SPECTROSCOPY

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(II M.SC PHYSICS)

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UNIT – III

ELECTRONIC SPECTROSCOPY OF ATOMS AND MOLECULES

Syllabus-Shape of atomic orbitals - energies of atomic orbitals - fine structure of hydrogen atom spectra - electronic spectra of diatomic molecules-Born - Oppenheimer Approximation - Frank-Condon Principle - Electronic spectra of polyatomic molecules-Re-emission of energy by an excited molecule - Photo electron Spectrometer.

Shape of atomic orbitals

Atomic orbitals are mathematical functions that describe the wave nature of electrons (or electron pairs) in an atom. There are four different kinds of orbitals, denoted s, p, d and f each with a different shape. To completely describe an electron in an atom, four quantum numbers are needed: energy (n), angular momentum (ℓ), magnetic moment (m_ℓ), and spin (m_s).

Quantum number	Symbol	Possible/allowed values	Function
Principal quantum number	n	1, 2, 3, 4, ……	Describes the energy and size of the orbital.
Orbital / Angular momentum quantum number	l	0, 1, 2, 3, …(n-1)	Describes the shape of the orbital and the electronic angular momentum
Magnetic quantum number	m_l	$-l$,…..-1,0,1…..l	Describe the direction and orientation of a particular orbital and describes the electrons behavior in magnetic field
Spin quantum number	m_s	+1/2 , -1/2	Describes the spin of the electron

Principal Quantum Number (n): $n = 1, 2, 3, \ldots, \infty$

- The principal quantum number, n, describes the energy of an electron and the most probable distance of the electron from the nucleus. In other words, it refers to the size of the orbital and the energy level an electron. All orbitals that have the same value of n are said to be in the same **shell** (**level**). For a hydrogen atom with n=1, the electron is in its *ground state*; if the electron is in the n=2 orbital, it is in an *excited state*. The total number of orbitals for a given n value is n^2.

Orbital / Angular momentum quantum number (l): l = 0, ..., n-1.

- The second quantum number, known as the angular or orbital quantum number, describes the sub shell and describes the shape of the orbital. .
- Orbital quantum number divides the shells into smaller groups of orbitals called **sub shells (sublevels**). Usually, a letter code is used to identify l to avoid confusion with n:

l	0	1	2	3	4	5	...
Letter	*s*	*p*	*d*	*f*	*g*	*h*	...

Magnetic Quantum Number (m_l): $m_l = -l, ..., 0, ..., +l$.

- It describes the orientation in space of a particular orbital. It is called the *magnetic* quantum number because the effect of different orientations of orbitals was first observed in the presence of a magnetic field. This quantum number divides the subshell into individual **orbitals** which hold the electrons; there are $2l+1$ orbitals in each subshell. Thus the *s* subshell has only one orbital, the *p* subshell has three orbitals, and so on.

Spin Quantum Number (m_s): m_s = +½ or -½.

- Specifies the **orientation of the spin axis** of an electron. Unlike n, l, and m_l, the electron spin quantum number ms does not depend on another quantum number. It designates the direction of the electron spin and may have a spin of +1/2, represented by↑, or –1/2, represented by ↓. This means that when ms is positive the electron has an upward spin, which can be referred to as "spin up." When it is negative, the electron has a downward spin, so it is "spin down."

Thus, it takes three quantum numbers to define an orbital but four quantum numbers to identify one of the electrons that can occupy the orbital.

Rules Governing the Allowed Combinations of Quantum Numbers

- The three quantum numbers (*n*, *l*, and *m*) that describe an orbital are integers: 0, 1, 2, 3, and so on.
- The principal quantum number (*n*) cannot be zero. The allowed values of *n* are therefore 1, 2, 3, 4, and so on.
- The angular quantum number (*l*) can be any integer between 0 and *n* - 1. If *n* = 3, for example, *l* can be either 0, 1, or 2.
- The magnetic quantum number (*m*) can be any integer between -*l* and +*l*. If *l* = 2, *m* can be either -2, -1, 0, +1, or +2.

Table of Allowed Quantum Numbers

n	*l*	m_l	Number of orbitals	Orbital Name	Number of electrons
1	0	0	1	1*s*	2
2	0	0	1	2*s*	2
	1	-1, 0, +1	3	2*p*	6
3	0	0	1	3*s*	2
	1	-1, 0, +1	3	3*p*	6
	2	-2, -1, 0, +1, +2	5	3*d*	10
4	0	0	1	4*s*	2
	1	-1, 0, +1	3	4*p*	6
	2	-2, -1, 0, +1, +2	5	4*d*	10
	3	-3, -2, -1, 0, +1, +2, +3	7	4*f*	14

The wavefunctions for the hydrogen atom is given by the equation

$$\psi_n = f\left(\frac{r}{a_0}\right)\exp\left(-\frac{r}{na_0}\right) \qquad \text{-----------------} \ (1)$$

Where $a_0 = h^2/4\pi^2mc^2$,

r is radial distance from the nucleus,

$f(r/a_0)$ is a power series of degree (n-1) in r/a_0,

n is the principal quantum number which can have only integral values, 1,2,3,….

The constant a_0 has the dimensions of length and so the quantity r/a_0 is a pure number. Thus for particular values of r and n, Ψ_n and Ψ_n^2 are also simply numbers and Ψ_n^2 represents the probability of finding the electron at chosen distance r from the nucleus when it is in the state represented by n.

Since the wave functions represent only a probability distribution of an electron it is difficult to define precisely the shape and size of an orbital. From the above equation, for very large values of r, Ψ_n and Ψ_n^2 has a small value. Thus an orbital tails off to infinity in all directions. However, the difficulty can be overcome if we draw a three dimensional shape within which the electron spends, 95 percent of its time. This can be taken as effective boundary of the electrons domain and it can be called the orbital.

Considering the wavefunction it is seen that the corresponding orbital must be spherical, for at any distance from the nucleus. The spherical orbitals associated with the value of $l = 0$ is called as *s orbitals.* The s orbitals are labeled according to their n quantum numbers 1s, 2s, ……..ns.

Orbitals with l=1 have twin-lobed shape. As n increases the shape also increases in size. Such orbitals are labeled as p orbitals. For a given value of n there are three p orbitals labeled as np_x, np_y, and np_z.. These three is connected with three values of m, i.e., m= +1, 0 and -1.

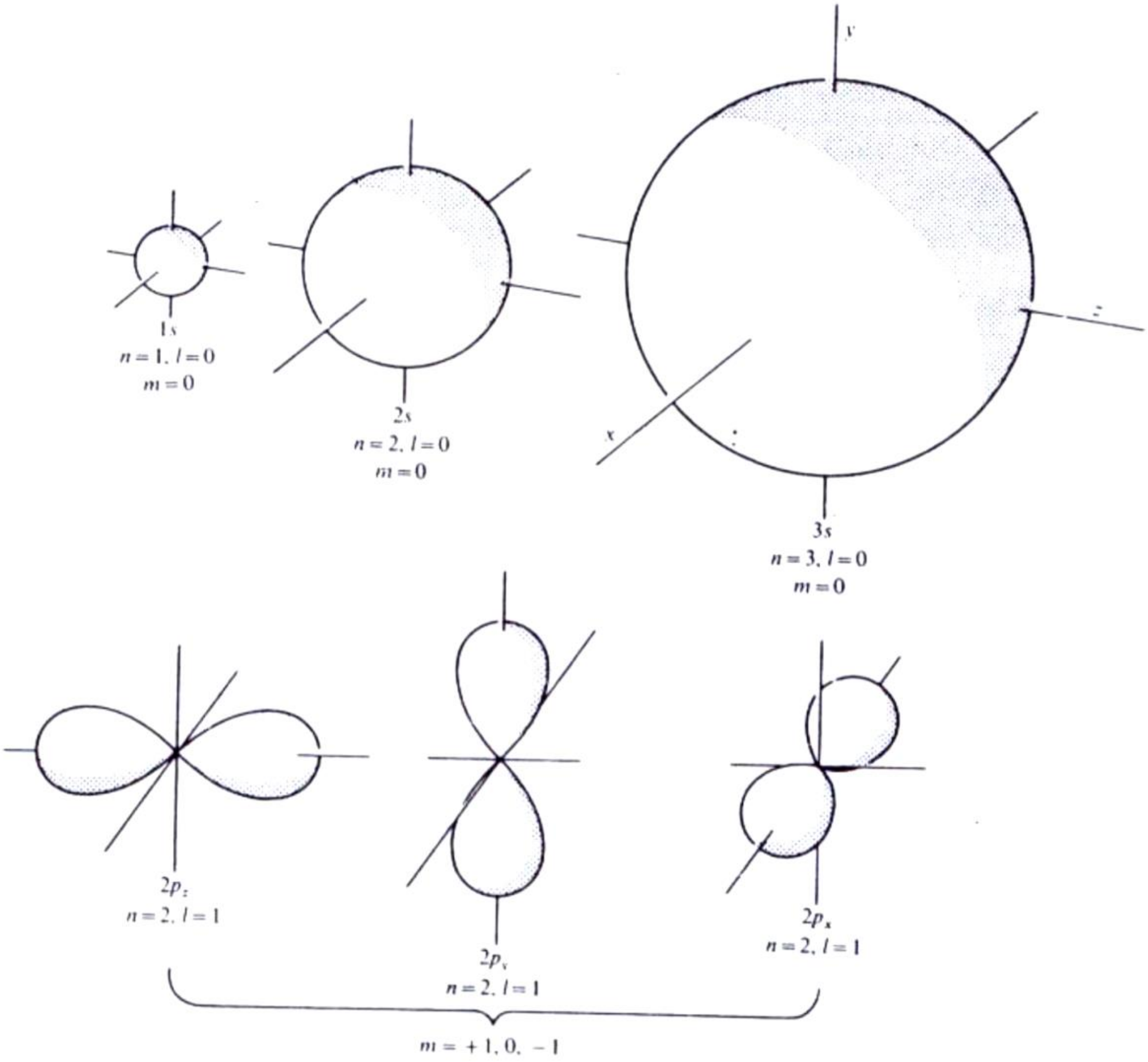


Fig. Electronic orbitals occupied by the electron in a hydrogen atom

For $l = 2$ the n is ≥ 3. The m values are $m = \pm 2, \pm 1$ or 0. The corresponding orbitals are called as *d* orbitals.

For $l = 3$ the n is ≥ 4. The m values are $m = \pm 3, \pm 2, \pm 1$ or 0. The corresponding orbitals are called as *f* orbitals .

Orbitals with higher values of l are less important. $l=4$ is labeled as g orbital and $l = 5$ is labeled as h orbital.

Energies of atomic orbitals - Fine structure of Hydrogen atom spectra

However large an atom its electrons take up orbitals of the s, p, d, ……. type and so the overall shape of each electrons domain is unaltered. The energy of each orbital varies considerably from atom to atome. There are two main contributions to this energy – (1) attraction between electrons and nucleus, (2) repulsion between electrons n the same atom. Hydrogen atom is the simplest atom, so the second factor is completely absent. Because of the absence of interelectronic effects all orbitals with the same n value have the same energy in the hydrogen. Thus the 2s and 2p orbitals are degenerate as the 3s, 3p and 3d. However the energies of the 2s, 3s,4s, …. Orbitals differ considerably. For the s orbitals given by eqn. 1

$$\psi_n = f\left(\frac{r}{a_0}\right) \exp\left(-\frac{r}{na_0}\right)$$

Schrödinger equation shows that the energy is:

$$E_n = -\frac{me^4}{8h^2\varepsilon_o^2 n^2} \quad \mathrm{J}$$

$$\varepsilon_n = -\frac{me^4}{8h^3 c\varepsilon_o^2 n^2} = -\frac{R}{n^2} \quad \mathrm{cm}^{-1} \qquad (n = 1, 2, 3, \ldots)$$

------ (2)

Where ε_0 is the vacuum permittivity and R is the Rydberg constant. Since p, d… orbitals have the same energies as the corresponding *s* (equation 2) represents all the electronic energy levels of the hydrogen atom.

The lowest value of ε_n is plainly ε_n = - R cm^{-1} (when n = 1), and so this represents the most stable or ground state.

ε_n increases with increasing n, reaching a limit, $\varepsilon_n = 0$ for $n = \infty$. This represents complete removal of the electron from the nucleus, i.e., the state of ionization. These energy levels (for n = 1 to 5 and *l* = 0, 1 and 2 only) are shown in below figure.

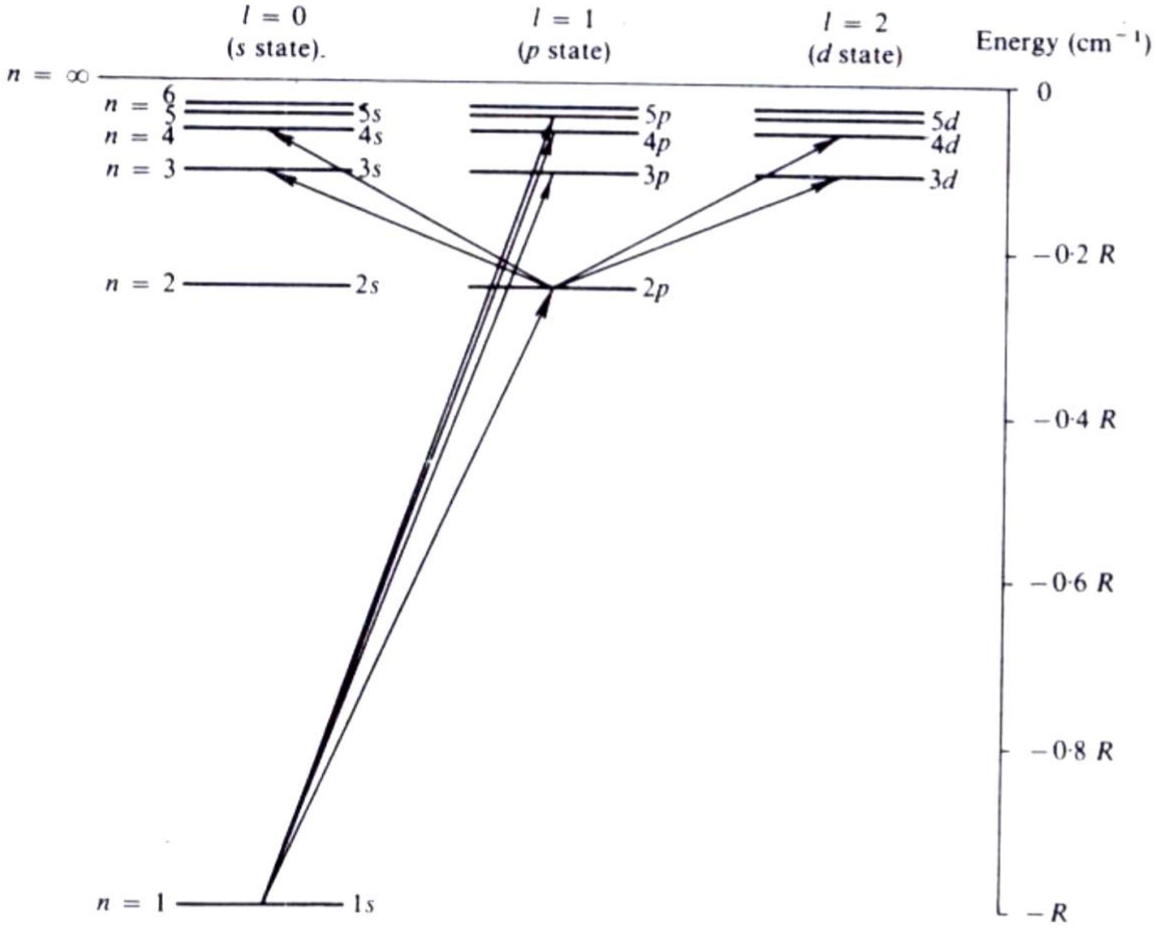


Figure – Electronic energy levels and transitions between them for the single electron of the hydrogen atom.

The three p states and five d states for each n are degenerate and not shown separately in the above energy level diagram. To discuss the spectra the selection rules are needed which governs the transitions. The Schrodinger equation shows these to be

$$\Delta n = \text{anything} \qquad \text{and} \qquad \Delta l = \pm 1 \text{ only} \qquad \text{-------------} \ (3)$$

From these selection rules it is seen that an electron in the ground state (the 1s) can undergo a transition into any p state

$$1s \rightarrow np \qquad (n \geq 2)$$

while a 2p electron can have transitions either into an state or a d state

$$2p \rightarrow ns \quad \text{or} \quad nd$$

Since s and d orbitals are here degenerate the energy of both these transitions will be identical. In general an electron in a lower state n″, can undergo a transition into a higher state n′, with absorption of energy

$$\Delta\varepsilon = \varepsilon_{n'} - \varepsilon_{n''} \quad \text{cm}^{-1}$$

$$\therefore \quad \bar{\nu}_{\text{spect.}} = -\frac{R}{n'^2} - \left(-\frac{R}{n''^2}\right) = R\left\{\frac{1}{n''^2} - \frac{1}{n'^2}\right\} \quad \text{cm}^{-1}$$

------ (4)

An identical spectral line will be produced in emission if the electron falls from state n′ to state n″. In both cases *l* must change by unity. Consider few transitions,

Transitions $1s \rightarrow n'p$, $n' = 2, 3, 4, \ldots$. For these

$$\bar{\nu}_{\text{Lyman}} = R\left\{\frac{1}{1} - \frac{1}{n'^2}\right\} = R - \frac{R}{n'^2} \quad \text{cm}^{-1}$$

$$= \frac{3R}{4}, \frac{8R}{9}, \frac{15R}{16}, \frac{24R}{25}, \ldots \quad \text{cm}^{-1} \quad (\text{for } n' = 2, 3, 4, 5, \ldots)$$

Hence we expect a series of lines at the wavenumbers given above. It is called Lyman series after its discoverer. The spectrum is given in the below figure together with a scale in units of R and in wavenumbers. We can see that the spectrum converges to the point R cm^{-1}, and from the observed spectrum the very precise value R = 109677.581 cm^{-1}, is obtained. This convergence limit is shown as dashed lines. It plainly represents complete removal of the electron i.e., ionization – and the energy required to ionize the atom is given in cm^{-1}, by the value of R.

Using the conversion factor 1 cm^{-1} = 1.987 x 10^{-23} J we have very precise measure of the ionization potential from the ground state 2.1781 x10^{-18} J (in eV it is 13.595).

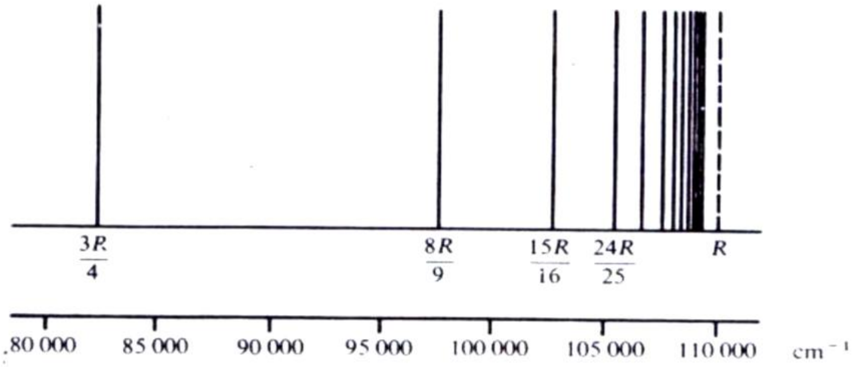


Fig – Representation of part of the Lyman series of the hydrogen atom showing the convergence (ionization) point.

Another set of transitions arises from an electron initially in the $2s$ or $2p$ states: $2s \rightarrow n'p$ or $2p \rightarrow n's, n'd$. For these we write:

$$\bar{\nu}_{\text{Balmer}} = R\left\{\frac{1}{4} - \frac{1}{n'^2}\right\} \quad \text{cm}^{-1}$$

$$= \frac{5R}{36}, \frac{3R}{16}, \frac{21R}{100}, \ldots \quad \text{cm}^{-1} \qquad (\text{for } n' = 3, 4, 5, \ldots)$$

Thus we expect another series of lines converging to $\frac{1}{4}R$ cm^{-1} ($n' = \infty$); this series, called the Balmer series after its discoverer, is observed and the value of $\frac{1}{4}R$ obtained from its convergence limit—which represents the ionization potential from the first excited state—is in excellent agreement with the value of R from the Lyman series.

Other similar line series (called the Paschen, Brackett, Pfund, etc., series) are observed for $n'' = 3, 4, 5, \ldots$; indeed these spectra were observed long before the modern theory of atomic structure had been developed. The spectral lines were correlated empirically by Rydberg, and he showed that an equation of the form given in Eq. 4 described the wavenumbers of each. It is after him that the Rydberg constant is named.

It should be mentioned that each line series discussed above shows a *continuous absorption* or *emission* to high wavenumbers of the convergence limits. The convergence limit represents the situation where the atomic electron has absorbed just sufficient energy from radiation to escape from the nucleus with zero velocity. It can, however, absorb more energy than this and hence escape with higher velocities and since the kinetic energy of an electron moving in free space is *not* quantized, *any* energy above the ionization energy can be absorbed. Hence the spectrum in this region is continuous.

ELECTRONIC SPECTRA OF DIATOMIC MOLECULES

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 is based on the fact that the nuclei are much heavier than the electrons. Consequently nuclei move much more slowly than the electrons. To the electrons the nuclei appear fixed. Thus in BO approximation the nuclear and electron motion is separated. It leads to a molecular wave function in terms of electron positions and nuclear positions. The wavefunction is assumed to be the product of the electronic, vibrational and rotational wave functions. The energy levels for each type of transition can be treated independently. The total energy of the molecule is the sum of the electronic, vibrational and rotational energy.

The approximation is widely used to speed up the computation of molecular wavefunctions and other properties for large molecules. The approach is named after Max Born and J. Robert Oppenheimer who proposed it in 1927.

In molecular spectroscopy, using the BO approximation means considering molecular energy as a sum of independent terms, e.g.:

$$E_{Total} = E_{electronic} + E_{vibration} + E_{rotation} + E_{nuclear\ spin}$$

These terms are of different orders of magnitude and the nuclear spin energy is so small that it is often omitted. The electronic energies consist of kinetic energies, interelectronic repulsions, internuclear repulsions, and electron–nuclear attractions, which are the terms typically included when computing the electronic structure of molecules.

As a first approach to the electronic spectra of diatomic molecules we use Born-Oppenheimer Approximation and this may written as

$$E_{Total} = E_{electronic} + E_{vibrational} + E_{rotational} \text{ -------------- } (1)$$

$$(E_{electronic} >> E_{vibrational} >> E_{rotational})$$

Which implies that the electronic, vibrational and rotational energies of a molecule are completely independent of each other. A change in the total energy of a molecule is written as

$$\Delta E_{\text{total}} = \Delta E_{\text{elec.}} + \Delta E_{\text{vib.}} + \Delta E_{\text{rot.}} \quad \text{J}$$

or

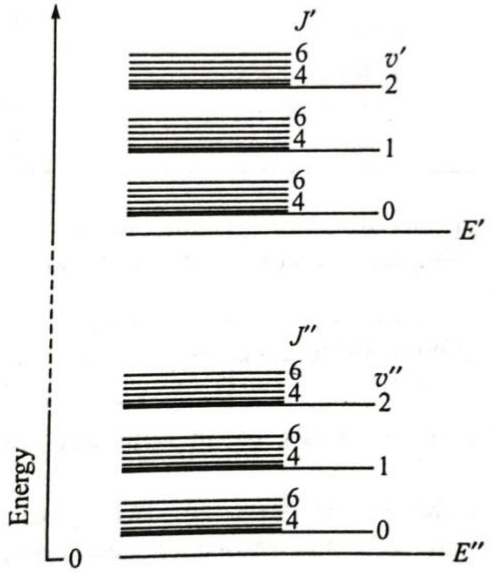
$$\Delta \varepsilon_{\text{total}} = \Delta \varepsilon_{\text{elec.}} + \Delta \varepsilon_{\text{vib.}} + \Delta \varepsilon_{\text{rot.}} \quad \text{cm}^{-1} \quad \text{-------- (2)}$$

The approximate orders of magnitude of these changes are:

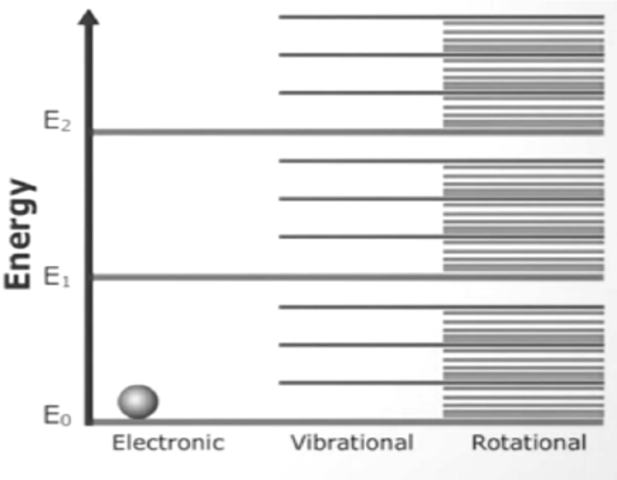
$$\Delta \varepsilon_{\text{elec.}} \approx \Delta \varepsilon_{\text{vib.}} \times 10^3 \approx \Delta \varepsilon_{\text{rot.}} \times 10^6 \quad \text{----- (3)}$$

It is seen that the vibrational changes will produce a ‘coarse structure’ and rotational changes a ‘fine structure’ on the spectra of electronic transitions.

It is noted that Pure rotational spectra are shown by molecules possessing a permanent electric dipole moment, vibrational spectra requires a change of dipole during the motion and electronic spectra are given by all molecules since changes in the electron distribution in a molecule are always accompanied by a dipole change. This means that homonuclear molecules (H_2 or N_2) which show no rotation or vibration-rotation spectra, do give an electronic spectra.



Quantized energy levels of a diatomic molecule: E″, E′—electronic levels; J″, J′—rotational levels; v″, v′—vibrational levels.

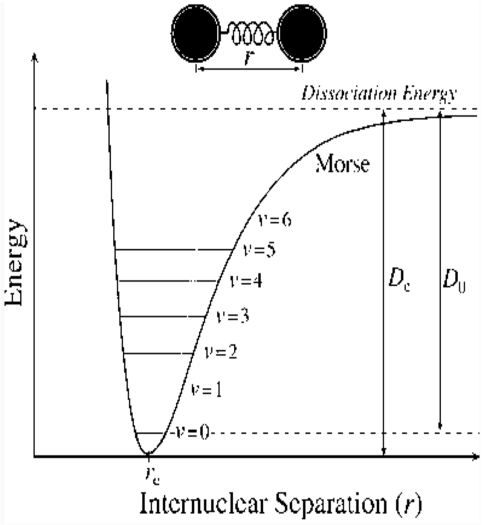


Franck Condon Principle

- Frank-Condon principle states that an “electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition”. That is during an electronic transition, the internuclear distance remains the same. This means the transition between electronic states will be vertical.

Alternatively Frank Condon principle states as “**Transition between electronic states occur vertically in a potential energy diagram”**

Morse curve, represents the energy when one atom is considered fixed on the r = 0 axis and the other is allowed to oscillate between the limits of the curve. “**The Morse Curve is represents the potential energy of an electronic state of a diatomic molecule”.**



Classical theory would suggest that the oscillating atom would spend most of its time on the curve at the turning point of its motion, since it is moving most slowly there. Quantum theory, agrees this view for high values of the vibrational quantum number. Quantum theory shows that for $\upsilon = 0$ the atom is most likely to be found at the centre of its motion i.e., at the equilibrium internuclear distance r_{eq}. For $\upsilon = 1,2,3,$ ……. the most probable positions steadily approach the extremities until, for high υ, the quantum and classical pictures merge. This behavior is shown in below figure.

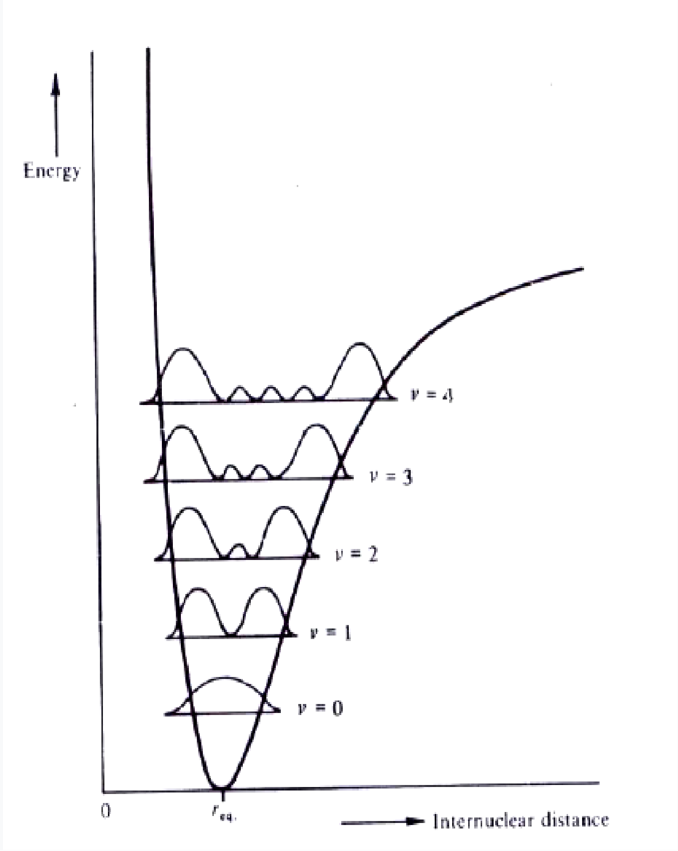


Fig. The probability distribution for a diatomic molecule according to the quantum theory. The nuclei are most likely to be found at distances apart given by the maxima of the curve for each vibrational state.

If a diatomic molecule undergoes a transition into an upper electronic state in which the excited molecule is stable with respect to dissociation into its atoms, then we can represent the upper state by a Morse curve similar in outline to that of the ground electronic state.

The below figure shows three possibilities. In (a) the upper electronic state having the same equilibrium internuclear distance as the lower. Now the Frank-condon principle suggests that a transition occurs vertically, since the internuclear distance does not change. If the molecule is consider to be initially in the ground state both electronically (ε'') and vibrationally ($\upsilon''= 0$), then the most probable transition is that indicated by the vertical line in fig (b). Thus the strongest spectral line of the $\upsilon''= 0$ progression will be the (0,0). However the quantum theory only says that the probability of finding the oscillating atom is greatest at the equilibrium distances in the $\upsilon= 0$ state. There is some chance of transition starting from the ends of the $\upsilon''= 0$ state and finishing in the $\upsilon' = 1, 2,$ etc states. The (1,0), (2,0), etc., lines diminish rapidly in intensity, however, as shown at the foot of figure (a)

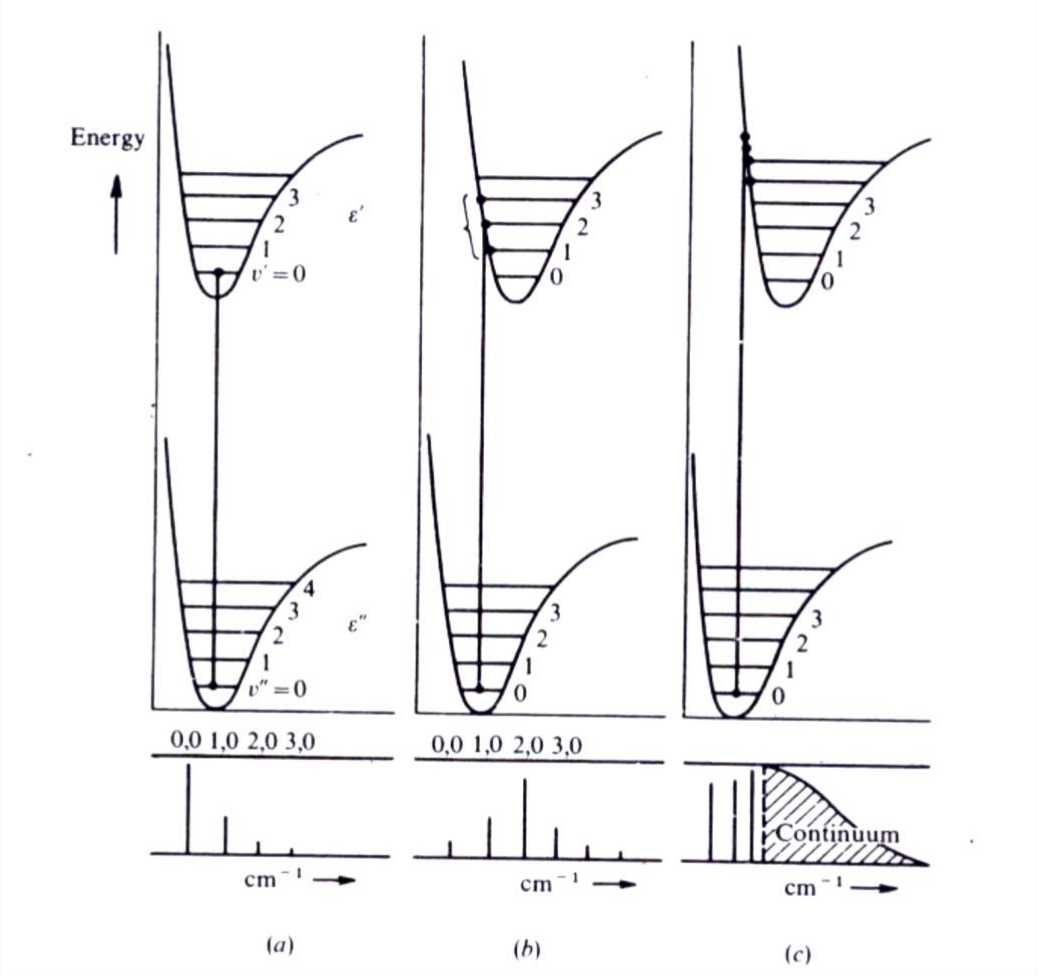


Fig. The operation of the Franck-Condon principle for (a) internuclear distances equal in upper and lower states. (b) upper state internuclear distance a little greater than that in the lower state and (c) upper state distance considerably greater.

Fig. (b) shows the case where the excited electronic state has a slightly greater internuclear separation than the ground state. Vertical transition occur from $\upsilon'' = 0$ to the upper vibrational state $\upsilon' = 2$. In fig (c) the upper state separation is drawn as considerably greater than that in the lower state and it is seen that, firstly, the vibrational level to which a transition takes place has a high υ' value. Further, transitions can now occur to a state where the excited molecule has energy in excess of its own dissociation energy. From such states the molecule will dissociate without vibrations and, since the atom which are formed may take up any value of kinetic energy, the transitions are not quantized and a continuum results. This is shown at the foot of the figure. Thus Franck-Condon principle is able to account for the intensities of lines in vibrational-electronic spectra.

Electronic Spectra of Polyatomic molecules

It is seen that the vibrational frequencies of a particular atomic grouping within a molecule, for example, CH_3, C=O, C=C, etc., are usually fairly insensitive to the nature of rest of the molecule. Other bond properties, such as length or dissociation energy, are also largely independent of the surrounding atoms in a molecule. Since all these properties depend, on the electronic structure of the bond, at least as an approximation it is necessary to study the spectrum and each bond in isolation. Bonds for which this approximation is adequate are usually said to have 'localized' molecular orbitals i.e., orbitals embracing a pair of nuclei only ; other molecules, for which this approximation is invalid, have non-localized orbitals and are often called 'conjugated'.

When each bond may be considered in isolation, it is evident that the complete electronic spectrum of a molecule is the sum of the spectra from each bond. The result is complex, but the information is contained within it. Thus if some band series can be recognized for a particular bond we immediately know the vibrational frequency of that bond and good estimate of its dissociation energy also. If the rotational structure is resolved, then moment of inertia is found from the line spacing and hence shape and size of the molecule.

Unlike diatomic molecules, the rotational fine structure is not observed in polyatomic molecules and the vibrational structure is present in the form of broad bands. The absence of rotational fine structure in polyatomics is due to the closely spaced rotational energy levels and high values of moments of inertia. Hence, spectra of polyatomics have poorer resolution as compared to spectra of diatomics. In spite of this limitation, spectra of polyatomics provide important information about electronic structure.

We make use of molecular orbital theory to understand theoretical aspects of spectra of polyatomics. In electronic transitions of polyatomics, we encounter three types of molecular orbitals: σ and σ^*, π and π^* *, and n (nonbondig) orbitals.

Orbitals without * are bonding orbitals and those with * are antibonding orbitals. The energy levels of all these molecular orbitals, in increasing order of energy, are shown in below Fig.

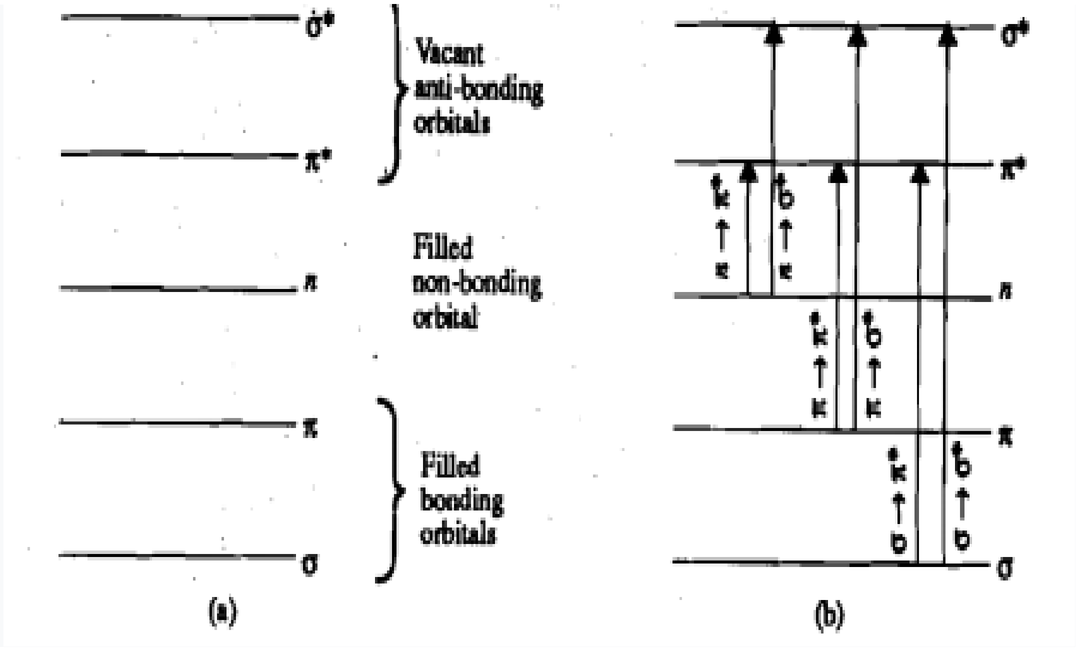


Fig. : Schematic diagram of (a) order of molecular orbital energies (b) possible electronic transitions.

When a molecule absorbs energy in the UV or visible region, an electron from a specific MO is excited to another of higher energy. The possible transitions of the electron between the MO's are:

$$\sigma - \sigma^*,\ n - \sigma^*,\ n - \pi^*,\ \pi - \pi^*,\ \pi - \sigma^* \text{ and } \sigma - \pi^*$$

The order of decreasing energy for these transitions is as follows:

$$\sigma - \sigma^* > \sigma - \pi^* \approx \pi - \sigma^* > \pi - \pi^* \approx n - \sigma^* > n - \pi^*$$

As we go to polyatomics, a simpler way to approach electronic spectra is to consider electronic excitations from various localized orbitals. On excitation, orbital shapes as well as molecular shapes can change significantly. For example, CO2 becomes bent and H – C ≡ C − H becomes zig-zag.

Among organic groups, common frequencies for excitations of -C = C-, > C = O, > C = N- bonds have been observed. In these molecules which contain double bonds, π → π* and n → π* transitions are observed. The n → π* transitions resulting from the excitation of a non-bonding electron is weak with a low value of extinction coefficient.

The σ → σ* transitions require a lot of energy and occur in the far ultraviolet region (wavelength 100 nm) of the electromagnetic spectrum. The n → π* transitions in conjugated ketones may occur in the visible region (400 to 700 nm).

The π → π* transitions for C = O, C = C, C ≡ C and C = N- occur at 166, 170, 170 and 190 nm respectively. The n → π* transitions in C = O and C = N- occur at 280 and 300 nm respectively. The extinction coefficients of π → π* transitions are in the order of ten to thirty thousand while those for n → π* are small. On conjugation, the wavelength of transitions increase. For example, -C=C-C=C and –C=C-C=C-C=C- have π → π* transitions at 220 and 260 nm respectively.

The Re-Emission of Energy by an Excited Molecule

After a molecule has undergone an electronic transition into an excited state there are several processes by which its excess energy may be lost. They are discussed below.

- Dissociation – The excited molecule breaks into two fragments. The energy required to separate the stable molecule into two unexcited atoms is known as dissociation energy. No spectroscopic phenomena, beyond the initial absorption spectrum, are observed unless the fragments radiate energy by one of the following processes.
- Re-emission – it is the reverse process of absorption process. The radiation emitted, which may be collected and displayed as an emission spectrum, is identical in frequency with that absorbed.

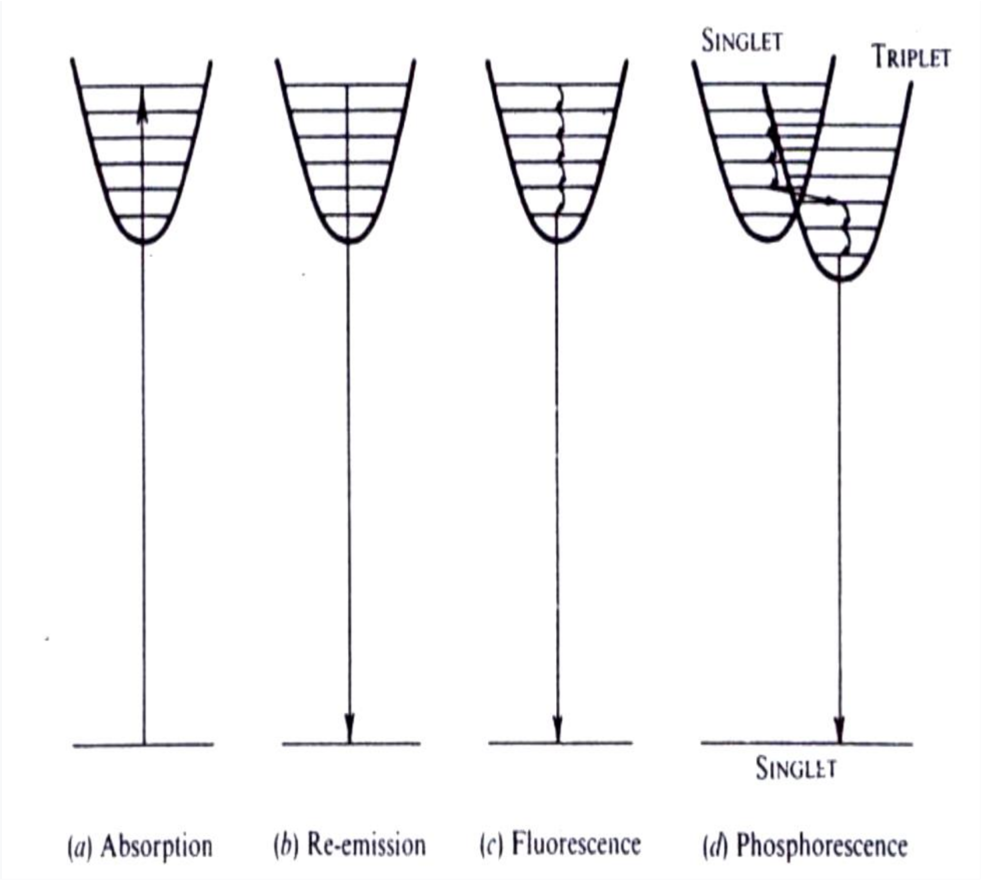


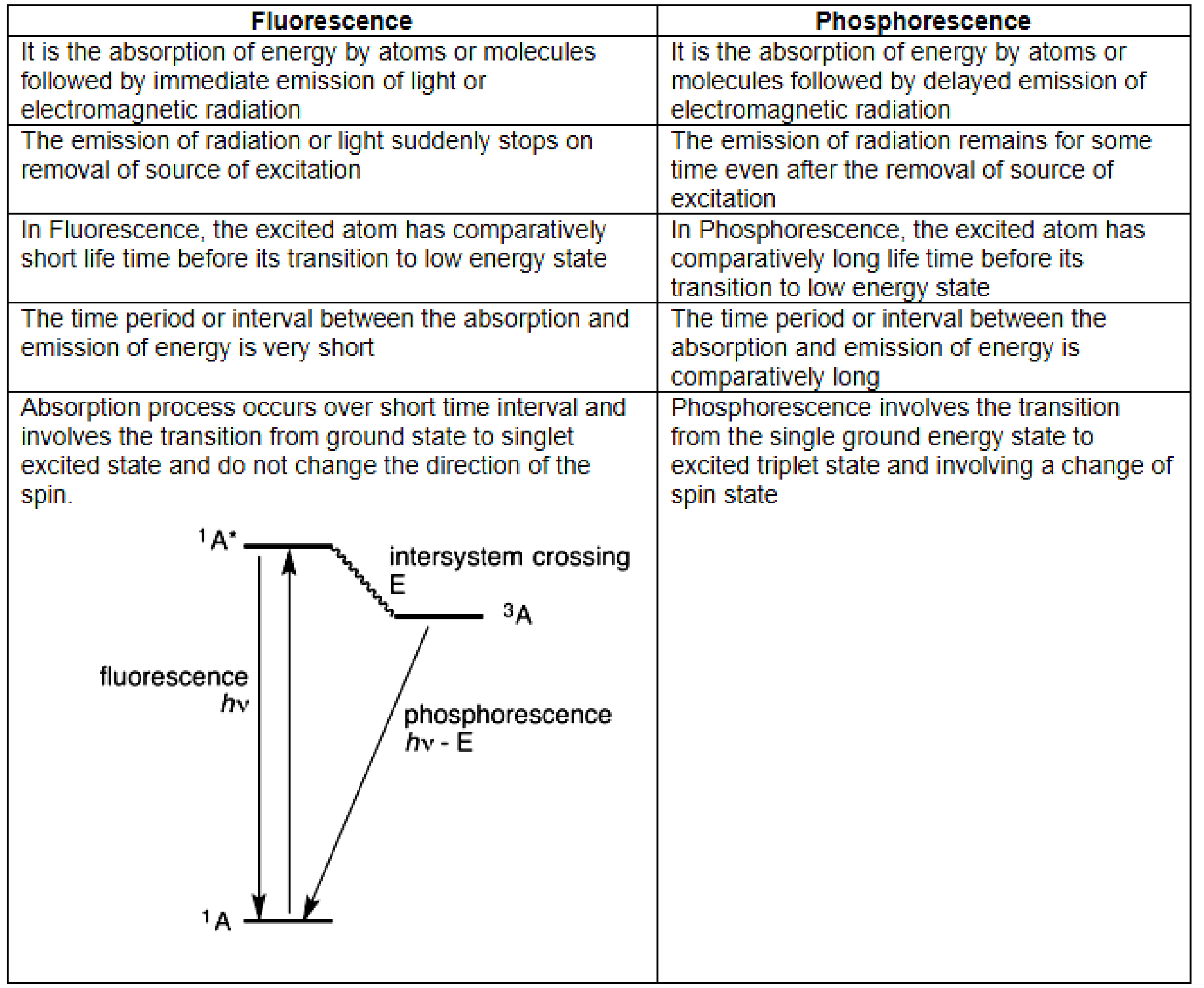
Fig. Showing the various ways in which an electronically excited molecule can lose energy

- Fluorescence – if the molecule is in a high vibrational state after electronic excitation, then excess vibrational energy may be lost by intermolecular collisions (illustrated in c of the figure). The vibrational energy is converted to kinetic energy and appears as heat in the sample, such transfer between energy levels is referred to as ‘radiation less’. When the excited molecule has reached a lower vibrational state, it may then emit radiation and revert to the ground state, the radiation emitted, called the fluorescence spectrum, is normally of lower frequency than that of the initial absorption. The time between initial absorption and return to ground state is very small, of the order of 10^{-8} seconds.
- Phosphorescence – This can occur when two excited states of different total spin have comparable energies. Thus in fig. d it is imagined that the ground state and one of the excited states to be singlets (that is $S=0$) while the neighboring excited state is a triplet ($S=1$). Although the rule $\Delta S = 0$ forbids spectroscopic transitions between singlet and triplet states, there is no prohibition if the transfer between the excited states occurs kinetically, i.e., through radiation less transitions induced by collisions.

Such transfer, however, can only occur close to the cross-over point of the two potential curves and once the molecule has arrived in the triplet state and undergone some loss of vibrational energy in that state, it cannot return to the excited singlet state. It will, therefore, eventually reach the $v' = 0$ level of the triplet state. Now although a transition from here to the ground state is spectroscopically forbidden, it may take place but much more slowly than an allowed electronic transition.

Thus, it is that a phosphorescent material will continue to emit radiation seconds, minutes, or even hours after the initial absorption. The phosphorescence spectrum, as a rule, consists of frequencies lower than that absorbed.

Differences between fluorescence and phosphorescence



Fluorescence	Phosphorescence
It is the absorption of energy by atoms or molecules followed by immediate emission of light or electromagnetic radiation	It is the absorption of energy by atoms or molecules followed by delayed emission of electromagnetic radiation
The emission of radiation or light suddenly stops on removal of source of excitation	The emission of radiation remains for some time even after the removal of source of excitation
In Fluorescence, the excited atom has comparatively short life time before its transition to low energy state	In Phosphorescence, the excited atom has comparatively long life time before its transition to low energy state
The time period or interval between the absorption and emission of energy is very short	The time period or interval between the absorption and emission of energy is comparatively long
Absorption process occurs over short time interval and involves the transition from ground state to singlet excited state and do not change the direction of the spin.	Phosphorescence involves the transition from the single ground energy state to excited triplet state and involving a change of spin state

Photo Electron Spectrometer

Principle – PES is based on the photoelectric effect. If a sample is irradiated with high energy photons of energy *hν*, electrons are emitted and part of the energy is carried off as kinetic energy of the emitted electrons. In PES, a monochromatic radiation is used to ionize the atoms and the kinetic energies of the emitted photoelectrons are measured.

Instrumentation - A Photo electron spectrometer requires four components

1. Electromagnetic radiation source of high intensity.
2. Sample in a chamber in a required physical state.
3. Electron energy analyzer to analyze the energy distribution of electrons emitted from the sample.
4. Detector to detect electrons whose energy has been measured by the electron analyzer.

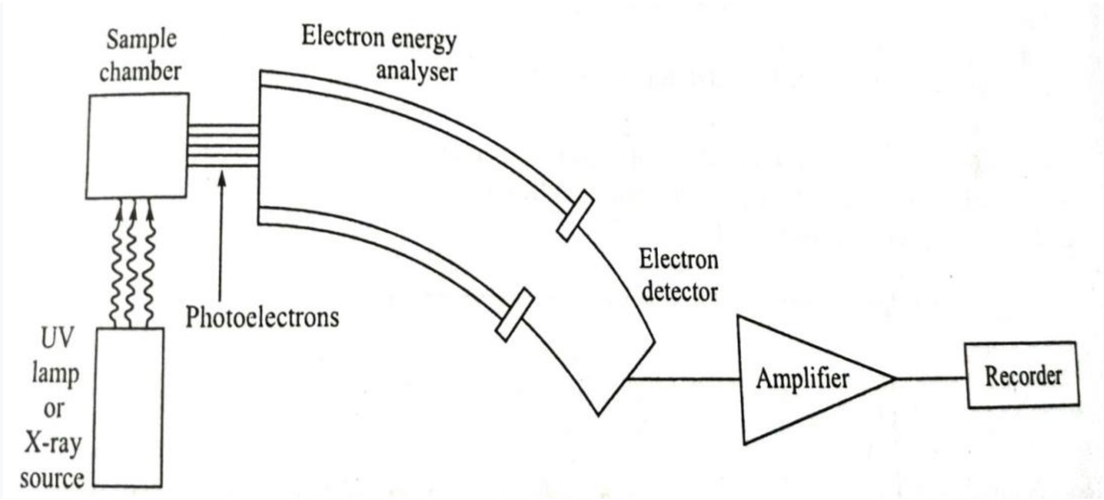


Fig-Photo Electron Spectrometer

Most frequently used UV source is either the 58.4 nm (21.21 eV) line of He-I or the 30.39 nm (40.81 eV) line of He - II. The width of these lines is approximately 0.1 eV. Other less monochromatic sources Ne-I at 73.58 nm (16.85 eV) and the Lyman line of atomic hydrogen at 121.55 nm (10.2 eV) are also used. A typical X-ray source consists of a twin anode of aluminium and magnesium giving Al$K_\propto$ (0.834 nm, 1486.6 eV) and Mg$K_\propto$ (0.989 nm, 1253.6 eV). The large line width of X-ray sources can be reduced by the use of monochromators.

The resolving power of the instrument decreases as the line width of the source increases. With the use of synchrotron radiation this problem is solved to a very great extent. The synchrotron radiation is given off by accelerated charged particles and it enables one to have continuously variable radiation from UV to X-ray region.

Electron energy analysers of different types are available. All of them are either; of the magnetic type or of the electrostatic type. In either case the analyzer must be shielded from the earth's magnetic field to avoid its effect on the motion of the electrons. Shielding of the electrostatic analyser is easier than that of magnetic analyser. When the photoelectrons are emitted they should reach the detector without being scattered by gas molecules. Also, the excitation source and the sample should be kept under clean conditions. Hence, the experimental chamber is usually made up of stainless less and equipped with the source, sample manipulator, electron energy analyser and arrangement for the detection of photoelectrons. The photoelectron signal is amplified and fed to a recorder or the data is stored in a computer. The whole set up except the recording system is kept in high vacuum.

UNIT – IV NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

SYLLABUS **-** Magnetic properties of nuclei – Resonance condition – Bloch equations – Shielding and deshielding effects – Chemical shift – Spin lattice and spin-spin relaxation time – Coupling constants – NMR Instrumentation.

Introduction to NMR

NMR Spectroscopy measures the absorption of electromagnetic radiation (radio waves) due to changes in nuclear spin orientation. NMR occurs only when the sample is in a strong magnetic field.

"transitions between magnetic energy levels'

NMR deals with transitions between energy levels because of different orientations of magnetic moment of nuclei placed in a magnetic field. These transitions are studied by means of a resonance method. "The magnetic energy levels are created by keeping the nuclei in a magnetic field".

The NMR spectroscopy is concerned with nuclei spin I = ½ . Examples are ^{1}H, ^{31}P, ^{19}F. Spectra cannot be obtained from nuclei with I = 0. NMR is a powerful tool for investigating nuclear structure.

Quantum description of NMR

According to quantum theory a spinning nucleus can only have values for the spin angular momentum given by

$$\text{Spin angular momentum } \mathbf{I} = \sqrt{\mathrm{I}\,(\mathrm{I}+1)}\; {}^{h}\!/_{2\pi}$$

Where I is the spin quantum number.

Magnetic moment of nucleus $\mu = \gamma \times spin\ angular\ momentum$

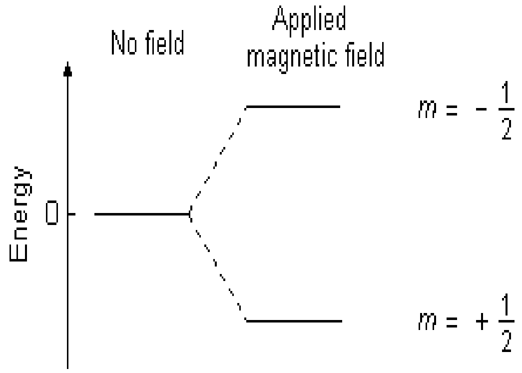
Where γ is the gyro magnetic ratio.

The rules for determining the net spin of a nucleus are as follows;

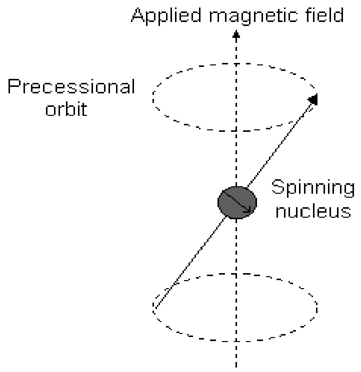
1. If the number of neutrons and the number of protons are both even, then the nucleus has NO spin.
2. If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
3. If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

The overall spin, *I,* is important. Quantum mechanics tells us that a nucleus of spin *I* will have 2*I* + 1 possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a *magnetic quantum number, m*.

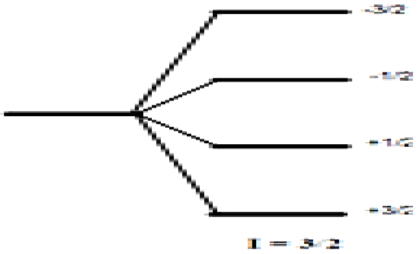
Energy levels for a nucleus with spin quantum number 1/2



Imagine a nucleus (of spin 1/2) in a magnetic field. This nucleus is in the lower energy level (i.e. its magnetic moment does not oppose the applied field). The nucleus is spinning on its axis. In the presence of a magnetic field, this axis of rotation will *precess* around the magnetic field;

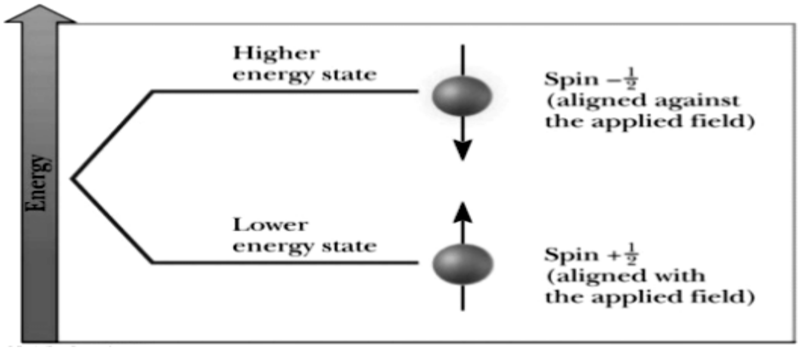


The splitting of spectral lines for spin 3/2 in magnetic field shown below



Magnetic Properties of Nuclei

When a charged particle such as a proton spins on its axis, it creates a magnetic field. Thus, the nucleus can be considered to be a tiny bar magnet. But when magnetic field is applied, the proton posses spin and their own magnetic field align themselves either or opposite to magnetic field. For example hydrogen has +1/2 spin state and -1/2 spin state. The proton with +1/2 spin state align themselves with field (lower energy) and with -1/2 spin state align opposite to field (higher energy).



Thus an important property of nucleus is its spin I or spin angular momentum = $I\hbar$. This gives rise to a magnetic moment to the nucleus. The following rules are used to determine the value of nuclear spin I.

i) If mass number A is odd and atomic number Z is even or odd then I is half integral. I = 1/2 , 3/2, …..

Example : ${}_{1}^{1}H,\ {}_{6}^{13}C,\ {}_{7}^{15}N, {}_{9}^{19}F, \dots\dots$

(Hydrogen has one proton and no neutron)

ii) If mass number A and atomic number Z are even, then I is zero.

I = 0

Example : ${}_{2}^{4}He,\ {}_{6}^{12}C,\ {}_{8}^{16}O, {}_{16}^{32}S, \dots\dots$

iii) If mass number A is even and atomic number Z is odd the I is integer

Example : ${}_{1}^{2}H,\ {}_{5}^{10}B,\ {}_{7}^{14}N, \dots..$

(Deuterium has one neutron)

Spin angular momentum **I** = $\sqrt{\mathrm{I}\ (\mathrm{I}+1)}$ ħ units

I = 0,1/2, 3/2, 5/2, …………..

The projection of spin angular vector I along a particular direction is

$$m_I = -I, (-I+1),\ldots\ldots(I-2), (I-1), I$$

giving (2I + 1) components. These components are all degenerate (having same energies) in the absence of external magnetic field.

When magnetic field is applied it splits up into (2I + 1) states.

Now the magnetic moment of nucleus $\mu = \gamma \times spin\ angular\ momentum$

Gyro magnetic ratio, $\gamma = \frac{magnetic\ moment}{angular\ momentum}$

$$\mu = \gamma \mathrm{I} \frac{h}{2\pi} = \gamma \mathrm{I} \hbar$$

The alternative expression for magnetic moment is

$$\mu = g_N \mu_N \mathrm{I}$$

where g_N is Nuclear g factor (small dimensionless algebraic number) and μ_N is nuclear magneton.

$$\mu_N = \frac{e\hbar}{2m_p} = 5.051 \times 10^{-27} J\, T^{-1}\, (Nm^2)$$

$$m_p - mass\ of\ proton\ (1.67 \times 10^{-27}\ Kg)$$

Resonance Condition

When a nucleus of magnetic moment μ is placed in a magnetic field B_0 the interaction energy,

$$E = -\mu B_0 = -\mu_0 B_0 \cos\theta = -\mu \frac{B_0 m_I}{I}$$

Since m_I can have 2I +1 values we will have 2I +1 energy levels. The energy separation between any two adjacent energy levels is given by,

$$|\Delta E| = \mu \frac{B_0 \Delta m_I}{I} = \frac{\mu B_0}{I} = \frac{g_N \mu_N\ I B_0}{I}$$

$$|\Delta E| = g_N \mu_N\ B_0$$

The basis of NMR experiment is to induce a transition from a lower level to next higher level. If γ is the frequency of electromagnetic radiation that induces transition between adjacent energy levels. Bohr's frequency condition is

$$h\upsilon = \frac{\mu B_0}{I} = g_N \, \mu_N \, B_0$$

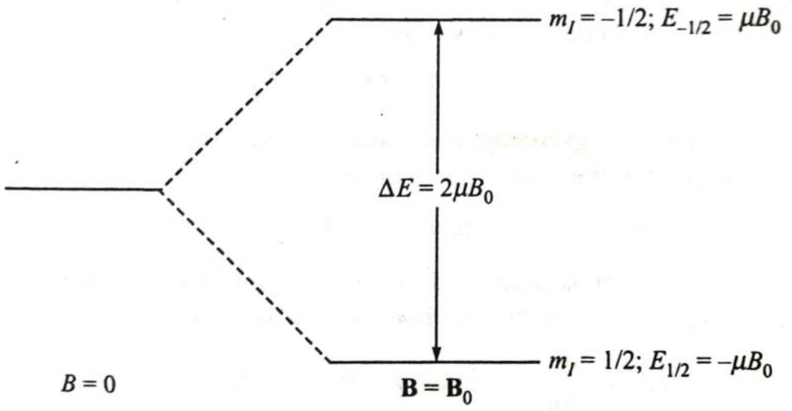
This is the resonance condition.

For a spin ½ system we will have two states, one corresponding to $m_I = +1/2$ and other $m_I = -1/2$.

Their energies are

$$E_{1/2} = -\mu B_0 \quad \text{and} \quad E_{-1/2} = +\mu B_0$$

The resonance condition reduces to $h\upsilon = 2\,\mu B_0$. This is represented in below figure.



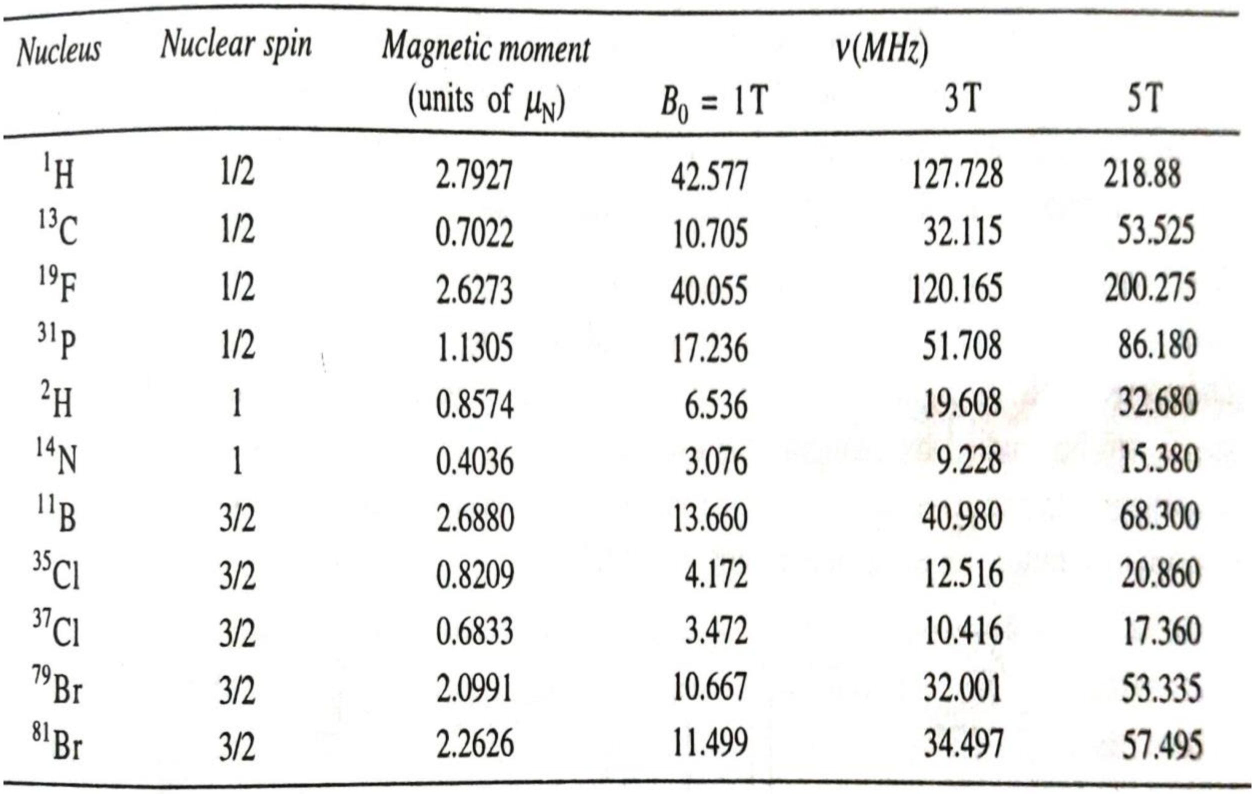
Energy levels of a spin 1/2 system in an external magnetic field $\mathbf{B} = \mathbf{B}_0$.

For Proton, $\mu = 2.79268\,\mu_N$, and therefore

$$\nu = \frac{2 \times 2.79{,}268 \times (5.051 \times 10^{-27}\ JT^{-1})}{6.626 \times 10^{-34}\ J.s}\ B_0 = (42.5772 \times 10^6\ T^{-1}s^{-1})\ B_0$$

Typical external magnetic fields used in NMR experiments are in the range of 1 to 5T.

Magnetic resonance parameters for some of the nuclei are given in below table.



Nucleus	*Nuclear spin*	*Magnetic moment* (units of μ_N)	*ν(MHz)* B_0 = 1T	3T	5T
^{1}H	1/2	2.7927	42.577	127.728	218.88
^{13}C	1/2	0.7022	10.705	32.115	53.525
^{19}F	1/2	2.6273	40.055	120.165	200.275
^{31}P	1/2	1.1305	17.236	51.708	86.180
^{2}H	1	0.8574	6.536	19.608	32.680
^{14}N	1	0.4036	3.076	9.228	15.380
^{11}B	3/2	2.6880	13.660	40.980	68.300
^{35}Cl	3/2	0.8209	4.172	12.516	20.860
^{37}Cl	3/2	0.6833	3.472	10.416	17.360
^{79}Br	3/2	2.0991	10.667	32.001	53.335
^{81}Br	3/2	2.2626	11.499	34.497	57.495

The frequencies fall in the radio frequency region of the electromagnetic spectrum and the sources used to induce the transitions are different from those used in other regions of spectroscopy. The resonance condition is achieved by applying a radiofrequency field oscillating at the Larmor frequency perpendicular to the external magnetic field. This oscillating field is produced by applying an oscillating voltage to a coil whose axis is perpendicular to the external static field. Proton is one of the most important nuclei having a spin I = ½ . It is a constituent in almost all organic molecules. The NMR of a proton nucleus is often called Proton Magnetic Resonance (PMR).

Relaxation Process:

- The process by which excess spin energy is shared either with the surroundings or with other nuclei is referred as a relaxation process. ***That is "the time taken for a fraction of 1/e =0.37 of the excess energy to be dissipated is called the relaxation time".***
- ***spin-lattice relaxation – (OR) longitudinal relaxation time T1-*** **the spins in the upper state transfer the excess energy to the surroundings (lattice).**
- ***spin–spin relaxation time (or) transverse relaxation timeT2*** **sharing of excess spin energy directly between nuclei is referred as *spin–spin relaxation time***

T_1 varies over a large range, being $10^{-2} - 10^{-4}$ sec for solids and $10^{-4} - 10$ sec for liquids. For solids, T_2 is the order of 10^{-4} seconds, while for liquids $T_2 \approx T_1$. The shape of the spectral lines depends significantly on the relaxation time.

BLOCH EQUATIONS – (Felix Bloch – 1946)

'A set of macroscopic equation used to calculate the nuclear magnetization M = (M_x, My, M_z) as a function of time (T_1 and T_2).

T_1 – Spin-Lattice Relaxation time (Longitudinal Relaxation time)

T_2 – Spin-Spin Relaxation time (Transverse Relaxation time)

The total magnetic moment or magnetization M of a sample of nuclear spins is the sum of the nuclear moments and is given by

$$\overrightarrow{\mathbf{M}} = \sum_i \mu_i - - - - - - - - 1$$

In terms of total spin angular momentum **I**

$$\overrightarrow{\mathbf{M}} = \gamma \mathbf{I} - - - - - - - - 2$$

The interaction of the applied field and magnetic moment produces a torque on the system and the motion of the nuclear magnetic moment in a magnetic field **B** is given by

$$\frac{d\mathbf{I}}{dt} = \overrightarrow{\mathbf{M}} \times \overrightarrow{\mathbf{B}} - - - - - - - - -3$$

Substitute 2 in eqn. 3

$$\frac{d\mathbf{M}}{dt} = \gamma(\overrightarrow{\mathbf{M}} \times \overrightarrow{\mathbf{B}}) ---------4$$

The vector product can be expanded as

$$\overrightarrow{\mathbf{M}} \times \overrightarrow{\mathbf{B}} = \begin{vmatrix} i & j & k \\ M_x & M_y & M_z \\ B_x & B_y & B_z \end{vmatrix}$$

$$= i\left(M_yB_z - M_zB_y\right) - j(M_xB_z - M_z\,B_x) + k(M_xB_y - M_yB_x)$$

$$= i\left(M_yB_z - M_zB_y\right) + j(M_z\,B_x - M_xB_z) + k\left(M_xB_y - M_yB_x\right) --- 5$$

This can be written as individual components

$$\left.\begin{aligned} \frac{dM_x}{dt} &= \gamma(M_yB_z - M_zB_y) \\ \frac{dM_y}{dt} &= \gamma(M_z\,B_x - M_xB_z) \\ \frac{dM_z}{dt} &= \gamma(M_xB_y - M_yB_x) \end{aligned}\right\} ------ 6$$

By convention, the static magnetic field is along the z-direction. This means that B_z has non-zero value. Whereas B_x and B_y are zero and as a consequence the spins precess around B_z.

M_y will be converted to M_x and M_x into M_y.

M_z will remain constant. This is the result that is seen when a sample is placed in a magnet. In order to get any changes in M_z under these conditions we have to add radiofrequency (RF) field terms.

Therefore eqn. 6 becomes (Put $M_z = 0$ in eqn 1 &2, $M_x, M_y = 0$ in 3)

$$\left.\begin{aligned} \frac{dM_x}{dt} &= \gamma(M_y B_z) \\ \frac{dM_y}{dt} &= -\gamma(M_x B_z) \\ \frac{dM_z}{dt} &= 0 \end{aligned}\right\} ------7$$

Including the relaxation terms in equation 6

$$\left.\begin{aligned} \frac{dM_x}{dt} &= \gamma\left(M_y B_z - M_z B_y\right) - \frac{M_x}{T_2} \\ \frac{dM_y}{dt} &= \gamma(M_z\, B_x - M_x B_z) - \frac{M_y}{T_2} \\ \frac{dM_z}{dt} &= \gamma\left(M_x B_y - M_y B_x\right) - \frac{(M_z - M_0)}{T_1} \end{aligned}\right\} ------8$$

Where M_0 is the equilibrium value.

The magnetic field components acting on the systems are

$$\left.\begin{aligned} B_x &= B_1 \cos \omega t \\ B_y &= -B_1 \sin \omega t \\ B_x &= B_0 \end{aligned}\right\} ------9$$

Substitute eqn 9 in 8

$$\left.\begin{aligned} \frac{dM_x}{dt} &= \gamma\left(M_y B_0 + M_z B_1 \sin \omega t\right) - \frac{M_x}{T_2} \\ \frac{dM_y}{dt} &= \gamma(M_z\, B_1 \cos \omega t - M_x B_0) - \frac{M_y}{T_2} \\ \frac{dM_z}{dt} &= -\gamma\left(M_x B_1 \sin \omega t - M_y B_1 \cos \omega t\right) + \frac{(M_0 - M_z)}{T_1} \end{aligned}\right\} ---10$$

Equation 10 is called as Bloch Equation.

Shielding and De-Shielding effects

The basic principle of NMR is to apply an external magnetic field B_0 and measure the frequency at which the nucleus achieves resonance.

Electrons orbiting around the nucleus generate a small magnetic field that opposes B_0. Thus the electrons are shielding the nucleus from B_0.

Shielding Effect – The higher the electron density around the nucleus, the higher the opposing magnetic field to B_0, then shielding is greater. Because the proton experiences lower external magnetic field, it needs a lower frequency to achieve resonance and therefore the chemical shift, shifts up field.

If induced magnetic field opposes the applied magnetic field, the stronger magnetic field required to flip the proton. The proton is then said to be shielded and the absorption spectra is shifted to **upfield**. Electron releasing substances (Alkyl groups) shields protons.

Thus, "*high electron density around a nucleus shields the nucleus from the external magnetic field and the signals are upfield in the NMR spectrum"*

De Shielding effect – Lower the electron density around the nucleus, the lower the opposing magnetic field to B_0 and therefore it is said to be de shielded. Because the proton experiences higher external magnetic field, it needs a higher frequency to achieve resonance and therefore the chemical shift shifts down field.

If induced magnetic field reinforces the applied magnetic field, the small external field is required to flip the spin of proton. Such proton is said to be deshielded and absorption spectra is shifted towards **downfield**. Electron withdrawing substances (halogens) deshields protons.

Thus, *"lower electron density around a nucleus deshields the nucleus from the external magnetic field and the signals are downfield in the NMR spectrum"*

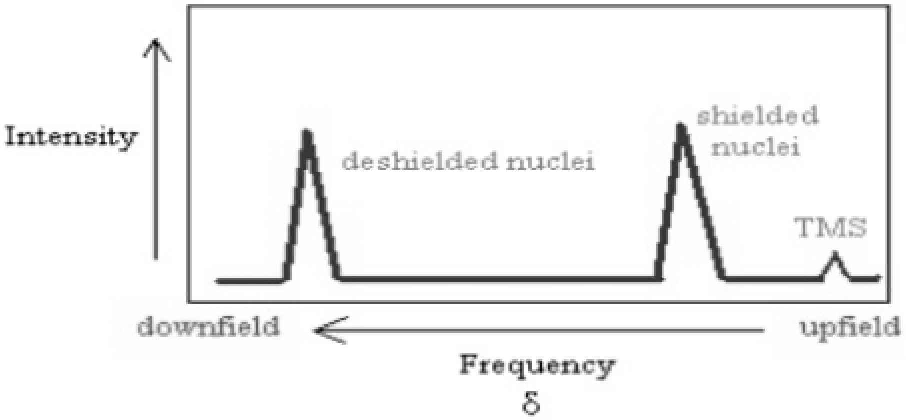


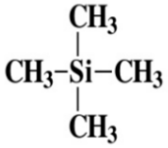
Figure – NMR spectrum, plot between the intensity of signals and magnetic field (frequency) in reference to TMS.

Difference between shielding and deshielding

Shielding	**Deshielding**
Nucleus feels weaker magnetic field	Nuclear feels stronger magnetic field.
Inner-shell electrons participate.	Valence electrons participate.
Occurs in the absence of electronegative groups.	Occurs in the presence of electronegative groups.
Caused by the closeness of dense electron cloud.	Caused by the removal of electron density.
Lower frequency is needed to achieve resonance.	Higher frequency is needed to achieve resonance.
Results in upfield chemical shift.	Results in downfield chemical shift.

Tetra Methyl Silane (TMS) is commonly used as standard reference in NMR spectroscopy due to the following reasons.

1. TMS is chemically inert and miscible with large range of solvents.
2. TMS has twelve protons that are magnetically equivalent.
3. TMS is highly volatile and low boiling point so it can be easily removed by evaporation after the spectrum is recorded.
4. TMS are less electronegative so the shielding is more and hence all the signal arrives in a down field direction.



$$\begin{array}{c} CH_3 \\ | \\ CH_3-Si-CH_3 \\ | \\ CH_3 \end{array}$$

Chemical Shift

- An NMR spectrum is a plot of the radio frequency applied against absorption.
- A signal in the spectrum is referred to as a resonance.
- The frequency of a signal is known as its chemical shift, δ.
- Chemical shift arises due to shielding /deshielding of protons by electrons.
- It is the difference between the between the absorption position of a sample proton and that of a reference proton (TMS-standard reference).
- **The shift of the resonance line in a given compound from of a standard reference sample is called the *chemical* shift (δ) of the compound.**
- It is measured in delta δ (unit is ppm) and tau τ scales. ($\tau = 10 - \delta$)

When magnetic field is applied, electrons circulate around the nucleus in such a way that it opposes the field. Thus the motion of electrons shields the nucleus from external field. Hence effective field experienced by nucleus is

$$B_{eff} = B_{app} - B_{induced}$$

$but, \quad B_{induced} = \sigma B_{app} \qquad where\ \sigma - shielding\ constant\ and\ B_{app} = B_0$

Therefore, $B_{eff} = B_0 - \sigma B_0 = B_0(1-\sigma)$

In general, $B_i = B_0(1-\sigma_i)$

$B_i -$ field experienced by i^{th} nucleus whose shielding constant is σ_i.

The chemical shift in absolute terms is defined by the frequency of the resonance expressed with reference to a standard compound which is defined to be at 0 ppm. The scale is made more manageable by expressing it in parts per million (ppm) and is independent of the spectrometer frequency.

$$\text{Chemical shift } \delta = \frac{\text{frequency of sample} - \text{frequency of reference}}{\text{spectromenter frequency}} \times 10^6 ppm$$

$$\boldsymbol{\delta = \frac{\upsilon_{sam} - \upsilon_{ref}}{\upsilon_0} \times 10^6 ppm}$$

Factors affecting chemical shift

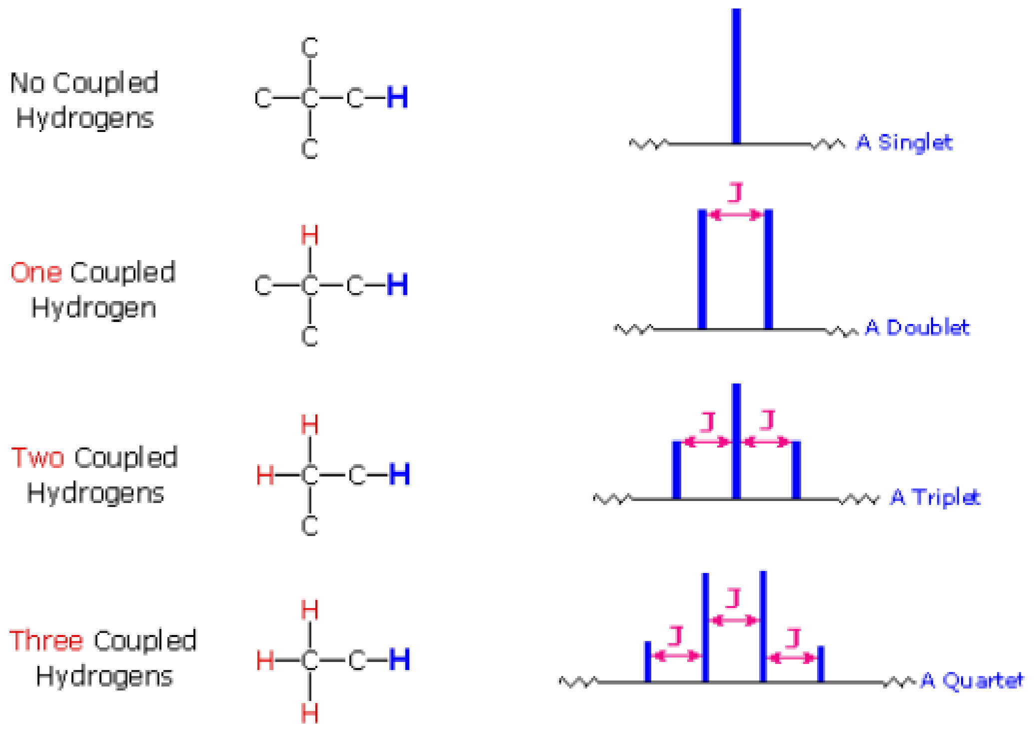
- Magnetic anisotropy – Electrons in $\pi -$ systems (like aromatics, alkenes, etc) interact with applied field which induces magnetic field that causes the anisotropy. Here anisotropy refers to non-uniform magnetic field. This result in both shielding and deshielding of protons
- Electro negativity - electronegative groups attached to the C-H system decrease the electron density around the protons and there is deshielding. Therefore chemical shift increases

Compound	δ
CH_3I	2.16
CH_3Br	2.65
CH_3Cl	3.10
CH_3F	4.26

- Hydrogen bonding – protons that are involved in hydrogen bonding changes the chemical shift values. If hydrogen bonding is more chemical shift value is large.

Coupling Constant (J)

- The **coupling constant**, **J** is a measure of the interaction between a pair of protons
- Coupling constant is the distance between the peaks in a simple multiplet.
- It is the measure of the amount of interaction between the two sets of hydrogens creating the multiplet.
- It measures how strongly a nucleus is affected by the spin states of its neighbor.
- Coupling constants are a measure of the effectiveness of spin-spin coupling and very useful in ^{1}H NMR of complex structures.
- It is measured in Hertz (Hz).

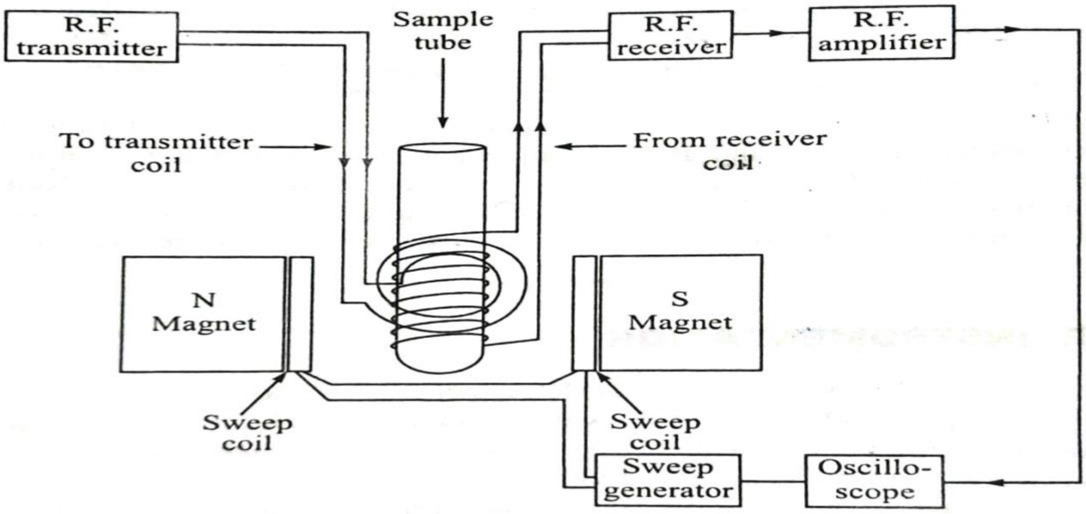


NMR Instrumentation :

The basic requirements of a typical NMR spectrometer are

- An electromagnet giving a powerful, stable and homogeneous magnetic field. The field must be a constant over the area of the sample and over the period of time of the experiment.
- A sweep generator which supplies a variable current to a secondary magnet. Then the total applied magnetic field can be varied over a small range.
- The sample container usually a glass tube (5mm OD) spun by an air–driver turbine to average the magnetic field over the sample container. This process is often referred to as the spinning of the sample.
- A r-f oscillator connected to a coil, called the transmitter coil, transmits the energy to the sample.
- A r-f receiver connected to the coil, called the receiver coil, encircles the sample. The transmitter and receiver coils and the sample holder are constructed into a single unit called *probe.*
- A read out system consisting of an r-f amplifier, recorder and other accessories to increase the sensitivity, resolution and accuracy. The read out system consist of computer that analyses and record the data

A schematic representation of the components is shown in Fig.



UNIT – V ESR AND MOSSBAUER SPCTOSCOPY

SYLLABUS - Theory of ESR – Resonance conditions – Experimental study – ESR spectrometer – ESR spectra of free radicals in solution – Mössbauer Spectroscopy – Recoilless emission and aborption – Mossbauer spectrometer – Application of Mossbauer spectroscopy – chemical shift.

Introduction

ESR is a spectroscopic technique confined to the study of those species heaving one or more unpaired electrons. Among the large number of paramagnetic systems, the most important ones are transition metal ions, free radicals, ions and molecules having an odd number of electrons etc. So this spectroscopy is also called *Electron paramagnetic resonance (EPR) spectroscopy.*

Theory of ESR

In ESR, the energy levels are produced by the interaction of the magnetic moment of an unpaired electron in a molecule ion with an applied magnetic field. The ESR spectrum results in due to the transitions between these energy levels by absorbing radiations of microwave frequency.

When an electron having magnetic moment μ is placed in a magnetic field B, the interaction energy,

$$E = -\mu\mathbf{B} = -\mu\, B\, cos\theta - - - - - 1$$

Where θ is the angle between μ and $\boldsymbol{B}$. $\cos \Theta = m_s/S$ If the system has only spin magnetic moment μ, then it is given by,

$$\mu = -g\mu_B S - - - - - - 2$$

g – gyromagnetic ration and μ_B is Bohr magneton

The eqn. 1 becomes,

$$E = \ g\ \mu_B\ m_s B - - - - - 3$$

For electron, $m_s = \pm 1/2$ and we get two levels with energies.

$$E_{-1/2} = -\frac{1}{2} g\mu_B\, B, \quad E_{1/2} = \frac{1}{2} g\mu_B\, B$$

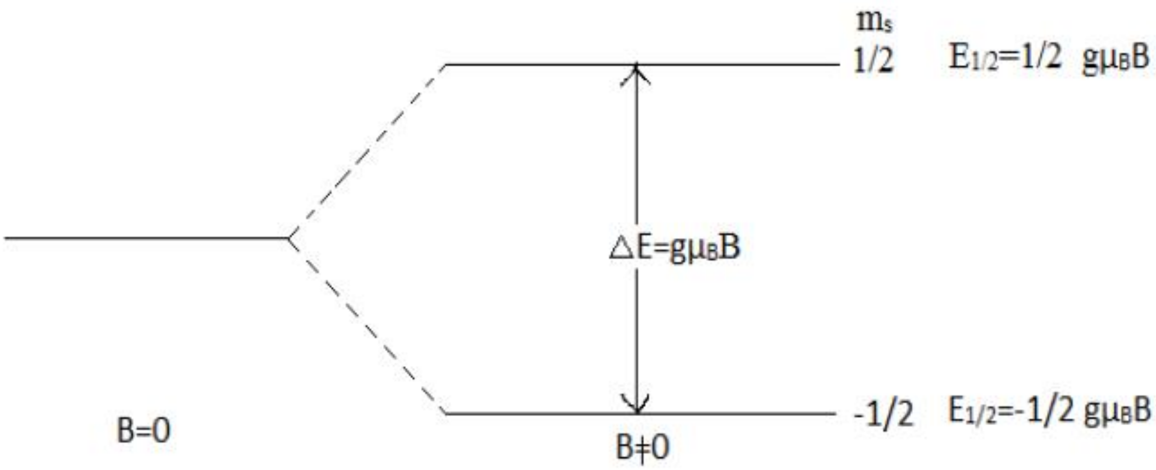


Fig. Zeeman splitting of an unpaired electron in a magnetic field B

If electromagnetic radiation of frequency υ satisfying the relation.

$$h\upsilon = E_{1/2} - E_{-1/2} = g\mu_B\, B ------ 4$$

is present, transition between these Zeeman levels occur which is studied by ESR. Eq.(4) gives the **Resonance condition for ESR** observation. For free electron, g = 2.0023. In a field of 0.34T, from Eq. 4

$$\gamma = \frac{2.0023(9.274 \text{x} 10^{-24}\ JT^{-1})0.34T}{6.626 \text{x} 10^{-34}\ J.Sec}$$

$$= 9528\, MH_z$$

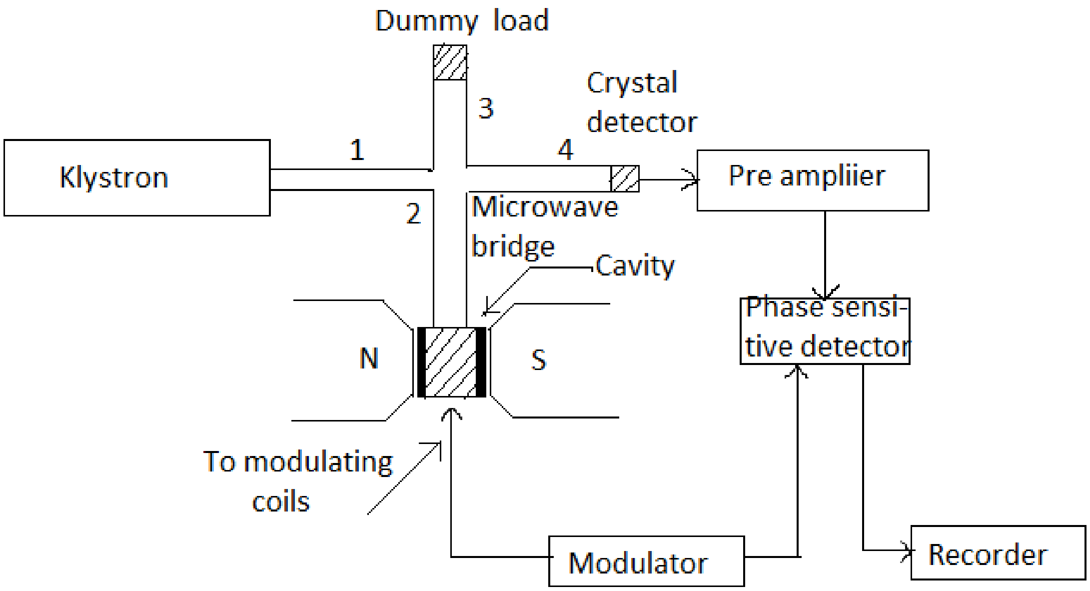
This frequency falls in the microwave region. Hence microwave source and techniques have to be applied for the observation of ESR.

Experimental study – ESR spectrometer

Some of the basic requirements of a ESR spectrometer are :

- An electromagnet capable of supplying a homogeneous magnetic field which can be varied linearly on either side of the magnetic field.
- Source of microwave radiation in the region of 9.5 GHz.
- Suitable sample cavity.
- Arrangements for transmitting the radiation energy in to the sample cavity.
- Detection system to measure the variation in microwave power.
- Suitable oscilloscope or recorder.

A simple block diagram of balanced bridge ESR spectrometer is given in below figure.



Description

The usual source of radiation is a klystron oscillator which produces monochromatic radiation of the required frequency. The radiation from the source is transmitted to the sample cavity through a microwave impedance bridge. The rectangular microwave cavity which contains the sample is kept in between the pole pieces of the electromagnet. A dummy load is kept in the third arm and a semi–conductor crystal in the fourth arm of the microwave bridge. The radiations that arrive in the 4th arm are detected by the crystal. It is then amplified and fed to a suitable recorder phase sensitive detectors are usually to detect ESR signals and represented as absorption or first derivative curves. The magnetic field is swept over a small range across the resonance condition by varying the current in a pair of sweep coils mounted on the cavity walls.

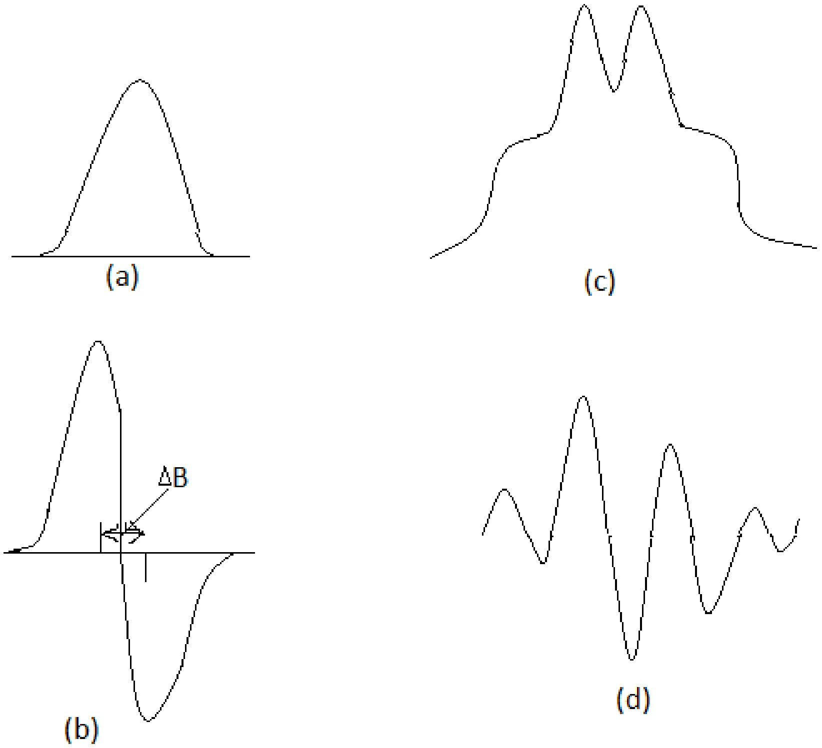


Fig. ESR signal (a) a single absorption line (b) its first derivative , (c) four equally spaced overlapping absorption lines, (d) first derivative of the spectrum in (c)

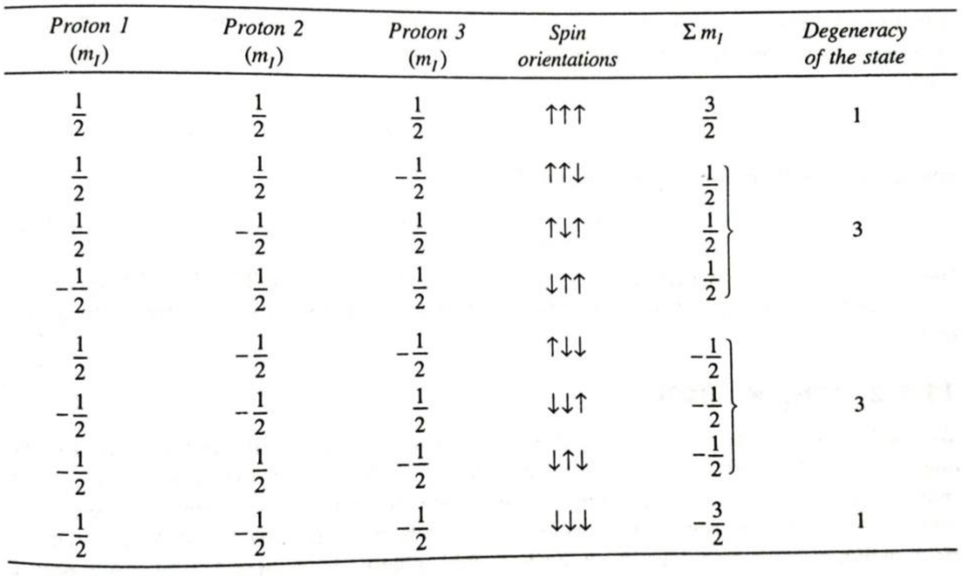
Working

When the bridge is in a balanced positive microwave power flows only in the two arms – the one cavity and the others to the dummy load. There will be any power in the fourth arm. Power in the fourth arm will be there only when the bridge is not balance. Thus, if balance exists, initially no signal appeal at the detector and when the sample absorbs, the balancing of the bridge is lost and power appears in the fourth arm. The width of ESR lines is fairly large and hence the spectrum is usually recorded in the first derivative mode which enables one to fix up the frequency position and estimation of intensity more precisely. Another advantage of derivative mode is that it gives a well defined line width ΔB. Even if there are overlapping signals, it is still possible to do a good estimate of ΔB.

ESR spectra of free radicals in solution

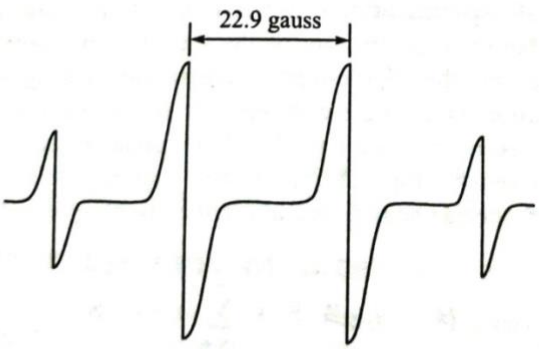
Methyl Radical (CH$_3$ Radical)

Methyl radial belongs to the type of an electron interacting with three equivalent protons, since the nuclear spin of carbon is zero. Spin arrangements for three equivalent protons are given in below table.



Proton 1 (m_I)	Proton 2 (m_I)	Proton 3 (m_I)	Spin orientations	Σm_I	Degeneracy of the state
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	↑↑↑	$\frac{3}{2}$	1
$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	↑↑↓	$\frac{1}{2}$	3
$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	↑↓↑	$\frac{1}{2}$	
$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	↓↑↑	$\frac{1}{2}$	
$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	↑↓↓	$-\frac{1}{2}$	3
$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	↓↓↑	$-\frac{1}{2}$	
$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	↓↑↓	$-\frac{1}{2}$	
$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	↓↓↓	$-\frac{3}{2}$	1

On the basis of selection rule four equally-spaced lines with relative intensities 1:3:3:1 are expected. In fact the experimental spectrum has four lines with the predicted intensities. Since the observed spectrum is symmetrical, the proton hyperfine coupling constant is isotropic and the unpaired electron density is distributed equally among the protons in the system.



This measurement cannot give the electron density on the carbon atom as its nuclear spin is zero. However, electron density on carbon can be investigated by studying the ESR of the radical $^{13}CH_3$. One expects eight lines in the spectrum since ^{13}C analysis led to a value of 41 G for the hyperfine coupling constant of ^{13}C. If the hybridization of carbon is sp^3, the structure of the radical will be pyramidal with a hyperfine constant greater than 100 G for $^{13}CH_3$. As the observed value is only 41 G, the hybridization for carbon is likely to be sp^2 which leads to a planar structure for the radical.

Benzene Anion $C_6H_6^-$

Benzene anion can be formed by the reaction of an alkali metal with benzene in a solvent such as tetrahydrofuran. Benzene anion $C_6H_6^-$ results, when the alkali metal atom transfer an electron to the benzene molecule. Fermi contact interaction is not expected from aromatic hydrocarbons as the unpaired electron transferred enters the lower unoccupied π molecular orbital which has a node in the molecular plane. However, due to a small unpairing of spins in the C-H bond, there will be a small but finite unpaired electron density at the hydrogen nucleus which is responsible for the ESR spectrum. The observed ESR spectrum of $C_6H_6^-$ is symmetrical with 7 lines indicating that the unpaired electron density is distributed equally among the six protons in the system. As the six protons are identical, total spin I = 3 and m_I = 3,2,1,0, -1, -2, -3. The spectrum will then consists of lines having intensity ratio 1:6:15:20:15:6:1. The spacing between the lines gives a hyperfine coupling constant of 3.6 G.

Mössbauer Spectroscopy

Introduction

Mössbauer spectroscopy, named after its discoverer who received a Nobel prize in 1961 this work, is concerned with transitions between energy levels within the nuclei of atoms. The heavier elements formed by the radioactive decay of an isotope of the same or a different element are initially produced in an excited nuclear state, after a very short delay, the excited nucleus reverts to the ground state and emits energy of a very high frequency, usually in the γ-ray region of the spectrum.

*"**Mössbauer spectroscopy** is the study of γ –ray absorption (or emission) spectra for transitions between nuclear states".*

Recoilless emission and absorption

Nuclear resonance absorption is in principle expected to occur when gamma radiation emitted in a transition from E_i to E_f is reabsorbed by another nucleus of the same kind according to the scheme depicted in below figure.

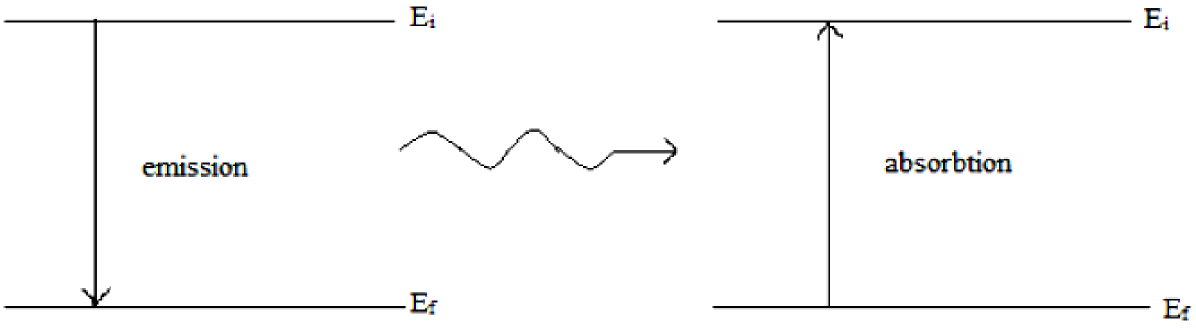


Fig. Nuclear resonance absorption

Consider an isolated atom of mass M having a nuclear excited state E_i above the ground state E_f . Let E_0 be the energy difference E_i - E_f and E_{re} be the kinetic energy of the recoil nucleus. If p is the recoil momentum

$$E_{re} = \frac{p^2}{2M} - - - - - - 1$$

As this energy has to come from E$_0$, the emitted gamma ray will have energy,

$$E_\gamma = E_0 - E_{re} - - - - 2$$

Therefore, the centre of the emitted spectral line will be shifted from the expected position E$_0$. By the law of conversation of momentum,

Recoil momentum of the atom = Momentum of the emitted γ –ray

$$p = \frac{E_\gamma}{c} \ - - - - 3$$

c is the velocity of light. Hence,

$$E_{re} = \frac{p^2}{2M} = \frac{E_\gamma^2}{2Mc^2} = \frac{(E_0 - E_{re})^2}{2Mc^2} = \frac{E_0^2}{2Mc^2} - - - - - - 4$$

Since E_{re} is small compared to E$_0$.

After absorption of the gamma ray by the same nucleus, the atom will have momentum and energy. This energy has to come from the radiation. Hence, in the absorption process, to excite the nucleus upto the same energy the gamma ray must have the energy E_γ' given by

$$E_\gamma' = E_0 + E_{re} - - - - - 5$$

The effect of recoil is thus to introduce a difference of $(E_\gamma' - E_\gamma)$ between the energies of the emitted and absorbed gamma rays in a resonant process.

$$E_\gamma' - E_\gamma = 2E_{re} \cong \frac{E_0^2}{Mc^2} - - - - - - - - 6$$

If $2E_{re} \ll \gamma$, the two curves would overlap and one would observe resonant absorption. Since E_{re} is proportional to E_0^2, it increases appreciably as we go from the optical region (~2eV) to the gamma ray region (~10 KeV) of the e.m. spectrum. The below figure illustrates the overlapping of emission and absorption lines, greater the overlap greater is the absorption. Thus, maximum absorption will occur when the recoil energy is zero. This can be achieved when the emitting and absorbing nuclei are bound in crystal lattices. In such a case, recoil energy is absorbed by the crystal lattice as a whole. This is what Mossbauer did to observe the resonance absorption.. In other words, by placing a suitable unstable nucleus in a matrix which absorbs most of the recoil energy one gets a good Mossbauer source. When this gamma ray is passed through a material containing a similar nucleus, absorption will occur.

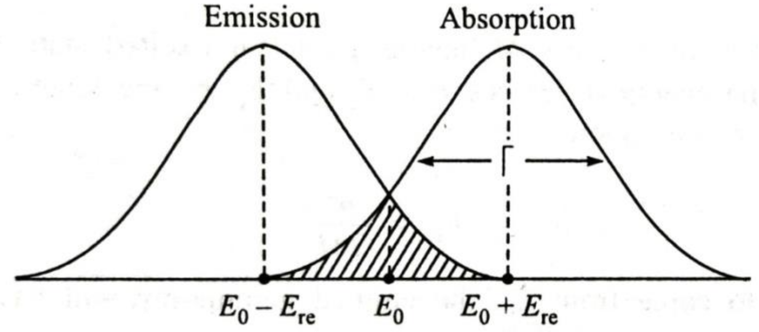


Fig. Overlap of emission and absorption lines in a nuclear transition

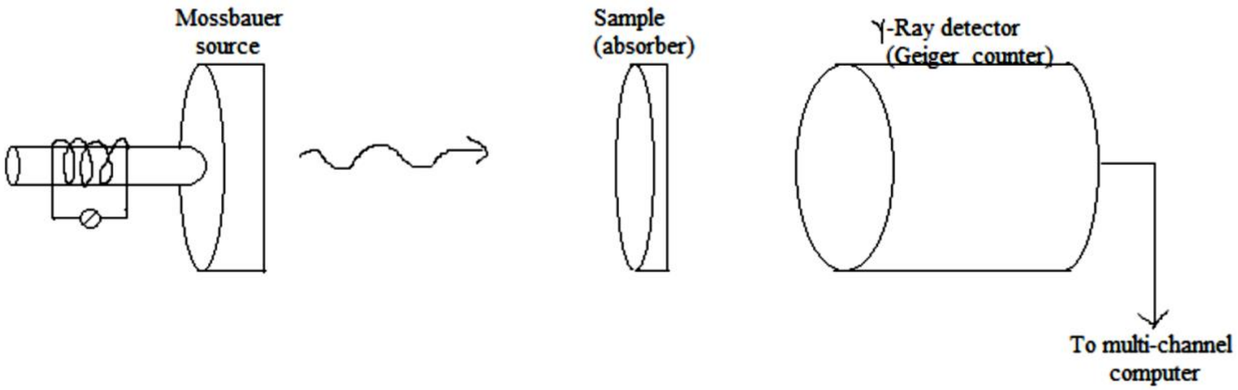
Mössbauer Spectrometer

Experimentally, two methods are possible for measuring the gamma – ray transmission as a function of Doppler velocity.

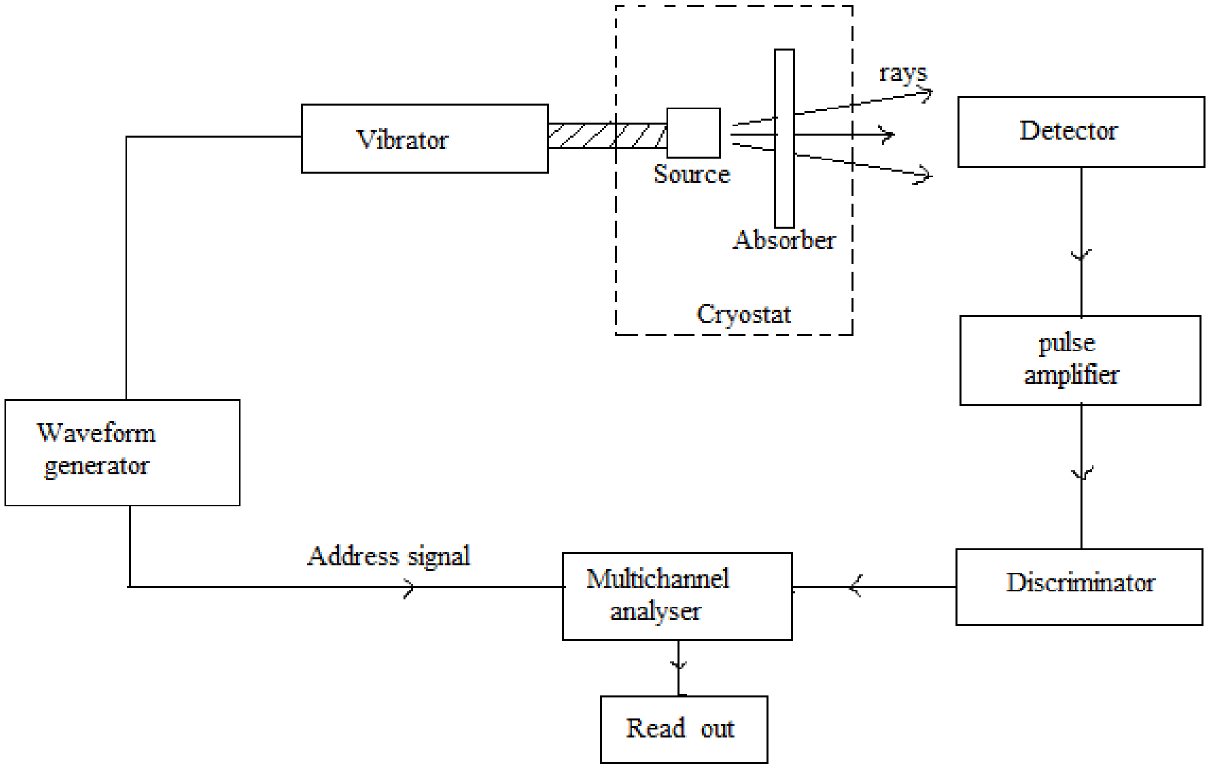
In one method, the source is mounted on a mechanical constant velocity device and the total number of counts is registered in a fixed time. The same is repeated at different velocities until the desired velocity is covered. A single channel analyser is used to limit the detection to only those pulses that have the required energy.

In the second method, the source is mounted on an oscillating drive which gives it a varying velocity relative to the sample. The detector output is fed to a multi-channel analyzer which collects and sums the results.

The general experimental arrangement of a Mossbauer spectrometer is given in below Fig



The schematic arrangements of a modern Mossbauer spectrometer is shown in below figure.



The source ^{57}CO is mounted on a loud speaker coil whose motion is controlled by a waveform generator. A saw tooth variation of velocity with time is generally used. This arrangement makes the sample to move back and forth at regular integrals. This oscillatory motion gives the source a varying velocity relative to the sample. The velocity will be zero at the turning points and maximum at the centre. The absorber which is also in the form of a foil covers the window of the detector. A scintillation counter or a gas – filled proportional counter are semi-conductor detector is used according to the situation. The signal from the detector as a function of the loud speaker velocity is fed to a multichannel analyzer which collects the results and sums it over each cycle. The discriminator rejects most of the nonresonant background radiation. The final Mossbauer spectrum is displayed as counts per second as a function of relative velocity between the source and absorber.

The Mossbauer Effect shown up strongly in the following way.

1. A relative velocity of 0.1mm/sec is sufficient to produce a marked reduction in the absorption of the 14.4Kev ^{57}Fe transition.
2. In certain cases, resonances are possible in room temperature, but in many cases, one has no cool the absorber and the source to liquid helium temperature. Due to this Doppler Effect is reduced to a minimum.

The absorption of the gamma – ray by the sample is shown up by a fall in counts per second is shown in below diagram.

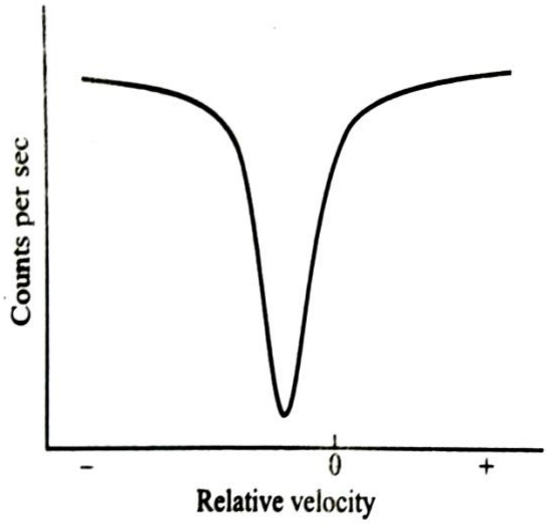
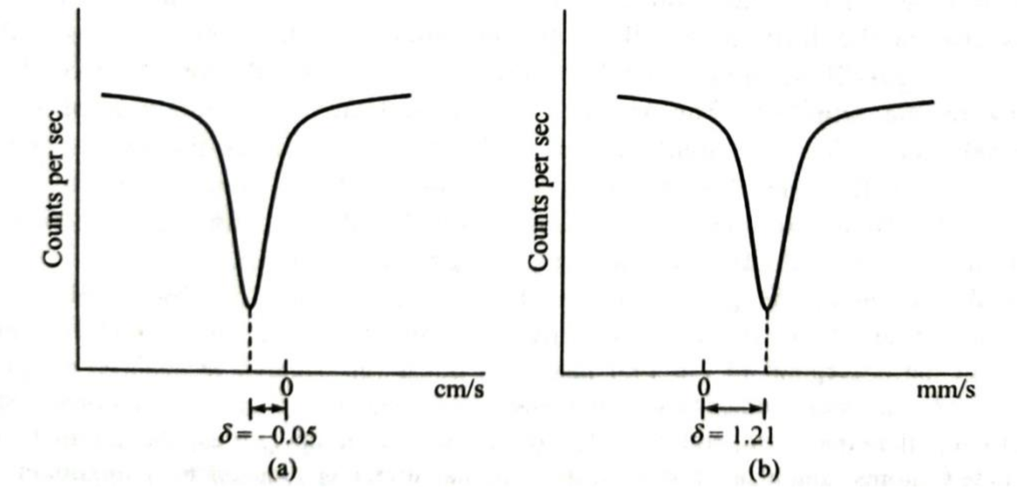


Fig. Typical Mossbauer Spectrum

Chemical shift / Isomer shift

In a Mossbauer experiment, if the environments of the emitting and absorbing nuclei are different, the energy of the nuclear transition E_0 may differ by a small amount. This energy difference in known as the ***isomer shift* (δ) or *chemical shift.***

The effect of isomer shift on the Mossbauer spectrum is the shift the resonance line from the zero position. The value of δ can be +ve or –ve depending on the sample. Isomer shift is the term more widely used since this effect depends on the energy difference in the ground and excited (isomeric) states.



Isomer shift in (a) $[Fe(CN)_6]^{-4}$ **(b)** $(C_6H_5)_4 S_n)$

Isomer shift arises because the nucleus of an atom is not a point charge as assumed, but has a finite charge distribution. The electrostatic interaction between the nuclear charge distribution and the electron charge distribution brings about a change in the energy levels of the nucleus. The shift in the energy levels of the nucleus is given by

$$\Delta E = \frac{2\pi}{5} Ze^2 \, R^2 \, |\,\psi(0)\,|^2$$

Where $|\psi\ (0)\ |^2$ represents the total electron density at the site of the nucleus. The charge in energy δ (Δ*E*) between the nuclear ground and first excited state . Hence,

$$\delta(\Delta E) = (\Delta E)_{ex} - (\Delta E)_{ga} = \frac{2\pi}{5} Ze^2 \, |\,\psi(0)\,|^2 \, (R_{ex}{}^2 - R_{gr}{}^2)$$

Writing R for radius of the equivalent sphere of uniform charge distribution and *dR* for $(R_{ex} - R_{gr})$

$$(R_{ex}^{\ 2} - R_{gr}^{\ 2}) = 2R\,dR = 2R^2 \frac{dR}{R}$$

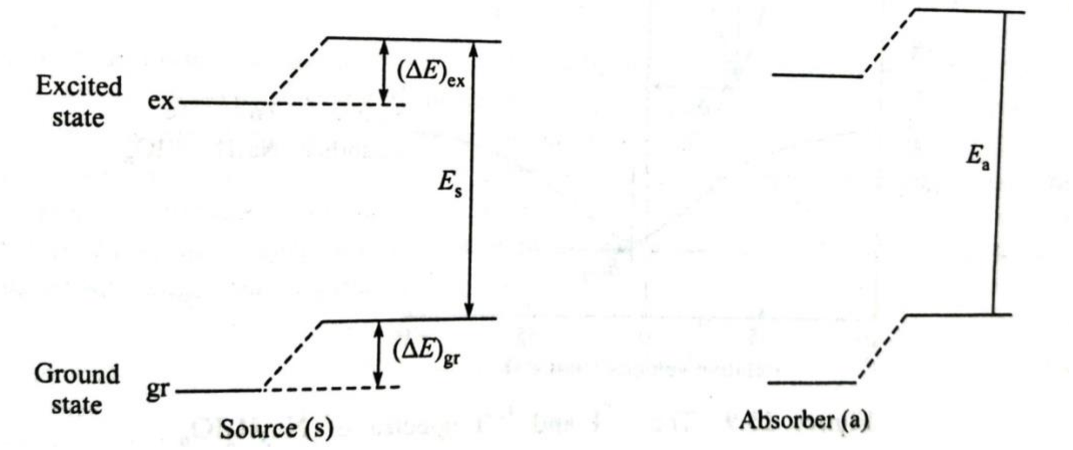


Fig. Representation of energy shifts responsible for isomer shift.

In the Mossbauer experiment, a source – absorber pair is involved and one measures only a difference in the nuclear electrostatic energy changes of the source and the absorber. Hence, the isomer shift δ is given by,

$$\begin{aligned}\delta &= \delta\ (\Delta E)_a - \delta\ (\Delta E)_s \\ &= \frac{4\pi}{5} Ze^2 R^2 \ \frac{dR}{R}\left[\,|\psi(0)|_a^{\,2} - |\psi(0)|_s^{\,2}\,\right]\end{aligned}$$

Where subscripts ‘a’ and ‘s’ refer to the absorber and emitter (source) respectively. The chemical term represents the difference in the total electron densities at the absorber and source nuclei and hence δ is sometimes referred to as chemical isomer shift. Chemical isomer shift is the Mossbauer parameter that gives the maximum amount of chemical information.

Applications of Mossbauer Spectroscopy

1. It is used as a tool for studies in solid state and chemistry is mainly based on the observation of hyperfine structure.
2. The narrow line width of nuclear transitions is possible to investigate small interactions between nucleus and orbital electrons which cannot be studied by other methods.
3. Mossbauer spectroscopy is used in the analysis of electronic structure, molecular structure, magnetic structure and crystal symmetry of compounds.
4. It is also used in surface studies, adsorption and catalysis at solid-liquid and solid-gas interfaces.
5. It is useful in the field of geology for identifying the composition of iron-containing specimens including meteors and moon rocks.
6. Mossbauer spectroscopy has been widely applied to bioinorganic chemistry, especially for the study of iron-containing proteins and enzymes. Often the technique is used to determine the oxidation state of iron.

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