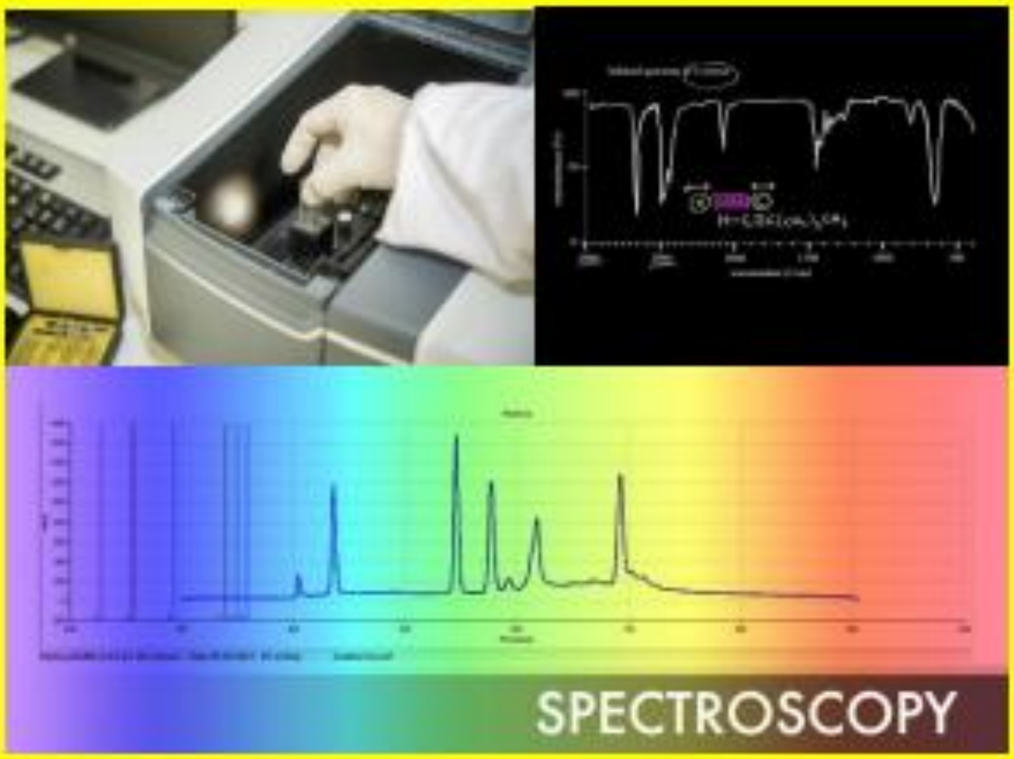
MSCPH507

M. Sc. IInd Semester

Spectroscopy



DEPARTMENT OF PHYSICS

SCHOOL OF SCIENCES

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Course Title and Code : Spectroscopy (MSCPH 507)
ISBN :
Copyright : Uttarakhand Open University
Edition : 2022
Published By : Uttarakhand Open University, Haldwani, Nainital- 263139
Printed By :

MSCPH507

Spectroscopy

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Course code: MSCPH507
Credit: 3

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UNIT 1

FINE STRUCTURE OF HYDROGEN AND HELIUM

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1.1 Introduction

The conception that matter is composed of small indivisible particles is redundant now. However, it took lot of time and rigorous efforts to come up with modern day experiments.

In late nineteenth century, most of the scientists were convinced that the matter is made up of atoms. In 1898, British scientist J.J. Thomson's suggested plum pudding model which stated that atoms are like positively charged solid spheres of matter and electron is embedded on it. It also stated that electrons are negatively charged. Lendard in 1903, observed that the cathode rays passes mostly undeviated through materials of small thickness. He proposed that the atoms are composed of positive tiny particles and electrons. However, these models were not consistent with each other. This was solved by Ernest Rutherford from 1906 to 1911. He performed a series of experiments in alpha particle scattering.

He bombarded the target (thin gold foil) with alpha particles and carefully studied their deflection patterns. He observed that most of the alpha particles passed undeviated/ small deviation through the gold foil. However, some of them showed large deflections and a very few completely rebounded back. Alpha particles completely reflect because it might have encountered very heavy mass on its path. However, most of them passed un-deflected. This was because the heavy mass occupied very less space and atom had lot of empty space in it.

After analysing quantitatively, he also suggested that the heavy mass/particle due to which the alpha particle showed complete or large deflections was positively charged and almost all the mass of atom was concentrated in it. He also estimated the size of the particle to be ~ 10^{-15} m. On the basis of these observations, he suggested a nuclear model. In accordance with this model, an atom contains positively charged particle – nucleus, placed at the center of the atom. Almost all the mass of the atom is concentrated at the nucleus of the atom. Outside the nucleus, electrons with some separation move around it. The space between nucleus and the electrons in an atom is empty and determines the size of the atom.

The amount of negative and positive charge is equal, thus explaining the charge neutrality of an atom. He also suggested that electrons are constantly in motion because the electrons at rest would experience coulombic attraction and fall into nucleus. However, the Rutherford couldn't explain much about electron's motion. It couldn't explain the absorption and emission spectra obtained for hydrogen and hydrogen like atoms.

Niel Bohr proposed an atomic model in 1913 which could explain the hydrogen spectral lines. He suggested that electrons would revolve around the nucleus in circular orbits under the coulombic attraction between positively changed nucleus and negatively charged electrons. His model is in accordance with classical laws of mechanics and as per classical laws, the electron orbit around the nucleus in fixed orbit. These electrons revolve with orbital angular momentum, $\vec{L}$ having a magnitude of $\frac{nh}{2\pi}$, where n is the orbit number 1, 2, ….. and h is the Planck's constant. This introduced the concept of quantisation. He also postulated that the electrons didn't radiate electromagnetically in the fixed allowed orbits, inspite of being in acceleration motion. This showed that the electrons moved in stationery orbits without falling into nucleus. He further stated that the electrons moving in an orbit having energy E_i when jumps to lower orbit having energy E_f emits. Electromagnetic radiation with frequency ν as $\nu = \frac{E_{f-E_i}}{h}$ $or\ \Delta E = h\nu$. Further, electron could also absorb energy quanta of suitable frequency and hence jump to higher orbit. This explained the observed absorption and emissions spectra in hydrogen as well as atoms with higher atomic number. The observed line spectra for various atoms could be now explained with the help of Bohr theory. However, the Bohr's theory couldn't explain the 'fine structure' of hydrogen atom. When the line structure was being observed under high resolution it showed several components of one spectral line with close energy. Sommerfield in 1916 tried to explain the existence of these components by considering the Bohr's circular orbits as elliptical. He evaluated total energy of the electron for a particular orbit. However, the introduction of elliptical orbit didn't add any new energy levels and hence failed to explain 'Fine Structure'. Therefore, he added relativistic corrections. This could explain the 'Fine Structure' to an extent.

The discrepancies were further removed by considering the Dirac theory which accounted the spin-orbit coupling effect and quantum – mechanical relativistic corrections. The fine structure of hydrogen atom shall be discussed later in this unit. To understand the quantum mechanical approach, the Schrödinger's treatment to hydrogen atom should be understood.

1.2 Objectives

After studying this unit, the learners should be able to:

- Explain and apply Schrödinger's Time-Independent Wave Equation
- Understand and describe the fine Structure of Hydrogen
- Apply Pauli's Exclusion principle and exchange symmetry
- State Hund's Rule
- Understand and explain the Helium Atom and it's Spectrum

1.3 Schrödinger's Time-Independent Wave Equation

With the development of de-Broglie idea of matter waves, Schröedinger presented his wave equation in 1926. This equation is known to be the fundamental equations in quantum mechanics as it represents a differential form of the de-Broglie waves associated with moving particles, similarly what Newton's second law of motion was described in classical mechanics for bulky objects.

A mathematical function ψ was introduced by Schrödinger. It is a complex function of variable space (the three axes) and time coordinates, associated with a moving particle. The mathematical representation of wave function ψ can be written as:

$$\bar{\psi} = \bar{\psi}(x, y, z, t)$$

where $\bar{\psi}$ is called the wave function of the moving particle, being the characteristic of the associated de-Broglie wave. It is postulated that $\bar{\psi}$ has the form of a solution of the classical wave equation.

The differential equation that represents the 3-Dimensional wave motion is:

$$\frac{\partial^2\bar{\psi}}{\partial x^2} + \frac{\partial^2\bar{\psi}}{\partial y^2} + \frac{\partial^2\bar{\psi}}{\partial z^2} = \frac{1}{v^2}\frac{\partial^2\bar{\psi}}{\partial t^2} \qquad \ldots(1)$$

where v is known as the wave velocity.

Now, the wavelength associated with a particle of mass 'm' moving with velocity 'v' is given by:

$$\lambda = \frac{h}{mv}$$

Using Einstein's postulate E = hν′ relating the frequency ν′ of the de-Broglie waves with the total energy E of the particle, we have

$$\therefore \frac{1}{v^2} = \frac{1}{\nu'^2\lambda^2} = \frac{m^2v^2}{E^2}$$

Making this replacement in equation (1),

$$\frac{\partial^2\bar{\psi}}{\partial x^2} + \frac{\partial^2\bar{\psi}}{\partial y^2} + \frac{\partial^2\bar{\psi}}{\partial z^2} = \frac{m^2v^2}{E^2}\frac{\partial^2\bar{\psi}}{\partial t^2}$$

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\bar{\psi} = \frac{m^2v^2}{E^2}\frac{\partial^2\bar{\psi}}{\partial t^2} \qquad \ldots(2)$$

The result of the above equation is of the formula $\bar{\psi} = \psi e^{-2\pi iEt/h}$ …(3)

Where ψ is the wave function of only space coordinates (here independent of time), i.e.

$$\bar{\psi} = \psi(x, y, z)$$

On differentiating the equation (3) w.r.t time *t*, we get

$$\frac{\partial^2\psi}{\partial t^2} = \psi e^{-2\pi iEt/h}\left(-\frac{2\pi iE}{h}\right)^2$$

$$= -\frac{4\pi^2E^2}{h^2}\psi e^{-2\pi iEt/h}$$

By substituting for $\bar{\psi}$ and $\frac{\partial^2\psi}{\partial t^2}$ in equation (2), we get

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\bar{\psi} = -\frac{4\pi^2 m^2 v^2}{h^2}\bar{\psi} \qquad \ldots(4)$$

Considering this case for particle having non-relativistic motion, the particle's kinetic energy *K=1/2mv*^{2}. Thus, if *V* is the potential energy of the particle, then we can write,

$$\frac{1}{2}mv^2 = K = E - V$$

Or
$$m^2v^2 = 2m(E - V)$$

Making this substitution in equation (iv), we get

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\bar{\psi} = -\frac{8\pi^2 m(E-V)}{h^2}\bar{\psi}$$

Let us use the mathematical symbol called 'Laplacian operator'

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

Above equation is known as '*Schrödinger's time-independent wave equation*' for a particle with its time-independent 'eigen function' ψ as its solution.

Since, you must be aware of the properties of eigen function (i.e. it must be finite everywhere, single-valued, continuous and should have continuous first derivative everywhere) during your graduation, let us now concentrate on the quantum mechanical interpretation for one electron atom (e.g. *H-atom*) being the simplest bounded system having a positively charged nucleus and negatively charged electron (-*e*), moving under Columbian attractive forces.

Consider one-electron of an atom having mass 'm' and the nucleus of mass 'M' move about at the centre of mass which is assumed to be fixed. We may consider substituting this actual atom by an equivalent model of atom in which the nucleus is considered to be infinitely massive and the electron has *reduced mass* 'μ' given by

$$\mu = \frac{Mm}{(M + m)}$$

The electron with reduced-mass moves about the infinitely massive (hence, also considered to be stationary) nucleus with the equivalent electron-nucleus separation as in the actual atom.

We consider an electron of reduced mass 'μ' moving under the three-dimensional Columbian potential defined as a function of (x, y, and z) such as:

$$V = V(x, y, z) = -\frac{Ze^2}{4\pi\epsilon_o\sqrt{x^2 + y^2 + z^2}}$$

where *x, y, z* are the rectangular coordinates of the electron relative to the nucleus, which is fixed and taken as the origin. The term '*radius vector*' $r = \sqrt{x^2 + y^2 + z^2}$ is the electron-nucleus separation.

You must be well aware till now about the Schröedinger equation as discussed previously.

In Cartesian coordinates, we have

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2\mu}{h^2}(E - V)\psi = 0$$

Since this equation involves three coordinates of V and hence, three equations must be required, it is always easy to use spherical polar coordinates viz. r, θ, φ (as shown in Fig.1)

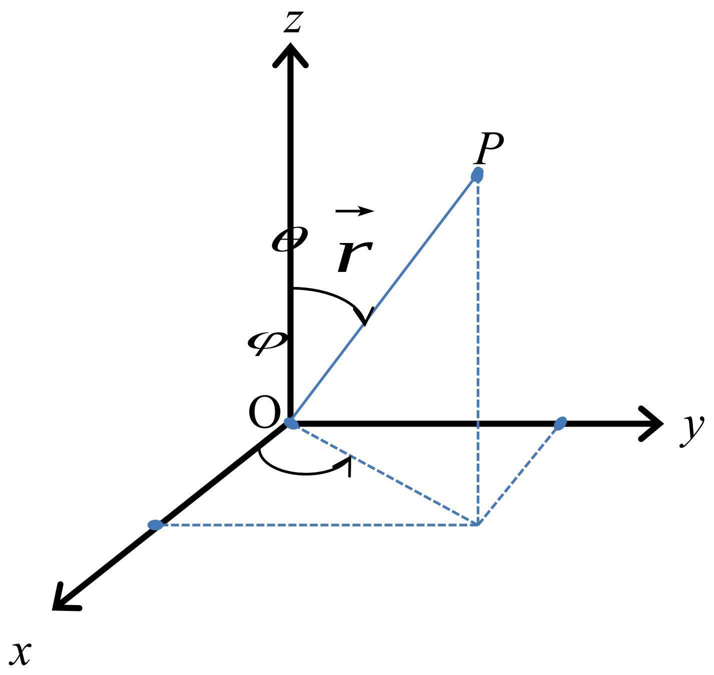

Fig. 1 The correlation between Cartesian coordinates *(x, y, z)* and Spherical polar coordinates *(r, θ, φ)* for a point P

The relation between Cartesian coordinates *(x, y, z)* and the spherical polar coordinates *(r, θ, φ)* of point *P* are:

$$x = r.sin\theta.cos\varphi,\ y = r.sin\theta.sin\varphi \text{ and } z = r.cos\theta$$

And polar angle $\theta = cos^{-1}\frac{z}{\sqrt{x^2+y^2+z^2}}$ and azimuthal angle $\varphi = tan^{-1}\frac{y}{x}$

In spherical polar coordinates, the Schröedinger equation comes out to be

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{8\pi^2\mu}{h^2}(E-V)\psi=0 \quad ...(5)$$

The potential energy V(r) can also be expressed as $V(r)=-\frac{Ze^2}{4\pi\epsilon_o r}$ ...(6)

Using the method of separation of variable, we first separate the radial component *r* and angular terms (θ, φ) assuming that

$$\psi(r,\theta,\varphi)=R(r).Y(\theta,\varphi)$$

where *R(r)* is the called as radial function depending upon the radius r alone, and Y(θ,φ) is known as angular function depending upon *θ* and *φ*. Thus, equation (1) can be rewritten as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial R}{\partial r}\right)Y+\frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right)R+\frac{1}{r^2 sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}R+\frac{8\pi^2\mu}{h^2}(E-V(r))RY=0$$

Multiplying the entire equation by $\frac{r^2}{RY}$ and rearranging, we get

$$\frac{1}{R^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)Y+\frac{8\pi^2\mu r^2}{h^2}(E-V(r))=-\frac{1}{Y}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]$$

The left side of this equation depends on the variable r, while the right side depends upon the other variables θ and φ. Hence, this equation can be correct only if both sides of it are equal to the same constant. Let this constant be *l*(*l*+1). Thus, we get a radial equation.

$$\frac{1}{R^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)Y+\frac{8\pi^2\mu r^2}{h^2}[E-V(r)]=l(l+1) \quad ...(7)$$

And angular equation

$$-\frac{1}{Y}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]=l(l+1)$$

The last equation cab be further separated by substituting

$$\psi(\theta,\varphi)=\Theta(\theta).\Phi(\varphi)$$

This equation gives

$$-\frac{1}{\Theta}sin\theta\frac{d}{d\theta}\left(sin\theta\frac{d\Theta}{d\theta}\right)+l(l+1)sin^2\theta=m_l^2 \quad ...(8)$$

$$and-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=m_l^2 \quad ...(9)$$

Equation (6), (7), and (9) can be written as

$$\frac{d^2\Phi}{d\phi^2}+m_l^2\Phi=0 \quad ...(10)$$

$$\frac{1}{sin\theta}\frac{d}{d\theta}\left(sin\theta\frac{d\Theta}{d\theta}\right)+\left[l(l+1)-\frac{m_l^2}{sin^2\theta}\right]\Theta=0 \qquad \ldots(11)$$

$$and\ \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{8\pi^2\mu}{h^2}\{E-V(r)\}-\frac{l(l+1)}{r^2}\right]R=0 \qquad \ldots(12)$$

Thus, we have fragmented the Schröedinger equation of Hydrogen atom into three ordinary differential equations, each having a single variable *r, θ, φ*, respectively. After finding the adequate solutions of these equations, we find the following quantum numbers:

Solution of the equations: The appearance of quantum numbers is explained ahead as:

1. The solution of Φ(φ) equation (10) is $\Phi_{ml}(\varphi)=Ae^{im_l\phi}$ …(13)
   where *A* is the known as the constant of integration. In order that it is an acceptable solution, the wave function Φ_{ml}must be a single-valued function of position, that is, it must have a single value at a given point in space. It is evident that the azimuth angles φ and φ+2π are actually the same angle. Hence it must by true that

$$\Phi_{ml}(\varphi)=\ \Phi_{ml}(\varphi+2\pi)$$

or $$Ae^{im_l\phi}\ =Ae^{im_l(\phi+2\pi)}$$

or $$1=\ e^{im_l(2\pi)}$$

or $$1=\cos(m_l 2\pi)+i\sin(m_l 2\pi)$$

This can only happen when m_l is 0 or positive or negative integer, i.e.

$$m_l=0,\pm1,\pm2,\pm3,\ldots$$

The constant m_l is a quantum number of the atom.

2. The solution of Θ(θ) equation (11) is known to be

$$\Theta_{l.m_l}(\theta)=N_{l.m_l}P_l^{|m_l|}(cos\theta) \qquad \ldots(14)$$

where $N_{l.m_l}$ is a constant and $P_l^{|m_l|}$ is '*Associated Legendre Polynomial*' which has different forms or different values of *l* and $|m_l|$, that is

$$l=|m_l|,\ |m_l|+1,\ |m_l|+2,\ |m_l|+3,\ldots$$

This requirement can be expressed as a condition on m_l in the following form:

$$m_l=0,\pm1,\pm2,\pm3,\ldots,\pm l$$

The constant *l* is another quantum number.

3. For solving equation (12) we must specify V(r). In the present case

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_o r}$$

Then, the solution of the equation is known to be

$$R_{n,l}(r) = N_{n,l}e^{-Zr/na_o}\left(\frac{2Zr}{na_o}\right)^l L_{n+1}^{2l+1}\left(\frac{2Zr}{na_o}\right) \qquad \ldots(15)$$

Where, $N_{n,l}$ is a constant and L_{n+1}^{2l+1} is 'Associated Laguerre Polynomial' which has different forms for different values of *n* and *l*. The parameter a_o is $= \frac{h^2\varepsilon_o}{\pi\mu e^2}$, which, in the old quantum theory, is the known as the smallest Bohr orbit of H-atom.

The solution to above equation is acceptable and it remains finite if the constant E in equation (12) is positive, or has one of the negative values of E_n (which corresponds to bound states), given by

$$E_n = -\frac{\mu Z^2 e^4}{8\varepsilon_o^2 h^2}\left(\frac{1}{n^2}\right)$$

where *n* is an integer, which must be equal to or greater than *l+1*. That is,

n = *l*+1, *l*+2, *l*+3, …

This requirement may be expressed as a condition on l in the form

l = 0, 1, 2, 3, … (n-1)

Here, the constant *n* is also a quantum number

The total eigen functions for one-electron atom can be written as:

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)\,\Theta_{l,m_l}(\theta)\,\Phi_{m_l}(\phi)$$

where R, Θ, Φ are given by equations (xiv), (xv) and (xvi). The constants $N_{n,l}$, $N_{l.m_l}$, and *A* elaborated in these equations are so adjusted that each equation is normalized. The exact normalized eigen function for ground state (corresponding for *n* = 1, *l* = 0, m_l = 0) of one electron atom is $\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/a_o}$

Physical interpretation of various quantum numbers: The three quantum numbers originated from the solutions of Schroedinger equation are:

n = 1, 2, 3,…

l = 0, 1, 2, 3,… (n-1),

$$m_l = 0, \pm1, \pm2, \pm3, \ldots, \pm l$$

These quantum numbers can be explained as:

Consider the case of one electron atom; we have the total energy of bound states atom obtained from Schröedinger Equation$E_n = -\frac{\mu Z^2 e^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n^2}\right)$. Since, the energy eigen values depends only on quantum number *n*, they were in excellent agreement experimental values based on with old quantum theory of Bohr model. Hence, *n* is said to be known as "Total" or "*Principal Quantum Number*".

To understand the value of *l*, we have to consider the radial wave equation based on equation (12): $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{8\pi^2\mu}{h^2}\{E - V(r)\} - \frac{l(l+1)}{r^2}\right]R = 0$

Here, the total energy of atom comprises of two components, viz. kinetic energy K and potential energy V (for its electrons). Further, kinetic energy is subdivided into radial components due to motion of electron round the nucleus and orbital component due to the nucleus itself. Therefore, we have

$$E = K_{rad} + K_{orb} + V(r)$$

Using this substitution in the radial equation, we have

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{8\pi^2\mu}{h^2}\{K_{rad} + K_{orb}\} - \frac{l(l+1)}{r^2}\right]R = 0$$

Since the radial component is basically originated due to electron motion, hence it is free from orbital counterpart. And this is only possible when the last two terms are equal to each other i.e.

$$K_{orb} = \frac{h^2}{8\pi^2\mu}\frac{l(l+1)}{r^2}$$

If angular momentum is denoted by $\underset{L}{\rightarrow}$, then we know that $L = \mu v r$ and therefore,

$$K_{orb} = \frac{1}{2}\mu v^2 = \frac{L^2}{2\mu r^2}$$

$$Or\ \frac{L^2}{2\mu r^2} = \frac{h^2}{8\pi^2\mu}\frac{l(l+1)}{r^2}$$

Or $$\mathrm{L}= \sqrt{(l(l+1)}\,\frac{h}{2\pi}$$

Since *l* varies from *0, 1, 2, 3,…(n-1)*, this proves that the electron can have discrete values of angular momentum. Finally, the total energy E is also quantized like the orbital angular momentum and it remains conserved. And this is just demonstrated by quantization of *l*. Hence, *l* is termed as the 'orbital' quantum number. The expression for angular momentum was obtained through the theory of Born-Sommerfield, where *k* was replaced by $\sqrt{(l(l+1)}$. The method for denoting the state is writing the total angular quantum number along with the various angular momentum states as letters {like: s (*l*=0), p(*l*=1), d(*l*=2), f(*l*=3), …}. For example, a state with n = 2 with l = 0 is shown as *2s* state. Similarly, another state with n = 3 and *l*=1 is written as *3p*.

The analysis of m_l originates when the atom is placed in an external magnetic field. You can imagine that when an electron is revolving round the nucleus, it behaves like a small loop of current having magnetic dipole when placed in an external magnetic field. Its potential energy depends upon its magnetic moment and its orientation with respect to the field. But here, the magnitude and direction of the magnetic moment depends upon the magnitude and direction of angular momentum $\vec{\mathrm{L}}$ of the electron. This also determines the magnetic potential energy. Since the direction of L is also quantized with respect to external magnetic field. If the field is along the z-axis, the component of $\vec{\mathrm{L}}$ can be defined as

$$L_z = m_l \frac{h}{2\pi}, \text{ where } \quad m_l = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l.$$

Since we can observe that m_l describes the quantization of $\vec{\mathrm{L}}$ in magnetic field (known as space quantization), and finally, the discretization of magnetic energy of the electron. Therefore, m_l is known as magnetic quantum number.

Therefore, *n*, *l*, and m_l are the three quantum numbers used to specify each of the eigen functions of single electron atom here n specifies the total energy (the eigen value), *l* specifies the angular momentum and m_l determines the z-component of the angular momentum of the electron. For a given value of n, there are different values of *l* and for every different value of *l* we have several values of m_l. Hence, several different eigen functions resembles to exactly the same eigenvalue E_n. And this property of eigen functions is said to be 'degenerate' state.

In accordance with old quantum theory the quantum-mechanical interpretations of energy states of single electron system matches well with each other. The differences that are crucial to understand is that in quantum mechanics, the electron should not be considered as moving around the nucleus in definite orbits. Here it is necessary to consider the relative probabilities of finding the electron in volume elements at various locations rather than is specific orbits. For this consideration, we relook the wave-function of single-electron system i.e.

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)\ \Theta_{l,m_l}(\theta)\ \Phi_{m_l}(\phi)$$

Where, the symbols have their usual meaning as specified above in equations (9), (10) and (11) respectively. We must know till now that the electron probability density, given by $|\psi|^2$ was mathematically formulated as:

$$|\psi|^2 = |R|^2.\ |\Theta|^2.\ |\Phi|^2, \text{ where } |\psi|^2 = \psi^*\psi$$

We observe that $|\Phi|^2 = \Phi^*\Phi$ will result in A^2 and since A is a constant; this shows that ψ is independent of Φ and does not directly determine probability density ($|\psi|^2$). This also dispels that the dependent factors were $|R|^2.\ |\Theta|^2$. From the relation of radial probability density for finding the electron between r and r+dr is given by $|R|^2(4\pi r^2 dr)$. The value of probability density P(r) is maxima at a_o and $4a_o$. These values of radii a_o and $4a_o$ corresponds to n=1 and n=2 Bohr's orbit where the electrons is most likely to be found. In Bohr's orbit at $4a_o$, the average distance of electron from the nucleus is given by

$$\bar{r} = \int_0^\infty r\,P(r)dr = \frac{n^2 a_o}{Z}\left[1 + \frac{1}{2}\left\{1 - \frac{l(l+1)}{n^2}\right\}\right]$$

where, a_o is the smallest Bohr orbit. This is same as for the Bohr-Sommerfeld elliptical orbit.

Solved Example No 1:

Question: Find the parity of N atom in ground state.

Solution- It is known that the parity is even if the sum of l values (Σl) for all the electron is even; and it carries an odd parity if Σl is odd.

The electronic configuration of N atom in ground state is given as:

$$1s^2\ 2s^2\ 2p^3$$

The value of l = 0 for s – electron and l = 1 for p – electron.

Therefore, Σl = 3

Hence, the parity is odd.

1.4 Fine Structure of Hydrogen

For hydrogen atom, when an electron transmits from one energy level to another, spectral lines are observed in an emission spectrum. The wavelengths of these lines are in accordance with Rydberg's formula. These are collectively known as Line spectra of hydrogen atom. When these spectral lines split due to spin - orbit coupling effect and quantum mechanical relativistic corrections, it gives rise to fine structure

1.4.1 Effect due to electron's spin and orbital motion

The interaction due to internal magnetic field of an atom and electron's spin magnetic dipole moment is partly responsible for the fine-structure of one electron atoms (excited state). It is well understood that the internal magnetic field of an atom arises due to the electron's orbital motion. Therefore, this type of interaction is called as spin-orbit interaction.

Let us consider electric field $\vec{E}$, defined as a gradient of potential function V(r), where *r* represents the distance between nucleus and electron of an atom.

$$\vec{E} = grad\,V(r)$$

$$= \frac{d\vec{V}(r)\hat{r}}{dr} \qquad \ldots(16)$$

where $\hat{r}$ is the unit vector in which electric field $\vec{E}$ is directed. The magnetic field caused due to the orbital motion of the associated electron moving with velocity v in electric field $\vec{E}$ is:

$$\vec{B} = \frac{1}{c^2}\left(\vec{E} \times \vec{v}\right)$$

$$= \frac{1}{c^2 r}\frac{dV(r)}{dr}(\vec{r} \times \vec{v}) \left\{\because \hat{r} = \frac{\vec{r}}{r}\ from\ (1)\right\} \qquad \ldots(17)$$

The orbital motion of an electron causes angular momentum $\vec{L}$, where $\vec{L}$ is further defined as $\vec{L} = m\vec{r} \times \vec{v}$, thus equation (17) may be written as

$$\vec{B} = \frac{1}{mc^2}\frac{1}{r}\frac{dV(r)\vec{L}}{dr} \qquad \ldots(18)$$

The magnetic field $\vec{B}$ orients the electron's spin magnetic moment μ_s and hence the magnetic potential energy of orientation, $\Delta E_{l,s}$. The expression of $\Delta E_{l,s}$is given as

$$\Delta E_{l,s} = -\mu_s.\vec{B} \qquad \ldots(19)$$

But spin magnetic moment is $* \ \mu_s = -g_s\left(\frac{e}{2m}\right)\vec{S}$, where $g_s = 2$ (for electrons) and $\vec{S}$ is spin angular momentum.

Thus, equation (19) can be written as: $\Delta E_{l,s} = -\frac{e}{m}\vec{S}.\vec{B}$ …(20)

Substituting the value of $\vec{B}$ from equation (18) into (20), we get

$$\Delta E_{l,s} = -\frac{e}{m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{S}.\vec{L} \qquad \ldots(21)$$

In accordance with 'Thomson precession' when nucleus is considered to be in rest, $\Delta E_{l,s}$is reduced by a factor of 2, i.e.

$$\Delta E_{l,s} = -\frac{e}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{S}.\vec{L} \qquad \ldots(22)$$

Let us now express the equation (22) in terms of *j*, *l* and *s* quantum numbers.

We know that $\vec{J} = \vec{L} + \vec{S}$ …(23)

Taking self dot products of equation (23), we get

$$\vec{J}.\vec{J} = \left(\vec{L} + \vec{S}\right).\left(\vec{L} + \vec{S}\right)$$

$$= \left(\vec{L}.\vec{L} + \vec{L}.\vec{S} + \vec{S}.\vec{L} + \vec{S}.\vec{S}\right)$$

$$= \left(\vec{L}.\vec{L} + 2\,\vec{L}.\vec{S} + \vec{S}.\vec{S}\right) \qquad \left(\because \vec{L}.\vec{S} = \vec{S}.\vec{L}\right)$$

$$\therefore \vec{S}.\vec{L} = \frac{1}{2}[\vec{J}.\vec{J} - \vec{L}.\vec{L} - \vec{S}.\vec{S}]$$

$$= \frac{1}{2}[J^2 - L^2 - S^2]$$

$$\vec{S}.\vec{L} = \frac{1}{2}[j(j+1) - l(l+1) - s(s+1)]\frac{h^2}{4\pi^2} \qquad \ldots(24)$$

$$\therefore \Delta E_{l,s} = -\frac{eh^2}{16\pi^2m^2c^2}[j(j+1) - l(l+1) - s(s+1)]\frac{1}{r}\frac{dV(r)}{dr} \qquad \text{\{from eq.22\} (25)}$$

As electron is in motion the terms $\frac{1}{r}\frac{dV(r)}{dr}$ is not fixed. Therefore, an average value during unperturbed motion must be considered. So,

$$\Delta E_{l,s} = -\overbrace{\frac{eh^2}{16\pi^2m^2c^2}}^{\frac{1dV(r)}{r\ dr}}[j(j+1) - l(l+1) - s(s+1)]\frac{1}{r}\frac{dV(r)}{dr} \qquad \ldots(26)$$

To evaluate the average value of $\frac{1}{r}\frac{dV(r)}{dr}$, the radial probability density of the required state and potential function V(r) is considered. The potential function V(r) for one-element atoms in Colombian field is:

$$V(r) = -\frac{1}{4\pi\epsilon_o}\frac{Ze}{r}$$

$$\frac{dV(r)}{dr} = -\frac{1}{4\pi\epsilon_o}\frac{Ze}{r^2} \qquad \ldots(27)$$

Substituting the value of $\frac{dV(r)}{dr}$ from (27) into (26), we get:

$$\Delta E_{l,s} = -\frac{Ze^2h^2}{4\pi\epsilon_o(16\pi^2m^2c^2)}[j(j+1) - l(l+1) - s(s+1)]\frac{T}{r^3} \qquad \ldots.(28)$$

Considering radial density function of H-Atom, the average value of $1/r^3$ can be evaluated as:

$$\frac{T}{r^3} = \frac{Z^3}{a_0^3n^3l(l+\frac{1}{2})(l+1)}, \text{ hen } l > 0 \qquad \ldots(29)\text{a}$$

where $a_0 = \left(\frac{4\pi\epsilon_oh^2}{4\pi^2mc^2}\right)$ …(29)b

a_0 is the radius of the smallest Bohr orbit for hydrogen atom. Substituting the value of $\frac{T}{r^3}$ from equation (29)a in (28), we get

$$\Delta E_{l,s} = -\frac{Ze^2h^2}{4\pi\epsilon_o(16\pi^2m^2c^2)}.\frac{Z^3}{a_0^3n^3l(l+\frac{1}{2})(l+1)}[j(j+1) - l(l+1) - s(s+1)] \qquad \ldots(30)$$

The above equation is simplified to the following equation:

$$\Delta E_{l,s} = \frac{R_\infty\alpha^2Z^4hc}{2n^3l(l+\frac{1}{2})(l+1)}[j(j+1) - l(l+1) - s(s+1)] \qquad \ldots(31)$$

Where, $R_\infty = \frac{me^4}{8\epsilon_0 h^3 c}$ (Rydberg constant for infinitely heavy nucleus) and $\alpha = \frac{e^2}{2\epsilon_0 hc}$ (Fine structure constant).

Due to spin-orbit coupling effect, term shift $\Delta T_{l,s}$ arises

$$\Delta T_{l,s} = -\frac{\Delta E_{l,s}}{hc}$$

$$= \frac{R_\infty \alpha^2 Z^4}{2n^3 l(l+\frac{1}{2})(l+1)}[j(j+1) - l(l+1) - s(s+1)] \qquad \ldots(32)$$

For one electron atom like hydrogen s=1/2 and $j = l \pm s = l \pm {}^1\!/_2$

Solving the term $[j(j+1) - l(l+1) - s(s+1)]$ is l and –(l+1) for j $= l + {}^1\!/_2$ and j $= l - {}^1\!/_2$, respectively .

The term shift corresponding to j $= l + {}^1\!/_2$ is

$$\Delta T'_{l,s} = -\frac{R_\infty \alpha^2 Z^4}{2n^3 l(l+\frac{1}{2})(l+1)} l \qquad \ldots(33)$$

The term shift corresponding to j $= l + {}^1\!/_2$ is

$$\Delta T''_{l,s} = \frac{R_\infty \alpha^2 Z^4}{2n^3 l\left(l+\frac{1}{2}\right)(l+1)}(l+1) \qquad \ldots(34)$$

Therefore, the coupling effect due to electron's spin and orbital motion causes splitting of one energy level into two levels with different *j*'s for a given *l*.

The difference in the energy levels is obtained by subtracting (33) from (34).

$$\Delta T_{l,s} = \Delta T'_{l,s} - \Delta T''_{l,s}$$

$$= \frac{R_\infty \alpha^2 Z^4}{2n^3 l\left(l+\frac{1}{2}\right)(l+1)}(2l+1)$$

$$= \frac{R_\infty \alpha^2 Z^4}{n^3 l(l+1)} \qquad \ldots(35)$$

Putting the values of $R_\infty = 1.097\times10^7 m^{-1}$ and α=1/137 for Hydrogen atom, due to spin-orbit interaction.

$$\Delta T' = 584\frac{Z^4}{n^3 l(l+1)} m^{-1} = 5.84\frac{Z^4}{n^3 l(l+1)} cm^{-1} \qquad \ldots(36)$$

From equation no. 36, it is clear that the splitting due to spin-orbit coupling increases with increasing atomic number (Z) and decreases with higher *n* and *l*.

1.4.2 Effect due to relativistic corrections

Apart from spin-orbit interactions, the relativistic effect also contributes in the splitting of energy levels of hydrogen atom. In order to evaluate the shift due to relativistic corrections, relativistic Hamiltonian function H for an electron is considered.

It is known that H=K+V where, k=$(p^2c^2 + m_o^2c^4)^{1/2} - m_oc^2$, is the relativistic kinetic energy, *V* is the relativistic potential energy, m_o is the rest mass of electron and p its linear momentum.

$$H = (p^2c^2 + m_o^2c^4)^{1/2} - m_oc^2 + V \qquad \ldots(37)$$

$$= m_oc^2\left(1 + \frac{p^2}{m_o^2c^2}\right)^{1/2} - m_oc^2 + V$$

$$= m_oc^2\left(1 + \frac{p^2}{2m_o^2c^2} - \frac{p^4}{8m_o^4c^4} + \cdots\right) - m_oc^2 + V$$

$$= \frac{p^2}{2m_o} - \frac{p^4}{8m_o^3c^2} + \cdots + V \qquad \ldots(38)$$

Neglecting the higher order terms, it is evident that the change in H due to relativistic correction is

$$-\frac{p^4}{8m_o^3c^2} \qquad \text{since} \left\{H = \frac{p^2}{2m_o} + V\right\}\text{without relativisticcorrection}$$

Considering $-\frac{p^4}{8m_o^3c^2}$ as perturbation term first order change in energy level can be evaluated.

The operator p is $-i\hbar\frac{\partial}{\partial q}$.

Therefore, $-\frac{p^4}{8m_o^3c^2}$ becomes $-\frac{1}{8m_o^3c^2}\left(-i\hbar\frac{\partial}{\partial q}\right)^4$

or $-\frac{1}{8m_o^3c^2}\hbar^2\nabla^4 \ldots(39)$

For hydrogen atom, let us consider ψ as unperturbed wave function, then first order shift in energy due to perturbation term is given as

$$\Delta E_r = -\int \psi^*\left(\frac{\hbar^4}{8m_o^3c^2}\right)\nabla^4\psi d\tau \qquad \ldots(40)$$

Evaluating the integral in equation no. 25 gives

$$\Delta E_r = -\frac{R_\infty\alpha^2Z^4hc}{n^3}\left(\frac{1}{l+\frac{1}{2}} - \frac{3}{4n}\right) \qquad \ldots(41)$$

Where α is the fine structure constant and R∞ is the Rydberg’s Constant.

Hence, the term shift due to relativistic correction is

$$\Delta T_{r=-}\frac{\Delta E_r}{hc} = -\frac{R_\infty \alpha^2 Z^4 hc}{n^3}\left(\frac{1}{l+\frac{1}{2}} - \frac{3}{4n}\right) \qquad \ldots(42)$$

To incorporate the combined effect of spin-orbit coupling and relativistic corrections in a H-atom spectrum, let us add equations 32 and 42.

1.4.3 Term shift

$$\Delta T = -\frac{R_\infty \alpha^2 Z^4}{2n^3 l\left(l+\frac{1}{2}\right)(l+1)}[j(j+1) - l(l+1) - s(s+1)] + \frac{R_\infty \alpha^2 Z^4}{n^3}\left(\frac{1}{l+\frac{1}{2}} - \frac{3}{4n}\right)$$

$$= \frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{1}{l+\frac{1}{2}} - \frac{j(j+1)-l(l+1)-s(s+1)}{2\left(l+\frac{1}{2}\right)(l+1)} - \frac{3}{4n}\right] \qquad \ldots(43)$$

Putting j=*l*+1/2 and s=1/2, we get

$$= \frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{1}{l+\frac{1}{2}} - \frac{l}{2l\left(l+\frac{1}{2}\right)(l+1)} - \frac{3}{4n}\right]\left[\frac{1}{l+\frac{1}{2}}\left(1 - \frac{1}{2l+2}\right) - \frac{3}{4n}\right]\left[\frac{1}{l+\frac{1}{2}}\left(\frac{2l+2-1}{2(l+1)}\right) - \frac{3}{4n}\right]$$

$$= \frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{1}{l+1} - \frac{3}{4n}\right] \qquad \ldots(44)$$

For j=*l*-1/2,

$$= \frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{1}{l+\frac{1}{2}} - \frac{\left(l-\frac{1}{2}\right)\left(l-\frac{1}{2}+1\right)-l(l+1)-\frac{3}{4}}{2l\left(l+\frac{1}{2}\right)(l+1)} - \frac{3}{4n}\right]$$

$$=\frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{2}{2l+1} - \frac{\frac{(2l-1)}{2}\left(l+\frac{1}{2}\right)-l^2-l-\frac{3}{4}}{2l\left(l+\frac{1}{2}\right)(l+1)} - \frac{3}{4n}\right]$$

$$= \frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{2}{2l+1} - \frac{\frac{(2l-1)(2l+1)}{4}-l^2-l-\frac{3}{4}}{2l\left(l+\frac{1}{2}\right)(l+1)} - \frac{3}{4n}\right]$$

$$= \frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{2}{2l+1} - \frac{\frac{(4l^2-1)}{4}-l^2-l-\frac{3}{4}}{2l\left(l+\frac{1}{2}\right)(l+1)} - \frac{3}{4n}\right]$$

$$= \frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{2}{2l+1} - \frac{l^2-\frac{1}{4}-l^2-l-\frac{3}{4}}{2l\left(l+\frac{1}{2}\right)(l+1)} - \frac{3}{4n}\right]$$

$$= \frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{2}{2l+1} - \frac{-(l+1)}{2l\left(l+\frac{1}{2}\right)(l+1)} - \frac{3}{4n}\right]$$

$$= \frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{2}{2l+1} + \frac{2}{2l\left(l+\frac{1}{2}\right)} - \frac{3}{4n}\right]$$

$$= \frac{R_\infty \alpha^2 Z^4}{n^3}\left(\frac{2}{2l+1}\right)\left[1 + \frac{1}{2l} - \frac{3}{4n}\right]$$

$$\Delta T = \frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{1}{l} - \frac{3}{4n}\right] \qquad \ldots(45)$$

Equation 44 and 45 cab be replaced by one single equation.

$$\Delta T = \frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right] \qquad \ldots(46)$$

Equation 46 is identical to equation of energy levels of hydrogen like atom given by Sommerfeld's relativistic equation; as

$$\Delta T = \frac{R_\infty \alpha^2 Z^4}{n^3}\left[\frac{1}{k} - \frac{3}{4n}\right]$$

As seen above, the equation is similar to the equation number 31, where k is equal to $j + \frac{1}{2}$

This equation is known as Dirac Equation.

By substituting the values of $R_\infty = 1.097 \times 10^7$ m^{-1}, α is Rydberg Constant where $\alpha = \frac{1}{137}$ (fine structure constant) and Z = 1 for hydrogen atom, we get term shift

$$\Delta T = \frac{584}{n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right] \text{ m}^{-1}$$

or $\Delta T = \frac{5.84}{n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right]$ cm^{-1}

Using, the term shift values in cm^{-1}, the fine structure of H_α line for n = 3 → n = 2 level is deduced as shown in Fig. 2

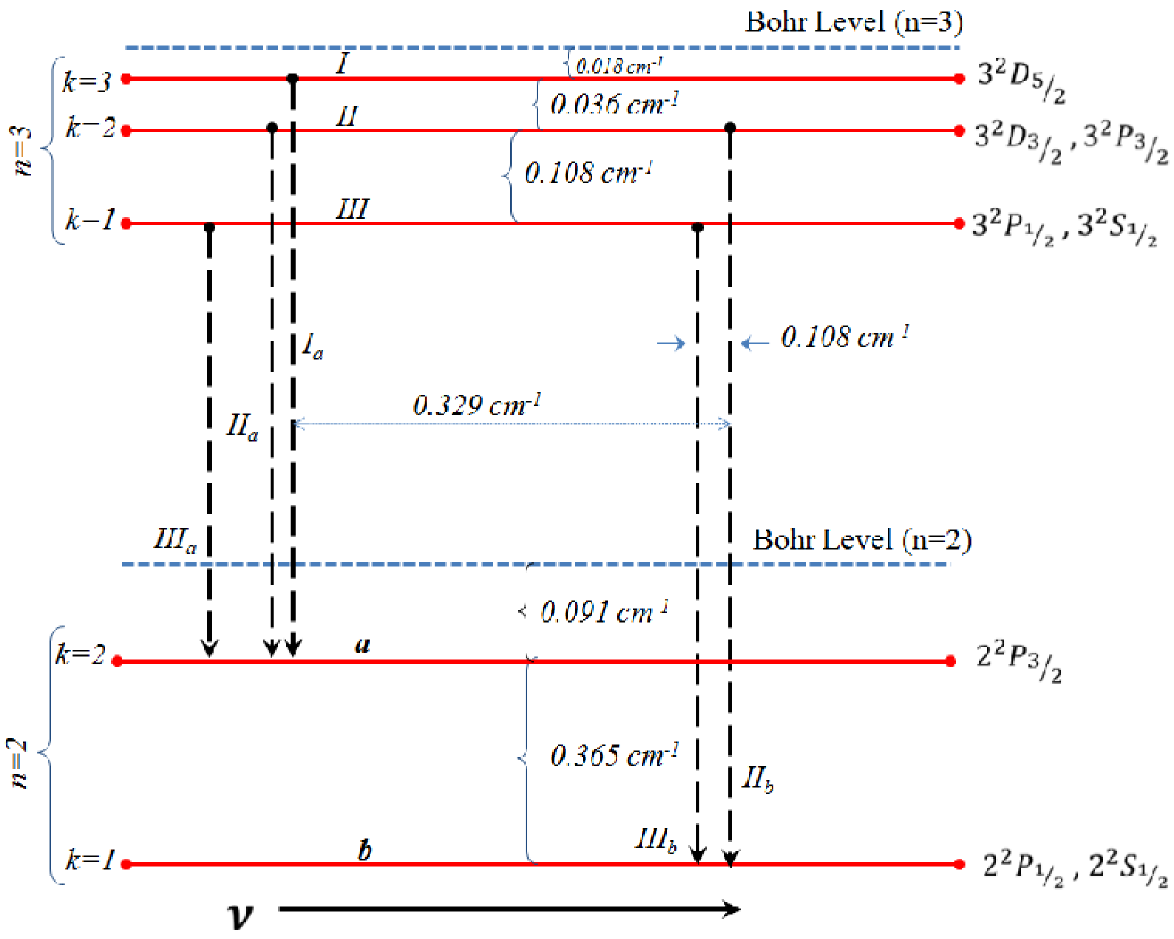

Fig. 2 The fine structure of H_α line for n = 3 → n = 2 level

The selection rules for fine structure of hydrogen atom are

$\Delta l = \pm 1$

$\Delta j = 0, \pm 1$ but $j = 0 \leftrightarrow j=0$ is not allowed

The above selection rules allow five transitions as shown in the figure. However, only doublets are observed in general practise instead of these five components. This happens due to thermal motion of the molecules that results into Doppler broadening. When the Doppler broadening effect is reduced carefully, all the five components can be observed.

Solved Example No 2:

The He^+ doublet splitting of first excited state $({}^2P_{\frac{1}{2}}$ - ${}^2P_{\frac{3}{2}})$ is 5.84 cm^{-1}. Evaluate the corresponding splitting value of H.

Solution- The doublet splitting separation due to spin-orbit interaction is given as:

$$\Delta T = \frac{R_{\infty}\alpha^2 Z^4}{n^3\ l(+1)}$$

Where, R_∞ is Rydberg's constant, $\propto$ is fine structure constant, Z is atomic number and n, l are constant for a given state.

$$\Delta T \propto Z^4$$

For He^+, Z = 2 and for H, Z = 1

Therefore, $\frac{\Delta T_{He}}{\Delta T_H} = (\frac{2^4}{1^4}) = 16$

$\Delta T_H = \frac{1}{16}\, \Delta T_{He^+} = \frac{1}{16} * 5.84 = 0.365\ cm^{-1}$

1.5 Pauli's Exclusion principle and exchange symmetry

To study the spectra of multi-electron atoms, the quantum mechanical properties of identical particles should be considered. As per the quantum mechanical wave theory, the particles that can be described by the symmetric total wave functions are called as 'Bosons'. Therefore,

$$\psi\ (1, 2, 3 \ldots\ldots.. N) = +\psi\ (1, 2, 3 \ldots..N)$$

From this it is inferred, that all the particles with the integral spins are known as Bosons. Examples are photons, gravitons, pions, etc.

Opposite to it, the particles that can be completely described by the asymmetric total wave functions are known as 'Fermions'. Therefore,

$$\psi\ (1, 2, 3 \ldots\ldots.. N) = -\psi\ (1, 2, 3 \ldots..N)$$

From this it can be inferred that all the particles with the half integral spins are Fermions. Examples are electrons, protons, neutrons, etc.

Pauli in Year 1925, formulated basic principle that governs the electronic configuration of the atoms. Pauli's Exclusion Principle states that "*no two fermions can exist in the same quantum state*". This can be further extended that the existence of two electrons with same spin orientation in one atomic orbital is not possible.

Let us consider two identical non – interacting particles 1 and 2 having quantum state, a and b, then the wave function of the system is

$$\psi_{ab}(1, 2) = \psi_a(1).\psi_b(2)$$

Let us now consider particle to be in state b and particle 2 in state a, then the wave function would be

$$\psi_{ba}(1, 2) = \psi_b(1).\psi_a(2)$$

As these particles are indistinguishable, ψ_{ab} and ψ_{ba}, both have equal likelihood. Therefore, the system can be described by linear combination of both.

$$\psi(1,2) = \frac{1}{\sqrt{2}}[\psi_a(1)\,\psi_b(2) \pm \psi_b(1)\,\psi_a(2)]$$

Where, $\frac{1}{\sqrt{2}}$ is the normalisation constant.

For Bosons, where total wave function is symmetric, the above equation becomes

$$\psi_{Bose}(1,2) = \frac{1}{\sqrt{2}}[\psi_a(1)\,\psi_b(2) + \psi_b(1)\,\psi_a(2)]$$

And for Formions (Anti – symmetric Wave),

$$\psi_{Formi}(1,2) = \frac{1}{\sqrt{2}}[\psi_a(1)\,\psi_b(2) - \psi_b(1)\,\psi_a(2)]$$

If the quantum states a ≡ b, then

$$\psi_{Bose}(1,2) \neq 0$$

$$\psi_{Formi}(1,2) \neq 0$$

Therefore, two Bosons can exist in the same quantum state whereas two Fermions cannot because because the wave function vanishes identically in case of fermions. This further indicates that fermions cannot be described by the same set of quantum numbers.

Solved Example No 3:

Consider a system comprising two Bose particles with same quantum number a construct normalised wave function.

Solution- Let the two Bose particles be 1 and 2. The normalised wave function is given as:-

$\psi_s\,(1, 2) = \frac{1}{\sqrt{2}}[\psi_a(1)\,\psi_b(2) + \psi_b(1)\,\psi_a(2)]$

where $\frac{1}{\sqrt{2}}$ is normalisation factor. Both the Bose particles are associated with same quantum number ‘a’. Therefore, a = b.

$\psi_s\,(1, 2) = \frac{1}{\sqrt{2}}[\psi_a(1)\,\psi_a(2) + \psi_a(1)\,\psi_a(2)]$

$= \sqrt{2}\,\psi_a\,(1)\,\psi_a\,(2)$

1.6 Hund’s Rule

These rules are as follows:-

1. The terms with largest multiplicity lie at the lowest.

2. The terms with largest L lie at the lowest for terms with same multiplicity.
3. The levels with lowest value of J lies at the lowest for half – filled or lesser in outermost sub shell and for more than half – filled sub shell, the level with longest J has lowest in energy for terms of an atom.

1.7 Helium Atom and it's Spectrum

1.7.1 He atom's spectrum

Two identical particles, when treated quantum mechanically act under the influence of exchange of forces. This force may be attractive or repulsive depending on the orientation of spin of the particles. If we consider two electrons, parallel spins repel, however the antiparallel spins attract.

A system having two electrons in an atom such as He atom may exist in singlet or triplet state. The two electrons two and two have spin quantum numbers as $s_1 = \frac{1}{2}$ and $s_2 = \frac{1}{2}$ respectively. Thus, the $\vec{S}$ (spin angular momentum) of the considered system is$\frac{h}{2\pi} \sqrt{S(S+1)}$. S can have all the values from $(s_1 + s_2)$ to $(s_1 - s_2)$ with a difference of one. Therefore, S = 1, 0.

S = 1 corresponds to antiparallel spins and S = 0 to parallel spins:

$s_1 = \frac{1}{2} \uparrow$ and $s_2 = \frac{1}{2} \uparrow$ gives S = 1

$s_1 = \frac{1}{2} \uparrow$ and $s_2 = \frac{1}{2} \downarrow$ gives S = 0

The Z component (S_Z) is given as $S_Z = M_s\, h/2\pi$, where M_s has all the possible values from +S to –S. That is

$M_s = 1, 0, -1$ for S = 1

And $M_s = 0$ for S = 0

Therefore, there are three possible values of M_s for S = 1, resulting into three possible spin states known as 'triplet states' whereas, for S = 0 the value of $M_s = 0$and thus singlet spin state arises due to parallel configuration and singlet state due to antiparallel configuration.

The He atom's emission spectrum for triplet and singlet states is shown in Fig. 3 below:

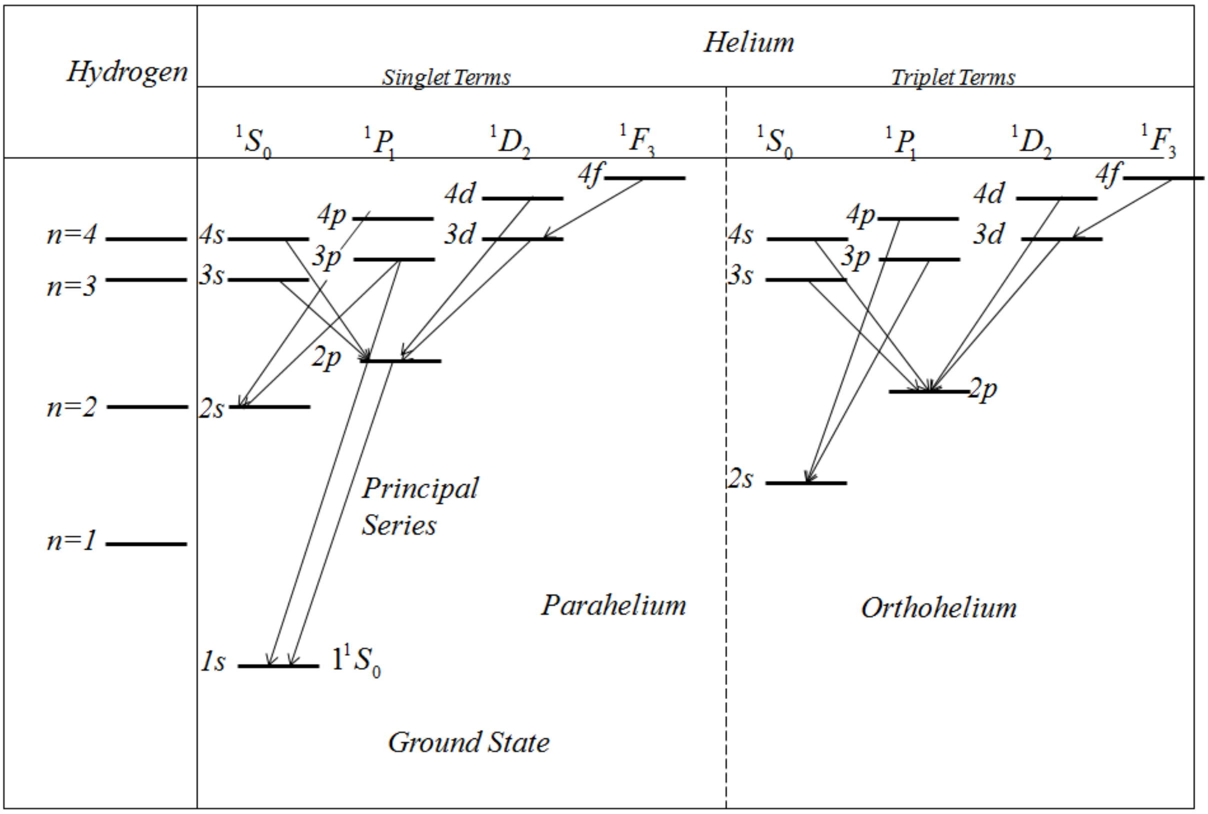

Fig. 3 The He atom's emission spectrum for triplet and singlet states

From the above figure, it may be inferred that for every single energy level of singlet state there corresponds a triplet state. The energy difference between the lowest excited state and state $^1S_0$ is quite large. The triplet states don't combine with the singlet states.

This non combination of triplet state with singlet state indicates the existence of two forms of helium – orthohelium and parahelium. In orthohelium form, the electron spins are parallel giving rise to the triplet state while, in the parahelium form, the spins of the electrons is antiparallel giving rise to the singlet state. In the process of collision, the orthohelium form may lose excitation energy and become parahelium. On the other hand, parahelium atom may gain this energy via collision to become orthohelium. Therefore, in general helium is found as the mixture of both. However, it is well understood that the splitting of He into two non-combing systems arises from quantum mechanical treatment.

1.7.2 Quantum Mechanical treatment of He atom

Let us consider a system comprised of two electrons. Then the general form of the normalised wave function, in space domain for symmetric and antisymmetric conditions is given as:

$\frac{1}{\sqrt{2}}\left[\psi_a(1)\,\psi_b(2) + \psi_b(1)\,\psi_a(2)\right]$ Symmetric Wave function ......(47)

$\frac{1}{\sqrt{2}}\left[\psi_a(1)\,\psi_b(2) - \psi_b(1)\,\psi_a(2)\right]$ Antisymmetric Wave function......(48)

Where a and b represent space quantum numbers.

The spin coordinate can have two orientations – spin up (+1/2) and spin down (-1/2). Thus there are only two possible wave functions - β^+ and β^-. Thus, there are only two possible wave functions corresponding to spin up and spin down states. These lead to four possible ways in which spin wave function can exist. The normalised form of these spin wave functions are given below.

$$\left.\begin{array}{l} \beta_1^+\beta_2^+ \\ \frac{1}{\sqrt{2}}[\beta_1^+\beta_2^- + \beta_1^-\beta_2^+] \\ \beta_1^-\beta_2^- \end{array}\right\} \longrightarrow \text{Symmetric (Triplet State).........(49)}$$

$$\frac{1}{\sqrt{2}}[\beta_1^+\beta_2^- - \beta_1^-\beta_2^+] \longrightarrow \text{Antisymmetric (Singlet State)........ (50)}$$

The first three forms (eqn 49) are for parallel orientation of electrons giving rise to the triplet states and the last form (eqn 50) is due to antiparallel orientation that results into singlet state.

It is also known that the total wave function may be written in terms of spin wave function and space wave function as:

$$\psi_{tot} = \psi\beta \qquad \text{........(51)}$$

Therefore the total wave function for He atom may be written as:

$$\left.\begin{array}{l} \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)\right]\beta_1^+\beta_2^+ \\ \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)\right]\frac{1}{\sqrt{2}}[\beta_1^+\beta_2^- + \beta_1^-\beta_2^+] \\ \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)\right]\beta_1^-\beta_2^- \end{array}\right\}$$

These forms represent the parallel orientation (Triplet State)

$$\frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)\right]\frac{1}{\sqrt{2}}[\beta_1^+\beta_2^- - \beta_1^-\beta_2^+]$$

This form represents the antiparallel orientation (Singlet state)

Due to first three forms of symmetric spin wave function (eqn 49), triplet state arises while the antisymmetric spin wave function (eqn 50) gives rise to singlet state. If we ignore the interaction due to coulomb field, all these four states are degenerate. However, if the coulomb interaction is considered, the exchange degeneracy gets removed and splits each state into singlet and three fold degenerate triplet state (Fig. 4). Therefore, splitting of He atom into Singlet – Triplet can be explained under coulomb effect.

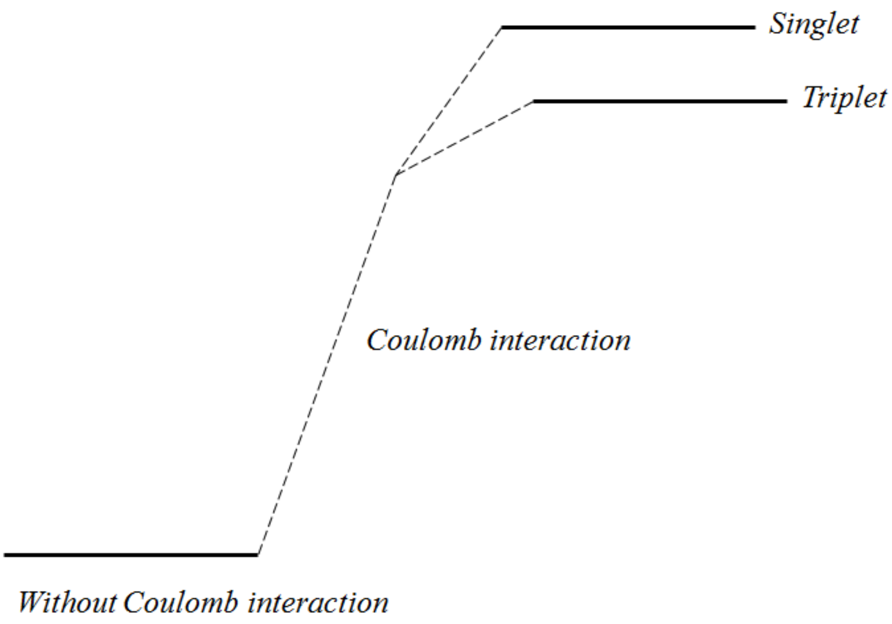

Fig. 4 Splitting of He atom into Singlet – Triplet can be explained under coulomb effect

The electrons in the ground state have same quantum numbers, that is a = b = 1s and hence there exists single wave function in the space domain as $\psi_{1s}(1)\,\psi_{1s}(2)$. This space wave function is symmetric with respect to the exchange of electrons. In order to satisfy the pauli's exclusion principle, the space wave function needs to be combined with antisymmetric spin wave function $[\frac{1}{\sqrt{2}}(\beta_1^+\beta_2^- - \beta_1^-\beta_2^+)$. Such a combination results into singlet state. This further indicates the absence of triplet state for the ground state.

Except for this ground state, there exist triplet states with singlet states for higher energy levels. The energy due to coulomb interaction $(\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_{12}})$between the two electrons is lesser in the triplet state compared to the singlet state. This is because the average distance (r_{12}) between the electrons is greater in triplet state compared to singlet state. Henceforth, the singlet states lie in the upper level compared to triplet states.

It is also observed that the energy level of the ground state is much lower compared to other higher levels. The electrons of the ground state are strongly bounded by the nucleus compared to higher energy levels. The perturbation may be adopted to calculate the energy of ground and higher levels of He atom.

Let us now consider He atom (Z = 2) having charge on nucleus (+Ze) and two electrons say 1 and 2. Then the Hamiltonian operator $(\hat{\mathrm{H}})$ is given as:

$$\hat{\mathrm{H}} = -\frac{h^2}{8\pi^2 m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_1} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_2} + -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_{12}} \qquad \text{...........(52)}$$

Where r_1 and r_2 are the distances between the nucleus and electrons 1 and 2 respectively. While, r_{12} is the distance between the electrons 1 and 2. Due to the coulomb repulsive potential energy between the two electrons, the term $\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r_{12}}$ is taken positive while all other forces are attractive. The motion of the nucleus and few interactions such as spin-spin and spin-orbit coupling are neglected in the present calculation as they are very weak compared to the coulomb interaction. The attractive potential energy between the nucleus and the electrons make the terms $\frac{1}{4\pi\varepsilon_o}\frac{Ze^2}{r_1}$ and $\frac{1}{4\pi\varepsilon_o}\frac{Ze^2}{r_2}$ make the terms negative. Hence the wave equation becomes:

$$\widehat{\mathrm{H}}\psi = [-\frac{h^2}{8\pi^2 m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{1}{4\pi\varepsilon_o}\frac{Ze^2}{r_1} - \frac{1}{4\pi\varepsilon_o}\frac{Ze^2}{r_2} + -\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r_{12}}]\psi \qquad \text{..........(53)}$$

And also, $\widehat{\mathrm{H}}\psi = E\psi$ ....(54)

The perturbation method is employed to solve eqn 53 and $\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r_{12}}$ is considered as the perturbing term. Here eqn 53 can be written as:

$(\widehat{\mathrm{H}}^\circ + \widehat{\mathrm{H}}')\psi = E\psi$

Where $\widehat{\mathrm{H}}^\circ + \widehat{\mathrm{H}}' = \widehat{\mathrm{H}}$

Thus the wave equation (for ground state – 1s1s) for unperturbed part can be written as:

$\widehat{\mathrm{H}}^\circ\psi^\circ = E^\circ\psi^\circ$ ....(55)

$$\left.\begin{aligned} &\text{Where } \psi^\circ = \psi^\circ{}_{1s}(1)\psi^\circ{}_{1s}(2) \\ &\text{And } \mathrm{E}^\circ = \mathrm{E}^\circ{}_{1s}(1)\mathrm{E}^\circ{}_{1s}(2) \end{aligned}\right\} \qquad \text{.......(56)}$$

The unperturbed wave function is treated as the product of two wave functions of hydrogen like atoms in the ground state. The eigen value of ψ° is the sum of the individual eigen values of $\psi^\circ{}_{1s}(1)$ and $\psi^\circ{}_{1s}(2)$ respectively.

We also know that the wave function of the hydrogen like atoms in the ground state is

$$\psi^\circ{}_{1s} = \frac{1}{\sqrt{\pi}}(\mathrm{Z}/\mathrm{a_o})^{\frac{3}{2}} \exp(-Zr/\mathrm{a_o}) \qquad \text{........(57)}$$

And the eigen value of the $\psi^\circ{}_{1s}$ is $\mathrm{E}^\circ{}_{1s} = -\mathrm{Z}^2\mathrm{E_H}$

Here, $E_H = \frac{me^4}{8\varepsilon_0{}^2h^2} = 13.6\text{ eV}$ ....(58)

Substituting the values from eqns 58 and 57 into 56, we get:

$$\left.\begin{aligned} &\psi^\circ = \frac{1}{\pi}(\mathrm{Z}/\mathrm{a_o})^3 \exp(-Z(r_1 + r_2)/\mathrm{a_o}) \\ &\mathrm{E}^\circ = -2\mathrm{Z}^2\mathrm{E_H} \end{aligned}\right\} \qquad \text{..........(59)}$$

As for He atom Z = 2

$$E^{\circ} = -8E_H$$

$$= -8 \times 13.6 \text{ eV}$$

$$= -108.8 \text{ eV}$$

However, the experimental results show that this value is -78.98 eV. This simply highlights the role of coulomb interaction between the two electrons play a key role in determining the energy state of He atom.

Therefore, the introduction of perturbation term representing coulombic repulsion term is done. Now, for the evaluation of first order energy perturbation evaluation of first order energy perturbation, we will consider the following equation:

$$E' = \int \psi^{\circ}\widehat{H}\psi' d\tau$$

$$E' = \iint \frac{1}{\pi}\left(Z/a_o\right)^3 \exp\left(-Z(r_1 + r_2)/a_o\right) \left(\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r_{12}}\right) \frac{1}{\pi}(Z/a_o)^3 \exp\left(-Z(r_1 + r_2)/a_o\right) d\tau_1\, d\tau_2$$

$$= \left(\frac{e^2}{\pi^2}\right)\left(\frac{Z}{a_o}\right)\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi}\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \frac{e^{\frac{-2Z(r_1+r_2)}{a_o}}}{4\pi\varepsilon_o r_{12}} r_1^2 dr_1 sin\theta_1 d\theta_1 d\varphi_1\, r_1^2 dr_2 sin\theta_2 d\theta_2 d\varphi_2$$

$$\text{Therefore,} \qquad E' = \frac{5Ze^2}{32\pi\varepsilon_o a_o} = \frac{5}{4}Z\left(\frac{e^2}{8\pi\varepsilon_o a_o}\right) = \frac{5}{4}ZE_H = \frac{5}{4} \times 2 \times 13.6 = 34.0eV$$

The total energy becomes: $E = E^{o} + E'$

$$= -108.8+34.0$$

$$= -74.8\text{eV}$$

This value is almost equal to the experimental results with an error limit of ~5%. However, for higher precision and accuracy, the variation method may be employed. If we consider He like atoms that are heavier than the He atoms like Li^{+}, Be^{++}, B^{+++} and many more, the error gets reduced. This is because the nuclear charge increases and the interaction between the nucleus and the electron become more important rather than the electron interaction and hence the perturbation term becomes more accurate.

1.6 Summary

The Schröedinger treatment on hydrogen and like atoms gives rise to principal quantum number, angular quantum number and azimuthal quantum number which further coined the concept of discreteness and quantization of energy. These quantum numbers and their discreteness could explain the line spectra of the hydrogen and hydrogen like atoms. Further, these discrete energy levels split due to electron's orbital and spin motion. The relativistic corrections in addition to spin-orbit coupling effect give rise to term shift. This term shift determines the fine structure of hydrogen and hydrogen like atoms.

For atoms with more than one electron, the Pauli's exclusion principle and the exchange symmetry becomes important. The Pauli's principle stated that no two fermions can exist in the same quantum state. Two particle systems like He atom have two identical particles. When such a system is treated quantum mechanically, they act under the influence of exchange of forces. This force may be attractive or repulsive depending on the orientation of spin of the particles. If we consider two electrons, parallel spins repel, however the antiparallel spins attract. Due to symmetric spin wave function, triplet state arises while the antisymmetric spin wave function gives rise to singlet state. If we ignore the interaction due to coulomb field, all these four states are degenerate. However, if the coulomb interaction is considered, the exchange degeneracy gets removed and splits each state into singlet and three fold degenerate triplet state. Therefore, splitting of He atom into Singlet - Triplet can be explained under coulomb effect. For every single energy level of singlet state there corresponds to a triplet state. The triplet states don't combine with the singlet states. This non combination of triplet state with singlet state indicates the existence of two forms of helium – orthohelium and parahelium. In orthohelium form, the electron spins are parallel giving rise to the triplet state while, in the parahelium form, the spins of the electrons is antiparallel giving rise to the singlet state. In general helium is found as the mixture of both.

The transitions taking place between the different energy states gives rise to spectral lines. By employing appropriate selection and intensity rules, these transitions between different energy levels are determined. In one electron atoms, all the states exist as doublets except the ground state. The fine structure is obtained due to the transitions between these doublets. However, the selection rules must be accounted for actually observable fine structure. A more complex fine structure is expected for more than one electron systems as these involve terms with higher multiplicities. However, the determination of these transitions is again governed by selection rules. Due to the closed shells in the atoms, the optical electrons available for transitions and hence spectra formation are few. Therefore, as the periodic number increases the complexity in the determination of fine structure of atoms doesn't increase. Apart from this, the selection rules also reduce its complexity. Furthermore, the application of Pauli's exclusion principle also reduces its complexity.

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1.8 Suggested Readings

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6. Max Born, R. J. B-. Stoyle, J. M. Radcliffe, , Atomic Physics (Dover Books on Physics), Dover Publications Inc.; Ed. 8th,1990, ISBN-10: 0486659844
7. Gerhard Herzberg, Atomic Spectra and Atomic Structure, Dover Books on Physics, (2010), ISBN-10: 0486601153

1.9 Terminal Descriptive type questions

Q-1. Consider a two- electron system and write its spin function for anti symmetric and symmetric combinations.

Q-2. Describe the helium atom with the help of energy - level diagram. State the conditions under which helium electrons transits into higher state.

Q-3. Treat helium atom quantum mechanically and hence explain its spectrum.

Q-4. Discuss the salient features of helium atom spectra. How does it differ from hydrogen spectra?

Q-5. Discuss the helium spectra for parahelium and orthohelium states.

Q-6. Evaluate the energy for ground state of He atom.

Q-7. Apply Pauli's exclusion principle to prove that the He atom exists in singlet state only in ground state.

Q-8. What do you understand by identical particles? Describe the exchange symmetry for identical particles wave function.

Q-9. Differentiate between symmetric and anti symmetric wave functions.

Q-10. State and discuss Pauli's exclusion principle for symmetric and anti symmetric wave functions.

Q-11. State the limitations of Bohr – Sommerfeld model. Discuss the quantum mechanical treatment on hydrogen atom.

Q-12. Discuss hydrogen atom quantum mechanically and hence explain all the quantum numbers involved.

Q-13. Obtain the energy levels and associated quantum numbers of a hydrogen by solving the radial part of the Schroedinger wave equation.

Q-14. Discuss the physical significance of quantum numbers obtained from hydrogen atom's Schroedinger equation.

Q-15. Discuss fine structure of hydrogen atom in light of spin – orbit coupling and relativistic corrections.

Q-16. Draw and explain the energy levels for fine structure of hydrogen atom. Elaborate the results from Dirac theory.

Q-17. Deduce the expressions for spin – orbit interaction energy and relativistic correction energy terms hence evaluate the net term shift for hydrogen like atoms.

Q-18. Consider hydrogen like atoms and apply first order perturbation theory to deduce the fine – structure splitting of n l due to spin – orbit interaction.

Q-19. Using Dirac theory to show transitions from n = 3 to n = 2 states for a hydrogen atom.

Q-20. Comment on the statement that the "the ground state of He atom lies much deeper compared to the H atom's ground level, however, the excited states lie closely to each other."

1.10 Numerical type (Self Assessment questions)

Q-1. The first order excited state ($^2P_{\frac{1}{2}}$ - $^2P_{\frac{3}{2}}$) doublet splitting values is 0.365 cm^{-1} for a H atom. Evaluate the corresponding splitting separation value of He^+ .

(Ans- 5.84 cm^{-1})

Q-2. Find the parity of O atom in ground state.

(Ans- Even Parity)

Q-3. The first order state ($^2P_{\frac{1}{2}}$ - $^2P_{\frac{3}{2}}$) doublet splitting value is 0.365 $cm^{-1}$for a H atom. Evaluate the corresponding splitting separation for Li^{++}.

(Ans- 29.6 cm^{-1})

Q-4. Prove that the total number of electrons is $2n^2$ for a closed shell (n is principal quantum number)

Q-5. Consider a wave function for two particles-

$\psi_3\,(1,2) = $ A $[\psi_a\,(1)\;\psi_b\,(2) \pm \psi_b\,(1)\,\psi_a\,(2)]$. Evaluate the value of A.

(Ans- $\frac{1}{\sqrt{2}}$)

Q-6. Write the exchange symmetric wave function for ground and excited state (1s 2s) of He atom.

UNIT 2 SPECTROSCOPIC TERMS

2.1 Introduction
2.2 Objectives
2.3 Spectroscopic Terminology
2.4 L-S Coupling
    2.4.1 Lande Interval Rule
    2.4.2 Normal and Inverted Multiplets
    2.4.3 Determination of Spectral terms
    2.4.4 Selection Rules in L-S coupling
2.5 *j-j* Coupling
    2.5.1 Selection Rules in j-j coupling
2.6 Summary
2.7 References
2.8 Suggested Readings
2.9 Terminal Descriptive type questions
2.10 Numerical type (Self Assessment Questions)

2.1 Introduction

The atomic models given by Rutherford, Bohr and Sommerfeld were incapable of explaining spectral lines due to fine structure splitting of simplest system (one electron atoms). Although, the Sommerfeld model could give some theoretical explanation to fine structure of spectral lines, it was partial success. The Sommerfeld model was incapable of predicting number of spectral lines correctly and the relative intensities among these spectral lines. Going forward, the findings of the relatively new experiments like Zeeman effect, Paschen - Back effect, Stark effect etc., could not get accommodated in the older atomic models. Bohr model suffered from one more major objection. It was based on two fundamental theories that opposed each other. The frequencies corresponding to emission spectra was explained and understood on the basis of quantum theory, however the motion of electrons in the stationary orbits was as per the classical laws. Therefore, the older models had become insufficient to explain and interpret new ideas related to atomic structure. This finally resulted in evolution of vector atom model. The vector atom model inculcated the conception of space quantization and the electron spin. Before detailing the concepts of 'quantization of space', 'spinning electron' and various coupling schemes, we shall first discuss the concept of orbital magnetic dipole moment and Bohr Magneton.

Let us consider one electron atom with orbital quantum number *l* that is orbiting around the nucleus. This orbiting electron serves as a tiny current loop and its movement produces magnetic field. An electron with electronic charge -e, mass m revolves around the nucleus in Bohr orbit of radius r with velocity v as illustrated in Fig.1 below. The current produced is given as:

$i = e/T$ (Magnitude only)

Where T is the electron's orbital time period

$T = (2\pi r)/v$

Therefore, $i = ev/2\pi r$

Also, we know that the magnetic dipole moment $\overrightarrow{\mu_l}$ in a current loop with area a and current i is given as:

$\overrightarrow{\mu_l} = iA$

$\overrightarrow{\mu_l} = \frac{ev}{2\pi r}\pi r^2$

$\overrightarrow{\mu_l} = \frac{evr}{2}$ ....(1)

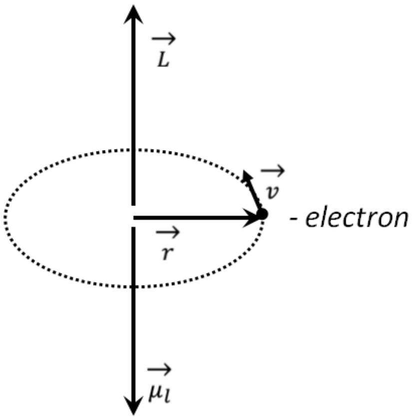


Fig. 1 Movement of electron in Bohr's circular orbit

As electron is negatively charged, the direction of $\overrightarrow{\mu_l}$ is opposite to that of $\vec{L}$. Also the magnitude of L is given as:

$L = mvr$ ......(2)

Thus from (1) and (2) equations we get

$\frac{\overrightarrow{\mu_l}}{L} = \frac{e}{2m}$ ......(3)

The ratio $\frac{\overrightarrow{\mu_l}}{L}$ is constant for an electron and is called as 'gyromagnetic ratio'.

The eqn 3 may be rewritten in vector form as:

$\overrightarrow{\mu_l} = -g_l \frac{e}{2m} \vec{L}$ ....(4)

Negative sign indicates that $\overrightarrow{\mu_l}$ and $\vec{L}$ are oppositely directed.

$\overrightarrow{\mu_l} = -g_l \frac{e}{2m} \vec{L}$, where $g_l = 1$ (orbital g factor)

The magnitude values of $\vec{L}$ (orbital angular momentum) and $\overrightarrow{\mu_l}$ (orbital magnetic momentum) are given as:

$\vec{L} = \frac{h}{2\pi} \sqrt{l(l+1)}$

$\overrightarrow{\mu_l} = \frac{eh}{4\pi m} \sqrt{l(l+1)}$

Where, *l* is orbital quantum number.

The quantity $\frac{eh}{4\pi m}$ is called Bohr magneton ($\overrightarrow{\mu_B}$) and has a value of $9.27 \times 10^{-24} Am^2$ for an electron.

$\overrightarrow{\mu_l} = \sqrt{l(l+1)}\mu_B$

The eqn number 4 can be written as

$\mu_l = -g_l \left({}^{2\pi\mu_B}/_{\mathrm{h}} \right) \vec{L}$

Solved Example 1:

Question: In terms of Bohr magneton, evaluate the spin dipole moment of an electron.

Solution: The spin magnetic moment is given as:

$\overrightarrow{\mu_s} = g_s \frac{e}{2m} \vec{S}$

The magnitude of μ_s is given as;

$\mu_s = g_s \frac{e}{2m} S$

For $g_s = 2$ and $s = \sqrt{s(s+1)}\frac{h}{2\pi}$

$s = \sqrt{3}/2\left(\frac{h}{2\pi}\right)$ for S = 1/2

Therefore, $\overrightarrow{\mu_s} = 2\frac{e}{2m}\frac{\sqrt{3}}{2}\frac{\mathrm{h}}{2\pi}$

$= \sqrt{3}\frac{eh}{4\pi m}$

But the Bohr magneton is $\mu_B = \frac{eh}{4\pi m}$

Therefore, $\mu_s = \sqrt{3}\mu_B$

Quantisation of Space

The quantisation of space was based on quantum theory. In the presence of magnetic field $\vec{B}$, the electron precesses along the direction of the magnetic field. The orbital angular momentum $\vec{L}$ traces a cone around$\vec{B}$. The angle between $\vec{B}$ and $\vec{L}$ is θ as shown in the fig. 2 below.

The z component L is given as:

$L_Z = L\ Cos\theta$

$Cos\theta = \frac{L_Z}{L}$

The magnitude of orbital angular momentum $\vec{L}$ and its Z component is given as:

$L = \frac{h}{2\pi}\sqrt{l(l+1)}$

$L_Z = m_l\frac{h}{2\pi}$

Where, *l* is orbital quantum number and m_l is magnetic orbital quantum number.

$Cos\theta = \frac{L_Z}{L}$

$Cos\theta = \frac{m_l}{\sqrt{l(l+1)}}$

$m_l = (0, \pm 1, \pm 2, \ldots\ldots\ldots, \pm l)$ for a given *l* in 2*l*+1 possible ways for a given *l*. These further states that ‘θ’ can have 2*l*+1 discrete values. These discrete orientations give rise to *space quantization.*

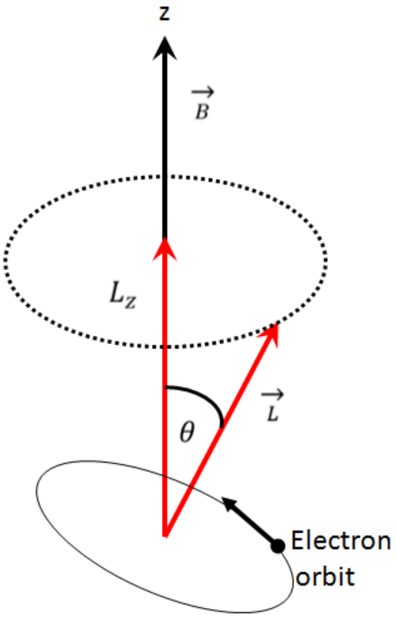


Fig. 2 Representation of angle θ between orbital angular momentum vector $\vec{\mathrm{L}}$ and external magnetic field $\vec{\mathrm{B}}$

The space quantization of orbital angular momentum $\vec{L}$ corresponding to $l = 1$ is shown in the fig. 3 below.

$$m_l = 1, 0, -1$$

$$L_Z = \frac{h}{2\pi}, 0, -\frac{h}{2\pi}$$

The orientations given by ‘θ’ is given as:

$$Cos\theta = \frac{m_l}{\sqrt{l(l+1)}}$$

$$Cos\theta = {}^{1}/_{\sqrt{2}} \; (for\ m_l = 1)$$

$$Cos\theta = 0 \; (for\ m_l = 0)$$

$$Cos\theta = -{}^{1}/_{\sqrt{2}} \; (for\ m_l = 1)$$

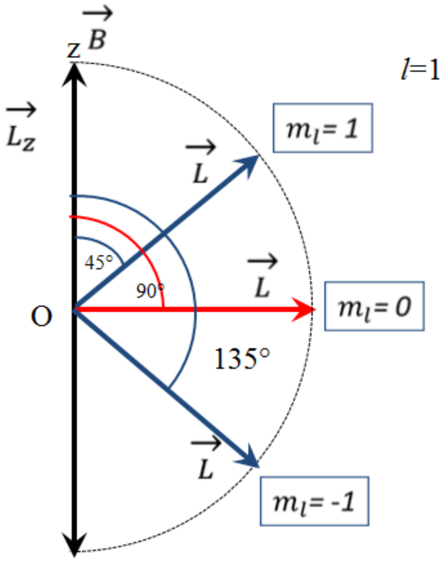


Fig. 3 Discrete orientations of orbital angular momentum $\vec{L}$ for l=1

Spinning Electron

The relativistic corrections inculcated by sommerfeld atomic model could explain fine structure of hydrogen atom to an extent. This explanation failed in case of atoms other than hydrogen. Further this theory couldn’t explain the experimental results obtained by Zeeman Effect. In 1925, Goudsmit and Uhlenbeck introduced the conception of *‘Spinning Electrons’*. They suggested that the electrons must be treated as charged particle that spins about its own axis. Thus the electron itself carries intrinsic spin angular momentum ($\vec{S}$) and magnetic spin dipole momentum ($\vec{\mu_s}$).

The magnitude values of $\vec{S}$ given as:

$$S = \frac{h}{2\pi}\sqrt{s(s+1)}$$

Where, s is spin quantum number and has a value of $s = \frac{1}{2}$

The z component S is given as:

$$S_Z = m_s \frac{h}{2\pi}$$

Where, m_s is called as the ‘spin magnetic quantum number’ and can have two possible values $m_s = \pm\frac{1}{2}$ according to 2s + 1 = 2. This states that the electron spin can have only two possible orientations in up and down directions.

Experimentally, it is been determined that the gyromagnetic ratio of the spinning electron $\left(\frac{\mu_s}{S}\right)$ is two times the gyromagnetic ratio due to the corresponding orbital motion $\left(\frac{\mu_l}{L}\right)$.

Therefore, $\overrightarrow{\mu_s} = -2\frac{e}{2m}\vec{S}$

Negative sign indicates that $\overrightarrow{\mu_s}$ and $\vec{S}$ are oppositely directed.

$\overrightarrow{\mu_s} = -g_l\frac{e}{2m}\vec{S}$ where $g_l = 2$ (spin g factor)

Vector Model of Atom

The spin ($\vec{S}$) and orbital ($\vec{L}$) angular momentums are combined to determine the total angular momentum of the electrons. Since the $\vec{S}$ and $\vec{L}$ are vector quantities, the total angular momentum ($\vec{J}$) is also a vector quantity.

The Orbital angular momentum ($\vec{L}$)

$L = \frac{h}{2\pi}\sqrt{l(l+1)}$

$L_Z = m_l\frac{h}{2\pi}$ (Z component)

l is the orbital quantum number, m_l is the orbital magnetic quantum number such that $m_l = l, l-1, \dots\dots\dots, 0, -l+1, -l$

The Spin angular momentum ($\vec{S}$)

$S = \frac{h}{2\pi}\sqrt{s(s+1)}$

$S_Z = m_s\frac{h}{2\pi}$ (Z component)

s is the spin quantum number, m_s is the magnetic spin quantum number such that $m_s = l, l - \pm 1/2$

Therefore the total angular momentum $\vec{J}$, is given as:

$\vec{J} = \vec{L} + \vec{S}$

$J = \frac{h}{2\pi}\sqrt{j(j+1)}$

$J_Z = m_j\frac{h}{2\pi}$ (Z component)

j is often called as inner quantum number, m_l is the magnetic inner quantum number such that $m_j = j, j-1, \dots\dots\dots, 0, -j+1, -j$

Also, $J_z = L_z + S_z$

$m_z = m_j + m_s$

Since m_l is the integral number and $m_s = \pm 1/2$, therefore $j = l \pm s$ is half integral number.

The quantum numbers $\vec{J}$, $\vec{L}$ and $\vec{S}$ are quantised and the relative orientations correspond to

$j = l - s$ for J > L

$j = l + s$ for J < L

In the vector model, the $\vec{L}$ and $\vec{S}$ precess around $\vec{J}$, as shown in fig. 4a; but when placed under the influence of external magnetic field $\vec{B}$, $\vec{J}$ precesses around $\vec{B}$ (Fig. 4b).

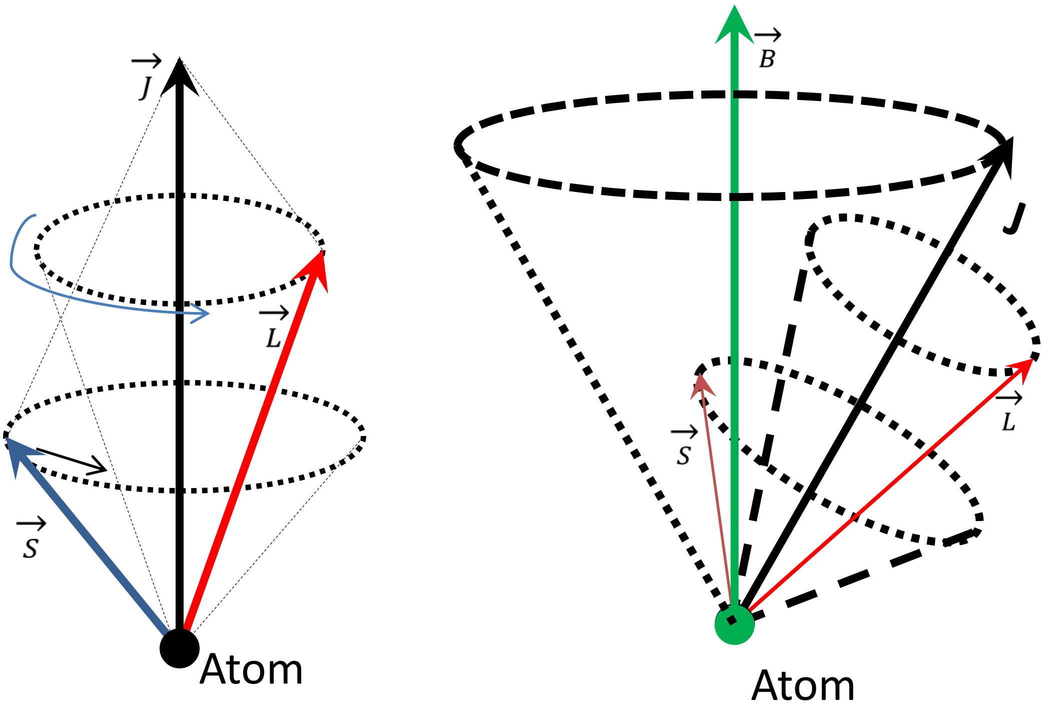


Fig. 4a Fig. 4b

Fig. 4 Representation of Vector model of an atom

Solved Example 2:

Question: Corresponding to j = $\frac{3}{2}$, evaluate the number of possible orientations of total angular momentum J along with z- axis.

Solution- The magnitude of J and its z axis component is given as :

J = $\sqrt{j(j+1)}\,\frac{h}{2\pi}$

And J_z = mj$\frac{h}{2\pi}$

Now for j= $\frac{3}{2}$

mj = $\frac{3}{2}, \frac{1}{2}, \frac{-1}{2}, \frac{-3}{2}$

Corresponding to mj and j, the angle θ between J and z axis is determined.

$$\cos\theta = \frac{J_z}{J} = \frac{mj}{\sqrt{j(j+1)}}$$

$$\sqrt{j(j+1)} = \sqrt{\frac{3}{2}}\ (\frac{3}{2}+1) = \frac{\sqrt{15}}{2}$$

$$\text{Therefore, } \cos\theta = \frac{2mj}{\sqrt{15}}$$

For mj = $\frac{3}{2}, \frac{1}{2}, \frac{-1}{2}, \frac{-3}{2}$ we have $\cos\theta$ as:

$$\cos\theta = 0.775, 0.258, -0.258, -0.775$$

Therefore, θ = 39.2° , 75.0° , 105° , 140.8°

There are four possible orientations.

2.2 Objectives

After studying this unit, the learners should be able to:

- Understand and explain the concepts of space quantisation, spinning electron and hence visualise vector model of an atom.
- Define various spectroscopic terminology
- Apply L-S coupling and *j-j* coupling schemes on the atoms and hence determine the spectroscopic terms
- Discuss Lande's interval rule and Normal and inverted multiplets
- Apply selection rules while determining the transitions during L-S and *j-j* coupling

2.3 Spectroscopic Terminology

There are few spectroscopic terms associated with the atomic spectra. To understand the coupling criteria and mechanism, the acquaintance with following terms is necessary.

1. *State:*
   It defines the overall motion of the electrons in atoms. Four quantum numbers associated with each electron defines the state of an atom. Ground state has lowest energy. States with same energies are denoted as degenerate states.

2. *Energy Level:*
   It is defined as aggregation of states with same energy, provided external electric or magnetic fields are absent. It is specified by total angular momentum J. The energy level of ground state is minimal.

3. *Sublevel:*
   In the presence of external magnetic or electric field, the energy levels spit into sublevels. These sublevels are specified by different magnetic quantum numbers.

4. *Spectroscopic Term:*
   It is defined as aggregation of levels specified by multiplicity and an orbital angular momentum. For example, ‘^3P’ term is weighed mean of ‘$^3P_0$’, ‘$^3P_1$’ and ‘$^3P_2$’.

5. *Configuration:*
   The electronic configuration of an atom is characterized by quantum numbers n and l associated with the orbitals of the electrons. For example the electronic configuration of ^5B is $1s^2$ $2s^2$ $2p^1$.

6. *Equivalent Orbitals:*
   It is defined as orbital having same value of n and l. The electrons present in these orbitals are known as equivalent electrons.

7. *Statistical Weight:*
   It is defined as the number of states present for a particular J. For a certain specific level, the statistical weight is calculated as 2J+1.

8. *Line Transition:*
   It is defined as transition between two energy two energy levels.

9. *Component:*
   It is defined as transition between two sublevels.

10. *Multiplet Transition:*
    It is defined as aggregation of transitions associated with two terms.

11. *Resonance Line:*
    The transition representing lowest frequency among all the transitions from ground to higher energy levels is known as resonance line.

Let us now consider an atom with N multielectrons and atomic number Z such that $N \leq Z$. The nucleus acquires the charge +Ze. The multielectrons are distributed as completely filled subshells around the nucleus and some as partially filled. The electrons in the outermost shell are optically active, only if it is partially filled. Five following prominent energy terms should be present in the Hamiltonian of the considered atom:

(a) The kinetic energy of the electrons
(b) The electrostatic energy of the electrons

(c) The residual electrostatic energy of the electrons
(d) The spin-spin correlation energy
(e) The spin-orbit interaction energy

In the heavier atoms, the spin-orbit energy term dominates over the other four energy terms and this type of atoms combine in accordance with *j-j* coupling. In the lighter atoms, the residual electrostatic energy of the electrons and the spin-spin correlation energy of electrons show dominance over the other terms and this type of atom combine in accordance with L-S coupling. Let us now discuss L-S and *j-j* couplings individually.

2.4 L-S COUPLING

Apart from the kinetic energy of the electrons and the electrostatic energy of the electrons, the perturbations due to residual electrostatic interaction, spin-spin correlation and spin-orbit correlations are involved in the Hamiltonian of an atom. As the spin-orbit correlations are much weaker compared to residual electrostatic interactions, spin-spin correlations for a lighter atom, the L-S coupling is followed by these atoms. Let us now discuss these two dominant effects independently.

(i) Spin-spin Correlation Effect:

As an effect of spin-spin interaction, a resultant spin angular momentum $\vec{S}$ is obtained due to strong coupling of individual spin angular momentum vectors $\vec{s}$ of individual optical electrons. The magnitude of $\vec{S}$ is $\frac{h}{2\pi}\sqrt{S(S+1)}$ and can have values as

$$\vec{S} = |\overrightarrow{s_1} + \overrightarrow{s_2} + \overrightarrow{s_3} + \ldots\ldots|\text{ min}, |\overrightarrow{s_1} + \overrightarrow{s_2} + \overrightarrow{s_3} + \ldots\ldots|\text{ min+1},(\overrightarrow{s_1}+\overrightarrow{s_2} + \overrightarrow{s_3}+\ldots\ldots)$$

The energies associated with different $\vec{S}$ is also different. The state with lowest energy has highest values of $\vec{S}$. This further indicates that the spin-spin interaction between the individual electrons splits the principal energy level with different values of $\vec{S}$ and multiplicity 2S + 1.

For 1 electron atom:
$S = s = \frac{1}{2}$
Thus, 2S+1 = 2 (Doublet level)

For 2 electron atom:
$s_{1}= 1/2$; $s_{2}= 1/2$
S = $|s_1 - s_2|$, $|s_1 - s_2|$ + 1, ...(s_1 + s_2)
= 0, 1
Thus, 2S+1 = 1 and 3 (Singlet and triplet levels)

For 3 electron atom:

$s_{1=}{}^{1}/_{2}$; $s_{2=}{}^{1}/_{2}$; $s_{3=}{}^{1}/_{2}$

For this evaluation, let us consider S′ as combination of two electrons and then couple with third electron $\left(s_{3=}{}^{1}/_{2}\right)$ individually. We know S′ = 0, 1

For S′ = 0 in combination with $s_{3=}{}^{1}/_{2}$ give $S = 1/2$.

For S′ = 1 in combination with $s_{3=}{}^{1}/_{2}$ give $S = \frac{1}{2}, \frac{3}{2}$.

Therefore, we get S = 1/2, 1/2, 3/2, that is., two sets of doublets and one set of quartets are obtained for three electron atom.

Let us generalize the possible values of S for N number of electrons:

S = 0, 1, 2, ... N (when N is even)
S = 1/2, 3/2, 5/2, ...N/2 (when N is odd)

Previously, it has been stated that the state with highest S has lowest energy. To understand this statement, an atom with two electrons is considered. We have seen that the spin-spin interaction effect splits the unperturbed energy level into singlet and triplet levels. As the total eigen function remains antisymmetric with respect to exchange of electrons, the distance between the two electrons is smaller for singlet state having antiparallel spins. This distance is larger for triplet state with parallel spins. Therefore, in the triplet state the electrostatic repulsion energy (positive) is less compared to singlet state and hence the triplet energy level lies deeper compared to singlet level.

(ii) The residual electrostatic interaction effect:

As an effect of residual electrostatic interaction, a resultant orbital angular momentum $\vec{L}$ is obtained due to strong coupling of individual orbital angular momentum vectors $\vec{l}$ of individual optical electrons. The magnitude of $\vec{L}$ is $\frac{h}{2\pi}\sqrt{L(L+1)}$ and can have values as:

$$\vec{L} = |\vec{l_1} + \vec{l_2} + \vec{l_3} + \ldots\ldots|\ \text{min}, |\vec{l_1} + \vec{l_2} + \vec{l_3} + \ldots\ldots|\ \text{min+1}, (\vec{l_1} + \vec{l_2} + \vec{l_3} + \ldots\ldots)$$

The energies associated with different $\vec{L}$ is also different such that the state associated with lowest energy has highest values of $\vec{L}$. As discussed in the earlier section, the energy levels split due to spin-spin interaction. Similarly, the energy levels also split due to residual electrostatic interaction. However, the separation in the split energy levels due to residual electrostatic interaction is lesser compared to spin-spin interaction. Each splitted energy level carries different values of $\vec{L}$.

For $\vec{L} = 0, 1, 2, 3, 4, \ldots$.... the associated levels are designated as S, P, D, F, G, ...

Let us evaluate for:

For 3p3d electrons:
$l_1 = 1\ ;\ l_2 = 2$
S = $|l_1 - l_2|$, $|l_1 - l_2|$ + 1, ….. (l_1 + l_2)
= 1, 2, 3 (For P, D and F states)

For 2p3p4d electrons:
For this evaluation, the two p electrons will be combined first (L′) as they are not tightly bound.

$l_1 = 1\ ;\ l_2 = 2$
Thus L′ = 0, 1, 2

Now let us combine with d electron ($l_3 = 3$) individually
L′ = 0 ; $l_3 = 2$
Thus L = 2 (D state)
L′=1 ; $l_3 = 2$
Thus L = 1, 2, 3 (P, D and F states)
L′=2 ; $l_3 = 2$
Thus L = 0, 1, 2, 3, 4 (S, P, D F and G states)

Therefore, overall we get one S, two P’s, three D’s, two F’s and one G state.

Earlier in this section, it is been mentioned that the state with lowest energy has largest value of L. The coulomb repulsion between two electrons is minimal at maximum distance. Thus, the electrostatic repulsion is least when the electrons are present at the opposite ends of a diameter of an orbit. In this condition, electrons revolve in same direction around the nucleus and their individual orbital angular moments are in parallel direction. From exchange symmetry of wave functions, it is very well known that the antisymmetric eigen function corresponds to parallel direction of two electrons. Thus, state with higher L, is associated with antisymmetric total wave function carries lower energy.

(iii) Spin- Orbit interaction effect:
As the spin-orbit interactions is weaker compared spin-spin interaction and residual electrostatic interaction, the spin angular moments and orbital angular moments couple individually first to resultant $\vec{S}$ and $\vec{L}$ respectively. Thereafter, the resultant spin angular momentum $\vec{S}$ and the resultant orbital angular moment $\vec{L}$ combine with each other to form resultant total angular moment $\vec{J}$ of the atom.
$\vec{J} = \vec{L} + \vec{S}$

The magnitude of $\vec{J}$ is $\frac{h}{2\pi}\sqrt{J(J+1)}$ and quantum number $\vec{J}$ has values as:

$$\vec{J} = \left|\vec{L} + \vec{S}\right|, \left|\vec{L} - \vec{S}\right| + 1, \ldots\ldots.(\vec{L} + \vec{S})$$

The number of J values are determined as (2S + 1) when L>S and (2L+1) when S>L. If S is integral value, J also has integral value and if S is half integral value, J also has half integral value. This further indicates that the splitting due to spin-orbit interaction is comparatively less spaced than splitting due to spin-spin interaction and residual interaction. These levels are characterised by quantum number J which has degeneracy (2J+1). The collection of these J levels form 'fine structure multiplet'. Further, the spacing between these multiplets is defined by *Lande Interval Rule.*

2.4.1 Lande Interval Rule

The spin-orbit interaction energy for the atoms obeying L-S coupling is given by:

$\Delta E_{l,s} = a(\vec{L} + \vec{S}),$
where 'a' is known as interaction energy constant.

We know that
$\vec{J} = \vec{L} + \vec{S},$

Let's take self-scalar product of above equation

$$\vec{J}.\vec{J} = \overrightarrow{(L + S)}.(\vec{L} + \vec{S})$$
$$\vec{J}.\vec{J} = \overrightarrow{L}.\overrightarrow{L} + \overrightarrow{S}.\overrightarrow{S} + 2\overrightarrow{L}.\overrightarrow{S}$$
$$2\overrightarrow{L}.\overrightarrow{S} = [|\vec{J}|^2 - |\vec{L}|^2 - |\vec{S}|^2]$$
$$\overrightarrow{L}.\overrightarrow{S} = \frac{1}{2}[|\vec{J}|^2 - |\vec{L}|^2 - |\vec{S}|^2]$$

Thus, $\Delta E_{l,s} = \frac{a}{2}[|\vec{J}|^2 - |\vec{L}|^2 - |\vec{S}|^2]$

$\Delta E_{l,s} = \frac{a}{2}[J(J+1) - L(L+1) - S(S+1)]\ h^2/4\pi^2$
{ As $\vec{J} = \sqrt{J(J+1)}h/2\pi$; $\vec{L} = \sqrt{L(L+1)}h/2\pi$ and $\vec{S} = \sqrt{S(S+1)}h/2\pi$ }

Thus, $\Delta E_{l,s} = A[J(J+1) - L(L+1) - S(S+1)]$
where $A = ah^2/8\pi^2$ (another constant).

As L-S coupling multiplet has same values of L and S for fine structure levels and only differs in values of j. Therefore, the energy difference for the fine structure levels having J as one level and J+1 for another level is given as:

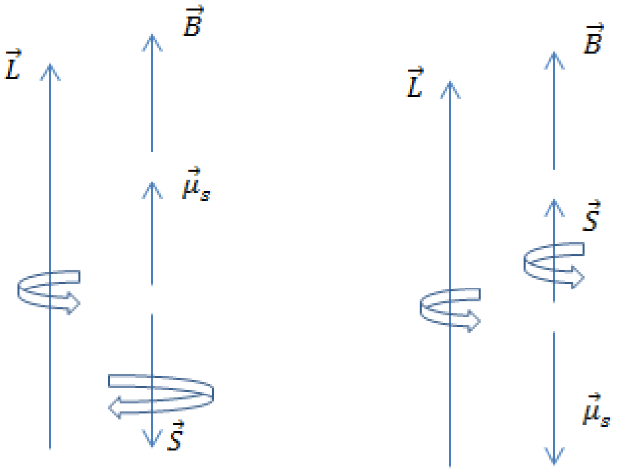
$$E_{J+1} - E_J = A[J(J+1)(J+2) - J(J+1)]$$

$$E_{J+1} - E_J = 2A[J+1]$$

This shows that the energy difference is proportional to the term (J+1). Larger the value of J, greater will be the energy difference and consequently larger spacing.

2.4.2 Normal and Inverted Multiplets

Generally, the lowest lying level in a multiplet carries lowest value of J. These types of multiplets are known as normal multiplets. However, the multiplets in which the lowest lying level is designated with highest value of J are known as inverted mutiplets.
The normal multiplets are stable in nature. The orbital angular momentum$\vec{L}$ and the magnetic field $\vec{B}$ caused by the motion of electrons in orbit (under the influence of nucleus) in same direction. In such a situation the spin magnetic moment $\vec{\mu}_s$ of the electron lies in the same direction as that of $\vec{B}$. This builds up a stable state as illustrated in fig. 5. As the electron is negatively charged $\vec{\mu}_s$ is in opposite direction to $\vec{S}$. Therefore, $\vec{L}$ and $\vec{S}$are in opposite directions and hence attain lowest energy as well as the lowest value of $\vec{J}$. In this condition $\vec{\mu}_s$ points opposite to $\vec{B}$, corresponding to inverted multiplet (least stable). Some perturbing influences give rise to inverted multiplets.



Normal Multiplet

Inverted Multiplet

Fig. 5 Orientations of $\vec{\mu}_s$, $\vec{B}$, $\vec{S}$ and $\vec{L}$ in normal and inverted multiplets

Solved Example 3:

Question: The energy levels with increasing energy in a multiplet are separated with 3:5 ratio for line spectrum of an arbitrary atom. Designate S, L and J quantum numbers to these levels via using Lande's interval rule.

Solution: Let us consider a normal mutiplet in accordance with the energies associated with a level, the lowest energy is designated with J and the consecutive higher levels are designated with J+1 and J+2 respectively. Then the energy (E) of of the levels with J+1 and J+2 level is 5/3 E. According to Lande interval rule, the energy interval of consecutive levels for a given multiplet is directly proportional to the J value of the upper level

$$E = 2A\,(J+1)$$

$$\frac{5}{3} = 2A\,(J+2)$$

By dividing the above two equations, we get

$$\frac{3}{5} = \frac{J+1}{J+2}$$

3(J + 2) = 5(J + 1)

3J + 6 = 5J + 5

2J= 1

J= $\frac{1}{2}$

The values of J with increasing energy levels are given as – J = $\frac{1}{2}$; $\frac{3}{2}$; $\frac{5}{2}$.

We also know,

$$\vec{J} = \left|\vec{L} + \vec{S}\right|, \left|\vec{L} - \vec{S}\right| + 1, \dots\dots.(\vec{L} + \vec{S})$$

The maximum and minimum values of J are $\frac{5}{2}$ and $\frac{1}{2}$ respectively.

$$\left|\vec{L} - \vec{S}\right| = \frac{1}{2}$$

$$\left|\vec{L} + \vec{S}\right| = \frac{5}{2}$$

If L> S

L-S = $\frac{1}{2}$

L+S = $\frac{5}{2}$

Subtraction and addition gives

L = $\frac{3}{2}$ and S = 1

But L cannot be half – integral, therefore S < L, then

S – L = $\frac{1}{2}$

S + L = $\frac{5}{2}$

Subtraction and addition gives,

S = $\frac{3}{2}$ and L= 1

2.4.3 Determination of Spectral Terms

Only the optical electrons present in the atoms are useful for the determination of spectral terms of L-S coupling. This is because the core electrons present in the atom do not contribute in the determination of angular momentum.

The odd or even spectral terms are determined by the electronic configuration. The odd electronic configuration results into odd spectral terms and even spectral term is associated with the even electronic configuration. The even or odd electronic configuration is further determined by l's of optical electrons. If the summation of l's (Σl) is odd, then the electronic configuration is odd and if the Σl is even then the electronic configuration is also even. The superscript °, is written after L symbol for only odd spectral term. Let us understand this statement with an example. A term '^{3}P' arising from an odd electronic configuration is written as '^{3}P°' and '^{3}P' arising from an even electronic configuration 2p 3p is simply written as '^{3}P'. Now we would determine the spectral terms of the atoms under below given three categories:

(a) *One optical electron atoms:*

Let us compute the spectral term for atoms with one optical electron such as hydrogen like atom. The ground state electronic configuration of hydrogen like atom is given as 1s

And for this configuration $= 1/2$; $l = 0$

Such that $S = s = 1/2$ and the multiplicity ⇒ 2S+1 = 2

$L = l = 0$ (S State)

$\vec{J} = \ |\vec{L} + \vec{S}|, |\vec{L} - \vec{S}| + 1, \dots\dots (\vec{L} + \vec{S}) = \ 1/2$

Hence, the spectral term for the ground state hydrogen like atom would be: $\boldsymbol{2S_{1/2}}$.

Let us now determine the spectral terms for the excited states of hydrogen like atoms:

2s,3s, 4s.........................$^2\boldsymbol{S}_{\boldsymbol{1/2}}$

2p, 3p, 4p.......................$^2\boldsymbol{P}^{\circ}{}_{\boldsymbol{1/2}}$, $^2\boldsymbol{P}^{\circ}{}_{\boldsymbol{3/2}}$

3d, 4d.............................$^2\boldsymbol{D}_{3/2}$, $^2\boldsymbol{D}_{5/2}$

Now, we would compute the spectral terms for alkali atoms. For this, let us consider Lithium (Li) as alkali atom, having electronic configuration as $1s^22s$.
The spectral term would be $^2\boldsymbol{S}_{1/2}$.

(b) Two or More Non-Equivalent optical electron atoms:

We would now compute the spectral term for an atom having two non-equivalent electrons in its outer shell, having an electronic configuration: 4p4d

For the above configuration

$s_{1=}\,1/2$; $s_{2=}\,1/2$; $l_1 = 1$; $l_2 = 1$

Thus, S =0,1 and multiplicity (2S+1) = 1, 3
L = 1, 2, 3 (P, D, F states)

Therefore, we have a total of six terms – three singlet and three triplet terms.
All these terms arise from odd electronic configuration – 4p4d and this configuration has $\Sigma l = 1+2 = 3$

The spectral terms associated with above configuration are:
$^1P^\circ$, $^1D^\circ$, $^1F^\circ$, $^3P^\circ$, $^3D^\circ$, $^3F^\circ$

Let us now evaluate J
$\vec{J} = |\vec{L} + \vec{S}|, |\vec{L} - \vec{S}| + 1, \ldots\ldots(\vec{L} + \vec{S})$

For Singlet terms we have,
$S = 0\,; L = 1\ gives\ J = 1 \Rightarrow\ ^1P_1^\circ$
$S = 0\,; L = 2\ gives\ J = 2 \Rightarrow\ ^1D_2^\circ$
$S = 0\,; L = 3\ gives\ J = 3 \Rightarrow\ ^1F_3^\circ$

For triplet terms, we have
$S = 1\,; L = 1\ gives\ J = 0, 1, 2 \Rightarrow\ ^3P_0^\circ,\ ^3P_1^\circ,\ ^3P_2^\circ$
$S = 1\,; L = 2\ gives\ J = 1, 2, 3 \Rightarrow\ ^3D_1^\circ,\ ^3D_2^\circ,\ ^3D_3^\circ$
$S = 1\,; L = 3\ gives\ J = 2, 3, 4 \Rightarrow\ ^3F_2^\circ,\ ^3F_3^\circ,\ ^3F_4^\circ$

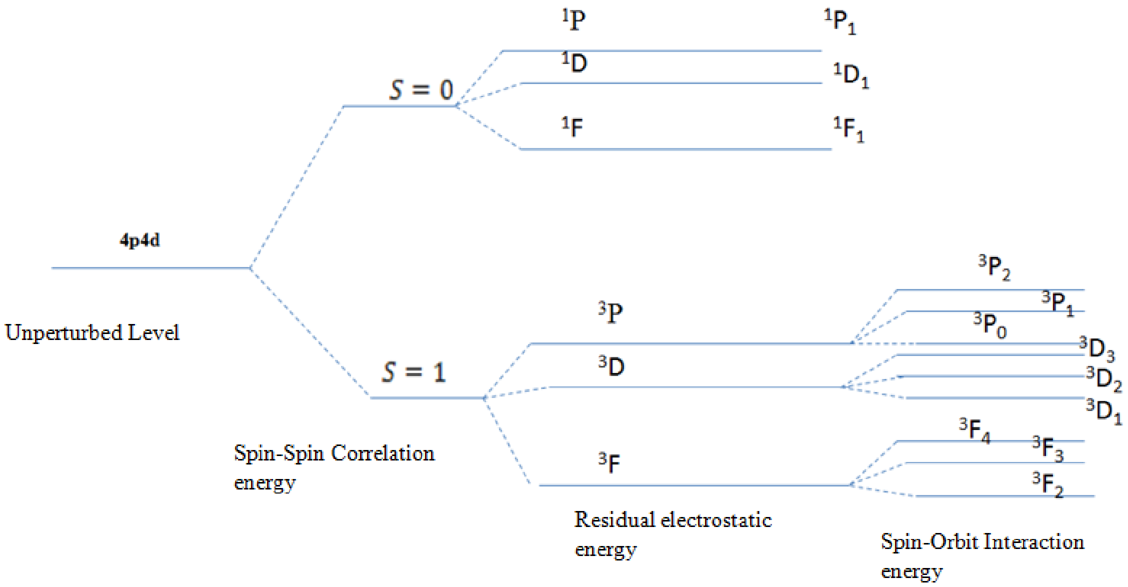


Fig. 6 Splitting of 4p4d level under L-S coupling scheme

This indicates that the single level representing the configuration 4p4d splits into 12 levels as shown in the fig. 6. The spin-spin interaction splits it into singlet (S = 0) and triplet (S = 1) levels. As shown in the figure, the triplet state lies lower to the singlet state owing to higher multiplicity. The residual electrostatic interaction further splits the two levels into three levels namely; P, D and F levels. Here also the F level lies at the lowest owing to highest l value. Now, due to spin orbit interaction, the triplet state is further split up into three fine-structure levels characterised by different J values. The spacing between these levels is determined by *Lande Interval Rule*, such that the levels with lowest J lie at the lowest for a given normal multiplet. Furthermore, each J level is 2J+1 fold degenerate. Henceforth, a total of 60 degenerate levels can be obtained for a level representing 4p4d electronic configuration.

Let us now evaluate for three non-equivalent optical electrons. For this, the spins of two electrons are first combined then the third spin is combined. Similarly, the orbital angular momentum of two electrons that are more closely bound is combined first and thereafter the third electron's orbital angular momentum is combined. The electronic configuration under consideration is 3d4s5p (Σl = 3; odd configuration)

Let's combine the spins first

$s_{1}= {}^{1}/_{2}$; $s_{2}= {}^{1}/_{2}$; $s_{3}= {}^{1}/_{2}$

Lets combine $s_{1}= {}^{1}/_{2}$ and $s_{2}= {}^{1}/_{2}$ first to get S′ = 0, 1. Then, $s_{3}= {}^{1}/_{2}$ is combined with S′ to get values as S = 1/2, 1/2, 3/2. Subsequently, the multiplicities 2S + 1 are 2, 2 and 4. These states correspond to two sets of ′doublets′ and one set ‘quartet’.

Let us now combine orbital angular moments

Consider 3d and 4s first

$l_1 = 2$; $l_2 = 0$

Thus, L′ = 2

Now combine the *l* for 5p electron ($l_3 = 1$).

Therefore, L = 1, 2,3 (P, D, F states)

Hence, there exists two sets of three doublets terms and one set of three quartet terms. The spectral terms are:

$^2P^\circ$, $^2D^\circ$, $^2F^\circ$, $^2P^\circ$, $^2D^\circ$, $^2F^\circ$, $^4P^\circ$, $^4D^\circ$, $^4F^\circ$ that is $^2P^\circ(2)$, $^2D^\circ(2)$, $^2F^\circ(2)$, $^4P^\circ$, $^4D^\circ$, $^4F^\circ$

By inculcating the spin orbit interaction, we get now:

$^2P^\circ_{1/2,\ 3/2}(2)$; $^2D^\circ_{3/2,\ 5/2}(2)$; $^2F^\circ_{5/2,\ 7/2}(2)$, $^2P^\circ_{1/2,\ 3/2,\ 5/2}$, $^4D^\circ_{1/2,\ 3/2,\ 5/2,\ 7/2}$, $^4F^\circ_{3/2,\ 5/2,\ 7/2,\ 9/2}$

A total of 23 levels are obtained.

(c) Two or more equivalent optical electron atoms:

The quantum numbers n and *l* are same for two equivalent electrons. To satisfy Pauli's exclusion principle, m_l and m_s (remaining quantum numbers) differ. Due to equivalence, certain spectral terms are not allowed. Let us understand this with example of two non equivalent and equivalent *p* electrons.

Non equivalent - 2p and 3p give rise to ^1S, ^1P, ^1D, ^3S, ^3P, ^3D

Equivalent – $2p^2$ gives rise to ^1S, ^1D and ^3P spectral terms respectively. Thus, ^3D, ^3S and ^1P are missing.

To determine the spectral terms for equivalent electrons, following points should be kept in mind:

1. $^1S_0$ term is always formed for closed sub-shell (S^2, p^6, d^{10}, ...)

   The maximum number of equivalent electrons in a closed sub-shell is 2(2*l* + 1). These exist in antiparallel pairs. These electrons have:

   $\Sigma m_{l} = 0$; $\Sigma m_{s} = 0$

   And hence $M_L = 0$; $M_S = 0$

   Correspondingly, L = 0 (S State)

   S = 0 and the multiplicity 2S + 1 = 1 (Singlet State)

   J = 0

   These above values are satisfied only for the term $^1S_0$. This suggests that the total spin and the angular momentums are zero for completely filled sub shell.

2. The electronic configuration $(nl)^q$ and $(nl)^{r-q}$ have same spectral terms. The symbol 'r' represents maximum number electrons present in a shell (2(2*l* + 1)) and 'q' being even

integral number. This implies that the electronic configurations like p^5 and p^1; d^8 and d^2 will have same spectral terms.

Let us now consider two equivalent *p* electrons (p^2) and evaluate its spectral term. For this we would place the atom under very strong magnetic field so that all the internal couplings are broken and individual $\vec{l}$ and $\vec{s}$ vectors exist. For a *p* electron $l = 1$, $m_l = -1, 0, 1$ and $m_s = 1/2, -1/2$. Therefore, m_l and m_s can possibly combine in following ways:

m_l	=	1	0	-1	1	0	-1
m_s	=	1/2	½	½	-1/2	-1/2	-1/2
		(a)	*(b)*	*(c)*	*(d)*	*(e)*	*(f)*

Thus, there exists six possible ways (*a, b, c, d, e, f)* of configuration. The above six combinations are for single p electrons. This can be done by taking these six ways twice at a time. However, m_l and m_s cannot be same for two equivalent electrons due to Pauli's exclusion principle. Such a type of combination allows fifteen possible ways (${}^6C_2 = 6!/2!(6-2)! = 15$)

The possible combinations are given as follows:

ab	ac	ad	ae	af;
	bc	bd	be	bf;
		cd	ce	cf;
			de	df;
				ef;

Under strong field two m_l and m_s values combine individually to form M_L and M_S respectively. Therefore, the following M_L and M_S are obtained.

m_{l_1}	=	1	0	-1	
M_L	=	2	1	0	1
M_L	=	1	0	-1	0
M_L	=	0	-1	-2	-1
		S	P	D	m_{l_2}

From the table, it is noticed that M_L can take values 2, 1 and 0.

(i) For $M_L = 2$; L = 2 (D State) and for Ms = 0
The spectral term as ${}^1D$ (S = 0)
Apart from $M_L = 2$, M_L has values -2, -1, 0, 1 and with $M_S = 0$ gives
The spectral term as ${}^1D$
Therefore the ${}^1D$ term abides with following combinations:

Combinations	ad	ae	af	bf	cf	
M_L	2	1	0	-1	-2	^1D
M_S	0	0	0	0	0	

(ii) For $M_L = 1$ and $M_S = 1$

The spectral term is ^3P (L = 1, S = 1)

For $M_L = 1, 0, -1$; L = 1(P State) and $M_S = 1$

The spectral term is ^3P and the combinations are

Combinations	ab	ac	bc	bd	cd	ce	de	df	ef	
M_L	1	0	-1	1	0	-1	1	0	-1	^3P
M_S	1	1	1	0	0	0	-1	-1	-1	

(i) For $M_L = 0$ and $M_S = 0$

Only one combination is justified and the spectral term is ^1S (L = 0, S = 0)

Combinations	bc	
M_L	0	^1S
M_S	0	

Therefore the spectral terms for two equivalent p electrons are ^1D, ^3P, ^1S. Henceforth, the fine structure levels are $^1D_2$, $^3P_{0,1,2}$, $^1S_0$.

The above exercise is bit cumbersome. These spectral terms can be evaluated by using ***Breit's Scheme.*** Under this scheme, a table as shown below is written bearing all possible values of M_L. The M_L values are evaluated by combining m_{l_1} and m_{l_2} values of two electrons respectively. The m_{l_1} and m_{l_2} values are written in row and column respectively. The summation of M_L are noted below m_{l_1} and towards the left of m_{l_2}. As shown in the table below, there exists three sets of nine M_L values in L shaped (dotted) lines. These sets are

2	1	0	-1	-2	*(i set)*
	1	0	-1		(*ii set)*
		0			(*iii set)*

For the above M_L values, the corresponding L = 2, 1 and 0 gives one D, P and S term.

Singlet (S = 0) or triplet (S = 1) are obtained by combing the spins of two electrons. The spin quantum number m_s of the electrons is same for the triplet state and hence to satisfy the Pauli's exclusion principle m_l should differ. Therefore, M_L values placed on the diagonal cannot be combined (m_{l_1} and m_{l_2} values are same at the diagonal). Thus, for S = 1, the M_L values are 1,0,-1 *(ii set)* and the corresponding term ^3P or $^3P_{0,1,2}$ fine - structure multiplet.

Let's discuss for Singlet state (S = 0) now. The spin quantum number m_s differ and hence any value of M_L is allowed. As the M_L values corresponding to set *ii* have been designated for term ^3P, the remaining sets *i* and *iii* are combined for Singlet state. Thus, the spectral terms obtained are $^1D_2$ and $^1S_0$.

Therefore, the two equivalent *p* electrons give the following spectral terms: $^1S_0$, $^1D_2$, $^3P_{0,\,1,\,2}$. The p^4 will also have same terms.

Let us repeat the above exercise for two d electrons which has electronic configuration $(nd)^2$. Write the Breit's scheme for the M_L values.

m_{l_1}	=	2	1	0	-1	-2	
M_L	=	4	3	2	1	0	2
M_L	=	3	2	1	0	-1	1
M_L	=	2	1	0	-1	-2	0
M_L	=	1	0	-1	-2	-3	-1
M_L	=	0	-1	-2	-3	-4	-2
		S	P	D	F	G	m_{l_2}

The above table deduces five sets of M_L values:

4	3	2	1	0	-1	-2	-3	-4	*i set*
	3	2	1	0	-1	-2	-3		*ii set*
		2	1	0	-1	-2			*iii set*
			1	0	-1				*iv set*
				0					*v set*

These L values = 0, 1, 2, 3, 4 (*set v, iv, iii, ii, i*) correspond to S, P, D, F, G respectively.

For the Triplet state (S = 1). As discussed in the above example (p^2 configuration) here only diagonal M_L values are not taken into consideration. Therefore, the limited M_L values are:

3	2	1	0	-1	-2	-3	*ii set*
		1	0	-1			*iv set*

For above M_L values; L = 3 and 1 which give 3F and 3P terms or $^3F_{2,\,3,\,4}$ and $^3P_{0,1,2}$ fine-structure multiplets respectively.

For Singlet state (S = 0); the M_L values of left out sets, that is *i, iii* and *v* are combined and term ^1G, ^1D and ^1S are obtained.

Therefore, the term values of two d electron are: $^1S_0$, $^1D_2$, $^1G_4$, $^3P_{0,1,2}$, $^3F_{2,3,4}$.

d^8 configuration will also have same spectral terms as stated above.

2.4.4 Selection Rules in L-S Coupling:

The atoms in which L-S coupling is applicable abide by following selection rules:

1. When an electron jumps to make one transition at a time then *l* value should change by one unit. That is $\Delta l = \pm 1$.

   The above selection rule follows 'Laporte Rule'. The Laporte rule states that in an electric – dipole transition, the parity of the electronic configuration must change and hence the Σl must change by an odd number for one electron atom. If two electrons are involved in a transition simultaneously then Δl will be odd for one electron and even for second electron. That is $\Delta l_1 = \pm 1$; $\Delta l_2 = 0,2$.
2. The total quantum number, n can take up any values.
3. For a complete atom, the L, S and J must follow:

   $\Delta L = 0, \pm 1$ ($\Delta L = 0$ is not allowed for one electron atom)

   $\Delta S = 0$

   $\Delta J = 0, \pm 1$ but for $J = 0 \not\leftrightarrow J = 0$

When the coupling between the spin and orbit is weak, L-S coupling holds good. The spacing between the fine-structure levels for a given multiplet is much less compared to spacings between different multiplets itself. This happens only in lighter atoms, thus the L-S coupling holds good. This we saw in case of He (Unit I, Section 1.7) that there was no inter combination between singlet and triplet state. As the atoms become heavier, the spin-orbit interaction starts predominating and hence the L-S coupling breaks up. This gives rise to j-j coupling in heavier atoms.

Solved Example No 4:

Question: The separation, between the adjacent components for a normal triplet state is $20 cm^{-1}$ and $40 cm^{-1}$ respectively for an atom following L-S coupling. The separations for higher states are $22 cm^{-1}$ and $33 cm^{-1}$ respectively. Evaluate the terms for the two states and draw energy level diagrams for the allowed transitions.

Solution: The quantum numbers J, J+1 and J+2 are associated with lowest for normal triplet state. By applying Lande's interval rule, we get,

$$\frac{J+1}{J+2} = \frac{20}{40}$$

This gives J=0,

Therefore, J=0, 1, 2 (in increasing energy order)

We know J=|L-S|, |L-S|+1,…., |L+S|. The minimum and maximum value of J is 0 and 2, respectively.

|L-S|=0,

(L+S)=2

If L>S, then L-S=0 and L+S=2

This gives S=1, so that 2S+1=3

L=1 (p state)

This gives the term ${}^3P_0$, ${}^3P_1$, ${}^3P_2$.

Let us evaluate for higher states,

$$\frac{J+1}{J+2}=\frac{22}{33}$$

This gives J=1,

Therefore, J= 1, 2,3, … (in increasing energy order)

Since J=|L-S|, |L-S|+1,…., |L+S|. The minimum and maximum value of J is 0 and 2, respectively.

|L-S|=1,

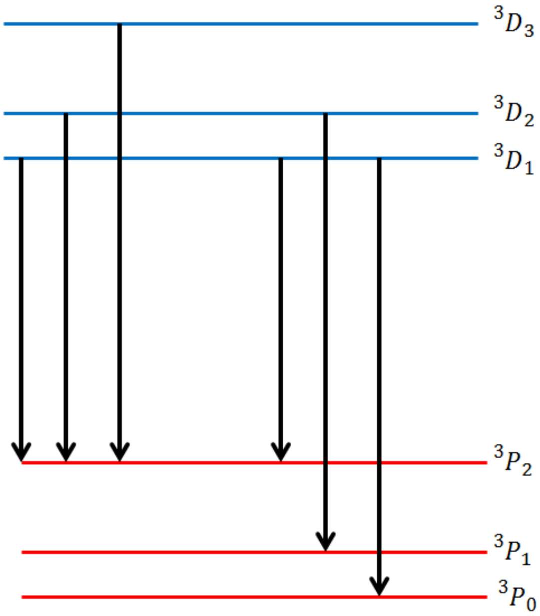
(L+S)=3

This gives S=1, so that 2S+1=3

L=2 (D state)

This gives the term ${}^3D_1$, ${}^3D_2$, ${}^3D_3$

By applying selection rule ΔJ=0, ±1



This gives a total of six transitions as shown in figure above.

2.5 *j-j* Coupling

In heavier atoms, the magnetic spin-orbit interaction factor present in the Hamiltonian, dominates over the spin-spin interaction and residual electrostatic interaction. This dominance results into *j-j* coupling. This spin-orbit interaction dominance also implies that the interaction between spin and orbit for a single electron is strongly coupled compared to spin momentum coupling and orbital momentum coupling in the individual electrons. Therefore, the splitting of the unperturbed energy level is more affected by spin-orbit interactions compared to spin-spin interactions and residual electrostatic interactions.

The resultant angular momentum j of magnitude $\sqrt{j(j+1)}h/2\pi$ is obtained due to strong coupling between spin and orbital angular momentums of individual electrons. The quantum number j takes vales from $j = l - 1/2$ to $j = l + 1/2$ (half integral values only). This implies that the well spaced split energy levels are obtained due to strong spin- orbit interaction. Each of these energy levels correspond to different j values such that $j = l - 1/2$ be lowest and $j = l + 1/2$ be highest.

Thereafter, this j of individual electrons combine due to residual electrostatic and spin-spin interaction with each other. The resultant total angular momentum $\vec{J}$ of an atom vary from $\vec{J} = |\vec{j_1} + \vec{j_2} + \vec{j_3} + \ldots\ldots|$ min, $|\vec{j_1} + \vec{j_2} + \vec{j_3} + \ldots\ldots|$ min+1,$(\vec{j_1}+\vec{j_2}+\vec{j_3}+\ldots\ldots)$ and magnitude as $\vec{J} = \sqrt{J(J+1)}h/2\pi$.

Let us understand the j-j splitting illustratively by considering the level having electronic configuration as 4p4d (fig. 7), For the p – electrons: $l_1 = 1$; $s_1 = \frac{1}{2}$; $l_1 = \frac{1}{2}, \frac{3}{2}$

For the d – electrons: $l_1 = 2$; $s_2 = \frac{1}{2}$; $j_1 = \frac{3}{2}, \frac{5}{2}$

The above values of j_1 and j_2 may possibly combine in following ways:

(1/2,3/2); (1/2,5/2); (3/2,3/2); (5/2,5/2)

Thus the j-j coupling splits the energy levels into four ways such that (1/2,3/2) is the lowest and (3/2,5/2) is the highest level. These levels further combine to give:

(1/2,3/2)$\Rightarrow$ J = 1, 2

(1/2,5/2)$\Rightarrow$ J = 2,3

(3/2,3/2)$\Rightarrow$ J = 0,1,2,3

(3/2,5/2)$\Rightarrow$ J = 0,1,2,3

It is relatively quite seldom to find pure j-j coupling. As atoms transit from being lighter to heavier there is a gradual shift from L-S to j-j coupling.

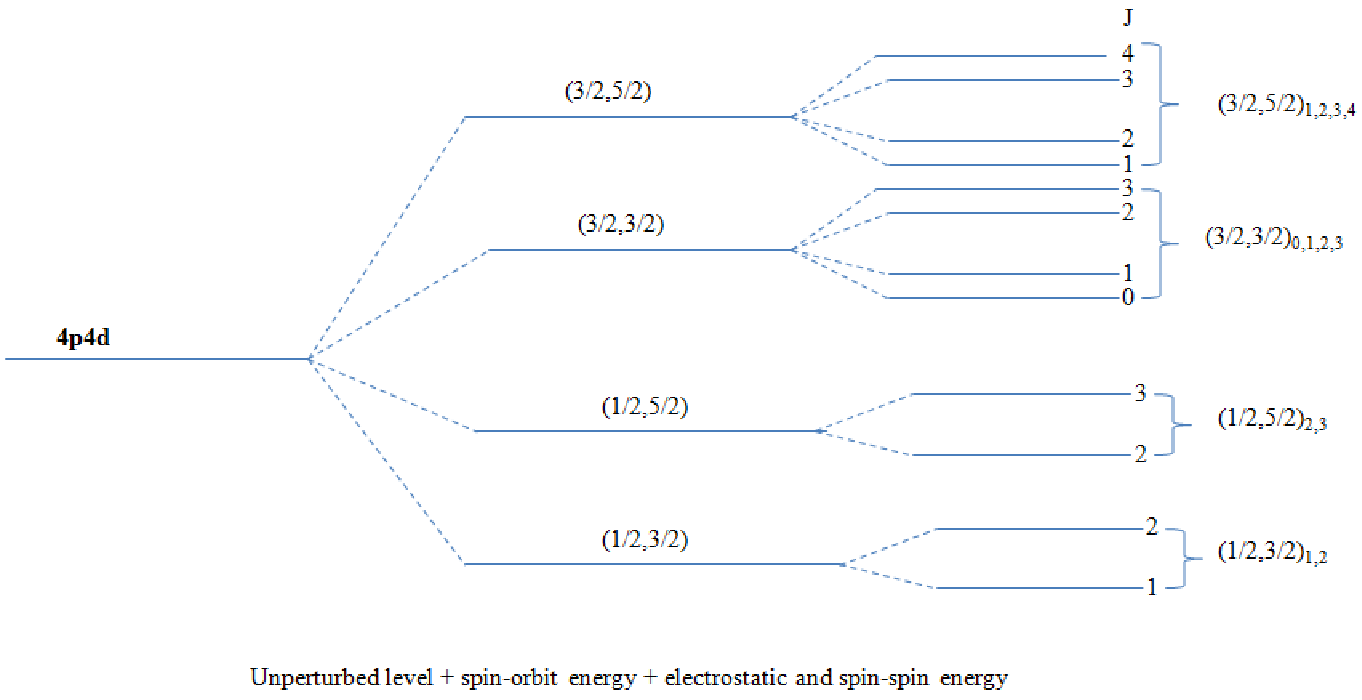


Fig. 7 Splitting of 4p4d level under *j-j* coupling scheme

2.5.1 Selection Rules in *j-j* Coupling

The atoms in which j-j coupling is applicable abide by following selection rules:

1. The selection rule follows 'Laporte Rule'. The Laporte rule states that in an electric -dipole transition, the parity of the electronic configuration must change and hence the Σl must change by an odd number for one electron atom. If two electrons are involved in a transition simultaneously then Δl will be odd for one electron and even for second electron. That is $\Delta l_1 = \pm 1$; $\Delta l_2 = 0{,}2$. This rule is same as for L-S coupling.
2. When an electron jumps to make one transition at a time then j value should follow $\Delta j = 0, \pm 1$ and for other electrons $\Delta j = 0$
3. For a complete atom, the J must follow:
   $\Delta L = 0, \pm 1$ but for J = 0 $\not\leftrightarrow$ J = 0
   $\Delta S = 0$ and $\Delta L = 0, \pm 1$ do not hold good for j-j coupling.

Solved Example 5:

Question: Two optically active electrons in two- valance electrons are associated with following quantum numbers as:

$n_1 = 6,\ l_1 = 3,\ s_1 = \frac{1}{2}$

$n_2 = 5,\ l_2 = 1,\ s_2 = \frac{1}{2}$

(a) Obeying the L-S coupling scheme, evaluate the possible values of L, S and J.
(b) Obeying the *j-j* coupling scheme, evaluate the possible values of J.

Solution: (a) Given Data:

$l_1 = 3,\ l_2 = 1$
Therefore, $L = |l_1 - l_2|, |l_1 - l_2| + 1,$ ----------------- $|l_1 + l_2|$
L= 2, 3, 4
$s_1 = \frac{1}{2}$; $s_2 = \frac{1}{2}$
Therefore, $S = |s_1 - s_2|, |s_1 - s_2| + 1,$ ----------------- $|s_1 + s_2|$
S = 0, 1
Therefore, J values are J $= |L - S|$, -----------------------$|L + S|$
For S = 0 and L = 2, 3, 4 the values of J = 2, 3, 4
For S = 1 and L = 2, 3, 4 the values of J = 1, 2, 3; 2, 3, 4 and 3, 4, 5

(b) Given Data:

For n_1, $l_1 = 3$, $s_1 = \frac{1}{2}$
Therefore, $j_1 = |l_1 - s_1|, |l_1 - s_1| + 1,$ ----------------- $|l_1 + s_1|$

$= \frac{5}{2}, \frac{7}{2}$

For n_2 , l_2 = 1, $s_2 = \frac{1}{2}$

Therefore, $j_2 = \frac{1}{2}, \frac{3}{2}$

This gives four combinations of j_1 and j_2 as:

$\left(\frac{1}{2}, \frac{5}{2}\right)$; $\left(\frac{1}{2}, \frac{7}{2}\right)$; $\left(\frac{3}{2}, \frac{5}{2}\right)$; $\left(\frac{3}{2}, \frac{7}{2}\right)$

These combinations give J values as follows:

$\left(\frac{1}{2}, \frac{5}{2}\right)$ Gives J = 2, 3

$\left(\frac{1}{2}, \frac{7}{2}\right)$ Gives J = 3 ,4

$\left(\frac{3}{2}, \frac{5}{2}\right)$ Gives J = 1, 2, 3, 4

$\left(\frac{3}{2}, \frac{7}{2}\right)$ Gives J = 2, 3, 4, 5

There are a total of 12 in number J values.

2.6 Summary

As the Bohr-Sommerfeld model became incapable of explaining the fine structure splitting, Zeeman effect, Paschen-Back effect, Stark effect etc.,. The, evolution of vector model of an atom seeded the concept of space quantization and spinning electrons. This further explained the splitting due to various interaction energies - the kinetic energy of the electrons, the electrostatic energy of the electrons, residual electrostatic interaction, spin-spin correlation and spin-orbit correlations that are involved in the Hamiltonian of an atom. This gave rise to splitting due to various coupling schemes namely L-S and *j-j* coupling. In the heavier atoms, the spin-orbit energy term dominates over the other interaction energy terms and this type of atoms combine in accordance with *j-j* coupling. In the lighter atoms, the residual electrostatic energy of the electrons and the spin-spin correlation energy of electrons show dominance over the other terms and this type of atom combine in accordance with L-S coupling.

As the spin-orbit interactions is weaker in L-S coupling, compared spin-spin interaction and residual electrostatic interaction, the spin angular moments and orbital angular moments couple individually first to resultant $\vec{S}$ and $\vec{L}$ respectively. Thereafter, the resultant spin angular momentum $\vec{S}$ and the resultant orbital angular moment $\vec{L}$ combine with each other to form resultant total angular moment $\vec{J}$ of the atom.

In heavier atoms, the magnetic spin-orbit interaction factor present in the Hamiltonian, dominates over the spin-spin interaction and residual electrostatic interaction. This dominance results into *j-j* coupling. This spin-orbit interaction dominance also implies that the interaction between spin and orbit for a single electron is strongly coupled compared to spin momentum coupling and orbital momentum coupling in the individual electrons. Therefore, the splitting of the unperturbed energy level is more affected by spin-orbit interactions compared to spin-spin interactions and residual electrostatic interactions.

The spectroscopic terms are further determined as per these coupling schemes and the allowed transitions follow the selection rules governed by these coupling schemes.

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2.8 Suggested Readings

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2.9 Terminal Descriptive type questions

Q-1. Discuss different types of coupling schemes in atoms with the help of illustrative examples.

Q-2. What do you understand by L-S coupling? Discuss various interaction energy terms involved in L-S coupling of an atom.

Q-3. Consider two-valance electron atom. Apply L-S and j-j coupling on this atom and prove that the numbers of terms are same under both the coupling schemes for ps electronic configuration.

Q-4. Differentiate between L-S and j-j coupling. Give examples to support your answer.

Q-5. Explain the concept of equivalent and non-equivalent electrons with the help of examples.

Q-6. Discuss vector model of an atom.

Q-7. Deduce an expression for magnetic dipole moment for a hydrogen atom. Also evaluate Bohr magneton.

Q-8. Discuss Lande's interval rule for L-S coupling.

Q-9. State various selection rules for j-j and L-S coupling schemes. Consider an oxygen atom and apply the selection rules to find the allow transitions from ^1D and ^1S terms.

Q-10. What is the condition of the atoms that L-S coupling transits into j-j coupling? Explain with the help of examples.

2.10 Numerical type (Self Assessment questions)

Q-1. Consider an electronic configuration$1s^2 2s^2 2p^1$. Evaluate the values of l, s and j for the corresponding L, S and J of an atom.

(Ans- $l = L = 1$; $s = S = \frac{1}{2}; j = J = \frac{1}{2}, \frac{3}{2}$)

Q-2. Evaluate the term symbol for an aluminium atom that has two 3s electrons and one 8p electron in the outer most shell.

(Ans- $^2P_{\frac{1}{2}}$)

Q-3. Two 3s electrons are present in the outer shell of magnesium. Evaluate term symbol of its ground state.

(Ans- $^1S_0$)

Q-4. Evaluate the spectroscopic notation for the following states;

(a) $L = 1; S = {}^1\!/_2$
(b) $L = 2; S = {}^7\!/_2$
(c) $L = 3; S = 3$

(Ans- (a) ${}^2P_{\frac{1}{2},\frac{3}{2}}$ (b) ${}^2P_{\frac{3}{2},\frac{5}{2},\frac{7}{2},\frac{9}{2},\frac{11}{2}}$ (c) ${}^7F_{0,1,2,3,4,5,6}$)

Q-5. Find the values of L, S and J for the spectroscopic term ${}^4D_{\frac{5}{2}}$.

(Ans- $= 2; S = \frac{3}{2}; J = \frac{5}{2}$)

Q-6. Compute the spectral terms for two equivalent d electrons.

(Ans- ${}^1S_0$; ${}^1D_2$; ${}^1G_4$; ${}^3P_{0,1,2}$; ${}^3F_{2,3,4}$)

Q-7. Consider an odd electron configuration $2p^2 3p$ and evaluate its spectroscopic terms.

(Ans- ${}^2S^0_{\frac{1}{2}}$; ${}^2P^0_{\frac{1}{2},\frac{3}{2}}(3)$; ${}^2D^0_{\frac{3}{2},\frac{5}{2}}(2)$; ${}^2F^0_{\frac{5}{2},\frac{7}{2}}$; ${}^4S^0_{\frac{3}{2}}$; ${}^4P^0_{\frac{1}{2},\frac{3}{2},\frac{5}{2}}$; ${}^4D^0_{\frac{1}{2},\frac{3}{2},\frac{5}{2},\frac{7}{2}}$)

Q-8. Diagrammatically represent the term values of $3p\,4d$ electronic configuration for L-S and j-j coupling.

Q-9. Compute the spectral terms arising from neutral nitrogen atom.

(Ans- ${}^2P^0_{\frac{1}{2},\frac{3}{2}}$; $D^0_{\frac{3}{2},\frac{5}{2}}$; and ${}^4S^0_{\frac{3}{2}}$)

Q-10. Evaluate the electronic configuration of N^+ and hence evaluate the spectral terms.

(Ans- $1s^2 2s^2 2p^2$; ${}^1S_0$; ${}^1D_2$; ${}^3P_{0,1,2}$)

Q-11. Prove that the neutral carbon atom gives spectroscopic terms as ${}^1S_0$, ${}^3P_{0,1,2}$ and ${}^1D_2$. Draw the energy level diagram for it.

Q-12. Consider the data of quantum numbers of two electrons in a two valance electron atom as:

$n_1 = 5;\ l_1 = 0;\ s_1 = \frac{1}{2}$

$n_2 = 4;\ l_2 = 1;\ s_2 = \frac{1}{2}$

Find the possible values of the l and j under (a) L-S coupling (b) j-j coupling

Q-13. Evaluate the angle between $\vec{J}$ and z axis largest value of j and m$_j$ (Given: $l = 4\ and\ s = \frac{1}{2}$)

(Ans – 25.2°)

UNIT 3 SPECTRA OF ALKALI EARTH ELEMENTS

3.1 Objectives
3.2 Introduction of Alkali Spectra
3.3 Ritz Combination Principle
3.4 Theory of comprehensive features of the Alkali spectra
3.5 Fine structure in Alkali Spectra: The Spinning Electron
3.6 The Ratio of Intensity (for the Doublets)
3.7 Essential factors of Alkaline Earth Spectra
3.8 Two valence electron Vector Model
3.9 Interaction Energy (Triplet separation) in L – S and j – j couplings
3.10 Comparison of the terms used in L – S and j – j couplings
3.11 Regularities in Complex Spectra
3.12 Summary
3.13References
3.14Suggested Readings
3.15Terminal Descriptive type questions
3.16 Numerical type (Self Assessment Questions)

3.1. Objectives

After studying this unit, the learners should be able to:

- Understand and explain the features of spectra of alkali or alkali like atoms.
- Better comprehend the absorption spectra and simultaneously the ionisation potential
- Apply the spin-orbit interaction to understand the doublet separation for an alkali atom.
- Elaborate in depth the splitting of S and P levels in alkali atoms resulting of the four series.
- Appreciate the quantitative intensity relation of the doublet spectra stated by Burger, Dorgelo and Ornstein.
- Understand the broad and fine-structure spectra of Alkaline Earth atoms with vector model of to valance electron atom.
- Apply the selection rules for analytical investigation of spin-orbit interaction showing the triplet and anomalous triplets splitting.
- Calculate the energy of interaction involving L-S and j-j coupling.

3.2. Introduction to Alkali Spectra

As we all know, hydrogen is the simplest atom, studied so far. Next that comes in line with respect to its spectra is the ‘Alkali Atoms’. These alkali atoms include Li, Na, K, Rb, Cs and Fr having their individual spectra whose experimental study was done by renowned scientists Bergmann, Rydberg, Living and Dewar. The study recognized that emission spectrum of the alkali atoms show spectral lines in form of four series. These include: A **principal** series of bright and constant lines, a **sharp** series of fine lines, a **diffuse** series of approximately broader lines and a **fundamental** (also called Bergmann) series in the infra-red region.

From the Balmer’s formula for hydrogen, Rydberg edged out that alkali series can be expressed by similar formulae, as given below:

As per Balmer’s formula,

$$\nu = \nu_{\infty} - \frac{R}{n^2}$$

Rydberg’s representation,

Principal: $\nu^{p}{}_{m} = \nu^{p}{}_{\infty} - \frac{R}{(m+p)^2}$, m =2, 3, 4…… ∞

Sharp: $\nu^{s}{}_{m} = \nu^{s}{}_{\infty} - \frac{R}{(m+s)^2}$, m =2, 3, 4…… ∞

Diffuse: $\nu^{d}{}_{m} = \nu^{d}{}_{\infty} - \frac{R}{(m+d)^2}$, m = 3, 4, 5…… ∞

Fundamental: $\nu^f{}_m = \nu^f{}_\infty - \frac{R}{(m+f)^2}$, m = 4, 5, 6…… ∞

Where ν_∞ of all the equations are the wave numbers of the convergence limits of its specific series and these terms are called as 'fixed terms'. The 'running terms' that is, p, s, d and f shows the Rydberg corrections for the specific series.

Rydberg perceived that different series of same atom have following relations among themselves:

1. The convergence limit is same in diffuse and sharp series ($\nu^d{}_\infty = \nu^s{}_\infty$).
2. The common convergence limit of sharp and diffuse series is equal to the first running term of the principal series.
$$\nu^s{}_\infty = \nu^d{}_\infty - \frac{R}{(2+p)^2}$$
3. The convergence limit of the principal series is equal to the running term (with m=1) of the sharp series.
$$\nu^p{}_\infty = \frac{R}{(1+s)^2}$$
4. The convergence limit of the fundamental series is equal to the first running term (with m = 3) of the diffuse series.
$$\nu^f{}_\infty = \frac{R}{(3+d)^2}$$

Therefore, keeping the above relations into consideration, the above Rydberg formulae can be represented as follows:

Principal: $\nu^p{}_m = \frac{R}{(1+s)^2} - \frac{R}{(m+p)^2}$, m =2, 3, 4…… ∞

Sharp: $\nu^s{}_m = \frac{R}{(2+p)^2} - \frac{R}{(m+s)^2}$, m =2, 3, 4…… ∞

Diffuse: $\nu^d{}_m = \frac{R}{(2+p)^2} - \frac{R}{(m+d)^2}$, m = 3, 4, 5…… ∞

Fundamental: $\nu^f{}_m = \frac{R}{(3+d)^2} - \frac{R}{(m+f)^2}$, m = 4, 5, 6…… ∞

Rydberg – Schuster Law: The difference in the wave number of the principal series limit and the sharp (or diffuse) series limit is equal to the wave number of the first line of the principal series:

$$\nu^{p}{}_{\infty} - \nu^{s\,(or\ d)}{}_{\infty} = \frac{R}{(1+s)^2} - \frac{R}{(2+p)^2} = \nu^{p}{}_{2}$$

Runge's law: The difference in the wave number of the diffuse series limit and the fundamental series limit is equal to the wave number of the first line of the diffuse series:

$$\nu^{d}{}_{\infty} - \nu^{f}{}_{\infty} = \frac{R}{(2+p)^2} - \frac{R}{(3+d)^2} = \nu^{d}{}_{3}$$

3.3. Ritz Combination Principle

The plausibility of the occurrence of other species was pinpointed by Ritz, as a result of the change in the 'fixed term' present in the formula for the main series. Such new series has been recognised in many different spectra's, even in that of hydrogen spectra.

For example, the main principal series and sharp series of the alkali spectra are explained in the form of abbreviations as follows:

$$\nu^{p}{}_{m} = 1S - mP, \text{ where m} = 2, 3, 4.....\infty \qquad ....1$$

$$\nu^{s}{}_{m} = 2P - mS, \text{ where m} = 2, 3, 4.....\infty \qquad ....2$$

Ritz predicted the series that was achieved by variation in the 'fixed term' 1S and 2P to 2S, 3S….. and 3P, 4P,….. . Thus, the principal series is now represented as

$$\left.\begin{array}{r} 2S - mP, \text{where m} = 3, 4, 5 \ldots\ldots\infty \\ 3S - mP, \text{where m} = 4, 5, 6 \ldots\ldots\infty \end{array}\right\} ....3$$

And the combination sharp series are represented as

$$\left.\begin{array}{r} 3P - mS, \text{where m} = 4, 5, 6 \ldots\ldots\infty \\ 4P - mS, \text{where m} = 5, 6, 7 \ldots\ldots\infty \end{array}\right\} ....4$$

It can be observed that the fixed terms that existed in equation number 3 are included in the running terms of equation 2. Moreover, the fixed terms occurring in equation 4 are included in the running terms of equation 1. Thus the final prediction of series is simple sum or the difference of the terms of the main series. The resulting series are therefore termed as the 'combination series' and the possibility of their occurrence is called as 'Ritz combination principle'.

3.4. Theory of comprehensive features of the Alkali spectra

It is understood till now that in case of alkali atoms, one can assume it to be consisting of an inert atom-as atom as its core composed of the nucleus and completed sub-shells, plus a single valence electron. In this case, the next incomplete sub-shell is s sub shell coming next after fully occupied outermost p sub-shell. It is known widely that during the optical excitation process, only the valence electron is responsible for its optical spectra. The inert gas atoms are neutral due their symmetrical distribution of charge throughout.

Considering the case of Na atom, it has the outer most configurations of 3s, which leads to an S-term. For other possible excitation terms, can be: 4s, 5s, 6s, … S-terms; 3p, 4p, 5p, … P-terms; 3d, 4d, 5d,…D-terms, 4f, 5f, 6f,… F-terms. With the constant energy of the core, the total optical energy of the optically active electron in that state is consider to be its total energy (taking the energy due to core as constant and as zero, here for the sake of simplicity). One can look into the quantum mechanics for considering the energies of H-atom. In H-atom, the total energy is dependent on shell *n* only. When we consider the case of alkali atom, the electron revolves around the 'central field' of the nucleus along with the core electrons. Mathematically, this is given by

$$E_{n,l} = -\frac{2\pi^2\mu(Z_{ne})^2e^2}{(nh)^2}$$

where μ is the reduced mass,

$Z_n e$ is the effective charge of the nucleus for nth shell.

The value of $Z_n e$ will be greater than that of e because of *Ze* charge of the nucleus by the *(Z-1)e* charge of the electron in the core, which is not equated or perfectly balanced. This results in the more negative energy of the alkali atoms as compared to H-atom. With same *n*. corresponding to above result, one can conclude that the energy levels of alkali atoms will be lower in energy values as compared to H-atom. Although, with increasing value of *n* levels in alkali atoms, energy will finally approach to those corresponding level of H-atom and try to stabilize the atom more and more with increasing screening effect.

In contrast to Hydrogen, the energy of an alkali atom not only depends on *n* but also depends on *l* values. Since the probability of finding the electron near the nucleus is largest for *l*=0 (*s*-electron) and decrease for increasing values of *l*. Thus for a given n, the energy is most negative for *s* electrons and further keeps on decreasing for *p,d,f,…* electrons. This is depicted in the Figure 1.

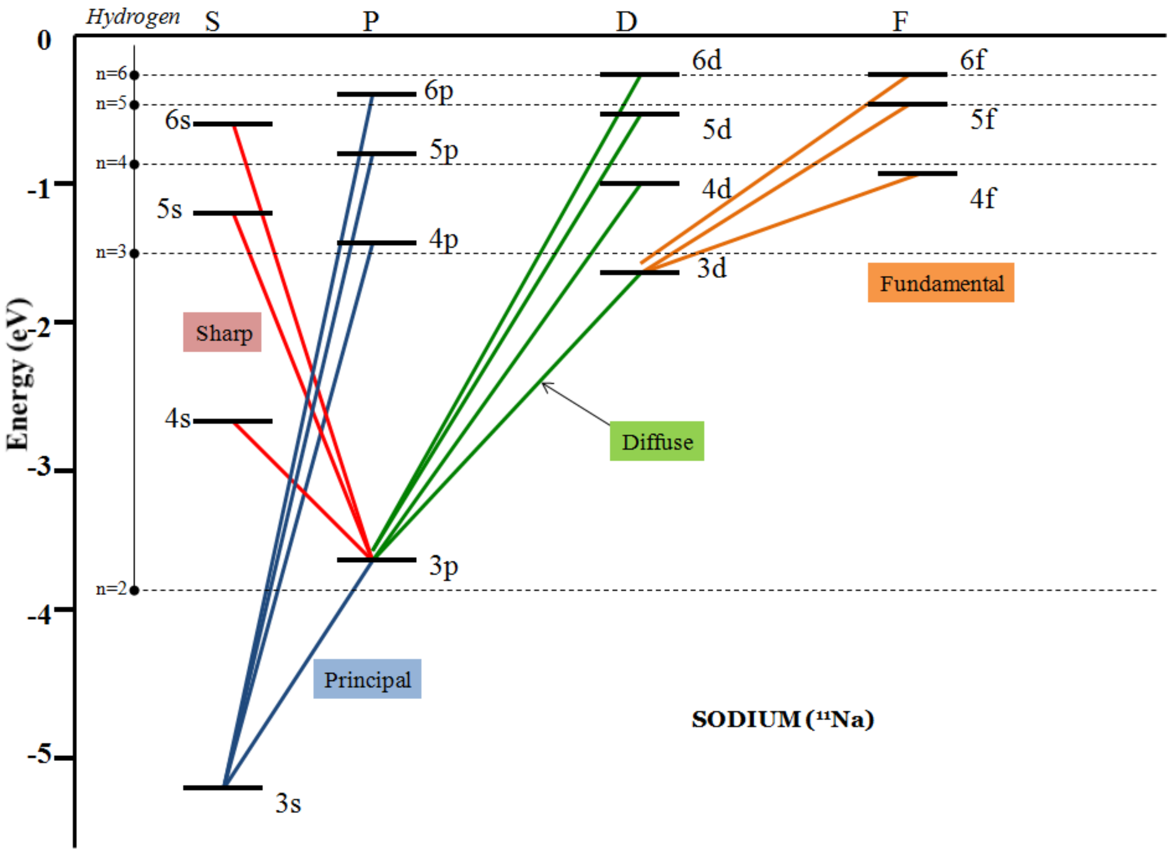

Figure 1.The alkali levels of Na atom, where the shift is greatest for *s* and becomes smaller for *p,d,f,…*levels.

The selection rule for such allowed transitions are Δn = any integer, and $\Delta l = \pm 1$. The observed transition in the emission spectra corresponds to the following series:

$np \rightarrow 3s$, $n > 2$, known as ***Principal Series***

$ns \rightarrow 3p$, $n > 3$, known as ***Sharp Series***

$nd \rightarrow 3p$, $n > 2$, known as ***Diffuse Series***

$nf \rightarrow 3d$, $n > 3$, known as ***Fundamental Series***

Experimentally, we have huge number of atoms, so we observe all the four series collectively. Ultimately, the principal series is observed because the entire excited electron returns to the ground state making this series as most intense.

The important observations noted from Figure 1 are stated as follows. The sharp and diffuse series have the same limit that corresponds to the jump of electron from infinity to 3p level. The absorption spectrum of Na is obtained when the light from a source is passed through the cooled vapours of Na. The absorption spectra of alkali atoms follow the selection rule of $\Delta l = \pm 1$. Usually at room temperature, the atoms in the vapour state are in ground energy state, the only possible absorption transition occurs as $3s \rightarrow np$, for n>2. This results as the principal series, which is the only series occurring both for absorption and as well as emission. The limit of this series corresponds to either the complete removal of 3s electron (in case of absorption) or de-exciting to 3s level from infinity (in case of emission). This gives the ionization potential of the atom, when converted in eV.

With the above understanding of the methodology of absorption, when the electron transits from 3s→3p, the only transition possible is 3p→3s which results in the only resonance yellow D-line in emission spectra. These are termed as resonance lines. Usually the other transition may results from other possible paths, say for e.g. the transition from 3s→4p and back to normal state may occur from (i) 4p→3s, (ii) 4p→4s→3p→3s, (iii) 4p→3d→3p→3s, thus emitting other lines in the spectrum as well.

3.5. Fine structure in Alkali Spectra: The Spinning Electron

Splitting of fine structure is obtained by the alkali atoms when the lines of the optical spectra are emitted from the atoms. The fine structure splitting is smaller for the light weighted atoms and increases promptly with the increase in the atomic number. Sharp series constitutes lines in close doublets with separation of similar wave number. In the same way, for the principal series, each line is also in doublet form but here the wave number separation declines speedily between the two components and the declination is towards the lines of increase in the wave number. On the other hand, diffuse as well as the fundamental series express a three component fine structure and therefore, are also known as 'Compound doublets' rather than the triplets. However, the fundamental series has negligible fine structure in the lines.

Alkali spectral analysis show that the line splitting are etched back to the level splitting and the S levels are single while other levels like P, D, F are the doublet levels. The spin of the electron give rise to the splitting of the levels. It is through the nuclear electric field, the electron moves and that creates the interaction between the spin magnetic moment (of the optically active electrons) and the internal magnetic field. This type of interaction is known as the Spin – Orbit interaction. This interaction causes the coupling of the orbital angular momentum $\vec{l}$ of the optical electron with that of the spin angular momentum $\vec{s}$ to give rise to the resultant $\vec{j}$ about which both the coupled momentums $\vec{l}$ and $\vec{s}$ precess further. $\vec{j}$ is also termed as the total angular momentum of the alkali atom as the angular momentum of the core is equal to zero. There are two values which the quantum number *j* can exhibit as the spin and orbital angular momenta are parallel or anti-parallel:

$$j = l \pm s = l \pm \frac{1}{2}$$

The placement of the spin with respect to the orbit results in the splitting of each energy level in two, one which corresponds to $j = l + \frac{1}{2}$ and the other corresponds to $j = l - \frac{1}{2}$. The exception is the S-level for which l = 0. The complete notation of levels is as given below:

Level	l	S	Multiplicity (2s+1)	j	Full notation
S	0	½	2	1/2	$^2S_{1/2}$
P	1	½	2	3/2, 1/2	$^2P_{3/2}$, $^2P_{1/2}$
D	2	½	2	5/2, 3/2	$^2D_{5/2}$, $^2D_{3/2}$
F	3	½	2	7/2, 5/2	$^2F_{7/2}$, $^2F_{5/2}$

The components in every doublet levels, analogous to the j's smaller value are more stable and thus placed deeper. The stable state arrives when the spin magnetic moment of the electron, $\overrightarrow{\mu_s}$ channels in the direction of the magnetic field $\vec{B}$ generated due to the orbital motion of the electrons in the nuclear electric field. Moreover, this $\vec{B}$ is in the same direction as that of the$\vec{l}$, which is the angular momentum. Since the electron is negatively charged, the directions of the spin moment $\overrightarrow{\mu_s}$ and $\vec{s}$ are opposite to each other. As $\overrightarrow{\mu_s}$ is in the same direction to that of $\vec{l}$ for a stable state, the latter becomes opposite to $\vec{s}$, while the value of j is very low, $j = l - s$. On the contrary, the higher value of j corresponds to the unstable or the less stable state, as shown in Figure 2.

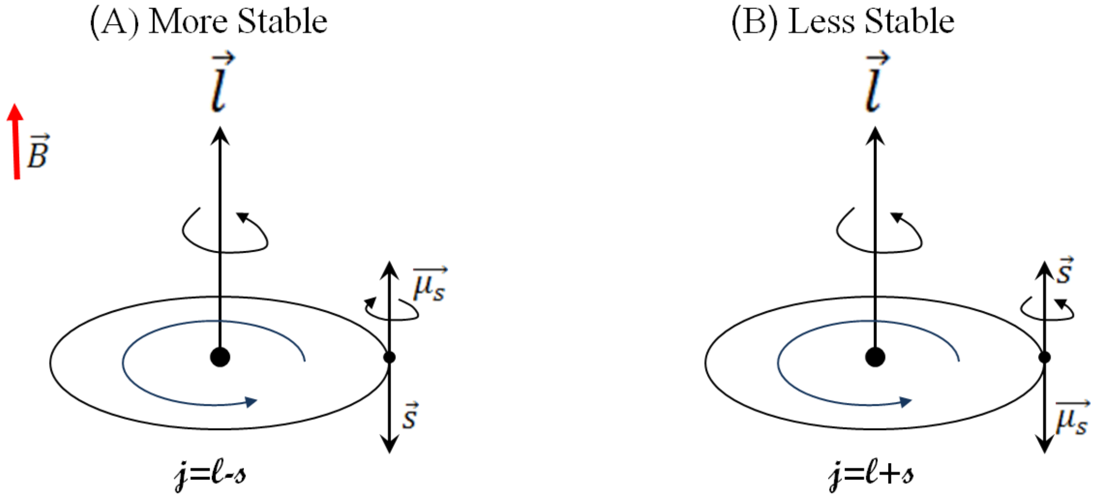

Figure 2. (A) The lower value of j corresponds to less stable state where $\vec{l}$ is opposite to $\vec{s}$ (B) the higher value of j corresponds to less stable state.

The interaction between the spin magnetic moment of an electron and an atom's internal magnetic field arising from the electron's orbital motion through the nuclear electric field is called as the Spin – Orbit Interaction. Although, it is a weak interaction, it is the partial reason behind the fine structure of the excited states of an electron atom. The spin – orbit interactions that acts on the optically active electron cause the splitting of the energy levels of the alkali atom, and can be calculated by deriving the expression for the interaction energy.

Let us take the $\vec{E}$ as the electric field, in which the electrons are moving with a gradient of a potential function *V(r)*. Here '*r*' is the distance between the electron and nucleus.

$$\vec{E} = grad\, V(r)$$

Since, $grad\, r = \frac{\vec{r}}{r}$

$$\vec{E} = \frac{\vec{r}}{r}\frac{dV(r)}{dr}$$

The magnetic field, that is, $\vec{B}$, which arises from the electron's orbital motion with velocity $\vec{v}$ in the electric field $\vec{E}$ can be written as

$$\vec{B} = \frac{1}{c}\left(\vec{E} \times \vec{v}\right)$$

$$\vec{B} = \frac{1}{cr}\frac{dV(r)}{dr}(\vec{r} \times \vec{v})$$

Since, the angular momentum of the electron is expressed as $\vec{l} = m\,\vec{r} \times \vec{v}$,

$$\vec{B} = \frac{1}{mc}\frac{1}{r}\frac{dV(r)}{dr}\vec{l}$$

The internal magnetic field $\vec{B}$ of the atom can cause different orientations for the spin magnetic moment $\overrightarrow{\mu_s}$ of the electron and the electron itself. For different orientations, the potential energy is also different. The magnetic potential energy of the orientation can be expressed as

$$\Delta E_{ls} = -\overrightarrow{\mu_s}.\vec{B}$$

But,

$\overrightarrow{\mu_s} = -g_s\frac{e}{2mc}\vec{s}$, where $g_s = 2$

Therefore, the above expression for the magnetic potential energy can be written in terms of the spin angular momentum of the electron, $\vec{s}$, which is given below

$$\Delta E_{ls} = -\frac{e}{2mc}\vec{s}.\vec{B}$$

Now, substituting the value of $\vec{B}$, we get

$$\Delta E_{ls} = -\frac{e}{m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{s}.\vec{l}$$

This is the energy in the reference frame in which the electron is at rest. The relativistic transformation to the normal reference frame in which the nucleus is at rest, the energy is reduced by the factor of 2. This is called as the 'Thomas Precession'. Therefore, the spin – orbit interaction energy can be expressed as

$$\Delta E_{ls} = -\frac{e}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{s}.\vec{l}$$

In the terms of quantum numbers, that is, l, s, and j, the expression can be written as

$$\vec{j} = \vec{l} + \vec{s}$$

If we take a self dot product of the above equation, we have

$$\vec{j}.\vec{j} = \left(\vec{l} + \vec{s}\right).\left(\vec{l} + \vec{s}\right)$$

Since, $\vec{s}.\vec{l} = \vec{l}.\vec{s}$

$$\vec{j}.\vec{j} = \left(\vec{l}.\vec{l}\right) + (\vec{s}.\vec{s}) + \overrightarrow{2s}.\vec{l}$$

Therefore,

$$\vec{s}.\vec{l} = \frac{1}{2}\left[\vec{j}.\vec{j} - \vec{l}.\vec{l} - \vec{s}.\vec{s}\right]$$

$$= \frac{1}{2}\left[j(j+1) - l(l+1) - s(s+1)\right]\frac{h^2}{4\pi^2}$$

Now,

$$\Delta E_{ls} = -\frac{eh^2}{16\pi^2m^2c^2}\left[j(j+1) - l(l+1) - s(s+1)\right]\frac{1}{r}\frac{dV(r)}{dr}$$

Generally, $\frac{1}{r}\frac{dV(r)}{dr}$ term is not constant during the motion of electron. Therefore, its average value is taken.

$$\boldsymbol{\Delta E_{ls} = -\frac{eh^2}{16\pi^2m^2c^2}\left[j(j+1) - l(l+1) - s(s+1)\right]\overline{\frac{1}{r}\frac{dV(r)}{dr}}}$$

This is the general expression for the interaction energy, provided that the $\frac{1}{r}\frac{dV(r)}{dr}$ average value is calculated through the probability density which is attained from the Hartree eigen functions.

The above equation reveals that the interaction energy, that is, $\Delta E_{ls} = 0$, when $l = 0$ as $j = s = \frac{1}{2}$. For the other values of l, ΔE_{ls} has two values, one being positive and the other being negative.

As per the Hartree theory, an orbital electron present in ‘n’ shell of an alkali atom moves in a potential field,

$$V(r) = -\frac{Z_n e}{r}$$

Here Z_n is a constant which is equal to $Z(r)$ examined at the average value of r for the shell n. The value of $Z(r)$ is such that $Z(r) \rightarrow Z$ as $r \rightarrow 0$ and $Z(r) \rightarrow 1$ as $r \rightarrow \infty$. The above quantity $Z_n e$ is called the effective nuclear charge for a particular shell n.

$$\frac{dV(r)}{dr} = -\frac{Z_n e}{r^2}$$

Therefore, the final equation can be expressed as follows:

$$\Delta \boldsymbol{E_{ls}} = -\frac{\boldsymbol{Z_n e^2 h^2}}{\boldsymbol{16\pi^2 m^2 c^2}}[\boldsymbol{j(j+1) - l(l+1) - s(s+1)}]\overline{\frac{\boldsymbol{1}}{\boldsymbol{r^3}}}$$

$\overline{\frac{1}{r^3}}$ is calculated using the radial eigen functions R_{nl}(r) of an alkali atom. The value of $\overline{\frac{1}{r^3}}$ is finally written as

$$\overline{\frac{1}{r^3}} = \frac{{Z_n}^3}{{a_0}^3 n^3 l\left(l+\frac{1}{2}\right)(l+1)}, \text{provided } l > 0$$

Where a_0 is the radius of the smallest Bohr orbit of hydrogen atom and $a_0 = \frac{h^2}{4\pi^2 m e^2}$.

Now if we introduce the value of a_0 in the above equation of interaction energy will be:

$$\Delta \boldsymbol{E_{ls}} = -\frac{\boldsymbol{Z_n e^2 h^2}}{\boldsymbol{16\pi^2 m^2 c^2}}[\boldsymbol{j(j+1) - l(l+1) - s(s+1)}]\frac{\boldsymbol{{Z_n}^3}}{\boldsymbol{{a_0}^3 n^3 l\left(l+\frac{1}{2}\right)(l+1)}}$$

The above equation can be simplified as

$$\Delta \boldsymbol{E_{ls}} = -\frac{\boldsymbol{R_\infty \alpha^2 hc\, {Z_n}^4}}{\boldsymbol{2n^3 l\left(l+\frac{1}{2}\right)(l+1)}}[\boldsymbol{j(j+1) - l(l+1) - s(s+1)}]$$

Where $R_\infty = \frac{2\pi^2 m e^4}{ch^3}$ is the Rydberg constant for a very boundlessly heavy nucleus and $\alpha = \frac{2\pi e^2}{hc}$ is the fine structure constant.

The shift of energy level in the wave number due to the spin – orbit interaction is

$$\boldsymbol{\Delta T_{ls} = \frac{-\Delta E_{ls}}{hc} = -\frac{R_\infty \alpha^2 \, {Z_n}^4}{2n^3 l\left(l+\frac{1}{2}\right)(l+1)}[j(j+1) - l(l+1) - s(s+1)]}$$

For a single optically active electron of an alkali atom,

$$s = \frac{1}{2} \text{ and } j = l \pm s = l \pm \frac{1}{2}$$

Substituting this,

$$j(j+1) - l(l+1) - s(s+1) = \; l, \;\; \text{for } j = l + \frac{1}{2}$$

$$j(j+1) - l(l+1) - s(s+1) = (l+1), \;\; \text{for } j = l - \frac{1}{2}$$

Now, the shift in the level, with respect to $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$ is expressed as

$$\Delta T_{ls'} = -\frac{R_\infty \alpha^2 \, {Z_n}^4}{2n^3\left(l+\frac{1}{2}\right)(l+1)}$$

$$\Delta T_{ls''} = -\frac{R_\infty \alpha^2 \, {Z_n}^4}{2n^3 l\left(l+\frac{1}{2}\right)}$$

Therefore, the spin – orbit interaction causes the splitting of the l- level into two different levels of j, one in upward direction and the other in downward direction. The separation between the two,

$$\Delta T = \; \Delta T_{ls''} - \Delta T_{ls'}$$

$$\Delta T = -\frac{R_\infty \alpha^2 \, {Z_n}^4}{2n^3\left(l+\frac{1}{2}\right)}\left[\frac{1}{l} + \frac{1}{l+1}\right]$$

$$\Delta T = -\frac{R_\infty \alpha^2 \, {Z_n}^4}{n^3 l(l+1)}$$

Putting the value of R_∞ = 1.097 × 10^5 cm^{-1} and $\alpha = {}^1\!/_{137}$, we get

$$\Delta T = 5.84 \frac{{Z_n}^4}{n^3 l(l+1)} \, \text{cm}^{-1}$$

If α is the screening constant, then $Z_n = Z - \sigma$, such that

$$\boldsymbol{\Delta T = 5.84 \frac{(Z-\sigma)^4}{n^3 l(l+1)} \, \textbf{cm}^{-1}}$$

This equation shows that the splitting of the levels for an alkali atom decreases with increase in 'n' for same level l. Further it increases with increase in the atomic number and decreases with increase in l (for same 'n'). Moreover, for the value of $l = 0$, the splitting is equal to zero.

For a given value of '*n*', the relative splitting of the P^2, D^2 and F^2 levels can be drawn as follows (in Figure 3):

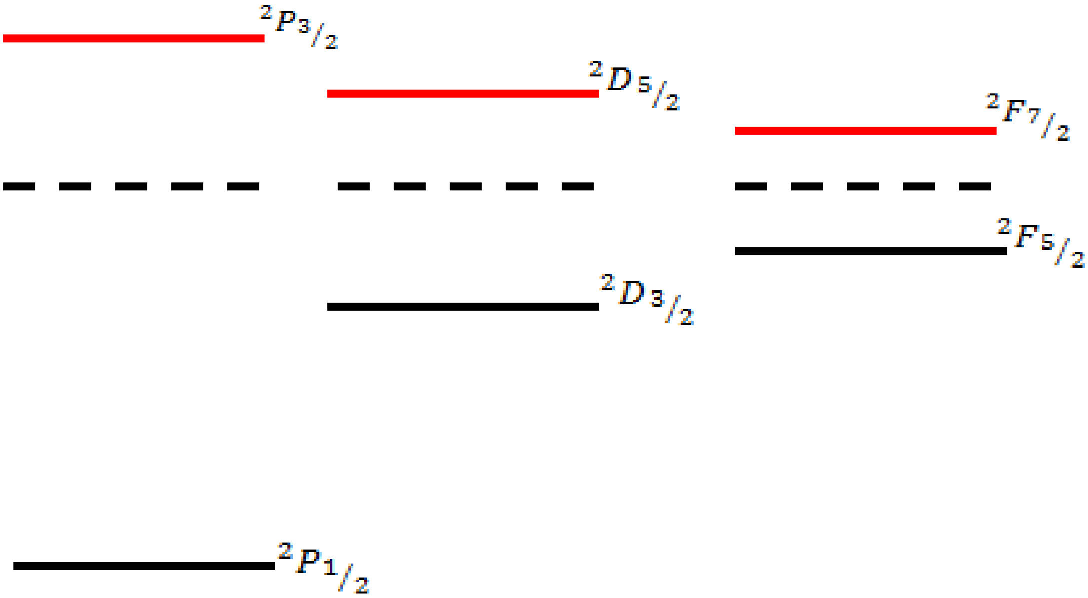

Figure 3. The relative splitting of the P^2, D^2 and F^2 levels.

The splitting of Alkali levels involved in the emission of the lines of the four series are shown in Figure 4. The S^2 are the single components and written as $^2S_{1/2}$. The splitting of ^2P is given as $^2P_{3/2}$ and $^2P_{1/2}$, where $^2P_{1/2}$ is deeper and there is decrease in splitting with increase in 'n'. In the same way, ^2D and ^2F levels can be splitted into $^2D_{5/2}$, $^2D_{3/2}$, $^2F_{7/2}$ and $^2F_{5/2}$, although these splitting are very small.

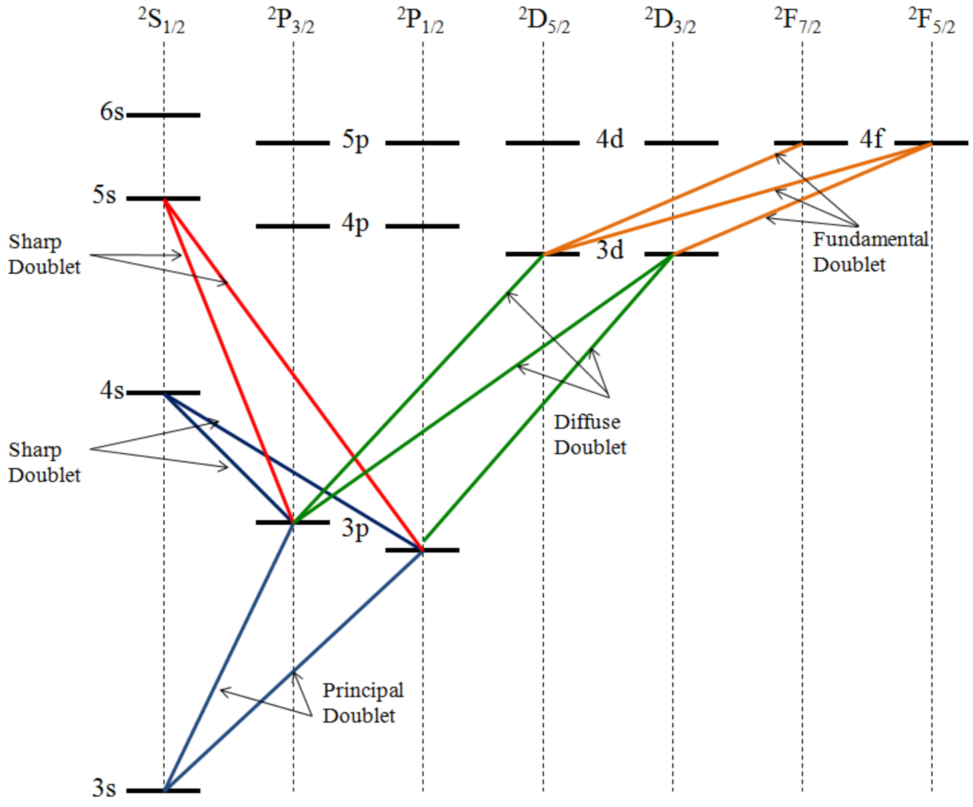

Figure 4. The emission of lines of the four series due to the splitting of involved alkali levels.

There are selection rules which are:

$$\Delta n = any\ integer\ (including\ zero)$$

$$\Delta l = \pm 1$$

$$\Delta j = 0, \pm 1$$

These rules provide an insight to the formation of the single as well as the compound doublet structure of the spectral lines.

As per example, let us take the resonance doublet of sodium atom, called as D_1 and D_2 lines. These lines arise from the $3^2P \rightarrow 3^2S$ transition, which is corresponding to the given two transitions:

$$3^2P_{1/2} \rightarrow 3^2S_{1/2}\ (D_1\ 5896\ Å)$$

$$3^2P_{3/2} \rightarrow 3^2S_{1/2}\ (D_2\ 5890\ Å)$$

The separation in the wave number between D_1 and D_2 lines and that between $3^2P_{3/2}$ and $3^2P_{1/2}$ is similar as shown in Figure 5. Other higher wave number lines of the principal series owe their doublet structure to the doubling of higher ^aP levels such as 4^2P, 5^2P, …….levels. As we know, increase in ‘n’ decreases the splitting of these levels it causes the decrease in the wave number separation between the doublet components.

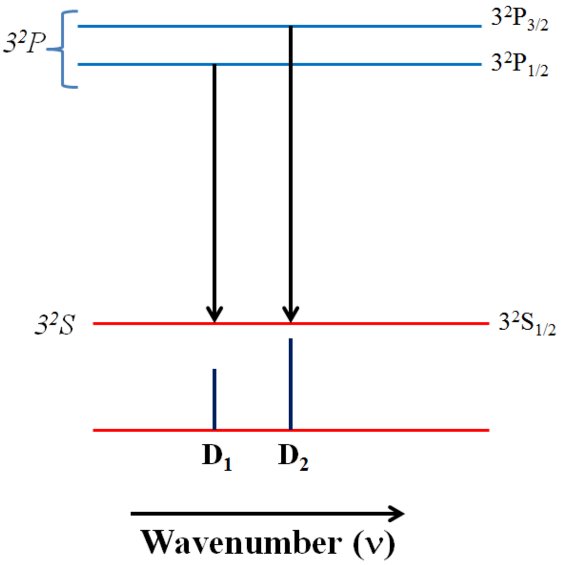

Figure 5. The separation in the wave number between D1 and D2 lines.

Now for the sharp series, the doublets are formed by the transition $n^2S_{1/2} \rightarrow 3^2P_{3/2}, 3^2P_{1/2}$. Here, the value of n = 4, 5, 6…. . In this type of series, separation in the wave number between the doublet components of all the lines is equal and similar to that between $3^2P_{3/2}$ and $3^2P_{1/2}$ levels where there is termination to all the transitions.

On the other hand, for the diffuse as well as the fundamental series, the lines display a three component structure and are called compound doublet. In the given Figure 6, transition $3^2D_{5/2}$, $3^2D_{3/2} \rightarrow 3^2P_{3/2}, 3^2P_{1/2}$ arise for a diffuse series. Here, both the ^2D and ^2P levels split and allow three transitions via selection rules.

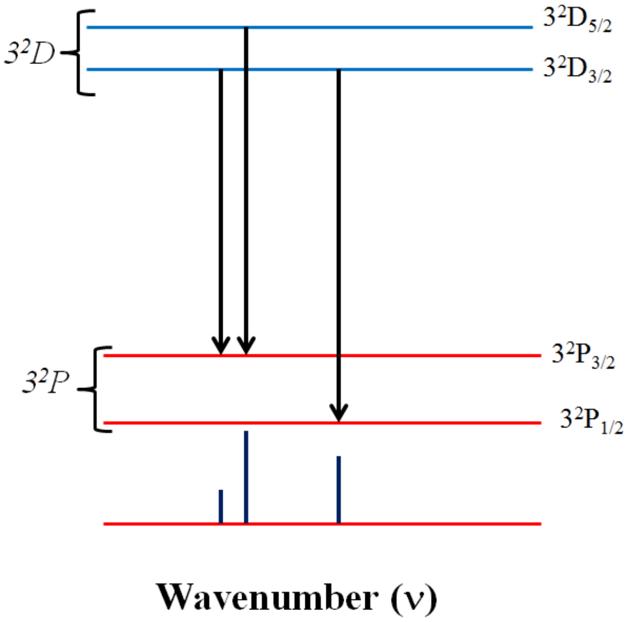

Figure 6. The splitting of allowed both the ^2D and ^2P levels.

However, the ^2D level splitting is too small to cause ordinary resolution to display only two components. Ignoring the ^2D level splitting, all the lines of the diffuse series have similar doublet separations since the lines of the sharp series are equal to the separation between $3^2P_{3/2}$ and $3^2P_{1/2}$ levels.

The lines of the diffuse as well as the fundamental series are called doublets, although it has three components to be called as triplets. This is because they come from the doublet level transitions. Here the term 'doublet' clearly refers to the multiplicity of the energy levels and not to the number of the components in the spectral lines.

3.6. The Ratio of Intensity (for the Doublets)

There are certain intensity rules that line intensities follow in doublet spectra:

1. The transition where j and l change in the similar manner give rise to the strongest line in any doublet.
2. If the same doublet contains more than one such lines, then the line having the highest value of j, is the strongest.

   Taking Figure 5 into consideration, we can see in the principal – series doublet, line $^2P_{3/2} - {}^2S_{1/2}$ is stronger than line $^2P_{1/2} - {}^2S_{1/2}$, as in the $^2P_{3/2} - {}^2S_{1/2}$ line, the value of j and l change in same way, that is, by -1. On the other hand, in line $^2P_{1/2} - {}^2S_{1/2}$, the value of j changes by zero while l changes by -1.

   Similarly, it can be seen in Figure 6, there is a diffuse – series compound doublet with two strong lines, $^2D_{5/2} - {}^2P_{3/2}$ and $^2D_{3/2} - {}^2P_{1/2}$, where both the value of j and l change in same way, that is, by -1. Having the higher value of j, makes the $^2D_{5/2} - {}^2P_{3/2}$, stronger. On the other hand, for the faint satellite, $^2D_{3/2} - {}^2P_{3/2}$, the values change differently, that is, the value of j changes by zero while l changes by -1.

   In the doublet spectra, quantitative intensity relations have been observed. The intensity ratio in the doublet of the sharp series line in sodium is 2:1. Similar ratio was observed for the diffuse and the principal series, if the ^2D level splitting is unresolved and if self-absorption is avoided, respectively.

   Burger, Dorgelo and Ornstein discovered the quantitative rules for the relative intensities, according to which these apply not only to the doublets, but to all the multiplets also. These are as follows:

   (A) The sum of the intensities of those lines of a multiplet arising from a common level is proportional to the quantum weight $2j + 1$ of that level.

   (B) The sum of the intensities of those lines of a multiplet ending on a common level is proportional to the quantum weight of that level.

   Taking an example of a principal series doublet (Figure 7), here are the two component lines beginning from the upper levels $^2P_{3/2}$ and $^2P_{1/2}$, and terminating on the common lower level $^2S_{1/2}$.

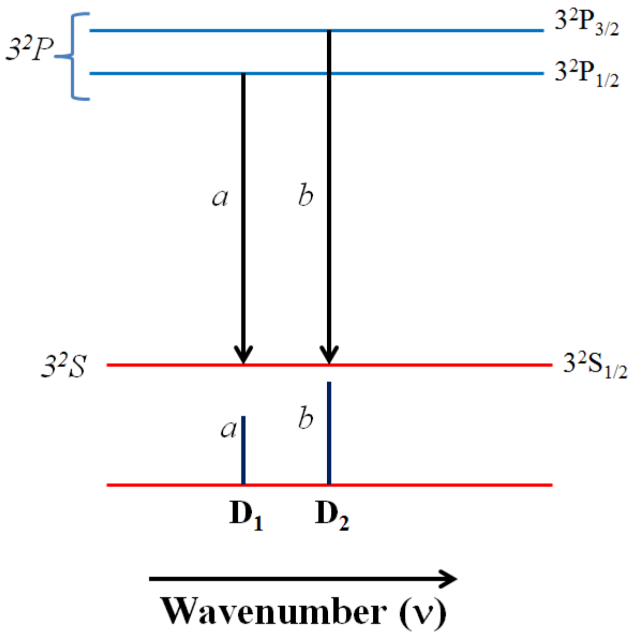

Figure 7. Schematic showing the generation of principle series doublet.

Ratio of the intensities would be same as the ratio of the quantum weights of the doublet levels. Therefore,

$$\frac{I_b}{I_a} = \frac{2\left(\frac{3}{2}\right)+1}{2\left(\frac{1}{2}\right)+1} = \frac{4}{2} = 2:1$$

Similarly the ratio can be calculated for the sharp series.

Now taking an example of diffuse – series compound doublet as shown in Figure 8 below. The line 'b' arises from the $^2D_{5/2}$ level while the lines 'a' and 'c' arise from the level $^2D_{3/2}$. Therefore,

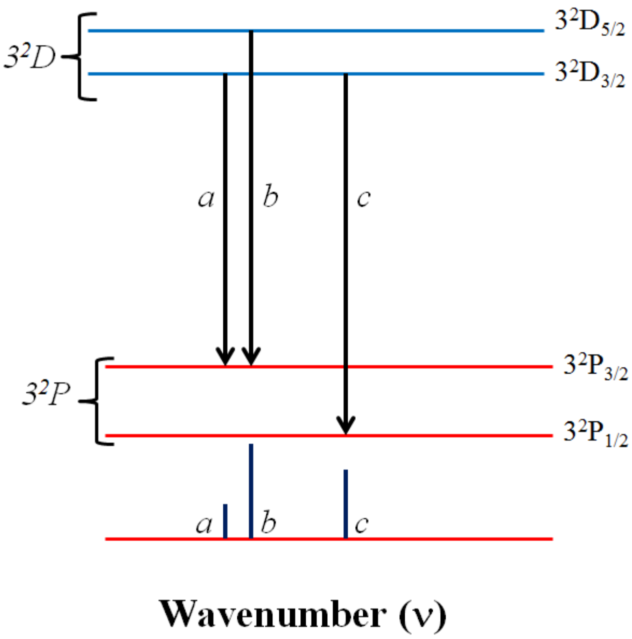

Figure 8. Schematic showing the diffuse series compound doublet.

$$\frac{I_b}{I_a + I_c} = \frac{2\left(\frac{5}{2}\right) + 1}{2\left(\frac{3}{2}\right) + 1} = \frac{6}{4} = 3:2$$

Further, the line 'c' terminates on the level $^2P_{1/2}$ while 'a' and 'b' terminates on the $^2P_{3/2}$ level.

$$\frac{I_c}{I_a + I_b} = \frac{2\left(\frac{1}{2}\right) + 1}{2\left(\frac{3}{2}\right) + 1} = \frac{2}{4} = 1:2$$

Thus, solving both the above equations, we get

$$c = \frac{5}{9}b\,, a = \frac{1}{9}b$$

This means that

$$a:b:c = \frac{1}{9}:1:\frac{5}{9}$$

Or it can be written as

$$a:b:c = 1:9:5$$

If 'a' and 'b' are not resolved, then we shall see two lines with an intensity ratio

$$(1+9):5 = 2:1$$

Similarly, the intensity ratio for the compound doublet of the fundamental series is calculated and is found to be 1:20:14 that will roughly be equal to 3:2.

This is the splitting between the levels $4^2P_{3/2}$ and $4^2P_{1/2}$.

Now, for the wavelength 4047.2 and 4044.1 Å, we have

$$dv = \frac{(4047.2 - 4044.1) \times 10^{-8} cm}{(4047.2 \times 10^{-8} cm) \times (4044.1 \times 10^{-8} cm)}$$

$$dv = \frac{3.1}{4047.2 \times 4044.1 \times 10^{-8} cm}$$

$$dv = 18.9\ cm^{-1}$$

This is the splitting between the levels $5^2P_{3/2}$ and $5^2P_{1/2}$.

3.7. Essential factors of Alkaline Earth Spectra

An alkaline earth atom constitutes two electrons in its valence shell, which are optically active, outside the subshells or the closed shells. Alkaline earth atoms include *Be, Mg, Ca, Sr, Ba* and *Ra.* Two types of spectral lines arise from the spectrum of such type of atoms, which are – Singlets and Triplets. As discussed in chapter 10, the lines of all the types can be categorised into four different series: Principal, sharp, diffuse and fundamental. There are certain relations among these series, which are as follows:

1. A common convergence limit has been observed between the singlet sharp (^1S) as well as the singlet diffuse (^1D) series. Similarly, the triplet sharp and diffuse (^3S and ^3D) have different common convergence limit.

2. The common limit of the singlet sharp and diffuse series (^1S and ^1D) and that of the principal series (^1P) have a difference of wave number and is equal to the wave number of the first member of the principal series (^1P). On the other hand, when we look into the triplet series, the wave number difference between the common convergence limit of triplet sharp and diffuse (^3S and ^3D) series and that of the convergence limit of triplet principal series (^3P), is equal to the wave number of the first member of the (^3S) sharp series. This is called as the *Rydberg – Schuster Law*.

3. *Runge Law* states that the difference in the wave number between the convergence limit of ^1S and ^1D series and that of the limit of ^1F series is equal to the wave number of the first member of the ^1D series. This law holds true for the triplet series also, that is, the wave number difference between the common limit of the triplet ^3S and ^3D series and that of the limit of ^3F series is equal to the wave number of the first member of the ^3D series.

4. When the fine structure is taken into consideration, the above relation holds true here also.

   A fine structure is observed in the lines of all the triplet series:

   (i) A three component fine structure is observed in all the lines of the principal series with decrease in the separation of the wave number approaching a single limit.

   (ii) On the contrary, similarity in the separation of the wave number approaching a triple limit although three component fine structure is observed in all the lines of the sharp series.

   (iii) A six component fine structure was observed in the all the lines of the diffuse and the fundamental series, approaching triple limit – three satellite and the other three strong ones. Due to the fine structure, these are called as compound triplets in contrast to the above simple triplets of principal and sharp series.

   (iv) There is another class of triplets, called anomalous triplets, within which some lines display a fine structure and features very different from the normal compound and simple triplets.

   (v) There are some other kinds of alkaline earth atom spectra which display lines that do not comply to any of the above mentioned series. These types of lines are called as Combination and inter-combination lines.

   All the features of the fine structures can be detailed by the vector model of an atom.

3.8. Two valence electron Vector Model

The vector model of an atom can be easily explained by several atomic spectra, within which different angular momenta present in the atom along with their combinations, have been described using the vectors and their quantum numbers. In the Vector Model, the quantum vector $\vec{l}$ has been used to express the orbital angular momentum of each electron while $\vec{s}$ has been used to express the spin angular momentum. In different conditions, the resultant vectors arise from the combination of these individual vectors in terms of which the atom’s spectral properties are described.

Suppose, for an alkaline earth atoms, with two valence rather optically active electrons present, the vector model constitutes four vectors ($\overrightarrow{l_1}$,$\overrightarrow{l_2}$,$\overrightarrow{s_1}$,$\overrightarrow{s_2}$) with the resultant vector $\vec{J}$. Two varying coupling schemes are responsible for the formation of the resultant vector and these are known as *L-S* coupling and *j-j* coupling as shown in Figure 9.

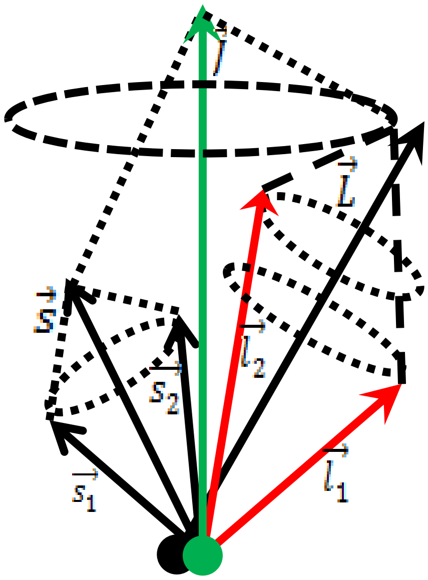

Figure 9: The vector model of L-S coupling.

The ***L-S* coupling** is a common type of coupling and exists in most of the lighter atoms. In this type of coupling the $\vec{l_1}$ and $\vec{l_2}$ of two electrons, that is the individual orbital angular momentum vectors are coupled to each other strongly, thus giving rise to a resultant orbital angular momentum vector $\vec{L}$. Therefore, the corresponding quantum number L can take the values

$$L = |l_1 - l_2|;\ |l_1 - l_2| + 1, \dots..(l_1 + l_2)$$

This can provide numerous terms of the atom. These terms are expressed as S, P, D, ….. as per the value of L= 0,1,2…. .

In similar manner, $\vec{s_1}$ and $\vec{s_2}$ of two electrons, that is the individual orbital angular momentum vectors are coupled to each other strongly, thus giving rise to a resultant orbital angular momentum vector $\vec{S}$. Therefore, the corresponding quantum number S can take the values

$$L = |s_1 - s_2|;\ |s_1 - s_2| + 1, \dots..(s_1 + s_2)$$

Since the value of $s_1 = s_2 = \frac{1}{2}$, the S = 0, 1.

Thus in value of multiciplicity (2S+1) is 1 and 3, which means that the two electrons give rise to singlet and triplet terms.

Now, for the formation of the total angular momentum $\vec{J}$ (resultant) of an atom, the spin – orbit interaction, that is $\vec{L}$ and $\vec{S}$ are less strongly coupled to each other. Therefore, both $\vec{L}$ and $\vec{S}$ move slowly around $\vec{J}$. Therefore, the values of quantum number $\vec{J}$ can be

$$J = |L - S|;\ |L - S| + 1, \dots..(L + S)$$

The spin orbit interaction is important for each and every multiplet term, which being a combination of fine structure levels, each designated with a *J* value.

Now this vector model can be used to describe the spectrum of the two electron atom, let's suppose Ca (Z=20). The configuration, generally called as ground state configuration is

$$\boxed{1s^2 2s^2 2p^6 3s^2 3p^6}\ 4s^2$$

For the electrons which are optically active,

$$l_1 = 0, l_2 = 0, s_1 = \frac{1}{2}, s_2 = \frac{1}{2}$$

Thus,

$$L = 0 \text{ (S-term)}$$

$$S = 0, 1 \text{ so that } (2S+1) = 1, 3$$

And

$$J = 0, 1$$

The terms used are $^1S_0$ and $^3S_0$. Since the electrons ($4s^2$) are equivalent, the term $^3S_1$ is excluded by Pauli's principle. Therefore, only singlet S- term $^1S_0$ arises from the normal atom.

The optically active electrons, either one or both present in the outer valence shell rise to the higher levels or states when the atom is excited. It seems true that excitation of just one of the optical electrons can give rise to the lines of all the eight series present in a spectrum.

Configuration	**Terms**
4s 5s, 4s 6s,….	5^1S_0, 6^1S_0, …… and 5^3S_1, 5^3S_1, …….
4s 4p, 4s 5p,…..	$4^1P^o{}_1$, $5^1P^o{}_1$, … and $4^3P^o{}_{2,1,0}$; $5^3P^o{}_{2,1,0}$; ……
4s 3d, 4s 4d,…..	3^1D_2, 4^1D_2,…… and $3^3D_{1,2,3}$; $4^3D_{1,2,3}$; …….
4s 4f,….	$4^1F^o{}_3$,…….. and $4^3F^o{}_{2,3,4}$; ……..

The energy levels with respect to the terms given in the table above, can be designed as per in Figure 10. When the spin – orbit interactions are studied, it displays different levels with triplet splitting of the levels of the same L which converges swiftly with the increasing value of n. Moreover, it shows that intervals of ^3P are broader than that of the respective intervals of ^3D. Similarly, the intervals of ^3D are broader than that of the respective intervals of ^3F.When the excited electron jumps back through any path, as per the selection rules, it emits different spectral series.

$$\Delta S = 0$$

$$\Delta L = \pm 1$$

$$\Delta J = 0, \pm 1, \text{but } J = 0 \not\leftrightarrow J = 0$$

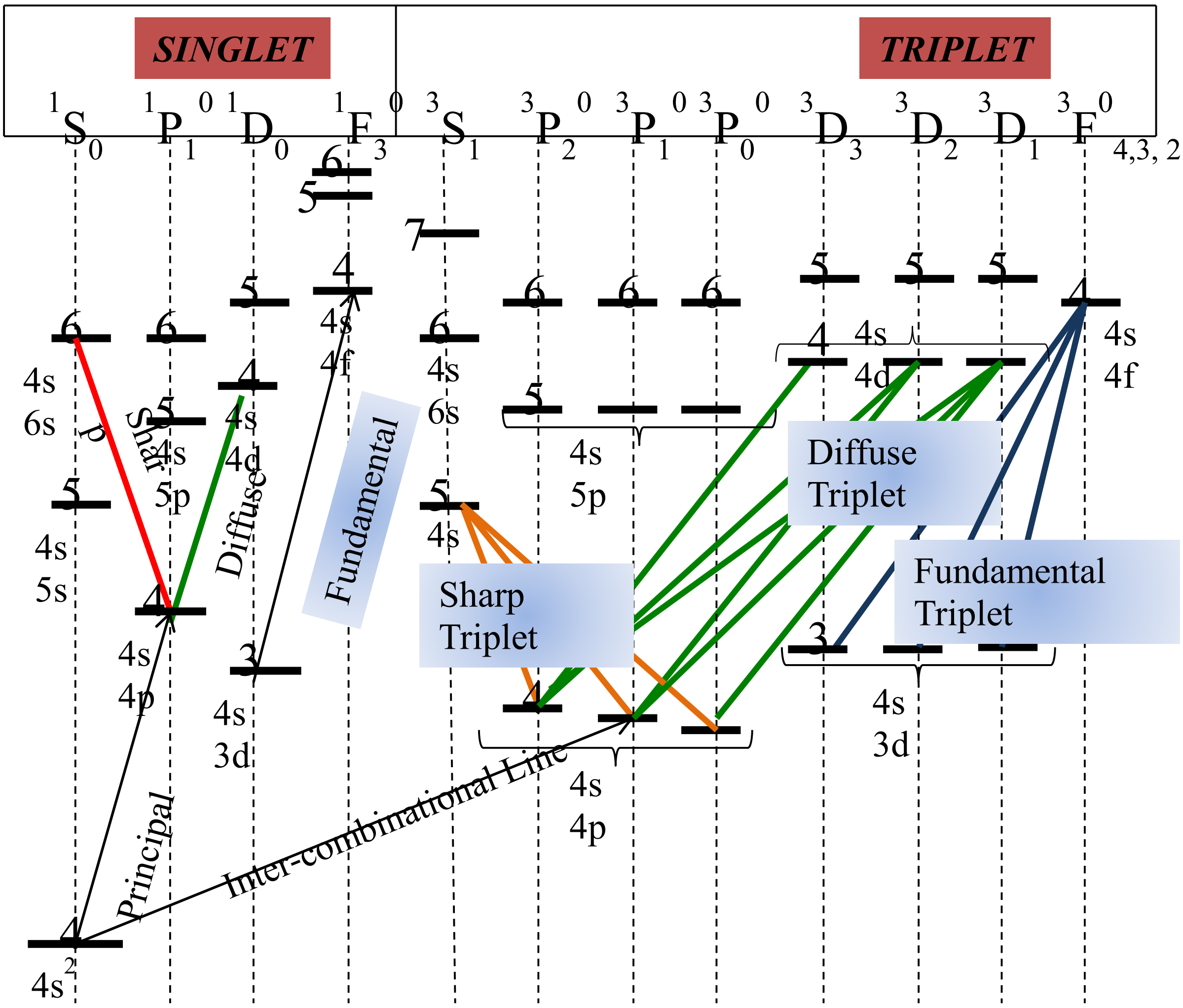

Figure 10. Energy levels corresponding to various configuration terms of excited states.

The permitted transitions can be expressed as in the Figure 10. Here, a singlet principal series arise from the transition of electrons from the $^1P^o{}_1$ level to the normal and lower level 4^1S_0. On the other hand, the triplet sharp series arise from the transition beginning from the $^3S_1$ series level and terminating on the lowest levels, that is, $4^3P^o{}_{2,\,1,\,0}$; the triplet diffuse series arise from the transition from $^3D_{3,\,2,\,1}$ to lowest $4^3P^o{}_{2,\,1,\,0}$ levels and the triplet fundamental series arise from the transition from $^3F^o{}_{4,\,3,\,2}$ to the lowest 3 $^3D_{3,\,2,\,1}$ levels. Those lines that start from the transitions between the levels that are higher as in the Figure 10 are called as the 'combination lines'. Seldom, the $^3P^o{}_1$ - $^1S_0$ transition, that is the transition that takes place between the triplet and the singlet levels, are also seen. These reflect to 'inter-combination lines'.

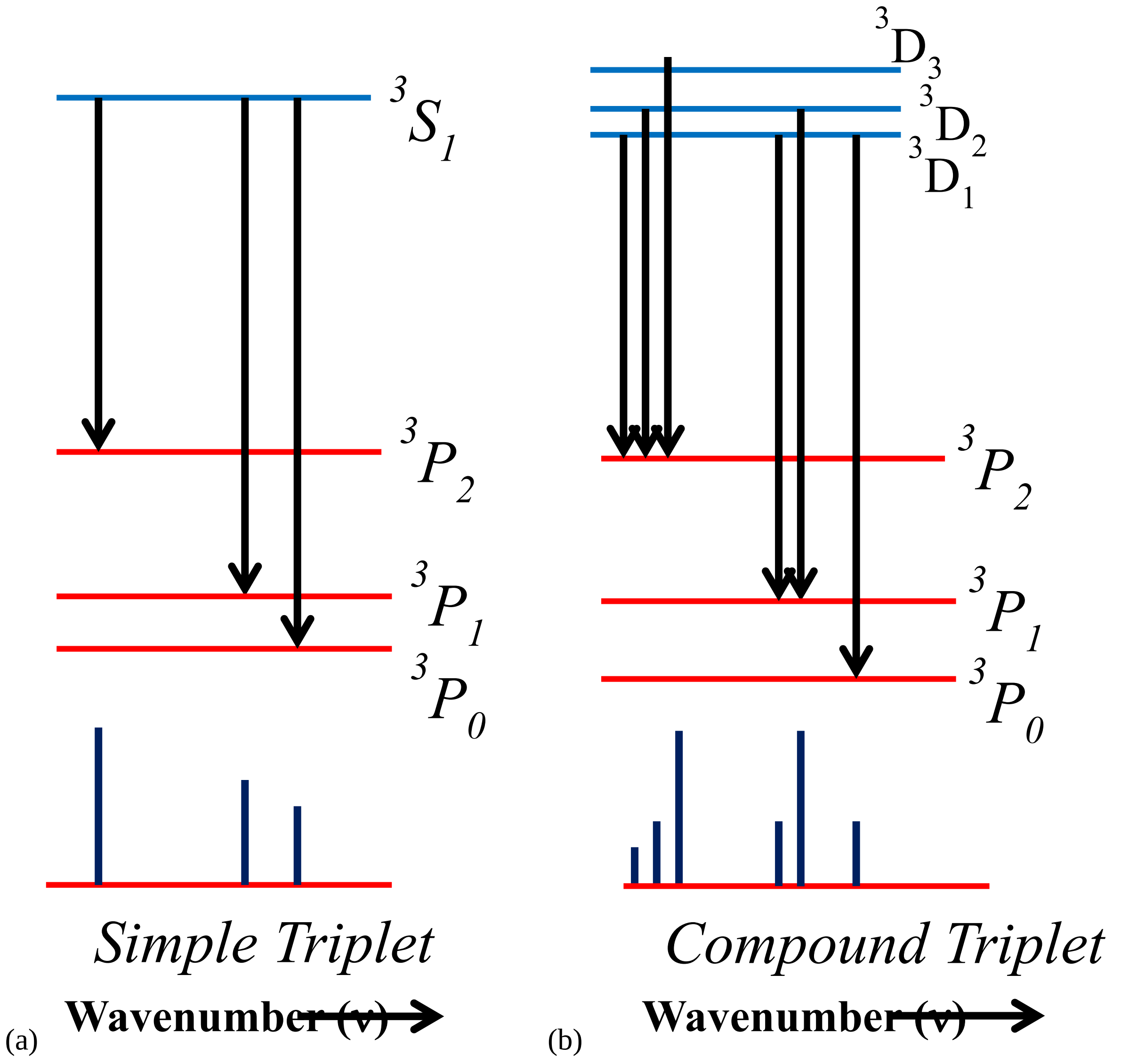

Figure 11. (a) Simple and (b) Compound triplet structure formation, respectively.

Figure 11(a) and (b) displays a simple as well as the compound triplet structure ($^3D \rightarrow {}^3P$), respectively. The order of the levels is regular as the lower *j* valued levels are placed lower. Moreover, the spacing obeys the Lande's interval rule. The $^3P_2 - {}^3P_1$ and $^3P_1 - {}^3P_0$ intervals exists in ratio 2:1, and that of $^3D_3 - {}^3D_2$ and $^3D_2 - {}^3D_1$ intervals exists in 3:2 ratio.

There are following rules which govern the relative intensities of the spectral lines. This rule says that where ΔL changes in the similar way as that of ΔJ. Out of these, the transition with the largest value of *L* and *J*, give rise to the strongest lines.

The Anomalous Triplets: The alkaline earth elements as well as the alkaline earth ion spectra's exhibit few multiplets with structure difference from that of simple or compound triplets, with respect to the intensities and the relative separations. These multiplets are then called as anomalous triplets and these are generated as a result of excitation of both of the optical electrons (Figure 12).

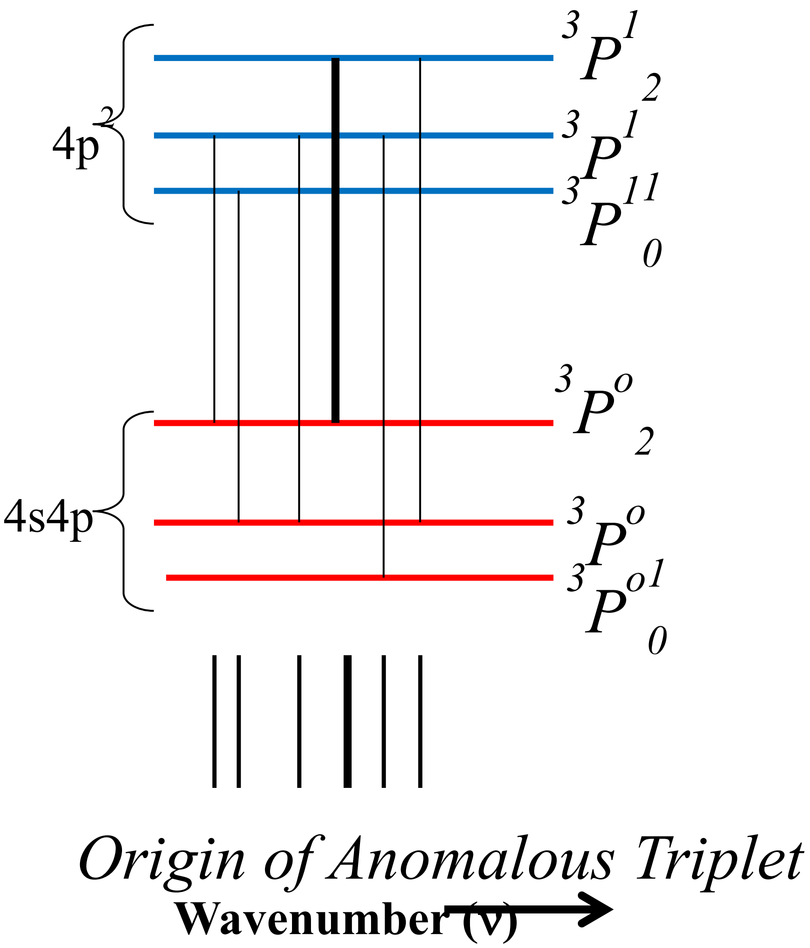

Figure 12. Depiction of the transition resulting in the formation of anomalous triplet.

A multiplet in *Ca* at 4300Å gives rise to six lines. An examination of this multiplet proposes its generation from the transition between two ^{3}P terms with same splitting. The lowest $4s\ 4p$ $^3P^o$ state constitutes the lower state of the multiplet while the upper state is an anomalous term which is labelled as $^3P'$ that is not included in the normal term series of the atom. In this term, both the optical electrons are excited to $4p$ subshell. This configuration gives three terms, that is, ^{3}P, ^{1}D, ^{1}S out of which ^{3}P only combines to all in a strong manner, as per the selection rule. If we write the symbol in full, we get transitions

$$4p^2\ {}^3P' \rightarrow 4s\ 4p\ {}^3P^o$$

In this scenario, $\Delta L = 0$, is possible, providing that $\Delta l = \pm 1$ (even ↔ odd) for that one electron that skips or jumps.

The ***j – j* coupling** scheme in the vector model of two electron atom constitutes the spin and the orbital vectors, $\vec{s_1}$ and $\vec{l_1}$ of one electron are coupled firmly to each other to give rise to a resultant $\vec{j_1}$ around which the two individual vectors precess swiftly. In the similar way, $\vec{s_2}$ and $\vec{l_2}$ of the another electron give rise to resultant $\vec{j_2}$. The two resultants $\vec{j_1}$and $\vec{j_2}$, themselves couple with each other strongly, thus giving rise to $\vec{J}$, which is the total angular momentum.

The individual resultant vectors precess quite slowly around the total angular momentum. (Figure 13)

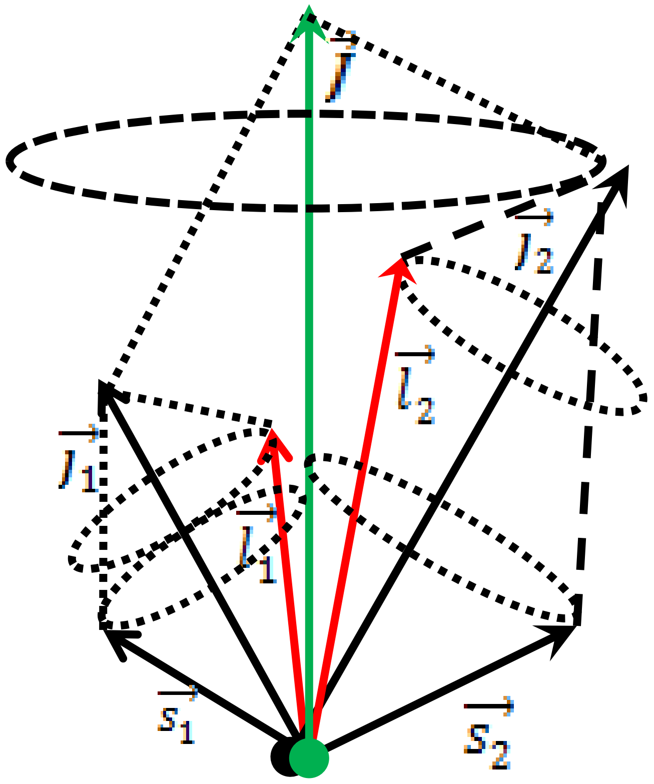

Figure 13. Vector model of two electron j-j coupling.

The terms and the J values for this type of coupling are similar to those of the $L - S$ coupling. Moreover, this type of coupling occurs seldom.

3.9. Interaction Energy (Triplet separation) in $L - S$ and $j - j$ couplings

For every different value of J, the atomic terms consists of multiplet components dues to spin-orbit interaction. This interaction is dependent on the fourth power of atomic number Z which gets further large in heavier atoms.

From the relation of the shift in fine-structure level from the hypothetical centre, for a single electron atom, the interaction energy is given by:

$$-\Delta T_{ls} = \frac{R_\infty}{2n^3 l\left(l+\frac{1}{2}\right)(l+1)}[j(j+1) - l(l+1) - s(s+1)]\text{cm}^{-1}$$

$$= a\frac{j^{*2} - l^{*2} - s^{*2}}{2}$$

Where $a = \frac{R_\infty \alpha^2 Z^4}{n^3 l\left(l+\frac{1}{2}\right)(l+1)} cm^{-1}$; $j^* = \sqrt{j(j+1)}, l^* = \sqrt{l(l+1)}, and\ s^* = \sqrt{s(s+1)}$

For two optical electrons there could be four possibilities of arrangement of angular momenta $l_1^*, l_2^*, s_1^*, s_2^*$ and these four possibilities can be paired um in six possible interactions the ways as $(a)\ l_1^*\ with\ l_2^*, (b)\ s_1^* with\ s_2^* (c)\ l_1^*\ with\ s_1^*, (d)\ l_2^*\ with\ s_2^*, (e)\ l_1^*\ with\ s_2^*, (f)\ l_2^*\ with\ s_1^*.$

It is seen that in L-S coupling, the interaction mentioned by processes (a), (b) are most probable over process (c) and (d), while the process I & (f) are least probable. Using the cosine law of $j^{*2} = l^{*2} + s^{*2} + 2l^{*2}s^{*2}\cos(l^*s^*)$,

Therefore, the general terms will be: $-\Delta T_{ls} = al^*s^*\cos(l^*s^*)$. For the above interactions, the related energies are:

$$\Delta T_1 = a_1 s_1^*\ s_2^* \cos(s_1^*\ s_2^*)$$

$$\Delta T_2 = a_2 l_1^*\ l_2^* \cos(l_1^*\ l_2^*)$$

$$\Delta T_3 = a_2 l_1^* s_2^* \cos(l_1^*\ s_2^*)$$

$$\Delta T_4 = a_2 l_2^*\ s_1^* \cos(l_1^*\ s_1^*)$$

Since, in s_1^* and s_2^* precess around in the fixed angles to form their resultant S*, and therefore its magnitude remains fixed. Similar observations were taken for l_1^* and l_2^* around L*. Again using the cosine law in terms to calculate S^{*2}, L^{*2}, we have,

$$\Delta T_1 = \frac{1}{2} a_1 (\mathrm{S}^{*2} - \mathrm{s}_1^{*2} - \mathrm{s}_2^{*2})$$

$$\Delta T_2 = \frac{1}{2} a_2 (\mathrm{L}^{*2} - \mathrm{l}_1^{*2} - \mathrm{l}_2^{*2})$$

Here L* and S* also precess around J* in the similar manner as l* and s* do for a single electron process around j*. The energy of interaction is due to coupling in between l_1^* and s_1^* and in between l_2^* and s_2^* is given by the terms ΔT_3 and ΔT_4, respectively. Since the angle between the vector changes continuously, we have to involve the average values obtained by the cosine functions between the vectors. This average value is given by

$$\overline{\cos(l_1^*\ s_1^*)} = cos(l_1^*\ L^*\ ) cos(L^*S^*) cos(S^*s_1^*)$$

And

$$\overline{\cos(l_2^*\ s_2^*)} = cos(l_2^*\ L^*\ ) cos(L^*S^*) cos(S^*s_2^*)$$

Using the average cosine values from $\Delta T_1, \Delta T_2$, and rearranging the terms from the cosine laws on the we get:

$$\Delta T_3 + \Delta T_4 = \frac{1}{2}(a_3c_3 + a_4c_4)(\mathrm{J}^{*2} - \mathrm{L}^{*2} - \mathrm{S}^{*2})$$

Where, $c_3 = \frac{l_1^{*2} - l_2^{*2} + L^{*2}}{2L^{*2}} . \frac{s_1^{*2} - s_2^{*2} + \mathrm{S}^{*2}}{2\ \mathrm{S}^{*2}}$ and

$$c_4 = \frac{l_2^{*2}-l_1^{*2}+L^{*2}}{2L^{*2}} . \frac{s_2^{*2}-s_1^{*2}+\mathrm{S}^{*2}}{2\,\mathrm{S}^{*2}}$$

Since for any of the sets of triplet, $l_1^*, l_2^*, s_1^*, s_1^*, L^*, S^*$ are having fixed magnitudes therefore $a_3, c_{3,} a_{4,} c_4$ are all constant and could be summed up as A. Therefore the equation reduces to,

$$\Delta T_3 + \Delta T_4 = \frac{1}{2} A(\mathrm{J}^{*2} - \mathrm{L}^{*2} - \mathrm{S}^{*2})$$

Now the formula for the fine structure can be written as,

$$T = T_0 - \Delta T_1 - \Delta T_2 - \Delta T_3 - \Delta T_4$$

Where T_0 can be assumed to be a hypothetical centre of gravity for the entire electronic configuration.

3.10. Comparison of the terms used in *L – S* and *j – j* couplings

The *L – S* coupling gives the singlet and triplet term, that is, ^{1}P and ^{3}P with high energy difference. The triplet term divides into three closely spaced components by the spin – orbit interactions. Thus, after splitting, there are four plausible states, $^1P_1$, $^3P_0$, $^3P_1$ and $^3P_2$ with value of J = 0, 1, 2. On the other hand, in the *j – j* coupling, this similar configuration gives broadly separated (j_1, j_2) terms $\left(\frac{3}{2}, \frac{1}{2}\right)$ and $\left(\frac{1}{2}, \frac{1}{2}\right)$. When a small interaction is taken into consideration, each term is divides into two closely spaced components. Here, for term $\left(\frac{3}{2}, \frac{1}{2}\right)$, the value of J is 2, 1. For term $\left(\frac{1}{2}, \frac{1}{2}\right)$, the value of J is 1, 0. Therefore, we can look that the number of the terms are similar along with the J values for both the type of coupling. The terms can be correlated in the Figure 14. Below.

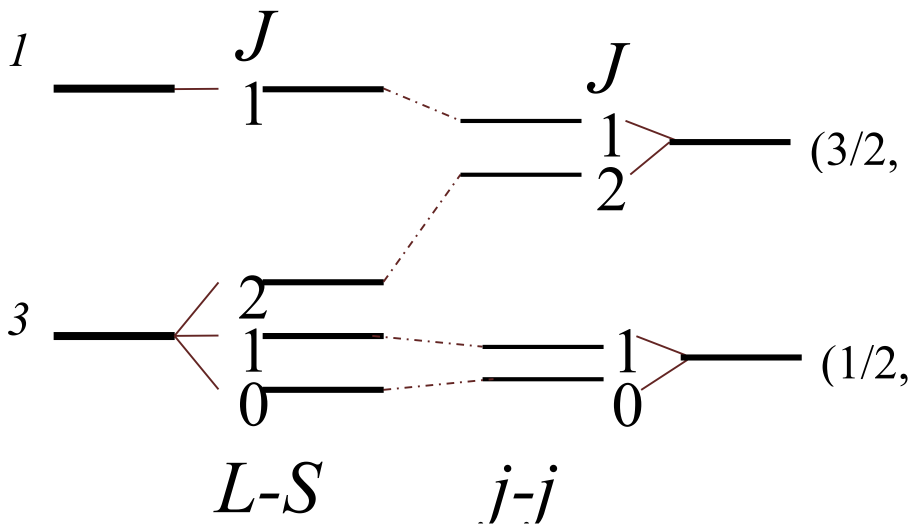

Figure 14. Correlation of two coupling is shown by dotted lines.

The coupling intermediate can exist with the extreme values but the terms can be determined through their J values as the total angular momentum of the atom is always conserved as the coupling changes.

3.11. Regularities in Complex Spectra

Atomic spectra of a complex atom constitute different regularities which are as follows:

(i). The Hartley Law of Constant Doublet separation

According to Hartley (1983), the components of the multiplets of a spectral series constitute constant wave separation. Let us take an example: same wave number separation is present in all the doublet lines of the sharp series of an alkali atom. It is an undeniable repercussion of the concept of energy levels. The transitions that are starting from or terminating on a doublet level gives two sets of lines, which are separated by the energy interval between two segments of the level.

(ii). The Rydberg – series relationships

According to the Rydberg's observation, the spectral lines of a complex atom splits into several series, with many recognized series can be denoted by a formula comparable to Balmer's formula of the hydrogen series

$$\boldsymbol{v_m = v_\infty - \frac{R}{(m+\mu)^2}};\ \mu < 1 \text{ and } m = 2,3,4, \ldots . \infty$$

Where, v_∞, also called convergence limit and μ are constant, which vary from one series to another. This can be interpreted from Schroedinger theory which explains that an electron which is at far distance from the nucleus travel through into the potential field and reach the field because of the singly charged nucleus, as that of hydrogen, due to the shielding effect of the inner electrons. Therefore, higher excited states of a neutral atom where only one electron is excited, reach for hydrogen.

(iii). The Alternation law of Multiplicities

According to this law, the spectral terms that generates from the consecutive elements present in the periodic table, alternates between even and odd multiplicities. As taking an example, the elements in fourth period, the multiplicities are:

K – Doublets

Ca – Singlets, Triplets

Sc – Doublets, Quartets

Ti – Singlets, Triplets, Quintets

This law is an effect of the combination of the spin properties of different valence electrons. Therefore, the even multiplicity arises from the odd number of electrons while the odd ones arise from the even number of electrons.
1 electron – Doublet
2 electrons – Singlet, Triplet
3 electrons – Doublet, Quartet
4 electrons – Singlet, Triplet, Quintet

(iv). Connection between member of same Chemical Group

The chemically similar atom spectra show noticeable connection. Such atoms have analogous electron configuration giving rise to analogous sets of excited energy levels, further results in similar spectra.

(v). The Displacement Law

Kossel and Sommerfeld stated this law in year 1919. According to this law, the energy level and the spectrum of any neutral atom of Z atomic number closely simulate the energy level and the spectrum of the singly ionised atom of atomic number Z+1 coming next in the periodic table. This law is based on the fact that the electron configuration of two such atoms would be same. Therefore, the spectrum of the hydrogen atom is similar to that of the He atom while the doublet series of Li, Na, K, … and so on, which are the alkali metals, are similar to the doublet series of Be^+, Mg^+, Ca^+,… and so on, the ionised alkaline earth metals.

(vi). Isoelectronic Sequences

The displacement law can also be applicable to the series with adjacent elements, each one of them ionised to a successively greater degree. Therefore, the series of atoms, whose electron configurations are similar, are called as an ‘Isoelectronic Sequence’. As per example, the atoms that form the isoelectronic sequence are as follows:

K – Z=19
Ca^+ – Z=20
Sc^{++}– Z=21
Ti^{+++}– Z=22

These can also be written as:
K I, Ca II, Sc III, Ti IV

The spectrum lines and the energy level generating from each of the atoms show great resemblance. For example, similar relative intensities for the various transitions, same type of fine structure splitting, etc.

3.12. Summary

This unit III is in continuation with previously discussed Unit I and II where most of the basic details and properties related to Hydrogen atom and its spectra were discussed. In this Unit III, we have summarised the whole unit in two halves. The first comprises of studies about the spectra of alkali and the second half considers the spectra about the alkaline earth spectra.

In first part, the fundamental introduction to the formation of four spectral lines were observed and elaborated. The Rydberg-Schuster Law and Runge's Law were found to be established in alkali series. The concept of 'combinational' series was established by Ritz combination principle. With the effect of increase in the shell value n, the alkali levels approach the corresponding H-levels because of the screening effect and also in comparison to hydrogen, it was found that the energy not only depends on n value but also on l. thus all alkali levels with a given n are shifted lower than the corresponding H-levels. The selection rule for the absorption spectra of Na atoms was revealed. It was noted that the optically active electron in atom absorbs quantised energy and gets excited to the higher levels. The concept of spin-orbit interaction leading to j was considered in details. The mathematical formulation for considering the screening effect gave a good agreement for doublet separation with experimental results. Quantitative rules for intensity relations were also discussed.

In the second half section of this unit, the essential features of alkaline earth spectra are elaborated in details. Vector Model, in which various angular momenta occurring in the atomic spectra are considered. In this model, the combined form of the resultant vectors, and subsequently their spectral properties were briefed. LS and jj coupling schemes are quantitatively and qualitatively discussed in details. Further, one can easily calculate the interaction energy for the triplet separation in L-S and j-j coup;ing using the mathematical operations therein.

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3.15. Terminal Descriptive type questions

1. How will you explain the common features of spectra of alkali like atoms?
2. Even though H and Na belong to the single valance electron system, distinguish between the spectra obtained for two atoms.
3. Show the conception of spinning electrons that result for the doubling of levels in the spectra of alkalis.
4. Using the spin-orbit interaction energy for a single non-penetrating valence electron, elaborate and discuss the separation of 2P and 2D terms of alkali spectra.
5. Explain the theoretical background along with the essential features of the spectra of alkaline earth elements.
6. Describe using the vector model of an atom for explaining its spectra with two electrons outside the closed shell.
7. Discuss the vector model of an atom consisting of the two valance electrons in terms of L-S and j-j couplings.

3.16. Numerical type (Self Assessment Questions)

1. The mean position of the first pair of lines of the principal series of sodium is 16960 cm^{-1}. If the convergence limit of the sharp series lines is at 24490 cm^{-1}, calculate the ionisation potential of sodium.

   Ans. The first principal line is obtained from the transition of 3s-3p and the convergence limit is obtained from 3p-∞. The sum of wave numbers will be (referring to Figure 1) 16960+24490=41450cm^{-1}. This corresponds to 3s-∞, resulting in the ionization of atom having energy 5.14eV. [Use 1eV=8066cm^{-1}].

2. The longest wavelength lines in the series $(n, l) \rightarrow (4,0)$ in potassium have wavelengths 7699.0, 7664.9, 4047.2, 4044.1Å respectively. Construct the relevant part of the energy level

diagram and calculate the splitting between the levels with the same values of *n* and *l* but different *j*.

Ans**.** The given wavelengths represent the first two doublets of the principal series of potassium, and arise from the transitions

$$4\,{}^2P_{3/2,\ 1/2} \rightarrow 4\,{}^2S_{1/2}$$

$$5\,{}^2P_{3/2,\ 1/2} \rightarrow 4\,{}^2S_{1/2}$$

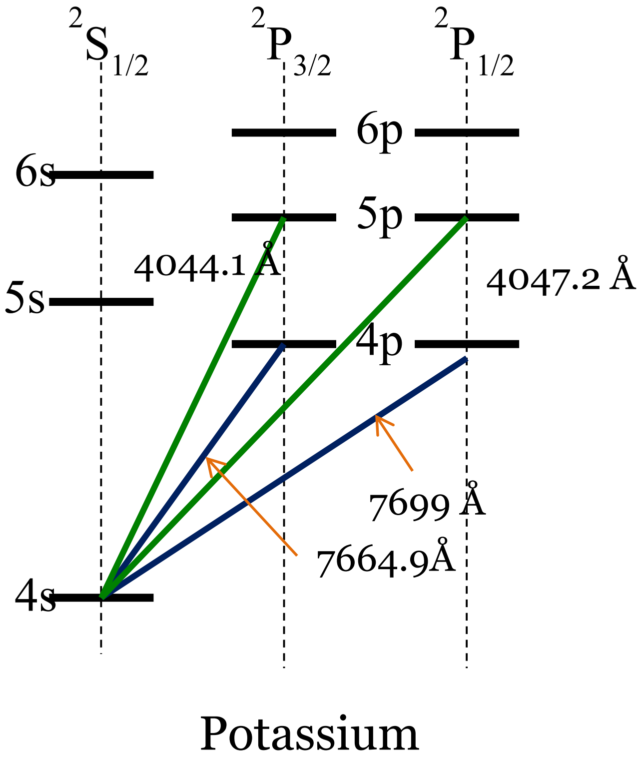

Diagram showing the splitting between the levels

The line splitting in the wave number are the corresponding level splitting with the same values of *n* and *l* but different *j*. We know that the wave number ν is the reciprocal of wavelength λ

$$\nu = \frac{1}{\lambda}$$

So that

$$d\nu = -\frac{1}{\lambda^2} d\lambda$$

Numerically, it can be written as

$$d\nu = \frac{d\lambda}{\lambda^2 \times \lambda_2}$$

For the wavelengths 7699.0 and 7664.9 Å, we have

$$d\nu = \frac{(7699.0 - 7664.9) \times 10^{-8} cm}{(7699.0 \times 10^{-8} cm) \times (7664.9 \times 10^{-8} cm)}$$

$$d\nu = \frac{34.1}{7699.0 \times 7664.9 \times 10^{-8} cm}$$

$$d\nu = 57.8\ cm^{-1}$$

UNIT 4 ZEEMAN EFFECT

STRUCTURE:

4.1. Introduction

4.2. Objectives

4.3. Zeeman effect and its experimental study

  4.3.1. Classical interpretation of normal Zeeman effect

  4.3.2. Vector atom model and Normal Zeeman effect

  4.3.3. Quantum mechanical interpretation of normal Zeeman effect

4.4. Anomalous Zeeman effect

  4.4.1. Quantum mechanical treatment of anomalous Zeeman effect

4.5. Paschen-Back effect

  4.5.1. Quantum mechanical treatment of Paschen-Back effect

4.6. Spin orbit correction

4.7. Summary

4.8. Glossary

4.9. Terminal Questions

4.10. References

4.11. Answers

4.1 INTRODUCTION

The Zeeman effect is a magneto-optical phenomenon in which spectral lines are affected by an applied magnetic field and split into several components. This was first observed by Zeeman in 1896 and hence called Zeeman effect. He found if a source of light giving line spectra be placed in a magnetic field, the lines were split into a number of component lines, symmetrically distributed about the original line. Doublets, triplets and even more complex system were observed.

Primarily, it was observed that a single spectral line splits into three components such that one line has got a large frequency, other a lower frequency than the frequency of original line and a third one has a frequency of original line. This was named as normal Zeeman effect. But later on, more complicated splitting was observed and was called anomalous Zeeman effect. However, when a huge magnetic field is applied the splitting is called Paschen-Back effect. The effect of electric field on spectral line was observed by Stark in 1913 and is called Stark effect.

4.2 OBJECTIVES:

This unit introduces the effect of magnetic field on the spectral lines of atom which is called as Zeeman effect. Depending on the strength of the magnetic field we have normal, anomalous Zeeman effect and Paschen-Back effect. In this unit we will study about these effects and their classical and quantum mechanical explanation. After going through this unit, the students will be able to know about

1. The normal Zeeman effect, anomalous Zeeman effect and Paschen-Back effect.
2. The experimental study of above effects.
3. The classical and quantum mechanical explanation of above.
4. The spin orbit interaction.

4.3 ZEEMAN EFFECT AND ITS EXPERIMENTAL STUDY

Zeeman effect was discovered by Pieter Zeeman in 1896. He observed that if a source of light producing line spectrum is placed in a magnetic field, the spectral lines are split up into components. When the splitting is into two or three lines, then it is called normal Zeeman effect because it can be explained easily by classical theory. But when the applied magnetic field is weak, then the splitting of a single line takes place into a number of components. This effect is called anomalous Zeeman effect. The normal Zeeman effect is observed rarely whereas the anomalous Zeeman effect is observed in general. The experimental arrangement for studying normal Zeeman effect is shown in fig. 4.1

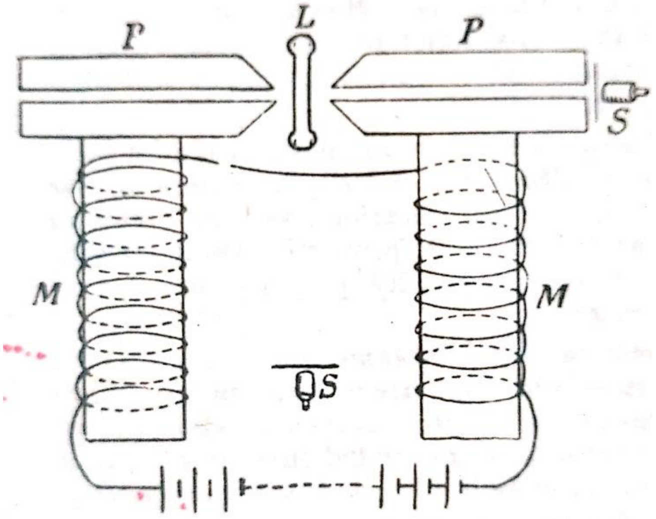

Figure 4.1: Experimental arrangement for studying Zeeman effect

In the given arrangement, an electromagnet MM capable of producing a very strong magnetic field and having conical pieces PP, through which holes are drilled lengthwise, is set up. A source L emitting spectral lines; say a sodium vapour lamp, is placed between the pole pieces. The spectral lines are observed with a high resolving power instrument with a constant deviation spectrometer S. The light can be viewed perpendicular as well as parallel to the magnetic field.

When light is viewed parallel to the magnetic field through the hole drilled in the pole pieces, a single line is observed to be split up into two components (doublet). One component has a higher frequency than the original line and the other lower. The original line is not observed. Also, the original line is not polarized but the other two components are circularly polarized in opposite direction. The outer components are known as σ components and the middle one is π component. The σ components are symmetrically situated about the original line, so the change in wavelength dλ, known as Zeeman shift, is the same in both cases (fig 4.2).

When light is observed perpendicular to the magnetic field, a triplet i.e., three component lines are seen. One component line is observed in the same position as the original line and the other two components, one on either side of this line are separated by equal amounts. These three components are plane polarized but the vibrations of the central line is parallel to the magnetic field while those of outer ones perpendicular to the field (fig. 4.2).

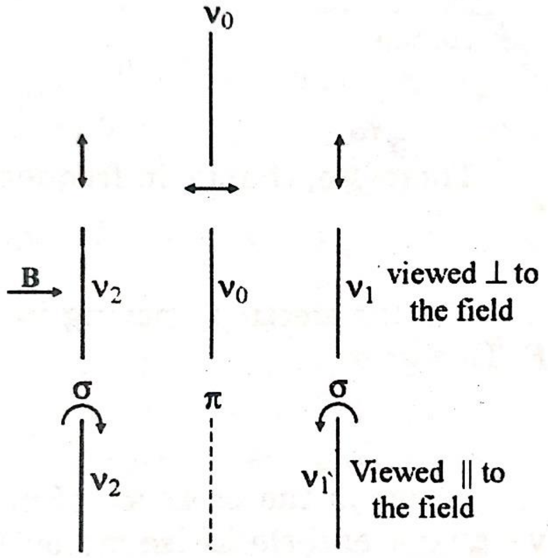

Figure 4.2: Normal Zeeman Effect

4.3.1 CLASSICAL INTERPRETATION OF NORMAL ZEEMAN EFFECT:

It is observed that when magnetic field is applied, a single spectral line splits up into three components such that one line has got a larger frequency, other a lower frequency than the original line and the third one has the same frequency as that of the original line. This is called normal Zeeman effect.

The normal Zeeman effect is explained on the basis of Lorentz classical theory. According to this theory if a source of light is placed in a magnetic field, the frequency of motion of electron moving in a circular orbit gets modified.

Let us consider an electron in an atom moving in a circular orbit of radius ‘r’ with a linear velocity ‘v’ and angular velocity ‘ω’. Let ‘e’ and ‘m’ be the charge and mass of electron respectively. The centripetal force acting on the electron towards the centre in the absence of the magnetic field,

$$F = \frac{mv^2}{r} = mr\omega^2 \qquad \text{………………..(1)}$$

Now, let an external magnetic field ‘B’ be applied in a direction perpendicular to the plane of the orbits of the two circular components. Then, an additional radial force of magnitude Bev acts on the electron. The direction of this force will be outwards from the center for clockwise motion but inwards towards the center for anticlockwise motion. The resulting complex motion of the electron subjected to an additional radial force is called Larmor precession. This produces change in the angular velocity without any change in the form of the orbit.

Let dω be the change in angular velocity caused by the magnetic field. For the circular motion in the clockwise direction, the additional radial force is directed away from the center,

Therefore $$F - Bev = mr\,(\omega + d\omega\,)^2 \qquad \text{………………….(2)}$$

$$mr\omega^2 - mr\,(\omega + d\omega\,)^2 = Be\omega r$$

Or $$-2mr\omega d\omega = Be\omega r \qquad neglecting\ \ (d\omega)^2$$

Or $$d\omega = -\frac{Be}{2m} \qquad \text{………………(3)}$$

For the circular motion in the anticlockwise direction, the additional radial force is directed towards the centre.

Therefore $$F + Bev = \ mr\,(\omega + d\omega\,)^2$$

Or $$d\omega = \ +\ \frac{Be}{2m} \qquad \text{………………..(4)}$$

The two cases can be combined into the equation

$$d\omega = \ \pm\frac{Be}{2m} \qquad \text{………………(5)}$$

If ν be the frequency of vibration of the electron,

Then $$\omega = 2\pi\nu$$

Or $$d\omega = 2\pi d\nu$$

Or $$d\nu = \ \frac{d\omega}{2\pi}$$

Therefore, change in frequency of the spectral line,

$$d\nu = \pm\ \frac{Be}{4\pi m} \qquad \text{…………….(6)}$$

If ν and λ are the frequency and wavelength of the original line,

$$\nu = \frac{c}{\lambda}$$

or
$$d\nu = -\ \frac{c}{\lambda^2}\, d\lambda$$

Therefore, the Zeeman shift

$$d\lambda = \pm \frac{Be\lambda^2}{4\pi mc} \qquad \text{..................(7)}$$

Taking a spectral line of known wavelength λ, and applying a magnetic field *B*, the Zeeman shift dλ is measured.

From equation (7),

$$\frac{e}{m} = \left(\frac{4\pi c}{B\lambda^2}\right) d\lambda$$

From above equation, $\frac{e}{m}$ can be calculated. $\frac{e}{m}$ is found to be 1.757×10^{11} CKg^{-1} which is in agreement with the value of $\frac{e}{m}$ of the electron obtained from Thomson's experiment.

4.3.2 VECTOR MODEL AND NORMAL ZEEMAN EFFECT:

We have studied that Lorentz was able to explain normal Zeeman effect quite satisfactorily using classical theory. Later, Debye was able to interpret the same using vector atom model where, the concept of electron spin was not taken into account, but only orbital motion was considered.

Here only the angular momentum possessed by the electron due to its orbital motion is taken into account. The magnitude of this orbital angular momentum which is quantized is given by

$$p_l = l.\frac{h}{2\pi} \qquad \text{..................(1)}$$

The corresponding magnetic moment is given by

$$\mu_l = l.\frac{eh}{4\pi mc} = \frac{e}{2mc}\, p_l \qquad \text{..................(2)}$$

The vectors l and μ_l will act along the same line, viz., perpendicular to the orbital plane. In the presence of external magnetic field B, the vector l will execute Larmor precession round the field direction as axis whose frequency is given by

$$\omega_{i = B}\,\frac{\mu_l}{p_l} = \frac{e}{2m}\,B \qquad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

The effect of this Larmor precession is to alter the energy of the system by an amount ΔE, which is given by

$$\Delta E = \omega_l \times \text{Projection of mechanical momentum on the field direction}$$

$$\Delta E = \frac{e}{2m}\,B\,p_l\cos\theta = \frac{eB}{2m}\,\frac{lh}{2\pi}\,\cos\theta$$

$$\Delta E = \frac{ehB}{4\pi m}\,m_l \qquad \ldots\ldots\ldots\ldots\ldots(4)$$

Since $\cos\theta = m_l$

Now change in energy means that each energy level of the undisturbed state of the atom is, splitted into a number of levels which is given by (2l + 1) and the magnitude of separation is proportional to the strength of magnetic field.

Now suppose that E_1 and E_2 are the energies of the two levels in the presence of magnetic field and E_{01} and E_{02} in the absence of magnetic field with the two values of m_l as m_{l_1} and m_{l_2}. Then we have

$$E_1 = E_{01} + \Delta E_1 = E_{01} + m_{l_1}\frac{ehB}{4\pi m} \qquad \ldots\ldots\ldots\ldots\ldots(5)$$

$$E_2 = E_{02} + \Delta E_2 = E_{02} + m_{l_2}\frac{ehB}{4\pi m} \qquad \ldots\ldots\ldots\ldots\ldots(6)$$

If transitions take place between these two above multiplet states, a multiplet group of lines will result. The frequency ν of any of these lines is obtained from equations (5) and (6) by using Bohr's frequency condition i.e.

$$E_1 - E_2 = E_{01} - E_{02} + \frac{ehB}{4\pi m}(m_{l_1} - m_{l_2})$$

$$h\nu = h\nu_0 + \Delta m_l\,\frac{ehB}{4\pi m}$$

$$\nu = \nu_0 + \frac{eB}{4\pi m}\Delta m_l \qquad \text{.............................} (7)$$

Here ν_0 is the frequency of the line in the absence of the field. Applying the appropriate selection rule; viz., $\Delta m_l = 0$ or ± 1 ; we have three possible lines,

$$\nu_1 = \nu_0$$

$$\nu_2 = \nu_0 + \frac{eB}{4\pi m}$$

$$\nu_3 = \nu_0 - \frac{eB}{4\pi m}$$

The frequency shift $d\nu$ produced by the field is therefore $\pm\, eB/4\pi mc,$ the same as derived by the classical theory for normal Zeeman effect. $eB/4\pi mc$, is called Lorentz unit. Fig. 4.3 represents normal Zeeman effect. For three transitions in a bracket change in the value of Δm_l is the same and hence they represent same change of energy and a single line.

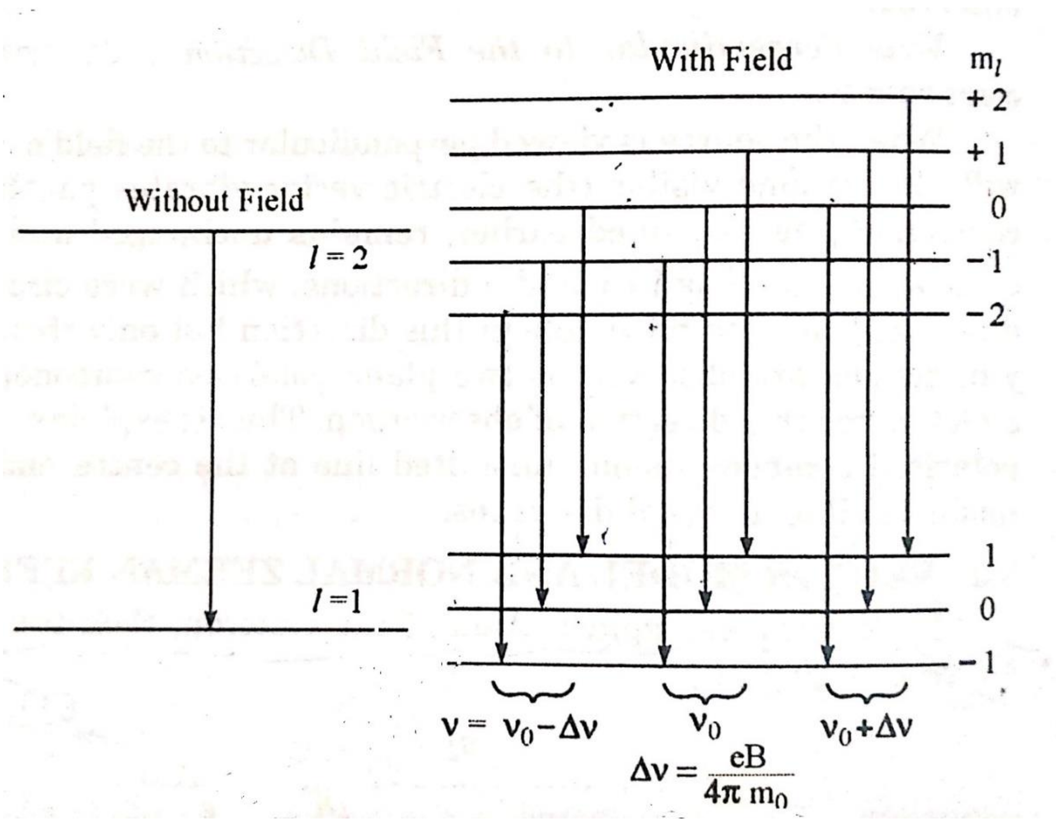

Figure 4.3: Normal Zeeman effect

4.3.3 QUANTUM MECHANICAL EXPLANATION OF NORMAL ZEEMAN EFFECT

Here the procedure is to calculate the interaction of magnetic field with the angular momentum of electrons. The magnetic moment of an electron moving in its orbit is given by

$$\mu_L = -\frac{e}{2mo} L$$

This magnetic moment interacts with external magnetic field and gives the perturbing Hamiltonian as

$$H' = - \mu_L.B$$

$$= \frac{e}{2mo} L \, . \, B$$

To calculate the splitting of spectrum lines, the operator forms of H' is used in the perturbation theory. The first order interaction energy is

$$\Delta E = \int \Psi^* \hat{L} \, \Psi \, d\tau$$

$$\Delta E = \frac{e}{2mo} \int \Psi^* \hat{L} \, \hat{B} \, \Psi \, d\tau$$

Let us assume that B is directed towards z axis; then

$$B = B_z$$

$$\Delta E = \frac{e}{2mo} \; B_z \int \Psi^* \hat{L} \, \Psi \, d\tau$$

But the average value of z-component of angular momentum is M_L h. Hence, change in energy value is (changing B_z to B)

$$\Delta E = \frac{eh}{2mo} \; B_z \, M_L$$

Therefore, the energy of the having the orbital quantum number M_{L1} is

$$E_1 = E^{(1)} + \frac{eh}{2mo} \; BM_{L1}$$

And $$E_2 = E^{(2)} + \frac{eh}{2mo} \; BM_{L2}$$

$$(E_2 – E_1) = (E^2 – E^1) + \frac{eh}{2moc} \; B \, \Delta M_L$$

$$h\nu = \; h\nu_0 + \frac{eh}{2mo} \; B \, \Delta M_L$$

$$\nu = \nu_0 + \frac{eB}{4\pi mo} \Delta M_L$$

The expression when subjected to selection rule $\Delta M_L = 0, \pm1$ gives rise to Zeeman normal triplet. $\Delta M_L = 0$ corresponds to π components and $\Delta M_L = \pm1$ gives σ components

Self-Assessment question (SAQ) 1: Choose the correct option-

1. The number of spectral lines seen in normal Zeeman effect is
a) Greater than 3
b) Equal to 3
c) Less than 3

2. In normal Zeeman effect we take
a) Only orbital motion in account
b) Only spin motion in account
c) Both the above

3. The rule for ΔM_L=0 gives
a) π component
b) σ component
c) none of above

4. 4 ANOMALOUS ZEEMAN EFFECT

When the applied magnetic field is weak as compared to the internal magnetic field, a single spectral line is splitted into a more complex - greater number of components. This is called anomalous Zeeman effect. The Lorentz or Debye theory was able to explain normal Zeeman effect but it was unable to explain anomalous Zeeman effect. To achieve this the idea of spin of electron was introduced. By introducing this the total angular momentum of the atom j^* becomes the vector sum of the orbital and spin angular moments, l^* and s^*, i.e.,

$$j^* = l^* + s^* \qquad \ldots\ldots\ldots\ldots\ldots (1)$$

In this case the coupling between l^* and s^* is intact, so that there is physical significance in compounding l^* and s^* into j^* and then considering the precession of j^* about B.

The magnetic moment due to orbital motion

$$\mu_l = l^* \frac{eh}{4\pi m} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

This μ_l *is* directed opposite to l^* because of negative charge of electron. Similarly, magnetic moment due to spin is given by,

$$\mu_s = 2s^* \frac{eh}{4\pi m} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

μ_s is directed opposite to s^*. This is shown in fig 4.4. Now since l^* and s^* precess around j^*, μ_l and μ_s will also precess around μ_j (μ_j is not in the line of the resultant of μ_l and μ_s).

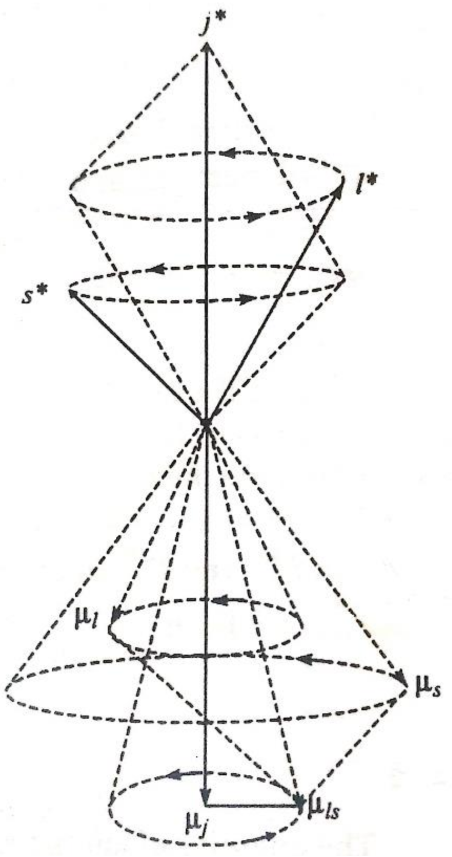

Figure 4.4: The precession of mechanical and magnetic moments

To find out the resultant magnetic moment of the electron, we resolve μ_{ls} into two directions, one along j^* and the other perpendicular to it. The perpendicular component average out to zero due to the continuous change in direction and the parallel components add together. We can say that the parallel components of μ_l and μ_s contribute for μ_j while perpendicular components do not. Hence

$\mu_j =$ Component of μ_l *along the* direction of j^* + component of μ_s along the direction of j^*

$$\mu_j = \frac{eh}{4\pi m}\, l^* \cos(l^* j^*) + \frac{eh}{4\pi m}\, 2s^* \cos(s^* j^*)$$

$$= \frac{eh}{4\pi m}\left[l^* \cos(l^* j^*) + 2s^* \cos(s^* j^*) \right]$$

Or

$$\mu_{j} = j^{*}g = [\, l^{*} \cos(l^{*} j^{*}) + 2s^{*} \cos(s^{*} j^{*})\,]$$

…………………………….(4)

In terms of Bohr Magneton.

But according to cosine law,

$$\cos(l^{*}j^{*}) = \frac{j^{*2} + l^{*2} - s^{*2}}{2j^{*}\, l^{*}}$$

and $$\cos(sl^{*}j^{*}) = \frac{j^{*2} + s^{*2} - l^{*2}}{2j^{*}\, s^{*}}$$

Putting the values in equation (4), we write

$$j^{*}g = \left[\frac{j^{*2} + l^{*2} - s^{*2}}{2j^{*}} + \frac{j^{*2} + s^{*2} - l^{*2}}{j^{*}}\right]$$

or $$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \qquad \text{……………(5)}$$

Writing $j^{*2} = j(j+1)$ and so on.

With this value of g, the total magnetic moment of the electron is

$\mu_{j} = j^{*}g$, in the unit of Bohr magneton.

If now the atom is placed in the weak magnetic field, the total angular momentum vector j^{*} precesses around the B direction. The result of this precession is the change in the energy of electron by the amount.

$$\Delta E = \mu_{j} B \cos(j^{*}B)$$

$$= j^{*}gh \cos(j^{*}B)$$

$$\Delta E = m_{j}gB \qquad \text{……………(6)}$$

This equation again shows that change in the energy is proportional to the magnetic field strength. In the ordinary unit of energy in the above expression,

$$\Delta E = m_j g \frac{eh}{4\pi m_0} B$$

Hence $$\Delta \nu = m_j g \frac{eB}{4\pi m_0}$$

$$\Delta \bar{\nu} = \Delta\, m_j g O$$

where $$O = \frac{eB}{4\pi m_0 c} = \text{Lorentz unit.}$$

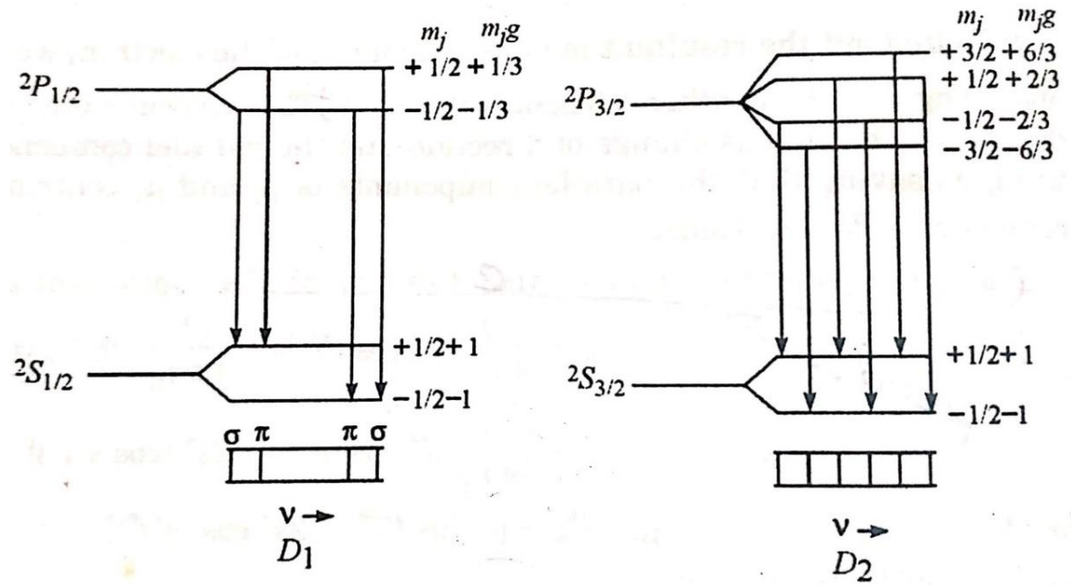

Figure 4.5: Anomalous Zeeman effect

Further, since m_j has $(2j + 1)$ values right from $-j$ to $+j$, so a given level is split up into $(2j + 1)$ sublevels with the application of magnetic field. When this m_j is subjected to the selection rule $\Delta\, m_j = 0$ or ± 1, we get the transition shown in fig. 4.5, for the sodium D lines. The longer wavelength components $3^2S_{1/2} - 3^2P_{3/2}$ splits into four lines. The magnitude of component separation is governed by the factor $\Delta\, m_j g$ showing fig. 4.6. Since g is different for different *values* of j, we get different components for the same change in the value of $\Delta\, m_j$. In this case $\Delta\, m_j = 0$ give rise to π components while $\Delta\, m_j = \pm 1$ gives to σ components.

Thus, it is clear that Lande's g factor is important in order to explain the anomalous Zeeman effect.

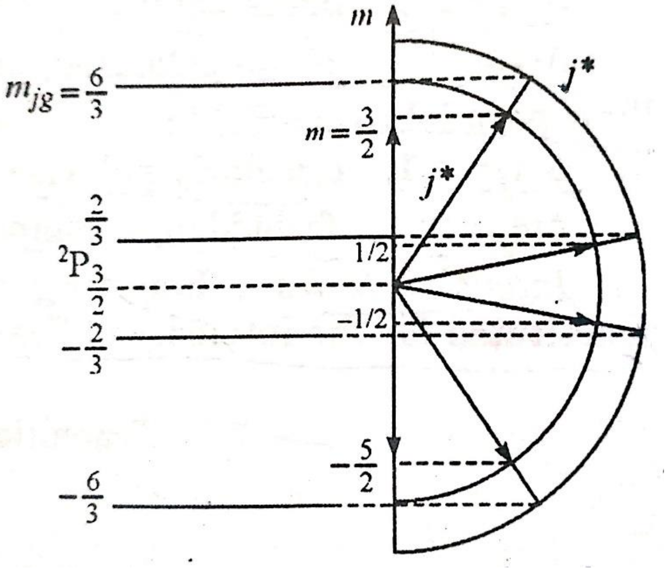

Figure 4.6: The orientations of total angular moment vector in magnetic field

4.4.1 QUANTUM MECHANICAL TREATMENT OF ANOMALOUS ZEEMAN EFFECT

When the source emitting spectral lines is subjected to weak magnetic field, the spin and the orbital angular momentum are separately conserved, and **L**, **S** and **J** are well defined. When we take the spin of the electron into account, the magnetic moment is given by

$$\mu_J = \mu_L + \mu_S,$$

$$\mu_J = - \frac{e}{2mo} [L + 2S]$$

The perturbing Hamiltonian comes out to be

$$H' = - \mu_J B$$

$$H' = \frac{e}{2mo} [L + 2S] . B$$

The change in energy value due to the perturbation is

$$\Delta E' = \int \Psi^* \hat{H}' \Psi \, d\tau$$

$$= \frac{e}{2mo} \hat{B} \int \Psi^* (\hat{L} + 2\hat{S}) \Psi \, d\tau$$

$$= \frac{e}{2mo}[(B.\hat{L}) + 2\,(\hat{B}.\hat{S})]$$

Further if **B** is directed along z-axis. B = B_z and

$$(\hat{B}.\hat{L}) = \frac{\hat{J}.\hat{L}}{\hat{J}^2}\,\hat{B}.\hat{J} = \frac{\hat{J}^2+\hat{L}^2+\hat{S}^2}{2\hat{J}^2}\,\hat{B}.\hat{J}$$

and $$(\hat{B}.\hat{S}) = \frac{J\,(J+1)+S(S+1)-L(L+1)}{2J\,(J+1)}\,BM_J\hbar$$

M_J is the Z component of total angular magnetic moment which is associated with the electron of the atom. The above relations follow from the fact that in a weak magnetic field L and S vectors precess rapidly round their resultant J and, hence, in the average only the component along J survives and the perpendicular component averages to zero. With the substitution, we get (Replace B_z by B)

$$\Delta E' = \frac{e}{2mo}\,B\,[\frac{J\,(J+1)+S(S+1)-L(L+1)}{2J\,(J+1)}]\,M_J\hbar$$

$$\Delta E' = g\,\mu_B\,BM_J$$

Where $$g = 1+\frac{J\,(J+1)+S(S+1)-L(L+1)}{2J\,(J+1)},$$

And $\mu_B = \frac{eh}{2mo}$ is Bohr magneton

The energy expression then becomes,

$$E_{J1} = E^{(1)} + \Delta E_{J1}$$

Or $$E_{J1} = E^{(1)} + \mu_B\,BM_{J1}\,g_1$$

$$E_{J2} = E^{(2)} + \mu_B\,BM_{J2}\,g_2$$

And $$\nu = \frac{E^{(2)} - E^{(1)}}{h} + \frac{eB}{4\pi mo}\,\Delta(M_J\,g)$$

Or $\bar{\nu} = \overline{\nu_0} + \Delta(M_J\,g)$, In Lorentz Unit.

The equation implies that anomalous splitting depends not on $\Delta(M_J)$ but on $\Delta(M_J g)$ informing, thereby, that it is ‘g’ which is responsible for anomalous splitting.

The expressions are same as derived on classical lines and with the selection rule $\Delta M_J = 0, \pm 1$, it explains anomalous Zeeman effect. $\Delta M_J = 0$ gives π components and $\Delta M_J = \pm 1$ gives σ components.

Self-Assessment question (SAQ) 2: Choose the correct option-

1. Anomalous Zeeman effect takes into account

a) Spin motion of electron

b) Orbital motion of electron

c) Both (a) and (b)

2. The ration of spin magnetic moment μ_s to the spin angular momentum $|\vec{s}|$ is

a) e/2m

b) 2e/2m

c) 0

d) 3e/2m

3. In the Anomalous Zeeman effect, the resonance line D_1 and D_2 of sodium arise from transition's

a) $^2P_{1/2} \rightarrow {}^2S_{1/2}$

b) $^2P_{3/2} \rightarrow {}^2S_{1/2}$

c) Both (a) and (b)

d) None of the above

4.5 PASCHEN – BACK EFFECT:

We have already studied that in Zeeman effect, the external magnetic field is weak as compared with the internal magnetic field due to spin and orbital motion of valence electron. Here the precession of l^* and s^* around j^* is much faster than that of j^* around B which makes no change due to motion of l^* and s^* into other motions. However, when the external magnetic field is increased in strength, the coupling between l^* and s^* breaks down and j^*loses its significance. l^* and $s^*$are quantized separately and precess more or less independently around B as shown in fig 4.7. This is known as Paschen – Back effect. Further, when the motion of l^* and s^*become separately quantized, the perpendicular component of magnetic moment, does not average out to zero and contributes to the total magnetic moment, i.e., now total magnetic moment is not equal to m_j. Due to this kind of splitting, whatever be the anomalous Zeeman pattern in the weak magnetic field it is converted into normal pattern in the strong magnetic field.

The angular velocities of two precessions are

$$\omega_l = B\frac{e}{2m0} \text{ and } \omega_S = B\frac{e}{2m0}\ 2.$$

Therefore, the change in interaction energy due to these two motions is the sum of two changes, i.e.

$$\Delta E = \Delta E_{lB} + \Delta E_{sB},$$

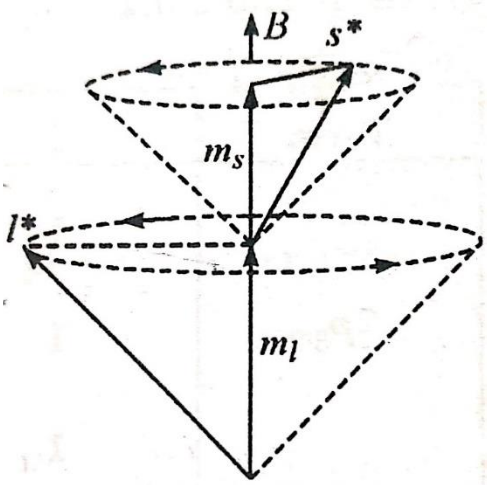

Figure 4.7: Precession of l* and s* vectors in Paschen-Back effect

Where

$$\Delta E_{lB} = B\frac{e}{2m0}\ l^*\frac{h}{2\pi}\cos(l^*B),$$
$$\Delta E_{sB} = B\frac{2e}{2m0}\ \frac{h}{2\pi}\cos(s^*B)$$

Or $$\Delta E_{lB} = \frac{eh}{4\Pi mo} Bm_l,$$

$$\Delta E_{sB} = \frac{eh}{4\Pi mo} 2Bm_s$$

Therefore, $$\Delta E = (m_l + 2m_s)\ B\ \frac{eh}{4\Pi mo}$$

The quantity, $(m_l + 2m_s)$ is known as strong field quantum number. In terms of the frequency change

$$\Delta\nu = \Delta(m_l \pm 2m_s)\,\frac{eB}{4\Pi mo}$$

And in terms of wave number

$$\Delta\bar{\nu} = \Delta(m_l \pm 2m_s)\,\frac{eB}{4\Pi moc}$$

$$= \Delta(m_l \pm 2m_s), \text{ in Lorentz unit}$$

Now since $\Delta m_l = 0$ or ± 1, and $\Delta\ m_s=0$ or ± 1.

We get three different frequencies. It means that the result is normal Zeeman triplet as said before. As a specific example, we consider a principal series doublet,

$$({}^2P_{3/2} \longrightarrow {}^2S_{1/2} \text{ and } {}^2P_{1/2} \longrightarrow {}^2S_{1/2})$$

In the strong field, P level is split up into six levels, because for a particular value of l(l+1), m_l has (2l + 1) values (here 1, 0, -1) and for each value of m_l, m_s has two values ($+\frac{1}{2}$ and $-\frac{1}{2}$); and levels with same value of ($m_l + 2m_s$) coincide. So, on the whole, we have five sub levels of P level and two sub levels of S level. The values of different quantum numbers are given in the table

Term	l	s	m_l	m_s	$m_l + 2\ m_s$	$a\ m_l\ m_s$
${}^2P_{3/2}$	1	$+\frac{1}{2}$	1	$+\frac{1}{2}$	2	$\frac{a}{2}$
	1	$+\frac{1}{2}$	0	$+\frac{1}{2}$	1	0
	1	$+\frac{1}{2}$	-1	$+\frac{1}{2}$	0	$-\frac{a}{2}$
${}^2P_{1/2}$	1	$+\frac{1}{2}$	1	$-\frac{1}{2}$	0	$-\frac{a}{2}$
	1	$+\frac{1}{2}$	0	$-\frac{1}{2}$	-1	0
	1	$+\frac{1}{2}$	-1	$-\frac{1}{2}$	-2	$\frac{a}{2}$
$2S_{1/2}$	0	$+\frac{1}{2}$	0	$+\frac{1}{2}$	+1	0
	0	$+\frac{1}{2}$	0	$-\frac{1}{2}$	-1	0

The allowed transitions are shown in fig. 4.8, with the coincidence of the transitions having the same value $\Delta(m_l + 2m_s)$.

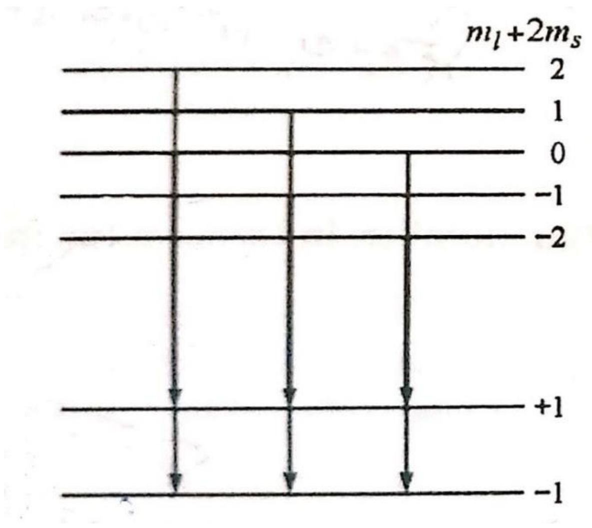

Figure 4.8: Paschen-Back effect

The allowed transitions in figure are correct up to the first approximation.

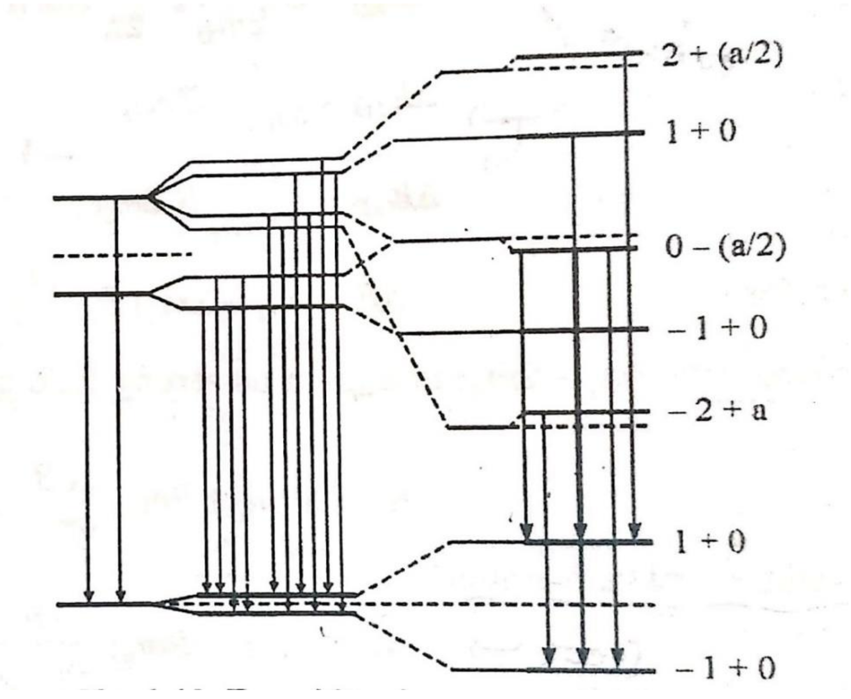

Figure 4.9: Transition from weak to strong magnetic field

4.5.1 QUANTUM MECHANICAL TREATMENT OF PASCHEN-BACK EFFECT

In a strong situation magnetic field L and S are not well defined and do not give a well-defined resultant J. In such a situation L and S precess independently round the direction of B. The values of equation 10 and equation 11 then modify as

$$(\hat{B}.\hat{L}) = (B_z\ L_z) = B\ M_L\ \hbar$$

$$(\hat{B}.\hat{S}) = (B_z\ S_z) = B_z\ M_s\ \hbar$$

The change in energy is

$$\Delta E' = \frac{eh}{2mo} B(M_L + 2M_S)$$

The strong field quantum number ($M_L + 2M_S$) when subjected to selection rule Δ ($M_L + 2M_S$) = 0, ±1, gives rise to Paschen-Back Effect.

Self-Assessment question (SAQ) 3: Choose the correct option

1. The strength of mag. Field is max. in
a) Normal Zeeman effect
b) Paschen-Back effect
c) Anomalous Zeeman effect

2. The total magnetic quantum number *J* precess around external magnetic field in
a) Normal Zeeman effect
b) Anomalous Zeeman effect
c) Paschen-Back effect

4.6 SPIN – ORBIT CORRECTION

In practice, the residual spin-orbit coupling changes the relative energies of the components of different terms. This can be allowed for by adding a small coupling term aM_LM_s in the expression for the magnetic interaction energy, which now becomes

$$-\Delta T = (M_L + 2M_S)L' + aM_L M_S$$

Where $L' = \frac{eB}{4\pi m_0 c}$ is the Lorentz unit.

As a result of this, each of the two σ-components of the normal triplet splits into narrow doublet, triplet, etc., according to original field-free transition was a doublet, triplet, etc., transition. In the present field-free transition $^2P \longrightarrow ^2S$, each σ-component split into a doublet with a separation just two-thirds that of the field free-doublet.

The Paschen-Back effect has experimentally been observed for very narrow multiplets only, such as the Li doublet having a field-free separation of 0.34 cm^{-1}. The reason is that the effect occurs when the magnetic splitting exceeds the fine-structure (field-free) splitting. The ordinarily available fields, for example, a field of 4.3 tesla can produce a magnetic splitting of about 2 cm^{-1}, which is larger than the fine-structure splitting of Li doublet, and Paschen-Back effect can easily be observed. On the other hand, this magnetic splitting is much less than the fine structure splitting of sodium resonance doublet (17 cm^{-1}). Hence a field of 4.3 tesla cannot produce Paschen-Back effect in sodium doublet. Instead, an abnormally large field is required.

So far, we have considered the cases when the external field is either very weak (Zeeman effect) or very strong (Paschen-Back effect), as compared to the internal field in the atom. For intermediate fields (comparable with internal field) complicated patterns are obtained.

Question: *The calcium line of wavelength* $\lambda = 4226.73\ \AA$ *(P→S) exhibits normal Zeeman splitting when placed in uniform magnetic field of 4 Webers/*m^2*. Calculate the wavelength of three components of normal Zeeman pattern and the separation between them.*

Sol. We know that

$$\nu = \nu_0 \pm \frac{eB}{4\pi m}$$

$$\Delta\nu = \nu - \nu_0 = \frac{eB}{4\pi m}$$

$$\Delta\nu = 1.7588 \times 10^{11} \frac{coulomb}{kg} \frac{1}{4\pi} 4 \times \frac{Webers}{m^2}$$

$$= 0.56\ \times 10^{11}\ cycles/sec$$

Since $\nu = \frac{c}{\lambda}$,

$$d\nu = -\frac{c}{\lambda^2} d\lambda$$

$$|d\lambda| = -\frac{\lambda^2}{c} d\nu$$

$$= \frac{(4226.70 \times 10^{-10} m)^2}{3 \times 10\ ^{8} m/sec} \times 0.56 \times 10^{11}\ cycles/sec$$

$$= 3 \times 10\ ^{-10}\ m$$

$$= 0.33\ \text{Å}$$

Thus, the wavelengths of three normal Zeeman components are

4226.40 Å, 4226.73 Å, 4227.06 Å

Question: *Determine the normal Zeeman effect of the cadmium red line of 6438* Å *when the atoms are placed in a magnetic field of 0.009 T.*

Sol. The change in wavelength is given by

$$dE = -ch \frac{1}{\lambda^2} d\lambda \text{ or } |d\lambda| = -\frac{\lambda^2}{ch} dE$$

$$dE = -\frac{e\hbar}{2m} B = \left(5.79 \times 10^{-5} \frac{e\ V}{T}\right)(0.009T)$$

$$= 5.21 \times 10^{-7} eV$$

$$|d\lambda| = -\frac{\lambda^2}{ch} dE = \frac{(6438\ \text{Å})(5.21 \times 10^{-7} e\ V)}{12.4 \times 10^{3} eV}$$

$$|d\lambda| = 1.74 \times 10^{-3}\text{Å}$$

Question: *The spin -orbit effect splits the 3P→3S transition into two lines, 5890 Å corresponding to* $^2P_{3/2}\rightarrow{}^2S_{1/2}$ *and 5896 Å corresponding to* $^2P_{1/2}\rightarrow{}^2S_{1/2}$*. Calculate, by using these wavelengths, the effective magnetic induction experienced by an outer electron in the sodium atom as a result of its orbital motion.*

Sol. We know that

$$|d\lambda| = \frac{\lambda^2}{c} d\nu$$

$$6 \times 10^{-10} = \frac{(5893 \times 10^{-10}\ m)^2}{3 \times 10^8\ m/sec} \Delta\nu$$

$$\Delta\nu = \frac{6 \times 10^{-10}\ \times 3 \times 10^8 m/sec}{(5893 \times 10^{-10}\ m)^2}$$

$$= \frac{18}{(5893)^2} \times 10^{18} cps$$

but

$$\Delta\nu = \frac{eB}{4\pi m}$$

$$\mathrm{B} = \frac{18}{(5893)^2} \times 10^{18} \times \frac{4 \times 3.14}{1.7588 \times 10^{11}}$$

$$B = 18.5\ T.$$

Question: *Evaluate the Lande g-factor for the* $^3P_1$ *level in the 2p3s configuration of the* ^6C *atom, and use the result to predict the splitting of the level when the atom is in an external magnetic field of 0.1 T.*

Sol: For the $^3P_1$ level, we have

L=1, S=1, J=1 and so

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

$$= 1 + \frac{1(1+1) - 1(1+1) + 1(1+1)}{2 \times 1(1+1)} = 1 + \frac{1}{2} = \frac{3}{2}$$

For J=1, the possible values of Mj are 1, 0, -1 and so the level is split into three components. The wave-number shift of the component is given by

$$\Delta T = \pm g M_j \frac{eB}{4\pi mc}$$

The Zeeman level corresponding to Mj=0 remains unshifted while those corresponding to Mj=±1 are shifted by

$$\Delta T = \pm g M_j \frac{eB}{4\pi mc}$$

$$\Delta T = \pm \frac{3}{2} \frac{(1.6 \times 10^{-19} C)(0.1\, NA^{-1} m^{-1})}{4 \times 3.14 \times (9.1 \times 10^{-31} Kg)(3.0 \times 10^{8}\, ms^{-1})}$$

$$= \pm 7.0\, m^{-1}$$

$$= \pm 0.07\, cm^{-1}$$

4.7. SUMMARY

Classically we have that when charge particle undergoes periodic motion, they emit light and the frequency of radiation is the characteristic of the element concerned. Now when these particles are subjected to external magnetic field, then we have studied that they undergo variation in frequency of emitted radiation. This effect was studied in 1896 by Zeeman. It was observed by him that a single spectral line splitted into three lines of frequencies greater than, less than and same as that of the original line. This was called normal Zeeman effect. This kind of splitting is explained classically as well as quantum mechanically by taking only orbital motion of the electron into account. When the applied magnetic field is less than internal magnetic field of the atom then we get multiple splitting of the spectral line which is called anomalous Zeeman effect. This is explained by taking the spin motion of electron also into account. When the external applied magnetic field is more than the internal field of the atom then the splitting obtained is due to Paschen-Back effect. In this case, the orbital and spin angular momentum are quantize separately and they precess independently around the external magnetic field.

4.8 Glossary

- Precession- to move around
- Spectral line- light of particular wavelength emitted by a source
- Discreate- separate and distinct
- Anomalous- deviation from normal or standard behavior
- Unperturbed- undisturbed

4.9. TERMINAL QUESTIONS

1. What are the normal and anomalous Zeeman effects? Use classical idea to explain normal Zeeman effect.
2. Explain clearly the phenomenon of anomalous Zeeman effect and Paschen-Back effect. Describe the spectral patterns expected for the yellow lines of sodium according to these two effects.
3. Describe the effect of weak magnetic field on the spectral lines emitted by an atom having two valance electrons.
   Calculate the Zeeman patterns for the transition sp $^3P_1 \rightarrow$sd $^2D_1$ in LS coupling.
4. Define Lande's splitting factor and derive expressions for its values for L-S and j-j coupling in a two-electron system.
5. Outline the theory of Paschen-Back effect and discuss the Paschen-Back pattern for a $^2P \rightarrow {}^2S$ transition.
6. An electron in He^+ is in an n=2 orbit. What is its magnetic moment due to its orbital motion according to Bohr theory?
7. What is the frequency difference in the photons emitted in the normal Zeeman effect corresponding to transitions from adjacent magnetic sublevels to the same final state in a magnetic field of 1.2 T?

4.10 REFERENCES

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S.L Gupta, V. Kumar and R.C. Sharma, Elements of Spectroscopy, Pragati Prakashan, 22 ed. Meerut, India, 2010

J. B. Rajam, Atomic Physics, SChand Publication, New Delhi, India, 2008

4.11 ANSWERS

Self-Assessment question (SAQ)1:

Ans. 1. (b)

Ans. 2. (a)

Ans. 3. (a)

Self-Assessment question (SAQ)2:

Ans. 1. (c)

Ans. 2. (b)

Ans. 3. (c)

Self-Assessment question (SAQ)3:

Ans. 1. (b)

Ans. 2. (b)

Terminal question

Ans. 6. 1.85×10^{-23} T

Ans. 7. 1.08×10^{10} Hz

CHAPTER 5 STARK EFFECT

Structure

5.1. Aims and Objectives

5.2. Introduction: Stark Effect

5.3. Stark Effect in Hydrogen Atom

5.4. Weak and Strong Field Stark Effect

5.4.1. Weak Field Effect

5.4.2. Strong Field Effect

5.4.2.1. Strong-Field Stark Splitting Of Hydrogen Levels

5.5. Quantum Mechanical Treatment of Stark Effect

5.5.1. The Unperturbed System

5.5.2. Important Results of Perturbation Theory

5.5.3. Effect of Electric Field on The Ground State Of Hydrogen

5.5.4. Effect of Electric Field on The Degenerate Energy Levels

5.5.4.1. The N=2 State Of Hydrogen in External Field

5.6. Hyperfine Structure

5.6.1. Isotope Effect

5.6.2. Nuclear Spin and Hyperfine Splitting

5.6.2.1. Vector Atom Model

5.6.3. Intensity Ratio and Determination Of Nuclear Spin:

5.8. Glossary

5.9. Terminal Questions

5.10. References

5.11. Answers

5.1. Aims and objectives

In the previous unit, we have studied about the effect of magnetic field on the spectral line. Now, in this unit we will study the effect of electric field on the spectral line which is called Stark effect. After going through this unit we will come to know:

1. What is Stark effect?
2. Stark effect in hydrogen atom.
3. The qualitative and Quantum mechanical treatment of Stark effect.
4. Hyperfine structure of spectral line.

5.2. INTRODUCTION: STARK EFFECT

In late 1913 Johannes Stark (1874–1957), the professor of experimental physics at the technical university of Aachen, discovered the effect of electric fields on spectral lines. This phenomenon is usually referred to as the Stark effect and is analogue of the magnetic field effect on spectral i.e. Zeeman effect. Stark worked with specially constructed discharge tubes. Stark's tube allowed stable electric fields of up to 100,000 Vcm^{-1}.

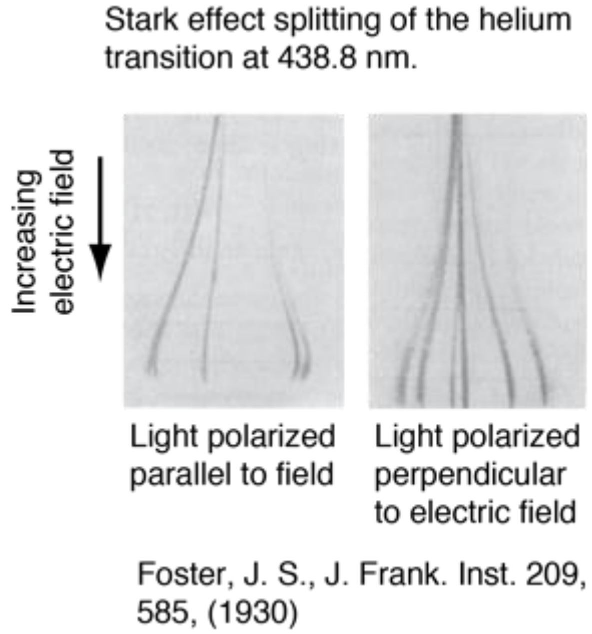
In numerous experiments, Stark demonstrated the following:

- The spectrum lines in the Balmer series of hydrogen split up into several components
- The number of these components increases with the series number
- Splitting and polarization of Balmer lines is symmetric to the original line
- The splitting seemed to be asymmetric for some other elements
- The distances between the hydrogen spectral-line components (in units of frequency or wavenumber) are all integer multiples of a smallest line distance
- The splitting interval Δ increases proportionally with the electric field E (i.e., $\Delta \sim E$ for not too small or too large E) first order stark effect or linear Stark effect
- For very small electric fields and atoms not subject to a permanent dipole moment, Δ actually increases by the second power of E ('quadratic Stark effect')

In the presence of external electric field, emission lines from atoms or ions (particle carrying an electric dipole moment) split into several polarised components. When viewed perpendicular to field, some of components of each line are plane polarised with electric field vector parallel to the field (π-components) and the other are polarised with electric field vector perpendicular to the field (σ-components). When viewed parallel to field, only σ-components appear which are now unpolarised. This phenomenon is called the Stark effect.

The magnitude of the wavelength separation and the relative intensity among the split line components depend on the field strength. The splitting of the emission lines is ascribed to the resolution of magnetic sublevels which are degenerate in the absence of an external field. The variation of relative intensity among the split line components is interpreted as a change of electric dipole moment between the magnetic sublevels of the transition; this change is caused by the wavefunction mixing. Stark effect generally increases as the square of the applied field strength (quadratic Stark effect). For hydrogen like system special condition prevail due to the level degeneracy and hence linear Stark effect (shift is linear in applied field strength) is obtained. The relationship for splitting of spectral line in stark effect is not simple and unique like Zeeman effect. So Stark effect is of no particular value as a help in analysis of spectrum but plays an important role in the theories of molecule formation from atom, broadening of spectral lines and dielectric constants.

The amount of splitting and or shifting is called the Stark splitting or Stark shift. In general, one distinguishes first- and second-order Stark effects. The first-order effect is linear in the applied electric field, while the second-order effect is quadratic in the field. When the split/shifted lines appear in absorption, the effect is called the inverse Stark effect.



Foster, J. S., J. Frank. Inst. 209, 585, (1930)

Figure 5.10

5.3. STARK EFFECT IN HYDROGEN ATOM

J. Stark discovered that the Balmer lines emitted by hydrogen atoms placed in an electric field of the order of 10^5 V/cm are split into a number of polarised components.

- All hydrogen lines from symmetrical patterns, but the pattern depends markedly on quantum number n of the term involved. The number of Stark lines, and the total width of the pattern increases with n. The line H_β shows a larger number of Stark components than H_α, the line H_γ showing still more larger numbers.
- The wave number shifts are integer multiples of a unit which is proportional to the strength of the electric field and is same for all hydrogen lines.
- Except for circular polarisation in longitudinal observation, the polarisation properties of Stark lines resemble those of the Zeeman lines. But, in contrast to Zeeman lines, the π-components shows greater shifts than the σ-components.
- The hydrogen lines involving the lower energy states (small n) shows only a symmetrical splitting proportional to the field strength about their field-free positions. This is known as the ‘first-order’ or ‘linear’ Stark effect.
- For lines involving higher states the Stark components shows unidirectional displacement proportional to the square of the field strength. This is known as the ‘second-order’ Stark effect.
- For hydrogen, at high field strength, a quadratic effect is superimposed on linear effect, and results essentially in a one-sided shift of the whole splitting pattern (Fig. 5.2)

In order to obtain theoretically the Stark effect splitting of H and H-like ions for low field strengths, relativity and spin effects have to be considered, and these then give an unsymmetrical splitting of the individual fine structure components.

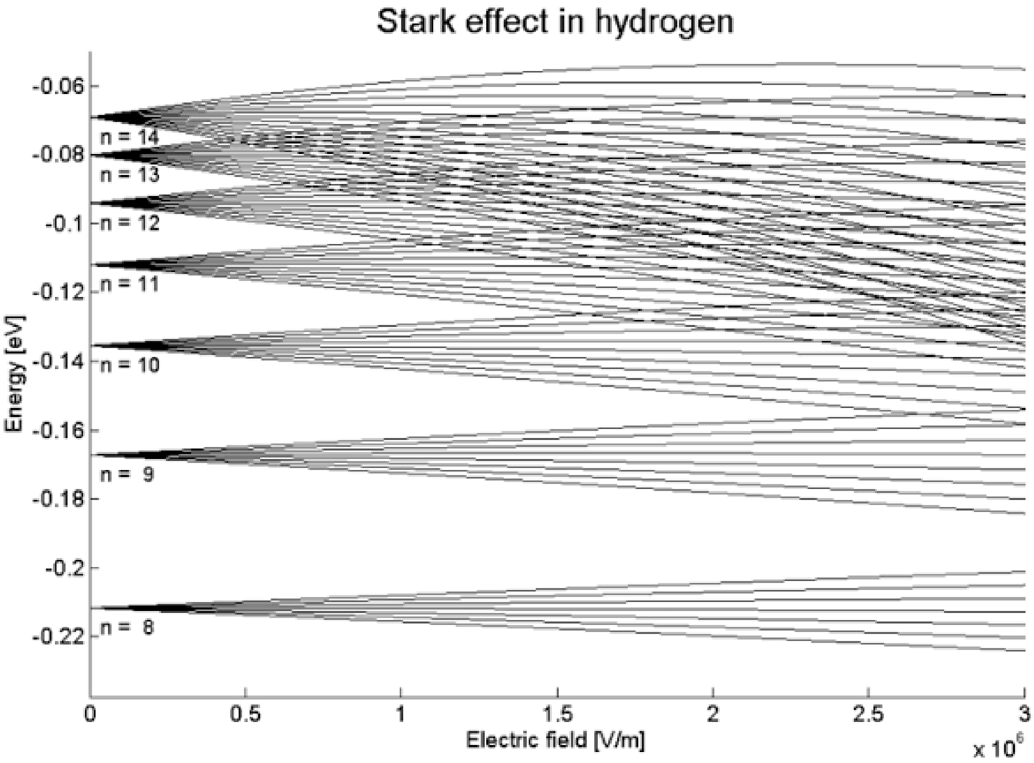


Fig. 5.11: Stark Effect in Hydrogen: The until then degenerate excited energy levels are split up if an exterior electric field is applied.

5.4. WEAK AND STRONG FIELD STARK EFFECT

The electric field is said to be WEAK when the splitting of energy level is smaller than the fine-structure splitting and STRONG when the splitting of the energy levels is greater than the fine-structure splitting.

5.4.1. WEAK FIELD EFFECT

A weak field for hydrogen atom is one for which the interaction energy between the electron's total angular momentum **j** and the electric field **F** is less than the magnetic interaction energy between orbital angular momentum **I** and spin momentum **s**, that is for which the Stark splitting is smaller compared with the fine-structure splitting. In such a field, **I** and **s** couple to form **j** which precesses around **F** with projection $m_j h/2\pi$, where

$$m_j = +j, j-1, j-2, \ldots, -j$$

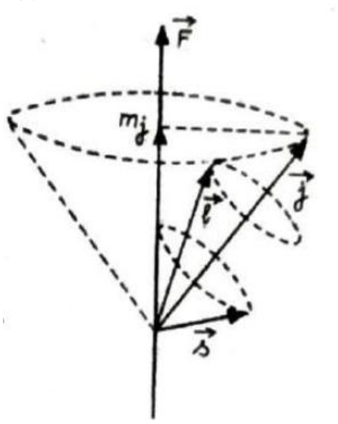


Figure 5.12

However, in contrast to Zeeman levels, the Stark levels +m_j and -m_j arising from a given unperturbed level have the same energy.

The energy levels of hydrogen atom for the two states n=2 and n=3 are shown in Fig 5.4. the field-free levels and theoretical pattern for H_α are given at the left, and the weak-field levels and Stark pattern at the right. The unperturbed levels for each $n(2^2P_{3/2}\ and\ 3^2D_{5/2})$ do not show Stark splitting because in these states the atom has no electric moment.

The selection rules for the weak-field Stark effect are the same as those for the Zeeman effect, i.e.

$$\Delta m_j = 0 \text{ gives } \pi \text{ components}$$

$$\Delta m_j = \pm 1 \text{ gives } \sigma \text{ components}$$

According to these rules, each of the fine-structure components should show symmetrical stark pattern, as shown at the lower right. However, since the fine-structure components of H_α have not been completely resolved, the weak-field stark pattern has never been observed.

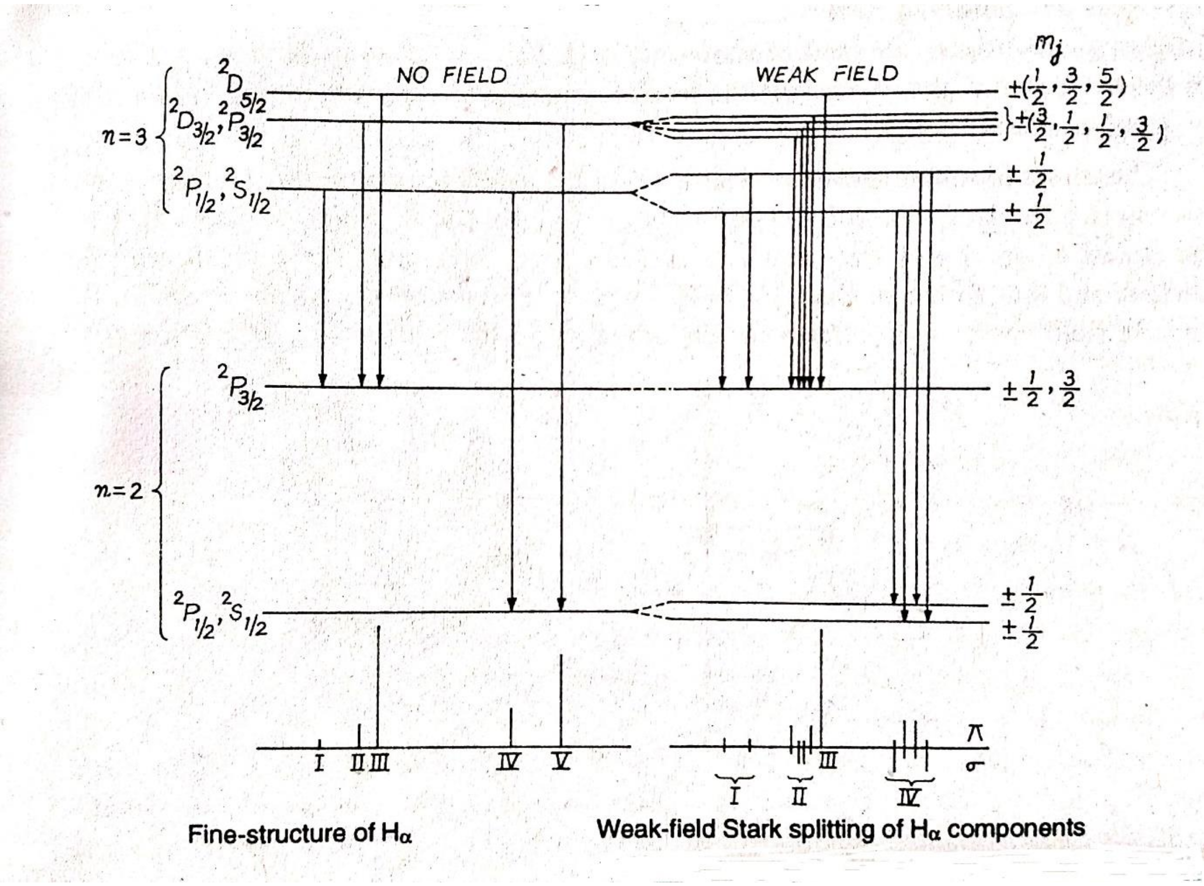


Figure 5.13: fine structure and weak field Stark effect for hydrogen Hα line

5.4.2. STRONG FIELD EFFECT

A strong electric field for hydrogen is one for which the interaction energy between the electron's total angular momentum **j** and the field **F** is greater than the magnetic interaction energy between electron's orbital momentum **I** and spin momentum **s**, that is, for which the (Stark) splitting of the energy levels due to the field is greater than the fine-structure splitting. The strong-Field Stark effect is actually been observed. In such a field the *magnetic coupling between **I** and **s** is broken down* and **I** is quantised with respect to and precesses independently around the field **F**. The spin is not acted on by **F**.

Schwarzschild and Epstein in 1916 explained the observed stark effect in Hydrogen atom and ionised helium by quantising hydrogen like atom in an electric field.

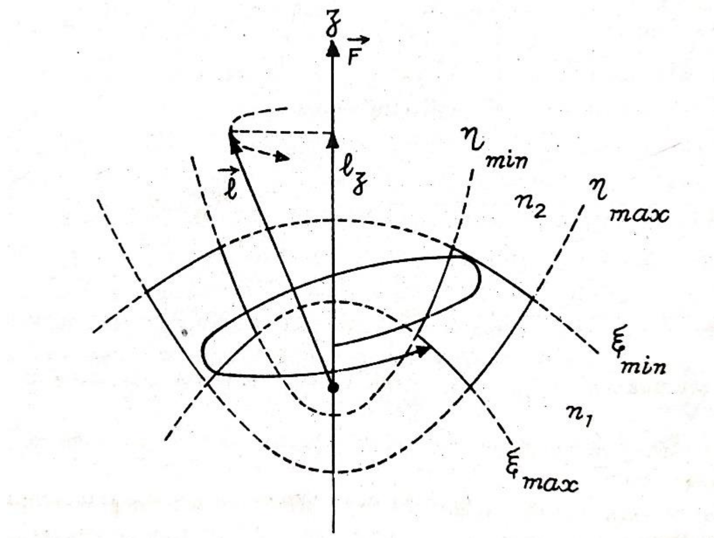


Figure 5.14

The effect of a homogeneous electric field **F**, parallel to the z-axis, on an electron moving in a Kepler ellipse is different from that of a magnetic field. For the Kepler motion the centre of gravity of the electron averaged over its orbit does not coincide with the nucleus and thus forms an electric dipole. The torque on the orbital dipole exerted by the electric field causes a precession the orbital about the z-axis. However, the orbital angular momentum **I** is not a constant, and the orbital quantum number l is no longer a "good" quantum number. The projection of **I** on the electric axis is l_z, given by $m_l \frac{h}{2\pi}$ where m_l is the electric quantum number. l_z is still a constant of motion and m_l retain its strict meaning. Calculation carried out in parabolic coordinates given the energy values as:

$$E = E_0 - \frac{3a_0 e}{2Z} Fn(n_2 - n_1)$$

Where E_0 is the electric field free energy of the atom, $a_0$is the Bohr radius, $n$is the usual total quantum number, and n_1 and n_2 are two new quantum numbers, subjected to the condition

$$m_l = n - n_2 - n_1 - 1$$

The allowed values are

$$n = 0, 1, 2, \dots\dots\dots, \infty$$

$$m_l = 0, \pm 1, \pm 2, \dots\dots\dots\dots, \pm(n-1)$$

$$n_1 = 0, 1, 2, \dots\dots\dots, (n-1)$$

$$n_2 = 0, 1, 2, \dots\dots\dots, (n-1)$$

n_1 limits the electron's motion to the region between the two paraboloids of revolution ξ_{min} and ξ_{max}; while n_2 limits it to the region between the two paraboloids of revolution η_{min} and η_{max}. Thus, confined to the region intersected by the two pairs of paraboloids, the electron has three periodic motions, one around the field **F** given by m_l, and one each along the η and ξ coordinates given by n_1 and n_1. Since the last two periods are not necessarily the same, the orbit is not closed and the electron in time covers every point in the intersected region.

5.4.2.1. STRONG-FIELD STARK SPLITTING OF HYDROGEN LEVELS

The term shift is given by

$$-\Delta T = \frac{\Delta E}{hc} = \frac{3a_0 e}{2Zhc} Fn(n_2 - n_1)$$

Pitting the known values of a_0, e, h and c, we get

$$-\Delta T = \frac{3(0.53 \times 10^{-10}\, m)(1.6 \times 10^{-19}\, C)}{2Z(6.63 \times 10^{-34}\, Js)(3.0 \times 10^{8}\, ms^{-1})} Fn(n_2 - n_1)$$

$$= \frac{6.40 \times 10^{-5}\, C/J}{Z} Fn(n_2 - n_1)$$

$$= \frac{6.40 \times 10^{-5}\, V^{-1}}{Z} Fn(n_2 - n_1)$$

If the field F is expressed in V/cm, then this becomes

$$-\Delta T = \frac{6.40 \times 10^{-5}}{Z} Fn(n_2 - n_1) \quad cm^{-1}$$

Thus, the Stark levels in a hydrogen like atom are all shifted by integral multiples of a fundamental amount from the original level.

The quantity $n(n_2 - n_1)$ represent the Stark shift. Allowed values of n, $n_1$and n_2 shows that there is exactly n^2 possible states for Stark effect similar to Zeman effect but certain levels fall together in Stark effect. Further, the Stark-shift for the ground state of Hydrogen is zero.

The selection rules for the strong-field Stark effect are as follows:

$\Delta m_l = 0$ gives π components

$\Delta m_l = \pm 1$ gives σ components

the transition $\Delta m_l = 1$ and $\Delta m_l = -1$ gives components circularly polarised in opposite sense. But a transition $\Delta m_l = -1$ occurs for every transition $\Delta m_l = 1$ and the superposition of the two gives linearly polarised components in transverse observation and unpolarised components in longitudinal observation.

n	n_2	n_1	$n_2 - n_1$	$n(n_2 - n_1)$	m_l $(n - n_2 - n_{1-1})$
1	0	0	0	0	0
2	1	1	0	0	-1
	1	0	1	2	0
	0	1	-1	-2	0

	0	0	0	0	1
3	2	2	0	0	-2
	2	1	1	3	-1
	2	0	2	6	0
	1	2	-1	-3	-1
	1	1	0	0	0
	1	0	1	3	1
	0	2	-2	-6	0
	0	1	-1	-3	1
	0	0	0	0	2

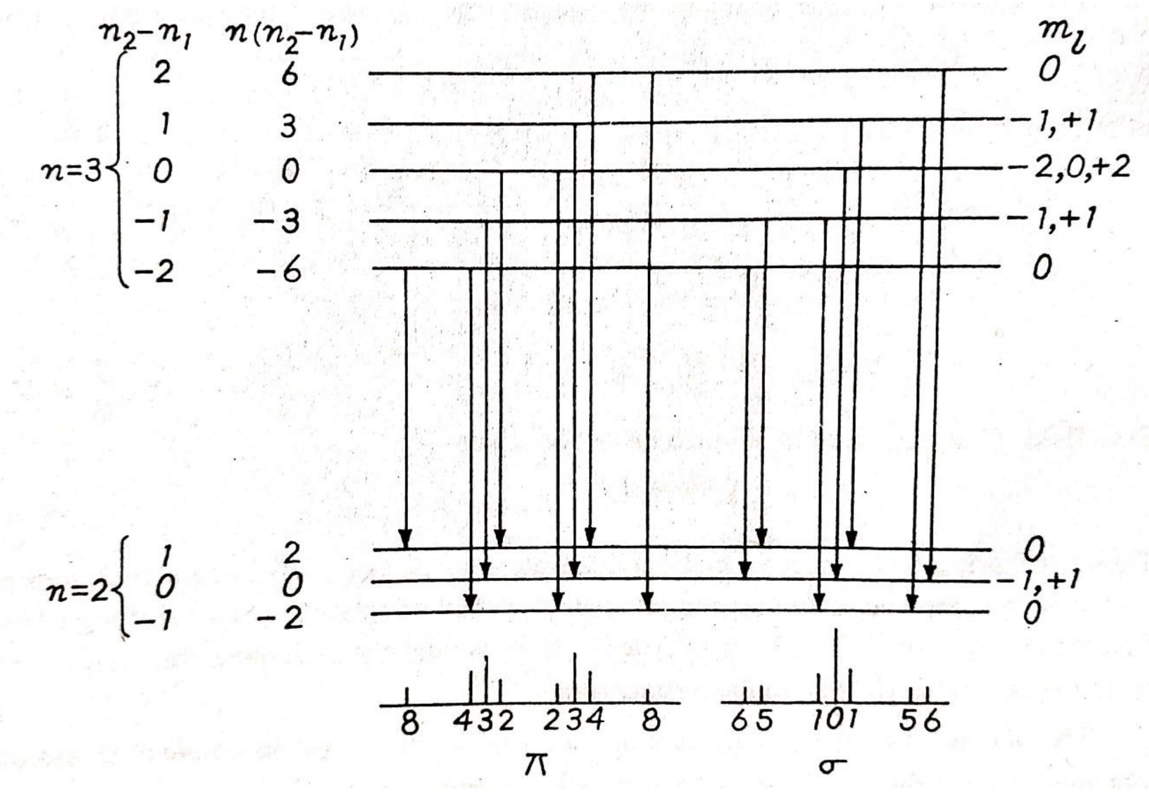


Figure 5.15: strong field first-order Stark effect for H_α line

The possible transitions for the H_α line and the resulting Stark pattern have also been shown. This has been found in good agreement with experimental observation in both the relative shifts and the intensities. The intensities were calculated by Schrödinger quantum mechanically.

Thus, the comparison of weak-field and strong-field Stark effect:

Electric Field	Level energy	Transition rules
Weak		$\Delta m_j = 0$ gives π components $\Delta m_j = \pm 1$ gives σ components
Strong	$E = E_0 - \frac{3a_0 e}{2Z} Fn(n_2 - n_1)$	$\Delta m_l = 0$ gives π components $\Delta m_l = \pm 1$ gives σ components

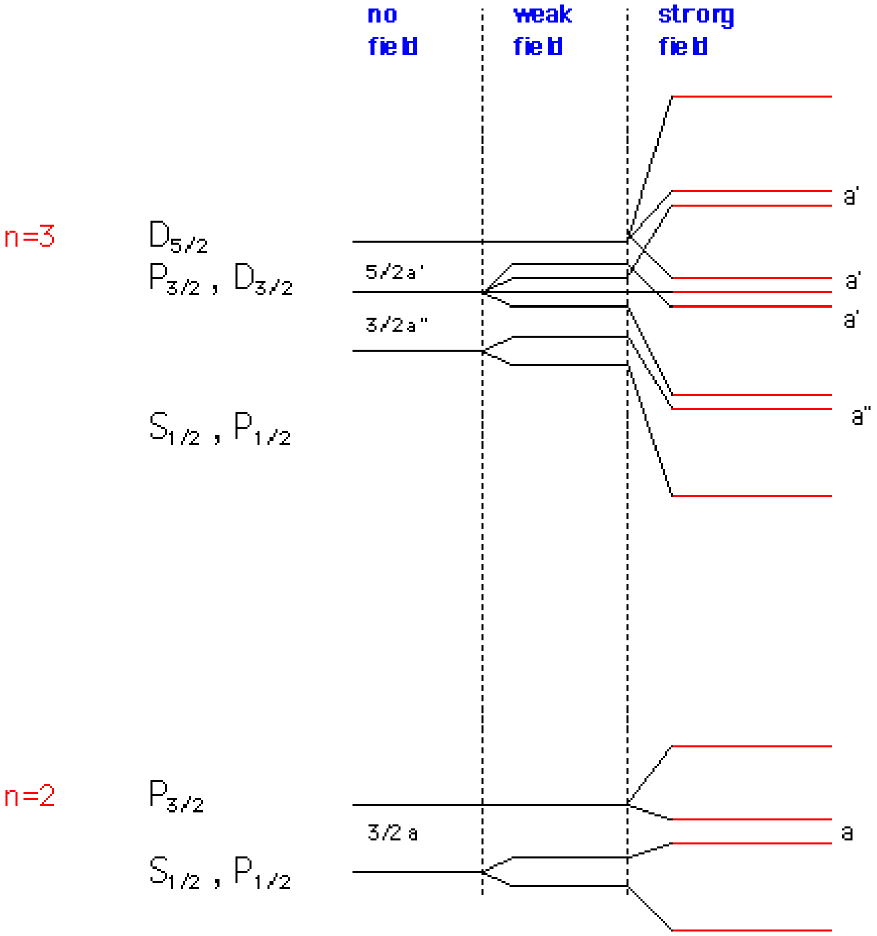


Figure 5.16: Comparison of level shifting for hydrogen in weak—field and strong field (n=2 and n=3 line)

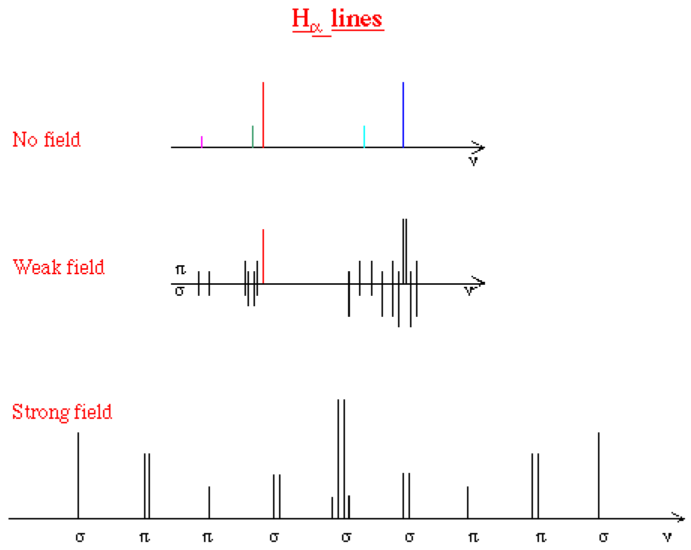
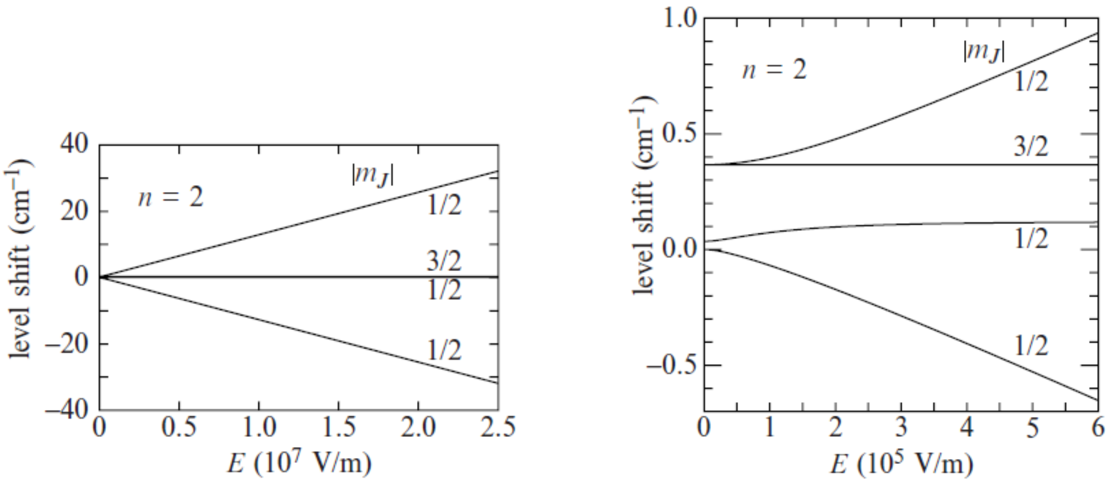


Figure 5.17: Comparison of Stark effect of hydrogen in weak--field, strong field and no-field



(a) *(b)*

Fig. 5.9: Energy level shifts against electric field strength for n = 2 of neutral hydrogen (a) in a wide field strength range and (b) in a weak field strength range where the intrinsic fine structure and Stark splitting are comparable

5.5. QUANTUM MECHANICAL TREATMENT OF STARK EFFECT

In this section we will discuss Stark Effect on the basis of perturbation theory of quantum mechanics. Stark Effect is the splitting of spectral line of an atom or ion (particle carrying an electric dipole moment) in a uniform external electric field. Splitting of spectral line is a result of shifting of energy level in the presence of external field. The shifting of energy level in external field can be understood by the theory of perturbation of Quantum mechanics, which was used to find the energy eigen values and wave function of a system with slightly modified potential then the potential for which exact solution of Schrödinger equation are known. The applied external field act as perturbation potential for known system. The first and second order energy correction in energy level will provide the shifted energy levels. By using these shifted energy levels, allow transition will give information of Stark effect.

The aim of the section is to solve the Schrödinger equation and find the eigenstates and the energy of the electron when a static electric field is applied to the atom. Unlike the analytical approach used until now, perturbation theory will be used in this section and after introducing the Schrödinger equation for the Stark effect, the perturbation theory method is presented.

5.5.1. THE UNPERTURBED SYSTEM

Before embarking on perturbation theory, we must understand the unperturbed system, its energies, eigenstates and their degeneracies. In the electrostatic model, the unperturbed energy levels in hydrogen are given by the usual Bohr formula,

$$E_n = -\frac{1}{2n^2}\frac{e^2}{a_0}$$

where a_0 is the Bohr radius. Here we ignore the small difference between the electron mass m and the reduced mass µ. These levels are n^2 -fold degenerate.

The eigenstates of Hydrogen have the form $|nlm\rangle$. The eigenfunction:

$$\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta)$$

For hydrogen, central force Hamiltonian is H_0

$$H_0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{k\,e^2}{r}; \qquad k = \frac{1}{4\pi\varepsilon_0}$$

5.5.2. IMPORTANT RESULTS OF PERTURBATION THEORY

The time-independent perturbation theory is used to find the energy eigen values and eigen function of the system whose Hamiltonian is slightly different from the system of known energy eigen values and eigen wavefunction. If H_0 is the unperturbed Hamiltonian, then the Hamiltonian of the system under consideration can be written as

$$H = H_0 + H'$$

Where H’ is the changes of Hamiltonian of the system under study i.e. perturbed Hamiltonian.

Result 1: The first-order correction to the energy is the average value of the perturbation over the corresponding unperturbed states of the system.

$$E_n^{(1)} = \langle\psi_n^0|H'|\psi_n^0\rangle$$

Result 2: The perturbative state corrections of first order are given by the superposition of all unperturbed states with energies different from the considered state.

$$\psi_n^{(1)} = \sum_{m\neq n} \frac{\langle m|H'|n\rangle}{E_n^0 - E_m^0} |\psi_m^0\rangle$$

Thus, the energy and wave function corrected to first order are

$$E_n = E_n^0 + \langle\psi_n^0|H'|\psi_n^0\rangle$$

$$\psi_n = \psi_n^0 + \sum_{m\neq n} \frac{\langle m|H'|n\rangle}{E_n^0 - E_m^0} |\psi_m^0\rangle$$

Result 3: The perturbative energy corrections of second order are determined by all unperturbed states with energy different from the considered state.

$$E_n^{(2)} = \left\langle\psi_n^0\middle|H'\middle|\psi_n^{(1)}\right\rangle$$

$$E_n^{(2)} = \sum_{m\neq n} \frac{|\langle m|H'|n\rangle|^2}{E_n^0 - E_m^0} |\psi_m^0\rangle$$

5.5.3. EFFECT OF ELECTRIC FIELD ON THE GROUND STATE OF HYDROGEN

Consider an atom situated at origin. Let an external electric field **E** applied along the positive z-axis. If **r** is the position vector of the electron, the electric dipole moment μ=-e**r** interacts with the electric field **E** giving an additional potential energy to the electron

H'= -μ.**E** = erE cosθ =eEz ; e-positive

Where θ is the angle the position vector makes with z-axis. Since this *extra energy term is very small, it can be treated as a perturbation* on the Hamiltonian of the system H°

$$H^o = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{k\,e^2}{r}; \quad k = \frac{1}{4\pi\varepsilon_0}$$

The ground state of the Hydrogen atom ($|nlm> = \psi_{100}$) is non-degenerate and first order correction to the energy

$$E^{(1)} = \langle\psi_{100}|eErcos\theta|\psi_{100}\rangle \qquad (5.1)$$

Where ψ_{100} is the hydrogen ground state wave function:

$$\psi_{100} = \frac{1}{(\pi a_0^3)^{1/2}}\, exp\left(-\frac{r}{a_0}\right)$$

The θ part of the integral in equation (5.1) vanishes as

$$\int_0^{\pi} cos\theta\ sin\theta\ d\theta = -\int_0^{\pi} cos\theta\ d(cos\theta) = 0$$

Hence, *the ground state of hydrogen atom will not show a first-order Stark effect* and we have to calculate the second-order energy shift.

The second-order energy shift presented in the next section, present a method of solving perturbation on the basis Dalgarno and Lewis method. They found an operator F (scalar function) such that

$$E\psi_1^0 = \psi_1^{(1)}$$

The second order energy correction

$$E_n^{(2)} = \left\langle \psi_n^0 \middle| H' \middle| \psi_n^{(1)} \right\rangle$$

$$E_1^{(2)} = \langle \psi_1^0 | H'F | \psi_1^0 \rangle$$

and

$$H'\psi_n^0 + H^0\psi_n^{(1)} = E_n^{(1)}\psi_n^0 + E_n^0\psi_n^{(1)}$$

$$H'\psi_1^0 + H^0F\psi_1^0 = E_1^{(1)}\psi_1^0 + FE_1^0\psi_1^0$$

Since $E_1^{(1)}$ is zero and $E_1^0\psi_1^0 = H^0\psi_1^0$,

$$(FH^0 - H^0F)\psi_1^0 = H'\psi_1^0$$

$$[F, H^0]\psi_1^0 = H'\psi_1^0$$

{Since the scalar function F commutes with -ke^2/r in H^0, the relation $\nabla^2(F\psi_1^0) = \mathrm{F}\nabla^2(\psi_1^0) + \psi_1^0\nabla^2 F + 2\nabla\psi_1^0.\nabla F$}

$$\frac{\hbar^2}{2\mu}(\psi_1^0\nabla^2 F + 2\nabla\psi_1^0.\nabla F) = H'\psi_1^0$$

This gives the differential equation that determines the operator F. Substituting the values of ψ_1^0 in the above equation

$$\nabla^2\mathrm{F} - \frac{2}{a_0}\frac{\partial F}{\partial r} = \frac{2\mu}{\hbar^2} eErcos\theta$$

The angular part of the right- hand side of the above equation comes from cosθ which is the Legendre polynomial P$_1$. Therefore, F may be assumed to be of the following form

$$F = f(r)\, P_1$$

This value of F when substituted in equation satisfied b f(r) which leads to

$$F = \frac{\mu}{\hbar^2} eE\, a_0 \left(\frac{r}{2} + a_0\right) rcos\theta$$

The second order correction is then

$$E_1^{(2)} = \langle \psi_1^0 | H'F | \psi_1^0 \rangle$$

$$= -\frac{\mu}{\hbar^2} e^2 E^2 a_0 \frac{1}{\pi a_0^3} \int_0^{\pi} \int_0^{2\pi} cos^2\theta sin\theta d\theta d\varphi \int_0^{\infty} \left(\frac{r^5}{2} + a_0 r^4\right) exp\left(-\frac{2r}{a_0}\right) dr$$

$$= -\frac{4}{3}\frac{\mu}{\hbar^2}\frac{e^2E^2}{a_0^2} \int_0^{\infty} \left(\frac{r^5}{2} + a_0 r^4\right) exp\left(-\frac{2r}{a_0}\right) dr$$

On solving, we get

$$E_1^{(2)} = -\frac{9}{4}\frac{\mu}{\hbar^2} e^2 E^2 a_0^4 = -\frac{9}{4k} a_0^3 E^2$$

Since $a_0 = \hbar^2/k\mu e^2$. The ground state energy corrected to second order is found to be

$$E_1 = E_1^0 - \frac{9}{4k} a_0^3 E^2$$

As the correction is proportional to the square of E, it is often referred to as the *quadratic Stark effect.*

The correction term $(-9/4k)a_0^3E^2$ is due to the distortion of the charge distribution of the 1s-electron by the electric field **E** and therefore we may say that the atom has been polarized b the field. The extent of this polarisation is measured by the polarizability α, which is defined as the ratio of the induced electric dipole moment μ to the external field **E**

$$\mu = \alpha \mathbf{E}$$

The energy of an induced dipole in an applied field is given by –(1/2) αE^2. Equating this energy change with the energy due to perturbation calculation

$$-\frac{1}{2}\alpha E^2 = -\frac{9}{4k} a_0^3 E^2$$

The polarizability of Hydrogen atom in its ground state is

$$\alpha = \frac{9}{2k} a_0^3$$

5.5.4. EFFECT OF ELECTRIC FIELD ON THE DEGENERATE ENERGY LEVELS

In the case of degenerate energy levels, unperturbed wave function of the system can be taken as the linear combination of degenerate wave functions. For simplicity let us consider a case in which E_n^0 is two-fold degenerate. Let ψ_n^0 and ψ_l^0 be eigenfunctions corresponding to eigenstate $E_n^0 = E_l^0$ and a linear combination of tow be

$$\phi = c_n \psi_n^0 + c_l \psi_l^0$$

Where c_n and c_l are constants.

First-order correction:

$$H'\psi_n^0 + H^0\psi_n^{(1)} = E_n^{(1)}\psi_n^0 + E_n^0\psi_n^{(1)}$$

$$H'|(c_n\psi_n^0 + c_l\psi_l^0) > +H^0|\psi_n^{(1)} >= E_n^{(1)}|(c_n\psi_n^0 + c_l\psi_l^0) > +E_n^0|\psi_n^{(1)} > \qquad (5.2)$$

Operating eq.(5.2) from left by $< \psi_n^0|$

$$c_n < \psi_n^0|H'|\psi_n^0 > +c_l < \psi_n^0|H'|\psi_l^0 > +< \psi_n^0|H^0|\psi_n^{(1)} >= c_nE_n^{(1)} + E_n^0 < \psi_n^0|\psi_n^{(1)} >$$

Since H^0 is Hermitian,

$$< \psi_n^0|H^0|\psi_n^{(1)} >= E_n^0 < \psi_n^0|\psi_n^{(1)} >$$

So

$$c_n < \psi_n^0|H'|\psi_n^0 > +c_l < \psi_n^0|H'|\psi_l^0 >= c_nE_n^{(1)}$$

$$(H'_{nn} - E_n^1)c_n + (H'_{nl})c_l = 0 \qquad (5.3)$$

Operating eq. (5.2) from left by $< \psi_l^0|$

$$(H'_{nl})c_n + (H'_{ll} - E_n^1)c_l = 0 \qquad (5.4)$$

Equation (5.3) and (5.4) together form a set of simultaneous equations for the coefficients $c_n$and c_l. A nontrivial solution of these equations exists only if the determinant of coefficients vanishes.

$$\begin{vmatrix} H'_{nn} - E_n^{(1)} & H'_{nl} \\ H'_{ln} & H'_{ll} - E_l^{(1)} \end{vmatrix} = 0 \qquad (5.5)$$

This is called the secular equation and its two solutions are:

$$E_{n\pm}^{(1)} = \frac{1}{2}(H'_{nn} + H'_{ll}) \pm \frac{1}{2}[(H'_{nn} - H'_{ll})^2 + 4|H'_{nl}|^2]^{(\frac{1}{2})}$$

Now the corrected energies are:

$$E_n = E_n^0 + E_{n+}^{(1)} \text{ and } E_l = E_n^0 + E_{n-}^{(1)}$$

Both the energies will be real as the diagonal matrix element H'_{nn} and H'_{ll} pf the Hermitian operator H’ are real. If $H'_{nn}=H'_{ll}$ and $H'_{nl}=0$, $E_{n+}=E_{n-}$ and the degeneracy is not removed in the first order.

When the two roots of eq. (5.5) are distinct, each can be used to calculate the ratio c_n/c_l either from eq. (5.3) or from (5.4). the normalization condition $c_n^2 + c_l^2 = 1$ allows us to calculate the values of c_n and c_l.

5.5.4.1. THE N=2 STATE OF HYDROGEN IN EXTERNAL FIELD

The first excited state (n=2) of hydrogen atom is four-fold degenerate, with $|nlm\rangle$: $|200\rangle$, $||210\rangle$, $|211\rangle$, and $|21-1\rangle$. Similar to previous discussion, let the applied external field is along the positive Z-axis which interacts with the electric dipole moment giving the perturbing Hamiltonian $H'=e\mathbf{E}z=eEr\cos\theta$.

For 4-fold degenerate state, the application of perturbation theory requires the evaluation of sixteen matrix elements of H’. The four diagonal matrix elements out of these sixteen elements are zero, since they correspond to the same parity (H’ is of odd parity). The off-diagonal matrix elements between states of different m values are zero since

$$\int_0^{2\pi} \exp[i(m'-m)\varphi]d\varphi = 0 \quad \text{if } m' \neq m$$

The remaining two matrix elements $\langle 200|H'|210\rangle$ and $\langle 210|H'|200\rangle$ are the only nonvanishing ones. These can be evaluated using the values of

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\frac{1}{a_0^3}\left(2-\frac{r}{a_0}\right)exp\left(-\frac{r}{2a_0}\right)$$

And

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\frac{1}{a_0^{3/2}}\frac{r}{a_0}exp\left(-\frac{r}{2a_0}\right)cos\theta$$

Therefore

$$\langle 200|H'|210\rangle = \frac{eE}{32\pi a_0^4}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\left(2-\frac{r}{a_0}\right)r^2 exp\left(-\frac{r}{a_0}\right)cos^2\theta r^2 sin\theta dr d\theta d\varphi$$

$$= \frac{eE}{16\pi a_0^4}\int_0^{\pi} cos^2\theta r^2 sin\theta d\theta \int_0^{\infty}\left(2r^4-\frac{r^5}{a_0}\right)exp\left(-\frac{r}{a_0}\right)dr$$

$$= -3eEa_0$$

So,

$$\langle 200|H'|210\rangle = -3eEa_0$$

$$\langle 210|H'|200\rangle = -3eEa_0$$

The perturbation matrix is therefore

$$H' = \begin{bmatrix} 0 & -3eEa_0 & 0 \\ -3eEa_0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

The secular determinant is then

$$\begin{bmatrix} -E_2^{(1)} & -3eEa_0 & 0 & 0 \\ -3eEa_0 & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{bmatrix} = 0$$

The four roots of this determinant are $3eEa_0$, $-3eEa_0$, 0 and 0. The state |200> and |210> are affected by the electric field whereas the state |211> and |21-1> are not. The four-fold degeneracy is thus lifted partially. Corresponding eigenstate can be evaluated using equation (5.3) and (5.4)

The eigenstate corresponding to the eigenvalues $3eEa_0$ is then (|200>-|210>)/$\sqrt{2}$. In a similar way the eigenstate for eigenvalue $-3eEa_0$ is (|200>+|210>)/$\sqrt{2}$.

Energy	**Eigenstate**
$E_2^0 + 3eEa_0$	$\frac{1}{2}(\|200 > -\|210 >)$
	$\|211 >, \|21-1 >$
E_2^0	$\frac{1}{2}(\|200 > -\|210 >)$

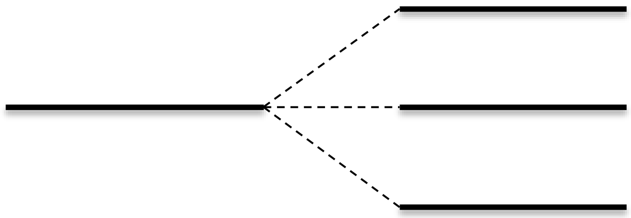


Fig. 5.10. Energies and wave functions of the first excited state of hydrogen atom in an electric field E.

The hydrogen atom in the first excited state thus possesses a permanent electric dipole moment of magnitude $3ea_0$ with three different orientations- one state parallel to the external electric field, one state antiparallel to the field and two states with zero component along the field. The states |211> and |21-1> do not possess dipole moments and therefore do not have a first-order interaction with the field.

Self-Assessment Questions (SAQ) 1:

1. The splitting of spectral line in Stark effect increase with
   a) Increase in **B**
   b) Decrease in **B**
   c) Increase in **E**
   d) Decrease in **E**

2. In the First-order Stark effect, the splitting is proportional to
   a) **E**
   b) Square of **E**
   c) Cube of **E**
   d) All of above

3. In strong field Stark-effect, the splitting of energy level is
   a) Less than fine structure splitting

b) Greater than fine structure splitting
c) Equal to fine structure splitting
d) None of the above

5.6. HYPERFINE STRUCTURE

In this section, we will go through the hyperfine structure of atoms. Various origins of the hyperfine structure are discussed. The coupling of nuclear and electronic total angular momentum is explained.

Many fine-structure components of spectral lines, when examined under high resolution, are further splitted into components with separations of the order of 2 cm^{-1}, which is very much smaller than those of the ordinary multiplet structure. This splitting is called the “hyperfine structure” and is caused by properties of the atomic nucleus. There are two type of nuclear effects that produce hyperfine structure.

The first is due to the presence of isotopic species in the element under investigation. The energy levels of isotopes are slightly displaced relative to each other, producing spectral transitions at slightly displaced relative to each other, producing spectral transition at slightly different wave numbers. Therefore, different isotopes of same element have slightly different spectral lines.

The second type of effect arises because the charged nucleus processes as spin angular momentum and the associated magnetic dipole moment. An interaction between the internal magnetic field produced by the orbital motion of the electrons in the atom and the spin magnetic dipole moment of the nucleus causes a hyperfine splitting of the spectral terms. As nuclear dipole moments are smaller than electronic magnetic dipole moments by~ 10^{-3}, the hyperfine splitting is smaller than the spin-orbit splitting by the same factor. Hyperfine structure, with energy shifts typically orders of magnitudes smaller than those of a fine-structure shift, results from the interactions of the nucleus (or nuclei, in molecules) with internally generated electric and magnetic fields.

5.6.1. ISOTOPE EFFECT

Different isotopes of an element have same number and arrangement of extranuclear electrons, differ from one another in mass. Since the nuclear mass enters into Rydberg constant for an atom, different isotopes have slightly different values of Rydberg constant. Correspondingly, the same transitions in different isotopes give rise to slightly different wave numbers.

Let us calculate the shift for H_β line (4861.33Å) due to presence of deuterium.

The Rydberg constant for hydrogen and deuterium

$$R_H = R_\infty \frac{1}{1+\frac{m}{M_H}} = 1.09677 \times 10^7\ m^{-1}$$

$$R_D = R_\infty \frac{1}{1+\frac{m}{M_D}} = 1.097074 \times 10^7\ m^{-1}$$

The transition formula for this transition from Balmer's formula

$$\frac{1}{\lambda_H} = R_H\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$\frac{1}{\lambda_D} = R_D\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$\frac{\lambda_D}{\lambda_H} = \frac{R_H}{R_D}$$

$$\frac{\lambda_D - \lambda_H}{\lambda_H} = \frac{R_H - R_D}{R_D}$$

$$\Delta\lambda = \lambda_D - \lambda_H = -\lambda_H\left(\frac{R_D - R_H}{R_D}\right)$$

$$= -4861.33\ \text{Å}\left(\frac{109707.4 - 109677.6}{109707}\right)$$

$$= -1.32\ \text{Å}$$

	Observed	*calculated*
H_α	*1.79*	*1.787*
H_β	*1.33*	*1.323*
H_γ	*1.19*	*1.182*
H_δ	*1.12*	*1.117*

Many cases of isotope-shift are not as simple as that for hydrogen. In fact, for the rare earth and heavier atoms, the main contribution to isotope shift is not due to a difference in mass but due to a change in nuclear radius with mass and the deviation of the nuclear magnetic field from being purely a coulombic one.

Sm^{150}→Sm^{152} shift is double that of Sm^{152}→Sm^{154}
Usual increase is not from Sm^{150}→Sm^{152}

5.6.2. NUCLEAR SPIN AND HYPERFINE SPLITTING

In many cases the isotope effect is not sufficient to explain the hyperfine structure. The number of hyperfine structure components is often considerably greater than the number of isotopes. In particular, elements which have only one isotope in appreciable amount also show hyperfine structure splitting. Likewise, the number of components of different lines is frequently quite different for one and the same element. These hyperfine structures can be quantitatively explained, when it is assumed that the "atomic nucleus possess an intrinsic angular momentum with which is associated a magnetic moment". This angular momentum can have different magnitudes for different nuclei and of course, for different isotope of the same element. This is known as Nuclear spin.

Thus, the atomic nucleus possesses an intrinsic spin angular momentum **I** with which is associated a magnetic dipole moment $\boldsymbol{\mu_I}$. Similar to electron, the magnitude of the nuclear angular momentum

$$\mathbf{I} = \sqrt{I(I+1)}\frac{h}{2\pi}$$

Where I is the "nuclear spin quantum number" which has different values for nuclei of odd mass numbers. Thus, angular momentum has different magnitude for different nuclei and also for different isotopes of the same element.

Just as **L**, **S** and **J** have quantised components along an axis in space, the component of **I** along z-axis is

$$\mathrm{I}_z = M_I\frac{h}{2\pi}$$

Where the nuclear magnetic quantum number M_I has 2*I*+1 values given by

$$M_I = I, I-1, I-2, \dots\dots\dots, -I$$

The motion of nuclear protons produces a magnetic moment $\mu_I$which is proportional to the angular momentum, and which we shall write

$$\mu_I = g_I\left(\frac{e}{2m_p}\right)\mathbf{I}$$

Where e and m_p are respectively the charge and mass of proton. The quantity g_I is called the 'nuclear g factor'. The magnitude of the nuclear magnetic moment is

$$\mu_I = g_I\left(\frac{e}{2m_p}\right)\sqrt{I(I+1)}\frac{h}{2\pi}$$

$$= g_I\sqrt{I(I+1)}\frac{eh}{4\pi m_p}$$

The quantity $\frac{eh}{4\pi m_p}$ forms a natural unit for the measurement of nuclear magnetic moment and is called the 'nuclear magnetron' μ_N. It is 1/1836 times the Bohr magnetron (because the mass of the proton is 1836 times the mass of electron). Thus

$$\mu_I = g_I\sqrt{I(I+1)}\,\mu_N$$

The component of μ_I along the z-axis is

$$\mu_{Iz} = g_I M_I\,\mu_N$$

Where $M_I = I, I-1, I-2, \dots\dots\dots, -I$

Since the maximum values of M_I is I, the maximum observed component of μ_I is $g_I I\,\mu_N$, and is commonly called the 'nuclear magnetic moment'. It is roughly 1000 times smaller than electron magnetic moment.

5.6.2.1. VECTOR ATOM MODEL

Let us now construct the vector atom model with nuclear spin taken into account. The total angular momentum of the whole atom is the sum of three angular momenta: the electron orbital angular momentum **L**, the electron spin singular momentum **S** and the nuclear spin singular momentum **I**. that is, the total angular momentum is

F=L+S+I=J+I

As a result of interaction between electron orbit and spin **L** and **S** precess rapidly around their resultant **J**. Further, the interaction between the nuclear magnetic moment and the magnetic field produced by the orbital and spin motions of the atomic electrons couples **I** with **J** (because nuclear magnetic moment is so much smaller than electronic magnetic moment). Correspondingly the energy differences are very much smaller.

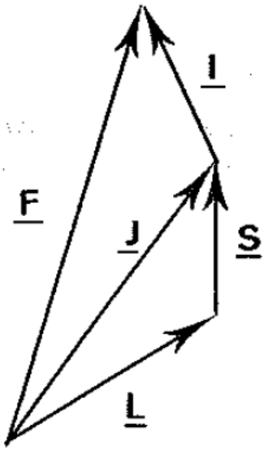


Figure 5.11

The quantised values of the total angular momentum F are $\sqrt{F(F+1)}\frac{h}{2\pi}$, where hfs quantum number F can take the values:

$$F = J + I, J + I - 1, J + I - 2, \dots\dots, -(J + I)$$

Giving 2J+1 values if $I \geq J$, or 2I+1 values if $I \leq J$. This means that as a result of I.J interaction, each fine-structure J-level split into 2J+1 (if $I \geq J$) or 2I+1 (if $I \leq J$) hfs levels, each characterised by an F value.

Interaction energy:

The I - J interaction energy can be shown to be given by

$$E_{I,J'} = \frac{1}{2}A'[F(F+1) - I(I+1) - J(J+1)]$$

Where A' is a constant. The various *hfs (hyperfine fine structure)* levels of a given term of a given atom have the same I and same J, but differ in F. Hence the separation between two *hfs* levels can be obtained by substituting first F+1, then F, in the above equation and taking the difference. This gives

$$\Delta E' = \frac{1}{2}A'[(F+1)(F+2) - F(F+1)]$$

$$= A'(F+1)$$

Thus, energy interval between consecutive *hfs* levels F and F+1 is proportional to the larger of the F values (Lande's interval rule). The order of *hfs* levels in some hypermultiplets is normal (smallest F level deepest) while in other it is inverted (largest F level deepest) (Fig. 5.12).

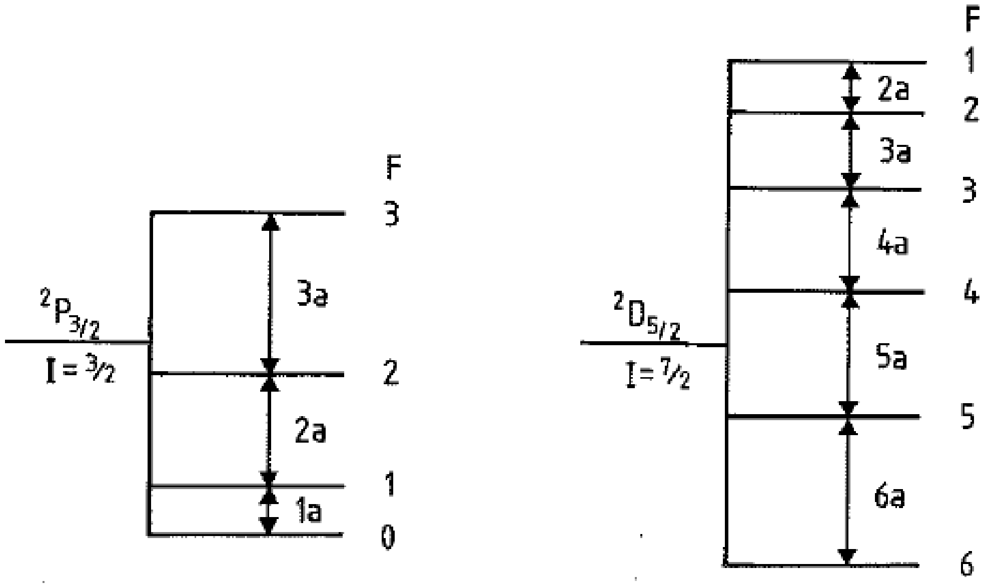


Figure 5.12

The selection rule for F electric dipole transitions is similar to that for j:

$$\Delta F = 0, \pm 1 \; but \; F = 0 \nleftrightarrow F = 0$$

Example 1:

For the H atom, with a proton as the nucleus, the experiments give the values

$I = 1/2$, $gI = +5.58 \Rightarrow (\mu_N)z = \pm 2.79\mu K$.

For the ground state $S^2_{1/2}$ is $j = 1/2$, $I = 1/2$

$\Rightarrow F = 0$ or $F = 1$.

This gives the two hyperfine components.

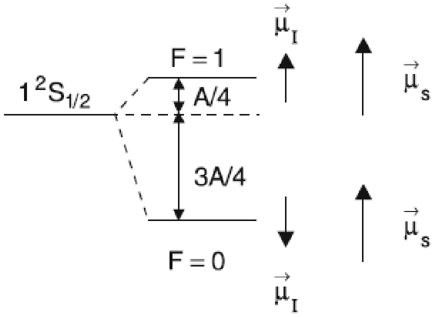
$$E_{I,J'} = \frac{1}{2} A' [F(F+1) - I(I+1) - J(J+1)]$$

$$E_{hfs}(F = 0) = E_{(1,0,1/2)} - \frac{3}{4} A$$

$$E_{hfs}(F = 1) = E_{(1,0,1/2)} + \frac{1}{4} A$$

with the separation $\Delta E = A = 5.8 \times 10^{-6}$ eV.

Figure 5.13: Hyperfine structure of the $1S^2_{1/2}$ state of the H atom. The hyperfine coupling constant is A = 0.047cm^{-1}.



$\Delta.v = \Delta E/hc = 0.047\ \text{cm}^{-1} \Rightarrow \Delta v = 1.42$ GHz, $\Delta\lambda = 21$ cm.

Example 2: For Hyperfine Structure of bismuth (I=9/2) line 4722 Å.

The fine-structure in bismuth shows j-j coupling. The transition corresponding to this line is

$$6p^2 7s, \left(\frac{1}{2}, \frac{1}{2}, \frac{3}{2}\right)_{\frac{1}{2}} \rightarrow 6p^3, \left(\frac{1}{2}, \frac{1}{2}, \frac{3}{2}\right)_{\frac{3}{2}}$$

With a nuclear spin I=9/2 and J=1/2, the initial state is split into two *hfs* levels with *F*= 5,4 which are in normal order. Again, with *I*=9/2 and *J*=3/2, the final state is split into four *hfs* levels with *F*= 6, 5, 4, 3 which are in inverted order.

The selection rule Δ*F*=0, ±1 (but $F = 0 \nleftrightarrow F = 0$) allows six transitions. Hence, the Bi line 4722 Å shows six Hyperfine components.

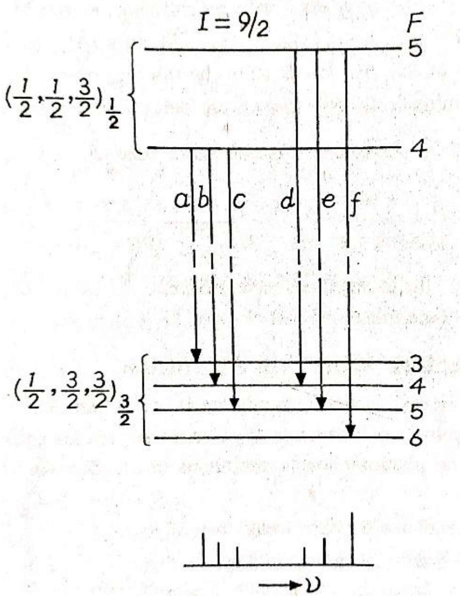


Figure 5.14

5.6.3. INTENSITY RATIO AND DETERMINATION OF NUCLEAR SPIN

When *hfs* components are observed due to the splitting of only one of the terms, a measurement of the intensity ratio of the observed components leads to the determination of nuclear spin. This is based on the 'sum rule', according to which the sum of the intensities of all the transitions starting from or ending on the same level is proportional to the statistical weight *2F+1* of that level. This situation arises in the *hfs* of the resonance lines (D_2, 5890 Å) of sodium. In this case, the ratio of the intensities of the two observed *hfs* components equal to the ratio of the weights *(2F+1)* of the *hfs* levels of the term $^2S_{1/2}$. When *I* is unknown, the *F* values of the two *hfs* levels of the term $^2S_{1/2}$ $\left(J = \frac{1}{2}\right)$ would be $I + \frac{1}{2}$ and $I - \frac{1}{2}$. Hence

$$Intensity\ ratio = \frac{2\left(I + \frac{1}{2}\right) + 1}{2\left(I - \frac{1}{2}\right) + 1} = \frac{I + 1}{I}$$

The observed intensity ratio is 5:3. Thus,

$$\frac{I + 1}{I} = \frac{5}{3}$$

$$I = \frac{3}{2}$$

Thus, the nuclear spin I is determined.

When the *hfs* components are observed due to the splitting of both the terms, as in case of Bi line 4722 Å (Fig. 5.14), then also an analysis of the hyperfine structure can also lead to the determination of nuclear spin. When all the hyperfine components are fully resolved, as in case of Bi, then constant wave-number difference occur between pairs of components. For example, we have

$$c - b = e - d$$

$$d - b = e - c$$

These differences correspond to level difference in the lower and the upper state respectively. We arrange the wave numbers of the hyperfine components in a square array such that along each row and along each column they increase (or decrease) regularly, and the difference between them in two successive rows and successive column is constant. Then, all the components in any row correspond to the same upper *hfs* level, while all those in any column correspond to the same lower *hfs* level. This will enable us to construct *hfs* energy levels for the upper and the lower states. For example, in the above case of Bi, when the wave numbers of the 6 observed components are filled in the square array, we obtain 2 *hfs* levels in the upper state and 4 in the lower state, as shown below:

F_{lower} F_{upper}	3		4		5		6
4	a	(b-a)	b	(c-b)	c		
			(d-b)		(e-c)		
5			d	(e-d)	e	(f-e)	f

Now, two case may arise:

- The upper and lower states have different J values and have also different number of *hfs* levels. In this case, number of *hfs* level is always (2J+1). We may apply the Land's interval rule to obtain the F values of the *hfs* levels from the interval ratio. Thus, all F values of the state whose J value is already known are determined. From this the nuclear spin I can be calculated. In the above case, for the lower state F= 3, 4, 5, 6 and J=3/2, so that

$$I = \frac{9}{2}$$

- The upper and the lower states have different J values but have the same number of *hfs* levels. In this case this number is always 2I+1; hence I may be evaluated.

Self-Assessment Questions (SAQ) 2:

1. The Hyperfine structure of spectral line arises due to

a) Isotope effect
b) Nuclear spin
c) Both ‘a’ and ‘b’
d) None of above

2. Numbers of Hyperfine components are present in Bi (6722 Å)
   a) 5
   b) 4
   c) 3
   d) 6

3. Intensity ratio of hyperfine components of sodium D_2 line (5890Å)
   a) 5:3
   b) 4:5
   c) 2:2
   d) 3:5

5.7. SUMMARY

The Stark effect is the shift in atomic energy levels caused by an external electric field. The magnitude of the wavelength separation and the relative intensity among the split line components depend on the field strength. Stark effect generally increases as the square of the applied field strength (quadratic Stark effect). For hydrogen like system special condition prevail due to the level degeneracy and hence linear Stark effect (shift is linear in applied field strength) is obtained.

Hyperfine structure is the splitting of individual multiplet (J→J transitions) components into a number of components lying extremely close together under the high resolution. The magnitude of the splitting is ~2 cm^{-1}. Hyperfine structure is caused by properties of the atomic nucleus, either due to presence of isotope or due to an interaction between the internal magnetic field produced by the orbital motion of the electrons in the atom and the spin magnetic dipole moment of the nucleus.

5.8. GLOSSARY

Polarisation- restrict vibration to one direction
Symmetrical- made up of similar part
Coupling- to join
Quantised- to have only certain values
Intrinsic- belonging
Isotope- elements having same atomic number and different atomic mass

5.9. TERMINAL QUESTIONS

1. Discuss Stark Effect with the overview of classical electrostatic.
2. Discuss the First order and Second order on the basis of Perturbation theory.
3. Why the hydrogen atom in the ground state does not show a first-order Stark effect?
4. Draw the Hyperfine structure of the fine structure component D_2 (5890 Å) of sodium (I=3/2). Transition $^2P_{3/2}$→$^2S_{1/2}$.
5. Draw the Hyperfine levels for $^2D_{5/2}$ of Bismuth (I=9/2). If the separation of $^2_2D_{5/2}$ and $^2_2D_{5/2}$ is 30 cm^{-1}. Calculate the separation of all adjacent Hyperfine levels.

5.10. REFERENCES

1. G. Aruldhas, Quantum Mechanics, PHI learning, New Delhi, India, 2009
2. G. Hertzberg, Atomic Spectra and Atomic Structure, Dover Publication, New York, USA, 1944
3. R. Kumar, Atomic and Molecular Spectra: Laser, Kedar Nath Ram Nath Publication, Meerut, India, 2011
4. J. J. Sakurai, Modern Quantum Mechanics, Addison, Wesley Publication House, USA, 1994
5. Wolfgang Demtröder, Atoms, Molecules and Photons: An Introduction to Atomic-, Molecular and Quantum-Physics, Springer-Nature, Germany, 2010

5.11. ANSWERS

Self-Assessment question (SAQ)1:

Ans. 1. (c)

Ans. 2. (a)

Ans. 3. (b)

Self-Assessment question (SAQ)2:

Ans. 1. (c)

Ans. 2. (d)

Ans. 3. (a)

Terminal question

Ans. 5. ${}_{3}^{2}D_{5/2} - {}_{4}^{2}D_{5/2}$ = 40 cm^{-1}

${}_{4}^{2}D_{5/2} - {}_{5}^{2}D_{5/2}$ = 50 cm^{-1}

${}_{5}^{2}D_{5/2} - {}_{6}^{2}D_{5/2}$ = 60 cm^{-1}

${}_{6}^{2}D_{5/2} - {}_{7}^{2}D_{5/2}$ = 70 cm^{-1}

UNIT 6 BREADTH OF SPECTRAL LINES

Structure

6.1 Objective
6.2 Introduction
6.3 Spectral Line Breadth
6.4 Causes of Spectral Line Breadth
    6.4.1 Natural Breadth
    6.4.2 Doppler Effect
    6.4.3 External Effects
        6.4.1.1 Collision Damping
        6.4.1.2 Pressure Broadening
        6.4.1.3 Stark Broadening
        6.4.1.4 Instrument Broadening
6.5 Voigt Profile
6.6 Summary
6.7 Glossary
6.8 Reference Books
6.9 Suggested Reading
6.10 Terminal Questions

6.1 Objectives

After studying this unit, you will come to know about:

1. Spectral line breadth.
2. Causes of spectral line breadth.
3. Define natural breadth
4. Define Doppler effect
5. Define external effects

6.2 Introduction

In the previous chapters, we have already discussed the two main important transition phenomena; Absorption and emission. Spectral lines are narrow emission or absorption features in the spectra of gaseous sources. Spectral lines are intrinsically quantum phenomena and have no explanation in classical physics. The classical concepts of ideal *particles* and *waves* are blurred in quantum mechanics: classical particles (e.g., electrons) and waves (e.g., radio waves) behave as both particles and waves.

An individual atom/molecule making a transition between energy levels emits one photon with a well-defined energy / frequency. However, profiles of real spectral lines are not infinitely narrow.

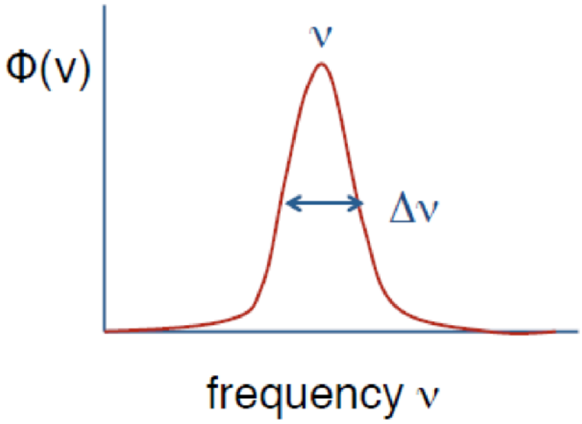


Figure 6.1: Width of the spectral line.

e.g. for an emission line, width of the spectral line Δν could be defined as the full width at half the maximum intensity of the line (Figure 6.1).

In molecular spectroscopy, the spectral lines depend on two factors:

1. Width of the spectral lines decides the sharpness or broadness of the line
2. Intensity of the spectral lines decides the strength of the signal

6.3 Spectral Line Breadth

If the spectral line is sharp, it will have no width i.e. it can be seen at a specific frequency only. If the spectral line is broad, it will have a certain width i.e. It is spread over a range of frequencies. The breadth of a spectral line is defined as the separation in the cm^{-1} between two points whose intensities are half that of the maximum intensity. Figure 6.2 represents a) a sharp spectral line and b) a spectral line having observable width. A spectral line is a dark or bright line

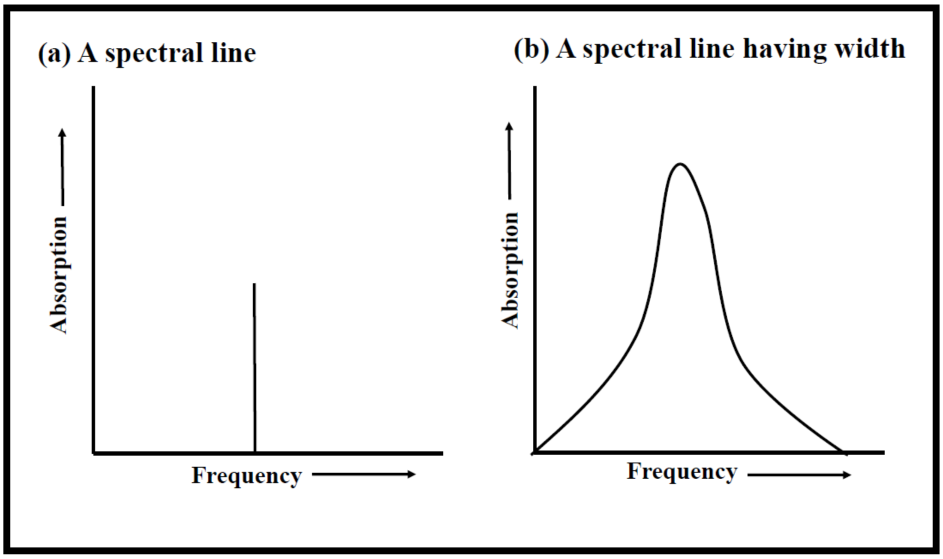


Figure 6.2: a) A sharp spectral line b) A sharp spectral line having width.

6.4 Causes of Spectral Line Breadth

Generally, the spectral lines observed are broad. The width or broadening depends on the following factors:

1. Natural Breadth

2. Doppler Effect
3. External Effects: (collision damping, pressure broadening, stark effect etc.)

6.4.1 Natural Breadth

This type of broadening is usually much smaller than other broadening mechanisms. Natural also known as intrinsic broadening. This type of spectral line broadening is one cause of the width Δν in a line profile function φ(ν). It arises from the spontaneous decay rate. In quantum mechanics by using the Heisenberg uncertainty principle, if we consider a bunch of atoms, their lifetimes are affected by the uncertainty in their energy states from. Such as given below:

$$\Delta E \Delta t \sim \hbar \tag{6.1}$$

Where E is the energy spread of a state and t is the mean time for which atoms remain in that state. A photon in a certain energy state will therefore have a range of possible frequencies when it decays to a lower state.

$$\Delta\nu \sim \frac{\Delta E}{h} \sim \frac{1}{2\pi\Delta t} \tag{6.2}$$

The value of mean life is inversely proportional to the energy breadth of the state. From this we can say that ground state and metastable states are sharp, while the other states are quite broad.

The line profile function resulting from Natural Broadening is the Lorentzian Profile. It is proportional to A_{10}. This shows that the larger values of A result in more broadening or wider profile function.

$$\phi(\nu) \propto A_{10} \tag{6.3}$$

If radiation is present, then stimulated emission effects must be added to the spontaneous emission ones. Overall though, natural line broadening is not the dominant broadening effect and isn't often directly observed, except in the line wings. Natural line width isn't often directly observed, except in the line wings in low-pressure (nebular) environments. Other broadening mechanisms usually dominate.

The half intensity breadth of a spectral line due to the transition from an excited state to the ground state is given by:

$$\Delta\nu \sim \frac{\Delta E}{h} \sim \frac{1}{2\pi\Delta t} \tag{6.4}$$

For the ordinary excited state, the value of mean time is 10^{-8} sec. Hence, by using the above formulae the value of energy breadth is given as: 10^{7} s^{-1}.

$$\Delta\nu = \frac{1}{2\pi\Delta t} \approx 10^{7} s^{-1}$$

For a visible wavelength (6000 Å). This corresponds to a wavelength broadening of

$$\Delta\lambda = \frac{\lambda^2}{c}\Delta\nu$$

$$\Delta\nu \approx \frac{(6000\times 10^{-10} m)^2}{3.8\times 10^{8} ms^{-1}}\times 10^{7} s^{-1}$$

$$= 10^{-4} \text{ Å}$$

This shows that the value of wavelength broadening is quite small and it cannot be measured by ordinary spectroscopic methods.

6.4.2 Doppler Effect

Unlike the other forms of broadening, Doppler broadening does not involve intra- or inter-atomic interactions. This type of broadening is due to the motions of the atoms with respect to an observer. Doppler broadening is sometimes called *inhomogeneous broadening* since each atom contributed its own frequency to the profile. Hence, removal of a (non-random) sample of atoms (e.g., by saturating a transition at a particular frequency) will distort the line shape.

Figure 6.3: Doppler broadening.

Two basic mechanisms:

1) Energy levels themselves are not infinitely sharp: emitted photons have a range of frequencies.
2) Atoms and molecules in the gas are moving relative to the observer: observed photons don't have the same frequency as the emitted photons because of the Doppler Effect.

Doppler Effect

It is named after an Austrian physicist Christian Doppler, who proposed it in 1842 in Prague. The Doppler effect also known as Doppler shift. It is defined as the change in frequency of absorbed or emitted radiation when the source is moving towards or away from the observer. It is observed in case of gaseous samples as the molecules of the gases are in a state of continuous random motion. If the source emitting the radiation is moving away from the observer or the observing instrument with a velocity ‘v’ , then the observer or instrument detects the radiation of frequency ϑ

$$\vartheta_0 = \vartheta /1+ v/c$$

where ϑ_0 is frequency of radiation detected by the observer, f is the frequency emitted by the source, v is the velocity of the radiation and c is velocity of light. If the source emitting the radiation is moving away from the observer or the observing instrument, then the observer or instrument detects the radiation of frequency ϑ_0.

$$\vartheta_0 = \vartheta \text{ /1- v/c}$$

The difference $\Delta\vartheta = \vartheta - \vartheta_0$ is called Doppler shift or broadening.

When the source of the waves is moving toward the observer, each successive wave crest is emitted from a position closer to the observer than the previous wave. Therefore, each wave takes slightly less time to reach the observer than the previous wave. Hence, the time between the arrivals of successive wave crests at the observer is reduced, causing an increase in the frequency. While they are travelling, the distance between successive wave fronts is reduced, so the waves "bunch together”. Conversely, if the source of waves is moving away from the observer, each wave is emitted from a position farther from the observer than "spread out". The previous wave, so the arrival time between successive waves is increased, reducing the frequency. The distance between successive wave fronts is then increased, so the waves. As the gas molecules are moving in different directions with different speeds, some towards and some away from the observer, so the spectral lines arise from all the resulting DOPPLER SHIFTS.

The shape of the Doppler shift resembles that of Maxwell's distribution of speeds as at a particular temperature the speed of the gas molecules is given by Maxwell's distribution.

Let us assume a Maxwell distribution of velocities: the probability that the velocity of an atom an ideal gas lies between ϑ and $\vartheta + d\vartheta$ is given by

$$dP = 4\pi\left(\frac{\mu}{2\pi RT}\right)^{\frac{3}{2}} e^{\left(\frac{-\mu v^2}{2RT}\right)^{\frac{3}{2}}}\, v^2 dv \qquad (6.5)$$

Here R is the universal constant and its value is given as: 8.31 J/(mol-K).

T is the temperature.

μ is defined as atomic weight.

We can write the Doppler shift as given below

$\Delta\vartheta = \vartheta - \vartheta_0 = \vartheta_0 \frac{v}{c}$

$$v = c\frac{\vartheta - \vartheta_0}{\vartheta_0} \tag{6.6}$$

Here, ϑ_0 is the source of light, ϑ is the apparent frequency measured by the observer, v is the velocity relative to the observer. On putting the value of v from equation 6.6 to equation 6.5, we will get the value of relative intensity in the terms of frequency as:

$$I(\vartheta) = constant\ e^{\frac{-\mu c^2(\vartheta - \vartheta_0)^2}{2RT{\vartheta_0}^2}} \tag{6.7}$$

Figure 6.4 gives the plot for the relative intensity expression. If we set the exponential term in tl the equation 6.7 as one half, we will get the situation at which the intensity drops to half of its n So by putting the exponential term in the equation 6.7 as ½;

$$e^{\frac{-\mu c^2(\vartheta - \vartheta_0)^2}{2RT{\vartheta_0}^2}} = \frac{1}{2} \tag{6.8}$$

By taking $\log_e$ both sides.

$$\frac{-\mu c^2(\vartheta - \vartheta_0)^2}{2RT{\vartheta_0}^2} = \log_e 2 \tag{6.9}$$

By rearranging terms in the equation 6.9.

$$\vartheta - \vartheta_0 = \frac{\vartheta_0}{c}\sqrt{\frac{2RT}{\mu}\log_e 2} \tag{6.10}$$

Multiplying equation 6.10 by 2 we will get line breadth as $\delta\vartheta$. Thus,

$$\delta\vartheta = 2(\vartheta - \vartheta_0)\sqrt{\frac{2RT}{\mu}\log_e 2} \tag{6.11}$$

$$\sqrt{\log_e 2} = \sqrt{0.693} = 0.832$$

$$\therefore \delta\vartheta = 1.66\frac{\vartheta_0}{c}\sqrt{\frac{2RT}{\mu}} \qquad (6.12)$$

Equation 6.12 represent Doppler broadening and it is directly proportional to the square root of the temperature and frequency and inversely proportional to the square root of the atomic weight. Equation 6.12 represent the Doppler broadening in terms of frequency, by using below\ equation we can convert half intensity line breadth in terms of wavelength.

Now, $\frac{\delta\vartheta}{\vartheta} = \frac{\delta\lambda}{\lambda}$

$$\delta\lambda = 1.66\frac{\lambda_0}{c}\sqrt{\frac{2RT}{\mu}} \qquad (6.13)$$

Equation 6.13 clearly represent that line breadth due to Doppler broadening increases with increasing temperature and decreases with increasing atomic weight.

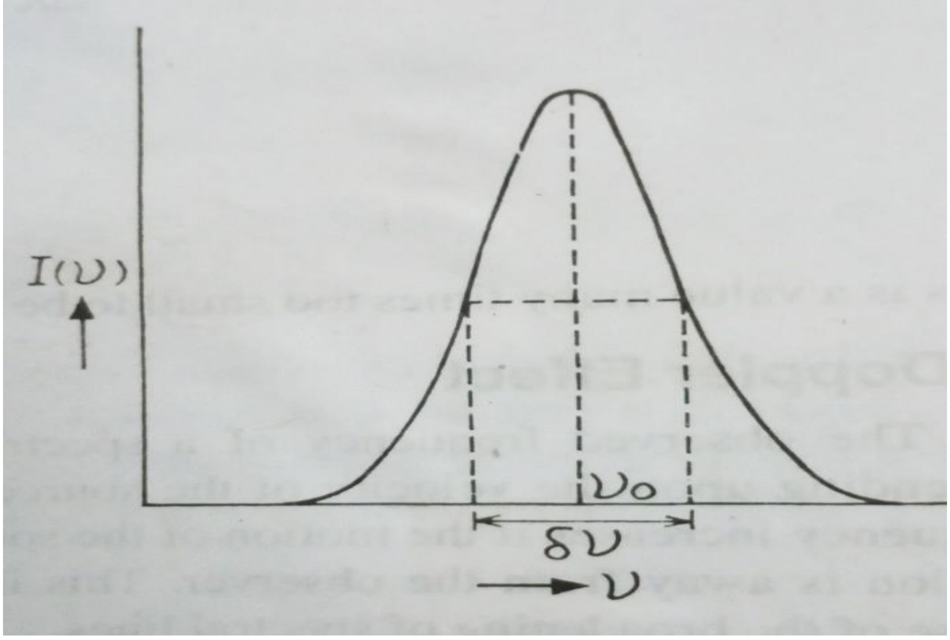


Figure 6.4

If we consider Doppler-broadened spectral lines at three different temperatures, we observe line broadens as the temperature is increased. The reason behind is that Doppler Broadening increases with temperature as molecular speed increases with rise in temperature. So in order to get maximum sharpness of the spectra, it is essential to work at low temperatures.

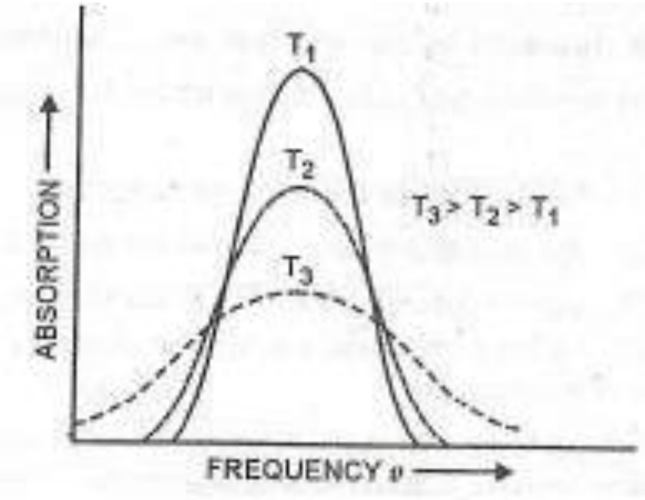


Figure 6.5: Shapes of Doppler-broadened spectral lines at three different temperatures.

6.4.3 External Effects

A number of external effects are also in nature that will cause the broadening in the spectral lines. Some of them are mentioned below:

- Collision Damping
- Pressure Broadening
- Stark Broadening
- Instrument broadening

Now in the coming sections we will discuss them.

6.4.1.1 Collision Damping

In a dense gas, atoms/molecules are colliding frequently. This effectively reduces the lifetime of states further, to a value smaller than the quantum mechanical lifetime. If the frequency of collisions is ν_{col}, then expect to get a collisional linewidth of about $\Delta\nu \sim \nu_{col}$.

Frequency of collisions increases with density - expect to see broader lines in high density regions as compared to low density ones. e.g. a main sequence star (small radius) has a higher density at the photosphere than a giant of the same surface temperature. Spectral lines in the main sequence star will be broader than in the giant.

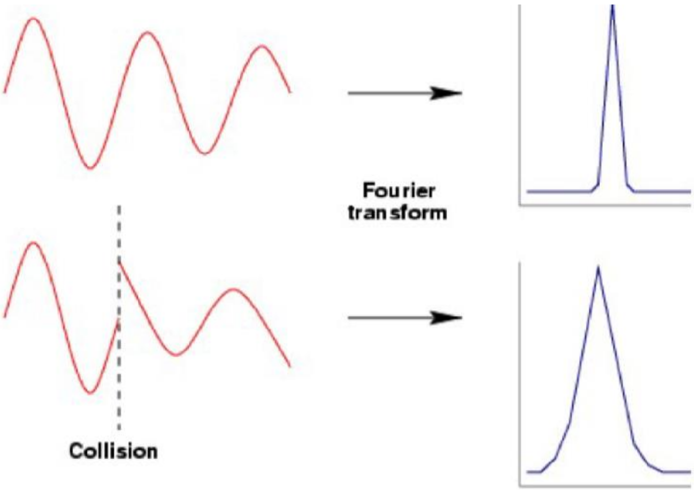


Figure 6.6: Collision Damping.

6.4.1.2 Pressure Broadening

At high pressure, the collision time for the two atoms are quite high in comparison with the mean time between collisions. When the emitting or absorbing atom is treated to a strong atomic field. It causes a shift in the spectral line (towards red) and line broadening asymmetrically. The shape of spectral lines due to collisions, referred to as pressure broadening, is given by the Lorentz profile.

6.4.1.3 Stark Broadening

The Stark effect was discovered in 1913 named after the physicist Johannes Stark. The Stark effect is defined as the shifting and splitting of spectral lines of atoms and molecules into several components due to the presence of an external electric field. It is an analogue of the Zeeman effect, where a spectral line is split into several components due to the presence of the magnetic field. In specific, the Stark effect is accountable for the Stark broadening of spectral lines by charged particles in plasmas. For most spectral lines, the Stark effect causes asymmetry in spectral line broadening.

6.4.1.4 Instrument Broadening

The spectrum is the spectroscopic signal that arises from physical processes in the material under study. The source of the distortion is the spectrometer slits or apertures, including entrance/exit slits, grating or gratings, confocal aperture, detector etc. through which radiation passes. The spectral distortion by the slits causes, among other phenomena, an increase in the observed band widths. Observed spectral line shape and line width are also affected by instrumental factors.

6.5 Voigt Profile

The combination of thermal broadening with the natural or collisionally broadened line profile is called the Voigt profile. This is the convolution of the Lorentz profile with a Doppler profile. Curves show the profile as the natural (or collisional) line width is increased. The Lorentz profile falls off slower than the Doppler profile, so the core remains roughly Gaussian, while the wings look like a Lorentz profile.

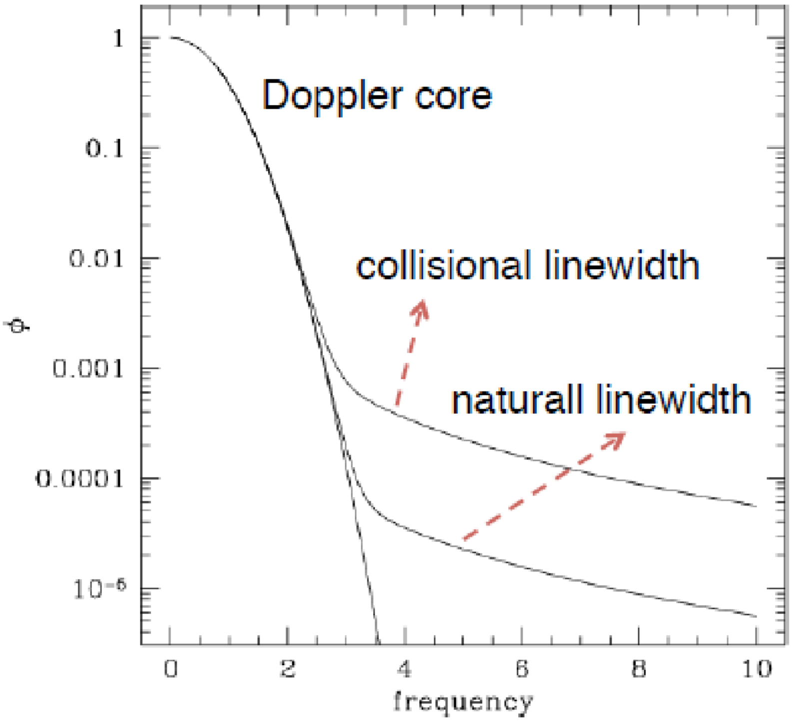


Figure 6.7: Voigt profile: combination of thermal and natural (or collisional) broadening

The wider Doppler broadening dominates near the center of the line, but since the Doppler profile decreases exponentially, natural and pressure broadening make a greater contribution farther from the center of the line. Most stellar spectra lines have a profile described by a Voigt profile. The use of Voigt profile are fit to observations of absorption towards quasars to measure temperatures and column densities of the gas along line of sight.

6.6 Summary

In this unit, you have studied the spectral line broadening and their causes in detail. Strength of different spectral lines depends upon the abundance of different elements, and on the excitation/ ionization state (described in part by the Boltzmann formula). Width of spectral lines depends upon: natural linewidth (small), collisional linewidth (larger at high density) and thermal linewidth (larger at higher temperature). You have also studied the dependence of temperature and pressure and different types of broadening. To check your progress, self-assessment questions (SAQs) are given place to place. Many terminal questions are given in the unit for practice and to make the concept clear.

6.7 Glossary

Spectrum	The set of colors into which a beam of light can be separated, or a range of waves.
rotational	A rotation is a circular movement of an object around a center of rotation.
vibrational	A molecular vibration is a periodic motion of the atoms of a molecule relative to each other,
Emission spectrum	The distribution of electromagnetic radiation released by a substance whose atoms have been excited by heat or radiation.
absorption spectrum	The spectrum formed by electromagnetic radiation that has passed through a medium in which radiation of certain frequencies is absorbed

Transition	The process or a period of changing from one state or condition to another
	The act of making something wider.
Doppler	Relating to, or utilizing a shift in frequency in accordance with the Doppler effect.
Collision	the act of colliding; a coming violently into contact

6.8 Reference Books

1. Atomic & Molecular spectra Laser: By Raj Kumar (KNRM Publication-Meerut)
2. Structure and properties of Material: By MA Wahab (Narosa Publishing House – Delhi)
3. Molecular Spectra and Molecular Structure I: G. Herzberg (Van-Nostrand Rein-hold, 1950)
4. Atomic Physics by J.H.Fewkes & John Yarwood. Vol. II (Oxford Univ. Press, 1991).
5. Physics of Atoms and Molecules, Bransden and Joachein. (Longman Scientific and Technical)

6.9 Suggested Readings

1. Fundamental of Molecular Spectroscopy. C N Banwell and E M Mc Cash (Tata Mc Graw Hills)
2. Gupta Kumar Sharma – Elements of Spectroscopy, Pragati Prakashan.
3. Modern Physics, Beiser, Tata McGraw Hill
4. 2. Optical Spectroscopy in Chemistry and Life Sciences, W. Schmidt; Wiley-VCH.
5. Atkins, P.W.; de Paula, J. (2006). "13.3: Linewidths". Physical Chemistry (8th ed.). Oxford University Press. pp. 436–438. ISBN 0198700725.

6.10 Terminal Questions

Long answer type questions:

1. Show that $\varphi(\nu)=\Delta\,\nu^{-2}$ well away from the center of a line with a Lorentzian broadening profile.
2. Calculate the line-of-sight thermal velocity dispersion $\Delta\nu_D$ of line photons emitted from a hydrogen cloud at a temperature of 10^4 K.
3. Calculate the natural broadening line width of the Lyman α line, given that $A_{ul}=5\text{x}10^8$ s^{-1}. Convert to km/sec via the Doppler formula.
4. Mention the difference between line and Doppler broadening.

Numerical type questions:

1. Estimate the fractional width of a spectral line of 5000 Å wavelength emitted from a level of a life time of 10^{-8} sec.
2. Calculate the Doppler half-life intensity breadth of the sodium D-lines at 5893 Å corresponding to the temperature of 500 K. Value of R= 8.31 J/(mol-K), c= $3\text{x}10^8$ m/s, atomic weight of sodium = 22.99 g/mol.
3. Calculate the Doppler half-life intensity breadth of the sodium D-lines at 5893 Å corresponding to the temperature of 400 K. Value of R= 8.31 J/(mol-K), c= $3\text{x}10^8$ m/s, atomic weight of sodium = 22.99 g/mol.
4. Calculate in Å the Doppler half-intensity breadth of mercury green line 5461 Å, if the light source is at 1000 K. Given R= 8.31 J/(mol-K), c= $3\text{x}10^8$ m/s, atomic weight of mercury = 200.59 g/mol.

Answer 1: 1.33 $\text{x}10^{-4}$ Å; 2: 0.02 Å; 4: 0.0087 Å

Objective Question

Question 1: One of the causes of the breadth of the spectral lines is:

a) Doppler effect

b) Dispersion

c) Reflection

d) Diffraction

Question 2: Doppler broadening most significant at:

a) Low P, high T, small λ

b) High P, high T, high λ

c) Small P, small T, small λ

d) Low P, Low T, Low λ

Question 3: Collision broadening is most significant at:

a) High P, low T, large λ

b) High P, low T, large λ

c) High P, low T, large λ

d) High P, low T, large λ

Question 4: The width or broadening depends on the which?

a) Natural Breadth

b) Doppler Effect

c) External Effects

d) All of the above

Question 5: In a real radiation spectrum the emission and absorption lines tend to overlap with each other due to

a) Vibrational transition

b) Electronic transitions

c) Presence of spectral lines of various gases

d) Line broadening

Question 6: The Doppler broadening mechanism dominates over other broadening under:

a) Low pressure and high temperature

b) High pressure and low temperature

c) Low temperature in infrared

d) High pressure in infrared

Answer 1: a; 2: a; 3: a; 4: d; 5: d; 6: a;

UNIT 7: X Rays

Structure

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7.1 Introduction

In 1895, Roentgen observed that when a beam of fast moving electrons struck on a suitable target, some rays are produced that have highly penetrating power. These rays were named as X-rays. Actually when fast moving electrons are deaccelerated, and according to classical electromagnetic theory, these deaccelerated electron emit electromagnetic radiations (Bremsstarhlung) which are known as X-rays.

For the production of X-rays we use a Coolidge tube. This tube has a target of a metal which have high melting point and high atomic numbers, for example tungsten, platinum, molybdenum etc. In this tube under lower pressure, electron are emitted from a filament and struck on a target (anode) due to high voltage difference (1000 to 30000 V) at anode. When we observe spectra of X-rays, we have two types of spectra, namely continuous spectra and characteristic (line) spectra. The continuous spectra arises due to deacceleration of electron when they hit the target. The intensity of continuous spectra depends on the energy of incident electron and not depends on target material. On the other hand, the line spectra arise when some electrons emitted from filament, penetrate the target material, hit and eject electron form inner shells of target atom. These spectra give the information about the target material.

7.2. Objective

After reading this unit we will able to understand

(i) continuous spectra of X-rays
(ii) Characteristic spectra or line spectra of X-rays
(iii) Significance of line spectra
(iv) Emission spectra
(v) Absorption spectra
(vi) Fine structure in X-rays
(vii) Doublets in X-rays spectra

7.3. X-Rays Continuous And Line Spectra

When the X-rays are produced at low potential applied between target and filament, some electrons penetrate the core of atoms of target material and deaccelerated. The deaccelerated electrons emit X-rays and give continuous spectra. The intensity of continuous spectra depends on the energy of incident electron and not depends on target material.

$$\lambda_{min} = \frac{hc}{eV} \text{ where V is applied potential}$$

$$\lambda_{min} = \frac{12400}{V}$$

The continuous spectra do not give the information about target material. Other type of radiation is line spectra, which consists of distinct spectral line whose frequencies are characteristic of the material of target. This type of spectra is also called characteristic spectra as it gives the information about atomic structure of atoms of target materials. The characteristic X-rays are produced when extremely high energy electrons penetrate well inside the atoms of target material, and hit the bounds electrons of K, L, M shells and bound electron is ejected from the shell (says K shell). As an electron ejected from K shell, an another electron from any higher energy shell say L, M. jump at the vacancy at K shell, and during thus transmission an x-ray emitted as shown in figure 1. The figure 2 shows the line spectra corresponding to such transition.

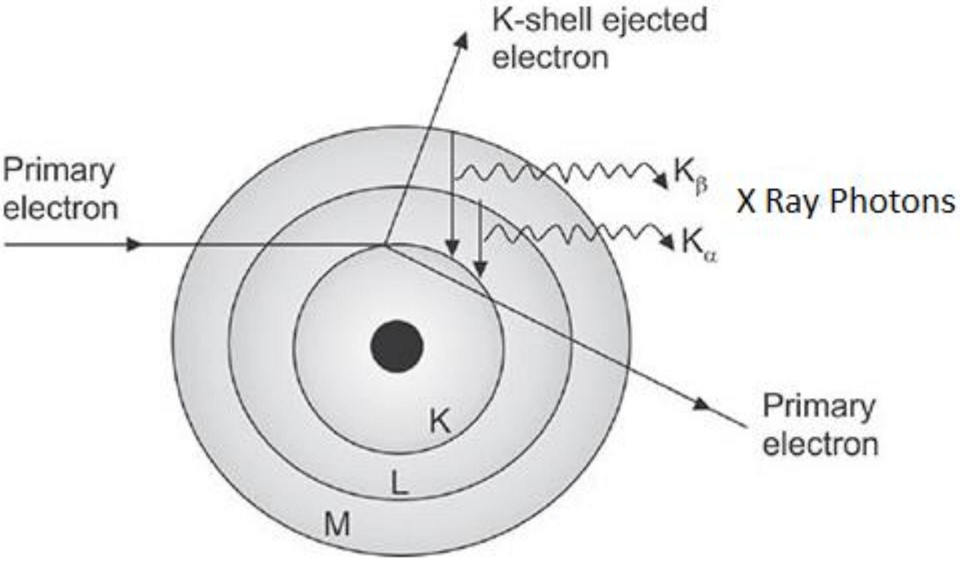

Figure 7.1: X Ray production by high energy electron penetration in an atom.

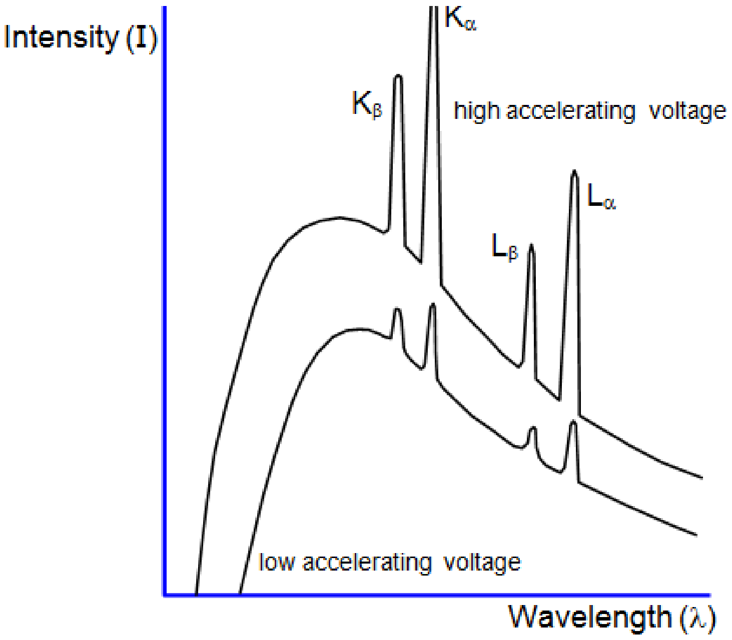

Figure 7.2: Characteristic X ray line spectra.

7.4 Explanation of Characteristic X-Ray Spectra

The most of element shows series of lines known as K series, L series and M series. On minute observation, each series contains number of lines named as K_α, K_β....., L_α, L_β.... and M_α, M_β.... etc. K. series appears when the x ray tube operated at highest voltage near 70,000 V as K electrons are strongly bound with nucleus and need maximum energy to eject. On the other hand, L series appear at voltage in the order of 2500 volt as M shell electrons are bound relatively loosely than K and L shell electrons.

Kossel first explained the feature of X-ray line spectra. Since electrons are arranged in K, L, M .... shells in normal state and K shell electrons are bound most strongly with positively charged nucleus. Thus K shell electrons require maximum energy to eject. Kossel explained that in an high energy electrons penetrates well inside an target atom, it eject the electron of K shell, and immediately an electron from outer shell, says L shell jump to K shell, X-ray photon of higher energy is emitted similarly an electron from N shell may jump to K shell. These lies of K series are designated as K_α, K_β, K_α, K_γ ..... respectively as shown in figure 7.3.

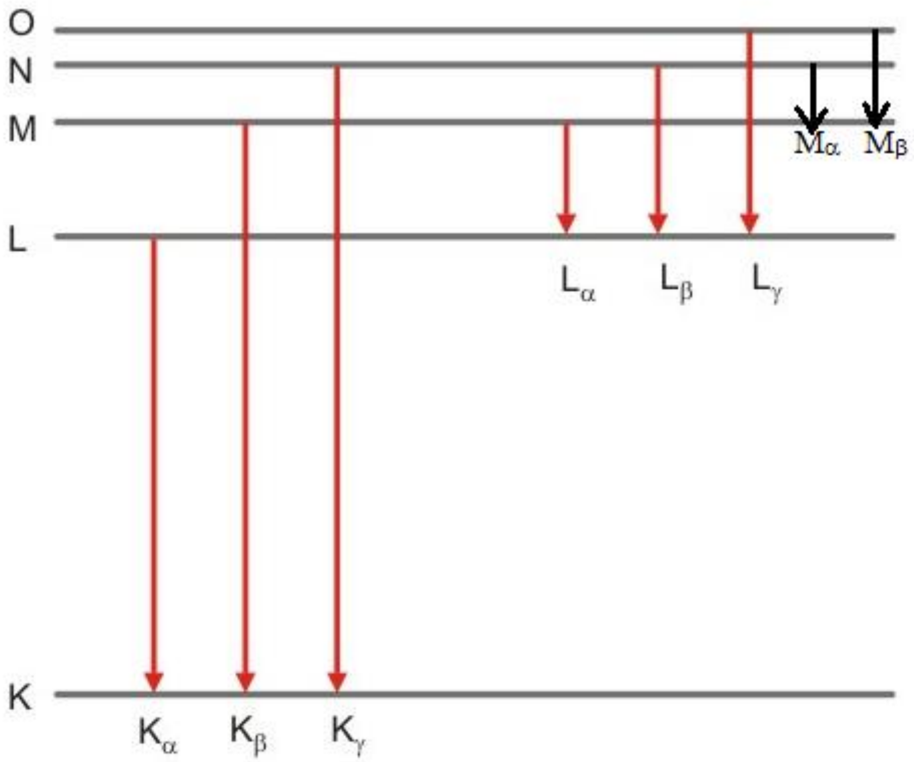

Figure 7.3: Characteristic X ray spectra.

In case of L series, an electron strikes the electron of L shell of target atom, and an electron from M, N, O shell jumps to L shell. Corresponding to these transitions L_α, L_β or L_γ lines arise as shown in figure 7.3. In the similar manner M, N.... series arise in X-ray spectra of a target material.

It is observed that when an electron from K shell is ejected, an electron from the L shell most likely fill the vacancy created at K shell and emits K_α line. Now a vacancy is created at L shell, and an electron from M shell most likely jumps from M shell and emit a phonon corresponding to L_α line. This process is continued until the vacancy reaches the outermost shell. Thus the emission of K series is always accompanied by L, M, N ... series as shown in figure 7.3.

Thus the x-ray lines are emitted when the potential is sufficient enough so that it can hit the particular K, L, M shell electron. Thus the necessary condition for the emission of K_α line, a accelerated fast moving electron must create a vacancy in the K shell of target material.

7.5 X-Rays Emission Spectra And Moseley Law

In 1913, Moseley studied the X-ray radiation of different elements. On this experiment he recorded the photographs of different – different elements. He observed K_α and K_β lines and later he observed that K_α and K_β lines are itself close doublets. These doublets are four lines designed as $K_{\alpha 1}$, $K_{\alpha 2}$, $K_{\beta 1}$, $K_{\beta 2}$.

Moseley found that as atomic number increases, K lines shift towards higher frequency. On this observation he stated that “The frequency of each corresponding K lines is approximately proportional to the square of atomic number of target element. The trend is shown in figure 4, and mathematically given as.

$$\nu = RA^2(Z-\sigma)^2$$

$$\sqrt{\frac{\nu}{R}} = A(Z-\sigma)$$

Where A and σ are constants for a given transition. In case of K_α line.

$$\sigma = 1,\ A^2 = \frac{3}{4}$$

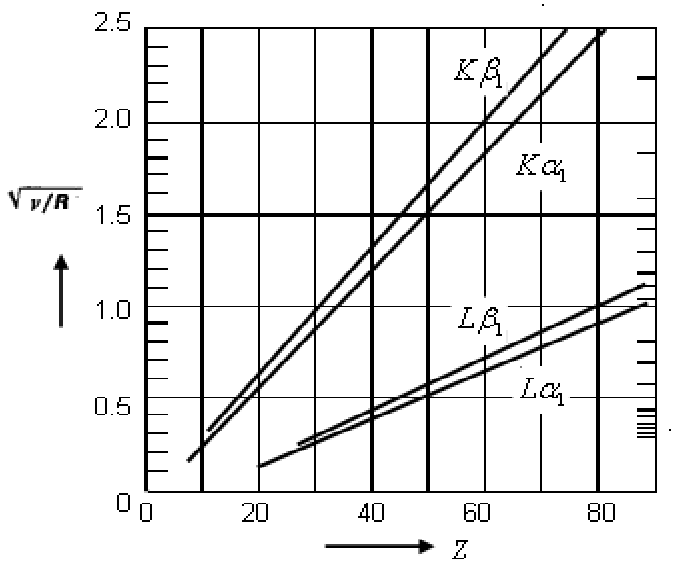

Figure 7.4: Moseley Law

by analogy with hydrogen line atoms the Moseley law can be given as

$$\nu = R(Z-1)\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$$

Similarly L_α, L_α series also composed of a number of lines.

7.6 X-ray Absorption Spectra

When a beam of X-rays passes through a film of a substance, and transmitted light is analyze through an X-ray spectrograph, an absorption spectra of that substance has been obtained. The absorption spectra of a substance are quite different from the emission spectra of some substance absorption lines are not observed corresponding to emission lines like K_α, K_β, K_γ .... In absorption spectra, a continuous region of absorption bounded by a sharp edge in the position of the limit of the emission of K series is observed as shown in figure 7.5. These edges are characteristics of absorber substance and called absorption edge. The frequency of absorption edge is ν_k is called K absorption limit.

It is clear that an x-ray emission line say K_α line occurs in the spectra when an electron jump from L shell to K shell of substance. In absorption spectra this line would be occurs when an electron jump from K shell to L shell. But it is not possible as L shell is already full with 8 electrons. Thus K_α line cannot be observed in the absorption spectra of X-ray.

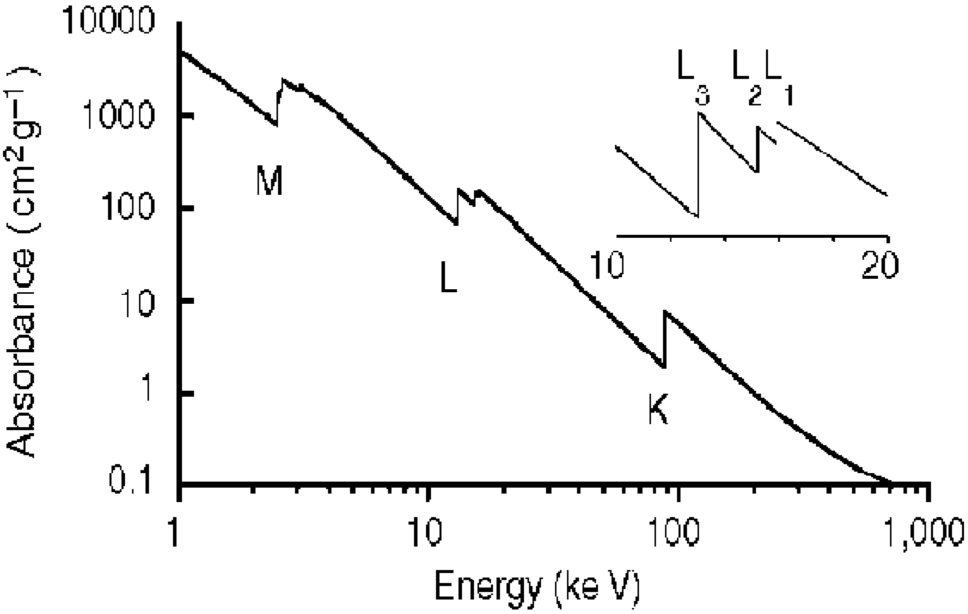

Figure 7.5: Absorption spectra of X ray.

Now we will explain the sharp edge occurred in the absorption spectra. In an x-ray photon has sufficient energy to eject an electron from it inner shells say k shell, such photon can be absorbed by k shell electron. But the frequency of such photon should be greater than a certain value say ν_k such that it can provide the energy required to remove the e^- of K shell (W_k)

Thus $h\nu_k = W_k$

The frequencies lower that this ν_k value would not be able to remove an K shell electron and such photon transmitted by substance. At frequency ν_k, the absorption process suddenly started and continues for frequencies greater than ν_k as shown in figure. Thus K absorption edge observed in the x-ray spectra corresponding to ν_k frequency. Absorption beyond the ν_k indicates that K electron ejected to infinity with kinetic energy say E_k as Einstein photoelectric equation ($E_k = h\nu_k – W_k$), where W_k is corresponding to work function.

In case of L series, when we observed the x-ray absorption we will observed three absorption edges designed a L_I, L_{II}, L_{III}. This occurs because L emission lines form three groups according to their escalation voltages. It indicates L shell has three energy levels the L series edges are shown in figure 7.5.

Similarly M absorption spectra shows S and N absorption spectra gives 7 edges.

7.7 Fine Structure of X-Rays Spectra

Kossel’s explained the x ray spectra on the basis of electron’s transmission in K, L, M, ... shell. But actually this explanation is only a rough approximation. When we observe the x-ray spectra more precision, we see each line of K series (K_β, K_α, K_γ....) is a doublet, and other series are more complex. These large numbers of lines are called fine structure. It is observed that absorption edges shows that K level is single L level is 3 fold and M level is 5 fold. The higher levels are shown by only heavier elements which are more complex.

The x ray levels arise due to removed of an electron from a shell. The x ray rotation of shell K, L, M are due by removal of electron from these shell respectively. When electron from 15 shell is removed the neutral atom raised to higher energy K state. If one electron remains in

15 subshell, this energy state is represented by $I^2$5½ as in the standard notation in spectroscopy for k level.

For next shell principal quantum number n=2, i.e. L shell, 25 level will again give rise to a state $2^2$5½. This is corresponding to L_1 level. In this shell there is another p subshell of 6 electrons. If an electron eject from this subshell, configuration becomes $2p^5$. This gives rise of some states as a single electron in p subshell. Hence the states arise as 2^2P½ and 2^2P 3/2. Corresponding to L_{II} and L_{III} levels as shown in figure. Hence L shell has 3 absorption edges corresponding to L_I, L_{II} and L_{III} states.

In case of third shell n=3 i.e. M shell, there as 3 subshells as 3s, 3p and 3d. The removal of an electron from this shell the possible incomplete subshells are 3s, $3p^5$, $3d^9$. These give the rise of the states $3^2$5½ , 3^2P½, $3^2P_{3/2}$, $3^2P_{5/2}$ respectively. These 5 states of M shells are represented by M_I, M_{II}, M_{III}, M_{IV}, M_v respectively. The levels are displayed in figure 7.6.

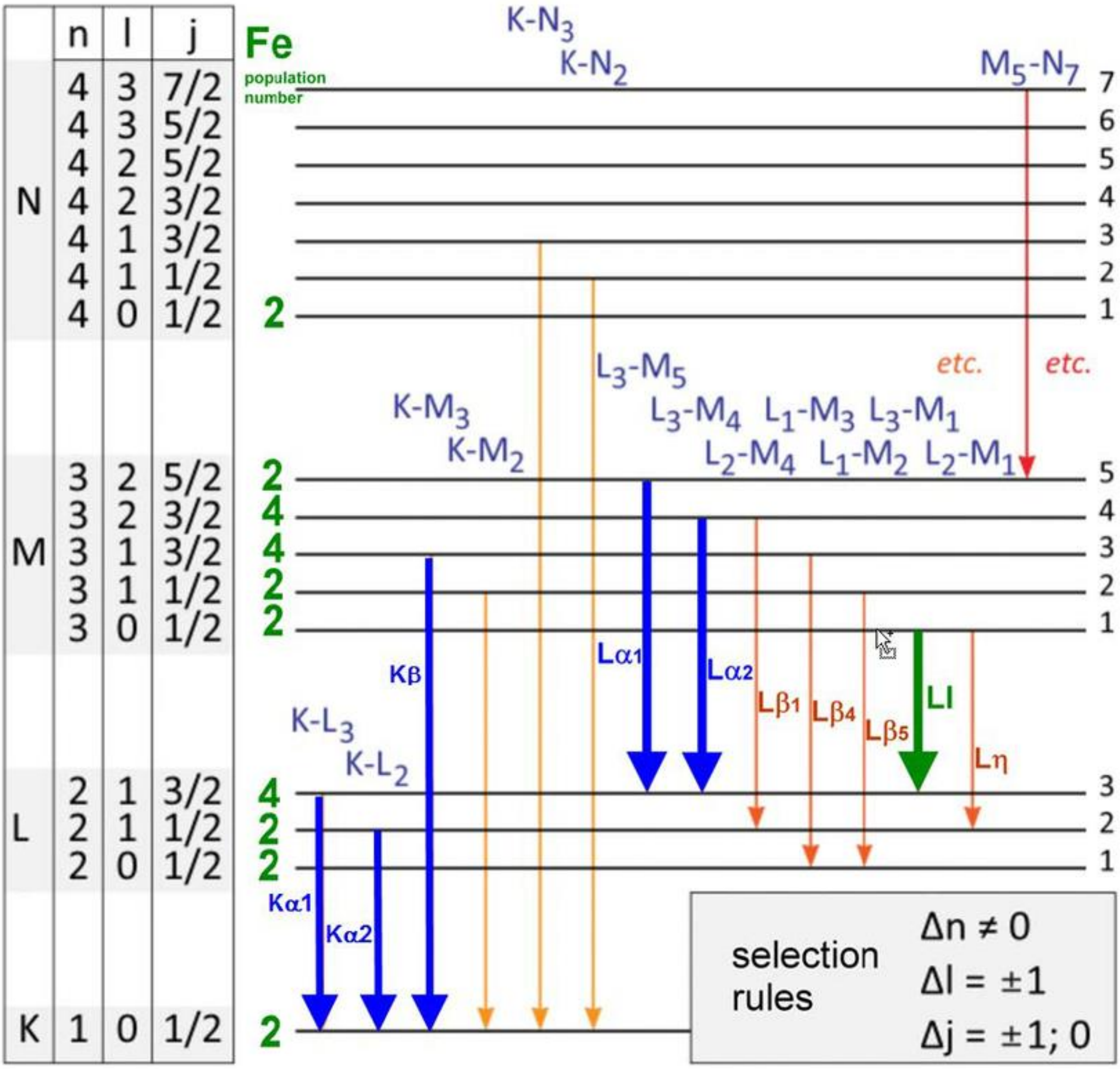

Figure 7.6: Fine structure of x-rays spectra

The selection rule for x-ray spectra is given as

$$\Delta n \text{ is arbitrary}$$

$$\Delta L = \pm 1$$

$$\Delta J = 0, \pm 1$$

Thus it is clear that the x-ray lines $K_{\alpha 1}$ and $K_{\alpha 2}$ arises due to transmission from K level to L_{II} and L_{III}. Similarly 3 groups of lines in L series appears due to transmission to L_{III}, L_{II}, L_{I} to M or N levels. Figure 6 displays the K and L series arise due to transmission. Similarly the M series can be shown due to transmission among different subshells of M and N.

7.8 X-Ray Spectra and Optical Spectra

We can compare x-ray spectra and optical spectra on the basis of following aspects.

(i) In the X ray spectra the tightly bond inner shell electrons say K shell or L shell electron are involved in transition. On the other hand, in optical spectra, the only outermost shell electrons are involved in the transition.

(ii) The frequencies of x ray spectra are about thousand times more than optical spectra. Since X ray spectra is related to complete removal of inner shell electrons hence the frequency range is quite higher.

(iii) In x ray spectra, the frequencies of x ray lines increase steadily, not periodically for different elements when their atomic number Z increases. This is because for heavy elements (more Z), the electrons of inner shells hold more strongly and need more energy for removal. Thus the X ray spectra of elements of nearby atomic number are very similar. On the other hand the in optical spectra, no similarity in the elements of nearby atomic number. This is because the structure of outermost shell changes for the elements of nearby Z.

(iv) In case of x ray spectra, the emission spectra consist of desecrate lines and absorption spectra consists of continuous region bounded by sharp edges. On the other hand, in optical spectra, emission lines are and absorption lines are same or both are identical.

SAQ 1 : In x ray emission, what happens when an high energy electron beam strikes on K shell electron?

SAQ 2 : What do you mean by K_α, K_β, K_γ .... lines?

SAQ 3 : What is the difference between emission spectra and absorption spectra?

SAQ 4 : Write down Moseley law.

SAQ 5 : What is absorption edge in x ray absorption spectra?

SAQ 6 : What is fine structure?

SAQ 7 : Give the selection rule for x ray spectra.

SAQ 8 : What are the range of frequencies of x ray spectra and optical spectra.

SAQ 9 : What happens when an electron from K shell of an element removed completely from its shells?

Example 1: Calculate the required voltage that must be applied to an x ray tube to produce x ray of wave length 0.1A (given e = 4.8 × 10^{-10}esu, C = 3 × 10^{10} cm/sec, h = 6.62 × 10^{-27} erg-5)

Solution: The electron is accelerated in x ray tube. If V is the accelerating voltage, e is change of electron then the energy E of emitted photons can be given as.

$$ev = E = h\nu = \frac{hc}{\lambda}$$

$$\nu = \frac{hc}{e\lambda} = \frac{6.62\times10^{-27}\,\text{erg}^{-5}\times3\times10^{10}\,\text{cm/5}}{4.8\times10^{-10}\,\text{esu}\times0.1\times10^{-8}\,\text{cm}}$$

= 413.75 esu

= 413.7 × 300 Volt

= 1.24 × 10^5 Volt

Example 2: How much energy goes into the quantum emitted when an L-electron drops into empty K shell in copper (Z = 29).

[guen R= 109737cm^{-1} and 1 cm^{-1}= 1.239 × 10^{-4} ev]

Solution: from moseley's law, x-ray wavelength is given by

$$\frac{1}{\lambda} = R(Z-1)^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

Where h_2=2 and n_1=1 for transmission from L shell (n = 2) to k shell (n = 2) corresponding to K_α line. Thus

$$\frac{1}{\lambda} = \frac{3}{4}\,R\,(Z-1)^2$$

$$= \frac{3}{4}\times109737\times 28^2$$

= 6.4525 × 10^{-7} cm^{-1}

Corresponding energy E = 6.4525 × 10^{-7} × 1.239 × 10^{-4}

7.9946 × 10^3 eV

Example 3: Calculate the wave length of K_α line of higher (given atomic number Z = 47, R = 109737 cm^{-1})

Solution: According to moseley law

$$\frac{1}{\lambda} = R(Z-1)^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$$

Where symbols are usual meaning and 1 and 2 are transition from L shell to K shell

$$\frac{1}{\lambda} = \frac{3}{4}\,\mathrm{R}\,(\mathrm{Z}-1)^2$$

$$\frac{3}{4}\times 109737\times 46^2$$

$$= 1.74 \times 10^{-8}\ \mathrm{cm}$$

$$\lambda = \frac{1}{1.74\times 10^{-8}}\,cm = 0.57\mathrm{A}$$

Example 4: If K_α radiation of M_0(Z=42) has wavelength 0.75A, calculate the wavelenght of K_α radiation of cu (atomic number Z = 29)

Solution: According to moseley law of K_α line

$$\frac{1}{\lambda} = R(Z-1)^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$$

$$\frac{1}{\lambda} = \frac{3}{4}\,\mathrm{R}\,(\mathrm{Z}-1)^2$$

$$\frac{\lambda_{\mathrm{cu}}}{\lambda_{\mathrm{mo}}} = \frac{(\mathrm{Z}_{\mathrm{Mo}}-1)^2}{(\mathrm{Z}_{\mathrm{Cu}}-1)^2} = \frac{41^2}{28^2}$$

$$\lambda_{\mathrm{Cu}} = \lambda_{\mathrm{Mo}}\times\frac{41^2}{28^2} = 0.75\times\frac{41^2}{28^2} = 1.60\mathrm{A}$$

7.9 Summary

1. When fast moving electrons are deaccelerated, these deaccelerated electron emit electromagnetic radiations (Bremsstarhlung) which are known as X-rays.

2. The intensity of continuous x ray spectra depends on the energy of incident electron and not depends on target material.

$$\lambda_{min} = \frac{hc}{eV}\ \text{where V is applied potential}$$

$$\lambda_{min} = \frac{12400}{V}$$

3. Kossel explained that in an high energy electrons penetrates well inside an target atom, it eject the electron of K shell, and immediately an electron from outer shell, says L shell jump

to K shell, X-ray photon of higher energy is emitted similarly an electron from N shell may jump to K shell. These lies of K series are designated as K_α, K_β , K_γ .

4. Moseley law states that as atomic number increases, K lines shift towards higher frequency. He stated that "The frequency of each corresponding K lines is approximately proportional to the square of atomic number of target element". Mathematically

$$\nu = RA^2(Z-\sigma)^2$$

$$\sqrt{\frac{\nu}{R}} = A\,(Z-\sigma)$$

5. Kossel's explained the x ray spectra on the basis of electron's transmission in K, L, M, ... shells. When we observe the x-ray spectra more precision, we see each line of K series (K_β, K_α, K_γ....) is a doublet, and other series are more complex. These large numbers of lines are called fine structure.

7.10 Glossary

X-rays	:	Electromagnetic radiation of wavelength of 0.01 to 1A
Line spectra	:	Dark or bright lines in continuous spectrum in a narrow frequency range
Emission line	:	if source emit specific wavelength of radiation
Absorption line	:	If a substance absorbs a specific wavelength from radiation
Fine structure	:	Splitting of a the main spectral line of a substance into two or more spectral lines
Optical spectra	:	Spectra arises due to outmost electron of atom
Selection rule	:	Also known as transitions rule give the possibility of transitions from one quantum state to another

7.11 References

1. Atomic and Molecular spectra. Raj Kumar, Kedarnath Ramnath Publication, Meerut

7.12 Suggested reading:

1. C.N. Benwell and E.M. McCash. Fundamental of molecular spectroscopy
2. Introduction to Atomic spectra. H.E. White.

7.13 Technical Questions

7.13.1 Short Answer type question

1. Give the Kossel's explanation of x-ray spectra

2. What is x-ray emission spectra?
3. Explain Moseley law.
4. What is absorption edge in x ray spectra?
5. What is fine structure? Discuss the fine structure of x ray.
6. Give comparison between x ray spectra and optical spectra.

7.13.2 Long Answer type questions

1. Explain emission spectra of X rays and deduce Moseley’s law.
2. Explain absorption spectra of X ray and discuss how it is different from emission spectra?
3. Discuss the fine structure of X rays. Give the diagram from the possible transition in x ray spectra.
4. Give a comparison between optical and x ray spectra an explain why in optical spectra of element of nearby atomic number are qualitatively very similar, while the optical spectra of these elements are different.

UNIT 8

MOLECULAR ENERGY STATES AND MOLECULAR SPECTRA

Structure

8.1 Objective
8.2 Introduction
8.3 Molecular Spectra
    8.3.1 Regions of the Electromagnetic Spectrum
    8.3.2 Effect of Electromagnetic Radiation
8.4 Types of Molecular Spectra
    8.4.1 Pure Rotational Spectra
        8.4.1.1 Salient Feature of Rotational Spectra
    8.4.2 Vibrational–Rotational Spectra
        8.4.2.1 Salient Feature of Vibrational–Rotational Spectra
    8.4.3 Electronic Spectra
        8.4.3.1 Salient Feature of Electronic Spectra
8.5 Atomic Spectra
8.6 Types of Molecular Energy States and Associated Spectra
8.7 The Born-Oppenheimer Approximation
8.8 Summary
8.9 Glossary
8.10 Reference Books
8.11Suggested Readings
8.12 Terminal Questions

8.1 Objectives

After studying this unit, you will come to know about:

1. Molecular spectra and its kinds.
2. Pure rotational spectra of diatomic molecules and its salient features.
3. Vibrational rotational spectra of diatomic molecules and its salient features.
4. Electronic spectra of diatomic molecules and its salient features.
5. Types of molecular energy states and associated spectra.
6. The Born-Oppenheimer approximation

8.2 Introduction

The absorption and emission of molecules arise from transitions between allowed energy states; ground and excited ones. The energy-level scheme of molecules is different from that of atoms and is relatively complicated; there are two main reasons for this. Firstly, we cannot classify molecular energy states according to the electronic angular momentum L (as we do in atoms) which is not conserved in molecules. Secondly, the nuclear motion in molecules cannot be ignored, as we can do in atoms. In a diatomic molecule, for example, the nuclei vibrate along the internuclear axis, and in addition the whole system rotates about its center of mass. The energy of each of these vibrational and rotational motion is quantized, with the result that there are many more energy levels in a molecule than in an atom.

Molecular spectroscopy is defined as the study of the interaction of electromagnetic waves and matter. So far we have studied about the interaction of electromagnetic waves with atoms, i.e. when the emitting substance is in atomic state. However, here the emitting substance is a molecule, which may contain two (diatomic) or more atoms (polyatomic). Molecular spectra are band spectra which appear as a continuous band when observed with a low resolving power instrument. With high resolving power instruments, molecular spectra disclose a three-fold structure:

1. Each band is composed of a large number of lines which are arranged with great regularity which are crowded together at the long wavelength side, i.e. at the band head and as they recede from the band head, the lines become more widely separated and also weaker.
2. There is a regular sequence in which the several bands follow one another, and thus constitute a group of bands.
3. There is a close and regular arrangement of different groups of bands which form a band system.

8.3 Molecular Spectra

The spectra emitted by molecules (When the emitting substance is in molecular state) is known as molecular spectra. It appears as a continuous band, therefore it is also known as band spectra. A band has a sharp intense edge on one side (band head) which decreased in intensity towards the other side. The study of molecular spectra is known as molecular spectroscopy.

8.3.1 Regions of the Electromagnetic Spectrum

The entire range of electromagnetic waves is known as the electromagnetic spectrum. This includes electromagnetic energy ranging from gamma rays to radio waves. In general the electromagnetic spectrum is mainly divided into six regions. In order of decreasing wavelength (increasing energy and frequency) different regions are mentioned below:

(i) Radio frequency region (100 to 10 m): Radio waves have the longest wavelength in the electromagnetic spectrum. To transmit a variety of data, radio waves are used. They are also used in wireless networking, television and amateur radio.

(ii) Microwave region (or far infra-red region) (1mm to 1m): Microwaves are essentially high frequency radio waves. They have wavelengths in the range of 1mm to 1m. Microwaves are used for many applications. They are beneficial for satellite communication, studying the Earth from space, radar technology etc.

(iii) Infra-red region (780 nm - 1000 µm): Infrared spectrum divided into the three main regions

Near Infrared (NIR): 0.7 – 1.3µm
Shortwave Infrared (SWIR): from 1.3 – 3 µm
Far or Thermal Infrared from 3 - 100 µm

Infrared radiation is mainly used in remote sensing.

(iv) Visible and ultraviolet region (1 nm to 750nm): Ultraviolet (UV) light has wavelengths of approximately 1 – 380 nm. The main source of ultraviolet energy is the Sun. The UV waves are invisible for the human, however some insects, can see them.

Visible light wavelengths range from 400 – 750 nm. Human eyes can see only this region of the electromagnetic spectrum. Each individual wavelength within the spectrum of visible light wavelengths is represented by a particular color. The visible portion of the electromagnetic spectrum is mainly used in remote sensing.

(v) X-ray region (0.01 – 10 nm): X-Rays range in wavelength from 0.01 – 10 nm. These rays are generated from superheated gas from exploding stars and quasars. The main important properties of the X-rays is that they are able to pass through a variety of materials. The most common use of X-rays are in the field of medical imaging and for checking cargo and luggage.

(vi) Gamma rays region (< 0.01 nm): Gamma rays are produced by the hottest objects in the universe, including neutron stars, pulsars, and supernova explosions. These rays are biologically hazardous.

8.3.2 Effect of Electromagnetic Radiation

There are two processes of interaction of electromagnetic radiation with the matter available. They are photo physical interaction and photochemical interaction. Both the photo physical and photochemical processes are used to study the nature and characteristics properties of molecules in their different energy states. If the chemical identity of a molecule is retained after the interaction, the process is called a photo physical process, if not, then it is called a photochemical process. The interaction of specific frequency with a molecule takes place between the electric field component of radiation and electric dipole moment of the molecule. Because of interactions, the transition of molecules can occur from ground state to excited state or vice versa. The energy level at which a molecule exists is referred to as its state. Two basic processes is observed when light interacts with matter:

- Absorption process
- Emission process

A molecule can move from one level to another level by using a finite amount of energy. Normally, a molecule exists in their most stable state referred to as the ground state or lower energy state. The transition from the ground state (E_0) to the excited state (E_1) requires some form of energy input. When the radiation interacts with molecules, it absorbs a suitable amount of energy and jump from its ground energy state to its nearest excited energy state by following the famous equation as:

$$\Delta E = E_1 - E_0 = h\nu = \frac{hc}{\lambda},$$

where λ is wavelength of incident radiation, υ is frequency of incident radiation, h is Planck's constant and c is the velocity of light. This process is known as absorption (Figure 8.1). Process of emission is just the opposite phenomenon of absorption. In this process, molecules that are in excited state decay to the lower levels by emitting radiation (Figure 8.1).

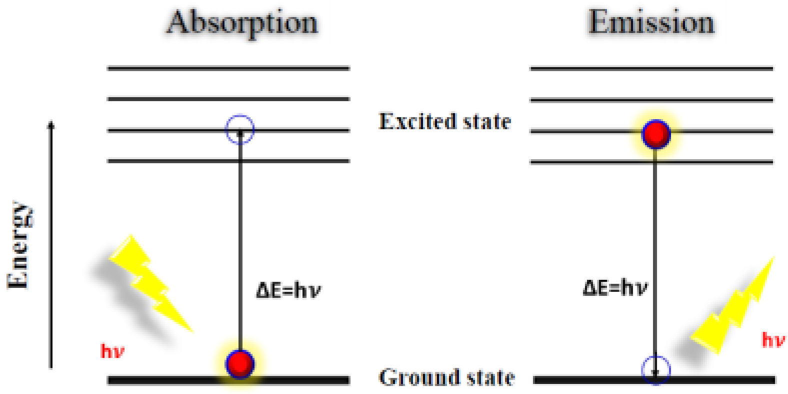

Figure 8.1: Absorption and emission process.

Electromagnetic radiation may also reorient the molecule along the direction of the field, which can break some bond. Now in the following sections, we will discuss different types of molecular spectra.

8.4 Type of Molecular Spectra

The molecular spectra can be divided into three spectral ranges corresponding to the different type of transition between molecular energy states.

1. **Pure rotational spectra**
2. **Vibration-rotational spectra**
3. **Electronic spectra**

8.4.1 Pure Rotational Spectra

These spectra are observed in absorption in the far infrared or in the microwave region. It involves transitions between rotational states of the molecules. Rotational spectroscopy is called pure rotational spectroscopy, to distinguish it from roto-vibrational spectroscopy (the molecule changes its state of vibration and rotation simultaneously) and vibronic spectroscopy (the molecule changes its electronic state and vibrational state simultaneously). For a molecule to exhibit a pure rotational spectrum it must possess a permanent dipole moment (otherwise the photon has no means of interacting "nothing to grab hold of"). Normally, a molecule must be polar to be able to interact with a microwave. A polar rotor appears to have an oscillating electric dipole. However, homonuclear diatomic molecules such as O_2, H_2, do not have a dipole moment and, hence, no pure rotational spectrum. For rotational spectroscopy, molecules are classified according to symmetry into spherical top, linear and symmetric top.

8.4.1.1 Salient Feature of Rotational Spectra

The salient features of the pure rotational spectra are given below:

1. The band which appears in the infra-red region is due to transition involving very small energy changes, about 0.005ev. With such a small quantum of energy, electronic and vibrational energy states will not be excited or in other words only transitions that are purely rotational in character will appear. Therefore bands that appear in the infra-red region arise due to the changes in the rotational energy of the molecule unaccompanied by changes in electronic or vibrational energy. Only those molecules which have permanent electric dipole moment can give rise to pure rotational spectra. Thus homonuclear diatomic molecules such as H_2, O_2, N_2 etc. do not exhibit pure rotation spectra. While heteronuclear diatomic molecules such as HF, HCl, HBr etc. exhibit pure rotation spectra.
2. In practice, rotational spectra are observed in absorption. For heteronuclear diatomic molecules such as HF, HCl, HBr, Co etc. the rotational spectra consist of a simple series of absorption maxima, which are very nearly equidistant on a wave number scale. A measurement of the frequencies of these maxima help to determine the moment of inertia and the internuclear distance.
3. The basic molecular requirement for the emission or absorption of radiation by a transition between rotational energy states is that the molecule must have a permanent dipole moment. This is in line with classical electrodynamics according to which a rotating molecule can lead to the emission of radiation, only if a changing dipole moment is associated with it. During the rotation of a heteronuclear diatomic molecule, having a permanent dipole moment, the component of this dipole moment in a fixed direction changes periodically with the frequency of rotation of the molecule, emitting radiations of the same frequency. However, homonuclear molecules have no dipole moment and hence there is no emission of infra-red radiation.
4. Further infra-red radiation can be absorbed by a rotating molecule and thereby increase rotation, only if a permanent dipole moment is present such a molecule interacts with the oscillating electric field of the incident radiation to absorb rotational energy and produce absorption spectra.

8.4.2 Vibration-Rotational Spectra

These spectra are observed in absorption in the near infra- red region. Each spectrum consists of an intense band (known as fundamental) which is followed by a few weak bands (known as overtones). If the molecule in its equilibrium position has a dipole moment, as is always the case for the heteroatomic molecules, this dipole moment will in general change if the internuclear distance changed. Thus, on the basis of classical electrodynamics the molecular vibration would lead to the emission of light at the oscillation frequency. Conversely, the oscillator could be set in vibration by absorption of light at this frequency. Therefore, all heteroatomic molecules in principle are said to be infrared active that is they can absorb or emit infrared radiation. Contrary, all homoatomic diatomic molecules do not have any dipole moment and cannot be set in vibration by absorption of infrared light. These molecules are said to be infrared inactive.

8.4.2.1 Salient features of vibrational-rotational spectra

1. When there are transitions between vibrational states of the same electronic state of molecule, we get vibrational-rotational molecular spectra. Such a spectra is observed in a near infra-red region of the electromagnetic spectrum.
2. Vibrational-rotational spectra, like pure rotational spectra, are observed only for molecules that have permanent dipole moments such as HCl, HCN, HF (heteronuclear diatomic molecules).
3. The internuclear distance changes when the nuclei of these molecules vibrate relative to each other. Thus these molecules possess an oscillating dipole moment, which according to classical electrodynamics emits radiations of frequency that fall in near infra-red region-conversely, if electromagnetic radiation falls on such a molecule then oscillating dipole interactions will the incident radiation and can absorb radiation of frequency of near infra-red region.
4. In practice, vibrational-rotational spectra are observed in absorption.

If the molecule in its equilibrium position has a dipole moment, as is always the case for the heteroatomic molecules, this dipole moment will in general change if the internuclear distance changed. Thus, on the basis of classical electrodynamics the molecular vibration would lead to the emission of light at the oscillation frequency. Conversely, the oscillator could be set in vibration by absorption of light at this frequency. Therefore, all heteroatomic molecules in principle are said to be infrared active that is they can absorb or emit infrared radiation. Contrary, all homoatomic diatomic molecules do not have any dipole moment and cannot be set in vibration by absorption of infrared light. These molecules are said to be infrared inactive.

Infrared transitions

W. Coblentz coined the first systematic use of infrared technique in 1905. Infrared R spectroscopy can be divided into three areas based on spectral region: far-IR, mid-IR, and near-IR. A molecule will be IR active when there is a change in dipole moment of the molecule with time. Due to change in dipole moments, the bond lengths and bond angles suffer a variation, which in turn appears as vibrational and bending modes. If one or more bond lengths of the molecule changes symmetrically, vibrational modes are known as symmetric stretching vibrational (υ) modes. Let us take an example of a linear CO_2 molecule.

There is a small net positive charge on C atom and O has small negative charges. In the symmetric stretching mode both the C=O bonds change simultaneously (Figure 8.2). If two bonds are in opposite atomic motions. One bond is elongating while the other is contracting. The vibration of molecules is known as asymmetric stretching (α) mode. In α stretching vibration shown in Figure 8.2 a periodic alteration in the dipole moment is observed. If one or more bond angles of the molecules change while bond lengths remain constant, vibrational mode is known as bending mode (δ). In the δ vibration, a change in dipole moment is also observed (Figure 8.2).

In CO_2, symmetric stretching mode for both the C=O bonds changes simultaneously and resultant dipole moment remains zero for the whole system as shown in Figure 8.2. As a result the symmetric υ mode remains "infrared inactive". Whereas, due to a periodic alteration in the dipole moment, α stretching vibration, is "IR active". In the δ vibration, a change in dipole moment is also observed and that results in "IR activity".

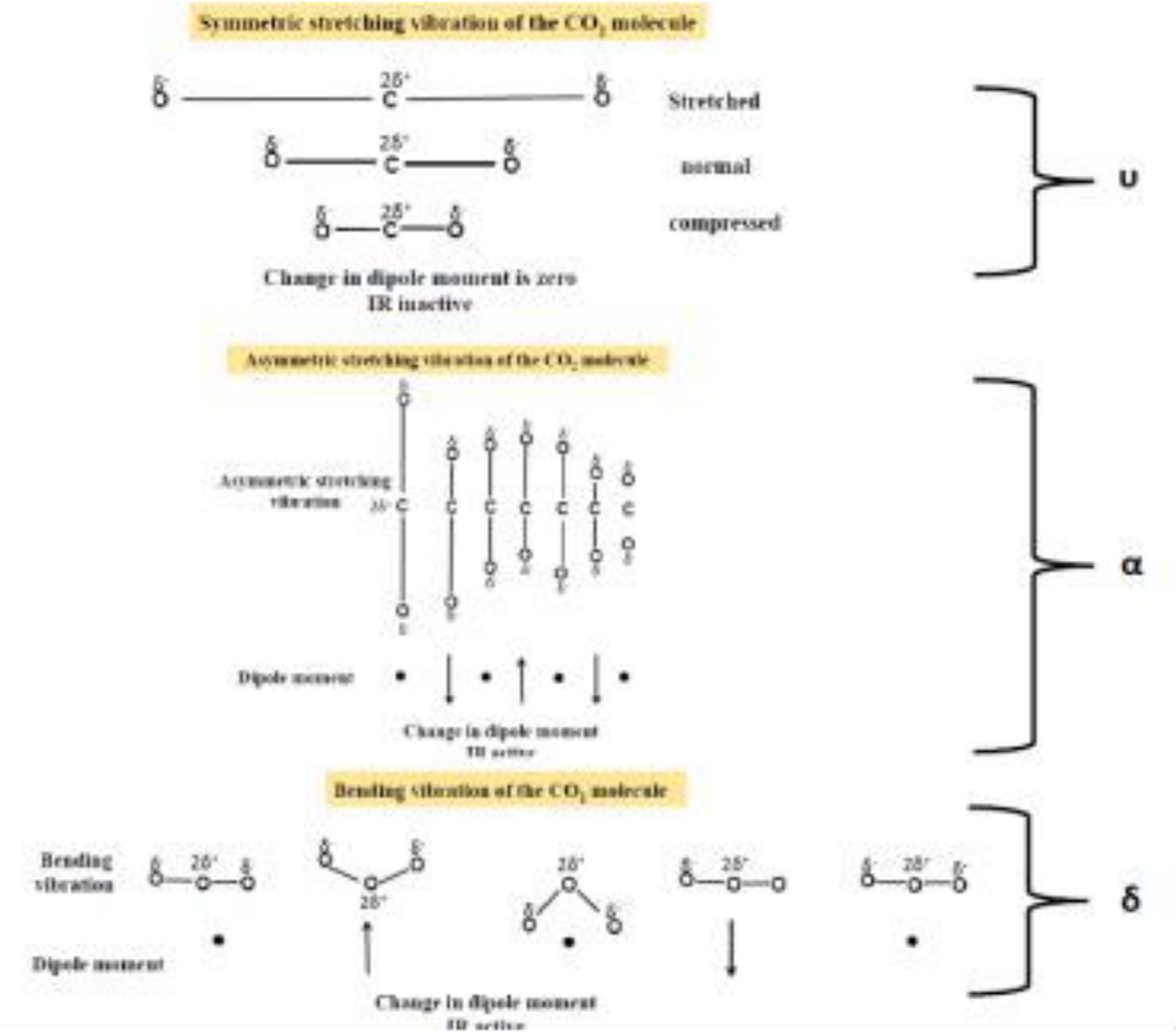

Figure 8.2: Different vibrational modes of carbon dioxide molecule showing the dipole moment and IR activity.

8.4.3 Electronic Spectra

These spectra are observed both in emission and absorption regions. Each spectrum consists of a large number of bands. Each band has a sharp edge (Band head) on one side which decreases in intensity towards the other side. Actually, a band is composed of a series of lines which draw further apart with the increase of distance from the band head. The band is said to be 'degraded' towards the side opposite to the bard-head. These spectra are observed for the hetro-nuclear as well as for the homonuclear diatomic molecules.

8.4.3.1 Salient Features of Electronic spectra

1. Electronic spectra is the most complex molecular spectra which appear in the visible and ultraviolet regions and involve the change in all the three energies (electronic, vibrational and rotational) of the molecule.
2. These spectra are obtained in emission and absorption regions.
3. The spectral band exhibits a fine structure which is more complicated. The head formation tendency is story and the bands are degraded either towards violet or toward the red. All molecules give electronic spectra.
4. Homo-nuclear molecules (H_2, N_2, O_2 etc.) do not give neither rotational nor vibrational-rotational spectra because of having no permanent dipole moments but they give electronic spectra because of the instantaneous dipole moment changes during the redistribution of change which results in the transition.

Electronic transitions

When an electron in its lowest energy state gains some energy and transfers to its excited states, is known as molecular electronic transition. This process involves promotion of an electron from a bonding or nonbonding molecular orbital to an antibonding molecular orbital. These transitions provide information regarding the structure of a molecule and determine many more molecular properties. Electronic transitions are measured by Ultraviolet and visible spectroscopy and fall in the ultraviolet and visible region (190 nm-700 nm) of the electromagnetic spectrum both in absorption and emission modes. The electronic transition is mainly possible by absorbing photon energy equivalent to the separation of energy levels between which the electron transited. Mostly four types of electronic excitation exist in molecules (**Figure 8.3**).

1. $\sigma \rightarrow \sigma^*$
2. $\pi \rightarrow \pi^*$
3. $n \rightarrow \sigma^*$
4. $n \rightarrow \pi^*$

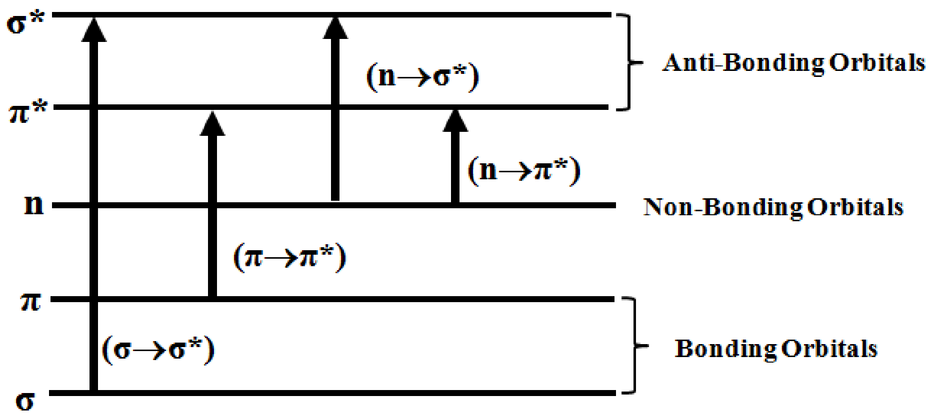

Figure 8.3: Possible transition between bonding (σ, π), anti-bonding (σ*, π*), and nonbonding (n) orbitals.

Energies associated with different molecular transitions are in the following order.
n→π* < π→π* < n→σ* < σ→π* < σ→σ*
The wavelength corresponding to the σ→σ* transition is located at the far ultraviolet region of the electromagnetic spectrum. The n→π* and π→π* are located at a near visible part of the spectrum. The strength of an electronic transition is expressed in terms of "oscillator strength" (*f*) and defined as the ratio of the experimental transition probability to that of the ideal case of a harmonic oscillator.

$$f = \frac{[\int \varepsilon_{\bar{v}} d\bar{v}]_{\exp}}{[\int \varepsilon_{\bar{v}} d\bar{v}]_{ideal}} = \frac{\int \varepsilon_{\bar{v}} d\bar{v}}{2.31\times 10^{8}}$$

It is a dimensionless quantity and totally allowed transition corresponds to the oscillator strength 1, when all the molecules are transferred to the higher energy state.

8.5 Atomic Spectra

When electrons of an atom are excited to higher energy states, the radiations that are absorbed in this process appear as the absorption spectra of atoms. In a similar way, electronic spectra of molecules arise when the electrons of a molecule are excited to higher energy states. The energy involved in this process is generally large and electronic spectra of molecules are usually found in visible and ultraviolet regions. Therefore electronic spectra arise due to the changes in the arrangement of molecular electrons. We shall discuss electronics spectra of diatomic molecules.

The electronic transition is the result of change in electronic energy. A small change in the electronic energy will be accompanied by a large change in the vibrational energy of the molecule. These vibrational energy changes give rise to vibrational transitions which form a group of various bands. Further, a small change in the vibrational energy will be accompanied by a large change in the rotational energy of the molecule. These rotational energy changes give rise to rotational transitions forming a series of lines in each band-the so called fine structure of each band.

8.6 Types Of Molecular Energy States And Associated Spectra

Molecular energy states arise from the rotation of a molecule as a whole and from the vibration of its constituent nuclei relative to one-another as well as from changes in its electronic configuration. Rotational states are separated by quite small energy-interval ($\approx$10^{-3}ev) and the spectra arising from transitions between these states are in the far infra-red or microwave region. Vibrational states are separated by somewhat larger energy intervals ($\approx$10^{-1}ev) and the vibrational spectra fall in the near infra-red region. The electronic states have higher energy separation ($\approx\approx$10ev) and the corresponding spectra fall in the visible and ultraviolet regions.

The two nuclei vibrate about their respective equilibrium positions along the internuclear axis, and the molecule rotates about the center of mass. Schrodinger's equation for the nuclear motion in a diatomic molecule is.

$$[-\frac{h^2}{8\pi^2 M_1}\nabla\frac{h^2}{8\pi^2 M_1}\nabla_1^2-\frac{\mathrm{h}^2}{8\pi^2 M_2}\nabla-\frac{\mathrm{h}^2}{8\pi^2 M_2}\nabla_2^2+V(r)]\varphi=E\varphi+V(r)]\varphi=E\varphi$$

When M_1 and M_2 are the masses of the nuclei and V(r) is the Potential energy function consisting of the instantaneous electronic energy and electrostatic energy of the two nuclei. φ is the nuclear eigenfunction which E is the eigenvalues for the whole molecule. Besides electronic bands. We have non-electronic bands also (for which $\nu\nu_e$=0) such bands are of two types: Vibration-rotational bands and pure rotational bands.

The explanation for three types of band spectra demands that the internal energy of a molecule, i.e. the energy other than the translational is essentially of three kinds, namely electronic, vibrational and rotational which are all quantised and thus the molecule possesses only certain discrete energy states. The transition between two energy states of a molecule, as a result of either absorption or emission of energy, will give rise to a spectral line in the spectrum of that molecule. Suppose energy difference of two states is (E$''$ – E") then the wave number (frequency in cm^{-1}) corresponding to the line, arising due to transition between these two states will be:

$$\nu=\frac{E^{'}-E^{''}}{hc}\nu=\frac{E^{'}-E^{''}}{hc}\ \mathrm{cm}^{-1},$$

where c is the velocity of light.

The three types of bands, discussed above, are correlated with

1. Change in the rotational energy
2. Simultaneous change of the rotational and vibrational energies, and
3. Simultaneous change in the rotational, vibrational and electronic energies.

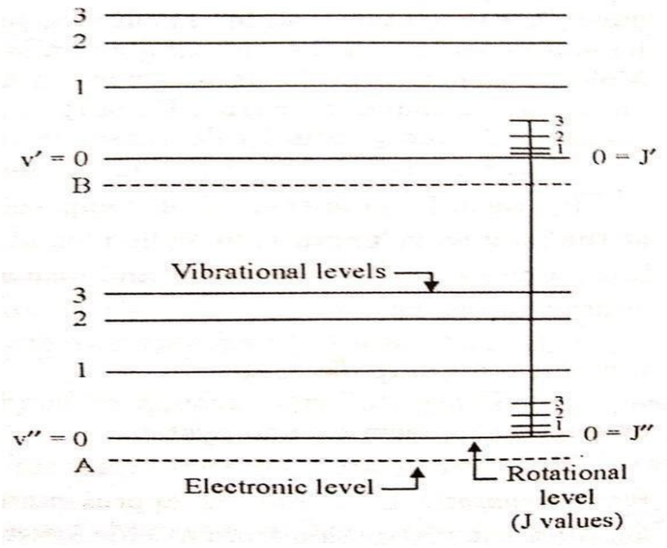

Figure 8.4: Diagram representing electronic, rotational and vibrational energy levels.

The diagram shows that:

i. A molecule has a number of discrete electronic levels with separation of the same order as in atoms. A transition between two electronic levels results in a radiation that falls in a visible or ultraviolet region.
ii. With each electronic level are associated a number of vibrational energy levels whose spacing decreases with increasing quantum number, *v*. A transition between two vibrational levels results in a radiation which falls in a near infrared region.
iii. With each vibrational level is associated a set of rotational levels whose spacing increases with increasing quantum number, *J*. A transition between two rotational energy levels results in a radiation that falls in a far infrared or microwave region.

Fig. 8.4, shows transition from: Electronic level A to electronic level B
Vibrational level v'' = 0to vibrational level v' = 0
Rotational level J'' = 1 to rotational level J' = 3

8.7 The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is the assumption that the electronic motion and the nuclear motion in molecules can be separated. It leads to a molecular wave function in terms of electron positions and nuclear positions.

This involves the following assumptions:

1. The electronic wave function depends upon the nuclear positions but not upon their velocities, i.e., the nuclear motion is so much slower than electron motion that they can be considered to be fixed.
2. The nuclear motion (e.g., rotation, vibration) sees a smeared out potential from the speedy electrons.

We know that if a Hamiltonian is separable into two or more terms, then the total Eigen functions are products of the individual Eigen functions of the separated Hamiltonian terms, and the total eigenvalues are sums of individual eigenvalues of the separated Hamiltonian terms.

Consider, for example, a Hamiltonian, which is separable into two terms, one involving coordinate q_1 and the other involving coordinate q_2.

$$H = H_1(q_1) + H_2(q_2)$$

With the overall Schrödinger equation being

$$H\psi(q_1, q_2) = E\psi(q_1, q_2)$$

If we assume that the total wave function can be written in the form

$$\psi(q_1, q_2) = \psi_1(q_1)\psi_2(q_2)$$

,

where $\psi_1(q_1)$ and $\psi_2(q_2)$ are Eigen functions of H_1 and H_2 with eigenvalues E_1 and E_2, then

$$H\psi(q_1, q_2) \ \underline{=} \ (H_1 + H_2)\psi_1(q_1)\psi_2(q_2) \tag{8.1}$$

$$\underline{=} \ H_1\psi_1(q_1)\psi_2(q_2) + H_2\psi_1(q_1)\psi_2(q_2) \tag{8.2}$$

$$\underline{=} \ E_1\psi_1(q_1)\psi_2(q_2) + E_2\psi_1(q_1)\psi_2(q_2) \tag{8.3}$$

$$\underline{=} \ (E_1 + E_2)\psi_1(q_1)\psi_2(q_2) \tag{8.4}$$

$$\underline{=} \ E\psi(q_1, q_2) \tag{8.5}$$

Thus the Eigenfunctions of H are products of the Eigenfunctions of H_1 and H_2, and the eigenvalues are the sums of eigenvalues of H_1 and H_2.

The Eigenfunctions and eigenvalues of this Hamiltonian, which will be given by solution of the time-independent Schrödinger equation

$$\left[T_N + T_e + V_{ee}(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{r},\mathbf{R})\right]\Psi(\mathbf{r},\mathbf{R}) = E\Psi(\mathbf{r},\mathbf{R}).$$

We first invoke the Born-Oppenheimer approximation by recognizing that, in a dynamical sense, there is a strong separation of time scales between the electronic and nuclear motion, since the electrons are lighter than the nuclei by three orders of magnitude. This can be exploited by assuming a quasi-separable ansatz of the form

$$\Psi(\mathbf{x},\mathbf{R}) = \phi_e(\mathbf{x},\mathbf{R})\phi_N(\mathbf{R})$$

where ϕ_N(R) is a nuclear wave function and ϕ_e(x, R) is an electronic wave function that depends parametrically on the nuclear positions. If we look again at the Hamiltonian, we would notice right away that the term V_eN would prevent us from applying this separation of variables. The Born-Oppenheimer (named for its original inventors, Max Born and Robert Oppenheimer) is based on the fact that nuclei are several thousand times heavier than electrons. The proton, itself, is approximately 2000 times more massive than an electron. 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, since there could be non-adiabatic effects that do not allow the electrons to follow in this ``instantaneous'' manner, however, in many systems, the adiabatic separation between electrons and nuclei is an excellent approximation. Another consequence of the mass difference between electrons and nuclei is that the nuclear components of the wave function are spatially more localized than the electronic component of the wave function. In the classical limit, the nuclear are fully localized about single points representing classical point particles.

After these considerations, $H_N(\mathbf{R})$ can be neglected since T_N is smaller than T_e by a factor of M/m. Thus for a fixed nuclear configuration, we have

$$H_{el} = T_e(\mathbf{r}) + V_{eN}(\mathbf{r},\mathbf{R}) + V_{NN}(\mathbf{R}) + V_{ee}(\mathbf{r})$$

Such that

$$H_{el}\phi_e(\mathbf{r},\mathbf{R}) = E_{el}\phi_e(\mathbf{r},\mathbf{R})$$

This is the “clamped-nuclei'” Schrödinger equation. Quite frequently $V_{NN}(\mathbf{R})$ is neglected in the above equation, which is justified since in this case $\mathbf{R}$ is just a parameter so that $V_{NN}(\mathbf{R})$ is just a constant and shifts the eigenvalues only by some constant amount. Leaving $V_{NN}(\mathbf{R})$ out of the electronic Schrödinger equation leads to a similar equation,

$$H_e \underline{=} T_e(\mathbf{r}) + V_{eN}(\mathbf{r},\mathbf{R}) + V_{ee}(\mathbf{r}) \qquad (8.6)$$

$$H_e\phi_e(\mathbf{r},\mathbf{R}) \underline{=} E_e\phi_e(\mathbf{r},\mathbf{R}), \qquad (8.7)$$

where we have used a new subscript “e" on the electronic Hamiltonian and energy to distinguish from the case where $V_{NN}$is included.

We now consider again the original Hamiltonian. If we insert a wavefunction of the form ψ(r, **R**)=ϕ_e(r, **R**)ϕ_N(**R**), we obtain

$$H\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}) = E_{tot}\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}) \qquad (8.8)$$

$$\{T_N(\mathbf{R}) + T_e(\mathbf{r}) + V_{eN}(\mathbf{r},\mathbf{R}) + V_{NN}(\mathbf{R})\}\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}) = E_{tot}\phi_e(\mathbf{r},\mathbf{R})\phi_N($$

Since T_e contains no $\mathbf{R}$ dependence,

$$T_e\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}) = \phi_N(\mathbf{R})T_e\phi_e(\mathbf{r},\mathbf{R})$$

However, we may not immediately assume

$$T_N\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}) = \phi_e(\mathbf{r},\mathbf{R})T_N\phi_N(\mathbf{R})$$

(this point is tacitly assumed by most introductory textbooks). By the chain rule,

$$\nabla_R^2\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}) = \phi_e(\mathbf{r},\mathbf{R})\nabla_R^2\phi_N(\mathbf{R}) + 2\nabla_R\phi_e(\mathbf{r},\mathbf{R})\nabla_R\phi_N(\mathbf{R}) + \phi_N(\mathbf{R})\nabla_R^2\phi_e(\mathbf{r},\mathbf{R})$$

Using these facts, along with the electronic Schrdöinger equation,

$$\{T_e + V_{eN}(\mathbf{r},\mathbf{R}) + V_{ee}\}\phi_e(\mathbf{r},\mathbf{R}) = H_e\phi_e(\mathbf{r},\mathbf{R}) = E_e\phi_e(\mathbf{r},\mathbf{R})$$

we simplify Equation to

$$\phi_e(\mathbf{r},\mathbf{R})T_N\phi_N(\mathbf{R}) + \phi_N(\mathbf{R})\phi_e(\mathbf{r},\mathbf{R})(E_e + V_{NN} \qquad (8.9)$$

$$-\left\{\sum_{A}\frac{1}{2M}(2\nabla_R\phi_e(\mathbf{r},\mathbf{R})\nabla_R\phi_N(\mathbf{R})+\phi_N(\mathbf{R})\nabla_R^2\phi_e(\mathbf{r},\mathbf{R}))\right\} \tag{8.10}$$

$$=E_{tot}\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}). \tag{8.11}$$

We must now estimate the magnitude of the last term in brackets. A typical contribution has the form $1/(2M)\nabla^2_R\phi_e(r, R)$, but $\nabla_R\phi_e(r, R)$ is of the same order as $\nabla_r\phi_e(r, R)$ since the derivatives operate over approximately the same dimensions. The latter is $\phi_e(r, R)P_e$, with P_e the momentum of an electron. Therefore

$$1/(2M)\nabla_R^2\phi_e(\mathbf{r},\mathbf{R})\approx p_e^2/(2M)=(m/M)E_e$$

Since m/M~1/10000 the term in brackets can be dropped, giving

$$\phi_e(\mathbf{r},\mathbf{R})T_N\phi_N(\mathbf{R})+\phi_N(\mathbf{R})E_e\phi_e(\mathbf{r},\mathbf{R})+\phi_N(\mathbf{R})V_{NN}\phi_e(\mathbf{r},\mathbf{R})=E_{tot}\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R})$$

$$\{T_N+E_e+V_{NN}\}\phi_N(\mathbf{R})=E_{tot}\phi_N(\mathbf{R}).$$

This is the nuclear Shrödinger equation we anticipated-the nuclei move in a potential set up by the electrons.

To summarize, the large difference in the relative masses of the electrons and nuclei allows us to approximately separate the wavefunction as a product of nuclear and electronic terms. The electronic wavefucntion $\phi_e(r,R)$ is solved for a given set of nuclear coordinates,

$$H_e\phi_e(\mathbf{r},\mathbf{R})=\left\{-\frac{1}{2}\sum_i\nabla_i^2-\sum_{i,I}\frac{Z_I}{r_{Ii}}+\sum_{i>j}\frac{1}{r_{ij}}\right\}\phi_e(\mathbf{r},\mathbf{R})=E_e(\mathbf{R})\phi_e(\mathbf{r},\mathbf{R}),$$

and the electronic energy obtained contributes a potential term to the motion of the nuclei described by the nuclear wavefunction $\phi_N(R)$.

$$H_N\phi_N(\mathbf{R})=\left\{-\sum_I\frac{1}{2M_I}\nabla_I^2+E_e(\mathbf{R})+\sum_{I>J}\frac{Z_IZ_J}{R_{IJ}}\right\}\phi_N(\mathbf{R})=E_{tot}\phi_N(\mathbf{R})$$

In the conclusion we can say that Born approximation enables us to solve the complete molecula wave equation in the the following way:

1. For a given electronic state of a molecule the electronic wave equation is solved for a range of nuclear coordinates (internuclear separations).
2. The eigenvalues E are the characteristic energies for the whole molecule in the given electronic state. A different set of wavefunction and energy eigen value is found for each electronic state of the molecule.
3. The total wavefunction of the system is the obtained by the product of wavefunctions of the coordinates of the nuclei and electrons.

Self Assessment Question (SAQ) 1: What do you understand by dipole moment?

Self Assessment Question (SAQ) 2: Why dipole moment is important in molecular spectroscopy?

Self Assessment Question (SAQ) 3: Homonuclear diatomic molecules are microwave inactive. Why?

Self Assessment Question (SAQ) 4: Heteronuclear diatomic molecule will show rotational spectrum or not?

Self Assessment Question (SAQ) 5: What is the main condition that a molecule will be microwave active or not? Give some examples.

Self Assessment Question (SAQ) 6: What is the main condition for a molecule to be IR active?

Self Assessment Question (SAQ) 7: What do you mean by degrees of freedom of a molecule? What is its value for a linear molecule and a nonlinear molecule?

Self Assessment Question (SAQ) 8: Which of the following molecules will show microwave spectrum: H_2, HCl, CH_4, CH_3Cl, CH_2Cl_2, H_2O, SF_6. Why?

8.8 Summary

In this unit, you have studied the electronic, vibrational and rotational spectra of diatomic molecules in detail. Transitions between different rotational levels give rise to pure rotational spectra of diatomic molecules. Transitions between different rotational levels give rise to pure rotational spectra in the microwave or far infrared region. This study helps in evaluation of molecular parameters. The transition between vibrational levels results in the vibrational spectra which are observed in the near infrared region. This gives information about molecular structure, bond length, interatomic distances etc. In electronic spectra which are obtained in visible and ultraviolet regions, transition from one electronic level to the other level takes place. This is accompanied by change in vibrational and rotational energy. This gives rise to vibrational coarse structure and rotational fine structure. We are able to get information about the rotational constants and vibrational frequencies of both ground and excited electronic states.

8.9 Glossary

Spectrum	The set of colours into which a beam of light can be separated, or a range of waves
rotational	A rotation is a circular movement of an object around a center of rotation.
vibrational	A molecular vibration is a periodic motion of the atoms of a molecule relative to each other,
Emission spectrum	The distribution of electromagnetic radiation released by a substance whose atoms have been excited by heat or radiation.
Absorption spectrum	The spectrum formed by electromagnetic radiation that has passed through a medium in which radiation of certain frequencies is absorbed
Transition	The process or a period of changing from one state or condition to another.

8.10 References Books

1. Atomic & Molecular spectra Laser: By Raj Kumar (KNRM Publication-Meerut)
2. Structure and properties of Material: By MA Wahab (Narosa Publishing House –Delhi)
3. Molecular Spectra and Molecular Structure I: G. Herzberg (Van-Nostrand Rein-hold, 1950)
4. Atomic Physics by J.H.Fewkes& John Yarwood. Vol. II (Oxford Univ. Press, 1991).
5. Physics of Atoms and Molecules, Bransden and Joachein. (Longman Scientific and Technical)
6. Molecular Spectroscopy, C N Banwell.
7. Fundamental of Molecular Spectroscopy. C N Banwell and E M Mc Cash (Tata Mc Graw Hills)

8.11 Suggested Readings

1. Modern Physics, Beiser, Tata McGraw Hill
2. Optical Spectroscopy in Chemistry and Life Sciences, W. Schmidt; Wiley-VCH.

8.12 Terminal Questions

Short and long answer type question

1. What is the meaning of Molecular spectra?
2. How many ranges in Molecular spectra can be classified?
3. Discuss various types of spectra.
4. Account for: “The molecules have rotational and vibrational states but atom do not”.
5. What are the salient features of rotational spectra?
6. Why do homonuclear diatomic molecules not exhibit pure rotation spectra?
7. Why is a vibrating diatomic molecule considered as an anharmonic oscillator?
8. Which physical quantities can we calculate from vibration rotation spectra?
9. Is electronic spectra exhibited by all molecules? Give proper reason.

Objective type question

1. The different types of energies associated with a molecule are __________
a) Electronic energy
b) Vibrational energy
c) Rotational energy
d) All of the mentioned

2. During the motion, if the centre of gravity of molecule changes, the molecule possess __________

a) Electronic energy
b) Rotational energy
c) Translational energy
d) Vibrational energy

3. The correct order of different types of energies is __________
a) Eel >> Evib >> Erot >> Etr
b) Eel >> Erot >> Evib >> Etr
c) Eel >> Evib >> Etr >> Erot
d) Etr >> Evib >> Erot >> E el

4. The region of electromagnetic spectrum for nuclear magnetic resonance is __________
a) Microwave
b) Radio frequency
c) Infrared
d) UV-rays

5. Which of the following is an application of molecular spectroscopy?
a) Structural investigation
b) Basis of understanding of colors
c) Study of energetically excited reaction products
d) All of the mentioned

Answer 1- d; 2-c; 3- a; 4-b; 5-d

UNIT 9 PURE ROTATIONAL SPECTRA

Structure

9.1 Introduction
9.2 Objectives
9.3 Salient features of rotational spectra
    9.3.1 Conditions for a molecule to show Rotational spectra
    9.3.2 Dipole moment
    9.3.3 Role of dipole moment in rotational transition
    9.3.4 Classification of molecules depending on rotation
        9.3.4.1 Linear molecules
        9.3.4.2 Symmetric top type molecules
        9.3.4.3 Spherical top type molecules
        9.3.4.4 Asymmetric top type molecules
9.4 Rotational Spectra of diatomic molecule
    9.4.1 Rigid Rotator
    9.4.2 Energy levels of Rigid Rotator
    9.4.3 Intensities of rotational spectral lines
    9.4.4 Effect of Isotope
9.5 Non Rigid Rotator
9.6 Linear Polyatomic Molecules
9.7 Symmetric Top Molecules
9.8 Asymmetric Top Molecules
9.9 Instrumentation for Rotational Spectroscopy
9.10 Applications of Rotational Spectroscopy
9.11 Summary
9.12 Glossary
9.13 References
9.14 Suggested Readings
9.15 Terminal Questions
    9.15.1 Short Answer type
    9.15.2 Long Answer type

9.1 Introduction

The story starts with the idea of the atom and molecule. An atom has a central nucleus with positively charged protons and uncharged neutrons in it and negatively charged electrons revolving around the nucleus. Usually atoms in nature cannot exist independently, rather atoms combine with other atoms of the same element or atoms of other elements. When atoms combine, they form a new structure called molecule. So molecular structure is a resultant of two or more atoms. Examples: Oxygen (O_2), Ozone (O_3), Water (H_2O), Sodium chloride (NaCl), Nitric acid (HNO_3) etc.

By knowing the various chemical and physical properties of molecules, we can get the knowledge about various properties of that molecule under consideration. To know a person, one has to interact with that person. Similarly to know a molecule you have to interact with that molecule. When a molecule interacts with some external field (electric or magnetic), the response that molecule shows due to that interaction, appears in the form of molecular spectra. The response may come in the form of absorption or emission of electromagnetic radiation. Spectroscopy is the output of that interaction in terms of measurement and interpretation of absorption and emission of radiation when atoms or molecules or ions move from one energy state to another state. To know the detail about the molecular structure and its properties, one requires a total knowledge about the quantum mechanics with investigation and theoretical interpretation of different spectroscopic techniques. Molecular spectroscopy measures various characteristics of absorbed or emitted radiation during transition between energy states by frequency (ν or ω), wavelength (λ), wavenumber ($\bar{\nu}\ or \bar{\varpi}$), energy ($\varepsilon$) as their units.

Molecule possesses different energy states. They are main rotational states, vibrational states and electronic energy states. Molecular rotational energy states arise from the rotation of molecular counter parts, i.e. atoms about their center of gravity as a whole. Molecular vibrational energy states arise from the vibrations of its atoms relative to each other due to periodic displacement of the atoms from their equilibrium position. Similarly the molecular electronic energy states may arise from changes in their electronic configuration since electrons associated with each atom are in continuous motion. In current unit we are going to discuss about the spectroscopy related to molecular rotational energy state transitions. Rotational energy states are separated by small energy interval (10^{-3}eV). The molecular spectra arise from the transition between two rotational energy states are observed in the microwave region of the electromagnetic spectrum with wavelength range from 0.1 mm to 1 cm.

9.2 Objectives

After studying this unit, you should be able to-

- understand the meaning of rotation of molecules
- understand the rotational spectra of linear and nonlinear rigid and nonrigid rotators,
- solve problems using rotational energy transitions
- apply the theory of rotation to identify the intensity of spectral lines

- apply the theory of rotation to identify the isotopic effects
- apply the rotation for polyatomic, symmetric top system

9.3 Salient Features Of Rotational Spectra

A molecule can have many forms of energy. It may have rotational energy due to its different bodily rotation about its center of gravity. It may have vibrational energy due to the periodic displacement of atoms from their equilibrium positions. It may also have electronic energy due to its electrons associated with each atom or bond are in varying motion. All these rotational, vibrational and electronic energies are quantized in nature (you know from the knowledge of Quantum Mechanics). A molecule exists in any energy level can show transition from one energy level to another energy level, either by absorbing or by emitting a finite amount of energy which is equivalent to the energy difference between that two specific adjacent energy levels.

Let us consider two possible rotational energy levels of a molecule as E_J and E_{J+1}. The transition can take place between E_J and E_{J+1} if the appropriate amount of energy can either be absorbed or emitted by the probe system. According to Max Planck, the absorbed/ emitted energy can take the form of electromagnetic radiation frequency or wavelength which has the simple form as (Fig 9.1)

$$\Delta E = E_{J+1} - E_J = nh\omega = nh\nu = \frac{nhc}{\lambda} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

Where energies are expressed in Joule, *h* is universal Plank constant (6.626x10^{-34} Joule-sec), frequencies (ω or ν) are expressed in Hertz or sec^{-1}, wavelength (λ) in meter or centimeter or nm or Å. For molecular rotational spectroscopy the boundaries of electromagnetic radiation are known as **Microwave** region. The detail of this region is as follows:

In terms of frequency (ν): 3 x10^{10} – 3 x10^{12} Hz
In terms of wavelength (λ): 1 cm – 100 μm
In terms of wavenumber ($\bar{\nu}$) : 1 – 100 cm^{-1}
In terms of energy (ε): 10 – 10^3 Joules/mole

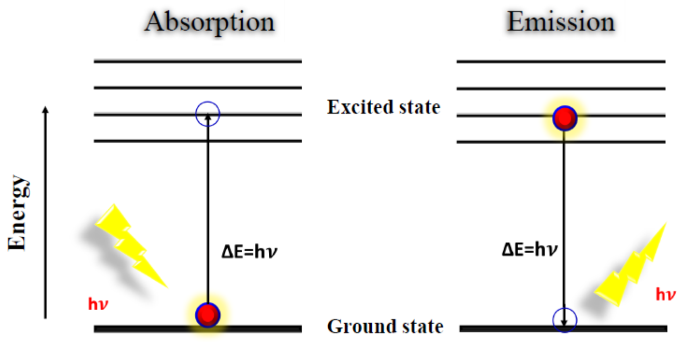

Fig 9.1: Absorption and emission process between rotational energy levels.

9.3.1 Conditions for a molecule to show Rotational spectra

When the interaction of electromagnetic radiation of proper frequency with a molecule (having rotational/vibrational/electronic energy levels) happens then different energy level transitions may appear. The rotational energy level transitions will only appear when the incident frequency is equivalent to the energy difference between two adjacent rotational energy levels as described in equation 1. The molecules having a **permanent dipole moment** are said to be eligible for rotational energy level transitions. So molecule with permanent dipole moment are said to be 'microwave active'. Usually heteronuclear molecules are generally microwave active. Example: HCl, H_2O etc. The molecules which do not have a permanent dipole moment, doesn't show rotational or microwave spectra and are said to be 'microwave inactive'. Usually homonuclear molecules are microwave inactive. Example: H_2, CO_2, O_2 etc.

9.3.2 Dipole moment

A **dipole** is defined as molecules or atoms with equal and opposite electrical charges separated by a small distance (Fig 9.2). In a molecule if one atom carries a permanent net positive charge and other atom carries a permanent net negative charge then the molecule is said to have a permanent electric dipole moment. Example: HCl. Hydrogen carries the positive charge and Cl carries the negative charge. H_2, CO_2 have no charge separation between the atoms and so they zero dipole moment.

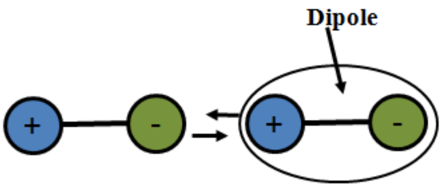

Fig 9.2: Dipole creation

9.3.3 Role of dipole moment in rotational transition

Let us consider the rotation of a simple diatomic molecule AB having a dipole moment due to its separated negative charge (A^-) and positive charge (B^+) densities. If we consider the pure rotation of AB where center of gravity does not move, then with time we can observe the positive and negative charges change their place periodically (Fig 9.3).

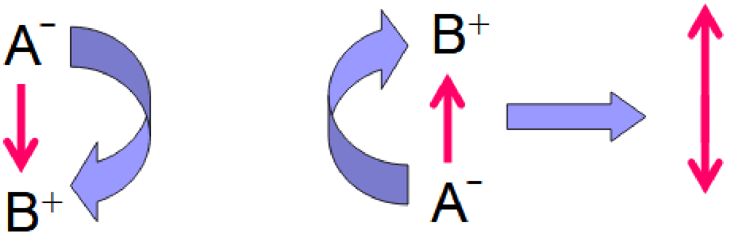

Fig 9.3: Rotating molecule

Let us start with a polar diatomic molecule HCl. Due to its rotation the component of dipole moment in a given direction fluctuates periodically. We can plot this fluctuation in Fig 9.4.

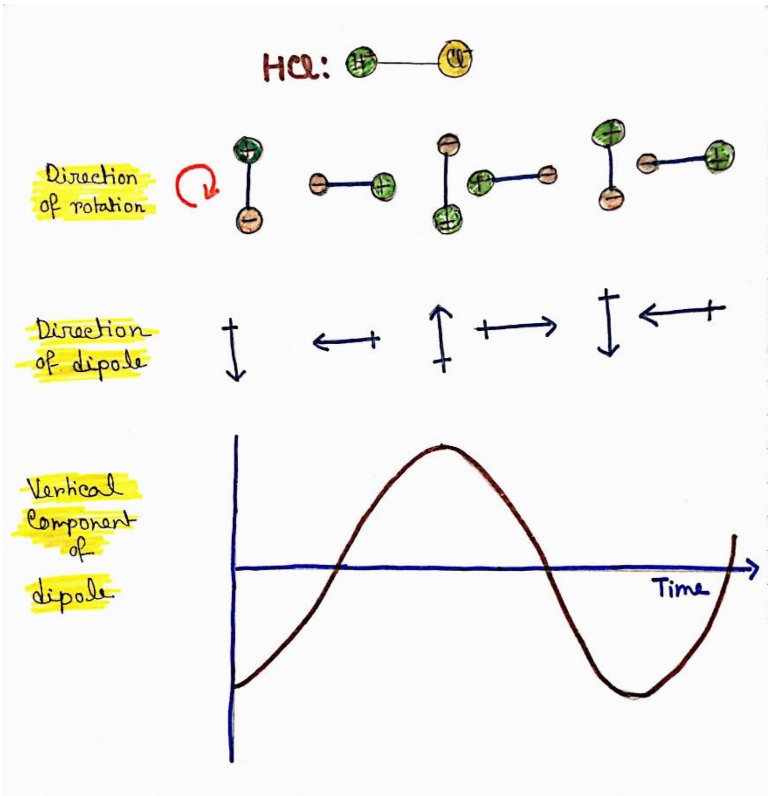

Fig 9.4: Periodic fluctuation of dipole moment of polar diatomic molecule due to rotation.

The fluctuation is same as that of the fluctuating electric field of radiation. If this fluctuating electric field interacts with the electric field of incident electromagnetic radiation, energy can be absorbed or emitted and pure rotation of the molecule will give rise rotational spectrum. So energy can be exchanged only if the molecule has a permanent dipole moment. If the permanent dipole of the molecule is zero, there will be no periodic variation and so no rotational spectrum.

9.3.4 Classification of molecules depending on rotation

Microwave or rotational spectroscopy is dependent on the rotating molecule. The complexity of rotational molecule is dependent on its dimension. The rotation of a three dimensional body is very much complex compared to one or two dimensional bodies. To describe the rotational motion it is convenient to explain the rotational component about three mutually perpendicular directions through the center of gravity which is known as principal axis of rotation. So a three dimensional body can be described by three principal moments of inertia, one about each axis as I_a, I_b and I_c where a, b, c are the three mutually perpendicular axes of rotation. Molecules can be classified into groups according to the values of I_a, I_b and I_c. Let us first describe the classification.

9.3.4.1 Linear molecules

All the atoms in this type of molecules are arranged in a straight line. Example: HCl, CO_2, OCS, C_2H_2 etc. Here the three axes or rotation are described as (Fig 9.4a):

H-Cl
O-C-O

a) The molecular or bond axis. Let it be a axis.
b) The direction of end over end rotation in the plane of the paper passing through the center of gravity of the molecule and perpendicular to a axis. Let it be b axis.
c) The direction of end over end rotation at right angles to the plane i.e. axis perpendicular to both a and b axes and passing through the center of gravity of the molecule. Let it be c axis.

As the nuclei of the atoms give the main contribution to mass and are situated in a axis, so the moment of inertia about a axis is tentatively zero (only approximation) and so I_a=0 for linear molecule. Again, since I_b and I_c are correspond to the end over end rotation and so they are equal ($I_b = I_c$).

So for linear molecule: I_a=0 and $I_b = I_c$.

(***Note:*** Moment of inertia is a measure of an object's resistance to changes in its rotation rate. It is the rotational analog of mass. A molecule can have three different moments of inertia I_a, I_b and I_c according to the axis of rotation.)

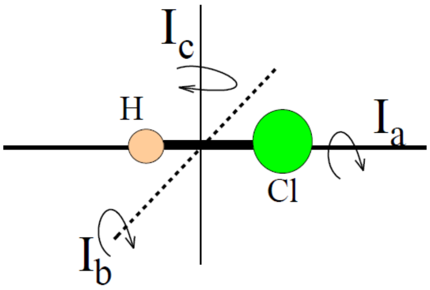

Fig 9.4a: Moment of inertia of linear HCl molecule.

9.3.4.2 Symmetric top type molecules

In symmetric top type molecules all the three moments of inertia are non-zero. Example: methyl chloride (CH_3Cl) where three hydrogen atoms are bonded tetrahedrally with carbon. Here C-Cl bond axis can be considered as a axis on which the center of gravity lies. This time I_a is not negligible since it involves the rotation of three massive hydrogen atoms of this axis. So $I_a \neq 0$. The two mutually perpendicular b and c axes lie in the plane perpendicular to a axis and these end over end in and out rotation are remain identical. So $I_b = I_c$. A molecule of this type spinning about a axis behaves like spinning top and known as symmetric top molecule.

So for symmetric top molecule: $I_a \neq 0$ and $I_b = I_c$.

There are two subdivisions of symmetric top molecule. They are: prolate symmetric top and oblate symmetric top.

For prolate symmetric top molecule $I_a < I_b = I_c$. Example: CH_3Cl, CH_3F.

For oblate symmetric top molecule $I_a > I_b = I_c$. Example: BF_3, BCl_3 (Fig. 9.5).

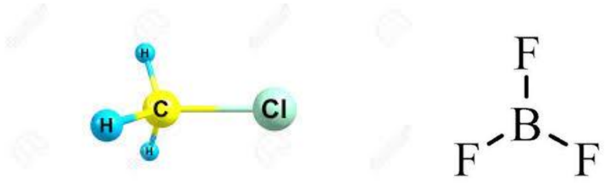

Fig 9.5. Methyl chloride (CH_3Cl) and Boron trifluoride (BF_3)

9.3.4.3 Spherical top type molecules

The molecule in which all three moment of inertia are equal is known as spherical top. Example: CH_4, CCl_4. Spherical top molecules have no dipole moment and so they are microwave inactive (Fig. 9.6).

So for spherical top molecule: $I_a = I_b = I_c$.

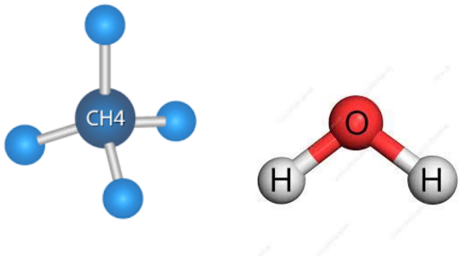

Fig 9.6. Methane (CH_4) and water (H_2O)

9.3.4.4 Asymmetric top type molecules

Molecules in this category have all three moment of inertia different. Example: H_2O, CH_3OH, CH_2CHCl. Majority of the natural molecules belong to the category of asymmetric top. (Fig. 9.6).

So for asymmetric top molecule: $I_a \neq I_b \neq I_c$.

Till now we have discussed different categories of molecules in terms of their moment of inertia. If we combine all then overall rotating molecules can be classified into four main groups as (Table 1):

Serial no	Moment of Inertia	Type of molecule
1.	I_a=0 and $I_b = I_c$.	Linear molecule
2.	$I_a \neq 0$ and $I_b = I_c$. $I_a < I_b = I_c$. $I_a > I_b = I_c$.	Symmetric top molecules prolate symmetric top oblate symmetric top
3.	$I_a = I_b = I_c$.	Spherical top molecule
4.	$I_a \neq I_b \neq I_c$.	Asymmetric top molecule

Table 9.1: Classification of rotating molecules in terms of moment of inertia.

Self Assessment Question (SAQ) 1: What do you mean by dipole moment? Why dipole moment is important in molecular spectroscopy?

Self Assessment Question (SAQ) 2: Homonuclear diatomic molecules are microwave inactive. Why? Heteronuclear diatomic molecule will show rotational spectrum or not?

Self Assessment Question (SAQ) 3: What is the main condition that a molecule will be microwave active or not? Give some examples.

9.4 Rotational Spectra Of Diatomic Molecule

Rotational energy states arise from the rotation of the molecule as a whole. A detailed picture of a particular molecule (bond length, force constant, bond angles) can be obtained from its permitted rotational energy level transition or from rotational spectrum. Let us consider the case of a simple heteronuclear diatomic molecule. The molecule can rotate as a whole about an axis passing through the center of gravity and perpendicular to the line joining the nuclei i.e. along internuclear axis. We will now try to investigate what type of spectrum this rotating system will show on the basis of quantum theory and will also try to compare the computed rotation spectrum with the experimental one.

9.4.1 Rigid rotator

We will start with the simple possible model of rotating diatomic molecule which is known as dumbbell model as shown in Fig 9.7. Two atoms of masses m_1 and m_2 considered to be point like are joined by a rigid bar (bond length) of distance R. The bar is considered as weightless. The bond length is represented as

$$R = r_{1+} r_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (2)$$

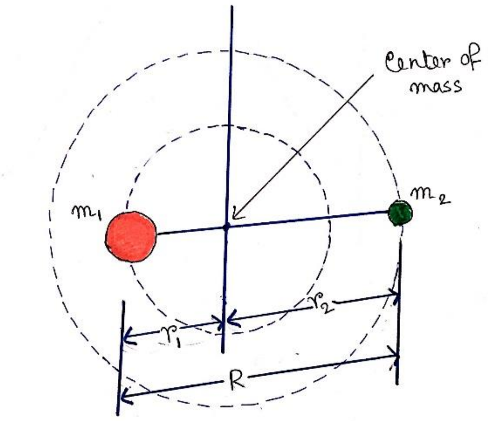

Fig 9.7. Rotation of rigid diatomic molecule with two masses m_1 and m_2 joined by a rigid bar of length $R=r_1+r_2$, about its center of mass or center of gravity C.

The molecule can rotate about its center of mass (C). From the definition of center of mass

$m_1r_1 = m_2r_2$ …………………………………… (3)

$m_1r_1 = m_2r_2 = m_2(R - r_1)$ from equation (2)

$r_1(m_1 + m_2) = m_2R$

$r_1 = \frac{m_2R}{(m_1+m_2)}$ and $r_2 = \frac{m_1R}{(m_1+m_2)}$ ………………….. (4)

The moment of inertia of this molecule about the axis passing through center of mass C and perpendicular to the line joining the atoms is

$I = m_1r_1^2 + m_2r_2^2$……………………………… (5)

$= m_2r_2r_1 + m_1r_1r_2$ using equation (3)

$= r_1r_2\,(m_1 + m_2)$……………………………….. (6)

$I = \frac{m_1\,m_2}{(m_1+m_2)}R^2 = \mu R^2$……………. (7) using equation (4)

Where we have used $\mu = {}^{m_1\,m_2}/_{(m_1 + m_2)}$ as reduced mass of the system. Equation 7 defines the moment of inertia in terms of atomic masses and the bond length. Here instead of considering the rotation of the dumbbell we have considered the rotation of single mass μ at a fixed point R from the axis of rotation. Such system is called as simple rigid rotator.

9.4.2 Energy levels of rigid rotator

To determine the possible energy states of rigid rotator, we have to use the concept of quantum theory. So we have to solve the Schrödinger equation in terms of amplitude of wave motion ψ for the system having mass μ, potential energy V, total energy of the mass point E as:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2\mu}{h^2}(E-V)\psi=0\ldots\ldots\ldots\ldots\ldots (8)$$

Here we have to consider $V=0$ since no potential energy is associated with the rotation as long as the rotator is considered as completely rigid. So the modified Schrödinger equation will be

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2\mu}{h^2}E\psi=0\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Where $x^2+y^2+z^2=R^2$ is a constant. The solution of the above equation (consult Arther Beiser, Modern Physics) in terms of ψ is single valued, finite and continuous occurs only for certain values of rotational energy levels E_J namely the Eigen values as

$$E_J=\frac{h^2J(J+1)}{8\pi^2\mu R^2}=\frac{h^2J(J+1)}{8\pi^2 I}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Where J is the rotational quantum number and can take the integer values $0, 1, 2, 3\ldots\ldots$Thus we have a series of discrete energy levels whose energy values increase quadratically with increasing J. Equation 10 is expressed in Joules. Now to calculate the emitted or absorbed rotational wavenumber we know that according to quantum theory the absorption of light quantum takes place as a result of the transition of the rotator from lower (E'') to higher (E') energy state, whereas the emission of a light quantum takes place as a result of a transition of the rotator from a higher to a lower energy state. The wave number of absorbed or emitted light quantum is (in units of cm^{-1}) expressed as

$$\bar{\upsilon}=\frac{E'}{hc}-\frac{E''}{hc}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Where $E/hc=\varepsilon_J$ is known as rotational term or energy in wavenumber (in units of cm^{-1}) and is expressed as

$$\varepsilon_J=\frac{E}{hc}=\frac{hJ(J+1)}{8\pi^2 cI}=BJ(J+1)\ldots\ldots\ldots\ldots (12)\quad \text{where } J=0,1,2,3\ldots\ldots$$

Where the constant $B=\frac{h}{8\pi^2 cI}$ is called as rotational constant. It is also expressed in units of cm^{-1}.

From equation 12 we can show the allowed energy levels (Fig 9.8a). For $J=0$ we have $\varepsilon_J=\varepsilon_0=0$ and so we can say that the molecule is not rotating at all. For $J=1$ the energy is $\varepsilon_J=\varepsilon_2=2B$ which is the lowest value of rotational energy. Similarly for higher values of J we get ε_J as 6B, 12B, 20B etc. It is important to mention here that in principle there no limit to get the values of ε_J with increasing J values but in practice there comes a point at which the centrifugal force of the rotating diatomic molecule will be greater than the strength of the bond length. At that point the molecule will be disrupted. It is not possible to achieve this situation at room temperature.

Using equation 11 we can write for the transition from higher to lower rotational level i.e. from *J'* → *J''* state the emitted frequency as

$$\bar{\upsilon} = \varepsilon_{J'} - \varepsilon_{J''} = BJ'(J'+1) - BJ''(J''+1) \text{ ………….. (13)}$$

To calculate the frequencies that are emitted or absorbed it is necessary to know the selection rule for the rotational quantum number *J*. The selection can be obtained by evaluating the matrix elements of the dipole moment (Herzberg, Molecular spectra and molecular structure) of the molecular system which show that only those rotational energy level transitions are allowed in which *J* changes by only one unit. All other transitions are spectroscopically forbidden. So the selection rule for the rotational transition of rigid diatomic rotator is

$$\Delta J = J' - J'' = \pm 1 \text{………………………… (14)}$$

In general we can consider *J''=J* and *J'=J+1* and for $\Delta J = +1$ we can have

$$\bar{\upsilon}_{J\rightarrow J+1} = \bar{\upsilon}_J = \varepsilon_{J+1} - \varepsilon_J = B(J+1)(J+2) - BJ(J+1)$$

$$= B[J^2 + 3J + 2 - (J^2 + J)]$$

$$= 2B(J+1) \;\; cm^{-1} \text{………………… (15)} \quad \text{with } J = 0,1,2,3\text{……}$$

Thus the spectrum of the simple rigid rotator consists of a series of equidistant absorption lines at *2B*, *4B*, *6B*…cm^{-1} (Fig 9.8a). Similar identical lines will be obtained for the rotational emission spectrum. The first of these lines observed at *2B* for *J=0*→*J=1* transitions in accord to equation 15 (with *J=0*) having the separation of successive lines as *2B*.

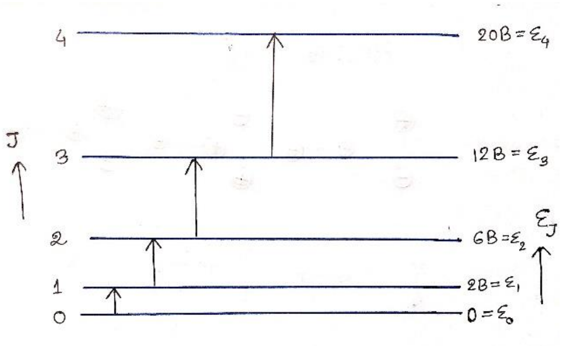

Fig 9.8a. Allowed rotational energies of a rigid diatomic molecule, their allowed transition probabilities according to selection rule and the spectrum arise from transition.

According to equation 11 and 15 the rotational frequency can be calculated as

$$\upsilon_{rot} = \bar{\nu}_J c = c2B(J+1) \approx 2cBJ \ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

which is approximately equal to the frequency of the spectral line that has this rotational energy state (*J*) as upper state i.e. if the rotational transition is from *J-1*→ *J*.

Example 1: Experimental rotation spectrum of HCl shows the first rotational line at 21.2 cm^{-1}. Using this value one can easily determine the moment of inertia and hence the bond length of HCl (Fig 9.8b).

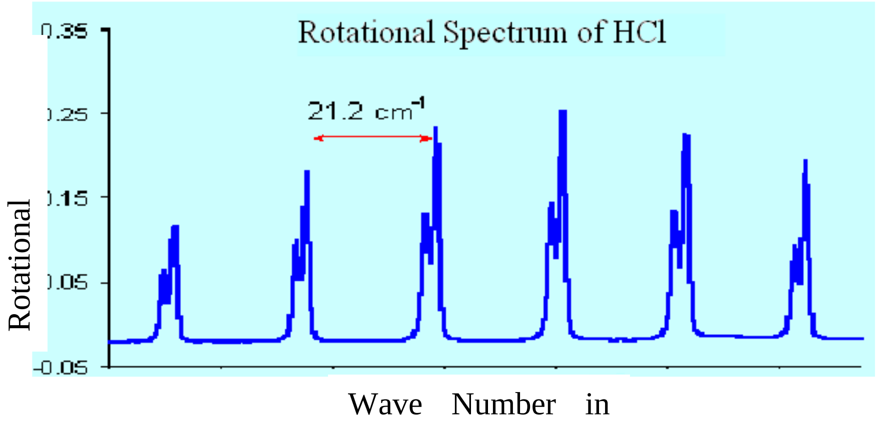

Fig 9.8b. Experimental Rotational spectrum of HCl with separation between any two lines is 21.2 cm^{-1}.

Here

$$\bar{\upsilon}_{0\to1} = 2B = 21.2 \text{ cm}^{-1}$$

$B = 10.6$ cm^{-1}=1060m^{-1}.Using the relation $I = \frac{h}{8\pi^2 Bc}$ we have $I_{HCl} = \frac{h}{8\pi^2 Bc} = 2.63x10^{-47} kgm^2$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{\left(\frac{1g}{mol}\right)\left(\frac{35g}{mol}\right)}{\left(\frac{36g}{mol}\right)(6.023x10^{23})} = 1.61x10^{-24} gm = 1.61x10^{-27} kg$$

$$R^2 = \frac{h}{8\pi^2 \mu Bc} = \frac{6.626x10^{-34} J.sec}{8\pi^2 (1.61x10^{-27} kg)(1060 \text{ m}^{-1})\left(\frac{3\text{x}10^8 m}{s}\right)} = 1.63x10^{-20} m^2$$

$$R = 1.27x10^{-10} m = 1.27\text{Å}$$

9.4.3 Intensities of rotational spectral lines

The pure rotational spectrum of a rigid diatomic molecule consists of a series of equidistant lines corresponding to the transitions, $J=0 \rightarrow J=1$, $J=1 \rightarrow J=2$, $J=2 \rightarrow J=3$ and so on. To identify the relative intensities of the different spectral lines from equation 15 and Fig 9.8a-c, we need the knowledge of the relative probabilities of transition between rotational energy levels. The factor that decides the intensity of lines is the number of molecules present in each energy level. So the line intensities will be directly proportional to the initial number of molecules in each level. The population of molecules in each level follows the Boltzmann distribution. We know that the rotational energy at the lowest energy level has been zero since $J=0$ (from equation 12), so if we have N_0 molecules in this lowest energy state then the number of molecules in any higher energy state J is given by according to Boltzmann distribution

$$N_J = N_0 e^{\left(-E_J/_{kT}\right)} = N_0 e^{\left(-BchJ(J+1)/_{kT}\right)} \text{.........}(17)$$

Where c is expressed in cm/sec, and B is in cm^{-1}. We can easily say that N_J is varying with J. Let us consider a typical case where B = 2 cm^{-1} and temperature as T= 300K. The relative population $(\frac{N_1}{N_0})$ at $J=1$ can be obtained as 0.98. So we see that there are almost as many molecules in the state $J=1$ at equilibrium as in the $J=0$ state. Again the population depends on the degeneracy of each level, which is $(2J+1)$ since each energy level is $(2J+1)$ fold degenerate. So taking degeneracy into account the total relative population at an energy E_J will be

$$Population \propto (2J+1) e^{\left(-E_J/_{kT}\right)} \text{................ } (18)$$

Differentiating equation 18 shows that the population is a maximum at the nearest J value to

$$J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} \text{................. } (19)$$

That is the rotational energy level to this J value will have the maximum population. So the transition originating from the level having this J value will have the maximum intensity as described in Fig 9.8c for HCL molecule at various temperature.

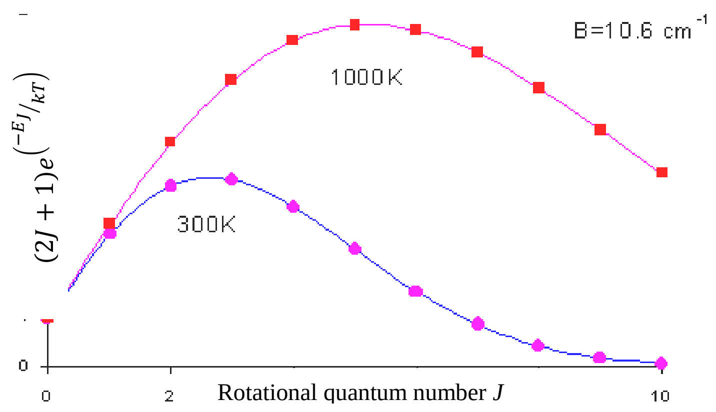

Fig 9.8c. Relative population of HCl including degeneracy with B value as 10.6 cm^{-1} at two different temperatures: 300K and 1000K.

9.4.4 Effect of Isotope

When an atom is replaced by one of its isotope, the interatomic bond distance remains the same as the electronic charge distribution does not change duo to this substitution. The resulting substance is identical chemically with the original. However a change in the total mass of the system due to changes in the nuclear mass appears and hence a change in the moment of inertia and *B* value of the molecular system appears. It is observed that if the atomic mass increases due to isotopic substitution the *B* value decreases as $B \propto 1/I$.

Example 2: Two isotopes of carbon monoxide. They are $^{12}C^{16}O$ having *B* value 1.921cm^{-1} and $^{m'}C^{16}O$ having *B'* value 1.836 cm^{-1}. The change in the *B* value reflects in the rotational energy levels of the two isotopes as described in Fig 9.9. The spectrum of the heavier species shows a smaller separation between the lines (*2B'*) than that of the lighter one (*2B*). For clarity the spectrum of heavier one is shown by dashed lines. Here the heavier mass is *m'*. Observation of the decreased separation of lines helps us to evaluate the precise atomic weights by using the relation (prime refers to the heavier atom)

$$\frac{B}{B'} = \frac{h}{8\pi^2 Ic}\frac{8\pi^2 I'c}{h} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046 \ldots\ldots\ldots\ldots\ldots\ldots (20)$$

Taking the mass of oxygen as 16 and that of ^{12}C to be 12 we have

$$\frac{\mu'}{\mu} = 1.046 = \frac{16m'}{16+m'} \times \frac{12+16}{12\times16}$$

$m' = 13$ which is the atomic weight of ^{13}C.

So rotation spectroscopy can give directly an estimate of the abundance of isotopes by comparison of absorption intensities.

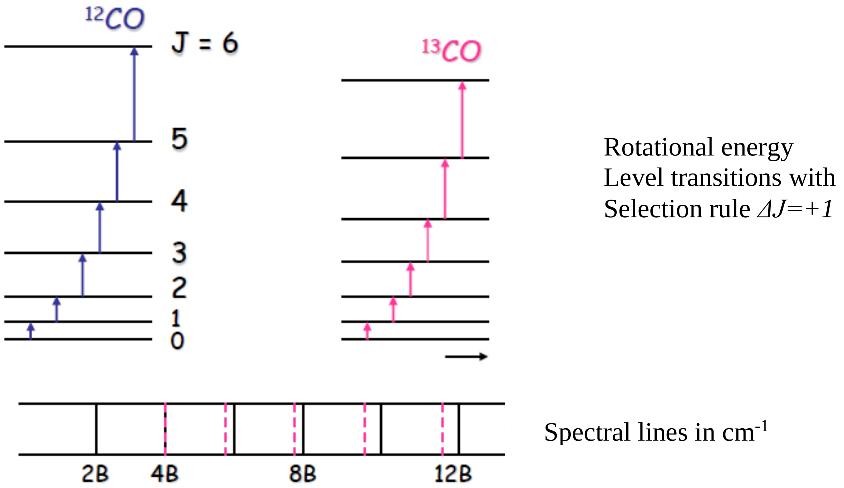

Fig 9.9. The effect of isotopic substitution on the energy levels and rotational spectrum of a diatomic molecule such as carbon monoxide. Dashed lines are for isotope.

Example2: Below is the rotational spectrum of HCl isotopes as $^1H^{35}Cl$ and $^1H^{37}Cl$. By identifying the wavenumber of transitions one can easily determine the atomic masses, bond length, and relative abundance of the isotopes (Fig 9.10).

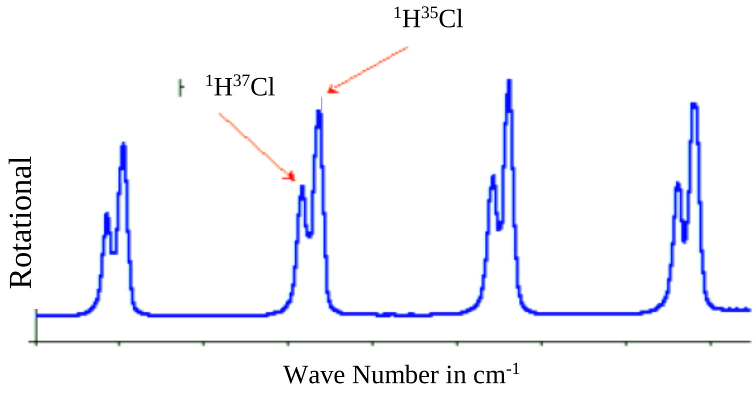

Fig 9.10. Rotational spectrum of a diatomic molecule hydrogen chloride isotopes.

Problem 1: What is the change in the rotational constant B when hydrogen is replaced by deuterium in the hydrogen molecule?

Solution: Denoting the isotopically substituted hydrogen by prime

$$\frac{B}{B'} = \frac{h}{8\pi^2 Ic}\frac{8\pi^2 I'c}{h} = \frac{I'}{I} = \frac{\mu'}{\mu}$$

$$\mu = \frac{m_H}{2} \qquad \mu' = \frac{m_D}{2} = m_H$$

$$\frac{B}{B'} = \frac{2m_H}{m_H} = 2, \quad B' = \frac{B}{2}$$

So change in rotational constant: $B - B' = \frac{B}{2}$

Problem 2: The first line (*J=0→J=1*) in the rotational spectrum of carbon monoxide ($^{12}C^{16}O$) has a frequency of 3.8424 cm^{-1}. Calculate the rotational constant and the C-O bond length in CO. Given Avogadro number is $6.023x10^{23}$ /mol.

Solution: For first line, 2B= 3.8424 cm^{-1}. B= 1.9212 cm^{-1} = 192.12 m^{-1}.

$$I = \mu R^2 = \frac{h}{8\pi^2 Bc},\ R^2 = \frac{h}{8\pi^2 \mu Bc}$$

So, $\mu = \frac{m_1 m_2}{m_1+m_2} = \frac{\left(\frac{12g}{mol}\right)\left(\frac{16g}{mol}\right)}{\left(\frac{28g}{mol}\right)(6.023x10^{23})} = 1.1385x10^{-23}gm = 1.1385x10^{-26}kg$

$$R^2 = \frac{h}{8\pi^2 \mu Bc} = \frac{6.626x10^{-34}J.sec}{8\pi^2(1.1385x10^{-26}kg)(192.12\ \mathrm{m}^{-1})\left(\frac{3\mathrm{x}10^8 m}{s}\right)}$$

$R = 1.131x10^{-10}m = 1.131\text{Å}$

Problem 3: What is the average period of rotation of HCl molecule if it is in the J=1 state. The internuclear distance of HCl is 0.1274nm. Given the mass of hydrogen and chlorine atoms are $1.673x10^{-27}$ kg and $58.06x10^{-27}$kg.

Solution: We have rotational energy of a classical oscillator $= \frac{1}{2}I\omega^2$

Rotational energy of quantum oscillator $E_J = \frac{h^2 J(J+1)}{8\pi^2 \mu R^2} = \frac{h^2 J(J+1)}{8\pi^2 I}$

Equation both the above equation we get $\omega^2 = \frac{h^2 J(J+1)}{4\pi^2 I^2}$

Also we can write angular frequency $\omega = \frac{h\sqrt{J(J+1}}{2\pi I}$

$I = \mu R^2 = \frac{(1.673x10-27\ kg)(58.06x10-27kg)(0.1274x10^{-9}m)^2}{59.733x10^{-27}kg} = 0.0264x10^{-45}\ kgm^2$

$$\omega = \frac{h\sqrt{J(J+1}}{2\pi I} = \frac{(6.626x10^{-34}J.sec)\sqrt{2}}{2\pi(0.0264\mathrm{x}10^{-45}kgm^2)} = 56.5116x10^{11}sec^{-1} = 56.5116x10^{11}Hz$$

Period of rotation $T = \frac{2\pi}{\omega} = \frac{2\pi}{56.5116x10^{11}sec^{-1}} = 1.112x10^{-12}sec$

Self Assessment Question (SAQ) 4: Which of the following molecules will show microwave spectrum: H_2, HCl, CH_4, CH_3Cl, CH_2Cl_2, H_2O, SF_6. Why?

Self Assessment Question (SAQ) 5: Distinguish between symmetric top (prolate and oblate), spherical top and asymmetric top molecules. Which are suitable for microwave spectroscopy?

Self Assessment Question (SAQ) 6: The intensity of $J=0 \rightarrow J=1$ is often not the most intense rotational line. Why?

Self Assessment Question (SAQ) 7: Outline the effect of isotopic substitution on the rotational spectra of molecules.

Self Assessment Question (SAQ) 8: Prove that for maximum population $J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$

Self Assessment Question (SAQ) 9: Choose the correct option-

(a) For linear diatomic molecule the relation of moment inertia are

(i) $I_b=0$ and $I_a = I_c$ (ii) $I_c=0$ and $I_b = I_a$ (iii) $I_a=0$ and $I_b = I_c$ (iv) $I_a\neq 0$ and $I_b = I_c$

Self Assessment Question (SAQ) 10: Fill in the blank-

(i) Region of rotational spectrum in terms of wavenumber is ……….
(ii) Relation between centrifugal distortion constant and rotational constant is ……………..
(iii) Prolate type asymmetric rotator can be represented by its moment of inertia as………..

9.5 Non rigid rotator

In rigid rotator model we have observed that the separation between the adjacent rotational lines remain fixed as *2B.* In reality it is found that the separation between the adjacent lines decreases steadily with increasing *J* value. If we check the experimental and computed rotational spectrum of hydrogen fluoride (HF) as given below in table 9.2, it is observed from the table that as *J* increases, *B* value also decreases for the experimental spectrum. The reason for this decreases in *B* may be observed if we calculate the internuclear distances from *B* value. It is observed that the bond length increases with *J*. We can say that our assumption of existence of rigid rotator is only an approximation. So the bond is not rigid as we assumed rather all bonds are elastic to a certain extent. It is quite obvious that the molecule cannot be a strict, rigid rotator when it is also able to carry out vibrations in the direction of the line joining the two nuclei. Therefore a better model for representing the rotations of the molecule is given by the "non rigid rotator" that is a rotating system consisting of two mass points which are not connected by a massless rigid bar rather by a massless spring.

Rotational transition	**B_{cal} in cm^{-1}**	**B_{exp} in cm^{-1}**	**Bond length r_{eq} in Å**
$J=0\rightarrow J=1$	**20.56**	**20.55**	**0.929**
$J=1\rightarrow J=2$	**20.56**	**20.48**	**0.931**
$J=2\rightarrow J=3$	**20.56**	**20.43**	**0.932**

J=3→J=4	**20.56**	**20.31**	**0.935**
J=4→J=5	**20.56**	**20.16**	**0.938**
J=5→J=6	**20.56**	**20.04**	**0.941**
J=6→J=7	**20.56**	**19.82**	**0.946**
J=7→J=8	**20.56**	**19.64**	**0.951**
J=8→J=9	**20.56**	**19.45**	**0.955**
J=9→J=10	**20.56**	**19.16**	**0.963**
J=10→J=11	**20.56**	**18.91**	**0.969**

Table 9.2: Rotation spectrum of hydrogen fluoride for different rotational energy level transitions.

In non-rigid rotator system the increase in bond length with J reflects the fact that the more quickly a diatomic molecule rotates the greater is the centrifugal force (as discussed in section 9.4.2). In such system as a result of greater action of centrifugal force, the internuclear distance, and consequently the moment of inertia increases with increasing rotation, which tends to move the atoms apart.

To explain how the elasticity of bond length may be quantitatively allowed for rotational spectrum, we have to consider the vibration energy of the molecule since the elastic bond length will stretch and compress periodically with a certain fundamental frequency dependent on the masses of the atoms and the elasticity (force constant) of the bonds. If we consider the motion of bond length as simple harmonic, the force constant is given by

$$k = 4\pi^2\overline{\omega}^2c^2\mu \text{ …………………….. (21)} \quad \text{with } \overline{\omega} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

with $\overline{\omega}$ as vibrational frequency (in cm^{-1}), c be the velocity of light, μ be reduced mass of the system. The variation of B with J can be determined by force constant as: the weaker the bond, the more quickly the molecule will distort under centrifugal force. Another consequence of elasticity is that the R and B varies during vibration as $B \propto 1/R^2$.

So for a correct treatment we have to use the complete Hamiltonian of the non-rigid rotator and apply Schrödinger wave equation to solve the Hamiltonian. The solution of the corresponding Schrödinger equation gives us the following energy Eigen value as

$$E_J = \frac{h^2J(J+1)}{8\pi^2I} - \frac{h^4J^2(J+1)^2}{32\pi^4I^2R^2k} \text{ Joule ………… (22)}$$

$$\text{or } \varepsilon_J = \frac{E}{hc} = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1} \text{ ………..(23)}$$

where, B is the rotational constant as defined earlier and D as centrifugal distortion constant and is expressed as a positive quantity.

$$D = \frac{h^3}{32\pi^4I^2R^2kc} = \frac{4B^3}{\overline{\omega}^2} \text{ cm}^{-1} \text{ ……………..(24)}$$

The above equation 23 is only applied for the simple harmonic force field. If the force field is anharmonic the expression will become

$$\varepsilon_J = \frac{E}{hc} = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + \cdots \text{ cm}^{-1} \text{ .... } (25)$$

From equation 24 it is evident that centrifugal distortion effect is greatest for molecules with smaller moment of inertia and small force constants. In a given molecule, the effect of *D* is to decrease the rotational energy (equation 23) which increases rapidly for higher rotational states. It is only in very rare cases the experimental data consider the introduction of the term *H*.

The selection rule for the non-rigid rotator is again $\Delta J = \pm 1$. So the frequency of transition for *J=1→J=J+1* is given by (only considering up to D term)

$$\bar{\nu}_{J\rightarrow J+1} = \varepsilon_{J+1} - \varepsilon_J$$

$$= B[(J+1)(J+2) - J(J+1)] - D[(J+1)^2(J+2)^2 - J^2(J+1)^2]$$

$$= 2B(J+1) - 4D(J+1)^3 \text{ cm}^{-1} \text{ ....(26)} \qquad \text{with } J=0,1,2,3\ldots\ldots$$

The first term in equation 26 is the same as that of rigid rotator. The additional term gives the shift of the lines of the spectrum of a rigid molecule which increase with *J* as $(J+1)^3$. Fig 9.11 gives the schematic representation of the energy levels and the spectrum of non-rigid rotator as well as rigid rotator. We can see that the rotational spectrum of non-rigid rotator is similar to that of rigid rotator expect each line is displaced slightly to low frequency. The knowledge of *D* allows us to determine the *J* value of the lines in an observed spectrum. Also the *D* value helps us to determine the vibrational frequency of the diatomic molecule.

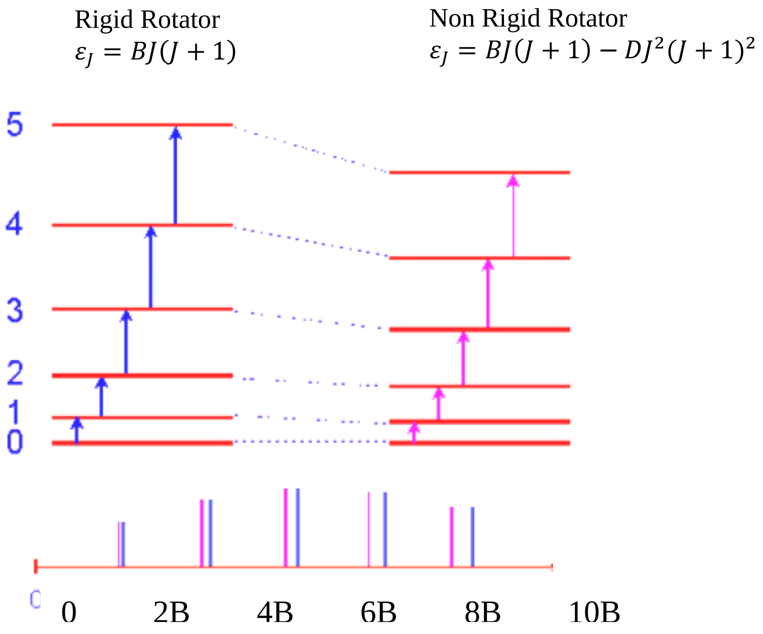

Fig 9.11. Representation of the energy levels and spectrum of rigid and non-rigid diatomic rotator.

Problem 4: Rotational and centrifugal distortion constants of HCl are 10.593 cm^{-1} and 5.3 x10^{-4} cm^{-1}. Estimate the vibrational frequency and force constant of the molecule.

Solution: Centrifugal distortion constant $D = \frac{h^3}{32\pi^4 I^2 R^2 kc} = \frac{4B^3}{\overline{\omega}^2}$ cm^{-1}

$$\overline{\omega} = \left[\frac{4(10.593\ \mathrm{cm}^{-1})^3}{5.3\ \mathrm{x}10^{-4}\ \mathrm{cm}^{-1}}\right]^{1/2} = 2995.2\mathrm{cm}^{-1}$$

Force constant $k = 4\pi^2\overline{\omega}^2 c^2 \mu$

$\mu = 1.6261 \mathrm{x} 10^{-27} kg$

$k=4\pi^2 x(3x10^8 m/sec)^2(1.6261x10^{-27}kg)(2995.2x10^2 m^{-1})^2$

$= 517.8Nm^{-1}$

Problem 5: Three consecutive lines of the rotational spectrum of a diatomic molecule are observed at 84.544, 101.355, 118.112 cm^{-1}. Assign these lines to their appropriate *J''→J'* Transitions and deduce the values of *B* and *D*. Also evaluate the approximate vibrational frequency of the molecule.

Solution: Frequency for $J \rightarrow J+1$ transition

$\bar{\nu}_{J\rightarrow J+1} = 2B(J+1) - 4D(J+1)^3 \mathrm{cm}^{-1}$. According to the given condition

84.544 cm^{-1}= $2B(J+1) - 4D(J+1)^3$

101.355 cm^{-1}= $2B(J+2) - 4D(J+2)^3$

118.112 cm^{-1}=$2B(J+3) - 4D(J+3)^3$ From the first two equations

16.811 cm^{-1}=$2B - 4D[(J+2)^3 - (J+1)^3]$

Since $D \ll B$, an approximate value of *B* can be obtained by neglecting the term in *D*. With $2B$= 16.811 cm^{-1} again neglecting the term in *D* we get,

84.544 cm^{-1}= $16.811\mathrm{cm}^{-1}\ (J+1)$

J=4.03=4(corrected to the integer)

So the line at 84.544 cm^{-1} correspond to $J=4 \rightarrow J=5$ transition. The line at 101.355 cm^{-1} is due to $J=5 \rightarrow J=6$ transition. The line at 118.112 $\mathrm{cm}^{-1}$is due to $J=6 \rightarrow J=7$ transition.

With these values we get

84.544 cm^{-1}=$2B \times 5 - 4D \times 125$

101.355 cm^{-1}=$2B\times 6-4D\times 216$. Solving these two equations we get

B= 8.473 cm^{-1} and D=3.7x10^{-4} cm^{-1}. Again by using the relation $D=\frac{h^3}{32\pi^4 I^2 R^2 kc}=\frac{4B^3}{\bar{\omega}^2}$

We can calculate $\bar{\omega}=2564.4\mathrm{cm}^{-1}$.

Self Assessment Question (SAQ) 11: What is centrifugal distortion? Explain the effect of centrifugal distortion on the moment of inertia and energy of a diatomic molecule. How centrifugal distortion can help to determine the force constant of a bond?

Self Assessment Question (SAQ) 12: The observed rotational spectrum of HF shows decrease in the line separation on the high frequency side. Why?

Self Assessment Question (SAQ) 13: Find the frequencies of the J=1→J=2 and J=2→J=3 rotational absorption lines in NO, who's molecules have the moment of inertia 1.65x10^{-46} kg m^2.

Self Assessment Question (SAQ) 14: Calculate the energies of the four lowest non zero rotational energy levels of the H_2 and D_2 molecules where D represents deuterium atom $H^2_{1.}$

9.6 Linear Polyatomic Molecules

Linear polyatomic molecules can also be treated similar to the diatomic molecules since I_a=0 and $I_b = I_c$. Similarly the energy levels E_J are given by the same formula identical to that of the diatomic molecules as

$\bar{\nu}_{J\to J+1}=\varepsilon_{J+1}-\varepsilon_J=2B(J+1)-4D(J+1)^3$ cm^{-1} with J=0,1,2,3……

Spectrum will show the same *2B* separation modified by the distortion constant. So the whole theory of diatomic molecules are equally applicable to all linear molecules. However there are some points are needed to be understand. They are:

1. The moment of inertia for end over end rotation of the polyatomic linear molecule is considerably greater than that of the diatomic molecule, The *B* value will be much smaller. Usually for diatomic molecules *B* value are observed to be 10 cm^{-1} while for linear triatomic molecule *B* value is observed as tentatively around 1 cm^{-1} or less. So for larger linear molecules it will be smaller more. As a result of this the spectral lines are observed to be more closely spaced.
2. The molecule should have a permanent dipole moment to be microwave active. Example: OCS molecule is microwave active, whereas OCO or CO_2 is not. Also isotopic substitution does not lead to microwave activity.
3. A noncyclic polyatomic linear molecule having N atoms contains N-1 individual bond lengths. So in a triatomic molecule like OCS, there we have two bond length as r_{CO} and r_{CS}. The molecule has only one moment of inertia for the end over end rotation of OCS. So only one value can be determined from the microwave spectrum of OCS. If we study the spectra OCS molecule for different transitions we will observe there is no existence

of centrifugal distortion and so *B* remains constant at 0.2027 cm^{-1}. And the moment of inertia comes out to be as I_b=137.95 x10^{-47} kg m^2. From this observation, it is impossible to deduce the values of the bond lengths r_{CO} and r_{CS}. To overcome this problem if we study the molecule with different atomic masses, but with the same bond lengths then we may get the value of different moment of inertia.

Let us consider the rotation of OCS where r_O, r_C, r_S represent the distances of the atoms from the center of gravity having corresponding masses as m_O, m_C, m_S (Fig-9.12).

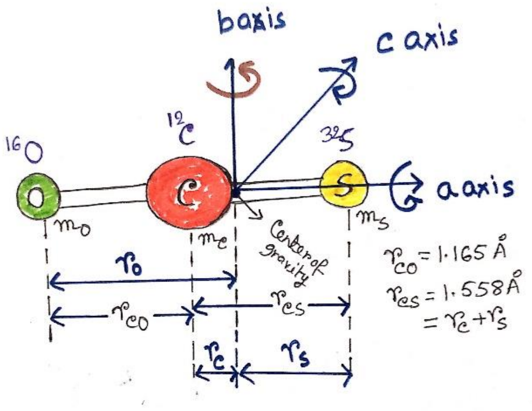

Fig 9.12. Linear polyatomic molecule carbon oxysulphide (OCS) showing the distances of each atom (r_o, r_c, r_s) from center of gravity.

Following the figure moments of OCS will be given by

$m_O r_O + m_C r_C = m_S r_S$ ……………………(27)

The moment of inertia will be

$I = m_O r_O^2 + m_C r_C^2 + m_S r_S^2$………………. (28)

Again we have $r_O = r_{CO} + r_C$ $\quad r_S = r_{CS} - r_C$ ……….(29)

Substituting equation 29 into equation 27 we get

$(m_C + m_O + m_S) r_S = m_S r_{CS} - m_O r_{CO}$…………………. (30)

$M r_S = m_S r_{CS} - m_O r_{CO}$……………………………. (31)

Where M is the total mass of the molecule. Now substituting equation 29 to equation 28 we get

$$I = m_O (r_{CO} + r_C)^2 + m_C r_C^2 + m_S (r_{CS} - r_C)^2$$
$$= M r_C^2 + 2 r_C (m_O r_{CO} - m_S r_{CS}) + m_O r_{CO}^2 + m_S r_{CS}^2$$

Substituting for r_C from equation 31 we get

$I = m_O r_{CO}^2 + m_S r_{CS}^2 - \frac{(m_O r_{CO} - m_S r_{CS})^2}{M}$…………………. (32)

If we consider the isotope of ^{16}OCS as ^{18}OCS then for mass of isotope of oxygen we may write $m_O{}'$ for m_O and by applying it in the equation 32 we will get the moment of inertia of the ^{18}OCS as

$I' = m'_O r_{CO}^2 + m_S r_{CS}^2 - \frac{(m'_O r_{CO} - m_S r_{CS})^2}{M'}$……………….. (33)

The analysis of the spectra of the parent ^{16}OCS and isotope ^{18}OCS molecules give I and I' from which the two unknown bond lengths r_{CO} and r_{CS} can be evaluated form the spectrum of the isotope. Point to be noted here that for isotopic substitution we have considered the bond length remains unaltered.

Self Assessment Question (SAQ) 15: The rotational constant for ^{12}H^{14}CN and ^{12}D^{14}CN are 1.4782 and 1.2077 cm^{-1}. Calculate the moments of inertia of these molecules and the internuclear distances of C-H and C≡N bonds.

9.7 Symmetric Top Molecules

Rotational energy levels of this type of molecules are more complicated than a linear molecule but due to the symmetry, the pure rotational spectra of symmetric top molecules are relatively simple. The condition for symmetric top molecule: $I_a \neq 0$ and $I_b = I_c$ .There are two directions of rotation in which the molecule might absorb or emit energy. They are one about the main symmetry axis and another one is perpendicular to this axis. As mentioned earlier, for the molecule CH_3Cl the main axis is C-Cl bond axis. So we need two quantum numbers (*K* and *J*) to describe the degree of rotation one for I_a and the other for I_b or I_c. The condition for the quantum number *K* is that it cannot be greater than *J*. *K* can be negative, so we can imagine positive and negative values of *K* to correspond with clockwise and anticlockwise rotation about the symmetry axis. In general *K* can take the values:

$K = J, J-1, J-2, \ldots\ldots 0, \ldots\ldots, -(J-1), -J$ …………….(34)

If we take the case of a rigid symmetric top molecule with no centrifugal distortion effect, the Schrödinger equation may be solved to give the allowed energy levels for rotation as

$\varepsilon_{J,K} = \frac{E_{J,K}}{hc} = BJ(J+1) + (A-B)K^2$ cm^{-1} ………..(35)

Where $B = \frac{h}{8\pi^2 c I_B}$ and $A = \frac{h}{8\pi^2 c I_A}$

The selection rule for the energy transitions are $\Delta J = +1$ and $\Delta K = 0$

If we apply the selection rule in equation 35 the frequency of transition will be

$$\bar{\nu}_{J,K\to J+1,K} = \varepsilon_{J+1,K} - \varepsilon_{J,K} = B[(J+1)(J+2) + (A-B)K^2 - [BJ(J+1) + (A-B)K^2]$$

$= 2B(J+1)$ cm^{-1} …………….(36)   with J=0,1,2,3…….

So we observe that the rotational spectrum is independent of K and hence rotational change about the symmetry axis do not give rise the rotational spectrum.

9.8 Asymmetric Top Molecules

These categories of molecules have three different moments of inertia and also have much more complicated rotational energy levels and spectra. No simple general expression for the energy and transition can be derived from this class of molecule. These classes of molecules generally treated by different approximation methods and so much complicated computation being required to deal these systems.

9.9 Instrumentation for Rotational Spectroscopy

The instrument required for rotation spectroscopy is known as microwave spectrometer. The instrument consists of source, monochromator, beam directors, sample and sample space, detector (Fig 9.13).

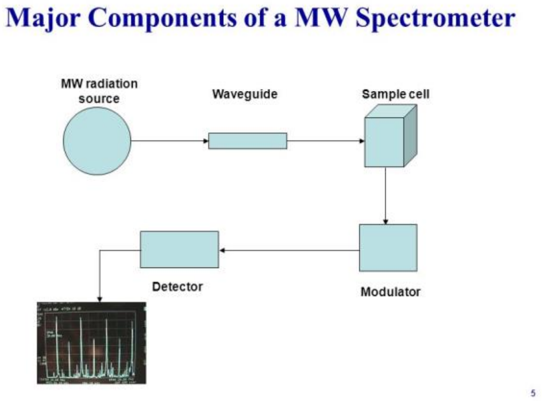

Fig 9.13. Schematic diagram of microwave spectrometer.

Source: Usual source used for microwave spectroscopy is klystron valve which acts as its own monochromator. In recent times Gunn diodes are used extensively as source since they need only 20 V power compared to the 300 V- 4000 V required for klystron source.

Beam director: This is achieved by using waveguides which is achieved by hollow tube of copper or silver with rectangular cross section inside which the radiation is confined.

Sample and sample space: Usually the sample are used in gaseous phase and is retained in a piece of evacuated waveguide by a very thin mica window.

Detector: Radio receiver is used as detector provided it can be tuned to the appropriate high frequency. Now simple crystal detector is also in use since it detects the radiation focused on it by the waveguide and the signal it gives is amplified for display on an oscilloscope.

9.10 Applications of Rotational Spectroscopy

Molecular structure: A whole molecular structure can be examined by rotational spectroscopy. Rotational constant can be obtained with a very high accuracy. Moment of inertia can be determined. The rotational spectroscopy can readily distinguish the presence of isotopes in a sample and can even detect the presence of different conformational isomers provided they have a different moment of inertia.

Dipole moment and nature of bond: Precise determination of electric dipole moment is possible from microwave spectroscopy by measurement of the Stark Effect (not discussed yet). Dipole moment can also throw light on the nature of the molecular bond present in the sample.

Chemical examination of interstellar space: Microwave spectroscopy has extended the analysis to the detection of simple stable molecules in space. Some 100 or molecules have been already been characterized by this process. Some of them are existence of water, ammonia and formaldehyde. Such observations are done by comparing the relative intensities of various rotational transitions of samples like ammonia which helps us to estimate the temperature of the interstellar material.

Microwave oven: Microwave oven is one of the major application areas of rotational spectroscopy for today's industry especially in the kitchen. Its mode of operation depends upon the absorption of the microwave radiation by the food in which it is bathed. Water molecule is the basic requirement of the microwave oven to operate. Water molecules present in food only absorb the microwave radiation and are raised to the higher rotational levels. The food molecules which are mainly biological in nature are too large in size to be able to rotate so they do not take part in rotational level transitions. With the presence of many rotational excited states, after absorption the excess rotational energies of the water molecules are re emitted as heat which is used to cook the food. In conventional oven, food is heated from outside and it is used till its food center has been raised to sufficiently high temperature which is time consuming process. For microwave heating, water molecules throughout the whole bulk food are excited and used to heat and cook the food. This is the reason why cooking time in microwave oven is lesser than normal oven.

It is essential to ensure that the door of microwave oven should be properly sealed under working so that no radiation is allowed to leak out.

Self Assessment Question (SAQ) 16: Microwave communication systems operate over long distances in the atmosphere. The same is true for radar which locates objects such as ships, aircrafts by microwave pulses they reflect. The region of molecular rotational spectra is microwave region of em radiation. Can you comment on why atmospheric gases do not absorb microwaves to any great extent?

Self Assessment Question (SAQ) 17: Microwave oven cannot be used to boil egg or to cook dry food. Why?

Self Assessment Question (SAQ) 18: A space probe was designed to seek CO in the atmosphere of Saturn by looking for lines in its rotational spectrum. If the bond length of CO is112.8 pm, at what wavenumber do the first three rotational transitions appear? What resolution would be needed to determine the isotopic ratio of ^{13}C to ^{12}C on Saturn by observing the first three ^{13}CO rotational lines as well? How could the experiment be extended to estimate the temperature of Saturn's atmosphere?

9.11 Summary

In this unit, you have studied about rotational spectroscopy. To present the clear understanding of rotational motion, some basic definitions like dipole moment, moment of inertia, energy, energy transition have been discussed. You have studied about the requirements of specific molecules to show rotational spectra. You have discussed about different categories of molecules like linear, symmetric top, asymmetric top in terms of their moment of inertia. You have also studied about the theories of rotational spectroscopy in detail for different linear molecular systems like diatomic rigid rotator, diatomic non-rigid rotator, polyatomic linear molecules, etc. You have also studied about the isotopic effect on the pure rotational spectra. In the unit, you have seen the characteristics of rotational spectra for symmetric and asymmetric top molecules. You have also studied the detailed instrumentation and techniques used to do rotational spectroscopy. You have been informed about different application areas of the use of rotational spectroscopy for the industry starting from your kitchen to interstellar space. Many solved examples are given in the unit to make the concepts clear. To check your progress, self assessment questions (SAQs) are given place to place.

9.12 Glossary

Spectroscopy – the study of the interaction between matter and electromagnetic radiation

Dipole moment- A *dipole moment* is the product of the magnitude of the charge and the distance between the centers of the positive and negative charges.

Moment of inertia- A quantity expressing a body's tendency to resist angular acceleration, which is the sum of the products of the mass of each particle in the body with the square of its distance from the axis of rotation.

9.13 References

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4. Molecular Spectra and Molecular Structure (I, II), G. Herzberg; D. Van Nostrand Comp. Inc, Princceton.

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9.14 Suggested Readings

1. Modern Physics, Beiser, Tata McGraw Hill

2. Optical Spectroscopy in Chemistry and Life Sciences, W. Schmidt; Wiley-VCH.

9.15 Terminal Questions

(Should be divided into Short Answer type, Long Answer type, Numerical, Objective type)

9.15.1 Short Answer type

1. How microwave oven works?

2. How many revolution per second does a CO molecule make when J=3? The CO bond length is 0.1131 nm.

3. Show that a substantial number of molecules of a gas are in excited rotational states at temperature 300K.

4. Mention the difference between rotational and vibrational spectra.

9.15.2 Long Answer type

1. Explain different types of rotator molecules in terms of their moment of inertia

2. Derive the rotational energy value for a diatomic rigid rotator by using the quantum mechanical model. Identify the transition frequency value for two rotational level transition.

3. Why the concept of non-rigid rotator is needed? What correction do you need to explain non-rigid rotator and why?

4. The energy levels of a rigid symmetric top molecule are given by
$\varepsilon_{J,K} = \frac{E_{J,K}}{hc} = BJ(J+1) + (A-B)K^2$ cm^{-1} .What are A, B, J, and K. State the selection rules for
allowed transitions.

5. Write notes on-

(i) Dipole moment (ii) Microwave oven (iii) Isotopic effect on rotational spectroscopy

9.15.2 Numerical type

1. Let the number of molecules in the first excited state are 98% of the number of molecules in the ground state at 23 ºC. Can one estimate the value of Rotational constant (*B*)?

2. Calculate the ratio of the number of molecules (N_J) in the rotational state *J=5 to J=0* in a
   Sample of HI at 300K. Use the moment of inertia of the HI molecule $4.31\text{x}10^{-47}$kg m^2.

3. Estimate the frequencies of the $J = 1 \rightarrow J = 2$ and $J = 2 \rightarrow J = 3$ rotational absorption lines in NO, whose molecules have the moment of inertia 1.65 x 10^{-46} kg.m^2.

4. The rotational constant for $H^{12}C^{14}N$ and $D^{12}C^{14}N$ are 1.4782 and 1.2077 cm^{-1} respectively. Calculate the moments of inertia of each molecule and bond lengths of C-H, C-D and $C \equiv N$ .Given the mass m_H=1.008 amu, m_D=2.014, m_C=12 amu, m_N=14.003 amu.

5. Consider a diatomic molecule as non – rigid rotator with rotational constant B=10.5 cm^{-1} and distortion constant D=$5.0\text{x}10^{-4}cm^{-1}$. Obtain vibrational frequency, and force constant of the molecule. Consider reduced mass of the molecule as $1.6\text{x}10^{-27}$Kg.

6. Three consecutive lines in microwave spectra are observed at 82.19 cm^{-1}, 123.15cm^{-1}, and 164 cm^{-1}. Obtain the value of the rotational constant and assign the *J* values between which the transition occurs for rotational line at 164 cm^{-1}.

7. Rotational and distortion constants of HCl molecule are 10.593 cm^{-1} and $5.3\text{x}10^{-4}$ respectively. If the force constant is 517.8 Nm^{-1} and vibrational frequency is 2995.2 $\text{x}10^2$ m^{-1}. Using these data can we obtain the reduced mass of the molecule? If yes, then find its value.

8. For ClF molecule, the bond length is 0.1630 nm and the centrifugal distortion is 10^{-4}B, where *B* is the rotational constant. Calculate the spacing between first four lines. Use atomic mass m_{Cl}= 35.45 amu and m_F= 19 amu.

UNIT 10 VIBRATIONAL SPECTRA

Structure

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10.1 Introduction

The atoms in a molecule do not remain in a fixed relative position, but vibrate about some mean position. A molecule may have many different modes of vibration. When sufficiently excited, a molecule can vibrate as well as it can rotate. So the vibrations of its atoms with respect to each other has an energy level spacing as we have already observed the rotational energy levels of molecules due to rotation of the atoms with respect to center of gravity. Transitions between these vibrational levels result vibrational spectra which give an insight into the discrete motion of the atoms in the molecular system. Vibrational frequencies of the molecule also help us to get valuable information regarding molecular structure, symmetry, bond length, inter and intramolecular interaction etc.

10.2 Objective

After studying this unit, you should be able to-

- define vibrational motion of atoms in molecule
- study the effect of vibrational motion on diatomic harmonic oscillator, anharmonic oscillator
- study the effects of vibration and rotation on molecule
- apply the laws vibrational spectroscopy for identifying different modes of normal vibrations in linear and nonlinear molecules
- apply the concept of vibrational spectroscopy to different infrared spectra of complex molecules
- learn to apply the knowledge of vibrational spectroscopy for different industrial applications

10.3 Slient Features Of Vibrational Spectra

For vibrational spectroscopy to be observed it is the vibration between atoms rather than rotation is important. The vibration gives rise to a **change in dipole moment** in the molecular system which results transitions between vibrational energy levels and give rise vibrational spectra. Vibrational energy states are separated by an energy interval of 10^4 Joule/mole. The molecular spectra arise from the transition between two vibrational energy states are observed in the infrared region of the electromagnetic spectrum with a wavelength range from 100 μm to 1 μm. Vibrational spectroscopy also known as infrared spectroscopy also. Let us discuss the vibrational spectra due to the change in dipole moment with an example. Consider linear carbon dioxide (CO_2) molecule. In CO_2, three atoms are arranged linearly with a small net positive charge on the carbon atom ($2\delta+$) and small negative charges on the oxygen atoms ($\delta-$) (Fig 10.1). If we consider the possibility of vibration, it can happen between two C=O bonds.

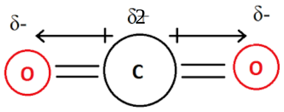


Fig10.1 Charge distribution in CO_2.

During the period of vibration between the atoms in CO_2 molecule as a whole, alternately stretching and compression of the C=O bonds happens simultaneously with respect to its center of gravity at C. For the symmetric stretching condition, both the C-O bonds on both sides of a central carbon atom stretched and compressed in equal amount with respect to C and so the resultant dipole moment remains zero throughout the whole vibration process (Fig 10.2). Since there is no change dipole moment is observed during "symmetric stretch", the particular vibration due to symmetric stretching mode is 'infrared inactive'.

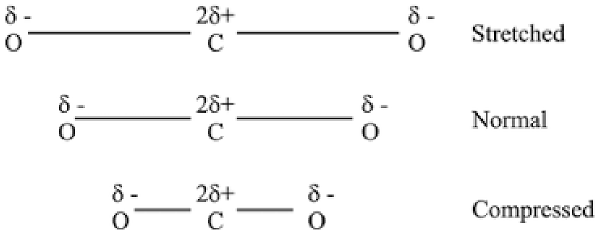


Fig10.2 Symmetric stretching vibration of CO_2 in terms of stretched and compressed mode with respect to center.

For antisymmetric stretching mode the amount of stretching or compression of both bonds are not equal and simultaneous. At the same time one bond stretches while the other is compressed or vice versa (Fig 10.3). As a result of this asymmetric stretching or compression, the total change in dipole moment for the whole CO_2 molecule shows a periodic alteration. Since a change in dipole moment exists for asymmetric stretching mode, the vibrations is thus 'infrared active'.

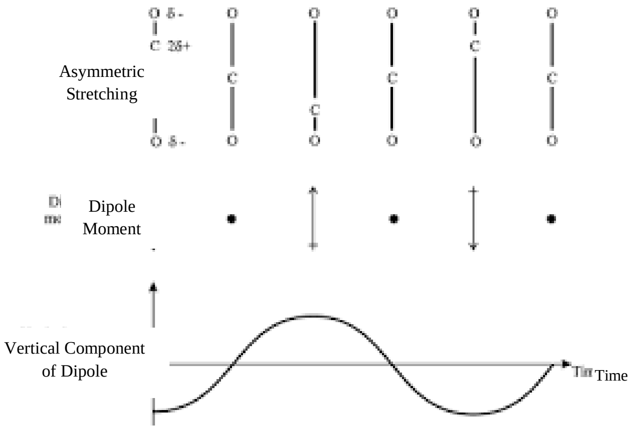


Fig10.3 Asymmetric stretching vibration of CO_2 in terms of stretched and compressed mode with respect to normal.

Another vibrational mode exists for this linear molecule which is bending mode. For bending mode also CO_2 shows change in dipole moment and so this mode also acts as 'infrared active' mode (Fig 10.4). We have to keep one point in mind that in neither of these vibrational motions does the center of gravity move. So change in dipole moment is the main requirement for the molecule to show vibrational or infrared spectroscopy. Homonuclear diatomic molecule has no change in dipole moment and so they are infrared inactive.

For molecular vibrational spectroscopy the boundaries of electromagnetic spectrum is known as Infrared region. The detail of this region is as follows:

In terms of frequency (ν): $3 \times 10^{12} - 3 \times 10^{14}$ Hz
In terms of wavelength (λ): $100\ \mu m - 1\ \mu m$
In terms of wavenumber ($\bar{\nu}$) : $100 - 10^{4}\ cm^{-1}$
In terms of energy (ε): $10^{3} - 10^{5}$ Joules/mole

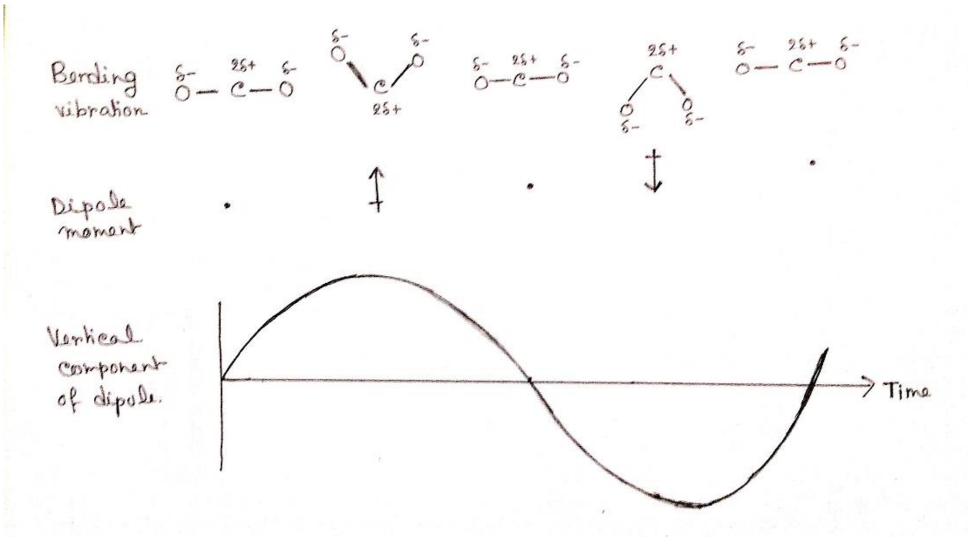


Fig10.4 Bending vibration of CO_2 and associated change in dipole moment with respect to normal.

10.4 Vibration Of Various Molecular Structures

10.4.1 Vibration of diatomic molecule

The simplest step to consider the possible assumption about the form of different vibrations is diatomic molecule. Let us start with the stable configuration of molecule. Two atoms in a stable diatomic molecule settle at an equilibrium internuclear distance (r_{eq}) when the balancing for attractive and repulsive forces appears between them. The repulsive force appears due to the repulsion between the positively charged nuclei of both atoms and between their negative electron clouds. The attractive force appears between the nucleus of one atom and electrons of the other. So squeezing the atoms more from their equilibrium position will generate repulsive force to rise rapidly, similarly pulling apart them will be resisted by the generation of attractive force. The restoring force exerted by the two atoms of the molecule on each other when they are displaced from their equilibrium position (r_{eq}) which is proportional to the change of the internuclear distance (r). The compression and extension of the bond length may follow the behavior of a spring which obeys Hook's law as

$f = -k(r - r_{eq})$………….. (1)

Where f is restoring force, k is the force constant, r is the distance of two atoms and r_{eq} is the mean internuclear distance or equilibrium distance.

Any attempt to disrupt r_{eq} or bond length requires an input energy as potential energy as described in equation (2) as

$V = \frac{1}{2}k(r - r_{eq})^2$……….. (2)

At the energy minimum, the internuclear distance is referred as the equilibrium distance r_{eq} or equilibrium bond length which can be described by a parabolic curve (red line) as Fig 10.5. For periodic motion each atom moves towards or away from each other so that the placement from the equilibrium position is the sine function of time. Such a motion of the two atoms can be reduced to the simple harmonic vibration of the single mass point about the equilibrium position. Such model is known as harmonic oscillator.

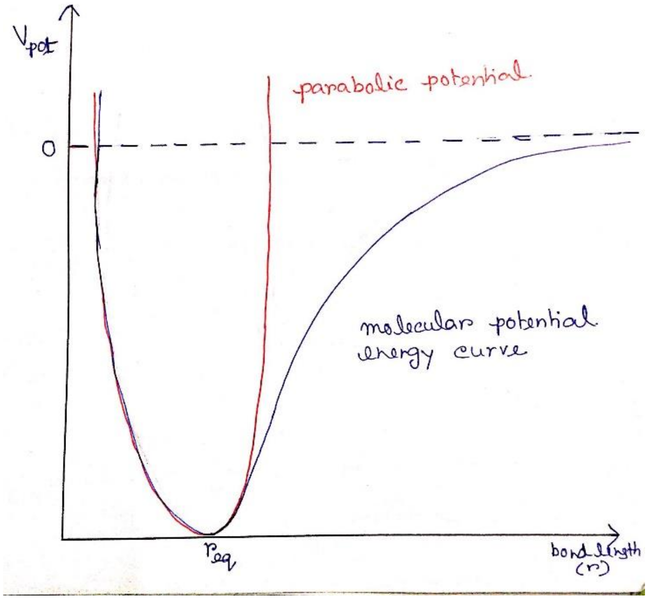


Fig10.5 Variation of Potential energy curve of diatomic molecule.

10.4.2 The harmonic oscillator

According to classical mechanics, a harmonic oscillator is defined as the mass point as mass (m) on which an acted force (f) is proportional to the distance (x) from the equilibrium position and is directed toward the equilibrium position. As force = mass x acceleration, so we may say

$$f = -kx = m\frac{d^2x}{dt^2} \text{………..} (3)$$

where k is the force constant. The solution of the differential equation 3 is well-known to us and can be expressed as

$$x = x_0 sin(2\pi\nu_{osc}t + \varphi) \text{…….} (4)$$

where x_0 is the amplitude of vibration and φ is the phase constant dependent on the initial conditions. The vibrational frequency ω_{osc} is given by equations 5a and 5b as

$$\omega_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \quad in\, Hz \text{………………..} (5a)$$

$$\bar{\omega}_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{m}} \quad in\, cm^{-1} \text{……………….} (5b)$$

Since force is negative derivative of potential energy V so we may express equation 2 as

$$V = \frac{1}{2}kx^2 = 2\pi^2 m{\omega_{osc}}^2 x^2 \text{…………..} (6)$$

This equation justifies the parabola nature (red line) of the potential energy curve in Fig 10.5.

Again we know that for diatomic molecule the restoring force is applied by the atoms on each other when they are forcefully displaced from their equilibrium position and the force is proportional to the change of r_{eq}. If we assume that this relation hold good for diatomic molecule then for mass m_1 and m_2 with their distances from r_1 and r_2 from the center of gravity (Fig 9.7 of unit 9), we can express the relations as

$$m_1\frac{d^2r_1}{dt^2} = -k(r - r_{eq})$$

$$m_2\frac{d^2r_2}{dt^2} = -k(r - r_{eq})$$

where r is the distance of two atoms and $r_{eq}=R$ is the mean internuclear distance or equilibrium distance. We can combine both the above equations as (by using equation 4 of unit 9)

$$\frac{m_1 m_2}{(m_1 + m_2)}\frac{d^2(r - r_{eq})}{dt^2} = -k(r - r_{eq}) \qquad since\ r_{eq}\ is\ constant.$$

$$\mu\frac{d^2(r - r_{eq})}{dt^2} = -k(r - r_{eq}) \dots\dots\dots\dots (7)$$

Equation 7 is identical with equation 3 of harmonic oscillator except that x is replaced by $(r - r_{eq})$, the change of internuclear distance from its equilibrium value. So we have reduced the vibration of two atoms of a molecule to the vibration of a single mass point μ whose amplitude equals to the change of internuclear distance of the molecule.

10.4.2.1 Energy levels of harmonic oscillator

If we assume the potential energy (V) of the two nuclei is given by equation 6 then the Schrödinger equation describing the motion of the representative particle in harmonic oscillator is given by

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2\mu}{h^2}\left(E - \frac{1}{2}kx^2\right)\psi = 0 \ldots\ldots\ldots\ldots\ldots (8)$$

Equation 8 gives a single valued, finite and continuous solution which vanish at infinity and do not exist for all Eigen values of E_v but exist only for a entrain quantized E_v values as

$$E_v = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\left(v + \frac{1}{2}\right) = h\omega_{osc}\left(v + \frac{1}{2}\right) \text{ Joules } \ldots\ldots\ldots\text{(9) with } v\text{=0,1,2,3}\ldots..$$

Where v is the vibrational quantum number. Converting the energy Eigen value in spectroscopic unit we get the energies of harmonic vibrator as

$$\varepsilon_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right)\bar{\omega}_{osc}\, cm^{-1} \ldots\ldots\ldots(10)$$

The values of equation 9 and 10 are the only energy values allowed by the quantum theory for the harmonic oscillator and so for the harmonically vibrating molecule. It should be noted that in contrast to the rigid rotator the state of lowest energy at $v=0$ does not have $E_v=0$ rather it has the value

$$E_0 = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\left(\frac{1}{2}\right) = \frac{1}{2}h\omega_{osc} \text{ Joules} \quad \text{with } \omega_{osc} \text{ in Hz} \quad \text{or}$$

$$\varepsilon_0 = \frac{1}{2}\bar{\omega}_{osc}\, cm^{-1} \qquad \text{With } \bar{\omega}_{osc} \text{ in cm}^{-1}\ldots\ldots\ldots\ldots\ldots(11)$$

So even in lowest vibrational state the vibrational energy is present. This energy $\frac{1}{2}\bar{\omega}_{osc}$ is known as zero point energy. Due to the existence of zero point energy, the diatomic molecule can never have zero energy value. As a result of that, the atoms can never be completely be at rest relative to each other. In spite of zero point vibration the state v=0 is known as vibration less state.

The prediction of zero point energy creates a basic difference between the quantum mechanical approach and classical approach to deal with molecular vibrations. Quantum mechanics insists that the molecule must always vibrate to some extent which justifies the existence of zero point energy. Classical mechanics has no objection to the molecule possessing no vibrational energy.

10.4.2.2 Spectrum of harmonic oscillator

The molecule with unlike or heteronuclear atoms in its equilibrium position always has a dipole moment. This dipole moment arises due to change in the internuclear distance. Example: HCl. Vibrational spectra will only be observed in heteronuclear molecules and not in homonuclear molecules since they don't have dipole moment or change in dipole moment. Example: N_2, O_2 etc. It is considered that the change in dipole moment with internuclear distance is linear. According to classical electrodynamics, the dipole moment changes with a frequency equal to the frequency of the mechanical vibration. This would lead to the emission of light of frequency ω_{osc} . Similarly the oscillator could be set in vibration by absorption of light of frequency ω_{osc}.

According to Quantum mechanics the emission of radiation takes place as a result of a transition of the oscillator from higher to lower state and absorption takes place for the transition of the oscillator from lower to higher state. The wavenumber (cm^{-1}) of emitted or absorbed light between two vibrational states is given by

$$\overline{\omega} = \frac{E_{v\prime}}{hc} - \frac{E_{v\prime\prime}}{hc} \text{ .... (12)}$$

Where v' and v'' are the vibrational quantum numbers of the upper and lower energy states. In order to determine which particular transition can actually occur we have to evaluate the expectation value of the density matrix (ρ) of the molecule. In your Quantum mechanics and Atomic and molecular physics courses you have already studied that the probability of transition from one quantum state $|\ n\ \rangle$to another quantum state $|m\ \rangle$ is given by

$$T_{nm} = \langle n|\rho|m\rangle \text{.......... (13)}$$

If $T_{nm} = \langle n|\rho|m\rangle \cong 0\ or\ \rightarrow 0$ then the transition is forbidden. If not then

$$T_{nm} = p\ \ with\ \ 0 < p < 1$$

So for harmonic oscillator the transition probability are zero except when p is between 0 and 1. If the two quantum or vibrational states are v' and v'' then the allowed transition will follow the selection rule for the vibrational quantum number as

$$\Delta v = v' - v'' = \pm 1 \text{ .... (14)}$$

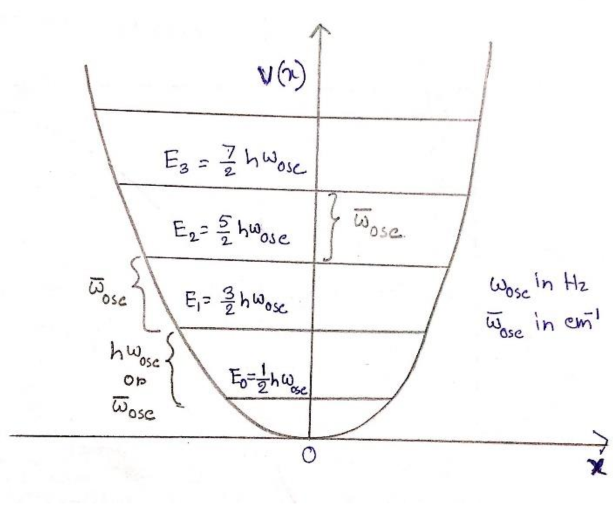
Applying the selection rule we can get the value of transition frequency for emission as

$$\overline{\omega}_{v+1\to v} = \varepsilon_{v+1} - \varepsilon_v = \left(v + 1 + \frac{1}{2}\right)\overline{\omega}_{osc} - \left(v + \frac{1}{2}\right)\overline{\omega}_{osc} = \overline{\omega}_{osc}\ \text{cm}^{-1}\text{.................(15)}$$

Similarly for absorption

$$\overline{\omega}_{v\to v+1} = \varepsilon_{v+1} - \varepsilon_v = \overline{\omega}_{osc}\ \text{cm}^{-1}$$

So the vibrational level transitions are equally spaced transitions between any two neighboring states which gives rise to same energy change (Fig 10.6).



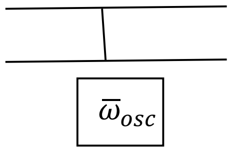


Fig10.6 Vibrational energy levels and allowed transition between them for harmonic oscillator model.

(Note: The frequency of the radiated light is equal to the frequency $\omega_{osc}(= c\overline{\omega}_{osc})$ of the oscillator.)

10.4.3 Diatomic molecule as Anharmonic oscillator

In real diatomic molecule the actual potential energy curve is not as simple parabola as it is for harmonic oscillator (Fig 10.5 (red one)). In an actual molecule when the two atoms are placed at larger distance from each other, the attractive force becomes zero and correspondingly the potential energy has a constant value as described in Fig 10.5 (blue line). The minimum of the curve reaches at equilibrium internuclear distance (r_{eq}). It its nearby points the potential energy curve can be represented approximately by a parabola. This is the reason why the model of harmonic oscillator represents the main characteristics of the vibrational spectrum very well.

If the bond between two atoms are stretched beyond a certain limit, the bond will break and the molecule will dissociates into two atoms. For small amplitude of stretching and compression of the bond length the bond may be considered as elastic, but for larger amplitude of stretching and compression of the bond length, tentatively for more than 10 percent change compared to the initial bond length, a complicated behavior of the potential energy curve appears. A purely empirical expression which fits the real potential energy curve of vibrating diatomic molecule is given by Morse function (Fig 10.7) was derived by P.M. Morse as

$$V(r) = D_{eq}\left[1 - exp\left\{a\left(r_{eq} - r\right)\right\}\right]^2 \text{ ....(16)}$$

Where D_{eq} is the dissociation energy, a is the constant for a given molecule, r_{eq} is the equilibrium internuclear distance corresponds to minimum $V(r)$.

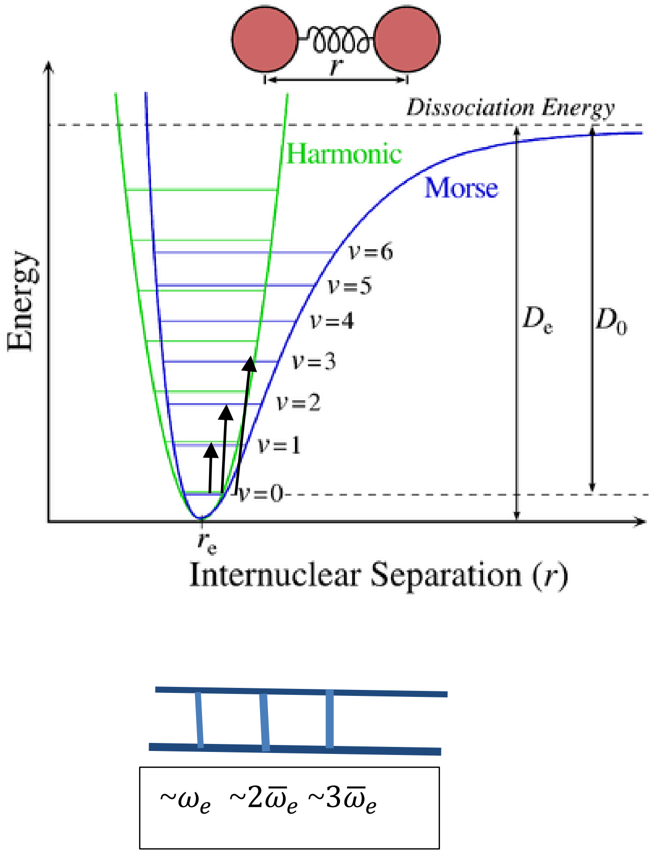


Fig10.7 The vibrational energy levels for harmonic and anharmonic oscillator and some transitions.

If we use the potential of equation 16 in the Schrödinger equation 8 and solve the newly formed Schrödinger equation of anharmonic oscillator we get the allowed vibrational energy eigen values corresponds to different energy levels as

$$\varepsilon_v = \frac{E_v}{hc} = \left(v+\frac{1}{2}\right)\overline{\omega}_e - \left(v+\frac{1}{2}\right)^2 x_e\overline{\omega}_e + \left(v+\frac{1}{2}\right)^3 y_e\overline{\omega}_e \; cm^{-1} \qquad \ldots\ldots\ldots(17)$$

with v= 0,1,2,3…..

Where $\overline{\omega}_e = \frac{\omega_{osc}}{c}$ is considered as the equilibrium oscillation frequency (expressed in wave number, we will describe about it in later section) of the anharmonic system, x_e and y_e are the anharmonicity constants which are very small and positive for bond stretching vibrations. So retaining only up to first anharmonic terms the equation (17) will become

$$\varepsilon_v = \frac{E_v}{hc} = \left(v+\frac{1}{2}\right)\overline{\omega}_e - \left(v+\frac{1}{2}\right)^2 x_e\overline{\omega}_e \; cm^{-1} \ldots\ldots\ldots\ldots\ldots (18)$$

as x_e is positive the effect of this anharmonicity is to crowd more closely the vibrational levels with increasing value of *v*. Some of these levels are shown in Fig 10.7. It should be mentioned that equation 18 is an approximation only as we can consider more precise expressions of energy levels also with rapidly diminishing magnitudes. These terms are only important for higher values of *v*. We can rewrite the equation 18 as

$$\varepsilon_v = \bar{\omega}_e \left\{1 - x_e\left(v + \frac{1}{2}\right)\right\}\left(v + \frac{1}{2}\right)\ cm^{-1} \ldots\ldots\ldots\ldots\ldots (19)$$

If we compare equation 18 with equation 10 of harmonic oscillator we get

$$\bar{\omega}_{osc} = \bar{\omega}_e \left\{1 - x_e\left(v + \frac{1}{2}\right)\right\}\quad cm^{-1} \ldots\ldots. (20)$$

So we may conclude that anharmonic oscillator behaves like the harmonic oscillator but with a oscillation frequency which decreases steadily with increasing *v*.

If we consider a vibrational energy state with $v=-1/2$, then according to equation 19, $\varepsilon=0$. It means the molecule will be at equilibrium point with zero vibrational energy. Then the oscillation frequency will be

$$\bar{\omega}_{osc} = \bar{\omega}_e\quad cm^{-1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (21)$$

For ground state (v=0), the oscillation frequency and zero point energy for anharmonic oscillator
will be

$$\bar{\omega}_0 = \bar{\omega}_e\left(1 - \frac{1}{2}x_e\right)\quad cm^{-1}\quad \text{And}\quad \varepsilon_0 = \frac{1}{2}\bar{\omega}_e\left(1 - \frac{1}{2}x_e\right)\ cm^{-1}\ \ldots\ldots (22)$$

So we see that zero point energy of anharmonic oscillator slightly differ from that of harmonic oscillator.

10.4.3.1 Spectrum of anharmonic oscillator

For anharmonic oscillator the selection rules are considered as

$$\Delta v = v' - v'' = \pm 1, \pm 2, \pm 3, \pm 4 \ldots\ldots.. \qquad \ldots\ldots. (23)$$

Thus the selection rules are same as the harmonic oscillator with some additional possibility of larger jumps between the energy levels like ±2, ±3….etc. Though the other possibilities of transitions are allowed but applications of Boltzmann distribution can show that the additional possibilities have rapidly diminishing probability and so these transitions have less observable intensity. Usually spacing between two lowest vibrational levels comes out to be of the order of 10^3cm^{-1}. At room temperature at around $T=300K$, if we apply Boltzmann distribution we can get

$$\frac{N_{v=1}}{N_{v=0}} = exp\left\{-\frac{6.63x10^{-34}x3x10^{10}x10^3}{1.38x10^{-23}x300}\right\} = \exp(-4.8) = 0.008\ldots\ldots\ldots\ldots(24)$$

So we can see that $v=1$ state has only about 0.01 per cent of the ground state population under room temperature. So to a very good approximation we need to consider only transitions originating from $v=0$ state. We can ignore all transitions originating at $v=1$ or more. The frequencies of first few possible transitions are described as (Fig 10.7):

1. **Fundamental absorption with considerable intensity:** ***v* = *0*→ *v* = *1*,** $\boldsymbol{\Delta v = \pm 1}$
   $\bar{\omega}_{0\rightarrow 1} = \Delta\varepsilon = \varepsilon_{v=1} - \varepsilon_{v=0}$
   $= \left(1+\frac{1}{2}\right)\bar{\omega}_e - \left(1+\frac{1}{2}\right)^2 x_e\bar{\omega}_e - \left\{\frac{1}{2}\bar{\omega}_e - \left(\frac{1}{2}\right)^2 x_e\bar{\omega}_e\right\}$
   $= \bar{\omega}_e(1-2x_e)$ cm^{-1} ……………….. (25)
2. **First overtone with small intensity:** ***v* = *0* → *v* = *2*,** $\boldsymbol{\Delta v = \pm 2}$
   $\bar{\omega}_{0\rightarrow 2} = \Delta\varepsilon = \varepsilon_{v=2} - \varepsilon_{v=0}$
   $= \left(2+\frac{1}{2}\right)\omega_e - \left(2+\frac{1}{2}\right)^2 x_e\bar{\omega}_e - \left\{\frac{1}{2}\bar{\nu}_e - \left(\frac{1}{2}\right)^2 x_e\bar{\omega}_e\right\}$
   $= 2\bar{\omega}_e(1-3x_e)$ cm^{-1} ………………… (26)
3. **Second overtone with negligible intensity:** ***v* = *0* →*v* = *3*,** $\boldsymbol{\Delta v = \pm 3}$
   $\bar{\omega}_{0\rightarrow 3} = \Delta\varepsilon = \varepsilon_{v=3} - \varepsilon_{v=0}$
   $= \left(3+\frac{1}{2}\right)\bar{\omega}_e - \left(3+\frac{1}{2}\right)^2 x_e\bar{\omega}_e - \left\{\frac{1}{2}\bar{\omega}_e - \left(\frac{1}{2}\right)^2 x_e\bar{\omega}_e\right\}$
   $= 3\bar{\omega}_e(1-4x_e)$ cm^{-1} ……………… (27)
   And so on…….

The three transitions are shown in Fig 10.7. As $x_e \approx 0.01$ is very small the three spectral frequencies fundamental, first overtone , second overtone may be considered as $\bar{\omega}_e, 2\bar{\omega}_e, 3\bar{\omega}_e$. By measurement of these frequencies one can easily evaluate x_e and $\bar{\omega}_e$.

Till now we have ignored the transition from *v=1* to higher states. If the temperature of the sample is high or if the vibration has a particularly low frequency means *v=1* level is not far from *v=0* level, the population of *v=1* state may be appreciable. The wave number of the transition from *v=1* to is given by

$$\bar{\omega}_{1\rightarrow 2} = \Delta\varepsilon = \varepsilon_{v=2} - \varepsilon_{v=1}$$

$$= \left(2+\frac{1}{2}\right)\bar{\omega}_e - \left(2+\frac{1}{2}\right)^2 x_e\bar{\omega}_e - \left[\left(1+\frac{1}{2}\right)\bar{\omega}_e - \left(1+\frac{1}{2}\right)^2 x_e\bar{\omega}_e\right]$$

$= \bar{\omega}_e(1-4x_e)$ cm^{-1} ……………(28)

This is very weak absorption frequency and it will be found close to and at slight lower wavenumbers than the fundamental frequency. Such weak absorptions bands are called as hot bands since high temperature is the main condition for their appearance. A hot band will increase in intensity as the temperature of the sample is increased.

10.5 Diatomic Vibrating Rotator

Till now we have considered the rotation and vibration of the molecule quite separately. However rotation and vibration can take place simultaneously and in fact the observed fine structure of the rotation bands suggests that rotation and vibration in molecule occurs simultaneously. So we will consider a model in which simultaneous rotation and vibration takes place simultaneously. The model is known as vibrating rotator or rotating oscillator.

The energies of rotations and vibrations are very different so we may say that a diatomic molecule can execute rotations and vibrations quite independently. The approximation which considers both motion is known as Born –Oppenheimer approximation. The approximation considers that combined rotational-vibrational energy is simply the sum of separate energies as

$E_{total} = E_{rot} + E_{vib}$ Joules………………… (29)

$\varepsilon_{total} = \varepsilon_{rot} + \varepsilon_{vib}$ cm^{-1} …………………......(30)

$\varepsilon_{J,v} = \varepsilon_J + \varepsilon_v$

Substituting the values of ε_J and ε_v from equation 23 of unit 9 and equation 18 of unit10 we get

$\varepsilon_{J,v} = \varepsilon_J + \varepsilon_v$

$= BJ(J+1) - DJ^2(J+1)^2 + \left(v+\frac{1}{2}\right)\bar{\omega}_e - \left(v+\frac{1}{2}\right)^2 x_e\bar{\omega}_e$ cm^{-1} ……… (31)

Where *J= 0,1,2…..* and *v= 0,1,2…..*

The selection rules for the combined notation will be same as that of individual notation as

$\Delta v = \pm1, \pm2, \pm3, \pm4 \ldots\ldots..$ and $\Delta J = \pm1$ …………(32)

Now consider the vibrational transition for $\Delta v = \pm1$ means transition from *v=0→v=1*. Also assume that *B* and *D* are same for both the states. Let us consider upper energy state by single prime and lower energy state by double prime. Then we get

$\bar{\omega} = \Delta\varepsilon_{J,v} = \varepsilon_{J',v=1} - \varepsilon_{J'',v=0}$

$= B[J'(J'+1) - J''(J''+1)] - D\left[J'^2(J'+1)^2 - J''^2(J''+1)^2\right]$

$+\left(1+\frac{1}{2}\right)\bar{\omega}_e - \left(1+\frac{1}{2}\right)^2 x_e\bar{\omega}_e - \left\{\frac{1}{2}\bar{\omega}_e - \left(\frac{1}{2}\right)^2 x_e\bar{\omega}_e\right\} cm^{-1}$

$= \bar{\omega}_e(1-2x_e) + B(J'-J'')(J'+J''+1) - D\left[J'^2(J'+1)^2 - J''^2(J''+1)^2\right] cm^{-1}$……(33)

Using the selection rule $\Delta J = +1 = J' - J'' = +1$ we get *R* branch frequencies as

$\bar{\omega}_R = \bar{\omega}_0 + 2B(J''+1) - 4D(J''+1)^3\ cm^{-1}\ \ with\, J'' = 0,1,2,3 \ldots\ldots\ldots$……..(34)

Again using the selection rule $\Delta J = -1 = J' - J'' = -1$ we get P branch frequencies as

$\bar{\omega}_P = \bar{\omega}_0 - 2B(J'+1) - 4D(J'+1)^3\ cm^{-1}\ \ with\, J' = 0,1,2,3 \ldots\ldots\ldots$…………(35)

Where we have used $\bar{\omega}_0 = \bar{\omega}_e(1 - 2x_e)$ which is the frequency of $v=0 \rightarrow v=1$ transition and known as band center or band origin or Q branch line. So the lines corresponding to $\Delta J = +1$ are called R Branch lines and lines corresponding to $\Delta J = -1$ are called P Branch lines. This notation is the part of the sequence like O, P, Q, R, S corresponds to $\Delta J = -2, -1, 0, +1, +2$ respectively.

Equations 34 and 35 may be combined into a single equation as

$$\bar{\omega}_{P,R} = \bar{\omega}_0 + 2Bm - 4Dm^3\ cm^{-1} \quad with\, m = \pm1, \pm2, \pm3 \dots\dots\dots \qquad \text{............(36)}$$

Where m replaces $J''+1$ in equation 34 and $J'+1$ in equation 35. It takes positive values for R branch lines and negative values for P branch lines. Usually D is extremely small so we may ignore D. Then equation 36 will be

$$\bar{\omega}_{P,R} = \bar{\omega}_0 + 2Bm\ cm^{-1} \quad with\, m = \pm1, \pm2, \pm3 \qquad \text{........(37)}$$

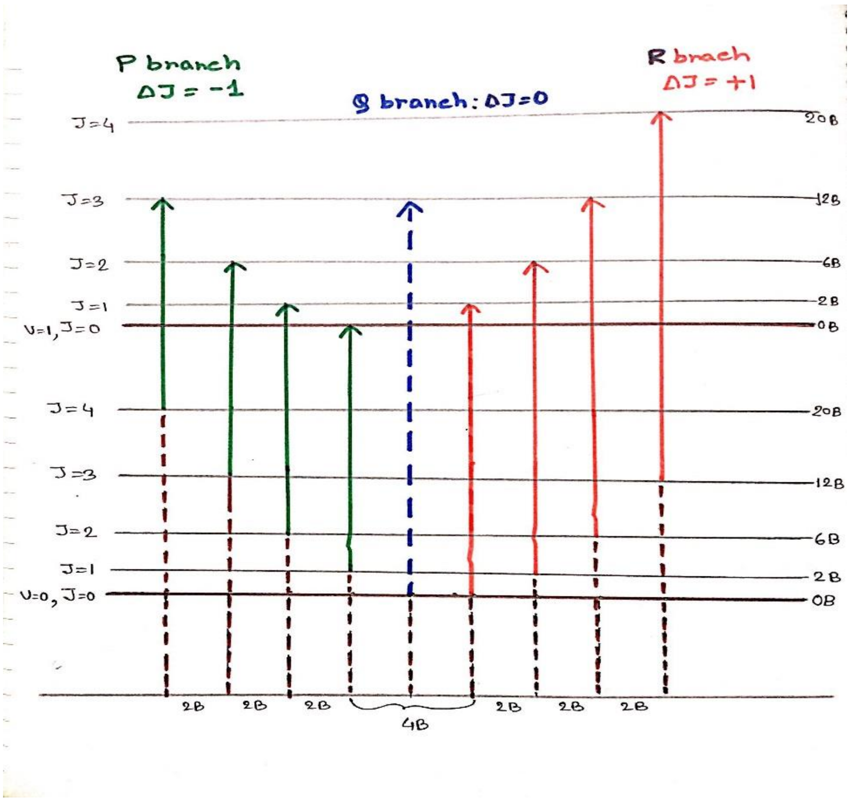


Fig10.8 Some transition for vibrating rotator between the energy levels with vibrational states *v=0* and *v=1*.

The vibration-rotation spectrum according to equation 37 will have both P and R branch lines each consisting of equally spaced lines with separation *2B*. The P branch lines will appear at the lower frequency side whereas R branch lines will appear at higher frequency side of band center. The spectrum is shown in Fig 10.8.

By analysing the spectrum one can calculate the value of band center and *B* from the spacing between lines. From *B* value one can calculate the value of bond length and force constant.

10.5.1 The fine structure of rotating vibrator spectrum-Breakdown of Born-Oppenheimer approximation

A detailed investigation of the experimental absorption band shows that the spacing between the rotational lines decreases as the frequency increases. So far we have assumed that vibration and rotation proceed independently without interaction. So constant rotational spacing *2B* should appear between the lines of *P* and *R* branches. It is a fact that a molecule vibrates 10^3 times during a course of single rotation. So it is a proven fact that bond length also changes during the rotation. Since bond length changes, so moment of inertia and *B* value also changes. For simple oscillator motion due to fixed equilibrium bond length it will not vary with vibrational energy (Fig 10.5). B is proportional to $1/r^2$. In real system i.e. in anharmonic oscillator, an increase in vibrational energy is accompanied by an increase in bond length with increase in vibrational amplitude and hence the value of B is dependent on the vibrational quantum number v. So B varies even more with the vibrational energy. So we may say that since r_{eq} increases with the vibrational energy, *B* is smaller in the upper vibrational state than in the lower. We can express the rotational constant as

$$B_v = B_e - \alpha\left(v + \frac{1}{2}\right) \ldots\ldots\ldots\ldots\ldots (38)$$

Where B_v is the rotational constant in vibrational level, B_e is the equilibrium rotational constant and α as the small positive constant for each molecule under consideration. If we restrict our discussion to the fundamental vibrational change means the change between $v=0 \rightarrow v=1$ vibrational energy levels, considering the respective *B* values as B_0 and B_1 with $B_0 > B_1$ we can get the transition frequency as

$$\bar{\omega} = \Delta\varepsilon_{J,v} = \varepsilon_{J',v=1} - \varepsilon_{J'',v=0}$$

$$= \bar{\omega}_e(1 - 2x_e) + B_1J'(J'+1) - B_0J''(J''+1)$$

$$= \bar{\omega}_0 + B_1J'(J'+1) - B_0J''(J''+1)\ \text{cm}^{-1} \ldots\ldots\ldots\ldots\ldots (39)$$

Again we have two conditions. Same as previous case for *R* branch, $\Delta J = +1 = J' - J'' = +1$

$$\bar{\omega}_R = \bar{\omega}_0 + B_1(J''+1)(J''+2) - B_0J''(J''+1)$$

$$= \bar{\omega}_0 + (J''+1)(B_1 + B_0) + (B_1 - B_0)(J''+1)^2\ cm^{-1} \quad with\, J'' = 0,1,2,3 \quad \ldots\ldots (40)$$

For *P* branch, $\Delta J = -1 = J' - J'' = -1$

$\bar{\omega}_P = \bar{\omega}_0 - (J' + 1)(B_1 + B_0) + (B_1 - B_0)(J'' + 1)^2\ cm^{-1}\ \ with\, J' = 0,1,2,3 \dots\dots\dots$ ….. (41)

If we combined equations 40 and 41 we get

$$\bar{\omega}_{P,R} = \bar{\omega}_0 + (B_1 + B_0)m + (B_1 - B_0)m^2\ cm^{-1}\ \ with\, m = \pm 1, \pm 2, \pm 3 \dots\dots\dots \qquad \dots\dots (42)$$

Where m is positive value for *R* branch lines and negative value for *P* branch lines. If $B_1 = B_0$ then equation 42 reduces to equation 37. For the case $B_1 < B_0$ then $(B_1 - B_0)m^2$ is always negative irrespective of the sign of m and its magnitude increase as m increases. As the first two terms are positive so the presence of this term is to crowd the rotational lines of the *R* branch with increasing m values. While for *P* branch lines the second and third terms are negative and so the lines become more widely spaced (Fig 10.9).

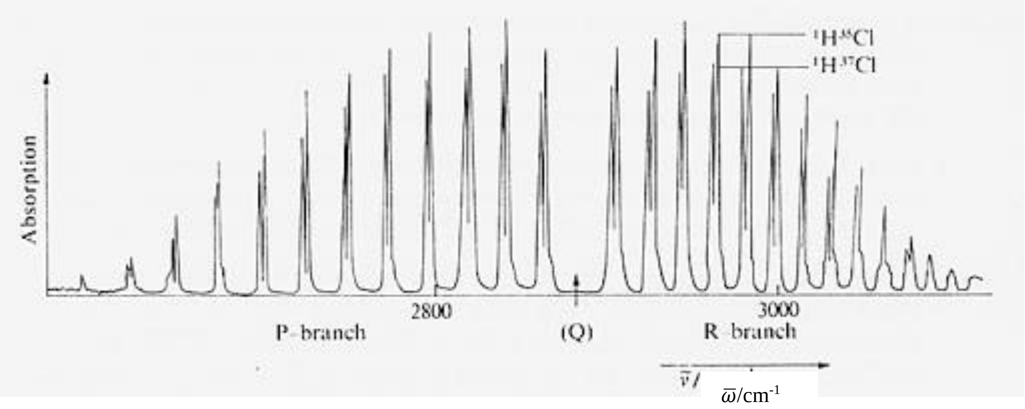


Fig10.9 P and R branch lines and their spacing between the lines in HCl molecule.

10.6 Vibbbrations of Polyatomic Molecule

A molecule having n atoms has *3n* degrees of freedom. The translational movement uses 3 and rotational movement uses 3 of *3n* degrees of freedom. So a nonlinear of atoms of n atoms has *3n-6* fundamental vibrations. For linear molecule since there is no rotation about the bond axis it will only have *3n-5* fundamental vibrations. Again for both the cases since molecules with n atoms has (*n-1*) bonds between the atoms, *n-1* number of the vibrations are for bond stretching motions. The other *2n-5* number of vibrations for non-linear molecule and *2n-4* vibrations for linear molecule are for bending motions. Let us consider two cases one for linear polyatomic molecule (CO_2) and other for non-linear polyatomic molecule (H_2O).

10.6.1 Fundamental vibrations for H_2O

H_2O is a non-linear triatomic molecule. For this according to previous mentioned rule there must be *3n-6 = 3* allowed fundamental vibrational motions. The three vibrational motions are referred as normal modes of vibrations. The three normal modes are: symmetric stretching (ω_1), asymmetric stretching (ω_3) and symmetric bending (ω_2).

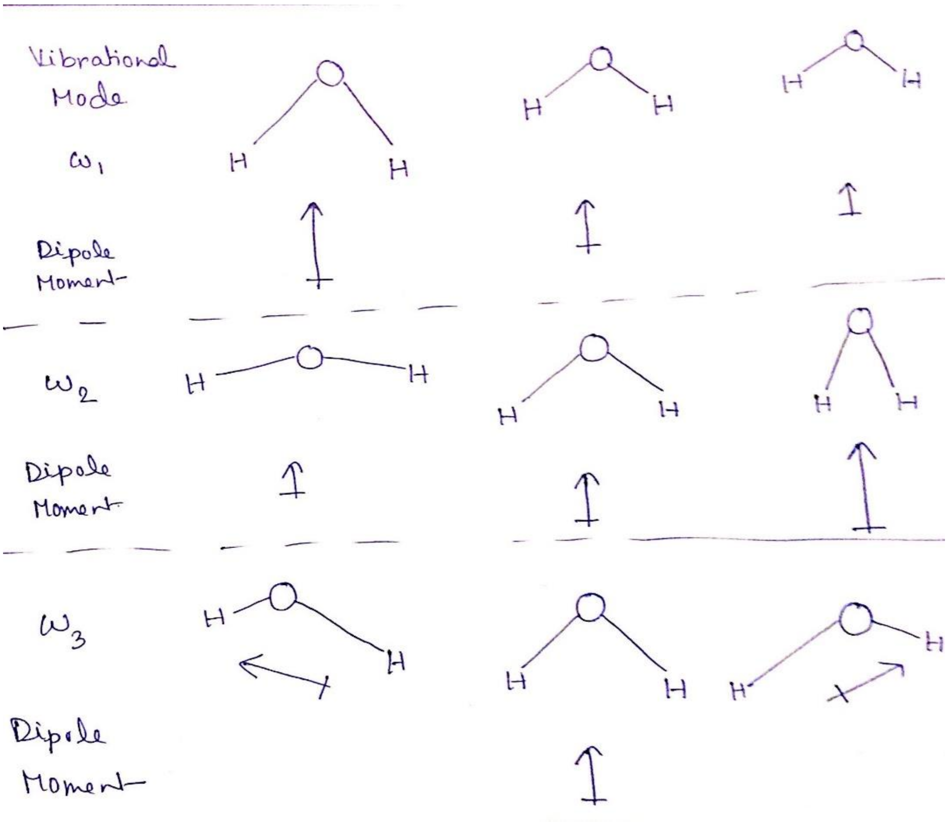
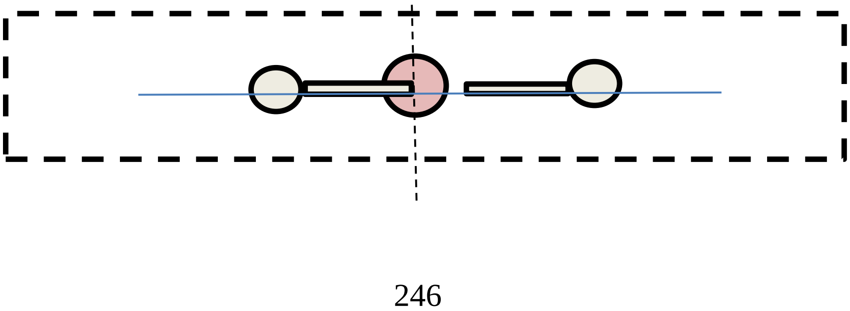


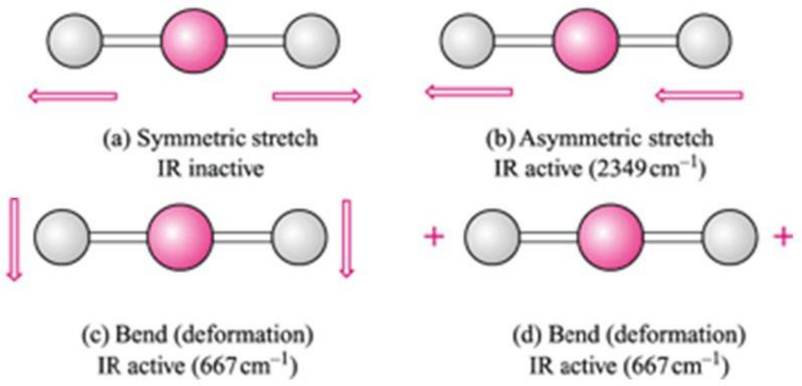
Fig10.10 Vibrational modes of water: symmetric stretching (ω_1), asymmetric stretching (ω_3), symmetric bending (ω_2)

In order to be infrared active there must be change in change in dipole moment during the vibrations. According to fig 10.10 each mode has a change in dipole moment so for H_2O molecule all modes are infrared active.

10.6.2 Fundamental vibrations for CO_2

CO_2 is a linear molecule and so it has 4 normal vibrations. For this molecule there are two different sets of symmetry axes. There is an infinite number of two fold axes. There is an infinite number of two fold axes (C_2) passing through the carbon atom at right angle to the bond direction. There is a ∞ fold axis (C_∞) passing through the bond axis itself.





(a) Symmetric stretch
IR inactive

(b) Asymmetric stretch
IR active (2349 cm^{-1})

(c) Bend (deformation)
IR active (667 cm^{-1})

(d) Bend (deformation)
IR active (667 cm^{-1})

Fig10.11 Vibrational modes of CO_2: symmetric stretching (ω_1), asymmetric stretching (ω_3), symmetric bending (ω_2).

Symmetric stretching mode produces o change in dipole moment so this vibtational mode is infrared inactive. Rest two modes are infrared active (Fig 10.11).

10.7 Isotope Effect

For isotopic molecules that is molecules that differ only by the mass of one or both of the nuclei but not by their atomic number, the vibrational frequencies are observed to be different. Assuming harmonic vibrations the vibrational frequency ω_{osc} is given by as equation 5 we can express

$$\omega_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad in\ Hz$$

The force constant k since it is determined by the electronic motion only, is exactly the same for different isotope molecules. But the reduced mass μ will be different for different isotopes. So if we try with the superscript i which distinguish an isotope molecule from the ordinary molecule then we have

$$\frac{{\omega_{osc}}^{i}}{\omega_{osc}} = \sqrt{\frac{\mu}{\mu^{i}}} = \rho \ \ldots\ldots. (43)$$

The behavior of isotopic molecule has a smaller frequency. This can be easily visualized if we consider that the larger of mass hanging on a spring, then is the smaller is its vibrational frequency. If the superscript i refers to the heavier isotope then the constant ρ will be smaller than 1. The values of ρ for the isotopic pairs $^{1}H^{35}Cl$ and $^{1}H^{37}Cl$ are 0.99924 and 0.71720. If we substitute equation 43 into equation 10 as

$$\varepsilon_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right)\overline{\omega}_e \ \ldots\ldots\ldots (10)$$

We find for the vibrational levels of two isotope molecules for the case of harmonic oscillators

$$\varepsilon_v = \left(v+\tfrac{1}{2}\right)\bar{\omega}_e \qquad {\varepsilon_v}^i = \left(v+\tfrac{1}{2}\right){\bar{\omega}_e}^i = \rho\bar{\omega}_e\left(v+\tfrac{1}{2}\right) \quad \ldots\ldots\ldots\ldots\ldots (44)$$

If anharmonicity is taken into account the calculation become more complicated and to solve the energy levels we need the applicability of some very good approximation method. After application of such approximations the energy values will be obtained as

$$\varepsilon_v = \frac{E_v}{hc} = \left(v+\tfrac{1}{2}\right)\bar{\omega}_e - \left(v+\tfrac{1}{2}\right)^2 x_e\bar{\omega}_e + \left(v+\tfrac{1}{2}\right)^3 y_e\bar{\omega}_e + \cdots$$

$${\varepsilon_v}^i = \left(v+\tfrac{1}{2}\right){\bar{\omega}_e}^i = \rho\bar{\omega}_e\left(v+\tfrac{1}{2}\right) - \rho^2 x_e\bar{\omega}_e\left(v+\tfrac{1}{2}\right)^2 + \rho^3 y_e\bar{\omega}_e\left(v+\tfrac{1}{2}\right)^3 + \cdots \quad \ldots\ldots\ldots (45)$$

or in other words we may write

$${\bar{\omega}_e}^i = \rho\bar{v}_e, \quad {\bar{\omega}_e}^i {x_e}^i = \rho^2 x_e\bar{\omega}_e, \quad {\bar{\omega}_e}^i {y_e}^i = \rho^3 y_e\bar{\omega}_e \ldots\ldots\ldots\ldots (46)$$

For isotopes the separations of the vibrational energy levels increase with the increasing *v* values. The energy level of the higher isotope always lie higher than those of the heavier.

10.8 Instrumentation for Vibratioanl Spectroscoy

Infrared spectroscopy is generally divided into three regions- the near IR region, mid IR region and far IR region. The essential components of the IR spectrometer are source, fore optics, monochromator, and beam directors with amplifier, sample, and detector. The block diagram of double beam IR spectrometer is shown in Fig 10.12.

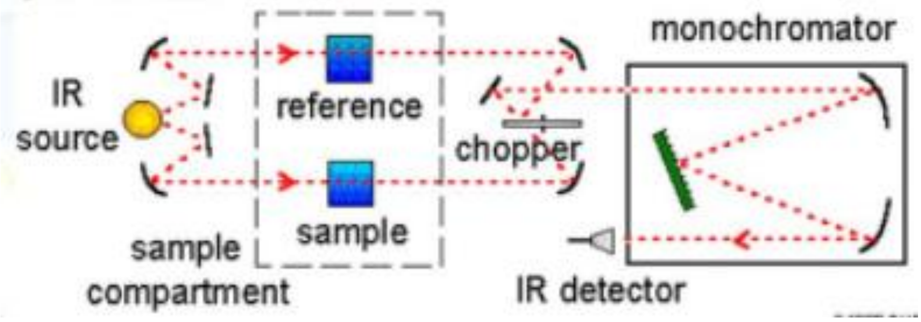


Fig 10.12. Schematic diagram of double beam IR spectrometer.

In double beam instrument the beam is splitted into two parts one is directed through the sample and the other is directed through the reference sample. The two beam are then compared either continuously or alternatively many times in a second. So in double beam instruments, the fluctuations in the source intensity, detector response and amplifier gain are compensated by observing the sample to reference signal ratio.

Source: The source is always which maintained at red or white light. The most commonly used sources are the globar filament and the Nernst glower. The Nernst glower consists of a spindle of rare earth oxide (thorium, cesium or zirconium) of about 2.5 cm long and 0.25 cm diameter with a peak around 1.4 μm (7100 cm^{-1}). The Nernst requires to be preheated before it will emit, but once red-heat is reached the temperature is maintained by the current. The globar is a low resistance rod of silicon carbide with black body peak between 1.8 to 2.0 μm (5500-5000cm^{-1}). It is more useful in longer wavelengths.

Fore optics: The fore optics consists of mirrors aluminized or silvered on their surfaces, and rotating chopper. Mirrors divide the source radiation into two equivalent beams of which one passes through the sample and the other passes through an equivalent path and is called the reference beam. The two beams meet at the rotating chopper. The rotating chopper alternately allows the sample beams through the spaces or reflects the reference beam with a predetermined period.

Monochromator: Monochromator splits the polychromatic radiation into its component wavelengths. It is achieved by using prisms or grating or both. Rock salt prisms usually used as monochromator for the region 650-4000 cm^{-1}.

Detector: Thermopiles, bolometers and Golay cells are used as detectors. The IR detectors measure the radiant energy by its heating effect. Two main types of sensing are used for detection. One sensing the heating effect of the radiation and the other depending on the photoconductivity. For both cases greater the effect at a given frequency, greater is the transmittance of the sample at that frequency. The detector does not show any signal when the energy transmitted by reference and sample cells are equal. If the sample absorbs radiation, there will be an inequality in two beams and a signal is produced. The signal is then fed to a gain amplifier which amplifies the low intensity signal to a useable level with minimum thermal and electrical noise.

Sample: The sample is held between plates of polished mineral salt rather than glass. Pure liquid samples are studied in thickness of about 0.01mm while solution should be at the order of 0.1-10 mm thickness. Gas samples are placed at pressure of up to 1 atm and are contained in long glass cell of 5 to 10 cm closed at their ends with rock salt windows. Recording of IR spectra of solid samples are more difficult because the solid particles reflect and scatter the incident radiation and so the transmittance becomes low. For solid samples three common techniques are used in recording the IR data. They are:

- **Mull Technique** = If the solid cannot be dissolved in a suitable solvent, it is best examined by grinding it very finely in paraffin oil (nujol) and then forming a suspension or mull. This mull can then held between salt plates in the same way as pure liquid of solvent. Here the main constraint condition is that refractive index of the sample liquid and its solid phase should not be very different otherwise the scattering will be high. For best result the sample particles must be less than that of the wavelength of radiation used.
- **Pellet Technique** = In this technique for handling solids, the sample should be grinded very finely with potassium bromide. Under high pressure this materials will flow

slightly and so the mixture can usually be pressed into a transparent disk. This may then be placed directly in the IR beam in a suitable holder. The main disadvantage of this method is that anomalous spectra may result from physical and chemical changes induced during grinding. A common change of this type is the absorption of water from atmosphere.

- **Solid films** = Spectra of solids may also be recorded by depositing a thin film of a solid on the suitable window material. A concerned layer of solution of the substance is allowed to evaporate slowly on the window material forming a thin uniform film. By changing the concentration thickness of the film can be adjusted.

Recorder: The amplified signal from the detector is moved to an attenuator which cuts down the radiation coming out of the reference beam until energy balance is restored. This is achieved by a motor which droves the attenuator into the reference beam when an absorption band is encountered and out of the beam when the band is passed over.

10.9 Applications for Vibrational Spectroscopy

Applications of infrared spectroscopy are spread in different areas. Invention Fourier transformed infrared (FTIR) spectroscopy added more interest in the field of IR spectroscopy. Different areas of applications are:

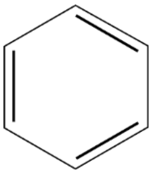
10.9.1 Identification of molecular constituents (skeletal vibrations and group frequencies)

Due to *3n-6* and *3n-5* rules a complex molecule is likely to have infrared spectrum due to its large number of normal vibrational modes. Identification of any molecular constituent is done by assigning the experimentally observed vibrations into various stretching and bending modes. The normal modes of a molecule can be divided into two major classes: skeletal or finger print vibrations and characteristic group vibrations.

10.9.1.1 Skeletal vibrations

The region in the range 700-1400 cm^{-1} is very important in IR absorption bands which contains mainly bending and certain stretching vibrations for most of the organic molecules in the form of linear or branched chain structure. A molecular or structural moiety can be identified by the assignments of the observed bands in this region. Some important group of molecules are

-C-O-C-



Such modes or vibrations are known as skeletal vibrations. Presence of functional groups generally show some marked changes in the pattern of skeletal bands. Skeletal modes of IR spectroscopy are used to gather information of different planets like Saturn, Uranus, and

Neptune etc. The atmosphere of these planets are mainly composed of hydrogen and helium. IR spectroscopy were proved to be extremely useful for the determination of different hydrogen and helium based constituents in these planets. Skeletal modes of IR spectroscopy are also very useful in comparing the spectra of natural and synthetic compounds.

10.9.1.2 Group vibrations

Group vibrations are frequencies that are associated with certain structural units such as $–CH_3$, $-OH$, $-NH_2$, $-C \equiv N$ etc. which appear a fairly constant region in the spectrum. Group frequencies are almost independent of the structure of the molecule as a whole. The approximate consistency of the position of the group frequencies form the basis of the structural analysis of an unknown compound. There are some factors which affects the group frequencies. They are

- Internal factors involving changes in the atomic mass, vibrational coupling, resonance effects, hydrogen bonding etc.
- External factors such as physical states (gas, liquid, solid, solution, solvent, concentration) and temperature. The effect of every factor is independent. So the influence of any factor on the particular group frequency can be identified individually.

It is observed that vibrations of lighter atoms ($–CH_3$, $-OH$, $-NH_2$ etc.) in terminal groups are observed at high frequency side of the IR spectrum. Whereas those of heavier atoms (-C-Cl, -C-Br, metal-metal etc.) are observed at low frequency side. $–CH_3$ group gives rise a C-H symmetric stretching absorption in the region between 2850-2890 cm^{-1}, asymmetric stretching absorption in the region between 2940-2980 cm^{-1}, a symmetric deformation mode at about 1375 cm^{-1} and asymmetric deformation mode at about 1470 cm^{-1}. Some important group frequencies are listed in the table 10.1. The idea of group vibrations also covers the motions of isolated features of a molecule which have frequencies not too far near those of the skeletal vibrations.

Group	**Approximate frequency (cm^{-1})**
$-OH$	3600
$-NH_2$	3400
$\equiv CH$	3300
$=CH_2$	3030
$-CH_3$	2970 (asymmetric stretch) 2870 (symmetric stretch) 1460 (asymmetric deformation) 1375 (symmetric deformation)
$-CH_2-$	2930(asymmetric stretch) 2860(symmetric stretch) 1470 (asymmetric deformation)
$-SH$	2580
$-C \equiv N$	2250
$-C \equiv C-$	2220
$>C=O$	1750-1600

>C=C<	1650
>C=N<	1600
>C=S	1100
>C-F	1050
-COOH	2800-3000 (symmetric OH) 1600-1750 (symmetric C=O) 1220-1300 (symmetric C-O)
-CHO	2700-2870 (symmetric C-H) 1670-1740 (symmetric C=O)

Table 10.1. Characteristic frequencies of some molecular groups

A very important consideration we have note at this point. As we know that IR spectrum only appears if the vibrations produces by the change in electrical dipole moment of the molecule. So it is reasonable to suppose that more polar a bond, the more intense will be the infrared spectrum arising from the vibrations of the bond. For this reason the ionic crystal lattices often give rise to very strong IR absorptions. The reverse effect is true for Raman spectroscopy.

It should be mentioned that complete interpretation of the IR spectrum of a complex molecule can be a very complicated tusk. Only practice can give necessary intuition for making correct assignment of the group frequencies.

10.9.2 Identification of molecular structure

From the observed *P, Q, R* branches of the IR spectra of polyatomic molecules, estimate of the rotational constants are possible. Then from B values moment of inertias and interatomic distances can be determined. IR spectroscopy is also useful is determining the shape of the molecule. For AB_2 type of polyatomic molecules, whether the molecule is linear symmetric type or linear nonsymmetrical type or bent symmetric or bent asymmetric type can be determined by their IR spectrum. If the IR spectrum shows some bands with P-R contour then the molecule is linear. If all the modes of linear molecule are IR active then the molecule is linear nonsymmetric. If all modes are not IR active then the molecule is linear symmetric. If no band shows the simple P-R structure, then the molecule is nonlinear. For nonlinear molecules the number of active fundamental bands decide whether the molecule is symmetric or nonsymmetric.

10.9.3 Characterization of transition phases of Ceramic material

Particle size and state of aggregation of ceramic type materials have a very strong effect in their IR spectra. So IR spectroscopy has been considered as a very effective tool in the characterization of the dihydroxylation behavior of ceramic material. Example-Boehmite (AlOOH) precursor gel, which is one of the most widely used gels in the operation of high temperature ceramics, abrasives and composites. At room temperature boehmite gel shows peaks at 485, 625, 742 cm^{-1} indicating the Al-O bonding in its octahedral structure. When temperature increases from 45°C-1100°C the structural changes appear in it from its octahedral form to tetrahedral form due to dihydroxylation. IR spectroscopy can be efficiently used to follow the structural changes taking place during this dihydroxylation process of boehmite precursor gel.

10.9.4 Characterization of Biological material

For different biological samples are applications of IR spectroscopy are

- Most biological samples are aqueous based and surface specific so their complex characteristics can only be evaluated by IR spectroscopy
- Most biological experiments require instruments with extremely high signal to noise ratio which is only achieved by FTIR spectrometers.
- Artificial devices used for temporary and permanent life support. Artificial surfaces are poorly tolerated by blood and so allotting is often initiated. FTIR is used to study the events that occur at the blood-biomaterial interface.
- For antibiotics and virus synthesis, an FTIR spectrometer is used to quantify the level of product in the fermentation mixture. The data is then transferred to another computer that evaluated the analysis and take appropriate control of action for the production through a preprogrammed logic operation. In this way IR spectroscopy is now extensively in use for biomedical research in the area of toxicology, mutagenesis and cellular research.

10.10 Summary

Throughout the present chapter we have considered the consequence of elasticity on bond length since the atoms in a molecule do not remain in fixed relative positions but vibrate about some mean position. We have considered first the case of diatomic molecule where we observed that the infrared or vibrational spectrum arises if molecular motion is in vibration. After that we have dealt with more practical case of diatomic molecule undergoing vibration and rotation simultaneously. Then we have extended our discussion to some more complex system like isotopes. We have observed that IR spectroscopy is extensively used in different areas of industry

10.11 Glossary

IR Spectroscopy- Infrared Spectroscopy

FTIR- Fourier Transformed Infrared

Elasticity- is the ability of a body to resist a distorting influence and to return to its original size and shape when that influence or force is removed.

Molecular vibration- A molecular vibration is a periodic motion of the atoms of a molecule relative to each other, such that the center of mass of the molecule remains unchanged.

Normal modes of vibration- The normal modes of vibration are: asymmetric, symmetric, wagging, twisting, scissoring, and rocking for polyatomic molecules.

10.12 References

1. The Infrared Spectra of Complex Molecules, L.J. Bellamy;Chapman and Hall, Vol I,II, 1980.

2. Fundamental of Molecular Spectroscopy, C.N. Banwell, E.M. McCash; Tata Mc Graw Hill.

3. Fourier Transformed Infrared Spectroscopy,P. R. Griffiths; J.A.D. de. Hareth; John Wiley 1986.

4. Molecular Spectra and Molecular Structure (I, II), G. Herzberg; D. Van Nostrand Comp. Inc, Princceton.

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10.13 Suggested Readings

1. Modern Physics, Beiser, Tata McGraw Hill

2. Optical Spectroscopy in Chemistry and Life Sciences, W. Schmidt; Wiley-VCH.

10.14 Solved Problems

Problem1: The frequency of OH stretching vibration in CH_3OH is 3300 cm^{-1}. Estimate the frequency of OD stretching vibration in CH_3OD.

Solution: $\frac{\omega_{OH}}{\omega_{OD}} = \sqrt{\frac{\mu_{OD}}{\mu_{OH}}} = \sqrt{\frac{16\times2}{18}\frac{17}{16\times1}} = 1.37$

$\omega_{OD} = \frac{3300}{1.37} = 2401$ cm^{-1}

Problem2: The fundamental and the first overtone for CO are 2143.26 cm^{-1} and 4260.04 cm^{-1}. Find the equilibrium vibrational frequency and anharmonicity constant for CO.

Solution: $\bar{\omega}_e - 2\bar{\omega}_e x_e = 2143.26 \ldots\ldots\ldots 1$

$2\,\bar{\omega}_e - 6\bar{\omega}_e x_e = 4260.04 \ldots\ldots\ldots 2$

Multiplying first equation by 3 and subtracting we get

$\bar{\omega}_e = 2169.74\, cm^{-1}$

Applying the value of $\bar{\omega}_e$ equation 1 or 2 we get x_e= 0.00617.

Problem3: The fundamental and the first overtone transition of $^{14}N^{16}O$ are given by 1876.06 cm^{-1} and 3724.20 cm^{-1} .Evaluate the equilibrium vibrational frequency, the anharmonicity constant, zero point energy and the force constant of the molecule.

Solution: Frequency of the fundamental: $\bar{\omega}_e(1-2x_e)$= 1876.06 cm^{-1}

Frequency of the first overtone: $2\bar{\omega}_e(1-3x_e)$= 3724.20 cm^{-1}. Solving these two equation we get

$\bar{\omega}_e = 1903.98\ cm^{-1}, x_e = 7.332x10^{-3}$

Zero point energy: $\varepsilon_0 = \frac{1}{2}\bar{\omega}_e\left(1-\frac{1}{2}x_e\right) = 948.5\ cm^{-1}$

$\mu = \frac{23.25x26.56}{23.25+26.56}x10^{-27} = 12.3975x10^{-27}$ kg

$k = 4\pi^2\mu c^2{\bar{\omega}_e}^2$=1598 N/m.

Problem4: The position of the lines in the fundamental band for *v=0→v=1* of CO is given by $\bar{\omega}\ (cm^{-1}) = 2143.3 + 3.813m - 0.0175m^2, \quad m = \pm1, \pm2, \pm3 \ldots\ldots$ Calculate B_0, B_1, B_e. Given α_e=0.018 cm^{-1}. Calculate also the equilibrium internuclear distance. Given that reduced mass of CO is 1.1385 $\times10^{-26}$ kg.

Solution: For the P branch lines m is positive and for R branch line m is negative. We know

$\bar{\omega}_{P,R} = \overline{v\omega}_0 + (B_1+B_0)m + (B_1-B_0)m^2\ cm^{-1}\ \ with\ m = \pm1, \pm2, \pm3$ so

$\bar{\omega}_{P_1} = 2143.3 + 3.813(-1) - 0.0175(-1)^2\ cm^{-1} = 2139.5\ \ cm^{-1}$

$\bar{\omega}_{P_2} = 2143.3 + 3.813(-2) - 0.0175(-2)^2\ cm^{-1} = 2135.6\ \ cm^{-1}$

$\bar{\omega}_{R_0} = 2143.3 + 3.813(+1) - 0.0175(+1)^2\ cm^{-1} = 2147.1\ \ cm^{-1}$

$\bar{\omega}_{R_1} = 2143.3 + 3.813(+2) - 0.0175(+2)^2\ cm^{-1} = 2150.9\ \ cm^{-1}$

Comparing the above equations we can get

B_1+B_0=3.183 cm^{-1} B_1-B_0=-0.0175 cm^{-1} . Solving them we can get

B_1=1.8978 cm^{-1} and B_0=1.9153 cm^{-1}

Again we know $B_v = B_e - \alpha\left(v+\frac{1}{2}\right), \quad B_e = B_0 + \frac{\alpha}{2} = 1.9153 + 0.009 = 1.9243\ cm^{-1}$

$$B_e = \frac{h}{8\pi^2\mu r_e^2 c}, \quad r_e^2 = \frac{h}{8\pi^2\mu B_e c}$$

r_e= 0.1129 nm

Problem5: The fundamental band for HCl is centred at 2886 cm^{-1}. Assuming that the internuclear distance is 1.276 Å, calculate the wave number of the first two lines of each of the P and R branches of HCl.

Solution: The reduced mass of HCl= $\frac{\left(1.008^{kg}/_{kmole}\right)\left(35.45^{kg}/_{kmole}\right)}{\left(36.46^{kg}/_{kmole}\right)\left(6.023x10^{26}/_{mole}\right)} = 1.6275x10^{27}kg$

The rotational constant $B = \frac{h}{8\pi^2 \mu r_e^2 c} = \frac{6.626\times10^{-34}J-S}{8\pi^2(1.6275x10^{27}kg)(1.276\times10^{-10}m)^2\left(3\times\frac{10^8 m}{s}\right)}$

$$= \quad 10.6129 \times 10^2 = 10.6129cm^{-1}$$

$\bar{\omega}_{P,R} = \bar{\nu}_0 + 2Bm\,cm^{-1} \quad with\, m = \pm1, \pm2, \pm3$

$\bar{\omega}_{P_1} = 2886 - 2 \times 10.6129 = 2864.77 \;\; cm^{-1}$

$\bar{\omega}_{P_2} = 2886 - 4 \times 10.6129 = 2843.55 \;\; cm^{-1}$

$\bar{\omega}_{R_0} = 2886 + 2 \times 10.6129 = 2907.23 \;\; cm^{-1}$

$\bar{\omega}_{R_1} = 2886 + 4 \times 10.6129 = 2928.45 \;\; cm^{-1}$

10.15 Self Assesment Questions

Self Assessment Question (SAQ) 1: What is the main condition for a molecule to be IR active?

Self Assessment Question (SAQ) 2: What do you mean by degrees of freedom of a molecule? What is its value for a linear molecule and a nonlinear molecule?

Self Assessment Question (SAQ) 3: What do you mean by normal modes?

Self Assessment Question (SAQ) 4: What are the selection rules of P,R,Q branch lines?

Self Assessment Question (SAQ) 5: For CO_2 molecule which mode is IR active and which mode is not? Why?

Self Assessment Question (SAQ) 6: What do you mean by zero point energy? What is its value? What do you mean by vibrational less state?

Self Assessment Question (SAQ) 7: What is the need of anharmonic oscillator to consider?

Self Assessment Question (SAQ) 8: What do you mean by dissociation energy?

Self Assessment Question (SAQ) 9: What do you mean by oscillation frequency? Write down its value.

Self Assessment Question (SAQ) 10: Why anharmonic constant appears? Express its value.

Self Assessment Question (SAQ) 11: What do you mean by equilibrium oscillation frequency?

Self Assessment Question (SAQ) 12: What do you mean by fundamental, first overtone, second overtone vibrations? Mention their values.

Self Assessment Question (SAQ) 13: Why the breakdown of Born-Oppenheimer approximation appears for vibrating rotator?

Self Assessment Question (SAQ) 14: In higher vibrational states what will happen to molecular bond length and why?

Self Assessment Question (SAQ) 15: What do you mean by skeletal and group frequencies? Which one is important to characterize the molecular structure?

Self Assessment Question (SAQ) 16: Why for astronomical studies Infrared spectroscopy plays a major role?

Self Assessment Question (SAQ) 17: What do you mean by FTIR spectroscopy?

10.16 Terminal Questions

(Should be divided into Short Answer type, Long Answer type, Numerical, Objective type)

10.16.1 Short Answer type question

1. IR spectrum of a symmetric AB_2 molecule gives 3 prominent lines. Check whether the molecule is linear or not?

2. Separation between P and R branch lines are different. Why?

3. What are hot bands? Why are they called so?

4. Homonuclear diatomic molecule does not show vibrational spectrum. Why?

5. The spacing between lines in P and R branch lines of CO_2 is 4B instead of 2B. Why?

6. How many normal modes would you expect to be observed in the infrared absorptionspectra of H_2O and CO_2 ?

10.16.2 Long Answer type question

1. Explain the effect of anharmonicity on the vibrational spectra of a diatomic molecule.

2. What parameters one can get from a study of the vibration-rotation spectrum of the heteronuclear diatomic molecule? Explain how are they estimated?

3. What are the effects of isotope on the spectrum of vibrating rotator?

4. Explain different vibrational modes with figures for H_2O and CO_2 and explain which modes of them are IR active and why?

5. Outline the theory of rotation-vibration spectrum of a diatomic molecule. How many normal Modes of vibrations are possible for these molecules: HBr, O_2. Why water can’t be used as a solvent for infrared spectroscopy?

6. How many normal modes of vibrations are possible for the following molecules OCS, SO_2, CH_4, CH_3I?

7. Assuming that the force constant for $C \equiv C$, $C = C$, and C-C are in the ratio of 3:2:1. The normal range of $C = C$ stretch absorption is 1630 – 1690 cm^{-1}. What range is expected for C-C, and $C \equiv C$ stretch vibration? Why monochromator (grating / prism) are made up of rock salts like NaCl / KBr?

8. Using a block diagram show essential components of IR spectroscopy.

10.16.3 Numerical and objective questions

1. Calculate the amplitude of vibration in the $v=0$ level of the molecule CO which has a force constant of 1870 N/m.

2. Assume that the H_2 molecule behaves like a harmonic oscillator with force constant k = 573 Nm^{-1}. Find the vibrational quantum number corresponding to its dissociation energy 4.5 eV. Given the atomic mass of H atom is 1.68×10^{-27}kg, and $h = 6.63 \times 10^{-34}$J-s.

3. The equilibrium vibrational frequency of the I_2 molecule is 215 cm^{-1}. The anharmonicity constant is 0.003. At temperature 300K what is the intensity of the band for transition v=1→v=2 relative to that of the transition for v=0→v=1?

4. The fundamental vibrational frequency of HCl is 2989 cm^{-1}. Find the force constant.

5. The position of the lines in the fundamental band for v=0→v=1 of HCl is given by $\bar{\omega}\ (cm^{-1}) = 2886.0 + 20.577m - 0.3034m^2, \quad m = \pm 1, \pm 2, \pm 3 \dots\dots$ Calculate B_0, B_1, B_e. Given $\alpha_e = 0.3019$ cm^{-1}.

6. Calculate the energy in cm^{-1} of the photon absorbed when HCl moleculegoes from the state $v=0, J''=1 \rightarrow v=1, J'=0$ and $v=0, J''=1 \rightarrow v=1, J'=2$. Assume that $v=0$ and $v=1$ states have the same B values. Given $\bar{\omega} = 2990$$cm^{-1}$, $x_e = 0.0174$, $r_{HCl} = 0.124$ nm.

Objective type question

1. Identify true or false:

a. A infrared spectrum is possible only for the molecules with a permanent dipole moment.

b. The selection rule for fundamental vibrational transition is $\Delta v = \pm 2$.

c. For linear molecule the number of vibrational frequencies are 6.

Unit 11 RAMAN SPECTRA

Structure

11.1 Introduction

11.2 Objective

11.3 Raman effect

11.4 Experimental Arrangement of Raman Effect

11.5 Quantum theory of Raman Effect

11.6 Intensity of Raman lines

11.7 Vibrational Raman spectra

11.8 Pure rotational Raman spectra

11.9 Raman shift

11.10 Comparison of Raman and Infrared spectra

11.11 Application of Raman spectra

11.12 Summary

11.13 Glossary

11.14 References

11.15 Suggested reading

11.16 Terminal questions

11.1 Introduction

Rayleigh theoretically study the scattering and shows that in scattering of light, the intensity of scattered light is inversely proportional to the forth power of wavelength $\left(I = \frac{1}{\lambda^4}\right)$. This is called Rayleigh scattering. We know the colour of sky is blue due to greater scattering of blue light as it is shorter wavelength. The scattering of lights takes place due to dust particles suspended in atmosphere. In Rayleigh scattering, only incident wavelengths are present in scattered light. No other wavelengths are present in scattered light therefore Rayleigh scattering is also called coherent scattering.

While studying the Rayleigh scattering, Raman found that when a beam of light was passing through some mediums like benzene or toluene, the scattered light contained some additional frequencies along with incident frequency (Rayleigh frequency). This effect was observed by CV Raman in 1928, and called Raman Effect.

11.2. Objective:

After studying this unit we will able to understand:

I. Raman effect and its discovery
II. Quantum theory of Raman effect
III. Pure rotational Raman effect
IV. Infra-red spectra and Raman spectra
V. Applications of Raman spectra

11.3 Raman Effect:

When a monochromatic beam of light passes through a gas, organic liquids like benzene or toluene, or a transparent solid, a small part of light scattered in all directions. The scattered light contains some other frequencies along with frequency of incident light (Rayleigh lines). The spectral lines of additional frequencies are called Raman lines. The frequency of incident light is called Rayleigh line or exciting line. The Raman lines corresponding to each Rayleigh line occur symmetrically on both ride of Rayleigh line as shown in figure 7.1. The lines on the low frequency side of Rayleigh line is called stoke line, while the lines on the higher frequency side is called anti-stoke lines. The intensity of antistoke lines are much weaker than stoke lines. It is also observed that the displacement of Raman Stoke lines from the Rayleigh line do not depend on the Rayleigh frequency.

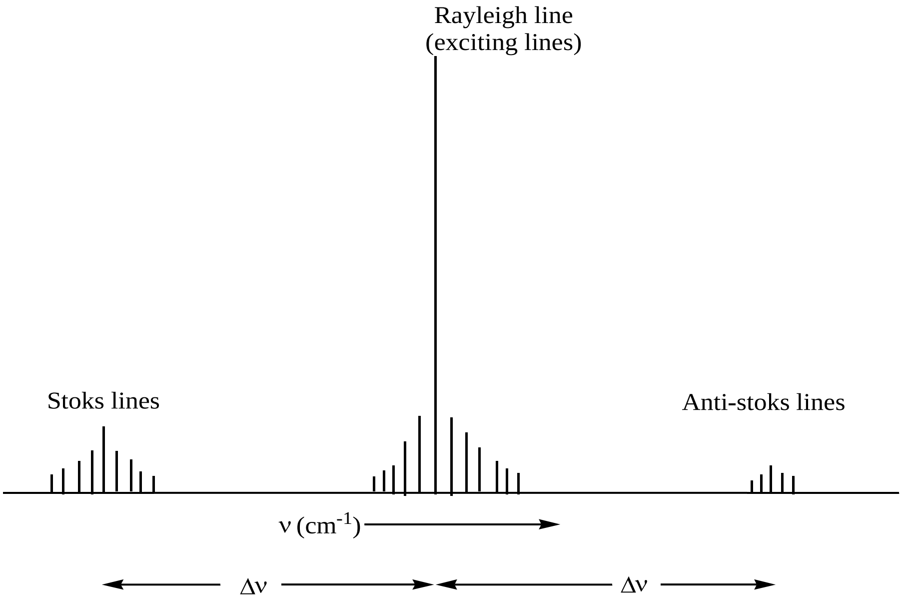

Figure 7.1: Raman Spectra of diatomic gas

If we change the frequency of incident light or used another Rayleigh line, we get other Raman lines for the same medium. However, the displacements of Raman lines from Rayleigh line are same. Thus for a particular material the displacement of Raman lines from Rayleigh line remains same. Thus the Raman displacements are characteristics of a scattering material.

Raman displacement is denoted by $\Delta\nu$ (in cm^{-1}) unit which is wavenumber and proportional to energy

$$\nu = \bar{\lambda} = \frac{\mathrm{E}}{\mathrm{hc}} = \frac{1}{\lambda} = \frac{\nu'}{c}$$

Where $\bar{\lambda}$ or ν is wave number, E is energy and ν' is frequency of incident light, h and c have its usual meanings $\Delta\nu$ denotes the Raman displacement from Rayleigh line.

Under low resolution we observe one stoke Raman line and one anti-stoke Raman line each having same displacement $\Delta\nu$. The Raman displacement $\Delta\nu$ is corresponding to main vibrational rotational absorption band near infrared band. On the other hand at high resolution, approximately equidistance lines are found on both side of Rayleigh line. This is pure rotational Raman spectrum as shown in figure 7.1.

11.4 Experimental Arrangement of Raman Experiment:

The basic arrangement for obtaining the Raman spectra is shown in figure 7.2. In this Experiment a liquid for which Raman spectra is to be obtained is filled in a tube which is called Raman tube figure 7.2. Raman tube is a thin walled glass tube about 15 cm long and 2 cm diameter. One end is closed with a optically plane glass from which scattered light can be emerged towards spectrometer and other is drawn out into the horn shape covered by black tape. This black colour horns shape end causes reflection of backward scattered light. The Raman tube is illuminated by a large spiral shaped lamp L wrapped around the Raman tube T.

The outer surface of lamp L is covered by a reflector R. Raman tube is surrounded by a jacket J, in which a filtering solution is used to filter one of the spectral line of mercury lamp.

The mercury arc lamp light source has three prominent lines at 2536, 4047Å and 4358Å. By using noviol glass and CCl_4 solution, the 4047Å line may be filtered. Similarly by using pale noviol and quinine, we can filter 4358Å line and finally we have only one prominent 2536Å prominent line for this experiment.

The scattered light passing through plane end of tube and a stop S and finally focused on the slit of a spectrometer G. Spectrograph or photograph of Raman spectra can be obtained by exposing the spectrograph plate for several hours.

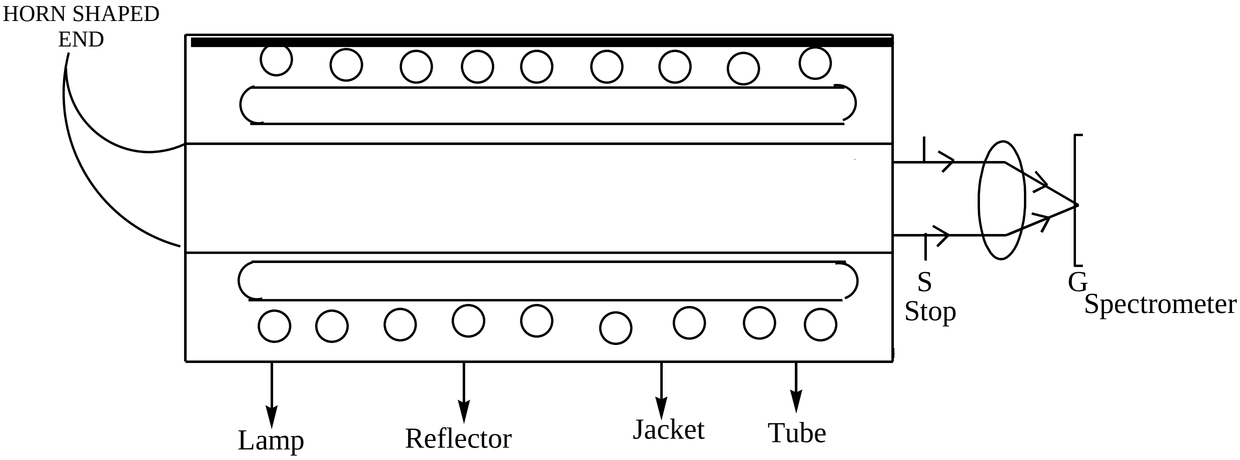

Figure 7.2: Experimental arrangement of Raman Spectra

11.5 Quantum Theory of Raman Effect:

According to quantum theory of light, a light wave consists of photons, and the energy of photons is given by $E = h\nu' = hc\nu$ where ν' is frequency of light and ν is wave number $\frac{1}{\lambda}$. When these light photons fall on a molecule of a liquid gas or solid material, the photon collides with molecules. There are two cases of collision called elastic and inelastic collusion.

I. If the collision is elastic, there is no transfer of energy from photon to molecule or molecule to photon. In this case the light is scattered without any modification in energy or frequency. This scattered light is corresponding to Rayleigh scattering line presence in Raman spectrum.

II. If the collision is inelastic, there is an exchange of energy from photon to molecule or molecule to photon. If the molecule is initially at energy state (say E_0), takes energy from the photon and goes to higher energy state of molecule say E^1, then photon is scattered with a smaller energy $(hcv - \Delta E)$ where $\Delta E = E' - E_0$ as shown in figure 7.3. In this case the frequency of Raman line is less than incident frequency. The scattered light has frequency $\frac{hcv - \Delta E}{h}$ and in term of wave number shift = $\frac{\Delta E}{hc}$ such Raman lines are called Stoke line.

There is another possibility called inelastic collision. If the molecule is initially at higher energy state E^1 and after collision it shifted to lower energy state E_0, now the scattered photon emerges with increased energy $(hcv + \Delta E)$ after gaining an addition energy ΔE. In this case the frequency of scattered light is greater than incident light. The frequency of scattered light is $\frac{hcv + \Delta E}{h}$ and the wave number shift is again $\frac{\Delta E}{hc}$ but now this line is in another side to Rayleigh line. Such Raman lines are called anti-stoke lines. The stoke line and anti-stoke lines are symmetrically situated on both side of Rayleigh (indent) line.

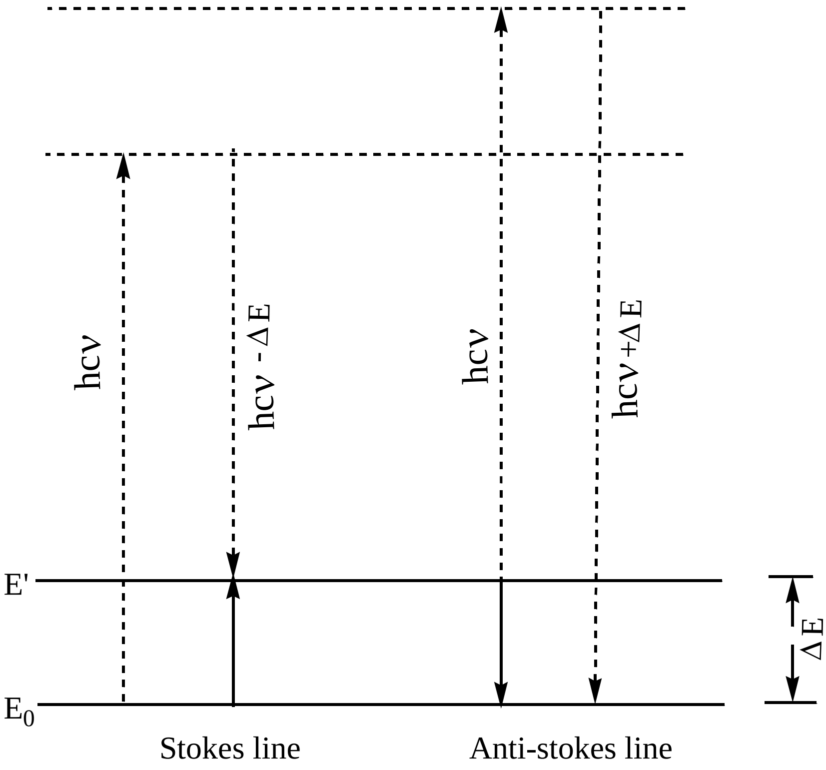

Figure 7.3: Quantum Theory of Raman Scattering

11.6 Intensity of Raman lines:

At normal temperature, the number of molecule in lower energy state is more than molecules in higher energy state E^1. When radiation falls on molecule there is more transition from lower to higher energy state. In this process molecules absorb energy from photons. However, the transition from higher to lower energy state in which photon absorbs energy from molecule is very few. Since Stoke lines are corresponding to transition from lower energy state to higher energy state therefore Stoke lines are more intense than anti-stoke line. In some case the anti-stoke lines are so faint or weak that they are not observed.

If the temperature increases, more molecules are available at higher energy state E^1 and transition from higher energy state to lower energy state also increase and consequently anti-stokes lines becomes brighter.

11.8 Pure Rotational Raman Spectra:

Pure rotational Raman spectra arises when the transition from one rotational energy state to another rotational energy state of a molecule.

In case of diatomic molecule, the energy involved in the different motion of molecules can be divided into three categories as translational, rotational, and vibrational energies. The rotational energy of a diatomic molecule is given by

$E_j = \frac{1}{2}\mathrm{I}\,\omega^2$ where I is moment of inertia and ω is angular frequency.

If J is angular momentum then we know $L = \mathrm{I}\omega$

or $E_j = \frac{1}{2}\frac{\mathrm{L}^2}{\mathrm{I}}$

Angular momentum can be given as $L = \sqrt{\mathrm{J}(\mathrm{J}+1)}\,\hbar$ where J is rotational quantum number and have values J = 0, 1, 2, 3………………..

thus $E_j = \mathrm{J}(\mathrm{J}+1)\frac{\hbar^2}{2\mathrm{I}}$ (1)

The selection rule for pure rotational transition is ΔJ = 0, ± 2

ΔJ = 0 is corresponding to Rayleigh line. The transition from J→J+2 (absorption) gives stoke rotational Raman line and J+2→J gives the Anti Stoke Raman rotational Raman lines as shown in figure 7.4.

From eq. 1 the rotational energy in terms of wave number can be expressed as

$$\frac{1}{\lambda} = v = \frac{E_j}{hc} = \frac{\hbar^2}{2\mathrm{Ihc}}\mathrm{J}(\mathrm{J}+1)$$

or $v = \frac{\mathrm{h}}{8\,\pi^2\mathrm{Ic}}\mathrm{J}(\mathrm{J}+1)$

$\frac{\mathrm{h}}{8\,\pi^2\mathrm{Ic}} = \mathrm{B}$ is another constant known as rotational constant. Then the wave number for rotational energy is can be expressed as

$v = B\,\mathrm{J}(\mathrm{J}+1)$ where J=0, 1, 2, 3……….

For rotational Raman lines the selection rule is ΔJ = ± 2, therefore the wave number of the rotational Raman lines are given by

$$v_{raman} = v_{rayleight} \pm \left[v_{j+2} - v_j\right]$$

$$= v_{rayleight} \pm \left[B\,(\mathrm{J}+2)(\mathrm{J}+3) - B\,\mathrm{J}(\mathrm{J}+1)\right]$$

$$= v_{rayleight} \pm B[4\,\mathrm{J}+6]$$

$$= v_{rayleight} \pm 4B(\,\mathrm{J}+3/2)$$

Thus rotation Raman Shift is

$$\Delta v = v_{raman} - v_{rayleight} = 4B(\,\mathrm{J}+3/2)$$

$$\Delta v = 6B, 10B, 14B, 18B \ldots\ldots\ldots\ldots\ldots\ldots$$

Thus in pure rotational Raman spectrums, a series of equidistance lines corresponding to different Raman shift are situated on both side of Rayleigh line. The separation between two successive lines is 4B as shown in figure 7.4.

Pure rotational molecular spectra can be shown by molecules that have permanent electric dipole moment. Thus the homonucleus diatomic molecule such as H_2, O_2, N_2, symmetric linear molecule O=C=O etc. do not exhibit rotational spectra. But homonucleus molecule exhibits rotational Raman spectra. Homonucleus molecules like H_2, N_2, O_2' the rotational Raman lines are alternately weak and strong due to symmetric properties of rotational energy levels. On the other hand hetronucleus molecule like HF, HCl, HBr, CO etc. exhibit rotational spectra.

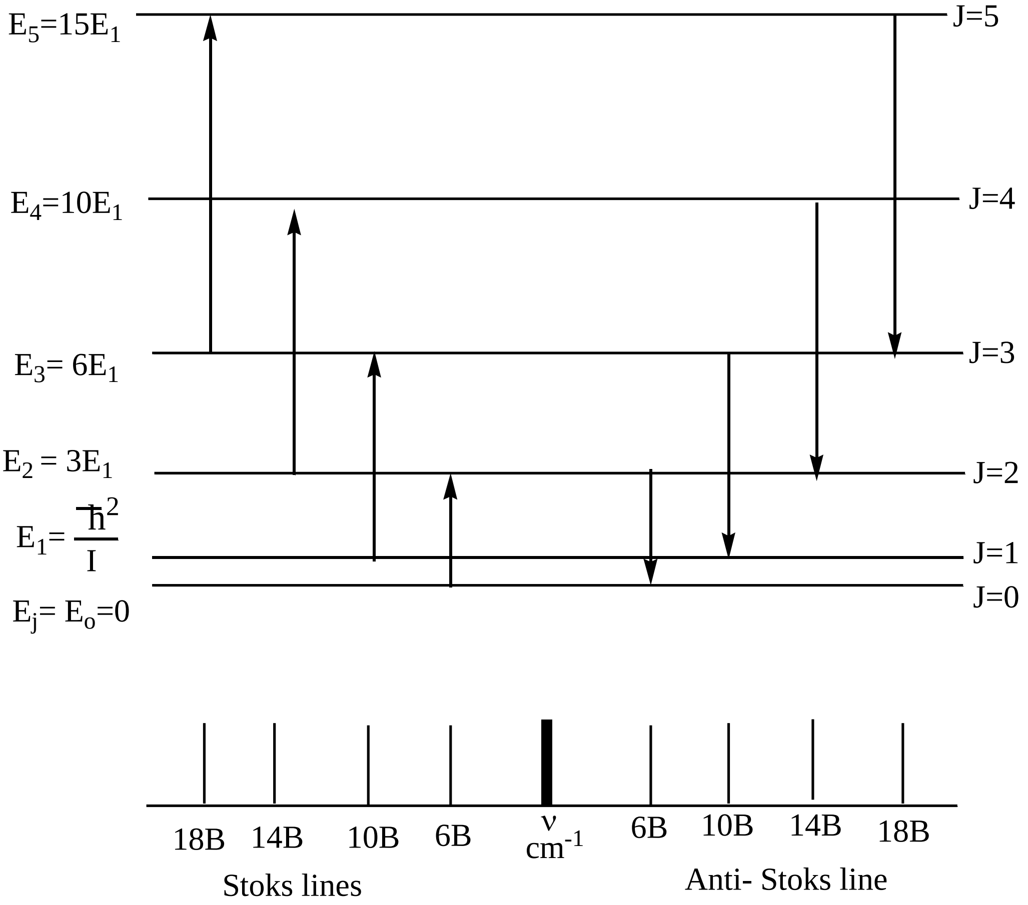

Figure 7.4: Pure rotational Raman Spectra

11.9 Vibrational Raman Spectrum:

The Vibrational Raman Spectrum arises when the transition takes place from one vibrational level to another vibrational level of the same electronic state of a molecule. Quantum mechanically, a molecule can be treated as a harmonic oscillator. If ν' is classical frequency of harmonic oscillator, then the energy E of such molecule can be given as

$$E=h\,\nu'\,(v+1/2)$$

Where v = 0, 1, 2, 3, 3………are integer number corresponding to different energy states. ν' is classical frequency given as

$\nu' = \frac{1}{2\pi}\sqrt{\frac{k}{m'}}$ where k = force constant and m' = reduced mass

In terms of wave number, the vibrational energy can be given as

$$G(v) = \frac{E}{hc} = \frac{\nu'}{c}(v + \frac{1}{2})$$

Where G(v) is known as vibration term and $\frac{\nu'}{c}$ is known as vibrational constant denoted by ω thus

$$\mathrm{G(v)} = \omega \left(\mathrm{v} + \frac{1}{2}\right) \text{ in cm}^{-1}$$

Corresponding to different vibrational levels v =1,2,3,4.......

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

In case of vibrational Raman spectrum, if ν is the wave number of incident light (Rayleigh line), Raman lines are symmetrically arise on either side of Rayleigh line. The selection rule (possible transition) for vibrational Raman spectrum is

$\Delta \nu = \pm 1$

Thus the vibrational Raman lines are situated on either side of Rayleigh line as

$$\nu_{raman} = \nu \pm \ [\mathrm{G(v+1)} \ - \mathrm{G(v)}]$$

If transition takes place from v =1 to v = 0 states then

$$\nu_{raman} = \nu \pm \left[\omega\frac{3}{2} - \omega\frac{1}{2}\right] = \nu \pm \omega$$

Similarly for transition v = 2 to v =1 state

$$\nu_{raman} = \nu \pm \left[\omega\frac{5}{2} - \omega\frac{3}{2}\right] = \nu \pm \omega$$

Thus in general the vibration Raman lines arises as

$$\nu_{raman} = \nu \pm \omega$$

Vibrational Raman shift is given as

$$\Delta\nu = \nu_{raman} \sim \nu = \omega$$

This is Raman Shift in terms of wave number corresponding to absorption band of vibrational energy levels and generally observed near infra-red spectrum.

11.10 Comparison between Raman and infrared spectra:

The infrared absorption spectra arises when a transition between vibration state v = 0 to v = 1 takes place. This transition is similar to vibration stoke Raman line in which some vibration state involved. Hence, there is an agreement between infrared and Raman spectra but the mechanism of production of both spectra are quite different.

In infrared spectra, we provide the radiation energy exactly same as energy difference between two different vibrational states; whereas in Raman spectra we provide a radiation of higher frequency and there is a change in energy corresponding to two energy states of molecule.

Further, in infrared band there is a change in molecular electric dipole moment due to molecular vibrational states. Thus permanent magnetic moment is must for occurrence of infrared spectra. On the other hand, Raman spectra arise due to polarizability of a molecule and no need of permanent dipole moment.

11.11 Application of Raman spectroscopy

11.11.1 Molecular structure:

Raman Effect is an important tool for study of structure of a molecule. Vibrational Raman spectra can be used for determining the force constant of diatomic molecule. As we know vibrational Raman shift $\Delta\nu=\omega$ where ω is vibrational constant given by $\omega = \frac{\nu'}{c}$. Here ν' is classical frequency of vibration of molecule and given as $\nu' = \frac{1}{2}\sqrt{\frac{k}{m'}}$. By this relation the force constant k can be obtained. On the other hand, by using Rotational Raman Spectra, the bond length of a molecule can be determined.

11.11.2 Structure of triatomic molecule:

With the help of Raman lines, its intensity and number of lines we can determine whether a triatomic molecule is symmetric or asymmetric. For structure infrared spectrum is also used along with the Raman spectrum for more information.

Theoretically we use rule of mutual exclusion. According to this rule a molecule with centre of symmetry transitions that are allowed in the infrared are for hidden in Raman spectra and vice versa. However, all transitions forbidden in one must occur in the other is not always true. Sometime some transitions may be forbidden in both Raman and infrared spectrum.

For example CO_2 has two strong bands in infrared absorption spectrum at 668cm^{-1} and at 2349cm^{-1}while a strong band at wave number 1389cm^{-1} in Raman spectra. As none of the bands appear both in Raman as well as infrared spectrum thus the CO_2 molecule has a centre of symmetry and CO_2 has linear structure as O-C-O.

Example1: In a Raman study of a material, the wavelength of a light source used is 5460Ǻ. The stoke line is observed at 5520Ǻ. Find the wavelength of anti stoke line

Solution: The light source provides the Rayleigh line for the Raman spectra. The location of Rayleigh line in terms of wave number ν can be given as

$$\nu = \frac{1}{5460\text{ X }10^{-8}\text{cm}} = 18318cm^{-1}$$

The stoke line is given as

$$\nu = \frac{1}{5520\text{ X }10^{-8}\text{cm}} = 18116cm^{-1}$$

The displacement in terms of wave number is

$$\Delta\,\nu = \nu - \nu_{stoke} = \text{ 18315 – 18116 = 199cm}^{-1}$$

The stoke line and anti-stoke lines are symmetrically located on either side of Rayleigh line. Therefore, the location of anti-stoke line is

$\Delta\,\nu = \nu + \nu_{antistoke}$

$\nu_{antistoke} = \nu + \Delta\,\nu = \text{18315+199=18514cm}^{-1}$

The corresponding wave length = $\frac{1}{18514\ cm^{-1}} = 5401\acute{\text{Å}}$

Example 2: When a celylene is irradiated with the 4358$\acute{\text{Å}}$ light source, a Raman line corresponding to vibration spectra is observed at 4768$\acute{\text{Å}}$. Calculate the fundamental frequency (frequency corresponding to vibrational constant) for this vibration.

Solution: The wave number corresponding to exciting line(Rayleigh line) is

$\nu = \frac{1}{4358X10^{-8}} = 22946cm^{-1}$

Raman line is located at

$\nu_{\text{raman}} = \frac{1}{4768X10^{-8}} = 20973cm^{-1}$

This is stoke line

In case of vibrational Raman spectra, the Raman displacement is given as

$\Delta\,\nu = \nu_{\text{ raman}} - \nu\ = \omega$

Where ω is vibrational constant $\frac{\nu'}{c}$ and ν′ is frequency.

Thus $\omega = 22946 - 20973 = 1973\text{ cm}^{-1}$

Hence, vibration frequency $\nu' = \omega c = 1973\text{ X }3\text{ X }10^{10}$

$$\nu' = 5.92\text{ x }10^{13}\text{cm}^{-1}$$

Example 3: A substance shows Raman lines at 4567Å when the wavelength of incident light (Rayleigh line) is 4358Å. Find out the positions of stoke and anti-stoke lines for the same substance when a light of 4047Å is used.

Solution: The wave number ν corresponding to incident light or Rayleigh line is

$$\nu = \frac{1}{4358X10^{-8}} cm^{-1} = 22946 cm^{-1}$$

The Raman line corresponding to 4567Å is

$$\nu_{raman} = \frac{1}{4567X10^{-8}} cm^{-1} = 21896 cm^{-1}$$

The Raman Shift or wave number displacement is

$$\Delta \nu = \nu - \nu_{raman} = 22946 - 21896$$

$$\Delta V = 1050 cm^{-1}$$

We know that the Raman shift is a characteristic of material and remains same for all incident light or Rayleigh line.

Now if the light used is of wavelength 4047Å, then in terms of wave number the Rayleigh line corresponding to incident light.

$$\nu = \frac{1}{4047 \ X \ 10^{-8}} = 24710 \ cm^{-1}$$

Since the Raman shift Δ ν remain same therefore position of Stoke line is

$$= \nu - \Delta \nu = 24710 - 1050 = 23660 cm^{-1}$$

Wave length of Stoke line $= \lambda_{stoke} = \frac{1}{23660 \ Cm^{-1}} = 42265$Å

Similarly Anti Stoke line $= \nu + \Delta\nu$

$$= 24710 + 1050 = 23760 \ Cm^{-1}$$

Wave length of anti-stoke line $\frac{1}{25760 Cm^{-1}} = 3.882 \ X \ 10^{8} cm$

= 3882Å

Self assessment questions (SAQ)

SAQ1: What are Raman lines?

SAQ2: Why Stoke lines are more intense than anti-stoke line?

SAQ3: Explain the unit of Raman displacement?

SAQ4: Give the Rotational energy in terms of rotational quantum number?

SAQ5: What is rotational constant?

SAQ6: What is classical frequency of molecular vibrations?

SAQ7: Define Vibrational Constant?

SAQ8: How structure of molecule can be studied with the help of Raman spectroscopy?

11.12 Summary

1. Rayleigh scattering, only incident wavelengths are present in scattered light. No other wavelengths are present in scattered light therefore Rayleigh scattering is also called coherent scattering. The frequency of incident light is called Rayleigh line or exciting line.

2. When a monochromatic beam of light passes through a gas, organic liquids like benzene or toluene, or a transparent solid, a small part of light scattered in all directions. In the spectral lines, if there are some additional frequencies, they are called Raman lines.

3. The Raman lines corresponding to each Rayleigh line occur symmetrically on both ride of Rayleigh line. The lines on the low frequency side of Rayleigh line is called stoke line, while the lines on the higher frequency side is called anti-stoke lines.

4. The intensity of antistoke lines is much weaker than stoke lines. Displacement of Raman Stoke lines from the Rayleigh line do not depend on the Rayleigh frequency.

5. Raman displacement is denoted by Δν (in cm^{-1} unit) which is wavenumber and proportional to energy

$$\nu = \bar{\lambda} = \frac{\mathrm{E}}{\mathrm{hc}} = \frac{1}{\lambda}$$

6. Rotational energy in terms of wave number

$$v = \frac{\mathrm{h}}{8\,\pi^2 \mathrm{Ic}} \mathrm{J}(\mathrm{J}+1)$$

$v = B\ \mathrm{J}(\mathrm{J}+1)$ where J=0, 1, 2, 3……..(J is rotational quantum number)

Where $\frac{\mathrm{h}}{8\,\pi^2\mathrm{Ic}} = \mathrm{B}$ is rotational constant.

7. Rotation Raman Shift is

$$\Delta v = v_{raman} - v_{rayleight} = \ 4B(\,\mathrm{J} + 3/2)$$

$$\Delta v = 6B, 10B, 14B, 18B \ldots\ldots\ldots\ldots\ldots\ldots.$$

8. In terms of wave number, the vibrational energy can be given as

$$G(v) = \frac{E}{hc} = \frac{\nu'}{c}(v + \frac{1}{2})$$

where v = 0, 1, 2, 3, ...are integer number corresponding to different energy states.

$$G(v) = \omega\left(v + \frac{1}{2}\right) \text{ in cm}^{-1}$$

9. vibrational Raman lines are situated on either side of Rayleigh line as

$$\nu_{raman} = \nu \pm [G(v + 1) - G(v)]$$

10. Vibrational Raman shift $\Delta\nu = \nu_{raman} \sim \nu = \omega$

11.13 Glossary

Rayleigh line: Wave number ν corresponding to incident light

Wave number: inverse of wavelength $\frac{1}{\lambda}$ = ν or $\left(\frac{E}{hc}\right)$

Spectrum: A band of colours

Selection rule: A rule specify the possibility of transition among the different energy levels

Rotational energy state: energy state arises due to rotations in molecule

Vibrational energy state: energy state arises due to vibration of molecule.

Rotational spectra: Spectrum due to transitions among rotational states

Vibrational spectra: Spectrum due to transitions among vibrational energy states of molecule.

Raman Displacement: separation between Rayleigh line and Raman line in terms of wave number ν.

Stoke line: particular wavelength (or wave number) present in the Raman spectra of a molecule on the low frequency side of Rayleigh line.

Anti-stoke line: Particular wavelength (or wave number) present in the Raman spectra on the higher frequency side of Rayleigh line.

11.14 References

Raj Kumar, *Atomic and molecular spectra*, KedarNath Raman, Nath Publication, Meerut

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11.15 Suggested Reading

1. CL Arora, *Atomic and Molecular Physics*, S Chand and Company Ltd., New Delhi
2. M. Alonso and EJ Finn, *Fundamental University Physics*, Addison-Wesley Publication Company.
3. HE., White., *Introduction to Atomic Spectra*, McGraw Hill Publication, New Delhi.
4. CN Banwell, *Fundamental of Molecular Spectroscopy*, Tata McGraw Hill Publication, New Delhi.
5. John R., *Introduction to Raman Spectroscopy*, FerraoKazuaNakamoto, Academic Press, New York

11.16 Terminal Questions

11.16.1 Short answer type questions

1. What is Raman Effect?
2. Explain the intensity of Stoke and anti-stoke lines?
3. Give the characteristic of molecular spectra.
4. Explain rotational Raman spectra.
5. Explain Vibrational Raman spectra.
6. What do you mean by Raman shift?
7. Give a comparison between Raman and infrared spectra.
8. With the help of Raman spectra, how the structure of a molecule can be studied.

11.16.2 Long answer type questions

1. Explain the Raman spectra with the help of experimental setup.
2. Explain rotational Raman spectra. Obtain the Rotational Raman shift with the help of vibrational constant.
3. Give the explanation of pure rotational Raman spectra. Find out the expression for rotational Raman shift and Rotational constant.
4. Give the applications of Raman spectrum.
5. Discuss the main features of vibrational and rotational Raman spectra of a diatomic molecule. Give the necessary theory.
6. Discuss Raman spectra of diatomic molecules and point out the similarities and differences in infrared and Raman spectra.

7. Describe the salient features of Raman spectra of a hetronucleus diatomic molecule and how this can be explained.
8. Explain how Raman spectra depends on polarisability of a molecule and entirely independent from the presence of permanent dipole moment.
9. Consider H_2 , N_2 , HCl and OH molecule. Explain which of these molecule show infrared spectrum and which will give Raman Spectrum.
10. Distinguish between scattering and Rayleigh scattering.

11.16.3 Numerical type questions

1. A sample is irradiated with a light source of wave length 3458 Å. If the stoke lines are observed at 4458 Å, find out the wavelength of anti-stoke line. [Ans. 4262 Å]

2. In the vibrational Raman spectra of HF, Raman lines are observed at 2670 Å and 3430 Å. What is the fundamental vibrational frequency of molecule? [Ans. 1.24×10^{14} Hz]

3. The exciting line in an experiment with Raman Effect is 5460 Å. If the stoke line has λ=5520 Å, Calculate the wavelength of anti-stoke line. [Ans. 5400 Å]

UNIT 12

ELECTRONIC SPECTRA

Structure

12.1 Introduction to Electronic spectra: Franck Condon Principle

12.2 Salient Features of Molecular Electronic spectra

12.3 Formation of electronic spectra; electronic transition

12.4 Vibrational Structure of Electronic Band-System in Emission

12.5 Electronic Band spectra in Absorption

12.6 Observed Intensity Distribution (Vibrational) in Band system

12.7 Rotational Intensity Distribution

12.8 Terminal Questions

12.9 References

12.1 Franck Condon Principal

when electrons of an atom are excited to higher energy states, the radiations that are absorbed in this process appear as the absorption spectra of atoms. In a similar way, electronic spectra of molecules arise when the electrons of a molecule are excited to higher energy states. The energy involved in this process is generally large and electronic spectra of molecules are usually found in visible and ultraviolet region. Therefore, electronic spectra arise due to the changes in the arrangement of molecular electrons. We shall discuss electronics spectra of diatomic molecules.

The electronic transition is the result of change in electronic energy. A small change in the electronic energy will be accompanied by a large change in the vibrational energy of the molecule. These vibrational energy changes give rise to vibrational transitions which form a group of various bands. Further, a small change in the vibrational energy will be accompanied by a large change in the rotational energy of the molecule. These rotational energy changes give rise to rotational transitions forming a series of line in each band-the so called fine structure of each band.

12.2 Salient Features of Molecular Electronic spectra

Electronic spectra is the most complex molecular spectra which appear in the visible and ultra violet regions and involve the change in all the three energies (electronic, vibrational and rotational) of the molecule. These spectra are obtained in emission and absorption regions. The spectral band exhibit a fine structure which is more complicated. The head formation tendency is story and the bands are degraded either towards violet or toward the red. All molecules give electronic spectra.Homo-nuclear molecules (H_2,N_2,O_2 etc.) do not give neither rotational nor vibrational- rotational spectra because of having no permanent dipole moments but they give electronic spectra because of the instantaneous dipole moment changes during the redistribution of change which results in the transition.

12.3 Formation of electronic spectra; electronic transition

Each electronic state of the molecule has a different potential energy curve. For stable electronic state, the curve, is characterized by a minimum at an equilibrium inter-nuclear distance γ_e a dissociation limit De, a set of discrete vibrational levels and sets of discrete rotational levels. Fig 5.1 shows the two potential energy curves for a diatomic molecule. The lower curve represents the ground state and the upper curve an electronically excited state of the molecule. The asymptote in the upper curve is higher by axe the electronic energy of excitation of the atom. Also

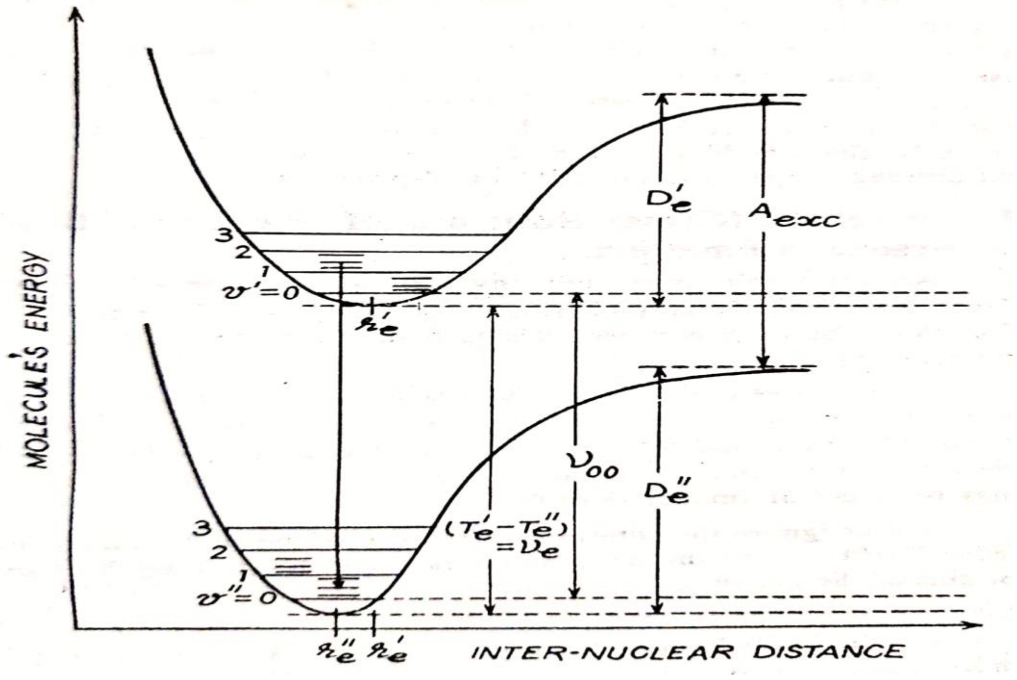

Fig 12.1 Both curve differ in shape as well as in position of minimum

When an electron of a molecule is raised from a low energy electronic state (ground state) to another of high energy, radiation is absorbed giving rise to absorption bands. The return of the excited molecule to lower electronic states results in an energy release giving rise to emission spectrum. Since during excitation a change takes place in vibrational and rotational level also, therefore the electronic emission is always accompanied by the vibrational transitions. Each vibrational transition of upper and lower electronic states, is accompanied by a number of transitions involving a rotational state. These rotational transitions give rise to a graph of fine lines known as band. The bands arising from all the vibrational transitions give rise to a bands-system.

$$\nu_e = (T'_e - T''_e) cm^{-1}$$

The bands of the system corresponding to the same upper vibrational level (ν') but different lower vibrational levels (ν'') are known as to form a ν'' - Progression and the bands corresponding to the same lower vibration level (ν'') but different upper vibrational level (ν') from a ν'- progression.

12.5.4 Vibrational Structure of Electronic Band-System in Emission

In an electronic transition, a change in all these energy (electronic vibrational and rotational) of the molecule takes place. The wave-numbers obtained from an electronic transition are.

$$\nu = \left(T_e' - T_e''\right) + \left(G' - G''\right) + \left(F' - F''\right)$$

Taking F'=F''=0 (neglecting rotational structure of the individual bands), the wave numbers of band system are.

$$\nu_G = \ \nu_e + G'(\nu') - G''(\nu'')$$

$$= \nu_e + \{w_e'\left(\nu' + \frac{1}{2}\right) - w_e'x_e'(\nu' + \frac{1}{2})^2 - \{w_e''\left(\nu'' + \frac{1}{2}\right) - \omega_e x_e''(\nu'' + \frac{1}{2})^2$$

As there is no limitation on the change in the vibrational quantum number ν for an electronic transition, therefore.

$$\Delta\nu = Unrestricted$$

That is, all transitions from each vibrational level of the upper electronic state can take place to each of the vibrational levels of the lower state. This gives rise to a large number of bands for a single electronic transition. Fig12.2 shows some of emission transition.

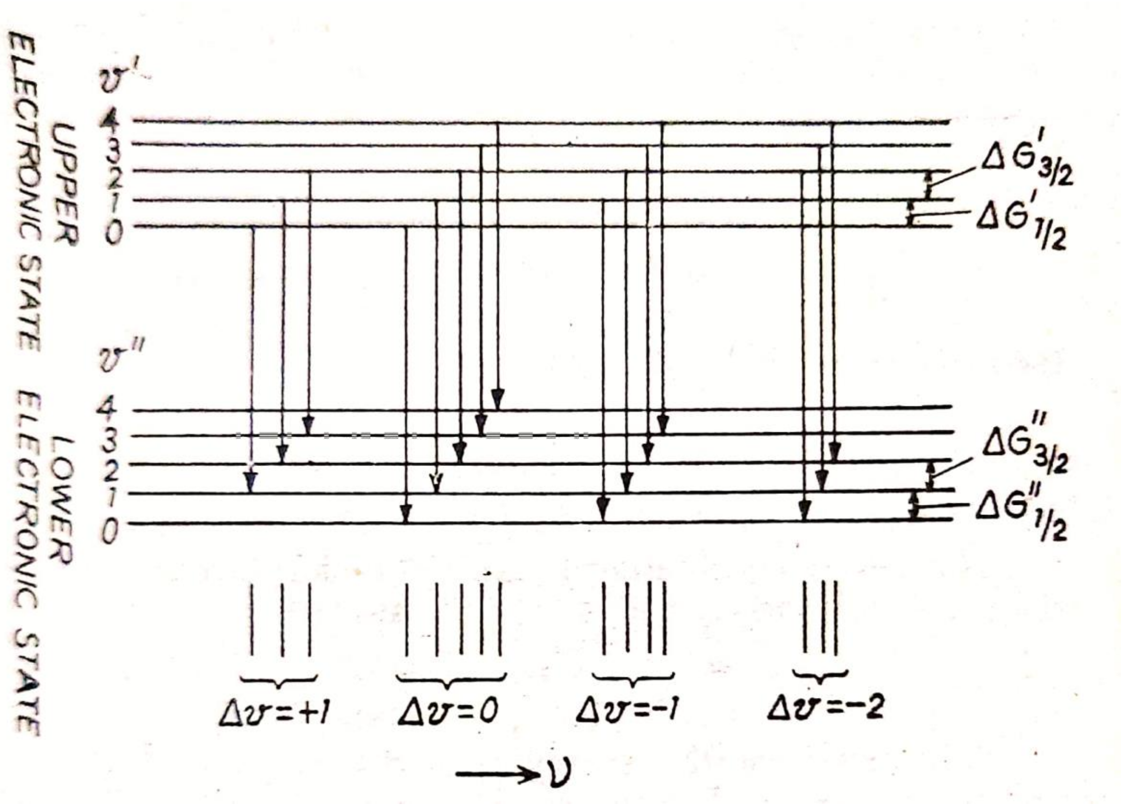

Fig.12.2

It can be band –system may be divided in to different groups. Each group contains a few close bands. These are known as sequences $(\Delta\nu = constant\ for\ each\ sequence)$. Bands of sequences lie along the diagonal or along a line parallel to diagonal of the (Deslandre table). Bands in the horizontal rows and in the vertical columns are knows as $\nu'' - and\ \nu'$ -progressions respectively.

12.5 Electronic Band spectra in Absorption

An electronic absorption spectrum consists of a series of bands which come more and more closer toward high wave-number side and ultimately give a continuum. All emission band systems are not observed in absorption. A large number of ν'' $-$Progressions (related to $\nu' = 0,1,2,---$)of emission bards occur while there is only a single ν'- Progression (related to $\nu'' = 0$) of bands occur in the absorption spectrum. Other progressions (related to $\nu'' = 0,1,2,---$) occur, if at all in very poor intersities Fig 5.3 shows the energy level diagram and the corresponding transitions. The bands coverage at a point corresponding to the transition.

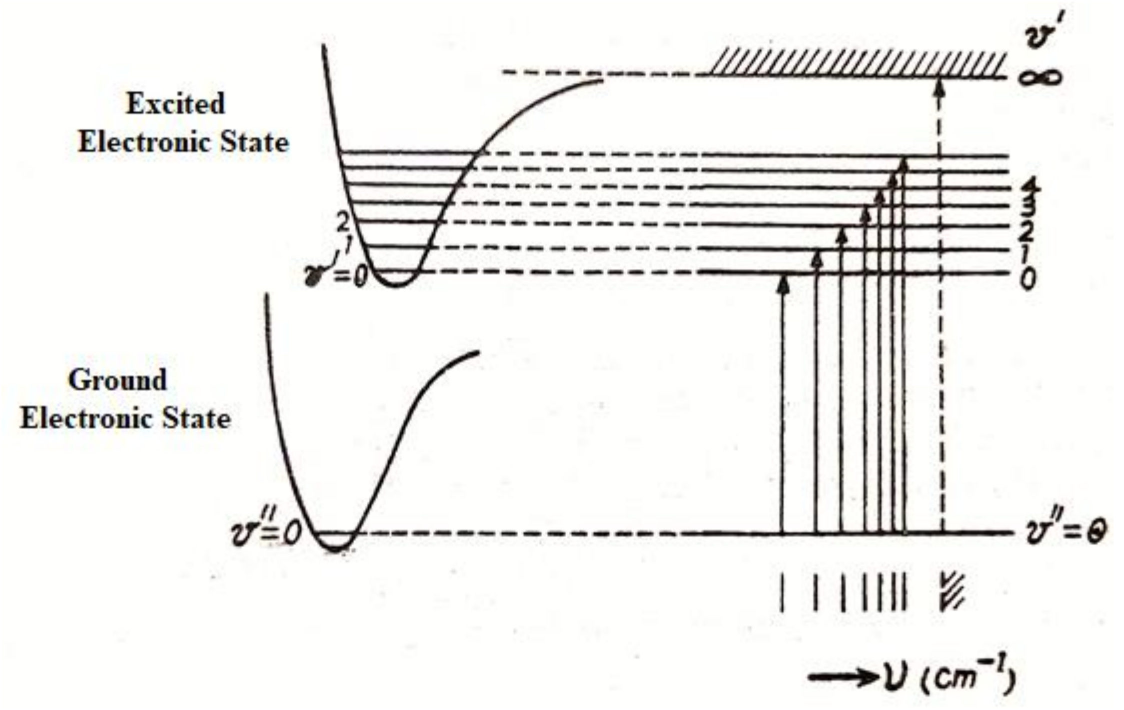

Fig.12.3

The wave numbers of the band-origins of a system are

$$\nu_0 = \nu_e + G^1(\nu^1) - G^{11}(\nu^{11})$$

$$= \nu e + \{w_e^1\left(\nu^1 + \tfrac{1}{2}\right) - w_e^1 x_e^1(\nu^1 + \tfrac{1}{2})^2\} - \{w_e^{11}\left(\nu^{11} + \tfrac{1}{2}\right) - w_e^{11} x_e^{11}(\nu^{11} + \tfrac{1}{2})^2\}$$

For the observed absorption progression of bands $\nu^{11} = 0$

$$\nu_0 = \nu_e + w_e^1\left(\nu^1 + \frac{1}{2}\right) - w_e^1 x_e^1(\nu^1 + \frac{1}{2})^2 - \frac{1}{2} we^{11} + \frac{1}{4}\omega_e^{"} x_e^{"}.$$

For the first few bands of this progression, we have $\nu' = 0,1,2,3, -----$

The wave numbers of these bands and wave number separations are

Wave numbers	First difference
$\nu_e + \frac{1}{2}\omega_e' - \frac{1}{4}\omega_e' x_e' - \frac{1}{2}\omega_e'' + \frac{1}{4}\omega_e'' x_e''$	$\omega_e' - 2\omega_e' x_e'$
$\nu_e + \frac{3}{2}\omega_e' - \frac{9}{4}\omega_e' x_e' - \frac{1}{2}\omega_e'' + \frac{1}{4}\omega_e'' x_e''$	$\omega_e' - 4\omega_e' x_e'$

$$\nu_e + \frac{5}{2}\omega'_e - \frac{25}{4}\omega'_e x'_e - \frac{1}{2}\omega''_e + \frac{1}{4}\omega''_e x''_e \qquad\qquad \omega'_e - 6\omega'_e x'_e$$

$$\nu_e + \frac{7}{2}\omega'_e - \frac{49}{4}\omega'_e x'_e - \frac{1}{2}\omega''_e + \frac{1}{4}\omega''_e x''_e$$

With the increase of v', first difference (wave-number separation between successive bands) decreases, that is levels come closer and closer. The second difference $(2\omega'_e x'_e)$ between the adjacent bands is the same. Thus the vibrational constant $\omega_e^{\cdot}$ can be determined if $\omega'_e x'_e$ is knows.

Potential Structure of Electronic Bonds: - The fine structure of individual bands of electronic spectra due to the rotation of the molecule, that is each line of band corresponds to a change in all the three energies of the molecule. The wave number of a line (J:J") is given as

$$\nu = \nu_e + \left(G' - G''\right) + (F' - F'')$$

$$= \nu_0 + F'(v'J') - F''(v''.J''),$$

where $\nu_0 = \nu_e + (G' - G'')$ is the band origin.

Putting the values of rotational terms F' and F" of the upper and lower electronic states, we get'

$$\nu = \nu_0 + B'_v J'(J' + 1) - B''_v J(\mathrm{J} + 1),$$

The selection rule is $\Delta J = \pm 1$

R-branch – Transitions corresponding to $\Delta J = J' - J'' = +1$

Provide one set of lines known as R-branch, Putting J'=J"+1, we get

$$\nu_R = \nu_0 + 2B'_v(3B_v' - B_v'')\mathrm{J}'' + (B'_v - B_v'')\mathrm{J}''^2$$

R-branch is a series of lines R(0),R(1),R(2),-------------having J"=0,1,2,----------

P-branch – Transitions corresponding to $\Delta J = J' - J'' = -1$

Provide another setoff lines known as P-branch. Putting J'=J"-1, we get

$$\nu_P = \nu_0 - (B_v' - B_v'')\mathrm{J}'' + (B'_v - B_v'')\mathrm{J}''^2$$

P-branch is a series of lines P(1), P(2), P(3),-------------having J"=1,2,3,----------in Fig 12..4 shows the transitions and the band-structure obtained. P-and P- branch can be incorporated in a single parabolic equation.

$$\nu = \nu_0 + (B'_v + B''_v)m + (B'_v - B''_v)m^2$$

where m = J"+1=1,2,3,------------ for R(0),R(1),R(2),------

m = J"+1=1,2,3,------------ for P(1),P(2),P(3) --------

and m= o for band origin,

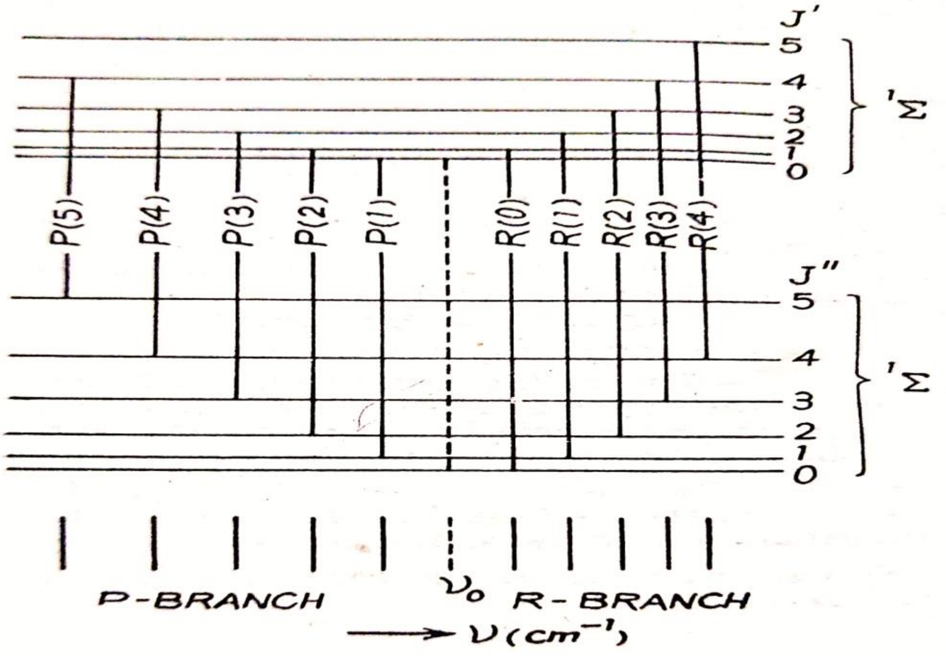

Fig.12.4

Fortrat Parabola:- The fig 12.5 shows the plots of above equation when $(B'_v - B_v")$ is negative (red- degraded band) and when $(B'_v - B_v")$ is positive (violet – degraded band). These are known as 'Fortrat Parabola' The vertex of the Parabola represents the band-head. Differentiating the able equation and equation dν/dm to zero, we get

$$\frac{d\nu}{dm} = (B'_v + B''_v) + 2(B_v' - B''_v)m = 0$$

This gives the value of m at which the vertex of the Fortrat Parabola (band-head) lies as

$$\text{m vertex} = -\frac{(B'_v + B_v")}{2(B'_v - B_v")}$$

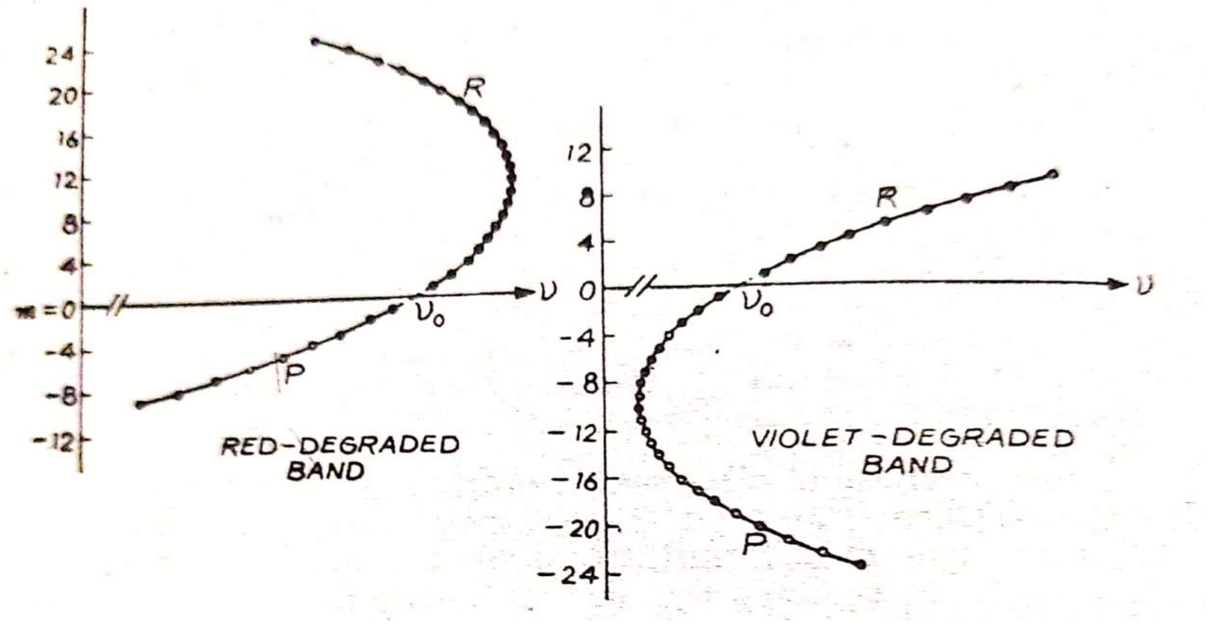

Fig.12.5

Putting this value, the wave number separation between band-head and band origin is obtained as

$$\nu_{Read} - \nu_0 = -(B_\nu' + B_\nu)\,\frac{(B_{\nu}{}' + B_{\nu}")}{2(B_{\nu}{}' - B_{\nu"})} \;+\; (\mathrm{B_v}' - \mathrm{B_v}"\,)\,\frac{(B_{\nu}{}' + B_{\nu}")^2}{4(B_{\nu}{}' - B_{\nu})^2}$$

$$= -\;\frac{(B_{\nu}{}' + B_{\nu}")^2}{4(B_{\nu}{}' - B_{\nu})^2}$$

Thus $\nu_{head} - \nu_0$ is positive for a band degraded to the red and negative for a band degraded to the violet.

12.6 Observed Intensity Distribution (Vibrational) in Band system

(Franck-Condon Principal) The Intensity distribution among the bands of a band-system of electronic spectra varies from one molecule to another and from one band-system to another of the same molecule. The intensity distribution of absorption bands of O_2,Co_2 and I_2 is shown in 12.6.

In the spectrum of O_2 (0,0) band is maximum intense and the intensity of successive bands $(v' - Progression)\; with\, v" = 0)$ decreases rapidly. In the spectrum of co_2 the intercity of bands along the progression first increases rapidly to a maximum and then decreases. In the spectrum of I_2, the intensity of bands increases gradually and the maximum reaches at a very high $v' - value$ .thus a long progression is obtained.

Franck- Condon Principle: - The Franck–Condon principle is a rule in spectroscopy and quantum chemistry that explains the intensity of vibronic transitions. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy. The intensity distributions can be explained with the help of Franck-Condon principal. This principle states that- ‘An electronic transition in a molecule takes place so rapidly in comparison to the vibrational motion of the nuclei that the intense and the velocity of the nuclei can be considered unaltered during the electronic transitions.

The principal also states that an electronic transition would take place only when the atoms in the lower electronic states are in their extreme position. Hence, transitions must be represented by vertical lines on the potential energy curves.

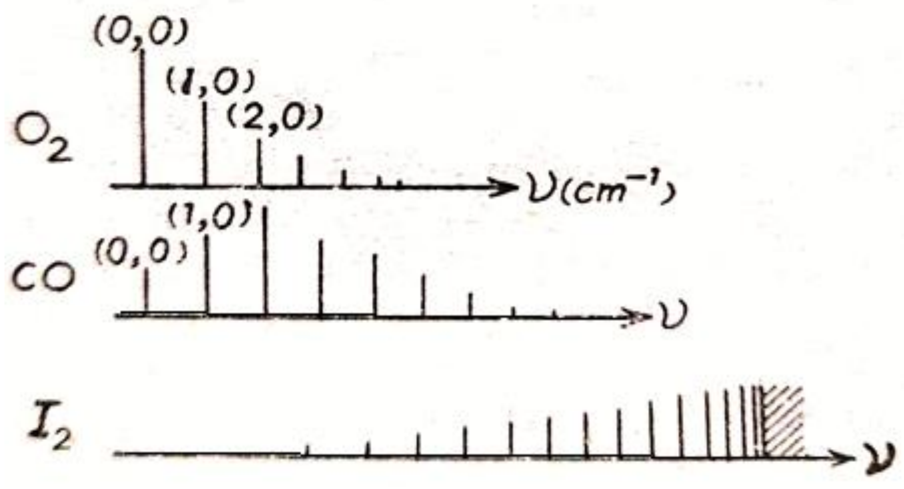

Fig12.6

Quantum Mechanical Formulation of Franck - Condon Principal:- In quantum mechanics, the intensity of spectroscopic transitions, between two states (total wave functions $\varphi' and\ \varphi''$) depends on the square of the corresponding transitions moment R(matrix element). If R be the average electronic transition moment, then

$$\text{R or R}v', v'' = \overline{R_e} \int \psi'_v \, \psi_v'' dr$$

Where r is the inter-nuclear distance. We may define the ‘Franck-Condon factor’ $q^{v',v''}$ as

$$q^{v',v''} = [\int \varphi'_v \varphi_v{}' \, dr]^2$$

The Franck-Condon factor and also the relative intensities depend upon the relative positions of the maxima and the nodes of the vibrational wave function ψ_ν in two states quantum mechanically we may state the principle as follows:-

A vibrational transition will have a large Franck-Condon factor only if one of the two turning points of a level of one electronic state lies nearly at the same inter nuclear distance as one of the two turning points of a level of the other state, except for $\nu = 0$ level for which the middle point of the level must be subetituted (in place of turning point)

Intensity Distribution in Absorption Bands: - Franck - Condon principle explains it. Fig 12.7 shows the three typical situations of absorption transitions between two electronic states in a diatomic molecule. The equilibrium in inter-nuclear distances are equal in both states in fig 12.7(a), slightly greater in upper state in (b), and much greater in upper state in (c) In fig 12.7(a), the transition $\nu" = 0 — \nu' = 0$ is the most probable one because of connecting the configurations of high probability and it appears as a vertical line (r remains unchanged).other transitions are also taking place but week in intensity. Thus (0,0) band has maximum intensity and for higher bands decreases rapidly. This is the case of o$_2$ molecule.

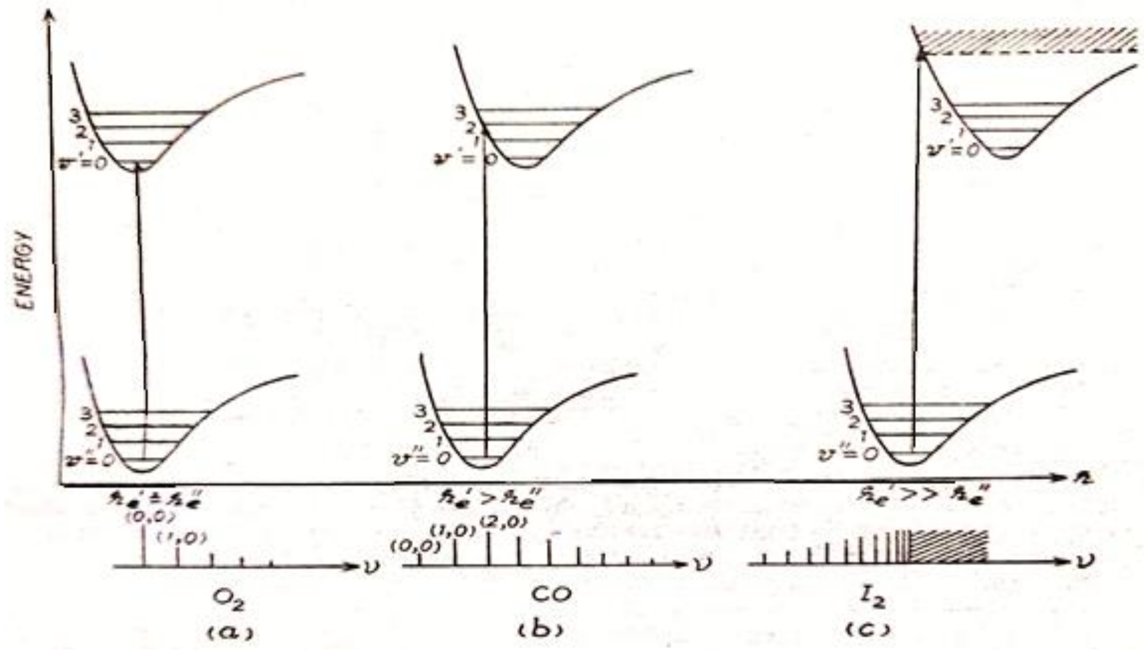

Fig.12.7

In fig 12.7(b), the most probable transition is $\nu" = 0 — \nu' = 2$. Other transitions to the $\nu' = 0,1,2,3,4, - - -$ are taking place but weak in intensity. Thus, the intensity first increase from

(0,0) band and after reaching a maximum for (2,0) band intensity decreases. This is the case of co molecule.

In fig 12.7(b), the most probable transitions is $\nu" = 0 — continnun$ of upper electronic state. Thus molecule is dissociated so that a progression of weak bands terminated to a continuum of maximum absorption intensity occurs. This is the case of I_2 molecule,

<u>Intensity Distribution in Emission Bands</u>:- The distribution of intensity in a band progression with $\nu' = 0$ in emission corresponds exactly to that of a progression with $\nu" = 0$ in absorption. The intensity maximum at a $\nu"$ value is obtained whose value depends on the relative portion of the maxima of the two potential curves. The larger value of ν” is obtained for intensity maximum for the greater difference $r'_e - r''_e$. The intensity distribution for band progression in emission (for $\nu' > 0$) is different from that for $\nu' = 0$. For O_2^+ and Co, the fig 12.7 shows the Condon parabola. This is a plot of intensities at the bands of a system in a $\nu' - \nu"$ array exactly similar to a Deslandre table and joining the most intense bands. Thus a Condon parabola may be defined as the locus of most intense bands in a $\nu' - \nu"$ array.

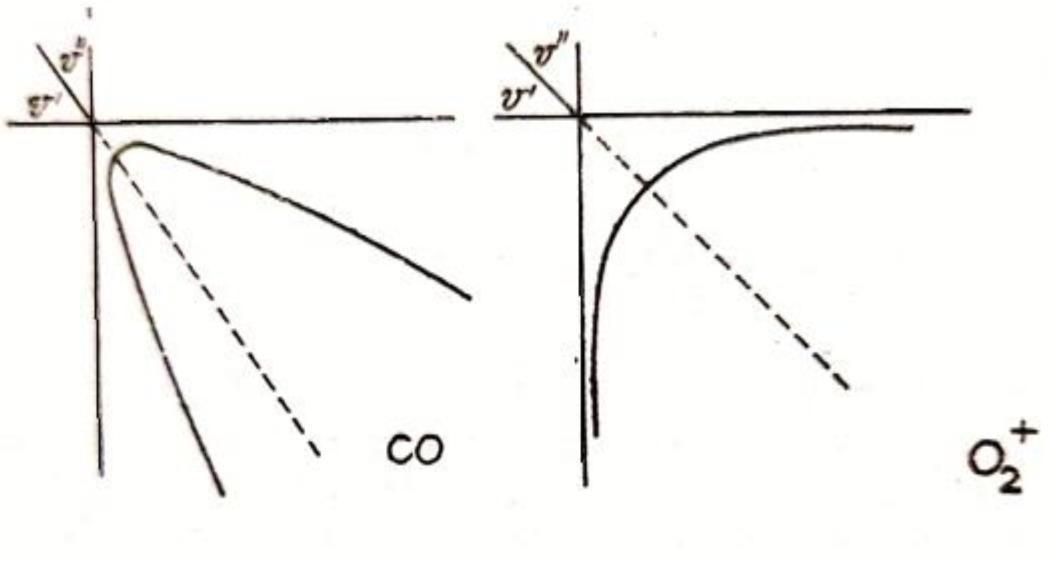

Fig.12.8

The potential curves are not symmetrical. This means transitions will be more probable from (or to) the one side than the other in accordance with Franck-Condon principal. Therefore, for a red-end degraded system, (r'>r"), the right part of the Condon parabola is stronger while for violet-end degraded system (r' < r"), the left part is stronger.

12.7 Rotational Intensity Distribution

The intensity of a line in an electronic band depends upon the rotational levels of the initial electronic state and upon the transition probability in emission or absorption of that line. For a transition $1_{\Sigma} - 1_{\Sigma}$, the value of intensity factor i for the lines of R –and P- branches is given by

$$i_{R(J)} = i_{P(J)} = J' + J'' + 1$$

If a graph between intensity and J is plotted, then in $1_{\Sigma} - 1_{\Sigma}$ electronic band an intensity maximum in each of R- and P-branches is found, fig. 12.9. with the increase of temperature, the maxima shift to higher J values. The R-branch is stronger in absorption while P- branch is stronger in emission.

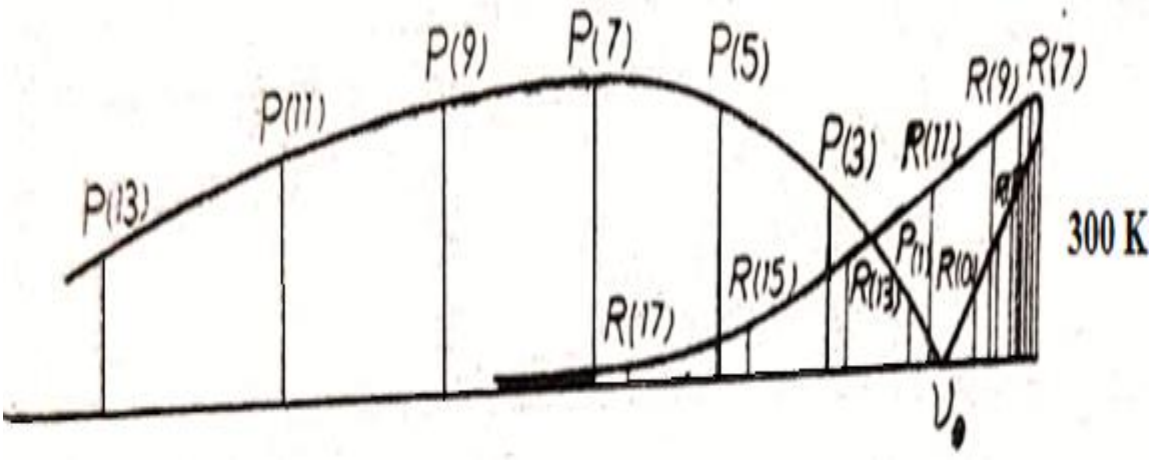

Fig.12.9

Solved Problems

Q.1 Rotational analysis of one band system is given by $\nu = 24762 + 25m - 2.1m^2\ cm^{-1}$.

Deduce the position of the band-head, the values of B$v' and Bv''$ and the degradation of the band.

Sol:- $\nu = 24762 + 25m - 2.1m^2cm^{-1}$ ----------------- (i)

The line of P and R branches of a band are represented by a single formula

$$\nu = \nu o + (B\nu' - B\nu'')m + (B\nu' - B\nu'')m^2$$

where ν_0 is the band origin. Comparing it with the eq.(1), we get

$$\nu_0 = 24762cm^{-1}, B\nu' + B\nu'' = 25cm^{-1}$$

and $B\nu' - B\nu'' = -2.1cm^{-1}$

solving these equations., we get.

$$B\nu' = 11.45cm^{-1} \; and \; B\nu'' = 13.55cm^{-1}$$

Now m venterx = - $\frac{B\nu' + B\nu''}{2(B\nu' - B\nu'')} = -\frac{25}{2x(-2.1)} = 5.9$

That is, the head lies at 6 (whole number). Putting m=6 in eq.(1) we get

$$\nu_{head} = 24762 + (25x6) - (2.1\,x\,6^2) = 24836.4cm^{-1}$$

This is clear that the band-head lies towards the high-frequency side of the band-origin so that

the band is degraded towards the law frequency side or 'toward the red'.

Q.2:- The 5'-0" transition is Hcl^{35} occurs at 99022 cm^{-1}. Calculate the position of the band origin of same transition for Pcl^{35} on the basis of the assumption that in both the electronic states the molecule behaves as harmonic oscillator. Given that.

$\omega_e' = 2710cm^{-1}$ $\omega_e'' = 2990cm^{-1}$ for Hcl^{35}

m'(Hcl) = .979889 m" (Hcl) = 1.90500

Sol:- $\rho = \sqrt{\left(\frac{0.979889}{1.90500}\right)} = 0.7172$

The origin of an electronic band is given by

$$\nu_0 = \nu_e + \nu_\nu$$

$$= \nu_e + [\omega_e'\left(\nu' + \frac{1}{2}\right) - \omega_e"(\nu" + \frac{1}{2})]$$

$$91022 = \nu_e + [2710\left(5 + \frac{1}{2}\right) - 2990\left(\frac{1}{2}\right)]$$

$$\nu_e = 77612\ cm^{-1}$$

This represents the energy difference between potential energy minima of two electronic state that remain unchanged. Position of new band origin is given by

$$\nu_0' = \nu_e + \rho\nu_\nu$$

$$= 77612+0.7172(\nu_0 - \nu_e)$$

$$= 77612+0.7172(91022-77612)$$

$$= 87230cm^{-1}$$

Q.3:- The zero point energy of the ground state of N_2 is 1176 cm^{-1} and that of its lowest excited state is 727 cm^{-2}. The energy difference between the minima of the potential energy cueves is 50,206 cm^{-1}. What is the energy of the $\nu' = 0$—$\nu'' = 0$ transition is cm^{-1}? What is the corresponding wavelength?

Sol:- The wave numbers of the band origins of a system are given by $\nu_0 = \nu_e + (\frac{E\nu' - E\nu"}{hc})$

In our case Zero point energy of ground state = $E\nu"$

Zero point energy of excited state =$E_0{}'$

Therefore, $\nu_0 = \nu_e + (\frac{E_0' - E_0"}{hc})$

$$\nu_e = 50206\ cm^{-1}$$

$$\frac{E_0\prime}{hc} = 727cm^{-1}$$

$$\frac{E_0\prime}{hc} = 1176\ cm^{-1}$$

So that frequency of (0-0) bands is

$$\nu_{00} = 50{,}206 + (727 - 1176)$$

= 50,206-449

= 49,757 cm^{-1}

Corresponding wave length of (0-0) band is given by

$$\lambda_{00} = \frac{1}{\nu_{00}} = \frac{1}{49{,}757}\ cm = 2010\ \text{Å}$$

Q.4:- The bands of a system are given by relation $\nu = 19221.2 + (1611.3U' - 40.7U^{12}) - (1495.7U" - 31.5U"^{2})$ where U = $\nu + \frac{1}{2}$ calculate the position of (0,0) band. Towards which side is the band degraded? Given that U'= ν+ $\frac{1}{2}$

Sol:- we know that band that band origin of the system is represented by

$$\nu_0 = \nu_e + (\omega_e' u' - \omega_e{}' x_e{}' u'^2) - (\omega_e'' u'' - \omega_e{}'' x_e{}'' u''^2)$$

Comparing it with

$$\nu = 19221.2 + \left(1611.3u' - 40.7u'^2\right) - (1495.74" - 31.54"^2)$$

we get $\nu_e = 19221.2\ cm^{-1}, \omega_e' = 1611.3cm^{-1}, \omega_e{}'x' = 40.7$

$\omega_e'' = 1495.7$cm^{-1}, $\omega_e{}''x" = 31.5$cm^{-1}

for (0,0) bard $\nu' = 0, \nu" = 0$

Hence u'= $\frac{1}{2}$ $and\ u" = \frac{1}{2}$

Substituting equation for ν_{00}. we get.

$\nu_{00} = \nu_e + (\frac{1}{2}\ \omega_e' - \frac{1}{4}\ \omega_e{}'x_e{}') - (\frac{1}{2}\ \omega_e'' - \frac{1}{4}\ \omega_e{}''x_e{}'')$

= 19221.2+$(\frac{1}{2}x1611.3 - \frac{1}{4}\ x40.7) - (\frac{1}{2}\ x\ 1495.7 - \frac{1}{4}x31.5)$

= 19276.7 cm^{-1}

As this case $\omega_e' > \omega_e$"

Hence B'>B or B'- B" is positive; so bands are degraded towards the violet.

MCQ Problem

1. Which statement is *correct* about the vibrational ground state of an H_2 molecule?

● The molecule is vibrating.

○ The molecule is in its lowest vibrational level but is not vibrating.

○ The molecule is static in its ground state.

○ In its vibrational ground state, the molecule has no vibrational energy.

2. Which value is the *correct* reduced mass of HF?

● 1.59×10^{-27} kg

○ 6.30×10^{26} kg

○ 5.72×10^{26} kg

○ 1.75×10^{-27} kg

3. Which statement is *incorrect* about CO_2?

○ CO_2 is linear.

○ CO_2 has two degenerate bending modes of vibration.

● The IR spectrum of CO_2 shows four absorptions.

○ CO_2 has two stretching modes of vibration.

4.Which of the following transitions between rotational energy levels is *not* allowed?

● $J = 1 \leftarrow J = 3$

○ $J = 1 \rightarrow J = 0$

○ $J = 1 \leftarrow J = 2$

○ $J = 0 \leftarrow J = 1$

5. For which of the following molecules could a pure rotational spectrum *not* be observed in the gas phase?

○ HCl

○ NO

● N_2

○ CO

Answers : (1) a (2) a (3) c (4) a (5) c

Short and Long Answer Problems

Q.1:- Write a note (short) on Franck-Condon principle?

Q.2 :- Give an account of the salient features observed in the electronic spectrum of a diatomic molecule. Discuss the conditions under which the band-heads are degraded towards violet red in the electronic spectrum.

Q.3:- Discuss rotational fine structure of electronic vibrational transitions. What is Fortrat diagram?

Q,4:- The band-head of the branch is always at J= $-\frac{1}{2}$, while that of the P-or R-branch may be any where explain.

Q.5:- Describe Franck-Condon principle in emission and absorption.

Q.6:- How did it become known as .Franck-Condon Principle?

Q.7:- The dissociation energy of H_2 molecule is 4.45 ev and that of D_2 molecule is 4.54ev. Find the zero-point energy of H_2 molecule.

Q.8:-You are given a Franck –Condon parabola. What information’s could be deduced from it about the molecule?

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UNIT 13

PHOTOACAUSTIC

Structure

13.0 Introduction to photoacoustic effect

13.1 Photothermal Phenomena and Detection Techenques

13.2 Electret Microphone and Piezoelectric Detection

13.3 Photo-thermal Beam Detection (PBD)

13.4 Photo-thermal Radiometry and Other Remote Sensing Techniques

13.5 Photo thermal Displacement Spectroscopy (PDS)

13.6 Photoelectric Detection:

13.7 Interferometric Detection

13.8 Theory of the Photoacoustic effect in condense media

13.9 Advantages of Photoacoustic Spectroscopy

13.10 Applications of Photoacoustic in different fields

13.0 Introduction to photoacoustic effect

Photoacoustic effect was discovered by Alexander G Bell in 1881. Bell accidently stumbled onto this effect as he was experimenting with this invention of the photo phone. Photoacoustic effect is essentially the generation of acoustic waves on irradiating certain substances by a modulated electromagnetic radiation ranging from radio frequency to X-rays. The photoacoustic effect or optoacoustic effect is the formation of sound waves following light absorption in a material sample. In order to obtain this effect, the light intensity must vary, either periodically or as a single flash. There are different mechanisms that produce the photoacoustic effect. The primary universal mechanism is photo-thermal its mechanism consists of the following stages:

- Conversion of the absorbed pulsed.
- Temporal changes of the temperatures at the loci.
- Expansion and contraction of temperature changes (diffusion of the thermal pulsations).

In applying the photoacoustic effect there exist various modes of measurement. Thus, when a sample is irradiated by a modulated electromagnetic waves, absorption of photons (Photon energy) generates excited internal energy levels. All or part of the absorbed photon energy is then transformed in to heat (thermal energy) through non-radiative relaxation processes in the sample. In a gas this heat energy appears as vibrational energy of the gas molecules, while in a solid or liquid, it appears as vibrational energy of ions or atoms. Photoacoustic (PA) generation is generally due to photo thermal heating effect apart from other mechanisms. Since the radiation incident on the sample is intensity modulated, the internal heating of the sample, which in turn produces acoustic signal of same frequency as that of modulating signal.

A condenser microphone can pick this signal. The sample to be studies is often enclosed in a PA cell.

(i) For the case of gases and liquids the sample generally fills the entire chamber where as in the case of solids, the sample fills only a portion of the chamber and the rest of the chamber is filled with a non-absorbing gas such as air. In addition, the cell also contains a sensitive microphone, which acts as acoustic transducer. Thus the periodic heating of the sample due to the absorption of modulated electromagnetic radiations results in a periodic heat flow from the sample to the gas, which itself does not absorb the radiation. This periodic heat flow in turn produces pressure variations in the gas medium at the same frequency at which the incident beam is modulated. A sensitive microphone placed in the PA cell and converted in to electrical signals directly monitors these pressure variations.

(ii) In case of sample in the form of thin film, bulk solid samples and liquids, it is possible to measure the heat production through subsequent pressure or stress variation in the sample itself by means of a piezoelectric transducer, which is placed in intimate contact with the sample. Thus the acoustic output signal amplitude directly gives the measure of absorption of the incident beam of radiation. This output is often processed through a ‘phase sensitive detection’ technique.

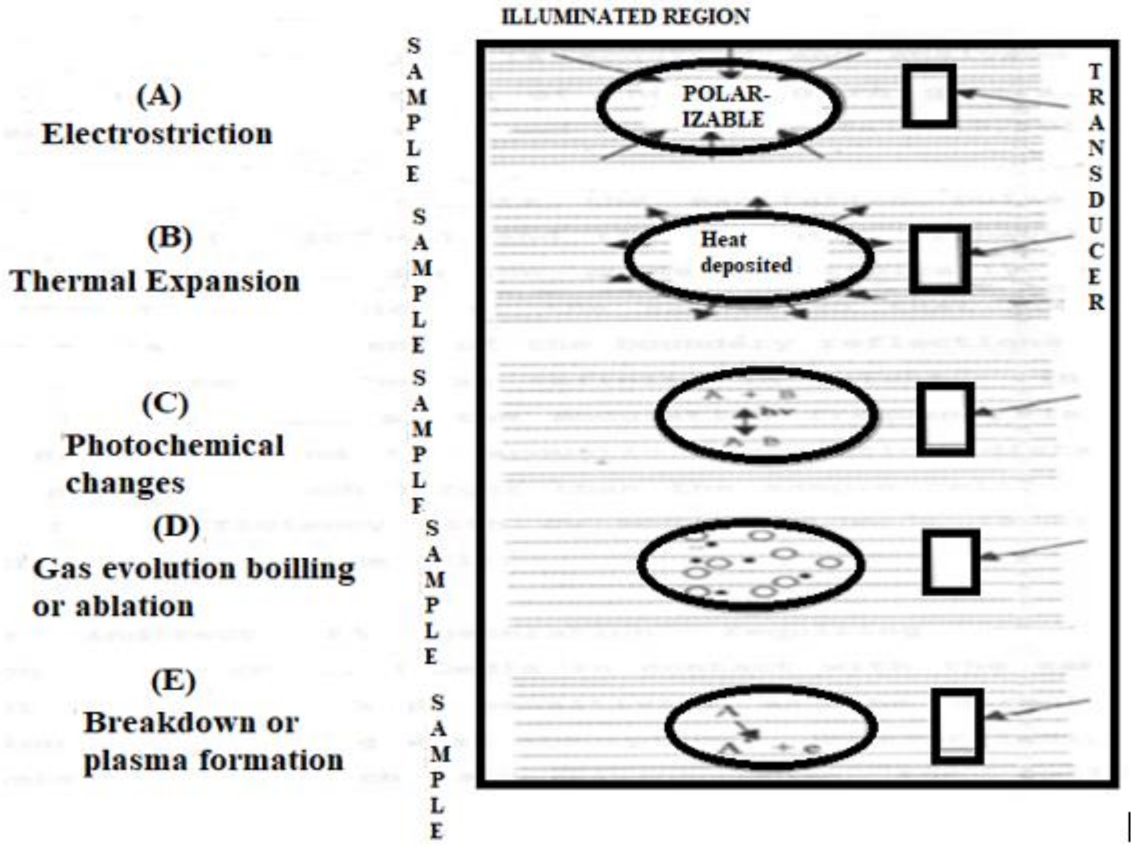


Fig.13.1 Common direct PA generations mechanism

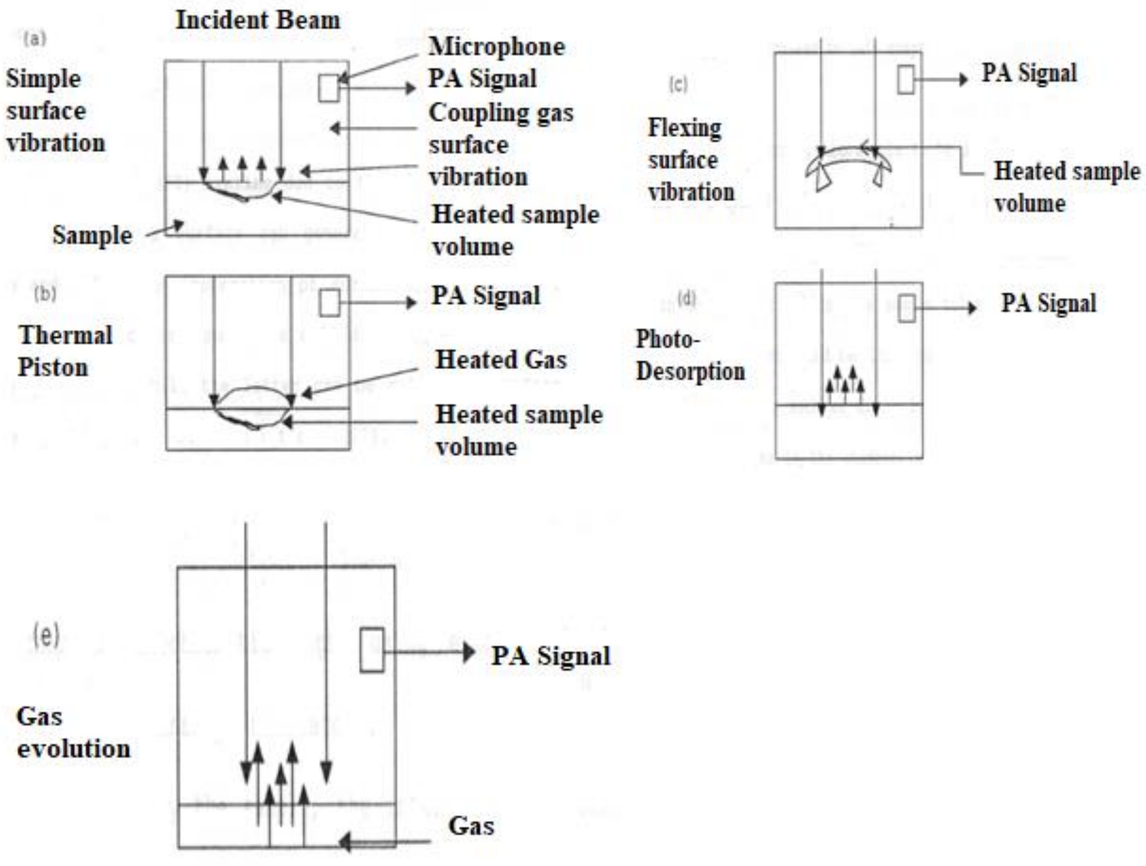


Fig 13.2 various possible cases of indirect PA Generation

Photothermal (PT) heating due to the absorption of an excited beam at a surface can generate surface acoustic wave and affect the propagation of surface acoustic waves. The former effect is sometimes called PA Rayleigh surface wave generation while the latter can be called as surface wave probing of PT generation.

13.0.1 Photothermal Phenomena and Detection Techenques

When the sample is illuminated by an intensity modulated beam, it gets heated up periodically due to the absorption of incident energy and subsequent excitation and non-radiative de-excitation phenomena This is a dissipative process in which the rate of energy transfer is determined by the thermal diffusivity $\alpha = k/\rho c$ and the distance of appreciable energy transfer is given by the thermal diffusion length it, which for periodically deposited heat $\mu=(2\alpha/\omega)^{1/2}$

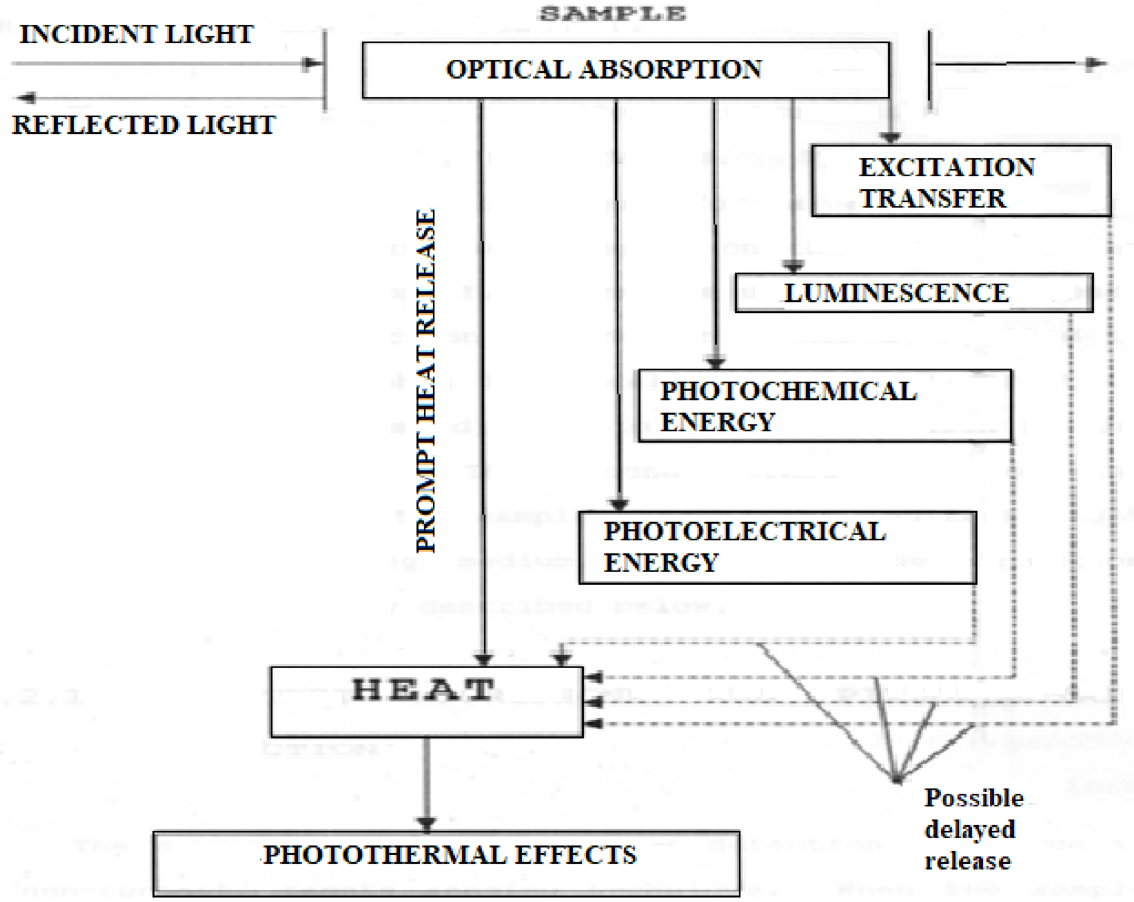
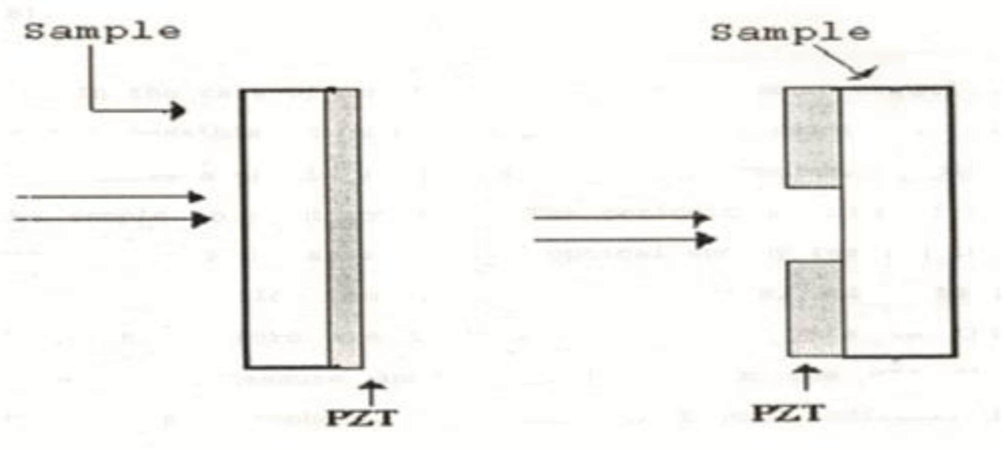


Fig.13.3 Block diagram showing the optical absorption and various possible de-excitation Channels.

Detection methods can either be applied to the sample directly when it is called direct PT effect or to the coupling medium adjacent to the sample which is the indirect PT effect. The second method lies on the assumption that only the sample absorbs the indirect light but not the coupling medium.

13.0.2 Electret Microphone and Piezoelectric Detection:

The conventional P A microphone detection technique is a non-contact, remote sensing technique. In this case, a displacement sensitive detector such as a capacitor microphone proves to be an excellent heat detector. With the availability of sensitive microphone and associated electronics, it is possible to detect temperature rise in a gas of 10^{-6} °C or a thermal input of the order 10^{-9} cal/cm^3 –sec. The response time of the gas-microphone system to the order of 100 µ sec or longer. In the case of solids or liquids, for measuring heat in the sample by means of a piezoelectric detector placed in intimate contact with the sample. It can detect temperature changes of 10^{-7} °C to 10^{-6} ^{O}C, which for a particular solids or liquids corresponds to thermal inputs of the order of 10^{-6} cal/cm^{3}-sec. Since the sample with a displacement sensitive detector such as microphone would be 10 to 100 times less sensitive than a pressure sensitive device such as a piezoelectric detector.



(a) (b)

Fig.13.4 Transducer assembly for PZT detection for solids (a) opaque and (b) transparent.

13.0.3 Photo-thermal Beam Detection (PBD)

This is a non-contact technique originally proposed by Boccara et al and Fournier et al. It is based on the concept of beam deflection by thermally induced changes in the refractive index. The absorption of a modulated pumping beam followed by the diffusion of the deposited heat causes a gradient in the refractive index in a thin layer of gas (or liquid) adjacent to the sample surface. Assuming that the probe beam passes through the coupling medium parallel to the sample surface at a distance x from the surface, it will be deflected by an angle ϕ from its original path Fig. 13.6. For small deflections, ϕ is given by

$$\emptyset = \left(\frac{L}{n_0}\right)\left[{}^{\partial n}/_{\partial T}\right]_{\cdot T_0}\left[\frac{\partial T_g}{\partial X}\right]_{\cdot X=X_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where T_g (x, t) = θ exp. ($-\sigma_g$.x).exp. (jωt) is the temperature distribution in the coupling medium(gas), no is the refractive index of the gas at ambient temperature (T_o) and L is the length of the sample illuminated by the pump beam.

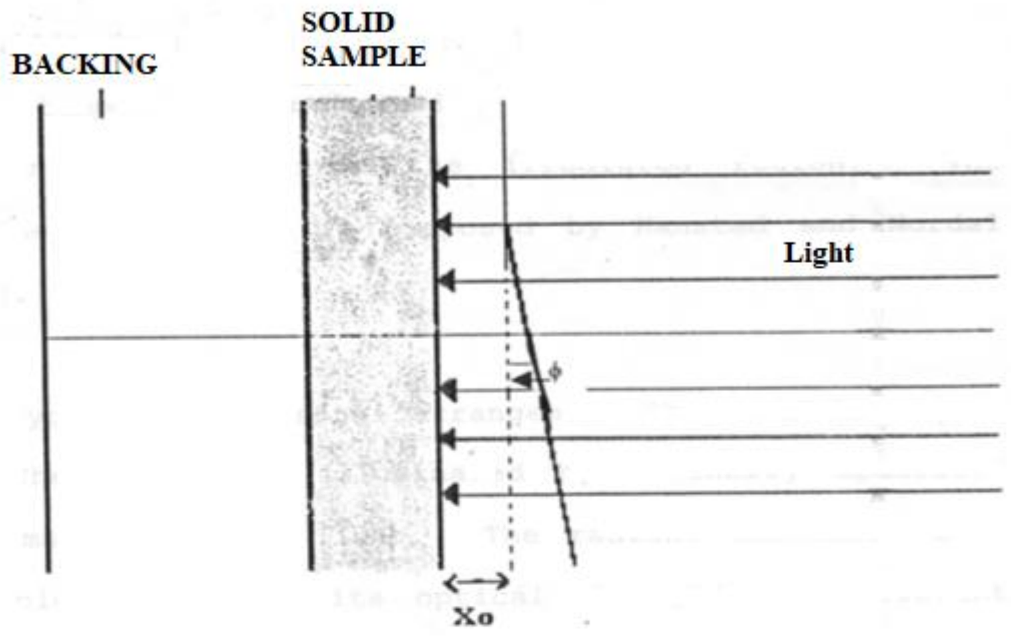


Fig.13.5 PBD experimental configuration

The PBD technique has been employed in the measurement of optical absorption coefficient of thin films, solids, liquids and gases and more recently to a quite diverse class of problems ranging from imaging to scanning microscopy.

13.0.4 Photo-thermal Radiometry and Other Remote Sensing Techniques:

Photo thermal radiometry (PTR) is a non-contact technique in which the specimen is irradiated with amplitude modulated light. This results in pulsating surface temperature and similar pulsation in the thermal radiation emanating from the irradiated region. The technique was originally proposed by Kanstad and Nordal. The thermal radiation from the illuminated area is collected by an appropriate optical system and focused on an infrared detector. The experiment can also be performed using pulsed laser with boxcar or transient detection.By Stefan-Boltzmann law, the total radiant energy emitted from a body of emissivity `e' at temperature T is given by

$$W = e\sigma T^4 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where σ is the Stefan's constant. For a temperature change δT due to the absorption of energy E from a radiation of wavelength λ, the change in radiant energy is

$$\delta W = 4\sigma e T^3 \, \delta T \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The PTR signal in a broadband detector over the entire thermal radiation spectrum may be written as

$$S = 4\sigma e T^3 \, A \, \mathrm{Sin}^2\theta \, dT \quad \ldots\ldots\ldots\ldots\ldots\ldots..(4)$$

where A is the detector area and θ the collecting angle.

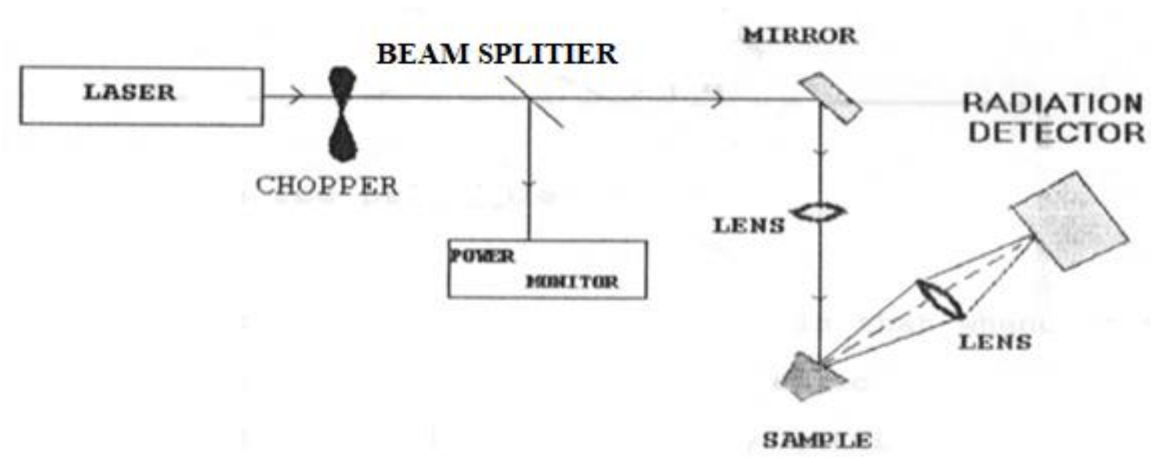


Fig.13.6 Experimental arrangement for PTR measurement

13.0.5 Photo thermal Displacement Spectroscopy (PDS)

The basic principle involved in PDS is that whenever a sample gets heated due to photo thermal effect, the surface expands due to thermal effect thereby getting displaced. The magnitude of displacement is related quantitatively to the optical absorption coefficient. A schematic representation of this technique is shown in figure 13.7. For an absorbing layer of thickness, 1, on a transparent substrate, the photo thermal surface displacement h is given by

$$h = \frac{\propto_{th} \beta P}{2Afc\rho} \quad \ldots\ldots\ldots\ldots\ldots\ldots..(5)$$

where αth - thermal expansion coefficient, R - the fraction of the absorbed light, P - incident power, f – modulating frequency, A - area of optically illuminated region, ρ – the mass density and c - specific heat capacity.

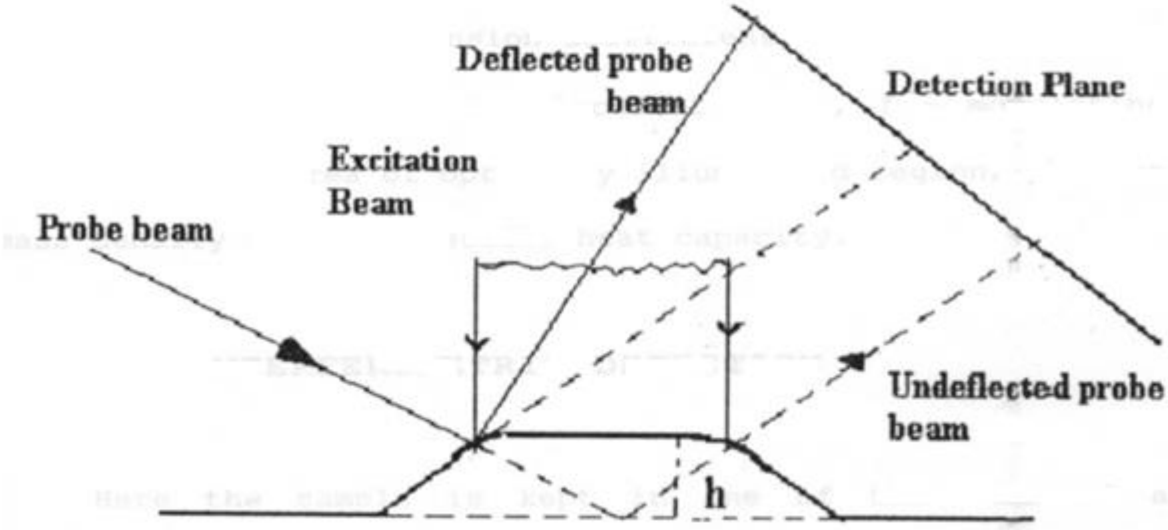


Fig.13.7 PDS principle

13.0.6 Photoelectric Detection

This is another example of contact type photo thermal detection technique. It is based on the use of pyroelectric thin films to detect the temperature change in the sample when exposed to modulated heating. In a pyroelectric material a temperature fluctuation induces an electrical current proportional to the rate of change of its average heat content

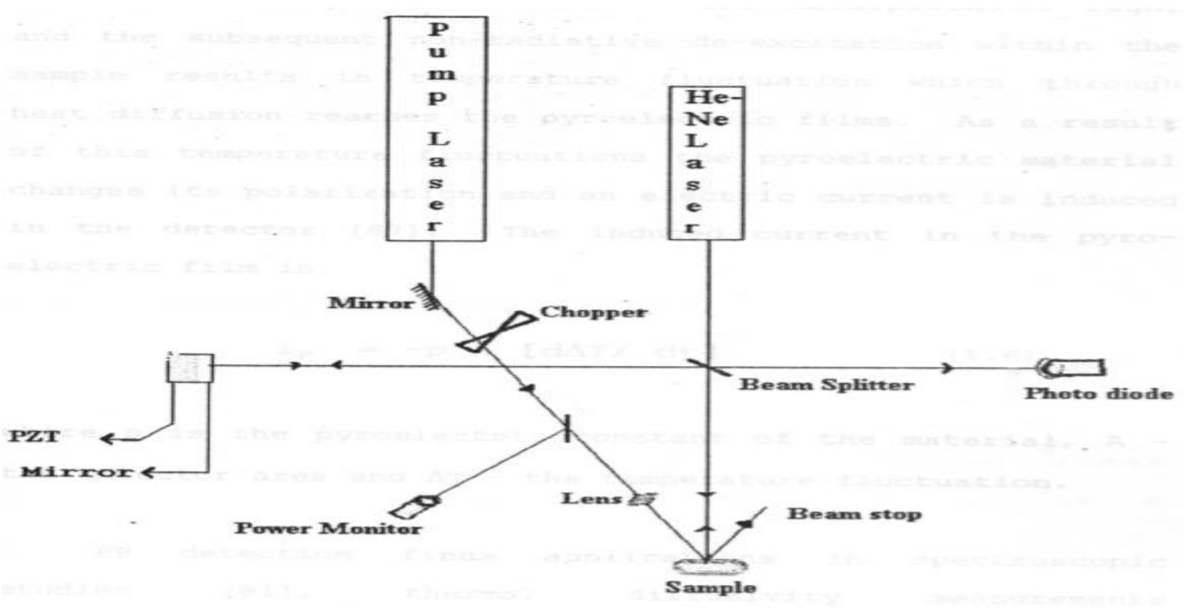


Fig.13.8 PDS-Interferometric method

The induced current in the pyroelectric film is

$$i_p = -p A [d\Delta T/ dt] \quad \text{……………….(6)}$$

where p is the pyroelectric constant of the material, A the detector area and ΔT - the temperature fluctuation.

13.0.7 Interferometric Detection

The sample Is kept in one of the arms of a Michelson interferometer and the position of the mirror in the other arm is modulated to overcome thermally induced drifts and the effect of mechanical vibrations on the interferometers (Fig.13.8). It is reported that the beam reflection approach is easier to implement and serves long term stability requirement.

13.0.8 Theory of the Photoacoustic effect in condense media

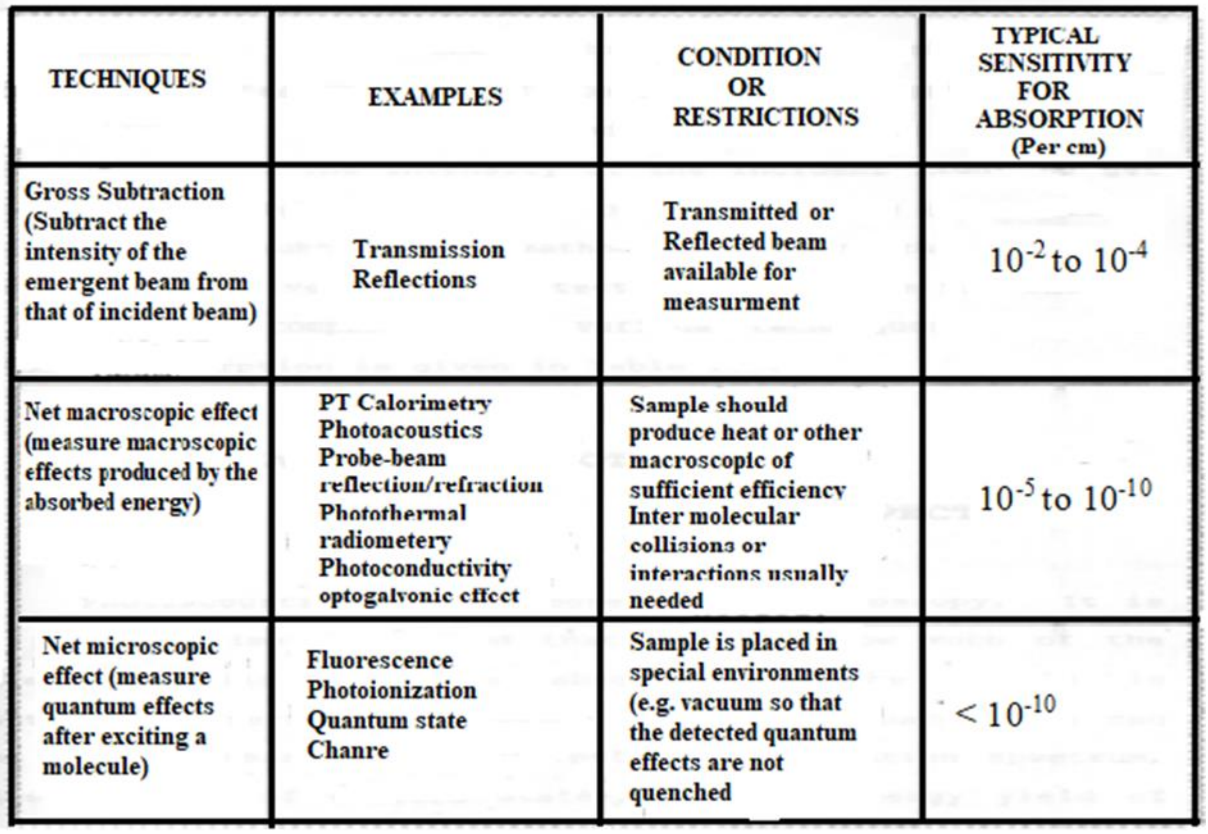
Though the photoacoustic effect was discovered as early as in 1881, the potentiality of the technique is not exploited until 1975 after the invention of microphone. There had been several theories to account for the photoacoustic effect in-gaseous media. There theories range from Bell's concept of air expulsion from the pores in the solid surface during heating to Rayleigh's convention that the signal is derived primarily from thermally induced mechanical vibrations of the solid. Experiments performed during the last few years indicate that the primary source of photoacoustic signal from a condensed sample, as measured by the gas microphone method, arises from the periodic heat flow from the sample to the surrounding gas with the subsequent change in the gas pressure within the cell.

The first attempt to develop an exact theory of photoacoustic effect in solid was carried out by porker in order to give a quantitative explanation for photo acoustic signal emanating from cell window while performing photo acoustic effect in condensed media was formulated by Rosencwaig and Gorsho. This theory now commonly referred to as the RG theory, shows they in a gas-microphone measurement of a PA signal, the signal depends both on the generation of an acoustic pressure disturbance at the sample-gas interface and on the transport of this disturbances through the gas to the microphone. The generation of the surface pressure disturbances depends in turns on the periodic variations of temperature at the sample-gas interface.

13.0.9 Advantages of Photoacoustic Spectroscopy

Since the photoacoustic signal is generated only after the absorption of optical signal, the light that transmitted or elastically, scattered by the sample does not interfere with the photoacoustic spectroscopic (PS) measurements. This is of greater importance when one works with essentially transparent media, such as polluted gasp that have few absorbing centers. Since the method is insensitive to the scattered radiation it Is possible to obtain optical absorption data on highly scattering materials such as powders, amorphous solids, gels and colloids. Another advantage is the capability of obtaining absorption spectra of optically opaque samples, since the method does not depend on the detection of photons.Coupled with this is the capability, unique to photoacoustic spectroscopy, of performing non-destructive depth profile analysis of absorption as a function of depth in to a material. The PA effect results from a radiation less energy conversion process and is therefore complementary to radiative and photo chemical processes. Thus PAS can be used as a sensitive, though indirect method for studying the phenomena of fluorescence and photosensitivity in matter.

Table 13.1 Comparison of various techniques optical absorption measurement for weak optical absorption measurement



TECHNIQUES	EXAMPLES	CONDITION OR RESTRICTIONS	TYPICAL SENSITIVITY FOR ABSORPTION (Per cm)
Gross Subtraction (Subtract the intensity of the emergent beam from that of incident beam)	Transmission Reflections	Transmitted or Reflected beam available for measurment	10^{-2} to 10^{-4}
Net macroscopic effect (measure macroscopic effects produced by the absorbed energy)	PT Calorimetry Photoacoustics Probe-beam reflection/refraction Photothermal radiometery Photoconductivity optogalvonic effect	Sample should produce heat or other macroscopic of sufficient efficiency Inter molecular collisions or interactions usually needed	10^{-5} to 10^{-10}
Net microscopic effect (measure quantum effects after exciting a molecule)	Fluorescence Photoionization Quantum state Chanre	Sample is placed in special environments (e.g. vacuum so that the detected quantum effects are not quenched	$< 10^{-10}$

13.1.0 Applications of Photoacoustic in different fields:

The applications of photo acoustic spectroscopy (PAS), which are directly related to the technological importance, are presented in the following points.

(a) **Application to solid**: In recent year’s substantial progress has been made in the fabrication of law loss optical materials for use in the visible and infrared spectral regions. This work how made necessary development of new techniques for measuring bulk and surface absorption at law levels. The absorption studies carried out in the infrared transmitting materials like Zn,Se and Uncoated sapphire could reveal the absorption coefficients at 10.6 Um and the influence of thickness. The studies revealed that the layer which acts as an antireflection coating on the surface of these materials at this wavelength region. This in turn brings out the developments of precision optics, which can improve the Co_2 laser efficiency. Similarly, the methods for the accurate determination of photoluminescence quantum efficiencies and relaxation processes are of considerable importance.

(b) **Application to weak Absorption in Gases**: One of the most significant applications of photoacoustic effect is the sensitive detection of pollutant gas species present in the atmosphere. The studies could attain a sensitivity limit of few parts per billion, which is considered to be a remarkable achievement the photoacoustic spectroscopic technology.

(c) **Application to thin films**: The use of Photoacoustic technique for measuring absorption in thin films, minelayers or even multilayers has been reported. For thin films of powders or for liquids, the pulsed Photoacoustic technique provides measurement of an absorption coefficient as low as 10^{-3} cm^{-1} for a thickness of 10^{-8} cm. the photoacoustic method has been successfully employed to measure the enthalpy of absorbed materials like pyridine on evaporated Polycrystalline nickel films this provide the absolute rate deposition of a single monolayer of surface absorption coefficient at various monolayer and the of deposition of layers on the substrate 'Consequently' this technique finds its application in the field of semiconductor industry in which the detailed analysis of the changes in Physical properties at each monolayer is often necessary to develop highly efficiently semiconductor devices since the photoacoustic signal is a function of the thermal propagation within the sample, it is possible to determine the thermal properties like thermal diffusivity and thermal conductivity with great accuracy normally not attainable with other technique.

(d) Microwave and Interference Spectroscopy

Originally studies of (PA) were carried out in the LW -Visible region of the electromagnetic spectrum. Such studies can be carried out at any wavelength provided, the material under study has absorption in the wavelength used. Several authors have used PP. detection for microscopic absorption studies over a wide range of materials. The use of PAS in the near IR region can be carried out using the same instrumentation as for UV-Visible region. The absorption bands observed in the near IR region for solid and liquid samples are attributable to overtones and combinations of the fundamental vibrational modes of particular bands. Most frequently observed bands are those relating to hydrogenic systems e.g.: -CH, -OH, and -NH.

(e) Surface Studies:

PAS can be used in the study of adsorbed and chemisorbed molecular species and compounds on the surface of metals, semiconductors and even insulators. Such studies can be done at any wavelength, provided the substrate is non-absorbing at that wavelength. The PAS experiment gives optical absorption spectra of the adsorbed or chemisorbed compounds on the surface of the substrate.

(f) Chemical Studies:

PAS is ideally suited to catalytic studies since catalytic substances are by their very nature difficult to investigate by conventional spectroscopic means. These difficulties arise from the fact that in heterogeneous catalysis the catalyst is often in the form of a fine powder.

(g)Photoacoustic in Biology and Medicine: A Photoacoustic method of determining the absorption of a material is widely being used in biological as well as in medical fields many of the above-mentioned samples occur naturally in insoluble states; many others are membrane bound or part of bone or tissue structure. These materials are found to function biologically with in a more or less solid matrix. Photoacoustic spectroscopy through its capability of providing optical data on intact biological matter, even with materials, which are optically opaque, holds great promise both as a research tool and as a diagnostic tool in biology and medicine.

(h)Miscellaneous Applications: Photoacoustic spectroscopy is a tool for the study of radiation chemistry. Another important area of application of photoacoustic spectroscopy is in photosynthesis. This technique can be used to measure energy conversion and storage, for molecular structure and interaction studies as well as oxygen evolution in photosynthetic systems. The bond gap energies of semiconductors can be obtained by photoacoustic spectroscopy. Study of the strength characteristics of thin films is another application of photoacoustic method.

Problems Sets

Q.1 What is photoacoustic effect.

Q.2 Explain about the different mechanisms for producing the photoacoustic effect.

Q.3 Discuss about the direct and indirect PA generation mechanism.

Q.4 Why does PAS require pulses of light instead of a continuous steady source of light to hit the

Sample.

Q.5 Draw the block diagram showing the optical absorption and various possible de-excitation

channels.

Q.6 write a short note on Electret Microphone and Piezoelectric Detection mechanism.

Q.7 Give brief idea of Experimental arrangement for PTR measurement.

Q.8 Give the Advantages of Photoacoustic Spectroscopy.

Q.9Write the applications of Photoacoustic in different fields.

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