energy gap is decreased and some more electrons can jump to the conduction band. Thus exhibits increased conductivity with increase of temperature.

Sometimes substances which are normally insulators can be converted in to the semiconductors by the addition of small amount of impurities (dopants). Such materials are known as extrinsic or impurities semiconductors. Depending on the nature of dopants added to the extrinsic semiconductors it has been classified in to two types

A. n -type extrinsic semiconductor
B. p-type extrinsic semiconductor

i) n -type extrinsic semiconductor:

These materials are obtained when an impurity atom to be added has more external electrons than the parent atoms. Eg: when pentavalent atoms such as phosphorous , arsenic or antimony are added to pure silicon or germanium (both containing four electrons). In this case each

phosphorous atom forms four covalent bonds with the neighboring four silicon atoms by using its four valency electrons and its fifth electron is left unused as shown in the fig.6.

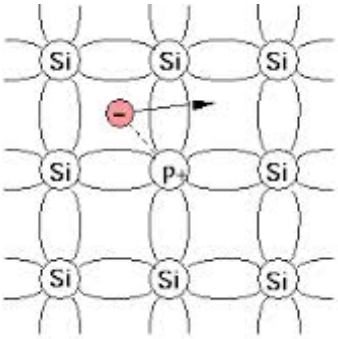


Figure 6: Doping of silicon by phosphorus

Thus the extra electron at the lattice point is occupied by phosphorous atoms compared to the lattice point occupied by silicon atoms. This extra electron is responsible for the conduction of electricity. These extra electrons occupy delocalized level which is just below the empty conduction band of silicon crystal. These extra electron can easily be excited to the empty conduction band by application of electric field or by thermal energy and thus silicon becomes semiconductor. Hence crystals of germanium are semiconductors because of the presence of extra electrons and hence behave as n-type extrinsic semiconductors.

ii) ***P-type extrinsic semiconductor:***

These materials are obtained when an impurity atom added has less external electron than the parent insulator atom. Eg: when boron or aluminum (both containing three electrons) atoms are added to pure tetravalent silicon or germanium. So, when silicon is doped with aluminum, aluminum forms three covalent bonds with silicon there by leaving one bond with silicon containing only one electron (from silicon). Thus in this bond, in the lattice there is an electron deficiency which creates a positive hole in the valency band of silicon as shown in the fig.7.

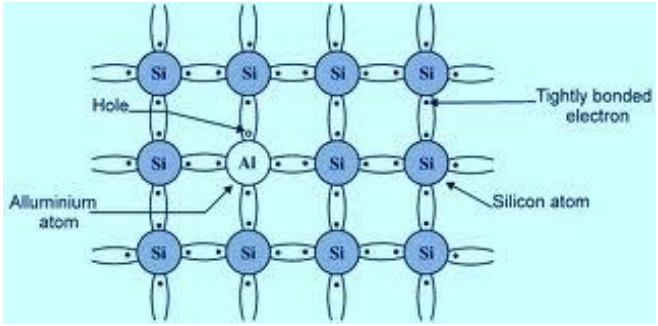


Figure 7: doping of silicon by aluminium

Positive holes are the places where elctrons are missing. These holes occupy the level (called acceptor impurity level) which present close to the filled valancy band of silicon crystal. The conductivity in these type of materials is due to movement of holes from one atom to another throught the crystal and these type of conductivity is known as p-type conductivity and materials ae known as the p-type extrensic semiconductors.

8.20 Summary of the unit:

Carbon forms thousands of stable compounds, similarly formation of molecules by similar atoms e.g., chlorine molecules, Cl_2 and formation of molecules by dissimilar atoms e.g., Hydrogen chloride, water, ammonia, which do not have properties indicating the presence of ionic constituents. Therefore it is not clear as what holds two or more atoms together in them. Lewis proposed that these elements attain inert gas configurations by sharing of electrons with atoms of similar or dissimilar elements. The electrons are shared in pairs each atom contributing one electron to pair. This theory was considerably extended by Langmuir who introduced the term covalent bond to describe the Lewis electron pair band.

8.21 Key words:

Atomic orbitals, Molecular orbitals; Octet Rule; Hydridization; Multicentred bond; Metals; Conductors; Insulators; Semiconductors; n –type; P-type.

8.22 Questions for self understanding:

1) Write a note on octet rule.

2) Discuss the advantage of octet rule

3) Explain in detail about linear combination of atomic orbitals.

4) Discuss the formation and characteristic of orbitals formed by following types of hybridisation

1. sp hybridization
2. sp^2 Hybridization
3. Sp^3 hybridisation

5) Write a note on molecular orbital treat ment of 3-centred-2electron (3C-2e) bond formation

6) List the physical properties of metals

7) What are the three common crystal structures addopted by metals?

8) Describe the varies theories of metallic bond

9) Discuss the enrgy band theory in detail

10) Expalin the electrical conductivity of metals and semi-metals on the basis of valence bond thory

11) Write a short notes on

a) Conductor
b) Semi-conductor
c) Insulator

12) Water are n-type and p-type semiconductors?explain their formation

8.23 References for further study:

1) An Introduction to Molecular Orbitals by Y. Jean, F. Volaton, J. Burdett. *Oxford University Press, USA*, **1993**.

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3) Advanced Inorganic chemistry by F. Albert Cotton, G. Vilkinson, C. A. Murillo, M. Bochmann; *Wiley-Interscience*; 6th Ed. **1999**.

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5) Inorganic Chemistry by Petter Atkins, Fraser Armstrong, Jonathan Rourke, Tina Overton, Mark Welle; *Oxford University Press* 5th Ed. **2011**.

UNIT – 9: Basic elements of laser; properties of laser light: directionality, intensity, monochromaticity, coherence; spontaneous and stimulated emission

Structure:

9.0 Objectives:

After studying this unit you will be able to

1. Define LASER.
   a. Recognize sources for ordinary light and monochromatic light.
2. Discuss the properties of LASER in detail.
3. List out applications of LASER.

9.1 Introduction:

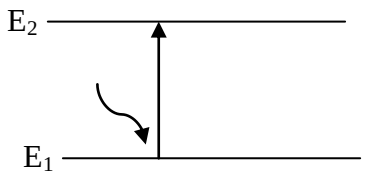
The word 'LASER' is an acronym for Light Amplification by Stimulated Emission of Radiation. It is a source which emits an intense, almost perfectly monochromatic, directional and highly coherent beam of light. Its working depends on the phenomenon of "stimulated emission", first predicted by Einstein in 1916.

Einstein considered the equilibrium between a matter and electromagnetic radiation in a black-body chamber at a constant temperature in which exchange of energy takes place due to absorption and spontaneous emission processes alone are not sufficient to explain the equilibrium. He then predicted that there must be a third process also, now called "stimulated emission". This prediction was paid little attention until 1954, when to Townes and Gordon developed a microwave amplifier (MASER) USING AMMONIA NH. In 1958, Schawlow and Townes showed that the maser principle could be extended in to the visible region and in 1960, Maiman built the first laser using ruby as the active medium. Soon after, Javan constructed the first gas laser, namely, the He-Ne laser. Since then, laser action has been obtained in a large variety of materials including liquids, ionized gases, plastics, dyes, semiconductors etc. at wavelengths from ultraviolet to radio-frequency regions, with power ranging from a few milliwatts to megawatts. Some lasers emit only in pulses, while other s emit a continuous wave.

An isolated atom may exist in ground state of energy or in excited state of energy. The atom can change its state in three ways. They are ,

9.1.1. Induced absorption:

Consider an atom initially at the ground state of energy E_1. If an electromagnetic radiation of frequency υ is incident on atom,



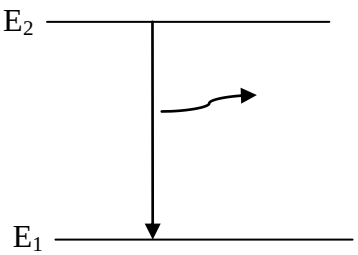
then the atom may absorb the energy and moves to the energy state E_2. This is possible provided $h\upsilon = E_2 - E_1$.

Such a process is called induced absorption.

Therefore "The process in which atom moves from lower energy state to higher energy state by absorbing the external energy is called "induced absorption".

9.1.2.Spontaneous emission:

Consider an atom in an excited state of energy E_2. The atom cannot remain in excited state for a long time. (i.e., for not more than 10^{-8} sec). Such an atom returns to its ground state by emitting photon of energy $h\upsilon = E_2 - E_1$.



This process is called Spontaneous emission. Therefore,

"The process in which an atom jumps from its higher energy state to the ground state on its own by emitting photon is called spontaneous emission".

Note:

i) Spontaneous emission is the cause of ordinary light

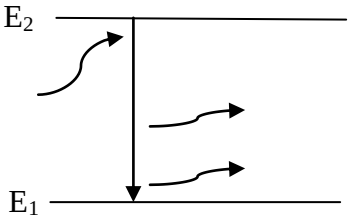
[i.e., Light from stars is because of spontaneous emission]

ii) The photons emitted during spontaneous emission are different from each other and their phases will be random.

9.1.3.Induced emission:

Consider an atom in an excited state of energy E_2.

If an electromagnetic radiation of frequency υ such that $h\upsilon = E_2 - E_1$ is incident on it. The interaction between the atom and photon makes the atom to return to its ground state by emitting a photon of same energy such that $h\upsilon = E_2 - E_1$.



[The emitted photon will be identical to the incident photon]

Therefore "The process in which an incident photon stimulates an atom to jump from higher energy state to ground state by emitting a photon identical to the incident photon is called induced emission".

Note: 1. Stimulated emission is possible if the atoms are in the excited state.

2. Stimulated emission is the cause for monochromatic light.

3. Stimulated emission leads to the emission of photons of the same energy and phase as that of the incident photon. Hence radiation obtained by stimulated emission is coherent.

4. The action of laser is based on the principle of stimulated emission.

9.2 Properties of laser beams:

It is perfectly monochromatic light

It can be focused to a small spot and hence can produce a high intensity

It is perfectly a parallel beam i. e, zero divergence.

All photons have same energy and the net intensity is high

Therefore, Laser radiation is characterized by an extremely high degree of monochromaticity, coherence, directionality and brightness.

9.2.1. Monochromaticity:

Monochromaticity of laser radiation results from the fact that all the photons are emitted because of a transition between the same two atomic or molecular energy levels, and hence have almost exactly the same frequency. Further, the laser cavity is resonant only for the frequencies of resonant cavity limits the frequency range. However, as the energy levels are not sharp, there is always a small spread to the frequency distribution, which may cover several discrete frequencies. The results that a small number of closely spaced frequencies may appear in a laser action i.e. the light are not monochromatic. In order to achieve the optimum monochromaticity, generally an etalon is placed within the laser cavity and arranged so that only well defined wavelength can travel back and forth between end mirrors.

One of the important factors which characterizes laser is the quality factor Q defined as the ratio of the emission frequency ν to the line width, that is, $Q = \frac{\nu}{\Delta\nu} = \frac{\lambda}{\Delta\lambda}$

Where ν is the central frequency of the laser beam. The degree of non – monochromaticity, ξ of laser radiation is the reciprocal of quality factor i.e. $\xi = \frac{1}{Q} = \frac{\Delta\nu}{\nu} = \frac{\Delta\lambda}{\lambda}$

***9.2.2.Coherence*:**

Coherence is the property, which results from the nature of the stimulated emission process. There are two types of coherence: temporal coherence and spatial coherence. Consider two points P and Q a distance L apart in the direction of propagation of laser beam as shown in fig. If a definite and fixed phase relationship exists between the waves' amplitudes at P and Q at time t and t + τ , then the wave shows temporal coherence for time τ .

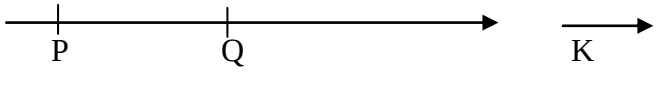


Diagram for explaining temporal coherence

The maximum separation L at which h the fixed relationships retained is called the coherence length L_c . The coherence length is related to the coherence time τ_c by

$$L_c = c\tau_c$$

The coherence time is related to monochromaticity of the laser by,

$$\tau_c \approx \frac{1}{\Delta \nu_L}$$

And

$$L_c \approx \frac{c}{\Delta \nu_L} \approx \frac{\lambda^2}{\Delta \lambda}$$

Spatial coherence in the simplest case tells us about the phase relationship between the field amplitudes at two points P and Q in a plane normal to the wave vector K as shown in fig.

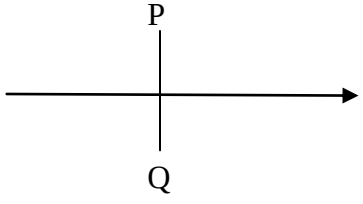


Diagram for explaining spatial coherence

Light that is emitted from different parts of the conventional light source is not phase – related. Therefore, the light from an extended light source will not spatially coherent.

A good measure of coherence of a light source is its ability to produce a stable interference fringes. Temporal coherence can best studied with a Michelson interferometer. The existence of spatial coherence between the fields at two points can be demonstrated in a young's slits experiment.

***9.2.3. Directionality*:**

Stimulated emission produces photons with almost precisely identical direction of propagation. The mirrors selectively amplify axial beam. The laser thus emits a narrow parallel beam from its output mirror. The extent of beam divergence is essentially determined by the diffraction limit of output aperture. From diffraction theory, the divergence angle θ_D is

$$\theta_D = \frac{\beta\lambda}{D}$$

Where λ and D are wavelength and diameter of the laser beam, respectively.

If the partial spatial coherent beam has given intensity distribution overt he diameter D and a given coherence area A_{sc}, its divergence is bigger than the diffraction limited divergence, then it can be shown

$$\theta_D = \frac{\beta\lambda}{(A_{sc})^2}$$

***9.2.4.Brightness*:**

It is defined, as the power emitted from unit area of the output mirror per unit solid angle. It is extremely high. The reason for this is that although the power may be small but it is distributed over solid angle which is small.

9.3 Applications of LASER:

- LASER is used in micro welding and cutting of metals.
- LASER is used in drilling holes in hard materials
- LASER beams are used in the production of holograms

- LASER beams are used in repairing retinal detachment of the eye.
- LASER beams are used in measurement of largest distances between the any objects [ex: between moon and earth]
- LASER beams are used in optical fiber.

9.4 Let us sum up:

In this unit you have learnt to

1. Definition of LASER.
2. Naming the sources for ordinary light and monochromatic light.
3. Explanation of the properties of LASER in detail.
4. To list out applications of LASER.

9.5 Self evaluation questions:

1. Explain the following terms
   (i) Stimulated absorption (ii) spontaneous emission (iii) stimulated emission
2. What are the properties of LASER? Explain.
3. Differentiate between Spatial coherence and temporal coherence.
4. Write a note on applications of LASER light.

9.6 References:

1. Introduction to Atomic and molecular spectroscopy by Vimal Kumar Jain
2. Atomic and Molecular Spectra: Laser by Raj Kumar

Unit –10: Einstein coefficients; light amplification, population inversion and threshold condition for laser oscillations; quality factor;

Structure:

10.0 Objectives:

After studying this unit you will be able to

1. Derive the Einstein's coefficients
2. What is principle of laser? Explain principle of laser.
3. Write a note on population inversion.
4. The mathematical treatment of necessary condition for light amplification (Population Inversion).

10.1 Introduction:

In 1916, Einstein proposed that there are three main processes that occur in the formation of an atomic spectral line namely, **spontaneous emission**, **stimulated emission**, and **absorption** which are discussed in detail in the previous chapter. With each is associated an **Einstein coefficient** which is a measure of the probability of that particular process occurring. Einstein considered the case of isotropic radiation of frequency ν, and spectral energy density $\rho(\nu)$

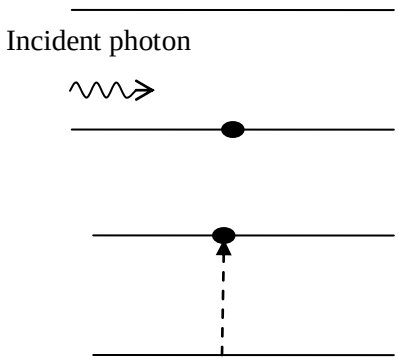
10.2 Einstein's coefficients:

10.2.1. Expression for energy density at thermal equilibrium:

Consider two energy states E_1 and E_2 of a system of atoms. Let N_1 and N_2 be the atoms with energy E_1 and E_2 per unit volume of the system. N_1 and N_2 are called the number density of atoms in the states 1 and 2 respectively. Let the radiation be incident on the system. Let '$U_\gamma d\gamma$' be the energy incident per unit volume of the system in the frequency range γ and $\gamma + d\gamma$. Here 'U_γ' is energy density.

Case i) Induced absorption

Here the radiation absorbed is a frequency γ. The number of such absorption per unit time, per unit volume is called rate of absorption. The rate of absorption depends upon,



a) The number density of lower energy state. i.e., N_1

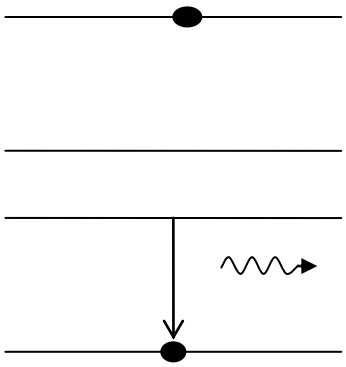
b) energy density, i.e., U_γ

$\therefore$ Rate of absorption α N_1U_γ

(or) Rate of absorption = B_{12} N_1U_γ ---- (1)

where 'B_{12}' is constant of proportionality called Einstein's coefficient of induced absorption.

Case ii) Spontaneous emission:

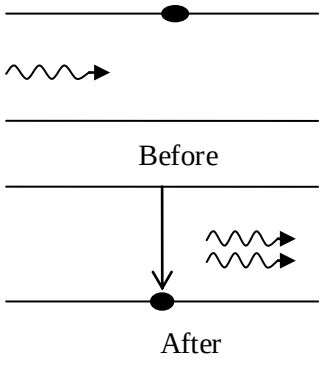


Here transition is voluntary. The number of spontaneous emissions per unit time, per unit volume is called rate of spontaneous emission. It depends upon only the number density in the higher energy state, i.e., N_2

$\therefore$ Rate of spontaneous emission = $A_{21}N_2$ ---- (2)

where 'A_{21}' is called Einstein's coefficient of spontaneous emission.

Case iii) Stimulated emission



Since the system requires an external photon of appropriate frequency γ, to stimulate the atom. The number of stimulated emissions per unit time, per unit volume, called rate of stimulated emission, is proportional to

a) the number density of the higher energy state, i.e., N_2

b) the energy density, i.e., U_γ

$\therefore$ Rate of stimulated emission = B_{21} N_2 U_γ ---- (3)

where 'B_{21}' is called Einstein's coefficient of stimulated emission.

Under thermal equilibrium, the number of photons absorbed by the system per second must be equal to the number of photons it emits per second by both the stimulated and the spontaneous emission processes.

i.e., Rate of absorption = Rate of spontaneous emission + Rate of stimulated emission

From equations (1), (2) and (3),

$$B_{12}\, N_1 U_\gamma = A_{21} N_2 + B_{21}\, N_2\, U_\gamma$$

Or, $$U_\gamma\,(B_{12}\, N_1 - B_{21}\, N_2) = A_{21} N_2$$

Or, $$U_\gamma = \frac{A_{21} N_2}{B_{12} N_1 - B_{21} N_2}$$

By rearranging the above equation, we get,

$$U_\gamma = \frac{A_{21}}{B_{21}} \left[\frac{1}{\frac{B_{12}}{B_{21}} \frac{N_1}{N_2} - 1} \right] \quad \text{---- (4)}$$

But, by Boltzmann's law, we have,

$$\left(\frac{N_2}{N_1} \right) = e^{-\left(\frac{E_2 - E_1}{KT} \right)} = e^{-\frac{h\nu}{KT}}$$

$$\therefore \quad \frac{N_1}{N_2} = e^{\frac{h\gamma}{KT}}$$

$\therefore$ Equation (4) becomes,

$$U_\gamma = \frac{A_{21}}{B_{21}} \left[\frac{1}{\frac{B_{12}}{B_{21}} e^{\frac{h\gamma}{KT}} - 1} \right] \quad \text{---- (5)}$$

According to Planck's law, the equation for 'U_γ' is

$$U_\gamma = \frac{8\pi h \gamma^3}{c^3} \left[\frac{1}{e^{\frac{h\gamma}{KT}} - 1} \right] \quad \text{---- (6)}$$

By comparing equations (5) and (6), we have,

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h \gamma^3}{c^3} \quad \text{and} \quad \frac{B_{12}}{B_{21}} = 1 \quad \text{or } B_{12} = B_{21}$$

i.e., the probability of induced absorption is equal to the probability of stimulated emission.

$\therefore$ At thermal equilibrium the equation for energy density is

$$U_\gamma = \frac{A}{B\left[e^{\frac{h\gamma}{KT}} - 1\right]}$$

10.2.2. Discussions on Einstein's coefficients:

i) Dependence of emission on frequency:

We know that, $\frac{A_{21}}{B_{21}} = \frac{8\pi h\gamma^3}{c^3}$ --- (1)

where 'A_{21}' is called Einstein's coefficient of spontaneous emission.

and 'B_{21}' is called Einstein's coefficient of stimulated emission.

$$\Rightarrow \frac{A_{21}}{B_{21}} \alpha \gamma^3$$

Since $\gamma = \left(\frac{\Delta E}{h}\right)$, When the energy difference between the two levels E_1 and E_2 is large, Then,

$$\left(\frac{A_{21}}{B_{21}}\right) >> 1 \quad OR \quad A_{21} >> B_{21}$$

$\Rightarrow$ For higher ΔE values, the probability of spontaneous emission is more.

ii) System in thermal equilibrium

We know that, $U_\gamma = \frac{8\pi h\gamma^3}{c^3}\left[\frac{1}{e^{\frac{h\gamma}{KT}} - 1}\right]$ -- (2) and $\frac{A_{21}}{B_{21}} = \frac{8\pi h\gamma^3}{c^3}$

$$\Rightarrow \frac{A_{21}}{B_{21}U_\gamma} = \left(e^{\frac{h\gamma}{KT}} - 1\right) \text{--- (3)}$$

Case (a): hγ >> KT: $e^{\frac{h\gamma}{KT}} >> 1$

Hence eqn (3) $\Rightarrow \left(\frac{A_{21}}{B_{21}}\right) >> 1 \quad OR \quad A_{21} >> B_{21}$

Spontaneous emissions are much larger.

Case (b): hγ = KT: Here $e^{\frac{h\gamma}{KT}}$ will be low and comparable to 1. ∴ A_{21} and B_{21} are comparable, which means that stimulated emission becomes significant

$B_{21} >> A_{21}$

Case (c): hγ << KT: $\left(e^{\frac{h\gamma}{KT}}-1\right)<<1$ and $\left(\frac{A_{21}}{B_{21}}\right)<<1$ OR $B_{21} >> A_{21}$

Hence for lower frequencies, stimulated emissions dominate. This is what we observe at room temperature.

iii)<u>Non-equilibrium conditions leading to amplification:</u>

We know that, Rate of emissions = $A_{21}N_2 + B_{21} N_2 U_\gamma$ ---- (4)

Rate of absorption = $B_{12} N_1 U_\gamma$ ---- (5)

$$\frac{\text{Rate of emissions}}{\text{Rate of absorption}} = \frac{A_{21}N_2 + B_{21} N_2 U_\gamma}{B_{12} N_1 U_\gamma} = \frac{N_2}{N_1}\left[\frac{A_{21} + B_{21}U_\gamma}{B_{12}U_\gamma}\right]$$

Since $B_{12} = B_{21}$

$$\frac{\text{Rate of emissions}}{\text{Rate of absorption}} = \frac{N_2}{N_1}\left[\frac{A_{21}}{B_{12}U_\gamma} + 1\right] \text{--- (6)}$$

If $\Delta E << KT$ i.e., $h\gamma << KT$, then $\left[\frac{A_{21}}{B_{12}U_\gamma} << 1\right]$

So that equation (6) becomes

$$\frac{\text{Rate of emissions}}{\text{Rate of absorption}} = \frac{N_2}{N_1}$$

We know that in normal condition $N_2 < N_1$. If we made $N_2 > N_1$ by some means, the system will be in non equilibrium condition since by Boltzmann factor.

In this case, rate of emission exceeds the rate of absorptions. Further if the photons emitted in a particular direction are returned in to the system by reflecting them back and forth, then the rate of stimulated emission exceeds the absorption rate. If right conditions are provided, all the stimulated emissions could be arranged to be identical in respect of wavelength, phase and direction to the starting stimulating radiation, then that itself has been amplified. To achieve this we should maintain $N_2 > N_1$ always. This forms the basis for functioning of every laser.

10.3 Requisites of a Laser system:

The important requisites of a typical laser system are as follows

1. an active medium
2. an energy source
3. an optical resonance cavity

10.4 Conditions for Laser action:

Let us consider an assembly of atoms of some kind that have metastable state of excitation energy hγ. Suppose we somehow raise the majority of the atoms to the metastable level. If now we introduce light of frequency 'γ' on the assembly, there will be more induced emission from the metastable level than induced absorption by the lower level. The result will be an amplification of original light. This is the concept of Lasers.

10.4.1. Population inversion:

Any material consists of collection of atoms, molecules or ions. Under normal circumstances there are always a large number of atoms in the lower energy state than in the excited state. Then by some means, we can make number of atoms (N_2) in the excited state is greater than the number of atoms (N_1) in lower state, then one can say that population inversion is attained by the atomic system.

Pumping:

The method of achieving population inversion is called pumping.

Since all laser emission involves radiation from excited states, the energy must be supplied to these atoms to produce the excited states. Methods of pumping, irrespective of the system of

levels (three level or four level) involved and of whether lasing is to be pulsed or continuous wave (CW)falls into following categories:

(a) Optical

(b) Electrical

(c) A thermal oven

(d) Chemical reaction

(e) Heavy particles

(f) Ionization radiation

(g) In view of the wide variety of techniques we will discuss only electrical pumping and optical pumping. Electrical pumping is accomplished by means of a sufficiently intense electrical discharge. In an electric discharge electrons are produced by ionization in strong electric field. The electrons achieve very high speed of 10^6 to 10^7 m/s . These electrons on collision transferred energy to atom or molecules of gas and raised them to excited states

$$M + e \longrightarrow M^* + e$$

Where M and M* represent the atom in the ground and excited states respectively. For a gas consisting of mixture of gases say X and Y, X serve only to transfer energy from electrons to Y.; X is excited to X* a long lived metastable state, by electron impact. The X is in excited state and Y is in ground state as shown in Figure. If the level Y to be pumped is of similar energy to that of X*, then there is an appreciable probability that after collision X* will transfer its energy to Y to raise it to excited state. The process is denoted by

$$X^* + Y \longrightarrow X + Y^* + \Delta E$$

Where the energy difference ΔE between X* and Y will be added or subtracted.

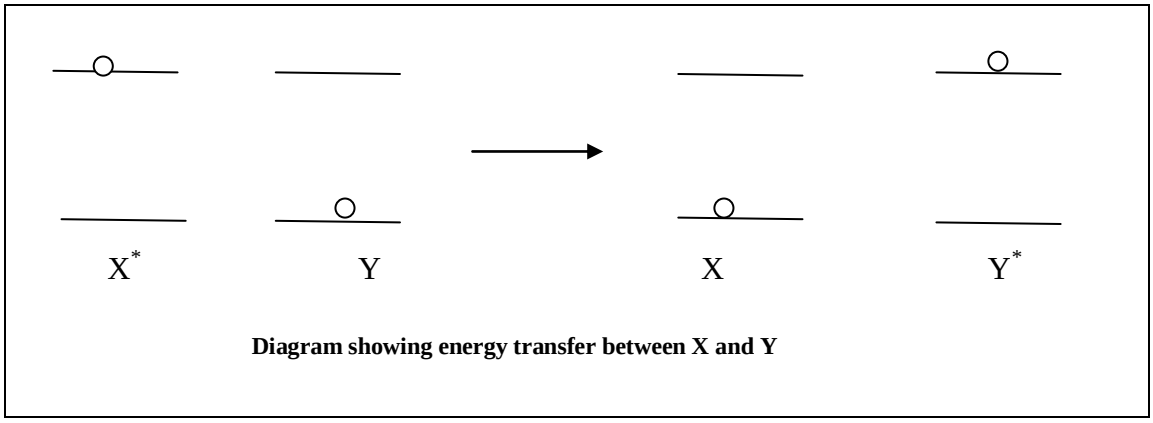


Diagram showing energy transfer between X and Y

For optical pumping, the excitation involves the transfer of the energy to the system from a high intensity light source, Optical pumping can be accomplished by many different light sources including inert gas flash lamp usually xenon at a pressure of about 100 torr. The result is a pulsed laser, the repetition rate being that of pumping source. CW optical pumping may be achieved by a continuously acting krypton or high pressure mercury lamp.

Electrical pumping is typically used in most gases and semiconductor lasers. On the other hand, optical pumping is often used in liquids (dye) lasers and crystalline solid state lasers. In solids and in liquids, electrons cannot easily be accelerated by electric field to excite the laser energy levels of impurities species. The line broadening mechanisms in solids and liquids produces an appreciable broadening.

Therefore, one is usually dealing with pump band rather than levels. These bands can therefore absorb a sizeable fraction of light emitted by flash lamps whose energy occurs over a broad wavelength region. However, non laser optical pumping is not feasible in gaseous systems. The gaseous system does not have in general broad absorption bands.

Population Inversion: A Necessary Condition for Light Amplification

Let us consider an assembly of atoms (an active medium) distributed over different energy states. Suppose a light beam of frequency ν, which coincides with one of the characteristic frequencies of the atoms, is passing through the medium. Now, one of the following two processes takes place:

(i) A light photon (of frequency ν) is absorbed by an atom in an energy state s E1 and the atom is excited to a higher energy state E_2, such that $h\upsilon = E_2 - E_1$.
In this case, the intensity of the beam passing through the medium gradually decreases, until the beam is totally attenuated.

(ii) A light photon (of frequency ν) is incident on an atom which is already in an excited energy state E_2. This atom decays to a lower energy state E_1, emitting a photon of same frequency. The emitted photon is in perfect coherence with the incident photon.
(This is stimulated emission of radiation). If these two photons are incident on two other atoms in the state E_2, they give rise to the emission of two more photons, thus resulting in four coherent photons. This process continues and the intensity of the light beam increases exponentially. This increase in light intensity is known as 'light amplification'.

Under ordinary conditions of thermal equilibrium, the number of atoms in higher energy state E_2 is considerably smaller than the number in lower energy state E_1 ($N_2 < N_1$), so that there is very little stimulated emission compared with absorption. If, however, by some means, the number of atoms in the higher energy state be made sufficiently larger than the number in the lower energy state, then stimulated emission is promoted.

The situation in which the number of atoms in the higher energy state exceeds that in the lower energy state ($N_2 < N_1$), is known as "population inversion". In this situation, the assembly of atoms would lase.

Stimulated emissions are further encouraged by increasing the radiation density $U(\nu)$ of the stimulating radiation. This is achieved by enclosing the emitted radiation in a "cavity' between two parallel reflectors. The radiation repeatedly travels back and forth, and the photons passing through the atoms go on multiplying by repeated stimulated emission. Hence a strong coherent beam of light emerges from the system.

10.4.2. Mathematical Treatment:

Let us consider a collection of atoms (an active medium) and let a nearly monochromatic light beam of frequency ν be propagating through the medium along the x direction. The intensity I_ν of a light beam of frequency ν is related to the energy density $U(\nu)$ of the light. If the light beam in question has frequencies in the range ν and $\nu + \Delta\nu$, then the relation between the intensity and the energy density can be written as

$$I_\nu \Delta\nu = cU(\nu)\Delta\nu$$

where *c* is the speed of light in the medium.

Let N_1 and N_2be the number of atoms per unit volume of the medium of energy states E_1 and E_2 respectively at any instant. In practice, the energy levels are not absolutely sharp, but have a finite energy spread due to Doppler Effect and certain other causes. Therefore, during the passage of the light beam of frequency ν through the medium, only certain number of atoms, say ΔN_1 out of N_1 atoms in the energy state E_1 undergo absorption transitions. Such upward transitions per unit volume is

$$\Delta N_1 B_{12} U(\nu) = \Delta N_1 B_{12} \left(I_\nu \big/ c \right)$$

Where B_{12} is Einstein's B coefficient. Similarly, the rate of downward induced transitions is:

$$\Delta N_2 B_{21} U(\nu) = \Delta N_2 B_{21} \left(I_\nu \big/ c \right)$$

During each upward transition, a quantity of radiation energy $h\nu$ is absorbed from the propagating light beam. Similarly, during each downward induced transition, an equal amount of energy is added to the light beam. So, the rate of change of spectral energy density of the beam in the frequency interval $\Delta\nu$ is

$$\frac{d}{dt}\{U(\nu)\Delta\nu\} = \left\{\Delta N_2 B_{21}\left(I_\nu \big/ c\right)\right\} h\nu - \left\{\Delta N_1 B_{12}\left(I_\nu \big/ c\right)\right\} h\nu$$

$$\frac{d}{dt}\{U(\nu)\Delta\nu\} = \left[\{\Delta N_2 B_{21}\} - \{\Delta N_1 B_{12}\}\right] h\nu \left(I_\nu \big/ c\right)$$

$$\frac{d}{dt}\{U(\nu)\Delta\nu\} = \left[\{\Delta N_2\} - \{\Delta N_1\}\right] B_{12} h\nu \left(I_\nu \big/ c\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

Because $B_{12} = B_{21}$. Here we have neglected the radiation arising out of spontaneous emission because such radiations propagate in random directions and are, in general, lost from the beam.

Suppose the light beam covers a distance dx in time dt in the medium, then $dx = cdt$

$$\therefore \frac{d}{dt}\{U(\nu)\Delta\nu\} = \frac{d}{dx}\{cU(\nu)\Delta\nu\} = \frac{d}{dx}\{I_\nu \Delta\nu\}$$

Therefore, eqn (i) can be written as

$$\frac{d}{dx}\{I_\nu \Delta\nu\} = [\{\Delta N_2\} - \{\Delta N_1\}]B_{12}h\nu\left(I_\nu \big/ c\right)$$

$$\frac{d}{dx}\{I_\nu\} = \frac{[\{\Delta N_2\} - \{\Delta N_1\}]}{\Delta\nu} B_{12}h\nu\left(I_\nu \big/ c\right)$$

Let us put $\frac{[\{\Delta N_2\} - \{\Delta N_1\}]}{\Delta\nu} B_{12}h\nu\left(1 \big/ c\right) = \alpha_\nu$

$$\therefore \frac{dI_\nu}{dx} = \alpha_\nu I_\nu$$

$$\therefore \frac{dI_\nu}{I_\nu} = \alpha_\nu dx$$

On integrating, $I_\nu = (I_\nu)_0 e^{\alpha_\nu x}$ ……(ii)

Where $(I_\nu)_0$ is a constant.

Now, since the levels E1 and E2 have finite widths, the spectral line due to transition between these levels has a finite frequency-spread $\Delta\nu$, say , about a mean frequency ν_0 . We can estimate the value of gain constant α_ν at this mean frequency ν_0 by putting $\Delta N = N$ in eqn. (ii), we get

$$(\alpha_\nu)_0 = \frac{[\{\Delta N_2\} - \{\Delta N_1\}]}{\Delta\nu} B_{12}h\nu\left(1 \big/ c\right)$$

Using the relation $\frac{A_{21}}{B_{21}} = \frac{8\pi h\gamma^3}{c^3}$

We get $(\alpha_\nu)_0 = \frac{c^3(N_2 - N_1)}{8\pi\nu_0^2} A_{21}$ ……(iii)

Now, there may be two cases:

If $N_2 > N_1$ (as a result of population inversion), then $(\alpha_\nu)_0$ is positive, and from eq.(iii), I_ν increases as x increases. This means that as the light beam progresses through the medium, its intensity I_ν increases exponentially, that is, there is an amplification of the intensity of the light beam. Thus, population inversion is necessary for light amplification.

If on the other hand, $N_2 < N_1$ as ordinarily happens, $(\alpha_\nu)_0$ is negative and I_ν decreases exponentially as x increases.

10.5 Let us Sum up:

In this unit you have learnt to

1. Derive the Einstein's coefficients
2. What is principle of laser? Explain principle of laser.
3. Write a note on population inversion.
4. The mathematical treatment of necessary condition for light amplification (Population *Inversion*)

10.6 Self Evaluation Questions:

1. Derive the Einstein's coefficients
2. What is principle of laser? Explain principle of laser.
3. Write a note on population inversion.
4. The mathematical treatment of necessary condition for light amplification (Population *Inversion*)

10.7 References:

1. Introduction to Atomic and molecular spectroscopy by Vimal Kumar Jain
2. Atomic and Molecular Spectra: Laser by Raj Kumar

UNIT 11: Optical and electrical pumping; optical resonator modes of a rectangular cavity; ammonia maser; Ruby, He-Ne, CO_2 and semi conductor laser:

Structure:

11.0 Objective:

After studying this unit you are going to understand

- The Optical and electrical pumping, optical resonator modes of a rectangular cavity, ammonia maser; Ruby, He-Ne, CO_2 and semi conductor laser.

11.1 Introduction:

The first requirement in the generation of laser is the creation of population inversion. Input energy in various forms have to be supplied to the gain media for excitation and transition of ground level atoms, molecules , ions or electrons as the case may be, to higher levels to create population inversion and consequent generation of laser.

Commonly used excitation techniques are

1. Optical pumping (solid state lasers),
2. Electrical discharge / radio frequency excitation (gas lasers),
3. Electron beam/injection current (semi conductor lasers),
4. Chemical (chemical lasers)
5. Thermal (Gas Dynamic lasers),
6. High-energy electrons from accelerator (free electron lasers) etc.,

The different types of excitation mechanism are obtained by optical, electrical, chemical and thermal process etc.

11.2 Pumping Techniques:

11.2.1. Electrical Pumping or Electron pumping:

In electrical pumping the pump energy is usually provided in the form of electric current. Electric glow discharge is a common method adopted for gas lasers. In this method an applied voltage produces an electric filed within the laser tube that accelerates the electrons within the gas. Those electrons collide with the gas atoms and excite the atoms to excited energy levels, some of which serve as upper laser levels. Lower-lying levels, those to which higher-lying levels can transition, typically decay to the ground state faster than the higher-lying levels, thereby establishing a population inversion between some of the higher and lower. In many instances the excitation is a two-step process in which the electrons first excite a long-lived or metastable

(storage) level or they ionize the atom, leaving an ion of that species and another electron. In either case, that level then transfers its stored energy to the upper laser level via a subsequent collision with the laser species.

Electron pumping is used primarily in gaseous or semiconductor gain Media. In gases, many electrons are produced when a few initial electrons within the gain Medium are accelerated by an electric field within the medium and these many electrons then Collide with neutral atoms, exciting those atoms to higher-lying energy levels and even ionizing some of the atoms (removing an electron). The freed electrons are also accelerated, producing an avalanche of electrons and therefore an electrical current within the medium. The electrons lose their energy by transferring it to the atoms during the collision process. Some of the lasers operate on a pulsed basis, applying a large amount of current for a short period of time. Others operate on a continuous basis, using a much smaller but continuous current.

In semiconductors, the electrons flow through the semiconducting material by applying a voltage across the *pn* junction with the positive voltage on the side of the *p*-type material. This leads to recombination radiation when the electrons combine with the holes in the junction. The heat loading of the semiconductor limits the current.

11.2.2. Optical pumping:

Optical pumping of lasers generally applies to the pumping of liquid (dye) Lasers and to dielectric solid-state lasers and is provided by either flash lamps or other lasers. The most common types of flash lamps used for pumping lasers are narrow, cylindrical quartz tubes with metal electrodes mounted on the ends, filled with a gaseous species such as xenon that serves as the radiating material within the lamp. A voltage is applied across the electrodes of the flash lamp and current flows through the gas, populating excited levels of the atoms within the gas that radiate and produce intense light emission. The process is similar to that of electron Excitation of lasers except that a population inversion is not produced and the radiating material of the lamp radiates via spontaneous emission, rather than by stimulated emission as in the case of a laser gain medium. The pumping wavelength of the flash lamp is determined by the gaseous medium inserted within the flash lamp tube. Xenon is the most common species because of both its radiating efficiency and its emission of a broad spectrum of wavelengths from which to choose

in matching the lamp emission to the pumping absorption bands of the laser. Laser pumping is used in cases in which the pumping energy must be concentrated into a relatively small volume or for a very short time, or if the pumping wavelength must be provided over a fairly narrow-wavelength bandwidth. Pumping lasers include the argon ion or doubled Nd:YAG lasers for pumping titanium-sapphire lasers, excimer lasers for pumping dye lasers, and gallium arsenide semiconductor lasers for pumping Nd:YAG lasers. In most cases the laser is focused to a relatively small gain region, a line focus for dye lasers and a spot focus for the other lasers.

This method is used when the laser media is in the form of optically transparent solid materials with active ions having strong absorption bands in the visible or near infrared region. A pump source, giving maximum emission at wavelengths to excite fluorescence in the solid lasing material is chosen. The different pump sources are: Noble gas filled flash lamps, metal vapor discharge lamps, tungsten-halogen filament lamps, semiconductor lasers, etc. Xenon flash lamps for pulsed operation and arc lamps for continuous wave operation of lasers are the most commonly employed optical pumps.

An optical reflector cavity is required to couple the high intensity light output efficiency from the flash lamp to the laser rod. Various reflecting geometries have been employed for this purpose. Elliptical reflector, with the laser rod at one focus and the flash lamp at the other, cylindrical reflector with the lamp and the rod in close proximity or the rod surrounded by the helical flash lamp, have all been used for efficient coupling of light on to the rod. End pumping as well as side pumping geometries have been employed for diode laser pumping of solid-state lasers. Examples of optically pumped solid state lasers are: Nd: YAG, Nd: Glass and alexandrite, etc. Two examples of diode pumping of Nd: YAG lasers are shown in figure 1.

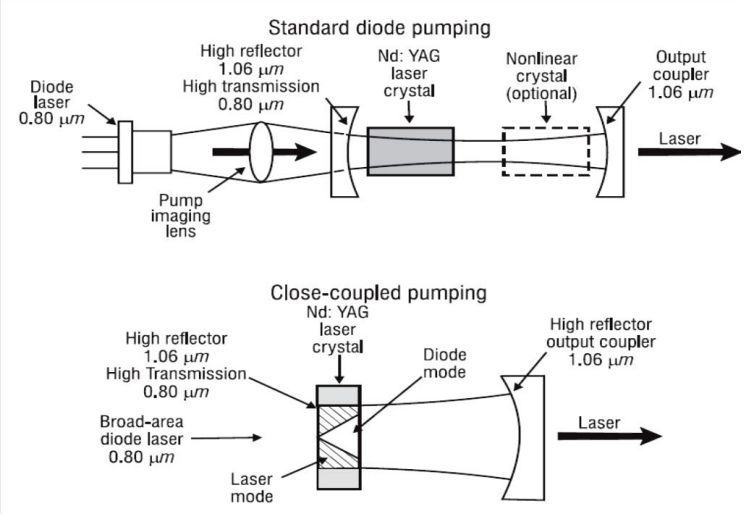


Figure 1: Examples of laser diode pumping of Nd: YAG lasers

11.3 Laser beam properties:

Laser beam properties such as direction and divergence of the beam, the beam profile, and the wavelength and frequency characteristics of the laser within the wavelength region of the laser gain bandwidth are determined largely by the laser mirrors. The factors determining those properties include mirror curvature, surface quality, and reflectivity as well as separation and location, assuming that the structure holding the mirrors is a secure, vibration-free structure. The unique electromagnetic wave properties produced by the mirrors are referred to as modes. Before discussing these mirror properties, we must consider the shape of the gain medium and the beam growth to the point of beam saturation. For a laser in which the amplifier length has a value of L and the mirrors have identical reflectivities R, with no other losses in the cavity, the threshold condition for the gain coefficient g is given as

$$g = \frac{1}{2L} \ln \frac{1}{R^2} \qquad \text{------ (1)}$$

This has dimensions of 1/length. Any value of g higher than that given by equation will produce a laser beam within the cavity. For a more complex laser cavity in which the mirrors have different reflectivities $R1$ and $R2$, and $a1$ and $a2$ represent other losses within the cavity (Beyond the amplifier), the expression for the threshold gain g is given as

$$g = \frac{1}{2L} \ln \left[\frac{1}{R_1 R_2 (1 - a_1)(1 - a_2)} \right] + \alpha \qquad \text{----- (2)}$$

The term α represents a potential absorption loss within the amplifier itself, which is present in only a few types of lasers. It is a distributed loss expressed in the same units as g or (1/length). For example, in solid-state lasers it is termed excited state absorption.

Problem1. Consider a He-Ne laser in which the mirror reflectivities might be $R1$ = 0.999 (99.9%) and $R2$ = 0.990 (99%) and the cavity losses are $a_1 = a_2$ = 0.002 (0.2%) and α = 0. For that situation calculate the gain per pass that would be necessary to operate the laser at threshold.

Solution: Using equation 2 for the gain coefficient, we can obtain

$$g = \frac{1}{2x20}\ln\left[\frac{1}{(0.999)(0.990)(1-0.002)(1-0.002)}\right] = 0.00038/cm = 0.038\%/cm$$

Hence the increase over a 20-cm-length amplifier would be gL = 20 cm × (0.00038)/cm = 0.0076 or 0.76% per pass.

The useful power from the laser is obtained by locating a partially transmitting "output" mirror at one end of the amplifier so that part of the beam "leaks out" of the mirror cavity as shown in figure. The initial gain in the amplifier must be greater than the loss of the transmitting mirror (plus other mirror and cavity losses) or the beam will not develop as described in Equations 1 and 2. A simple expression for the optimum mirror transmission T_{opt} in terms of the small-signal-gain coefficient g, the actual amplifier length L, and the absorption loss a (averaged over a single pass from one mirror to the other) can be expressed as

$$T_{opt} = (gLa)^{\frac{1}{2}} - a \quad \text{------ (3)}$$

Problem2. For the He-Ne laser given in Example 1, assume that the gain is 10 times the threshold value or g = 10 × 0.00038 = 0.0038 and L = 20 cm. Also assume that the absorption loss $\boldsymbol{a}$ is an average of $\boldsymbol{a_1}$ and $\boldsymbol{a_2}$ as defined above, or a = 1/2(a_1 + a_2) = 0.002. Compute the optimum mirror transmission for that situation.

Solution: Using Equation 3 we have for T_{opt}

A mirror reflectivity of 98.96% or approximately 99% would be the appropriate reflectivity of the output mirror. This was in fact the transmission used in Example 1 for R2.

$$T_{opt} = [(0.0038)(20)(0.002)]^{\frac{1}{2}} - 0.002 = 1.04\%$$

The laser beam output intensity I_{max} emitted from the output mirror can also be estimated in terms of the saturation intensity I_{sat}, $T_{opt,}$ and the average absorption per pass a in the following expression.

$$I_{\max} = \left[\frac{T_{opt}^2}{2a} \right] I_{sat} \quad \text{---- (4)}$$

Problem3. For the He-Ne example given above, estimate the power output from the laser. Using Equation (4) and the conditions described in the example above, T_{opt} = 0.0104, a = 0.002, as well as the value of the saturation intensity I_{sat} = 6.2 W/cm^2.

Solution: $I_{\max} = \left[\frac{T_{opt}^2}{2a} \right] I_{sat}$

We find that the maximum output power is I_{max} = 167 mW.

11.4 Optical cavity or **optical resonator:**

This is an arrangement of mirrors that forms a standing wave cavity resonator for light waves. Optical cavities are a major component of lasers, surrounding the gain medium and providing feedback of the laser light. They are also used in optical parametric oscillators and some interferometers. Light confined in the cavity reflect multiple times producing standing waves for certain resonance frequencies. The standing wave patterns produced are called modes; longitudinal modes differ only in frequency while transverse modes differ for different frequencies and have different intensity patterns across the cross section of the beam.

Different resonator types are distinguished by the focal lengths of the two mirrors and the distance between them. (Flat mirrors are not often used because of the difficulty of aligning them to the needed precision.) The geometry (resonator type) must be chosen so that the beam remains stable (that the size of the beam does not continually grow with multiple reflections). Resonator types are also designed to meet other criteria such as minimum beam waist or having no focal point (and therefore intense light at that point) inside the cavity.

Optical cavities are designed to have a large Q factor a beam will reflect a very large number of times with little attenuation. Therefore the frequency line width of the beam is very small indeed compared to the frequency of the laser.

11.4.1. Longitudinal cavity modes:

When the beam is developing within the mirror cavity, traveling back and forth, certain wavelengths within the gain bandwidth of the laser tend to be more enhanced than others. These are wavelengths (or frequencies) in which the light beam in the cavity forms a *standing wave*. Such an effect occurs when an exact number of half-wavelengths of the light fit within the separation distance between the mirrors. Typically there will be several hundred thousand wave peaks for each standing wave that occurs within the cavity. Hence, each standing wave must have a wavelength such that an integral number of oscillating waves fits in the space separating the mirrors. If more than one standing wave is present, each standing wave (longitudinal mode) will be separated in frequency from the next one by a fixed exact amount that depends upon the laser cavity length *d*. That frequency separation Δν between longitudinal modes can be obtained by dividing the speed of light *c* by twice the cavity length

$$\Delta \nu = \frac{c}{2d} \quad \text{----- (5)}$$

In Figure 2, several of these modes are shown occurring within the frequency bandwidth of a typical gas laser. Typically, the separation in frequency is of the order of 500 MHz (5×10^8 Hz) whereas the laser frequency itself is of the order of 500,000,000,000,000 Hz (5×10^{14} Hz).

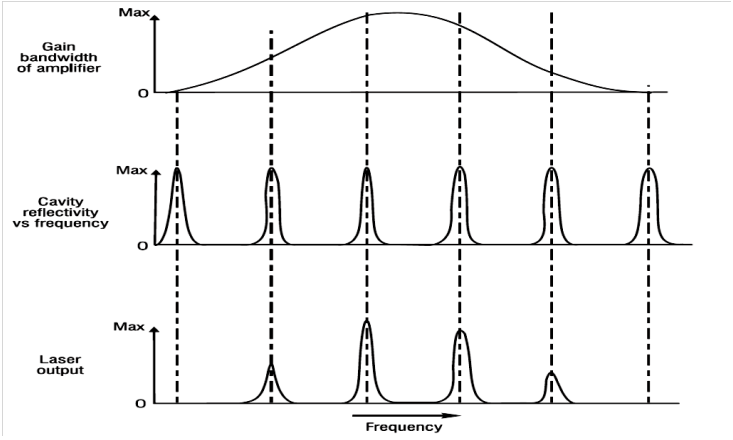


Figure 2: Several longitudinal modes are shown occurring within the gain bandwidth of a typical gas laser

Each discrete standing wave is referred to as a longitudinal mode associated with the laser cavity. Figure 3 shows two such modes within a cavity. There will always be at least one longitudinal mode and there could be many more, depending on the frequency or wavelength bandwidth of the laser gain medium. If more than one longitudinal mode is being generated, they will be indistinguishable unless a spectrum analyzer is used to analyze the beam. They all travel in the same direction, and their color will be indistinguishable because their wavelengths (frequencies) are so similar, as indicated above.

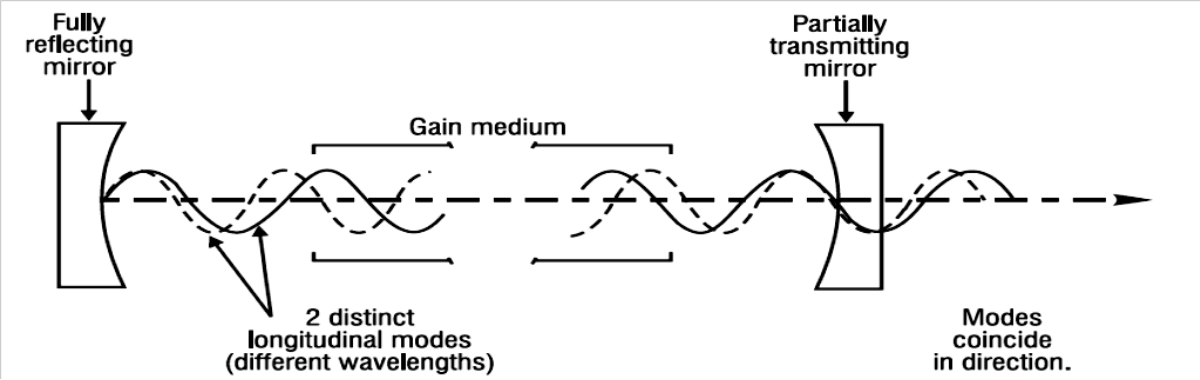


Figure 3: Two distinct longitudinal modes operating simultaneously in the same laser Cavity

11.4.2. Transverse modes:

The presence of more than one longitudinal mode involves much light beams traveling exactly the same path through the amplifier but differing in wavelength depending upon the total number of wave cycles that fit between the mirrors. Contrary to this, different transverse modes involve slightly different optical paths through the amplifier and thus have slightly different directions when they emerge from the laser as shown in Figure 4. Because of the different optical path lengths, they also have slightly different frequencies. Each of these stable modes evolves because the light traveling that particular pathway recurs exactly from one round trip of the beam to the next, therefore developing into a steady beam. Each transverse mode traveling over its unique path might also consist of several longitudinal modes separated in frequency.

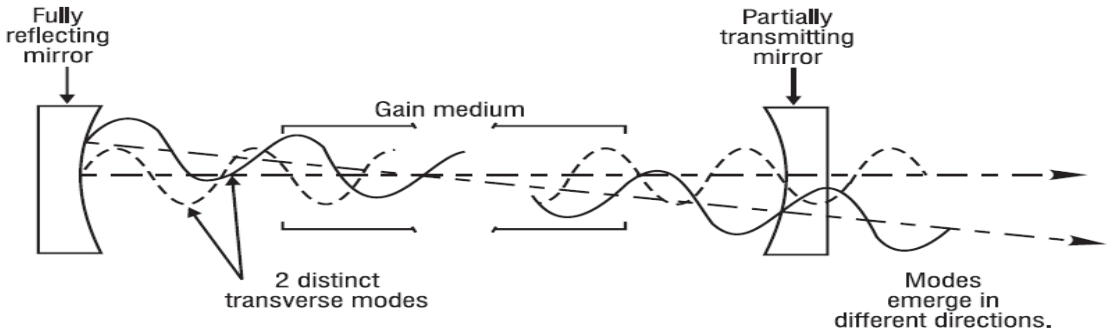


Figure 4: Two transverse modes occurring simultaneously within a laser cavity.

11.4.3. Resonator type:

The most common types of optical cavities consist of two facing plane (flat) or spherical mirrors. The simplest of these is the plane-parallel or Fabry–Pérot cavity, consisting of two opposing flat mirrors. While simple, this arrangement is rarely used in large-scale lasers due the difficulty of alignment; the mirrors must be aligned parallel within a few seconds of arc, or "walk off" of the intracavity beam will result in it spilling out of the sides of the cavity. However, this problem is much reduced for very short cavities with a small mirror separation distance ($L <$ 1 cm). Plane-parallel resonators are therefore commonly used in microchip and micro cavity lasers and semiconductor lasers. In these cases, rather than using separate mirrors, a reflective optical coating may be directly applied to the laser medium itself. The plane-parallel resonator is also the basis of the Fabry–Pérot interferometer.

For a resonator with two mirrors with radii of curvature R_1 and R_2, there are a number of common cavity configurations. If the two curvatures are equal to half the cavity length ($R_1 = R_2 = L / 2$), a concentric or spherical resonator results. This type of cavity produces a diffraction-limited beam waist in the centre of the cavity, with large beam diameters at the mirrors, filling the whole mirror aperture. Similar to this is the hemispherical cavity, with one plane mirror and one mirror of curvature equal to the cavity length.

A common and important design is the confocal resonator, with equal curvature mirrors equal to the cavity length ($R_1 = R_2 = L$). This design produces the smallest possible beam diameter at the cavity mirrors for a given cavity length, and is often used in lasers where the purity of the transverse mode pattern is important.

A concave-convex cavity has one convex mirror with a negative radius of curvature. This design produces no intracavity focus of the beam, and is thus useful in very high-power lasers where the intensity of the intracavity light might be damaging to the intracavity medium if brought to a focus.

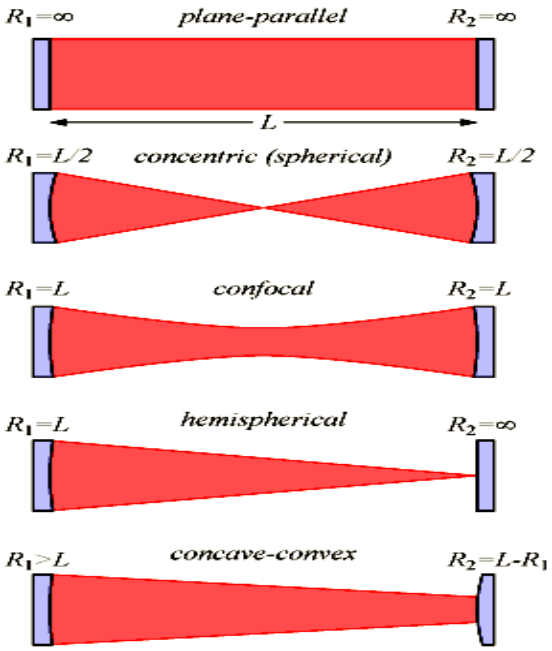


Fig 5. Radiation pattern

11.4.4. Modes of a Rectangular Cavity:

Consider a rectangular cavity of dimensions $2a \times 2b \times d$ as shown in Figure.6

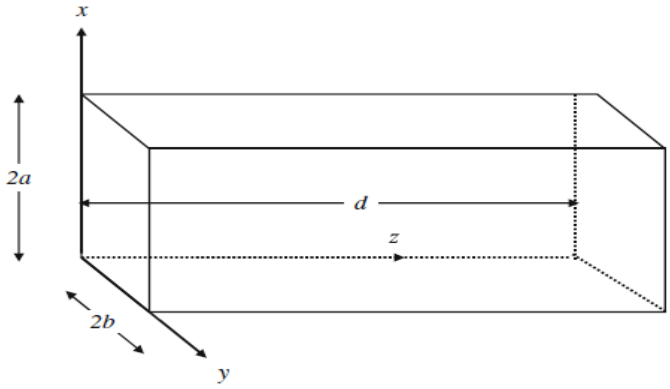


Fig 6. rectangular cavity

Starting from Maxwell's equations one can show that the electric and magnetic fields satisfy a wave equation of the form given by

$$\nabla^2 E - \frac{n_0^2}{c^2}\frac{\partial^2 E}{\partial t^2} = 0 \text{ ---------- (6)}$$

Where c represents the velocity of light in free space and n_0 represents the refractive index of the medium filling the rectangular cavity. If the walls of the rectangular cavity are assumed to be perfectly conducting then the tangential component of the electric field must vanish at the walls. Thus if $\hat{n}$ represents the unit vector along the normal to the wall then we must have

$$E \times \hat{n} = 0 \text{ ---------- (7)}$$

on the walls of the cavity.

Let us consider a Cartesian component (say x component) of the electric vector this will also satisfy the wave equation, which in the Cartesian system of coordinates will be given by

$$\frac{\partial^2 E_x}{\partial x^2} + \frac{\partial^2 E_x}{\partial^2 y^2} + \frac{\partial^2 E_x}{\partial^2 z^2} = \frac{n_0^2}{c^2}\frac{\partial^2 E_x}{\partial^2 t^2} \text{ ---------- (8)}$$

In order to solve Eq. (8) we use the method of separation of variables and write

$$E_x = X(x)Y(y)Z(z)T(t) \text{ ---------- (9)}$$

Substituting this in Eq. (8) and dividing by *Ex* We obtain

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial^2 y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial^2 z^2} = \frac{n_0^2}{c^2 T}\frac{\partial^2 T}{\partial^2 t^2} \text{ ------ (10)}$$

Thus the variables have indeed separated out and we may write

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = -k_x^2 \text{ ---------- (11)}$$

$$\frac{1}{Y}\frac{\partial^2 Y}{\partial^2 y^2} = -k_y^2 \text{ ---------- (12)}$$

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial^2 z^2} = -k_z^2 \text{ ---------- (13)}$$

and

$$\frac{n_0^2}{c^2 T} = \frac{\partial^2 T}{\partial t^2} = -k^2 \text{ ---------- (14)}$$

Where,

$$k^2 = k_x^2 + k_y^2 + k_z^2 \text{ ---------- (15)}$$

Equation (14) tells us that the time dependence is of the form

$$T(t) = Ae^{-i\omega t} \text{ ---------- (16)}$$

Where $\omega = c\ k/n_0$ represents the angular frequency of the wave and A is a constant. It should be mentioned that we could equally well have chosen the time dependence to be of the form $e^{i\omega t}$. Since Ex is a tangential component on the planes $y = 0$, $y = 2b$, $z = 0$, and $z = d$, it has to vanish on these planes and the solution of Eqns. (12) and (13) would be sin $k_y y$ and sin $k_z z$, respectively, with

$$k_y = \frac{n\pi}{2b}, k_z = \frac{q\pi}{d}, where(n),(q) = 0,1,2,3..... \text{ ---------- (17)}$$

Where we have intentionally included the value 0, which in this case would lead to the trivial solution of E_x Vanishing everywhere .In a similar manner, the x and z dependences of E_y would be sin $k_x x$ and sin $k_z z$, respectively, with

$$k_x = \frac{m\pi}{2a}, where(m) = 0,1,2,3,.... \text{ ---------- (18)}$$

and k_z given by Eq. (17). Finally the x and y dependences of E_z would be sin $k_x x$ and sin$k_y y$ respectively. Now, because of the above forms of the x dependence of E_y and E_z, $\partial E_y / \partial y$, and $\partial E_z / \partial z$ would vanish on the surfaces $x = 0$ and $x = 2\ a$. Thus on the planes $x = 0$and $x = 2a$, the equation $\nabla . \mathbf{E} = 0$ leads to $\partial \mathbf{E}_x / \partial x = 0$.Hence the x dependence of E_x will be of the form cos$k_x x$ with k_x given by Eq. (18). Notice that the case $m = 0$ now corresponds to a nontrivial solution.

In a similar manner, one may obtain the solutions for E_y and E_z. The complete solution (apart from the time dependence) would therefore be given by

$$E_x = E_{0_x} \cos k_x x \sin k_y y \sin k_z z$$

$$E_y = E_{0_y} \sin k_x x \cos k_y y \sin k_z z \text{ -------- (19)}$$

$$E_z = E_{0_x} \sin k_x x \sin k_y y \cos k_z z$$

where E_{0x}, E_{0y}, and E_{0z} are constants. The use of Maxwell's equation $\nabla . \mathbf{E} = 0$, immediately gives

$$\vec{E}_0 . \vec{k} = 0 \text{ ----- (20)}$$

Where, $\vec{k} = \hat{x}k_x + \hat{y}k_y + \hat{z}k_z$

Since the coefficients E_{0x}, E_{0y} and E_{0z} have to satisfy. Eqn (20) It follows that for a given mode, i.e., for a given set of values of *m*, *n*, and *q* only two of the components of E_0 can be chosen independently. Thus a given mode can have two independent states of polarization. Note that when one of the quantities *m*, *n*, or *q* is zero, then there is only one possible polarization state associated with the mode. Thus if we consider the use with $m = 0$, $n \neq 0$, $q \neq 0$, then

$E_x = E_{0x} \sin k_y y \sin k_z z$, $E_y = 0$, $E_z = 0$. Thus the only possible case is with the electric vector oriented along the *x*-direction. Using Eqns (15), (17), and (18), we obtain

$$\omega^2 = \frac{c^2 k^2}{n_0^2} = \frac{c^2}{n_0^2}(k_x^2 + k_y^2 + k_z^2) = \frac{c^2 \pi^2}{n_0^2}\left(\frac{m^2}{4a^2} + \frac{n^2}{4b^2} + \frac{q^2}{a^2}\right)$$

or

$$\omega^2 = \frac{c^2 \pi}{n_0}\left(\frac{m^2}{4a^2} + \frac{n^2}{4b^2} + \frac{q^2}{a^2}\right)^{\frac{1}{2}} \text{ ---------- (21)}$$

which gives us the allowed frequencies of oscillation of the field in the cavity. Field configurations given by Eq. (19) represent standing wave patterns in the cavity and are called modes of oscillation of the cavity. These are similar to the acoustic modes of vibration of an acoustic cavity (like in a musical instrument such as a guitar and veena) and represent the only possible frequencies that can exist within the cavity.

11.5 Ammonia maser

A **maser** is a device that produces coherent electromagnetic waves through amplification by stimulated emission. The word "maser" is derived from the acronym **MASER**: Microwave Amplification by Stimulated Emission of Radiation".

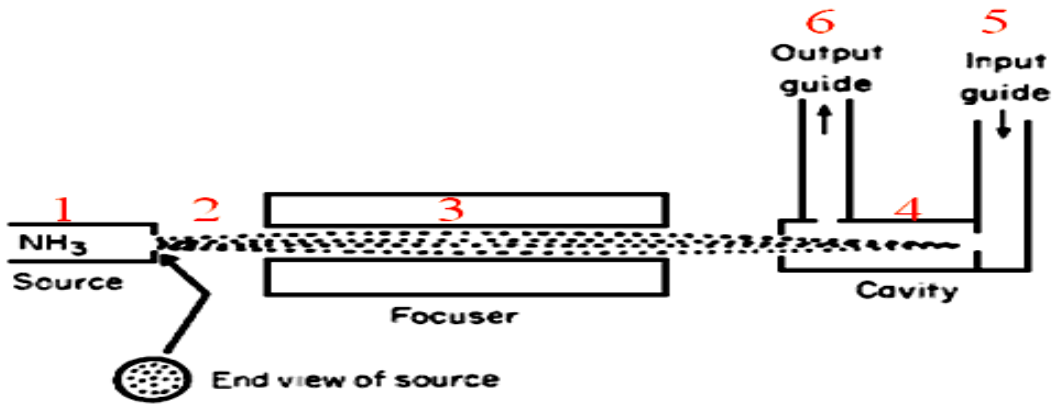


Fig 7. Ammonia Maser

i) Working:

1. A heater gives energy to molecules of ammonia (NH_3) in the source at this point about half of the molecules are in an excited state, the other half are not.

2. The ammonia molecules stream into the focuser (also called a separator), which is evacuated.

3. The focuser removes molecules in the lower quantum state from those in the upper quantum state (for these would absorb rather than emit photons at the desired frequency) while *focusing* those in the upper state. The energy states can be *separated* by a system of focusing electrodes. The electric dipole moments induced in the NH_3 molecules interact with the electric field produced by the electrodes. The internal energy of an upper state molecule is increased and that of a lower state molecule is decreased so that, in the non-uniform electric field, the lower state molecules move towards the higher field region and the upper state molecules move to the lower field region

4. The ammonia molecules that pass into the resonant cavity (tuned to 24GHz) are almost all excited. They constitute an inverted population. The cavity has a very high Q, so there is sufficient noise power to initiate transitions from the upper state the lower state. Photons from these transitions can then *stimulate* emission from other molecules.

5. When it is used as an amplifier, the signal to be amplified is injected into the cavity that enters the cavity via an input waveguide. This radiation leads to even more rapid stimulated emission by the excited molecules.

6. The resultant coherent radiation detected at the output waveguide is an amplified version of the input signal.

ii) Applications:

a. Masers are low-noise amplifiers. Since molecules are uncharged, the usual shot noise in electronic amplifiers is missing, and essentially no noise in addition to thermal noise is present in maser amplifiers. This radiation reflects back and forth inside the cavity, whose size is specially chosen and regulated to reinforce waves of just this frequency.
b. The maser is functioning as a self-oscillator

11.6 Types of Lasers:

Many materials have been found to have the required characteristics to form the laser gain medium needed to power a laser, and these have led to the invention of many types of lasers. Based on the lasing material used laser can be broadly classified into four categories: gas discharge lasers, semiconductor diode lasers, optically pumped lasers, and "other," a category which includes chemical lasers, gas-dynamics lasers, x-ray lasers, combustion lasers, and others developed primarily for military applications.

Solid state laser materials are commonly made by doping a crystalline solid host with ions that provide the required energy states. Example Nd: YAG laser. Gas lasers use a gas as the gain medium, for ex. CO_2 laser. OTHER LASERS TYPES use different mechanisms for laser light generation. One such method is Dye laser.

11.6.1: He-Ne Laser

A **helium–neon laser** or **He-Ne laser** was the first gas laser whose gain medium consists of a mixture of helium and neon inside of a small bore capillary tube, usually excited by a DC

electrical discharge. The best known and most widely used He-Ne laser operates at a wavelength of 632.8 nm in the red part of the visible spectrum.

He-Ne lasers can also be operated at the 543.5-nm green wavelength and several infrared wavelengths. Initiation of a relatively low electrical current through a low-pressure gas discharge tube containing a mixture of helium and neon gases produces the population inversion. With this gas mixture, helium metastable atoms are first excited by electron collisions with helium ground-state atoms. This energy is then transferred to the desired neon excited energy levels, thereby producing the required population inversion with lower-lying helium energy levels.

i) Construction and working

The gain medium of the laser, as suggested by its name, is a mixture of helium and neon gases, in approximately a 10:1 ratio, contained at low pressure in a glass envelope. The gas mixture is mostly helium, so that helium atoms can be excited. The excited helium atoms collide with neon atoms, exciting some of them to the state that radiates 632.8 nm. Without helium, the neon atoms would be excited mostly to lower excited states responsible for non-laser lines. A neon laser with no helium can be constructed but it is much more difficult without this means of energy coupling. Therefore, a He-Ne laser that has lost enough of its helium (e.g., due to diffusion through the seals or glass) will most likely not lase at all since the pumping efficiency will be too low. The energy or pump source of the laser is provided by a high voltage electrical discharge passed through the gas between electrodes (anode and cathode) within the tube. The optical cavity of the laser usually consists of two concave mirrors or one plane and one concave mirror, one having very high (typically 99.9%) reflectance and the output coupler mirror allowing approximately 1% transmission.

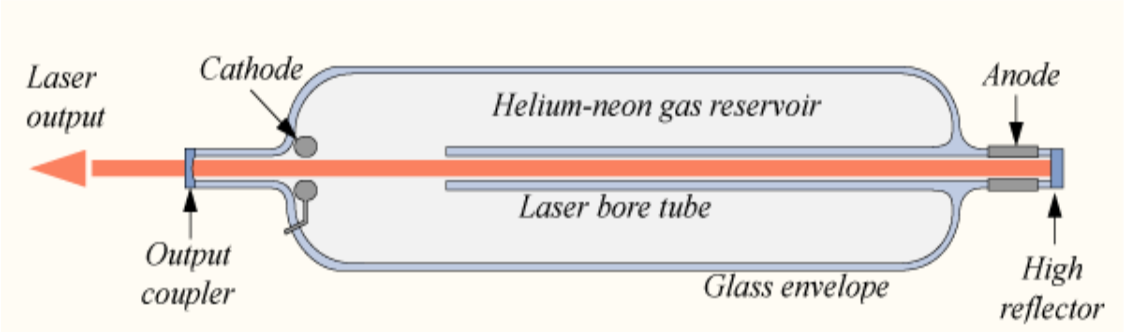


Fig 8. Schematic diagram of a helium-neon laser

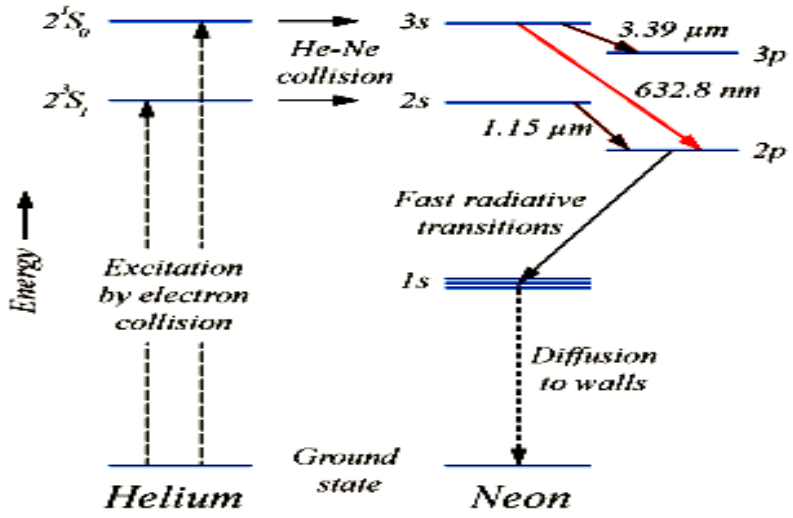


Fig 9. Energy level diagram of a He-Ne laser

The mechanism producing population inversion and light amplification in a He-Ne laser plasma originates with inelastic collision of energetic electrons with ground state helium atoms in the gas mixture. As shown in Fig 9, these collisions excite helium atoms from the ground state to higher energy excited states, among them the 2^3S_1 and 2^1S_0 long-lived metastable states. Because of a fortuitous near coincidence between the energy levels of the two He metastable states, and the $3s_2$and $2s_2$ levels of neon, collisions between these helium metastable atoms and ground state neon atoms results in a selective and efficient transfer of excitation energy from the helium to neon. This excitation energy transfer process is given by the reaction equations:

$$He^*(2^3S_1) + Ne^1S_0 \rightarrow He\ (^1S_0) + Ne^*2s_2 + \Delta E$$

And

$$He^*(2^1S) + Ne^1S_0 + \Delta E \rightarrow He\ (^1S_0) + Ne^*3s_2$$

where (*) represents an excited state, and ΔE is the small energy difference between the energy states of the two atoms, of the order of 0.05 eV or 387 cm^{-1}, which is supplied by kinetic energy. Excitation energy transfer increases the population of the neon $2s_2$ and $3s_2$ levels manifolds. When the population of these two upper levels exceeds that of the corresponding lower level neon state, $2p_4$ to which they are optically connected, population inversion is present. The

medium becomes capable of amplifying light in a narrow band at 1.15 μm (corresponding to the $2s_2$ to $2p_4$ transition) and in a narrow band at 632.8 nm (corresponding to the $3s_2$ to $2p_4$ transition at 632.8 nm). The $2p_4$ level is efficiently emptied by fast radiative decay to the 1s state, eventually reaching the ground state.

The remaining step in utilizing optical amplification to create an optical oscillator is to place highly reflecting mirrors at each end of the amplifying medium so that a wave in a particular spatial mode will reflect back upon itself, gaining more power in each pass than is lost due to transmission through the mirrors and diffraction. When these conditions are met for one or more longitudinal modes then radiation in those modes will rapidly build up until gain saturation occurs, resulting in a stable continuous laser beam output through the front (typically 99% reflecting) mirror.

The visible output of the red He-Ne laser, long coherence length, and its excellent spatial quality, makes this laser a useful source for holography and as a wavelength reference for spectroscopy. A stabilized He-Ne laser is also one of the benchmark systems for the definition of the meter.

He-Ne lasers are generally present in educational and research optical laboratories.

Application:

Red He-Ne lasers have many industrial and scientific uses.

- They are widely used in laboratory demonstrations in the field of optics in view of their relatively low cost and ease of operation compared to other visible lasers producing beams of similar quality in terms of spatial coherence (a single mode Gaussian beam) and long coherence length (however since about 1990 semiconductor lasers have offered a lower cost alternative for many such applications).
- A consumer application of the red He-Ne laser is the Laser Disc player, made Pioneer.
- The laser is used in the device to read the optical disk.

11.6.2: Ruby Laser:

A **ruby laser** is a solid-state laser that uses a synthetic ruby crystal as its gain medium. The first working laser was a ruby laser made by Theodore H. Maiman at Hughes Research Laboratories on May 16, 1960.

The ruby mineral (corundum) is aluminum oxide with a small amount (about 0.05%) of chromium which gives it its characteristic pink or red color by absorbing green and blue light.

The Ruby rod's ends are polished with great precision. The finely polished ends of the rod are silvered; one end completely, the other only partially. The rod, with its reflective ends, then acts as a Fabry–Pérot etalon (or a Gires-Tournois etalon). Modern lasers often use rods with antireflection coatings, or with the ends cut and polished at Brewster's angle instead. This eliminates the reflections from the ends of the rod. External dielectric mirrors then are used to form the optical cavity. Curved mirrors are typically used to relax the alignment tolerances and to form a stable resonator, often compensating for thermal lensing of the rod.

The rod is then placed inside a xenon flash lamp. After receiving a pumping flash from the flash tube, the laser light emerges for as long as the excited atoms persist in the ruby rod, which is typically about a millisecond. The ruby laser, which lases at the extreme red end of the visible spectrum at 694 nm, was the very first laser demonstrated.

A ruby laser is pumped with very high energy from the flashtube, to achieve population inversion. The rod is often placed between two mirrors, forming an optical cavity, which oscillate the light produced by the ruby's fluorescence, causing stimulated emission.

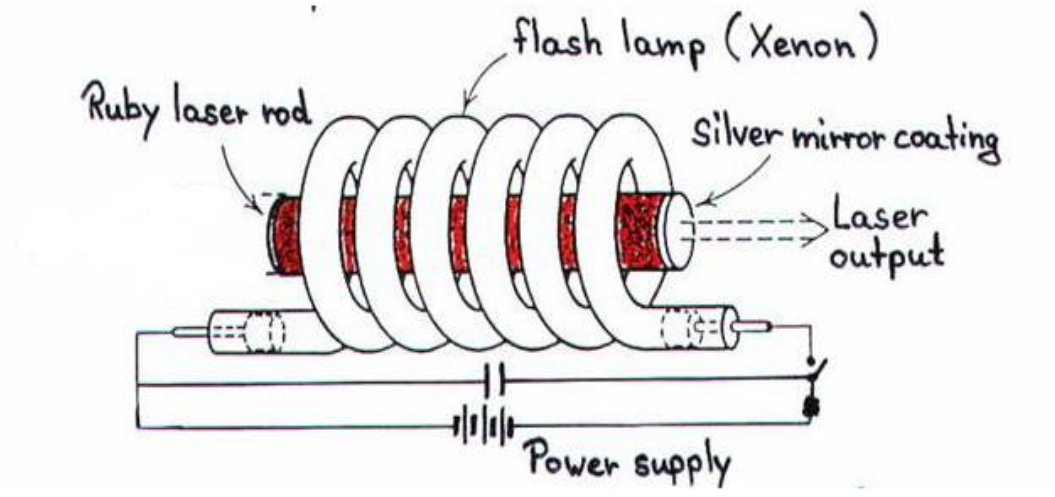


Fig 10. Ruby Laser

The ruby laser is a three level solid state laser. The active laser medium (laser gain/amplification medium) is a synthetic ruby rod that is energized through optical pumping, typically by a xenon flashtube. Ruby has very broad and powerful absorption bands in the visual spectrum, at 400 and 550 nm, and a very long fluorescence lifetime of 3 milliseconds. This allows for very high energy pumping, since the pulse duration can be much longer than with other materials. While ruby has a very wide absorption profile, its conversion efficiency is much lower than other mediums. Ruby also absorbs some of the light at its lasing wavelength. To overcome this absorption, the entire length of the rod needs to be pumped, leaving no shaded areas near the mountings. The active part of the ruby is the dopant, which consists of chromium ions suspended in a synthetic sapphire crystal.

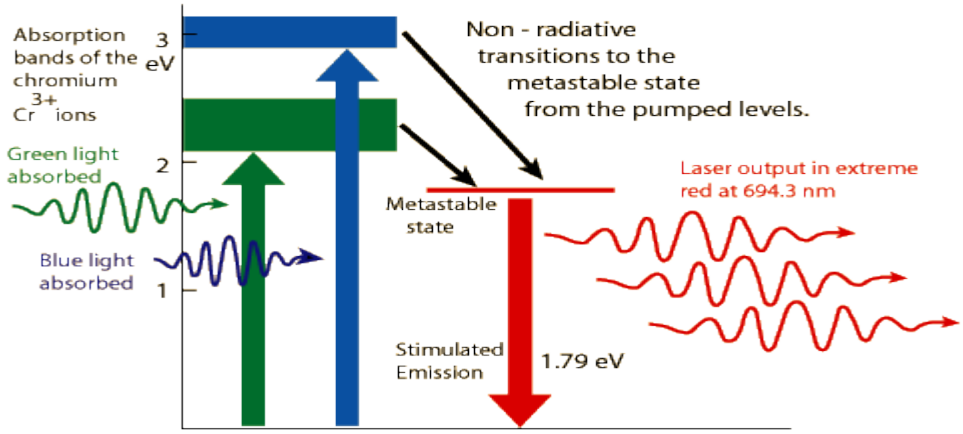


Fig 11. Energy level diagram

The dopant often comprises around 0.05% of the crystal, and is responsible for all of the absorption and emission of radiation. Depending on the concentration of the dopant, synthetic ruby usually comes in either pink or red.

The energy-level arrangement of the ruby laser, with the ground state as the lower laser energy level, makes for a very ineffective pumping process, in which very large amounts of pump light are required before gain is achieved. Therefore, this laser is not as efficient as other solid-state lasers and is not used much anymore.

Applications:

- One of the first applications for the ruby laser was in range finding. By 1964, ruby lasers with rotating prism q-switches became the standard for

military rangefinders, until the introduction of more efficient Nd:YAG range finders a decade later. Ruby lasers were used mainly in research.

- The ruby laser was the first laser used to optically pump tunable dye lasers and is particularly well suited to excite laser dyes emitting in the near infrared.
- Ruby lasers are used in drilling holes through diamond.
- Holography's around the world produce holographic portraits with ruby lasers, in sizes up to a meter square. Because of its high pulsed power and good coherence length, the red 694 nm laser light is preferred to the 532 nm green light of frequency-doubled Nd: YAG, which often requires multiple pulses for large holograms.
- Many non-destructive testing labs use ruby lasers to create holograms of large objects such as aircraft tires to look for weaknesses in the lining.
- Ruby lasers were used extensively in tattoo and hair removal, but are being replaced by alexandrite and Nd: YAG lasers in this application.

11.6.3: Semiconductor lasers (solid state laser):

The semiconductor or diode lasers are the smallest of all the known lasers; they have a size of a fraction of a millimeter. The laser consists of a semiconducting crystal, such as gallium arsenide, lead selenide, etc, with parallel faces at the ends to serve as partially reflective mirrors. The entire laser package is very small and can be incorporated into an integrated circuit board, if required.

A semiconductor, as the name implies, is half-way between a conductor and an insulator (non-metal), so far as its electrical conductivity is concerned. The semiconducting materials containing gallium and arsenic compounds have been found to generate infrared rays when the current is passed through them. This implies that these semiconductors convert electrical energy into photons. But, these were ordinary incoherent light rays and were not produced by the' laser action, However, when the gallium arsenide crystal is through it, the laser action does take place. Many semiconductors serve as laser materials and they have been made to 'lase' under the

stimulation of electricity instead of light which is used for the other solid-state lasers. There are two types of semiconductors, viz., n-type and p-type.

To understand the functioning of these devices, it is necessary to know the nature of the electronic energy states in a semiconductor. A typical semiconductor has bands of allowed energy levels separated by forbidden energy gap region. In an intrinsic semiconductor, there are just enough electrons present to fill the uppermost occupied energy band (valence band) leaving the next higher band (conduction band) empty. In an n-type semiconductor, a small amount of impurity is added intentionally so that the material is made to have an excess of electrons, which thus becomes negative. On the other hand, by adding a different type of impurity in a p-type semiconductor, the material can be made to have an excess of holes (vacancy of electrons), which thus becomes positive.

The semiconductor laser consists of a tiny block (about one square millimeter in area) of gallium arsenide. When the p- and n-type layers are formed in an intimate contact, the interface becomes a p-n junction. When direct current is applied across the block, the electrons move ii across the junction region from the n-type material to the p-type material, having excess of holes. In this process of dropping of the electrons into the holes, recombination takes place leading to the emission of radiation. The photons travelling through the junction region stimulate more electrons during the transition, releasing more photons in the process. The laser action takes place along the line of the junction. Due to the polished ends of the block, the stimulated emission grows enormously and a beam of coherent light is emitted from one of the two ends. With a gallium arsenide laser, a continuous beam of a few militates power is easily obtained.

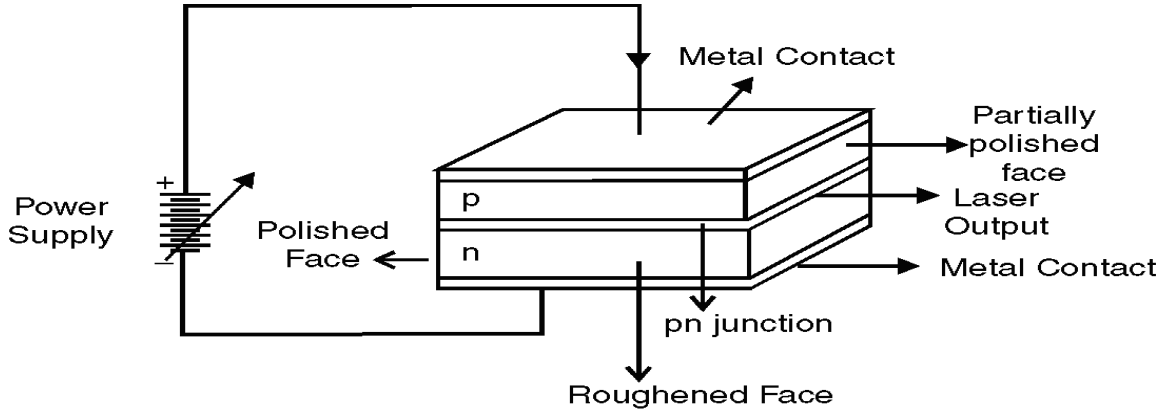


Fig 12(a). Semi conductor Diode

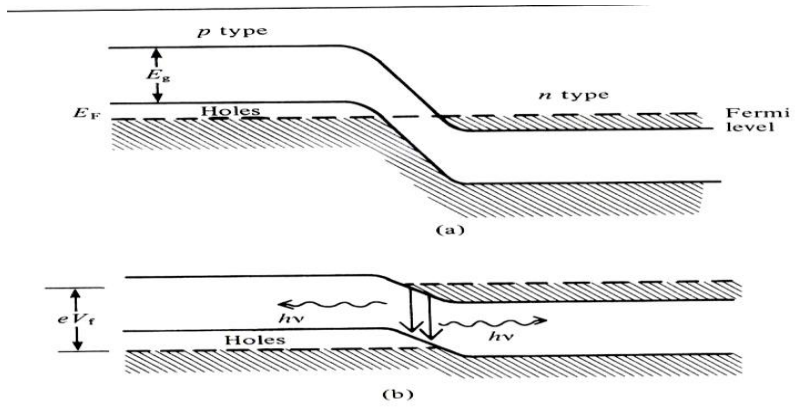


Fig 12(b). Fermi energy level

The semi conducting lasers are also called junction lasers or junction diode lasers because they produce laser energy at the junction of two types of impurities in a semiconductor. They are also called injection lasers because electrons are injected into the junction region.

The technology of semiconductor lasers has undergone considerable development with the important goal of achieving room-temperature operation, low threshold energy, high output powers, wavelength diversity and long lifetimes. By constructing a row of p-n junctions positioned next to each other, all the separate gain media can be forced to emit together in a phased array to produce an effective combined power output. In this way, gallium aluminum arsenide diode lasers have been operated continuously at room temperature with output in the range of several watts. In addition, electrical to optical power conversion efficiencies of greater than 50 per cent have been obtained. The semiconductor lasers, being simple in construction and light In weight with compact units and requiring little auxiliary equipment, are very suitable for applications where high powers are not required. They are primarily used in the area of communication in which the near-infrared laser beams can be transmitted over long distances through low loss optical fibers. In addition, they have found a large market as reading devices for compact disc players.

Application

- The largest applications of semiconductor lasers are in communication, in which the laser provides the signal, and in compact disk players, in which the laser is focused into the disk grooves and reflected to detect the digitally coded information.

- They are also used in high-speed printing systems and laser pointers and as pump sources for solid-state lasers (mainly Nd:YAG).

11.6.4 CO_2 Laser:

Carbon Dioxide lasers (CO_2) lasers are gas lasers originally conceived and devised by Patel (1964). The CO_2 laser behaves basically as a four level laser and uses transitions between two vibrational levels. The carbon dioxide (CO_2) gas laser emits infra red radiation with a wavelength between 9 and 11µm, although emission at 10.6µm is the most widely used. Several types of CO_2 laser that are available, of which the waveguide, the low power sealed tube and the transversely excited atmospheric (TEA) lasers are used for small scale materials processing applications. For sealed tube lasers several thousand hours of operation are possible before the tube has to be cleaned and re-filled or replaced and a good beam quality with power up to 200W is available.

The principle of operation of sealed tube CO_2 laser is described below.

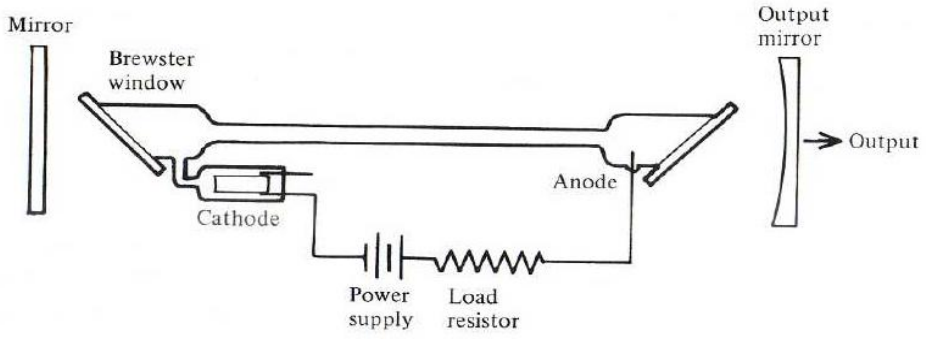


Fig 13. Schematic diagram of sealed tube CO_2 laser

i) Construction:

It is a gas laser in which an electric current is discharged through a gas to produce light. It consists of long narrow glass tubes, filled with the lasing gas mixture. Electrodes at either end of the tube provide the discharge current. A totally reflecting and partially transmitting mirror, usually made from polished metal and coated zinc selenide respectively, form the resonant cavity. The tube is sealed using Brewster angled windows as shown in figure 3.

As the electric discharge in the tube breaks down the CO_2, an ordinary gas mixture would stop working very quickly and so methods are provided to cause the CO_2 to regenerate, either by addition of hydrogen or water or by the use of catalytic action. With these lasers DC and sometimes RF discharges are used.

ii) Principle of working:

For operation of the CO_2 laser, the necessary processes are:

1. Excitation of N_2 vibration by electron impact.
2. Transfer of vibrational energy from N_2 to the nearly resonant v_3 mode of CO_2.
3. Laser transition from v_3 to v_1 mode.
4. Sharing of population between v_1 and $2v_2$ modes and relaxation within the v_2 manifold.
5. The vibrational energy in the v_2 manifold converted into translational energy by collisions with He.

In the CO_2 molecule, the individual atoms are bound by a force which acts much like that of the force due to a spring - a harmonic oscillator. Molecules vibrate due to their lacking fixed orientations within the molecule shown in fig5. They are able to rotate and spin because they are in a gaseous state.

These states, as in electronic states, are quantized. Transitions between Vibrational energy states results in photon emission in the infrared.

Figure shows the energy level diagram of The CO_2 laser. The CO_2 behaves basically as a four level laser and uses transitions between two vibrational levels. The main excitation process involves the excitation of N_2 molecule into their first excited vibrational state. Collisions of CO_2 molecules with excited N_2 molecules result in resonance excitation of CO_2 molecules because of asymmetric stretching vibration frequency. The excited CO_2 molecule undergoes laser action by transition between the vibrational levels (001) and (100) and the accompanying rotational levels. The separation of lasing Vibrational levels of CO_2 is in the range 9 – 11 microns.

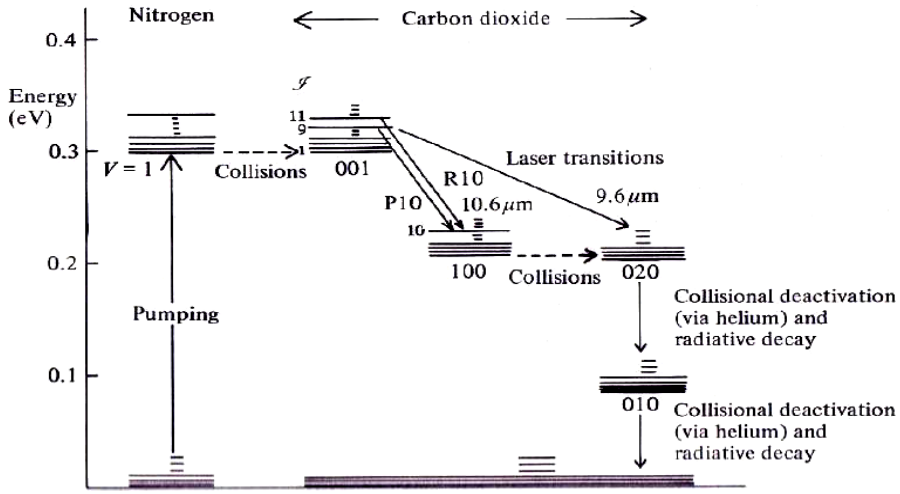


Fig 14. Energy level diagram of CO_2 laser

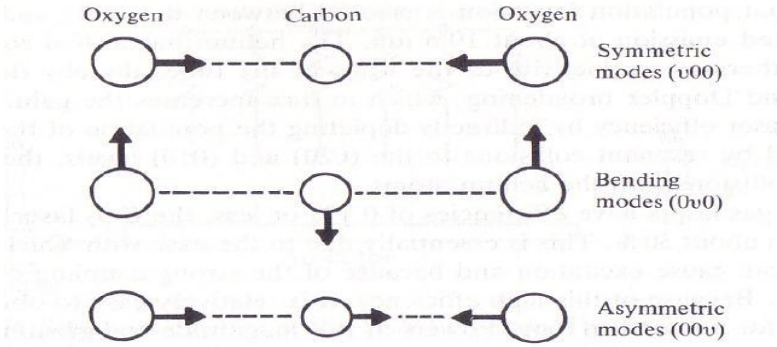


Fig 15. The Vibrational Modes of CO_2 laser

The CO_2 laser producing wave length of 10.6 microns has higher efficiency than any other industrial laser at present. The excited CO_2 molecule also decays spontaneously and directly to the ground state liberating this energy as heat. Some of this heat can be removed by introducing an inert gas which helps to transfer the heat to the wall of the containing tube. When in one of these lower energy levels, a collision between CO_2 and He atoms results in a transfer of the energy to the He atom, and helps the CO_2 molecules to return to the ground state.

11.7 Questions for self study:

1. Explain optical and electrical pumping.

2. What is meant by optical resonator and explain modes of a rectangular cavity.
3. Explain ammonia maser and its uses.
4. Describe the construction and working of Ruby laser.
5. Explain the working principle of He-Ne laser and mention some of its applications.
6. Describe the construction and working of CO_2.
7. Describe the construction and working of Semi conductor laser and mention its applications.

11.8 References:

1. Fundamental and applications of lasers by K.Thyagarajan and Ajoy Ghatak
2. Principles of lasers and optics by William C.Chang.
3. Laser principles by Nambiar.K.R

UNIT 12: Excitation mechanism. Selected applications of laser: holography and optical communication (basic principles only).

Structure:

12.0 Objective:

After studying this unit you are going to understand

- Excitation mechanism, holography and optical communication

12.1 Introduction:

The first requirement in the generation of laser is the creation of population inversion. Input energy in various forms have to be supplied to the gain media for excitation and transition of ground level atoms, molecules, ions or electrons as the case may be, to higher levels to create population inversion and consequent generation of laser.

12.2 Excitation Mechanism:

Commonly used excitation techniques are optical pumping (solid state lasers), electrical discharge / radio frequency excitation (gas lasers), electron beam / injection current (semiconductor lasers), chemical (chemical lasers), thermal (Gas Dynamic Lasers), high-energy electrons from accelerator (free electron lasers) etc.

The different types of excitation mechanisms are optical, electrical, chemical, thermal, laser etc.

12.2.1. Optical pumping:

This method is used when the laser media is in the form of optically transparent solid materials with active ions having strong absorption bands in the visible or near infrared region. A pump source, giving maximum emission at wavelengths to excite fluorescence in the solid lasing material is chosen.

The different pump sources are : Noble gas filled flash lamps, metal vapor discharge lamps, tungsten-halogen filament lamps, semiconductor lasers, etc. Xenon flash lamps for pulsed operation and arc lamps for Continuous wave operation of lasers are the most commonly employed optical pumps.

An optical reflector cavity is required to couple the high intensity light output efficiently from the flash lamp to the laser rod. Various reflecting geometries have been employed for this

purpose. Elliptical reflector, with the laser rod at one focus and the flash lamp at the other, cylindrical reflector with the lamp and the rod in close proximity or the rod surrounded by the helical flash lamp, have all been used for efficient coupling of light on to the rod. End pumping as well as side pumping geometries have been employed for diode laser pumping of solid-state lasers.

12.2.2. Electrical Pumping

In electrical pumping the pump energy is usually provided in the form of electric current. Electric glow discharge is a common method adopted for gas lasers. In this method an applied voltage produces an electric field within the laser tube that accelerates the electrons within the gas. Those electrons collide with the gas atoms and excite the atoms to excited energy levels, some of which serve as upper laser levels. Lower-lying levels, those to which higher-lying levels can transition, typically decay to the ground state faster than the higher-lying levels, thereby establishing a population inversion between some of the higher and lower. In many instances the excitation is a two-step process in which the electrons first excite a long-lived or metastable (storage) level or they ionize the atom, leaving an ion of that species and another electron. In either case, that level then transfers its stored energy to the upper laser level via a subsequent collision with the laser species

Electric current is typically used to pump semiconductor lasers. When a voltage is applied across the junction, with the positive voltage on the *p* side, the electrons are pulled through the junction toward the positive electrode and the holes are attracted to the negative side, producing an electrical current flow across the junction. The electrons and holes meet within the junction and are attracted to each other because of opposite charges. When they meet, they recombine and emit radiation and also can produce a population inversion. This inversion occurs between energy levels located above and below the semiconductor band gap. This energy typically corresponds to a wavelength in the infrared.

12.2.3. Chemical Pumping:

In this method, initially a chemical reaction generates a large amount of excited

molecules and then another gas is introduced in to the system. Now depending on the system, one of the two following things can happen. Either it takes energy from the excited molecule, or it reacts with those particles, producing an excited molecule. These excited molecules produce population inversion.

Examples of chemically Pumped lasers: COIL (chemical oxygen-Iodine laser), DF (deuterium with fluorine), HF (hydrogen with fluorine) lasers etc.

12.2.4. Thermal pumping:

In gas dynamic laser, Pumping is through adiabatic expansion cooling of hot gases. The technique is to expand hot gases through specially shaped nozzles from a high pressure, high temperature chamber into a low-pressure chamber, thus creating a highly non-equilibrium state in the resonator. Due to adiabatic expansion, the upper level population is frozen and the lower level population is depleted, resulting in strong population inversion.

Example of thermally excited laser: Carbon dioxide gas dynamic laser (CDGDL).

12.3 Pumping through Laser:

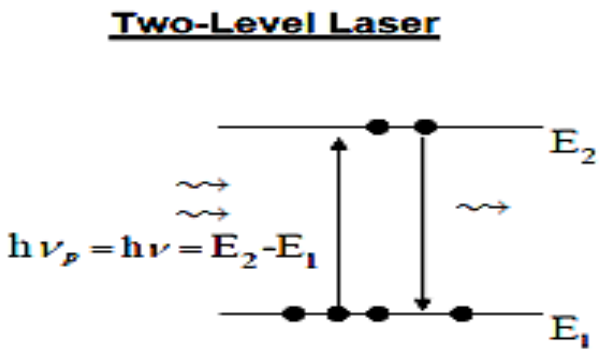
In this method, Lasers with output in the spectral region matching the absorption band of the active media are employed for excitation. For Ti: Sapphire laser, the peak of the absorption band is around 500 nm.

Hence, frequency doubled Nd: YAG laser (532 nm) for pulsed operation and Argon ion laser (514 nm) for CW mode of operation are used for excitation to create population inversion and subsequent laser emission.

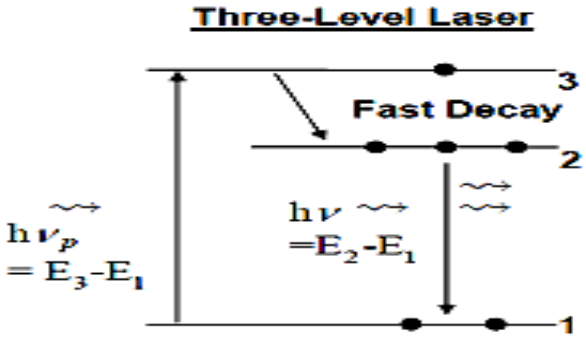
Examples of Laser pumped lasers: - Ti: Sapphire laser, Diode laser pumping of Nd: YAG laser .

Energy level Schemes for Pumping

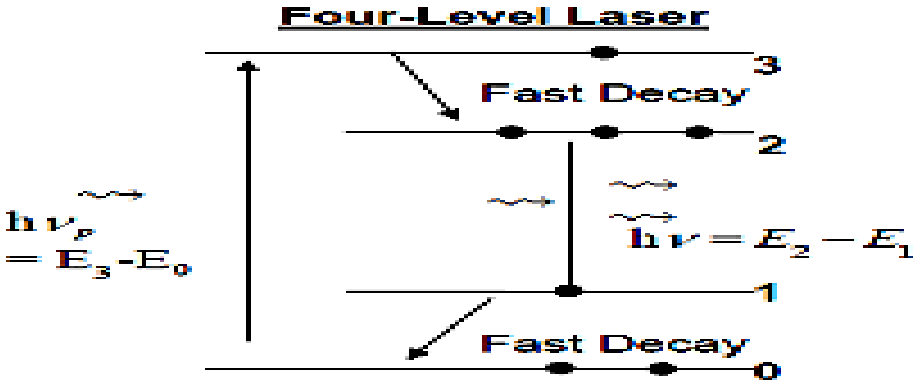
With a two-level system one cannot achieve Population inversion since the probabilities of stimulated absorption and emission are the same when $N_2=N_1$ is once reached and there is no further increase of N_2 by irradiation possible.



In a **three level** system one pumps the third energy level (e.g.: with help of a flash light or by ion acceleration inside the lasing material) which best consists actually of a lot of closely spaced energy levels in order to make the pumping efficient as the source used will supply a wide range of frequencies. If the third level shows a rapid decay to the second but not to the first and lowest level the second will fill up until Population inversion.



A four level system means that added to the "pump" there is a so called "sink" E_1 to E_0 which is characterized by a low life time and depopulates E_1 thereby increasing the ratio N_2/N_1. It is easier to get large inversion.



12.4 Holography:

Introduction:

The most widespread method of obtaining optical images is the photographic method. The image of a 3-dimensional object is recorded on a 2-dimensional photographic plate. Absorption of light in the light sensitive layer. Absorption of light in the light sensitive layer results into chemical reactions and in formation of a latent image. This is transformed into a visible one by the process of developing.

When a observe a photograph from various directions, we does not get new angles of approach and cannot see what's happening on the other side of the object. This is because the conventional photograph is a flat 2-dimensional record of the object. It records only the intensity of the scattered light from the objects and hence their 3-dimensional character is almost completely lost. For the 3-dimensional representation the details of intensity and phases of light waves received from different parts of the object are required. The photographic technique of producing 3-dimensional image of an object is called holography. The resulting photography is called hologram.

The word 'Holography' originates from the Greek word 'holes' meaning the whole. Holography means complete recording. This technique was developed by Gabor in 1949. In this technique a light wave is a carrier of information and it is recorded in terms of wave parameters, amplitude and phase components.

Holography is a technique that allows light scattered from an object to be recorded and later reconstructed. Thus the process doesn't record the image of the object but rather records the reflected light wave.

Holography is a technique which enables three-dimensional images to be made. It involves the use of a laser, interference, diffraction, light intensity recording and suitable illumination of the recording. The image changes as the position and orientation of the viewing system changes in exactly the same way as if the object were still present, thus making the image appear three-dimensional.

The holographic recording itself is not an image; it consists of an apparently random structure of varying intensity, density or profile.

Principles of Holography

The basic principle of holography can be explained in two steps

1. Recording of the hologram
2. Reconstruction of the image.

Working:

Holography is a technique that enables a light field, which is generally the product of a light source scattered off objects, to be recorded and later reconstructed when the original light field is no longer present, due to the absence of the original objects. Holography can be thought of as somewhat similar to sound recording, whereby a sound field created by vibrating matter like musical instruments or vocal cords, is encoded in such a way that it can be reproduced later, without the presence of the original vibrating matter.

Holography applications

Holography may be better understood via an examination of its differences from ordinary photography:

- A hologram represents a recording of information regarding the light that came from the original scene as scattered in a range of directions rather than from only one direction, as in a photograph. This allows the scene to be viewed from a range of different angles, as if it were still present.
- A photograph can be recorded using normal light sources (sunlight or electric lighting) whereas a laser is required to record a hologram.
- A lens is required in photography to record the image, whereas in holography, the light from the object is scattered directly onto the recording medium.

- A holographic recording requires a second light beam (the reference beam) to be directed onto the recording medium.
- A photograph can be viewed in a wide range of lighting conditions, whereas holograms can only be viewed with very specific forms of illumination.
- When a photograph is cut in half, each piece shows half of the scene. When a hologram is cut in half, the whole scene can still be seen in each piece. This is because, whereas each point in a photograph only represents light scattered from a single point in the scene, *each point* on a holographic recording includes information about light scattered from *every point* in the scene. Think of viewing a street outside your house through a 4 ft x 4 ft window, and then through a 2 ft x 2 ft window. You can see all of the same things through the smaller window (by moving your head to change your viewing angle), but you can see more *at once* through the 4 ft window.
- A photograph is a two-dimensional representation that can only reproduce a rudimentary three-dimensional effect, whereas the reproduced viewing range of a hologram adds many more depth perception cues that were present in the original scene. These cues are recognized by the human brain and translated into the same perception of a three-dimensional image as when the original scene might have been viewed.
- A photograph clearly maps out the light field of the original scene. The developed hologram's surface consists of a very fine, seemingly random pattern, which appears to bear no relationship to the scene it recorded.

12.5 Optical communication:

Optical communication, also known as optical telecommunication, is communication at a distance using light to carry information. It can be performed visually or by using electronic devices. The earliest basic forms of optical communication date back several millennia, while the earliest electrical device created to do so was the photo phone, invented in 1880.

An optical communication system uses a transmitter, which encodes a message into an optical signal, a channel, which carries the signal to its destination, and a receiver, which reproduces the message from the received optical signal. When electronic equipment is not

employed the 'receiver' is a person visually observing and interpreting a signal, which may be either simple (such as the presence of a beacon fire) or complex (such as lights using color codes or flashed in a Morse code sequence).

Free-space optical communication has been deployed in space, while terrestrial forms are naturally limited by geography, weather and the availability of light. This article provides a basic introduction to different forms of optical communication.

12.6 Questions for self study:

1. Explain the concept of excitation mechanism.

2. Briefly explain about holography and their uses and optical communication

12.7 References:

1. Basics of Holography by P. Hariharan
2. The Complete Book of Holograms: How They Work and How to Make Them (Dover Recreational Math) Paperback by Joseph E. Kasper , Steven A. Feller
3. Optical communication by M.M. Rao
4. Optical communication by V.S. Bagad

UNIT 13: Laser Spectroscopy, Raman Scattering and their use in pollution studies.

Structure:

13.0 Objectives:

To understand the scattering phenomenon, contribution of Sri. C.V.Raman in the field of scattering of light, Raman spectroscopy, using this the study of environmental applications and other important uses can be studied.

13.1 Introduction:

Raman spectroscopy is a major technique used in many science and technology field. Some of the concepts can be observed in this chapter. Raman scattering, Rayleigh scattering and Raman effect explain with phenomenon of scattering in the system, resulting in the energy of the laser photons shifted up or down gives laser Raman spectroscopy applications in the environmental studies.

13.2 Raman Scattering:

The molecules scatter light. Scattering occurs when a photon interacts with a molecule, but no absorption occurs. The electric field of the light perturbs the electron distribution of the molecule momentarily, but no transition occurs. Because the molecule does not go from one stationary state (lower state) to another (higher state) energy level, there are no selection rules. Figure 13.0, indicates scattering occurring by a transition to virtual state (non-stationary state); the molecule immediately returns to the ground electronic state and theist photon is scattered. If there is no change in energy of the scattered photon, the scattering is elastic; it is known as Rayleigh scattering. The intensity of the scattered light is proportional to the square of the polarizability of the molecule, and if the wavelength is not too close to an absorption band, the scattering is inversely proportional to the fourth power of the wavelength. These wavelength dependence explains the blue sky and red sunsets, although for the best red sunsets the scattering particles are dust, not molecules, and the wavelength dependences is more complicated.

The polarizability, α, is a measure to induce a dipole in a molecule by applying an electric field. The polarizability tells us how easy it is to distort the distribution of electrons of the molecule. The quantitative definition is

$$\mu_{ind} = \alpha E \qquad 1$$

Where μ_{ind} is the dipole induced and E is the electric field. The usual units for α are cm^3. The electric field is then in esu-volt cm^{-1} and μ_{ind} is esu cm. In SI units a is in m^3 and

$$\mu_{ind} = 4\pi\varepsilon_o \alpha E \qquad 2$$

With μ_{ind} in coulomb m and E in volt m^{-1}.

In Raman scattering the molecule returns to a different energy level after interaction with the light. As shown in fig 13.1, having excited vibrational level ground electronic state level. In These transition the Raman scattering occurs. The scattered photon has a longer wavelength (lower energy) than does the incident photon. The scattered photon

can have a shorter wavelength if the molecule was originally in an excited vibrational state and returned to the ground vibrational state. In either case the scattering is inelastic; there has been energy transfer between the molecule and the light. The selection rule for Raman scattering is that the polarizability of the molecule must change with the vibration in order into have a transition to a different energy level. Thus N_2 and O_2 will show vibrational Raman spectra, because their vibrations cause a change in polarizability. For CO_2 its asymmetric stretch and its bend will. We see that some vibrations can be measured using Raman, but not infrared; some can be measured using Raman, but not infrared; some can be measured using infrared, but no Raman; and some can be measured both ways.

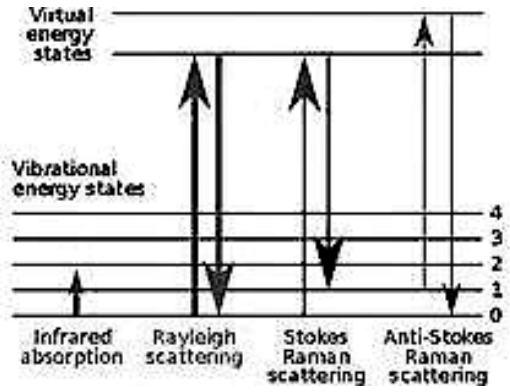


Figure 13.0: Energy-level diagram for IR absorption, elastic (Rayleigh) scattering, and inelastic (Raman) scattering. Transitions between vibrational energy levels of the ground electronic state absorb IR radiation; not all transitions are allows. For elastic scattering the frequency of the incident light is equal to the frequency of the scattered light. For inelastic scattering the frequency of the scattered light is different from that of the incident light. The virtual state shown can have any energy; the scattering of light occurs in any region of the spectrum.

Raman spectroscopy, which began in the early twentieth century, was named in honor of, C.V. Raman, who, along with K.S. Krishnan, published the first research paper on this discover. In turn, Raman's techniques were inspired by the theoretical work of A. Smekal: indeed, for many years, Raman scattering is one of two spectroscopic methods normally used to probe molecular vibrations. It was the tool of choice for this purpose until the 1940s. It was at that time that commercial IR spectrometers were first introduced and IR became the dominant tool for vibrational analysis. Between then and the late 1960s, Raman spectroscopy was virtually lost in obscurity. The radiation source during that era was typically the 435.8nm line of a coiled low-pressure Hg arc lamp. During the late 1960s, however, laser power sources became available. These lasers, with their ability to focus large numbers of photons into small volumes, gave rise to the renaissance of Raman spectroscopy. When a beam of light passes through a medium, a certain amount of the light is scattered and can be detected by making observations perpendicular to the incident beam. Most of the light is scattered without a change in wavelength, an effect known as Rayleigh scattering. However, if the incident light is monochromatic (i.e., if only a narrow range of wavelength is represented), a small amount of the scattered light may have either higher or lower wavelengths than the original light. The spectrum consists then of lines of both longer and shorter wavelengths than the incident wavelength. This effect was first observed in 1928 by the Indian physicist Sir Raman (1888-1970) and his co-worker Sir K.S. Krishnan (1898-1961) and is known as the Raman-effect.

The interaction occurs between a molecule and a photon result Raman effect. If a photon had a perfectly elastic collision with the molecule, it would be scattered with no change of frequency. The radiation would then be emitted in all directions, with an intensity inversely proportional to the fourth power of the wavelength. Because of this dependency, shorter wavelengths are more prominent in scattered light and particles suspended in a gas are rendered visible by a light beam.

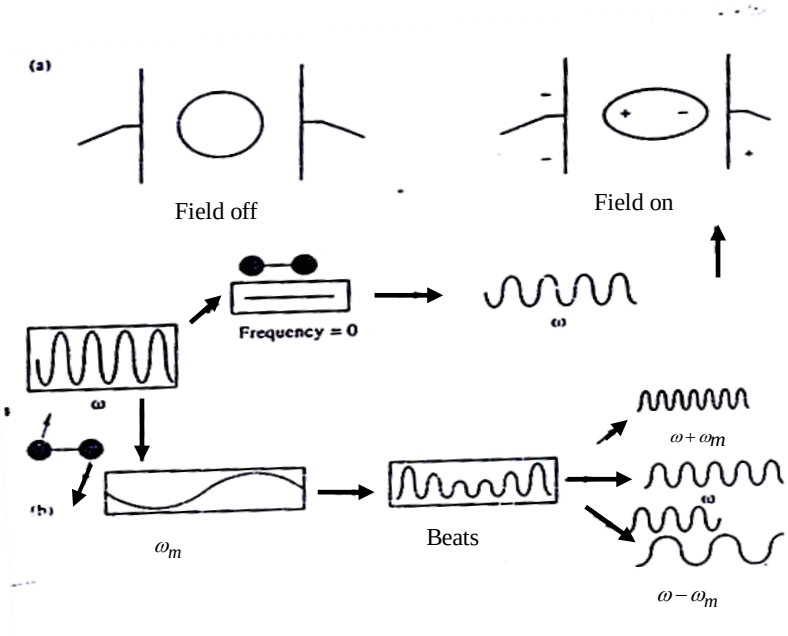


Figure 13.1. (a) A spherically symmetric charge distribution with no dipole moment is distorted to become a dipolar charge distribution when a field is applied. (b) When a molecule has only static polarizability (the frequency of motion is zero), it scatters the frequency of incident radiation as indicated at the top (Rayleigh scattering). If the molecule undergoes any motion (rotational, vibrational, or electronic at frequency) at ω_m scatters radiation at ω (Rayleigh scattering) and ($\omega - \omega_m$) and ($\omega + \omega_m$)(Raman scattering).

In an elastic collision, energy is exchanged between the molecule and the incident photon according to quantum rules. The selection rule for rotational transitions in Raman spectroscopy is

$$\Delta J = O, \pm 2 \qquad 3$$

The reason for this Raman scattering has two-photon process, with one photon going in and one coming out, and as a result the angular momentum of the photons can remain unchanged or change by two units. If enough energy is available, a vibrational transition may occur, and the selection rule is then the same as for the infrared spectra of anharmonic oscillators; namely Dv= ±1, ±2, Generally only the lowest vibrational level is occupied to any extent and the transition v = 1← v = O with rotational states superimposed gives the strongest Raman band.

13.2.1 Theory of Raman Spectroscopy:

Rayleigh scattering

When a molecule is placed in an electric field, the positive and negative charges are pulled to opposite direction. Thus a dipole moment is induced in the molecule. This happens even when the molecule has a permanent dipole moment.

The induced dipole moment μ_i

$$\mu_i = \alpha^* \qquad 4$$

at moderate field strengths. The proportionality constant α is called the **polarizability.** Consider now a molecule subjected to radiation of frequency ω_o.

$$E=E_o \cos\omega_o t \qquad 5$$

Since the electric field oscillates according to the induced dipole moment of the molecule also oscillates. The induced moment therefore is given by

$$\mu_i = aE_o \cos\omega_o t \qquad 6$$

According to classical electromagnetic theory, an oscillating dipole radiates (scatters) at the frequency of oscillation. The scattering at the frequency of impinging radiation is called Rayleigh or elastic scattering.

Raman Effect

The molecules rotate and vibrate with their characteristic frequencies. Since induced moments depend on bond lengths and molecular orientation, the polarizability of a molecule changes as it rotates and vibrates. Let us consider one particular frequency to illustrate the effect of changing polarizability. If ω_m is the frequency of rotation or vibration, the polarizability of the molecule varies with time according to the equation

$$\alpha = \alpha_o + \alpha' \cos\omega_m t \qquad 7$$

Therefore, the induced moments also vary with time:

$$\mu_i(t) = \alpha_o E_o \cos\omega_o t + \alpha' E_o \cos\omega_o t \cos\omega_m t \qquad 8$$

With the aid of a standard trigonometric relation, we can express this result in an alternative form:

$$\mu_i(t) = \alpha_o E_o \cos\omega_o t + \frac{1}{2}\alpha' E_o[\cos(\omega_o - \omega_m)t + \cos(\omega_o + \omega_m)t \qquad 9$$

We see from Eq.7, that the induced dipole oscillates at the frequencies ω_o (Rayleigh scattering), $(\omega_o - \omega_m)$, and $(\omega_o + \omega_m)$. As a consequence, the molecules scatter radiation at these frequencies. The inelastic scattering at the sum and difference frequencies is known as the Raman Effect. Fig 13.1 illustrates the mechanism of Raman scattering.

Let us determine the relation between Raman Scattering and the beats. The techniques for both these phenomena are same, namely, the superposition of waves of different

frequency. If we monitor the intensity of radiation as a function of time, we will observe the optical beats. By monitoring the intensity of radiation as a function of frequency, we will observe scattering at different frequencies. Inelastic scattering and beat phenomena are two aspects of the same process.

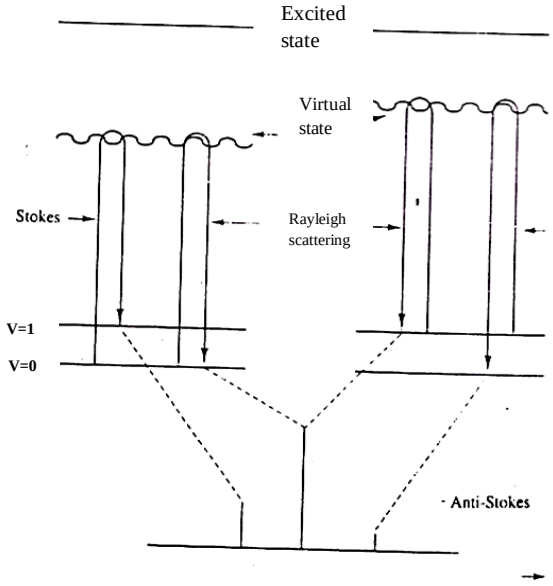


Figure 13.2. Relation between Rayleigh, Stokes and anti-Stokes Raman scattering

Fig.13.2 gives the relation between molecular energies and Raman scattering. Only two vibrational states in the lower electronic level are shown in the figure. In the Raman studies the sample is exposed to radiation of a frequency not absorbed by the molecules. A Raman spectrum consists of weak scattered lines on both sides of an intense Rayleigh peak. Molecules in the v = o state scatter radiation at ($v_o - v_m$) (v_m is the vibrational frequency). The resulting peak, which appears on the low- frequency side of the Rayleigh peak, is called the stokes line. The peak on the high–frequency sides of the Rayleigh peak is called the anti-stokes line. This peak is due to scattering by the molecules in the v=1 states. Since the numbers of molecules in the v = 1 state are lower than those in the v = o state, the anti-stokes line is weaker than the Stokes line. Molecules gain energy in stokes transitions and lose energy in anti-Stokes transitions.

13.3: Laser Spectroscopy:

In the early 1960's discovery laser that has been applied in a spectroscopic experiment of one form or another. In that early period, the ruby laser and rare gas ion lasers, operated only on a fixed frequency, often providing only a single lasing wavelength, or at most lasing on a few narrow atomic or ionic resonances. As such, they were only tunable across the available optical cavity modes lying within the narrow gain profile of the relevant resonance (figure 13.3). These sources, such as lasers are difficult to employ spectroscopically, with the obvious exception of their application in spectroscopic methods such as Raman spectroscopy where excitation on a single narrow frequency band is clearly desirable. It was, therefore, not until the development of broadly tunable lasers such as the organic molecular dye laser that the modern age of laser spectroscopy began to dawn and it is upon such tunable laser sources

that the following discussing will focus. Although spectroscopic measurements of one form or another can be made across the entire electromagnetic spectrum, the majority of studies, and those probably most relevant to our current contest, are made in the region stretching from the microwave, with wavelengths of around 1 cm, to the vacuum ultraviolet, beyond 200 nm. Each region reflects a particular type of energy level transition and hence spectroscopy. Rotational in the microwave and far-IR (ca. 1 cm- 50 µm), vibrational in the mid –and near-IR (ca.50-1 µm) and electronic in the near-IR through the visible to the UV and VUV and beyond (ca.1µm-100 nm).in each of these regions suitable sources of tunable radiation have existed for a long time.

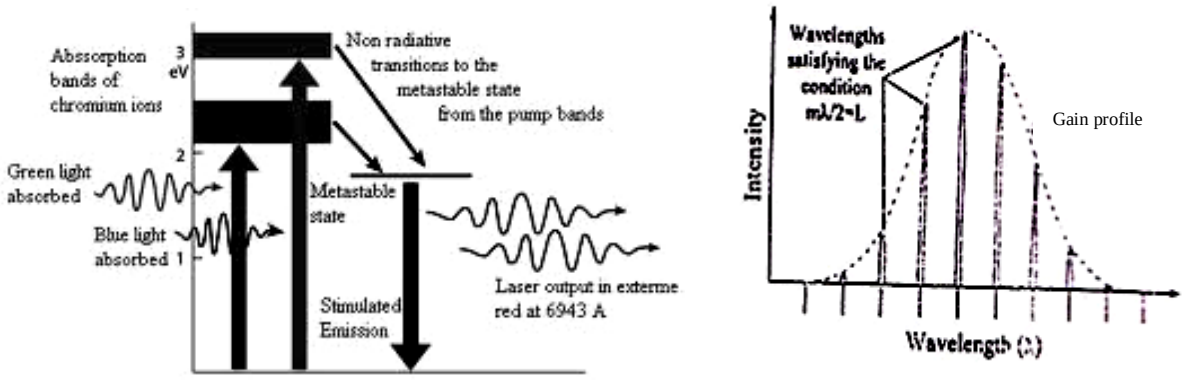


Figure 13.3(a) Energetic of the ruby laser,(b) Emission spectrum of a typical laser.

13.4: Environmental Applications of Laser Raman spectroscopy:

Several examples where Raman spectroscopy has played an important role in environmental analyses will be presented.

13.4.1: Remote Raman Sensing:

A light scattering technique called differential absorption (LIDAR) has become a useful technique for measurement of stratospheric molecules. LIDAR is a spectroscopic method whereby the Rayleigh (wavelength of incident light is not changed) scattering from an intense laser beam is collected by a telescope. An eximer laser supplies pulses of radiation and the return radiation is examined with respect to the time elapsed and the intensity in order to produce a concentration-versus-height profile of the analyte. In the DIAL Modification, two wavelengths are used, one of which is less strongly absorbed. Typically, lasers emitting at 308 and 353nm are used for this process. DIAL works well in a clean atmosphere where almost all the scattering is Rayleigh scattering. The scattering of aerosols is ignored or accounted for with a small correction factor. However, introduction of volcanic SO_2, such as occurred with the eruption of Mount Pinatubo, causes rapid changes in particle size and aerosol concentration. In order to circumvent this difficulty, McGee and colleagues modified the LIDAR to detect Raman signals from the N_2 molecules. The scattering from the N_2 is shifted by 2331 cm^{-1} with respect to the incident wavelength and return depends on the molecular density. Aerosols do not contribute directly to the Raman return and thus

backscattering from these is absent. Thus the extinction due to the aerosols can be calculated from the non absorbed beam. Using this technique, McGee and colleagues were able to produce ozone profiles that are valid from 15 to 50 km into the atmosphere.

13.4.2: Ground Water Analysis:

Polluting materials in trace amounts, such as metallic ions, find their way into the water system. It is necessary to be able to detect these materials in situ and in real time. Recently, such a method was found involving the SERS technique using optical fibers. The technique monitors the ions in aqueous solutions, measuring the changes in the Raman spectra of indicators, which form complexes with the metallic ions. The indicators used were Eriochrome Black T (EBT), 4-(2-pyridylazo) resorcinol (PAR), cresol red, methyl red and 4-pyridinethiol.

Figure 13.4 illustrates the spectra of EBT – CU^{2+}, of blank EBT, and the difference spectrum (traces a, b, c, respectively). The intensity of the band at 1,403cm^{-1} in the difference spectrum corresponds to the Cu^{2+} concentration in solution. The 1,274 cm^{-1} band present in the uncomplexed EBT (trace b) disappears upon complexation. A calibration curve for detection of cu^{2+} with EBT was made by plotting I_{1403}/I_{1274} v/s pCu^{2+}(-log Cu^{2+})concentration. This illustrated in figure 13.5.

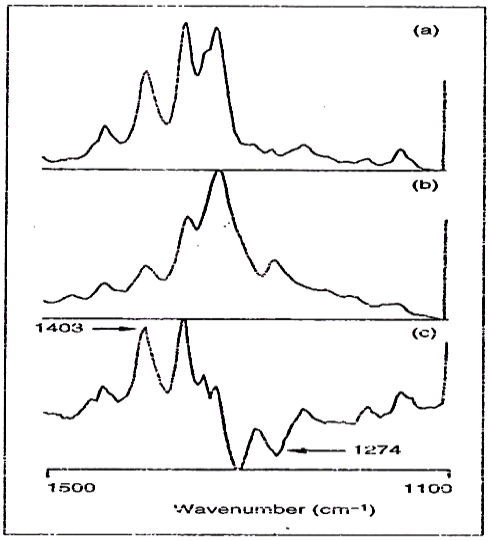


Figure 13.4; Surface-enhanced resonance Raman (SERRS) spectra of (a) $1.8x10^{-4}$ MEBT and $1.8x10^{-4}$ Cu^{2+};(b)) $1.8x10^{-4}$ MEBT only; and (c) the difference spectrum of (a)-(b).(a) and (b)were obtained with 3-s integration time and 20 mW of 531nm light for resonance excitation of EBT.

Figure 13.4a shows the spectrum of blank PAR. Figure 13.4b shows its spectrum in the presence of $Pb^{2+,}$ and fig 13.4c the spectrum in the presence of Fe^{2+}. Similar calibration curves could be formulated. For the $Pb^{2+,}$ *concentration, plotting of* I_{1323}/I_{1005} v/s pPb^{2+}(-log Pb^{2+}) can be used for the detection of Pb^{2+}.Likewise, a plot of I_{1329}/I_{1362} Vs. $_pFe^{3+}$ can be used for detection of the Fe^{3+} concentration in ground water by the SERS technique. The technique is particularly effective when used with optical fibers. Silver substrates provide the largest enhancements of the Raman signal, but rapidly degrade in air or water. A method of forming

a durable, strongly enhancing SERS surface on silver is to roughen the fiber end followed by depositing a layer of silver, whereby some of degradation of the silver surface is avoided.

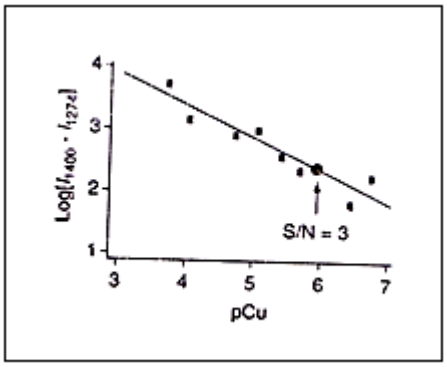


Figure 13,5; Calibration curve for detection of Cu^{2+} with EBT. The detection limit of 85 ppb is illustrated where S/N=3

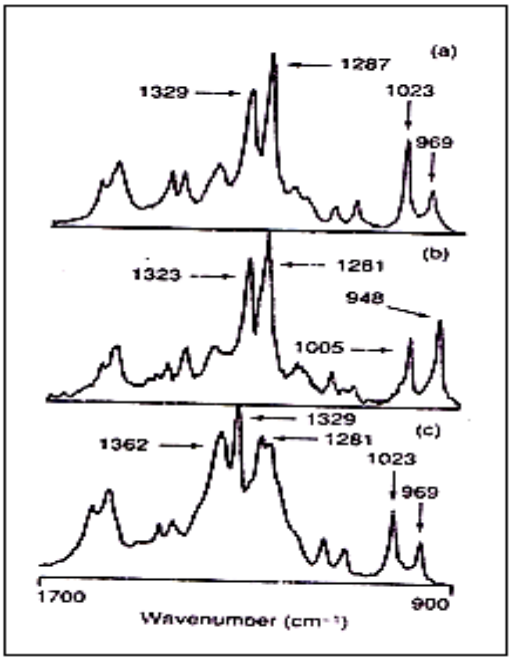


Figure 13.6; SERS spectra of etched silver foil that is coated with anchored of the indicator PAR disulfide (PARDS) immersed in (a) a blank solution showing PARDS only, (b) in the presence of Pb^{2+}, and (c) in the presence of Fe^{3+}. Spectra were obtained with 5-s integration time and 5nm light for resonance excitation of PARDS.

13.4.3: Fresh water and seawater analysis:

The amounts of trace of nitrite ion (NO_2^-) are indicative of the net amount of pollution and eutrophication. The various experimental techniques that can measure nitrite ion concentrations, such as colorimetry, chemiluminescence or flourimetry, are not capable of detecting subnanomole amounts of nitrite. These also suffer from interference problems. A highly sensitive and selective method for the determination of low concentrations of nitrite in aqueous solutions using Surface–Enhanced Resonance Raman (SERRS) has been developed.

The dye has an azo form as shown fig. 13.7 (1) and 13.7(2a) and a hydrazone form as shown in figure (2b). The hydrazone form is the predominant form. The structural difference between the azo and hydrazone forms is that the N=N bond is associated with the azo forms (1) and (2), and the quinoid ring is associated with the hydrazone form 13.7 (2b). The SERRS spectra of the azo dye at high, neutral and low pH solutions are shown in Fig 13.8. Figure 13.9 shows the SERRs spectra compared to the resonance spectra (RR) at pH 2 and 12. The experimental observed Raman bands and the tentative assignments are listed and shown in Table.1. In basic solutions the SERRS spectrum of the azo dye looks the same as the RR spectrums shown in fig. 13.9. In acidic solutions, they differ, with two new bands at 1,328 and 1,283cm^{-1} appearing in the SERRS spectrum shown in figure 13.8. For the purpose of quantitative analyses the Raman measurements were made at high pH. The SERRS spectrum (Fig. 13.10) in basic solution has the bands at 1,422cm^{-1},(N=N bond) and at 1328 and 1383 cm^{-1} which show high selectivity and can be used for analytical purposes. Figure 13.11 indicates the analytical curves for the azo dye, it may be observed that linear relationship exist between the SERRS intensity and the dye concentration. For purposes of accuracy, an internal standard such as pyridine (10^{-3}M) was added to compensate for changes in excitation energy and for variations in sample positioning and optical alignment. Figure 13.11 shows the SERRS spectra of the azo dye in seawater, a was 35m deep, and b, 500m deep.

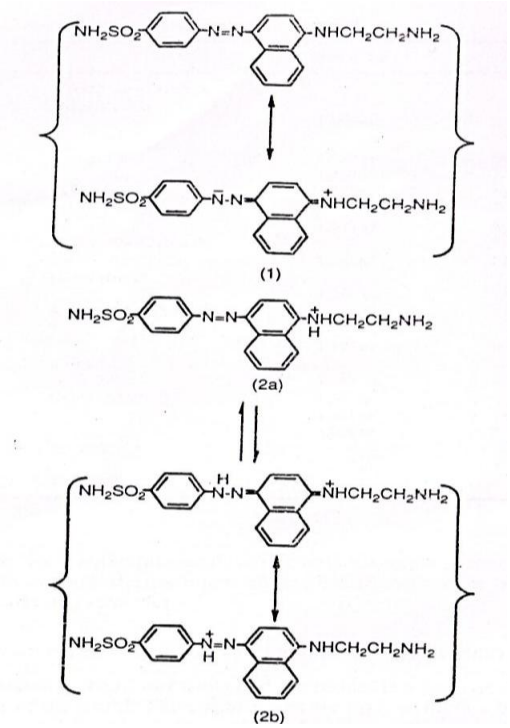


Figure 13.7; Structures of (1) basic and (2) acidic form of the azo dye.

Limits of detection for the nitrite ion are 0.02 nm. Reproducibility of the method is satisfactory, simple, faster, and demonstrates advantages over the high-sensitivity laser – induced fluorescent techniques.

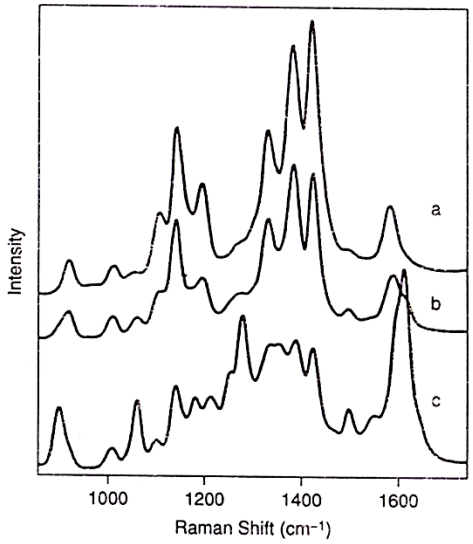


Figure 13.8; SERRS spectra of 1µm azo dye in different pH solution; (a) pH=12; (b) pH=7; (c) pH=1.

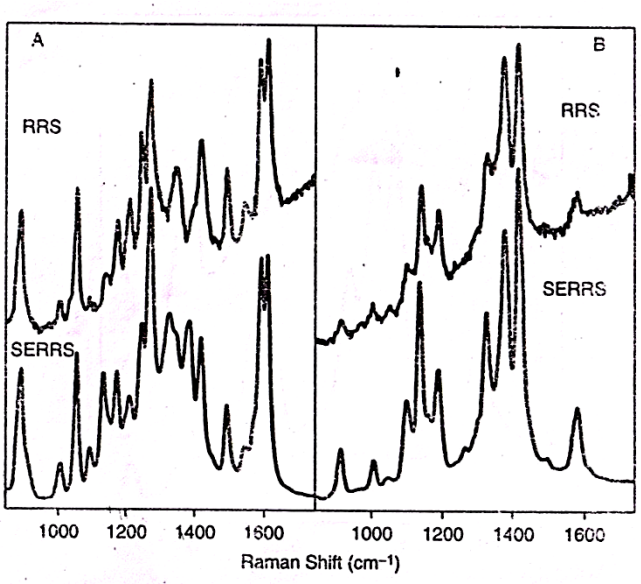


Figure 13.9; Comparison of SERRS spectra and RR spectra of 10µM azo dye in different pH solution (a) pH=2; (b) pH=12.

Table: 1: Tentative Assignment of Observed Raman Bands

Ph =2		Ph=12	
1.620v	**N'-ring c=C stretch**		
1.597vs	**S-ring stretch**		
		1.582m	**8a or 8b**
1.546vs	**?**		
1.496m	**S-ring 19a**	**1.499vs**	**S-ring 19a**
		1.450vvw	**N'-ring 19b**
		1,422vs	**N=N stretch**
1.425 sh	**C-N' stretch**	**1.383vs**	**S-ring 19b**
1.351sh	**N'-ring C---C stretch**		
		1.328s	**Ph-NMe_2**
1.278s	**C-N stretch**		
		1.266vw	**S-ring 14**
1.253s	**S-ring Ph-NH-N**		
1.214m	**?**		
		1.193 m	**9a**
1.177m	**S-ring 9a**		
		1.163vw	**9a coupled**
1.145 w	**C-N stretch**	**1.142 s**	**C-N stretch**
		1.101 m	**18b**
		1.006 w	**?**
1.062 s	**18a or b**		
		915m	**5**
897m	**3**		

Which require low temperatures and more complex sample preparation. The technique demonstrates the usefulness of the SERRS method for trace analysis in fresh water and seawater.

13.4.4: Characterization of Organophosphorus Pesticides:

Characterization of organophosphorus Pesticide contamination of our fruits and vegetable is a primary concern of many nations of the world. These substances are toxic to human beings, and therefore, some advances method for analyzing them is necessary. In addition, the method should be noninvasive and not dangerous to the experimentalist. Attention has turned to study of these materials by the Raman technique. Although at first thought one might consider IR spectroscopy to be a reliable technique, the sampling techniques, such as mulling with KBr or CsI, involve grinding of the pesticide, and this could be harmful. Although precautions could be taken by sampling in a glove box, this would require time.

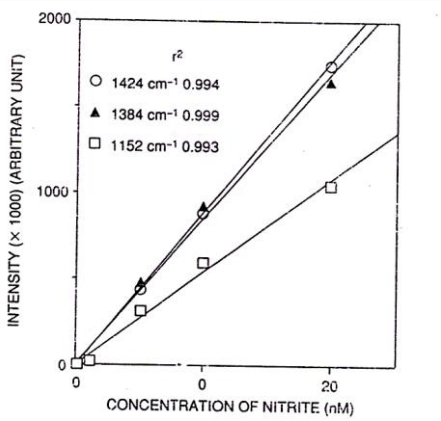


Figure 13.10; Analytical curves of azo dyes.

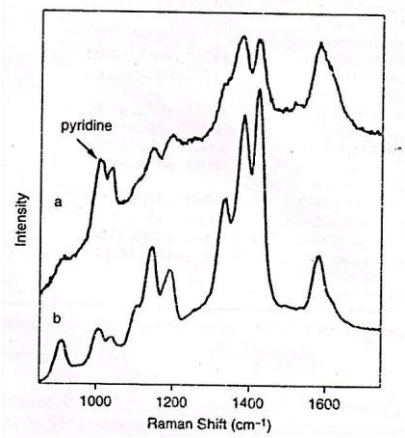


Figure 13.11; SERRS spectra of azo dye in seawater with internal standard (1mM pyridine) at different depths; (a) 35m; (b) 500m.

The Raman spectroscopy used to characterize organophosphorus pesticides has been reported and appears to demonstrate characteristic functional bands that enable one to distinguish between different pesticides. Table 1 lists the six most intense Raman frequencies. Characteristic functional frequencies were identified for the P=S, P=O, P=S, P-$(OCH_3)_2$, and $P(OC_2H_5)_2$ groups. No among these pesticides photodecomposition a will not observed.

13.4.5: Forensic analysis and illicit drugs:

The Raman spectroscopy has not played a role in forensic science because of the fluorescent problems and the sample alignment, which is time consuming. The development of FT-Raman spectroscopy, the technique is now being reexamined, for the application in forensic science follows.

A FT-Raman spectrometer with excitation from a **Nd: YAG** laser at 1.064μm and an **GaInAs** detector was used to collect the Raman data. The range for the Raman spectra was 400-3,200 cm^{-1} at a resolution of 6 cm^{-1} and 200 mW power.

The Raman spectra of three pure alkaloids (heroin, morphine and codeine) observed in the 400-1,800 cm^{-1} range shows the spectra of a cut sample of amphetamine sulfate, the

cutting agent, sorbitol, the subtraction spectrum, and pure amphetamine sulfate. Subtraction of the cutting agent from the cut sample gives the spectrum of amphetamine sulfate, which agrees with the spectrum of pure amphetamine. It appears that the technique is well suited for identification of illicit drugs. The technique utilizes small samples with no sample preparation and is non-destructive. The only possible problems that might be encountered are those where the material is contaminated with a highly fluorescent compound (e.g., a fluorescent cutting agent), or a very dark material and a thermally sensitive substance, fluorescence of the sample makes the identification of the drug virtually impossible. The capability of attaching a microscope to an FT-Raman, which is now commercially available, should make this technique even more attractive.

13.5: Summary:

In this unit importance of Raman scattering, Rayleigh scattering , Raman effect occurs and their theory are presented laser Raman spectroscopy discussed with the help of transition diagram. The use of laser Raman spectroscopy in environmental studies explained with relevant examples, these information helps to understand about Raman effect and application.

13.6: Key words:

Raman effect: in 1928. Indian physicist Raman discovered that when a monochromatic light illuminates molecules with internal modes of vibration a very small portion of the incident light is scatter off from the molecules with its color either red-shifted or blue shifted.
Raman scattering: in elastic scattering of a photon
Laser Raman spectroscopy: Study of Raman scattering phenomena using laser source

13.7: Questions for self study:

1. Explain the scattering of light Raman and Rayleigh scattering with energy level diagram
2. Why anti-Stokes lines are less intense than stokes line
3. Explain Raman Effect and laser Raman spectroscopy and explain only any three.

13.8: References:

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UNIT 14: Non-linear interactions, Harmonic generation, Multiphoton processes.

Structure:

14.0 Objectives:

The use of laser light, interaction of monochromatic light with various object or medium resulting harmonic generation also higher order harmonic generation, gives the non-linear interactions. Multiphoton processes and its important applications in various fields.

14.1 Introduction:

The interaction of high intensity laser beams with different material resulted in the observation of many new phenomena. This prompted a large number of experimental and theoretical investigations. Most of the new phenomena are observed since intense laser beams evoke non-linear response from a very large variety of materials. This leads to the development of the now area of non-linear optics.

The Self-focusing technique is most interesting and basic problems of non-linear optics. It limits the use of high power laser beams since it is responsible for optical damage created by the beams in solids used in the design of high power laser amplifiers or within the laser cavities. These limitations are due to filamentation of laser beams which is a process distinctly different from self-focusing, as would be emphasized.

There are various physical situations when filamentation of intense laser beams takes place much before the size of the beam shrinks a significantly due to self-focusing. Self-focusing and / or filamentation have a strong influence on many nonlinear optical processes like stimulated Raman or Brillouin scattering, harmonic generation, two-photon absorption and optical breakdown of gases. The knowledge of self-focusing and filamentation is essential for quantitative land sometimes even qualitative understanding of the experimental results concerning the above non-linear optical processes. As has been remarked earlier, the important use of self-focusing is concerned with the avoidance of self-focusing and prevention of optical breakdown and damage produced by intense laser beams in materials. The explanation of harmonic, second and harmonic generations with the higher order non-linear effects with examples the materials used to generate the non-linear interactions homogeneous broadening multiphoton process, excitation, and multiphoton microscopy with examples.

14.2 Harmonic generation:

The Nonlinear properties in optical region have been experimentally demonstrated by the harmonic generation of light observed for the first time by Franken and coworkers in 1961. They observed ultraviolet light at twice the frequency of a ruby laser light (λ =6493Å) when the light was made to traverse a quartz crystal. This experiment attracted widespread attention and marked the beginning of the experimental and theoretical investigation of nonlinear optical properties. A simple scheme for this experiment is shown in figure 14.0.

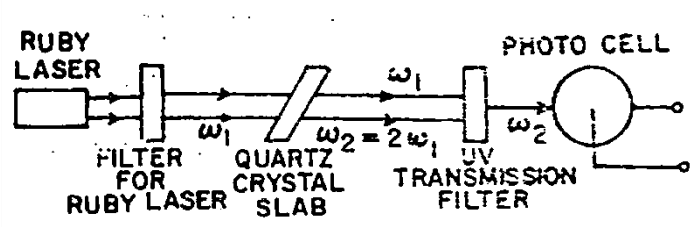

Figure 14.0; Second Harmonic generation

Been of ruby laser (λ =6493Å) with average power of the order of 10 kW is focused on a quartz slab. The transmitted light then was passed through a filter, which cuts off the red light and allows UV light to pass through and emerging light was incident on a photocell. Radiation with wavelength λ =3471Å and the power 1mW was observed in the transmitted light.

A dielectric medium when placed in an electric field is polarized, if the medium does not have a transition at the frequency of the field. Each constituent molecule acts a dipole, with a dipole moment P_1. The dipole moment vector per unit volume P is given by

$$P = \sum_I P_i \qquad 1$$

Where the summation is over the dipoles in the unit volume. The orienting effect of the external field on the molecular dipoles depends on both the properties of the medium and on the field strength. Thus, we can write

$$P = \epsilon_0 \chi^E \qquad 2$$

Where x is called the polarizability or dielectric susceptibility of the medium. This relation is valid for the field strengths of conventional sources. The quantity x is a constant only in the sense of being independent of E; its magnitude is a function of the frequency. With sufficiently intense laser radiation the relation (2) does not hold good and has to be generalized to

$$P = \epsilon_0 (\chi^{(1)} E^1 + \chi^{(2)} E^2 + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots.) \qquad 3$$

Where $\chi^{(1)}$is the same as in equation (2); the coefficients $\chi^{(2)}$, $\chi^{(3)}$,…..define the degree of nonlinearity and are known as nonlinear susceptibilities. If the field is low, as it is in the case of ordinary light sources, only the first term of equation (3) can be retained. It is in for this reason that the pre-laser optics is known as linear optics. Higher the values of the electric field, more significant become the higher order terms. It may be noted that optical characteristics of a medium, such as dielectric permittivity, refractive index, etc, which depends upon susceptibility, also become functions of the field strength E, if it is sufficiently high. The medium of which the polarization is described by a nonlinear relation of the type equation (3) is called la “nonlinear medium”.

Suppose now that the field incident on a medium has the form

$$E = E_0 \cos\omega t \qquad 4$$

Substituting this in equation (3), we have

$$P = \epsilon_0 \chi^{(1)} E_0 \cos \omega t + \epsilon_0 \chi^{(2)} E^2_0 \cos^2 \omega t + e_0 \chi^{(3)} E_0^3 \cos^3 \omega t + \ldots\ldots \qquad 5$$

Using the trigonometric relations

$$\cos^2 \theta = 1+\cos 2\theta/2; \cos^3\theta = \cos 3\theta + 3\cos\theta/4 \qquad 6$$

We can transform equation (5) to the form

$$P = 1/2\, \epsilon_0 \chi^{(2)} E_o + \epsilon_o \{\chi^{(1)} + 3/4 \chi^{(3)} E_o^2\} E_o \cos \omega t$$
$$+ 1/2\, \epsilon_o \chi^{(2)} E_0^2 \cos \omega t + \tfrac{1}{4}\, \epsilon_0 \chi^{(3)} E_0^3 \cos 3\omega t + \ldots. \qquad 7$$

The first term is a constant which gives rise to a dc field across the medium, the effect of which is of comparatively small practical importance. The second follows the external polarization and is called the first for fundamental harmonic of polarization; the second harmonic of polarization, the fourth is called the third harmonic of polarization, and so on.

14.2.1 Second and Higher Harmonics Generation:

The polarization oscillating at frequency 2ω radiates an electromagnetic wave of the same frequency, which propagates with the same velocity as that of the incident wave. The wave observed, has the same characteristics of directionality and monochromaticity as the incident wave and is emitted in the same direction. This phenomenon is known as the Second Harmonic generation (SHG).

The important crystalline materials, the nonlinear polarizability $\chi^{(2)}$ depends on the direction of propagation, polarization of the electric field and the orientation of the optic axis of the crystal. Since the in such crystalline materials the vectors P and E are not necessarily parallel the coefficients x must be treated as tensors. The second order polarization, therefore, may be represented by the equation of the type

$$P_i^{(2)} = \epsilon_0 \sum_{jk} \chi_{ijk}^{(2)} E_j E_k \qquad 8$$

Where i, j, k are the coordinates of x, y, z., Most of the coefficient χ_{ijk}, however, are usually zeroed and we have to deal with one or two components. It must be mentioned here that the second harmonic generation represented by equation (8) occurs only in certain type of crystals. Consider, for example, a crystal that is isotropic. In this case χ_{ijk} is independent of direction and, hence, is a constant. If we now reverse, the direction of the axis (x→ -x, y→ -y, z→-z) leaving electric field and dipole moment unchanged in direction, the sign of these two must change therefore,

$$P_1^{(2)} = \epsilon_0 \sum_{j,I} \chi_{ij}^{(2)} (-E,) (-E1) = +P_1^{(2)} \qquad 9$$

Which means $P_1^2 = 0$ and hence, $\chi^2_{ijk} = 0$ Second harmonic generation, therefore, cannot occur in an isotropic medium such as liquids or gases nor in centro-symmetric crystals (i.e. crystal symmetrical about point). Only crystals that lack inversion symmetry exhibit SHG.

For materials like non-centro-symmetric materials (e.g. anisotropic crystals, such as uniaxial crystals) both the quadratic and cubic terms are present. However, generally, the cubic term is substantially smaller than the second order term and may be ignored. For such materials, the equation form will be

$$P=\epsilon_0 \chi^{(1)}E+\epsilon_0 \chi^{(2)}E^2 \qquad 10$$

And the medium is said to have second order linearity.

In the case of centro-symmetric materials, the expression (3) will lack terms in even powers of E and it will reduce to

$$P=\epsilon_0 \chi^{(1)}E+\epsilon_0 \chi^{(3)}E^3 +\ldots\ldots \qquad 11$$

Or in vector notation

$$P = \epsilon_0 \chi^{(1)}E + \epsilon_0 \chi^{(2)}E^2E \ +\ldots \qquad 12$$

Therefore, third harmonic generation (THG) is, possible in crystals that exhibit inversion symmetry. The advancement of Q – switched lasers had made it possible to generate third harmonic in crystals. However, the energy conversion efficiency in such cases is very low. i.e in calcite the maximum energy conversion in the third harmonic was 0.01%.

The experimental observations of the third harmonic were also performed by Maker and Terhune using giant pulse lasers. Zwernemann and Beeker have performed experimentally enhancement of third harmonic generation (THG) at 9.33μm in CO by having the interaction take place in a waveguide. They have given a theoretical determination of the most suitable waveguide in which the interaction can take place. Therefore the process of generation of higher order harmonics can be explained on the same lines.

14.2.2 Higher Order Nonlinear Effects:

The higher order other than 2 or 3 nonlinear effects of are present in many high-power laser experiments but are not dominant and are thus difficult to detect. Explicitly reported are the generations of higher-order-frequency harmonics mainly in noble gases. For technical applications the stepwise frequency transformation based on second and third harmonic effects is usually more efficient. This is a consequence of the much larger nonlinear coefficients $X^{(2)}$ and $X^{(3)}$ compared to, e.g. $X^{(4)}$, $X^{(5)}$ and so on for known materials. Further these materials have to be transparent over a wide spectral range because absorption will decrease the efficiency. Even though the resonance effect working with wavelengths close to matter absorption can increase the nonlinear effect drastically. Hence a suitable compromise will enhance the harmonic output.

The applied atom vapors for generation of higher frequencies do not automatically give phase matching. Thus by tuned mixing of different atoms with different refractive indices at the wavelength of the fundamental and the high harmonics, phase matching can be achieved in isotropic materials.

For example, the generation of the fifth harmonic in Ne vapor is described, which in combination with the generation of twice the second harmonic, finally results in the generation of the 20^{th} harmonics of the original Nd: YAG laser light. The process is depicted in Fig. 14.1.

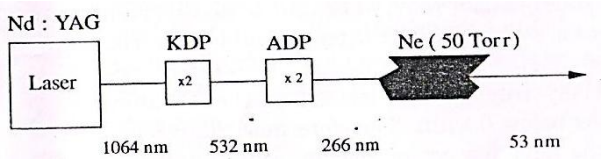

Fig: 14.1; Generation of the fifth harmonic in Ne vapor by pumping with the fourth harmonic of a Nd:YAG laser resulting in the 20^{th} harmonic of the laser radiation

The efficiency in this experiment was less than 10^{-6} although it was performed close to the resonance of Ne atomic absorption and thus the nonlinear coefficient is distinctly enlarged. Another example also reported seventh harmonic generation of the radiation of a Krypton fluoride excimer laser with a wavelength of 248 nm in He vapor. The resulting output of seventh harmonic shows a wavelength of 35.4nm.

The generation of even higher harmonics for for generating coherent light at wavelengths below 20 nm was obtained using very high powers in the range of TW and more with short pulses in the ps of fs range. The generation of the fifth- harmonics in and of the seventh-harmonic, Much higher harmonics are observed. For example, 221th-harmonic as discrete harmonic peak of coherent light with a wavelength of 3.6nm was observed in He using a high-power Ti:-sapphire laser pulse with a width of 26 fs, an energy of 20 mJ, a wavelength of 800nm and a focal spot diameter of 100µm resulting in an intensity of 6×10^{15} Wcm^{-2} . Ne or He gas was used at 8 Torr. Coherent emission was observed up to the 297^{th} harmonic of the laser light corresponding to a wavelength of 2.7 nm, another technique is based on a seeded free electron laser allowing the generation of laser light with wavelengths in the nm range.

XUV generation from laser-induced plasmas should be mentioned although it is not frequency conversion technique. The very intense light excites atoms which emit light, e.g., in the spectral range of the "water window" between 2 and 4 nm which is important for applications. These point sources are very useful for lithography and X-ray microscopy.

14.3 Materials for Non-resonant Nonlinear Interactions:

The various types of materials are used for the non-resonant nonlinear optical effects in photonics are known and to some extent used in commercial devices there is still a need for better suitable materials with higher nonlinear coefficients, higher damage threshold, lower costs and higher reliability. This is especially true for wavelengths in the IR above 1.2

µm and for short wavelengths below 0.3µm.Therefore new materials of all kinds can be expected in the next few years; and information can be obtained from scientific articles and product catalogs.

a) Inorganic Crystals

Crystals are produced for all kinds of frequency transformation technologies such as harmonic generation, frequency mixing and electro-optical effects. They may be categorized into two groups:

(i) Grown from solution: These crystals are hygroscopic and in contrast to the group below thermal shock sensitive, mostly fragile and comparatively soft. But they are available in large sizes of good optical quality and are mostly cheaper.
(ii) Grown from melt: These crystals are non-hygroscopic and thus much more useful than those above.

Known materials are, e.g. KDP, KD*P, ADP, AD*P and $LiNbO_3$. More recently developed crystals are KTP, CDA, CD*A, RDA, RDP, BBO, LBO and BANANA.

b) Organic Materials

The organic materials can exhibits very high nonlinear coefficients, high damage threshold and good transparency at short wavelength region. Because of the large variety of these compounds an inestimable number of possibilities exist in principle. Molecules having large conjugated π-electron system from a large number of multiple bonds will show a large inducible dipole moment from these delocalized electrons. This can even be enhanced by donor (N-atoms) and acceptor (O-atoms) groups.

Some of these organic molecules can be crystallized with sufficient optical quality. Known examples of crystals without an inversion center are urea, DAN, MNA, MAP, COANP, PAN and MBANP.

The inversion symmetry can be broken by applying these materials surfaces. SHG with high efficiencies was demonstrated this way. Liquid crystals are especially applied in such setups.

An amorphous organic matter will be new applications in photonics as in optical fibers, in optical switches and storage or in optical phase conjugation. Different polymer materials have been proposed and are still used.

The main difficulty to now is the long-term stability of these systems. Limited photo-stability and possible chemical reactions restrict their application. New materials will hopefully not be so restricted in the future. Using a well-designed resonance enhancement by tuning the absorption of these compounds for the required wavelengths will allow much higher nonlinearities.

c) Liquids

The new organic liquids or solutions are used in non-resonant photonic applications for "white light" generation, optical phase conjugation and Raman shifting of the incident light. These are various from the nonlinear absorbers and laser materials for dye lasers in resonant applications, and in this case the transparent matter operates again by its induced dipole moments, based on the electron distribution in different electronic or vibrational states of the organic molecules in a similar way as that just described above.

These materials are useful, e.g. CS_2, CCI_4, $TiCI_4$, Freon, hexane, benzene, alcohol and almost all other solvents, For nonlinear applications with high light powers the chemically specified purity is sometimes not sufficient. Small particles can disturb the nonlinear interaction and promote optical break down by the resulting inhomogeneous high local field. Therefore lavish cleaning with filters or "pump and freeze" procedures may be necessary before use.

d) Liquid Crystals

The fundamental geometrical orientation and order of molecular systems in liquid crystals can be applied in photonics for changing the polarization of a transmitting light beam. This can be achieved in liquid crystals displays and projectors based on electro-optically switching the orientation of the molecules by an external electric field. But the orientation of the molecules in the liquid crystal can be changed via polarized pump light, too, and thus opto-optical switching becomes possible. Also, liquid crystals can be used for frequency conversion and four-wave mixing techniques.

e) Gases

The useful noble gases and gases of organic molecules are used in a way similar to liquids for optical phase conjugation and Raman shifting. The mechanisms are the same as described for liquids and references are given there. These gases show the advantage of easy "self-repairing" if damage threshold is exceeded and, e.g. optical breakdown occurred. Thus high – power applications are possible with nonlinear processes in gases.

Typical applied nonlinear gases are SF_6, N_2, Xenon, CH_4, C_2F_6, CO and CO_2 used at pressures of 10-100 bar. The damage threshold in gases is mostly determined by impurities. It can be improved by at least one order of magnitude by cleaning, e.g. with high electric fields.

14.4 Nonlinear interactions of Light and Matter with Absorption:

As explain in the earlier section nonlinear interactions of light with matter are of fundamental importance for photonic applications. It may be worth with reading these sections before continuing. All the matter shows some absorption in almost all spectral regions as a consequence of the Lorentz an line shape of the electronic transitions with indefinite wings. But if the absorption coefficient is smaller than about 10^{-6} cm^{-1} the share of the resonant nonlinear interaction can often be neglected. This nonlinear non-resonant light-matter interaction is described in the previous section. But many photonic applications are

based on resonant nonlinear interactions such as, e.g. stimulated emission in lasers or passive Q-switching and mode locking. Other application such as optical switching and storage may become important, based on nonlinear absorbing devices. In any case the resonance enhancement of very weakly absorbing materials may promote non-resonant nonlinear effects by strongly increased nonlinear coefficients.

Therefore detailed information about nonlinear absorption, which Is also known as, nonlinear transmission and transient absorption effects, and their experimental and theoretical evaluation is essential for successful operation of nonlinear photonic devices in both resonant and non-resonant cases. Although the resonant nonlinear interaction is always accompanied by non-resonant effects (as vice versa) under conditions of strong absorption the non-resonant part may be neglected. Therefore the resonant interaction of light with matter will be described first and combined interactions at the end.

General Remarks

In general the nonlinear interaction can be described by the formulas, based on the nonlinear polarization of matter as a function of the electric field strength if all values are used as complex values. The imaginary part of the X-tensor and the resulting imaginary part of the refractive index n will contribute to the absorption. This method may be useful in cases of small absorption with little structure in the required spectral range. But if nonlinear absorption effects are dominant other descriptions which consider the detailed structure of the energy levels of the matter, their transition moments and the relaxation times between them may be more useful. Again it is worth distinguishing between coherent and incoherent interactions (see Fig.14.2).

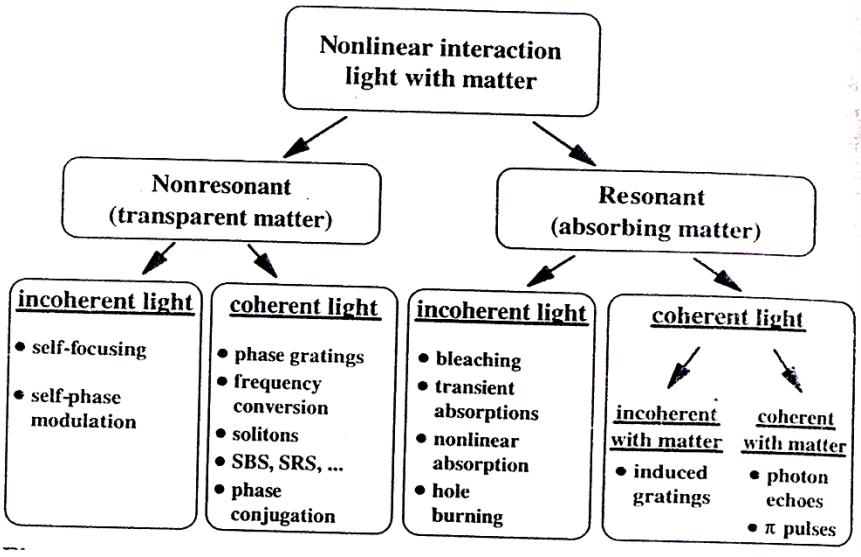

Fig. 14.2. Scheme of nonlinear interactions of light with matter which may be transparent or not at the required wavelengths

Nonlinear interactions in absorbing matter can show two levels of coherence: First the used light fields can be coherent and thus they can produce nonlinear absorption gratings. Second, the induced dipole moment in the matter can oscillate in phase with the applied electric field.

Quantum effects ¯such as the generation of π –pulses and photon echoes can occur. Precondition for this complete coherent interaction is an internal phase coherence time of the matter, T_2, longer than the relevant experimental time, e.g. the pulse width.

14.5 Homogeneous and Inhomogeneous Broadening:

In majority of cases matter absorption observed broad-bands over a few nm up to few 100nm. In particular mixtures of organic molecules such as, e.g. those used in dye lasers or for Q-switching and mode locking may have broad absorption bands. These bands which are easily observable with conventional UV-V is spectrometers as the sum spectra of all participating particles in the matter. Thus for a single particle the absorption lines may be shifted or broadened by: Particle-environment interactions; Particle-particle interaction; Combined transitions; Doppler shifts.

The following mechanisms may cause additional broadening of the observed optical absorption and emission bands of crystals or molecular systems;

* Combinations of electronic transitions;

* Combinations of electronic transitions with a large number of possible simultaneous vibrational transitions;

* Combinations of electronic transitions with conformational transitions of the molecules;

* Participation of rotational transitions;

* Molecule-solvent (intermolecular) interaction;

* Molecule-molecule interactions (aggregation);

* Slightly different conformations or chemical structure of the particle.

The resulting sum spectrum of the sample show broad spectra. In contrast to conventional optical experiments under steady – state conditions with low intensities in nonlinear optics the broadening mechanisms of the absorption and emission bands can be very important.

In particular we have to be able to distinguish whether these bands are spectrally homogeneously or in-homogeneously broadened with respect to the conditions of the application or the experiment. Homogeneously broadened absorption or emission bands change their amplitude but not their structure during excitation. In-homogeneously broadened bands can change structure and amplitude under excitation.

In the case of homogeneously broadened absorption or emission bands each particle such as e.g. the molecules shows the same absorption spectrum and therefore the sum spectrum of the sample has the same shape as the spectra of the single particles.

In-homogeneously broadened absorption or emission bands can be caused by slightly different particle state, e.g. in slightly different environments or in different vibrational states,

and then the matter is called spectrally in-homogeneously broadened. If the particles are in-homogeneously broadened each particle shows a shifted absorption spectrum.

14.6 Multiphoton processes:

The emission resulting from one-photon excitation (1PE). By 1PE it means that an excited fluorophore has reached the excited state by absorption of a single photon. We now consider two-photon (2PE) and three-photon (3PE) excitation. The term 2PE indicates that the fluorophore has reached the excited state by absorption of two photons. We will only consider simultaneous absorption of two or more photons. We will not consider sequential absorption where there is a well-defined intermediate state.

Multiphoton process means an interaction between radiation and matter accompanied by absorption or emission or both, of not less than two photons per elementary act. Consider, for example, Absorption and emission of a photon – a two level system as shown in figure (14.3). The atom absorbs energy ħω and changes from level 1 to level 2. After a short while it returns to level 1 by emitting a photon of the same energy. The state of the atom remains unaltered as far as its energy is concerned; but the emitted photon, although has the same energy as the incident photon, may be in a different state in that it may in a different state in that it may have a different momentum, direction and polarization. The atom has acted in this transformation as an intermediary.

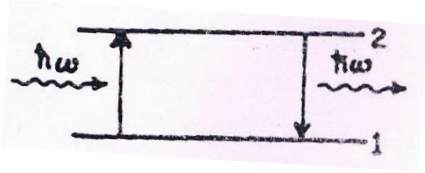

Figure 14.3. Absorption and emission of a photon – a two level system

Consider now another process of three level system as shown in figure (14.4). The molecule absorbs a photon of energy $\hbar\omega_{13}$ and shifts from level 1 to 3 and emits a photon of energy $\hbar\omega_{32}$ by dropping from level 3 to level 2. In this process photon frequency ω_{13} has been converted into a frequency ω_{32} through the intermediary role played by the molecule; but in this case the state of the intermediary is also changed.

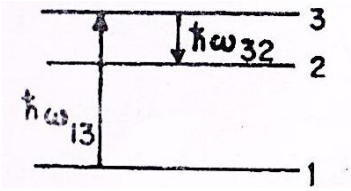

Figure: 14.4. Absorption and emission of a photon – three level system

Multiphoton absorption of visible photons may result in ionization of atoms. At a given laser intensity the ion rate recorded as a function of the laser intensity shows narrow maxima if one-, two-, or three-photon resonance occur. If, for instance, the ionization potential is smaller than 3ħω, resonance in the ionization yield are observed, either when the laser frequency ω is in resonance with a two – photon transition between the levels. At sufficient

intensities this multiphoton excitation of high vibrational –rotational states may lead to the dissociation of the molecule.

Until 1990 multiphoton spectroscopy was considered to be an exotic phenomenon that was used primarily in chemical physics and optical spectroscopy. Two-photon absorbance or excitation requires high peak powers to increase the probability that two photons are simultaneously available for absorption. Because of the interaction of two photons with the fluorophore, the selection rules for light absorption are, in principle, different from those for one-photon spectroscopy. Because of the different selection rules, two-photon spectroscopy can be used as a tool to study the excited-study symmetry of organic chromophores. Multiphoton experiments require complex lasers and high optical powers. It did not seem possible to use multiphoton excitation (MPE) in optical microscopy because the high power would damage the biological samples. Surprisingly, MPE is now widely used in fluorescence microscopy. Multiphoton microscopy (MPM) is possible because of the favourable properties of titanium-sapphire (Ti:sapphire) lasers and the development of laser-scanning microscopes. Multiphoton excitation is usually less damaging to biological samples than in one-photon excitation. Multiphoton microscopy was introduced in 1990 and is now used extensively in cell imaging.

14.6.1 Multiphoton Excitation:

The phenomenon of multiphoton excitation can be depicted in a Jablonski diagram (Figure 14.5). For one-photon absorption a single photon elevates the fluorophore to the excited state. Depending upon the absorption spectrum and the excitation wavelength the fluorophore may be excited to higher vibration levels of the S_1 state.

MPE is accomplished using longer-wavelength excitation to avoid the much stronger single-photon absorption of the fluorophore (Figure 14.5), so that 2 or 3 photons are needed to reach the same energy level due to one-photon absorption. This diagram can give the impression that a fluorophore absorbs the photons sequentially. However, MPE is due to simultaneous absorption of multiple photons, which is why no intermediate states are shown in Figure 14.5 High illumination intensities must be used for MPE because two or more photons must interact simultaneously with the fluorophore. MPE is a nonlinear process. The extents of 2PE and 3PE are proportional to the intensity raised to the second or third power, respectively. To date all fluorophores examined with MPE have displayed the same emission spectra and lifetimes as if they were excited by one-photon absorption. Since the selection rules for optical excitation are different for 1PE, 2PE, and 3PE, the fluorophores may be placed into different excited states with different modes of excitation. However, the flurophores emit from the same excited state, independent of one or multiphoton absorption. Hence we can still use a Jablonski diagram with S_1 emission to describe multiphoton excitation.

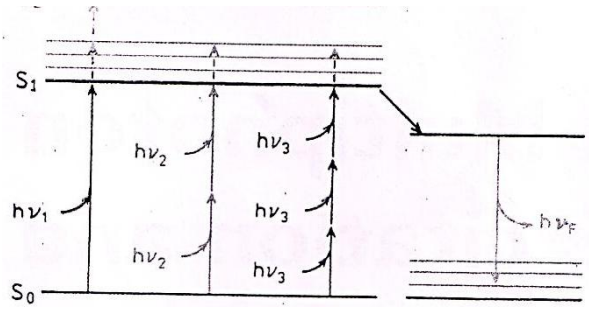

Figure 14.5, Jablonski diagram for one-,two- and three-photons excitation.

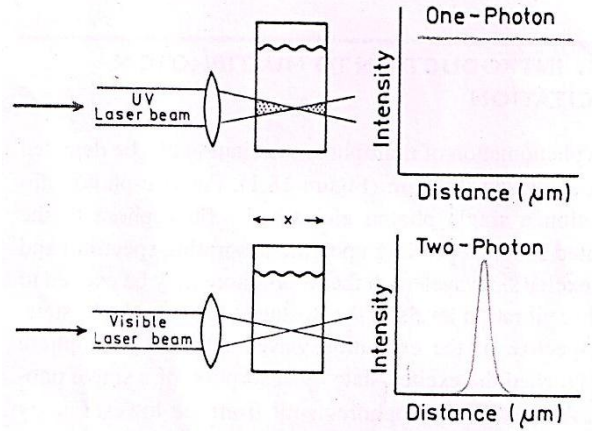

Figure 14.6; Schematic comparison of one- and two-photon excitation.

The quadratic or higher-order dependence of MPE on the incident intensity is a favourable property for optical imaging. Assume a wavelength for 1PE is incident on a cuvette (Figure 14.6). The amount of light absorbed in any plane at a distance is proportional to the incident intensity at this plane. Focusing a beam on the centre of a cuvette changes the size of the beam but does not change the total amount of light passing through a plane at a position x. The emission intensity is constant at all positions x across the cuvette, assuming the absence of inner-filter effects.

Now consider 2PE with a longer wavelength. The amount of light absorbed is proportional to the square of the intensity. Focusing the beam decreases its size but increases its intensity. As a result the amount of light absorbed is not constant across the cuvette, but shows a maximum at the focal point where the incident intensity is highest. This effect can result in strongly localized excitation. Figure 14.7 shows a fluorescein solution illuminated with wavelengths for 1PE and 2PE. For 1PE the fluorescein is excited across the cuvette. For 2PE the fluorescein is only excited in a small spot at the focal point of the laser beam.

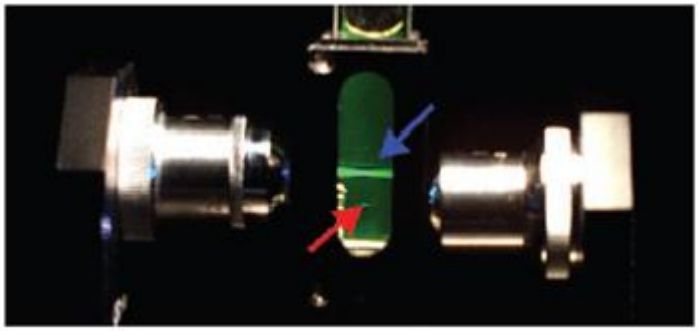

Figure 14.7. Comparison of one-photon excitation (blue arrow) and two-photon excitation (red arrow) of a fluorescein solution. Courtesy of Dr.Peter T. C. So from the Massachusetts Institute of Technology.

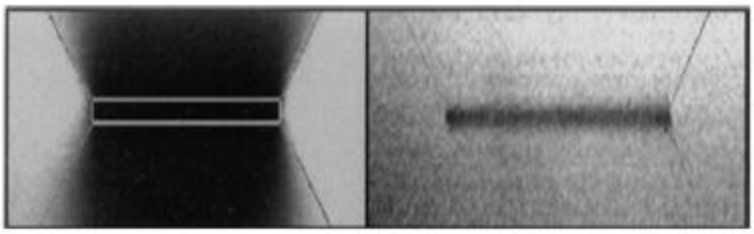

Figure 14.8. Photo bleaching of rhodamine in a Formvar Iayer with one- (left) and two-photon excitation (right).

Most fluorophores photo bleach rapidly in fluorescence microscopy. Localized excitation is an advantage under these conditions. If a biological sample undergoes 1PE the light is absorbed at all depths in the sample, not just in the focal plane. As a result the entire thickness of the sample undergoes photo bleaching (figure 14.8) and photo-damage occurs across the entire thickness of the sample. For three-dimensional reconstruction of the cell image it is necessary to obtain images from multiple focal planes. This is difficult with 1PE because all planes are bleached irrespective of the position of the focal plane.

The right side of Figure 14.8 shows photobleaching with 2PE, which is now strongly localized in the focal plane. The fluorophores are still photo-bleached, but it is possible to image above and below the focal plane because the fluorophores in these regions are not photo bleached. The adverse effects due to absorption are localized to the focal plane, which may be less damaging to the specimen than when photo bleaching occurs across the entire thickness. MPE is usually performed using wavelengths from 720 to 950 nm, where there is minimal absorption by water and intrinsic chromospheres.

14.6.2 Cross-Sections for Multiphoton Absorption:

We are all familiar with the absorption coefficients for one photon absorption, which are usually expressed as the molar extinction coefficients in units of M^{-1} cm^{-1}. For a single molecule the absorption can be described in units of cm^2, which is the effective area over which a single molecule absorbs the incident light. For 1PE the optical cross-sections σ_1 range from 10^{-15} to $10^{-17}cm^2$. Cross-sections of 10^{-15}, 10^{-16} and 10^{-17} cm^2 correspond to squares

with sides of 3, 1, and 0.3 Å, respectively. One-photon cross-sections are thus comparable to the size of fluorophores and can be understood intuitively.

It is more difficult to have an instructive understanding of cross-sections for multiphoton absorption. For 2PE the cross-sections are in units of cm^4 s/photon. The values of the 2PE cross-sections are reported in terms of GM (Goppert-Mayer) units, where 1 GM = 10^{-50} cm^4 s/photon. The units are named after Maria Goppert-Mayer, who developed the theory for two-photon absorption processes. [13-14] these units for the 2PE cross-sections are more difficult to understand than the cross-sections for 1PE in units of area.

The physical origin of the 2PE cross-sections can be understood by some simple considerations. For one-photon absorption the number of photons absorbed per second (NA_1) is given by

$$NA_1 \text{ (Photon/s)} = \sigma_1 \text{ (cm}^2\text{)} \; I \text{ (photon/cm}^2\text{s)} \qquad 13$$

Where I is the intensity and σ_1 is the cross-section for one-photon absorption. The units are given within the parentheses. The cross-section in cm^2 is multiplied by the number of photons passing near the molecule per second to yield the number of photons absorbed per second. To obtain NA_1 in photons per second the cross-section must be in units of cm^2.

Now consider two-photon absorption. The number of photons absorbed per second by 2PE (NA_2) is given by

$$NA_2 \text{ (Photons/s)} = \sigma_2 \, I^2 \; \text{(photon/cm}^2\text{s)}^2 \qquad 14$$

In order for the units to match on both sides of eq. 18.2 the units of σ_2 must be cm^4s/photon. Similarly, for 3PE

$$NA_3 \text{ (Photons/s)} = \sigma_3 \, I^3 \; \text{(photons/cm}^2\text{s)}^3 \qquad 15$$

and the units of a three-photon cross-section are $cm^6 \, s^2$/$photon^2$.

14.6.3 Two--Photon Absorption Spectra

Since selection rules for one and two-photon optical transitions are different there is no reason to expect the one- and two-photon absorption spectra to be the same. Figure 14.9 shows these spectra for some commonly used fluorophores. Note that the y-axis is a logarithmic scale and the one-photon spectra are plotted on an arbitrary scale. For visual comparison the spectra are usually plotted on the same wavelength scale where the one-photon spectrum is plotted using twofold longer wavelengths. The x-axis is usually the wavelengths used for two-photon absorption measurements. Occasionally the data are plotted on the one-photon wavelength scale. The correct scale is usually apparent from the known one-photon absorption spectra of the fluorophores.

The one- and two-photon absorption spectra are different for the three fluorophore shown in Figure 14.9, which has been found for most fluorophores. An important feature of the two-photon absorption is that, on a relative scale, the absorption is stronger at wavelengths below twice the long-wavelength absorption. For example, the one-photon absorption of RhB is much weaker at 400nm than at 500 nm (middle panel). The two-photon absorption is stronger for RhB at 800 nm than at 1000 nm. This is convenient because two-photon microscopy is almost exclusively done using Ti:sapphire lasers, which have an output

from 720 to 1000 nm. Additionally, the shape of the two-photon absorption spectra often allows simultaneous excitation of several fluorophores using a single wavelength.

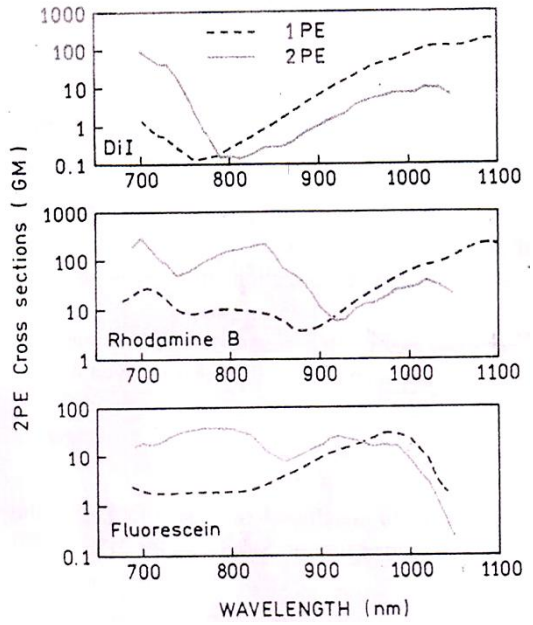

Figure 14.9; One- and two-photon absorption spectra of three commonly used fluorophores. The one-photon spectra are plotted on an arbitrary scale

Additional two-photon absorption spectra are shown in Figure 14.10. It is difficult to measure their spectra because the amount of light absorbed depends strongly on the exact spatial and temporal profile of the pulses. For this reason two-photon cross-sections are usually measured relative to a standard, typically bis-MSB, which appears to be the best characterized two-photon standard. Fortunately, fluoresceins have large cross-sections at Ti:sapphire wavelengths. The cross-sections of UV-absorbing fluorophores such as indo-1(IC) of fura-2 with calcium (FC) are small above 700 nm because two photons at wavelengths above about 700nm do not contain enough energy to reach the S_1 state.

One-photon absorption spectra often show regions of low absorption at wavelengths below the long-wavelength absorption. The low absorption at wavelengths below the $S_0 \otimes S_1$ transition makes it difficult to excite more than one dye at a time using a laser source. The larger width of the two-photon absorption spectra makes it easier to excite multiple fluorophores using one wavelength. This possibility is shown in Figure 14.11 for five fluorophores that were all excited using 800 nm from a Ti:sapphire laser.

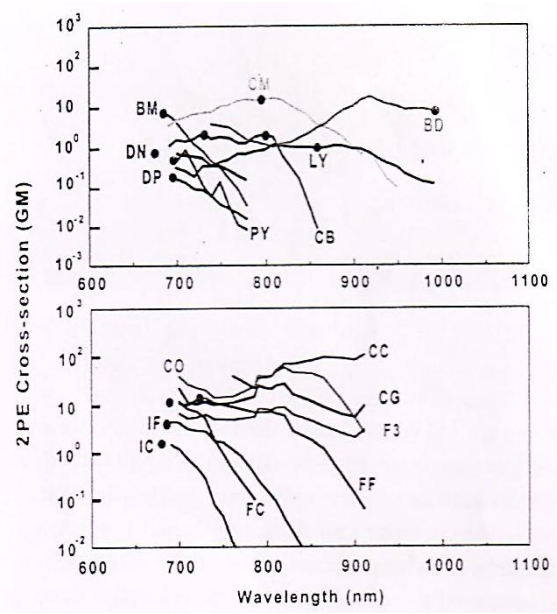

Figure 14.10. Two-photon fluorescence excitation spectra of fluorophores.

For BM (bis-MSB), data represent two-photon absorption cross-sections. For all the other fluorophores, data represent two-photon action cross-sections i.e., the product of the fluorescence emission quantum efficiencies and the two-photon absorption cross-sections. Units are Goppert-Mayer (GM); 1 GM = 10^{-50} CM^4 s/photon. Spectra are excited with linearly polarized light using a mode-locked Ti:sapphire laser. The black dot indicates twice the wavelength of the one-photon absorption maximum of the fluorophore. The fluorophores illustrated in α are as follows: BM, p-bis(o-methylstyryl)benzene; CM, Cascade Blue hydrazine trisodium salt; LY, Lucifer Yellow CH ammonium salt; BD (BODIPY), 4,4-difluoro-1,3,5,7,8 pentamethyl-4-bora-3a, 4a-diazaindacene-2, 6-disulfonic acid disodium salt; DP (DAPI not DNA bound), 4,6-diamidino-2-phenylindoledyhydrochloride; DN (dansyl), 5-dimethylaminonaphthalene-1-sulfonyl hydrazine: PY, 1,2-bis-(1-pyrenedecanoyl)-sn-glycero-3-phosphocholine: and CM, coumarin 307. The fluorophores illustrated in b are as follows: IC, indo-1 with Ca^{2+} ; IF, indo-1 without Ca^{2+}; Fc, fura-2 with Ca^{2+}; FF, fura-2 without Ca^{2+}; CG, calcium crimson Ca^{2+}; Co, calcium orange with Ca^{2+}; CC, calcium crimson Ca^{2+}; and F3, flu0-3 with Ca^{2+}.

14.6.4 Two-Photon excitation of DNA-bound fluorephore:

At present MPE is used primarily for cellular imaging or for fluorescence correlation spectroscopy. Both of these applications make use of the small excited volumes obtained using MPE with a focused laser beam. Prior to describing MPE microscopy it is informative to see the effects of MPE on the fluorophores themselves. Figure 14.12 shows emission spectra of DAPI bound to DNA when excited at 360, 830, and 885 nm. The emission spectra are the same at each excitation wavelength, showing that emission occurs from the lowest singlet state irrespective of the mode of excitation. Although not shown, the intensity decays are the same for these excitation wavelengths. when excited at 360 nm a twofold decrease in fluorescence intensity, as expected for a one-photon process. When excited at 830 and 885 nm, the emission intensity decreases four- and eight-fold, respectively. This indicates that 2PE occurs at 830 nm and 3PE occurs at 885 nm.

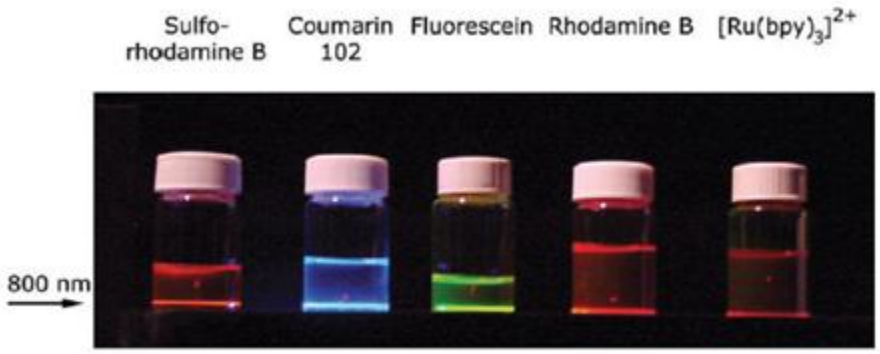

Figure 14.11. Simultaneous excitation of several fluorophores using the 800-nm output of a regenerative amplified Ti:sapphire laser. The laser is incident near the bottom of the bottles. The upper lines are reflections off the surface.

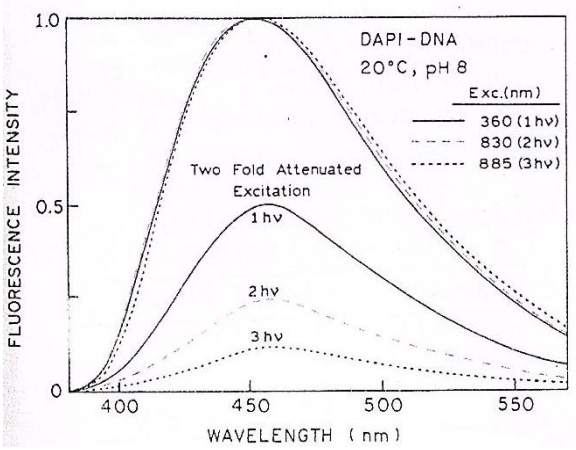

Figure 14.12; Normalized emission spectra of DAPI-DNA for excitation at 360, 830 and 885 nm. Also shown are the emission spectra with a twofold attenuation of the excitation. The excitation source at 830 and 885 nm was a femtosecond Ti:sapphire laser; 80MHz repetition rate with a pulse width near 80 fs.

The mode of excitation can be determined by the dependence of the emission intensity on incident power (Figure 14.13). For excitation at 830 and 885 nm a plot of DAPI emission intensity versus incident power yields slopes of 2.01 and 2.85, respectively. The mode of excitation switches from 2PE to 3PE between these wavelengths. The reason for this switch can be found in the DAPI absorption spectrum. The long-wavelength absorption ends near 420 nm. Above 840 nm 2PE can no longer occur because the energy of the combined photons is not adequate to reach the S_1 state. As a result the mode of excitation changes to 3PE. The 2PE-to-3PE transition occurs on the long-wavelength edge of the DAPI absorption. This is a result of the 2PE cross-section being much larger than the 3PE cross-section, so that 2PE dominates wherever possible. It was initially surprising that 3PE could be observed without detectible damage to the sample.

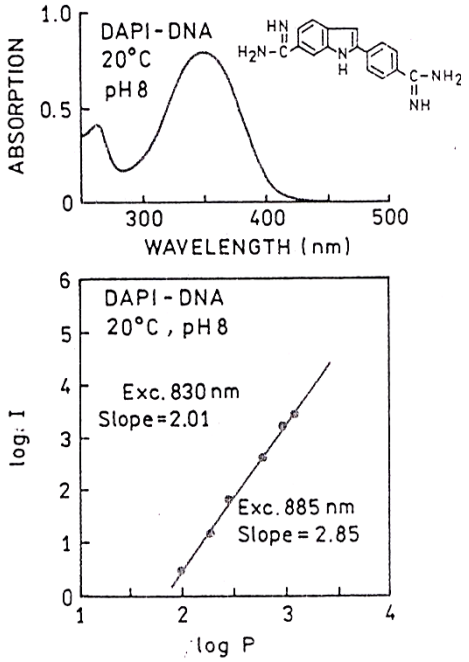

Figure 14.13. Absorption spectra and power-dependent intensities of DAPI-DNA. The laser power is in milli watts.

14.6.4 Multiphoton Microscopy

At present the dominant use of MPE is for optical imaging. Multiphoton microscopy (MPM) requires complex instruments that are often maintained by dedicated personnel. Most MPMs use a Ti:sapphire laser source (Figure 14.13-14.14). There may be a pulse picker to decrease the repetition rate. The optical path contains components for focusing the beam and for adjusting its intensity. In order to obtain an image the focused laser beam is raster scanned across the sample by the scanning unit. In this instrument there is also a CW He-Ne laser for conventional confocal laser-scanning microscopy (CLSM) with one-photon excitation. When using MPE all the emitted light comes from the focal spot, and there is

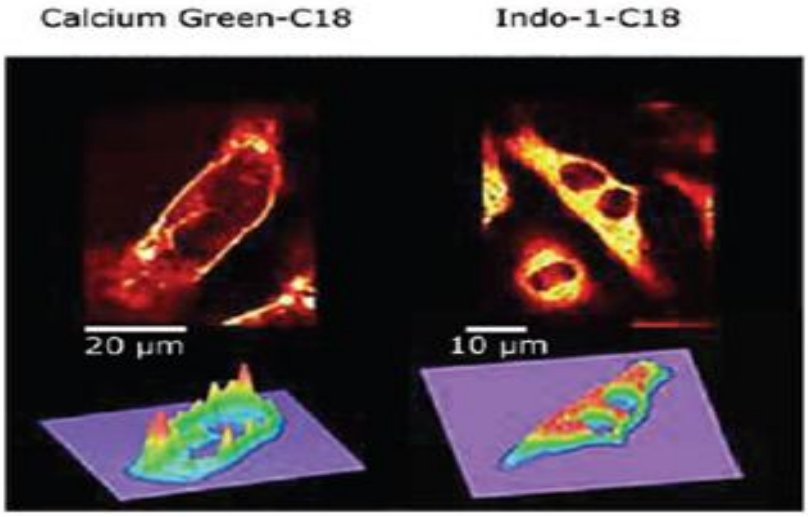

Fig. 14.14. Multiphoton microscopy images of neonatal rat cells labeled with lipid conjugate of calcium green or indo-1

minimal out-of-plane fluorescence. For this reason the multiphoton-induced fluorescence is usually measured using a PMT behind the objective, which provides higher sensitivity than passing the emission back through the scanning unit as is done with CLSM.

Several detectors are shown below the base plate of the microscope. Prior to reaching the detector the signal is passed through a short-pass (SP) filter to remove the longer wavelength excitation from the emission. Separate detectors are available for measuring lifetimes or emission spectra.

14.6.6 Three-Dimensional Imaging of Cells:

A longstanding goal of multiphoton microscopy has been to obtain three-dimensional cellular images. this is possible because the localized excitation allows collection of images at various focal planes in the cell (Figure 14.15). Using these 2D images it is possible to reconstruct a 3D image. Figure 14.16 shows a 3D reconstruction of a live PC12 cell stained with acridine orange. This probe emits in the green when bound to nuclear DNA and red when present in acidic organelles.

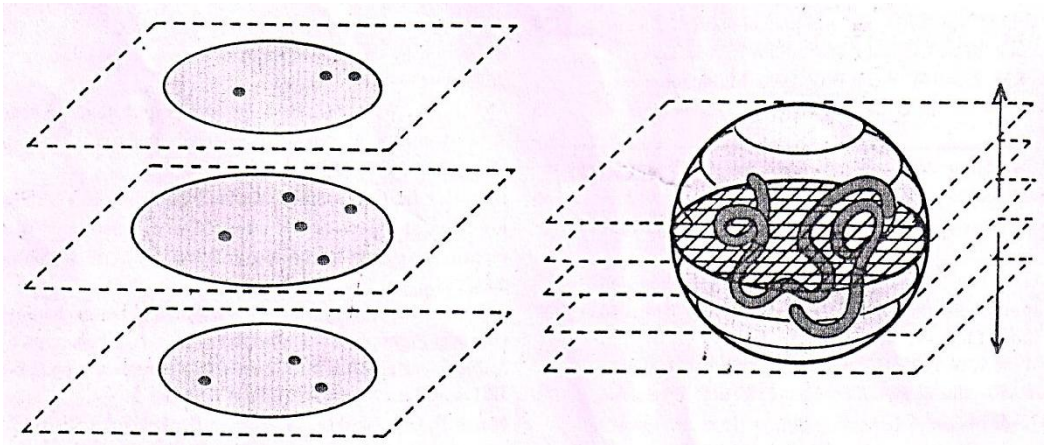

Figure: 14.15. Three-dimensional cell imaging using confocal or multiphoton microscopy.

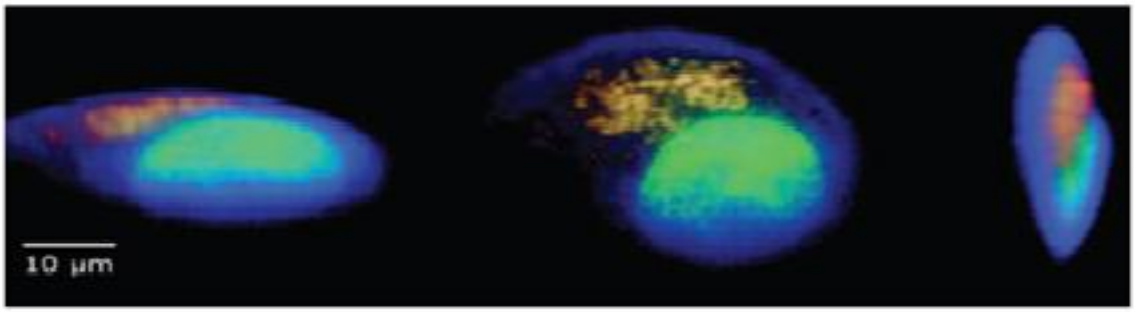

Figure: 14.16. Three-dimensional reconstruction of a live PC cell stained with acridine orange, which emits green (525 nm) when bound to DNA and red (650 nm) when present in acidic organelles. The perspective on the left is rotated 60^0 from the cells around the horizontal axis. The perspective on the right is rotated 90^0 around the vertical axis. Figure courtesy of Dr. Stefan Hall, Max-Planck Institute for Physical Chemistry, Gottingen, Germany.

14.7 Summary:

In the unit, with the help of non-linear interaction how the higher order harmonic generation will occurs and its function for the interpretation of out put source, observation of homogeneous and inhomogeneous broadening occurs multiphoton processes with their applications, interpretation are dealt in detail.

14.8 Key words:

Nom-linear interaction
Non-linear effect
Homogeneous broading
Multiphoton process

14.9 Question for self study:

1.What are the non-linear interaction, explain with example?
2. Define harmonic generation. How the second harmonic generation can be observed experimentally.
3. Write note on higher order non-linear effect.
4. What are the materials for non-resonant non-linear interaction Explain.
5. What are the homogeneous and inhomogeneous broading?
6. What is mean be multiphoton processes and explain their application?

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UNIT 15: Generation of short laser pulses, Time profiles of pulsed laser, Applications

Structure:

15.0. Objectives:

This content is useful to understand who the laser pulses time profile can be obtained. Pulse generation methods and their uses in various scientific fields

15.1. Introduction:

The discovery of fast processes, i.e., electron motions in atoms or molecules, radiative or collision-induced decays of excited levels, or the dynamics of an optically pumped system toward thermal equilibrium, opens the way to study in detail the dynamic properties of excited atoms and molecules etc. Knowledge of dynamical observation is of fundamental importance for many branches of physics, chemistry, engineering or biology. Examples are predissociation rates of excited molecules, femto second chemistry, or the understanding of the visual process and its different steps from the photoexcitation of rhodopsin molecules in the retina cells to the arrival of electrical nerve pulses in the brain.

To study these observation experimentally, one needs a good time resolution, i.e., minimum time interval Δt must still be shorter than the time scale T of the process under the observation. While the previous chapters explains non-linear interaction and multiphoton processes, this chapter concentrates on experimental techniques that allow high time resolution

The discovery of ultrashort laser pulses and of new detection technique that allow a very high time resolution has brought about development in the study of fast processes. The observed time resolution has been pushed recently into the attosecond range (1 as $= 10$ s). Spectroscopists can now quantitatively follow up ultrafast processes, which could not be resolved fifteen years ago.

The spectral resolution $\Delta\nu$ of most time-resolved techniques is, in principle, confined by the Fourier limit $\Delta\nu = a/\Delta T$, where ΔT is the duration of the short light and the factor $a \cong 1$ depends on the profile I(t) of the pulse. The spectral bandwidth $\Delta\nu$ of such *Fourier-limited pulses* is still much narrower than that of light pulses from incoherent light sources, such as flashlamps or sparks. Time-resolved coherent methods based on regular trains of short pulses even circumvent the Fourier limit $\Delta\nu$ of a single pulse and simultaneously reach extremely high spectral and time resolutions. Techniques for measuring lifetimes of excited atoms or molecules and of fast relaxation are obtained. These uses give the relevance of pico and femto second molecular physics and chemistry etc., for our understanding of fundamental dynamical observations in molecules.

15.2. Generation of Short Laser Pulses:

For a long time, microsecond pulses shows the shortest available pulses. Recently nanosecond range be reached by using special discharge circuits with low inductance and with pulse-forming networks, the time duration of the pulse is not necessarily limited by the duration of the pump pulse, but may be much shorter. Before we explaining present different techniques of ultrashort laser pulses, we will discuss the relations between the relevant factors of a laser that determine the time

profile of a laser pulse

15.3 Time Profile of Pulsed Lasers:

The time profile of the laser pulse is not only determined by the amplification per round trip $G(t)$ but also by the relaxation times τ_i, τ_k of the upper and lower laser levels. If the times are short compared to the rise time of the pump pulse, quasi-stationary laser emission is reached, where the inversion $\Delta N(t)$ and the output power $P_L(t)$ have a smooth time profile, determined by the balance between pump power $P_P(t)$,which creates the inversion, and laser output power $P_L(t)$, which decreases it. Such a time behavior, which is depicted in Fig. 15.0a, can be found, for instance, in many pulsed gas lasers such as the excimer lasers.

The increasing laser power $P_L(t)$ decreases the population inversion by stimulated emission, the lower level is not sufficiently quickly depopulated, it forms a bottleneck for maintaining threshold inversion. These laser pulse itself limits its duration and it ends before the pump pulse ceases (self-terminating laser, Fig. 15.0b). If the relaxation times τ_i, τ_k are long compared to the rise time of the pump pulse, a ΔN large inversion may build up before the induced emission is strong enough to deplete the upper level.

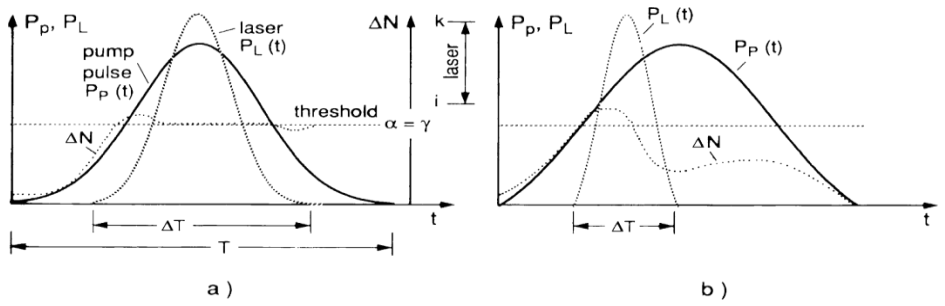

Fig.15.0 a,b. Time profile of the pump power $P_P(t)$,the inversion density $\Delta N(t)$, and laser output power $P_L(t)$; (a) for sufficiently short lifetime τ_i, of the lower laser level; and (b) for a self-terminating laser with $\tau_i^{eff} > \tau_k^{eff}$.

The corresponding high gain leads to a large amplification of induced emission and the laser power P_L may become so high that it depletes the upper laser level faster than the pump can refill it.

For time-resolved laser spectroscopy, pulsed dye lasers are of particular relevance due to their continuously tunable wavelength. They can be pumped by flashlamps ($T \cong 1$ μs to 1 ms),by other pulsed lasers, for example, by (T =2−10 ns), or frequency-doubled Nd:YAG lasers (T =5−15 ns). Because of the short relaxation time $\tau_i, \tau_k (\cong 10^{-11}$s) s), no spiking occurs and the situation of Fig. 15.0a is realized. The dye laser pulses have durations between 1 ns to 500 μs, depending on the pump pulses; typical peak powers range from 1 kW to 10MW and pulse repetition rates from 1Hz to 15 kHz.

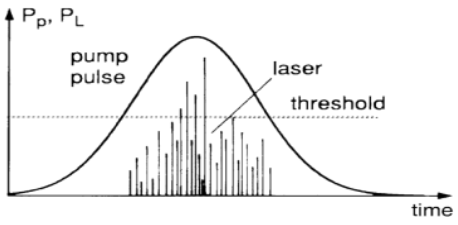

Fig.15.1. Schematic representation of spikes in the emission of a flashlamp pumped solid state laser with long relaxation time τ_1, τ_k.

15.3.1 Q-Switched Lasers:

To obtain a single, powerful pulse of a flashlamp-pumped laser from of the irregular sequence of many spikes, the technique of Q-switching was developed. Q-switching is based on the following principle. Until a selected time t_0 after the start of the pump pulse at t =0, the cavity losses of a laser are kept so high by a closed "optical switch" inside the laser resonator that the oscillation threshold cannot be reached. Therefore a large in version ΔN is built up by the pump (Fig. 15.2). If the switch is opened at $t=t_0$ the losses are suddenly lowered (that is, the quality factor or Q-value of the cavity jumps from a low to a high value. Because of the large amplification $G \propto B_{ik}\rho\Delta N$ for induced emission, a quickly rising intense laser pulse develops, which depletes in a very short time the whole inversion that had been built up during the time interval t_0. The time profile of the pulse depends on the rise time of Q-switching. Typical durations of these giant pulses are 1−20 ns and peak powers up to 10^9W are reached, which can be further increased by subsequent amplification stages

Such an optical switch can be realized, for instance, if one of the resonator mirrors is mounted on a rapidly spinning motor shaft (Fig. 15.3). Only at that time t_0 where the surface normal of the mirror coincides with the resonator axis is the incident light reflected back into the resonator, giving a high

Q-value of the laser cavity: The optimum time t_0 can be selected by imaging the beam of a light-emitting diode (LED) after reflection at the spinning mirror onto the detector D, which provides the trigger signal for the flashlamp of the Q-switched laser.

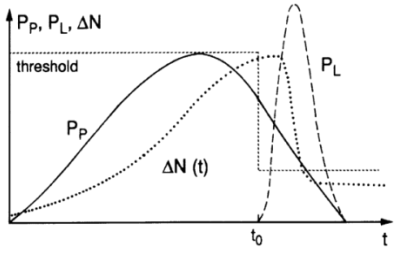

Fig.15.2. Pump power *P(t)*, resonator losses *γ(t)*, inversion density *ΔN(t)* and laser output power *P (t)* for a Q- switched laser

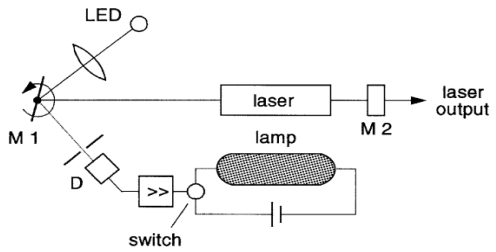

Fig. 15.3. Experimental realization of Q-switching by a rapidly spinning cavity mirror M_1

This technique, however, has some disadvantages: the spinning mirror is not very stable and the switching time is not sufficiently short. Therefore other Q-switching methods have been developed that are based on electro-optical or acousto-optical modulators.

15.3.2. Cavity Dumping:

The principle of Q-switching inverse technique, called cavity dumping, is used. The laser cavity consists of highly reflecting mirrors in order to keep the losses low and the Q-value high. Often an acousto-optic switch is used, for example, for argon lasers and cw dye lasers. Its basic principle is explained in Fig.15.4. A short ultrasonic pulse with acoustic frequency f_s and pulse duration $T>>1/f_s$ is sent at $t=t_0$ through a fused quartz plate inside the laser resonator. The acoustic wave produces a time-dependent spatially periodic modulation of the refractive index n(t,z), which act as a Bragg grating with the grating constant $\Lambda=c_s/f_s$, equal to the acoustic wavelength Λ where c_s is the sound velocity.

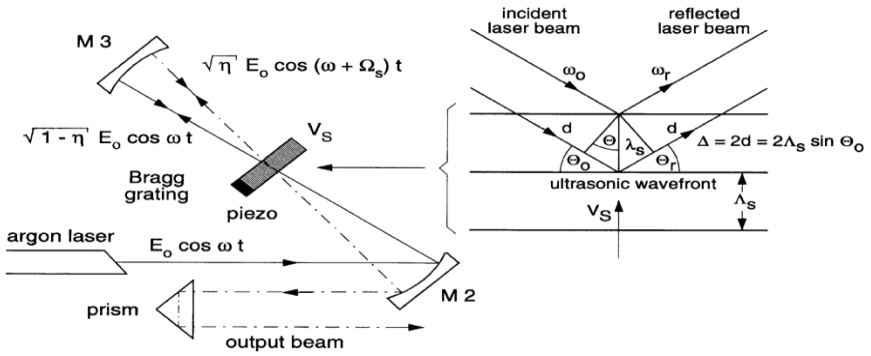

Fig.15.4. Cavity dumping of a cw argon laser by a pulsed acoustic wave. The insert shows the Bragg reflection of an optical wave at a running ultrasonic wave with wavelength Λ

When an optical wave $E_0\cos(\omega t-k.r)$ with the wavelength $\lambda=2\pi/k$ passes through the Bragg plate, the fraction Π of the incident intensity I_0 is diffracted by an angle θ determined by the Bragg relation:

$$2\Lambda\sin\theta = \lambda/n$$

The fraction η depends on the modulation amplitude of the refractive index and thus on the power of the ultrasonic wave.

When the optical wave is reflected at an acoustic wave front moving with the velocity v_s its frequency ω suffers a Doppler shift, which is , according to with $c=\lambda\cdot\omega/2\pi$ and $v=\Lambda\Omega/2\pi$

$$\Delta\omega=2n v_s/c\omega\sin\theta = 2\,n\,(\Lambda\Omega/\lambda\omega)\omega\sin\theta=\Omega,$$

And turn out to be equal *to acoustic frequency* $\Omega=2\pi f_s$. the amplitude of the deflected fraction is $E_1=\sqrt{\Pi}E_0\cos(\omega+\Omega)t$, that of the unaffected transmitted wave $E_2=\sqrt{1-\Pi}E_o\cos\omega t$. . After reflection at the mirror M3 the fraction $(1-\Pi)^{1/2}E_1$ is transmitted and the fraction $\Pi^{1/2}$ E_2 is deflected by the Bragg plate into the direction of the out coupled beam. This time, however, the reflection occurs at receding acoustic wave fronts and the Doppler shift is $-\Omega$ instead of $+\Omega$. The total amplitude of the extracted wave is therefore

$$E_c=(\Pi)^{1/2}\,(1-\eta)^{1/2}E\,[\cos(\omega+\Omega)t+\cos(\omega-\Omega)t]$$

The average output power $P_c\alpha\ E_c^2$ of the light pulse is then with $\omega>>\Omega$ and $(\cos^2\omega) = 0.5$:

$$P_c(t)= \eta(t)[1-\eta(t)]P_0\cos^2\Omega t\ ,$$

where the time-dependent efficiency $\eta(t)$ is determined by the time profile of the ultrasonic pulse and P_0 is the interactivity during the ultrasonic pulse the fraction $2\eta(1-\eta)$ of the optical power $\frac{1}{2}\varepsilon_0 E_0^2$, stored within the laser resonator, can be extracted in a short light pulse, which is still modulated at twice the acoustic frequency Ω. With $\eta = 0.3$ one obtains an extraction efficiency of $2\eta(1-\eta)=0.42$.

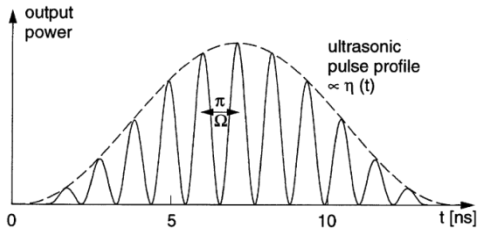

Fig. 15.5. Intensity profile of a cavity-dumped laser pulse, showing the intensity modulation at twice the ultrasonic frequency Ω

The technique of cavity dumping is mainly applied to gas laser and cw dye lasers. One achieves pulse durations $\Delta T = 10-100$ ns, pulse-repetition rates of 0-4 MHz, and peak powers that may be 10-100 times higher than for normal cw operation with optimized transmission of the output coupler (Fig. 15.5). The average power depends on the repetition rate f. typical value for $f = 10^4 - 4\times10^6$ Hz are 0.1−40% of the cw output power. The disadvantage of the acoustic cavity dumper compared to the Pockels cell of is the intensity modulation of the pulse at the frequency 2Ω.

15.3.3. Mode Locking of Lasers:

If coupling between the phases of these simultaneously oscillating mode scan be established, a coherent superposition of the mode *amplitudes* may bereached, which leads to the generation of short output pulses in the picosecond range. This mode coupling or *mode locking* has been realized by optical modulators inside the laser resonator (*active* mode locking) or by saturable absorbers (*passive* mode locking) or by a combined action of both locking techniques.

a) Active Mode Locking

If the intensity of a monochromatic light wave

$$E = A_0 \cos(\omega t - kx),$$

is modulated at the frequency $f = \Omega/2\pi$ (for example, by a Pockels cell or an acousto-optic modulator), the frequency spectrum of the optical wave contains,

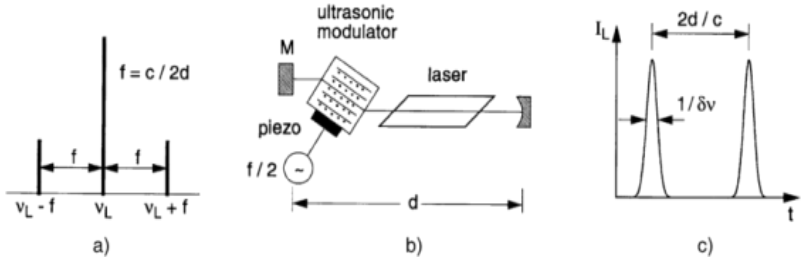

Fig. 15.6.a-c. Active mode locking : (a) sideband generation; (b) experimental arrangement with a standing ultrasonic wave inside the laser resonator; (c) idealized output pulses.

besides the carrier at $\omega = \omega_0$, the sidebands at $\omega = \omega_0 \pm \Omega$ (that is, $\nu = \nu_0 \pm f$) if the modulator is placed inside the resonator with the mirror separation d and the mode frequencies $\nu_m = \nu_0 \pm m \cdot c/2d$ ($m = 0,1,2,..$), the sidebands coincide with resonator mode frequencies if the modulation frequency f

equals the mode separation $\Delta\nu = c/2d$. Since they pass the intracavity modulator they are also modulated and new sidebands $\nu = \nu_0 \pm 2f$ are generated. This continues until all modes inside the gain profile participate in the laser oscillation. The time t, the amplitudes of all modes have their maximum at the location of the modulator and this situation is repeated after each cavity round-trip time T=2d/c (Fig. 15.6.c).

If the amplitude A_0 is time independent (cw laser), this shows a sequence of equidistant pulses with the separation $T=2d/c=1/\Delta\nu$

which equals the round-trip time through the laser resonator. Therefore pulse width

$$\Delta T = 2\pi/[2m+1]\Omega = 2\pi/N\Omega = 1/\delta\nu,$$

is obtained by the number N of phase-locked modes and is inversely proportional to the spectral bandwidth $\delta\nu$ of the gain profile above threshold (Fig.15.7.)

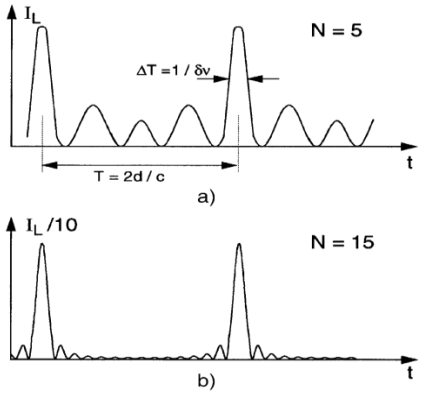

Fig.15.7.a.b. Schematic profile of the output of a mode-locked laser: (a) with 5 modes locked; (b) with 15 modes locked

The peak power of the pulses, which can be derived from the intensity maxima in 15.7 at times $t=2\pi q/\Omega = q(2d/c)(q=0,1,2,\ldots)$, is proportional to N^2. The pulse energy is therefore proportional to $N^2\Delta T \propto N$. intensity as N increases.

b) Passive Mode Locking

The passive mode locking is a method that has less experimental effort than active mode-locking; it can be applied to pulsed as well as to cw lasers. Pulse widths below 1 ps have been realized. The basic principles as follows, instead of the active modulator, a saturable absorber is put inside the laser resonator, close to one of the end mirrors (Fig15.8). The absorbing transition short relaxation times τ_I ,τ_k. In order to reach oscillation threshold in spite of the absorption losses the gain of the active medium must be correspondingly high. In the case of a pulsed pump source, the emission of the active laser medium a ta time shortly before threshold is reached consists of fluorescence photons, which are amplified by induced emission.

The peak power of the resulting photon avalanches fluctuates more or less randomly. Because of nonlinear saturation in the absorber, the most intense photon avalanche suffers the lowest absorption losses and thus experiences the largest net gain. It therefore grows faster than other competing weaker avalanches, saturates the absorber more, and increases its net gain even more.

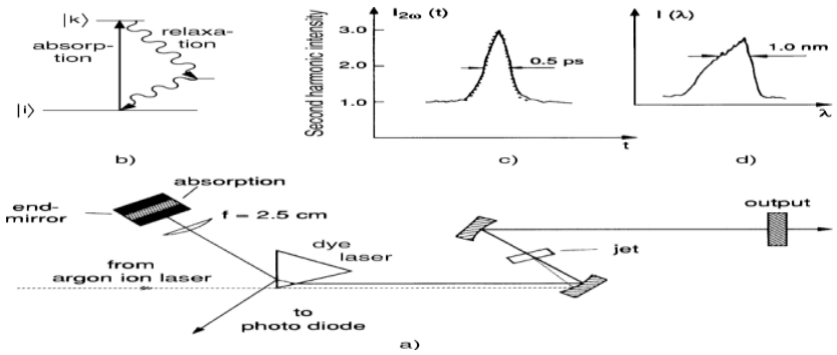

Fig.15.8.a-d, Passive mode locking of a cw dye laser (a) experimental arrangement; b) level scheme of absorber; (c) time profile; and (d) spectral profile of a mode-locked Pulse

After a few resonator round trips this photon pulse has become so powerful that it depletes the inversion of the active laser medium nearly completely and therefore suppresses all other avalanches.

These nonlinear interaction of photons with the absorbing and the amplifying media leads under favorable conditions to mode-locked laser operation starting from a statistically fluctuating, unstable threshold situation. After this short unstable transient state the laser emission consists of a stable, regular train of short pulses with the time separation $T = 2d/c$, as long as the pump power remains above threshold.

This more qualitative representation illustrates that the time profile and the width ΔT of the pulses is determined by the relaxation times of absorber and amplifier. In order to suppress the weaker photon avalanches reliably, the relaxation times of the absorber must be short compared with the resonator round-trip time.

Table: Summary of different mode-locking techniques. With active mode locking of cw lasers an average power of 1 W can be achieved

Technique	Mode locker	Laser	Typical pulse duration	Typical pulse energy
Active mode locking	Acousto-optic modulator Pockels cell	Argon, cw HeNe, cw Nd:YAG, pulsed	300 ps 500 ps 100 ps	10 n J 0.1 nJ 10 µJ
Passive mode locking	Saturable absorber	Dye, cw Nd:YAG	1 ps 1-10 ps	1 nJ 1 nJ
Synchronous pumping	Mode-locked pump laser & matching of resonator length	Dye, cw Color center	1ps 1 ps	10 nJ 10 nJ
colliding pulse mode locking CMP	Passive mode locking and eventual synchronous pumping	Ring dye laser	<100 fs	≈1 nJ
Kerr lens mode-locking	Optical Kerr effect	Ti:sapphire	<10 fs	≈1-10 nJ

There are several versions of the experimental realizations of mode-locked or synchronously pumped lasers. Table gives a short summary of typical operation parameters of the different techniques. More detailed representations of this subject can be obtained.

Many different techniques have been used for obtaining time resolution in luminescence spectroscopy. An excellent discussion of various techniques has been given recently by Fleming. The most direct technique is to use a fast photomultiplier or a photo detector in conjunction with fast electronics. The best time resolution that can be obtained with a photomultiplier directly is about 50ps .while photo detectors can be mode with much faster response time, their low sensitivity restricts their use to the detection of strong signals, such as from laser .using a technique called time correlated photon counting in conjunction with fast photomultiplier it is possible to improve the time resolution to approximately 10ps;but careful deconvolution is required to obtain such time resolution. Another technique for obtaining time resolutions of 10ps is to measure the phase shift between a sinusoidal excitation source and the luminescence. However, analysis of the data becomes difficult if several time constants are present in the luminescence decay.

The various aspects of frequency mixing techniques for time resolved luminescence spectroscopy. Here, we will discuss the primarily on the technique of sum frequency generation, also known as upconversion, because the availability of excellent photomultiplier in the blue and UV spectral region makes this an extremely attractive technique for time resolved luminescence spectroscopy.

15.4 A. Experimental arrangement:

A. Time Resolution

The time resolution in a properly designed system is governed primarily by two factors; to pulse width of the laser and the group velocity dispersion in the nonlinear crystal. Since the group velocity dispersion is not zero, this imposes limitations on the thickness of the crystal for a given time resolution. The efficiency of mixing decreases as the crystal thickness decreases, the ultimate time resolution attainable depends on the strength of the luminescence signal and the sensitivity of the detection system. Note that the spectral bandwidth of the nonlinear crystal may broaden the pulse width of the sum frequency photons. However this does not contribute to the attainable time resolution. There should be no dispersive elements in the path of the IR beam if the luminescence extends over a wide spectral range.

B. Spectral Resolution

If observed luminescence spectrum is broad, the spectral resolution is determined by the bandwidth of the nonlinear crystal. In order to obtain better spectral resolution, one can disperse the upconverted signal in a spectrometer. The use of a spectrometer also helps in reducing stray light at the detector.

The spectrometer complicates data acquisition for the following reason. The spectral bandwidth of the nonlinear crystal is generally larger than the desired spectral resolution but

may be small compared to the spectral range of interest. In this case one needs to vary the angle of the nonlinear crystal to cover the entire spectral range. Thus the spectrometer wave length has to be varied in synchronism with the crystal angle in a predetermined manned .tis can be achieved most simply if both the angle and the spectrometer wavelength are controlled by stepper motors.

C. Rejection of stray light

The luminescence wavelengths close to the exciting laser wave length, the second harmonic of the pump laser may generated with sufficient intensity even if this processes is not properly phase matched. This signal may in fact be stronger than the weak upconverted luminescence signal very close to the wavelength the use spectrometer helps in reducing this unwanted signal at detector. A double spectrometer maybe necessary if the problem is serious. Another solution to this problem is to use a different mixing configuration so that the IR and the P have different polarizations. The second harmonic generation (SHG) will be further suppressed because the actual angle will be far from the phase matching angle for SHG. Castner et al. have used type II upconversion in area for this and other reasons. To reduce the stray light due to SHG of the laser, it is important to prevent SHG beam from hitting the entrance slit of the spectrometer. This can be best done by using a non collinear geometry for the IR and the P beam, so that there is a sufficient angular spread between the SHG and the sum frequency beams.

D. Spectral Calibration

The equation for the efficiency of the mixing process indicate, there is a dependency of the efficiency on wavelength, arising from the dispersion of the indices of refraction and the dependence of the effective nonlinear coefficient on the phase matching angle. While this variation is rather slow, any precise measurement of the spectra must account for it. Furthermore, the use of a spectrometer and a photomultiplier also introduce wavelength dependent efficiency factors.

E. Detection of upconverted photons

There are two source of noise for the upconverted photons. If observed the signal is sufficiently above the dark count rate of the photomultiplier, then the fluctuations I n the laser may by the primary noise source. Under these conditions, any reasonable means of detecting the photomultiplier current will be adequate. However, the signal levels are generally low, and the shot noise arising out of the dark current of the photomultiplier may maybe the limiting noise factor. In this case, it is advisable to cool the photomultiplier to reduce the dark noise and to use photon counting technique to discriminate against thee small noise pulses (fig. 15.8.f).

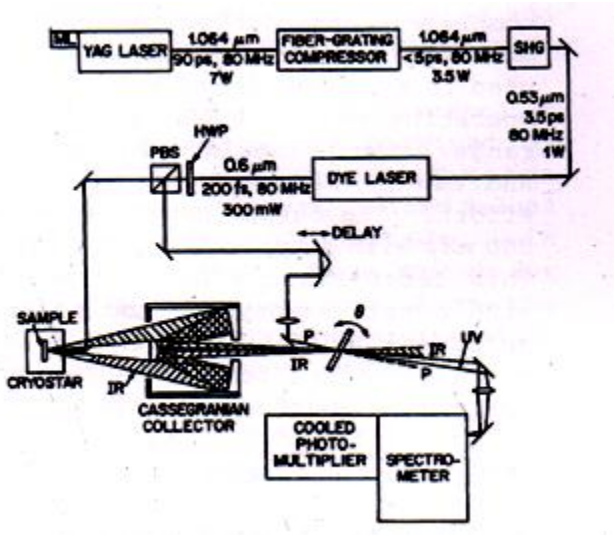

Fig.15.8.f Experimental arrangement of upconvertion

F. Determination of the zero delay

The determination of the zero time delay is necessary in all ultrafast determinations. The determining the zero in a luminescence upconversion system is by obtaining cross correlation trace between the scattered laser light from the sample under investigation and a delayed laser beam at the non linear crystal used for frequency up conversion. Such trace provides not only an accurate zero but also an accurate measure of the system response time. However, sometimes, the non linear crystal is cut at such an angle that it is not possible to obtain a cross correlation trace. In such case , one can get the zero by replacing the nonlinear crystal with another appropriately cut crystal at precisely the same position in some cases it may also be possible to use the fast luminescence from the sample to determine the zero with an order accuracy of better than 100 fs.

15.4. B. Experimental Arrangements

The experimental observation of optical cooling, which uses a collimated bean of atoms and a counter propagating cw laser (day laser or diode laser, Fig. 15.9) the following difficulties have to be overcome: during the deceleration time the Doppler-shifted absorption frequency $\omega(t)=\omega_0+k\text{-}\upsilon(t)$ changes with the decreasing velocity u, and the atoms would come out of resonance with the monochromatic laser. Three solutions have successfully tried either the laser frequency.

$\omega(t)= \omega_0+k\text{-}\upsilon(t) \pm \gamma$

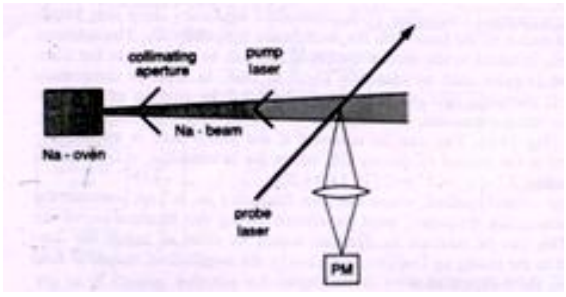

Fig: 15.9. Simplified experimental realization for the deceleration of action atoms in a collimated beam by photon recoil

is synchronously tuned with the changing velocity v9t) in order to stay within the line width y of the atomic transition, or the absorption frequency of the atom is appropriately altered along the deceleration path.

The second technique, where the laser frequency ω_L is kept constant, the atomic absorption frequency must be altered during the declaration of the atoms. Thos can be realized by Zeeman tuning. In order to match the Zeeman shift to the changing Doppler shift $\Delta\omega(z)$, the longitudinal magnetic field must have the z-dependence (Fig.15.10).

$$B = B_o\sqrt{1-\frac{2az}{v_o^2}}$$

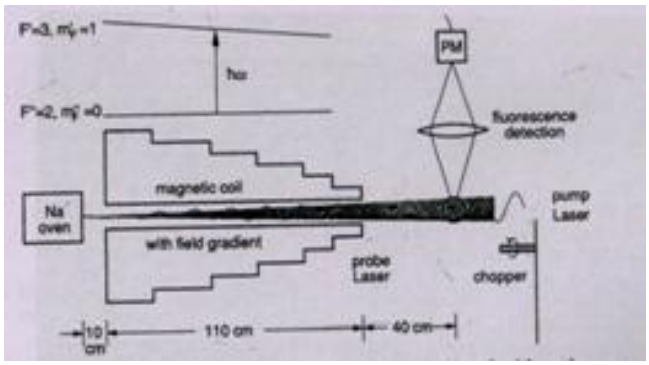

Fig 15.10. Laser cooling of atoms in a collimated beam with a fixed laser frequency and Zeeman tuning of the atomic absorption frequency.

For atoms that enter the at z=0 with the velocity v_0 and experience the negative acceleration $\alpha(m/s^2)$ by photon recoil. This field dependence B(z) can be realized by a proper choice of the winding $N_w(z)$ per centimeters of the magnetic field coil.

Most optical cooling experiments have been performed upto now on Alkali atoms, such as Na or Rb, using a single mode cw dye laser. The velocity decreases of the atoms is monitored with the tunable probe laser 12, which is sufficiently weak that is does not affect the velocity distribution. The probe laser induced fluorescence $I_{FL}(\omega_2)$ is measured as a function of the Doppler shift. Experiments have shown that the atoms could be completely stopped and there velocity could even be reversed. An example of the compression of the thermal velocity distribution into a narrow range around V=200m/s is illustrated in Fig 14.11 for Na atoms.

A very interesting alternative laser for optical cooling of atoms in a collimated beam is the modeless laser, which has a broad spectral emission. Such a laser can cool all atoms regardless of their velocity if its spectral width $\Delta\omega_L$ is larger than the Doppler shift $\Delta\omega_D=V_Ok$ (Fig. 15.12)

With the following experimental trick it is possible to compress the velocity distribution $N(V_z)$ of atoms in a beam into a small interval ΔV_z around a wanted final velocity V_F. The beam from modeless laser propagates anti collinearly to the atomic beam

and cools the atoms. A second single mode laser intersects the atomic beam under a small angle α against the beam axis, if it is tuned to frequency.

$$\omega_2=\omega_0+kv_f\cos\alpha$$

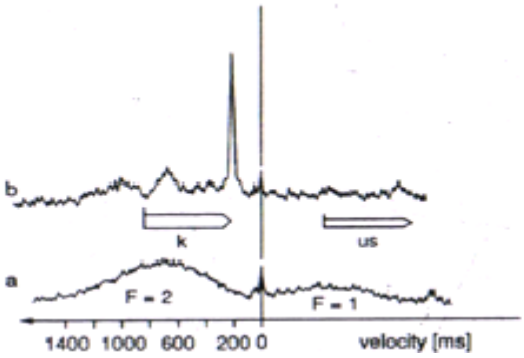

Fig 15.11.(a) Compression of the thermal velocity distribution Na atoms by optical cooling into an narrow velocity range V=200m/s(b) the sharp resonance at V=0 is caused by the probe; laser perpendicular to the atomic beam. The arrow k gives the tuning range of the cooling laser, the arrow μs gives that of the upper side band, which pumps the transition.

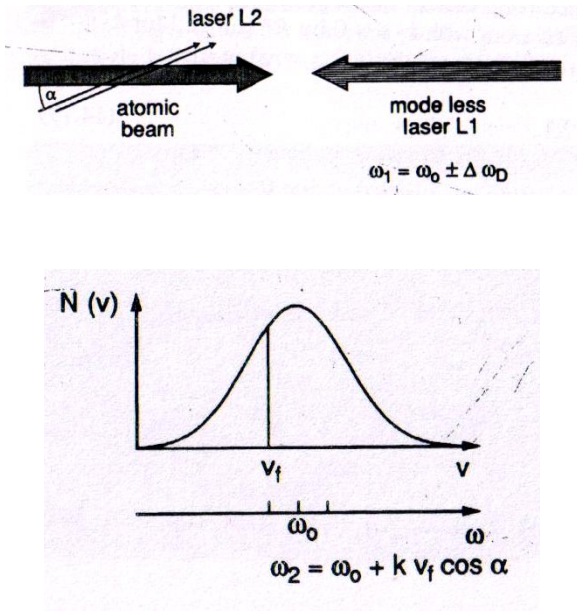

Fig 15.12. Cooling of all atoms with a counter propagating modeless laser. A cooling stop at a selectable velocity V_f can be realized with a second co-propagating single mode laser.

It accelerates the atoms as soon as they have reached the velocity V_f. This second laser therefore acts as a barrier for the lower velocity limit of cooled atoms.

The photon recoil can be used not only for the declaration of collimated atomic beams but also for the deflection of atoms, if the laser beam crosses the atomic beam perpendicularly. In order to increase the transferred photon momentum, and with it the deflection angle, an experimental arrangement is chosen where the laser beam crosses the atomic beam many times in the same direction. The deflection angle ð per absorbed photon, which is given by $\tan\eth=hk/(mv_z)$, increases with decreasing the atomic velocity V_z . optically

cooled atoms can therefore be deflected by large angles. Since the atomic absorption frequency differs for different isotopes, this deflection can be used for spatial isotope separation if other methods cannot be applied (fig. 15.13).

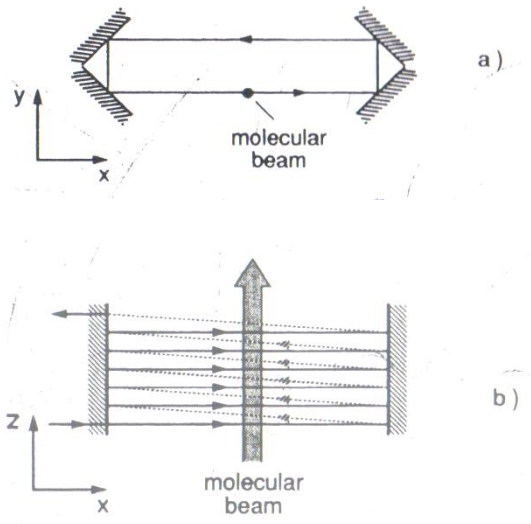

Fig 15.13.Deflection of atom in a collimated atomic beam using a multiple path geometry. The molecular beam travels into the z-direction (a) view into the z-direction (b) view into the y-direction. On the dashed return paths the laser beam does not intersect the atomic beam.

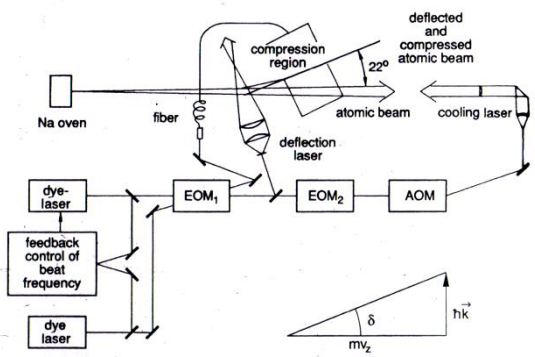

Fig 15.14. Cooling, Deflection and Compression of atoms by photon recoil. The electro optic modulators (EOM) and the acousto-optic modulator(AOM) serve for sideband generation and frequency tuning of the cooling laser sideband.

An interesting application of atomic deflection by photon recoil is the collimation and focusing of atomic beams with laser. Assume atoms with the velocity $v=v_x<<v_z,0,v_z$pass through a laser resonator, where an intense standing optical wave in the ±x-direction is present. If the laser frequency ω_L is kept slightly below the atomic resonance frequency ω_0, atoms with transfers velocity components V_x are always pushed back to the z-axis by photon recoil because that part of the laser wave with the k-vector antiparallel to V_X always has large absorption probability than the component with k parallel to V_X. The velocity component V_x is therefore reduced and the atomic beam is collimated.

If the atoms have been optically cooled before they pass the standing laser wave, the experience a large collimation in the maximum of the standing wave, but are not affected in

the nodes. The laser wave acts like a transmission grating that "channels" the transmitted atoms. A schematic diagram of an apparatus for optical cooling of atoms deflection of the slow down atoms, and focusing is depicted in Fig 15.14.

15.5. Application of Cooled atoms and molecules:

In optical cooling and deflection of atoms open new areas of atomic and molecular physics. Collisions at very small relative velocity, where the de-Borglie wavelength $\lambda_{DB}=h/(mv)$ is large can now be studied. They give information about the long range part of the interaction potential, where new phenomena arise, such as retardation effects and magnetic interactions from the electron or nuclear pins. One example is the study of collision between Na atoms in their $3^2S_{1/2}$ ground state. The interaction energy depends on the relative orientation of the two electron spins S=1/2. The atoms with parallel spin from a Na_2 molecule in a $^3\Sigma_u$ state while atoms with antiparallel spins from a $Na_2(^1\Sigma_g^+)$ molecules. At large inter nuclear (r>1.5nm) distances the energy differences between $^3\Sigma_u$ and $^1\Sigma_g$ potential become comparable to the hyperfine splitting of the $Na(3^2S_{1/2})$ atoms. The interaction between the nuclear spins and the electron spins leads mixing of the $^3\Sigma_u$ and $^1\Sigma_u$ states with corresponds in the atomic model of colliding atoms to spin-flip collision.

Collision between cold atoms in a trap can be studied experimentally by measuring the loss rate of trapped atoms under various trap conditions. It turns out the density of exited atoms cannot be neglected compared with the density of ground state atoms, and the interaction between exited and ground state atoms plays an essential role. For collision at very low temperatures the absorption and emission of photos during the collisions is important, because the collision time $\tau_C=R_C/V$ becomes very long at low relative atomic velocities v. the two dominant energy transfer processes are collision-induced fine-structure transitions in the exited state and radiative redistribution, where a photon is absorbed by an atom at the position r_1 in the trap potential V(r) and another photon with a slightly different energy is reemitted after the atom has moved to another position r_2 .

Another application is the deflection of the atoms by photon recoil. For sufficiently good beam collimation, the deflection from single photons can be deducted. The distribution of the transverse-velocity components contains information about the statistics of photons absorption. Such experiments have successfully demonstrated the anti bunching characteristics of photons absorption. The photon statistic is directly manifest in the momentum distribution of the deflected atoms. Optical collimation by radial recoil can considerably decreases the divergence of atomic beams and thus the beam intensity. This experiments in crossed beams that could not be performed before because of a lack of intensity.

The important application of cold trapped atoms is their use an optical frequency standard. They offer two major advantages reduction of the Doppler effect and prolonged interaction times on the order of 1s or more. Optical frequency standards may be realized either by atoms in optical traps or by atomic fountains.

For realization of an atomic fountain, cold atoms are released in the vertical direction out of an atomic trap. They are decelerated by the gravitational field and return back after having passed the culmination point with $v_z=0$.

There are many possible applications of cold trapped molecule.

One example is the spectroscopy of highly forbidden transition, which because possible because of the long interaction time. Another aspect is a closer look at the chemistry of cold trapped molecules, where the reaction rate and the molecular dynamics are dominated by tunneling and a manipulation of molecular trajectories seems possible. Experiments on testing time reversal symmetry via a search for a possible electric dipole moment of the proton or the electron are more sensitive when cold molecules are used.

15.6 Summary:

The Generation of short laser pulses gives the microscopic information of many interactions in various fields. Techniques of obtaining the short laser pulses with the help different technique like Q-switching laser cavity dumping, mode locking of lasers. Experimental arrangement and applications.

15.7: Key words:

Short laser pulses

Time profiles of pulsed laser

Q-switching lasers.

Mode locking of lasers

15.8: Question for self study:

1. Methods of generation of short laser pulses? Explain with example?
2. Define time profiles of pulsed laser observed experimentally with relevant diagram.
3. Write note on Q-switching and Cavity dumping techniques
4. What are the Mode locking of lasers? Discuss with examples.
5. Explain in detail application of short pulse lasers.

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UNIT 16: Optical fibers, Light Wave Communication and Applications of Lasers.

Structure:

16.0 Objectives:

To understand the transmission of light or digital signal using optical fiber results optical fiber communication system. Advance medical applications of laser spectroscopy which are used for various treatments of human body, industrial applications and other applications.

16.1 Introduction:

In 1870 John Tyndall, a natural philosopher living in England, demonstrated one of the first guided light systems to the Royal Society. His experiment involved using water as a medium to prove that light rays bend. The fibers are not electrically conductive, so they may be used in areas where isolation from electrical and electromagnetic interference is a problem. With the much higher information capacities, multiple channel routes using optic fibers can be compressed into much smaller cables, greatly reducing congestion in over crowed cable ducts. With present technology, fiber-optic communications systems are still more expensive than equivalent wire or radio systems, but this situation is changing rapidly, Fiber-optic systems will rapidly become competitive with other systems in price and eventually replace them.

The present context the technological system need very high speed communication system for development of science and technology. Demonstration of Fiber optic communication system. Medical applications of laser spectroscopy for treatment of various diseases and industrial application of lasers.

Need for ultra high speed communications

The large increase in the availability of inexpensive, high-speed information technology personal computers has led to the deployment of large-scale distributed computing technology with the capability of serving a large number of users. These systems permit the users to share software and databases to accomplish tasks that were once the sole province of mainframe share computers; they are feature by centrally located file servers which store the main programs, files and back up the PC systems, thus avoiding disk crash calamities, Direct communication between computers is now necessary in many networking system, leads to greatly expanded requirements for high-speed digital communication channels. There are many applications that require extremely high-speed interconnections;

- Rapid access to very large databases. This application is one of the primary reasons for the presence of high-speed PCs in many offices today. Processor speeds of 100 MHz are certainly not required for word-processing applications.

- High-definition image transmission which includes
- Medical images such as X-rays, magnetic resonant images (MRIs), and computerized axial tomography (CAT) scans for intercity medical teleconferencing.

- Video cables transmitting high-definition TV
- Three dimensional (3D) images for robotics and next generation surveillance and tracking systems.
- Computer-computer comm. Communications and internal communication within supercomputers. In particular, there has been interest in employing optical communications within massively parallel machines.
- Information Superhighway communications, TV cable with a massive number of channels.

At present the fiber-optic communication systems (FOCS) is the strongest method for achieving the communication speeds required for the above- mentioned tasks. The data rates is excess of 10 Gbits/s have been achieved in the laboratory, and practical systems with data rates in excess of 1 Gbits/s are being deployed by major communication carriers throughout the world. In the remainder of the test we shall see why FOCS has the potential to achieve the aforementioned tasks and thereby fulfill foreseeable communication requirements well into the twenty-first century. Although the only potential competitor for FOCS at these data rates is superconducting cables, that technology is barely in its infancy.

16.2 Elements of an optical fiber transmission links:

Figure 16.0 shows the optical fiber transmission containing the various elements. The transmitter consisting of a light source and its associated drive circuitry, a cable offering mechanical and environmental protection to the optical fibers contained inside, and a receiver consisting of a photo detector plus amplification and signal-restoring circuitry. Additional components include optical amplifiers, connectors, splicer's, couplers, and regenerators helps for restoring the signal-shape characteristics. In addition to protecting the glass fibers during installation and service, the cable may contain copper wires for powering optical amplifiers or signal regenerators, which are needed periodically for amplifying and reshaping the signal in long-distance links.

The optical fiber cables can be installed either aerially, in ducts, undersea or buried directly in the ground. As a result of installation and/or manufacturing limitations individual cable lengths will range from several hundred meters to several kilometers. Practical considerations such as reel size and cable weight determine the actual length of a single cable section. Shorter segments tend to be used when the cables are pulled through ducts. Longer lengths are used in aerial, direct-burial or undersea applications. Splicing together individual cable sections forms continuous transmission lines for these long-distance links. For installations in undersea the splicing and repeater installation functions are carried out on board a specially designed cable laying ship.

The most important characteristics of an optical fiber is its attenuation as a function of wavelength. Early technology made exclusive use of the 800 to 900 nm wavelength band, since, in this region, the fibers made at that time exhibited a local minimum in the attenuation curve and optical sources and photo detectors

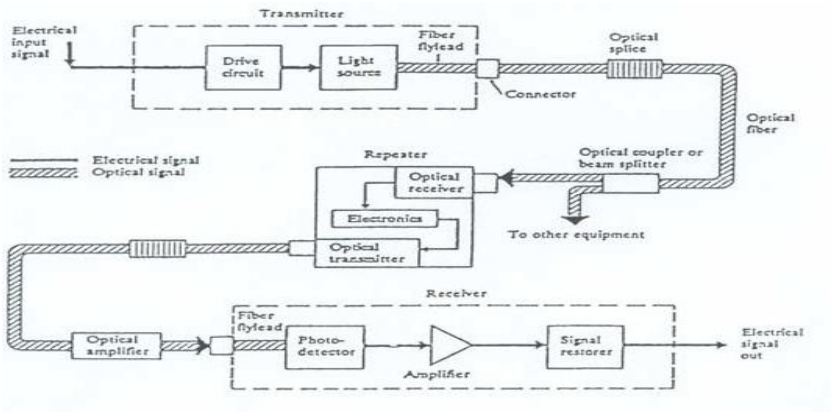


Fig.16.0; Components in an optical fiber communication

at these operating at these wavelengths were available. This region is referred to as the first window. By reducing the concentration of hydroxyl ions and metallic impurities in the fiber material in the 1980s manufactures were able to fabricate optical fibers with very low loss in the 1100 to 1600 nm region. This spectral band is referred to as the long wavelength region. Two windows are defined here the second window, centered around 1310 nm and the third window, centered around 1550 nm.

In 1998, a new ultrahigh purifying process patented by Lucent technologies eliminated virtually all water molecules from the glass fiber material. By dramatically reducing the water attenuation peak around 1400 nm, this process opens the transmission region between the second and third windows to provide around 100 nm more bandwidth than in conventional single mode fibers. This particular fiber, which was specifically designed for metropolitan networks, will give local service providers the ability to deliver most effectively up to hundreds of optical wavelengths simultaneously.

The important concepts of design and installation of an optical fiber communication system require measurement techniques for verifying the operational characteristics of the constituent components. In addition to optical fiber parameters, system engineers are interested in knowing the characteristics of passive splitters, connectors, and couplers and electro optic components, such as sources, photodetectors and optical amplifiers. Furthermore, when a link is being installed and tested, the operational parameters of interest include bit error rate, timing jitter and signal to noise ratio as indicated by the eye pattern. During the time of operation, measurements are needed for maintenance and monitoring functions to determine factors such as fault locations in fibers and the status of remotely located optical amplifiers.

16.3 Medical applications of Laser Spectroscopy:

Numerous books have been published on laser applications in medical research in hospital practice. Most of these applications rely on the high laser output power, which can be focused into a small volume. The strong dependence of the absorption coefficient of living tissue on the wavelength allows selection of the penetration depth of the laser beam by

choosing the proper laser wavelength. for example, skin carcinoma or portwine marks should be treated at wavelengths for a small penetration depth in order to protect the deeper layers of the epidermia from being damaged, while cutting of bones with lasers or treatment of subcutaneous cancer must be performed at wavelengths with greater penetration depth The most spectacular outcomes of laser applications in medicine have been achieved in laser surgery, dermatology, ophthalmology and dentistry. There are, however, also very promising direct applications of laser spectroscopy for the solution of problems in medicine, they are based on new diagnostic techniques and are discussed in this section.

16.3.1 Applications of Raman spectroscopy in Medicine:

During surgery on a patient, the optimum concentration and composition of narcotic gases can be indicated by the composition of the respiratory gases, that is, with the concentration ratio of $N_2;O_2;C0_2$. This ratio can be measured in vivo with Raman spectroscopy. The gas flows through a cell that is placed inside a multipass arrangement for an argon laser beam. Several detectors with special spectral filters are arranged in a plane perpendicular to the beam axis. Each detector monitors a selected Raman line, which allows the simultaneous detection of all molecular components of the gas.

The sensitivity of the method is illustrated by fig.16.1 which depicts the time variation of the CO_2,O_2 and N_2 concentration in the exhaled air of a human patient. Note the variation of the concentrations with changing breathing periods. The technique can be used routinely in clinical practice for anesthetic control during operations and obviously also for alcohol tests of car drivers.

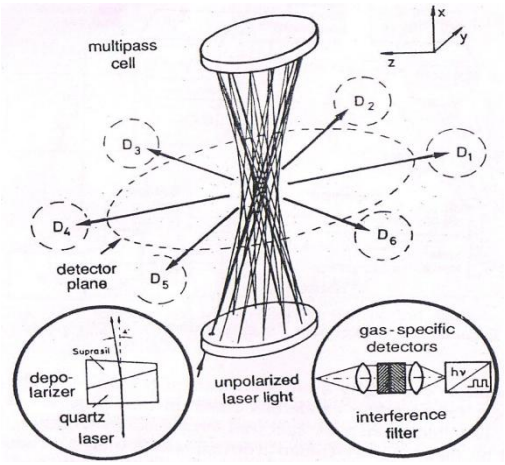


Figure 16.1; Multipass cell and spectrally selective detector arrangement for sensitive Raman spectroscopy and diagnostics of another molecular gases.

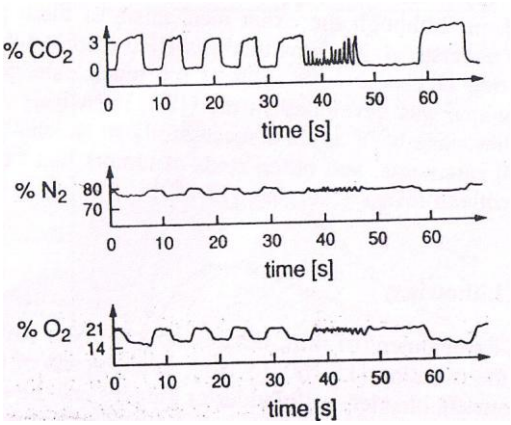


Fig.16.2; Co_2, N_2 and O_2 concentraction of respiratory gases for varying breath periods, measured in vivo with the arrangement of fig 16.1.

Instead of Raman spectroscopy, infrared absorption spectroscopy can be used in cases of infrared active transition, for example, for CO, CO_2, NO and CH_4. With cavity ring down spectroscopy a high sensitivity can be reached and spurious molecular concentrations resulting from fermentation processes in the stomach can still be detected.

16.3.2. Heterodyne Measurements of Ear Drums:

A large fraction of ear disease of elderly people is due to changes in the frequency response of the ear drum. While until now investigations of such changes had to rely on the subjective response of the patient, novel laser spectroscopic techniques allow objective studies of frequency dependent vibrational amplitudes of the ear drum and their local variation for different location on the drum with a laser Doppler vibrometer fig. 16.3. The experimental arrangement is illustrated in fig 16.4., the output of a diode laser is fed through an optical fiber to the ear drum. The light reflected by the drum is collected by a lens at the end of the fiber and is sent back through the fiber, where it is superimposed on a photodetector behind a beam splitter with part of the direct laser light. The ear is exposed to the sound waves of a loudspeaker with variable audio frequency f. the frequency ω of the light reflected by the vibrating ear drum is Doppler shifted. The amplitude A (f) of the illuminated area of the vibrating drum can be derived from the frequency spectrum of the heterodyne signal. In order to transfer the heterodyne spectrum in a region with less noise, the laser light is modulated at the frequency $\Omega \approx$ 40 MHz by an optoacoustic modulator producing sidebands at $\omega \pm \Omega$.

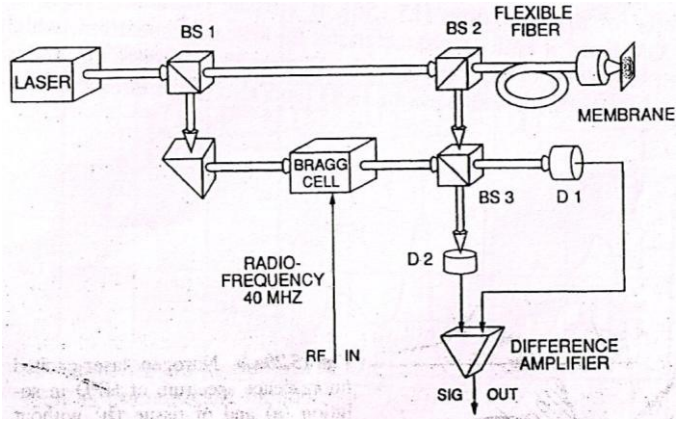


Figure 16.3; Principle of laser Doppler vibrameter.

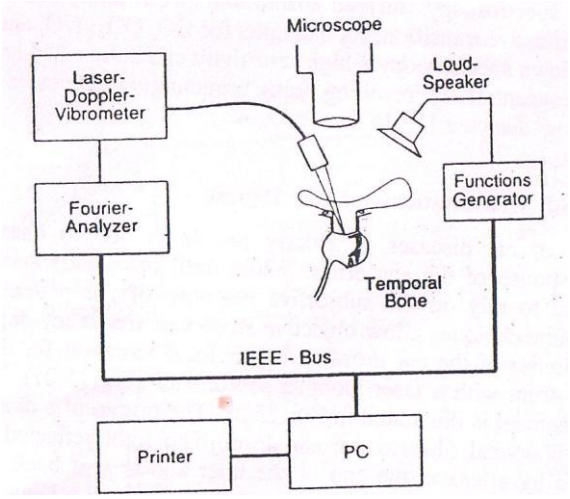


Figure 16.4; Heterodyne measure of frequency-dependent vibrations of the ear drum and their local vibrations.

16.3.3. Cancer Diagnostics and Therapy with the HPD Technique:

Recently, a method for diagnostics and treatment of cancer has been developed that is based on photoexcitation of the fluorescing substance hemato porphyrin derivative (HPD). A solution of this substance is injected to the veins and is distributed in the whole body after a few hours. While HPD is released by normal cells after 2-4 days, it is kept by cancer cells for a longer time. If a tissue containing HPD is irradiated by a UV laser, it emits a characteristic fluorescence spectrum, which can be used for a diagnostic of cancer cells. Fig 16.5 shows the emission spectrum of a tissue with and without HPD, and also the fluorescence of pure HPD in a liquid solution excited by a nitrogen laser at $\lambda = 337$nm. The experimental arrangement for detecting cancerous tissue in rats is exhibited in fig.16.6. The fluorescence is spectrally resolved by grating and spatially separated by three slightly folded mirrors, which image a cancer region and a region of normal cells onto different parts of the diode array of an optical multichannel analyzer.

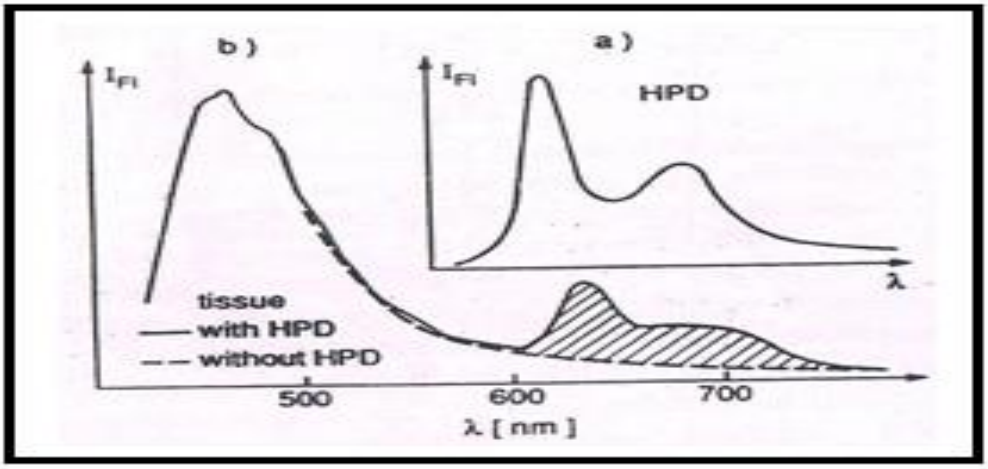
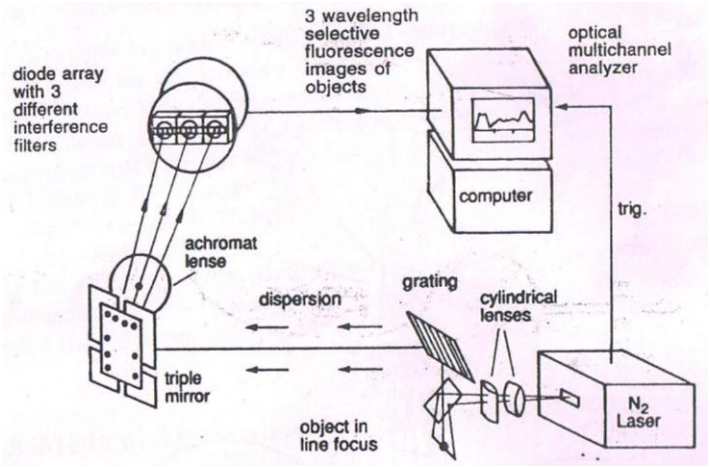


Fig 16.5 a,b; Nitrogen laser-excited fluorescence spectrum of HPD in solution (a) and of tissue (b) without HPD (dashed curve), and with HPD (solid line) two days after injection. The hatched area represents the additional absorption of HPD.



Fig;16.6; Experimental arrangement for cancer diagnostics of rat tissue.

A computer subtracts the fluorescence of the normal tissue from that of a cancerous tissue. Absorption of photons in the range 620 – 640 nm brings HPD into an excited state, which reacts with normal oxygen in the O_2 ($^3\Pi$) state and transfer it into the O2 (IΔ) state, which apparently reacts with the surrounding cells and destroys them. Although the exact mechanism of these processes is not yet completely understood, it seems that this HPD method allows a rather selective destruction of cancer cells without too much damage to the normal cells. The technique was developed in the USA, intensively applied in Japan , and has since been applied successfully to patients with esophageal cancer, cervical carcinoma, and other kinds of tumors that can be reached by optical fibers without invasive surgery.

16.3.4. Laser Lithotripsy:

Thanks to the development of thin, flexible optical fibers with a high damage threshold for the radiation, inner organs of the human body, such as the stomach, bladder, gallbladder or kidneys, can be selectively irradiated by laser radiation. A new technique for breaking kidney stones to pieces by irradiation with pulsed lasers (laser lithotripsy) has found

increasing interest because it has several advantages compared to the ultrasonic shockwave lithotripsy.

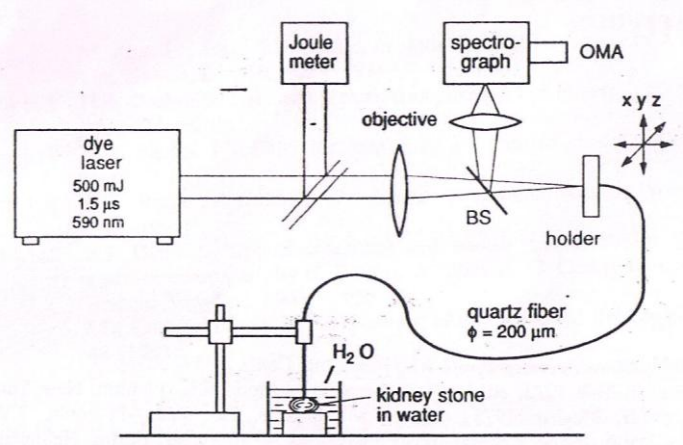


Fig.16.7; Experimental arrangement for the spectral analysis of kidney stone for the determination of stone composition

An optical fused quartz fiber is inserted through the urinary tract until it nearly touches the stone that is to be broke. This can be monitored by x ray diagnosis or by endoscopy through a fiber bundle that contains, besides the fiber for guiding the laser beam, other fibers for illumination, viewing and monitoring the laser-induced fluorescence (fig. 16.7).

If the pulse of a flashlamp- pumped dye laser is transported through the fiber and focused onto

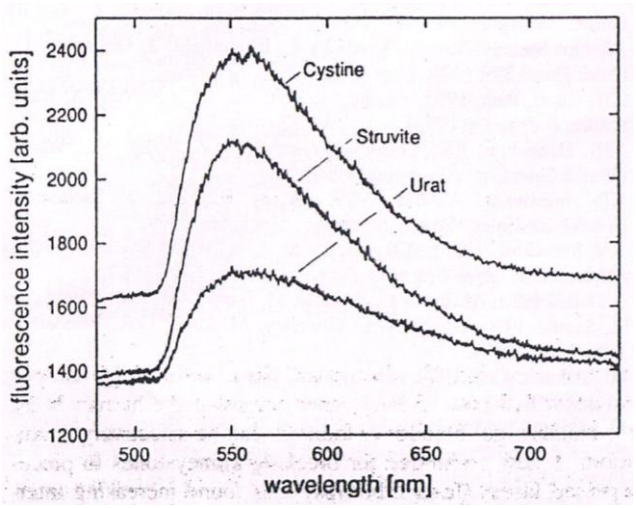


Fig.16.8; Fluorescence of three different kidney stone materials excited with a dye laser at λ=497 nm at low intensities to prevent plasma breakdown.

the kidney stone, the rapid evaporation of the stone material results in a shock wave in the surrounding liquid, which leads to destruction of the stone after several laser shots. The necessary laser power and the optimum wavelength depend on the chemical composition of the stone, which generally varies for different patients; It is therefore advantageous to know the stone composition before destruction in order to choose optimum laser conditions. This

information can be obtained by collecting the fluorescence of the evaporated stone material at law laser powers through an optical fiber. The fluorescence spectrum is monitored with an optical multichannel analyzer and a computer gives, within seconds, the wanted information about the stone composition.

First demonstrations of the capability of spectral analysis of kidney stones in vitro are illustrated in fig. 16.8 where the fluorescence spectra of different kidney stones that had been irradiated in water surrounding outside the body, and that were detected with the arrangement of fig. 16.6 are shown . Further information on laser lithotripsy and spectroscopic control of this technique can be found in.

Laser induced interstitial thermotherapy represents a minimally invasive therapy, where the cancerous tissue is irradiated by laser light guided through an optical fiber. Planning the operation anticipates the knowledge of the absorption and scattering properties of cancerous tissue compared to healthy tissue. Several optical and computational techniques have been developed that can

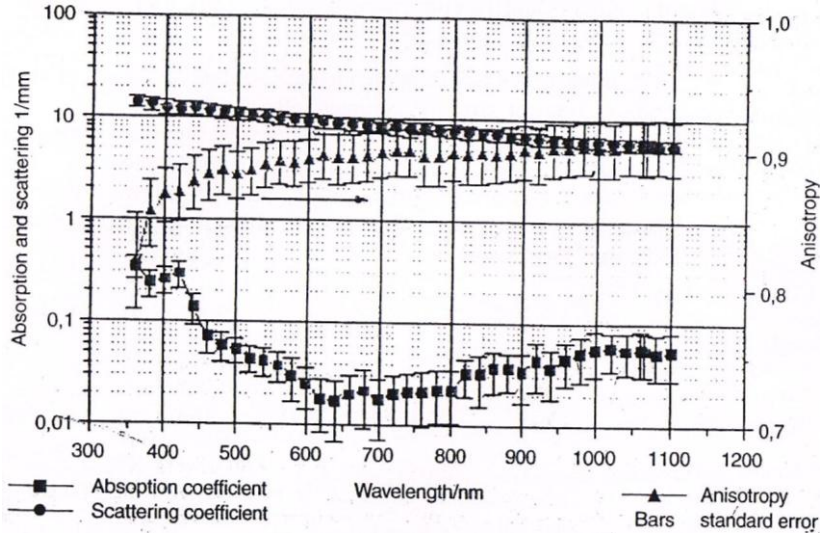


Figure 16.9; Optical properties of human gray matter determined in vitro in with an integrating-sphere setup and an inverse Monte Carlo technique.

Be used to localize the cancerous tissue and to optimize the optical radiation dose. Here the wavelength dependence of the absorption and scattering coefficients is determined in foregoing experiments. Fig 16.9 shows for illustration the spectral dependence of both coefficients and also the anisotropy of the scattering in human brain tissue determined in vitro.

16.3.5. Fetal Oxygen Monitoring:

Monitoring the oxygen concentration of a baby during longer birth processes is of crucial importance for the lasting health of the child. Until now the available equipment was not well adapted for clinical applications. Here a laser based technique, using light scattering measurements seems to be very successful. The laser light is transported to the skull of the baby through an optical fiber and the scattered light is collected by a second fiber, placed

some centimeters distant from the first. The collected light is then monitored as a function of the wavelength. Since the scattering cross section depends on the oxygen concentration, after calibration this method allows the determination of the wanted O_2 concentration.

16.4 Lasers in industrial Applications:

The precision properties of laser light have been of immense help in industry, particularly in testing the quality of optical components; lenses, prisms, etc. Accuracy in the measurement of the sizes of physical quantities is considerably increased. The length of a meter bar can now be measured by an automatic fringe counting method.

The ability of the laser beam to concentrate large power in a small volume is easily utilized for drilling of small holes and for the welding of small metal parts. Lasers are found to be vey effective in cutting different types of material. A CO_2 laser of 100 W continuous output can cut a cloth at a speed a 1m/s, this it can prepare cut pieces for about 50 suits in an hour, laser cutting technology is widely used in the fabrication of spacecraft. A CO_2 laser of 3kW continuous output cuts titanium sheets of 50 mm thickness at a velocity of 0.5 m/ minute.

Lasers have been used as light sources for telephoto pictures. Pulsed Q-switched lasers are suitable for technical motion picture photography. Ellis and Fourney obtained pictures of bubble formation at the rate of 200,000 frames per second with a Q-switched ruby laser. The spiky output from a normal ruby laser has been found to be useful in high-speed photography. The intensity of individual spikes is high enough for the light reflected from a moving object to be recorded on a photographic plate. The successive positions of a bullet travelling at a speed of 20,000 cm/sec have photographed using a ruby laser.

One obvious use of high power source of relatively narrow band radiation, such as free electron laser, is in industrial chemistry, to supply energy to specific reactions, for, example, one could use such a source to clean the exhaust gases from combustion by selectively decomposing noxious substances. Similarly one could purify the feedstocks for chemical processes by selective destruction of contaminants.

It has been observed that finger print- prints can be detected under a laser light where the normal method of obtaining fingerprints through dusting power is ineffective. It is likely that people carry some kind of fluorescent contaminant on hands, picked up from miniute traces of ink, paints, etc. if the blue light of an argon-ion laser is directed at suspected fingerprints. Later fingerprints emit a part of the beam energy as yellow-light fluorescence. The laser technique can also be used for detection and analysis of older finger prints on, say, documents, currency bille, cloth, etc. This is possible because finger prints contain ultraminute quantities of stable amino acids, which when treated with certain chemicals become fluorescent.

16.5 Applications of Lasers in Communication:

The large techniques commonly used for transmitting a large volume of messages over long distance are;

i. Coaxial-cable system; the cable consists of a copper tube about 3/8 inch in diameter with a single copper-wire conductor in the centre. The cables carry radio waves with frequencies from 500,000 to 20,000,000 cycles per second. Amplifying equipment is located every two to four miles along the cables.
ii. Microwave-radio relay; The relay towers are located some 20 to 30 mil apart. The system employs microwave radiation in the frequency band between 1 billion to 10 billion cycles per second.
iii. Wave-guide; A simple hollow tube two inches in diameter is used as a waveguide to transmit millimetre waves with frequencies between 30 billion to 90 billion cycles per second.
iv. Artificial Earth satellite; This broad band communication operates within the microwave radio band.

16.6 Lasers in Holography Applications:

Laser holograms were prepared for the first time by Leith and Upatnicks. Denisyuk using thick layers of photosensitive material recorded three dimensional holograms. The basic principle of holography can be explained in two steps; (i). recording of the hologram and (ii). reconstructing the image.

Construction of a hologram using laser; The entire arrangement is on vibration isolation table. The laser beam is split into two i). to illuminate the object, the beam falling on the object after scattering reaches the recording material. (ii). The other beam after expansion reaches the recording material.

At the recording plane interference of object beam and reference beam takes place. On developing and processing what we get is called “hologram” which is nothing but recorded interference, say “grating”. Since the fringe spacing of the interference pattern is less than microns, the photosensitive grains in the recording material must be much smaller in size to record it. This makes the film/plate slow in speed; hence slightly longer exposure (of the order of few seconds) is required. Since the earth is always having vibrations of the order of few microns, the recording table with its components vibrates while recording fine interference pattern. Unless we avoid the earth vibration we won’t get good recording. Hence vibration isolation table is required. This table is a heavy one floating on compressed air bed/pillars so that earth vibrations are arrested by this arrangement.

Reconstruction of a hologram using laser: when the reference beam is used for reconstruction, the hologram (the grating structure) diffracts the light and the diffracted light received is identical to the object wave received by the recording material at the time of recording. Hence it appears as if the object is really present. By moving the head the observer can get three dimensional effects. Since while recording the secondary waves from each and every point on the object reach the entire plate, each bit of the plat has full information about the object.

While recording if the object wave and reference wave are made to interfere from opposite directions, in the recording material Bragg plane fringes are created. On

development this hologram can be viewed under white light. Depending on the angle of reconstruction θ, the wavelength λ satisfying the Bragg condition ($2d\sin\theta = n\lambda$) is reconstructed, i.e. color of the image will change while you change the direction of viewing, by using a lens in between the object and the recording material. One can focus the object into a tiny spot (of the order of few microns) and store the image. Thus very high-density data can be stored in hologram. Also different positions of a single object can be stored on a single hologram by changing the angle of the reference beam alone while recording. While reconstruct if we change the direction of viewing, it will appear as if the object is in motion. This technique is called multiplexing.

16.7 Summary:

In this unit, with the concept of optical fibers, how the communication system is development and working in details. The medical and engineering application details in the last section.

16.8 Key words:

Optical fiber communication

Medical application

Industrial

Holography

16.9 Question for self study:

1. Explain optical fibers ? why this needed for high speed communication?
2. Explain optical fiber communication, with neat diagram?
3. List the application of lasers, explain the medical applications of laser with neat diagrams.
4. Write a note on holography and industrial application of lasers.

16.10 References:

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