

UNIT-1**Structure:**

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1.0 Objective of the unit

After learning this unit you are able understand

- Properties and components of radiations
- Relation between wavelength, frequency and energy of radiation
- Electromagnetic radiation.
- Wave nature of matter
- Particle nature of matter
- Dual nature of matter
- Interaction of matter with radiation.

1.1 Introduction

The theory of relativity was largely the work of one man, the quantum theory developed by Albert Einstein was principally over a period of thirty years through the efforts of many scientists. Explanation of black body radiation was the first contribution by Max Planck in 1900, who proposed that the energies of any harmonic oscillator such as the atoms of a black body radiator, are restricted to certain values, each of which is an integral (ie, whole number) multiple of a basic, minimum value. The energy E of this basic quantum is directly proportional to the frequency ν of the oscillator, or $E = h \nu$, where h is a constant called Planck's constant, having the value 6.63×10^{-34} joule-second. In 1905, Einstein proposed that the radiation itself is also quantized according to this same formula, and he used the new theory to explain the photoelectric effect. Bohr used the quantum theory in 1913 to explain both atomic structure and atomic spectra, showing the connection between the electrons energy levels and the frequencies of light given off and absorbed.

Quantum mechanics, the mathematical formulation of the quantum theory, was developed during the 1920s. In 1924, Louis de Broglie proposed that not only do light waves exhibit particle like properties, as in the photoelectric effect and atomic spectra but particles also exhibit wavelike properties. This hypothesis was confirmed experimentally in 1927 by C. J. Davisson and L. H. Germer, who observed diffraction of a beam of electrons analogous to the diffraction of a beam of light. The wave mechanics of Erwin Schrödinger (1926) involves the use of a mathematical entity, the wave function, which is related to the probability of finding a particle at a given point in space. The matrix mechanics of Werner Heisenberg (1925) makes no mention of wave functions or similar concepts but was shown to be mathematically equivalent to Schrödinger's

theory. The important discovery of the quantum theory is the uncertainty principle enunciated by Heisenberg in 1927, which places an absolute theoretical limit on the accuracy of certain measurements as a result, the assumption by earlier scientists that the physical state of a system could be measured exactly and used to predict future states had to be abandoned.

1.2 Relationship of Energy and Matter

According to the earlier theories of classical physics, energy is treated as a continuous phenomenon. The matter is assumed to occupy a very specific region of space and to move in a continuous manner. According to the quantum theory, energy is held to be emitted and absorbed in tiny, discrete amounts. Therefore an individual bundle or packet of energy, called a quantum (or quanta), behaves in some situations much like particles of matter. These particles exhibit wave like properties when in motion and are no longer viewed as localized in a given region but rather as spread out to some degree. For example, the light or other radiation is given off or absorbed by an atom has only certain frequencies (or wavelengths), can be seen from the line spectrum associated with the chemical element represented by that atom. The quantum theory shows that those frequencies correspond to definite energies of the light quanta or photons and result from the fact that the electrons of the atom can have only certain allowed energy values, or levels when an electron changes from one allowed level to another, a quantum of energy is emitted or absorbed whose frequency is directly proportional to the energy difference between the two levels.

1.3 Properties of Matter (Particle)

There are four different properties of matter. They are weight, volume, mass, and density. The most important one is mass. Mass is the amount of matter in an object and it never changes unless matter is taken out from the object. Mass also has a direct relationship with inertia. Inertia is the resistance of motion of an object. If an object has a greater mass, then it has a greater inertia. Also, you can find mass by measuring it on a triple beam balance.

Volume is another general property of matter. Anything that takes up space has volume. In fact, volume *is* the amount of space an object takes up. You can find a straight-edged object's volume by measuring the Length x Width x Height. For irregular shaped objects, you'd probably want to use a graduated cylinder. Liters and milliliters are used to measure the volume of liquids, while cubic centimeters are used to measure solids.

The third general property of matter is density. Density is very important because it enables you to compare different objects. For instance, water has a density of 1 gram/cc and wood is 0.8 grams/cc. Therefore, wood will float in water because its density is less than that of water. The equation for density is $\text{Density} = \text{Mass}/\text{Volume}$. Also, if you split an object in half, it will still have the exact same density

Weight is the fourth general property of matter. It is defined as the measure of force of attraction between objects due to gravity. Gravity is what keeps you and me on the ground. Weight, unlike mass, changes with location. The farther you are from the center of the Earth, the less you weigh. The metric unit for weight is the newton, even though in America the most common unit is the pound. The equation for weight is $\text{Weight} = \text{Mass} \times \text{Acceleration due to gravity}$, but I personally think the easiest one is for every kilogram of mass, there 9.8 newtons of weight

1.4 Properties of Wave:

A wave doesn't *stop* when it reaches the end of the medium. Rather, a wave will undergo certain behaviors when it encounters the end of the medium. Specifically, there will be some reflection off the boundary and some transmission into the new medium. The transmitted wave undergoes refraction (bending) if it approaches the boundary at an angle. If the boundary is merely an obstacle implanted within the medium, and if the dimensions of the obstacle are smaller than the wavelength of the wave, then there will be very noticeable diffraction of the wave around the object. Each one of these behaviors - reflection, refraction and diffraction - is characterized by specific conceptual principles and mathematical equations.

1.5 Wave properties of Light

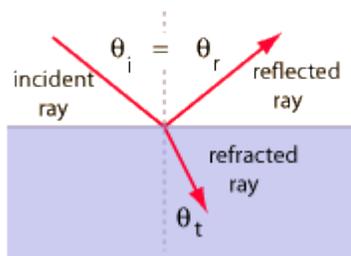
Light exhibits behaviors that are characteristic of both waves and particles. Certain behaviors of light that are characteristic of wave and would be difficult to explain with a purely particle-view.

- 1) Light reflects in the same manner that any wave would reflect.
- 2) Light refracts in the same manner that any wave would refract.
- 3) Light diffracts in the same manner that any wave would diffract.
- 4) Light undergoes interference in the same manner that any wave would interfere.

Reflection:

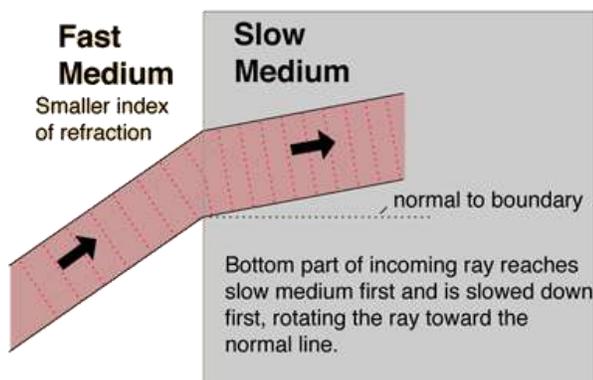
When light wave incident upon a surface, the partial light is bounce back this is called reflected light and the phenomenon is called reflection. And partial light wave transmitted through surface and is called refracted light and the phenomenon is called refraction. The angle relationships for

both reflection and refraction can be derived from Fermat's principle. The angle of incidence is equal to the angle of reflection is sometimes called the law of reflection



Refraction:

Refraction is the bending of a light wave when it enters from one medium to another medium if the speed of light is different in two mediums. The light when it passes from a fast medium to a slow medium bending of the light waves toward the boundary between the two media. The amount of bending depends on the refraction indices of the two media and is described quantitatively by Snell's law. Refraction is responsible for image formation by lenses and eye.



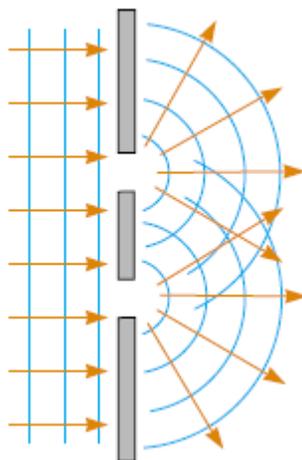
Diffraction:

Light bends when it passes around an edge or through a slit. This bending is called *diffraction*. The amount of bending depends on the wavelength of light and the size of the opening (edge of the object). If the opening is much larger than the light's wavelength, the bending will be almost unnoticeable. However, if the two are closer in size or equal, the amount of bending is considerable, and easily seen with the naked eye.

Interference:

When two sets of light combine with each other to produce a resultant wave, the way in which this combined wave is produced is called interference. When propagative light waves superimposed, they will add their crests if they meet in the same phase this phenomenon is called constructive interference, or the troughs will cancel the crests if they are out of phase these

phenomena is called destructive interference. Bright or dark bands are caused by beams of light that are in phase or out of phase with one another respectively.



1.6 Particle Properties of Light

Until the early 20th century physicists and chemists used to explain the phenomena in the world around them using theories such as mechanics, electromagnetism, thermodynamics and statistical physics and are called as classical theories. At the turn of the 19th century more and more experiments did show effects that could not be explained by these classical theories. This indicated a need for a new theory that is now known as quantum mechanics. In the early years of the 20th century experimental observations did hint at the fact that light might also possess particle properties, i.e., that any radiation transports energy in quanta of energy that is called photons. The photoelectric effect, X-ray diffraction and Compton effects represent the particle nature of light. These effects are difficult to explain on the basis of pure wave nature of light.

Photo electronic effect:

A photon of energy $h\nu$ (where h is Planck's constant) strikes an electron inside a metallic conductor, it can knock the electron out of the metal. This is called photoelectric effect. To explain this effect Einstein claimed that light was made of particles called quanta, that each had some small fixed energy which depended on the wavelength of the light. *The shorter the wavelength, the more energy each of these quanta had, the longer the wavelength the smaller the energy of the quanta.* So quanta of red light would have less energy than quanta of blue light. Einstein also reasoned that light should *behave and interact* like any other particle.

X-ray diffraction:

X-rays are high-energy photons that are produced when electrons make transitions from one atomic orbit to another. These transitions can be generated via the photoelectric effect. An electron in an alternating electromagnetic field will oscillate with the same frequency as the field. When an X-ray beam hits an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In almost all directions and results destructive interference, ie, the combining waves are out of phase and there is no resultant energy leaving the solid sample. However the atoms in a crystal are arranged in a regular pattern in a definite directions results constructive interference. The waves will be in phase and there will be well defined X-ray beams leaving the sample at various directions. Hence, a diffracted beam may be described as a beam composed of a large number of scattered rays mutually reinforcing one another.

The Compton Effect:

The Compton Effect is the elastic scattering of photons from electrons. Compton found that, when the monochromatic X rays are illuminated on graphite the wavelength of the scattered X rays will be longer as the scattering angle becomes larger. This is called Compton effect. This cannot be explained with the classical theory. According to the classical theory, the incident X rays oscillate the charged particle (electron at present) and the oscillating charged particle radiates around the same frequency of electromagnetic waves (X rays). Accordingly the frequency of the radiated (scattered) X rays must be the same as that of the incident X rays. Compton analyzed Compton scattering as follows. He thought that the incident X rays collide against the electron in the graphite as a "particle" with the energy $h\nu$ and the momentum $h\nu/c$.

1.7 Dual Nature of Electron

In 1905, Einstein suggested the concept of light having a dual nature, ie, particle and wave nature. In a similar way, Louise de Broglie suggested that a small particles (electron) are also exhibits a dual nature. de Broglie also derived a mathematical expression to prove the wave nature of small particles (electron).

According to Einstein's mass energy relation, $E = mc^2$ ----- (1)

Broglie compared the above relation with the relation for energy of wave. According to quantum theory the energy of a radiation with frequency ν is equal to

$$E = h\nu \text{ ----- (2)}$$

Where h is Planck's constant and its value is equal to $6.625 \times 10^{-34} \text{ m}^2\text{Kg/s}$.

From equation 1 and 2

$$h\nu = mc^2$$

$$\frac{hc}{\lambda} = mc^2 \quad (\text{as } \nu = \frac{c}{\lambda})$$

$$h = \lambda mc \text{ or}$$

$$\lambda = \frac{h}{mc} \text{----- (3)}$$

$$\lambda = \frac{h}{p} \quad (\text{as } mc = p \text{ is a momentum})$$

Equation (3) is called the de Broglie wave equation and it defines the wavelength of a particle of mass m moving with a velocity c . The wavelength of a particle is inversely proportional to mass and velocity of the particle.

If we apply this relation to electrons in an atom moving at a constant speed along a circular orbit around the nucleus, then the circumference of the circular orbit of the electron must be an integral multiple of the wavelength of de Broglie wave as shown in the figure 1.

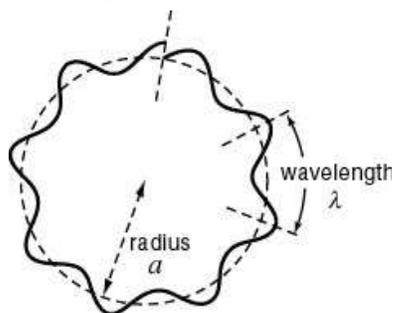


Figure 1: de Broglie wave motion of an electron in circular orbit

For the stationary particle i.e., particle does not move, then $c = 0$ therefore wavelength is

$$\lambda = \frac{h}{mc} = \frac{h}{m \times 0} = \infty (\text{Infinity})$$

This shows that the wave nature of particle is only observed when the particle is in motion.

Electron carrying a negative charge can be knocked out from the orbit by providing sufficient amount of energy. And the knocked-out electron can easily be accelerated using an accelerating

voltage. We know that any small objects that moves will have a wavelength associated with them called de Broglie wavelength. Therefore by accelerating an electron we can create a wave with discrete range of wavelength. Faster acceleration gives shorter wavelength waves and vice versa.

1.8 Electromagnetic radiation

Electromagnetic waves are produced by accelerating charges. From our elementary study of physics we know that a moving charge particle generate an electric field around it, and an oscillating electric field generates an oscillating magnetic field and vice versa. Therefore the electromagnetic wave has two components, the electric radiation field and the magnetic radiation field. The magnitude of the electric radiation field is directly proportional to the acceleration.

Therefore electromagnetic waves are defined as a wave consisting of electric and magnetic fields, oscillating at right angles to each other and perpendicular to the direction of propagation (figure 2).

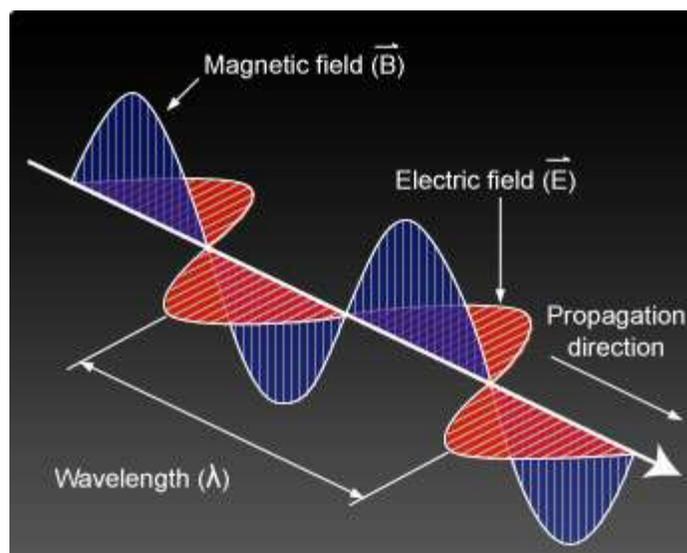


Figure 2: Propagation of electromagnetic wave

When electrons move, they create a magnetic field. When electrons move back and forth or oscillate, their electric and magnetic fields change together, forming an electromagnetic wave. This oscillation can come from atoms being heated and thus moving rapidly or from alternating current (AC) electricity. The opposite effect occurs when an electromagnetic wave hits matter. In such a case, it could cause atoms to vibrate, creating heat, or it can cause electrons to oscillate, depending on the wavelength of the radiation.

1.9 Properties of Electromagnetic Waves

Electromagnetic waves are very different from mechanical waves. Electromagnetic waves travel in vacuum, i.e., no medium is required for the electromagnetic wave to travel through. Other waves such as sound waves cannot travel through a vacuum. An electromagnetic wave has no mass, but has energy and momentum. The electromagnetic waves travel with a speed of light, and energy carried by an electromagnetic wave is proportional to the frequency of the wave. The wavelength and frequency of the electromagnetic wave are connected through equation 4

$$C = \gamma \lambda \text{ ----- (4)}$$

Electromagnetic waves are not deflected by electric or magnetic fields. Also, electromagnetic waves can show interference or diffraction. Electromagnetic waves are transverse waves and can be polarized.

1.10 Characteristics of electromagnetic waves

Electromagnetic waves are transverse waves, similar to water waves in the ocean. As we learned in wave motion, all waves including electromagnetic waves have amplitude, wavelength, velocity, and frequency.

Amplitude

The amplitude of electromagnetic waves relates to its intensity or brightness (as in the case of visible light). With visible light, the brightness is usually measured in lumens. With other wavelengths, the intensity of the radiation, which is power per unit area or watts per square meter, is used. The square of the amplitude of a wave is the intensity.

Wavelength

The wavelengths of electromagnetic waves go from extremely long to extremely short and everything in between. The wavelengths determine how matter responds to the electromagnetic wave.

Velocity

The velocity of electromagnetic waves in a vacuum is approximately 186,000 miles per second or 300,000 kilometers per second, the same as the speed of light. When these waves pass through matter, they slow down slightly, according to their wavelength.

Frequency

The frequency of any waveform equals the velocity divided by the wavelength. The units of measurement are in cycles per second or Hertz.

1.11 Let us sum up

The nature of electrons seems odd. Seemingly they exist in different places at different points in time, but it is impossible to say where the electron will be at a given time. Just as light is thought to have a dual nature, sometimes showing the characteristic of a wave, and sometimes that of a particle (photon), quantum theory attributes a similar dual wave-particle nature to subatomic particles. Electrons that orbit around the nucleus interact with each other by showing interference patterns, not unlike those of wave interference. If the velocity of the electron is thought of as its wavelength, the crests of neighbouring electron waves amplify or cancel each other, thereby creating a pattern that corresponds to Bohr's allowed orbits.

To explain all experiments with EM radiation, one must assume that light can be described both as *wave* (Interference, Diffraction) and *particles* (Photoelectric Effect, Frank-Hertz Experiment, x-ray production, x-ray scattering from electron) and to observe wave properties one must make observations using devices with dimensions comparable to the wavelength. Louis de Broglie postulated that the dual nature of the light must be “expanded” to all matter. In other words, all material particles possess wave-like properties, characterized by the wavelength, λ_B , related to the momentum p of the particle in the same way as for light. More over de Broglie's waves *are not* EM waves. He called them “pilot” or “material” waves and λ_B depends on the momentum and not on physical size of the particle. The principle of complementarity states that the wave and particle models of either matter or radiation are complement each other. Both models cannot be used exclusively to describe matter or radiation and no measurements can simultaneously reveal the particle and the wave properties of matter.

1.12 Key words

Energy; Matter; Light; Electron; Wave; Dual Nature of Electron; Electromagnetic radiation; Dual nature; Amplitude; Wavelength; Velocity; Frequency.

1.13 References for further study:

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2. Quantum Chemistry by R. K. Prasad, *New Age International Publications, New Delhi, 1997*.

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1.14 Questions for self study:

- 1) Mention describes three wave nature properties of light.
- 2) Explain three wave particle properties of light.
- 3) What is dual nature of electron?
- 4) Derive the de Broglie wave equation for electron?
- 5) What is electromagnetic radiation and how it should produce?
- 6) What are the properties of electromagnetic radiation?

UNIT 2**Structure**

- 2.0 Objective of the unit
- 2.1 Introduction
- 2.2 Relationship of Energy and Matter
- 2.3 Electromagnetic Spectra
 - Radiofrequency region
 - Microwave region
 - Infra-red region
 - X-ray region
 - γ -ray region
- 2.4 Energy level of atom
- 2.5 Interaction of electromagnetic radiation with atom
- 2.6 Energy level diagram for molecule
- 2.7 Molecular energy levels and associated spectra
- 2.8 Let us sum up
- 2.9 Key words
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2.1 Objectives of the unit

After studying this unit you are able to.

- Describe the relationship between energy and matter.
- Identify the different regions in the electromagnetic spectra.
- Explain the interaction of molecules with different regions of ES.
- Explain the energy levels of atom and molecules.
- Identify the molecular energy levels and associated spectra.

2.2 Introduction

Radiation is energy that travels through media. The visible light that comes from a lamp in our house, the radio waves that come from a radio station, the microwave used for cooking in kitchen, the infrared light and ultraviolet light used in industries and laboratories for various propose, the X-rays used in medical filed are some of the example of radiations which we are used in our daily life. All these radiations are the types of electromagnetic (EM) radiation. Each type of radiations have particular property and have definite characters, hence radio waves cannot be used for cooking similarly X-rays are not use full to transmit radio signals. The some of the uses of these radiations are,

Radio: Our radio captures radio waves emitted by radio stations, bringing our favorite tunes. Radio waves are also emitted by stars and gases in space.

Microwave: Microwave radiation will cook our popcorn in just a few minutes, but is also used by astronomers to learn about the structure of nearby galaxies.

Infrared: Night vision goggles pick up the infrared light emitted by our skin and objects with heat. In space, infrared light helps us map the dust between stars.

Visible: Our eyes detect visible light. Fireflies, light bulbs, and stars all emit visible light.

Ultraviolet: Ultraviolet radiation is emitted by the Sun and is the reason skin tans and burns. "Hot" objects in space emit UV radiation as well.

X-ray: A dentist uses X-rays to image our teeth, and airport security uses them to see through our bag. Hot gases in the universe also emit X-rays.

Gamma ray: Doctors use gamma-ray imaging to see inside our body. The biggest gamma-ray generator of all is the Universe.

In this unit we will discuss what are electromagnetic waves and their effect on atom and molecule when they are observed.

2.3 Electromagnetic Spectra:

Electromagnetic waves exist with an enormous range of frequencies. This continuous range of frequencies is known as the *electromagnetic spectrum*. The entire range of the spectrum is

divided into specific regions. This subdividing of the entire spectrum into smaller spectra is done on the basis of how each region of electromagnetic waves interacts with matter. Figure 1 depicts the electromagnetic spectrum and its various regions. The longer wavelength or lower frequency of the region is located on the far left of the spectrum. The shorter wavelength or higher frequency region is located on the far right of the spectrum. Two very narrow regions within the spectrum are the visible light region and the X-ray region.

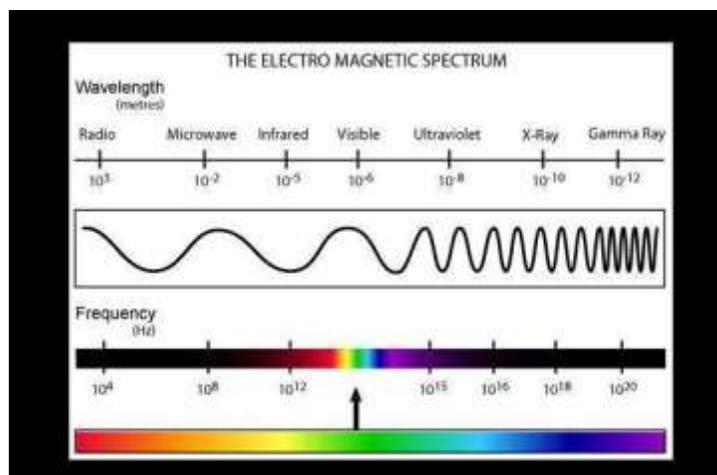


Figure 1: over view of the entire electromagnetic spectrum

Electronic spectrum is divided into 6 major sub regions. In increasing order of frequency, the regions are named as follows

1. *Radiofrequency region:*

The frequencies of electromagnetic spectrum corresponding to this region are lying between 3×10^6 to 3×10^{10} Hz and wave length corresponding to 10m to 1cm. The energy changes involved in the atom or molecule due to absorption radiation in this region is the reversal of spin of a nucleus or electron, and is of the order 0.001-10 joules/mole. Nuclear magnetic resonance (NMR) spectroscopy is studied in this radiofrequency region.

2. *Microwave region:*

The frequencies of electromagnetic spectrum corresponding to this region are lying between 3×10^{10} to 3×10^{12} Hz and wavelength corresponding to 1cm-10 μ m. Separations between the rotational energy levels of the molecules are of the order 100 joules/mole and falling in this region. Therefore rotational spectroscopy is studied in this microwave region.

3. *Infra-red region:*

The frequencies of electromagnetic spectrum corresponding to this region are lying between 3×10^{12} to 3×10^{12} Hz and wavelength corresponding to $100 \mu\text{m}$ - $1 \mu\text{m}$. Separation between the vibrational energy levels of the molecules are of the order 10^4 joules/mole and falling in this region. Therefore vibrational spectroscopy is studied in this Infra-red region.

4. Visible and Ultra-violet region:

The frequencies of electromagnetic spectrum corresponding to this region are lying between 3×10^{14} to 3×10^{16} Hz and wavelength corresponding to $1 \mu\text{m}$ to 10nm . The separation between the energies of electrons in an atom or molecules is 100kJoules/moles and falling in this region. Therefore Electronic spectroscopy is studied in this visible and ultra-violet region.

5. X-ray region:

The frequencies of electromagnetic spectrum corresponding to this region are lying between 3×10^{16} to 3×10^{18} Hz and wavelength corresponding to 10nm to 100pm . Absorption of energy in this region involves the energy changes of the inner electrons of an atom or molecules and may be order of $1000 \text{kJoules/moles}$. Diffraction studies of crystal structure are studied in this X-ray region.

6. γ -ray region:

The frequencies of electromagnetic spectrum corresponding to this region are lying between 3×10^{18} to 3×10^{20} Hz and wavelength corresponding to 100pm to 1pm . Energy changes involving the rearrangement of nuclear particles, having energies of 10^9 to 10^{11} joules per gram of atom.

2.4 Energy level of atom

According to Bohr's atomic model, electrons travel around the nucleus in specific permitted circular orbits. Each orbit is at the fixed distance from the nucleus and has definite energy (**Figure 2**). As long for as electron circulating in these orbits they don't emit radiation, ie, they did not lose or gain energy.

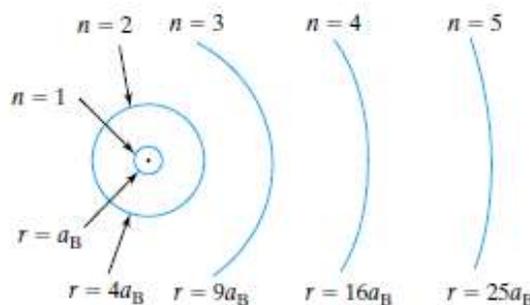


Figure 2: energy level of the orbits in an atom

All the electrons try to occupy the orbit which is lowest in energy and electron resides in this are called ground state. The energy difference between the two orbits is equal to

$$\Delta E = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{----- (2)}$$

Where R is called Rydberg constant and its value equal to $1,09,679\text{cm}^{-1}$ and n_1 and n_2 are the two different orbitals.

The electron in atom at ordinary temperature resides in the lowest energy state i.e., ground state. When electromagnetic radiation correspond to energy of ΔE in the equation 2 is absorbed, the electrons move to higher energy level i.e., 2,3,4,5,6.....etc, depending on the values of n_1 and n_2 . Electron in the higher energy level is unstable and returns to one or other energy levels by emitting the excess of energy as a photon. This gives the electronic spectra of an atom (**Figure 3**). Transitions connecting the $n_1 = 1$ level to higher levels is usually referred to as the Lyman series, with $n_2 = 2 \rightarrow n_1 = 1$ designated Lyman- α or $\text{Ly}\alpha$, $n_2 = 3 \rightarrow n_1 = 1$ as $\text{Ly}\beta$, etc. Transitions connecting $n_1 = 2$ to higher levels make up the Balmer series, for $n_1 = 3$ we get the Paschen series (Pa), and $n_1 = 4$ gives the Brackett series (Br); similarly $n_1 = 5$ the Pfund series (Pf).

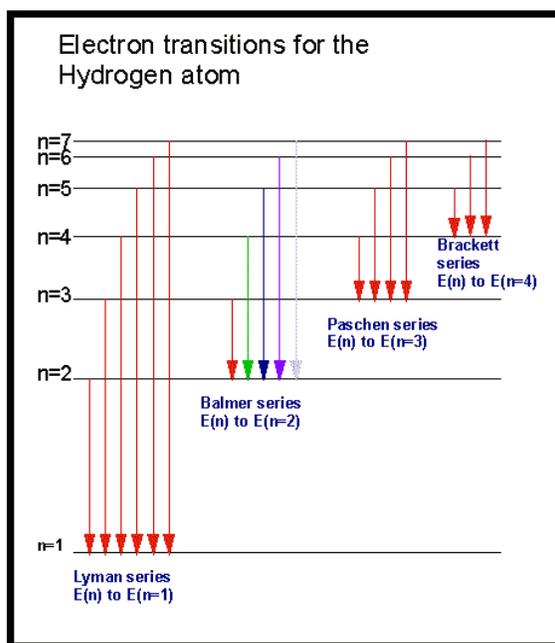


Figure 3: Electronic spectra of Hydrogen atom

The Lyman series lie in the ultraviolet. The $\text{Ly}\alpha$ line at 1216 \AA is one of the strongest lines from atomic hydrogen. Since subsequently higher levels are closer together in energy, all series have a

limit for transitions to large n . For the Lyman series this limit lies at 912 \AA , corresponding to the ionization potential of H of 13.6 eV . The Balmer series lie in the optical, while the Paschen, Brackett, and Pfund series are in the infrared.

2.5 Interaction of electromagnetic radiation with atom

When electromagnetic radiation strike an atom it can cause number of changes, an electron residing in a low-energy molecular is promoted to a higher-energy orbital. The change in energy levels is called a *transition*. Such a transition happens only when the energy $h\nu$ of the electromagnetic radiation is exactly the same as the energy difference between the two orbital energies. The transition of an electron between different energy levels is called an *electronic transition*, and the absorption process is called *electronic absorption*. These electrons will remain in the excited state for a certain period of time, and then will return to lower energy state while emitting energy in the exact amount of the difference between the two energy levels this is called *emission process*. The electromagnetic radiation may be transmitted completely through the substance it encounters. If absolutely no energy is absorbed by the material, it is said to be *transparent* to the radiation. For example, lead glass is transparent to visible light but not X-rays, similarly thicknesses of black paper sheets are transparent to X-rays, but not visible light. The velocity of the radiation is usually slower in the transparent medium as a result the radiation usually undergoes *refraction*.

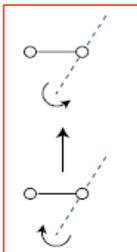
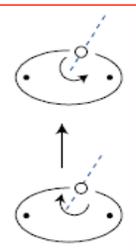
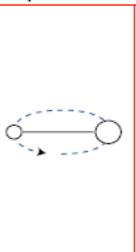
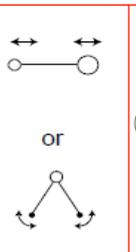
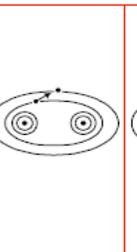
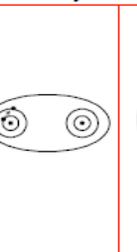
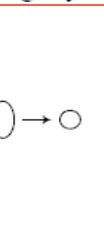
Change of Spin		Change of Orientation	Change of Configuration	Change of Electron Distribution		Change of Nuclear Configuration
nmr	esr	μ wave	IR	vis-UV	X-ray	g-ray
						
10^{-2}	1	100	10^4	10^6	10^8	10^8
10 m	100 cm	1 cm	100 μm	1 μm	10 nm	10 pm
13×10^8	3×10^8	3×10^{10}	3×10^{12}	3×10^{14}	3×10^{16}	3×10^{18}
10^{-3}	10^{-1}	10	10^3	10^5	10^7	10^9
				cm ⁻¹	wavenumber	
					wavenumber	
				Hz	frequency	
				joules/mole	energy	

Figure 4: Over view of Interaction of molecule with different electromagnetic spectrum regions

2.6 Energy level diagram for molecule:

Molecules are formed by uniting two or more atoms. The formation of bond between the atoms in a molecule is due to overlapping of atomic orbitals. According to molecular quantum mechanics, since nuclei are much heavier than the electron, nuclei are treated as stationary so that electrons move relative to them. When atomic orbitals come close together they overlap to form molecular orbitals. Each molecular orbital can hold maximum of two electrons with opposite spin in accordance with Pauli's exclusion principle. Atoms are not stationary they are spinning around an axis passing through its nucleus. Like simple atoms molecules are also not stationary, they are rotating and vibrating. These contribute to the total energy of the molecules. The overall energy E associated with a molecule in a given state can be written as

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$

where $E_{\text{electronic}}$ is the electronic energy of the molecule, $E_{\text{vibrational}}$ is its vibrational energy, and $E_{\text{rotational}}$ is its rotational energy.

Three types of energy changes occur when molecules are excited by electromagnetic radiation. Molecules exhibit two additional types of radiation-induced transitions: vibrational transitions and rotational transitions. The vibrational energy of a molecule is associated with the bonds that hold the molecule together. The vibrational energy of a molecule is quantized and can only assume certain discrete levels. Transitions between vibrational levels are vibrational transitions.

where $E_{\text{electronic}}$ is the electronic energy of the molecule, $E_{\text{vibrational}}$ is its vibrational energy, and $E_{\text{rotational}}$ is its rotational energy.

2.7 Molecular energy levels and associated spectra

A diatomic molecule is a stable arrangement of two atoms separated by a distance called bond length. If the molecule is formed by two same atoms then the molecule is said to be homonuclear molecule, ex: H_2 , O_2 , N_2 , Cl_2 , Br_2 , etc.... If the molecule is formed by two or more different atoms, then molecule is said to be heteromolecule, ex: HCl , CO , HCN , NO , etc...

Energy-level of molecule is different from that of individual atoms. Like atomic-energy states we cannot classify molecular energy states according to the electronic angular momentum L (which is not conserved in molecule). In diatomic molecule the total charge is distributed symmetrically about the intramolecular axis so that the component of angular momentum about this axis is conserved. In addition the nuclei vibrate along the internuclear axis, the whole molecule rotates

about the centre of mass. These nuclear motions in the molecule cannot ignore. The energy of each of these vibrational and rotational motions is quantized. Hence the energy levels in a molecule are more complex than in an atom (Figure 5).

When a molecule absorbs radiation, its energy increases which is equal to

$$E = h\nu = \frac{hc}{\lambda}$$

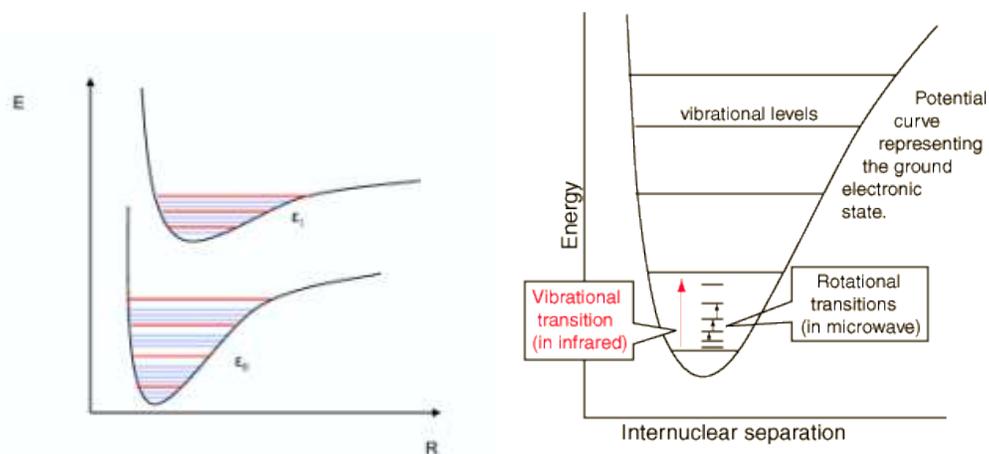


Figure 5: Molecular energy levels and associated spectra

By absorbing appropriate quantity of energy which is exactly equal to the energy difference between two levels ($\Delta E = hc/\lambda$). The molecule is promoted to the next higher level and is said to be in the excited state. The excited molecule returns to the ground state by emitting this observed energy as radiations.

The portions of electromagnetic radiation which do not absorb and may simply pass through the matter or undergo scatter or reflecting with or without change of wavelength. Apart from the transition energy, as already mentioned the internal energy of a molecule is equal to the sum of the rotational, vibrational, and electronic energies.

$$\text{ie, } E_{\text{int}} = E_{\text{elc}} + E_{\text{vib}} + E_{\text{rot}}$$

Like atomic spectra, molecular spectra are obtained by transition between energy states of the molecule. The molecular energy states are arising from the rotations and vibrations of its constituent nuclei relative to one other, as well as from the change in its electronic configuration. The energy states corresponding to rotation are separated by quite small energy-level ($\approx 10^{-3}$ eV). Vibrational energy states are separated by somewhat larger energy interval ($\approx 10^{-1}$ eV). The electronic energy states have higher energy separation (≈ 10 eV).

The molecular spectra are divided into three spectral ranges corresponding to the different types of transition between molecular energy states. They are

- a) Electronic spectra
- b) Vibrational-rotational spectra and
- c) Pure rotational spectra.

Electronic spectra are observed both in emission and absorption in the visible and the ultraviolet regions. Each electronic spectrum consists of quite a large number of bands and each individual band as a sharp edge. This is called band-head, in which the intensity falls suddenly to zero. Under high resolution spectra a band is found to be composed of a series of lines which draw further apart as the distance from the band-head increases. The electronic spectra are observed for the hetero nuclear as well as the homo nuclear diatomic molecules.

Vibrational-rotational spectra are observed in the near infrared region ($1\mu - 10^2\mu$; $1\mu = 10^{-6}\text{m} = 10^4 \text{ \AA}$). Each spectrum consists of an intensive band called fundamental bands, which are accompanied by a few weak bands. Vibrational-rotational spectra are observed only for hetero nuclear molecules. The homo nuclear molecules like H_2 , N_2 , O_2 do not produce vibrational-rotational bands.

Pure rotational spectra are observed in far-infrared ($10^2\mu - 10^3\mu$) or in the microwave ($10^3\mu - 10^4\mu$) region. Each spectrum is composed of a series of nearly equidistant lines. Like vibrational-rotational spectra, the pure rotational spectra are observed only for hetero nuclear diatomic molecules.

2.8 Let us sum up

For many years, scientists have exploited the ways that radiation interacts with matter. The particular effects that matter has upon light (and vice versa) depend on the energy content of the radiation and the type of matter. In all cases scientists measure the wavelengths and/or frequencies of radiation absorbed by the matter. When a substance is exposed to electromagnetic radiation, it undergoes changes that may or may not be reversible and that depend on the energy of the radiation. For example, gamma radiation can cause matter to lose electrons and undergo irreversible changes. In the case of living matter, radiation of this high energy can cause mutations in the tissue that may result in cancer or some other disease. However, it is more concerned with what happens to a substance when it is exposed to light of much lower

frequencies and energies. Two principal regions of light are most important in characterizing evidence: the ultraviolet/visible (UV/visible) and the infrared (IR).

All matter consists of atoms that are made up of negatively charged electrons circulating in orbitals existing in approximately concentric spheres around the nucleus. Nucleus is made up of positively charged protons and neutral neutrons. In a neutral atom or molecule, there are equal numbers of electrons and protons, so there is no net positive or negative charge. When atoms combine to make molecules (the building blocks of compounds, materials, or substances), they do so by sharing or donating/accepting electrons to form covalent or ionic bonds. Valence electrons in atoms and in molecules can be promoted to a higher energy level by absorbing energy from light or other energy sources. This process is said to be *quantized* because the atom or molecule can only absorb the exact amount or quantum of energy that corresponds to the difference in energy between the occupied and unoccupied energy level. In other words, a molecule will absorb energy and promote an electron if it is exposed to a photon of the proper energy.

2.9 Key words

Electromagnetic Spectra; Radiofrequency region; Microwave region; Infra-red region; X-ray region; γ -ray region

2.10 References for further study

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2.11 Questions for self study

- 1) Derive the relationship between energy and matter.
- 2) What are the different regions associated with electromagnetic radiation?
- 3) Explain the differences between energy levels of atom and molecule.

- 4) Explain the consequences of interaction of molecule with different regions of electromagnetic radiation.

UNIT 3.0**Structure:**

- 3.0 Objectives of the unit
- 3.1 Introduction
- 3.2 Electron Spin Resonance
- 3.3 Basic principle of ESR spectroscopy
- 3.4 Spectroscopic splitting factor
- 3.5 Relaxation, Saturation and Sensitivity
 - a) Spin Relaxation Mechanisms
 - b) Spin-lattice relaxation
 - c) Spin-spin relaxation
- 3.6 Width and Position of the spectral line
- 3.7 Energy Level Structure and the g-factor
- 3.8 Spin-spin Splitting (Hyperfine Splitting)
- 3.9 Results of Nuclear-Electron Interactions
- 3.10 The Hyperfine Coupling Constant
- 3.11 Isotropic and Anisotropic Interactions
- 3.12 Super hyperfine Splitting
- 3.13 Spin-orbit interaction
- 3.14 Effect of spin orbit coupling
- 3.15 Crystal field effect
- 3.16 Summary of the unit
- 3.17 Key words
- 3.18 References for further study
- 3.19 Questions for self study

3.0 Objectives of the unit

After studying this unit you are able to learn

- The meaning of electron spin
- The resonance phenomenon under the influence of magnetic field
- Understand the Basic principle of ESR spectroscopy
- Understanding the Relaxation, Saturation in ESR spectroscopy
- Understand the energy Level Structure
- Understand the significance of g-factor
- Explain the Isotropic and Anisotropic Interactions
- Understand the hyperfine splitting and its significance
- Width and Position of the spectral line

3.1 Introduction

The electron spin resonance spectroscopy is relevant to the study of atoms, ions, free radicals and molecules possessing an odd number of electrons or unpaired electrons, which display characteristic magnetic properties arising from the spin properties of unpaired electrons. Under the influence of external applied magnetic field the magnetic moment of the spinning electron may occupy either of the two possible orientations. Aligned or opposed to the applied magnetic field leading to the two energy levels for the electron spin. The absorption of energy causes the magnetic moment of the spinning electron to flip from the lower to higher energy state.

ESR spectroscopy is also called as electron paramagnetic resonance (EPR) spectroscopy and was first observed in 1945 by Zavoisky at Kazan. In very shorter period this leads to an important method for obtaining information about paramagnetic substances. The electron spin resonance and Nuclear Magnetic Resonance (NMR) are collectively referred to as magnetic resonance phenomena, because ESR and NMR are similar in their theoretical principles. However the NMR is observed in radio frequency region and the ESR is observed in microwave region of the electromagnetic spectrum. An ESR spectrum is observed only for systems containing unpaired electrons. Thus the systems which can be investigated by ESR spectroscopy are organic or inorganic free radicals and ions of transition metals which contain unpaired d or f electrons. One of the most important uses of ESR technique is the detection of extremely short-lived (transient) free radical intermediates in chemical reactions. ESR spectrum can be recorded in two modes, they are absorption mode and the derivative mode. Generally the ESR are broad (ie, not sharp)

therefore it is difficult to locate the peak in the absorption mode, but it is quite easy to locate it in the derivative mode. Hence ESR spectra are generally recorded in the derivative mode.

3.2 Electron Spin Resonance

ESR has been defined as the form of spectroscopy concerned with microwave induced transition between magnetic energy level of electron having a net angular momentum. ESR differs from simple microwave spectroscopy by being applicable only for paramagnetic materials. ESR requires the presence of unpaired electrons in the sample therefore it is restricted to paramagnetic substances and those substances which can be converted to a paramagnetic form with sufficient stability.

The following types of substances can be investigated by ESR

- 1) Atom and ions: all configurations with an odd number of electrons must possess angular momentum and therefore must be paramagnetic in nature and can be detected by ESR.
- 2) Molecules and molecular ions: molecules such as NO and NO₂ have an odd number of electrons and therefore are paramagnetic. The molecule such as O₂ although having an even number of electrons, has a partially filled molecular shell and therefore is paramagnetic in nature and can be detected by ESR.
- 3) Transition group impurities: These are atoms or ions with incomplete 3d, 4d, 5d, 4f or 5f shells. However not all the valence states of the transition metal ions are paramagnetic in nature. The paramagnetic ions most commonly observed are V⁴⁺, V²⁺, Ti³⁺, Cr³⁺, Mn²⁺, Fe³⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Pd²⁺, Ru²⁺, Os⁴⁺, Gd³⁺, Eu²⁺, Mo⁵⁺, Ir⁴⁺, etc...
- 4) Donors and acceptors such as phosphorous donor impurities in silicon.
- 5) Organic and inorganic radicals.
- 6) Activator and co-activators in phosphorus such as self activated ZnS.
- 7) Conduction electrons.

3.3 Basic principle of ESR spectroscopy

Electron is a charged particle with angular momentum and hence possesses magnetic moment. The two spin states of a single electron have the same energy level. By virtue of its charge and spin electron acts as a bar magnet and can interact with an external magnetic field B. In the absence of an external applied magnetic field the two spin energy states of an electron are equal. In the influence of an external applied magnetic field the spin energy states of electron separate and these energies of spin states increase linearly as the magnetic field increases. *The energy differences studied in EPR spectroscopy are due to the interaction of unpaired electrons in the*

sample with an external magnetic field produced by the EPR spectrometer. This effect is called Zeeman Effect.

When strength of the field B is zero, magnetic moment of odd electron have randomized direction, but in presence of B individual magnetic moment arising due to electron spin of the unpaired electron oriented in two ways. When the magnetic moment of electron μ is aligned along the applied magnetic field (ie, parallel) which has lowest energy. Other hand when the magnetic moment of electron μ is aligned against the applied magnetic field (ie, antiparallel) which has highest energy. The two states are labeled by the projection of electron spin, M_s , on the direction of the magnetic field. Because the electron has a spin $\pm 1/2$, the parallel state is assigned as $M_s = -1/2$ and the antiparallel state is $M_s = +1/2$ as shown in figure 1. The energy difference between these two energy states (ΔE) is calculated theoretically as follows

We know that an electron possesses a spin S whose values is $1/2$. The magnetic momentum associated with this spin is given by

$$\vec{\mu} = -g_e \mu_B \vec{S} \text{----- (1)}$$

The energy associated with electron spin S in the applied magnetic field in the direction of Z axis is

$$E = -\mu B_Z \text{----- (2)}$$

The component of spin S along the magnetic field direction is S_z , applying the value of μ then equation 2 becomes

$$E_z = -g_e \mu_B B_z \text{----- (3)}$$

For an electron $S_z = \pm 1/2$

$$\text{There fore } E_{+\frac{1}{2}} = \frac{1}{2} g_e \mu_B B_z$$

$$\text{and } E_{-\frac{1}{2}} = -\frac{1}{2} g_e \mu_B B_z$$

As already mention in absence of B_Z these to energy levels are equal (ie, degenerate). In the influence of B_Z the degeneracy is removed and there is an energy separation between the two states as shown in figure 1. The difference between the two energy sates is directly proportional to the strength of the applied magnetic field. The transition between the two levels can be induced by the microwave radiation frequency at perpendicular to B . Thus the ESR frequency of the odd electron can be calculated using quantum mechanics as follows.

From quantum mechanics, we obtained the most basic equations of EPR

$$E = g\mu_B B m_s = \pm 1/2 g\mu_B B \text{----- (3)}$$

$$\Delta E = E_H - E_L = \frac{1}{2} g\mu_B B_0 - (-\frac{1}{2} g\mu_B B)$$

$$\Delta E = g\mu_B B = h\gamma \text{----- (4)}$$

where: ΔE is the energy difference between the two spin states h is Planck constant γ is the microwave frequency g is the proportionality factor which is a function of electron's environment and it is called as Zeeman splitting factor,

3.4 Spectroscopic splitting factor:

From the relationship of equation 4, there are two important factors to note: the two spin states ($E_{+1/2}$ and $E_{-1/2}$) have the same energy when there is no applied magnetic field. Application of magnetic field provides a magnetic potential energy which splits the electronic spin state and the energy difference between the two spin states increases linearly with increasing magnetic field strength. If radiation is supplied with suitable frequency the spin can be made to flip in to opposite direction. These spin flips can be considered as transition between the energy states that become separated in energy in the influence of applied magnetic field.

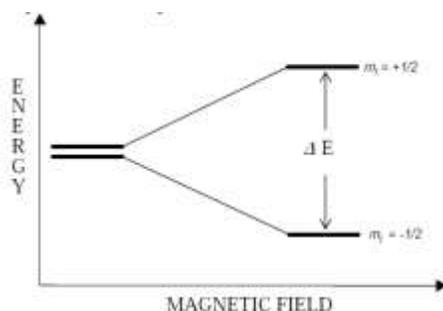


Figure 1: Splitting of energy level in the influence of applied magnetic filed

At the thermal equilibrium and external applied magnetic field, the spin population is split between the two Zeeman levels (Figure1) according to the Maxwell–Boltzmann law. Absorption

can occur as long as the number of particles in the lower state is greater than the number of particles in the upper state.

3.5 Saturation and Sensitivity

Ratio of number of electrons in upper energy level to those in lower energy level is given by Boltzmann law

$$\frac{n_1}{n_2} = e^{-\frac{\Delta E}{kT}} = e^{-\frac{g\mu_B B}{kT}} \quad \text{----- (5)}$$

where k is the Boltzmann constant.

At ordinary temperatures and applied magnetic fields, the exponent is very small and the exponential is expressed as $1 - X$. Thus

$$\frac{N_{upper}}{N_{lower}} = 1 - \frac{g\mu_B B}{kT} \quad \text{----- (6)}$$

At 298K and in a field of about 3000G the distribution shows that $N_{upper}/N_{lower} = 0.9986$, which means that difference between N_{upper} and N_{lower} is very small. The populations of the two energy levels are nearly the same, but the slight excess in the lower level. This gives rise to a net absorption.

$$\begin{aligned} N_{lower} - N_{upper} &= N_{lower} \left[1 - \left(1 - \frac{g\mu_B B}{kT} \right) \right] \\ &= \frac{N g \mu_B B}{2kT} \quad \text{----- (7)} \end{aligned}$$

Equation (7) tells us that EPR sensitivity (net absorption) increases as temperature decreases and magnetic field strength increases, and magnetic field is proportional to microwave frequency. Hence there must be an unsaturation condition occurs (ie, the number of particles in the lower state is greater than the number of particles in the upper state) resulting in absorption of energy by electron present in lower state and jump to higher energy level, which leads to equal population in both state and this is called as Saturation Condition. Therefore there is no further absorption of radiation from electrons and no further resonance state take place.

Like most spectroscopic techniques, when the radiation is absorbed, a spectrum is produced similar to the one on the left (ie, b) in figure 2. In EPR spectrometers a phase-sensitive detector is

used, this results in the absorption signal being presented as the first derivative so the absorption maximum corresponds to the point where the spectrum passes through zero. This is the point that is used to determine the center of the signal.

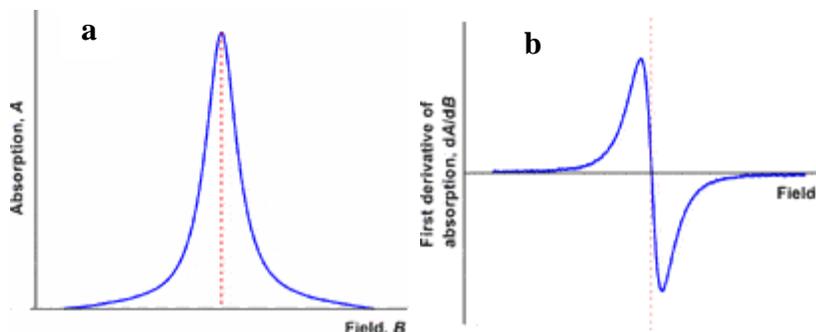


Figure 2: ESR absorption spectra of an electron. a) Absorption spectra and b) First derivative of absorption spectra.

3.6 Spin Relaxation Mechanisms

The slight excess in the lower energy level leads to energy absorption. In order to maintain a population excess in the lower energy level, the electrons from the upper level give up the energy equal to $\Delta E = h\nu$ and return to the lower level. The process of this energy releasing is called *spin relaxation process*. Relaxation time should be sufficiently rapid to prevent saturation of upper energetic level at the same time sufficiently slow to yield narrow spectral peaks. The spin relaxation process taking place in two ways they are *spin-lattice relaxation* and *spin-spin relaxation*.

a) Spin-lattice relaxation

Spin-lattice relaxation implies interaction between the spin system and the lattice ie, surrounding molecule. Vibrational, rotational and/or translational energies are dissipated within the lattice. The spin lattice relaxation is characterized by a relaxation time T_{1e} , which is the time for the spin system to lose $1/e^{\text{th}}$ of its excess energy. To maintain the population difference of the spin states the rapid dissipation of energy (short T_{1e}) is essential. Hence slow spin-lattice relaxation is occurred in systems containing free radicals, especially at low temperatures. This will cause saturation of the spin system thereby population difference of the upper and lower spin states approaches zero, and EPR signal ceases.

b) Spin-spin relaxation

Spin-spin relaxation is also called Cross relaxation, by which energy exchange happens between electrons in a higher energy spin state and nearby electrons or magnetic nuclei in a lower energy state, without transferring to the lattice. The spin–spin relaxation can be characterized by spin-spin relaxation time T_{2e} .

3.7 Width of the spectral line

When both spin–spin and spin–lattice relaxations contribute to the EPR signal, the resonance line width (ΔB) can be written as

$$\Delta B \propto \frac{1}{T_{1e}} + \frac{1}{T_{2e}} \text{-----} (8)$$

From the equation, it is clear that when $T_{1e} > T_{2e}$, ΔB depends primarily on spin–spin interactions. Decreasing the spin-spin distance, which is the spin concentration, T_{1e} will become very short, approximately below 10^{-7} sec, thus the spin-lattice relaxation will have a larger influence on the line width than spin-spin relaxation. In some cases, the EPR lines are broadened beyond detection. When a spin system is weakly coupled to the lattice, the system tends to have a long T_{1e} and electrons do not have time to return to the ground state, as a result the population difference of the two levels tends to approach zero and the intensity of the EPR signal decreases. This effect, known as saturation, can be avoided by exposing the sample to low intensity microwave radiation. Systems with shorter T_{1e} are more difficult to saturate.

3.8 ESR absorption positions (The g factor)

Equation 4 shows that an ESR absorption will occur at a frequency $\gamma = \Delta E/h$ Hz. Thus the position of an ESR absorption may be expressed in terms of absorption frequency ie, absorption position, which varies with applied field B.

The different ESR spectrometers operate at different magnetic fields, hence it is desirable to express ESR absorption position in the same form ie, independent of the field strength. Thus the absorption positions are more consequently in terms of the observed g values. From equation 4

$$\text{we get } g = \frac{\Delta E}{\mu_B B} = \frac{h\gamma}{\mu_B B} \text{-----} (9)$$

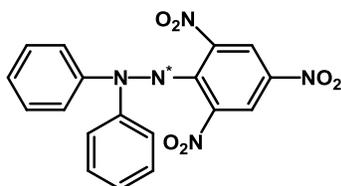
$$\text{(for free electron } \mu_B = 9.273 \times 10^{-24} \text{ JT}^{-1}\text{)}$$

For example ESR absorption was observed at 8388.255 MHz in a field of 0.30 T. the ESR

$$\text{absorption position appears at a } g = \frac{6.626 \times 10^{-34} \times 8388.255 \times 10^6}{9.273 \times 10^{-24} \times 0.30}$$

$$\begin{aligned}
 &= \frac{6.626 \times 10^{-4} \times 8388.255}{9.273 \times 0.30} = 19979.35 \times 10^{-4} \\
 &= 1.9979 \\
 &\approx 2.00.
 \end{aligned}$$

For measuring the g values of free radicals it is convenient to measure the field separation between the center of the spectrum of the unknown sample and that of a reference substance whose g value is accurately known. The most widely used reference is 1,1-diphenyl-2-picrylhydrazyl free radical (DPPH) which is completely in free radical state and its g value is 2.0036. The reference substance is placed along with the unknown sample in the same dual resonant cavity.



Two signals will be observed simultaneously with a field separation of ΔB . The g factor for unknown sample is given by

$$g = g_{ref} \left(1 - \frac{\Delta H_0}{H} \right)$$

Where g_{ref} is the g factor for the reference and H is the resonance frequency. ΔH_0 is positive if the unknown sample has its center at a higher field than the reference sample. For a free electron, the proportionality factor is 2.00232. For organic radicals, the value is typically quite close to that of a free electron with values ranging from 1.99 - 2.01. For transition metal compounds, large variations can occur due to spin-orbit coupling and zero-field splitting and results in values ranging from 1.4-3.0.

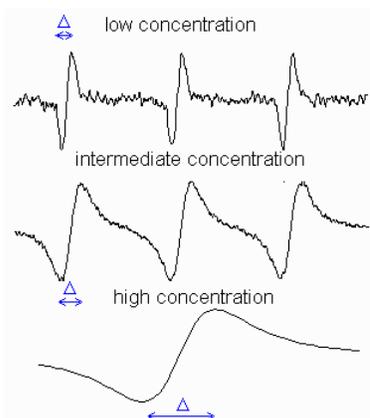


Figure 3: Effect of solvent concentration on line width ESR spectrum

The EPR signal shape varies with concentration of the sample (intensities were scaled to the same height). The line widths of the resonant transitions are not infinitely small and can be altered by the environment. At low concentrations of the sample, each line has a width because of the heterogeneous broadening

Problem 1: Calculate the ESR frequency of an unpaired electron in a magnetic field of 3000 G.

Solution:

$$\text{We know that } \Delta E = h\gamma = g\mu_B B_0$$

$$\therefore \gamma = g\mu_B B_0 / h \text{ Hz}$$

For free electron $g = 2.00$ and $\mu_B = 9.73 \times 10^{-24} \text{ JT}^{-1}$.

$h = 6.626 \times 10^{-34} \text{ Js}$ (Plank's constant)

Given $B_0 = 3000 \text{ G} = 0.3 \text{ T}$

Substituting all values in above equation, then we get

$$\begin{aligned} \gamma &= \frac{2.00 \times 9.73 \times 10^{-24} \times 0.30}{6.626 \times 10^{-34}} \\ &= 8.397 \times 10^9 \text{ Hz} \\ &= 8397 \text{ MHz or} \\ &= 8.397 \text{ kHz} \end{aligned}$$

Problem 2: Calculate the g value if the methyl radical shows ESR signal at 3290G in a spectrometer operating at 9230MHz

$$\text{We know that } \Delta E = h\gamma = g\mu_B B_0$$

$$\therefore g = h\gamma / \mu_B B_0$$

For free electron $\mu_B = 9.73 \times 10^{-24} \text{ JT}^{-1}$.

$h = 6.626 \times 10^{-34} \text{ Js}$ (Plank's constant)

Given $B_0 = 3290 \text{ G} = 0.3290 \text{ T}$

$\gamma = 9230 \text{ MHz} = 9.230 \times 10^9 \text{ Hz}$

Substituting all values in above equation, then we get

$$\begin{aligned} g &= \frac{6.626 \times 10^{-34} \times 9.230 \times 10^9}{9.73 \times 10^{-24} \times 0.3290} \\ g &= 2.00461 \end{aligned}$$

3.9 Multiplet structures in ESR spectroscopy

There are two types of multiplet structure in ESR spectroscopy they are i) Fine and ii) Hyper fine splitting.

a) *Fine structure*

It occurs only in crystals containing more than one unpaired electronic spins. Suppose the crystal which contains molecules or ions with two parallel rather than unpaired electron spins. In this case there would be a total spin of 1 ie, $S=1$ and $2S+1=3$ thus it is a triplet state. Molecular triplet states are generally unstable and they revert to ground state with paired spins. However by cooling the crystal to low temperature the triplet state is maintained and examined by ESR spectroscopy and these parallel spin are not interact with each other and give two fine-structure lines.

For example; when naphthalene is irradiated with UV light its individual molecule undergo triplet excited state which revert quite rapidly to the ground state with paired spin. However by cooling the sample to low temperature triplet state can be maintained and the ESR spectrum of naphthalene recorded in its triplet excited state consist of two fine-structure lines. Similarly transition metal ions are quite stable in their triplet states and can be easily studied by ESR spectroscopy at room temperature.

In general if there are 'n' number parallel electrons spins present in a molecule there will be 'n' equally spaced resonance lines in the ESR spectrum.

a) *Spin-spin Splitting (Hyperfine Splitting)*

Hyperfine structure is resulting from the coupling of unpaired electronic spin with neighboring nuclear spins.

In addition to the applied magnetic field, unpaired electrons are also sensitive to their local environments. Frequently the nuclei of the atoms in a molecule or complex have a magnetic moment, which produces a local magnetic field at the electron. The interaction between an unpaired electron and nuclei with non zero nuclear spin is called the *hyperfine interaction*. This leads to splitting of the ESR line in to multiplet structures and is called as *hyperfine structure or hyperfine spectrum*

When an unpaired electronic spin couples with a nucleus with spin I then absorption signals of the electron is split in to a multiplet with $2I+1$ lines of equal intensity. In general if unpaired electron couples with n number of nucleus with equal spin I then the number of lines given by

ESR spectra is equal to $(2nI + 1)$. In other word if unpaired electron couples with n number of nucleus with spin I_a and m number of nucleus with spin I_b , then the overall pattern is determined by first applying the coupling to the nearest nuclei, then splitting each of those lines by the coupling to the next nearest nuclei ie, the number of lines given by ESR spectra is equal to $(2nI_a + 1)(2mI_b + 1)$ and so on.. Since there are multiple nuclei interacting, the relative intensities of the lines follow the binomial distribution shown below.

# of Equivalent Nuclei	Relative Intensities
1	1:1
2	1:2:1
3	1:3:3:1
4	1:4:6:4:1
5	1:5:10:10:5:1
6	1:6:15:20:15:6:1

For example a hydrogen atom contains one proton and one electron. There are two energy level for a free electron in an applied field as shown in figure 2a with $M_s = -\frac{1}{2}$ aligned with field and $M_s = +\frac{1}{2}$ aligned opposing the field. Thus the ESR spectrum of a free electron would give single peak corresponding to transition between these energy levels. But each of the two energy levels of the electron in hydrogen atom is split in to two energy levels by interacting with the nuclear spins of proton $m_I = \pm\frac{1}{2}$, and four different energy levels are obtained as shown in figure 2b. Therefore ESR spectrum of hydrogen atom consists of two lines corresponding to two transitions shown by two arrows in figure 2b. The two peaks are of equal intensity because the probability of orientations of the nuclear spin of hydrogen atom causing different energy levels is equal.

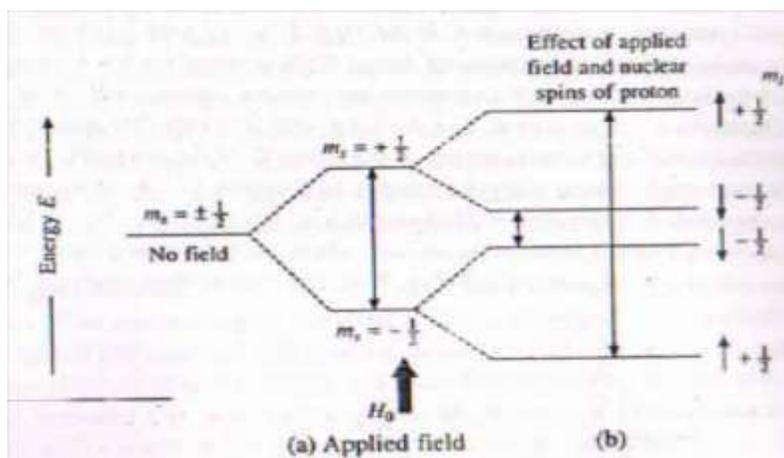
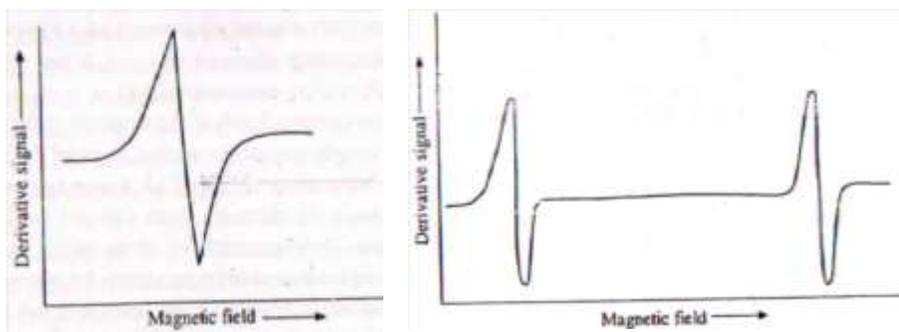


Figure 4: Hyper spin splitting of an electron in Hydrogen atom the influence of applied magnetic filed



Similarly, in the case of methyl radical, there are 3 hydrogen atoms are present. Therefore each of the two energy levels of the single unpaired electron on the carbon atom is coupled with nuclear spin of 3 hydrogen atoms. The number of peaks in the ESR signal of methyl radical is split into four energy levels according to the formula $2nI + 1$ ie, $(2 \times 3 \times \frac{1}{2}) + 1 = 4$ peaks. (m_I for a single hydrogen nucleus is $\pm\frac{1}{2}$ and that for the three hydrogen nuclei $\pm 3 \times \frac{1}{2} = \pm\frac{3}{2}$). The observed relative intensities of the component peaks are in the ratio 1:3:3:1.

The EPR spectrum of the radical anion of benzene, $[C_6H_6]^-$ in which the electron is delocalized over all six carbon atoms and therefore exhibits coupling to six equivalent hydrogen atoms. As a result, the EPR spectrum shows $[(2 \times 6 \times \frac{1}{2}) + 1 = 7]$ seven lines with relative intensities of 1:6:15:20:15:6:1.



Figure 5: EPR Spectrum of benzene radical anion

The ESR spectrum of radical anion of pyrazine is little complex. In this case electron is delocalized over the six atoms with two different nuclear spins (ie, 4 carbon atoms and 2 nitrogen atoms). First electron coupling to two equivalent nitrogen $\{^{14}N (I = 1)\}$ nuclei gives a quintet $[(2 \times 2 \times 1) + 1 = 5]$ with the relative intensities of 1:2:3:2:1 which are further split into quintets with relative intensities of 1:4:6:4:1 by coupling to four equivalent hydrogen.

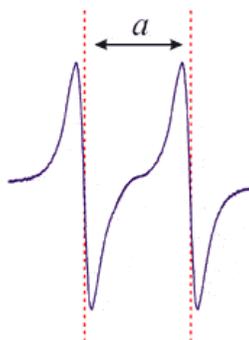


Figure 6: EPR Spectrum of pyrazine radical anion

Hyperfine interactions can be used to provide a great deal of information about the sample including information about the number and identity of nuclei in a complex as well as their distance from the unpaired electron.

3.10 The Hyperfine Coupling Constant

The hyperfine coupling constant 'a' is directly related to the distance between peaks in a spectrum and its magnitude indicates the extent of delocalization of the unpaired electron over the molecule.



This constant is calculated using following equation. The total energy related to electron transitions in EPR.

$$\Delta E = g\mu_e M_s B + \sum_i g N_i \mu N_i M_i (1 - \sigma_i) + \sum_i a_i M_s M_i \text{ ----- (13)}$$

The first two terms correspond to the Zeeman energy of the electron and the nucleus of the system, respectively. The third term is the hyperfine coupling between the electron and nucleus where a_i is the hyperfine coupling constant. Figure 7 shows splitting between energy levels and their dependence on magnetic field strength. In this figure, there are two resonances where frequency equals energy level splitting at magnetic field strengths of B_1 and B_2 .

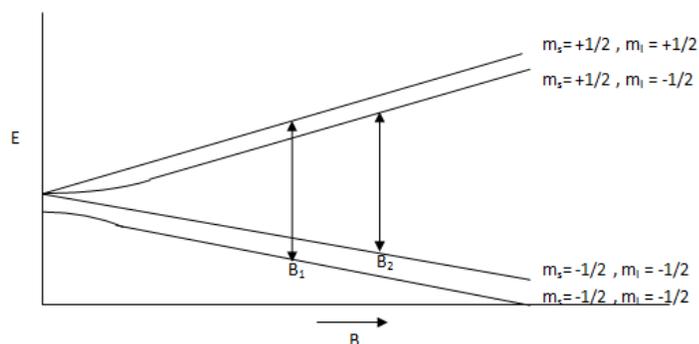


Figure 8: Splitting between energy levels and their dependence on magnetic field strength

The below parameters are essential in the derivation of the hyperfine coupling constant. By manipulating the total energy equation the following two relations may be derived.

$$B_1 = hv - a/2g\mu_e$$

$$B_2 = hv + a/2g\mu_e$$

From this, the hyperfine coupling constant 'a' may be derived where g is the g-factor.

$$\Delta B = B_2 - B_1 = hv + a/2g\mu_e - hv - a/2g\mu_e$$

$$a = g\mu_e \Delta B \text{ ----- (14)}$$

The EPR spectra of paramagnetic compounds can provide useful information. Analysis of the coupling patterns can provide information about the number and type of nuclei coupled to the electrons. The magnitude of *a* can indicate the extent to which the unpaired electrons are delocalized and *g*-factors can show whether unpaired electrons are based on transition metal atoms or on the adjacent ligands.

3.11 Isotropic and Anisotropic Interactions

Electron-nuclei interactions have several mechanisms, the most prevalent being Fermi contact interaction and dipole interaction. Dipole interactions occur between the magnetic moments of the nucleus and electron as an electron moves around a nucleus. However, as an electron approaches a nucleus, it has a magnetic moment associated with it. As this magnetic moment moves very close to the nucleus, the magnetic field associated with that nucleus is no longer entirely dipolar. The resulting interaction of these magnetic moments while the electron and nucleus are in contact is radically different from the dipolar interaction of the electron when it is outside the nucleus. This non-dipolar interaction of a nucleus and electron spin in contact is the Fermi contact interaction. A comparison of this is shown in Figure 9. The sum of these interactions is the overall hyperfine coupling of the system.

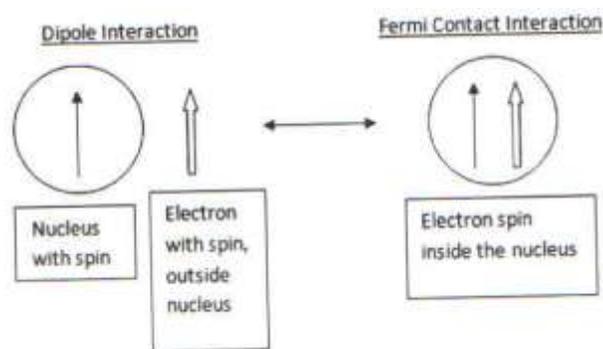


Figure 9: Different electron-nuclei interactions resulting in hyperfine coupling

Fermi contact interactions predominate with isotropic interactions, meaning sample orientation to the magnetic field does not affect the interaction. Due to the fact that this interaction only occurs when the electron is inside the nucleus, only electrons in the s orbital exhibit this kind of interaction. All other orbital (p,d,f) contain a node at the nucleus and can never have an electron at that node. The hyperfine coupling constant in isotropic interactions is denoted 'a'.

Dipole interactions predominate with anisotropic interactions, meaning sample orientation does change the interaction. These interactions depend on the distance between the electron and nuclei as well as the orbital shape. The typical scheme is shown in Figure 10. Dipole interactions can allow for positioning paramagnetic species in solid lattices. The hyperfine coupling constant in isotropic interactions is denoted 'B'

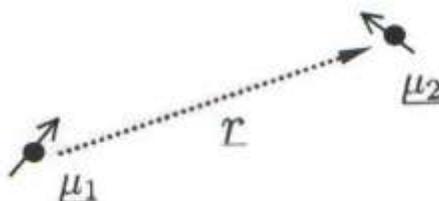


Figure10: Interaction between two dipoles with radius 'r'

3.12 Superhyperfine Splitting

Further splitting may occur by the unpaired electron if the electron is subject to the influence of multiple sets of equivalent nuclei. This splitting is on the order of $2nI+1$ and is known as superhyperfine splitting. The hyperfine structure splits fine structure into smaller components, the superhyperfine structure further splits these hyperfine structure. As a result, these interactions are extremely small but are useful as they can be used as direct evidence for covalency. The more covalent character a molecule exhibits, the more apparent its hyperfine splitting.

For example, in a CH_2OH radical, an EPR spectrum would show a triplet of doublets. The triplet would arise from the three protons, but superhyperfine splitting would cause these to split further into doublets. This is due to the unpaired electron moving to the different nuclei but spending a different length of time on each equivalent proton. In the methanol radical example, the electron lingers the most on the CH_2 protons but does move occasionally to the OH proton.

3.13 Spin-orbit interaction

The energy levels of atomic electrons are affected by the interaction between the electron spin magnetic moment and the orbital angular momenta of the electron. It can be visualized as a

magnetic field caused by the electron's orbital motion interacting with the spin magnetic moment. This effective magnetic field can be expressed in terms of the electron orbital angular momentum. The spin-orbit interaction is also a magnetic interaction, but with the magnetic field generated by the orbital motion of an electron within the atom itself. It has been described as an "internal Zeeman effect". H_L represents spin-orbit coupling and may be expressed in the simpler form.

$$H_{LS} = \lambda_{LS} L \cdot S \quad (15)$$

Here L and S are the orbital and spin angular momenta of the free ion values and H is the spin-orbit coupling constant of the ion. The magnitude of this interaction is generally between 10^2 and 10^3 cm^{-1} .

3.14 Effect of spin orbit coupling

When the unpaired electron is placed in a chemical environment or in a transition metal complex, the "g" value does not agree with the expected value. It is explained as follows: The chemical environment or the crystal field strongly perturbs the orbital motion of the electron. Therefore, the orbital degeneracy if any is partly removed or quenched. On the other hand, the spin – orbit coupling tends to sustain certain amount of orbital degeneracy. ie, complete removal of orbital degeneracy is prevented by spin – orbit coupling but higher fold degeneracies are often decreased by this effect. This sustaining effect implies that if an electron has orbital angular momentum, this is maintained by coupling to the spin angular momentum and if it has a 7spin angular momentum this tends to generate orbital angular momentum. Because of this quenching and sustaining competition, the orbital degeneracy is partly but not completely removed and a net orbital magnetic moment results. Hence, g-value is different from 2.0023, which would be expected if the orbital degeneracy were completely removed.

3.15 Crystal field effect

The relative magnitudes of crystal field and spin– orbit coupling determine the properties of the transition metals to a large extent. These two have opposite effects on the orbital degeneracy, crystal field tries to remove while the spin– orbit coupling prevents the removal of orbital degeneracy. Three cases can be distinguished

- (i) Spin–orbit coupling is very much greater than the crystal field.
- (ii) Effect of crystal field is strong enough to break the coupling between L and S
- (iii) Effect of crystal field is very large so that L - S coupling is broken down completely.

3.16 Let summerrize the unit

Electron Paramagnetic Resonance (EPR), also recognized as Electron Spin Resonance (ESR) and Electron Magnetic Resonance (EMR), is a branch of spectroscopy which involves the process of resonant absorption of microwave radiation by paramagnetic ions or molecules containing one or more unpaired electrons (i.e. $S > 0$) in the presence of a static magnetic field. It is discovered by Zavoisky in 1945 and became a powerful technique, applicable to systems with a net electron spin angular momentum. EPR has developed into a potent, multipurpose, non-destructive and non-intrusive analytical method. EPR can provide valuable information on structural and dynamical aspects, even from current chemical and/or physical processes without influencing the process itself. Therefore, EPR is considered as an ideal complementary technique for other methods in a wide range of studies in the areas of Chemistry, Biology, Medicine and Physics.

EPR spectroscopy provides an experimental route to study the magnetic interactions in paramagnetic materials. High sensitivity and the ability to investigate low concentrations of paramagnetic ions in powders, polymers, and frozen solutions are key advantages of EPR spectroscopy. Additional techniques employing both EPR and NMR method (for example, ENDOR-electron nuclear double resonance) are available and extend the scope of such investigations. EPR spectroscopy can be combined with chemical techniques such as spin trapping to detect and follow free radical reactions in biological systems, etc.

3. 17 Key words

Electron Resonance Spectroscopy, Spin relaxation, Spin-orbit interaction, Spin-lattice interaction, Splitting pattern, coupling constant, Hyperfine spitting,

3. 18 References for further study

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3.19 Question for self study

1. Why microwaves are necessary to study the electron spin resonances?
2. What is the g-factor? What does it mean if the value is 2?
3. Explain the basic principle of ESR spectroscopy.
4. Write a note on a) Spin Relaxation Mechanisms b) Spin-lattice relaxation c) Spin-spin relaxation.
5. Explain the significance of hyperfine interaction.
6. Write a note on a) Isotropic and Anisotropic Interactions b) Superhyperfine Splitting c) Spin-orbit interaction.
7. Define Effect of spin orbit coupling and Crystal field effect.
8. Describe width and position of spectral line in ESR spectra.

UNIT 4**Structure**

- 4.0 Objectives of the unit
- 4.1 Introduction
- 4.2 Zero-field splitting
- 4.3 Magnetoanisotropy and Dipole-dipole interactions
- 4.4 Kramer's degeneracy
- 4.5 Experimental apparatus
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 - c) ESR spectra of 1,4-Benzosemiquinone radical atom:
 - d) Naphthalene negative ion:
 - e) Anthracene negative ion:
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- 4.6 Applications of ESR spectroscopy:
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 - iv) Spin labels
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- 4.7 ESR in molecular biotechnology:
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4.0 Objectives of the unit

After studying this unit you are able to

- Describe the Zero-field splitting
- Understand the magnetoanisotropy and Dipole-dipole interactions
- Explain the Kramer's degeneracy
- Understand the experimental apparatus and Instrumentation of ESR spectroscopy
- Interpret the ESR spectra
- Understand the application of EPR spectra

4.1 Introduction

Professor Hendrik Anthony Kramers' has given the names Kramers' doublets, Kramers' degeneracy and Kramers' centers. Kramers' theorem is a keystone to EPR. Kramers' theorem states that a purely electrostatic field can never reduce the degeneracy of the system, if it has an odd number of electrons. Such degeneracy as remains (generally two-fold) can be lifted only by an external magnetic field. He showed that a system containing an odd number of electrons, for example, $S = 1/2, 3/2, 5/2$ etc., even with no symmetry, and with no magnetic field, must be at least doubly degenerate. A non-Kramers' center will have $S = 1, 2, 3$, etc. A corollary of this is that systems with odd numbers of electrons will relax differently from one with even numbers of electrons.

Another concerned theorem is the Jahn-Teller Theorem. It was published in 1937 and states: "any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy". This is the most fascinating phenomenon in transition metal chemistry in general and EPR in particular, providing a general approach to understanding the properties of molecules and crystals and their origins. The chief applications of this theorem in transition-metal chemistry are in connection with octahedrally coordinated metal ions with high-spin d^4 , low-spin d^7 , and d^9 configurations in each of these cases the t_{2g} orbitals are all equally occupied (either all half filled or completely filled) and there is a single electron or a single vacancy in the e_g orbitals. Either an e_g or an e_g^3 configuration gives rise to a doubly degenerate (E) ground state, and thus a distortion of the octahedron is expected. In other words, high spin d^4 , low-spin d^7 , and d^9 ions should be found in distorted, not regular, octahedral environments. It is to be noted here

that Jahn-Teller theorem does not predict the direction and amount of distortion. It only predicts about the possibility of distortion from octahedral symmetry.

4.2 Zero-field splitting (zfs)

Zero-field splitting (zfs) is the removal of spin microstate degeneracy for systems with $S > 1/2$ in the absence of an applied magnetic field. i.e., the degeneracy is removed as a consequence of molecular electronic structure and/or spin density distribution. Zero-field splitting causes magnetic anisotropy, and has profound effects on magnetic *properties*.

4.3 Magnetoanisotropy and Dipole-dipole interactions

Magnetoanisotropy is referred as the non-uniform distribution of magnetic properties in three dimensional spaces. For two electrons *i.e.*, two magnetic dipoles in two orbitals of different energies, the six microstates arise and they are

- 1 closed shell singlet with both electrons in the lower energy orbital
- 1 open shell singlet with an electron in each orbital
- 3 belonging to the triplet with an electron in each orbital
- 1 closed shell singlet with both electrons in the higher energy orbital

For all three possible singlet states, it is (obviously) not possible to split the microstate. For the triplet state, $S = 1$ and $M_S = +1, 0, -1$. In the absence of an applied field, these microstates should be *degenerate*, and this is strictly true if the two unpaired electrons are distributed in a *spherical geometry*. i.e. If there is no direction in which the electrons can “move” in order to minimize the repulsive dipole-dipole interactions, the three microstates remain at the same energy. If, however, the molecular orbitals are not spherically distributed, a ZFS can arise such that the degeneracy of these microstates is lifted due to the geometry of the molecule (figure 1).

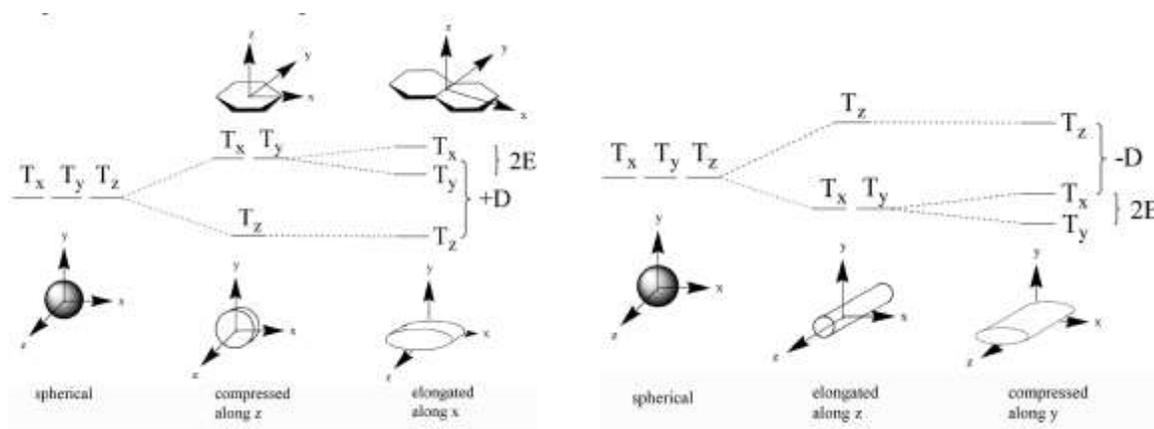


Figure 1: Splitting of T^3 ground state ZFS into D and E.

The ZFS of the microstates arising from the 3T ground state is commonly described by the ZFS parameters D and E .

- D and E are clearly energy terms describing the extent of ZFS splitting in the “axial and “equatorial” (or “rhombic”) directions respectively.
- D is (+)ve for an oblate spin distribution, i.e., a flattening in one direction or compression long one axis
- ΔD is (-)ve for a prolate spin distribution, i.e., an elongation in one direction or lengthening of one axis
- $\Delta E = 0$ for a triplet species with:
 - a) 3-fold or higher symmetry and
 - b) axial symmetry

EPR is the technique most used to determine D and E .

4.4 Kramer's degeneracy

In the absence of spin-orbit interactions the ground state of any system with time reversal invariance and an odd number of electrons is degenerate because the spin direction is arbitrary. However in this case electrons with up and down spin can be considered independently. Therefore the energy level of a system containing an odd number of spin $-1/2$ particles (electrons) is at least double degenerate in the presence of pure electric field (or in the absence of an external field). *This degeneracy is known as Karmer's degeneracy.* This degeneracy is due to the time reversal invariance and charge conjugation. The Karmer's degeneracy is removed by placing the system in an external magnetic field if, by applying magnetic field.

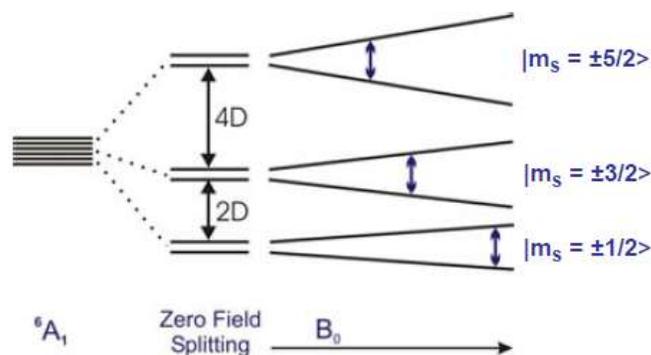


Figure2: The $S = 5/2$ multiplet forms three Kramer's doublets that are separated from the others by energies significantly larger than the $\approx 0.3\text{-cm}^{-1}$ microwave quantum (X-band).

The ESR spectra are most commonly recorded by varying the strength of applied magnetic field B_0 and keeping the frequency constant. However it can also be done by varying the frequency and keeping B_0 constant.

4.5 Experimental apparatus

The ESR spectrometer consists of the following components,

- 1) Microwave source,
- 2) A resonant cavity,
- 3) A magnet and power supply with field control and field sweep,
- 4) The modulation and detection systems.

Monochromatic coherent microwaves are generated by the klystron tube and the desired frequency level of MW is adjusted using the attenuator. The circulator directs the microwaves to the cavity where the sample is mounted. The cavity was placed between two electromagnets, which generate wide range of magnetic field B_0 . The magnitude of B_0 is changed by varying electromagnet current. *Continuous wave EPR* spectra are recorded by putting a sample into a MW irradiation field of constant frequency ν and sweeping the external magnetic field B_0 until the resonance condition is fulfilled. At resonance, a portion of the microwaves are absorbed by a sample. The microwaves are reflected back from the cavity and detected by a diode detector. The diode is mounted to lie in the direction of the electric vector of the microwaves and generates a direct current proportional to the microwave power reflected from the cavity. In principle the absorption of microwaves by the sample could be detected by the decrease in current. The detected diode current is then amplified using a frequency sensitive amplifier by eliminating much of the noise. The detected ac signal is the change in sample absorption and so what is observed is the first derivative of the absorption curve. Most commonly, EPR spectra are run at one of two fixed frequencies with associated field strength:

X-Band 0.33T / 9GHz

Q-Band 1.4 T / 32GHZ

Instrumentation:

In the ESR spectra the transitions occur at frequencies in the microwave region, thus the instrumentation for the ESR require microwave source. The schematic diagram of an ESR spectrometer is shown in figure 2. The description of various components of the instrument is given as follows.

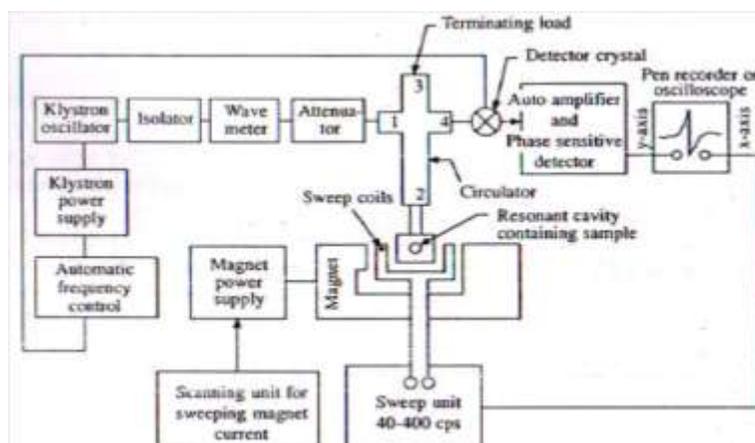


Figure 2: Schematic diagram of an ESR spectrometer

g) Source of the Microwave radiation:

It consists of following items

- a) *Klystron valve* is a powerful source of radiation of a small frequency range. For free radical studies, klystron is normally operated in the microwave region of 3cm wavelength. The frequency of the monochromatic radiation is determined by the voltage applied to klystron. A klystron oscillator is generally operated at 950MHz.
- b) *Isolator* is a strip of ferrite material. It minimizes variations in the frequency of microwaves produced by klystron. The variations in frequency are caused by the backward reflections in the regions between the klystron and the circulator.
- c) *Wave meter* is put in-between the wave meter and attenuator to know the frequency of microwaves produced by the klystron. The wave meter is usually calibrated in frequency units (MHz) instead of wavelength.
- d) *Attenuator* is put in-between the wave meter and circulator. It has absorption of element and corresponds to neutral filter in light absorption measurements. It adjusts the level of the microwave power incident upon the sample.

ii) Circulator or Magic-T

From the attenuator, the microwave radiations enter the microwave circulator (bridge). Figure 3 indicates the operation of a four-port circulator which works as a balanced bridge with all advantages of null method in electrical circuits. The microwave radiations enter arm 1 and arm 2 is attached to resonant cavity which contains the sample. Arm 3, which has a balancing load, absorbs any power reflected from the detector arm 4 which is connected to the detector. The

microwave circulator does not allow the microwave power to pass in a straight line from one arm to the opposite arm.

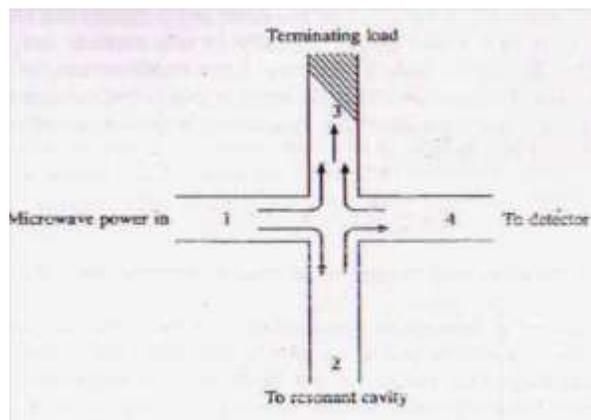


Figure 3: A four-port microwave circulator showing the direction of microwave transmission among the four arms.

iii) *Resonant cavity:*

The resonant cavity is considered as the heart of an ESR spectrometer because it contains the sample. In the cavity system the applied magnetic field can be minimized along the sample dimension and also maximum microwave power can be introduced to the sample. The sample may be introduced in the form of a single crystal, solid powder, liquid or solution in a tube of about 5mm diameter. For studying anisotropic effects in single crystals and solid samples, rotatable sample cavities are generally used. In most of the ESR spectrometers dual resonant cavities are used for the simultaneous observation of a sample and a reference material. By using a reference material the sources of error are compensated by comparing relative signal heights.

iv) *Magnet system:*

ESR spectrometer consists of an electromagnet placed around each side of the resonant cavity and provides a homogeneous magnetic field. An electromagnet which is capable of producing a steady field from 50 to 5500 gauss is essential to studying the sample whose 'g' factor ranges from 1.5 to 6. The strength of the magnetic field can be varied (swept) over a small range (zero to 500 gauss) by varying the current in a pair of sweep coils. The resonant cavity is placed between the pole pieces of the electromagnet. The magnetic field should be uniform and stable over the volume of the sample. The stability of the field is maintained by energizing the magnet with a highly regulated power supply.

v) *Crystal detector:*

The most of the commonly used detector is a semiconducting silicon-tungsten crystal which acts as a microwave rectifier and converts the microwave power in to a direct current output.

iv) *Auto amplifier and phase sensitive detector:*

The signal in the form of direct current received from the detector undergoes narrow band amplification by the operation of the auto amplifier. This amplified signal contains a lot of noise and reduced by using phase sensitive detector, which reject the all noise components except those in a very narrow band.

vii) *Recorder:*

The signal from the phase sensitive detector and sweep unit is recorded by an oscilloscope or a pen recorder.

Working of an ESR spectrometer:

The sample whose ESR spectrum is to be recorded is placed in the resonant cavity. The cavity serves as a very long path length cell in which the waves are reflected to-and-fro for thousands of times. The microwave produced by the klystron oscillator is passes through the oscillator wave meter and attenuator and they are received by the circulator through arm 1. The microwave power entering to arm 1 is divided between arm 2 and arm 3. Generally arm 3 has balancing load, if the impendence arm 2 and arm 3 are same, then circulator (bridge) is balanced and no power will be received by the crystal detector through arm 4. If the impendence of arm 2 changes due to some ESR absorption by a sample, then bridge becomes unbalanced and some microwave power will enter in to the crystal detector through arm 4. The detector acts as a rectifier and converts the microwave power in to direct current. If the strength of the magnetic field around the resonant cavity containing the sample is changed to the value required for resonance, then the recorder will shows an absorption curve, ie, an absorption ESR spectrum and the absorption curve is obtained by plotting intensity against the strength of the magnetic field and has no fine structure. When the main field is swept slowly over a period of several minutes, the recorder will show the first derivative of the absorption curves plotted against the strength of the magnetic field. Because of instrumental considerations associated with the signal-to-noise ratio ESR spectra are generally recorded as first derivative spectra.

For low-frequency modulation (400 Hz or less) the coils can be maintained outside the cavity and even on the magnet pole pieces. Since higher modulation frequencies cannot penetrate metal

effectively, the modulation coils must be mounted inside the sample cavity in case of higher-frequency modulation.

Sample handling:

As already mentioned the sample may be in the form of a single crystal, solid powder, solution or frozen solutions and is usually contained in a tube of about 5mm diameter. A sample volume of 0.15 to 0.5 ml can be used for sample which does not have a high dielectric constant. For a sample with high dielectric constant, flat cells with a thickness of 0.25 mm and sample volume of 0.05ml are generally used.

Water, alcohol and other solvents with high dielectric constant are not generally used in ESR studies because they strongly absorb microwave power. However where there is no alternative choice of solvent other than water, alcohol and other high dielectric constant solvents.

When a sample is used in the form of a frozen solution, the best results are obtained if the solvent freezes to form a glass. It is observed that symmetrical molecules do not form good glass, eg, methyl cyclohexane forms good glass while cyclohexane does not.

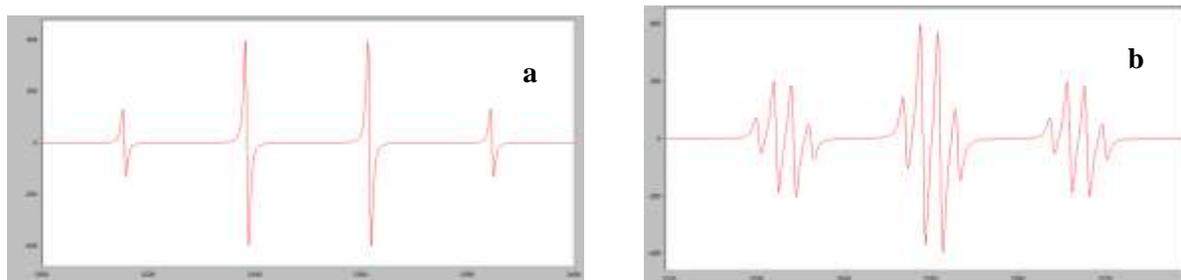


Figure 4: a) Simulated EPR spectrum of the $\bullet\text{CH}_3$ radical. b) Simulated EPR spectrum of the $\text{H}_2\text{C}\cdot\text{O}-\text{CH}_3$ radical.

a) ESR spectra of 1,4-Benzosemiquinone radical atom:

1,4-Benzosemiquinone radical anion has one unpaired electron having $S = \pm\frac{1}{2}$. This electron interacting with four equivalent proton with spin $m_I = +2, 1, 0, -1, -2$. The ESR spectrum consists of a quintet, ie, five equally spaced lines as shown in figure with 1: 4: 6: 4: 1.

b) Naphthalene negative ion:

In this case there are two sets (α and β) of four equivalent protons each. The ESR spectrum would thus shows $(4 + 1) \times (4 + 1) = 25$ lines.

c) Anthracene negative ion:

In this case there are three sets of equivalent protons, ie, four equivalent sets of α and β protons and two equivalent sets of γ protons. The ESR spectrum consist of $(4 + 1)(4 + 1)(2 + 1) = 75$ lines.

d) Triphenylmetyl radical:

It has three sets of equivalent protons. Sets of α and β consist of six equivalent protons each and a set of γ consist of three equivalent protons. The ESR spectrum consists of $(6 + 1) (6 + 1)(3 + 1) = 196$ lines.

In general the ESR spectrum of a system where the unpaired electron interacts with n equivalent protons contains n + 1 lines and their relative intensities are given by pascal's triangle.

4.6 Applications of ESR spectroscopy

All application of ESR is based on three aspects, which are,

1. Study of free radicals,
2. Investigation of molecules in the triple state, and
3. Study of inorganic compounds.

vii) Study of free radicals

Even in very low concentration of sample ESR can study via free radicals. It is also applied in determination of structure of organic and inorganic free radicals. The intensity of ESR signal is directly proportional to the number of free radicals present. Hence using ESR we can measure relative concentration of free radicals.

viii) Investigation of molecules in the triple state

A triple state molecule has a total spin $S=1$ so that, its multiplicity can be given as $2S+1=3$. While free radicals with $S= \frac{1}{2}$ has an odd number of unpaired electrons. A triple state molecule has an even number of electrons and two of them unpaired. Therefore in triple state molecule the unpaired electrons must interact whereas in diradical, the unpaired electrons do not interact because they are a great distance apart.

ix) Study of inorganic compounds

ESR is very successful in the study of inorganic compounds and it can be used to study for knowing the exact structures of solvated metal ions. ESR is also used in the study of catalysts and the determination of oxidation state of metal. eg. Copper is found to be divalent in copper protein complexes whereas it is found to be mono valent in some biologically active copper complexes. The information of unpaired electrons is very useful in various aspects in

applications of ESR. Like, Spin labels, Structural determination, and Reaction velocities and reaction mechanisms.

x) **Spin labels**

Groups with unpaired electron can be attracted to macromolecules such as protein and membranes to obtain a great deal of information about their structure. The *nitroxide molecules* bound to macromolecules are called spin labels. These spin labels are stable molecules that possess an unpaired 2p electron. A commonly used **TEMPOL** (2,2,6,6-tetramethyl piperidinol-n-oxyl). The hyperfine structure of an ESR spectrum is a kind of fingerprint that helps to identify the free radicals present in the sample. Spin labels give very useful information about the molecules to which they are bound. Also, we can get information like, the rate of motion of macromolecules to which they are bound or the amount of thermal motion in a membrane in which they have been inserted. The spin label can give information about the polarity of its environments.

xi) **Structural determination**

The ESR technique cannot be applied to determine molecular structure because the information obtained from the hyperfine structure is mostly about the extent of delocalization and Fermi contact interaction. It does not tell us about the arrangement of the atoms in the molecule although the symmetry of the molecule can be sometimes deduced from the sets of equivalent nuclei. In certain cases ESR is able to provide useful information about the shape of the radicals.

xii) **Reaction velocities and reaction mechanisms**

A large number of organic reactions are known which proceed by a radical mechanism. Most of the radicals formed during organic reaction are not stable but are very reactive. The ESR spectroscopy can be used to study very rapid electron exchange reactions.

xiii) **Analytical applications**

Mn^{+2} ions can be measured and detected even when present in trace quantities. The method is very rapid and can be measured in aqueous solution over the range from 10^{-6} M to 0.1M. ESR method has proved to be a rapid and convenient method for determination of Vanadium in petroleum products. ESR can also be used to estimate Cu(II), Cr(II), Gadolinium(III), Fe(III) and Ti(III). The ESR spectroscopy has been used to estimate polynuclear hydrocarbons, which are first, converted into radical cations and then absorbed in the surface of an activated silica-alumina catalyst.

xiv) Biological systems

ESR technique is used to study the variety of biological system such as, leaves, seeds, and tissue preparation, it is found that a definite, correlation exists between the concentration of *free radicals* and the metabolic activity of the plant material. ESR has studied the presence of *free radicals* in healthy and diseased tissues. Most of the oxidative enzymes function via one electron redox reaction involving the production of either enzyme bound *free radicals* or by a change in the valence state of transition metal ion. This has been confirmed by ESR studies. Much of the ESR work on photosynthesis has been carried out with photosynthetic bacteria. The oxidation of bacteriochlorophyll in vitro produces an ESR signal.

4.7 ESR in molecular biotechnology

DNA: ESR is used to investigate the nucleotide-centered free radicals in DNA, either produced by irradiation, or indirectly by other free radicals. ESR is applied to analysis of DNA hydration and the process of the hole or electron transfer from the hydration layer to DNA due to water ionization, and to the analysis of DNA repair by DNA photolyase, by detection of flavin radical formation. ESR is useful in analysis of Reverse Transcriptase (RT) inhibition by polynucleotide.

RNA: ESR was employed to structure dependent molecular dynamics of Trans Activator Responsive (TAR) RNA of HIV-1. ESR is also used to determine the map of protein-RNA interactions between RNA and ribonuclease P from E.coli.

Protein structure and dynamics: The free radical damage of proteins in the field of research is still waiting for the complete exploration. Example of the ESR investigations of the interactions between ligands and target protein is the study on the iron siderophore complex and its binding to site directed spin labeled ferric enterobactin receptor responsible for iron uptake by enterobacteria.

Activity of enzymes: ESR can effectively screen potential inhibitors interaction with the enzymes with high speed. Now a day, ESR is used in the analysis of enzymatic activity of nitric oxide synthetase (NOS), the main enzymes delivering NO in biological systems.

Membranes: The existence of phospholipid bilayers in biological systems is confusing from the point of view of evolutionary biology. The model of Fluid Mosaic appears too simple to satisfactorily represent the details of membrane structure and the respective functions. The common view of the architecture of membrane has changed by the recent ESR evidence of the existence of structural domains stabilized by membrane proteins in the form of “rafts”.

Glycobiology: Spin labeled sugars, sugar residues, and spin labeled components interacting with sugar applied in two basic fields of carbohydrate research: Sugar metabolism (degradation and transport), Structural biochemistry of glycoproteins and membranes.

- 1) ESR is employed to analyze the process of sugar transport in bacteria.
- 2) ESR was applied to the analysis of the influence of diabetes on the properties of erythrocytes showing the decrease in erythrocyte deformability due to the non-enzymatic glycation of hemoglobin. Thus, structural investigation often reveals medical aspects.

4.8 ESR in medical biotechnology

Activation and transport of drugs: ESR is useful in several pharmacological investigations like interactions between DNA binding drugs and DNA. ESR may be used to characterize some herb derived products which act by increasing the level of free radicals and other reactive species produced during light induced oxidative stress of the cell. In vivo ESR experiments revealed that multimellar liposomes enhance the topical delivery of hydrophilic compound, drugs used to be more effective when applied in liposomes then in solutions.

Imaging: ESR imaging is a valuable tool for spatially resolved redox mapping of living tissues. Redox status of tumor tissues is significant for understanding tumor physiology, and for determining the effects of chemotherapy and radiation.

4.9 ESR in classical biotechnology

Plant biotechnology: ESR is helpful even at developing artificial photosynthesis, which is biggest biotechnological challenge for the mankind.

Food production and storage: Commercially, ESR is used to analyze shelf life of beer and wine. It is based on free radicals generated in beer or wine due to the action of light, or spontaneously during the process of storage, contribute to the degradation and flavor changes of product. The level of free radical would depend on antioxidants presents in the solutions. Therefore antioxidant capacity of beer or wine helps to predict stability. Similar approach is applied to other food products, such as oils or milk. ESR measurement revealed also photosensitizing action of the important milk ingredient, vitamin-B₂, which may affect quality of the product. ESR also used in food science, and the field is hydration, water diffusion, and small molecule mobility in food systems, or sugar-water systems used to model much more complicated systems.

4.10 Summary of the unit

The ESR method is employed for studies of paramagnetic substances most commonly in liquids and solids. A spectrum is obtained in continuous wave (CW) ESR by sweeping the magnetic field. The substances are characterized by measurements of the g-factor at the centre of the spectrum and of line splitting due to hyperfine structure from nuclei with spin I is not equal to zero. Zero-field splitting (or fine structure) characteristic of transition metal ion complexes and other substances with two or more unpaired electrons ($S \geq 1$) can be observed in solid samples. Concentration measurements with the CW-ESR method are common in other applications. High field and multi-resonance methods employed in modern applications improve the resolution of the g-factor and of the hyperfine couplings, respectively. Pulse microwave techniques are used for measurements of dynamic properties like magnetic relaxation but also for structural studies.

4.11 Key words

Zero field splitting; kramers's degeneracy; esr spectra interpretation; magnitude of g value; esr instrumentation; esr application.

4.12 References for further study

1. Chatwal G. R. and Anand S. K., Electron spin resonance spectroscopy, in Instrumental methods of chemical analysis, by Anand A. and Arora M. *Himalaya publishing house, 5th Ed, 2002.*
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5. Physical Methods in Inorganic Chemistry; R. S. Drago, *Affiliated East-West Press Pvt. Ltd., New Delhi, 1st Ed, 1968.*
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4.13 question for self study

1. What is the number of peaks for benzene radical in EPR due to hyperfine coupling and what are their relative intensities?

2. What is the number of peaks for $\text{CH}_2(\text{OCH}_3)$, a methoxymethyl radical in EPR due to hyperfine coupling?
3. Which of the following will not show ESR spectrum? Explain the reason.
 - a) Cyclopentadiene, b) Benzene dianion ($\text{C}_6\text{H}_6^{2-}$), c) Cyclopentadienyl anion, d) Anthracene anion.
4. How many lines are expected in the ESR spectrum of the following?
 - a) Radical anion derived from p-xylene
 - b) 1,3,5-cycloheptatrienyl radical.
5. Draw the energy level diagram showing the transition responsible for ESR spectrum of methyl free radical.
6. Calculate the magnetic field at which resonance occurs if the ESR spectrometer is operating at 9302 MHz and the g value for benzene anion is 2.0025.
7. Deduce the structure of the chemical species which is obtained by the alkali metal reduction of benzene at -70°C and exhibits seven lines in its ESR spectrum.
8. Will $^{13}\text{CO}_2^-$ exhibit ESR spectrum? If yes predict the number of lines and their relative intensity in its ESR spectra.
9. Triiodomethyl radical $[\text{CI}_3]^*$ exhibits sixteen lines in its ESR spectrum. Calculate the spin of the iodine nucleus.
10. Which of the following compounds will not exhibit ESR spectrum?
 - a) NO, b) CO_2^- , c) C_6H_5^+ , d) O_2

UNIT 5**Structure**

- 5.0 Objectives of the unit
- 5.1 Introduction
- 5.2 Microwave region
- 5.3 Interaction of radiation with matter
- 5.4 Moment of Inertia
- 5.5 Classification molecule based on symmetry
- 5.6 Linear molecule
- 5.7 Spherical top
- 5.8 Symmetric top
- 5.9 Asymmetric top
- 5.10 Dipole moment
- 5.11 Rotational energy levels of molecule
- 5.12 The Selection rules
- 5.13 Summary of the unit
- 5.14 Key words
- 5.15 References for further study
- 5.16 Questions for self study

5.0 Objectives of the unit

After studying this unit you are able to learn

- Explain the Moment of Inertia of rotating molecule.
- Identify the symmetry of given molecule.
- Recognize the rotating axis of linear molecules to exhibit rotation spectra.
- Recognize the rotating axis of Spherical top molecules to exhibit rotation spectra.
- Recognize the rotating axis of Symmetric top molecules to exhibit rotation spectra.
- Recognize the rotating axis of Asymmetric top molecules to exhibit rotation spectra.
- Explain the dipole moment.
- Calculate the rotational energy levels.
- Identify selection rules for rotation spectra.

5.1 Introduction:

The electromagnetic radiation is characterized by two properties, namely amplitude and periodicity (**Fig. 1**). The periodicity may be described in terms of its wavelength, wave number or frequency. Wavelength (λ) is the distance between any two consecutive points in the same phase, say between successive crests or troughs. Many units of length are used to describe wavelength and the commonly used units are nanometres ($\text{nm} = 10^{-9} \text{ m}$) or Angstroms ($\text{\AA} = 10^{-8} \text{ cm}$). The radiation is often characterized by wave number ($\bar{\nu}$) which is defined as number of waves contained per unit length, usually one centimetre. It has the dimension of reciprocal centimetre (cm^{-1}). The wave length and wave number are related, $\bar{\nu} = 1/\lambda$.

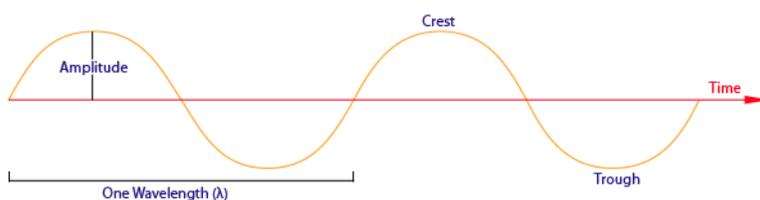


Figure1: Electromagnetic radiation (λ = wave length, A = amplitude).

All radiation travel uniformly with the velocity of light in vacuum (c) and the c/λ is called the frequency (ν) of the radiation. This frequency is expressed as the number of waves that pass a particular point per second (unit time). It is now referred to as hertz (Hz) and has reciprocal second (s^{-1}) as the unit. Both frequency and wave number are thus directly proportional to the energy of the radiation. When a particular radiation is characterized by a single frequency, it is

said to be monochromatic. When the beam of radiation of different frequency, it is said to be polychromatic.

Electromagnetic radiation has, as the name implies, both an electric field (E) and a magnetic field (H) associated with it. These fields oscillate in a periodic manner (sinusoidally) at mutually perpendicular directions and to the direction of propagation of radiation. In natural light, all transverse directions for the electric and magnetic fields are equally represented. However, with plane polarized light, the electric vector is confined to a particular plane. In **Fig. 2** a radiation with electric and magnetic fields oscillating in fixed planes in space shown.

5.2 Microwave region

$3 \times 10^{10} - 3 \times 10^{12}$ Hz; 1 cm – 100 μm wave length. Separations between the rotational levels of molecules are of the order of 100 joules/mole.

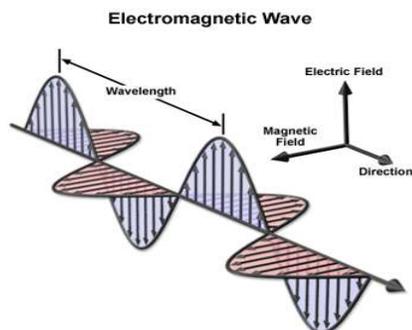


Figure 2: The propagation of EM radiation.

5.3 Interaction of radiation with matter

Spectroscopy involves study of the interaction of electromagnetic radiation with matter. Due to this interaction, electromagnetic radiation characteristic of the interacting system may be absorbed or emitted. The experimental data consist of the nature (frequency or wavelength) and the amount (intensity) of the characteristic radiation absorbed or emitted. These data are correlated with the molecular and electronic structure of the substance and with intra-and intermolecular interactions.

An isolated molecule in space has various forms of energy by virtue of its different kinds of motion and intramolecular interactions. For instance, the molecule possesses translational energy by virtue of the motion of the molecule as a whole. It may possess rotational energy due to bodily rotation of the molecule about an axis passing through the centre of gravity of the molecule. The molecule possesses vibrational energy due to periodic displacement of its atoms from their equilibrium positions. It also possesses electronic energy since the electrons

associated with each atom and bonds are in constant motion. Further, it possesses nuclear energy and energy due to nuclear and electron spins. As a first approximation, the total energy of a molecule can be expressed as the sum of the constituent energies, that is,

$$E_{total} = E_{trans} + E_{rot} + E_{vib} + E_{el} + \dots$$

It is assumed that the various types of energy associated with different motions of the molecule are independent of one another. A molecule can have many levels of these different energies. By absorption of a finite amount of energy, a molecule can go over from one energy level to a higher energy level.

Consider two energy states of a system say two rotational energy levels labelled E_1 and E_2 as shown in **Fig .3**. The subscripts 1 and 2 which distinguish the levels are referred to as 'quantum numbers'. Any expression to define the energy levels will involve one or more quantum numbers. A transition which takes the system from the lower level E_1 to the higher level E_2 can occur provided an appropriate amount of energy $\Delta E = E_2 - E_1$ is absorbed by the system. On the other hand, if the system is already at the higher energy level E_2 , by emission of energy ΔE , a transition to the lower energy level E_1 can take place. The frequency of the electromagnetic radiation absorbed (or emitted) in the process is given by the Planck's equation,

$$\Delta E = h\nu \text{ (ergs)}$$

$$\text{i.e., } \nu = \Delta E/h \text{ (Hz)}$$

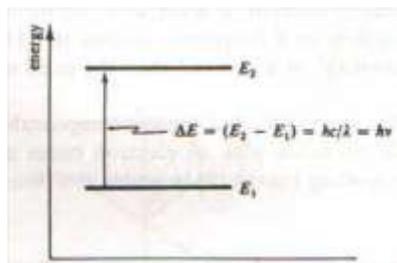


Figure 3: A typical transition for the absorption of light or EM radiation.

This is the basic equation of all spectroscopic studies. Thus, a molecule in level E_1 by absorbing radiation of frequency $\nu = \Delta E/h$ can occupy the energy level E_2 . A detector used to analyze the radiation will reveal that the intensity of the beam has decreased after its interaction with the molecule. If a radiation beam containing a range of frequencies were used, only the radiation of frequency $\nu = \Delta E/h$ would decrease in intensity and the intensity of the radiation of other frequencies would remain undiminished. Thus, in absorption spectroscopy, one observes what frequencies of radiation are absorbed from the incident radiation as it passes through the sample.

An absorption spectrum, which is a plot of the intensity of the radiation absorbed against the frequency of the radiation obtained. The interaction may occur through the electric or magnetic field associated with the electromagnetic radiation with appropriate electric or magnetic fields produced by changes taking place in the molecule. If there is no interaction between the molecule and the radiation, no absorption can occur. The interaction of electromagnetic radiation with the system is determined by the selection rules.

5.4 Moment of Inertia

Moment of inertia (I), also called mass moment of inertia or the angular mass, is a measure of an object's resistance to changes in its rotational rate. It is the rotational analog of mass.

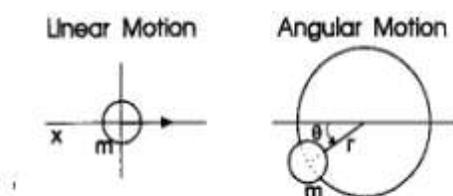


Figure 4: Linear and circular motion of a particle of mass.

Therefore the moment of inertia of an object about a given axis describes how difficult it is to change its angular motion about that axis.

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

$$I = \sum_i m_i r_i^2$$

where m_i is the mass of the atom i and r_i is the perpendicular (shortest) distance between this atom and the axis.

$$\text{ie, } I = m_1 r_1^2 + m_2 r_2^2 \dots \dots \dots (1)$$

By the definition

$$m_1 r_1 = m_2 r_2 \dots \dots \dots (2)$$

$$\text{and } r = r_1 + r_2 \dots \dots \dots (3)$$

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

$$r_1 = \frac{m_2}{m_1 + m_2} r ; r_2 = \frac{m_1}{m_1 + m_2} r \dots\dots\dots(4)$$

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

$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r^2 \dots\dots\dots(5)$$

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

$$\therefore I = \mu r^2 \dots\dots\dots(6)$$

The Classical angular momentum L of the System is given by

$$L = I\omega_r \dots\dots\dots(7)$$

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

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

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

5.5 Classification molecule based on symmetry

All gas phase molecules have quantized rotational energy levels hence pure rotational transitions are possible. A molecule can, in general, rotate about three geometric axes and can have three different moments of inertia relative to these axes. The internal axis system of a molecule is chosen to have its origin at the center of mass and is rotated so that the moment of inertia tensor is diagonal. This is the principal-axis system for a rigid molecule. Hence molecules can be classified into five main groups depending on their moments of inertia. The molecular symmetry determines the x, y and z labels but, it is the size of the moments of inertia that set the A, B and C labels. In terms of the A, B and C labels, it is conventional to classify molecules into five categories:

1. Linear molecules, $I_A = 0, I_B = I_C$.

2. Spherical tops, $I_A = I_B = I_C$.
3. Prolate symmetric tops, $I_A < I_B = I_C$, e.g. CH_3Cl .
4. Oblate symmetric tops, $I_A = I_B < I_C$, e.g. BF_3 .
5. Asymmetric tops, $I_A < I_B < I_C$.

The three moments of inertia I_A , I_B and I_C can be used to classify molecules into four different types of “tops”:

5.6 Linear molecule [$I_C = I_B$; $I_A = 0$] e.g. $\text{C} = \text{O}$, $\text{HC} \equiv \text{CH}$.

There are three axes of rotation : (a) about the molecular axis, (b) end-over-end rotation in the plane of the paper and (c) end-over-end rotation perpendicular to the plane of the paper. The rotation about the molecular axis will involve much lower moment of inertia since only the electrons will contribute to the motion. As an approximation, the moment of inertia about the molecular axis is taken as zero, that is $I_a = 0$. Obviously the moments of inertia about the axis defined above in (b) and (c) are the same, that is, $I_b = I_c$. Thus linear molecules for example CO , HCl , HCN , C_2H_2 , HCCl , OCS , etc., are characterized by $I_a = 0$, and $I_b = I_c$. Moments of inertia for representative linear molecules CO and OCS are given in **Fig 5**.

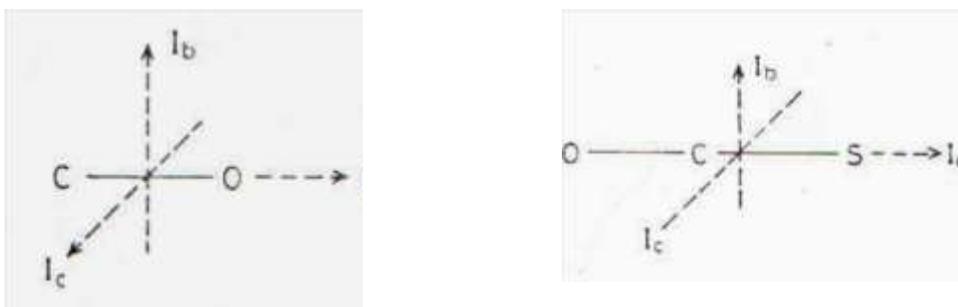


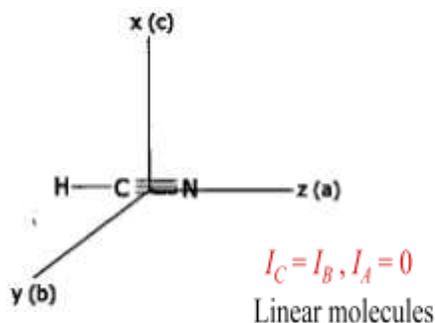
Figure 5: Moments of inertia for linear molecules: CO and OCS .

$$r(\text{C-O}) \text{ 1.130 } \text{\AA}$$

$$I_a = 0; I_b = I_c = 9.534 \text{ amu } (\text{\AA})^2$$

$$r(\text{C-O}) \text{ 1.165 } \text{\AA}, r(\text{C-S}) \text{ 1.558 } \text{\AA}$$

$$I_a = 0; I_b = I_c = 83.21 \text{ amu } (\text{\AA})^2$$



Other examples:

- HCl
- CO_2
- $\text{H-C}\equiv\text{C-H}$
- $\text{H-C}\equiv\text{C-C}\equiv\text{C-C}\equiv\text{C-H}$
- LiF

5.7 Spherical top [$I_C = I_B = I_A$] e.g. CH_4 , SF_6 .

These molecules have all the three moments of inertia equal, that is, $I_a = I_b = I_c$. The spherical top molecules (for example CH_4 , SF_6 , etc.) do not possess any permanent dipole moment and hence they exhibit no rotational spectrum.

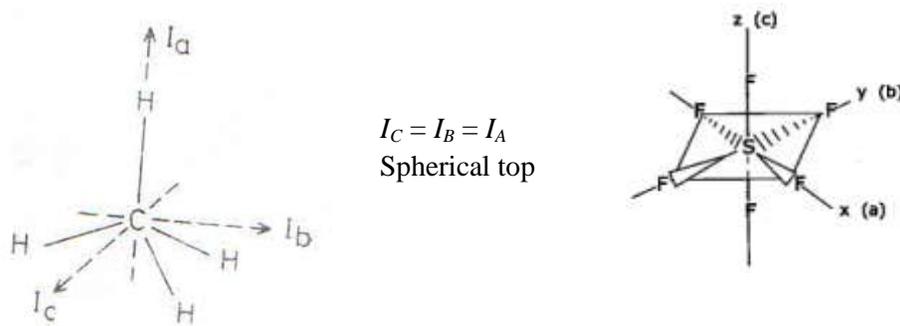


Figure 6: Moments of inertia for spherical top molecules CH_4 and SF_6 .

$$r(\text{C-H}) \text{ 1.092 \AA,}$$

$$r(\text{S-F}) \text{ 1.564 \AA,}$$

$$I_a = I_b = I_c = 3.180 \text{ amu (\AA)}^2$$

$$I_a = I_b = I_c = 185.888 \text{ amu (\AA)}^2$$

Moments of inertia for typical spherical top molecules CH_4 and SF_6 are given in **Fig 6**. Other examples: CCl_4 , and molecules with O_h , T_d , or I_h point groups are considered spherical top molecule.

5.8 Symmetric top [$I_C = I_B \neq I_A$] e.g. BF_3 , CH_3Cl .

These molecules have equal moments of inertia about two axes of rotation, while the moment of inertia about the remaining axis is not equal to either of the other two moments of inertia. Thus molecules are a special case of symmetric tops where the moment of inertia about the unique axis (I_a) is not zero. Further division is possible for symmetric top molecules. When a molecule possesses moments of inertia, $I_b = I_c > I_a$ (that is, I_a is the axis of smallest principal moment of inertia), it is referred to as a prolate, for example $\text{CH}_3\text{C}=\text{CH}$, CH_3F , etc. For CH_3F , the moment of inertia about the C—F axis corresponds to I_a and the axes corresponding to I_b and I_c are at 90° to each other and to I_a axis. When the moments of inertia of a molecule follow the pattern $I_b = I_c < I_a$, it is referred to as an oblate. Benzene, BF_3 , etc., are examples of oblate type of symmetric top molecules. Moments of inertia for representative symmetric top molecules NH_3 and BF_3 are given in **Fig 7**.



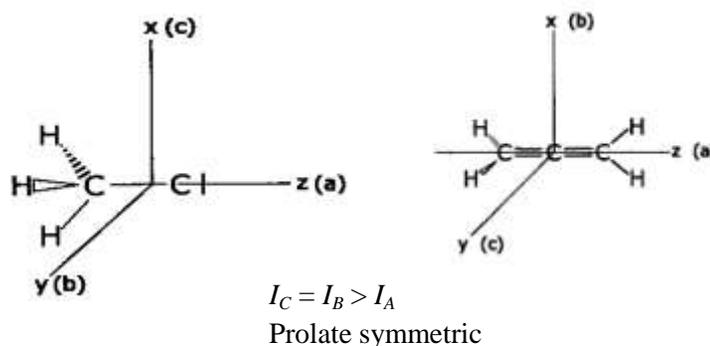
$r(\text{N-H})$ 1 **Figure 7:** Moments of inertia for symmetric top molecules NH_3 and BF_3

$$I_a = I_b = 2.667 \text{ amu } (\text{\AA})^2;$$

$$I_a = I_b = 47.79 \text{ amu } (\text{\AA})^2;$$

$$I_c = 1.693 \text{ amu } (\text{\AA})^2$$

$$I_c = 95.58 \text{ amu } (\text{\AA})^2$$



5.9 Asymmetric top [$I_A \neq I_B \neq I_C$] e.g. H_2O , CH_3OH .

These molecules which form a majority have all the three moments of inertia different, that is $I_a \neq I_b \neq I_c \neq 0$. Some examples are SO_2 , H_2CO , CH_3CHO , CH_2F_2 , pyridine, etc. Moments of inertia for representative asymmetric top rotors, H_2CO and SO_2 are given in **Fig 8**.

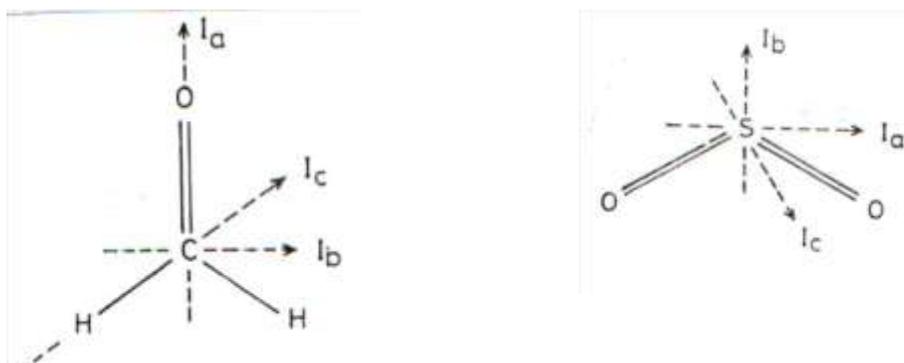


Figure 8: Moments of inertia of asymmetric top molecules: H_2CO and SO_2 .

$$r(\text{C-O}) 1.216, r(\text{C-H}) 1.09 \text{ \AA}$$

$$r(\text{S-O}) 1.431 \text{ \AA},$$

$$I_a = 1.86 \text{ amu}(\text{\AA})^2$$

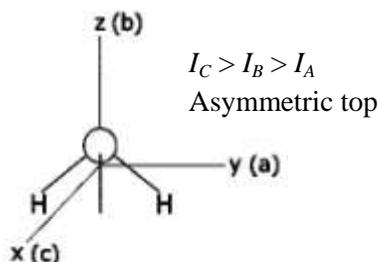
$$I_a = 8.37 \text{ amu}(\text{\AA})^2$$

$$I_b = 12.96$$

$$I_b = 48.80$$

$$I_c = 14.76$$

$$I_c = 57.17$$



Most of the molecules are asymmetric top.

The internal molecular axes x , y , and z (or a , b , and c) are labelled according to a certain set of rules based on molecular symmetry. An additional labelling scheme is also used that is based on the size of the moments of inertia.

5.10 Dipole moment:

Dipole moment (μ) is the measure of net molecular polarity, which is the magnitude of the charge Q at either end of the molecular dipole times the distance r between the charges.

$$\mu = Q \times r$$

Dipole moment tells about the charge separation in a molecule. The larger the difference in electronegativities of bonded atoms in a molecule, the larger the dipole moment. For example, in CH_3Cl molecule, chlorine is more electronegative than carbon, thus attracting the electrons in the $\text{C}-\text{Cl}$ bond toward itself (Figure 9). As a result, chlorine is slightly negative and carbon is slightly positive in $\text{C}-\text{Cl}$ bond. Since one end of $\text{C}-\text{Cl}$ is positive and the other end is negative, it is described as a polar bond. The vector will point from plus to minus charge and run parallel with the bond between two atoms. The symbol δ indicates the partial charge of an individual atom. In addition, the direction of vector implies the physical movement of electrons to an atom that has more electronegativity when two atoms are separated by a distance of r .

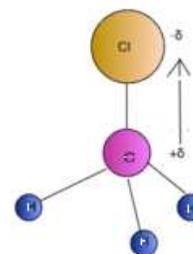


Figure 9: Representation of dipole moment in CH_3Cl molecule

5.11 Rotational energy levels of molecule

As mentioned earlier molecular energy states arise from the rotation of the whole molecule, from the vibration of its atoms, and from changes in its electronic configuration. The rotational energy states are separated by quite small intervals of the order of 10^{-3} eV. This corresponds to

the microwave spectrum (10^{-4} - 10^{-2} m). The vibrational energy states are separated by little higher energy compare to rotational energy state, and of the order 10^{-1} eV.

The rotational energy of a molecule is given by

$$E_J = \frac{1}{2} I \omega^2 \text{----- (9)}$$

where I is the moment of inertia and is equal to $I = \mu r^2$, where μ is the reduced mass and r is the internuclei distance.

From quantum chemistry calculation, the orbital angular momentum is quantized, therefore the rotational energy is

$$E_J = \frac{\hbar^2}{2I} J(J+1) \text{ joules----- (10)}$$

Where J is the rotational quantum number and has value $J = 1, 2, \dots$ and each level is $(2J + 1)$ fold degenerate.

The transition frequency of rotational energy is given

$$\gamma_J = \frac{E_J}{hc} \text{----- (11)}$$

Substituting the value of E_J in equation 3 we get

$$\gamma_J = \frac{h}{8\pi^2 I c} J(J+1) \text{ cm}^{-1}$$

$$\text{or } \gamma_J = BJ(J+1) \text{ cm}^{-1} \text{----- (12)}$$

where B is called rotational constant and which is equal to $B = \frac{h^2}{8\pi^2 I}$ joules.

If γ^I and γ^{II} are represented the lower and upper state energy frequencies respectively then

$$\Delta\gamma = \gamma^I - \gamma^{II}$$

$$\therefore \Delta\gamma = B[J^I(J^I + 1) - J^{II}(J^{II} + 1)] \text{----- (13)}$$

5.12 The Selection rules

The selection rule for a transition between any two rotational states is quantum mechanically given by

$$[\mu_{nm}] = \int \psi_n \mu \psi_m d\tau$$

where μ is the permanent dipole moment of the molecule and ψ_m and ψ_n are the initial and final rotational energy states respectively. The dipole moment being a vector quantity can be expressed by its three components along the Cartesian coordinate axes, $\mu = \mu_x + \mu_y + \mu_z$, $\mu^2 = \mu_x^2 + \mu_y^2 + \mu_z^2$. The transition moment integral can now be split in terms of the components of the dipole moment,

$$[\mu_{nm}^x] = \int \psi_n x \psi_m d\tau$$

$$[\mu_{nm}^y] = \int \psi_n y \psi_m d\tau$$

$$[\mu_{nm}^z] = \int \psi_n z \psi_m d\tau$$

If at least any one of the integrals is nonzero, then the transition is allowed and forbidden otherwise. The intensity of an allowed rotational transition depends on the square of the transition dipole moment. Consequently, the intensity of the rotational line depends on the square of the permanent dipole moment of the molecule.

It can be shown from Schrodinger equation that for a diatomic rigid rotor, in the absence of an external electric or magnetic field, only transitions in which J changes by one unit, that is, $\Delta J = \pm 1$ are allowed and all other transitions are forbidden. Thus the selection rule for rotational spectra is **$\Delta J = \pm 1$** . *Further, only hetero nuclear diatomic molecules will exhibit the rotational spectrum since homonuclear diatomic molecules do not possess permanent dipole moment.*

15.13 Summary of the unit:

Interaction of electromagnetic radiation of proper frequency with molecule results in rotational energy transitions. Consider a diatomic molecule having a dipole moment which will be along the bond. If the molecule rotates about an axis perpendicular to the bond, then the direction of the dipole moment changes continuously in a perpendicular variation in a given direction. This generates a fluctuating electric field which interacts with the electric field of the electromagnetic radiation leading to pure rotational spectrum. Hence energy can be exchanged only if the molecule has a permanent dipole moment. Homo-nuclear diatomic molecules such as N_2 , O_2 , H_2 etc.... and hetero-nuclear molecule such as CO_2 , CS_2 and spherically top molecules do not

possess a permanent dipole moment. Hence they will not show microwave spectrum. Even isotopic substitution does not produce activity, since it changes only the mass of nucleus. Molecules such as CO and HCl will show rotational spectra since they possess permanent dipole moment.

The very basic requirement for the rotational spectra is that the molecules must have a permanent dipole moment. This is because, according to classical electrodynamics, a rotating molecule can exhibit electric and magnetic component provided a changing dipole moment is associated with the molecule. Hence, all hetero nuclear diatomic molecules, whose centres of positive and negative charges do not coincide, have a permanent dipole moment. A rotating molecule can absorb microwave radiation and thereby increase the rotational energy only if a permanent dipole is present. Such a molecule interacts with the electric field of the incident radiation to absorb rotational energy and produce the absorption spectrum.

Salient Features of Rotational Spectra:

- a) Pure rotational spectra arise from transitions between rotational energy states and are observed in microwave (or) far infra red region of the electromagnetic spectrum.
- b) Only molecules having permanent electric dipole can give rise to rotational spectra. It means homonuclear diatomic molecules such as H₂, O₂, N₂ etc..., symmetric linear molecules such as CO₂ and spherical top polyatomic molecules such as CH₄ do not exhibit rotational spectra.
- c) In practice, pure rotational spectra are observed in absorption. For heteronuclear diatomic molecules such as HCl, HBr etc..., the rotational spectra consist of a series of absorption maxima which are very nearly equidistant on wave number scales.

15.14 Key words:

Microwave radiation; Moment of Inertia; Symmetry; Linear; Spherical top; Symmetric top; Asymmetric top; Dipole moment; Rotational energy; Selection rules.

15.15 Reference for further study:

- 1) Atomic and Molecular spectra: Laser by Raj Kumar, *Kedar Nath Ram Nath*; 4th Ed **2012**.
- 2) Molecular structure and Spectroscopy by G. Aruldas, *Prentice-Hall of India Private Limt*; **2001**.
- 3) Molecular Rotation Spectra by H.W Kroto, *Courier Dover Publications*; **2003**.
- 4) Vibrational and Rotational Spectroscopy of Polyatomic Molecules by M. Mueller, *Kluwer Academic Publishers*; **2002**.

5) Rotational Spectroscopy by HC Wolf, *Springer Berlin Heidelberg*; **1995**.

5.16 Questions for self study

- 1) How do you distinguish between symmetric top and asymmetric top molecules?
- 2) Why microwave spectra are difficult to be observed in case of liquids and solids?
- 3) Differentiate between prolate and oblate symmetric top molecule.
- 4) State the requirement for a sample to be satisfactory for microwave spectral study.
- 5) How rotational energy of linear molecule differs from that of symmetric top molecule?
- 6) What types of molecules give rotational spectra? State which of the following molecules give rotational spectra, H_2 , HCl , CH_4 , CH_3Cl .
- 7) Give the different region of the electromagnetic spectrum. Mention the kinds of spectra observed in different regions
- 8) How are molecules classified based on the three principle moments of inertia?
- 9) Give a brief account on the classification of polyatomic molecule on the basis of moment of inertia.

UNIT 6**Structure**

- 6.0 Objectives of the unit
- 6.1 Introduction
- 6.2 Rotation Spectra of Diatomic Molecules
- 6.3 The Rigid Diatomic Molecule
- 6.4 The Non-rigid Rotator
- 6.5 Effect of Isotopic Substitution on Rotation Spectra
- 6.6 Intensities of the Spectral lines
- 6.7** Application of rotational spectra
 - Molecular structure determination
 - Dipole moment determination
 - Atomic mass determination
 - Nuclear quadrupole moment measurement
- 6.8 Solved problems
- 6.9 Summary of the unit
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- 6.12 Question for self study

6.0 Objectives of the unit:

After studying this unit you are able to

- Derive the energy levels for rotation spectra of diatomic molecule.
- Obtain the energy level diagram for rigid-rotator.
- Obtain the energy level diagram for non-rigid rotator.
- Study the effect of isotopic substitution on rotation spectra.
- Derive the expression for intensity of spectral lines.

6.1 Introduction

The rotation of a diatomic molecule is best described in terms of its angular velocity, ω about the center of gravity of the molecule. Diatomic molecules with a permanent dipole moment can absorb electromagnetic radiation via their rotational motion. Thus, CO, NO, and HCl will all exhibit rotational spectra but S₂ or H₂ will not.

An important quantity for describing the energy of rotation is the moment of inertia. The moment of inertia (I) of a molecule is defined as the mass of each atom multiplied by the square of its distance from the rotational axis through the center of mass of the molecule. Suppose that molecules are rigid rotors, bodies that do not distort under the stress of rotation. The potential energy may be set to zero since there is no change in bond length during the rotation. In reality, a chemical bond is not rigid but it is free to stretch or compress. At high rotational speed, the bond will stretch and the molecular geometry will distort as a result of centrifugal forces. Centrifugal distortion reduces the rotational constant and consequently the energy levels are slightly closer than the rigid-rotor expression predicted.

6.2 Rotation Spectra of Diatomic Molecules

The rotational energy, along with all other forms of molecular energy, is quantized. This means that a molecule cannot have any arbitrary amount of rotational energy (i.e., any value of angular momentum) but its energy is limited to certain definite values depending on the shape and size of the molecule concerned. The permitted energy values of rotational energy levels may in principle be calculated for any molecule by the Schrodinger equation for the system represented by that molecule.

6.3 The Rigid Diatomic Molecule

For a diatomic molecule AB of masses m_1 and m_2 are joined by a rigid bond whose length is

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

The molecule rotates end-over-end about a point C, the centre of gravity of the molecule. This is defined by the moment or balancing equation:

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

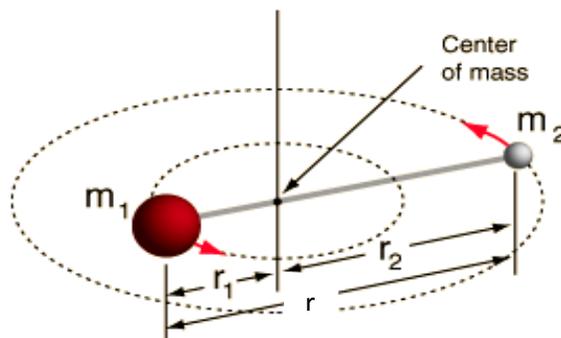


Figure 1: A rigid diatomic rotator.

The moment of inertia about C is defined by

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= m_2 r_2 r_1 + m_1 r_1 r_2 \quad (\text{from Eq.2})\text{-----(3)} \\ &= r_1 r_2 (m_1 + m_2) \end{aligned}$$

However, from equations (1) and (2), $m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$

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

Replacing (4) in (3),

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

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$, and μ is called the reduced mass of the system. Eq. (5) defines the moment of inertia in terms of atomic mass and the bond length.

By the use of the Schrodinger equation it may be shown that the rotational energy levels allowed to the rigid diatomic molecule are given by the expression:

$$E_J = \frac{h^2}{8\pi^2 I} J(J + 1) \text{ Joules} \quad \text{where } J = 0, 1, 2, \dots \text{(6)}$$

In this expression h is Planck's constant, and I is the moment of inertia. The quantity J , which can take integral values from zero upwards, is called the rotational quantum number. Its restriction to

integral values arises directly out of the solution to the Schrodinger equation and is by no means arbitrary, and it is this restriction which effectively allows only certain discrete rotational energy levels to the molecule.

Eq. (6) expressed the allowed energies in joules; we, however, are interested in differences between these energies, i.e., the corresponding frequency. $\nu = \Delta E/h$ Hz, or wave number, $\bar{\nu} = \Delta E/hc$ cm^{-1} , of the radiation emitted or absorbed as a consequence of changes between energy levels. In the rotational region, spectra are usually discussed in terms of wave number, so it is useful to consider energies expressed in these units.

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

where c , the velocity of light, is here expressed in cm s^{-1} , since the unit of wavenumber is reciprocal centimetres. Eq. (7) is usually abbreviated to,

$$\epsilon_J = B J(J+1) \text{ cm}^{-1} \quad (J = 0, 1, 2, \dots) \dots \dots (8)$$

where B , the rotational constant, is given by

$$B = \frac{h}{8\pi^2 I} J(J+1) \text{ cm}^{-1} \dots \dots \dots (9)$$

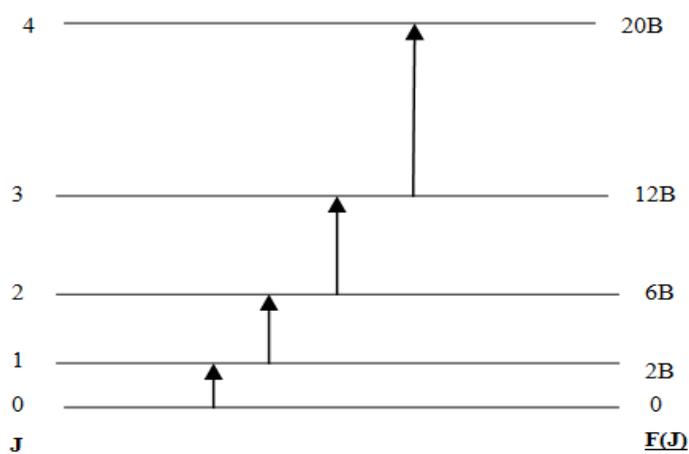


Figure 2: The allowed rotational energies of a rigid diatomic molecule.

From Eq. (9) we can show the allowed energy levels diagrammatically as in **Fig. 2**. For $J = 0$ we have $\epsilon_J = 0$ and we would say that molecule is not rotating at all. For $J = 1$, the rotational energy is $\epsilon_J = 2B$ and a rotating molecule then has its lowest angular momentum. We may continue to calculate ϵ_J with increasing J values.

In order to discuss the spectrum, we need to consider the difference between the levels. If the molecule to be in $J = 0$ state (the ground state in which no rotation occurs), the incident radiation be absorbed to rise it to the $J = 1$ state. The energy absorbed will be,

$$\begin{aligned}\epsilon_1 - \epsilon_0 &= 2B - 0 = 2B \text{ cm}^{-1} \\ \nu_{0 \rightarrow 1} &= 2B \text{ cm}^{-1} \text{-----(10)}\end{aligned}$$

In other words, an absorption line will appear at $2B \text{ cm}^{-1}$. If the molecule is raised from the $J = 1$ to the $J = 2$ level by the absorption of more energy, then we see that

$$\nu_{1 \rightarrow 2} = \epsilon_2 - \epsilon_1 = 6B - 2B = 4B \text{ cm}^{-1} \text{-----(11)}$$

In general, to raise the molecule from the state J to state $(J+1)$, we have,

$$\begin{aligned}\nu_{J \rightarrow J+1} &= B(J+1)(J+2) - BJ(J+1) \\ &= B[J^2 + 3J + 2 - (J^2 + J)] \\ \nu_{J \rightarrow J+1} &= 2B(J+1) \text{ cm}^{-1} \text{-----(12)}\end{aligned}$$

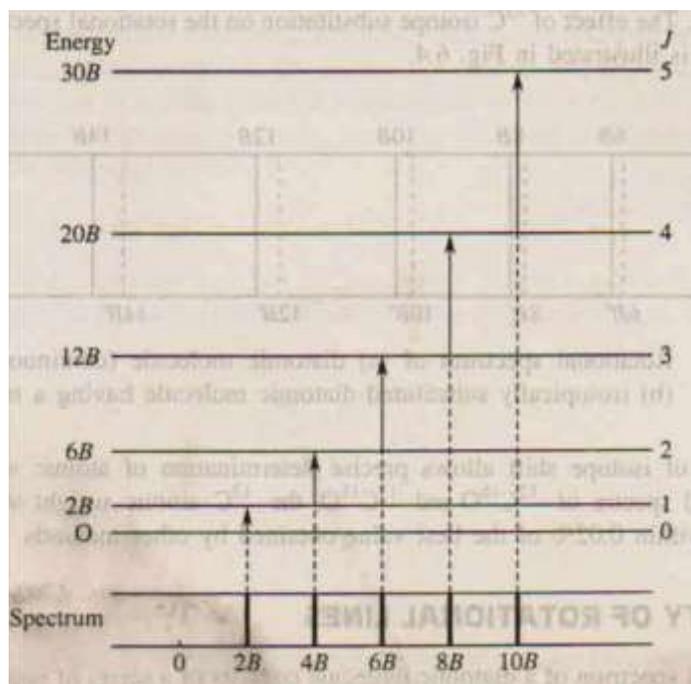


Figure 3: Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from them.

Thus a stepwise raising of the rotational energy results in an absorption spectrum consisting of lines at $2B, 4B, 6B, \dots \text{ cm}^{-1}$, while a similar lowering would result in an identical emission spectrum. This is shown at the foot of **Fig 3**.

In deriving this pattern we have made the assumption that a transition can occur from a particular level only to its immediate neighbour, either above or below. But for instance, the transitions are

not showed for $J = 0 \rightarrow J = 2 \rightarrow J = 4 \dots$. Hence, we need to consider only transitions in which J changes by one unit, and all other transitions being spectroscopically forbidden. Such a result is called a selection rule, and we may formulate for the rigid diatomic rotator as,

$$\text{Selection rule: } \Delta J = \pm 1 \text{-----(13)}$$

The spectrum will be observed only if the molecule is hetero nuclear. If it is homonuclear, there will be no dipole component change during the rotation, and hence no interaction with radiation. Thus molecules such as HCl and CO will show rotational spectra, while N_2 and O_2 will not. Also, the rotation about the bond axis was rejected since the moment of inertia is very small about the bond axis. This means that, a molecule requires a great deal of energy to be raised from the $J = 0$ to the $J = 1$ state, and such transitions do not occur under normal spectroscopic conditions.

6.4 The Non-rigid Rotator

The internuclear distances could be calculated from the microwave spectra. Experimental investigations have shown that, the successive lines in the rotational spectrum are not evenly spaced, but the frequency separation decreases with increasing values of J . This is shown by the spectrum of HF given in **Table 1**. The reason for this decrease may be seen if we calculate internuclear distances from the B values. The bond length increases with J , and thus a rigid bond is only an approximation. All bonds are elastic to some extent, and the increase in length with J nearly reflects the fact that the more quickly a diatomic molecule rotates the greater is the centrifugal force tending to move the atoms apart. Thus the bond length tends to increase with the frequency of rotation. This increases the effective moment of inertia of the molecule and decreases the rotational energy as compared to that of rigid rotator.

Table 1: Rotational spectrum of HF

J	$\nu_{\text{obs}} (\text{cm}^{-1})$	$\nu_{\text{cal}} (\text{cm}^{-1})$	$\Delta\nu_{\text{obs}} (\text{cm}^{-1})$	B (cm^{-1})	r (\AA)
0	41.08	41.11			
1	82.19	82.18	41.11	20.56	0.929
2	123.15	123.14	40.96	20.48	0.931
3	164.0	163.94	40.85	20.43	0.932
4	204.62	204.55	40.62	20.31	0.935
5	244.93	244.89	40.31	20.16	0.938

6	285.01	284.93	40.08	20.04	0.941
7	324.65	324.61	39.64	19.82	0.946
8	363.93	363.89	39.28	19.64	0.951
9	402.82	402.70	38.89	19.45	0.955
10	441.13	441.00	38.31	19.16	0.963

The Schrodinger wave equation may be set up for a non-rigid molecule, and the rotational energy levels are found to be:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2 \text{ joules}$$

$$\epsilon_J = \frac{E_J}{hc} = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1} \text{-----(14)}$$

where B is the rotational constant as defined previously and D is the centrifugal distortion constant, is given by,

$$D = \frac{h^3}{32\pi^4 I^2 r^2 k} \text{ cm}^{-1} \text{-----(15)}$$

which is a positive quantity. Equation (14) applies for a simple harmonic force field only, if the force field is anharmonic, the expression becomes,

$$\epsilon_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 \text{ cm}^{-1} \text{-----(16)}$$

where H, K, etc., are small constants dependent upon the geometry of the molecule. They are, however, negligible compared with D and most modern spectroscopic data are adequately fitted by Eq. (14).

From the defining equations of B and D it may be shown directly that,

$$D = \frac{16B^3\pi^2\mu c^2}{k} = \frac{4B^3}{\omega^2} \text{-----(17)}$$

Where ω the vibrational frequency of the bond and k is the force constant, is given by

$$k = 4\pi^2 c^2 \omega^2 \mu \text{-----(18)}$$

where c is the velocity of light and μ is the reduced mass. The vibrational frequencies are usually of the order of 10^3 cm^{-1} , while B we have found to be of the order of 10 cm^{-1} . Thus we see that D, being of the order 10^{-3} cm^{-1} , is very small compared with B. For small J, therefore, the correction term $DJ^2(J+1)^2$ is almost negligible, while for J values of 10 or more it may become appreciable.

Fig 4 shows the lowering of rotational levels when passing from rigid to the non-rigid diatomic molecule. The spectra are also compared, the dashed lines connecting corresponding energy levels and transitions of the rigid and the non-rigid molecules. It should be noted that the selection rule for non-rigid rotator is still $\Delta J = \pm 1$.

We may easily write an analytical expression for the transitions,

$$\begin{aligned} \epsilon_{J+1} - \epsilon_J &= \nu_J = B[(J+1)(J+2) - J(J+1)] - D[(J+1)^2(J+2)^2 - J^2(J+1)^2] \\ \nu_J &= 2B(J+1) - 4D(J+1)^3 \quad \text{cm}^{-1} \end{aligned} \quad (2.19)$$

where ν_J represents equally the upward transition from J to $J+1$, or the downward from $J+1$ to J . Thus we see analytically, and from **Fig 4**, that the spectrum of the elastic rotator is similar to that of the rigid molecule except that each line is displaced slightly to lower frequency, the displacement increasing with $(J+1)^3$.

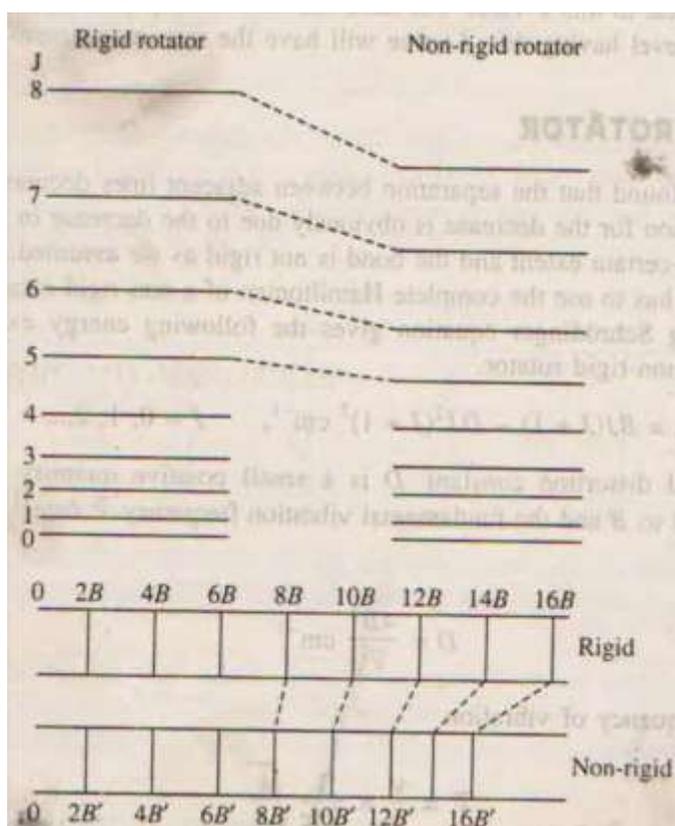


Figure 4: The change in rotational energy levels and spectrum when passing from a rigid to a non-rigid diatomic molecule. Energy levels on the right are calculated using $D = 10^{-3}B$.

6.5 Effect of Isotopic Substitution on Rotation Spectra

When a particular atom in a molecule is replaced by its isotope, the resulting element identical in every way except for its atomic mass, i.e., the resulting substance is identical chemically with the

original. In particular, there is no appreciable change in internuclear distance on isotopic substitution. There is, however, a change in total mass and hence in the moment of inertia and B value for the molecule.

Considering carbon monoxide as an example, we see that, on going from $^{12}\text{C}^{16}\text{O}$ to $^{13}\text{C}^{16}\text{O}$, there is a mass increase and hence a decrease in the B value. If we designate the ^{13}C molecule with a prime we have $B > B'$. This change will be reflected in the rotational energy levels of the molecule. **Fig. 5** shows the relative lowering of the ^{13}C levels with respect to those of ^{12}C . The diagram at the foot of **Fig. 5** shows that the spectrum of the heavier species will show a smaller separation between the lines ($2B'$) than that of the lighter one ($2B$). Again the effect has been much exaggerated, and the transitions due to the heavier molecule are shown dashed.

Observation of this decreased separation has led to the evaluation of precise atomic weights. Gilliam *et al.*, found that the first rotational absorption of $^{12}\text{C}^{16}\text{O}$ to be at 3.84235 cm^{-1} , while that of $^{13}\text{C}^{16}\text{O}$ was at 3.67337 cm^{-1} . The values of B determined from these figures are,

$$B = 1.92118\text{ cm}^{-1} \text{ and } B' = 1.83669\text{ cm}^{-1}$$

where the prime refers to the heavier molecule, then we have

$$\frac{B}{B'} = \frac{h}{8\pi^2 I c} \cdot \frac{8\pi^2 I' c}{h} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046 \text{-----} (20)$$

where μ is the reduced mass, and the internuclear distance is considered unchanged by isotopic substitution. Taking the mass of oxygen to be 15.9994 and that of carbon-12 to be 12.00, we have:

$$\frac{\mu'}{\mu} = 1.046 = \frac{15.9994m'}{15.9994+m'} \times \frac{12+15.9994}{12 \times 15.9994} \text{-----} (21)$$

from which m' , the atomic weight of carbon-13, is found to be 13.0007. This is within 0.02 per cent of the best value obtained in other ways.

It is noteworthy that the data quoted above were obtained by Gilliam *et al.*, from $^{13}\text{C}^{16}\text{O}$ molecules in natural abundance (i.e., about one per cent of ordinary carbon monoxide). Thus, besides allowing an extremely precise determination of atomic weights, microwave studies can give directly an estimate of the abundance of isotopes by comparison of absorption intensities.

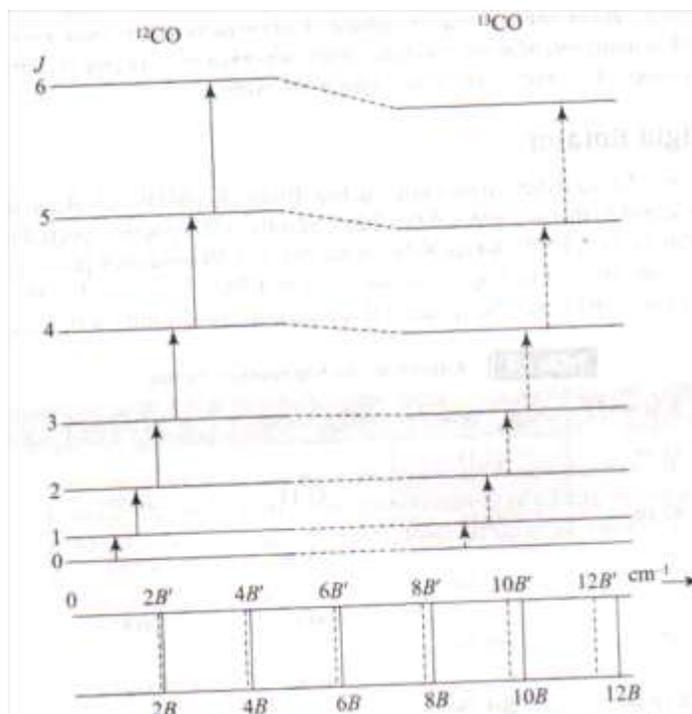


Figure 5: The effect of isotopic substitution on the energy levels and rotational spectrum of a diatomic molecule.

6.6 Intensities of the Spectral lines

The intrinsic probabilities of the transitions are identical. The intensities of the spectral lines arising from different J levels will therefore be directly proportional to the number of molecules present in each level. Boltzmann distribution law governs the population of levels for molecules at thermal equilibrium. The relative population in the upper level J' to that in the lower level J'' is given by

$$\frac{N_{j'}}{N_{j''}} = e^{-\frac{\Delta E}{kT}} \text{-----(22)}$$

where ΔE is the energy difference between the two rotational states, k is Boltzmann constant and T is the temperature in Kelvin. Taking a representative value of B as 2.0 cm^{-1} at room temperature (300 K), the population in the J state relative to that in $J = 0$ state is given by

$$\frac{N_j}{N_{j''}} = e^{-\frac{BhcJ(J+1)}{kT}} \text{----- (23)}$$

Substituting the values, for $J = 1$,

$$\frac{N_1}{N_0} = e^{\frac{-2.0 \times 6.63 \times 10^{-34} \times 3 \times 10^{10} (1)(2)}{1.38 \times 10^{-23} \times 300}} \text{-----}(24)$$

Thus there are almost as many molecules in the $J = 1$ level as there are in the $J = 0$ level at thermal equilibrium. This is because of the smaller energy difference between two rotational states compared to kT . A more rapid decrease in the ratio of N_J/N_0 occurs for larger values for B and with increasing J values.

The rotational transitions consist of successive jumps from each rotational level to the one immediately above. Consequently, the absorption spectrum will appear as a series of equally spaced lines. The spectral lines are given by

$$\nu_J = 2B(J + 1), \text{ with } J = 1, 2, \dots \text{---}(25)$$

One of the factors which determine the intensity of the spectral lines is the degeneracy of the rotational energy states. The degeneracy corresponds to certain allowed orientations of the rotation relative to a fixed reference direction, usually referred to as the Z-axis. By imposing an external electric or magnetic field along this axis, the degeneracies are lifted so that different orientations now have slightly different energies. In general, it can be shown that each rotational energy level is $(2J + 1)$ fold degenerate in the absence of an external field. Thus the molecular population in each rotational level decreases exponentially with increasing value of J (**Fig 6**) because of Boltzmann distribution law, while the number of degenerate levels available increases rapidly with J values. The relative population at energy E_J is given by,

$$\text{Relative population} \propto (2J + 1) e^{-\left(\frac{E_J}{kT}\right)} \text{-----} (26)$$

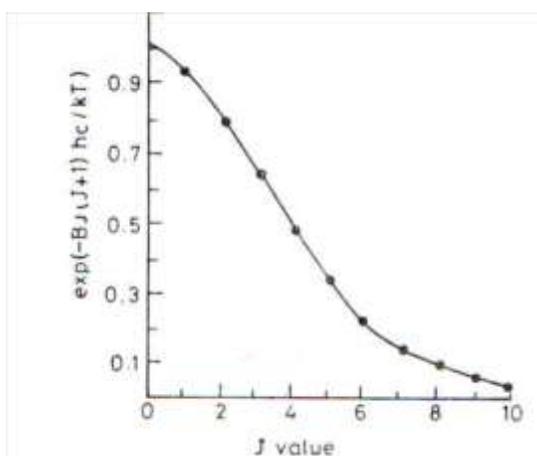


Figure 6: The Boltzmann population of rotational energy levels with $B = 10.0 \text{ cm}^{-1}$ and $T = 300 \text{ K}$.

A plot of the total relative population of the rotational energy levels including degeneracy for a diatomic molecule is shown in **Fig 7**, and the curve indicates that the population rises to a maximum and then decreases. The degeneracy factor $(2J + 1)$ overcomes the exponential factor causing the population of levels with low J to increase with increasing J . For high J values, the opposite holds true. Maximum population is obtained for an intermediate value of J . A spectrum similar to the one shown in **Fig 8** may be obtained.

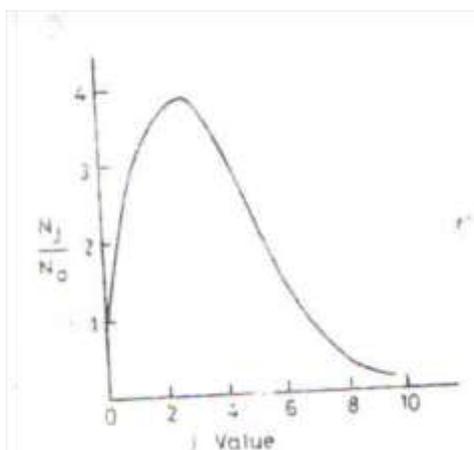


Figure 7: The total relative population distribution of the rotational energy levels of a diatomic molecule taking $B = 10.4 \text{ cm}^{-1}$ and $T = 300 \text{ K}$.

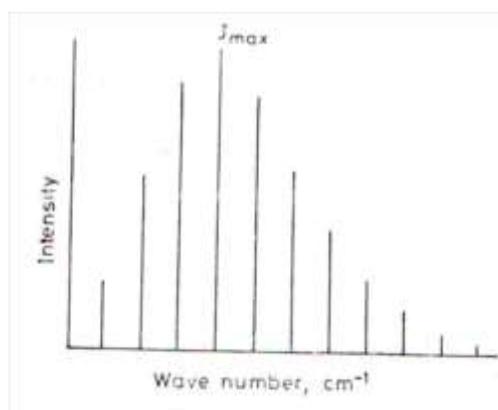


Figure 8: Typical rotational absorption line spectrum.

The value of J for which maximum intensity of the spectral line may be derived by the following method:

$$\text{Since } \frac{N_J}{N_0} = (2J + 1) \frac{e^{-BhcJ(J+1)/kT}}{kT}$$

$$\text{That is } N_J = N_0(2J + 1)e^{-\frac{BhcJ(J+1)}{kT}} \text{ -----(27)}$$

Treating J as a variable, differentiation of Eq.(27) for maximum,

$dN_J/dJ = 0$ gives,

$$\frac{dN_J}{dJ} = \left[2N_0 + N_0(2J + 1) \left(\frac{-Bhc}{kT} \right) 2J + 1 \right]$$

This on simplification, finally the J value for maximum population is given by,

$$J = \left(\sqrt{\frac{kT}{2Bhc}} \right) - \frac{1}{2} \text{-----(28)}$$

Consequently, transitions between levels with very high or very low values of J will have low intensities while the intensity of the spectral line will be maximum at the nearest integral J value given by the equation (28).

The rotational spectrum of HCl is considered for illustration. The spectrum showed in **Fig 9** displays lines at 20.7, 41.5, 62.0, 83.0, 103.8 cm^{-1} , etc. The spectral lines are easily assigned to ($J \rightarrow J + 1$) as $0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$, $3 \rightarrow 4$, $4 \rightarrow 5$ transitions, respectively occurring at $2B$, $4B$, $6B$, $8B$ and $10B$. The average of the above five $2B$ values is 20.8 cm^{-1} .

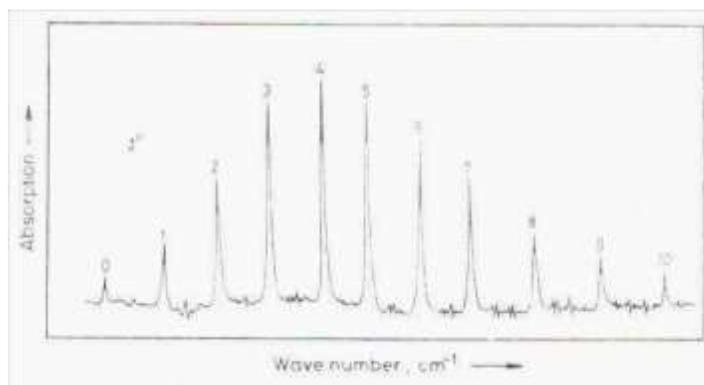


Figure 9: Microwave spectrum of HCl.

6.7 Application of rotational spectra

The details about molecular structure will get from the study of rotational spectra. Rotational constant B can be obtained with very high accuracy.

a) Molecular structure determination

The information about the position of atoms in a molecule is obtained from the three rotational constants mentioned below, from which the three principal moments of inertia I_a , I_b and I_c of the molecule can be calculated.

$$A = \frac{h}{8\pi^2 I_a}, \quad B = \frac{h}{8\pi^2 I_b} \text{ and } C = \frac{h}{8\pi^2 I_c}.$$

In a diatomic molecule, there is only one observable principal moment of inertia which along with atomic masses gives the interatomic distance.

ie, $I = \mu r^2$, $\therefore r = \sqrt{I\left(\frac{1}{m_1} + \frac{1}{m_2}\right)}$ where m_1 and m_2 are the masses of the two atoms in a diatomic molecule.

In case of linear molecule having n atoms, there is $(n-1)$ bond distance to be determined. In this case also only one bond distance can be obtained from rotational spectra.

b) Dipole moment determination

Precise determination of electric dipole moment is possible from microwave spectroscopy by measurement of the Stark effect. Dipole moment value as low as 0.05 Debye can be measured. Dipole moment measurement helps to analyze the nature of molecular bond present in the molecule. Dipole moment value of some of the molecules determined by microwave spectroscopy is given in Table 2.

Table 2: Molecular constants from rotational spectra

Molecule	Bond length (Å)	Bond angle	Dipole moment (Debye)
FCI	1.6281	-	0.88
BrCl	2.138	-	0.57
OCS	1.164 (C = O)	-	0.71
	1.558 (C = S)	-	
HCN	1.064 (C - H)	-	3.00
	1.156 (C ≡ N)	-	
ClCN	1.629 (C - Cl)	-	2.802
	1.163 (C - N)	-	
NH ₃	1.090	107° 20'	1.468
NF ₃	1.371	103°	0.234
CH ₃ Cl	1.095 (C - H)	109°	1.869
	1.781 (C - Cl)	(HCH)	
H ₂ O	0.958	104° 30'	1.846

c) Atomic mass determination

A very high resolution microwave spectra can be used for the determination of atomic masses. The rotational spectra of molecules and their isotopes gives rotational constants B and B' respectively, where prime refers to the isotope molecule. Ratio of these two can be used to get atomic mass of the molecule as shown below.

$$B = \frac{h}{8\pi^2 I} \text{ and } B' = \frac{h}{8\pi^2 I'}$$

$$\therefore \frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu}$$

From the known value of μ , one can evaluate μ' from which the mass of the isotope can be estimated.

d) Nuclear quadrupole moment measurement

Measurement of the quadrupole hyperfine structure in molecules gives the quantity e^2qQ , the quadrupole coupling constant. For the evaluation of eQ , the knowledge of quantity q is necessary which can be established from many other studies. However, knowledge of q is not necessary for the determination of the ratio of the quadrupole moment of different isotopes of the same elements and these can be precisely evaluated from microwave measurements. Some of the important quadrupole moments determined from microwave spectra are listed in Table 3.

Table 3: Nuclear quadrupole

Nucleus	Quadrupole moment (10^{-24} cm^2)	Nucleus	Quadrupole moment (10^{-24} cm^2)
^{10}B	0.06	^{37}Cl	- 0.052
^{11}B	0.03	^{79}Br	0.28
^{14}N	0.02	^{81}Br	0.31
^{17}O	- 0.005	^{127}I	- 0.75
^{35}Cl	- 0.066	^{129}I	- 0.47

6.8 Solved 1

1) The moment of inertia of the CO molecule is $1.45 \times 10^{-46} \text{ kg} \cdot \text{m}^2$. Calculate the energy and the angular velocity in the lowest rotational energy level of the CO molecule ($h = 6.63 \times 10^{-34} \text{ Js}$).

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

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

For the lowest rotational energy level $J = 1$

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

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

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

The angular velocity is

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

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

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

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

Where J refers to lower state

For the transition $J = 0$ we have

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

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

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

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

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

$$\bar{\nu} = 20.68 \times 15$$

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

The corresponding wavelength is

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

(or)

$$\lambda = 32 \mu\text{m}$$

3) Microwave causes molecules to rotate more energetically. A molecule absorbs microwave photon of wavelength 20cm, calculate the energy difference between the two rotational levels in joules

Solution: Here wavelength, $\lambda = 20 \text{ cm} = 20 \times 10^{-2} \text{ m} = 0.2 \text{ m}$

Difference between the two rotational levels = energy of microwave radiation absorbed.

$$\begin{aligned} &= h\nu = hc/\lambda \\ &= \frac{6.6 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{0.2 \text{ m}} \\ &= 9.9 \times 10^{-25} \text{ J} \end{aligned}$$

4) In the rotational spectrum of $^{12}\text{C}^{16}\text{O}$ absorption lines are observed at a constant separation of 3.84236 cm^{-1} . Calculate angular velocity in radian second in $J = 1$ level.

Solution:

$$\text{Here, } 2B = 3.84236 \text{ cm}^{-1}$$

$$\text{So, } B = 1.92118 \text{ cm}^{-1} = 1.92118 \times 10^2 \text{ m}^{-1}$$

Rotational energy in the $J = 1$ level is given by equation,

$$\begin{aligned} E_1 &= 2Bhc \\ &= 2 \times 1.92118 \times 10^2 \text{ m}^{-1} \times 6.6 \times 10^{-34} \text{ Js} \times 10^8 \text{ ms}^{-1} \\ &= 76.079 \times 10^{-24} \text{ J} \end{aligned}$$

$$\text{ie, } \frac{I\omega^2}{2} = 76.079 \times 10^{-24} \text{ J}$$

$$\therefore \omega^2 = \frac{2 \times 76.079 \times 10^{-24} \text{ j}}{I} = \frac{76.079 \times 10^{-24} \text{ j}}{14.5694 \times 10^{-47} \text{ kg m}^2} = 10.4437 \times 10^{23} \text{ s}^{-2}$$

Hence angular velocity $\omega = 10.22 \times 10^{11} \text{ rad s}^{-1}$

5) What is the change in the rotational constant B when hydrogen is placed by deuterium in the hydrogen molecule?

Solution:

Denoting the isotopically substituted hydrogen by primes

$$\frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu}$$

$$\mu = \frac{m_H}{2}, \quad \mu' = \frac{m_D}{2} = m_H$$

$$\frac{B}{B'} = \frac{2m_H}{m_H} = 2 \quad \text{because } B' = B/2$$

Change in rotational constant $B-B' = B/2$

6) The first line in the rotation spectrum of carbon monoxide has frequency of 3.8424cm^{-1} . Calculate the rotational constant and hence C-O bond length in carbon monoxide. Avogadro number is 6.022×10^{23} .

Solution

$$2B = 3.8424 \text{ cm}^{-1}, \quad \therefore B = 1,9212 \text{ cm}^{-1}$$

$$I = \mu r^2 = \frac{h}{8\pi^2 Bc}$$

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

$$\mu = \frac{12 \times 15.9949}{27.9949 \times 6.022 \times 10^{23}} = 1.1385 \times 10^{-23} \text{ g}$$

$$\therefore r^2 = \frac{6.625 \times 10^{-27}}{8\pi^2 \times 1.1385 \times 10^{-23} \times 1.9212 \times 3 \times 10^{10}}$$

$$r = 1.131 \times 10^{-8} \text{ cm} = 1.131 \text{ \AA}$$

7) The first rotational line of $^{12}\text{C}^{16}\text{O}$ is observed at 3.84235 cm^{-1} and that of X^{16}O at 3.67337 cm^{-1} . Calculate the atomic weight of X, assuming the mass of ^{16}O to be 15.99949.

Solution

Let B is the rotational constant of $^{12}\text{C}^{16}\text{O}$ and B' is that of X^{16}O

$$\frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu} \text{ ----- (1)}$$

Let the atomic weight of X be m

$$\text{Then } \frac{\mu'}{\mu} = \frac{27.9949}{12 \times 15.9949} \times \frac{m \times 15.9949}{m + 15.9949} \text{ ----- 2}$$

$$\therefore \frac{B}{B'} = \frac{3.84235}{3.67337} = 1.046 \text{ ----- 3}$$

Sustituting values of 2 and 3 in equation 1 and simplifying we get,

$$m = 13.001$$

$$\therefore X \text{ } ^{16}\text{O} \text{ is } ^{13}\text{C}^{16}\text{O}$$

6.9 Summary of the unit

For the purposes of studying the rotational spectra of molecules it is essential to classify them according to their principal moments of inertia. The moment of inertia I of any molecule about any axis through the centre of gravity is given by expression

$$I = \sum_i m_i r_i^2$$

The rotational energy levels E_r of a diatomic molecule, in the rigid rotor approximation, is given by

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

In this equation, I is the moment of inertia [equal to μr^2 where the reduced mass μ is equal to $m_1 m_2 / (m_1 + m_2)$] and the rotational quantum number $J = 0, 1, 2, \dots$. The same expression applies to any linear polyatomic molecule but, because I is likely to be larger than for a diatomic molecule, the energy levels tend to be more closely spaced. In practice, what is measured experimentally is not energy but frequency, in the microwave regions. Therefore we convert the energy levels of above equation to what are known as term values $F(J)$ having dimensions of either frequency, by dividing by h , or wave number, by dividing by hc , gives.

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

$$F(J) = \frac{E_r}{hc} = \frac{h}{8\pi^2 cI} J(J+1) = BJ(J+1)$$

Thus a series of spectral lines with wave number values $2B, 4B, 6B, \dots, \text{cm}^{-1}$, is expected for the rotational spectrum of a rigid diatomic molecule. The separation between any two adjacent

lines is equal to $2B$. As the rotational levels are closely spaced compare to kT , many of the lower lines will have reasonable population leading to a spectrum with sufficient lines.

6.10 Key words

Diatomic molecule; Rigid rotator; Non-rigid rotator; Isotope; Nuclear quadrupole.

6.11 Reference for further study

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6.12 Question for self study

- 1) Obtain an expression for the rotational energy levels of a diatomic molecule.
- 2) Write down the expression for the energy of a rigid rotator model of a diatomic molecule and predict the pure rotational spectrum of the molecule
- 3) Discuss and explain briefly the principal features of the pure rotational band spectrum of a diatomic molecule. Show in a diagram the allowed rotational energy levels in terms of rotational constant.
- 4) Predict the effect of isotopic substitution on rotation spectra and the information that can be obtained from such a study.
- 5) Describe the difference between the rotational spectra of diatomic molecule with respect to rigid and non-rigid model.
- 6) Explain briefly the factors that determine the intensities of rotational lines for linear molecules.
- 7) Obtain an expression for the moment of inertia of a rigid rotator diatomic spectrum.
- 8) Write the physical meaning of rigid and non-rigid rotators?
- 9) When and why is the rotational motion of a diatomic molecule considered to resemble that of rigid and non-rigid rotator?

- 10) The rotational constant for H^{35}Cl is observed to be 10.5909 cm^{-1} . What is the B value for H^{37}Cl ?
- 11) Explain briefly the factors that determine the intensities of rotational lines for linear molecules.
- 12) Obtain an expression for the moment of inertia of a rigid rotator diatomic spectrum.
- 13) Discuss the principle involved in the determination of bond length using microwave spectrum.
- 14) How does the pure rotational spectrum of a rigid symmetric top molecule differ from that of non-rigid symmetric top? Explain.
- 15) Discuss the rotation spectra of diatomic molecules from the following view points: (i) Region of occurrence (ii) Criteria for absorption of radiation (iii) Rotational energy and selection rules and (iii) Molecular parameters obtained.
- 16) The bond length of HF molecule is 0.0097 nm (a) what is the moment of inertia of the HF molecule? (b) What is the value of rotational constant in joules and in cm^{-1} ? (c) Find the wave numbers of the first four transitions. (d) Mention the spectral region in which these absorption occurs.
- 17) How many revolutions per second does a CO molecule make when $J = 4$? The rotational constant of CO molecule is 1.9313 cm^{-1} .
- 18) The CH and CN bond lengths of the linear molecule HCN are 1.063 \AA and 1.155 \AA respectively. Calculate the moment of inertia I and rotational constant B for HCN and DCN molecule.
- 19) The frequencies of the $J = 1 \rightarrow J = 2$ transition $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ and $^{16}\text{O}^{12}\text{C}^{34}\text{S}$ are $24,325.92\text{ MHz}$ and $23,732.33\text{ MHz}$, respectively. Calculate the C-O and C=S bond lengths.
- 20) The rotational constant for H^{35}Cl is found to be 10.5909 cm^{-1} . What are the values of B for H^{37}Cl and for D^{35}Cl

UNIT 7**Structure**

- 7.0 Objectives of the unit
- 7.1 Introduction
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- 7.3 The absorption laws (Lambert's law)
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- 7.5 Beer's Law
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7.0 Objectives of the unit

After studying this unit you are able to

- Explain the Salient features of molecular electronic spectra.
- Derive the absorption laws.
- Explain the significance of absorption coefficient.
- Explain the theory of molecular absorption.
- Identify the different types of electronic transition.
- Identify the different types of bands formed in absorption spectra.
- Identified the allowed and forbidden transitions.
- Explain the chromophore and auxochrome.

7.1 Introduction

When radiation passes through a transparent material, a portion of the radiation may be absorbed. As a result of energy absorption, atoms or molecules pass from a state of low energy (the initial or ground state) to a state of higher energy (the excited state). The electromagnetic radiation that is absorbed has energy exactly equal to the energy difference between the excited and ground states. In atomic spectra, when electrons of an atom are excited to higher energy states, the radiations that are absorbed in this process appear as 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 molecular electrons.

Electronic spectroscopy involves the promotion of electrons (σ , π , n^* electrons) from the ground state to the higher energy state. For visible and ultra-violet spectrum, electronic excitations occur in the range 200 – 800 nm and involve the promotion of electrons to the higher energy molecular orbitals. Since the energy levels of a molecule are quantised, the energy required to bring about the excitation is a fixed quantity. Thus, the electromagnetic radiation with only a particular value of frequency will be able to cause excitation. If the substance is exposed to radiation of some different values of frequency, energy will not be absorbed and thus, light or radiation will not suffer any loss in intensity. If radiation of a desired or correct frequency is made to fall on the sample of the substance, energy will be absorbed and electrons will be promoted to the higher

energy states. Thus, light radiation on living the sample after absorption will be either less intense or its intensity may be completely lost.

7.2 Salient features of molecular electronic spectra

- (1) It appears in the visible and ultraviolet regions.
- (2) It involves a change in electronic, vibrational and rotational energies of the molecule.
- (3) They are studied both in emission and absorption, and the bands show a fine structure usually more complicated than in vibrational-rotational bands.
- (4) All molecules exhibit electronic spectra. Homonuclear molecules such as H_2 , N_2 , O_2 which neither give rotational nor rotational-vibrational spectra (as they do not possess permanent dipole moment) exhibit electronic spectra. The reason is that the instantaneous dipole moment changes during the redistribution of electronic charge accompany the electronic transition.

7.3 The absorption laws

There are two laws which govern the absorption of light by the molecule. These are

- (i) Lambert's law and
- (ii) Beer's law

Lambert's law It states that '*when a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation*'.

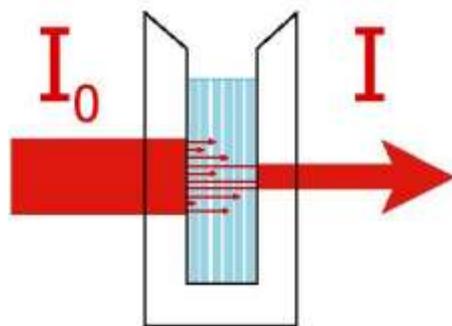


Figure 1: representation of Lambert's law

Mathematically, the law is expressed as

$$-\frac{dI}{dx} = kI$$

Where I = intensity of radiation after passing through a thickness x , of the medium.

dI = infinitesimally small decrease in the intensity of radiation on passing through infinitesimally small thickness, dx of the medium.

$-\frac{dI}{dx}$ = rate of decrease of intensity of radiation with thickness of the absorbing medium.

k = proportionality constant or absorption coefficient. Its value depends upon the nature of the absorbing medium.

Let I_0 be the intensity of radiation before entering the absorbing medium ($x = 0$). Then I , the intensity of radiation after passing through any thickness, say x of the medium can be calculated as,

$$\ln \frac{I}{I_0} = -kx \text{ or } \frac{I}{I_0} = e^{-kx}$$

$$\text{or } I = I_0 e^{-kx}$$

The above Lambert's law equation can also be written by changing the natural logarithm to the base 10.

$$I = I_0 10^{-ax}$$

Where a = extension coefficient of the absorbing medium and is given by, $a = k/2.303$.

7.4 Absorption coefficient

Absorption coefficient is a measure of the rate of decrease in the intensity of electromagnetic radiation as it passes through a given substance or the fraction of incident radiant energy absorbed per unit mass or thickness of an absorber

The absorption coefficient determines how far the light of a particular wavelength can penetrate into a material before it is absorbed. The material with a low absorption coefficient means, the light is poorly absorbed. The absorption coefficient depends on the material and also on the wavelength of light which is being absorbed. The extinction coefficient or absorption coefficient also describes how well a substance scatters and absorbs them radiation. Some substance like glass would have a very low extinction coefficient for visible light as it is hardly absorbed or scattered even through very thick panes of glass, whereas something like wood would have a very high coefficient, since almost all light is scattered and absorbed within a very small distance.

7.5 Beer's Law: This law states that 'when a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the concentration of the solution'.

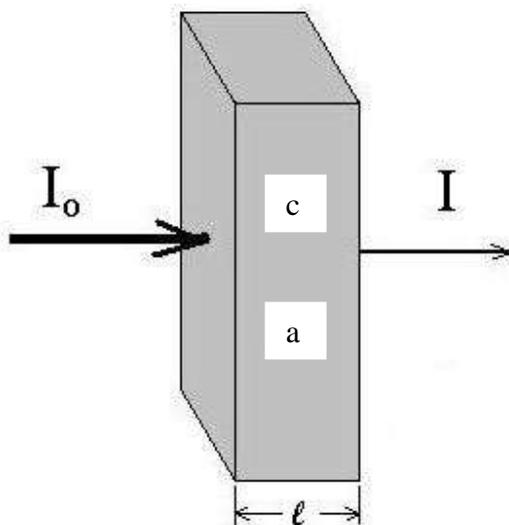


Figure 1: representation of Beer's law.

Mathematically this law is stated as $-\frac{dI}{dx} = k'IC$

where c = concentration of the solution in mol lit^{-1} . k' = molar absorption coefficient and its value depends on the nature of the absorbing substance.

Suppose I_0 be the intensity of the radiation before entering the absorbing solution (when $x = 0$), then the intensity of radiation, I after passing through the thickness x , of the medium can be calculated.

$$\text{Therefore, } I = I_0 e^{-k'cx}$$

The above equation can also be written by changing the nature of logarithm to the base 10.

Here $k'/2.303 = a'$, where a' = molar extension coefficient of the absorbing solution.

7.6 Theory of Molecular Absorption

Let us consider the case of a diatomic molecule. If one of its atoms is excited then the molecule is said to be excited. For each of the electronic states, there is different dependence of the molecule's energy on its internuclear separation. That is, each electronic state of the molecule has

a different potential energy curve characterized by a minimum. When a transition of the molecule from one electronic state to the other takes place, the emitted or absorbed radiation falls in the visible or ultraviolet region of the electromagnetic spectrum (because the order of energy separation between different electronic states is from 1 to 10 eV). The electronic transition is accompanied by a number of transitions involving a vibrational level of the upper and a vibrational level of the lower electronic state, called vibration coarse (gross) structure of electronic band system. Further, each vibrational transition is, in turn, accompanied by a number of transitions involving a rotational level of the upper and a rotational level of the lower vibrational state. This is called rotational fine structure of electronic band system.

Thus a single electronic transition in a molecule gives rise to a band system. The bands of the system which correspond to the same upper vibrational state (v') but different lower vibrational levels (v'') are said to form a v'' progression while the bands which correspond to same lower vibrational level (v'') but different upper vibrational levels (v') form a v' - progression.

To a close approximation, the total energy E of the molecule in a given quantum state may be supposed as made up of the electronic energy, E_e , the vibrational energy E_v and the rotational energy E_r as shown in **Fig 3**.

$$\text{Thus, } E = E_e + E_v + E_r$$

In the form of energy changes, we write as

$$\Delta E = \Delta E_e + \Delta E_v + \Delta E_r \text{ ergs}$$

$$\frac{\Delta E}{hc} = \frac{\Delta E_e}{hc} + \frac{\Delta E_v}{hc} + \frac{\Delta E_r}{hc} \text{ cm}^{-1}$$

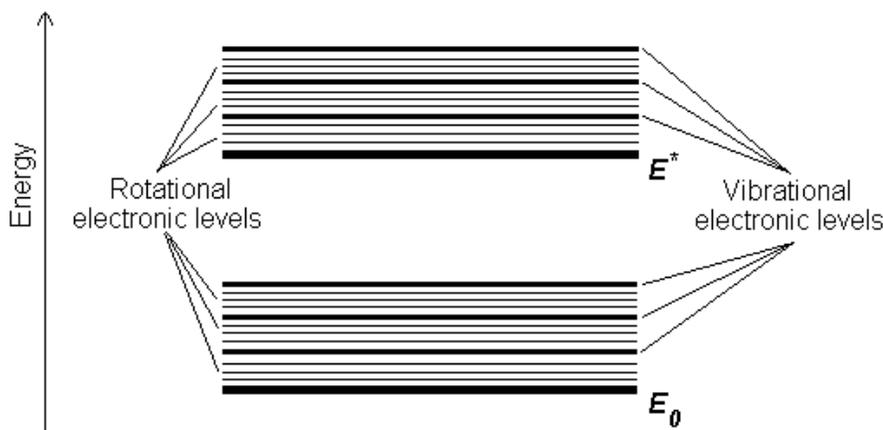


Figure 3: molecular energy levels on its internuclear separation.

7.7 Franck-Condon Principle

The probability of transition between two given vibrational levels of two electronic states A and B is determined by Franck-Condon Principle. The principle, as discussed below, suggests that:

- (i) *The observed transitions between two states should start from extreme positions of vibrational levels.*
- (ii) *They should be represented by vertical lines.*

We shall now discuss how the above two predictions result from the Frank-Condon Principle. The principle stems from the idea that electrons move and rearrange themselves much faster than the nuclei of molecules. For example, if one calculates the time for an electron to circle a hydrogen nucleus (10^{-16} sec) then it comes out to be a thousand times shorter than the typical period of vibration of molecule (10^{-13} sec). It means an electronic configuration will change in a time so short that the nuclei will not change their positions. As the internuclear distance of a vibrating molecule in the course of transition between two electronic states does not change appreciably, such a transition should then be represented by a vertical line **Fig. 4**.

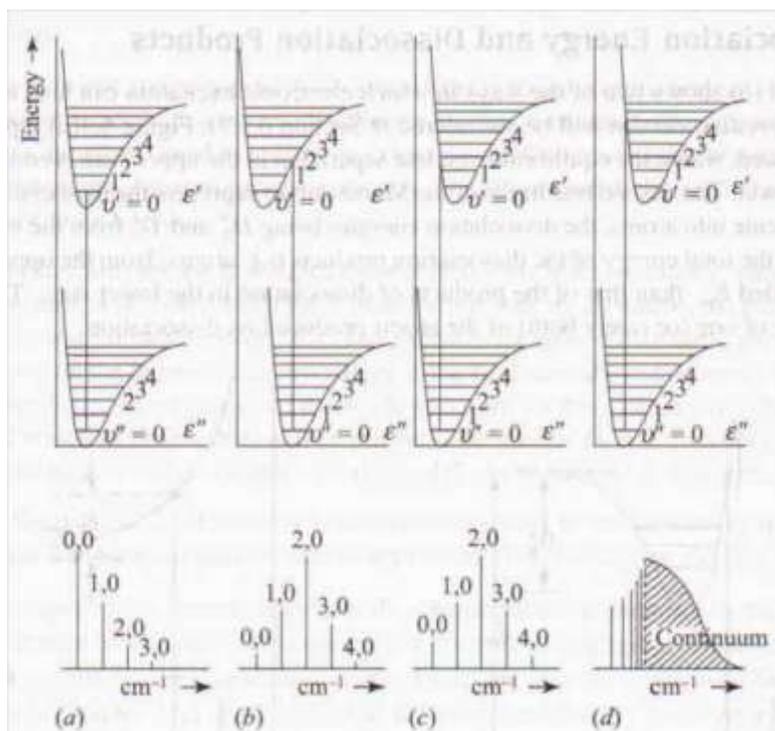


Figure 4: The operation of the Frank-Condon principle for a) internuclear distances equal in the upper and lower states, b) upper state internuclear distance is little less than that in the lower state, c) upper state distance is little greater than in the lower and d) upper state distance considerably greater

Further, Frank-Condon principle states that transitions from one state to another are most probable when nuclei are in their mean positions, for example, at L and N for the level LN. This is because the nuclei spend at these positions longest time on account of vibrational kinetic energy being zero there and also quantum mechanically square of the vibrational eigen function is greatest at the extreme positions implying that the probability of finding the nuclei is greatest there. However, for the lowest vibrational energy level ($v = 0$), quantum mechanics predicts that the most probable position for the nuclei to remain in, corresponds to equilibrium position (i.e., minima of the curve, r_e). Thus the most probable internuclear distance for the vibrational levels other than $v = 0$, corresponds to the extreme positions and to mid-position for $v = 0$. It means transitions would start from extreme positions for levels other than $v = 0$ as for the latter they would start from the mid-point. Since these transitions are most probable, the corresponding vibrational bands will be most intense.

7.8 Origin of UV-Visible spectroscopy

UV-visible spectra originate from electronic transitions within a molecule. These transitions involving promotion of valence electrons from the ground state to higher-energy state (excited state) are called electronic excitations and are caused by the absorption of radiation energy in the UV-Visible regions of the electromagnetic spectrum. Since various energy levels of molecules are quantized, a particular electronic transition occurs only by the absorption of specific wavelength of radiation corresponding to the required quantum of energy.

7.9 Types of Electronic Transitions:

According to the molecular orbital theory, when a molecule is excited by the absorption of energy (UV or visible light), its electrons are promoted from a bonding to an antibonding orbital.

- (i) The antibonding orbital which is associated with the excitation of σ electron is called σ^* antibonding orbital. So σ to σ^* transition takes place when a (sigma) electron is promoted to antibonding (σ^*) orbital. It is represented as $\sigma \rightarrow \sigma^*$ transition.
- (ii) When a non-bonding electron (n) gets promoted to an antibonding sigma orbital (σ^*), then it represents $n \rightarrow \sigma^*$ transition.
- (iii) Similarly $\pi \rightarrow \pi^*$ transition represents the promotion of π electrons to an antibonding π orbital, i.e., π^* orbital. Similarly, when an n -electron (non-bonding) is promoted to antibonding π orbital, it represents $n \rightarrow \pi^*$ transition. The energy required for various transitions obey the following order: $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$ (**Fig 5 a and b**).

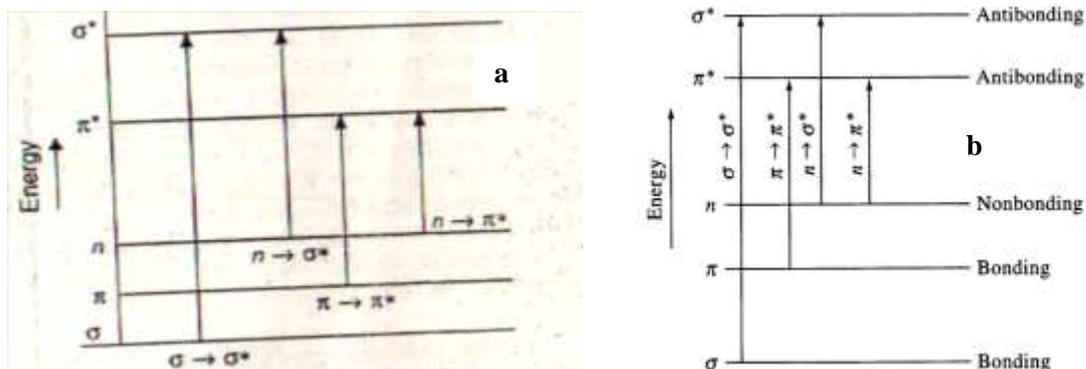


Figure 5: a) Electronic excitation energies.

b) Electronic excitation energy levels.

(a) $\sigma \rightarrow \sigma^*$ transition:

It is a high energy process since σ bonds are in general very strong (Fig 6). The organic compounds in which all the valence shell electrons are involved in the formation of sigma bonds do not show absorption in the normal UV region (180 – 400 nm). For saturated hydrocarbons like methane, propane etc., absorption occurs near 150 nm.

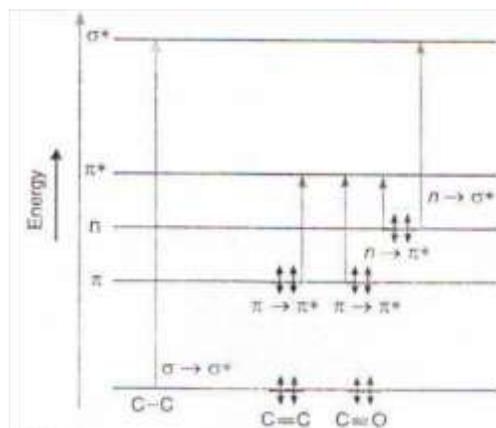


Figure 6: Various transitions involved in Electronic spectroscopy.

(b) $n \rightarrow \pi^*$ transition:

This type of transition takes place in saturated compounds containing one hetero atom with unshared pair of electrons (n electrons) (Fig 6). Some compounds undergoing this type of transitions are saturated halides, alcohols, ethers, aldehydes, ketones, amines etc. Such transitions require comparatively less energy than that required for $\sigma \rightarrow \sigma^*$ transitions. Water absorbs at 167 nm, methyl alcohol at 174 nm and methyl chloride absorbs at 169 nm. In

saturated alkyl halides, the energy required for such a transition decreases with the increase in the size of the halogen atom (or decrease in the electronegativity of the atom).

Let us compare $n \rightarrow \sigma^*$ transition in methyl chloride and methyl iodide. Due to the greater electronegativity of chlorine atom, the n electrons on chlorine atom are comparatively difficult to excite. The absorption maximum for methyl chloride is 172-175 nm whereas that for methyl iodide is 258 nm as 'n' electrons on iodine atom are loosely bound. Since this transition is more probable in case of methyl iodide, its molar extinction coefficient is also higher compared to methyl chloride. $n \rightarrow \sigma^*$ transitions are very sensitive to hydrogen bonding. Alcohols as well as amines form hydrogen bonding with the solvent molecules. Such association occurs due to the presence of non-bonding electrons on the hetero atom and thus, transition requires greater energy.

(c) $\pi \rightarrow \pi^*$ transitions:

This type of transition occurs in the unsaturated centres of the molecules, i.e., in compounds containing double or triple bonds and also in aromatics. The excitation of π - electrons requires smaller energy and hence, transition of this type occurs at longer wavelength (**Fig 6**). A π electron of a double bond is excited to π^* - orbital. For example, alkenes, alkynes, carbonyl compounds, cyanides, azo-compounds etc., show $\pi \rightarrow \pi^*$ transition.

Consider an alkene: This transition requires still lesser energy as compared to $n \rightarrow \sigma^*$ transition and therefore, absorption occurs at longer wavelengths. Absorption usually occurs within the region of ordinary ultra-violet spectrophotometer. In unconjugated alkenes, absorption bands appear around 170 – 190 nm. In carbonyl compounds, the band due to $\pi \rightarrow \pi^*$ transition appears around 180 nm and is most intense, i.e., the value of extinction coefficient is high. The introduction of alkyl group to olefinic linkage produces a bathochromic shift of the order of 3 to 5 nm per alkyl group. The shift depends upon the type of the alkyl group and the stereochemistry about the double bond.

(d) $n \rightarrow \pi^*$ transition:

In this type of transition, an electron of unshared electron pair on hetero atom gets excited to π^* antibonding orbital. This type of transition requires least amount of energy out of all the transitions discussed above and hence occurs at longer wavelengths (**Fig 6**).

Saturated aldehydes show both the types of transitions, i.e., low energy $n \rightarrow \pi^*$ and high energy $\pi \rightarrow \pi^*$ occurring around 290 nm and 180 nm, respectively. Absorption occurs at lower wave

length is usually intense. In simple cases, it is quite easy to tell whether the transition is $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ since the extension coefficient for the former is quite low as compared to that of the latter. The exact electronic structure of the molecule in the excited state (by the absorption of UV or visible light) is not known but the electronic transition involves the redistribution of electrons within the molecule.

7.10 Formation of absorption bands:

The radiation energy passed through a sample is sufficient to induce various electronic transitions as well as transitions in accompanying vibrational and rotational energy levels (**Fig 7a**). However, these transitions have very small energy differences, but the energy required to induce an electronic transition is higher than that required to cause transition in the accompanying vibrational and rotational energy levels. Thus, the electronic absorption is superimposed upon the accompanying vibrational and rotational absorptions resulting in the formation of broad bands (**Fig 7b**). More clearly not only a single but a large number of every close wavelength are absorbed and the closeness of the resulting discrete spectral lines causes them to give broad absorption bands in case of complex molecule.

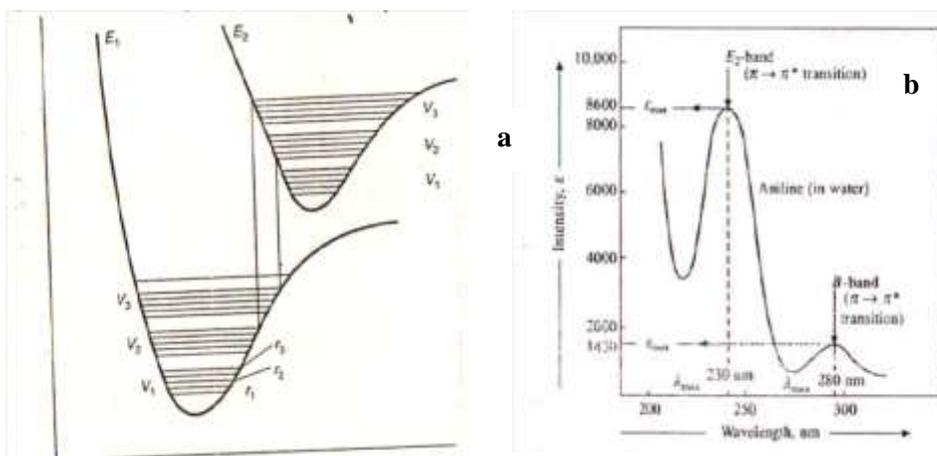


Figure 7: a) Energy curve for diatomic molecule, b) UV absorption spectrum of aniline

7.11 Designation of absorption bands

UV-visible absorption bands may be designated by the type of electronic transition from which they originate eg. $\sigma \rightarrow \sigma^*$ band $\pi \rightarrow \pi^*$ band etc.....The following letters are used to designate the absorption bands because more than one band may arise due to the same type of electronic transition.

K-Bands (Conjugated; German: Konjugierte): These bands originate from $\pi \rightarrow \pi^*$ transition in compounds having a π - π conjugated system (a system having at least two multiple bonds separated by one single bond) e.g. 1,3-butadiene.

R-Bands (Radical-like; German: Radikalartig): these bands originate from $n \rightarrow \pi^*$ transitions of a single chromophoric group. e.g. Carbonyl or nitro group.

B-Bands (Benzenoid bands): These bands originate from $\pi \rightarrow \pi^*$ transitions in aromatic or heteroaromatic compounds. For example Benzene, acetophenone

E-Bands (Ethylenic bands): similar to B-bands, these are characteristics of aromatic and heteroaromatic compounds and originate from $\pi \rightarrow \pi^*$ transitions of the ethylenic bond present in the aromatic ring. E-band which appears at a shorter wavelength and is usually more intense is called E_1 -band. The low intensity band of the same compound appearing at longer wavelength is called E_2 -band ((**Fig 7b**)).

7.13 Transition probability: allowed and forbidden transitions

When a molecule is exposed to UV radiation, it may or may not absorb the radiation, i.e., it may or may not undergo electronic excitation. The molar absorptivity at maximum absorption is given by the expression

$$\epsilon_{\max} = 0.87 \times 10^{20} \cdot p \cdot a$$

Where 'p' is the transition probability with values from 0 to 1 and 'a' is target area of the absorbing system, i.e., chromophore.

Hence there is a direct relationship between the area of the chromophore and the absorbing intensity ϵ_{\max} . In addition, there are other factors also govern the transition probability.

Depending upon the symmetry and value of ϵ_{\max} the transition can be classified as

- a) Allowed transition and
- b) Forbidden transition

a) Allowed transition

The transition with value of ϵ_{\max} (extinction coefficient) more than 10^4 are usually called as allowed transition. They generally arise due to $\pi \rightarrow \pi^*$ transition (The type of transition is a function of symmetry which in turn depends on molecular vibrations)

Ex. In 1,3-butadiene, the absorption at 217nm, ϵ_{\max} 21,000 results from the allowed transition.

b) Forbidden transition

The transition with value of ϵ_{\max} (extinction coefficient) less than 10^4 are usually called as allowed transition. Forbidden transitions are generally caused by $n \rightarrow \pi^*$ transition.

Ex. In carbonyl compounds the absorption near 300nm with ϵ_{\max} values 10-100 results from the forbidden transition.

7.14 Symmetry restrictions in electronic transitions

The allowed or forbidden transition is related with the geometries of the lower and higher energy molecular orbitals and also on the symmetry of the molecule. The symmetrical molecules have more restrictions on their electronic transitions than the less symmetrical molecules. For example, benzene is a highly symmetrical molecule and has simple electronic absorption spectra. Between symmetrical and totally unsymmetrical and totally unsymmetrical molecules a large number of organic compounds fall which absorb light in the ultra-violet-visible region. To decide whether the transition is allowed or forbidden for such molecules, it is important to consider

- 1) The geometry of the molecular orbital in the ground state.
- 2) The geometry of the molecular orbital in the excited state and
- 3) The orientation of the electric dipole of the incident light that might induce the transition.

The transition will be an allowed transition if the above three factors have an appropriate symmetry relationship.

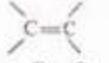
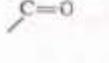
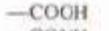
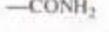
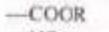
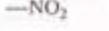
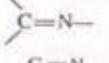
7.15 Chromophore

A covalently unsaturated group responsible for absorption in the UV or visible region is known as a chromophore.

Ex, $C=C$, $C\equiv C$, $C=O$, $C\equiv N$, $N=N$, NO_2 etc....., chromophore group may or may not impart colour to a compound, it depends on whether the chromophore group absorbs radiations in the visible or UV region, If a chromophore group absorb radiation in the visible region only then it appears coloured.

Chromophore like $C=C$, $C\equiv C$ having π electrons undergo $\pi \rightarrow \pi^*$ transitions and those having both π and non-bonding electrons eg. $C=O$, $C\equiv N$, $N=N$ undergo both $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions. Since the wavelength and intensity of absorption depends on a number of factors, there are no of set rules for the identification of a chromophore. Characteristics of some chromophores commonly present in organic molecules are listed in below Table 1.

Table -1. Characteristics of some common unconjugated chromophore.

Chromophore	Example	λ_{\max} (nm)	ϵ_{\max}	Transition
	Ethylene	171	15,530	$\pi \rightarrow \pi^*$
	Acetylene	150	-10,000	$\pi \rightarrow \pi^*$
		173	6000	$\pi \rightarrow \pi^*$
	Acetaldehyde	160	20,000	$n \rightarrow \sigma^*$
		180	10,000	$\pi \rightarrow \pi^*$
		290	17	$n \rightarrow \pi^*$
	Acetone	166	16,000	$n \rightarrow \sigma^*$
		188	900	$\pi \rightarrow \pi^*$
		279	15	$n \rightarrow \pi^*$
	Acetic acid	204	60	$n \rightarrow \pi^*$
	Acetamide	178	9500	$\pi \rightarrow \pi^*$
		220	63	$n \rightarrow \pi^*$
	Ethyl acetate	211	57	$n \rightarrow \pi^*$
	Nitromethane	201	5000	$\pi \rightarrow \pi^*$
		274	17	$n \rightarrow \pi^*$
	Acetoxime	190	5000	$n \rightarrow \pi^*$
	Acetonitrile	167	Weak	$\pi \rightarrow \pi^*$
	Azomethane	338	4	$n \rightarrow \pi^*$

7.16 Auxochrome

A covalently saturated group which itself does not act as a chromophore, but when attached to a chromophore, changes both the wavelength and the intensity of the absorption maximum is known as auxochrome. Eg. NH_2 , OH, SH, Halogens etc....,

Auxochromes generally increase the value of λ_{\max} and ϵ_{\max} by extending conjugation through resonance and these are called colour enhancing groups. Ex, benzene shows λ_{\max} 256nm, ϵ_{\max} 200, whereas aniline shows λ_{\max} 280nm, ϵ_{\max} 1430 (both increased). Hence NH_2 group is an auxochrome.

7.17 Summary of the unit

Many molecules absorb ultraviolet or visible light. The absorbance of a solution increases as attenuation of the beam increases. Absorbance is directly proportional to the path length, b , and the concentration, c , of the absorbing species. This was explained by Beer's Law, which states that $A = ebc$, where e is a constant of proportionality, called the absorptivity. Different molecules absorb radiation of different wavelengths. An absorption spectrum will show a number of absorption bands corresponding to structural groups within the molecule.

Ultraviolet and visible (UV-Vis) spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Ultraviolet and

visible light are energetic enough to promote outer electrons to higher energy levels. The UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert Law.

7.18 Key words

Absorption coefficient; Lambert's law; Beer's Law; Franck-Condon Principle; Allowed transition; Forbidden transition; Chromophore; Auxochrome

7.19 References for further study

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- 2) Elementary Organic spectroscopy: Principles and Chemical Applications by Y. R. Sharma, *S.Chand and Company Ltd.* **2005**.
- 3) UV/Vis Spectroscopy by ErnÖ Pretsch, Philippe Bühlmann, Martin Badertscher, *Springer Berlin Heidelberg*, **2009**.
- 4) Atomic and Molecular Spectroscopy by Gupta, Mool Chand, *New Age International*, **2007**.
- 5) Basic Atomic and Molecular Spectroscopy Volume 11 of tutorial chemistry texts by J. M. Hollas, *Royal Society of Chemistry*, **2002**.

7.20 Questions for self study

- 1) What is electronic spectroscopy?
- 2) Discuss various types of electronic transitions
- 3) Why is absorption bands formed in UV spectrum is broad?
- 4) Arrange all the expected electronic transition for 2-pentanone in order of their increasing energy?
- 5) What are absorption laws?
- 6) What is meant by absorption coefficient? Discuss its significance.
- 7) Write short note on theory of molecular absorption.
- 8) Write a note on K-band, R-band, E-band and B-band
- 9) Write a note on Franck-Condon principle.
- 10) What is meant by a) Allowed transition b) forbidden transition.
- 11) Discuss in detail about symmetry restrictions in electronic transition.
- 12) What are chromophore give three examples?
- 13) What are auxochrome give three examples?

UNIT 8**Structure**

- 8.0 Objectives of the unit
- 8.1 Introduction
- 8.2 Solvent Effect on Spectral Lines
- 8.3 Absorption and intensity shifts
 - Bothochromic effect (shift) or Red shift
 - Hypsochromic effect (shift) or Blue shift
 - Hyperchromic effect
 - Hypochromic effect
- 8.4 Conjugated system and transition energies
- 8.5 Woodward-Fieser Rules for Calculating Absorption Maximum in Dienes
- 8.6 Homoannular dienes
- 8.7 Heteroannular dienes
- 8.8 Exocyclic conjugated double bonds
- 8.9 Woodward-Fieser Rules for Calculating Absorption Maximum α , β -unsaturated Carbonyl Compounds
- 8.10 Rules for Calculating Absorption Maximum for Derivatives of Acyl Benzenes
- 8.11 Summary of the unit
- 8.12 Key words
- 8.13 References for the further study
- 8.14 Question for self study

8.0 Objectives of the unit

After studying this unit you are able to

- Explain solvent effect on absorption spectral lines.
- Explain absorption and intensity shift upon changing solvent.
- Recognize red shift and blue shift.
- Identify homoannular and heteroannular double bonds.
- Calculate the λ_{\max} for different organic compounds.

8.1 Introduction

Solvents play an important role in UV spectra. Compound peak could be obscured by the solvent peak. So a most suitable solvent is one that does not itself get absorbed in the region under investigation. A solvent should be transparent in a particular region. A dilute solution of sample is always prepared for analysis. It is clear that polar solvents give rise to broad bands, non-polar solvents show more resolution. Completely removing the solvent gives the best resolution. This is due to solvent-solute interaction. The solvent can interact with the solute in its ground state or excited state through intermolecular bonding. Polar solvent like water has the ability of hydrogen bonding with the solute if the solute has a hydrogen bonding component, or simply through induced dipole-dipole interactions. The non-polar solvents can interact through polarizability. This is due to the solvent's tendency to align its dipole moment with the dipole moment of the solute. Depending on the interaction, this can cause the ground state and the excited state of the solute to increase or decrease, thus changing the frequency of the absorbed radiation. Due to this, there are many different transition energies that become average together in the spectra. This causes peak-broadening. The effects of peak broadening are most severe for polar solvent, less so for non-polar solvents, and absent when the solute is in vapor phase.

8.2 Solvent Effect on Spectral Lines

A most suitable solvent is one which does not itself absorb in the region under investigation. A dilute solution of the sample is always prepared for the spectral analysis. Most commonly used solvent is 95 % ethanol. Ethanol is a best solvent as it is cheap and is transparent down to 210 nm. Commercial ethanol should not be used as it contains benzene which absorbs strongly in the ultraviolet region. Some other solvents which are transparent above 210 nm are n-hexane, methyl alcohol, cyclohexane, acetonitrile, diethyl ether etc. Some solvents with their upper wavelength limit of absorption are given in **Table 1**.

Table 1: Solvents used in UV-spectroscopy

Solvent	Upper wave length limit (nm)
Ethanol	210
Hexane	210
Methanol	210
Cyclohexane	210
Diethyl ether	210
Water	205
Benzene	280
Chloroform	245
THF (tetrahydrofuran)	220
Carbon tetrachloride	265

Hexane and other hydrocarbons can be used as these are less polar and have least interactions with the molecules under investigation. For ultra-violet spectroscopy, ethanol, water and cyclohexane serve the purpose best.

The position and the intensity of absorption maximum are shifted for a particular chromophore by changing the polarity of the solvent. By increasing the polarity of the solvent, compounds like dienes and conjugated hydrocarbons do not experience any appreciable shift. Thus, in general, the absorption maximum for the non-polar compounds is the same in alcohol (polar) as well as in hexane (non-polar). The absorption maximum for the polar compounds is usually shifted with the change in polarity of the solvents. α , β - unsaturated carbonyl compounds show two different shifts.

(i) $n \rightarrow \pi^*$ transition (less intense): In such a case, the absorption band moves to shorter wavelength by increasing the polarity of the solvent. In $n \rightarrow \pi^*$ transition, the ground state is more polar as compared to the excited state. The hydrogen bonding with solvent molecules takes place to lesser extent with the carbonyl group in the excited state. For example, absorption maximum of acetone is at 279 nm in hexane as compared to 264 nm in water.

(ii) $\pi \rightarrow \pi^*$ transition (intense): For such a case, the absorption band moves to long wavelength by increasing the polarity of the solvent. The dipole interactions with the solvent molecules lower the energy of the excited state more than that of the ground state. Thus, the value of absorption maximum in ethanol will be greater than that observed in hexane.

In short, π^* orbitals are more stabilised by hydrogen bonding with polar solvents like water and alcohol. It is due to greater polarity of π^* orbital compared to π orbital. Thus, small energy will

be required for such a transition and absorption shows a red shift. $n \rightarrow \sigma^*$ transitions are also very sensitive to hydrogen bonding. Alcohols as well as amines form hydrogen bonding with the solvent molecules. Such associations occur due to the presence of non-bonding electrons on the hetero atom and thus transition requires greater energy. In general, if a group (carbonyl) is more polar in the ground state than in the excited state, then increasing polarity of the solvent stabilizes the non-bonding electron in the ground state due to hydrogen bonding. Thus, absorption is shifted to lower wavelength. If a group is more polar in the excited state, then absorption is shifted to longer wavelength with increase in polarity of the solvent which helps in stabilizing the non-bonding electrons in the excited state. *It has been found that increase in polarity of the solvent generally shifts $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ bands to shorter wavelengths and $\pi \rightarrow \pi^*$ bands to longer wavelengths (Fig 1).*

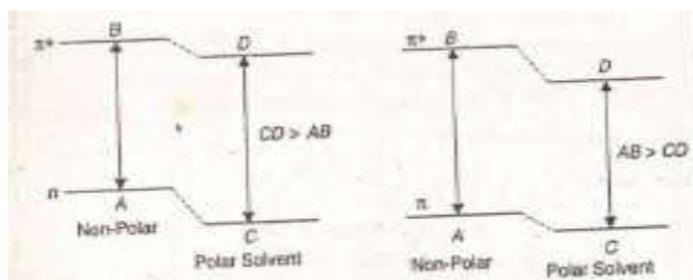


Figure 1: Absorption shift with change in polarity of the solvent.

8.3 Absorption and intensity shifts

The shift of absorption position and absorption intensity due to change, presence or removal of chromophore, auxochrome and/or solvent is denoted by particular terminology in absorption spectroscopy and they are

Bothochromic effect (shift) or Red shift

The shift of an absorption maximum to a longer wavelength due to the presence of an auxochrome or solvent effect is called a bathochromic shift or red shift.

For example benzene shows λ_{\max} 256 nm and aniline shows λ_{\max} 280 nm. Thus, there is a bathochromic shift of 24 nm in the λ_{\max} of benzene due to presence of the auxochrome, NH_2 . Similarly bathochromic shift of $n \rightarrow \pi^*$ band is observed in carbonyl compounds on decreasing solvent polarity. Eg. λ_{\max} of acetone is at 264.5 nm in water is shifted to 279 nm in hexane.

Hypsochromic effect (shift) or Blue shift

The shift of an absorption maximum to a shorter wavelength is called hypsochromic or blue shift. This is caused by the removal of conjugation or change in solvent polarity. For example, aniline shows λ_{\max} 280 nm whereas anilinium ion (acidic solution of aniline) shows λ_{\max} 254 nm. This hypsochromic shift is due to the removal of $n \rightarrow \pi^*$ conjugation of the lone pair of electrons of the nitrogen atom of aniline. Protonated aniline has no lone pair electrons for conjugation with benzene ring. Similarly there is a hypsochromic shift of 10-20 nm in the λ_{\max} of $\pi \rightarrow \pi^*$ bands of carbonyl compounds on going from the solvent ethanol to hexane.

Hyperchromic effect

An effect which leads to an increase in absorption position intensity i.e., ϵ_{\max} is called hyperchromic effect. The introduction of auxochrome usually causes hyperchromic shift. For example, benzene shows B-band at 256 nm with ϵ_{\max} 200, whereas aniline shows B-band at 280 nm with ϵ_{\max} 1430. The increase of 1230 in the value ϵ_{\max} of aniline compared to that of benzene is due to the hyperchromic effect of the auxochrome NH_2 .

Hypochromic effect

An effect which leads to a decrease in absorption intensity ϵ_{\max} is called hypochromic effect. This is caused by the introduction of a group which distorts the chromophore. For example, biphenyl shows λ_{\max} 252 nm with ϵ_{\max} 19,000, whereas 2, 2'-dimethylbiphenyl shows λ_{\max} 270 nm with ϵ_{\max} 800, the decrease of 18,200 in the value of ϵ_{\max} of 2,2'-dimethylbiphenyl is due to the hypochromic effect of the methyl groups which distort the chromophore by forcing the ring out of coplanarity resulting in the loss of conjugation.

All the effects discussed above are summarized in **Fig. 2**.

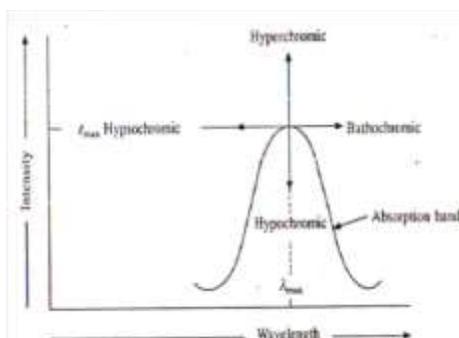


Figure 2: Shift in absorption position and

8.4 Conjugated system and transition energies

When two or more chromophoric groups are conjugated, the absorption maximum is shifted to a longer wavelength (lower energy) and usually to a greater intensity compared to the simple unconjugated chromophore. This is because the conjugation reduces the energy gap between electronic transition levels i.e., conjugation lowers the energy required for electronic transition. We know that as the energy of electronic transitions decreases, usually their probability increases and so ϵ_{\max} also increases.

8.5 Woodward-Fieser Rules for Calculating Absorption Maximum in Dienes

Longer the conjugated system, greater is the wave-length of absorption maximum. The intensity of absorption (ϵ_{\max}) also increases with the increase in the length of the chromophore. The conjugated polyene system appears coloured to the naked eye if there are more than five bonds in conjugation and absorption occurs around or above 400 nm (visible region). The presence of alkyl group on the double bond also causes bathochromic shift.

Woodward formulated a set of empirical rules for calculating or predicting the λ_{\max} in case of conjugated acyclic and six membered ring dienes. These rules were later modified by Fieser and Scoot in 1948 on the basis of wide experience with dienes and trienes and are called Woodward-Fieser rules. According to these rules, each type of diene has a certain fixed basic value and the value of absorption maximum (λ_{\max}^*) depends upon

- (i) The number of alkyl substituents or ring residues on the double bond.
- (ii) The number of double bonds with extend conjugation and
- (iii) The presence of polar group such as -Cl, -Br, -OR, -SR etc.

The ring residue is a C-C bond, not a part of the conjugated system but attached to any one of the carbon atoms of the conjugated polyene system. The various rules for calculating the absorption maximum in case of dienes and trienes are summarised in the **Table 2**.

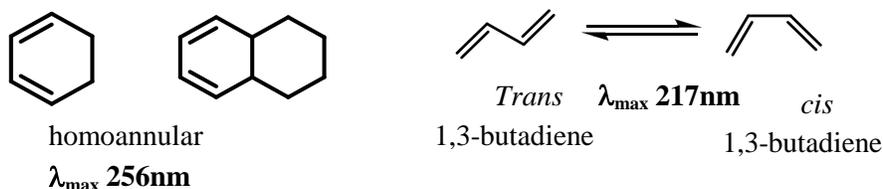
Table 2: Conjugated dienes and trienes (solvent: Ethanol; Transition involved: $\pi \rightarrow \pi^*$)

Parent value for Butadiene system or acyclic conjugated diene	217 nm
Acyclic Triene	245 nm
Homoannular conjugated diene	253 nm
Heteroannular conjugated diene	215 nm
Increment of each substituent	
Alkyl substituent or ring residue	5 nm
Exocyclic double bond	5 nm

Double bond extending conjugation	30 nm
Auxochrome	
-OR	+ 6 nm
-SR	+ 30 nm
-Cl, -Br	+ 5 nm
-NR ₂	+ 60 nm
OCOCH ₃	0 nm

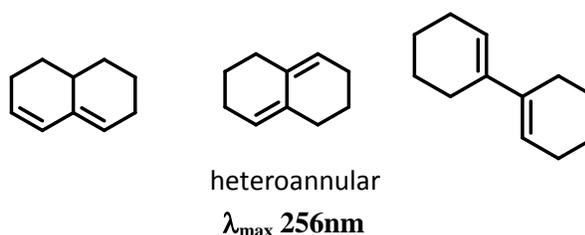
8.6 Homoannular dienes

In homoannular dienes, conjugated double bonds are present in the same ring and having cis configuration. The cis configuration causes strain which raises the ground state energy level of the molecule leaving the high energy excited state relatively unchanged. Thus, the transition energy is lowered resulting in the shift of absorption position to a longer wavelength. Acyclic dienes exist mostly in the stainless trans configuration which relatively lower ground state energy level. Thus, their absorptions appear at shorter wavelengths. Hence 1,3-cyclohexadiene shows λ_{\max} 256 nm, where as 1,3-butadiene shows λ_{\max} 217 nm. Also due to the shorter distance between the two ends of chromophore, cis-dienes give lower ϵ_{\max} (~10,000) than that of the trans diene (~20,000).



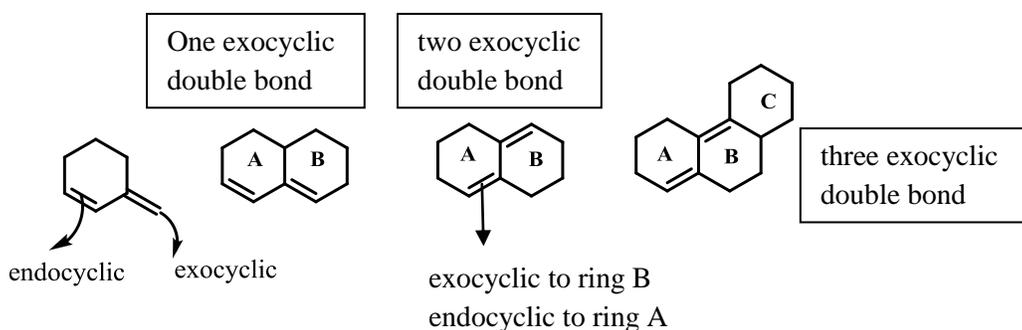
8.7 Heteroannular dienes

In heteroannular dienes, conjugated bonds are not in the same ring and these have trans configuration



8.8 Exocyclic conjugated double bonds

The carbon-carbon double bonds projecting outside a ring called exocyclic double bonds.

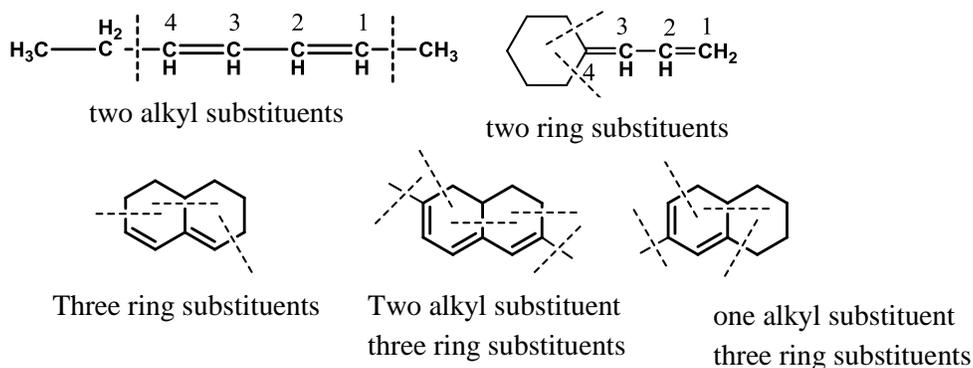


Note that the same double bond may be exocyclic to one ring, while endocyclic to the other and sometimes the same double bond may be exocyclic to two rings simultaneously.

8.9 Alkyl substituents and ring residues:

Only the alkyl substituents and ring residues attached to the carbon atoms constituting the conjugated system of the compound are taken into account.

Following examples indicating such carbon atoms by numbers and the alkyl substituents and ring residues by dotted lines.



In compounds containing both homoannular and heteroannular diene systems, the calculations are based on the longer wavelength i.e, homoannular diene system.

The calculated and observed values of λ_{\max} usually match within ± 5 nm. The following examples are illustrated using above rules.

(1) Calculate the absorption maximum in the ultra-violet spectrum of 2, 4-Hexadiene.

Solution: The basic unit in 2, 4-hexadiene is butadiene. There are two alkyl substituents (one each double bond) on it, thus,



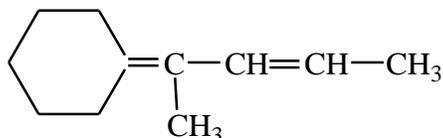
$$\text{Basic value} = 217 \text{ nm}$$

$$2\text{-alkyl substituent} (2 \times 5) = 10 \text{ nm}$$

Calculated value = 227 nm

Observed value is also found to be 227 nm

- (2) Calculate the absorption maximum in the UV spectrum of



Solution: It is a butadiene system. There are two alkyl substituents and two ring residues on the double bonds. Moreover, there is an exo-cyclic double bond.

The values of absorption maximum are calculated as follows:

Basic value = 217 nm

2-alkyl substituent (2 x 5) = 10 nm

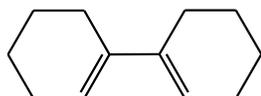
2-ring residues (2 x 5) = 10 nm

1-Exocyclic double bond = 5 nm

Calculated value = 242 nm

The observed value is also found to be 242 nm

- (3) Calculate λ_{\max} for



Solution: It is an example for heteroannular diene and there are four ring residues on the double bond, thus,

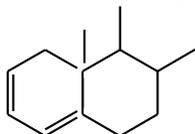
Basic value = 215 nm

Four ring residues (4 x 5) = 20 nm

Calculated value = 235 nm

The observed value is also found to be 234 nm.

- (4) Calculate the absorption maximum of the compound in ethanol



Solution: It is an example for homoannular conjugated diene and there are three ring residues on it. Moreover, it contains an exocyclic double bond in it, thus,

Basic value = 253 nm

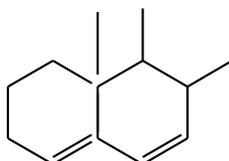
3 – Ring residues (3 x 5) = 15 nm

1 – exocyclic double bond = 5 nm

Calculated value = 273 nm

Observed value = 274 nm

(5) Calculate the value of absorption maximum of the compound in ethanol



Solution: It is a homodiene system. There are five ring residues on the double bonds, one exocyclic bond and also two double bonds with extended conjugation.

Basic value = 253 nm

2-double bond extended conjugation (2 x 30) = 60 nm

5- ring residues (5 x 5) = 25 nm

1-exocyclic double bond (1 x 5) = 5 nm

Calculated value = 343 nm

Observed value = 345 nm

8.9 Woodward-Fieser Rules for Calculating Absorption Maximum α , β -unsaturated Carbonyl Compounds

Woodward and Fieser framed certain empirical rules for estimating the absorption maximum α , β -unsaturated carbonyl compounds. The rules were later modified by Scott, and are as follows:

(a) The basic value of α , β -unsaturated ketone is taken as 215 nm. The α , β -unsaturated ketone may be a cyclic or six membered.

For a compound, = CH—COX, basic value is 215 nm, if X is an alkyl group. If X = H, basic value becomes 207 nm. The basic value is 193 nm if X is OH or OR.

(b) If the double bond and the carbonyl group are contained in the five membered ring (cyclopentanone), then for such an β -unsaturated ketone, the basic value becomes 202 nm.

The structural increments for estimating λ_{\max} for a given α , β -unsaturated carbonyl compound are as follows :

(i) For each exocyclic double bond + 5 nm

(ii) For each double bond endocyclic in five or seven membered

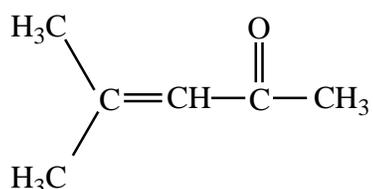
- ring except cyclo-pent-2 enone + 5 nm
- (iii) For each alkyl substituent or ring residue at the α -position + 10 nm
- β - position + 12 nm
- γ - or δ - or higher position + 18 nm
- (iv) For each double bond extending conjugation + 30 nm
- (v) For a homoannular conjugated diene + 39 nm
- (vi) Increments for various auxochromes in the various α -, β -, γ - etc. positions are given in

Table 3.**Table 3:** Chromospheres increments in carbonyl compounds

Chromophore	Increments in nm for positions w r t the C=O groups			
	α -	β -	γ -	δ -
-OH	+ 35	+ 30	-	+ 50
-OAc	+ 6	+ 6	+ 6	+ 6
-Cl	+ 15	+ 12	-	-
-Br	+ 25	+ 35	-	-
-OR	+ 35	+ 30	+ 17	+ 31
-SR	-	+ 85	-	-
-NR ₂	-	+ 95	-	-

Making use of the above rules, the absorption maximum for various α , β -unsaturated compounds can be estimated.

Example (1): Calculate the λ_{\max} (ethanol) for the given structure,



Solution:

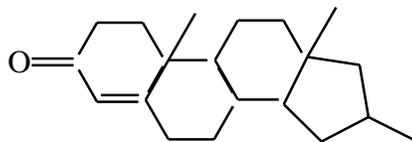
Basic value = 215 nm

2 β -alkyl substituents (2 x 12) = 24 nm

Calculated value = 239 nm

The observed value is found to be 237 nm

Example (2): Calculate the λ_{\max} for the given structure



Solution:

Basic value = 215 nm

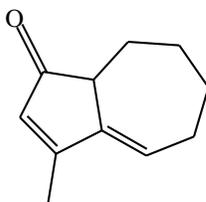
β -ring residues (2 x 12) = 24 nm

1-exocyclic double bond = 5 nm

Calculated value = 244 nm

The observed value is found to be 241 nm

Example (3): Calculate the λ_{\max} for the given structure:



Solution: It is an α, β -unsaturated cyclopentanone system

Basic value = 202 nm

1- β -alkyl substitution (1 x 12) = 12 nm

1-exocyclic double bond = 5 nm

1-double bond extending conjugation = 30 nm

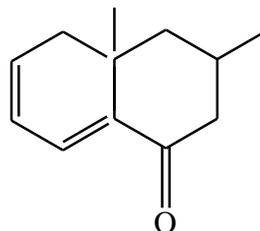
1- γ ring residue = 18 nm

1- δ ring residue = 18 nm

Calculated value = 285 nm

The observed value is found to be 287 nm

Example (4): Calculate the λ_{\max} for the given structure



Solution:

Basic value = 215 nm

 α - ring residue = 10 nm δ -ring residue = 18 nm

1-exocyclic double bond = 5 nm

Homoannular conjugated diene = 39 nm

1-double bond extending conjugation = 30 nm

Calculated value = 317 nm

The observed value is found to be 319 nm

8.10 Rules for Calculating Absorption Maximum for Derivatives of Acyl Benzenes

Like Woodward Fieser rules, Scott devised a set of rules for calculating the absorption maximum for the derivatives of acyl benzenes. These rules help in estimating the position of absorption maximum in ethanol in a number of monosubstituted aromatic ketones, aldehydes, acids and esters

For a compound of the type

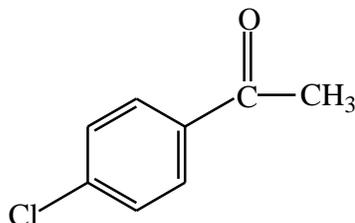
- (i) The basic value is 246 nm if X is an alkyl group or alicyclic residue.
- (ii) If X is hydrogen atom, the basic value becomes 250 nm and
- (iii) The basic value is 230 nm if X is OH or OR. The structural increments in nm for further substitution on the aromatic ring in the ortho, meta and para positions are given in **Table 5**.

Table 4: Auxochrome acting as substituent

Auxochrome	Increment in nm Position of substituent		
	Ortho	Meta	Para
Alkyl	+ 3	+ 3	+ 10
OH, OR	+ 7	+ 7	+ 25
Cl	0	0	+ 10
Br	+ 2	+ 2	+ 15
NH ₂	+ 13	+ 13	+ 58
NHAc	+ 20	+ 20	+ 45
NR ₂	+ 20	+ 20	+ 85

O ⁻	+ 11	+ 20	+ 75
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Example (1): Calculate the absorption maximum in ethanol for p-chloroacetophenone,



Solution: In this case, X is an alkyl group and thus the basic value is 246 nm.

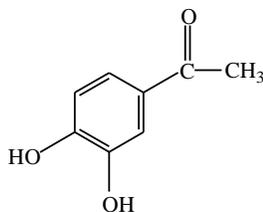
Basic value = 246 nm

Cl - substitution at para position = 10 nm

Calculated value = 256 nm

The observed value is found to be 254 nm

Example (2): Calculate the absorption maximum in ethanol for the following compound.



Solution:

Basic value = 246 nm

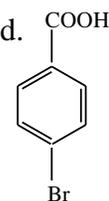
OH - substitution at meta = 7 nm

OH - substitution at para = 25 nm

Calculated value = 278 nm

The observed value is found to be 281 nm

Example (3): Calculate the absorption maximum in ethanol for the following compound.



Solution:

Basic value = 230 nm

Br - substitution at para = 15 nm

Calculated value = 245 nm

The observed value is found to be 245 nm

8.11 Summary of the unit

A good solvent should not absorb ultraviolet radiation in the same region as the substance whose spectrum is being determined. Usually solvents which do not contain conjugated systems are most suitable for this purpose, although they vary as to the shortest wavelength at which they remain transparent to ultraviolet radiation. The solvents most commonly used are water, 95% ethanol, and n-hexane. There are several types of electronic transitions available to a molecule including: σ to σ^* (alkenes) π to π^* (alkenes, carbonyl compounds, alkynes, azo compounds) n to σ^* (oxygen, nitrogen, sulfur, and halogen compounds) n to π^* (carbonyl compounds)

The solvent used in the absorption spectra has an ability to influence the wavelength of ultraviolet light (λ_{\max}) which will be absorbed by molecule. Transitions of the $n \rightarrow \pi^*$ type are shifted to shorter wavelengths by polar solvents. In some cases the excited states may form stronger hydrogen bonds with solvents than the corresponding ground state. In such cases, a polar solvent would shift absorption to longer wavelength, since the energy of the electronic transition would be decreased. Transitions of the type $\pi \rightarrow \pi^*$ are shifted to longer wavelengths by polar solvents.

Although the λ_{\max} values of conjugated systems often requires difficult calculations using MO theory, they can be readily estimated using a set of empirical rules, depending on whether the basic chromophore is a conjugated diene or an α,β -unsaturated carbonyl compound or a benzoyl derivative. For 1,3-butadiene, the *s-trans* conformer is rather more stable than the *s-cis* conformer, but for other substituted dienes the reverse is usually the case, because of steric hindrance between substituents. In general, the extent of p-orbital interaction is rather greater in *s-cis* conformers than in corresponding *s-trans* conformers, leading to higher λ_{\max} values for the former, as indicated in diagram below. The Woodward-Fieser rules break down when applied to molecules that have some kind of strain (steric or ring strain) around the chromophore. They also give poor prediction of λ_{\max} for “cross-conjugated” molecules (molecules whose conjugation is

extended other than at either end of the chromophore). In most cases, resonance (delocalization) is impeded due to distortion caused by strain, and so the Woodward-Fieser rules predict λ_{\max} values that are too high.

8.12 Key words:

Solvent Effect; intensity shifts; Bathochromic effect; Hypsochromic effect; Hyperchromic effect; Hypochromic effect; Woodward-Fieser Rules.

8.13 References for the further study:

- 1) Engineering Chemistry by Dr. B.S. Chavhan, *University science presses*, 3rd Ed. **2009**.
- 2) Elementary Organic spectroscopy: Principles and Chemical Applications by Y. R. Sharma, *S.Chand and Company Ltd.* **2005**.
- 3) UV/Vis Spectroscopy by ErnÖ Pretsch, Philippe Bühlmann, Martin Badertscher, *Springer Berlin Heidelberg*, **2009**.
- 4) Atomic and Molecular Spectroscopy by Gupta, Mool Chand, *New Age International*, **2007**.
- 5) Basic Atomic and Molecular Spectroscopy Volume 11 of tutorial chemistry texts by J. M. Hollas, *Royal Society of Chemistry*, **2002**.

8.14 Question for self study:

- 1) Explain the following:
 - a) Effect of increasing solvent polarity on $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions.
 - b) Transition probability.
- 2) Write a note on
 - a) Bathochromic and Hypsochromic shifts.
 - b) Hyperchromic and hypochromic effects.
- 3) Describe Woodward-Fieser rules for calculating the absorption maximum in diene.
 - 4) Arrange the following compounds in the order of their increasing wavelength of UV absorption maximum:
 - a) Ethylene b) Naphthalene c) Anthracene d) 1,3 butadiene.
- 5) Explain why
 - a) PhMe, Ph₂CH₂ and Ph₃C have similar UV spectra ($\lambda_{\max} \sim 262$ nm).
 - b) The UV spectrum of anilinium cation resembles that of benzene
 - c) The ethanolic solution of phenol shows λ_{\max} 210 nm but on addition of dilute NaOH to the solution, the λ_{\max} is shifted to 235 nm.

6) How will you distinguish between the following pairs of compounds by UV spectroscopy

- 1,3-pentadiene and 1,4-pentadiene.
- Benzene and Anthracene.
- 1,3-hexadiene and 1,3-cyclohexadiene.

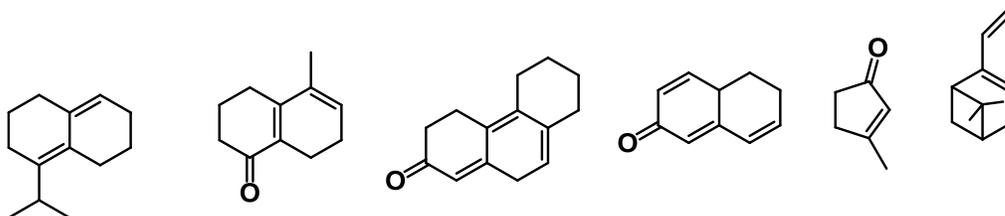
7) Which of the following do not absorb in the near UV region:

Benzene; 2-propanol; acrolein, ethanol, methyl iodide, heptene, water, acetaldehyde, dioxane and benzoic acid.

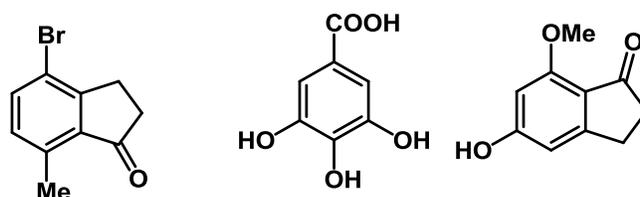
8) Explain why?

- Methyl iodide has both λ_{\max} and ϵ_{\max} higher than methyl chloride.
- No $n \rightarrow \sigma^*$ transition is observed in protonated triethylaniline
- Dimethylamine has higher value of λ_{\max} in hexane solution than that in water.

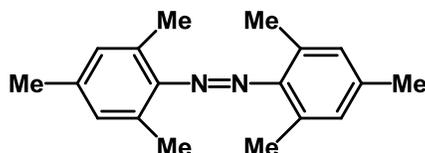
9) Using Woodward-Fisher rules, calculate the λ_{\max} of UV absorption for the following compounds:



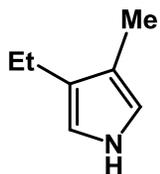
10) Calculate the λ_{\max} for the following benzene derivatives:



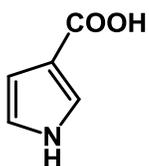
11) Explain why the cis isomer of the following compound is colourless, whereas its trans isomer is coloured:



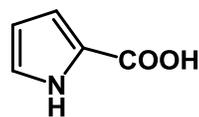
12) Explain the increasing order (a)→ (c) of the λ_{\max} in ethanol for the following pyrrole derivatives:



(a)
 λ_{\max} 230nm
 ϵ_{\max} 5670



(b)
 λ_{\max} 245nm
 ϵ_{\max} 4800



(c)
 λ_{\max} 262nm
 ϵ_{\max} 12,000

UNIT 9**Structure**

- 9.0 Objectives of the unit
- 9.1 Introduction
- 9.2 Harmonic oscillator for single particle
- 9.3 Harmonic oscillator for two particles attached to each other
- 9.4 Vibration of Diatomic molecules
- 9.5 Vibrational energy of simple harmonic oscillator
- 9.6 The Anharmonic Oscillator
- 9.7 Difference between harmonic and anharmonic oscillators
- 9.8 The diatomic vibrating Rotator
- 9.9 Summary of the unit
- 9.10 Key words
- 9.11 References for further study
- 9.12 Questions for self study

9.0 Objectives of the unit

After studying this unit you are able to

- Calculate energy for harmonic oscillator for single particle system.
- Calculate energy for anharmonic oscillator for two particle system.
- Calculate vibrational energy of simple harmonic oscillator.
- Calculate vibrational energy of anharmonic oscillator.
- Identify the difference between harmonic and anharmonic oscillators.
- Derive the equation for diatomic vibrating rotator.

9.1 Introduction

A chemical bond is an *attraction force* between atoms or molecules. The bond length or bond distance between two atoms in a molecule is the average distance between nuclei of two bonded atoms in that molecule. The bond acts as a spring, hence it is harder to compress the molecules than to stretch it. Too much stretch can break the bond.

The chemical bond at room temperature is not rigid and always vibrating in order to minimize the electrostatic forces exerted from nuclei and electrons. The mode of vibration is depends on nature of bonded atoms i.e., mass, size etc..., and also on the bond length. So, study of vibrational motion in a molecule gives information about the chemical bond. The potential felt by the nuclei in a diatomic molecule is shown in **Fig. 1**.

At low energies, the molecule will sit near the bottom of this potential energy surface (PES). Therefore, no matter what the detailed structure of the molecule is, the nuclei will “feel” a nearly harmonic potential. Hence, the motion of the nuclei along the PES is called vibrational motion, and clearly at low energies the nuclear motion is a harmonic oscillator. In diatomic molecule, there is only one degree of freedom (the bond length), and so it is reasonable to model diatomic vibrations using a 1D harmonic oscillator

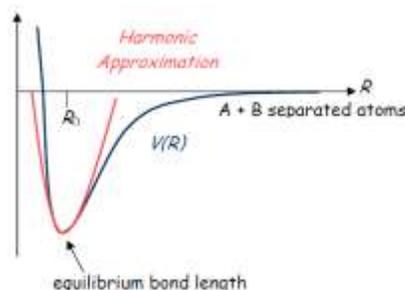
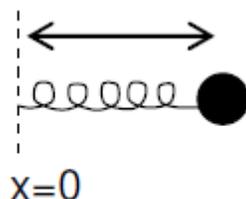


Figure 1: potential felt by the nuclei in a diatomic molecule.

9.2 Harmonic oscillator for single particle

The harmonic oscillator for single particle will be described by model, spring attached to anchor at one end and particle or atom at other end, this is the only end that moves as shown in **Fig. 2**.



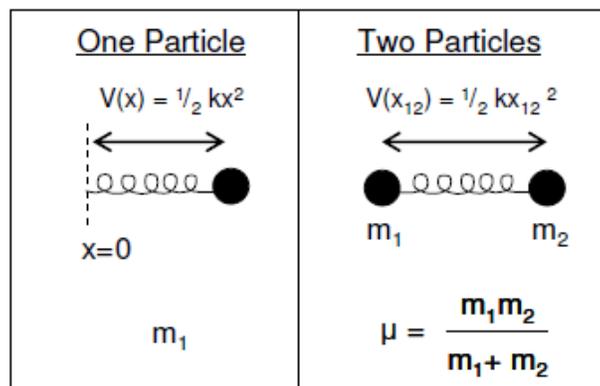
Hence, according to **Figure 2**: model of harmonic oscillator for single particle.

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

k = force constant (not to be confused with wave vector or Boltzmann constant)

9.3 Harmonic oscillator for two particles attached to each other

In molecular vibrations, both ends are able to move and both ends have mass. Furthermore, the distance for potential energy is deviation from equilibrium bond distance – not the total distance separating the atoms.



9.4 Vibration of Diatomic molecules

A diatomic molecule will be formed by the combination of two atoms. They may be doing so because of some internal electronic rearrangement. In this molecule there will be repulsion between the positively charged nuclei of both atoms, and between their negative electron cloud, on the other hand there is an attraction between the nucleus of one atom and the electrons of the other and vice versa. The two atoms settle at a mean internuclear distance such that these forces are just balanced and the energy of the whole system is at a minimum. Attempts to squeeze the atoms more closely together will cause repulsive force to rise rapidly, while pulling them apart is

resisted by the attractive force. In either case, an attempt to distort the bond length requires an input of energy, and conversely any excess of energy causes compression and expansion of the bond. *This particular compression and expansion of the molecule is called molecular vibration. The frequency with which the vibration takes place is called vibrational frequency or oscillation frequency.* A plot of energy against internuclear distance will be as shown in **Fig. 3**. At the maximum, the internuclear distance is referred to as equilibrium distance, r_{eq} or simply bond length.

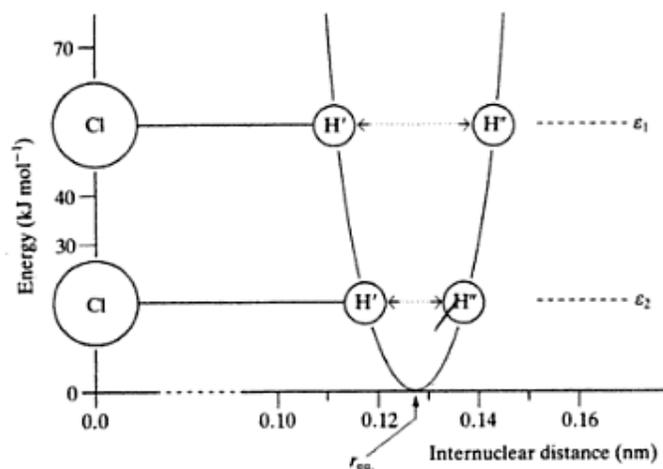


Figure 3: Energy of HCl as the bond is compressed and expanded.

The compression and expansion of a bond may be likened to the behaviour of a spring, and we may extend the analogy by assuming that the bond, like a spring, obeys Hooke's law. We may write,

$$f = -k(r - r_{eq}) \text{----- (1)}$$

where f is the restoring force, k the force constant, and r the internuclear distance. In this case the energy curve is parabolic and has the form,

$$E = 1/2 k(r - r_{eq})^2 \text{----- (2)}$$

This model of a vibrating diatomic molecule is called simple harmonic oscillator model, and this is only an approximation which forms an excellent starting point for the discussion of vibrational spectra. The zero of curve is found at $r = r_{eq}$, and any energy in excess of this, for example at E_2 , arises because of expansion or compression of the bond. The **Fig. 3** shows that if one atom (Cl) is considered to be stationary on the $r = 0$ axis, the other (H) will oscillate between H' and H'' . If the energy is increased to E_1 , the oscillation will become more vigorous that degree of compression and expansion will be greater but the vibrational frequency will not change. This

oscillation frequency depends upon the force constant and the mass of the atoms. Classically it can be shown that

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz} \text{ ----- (3)}$$

$$\omega_{osc} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \text{ -----(4)}$$

Where 'c' is the velocity of light. *This vibrational frequency is termed as fundamental vibration frequency of the molecule.*

9.5 Vibrational energy of simple harmonic oscillator

Vibrational energies, like all other molecular energies are quantized, and the allowed vibrational energies for any particular system may be calculated from the Schrodinger equation. For the simple harmonic oscillator this will be,

$$E_v = \left(v + \frac{1}{2}\right) hc\omega_{osc} \text{ joules} \quad (v = 0, 1, 2 \dots) \text{----- (5)}$$

where 'v' is called vibrational quantum number. Converting to the spectroscopic units, cm^{-1} , we have

$$\epsilon_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right) \omega_{osc} \text{----- (6)}$$

$$\text{When } v = 0 \text{ then } E_v = \frac{1}{2} hc\omega_{osc} \text{ joule ----- (7)}$$

This means that the diatomic molecule (indeed any molecule) can never have zero vibrational energy. i.e., the atoms can never be completely at rest relative to each other. *This quantity is known as the zero-point energy.*

Further, use of the Schrodinger equation leads to the simple selection rule for the harmonic oscillator undergoing vibrational changes.

$$\Delta v = \pm 1$$

To this we must, of course, add the condition that vibrational energy changes will only give rise to an observable spectrum if the vibration can interact with radiation, i.e., if the vibration involves a change in the dipole moment of the molecule. Thus, *vibrational spectra will be observable only in heteronuclear diatomic molecules since homonuclear molecules have no dipole moment.*

$$E_v = \left(v + \frac{1}{2}\right) hc\omega_{osc}$$

$$E_{v'} = \left(v' + \frac{1}{2} \right) hc\omega_{osc}$$

$$\Delta E = hc\omega (v - v')$$

For $\Delta v = +1$, then $\Delta E = hc\omega$

or $h\nu = hc\omega$ or $\nu = \omega$ ----- (8)

Thus for a harmonic oscillator the frequency of the radiation emitted or absorbed should be equal to the frequency of vibration of the system ω . According to the above argument, the vibration spectrum should consist of a single line provided there are accompanying rotational energy changes as shown in **Fig 4**.

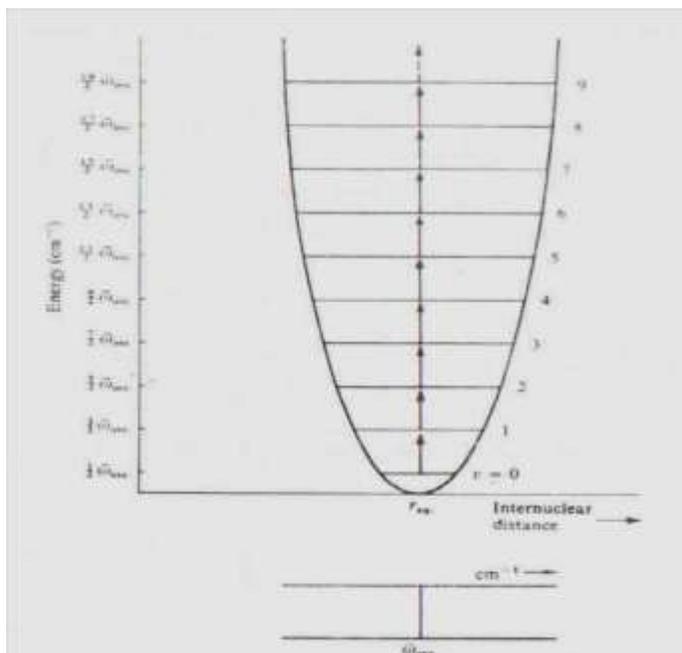


Figure 4: The vibrational energy levels and allowed transition between them for a diatomic molecule undergoing simple harmonic motion.

Solved problems:

- 1) The force constant of the bond in CO molecule is 1870 Nm^{-1} . Find the energy of the lowest vibrational level. The reduced mass of the CO molecule is $1.14 \times 10^{-26} \text{ kg}$; $h = 6.63 \times 10^{-34} \text{ Js}$ and $1\text{eV} = 1.60 \times 10^{-19} \text{ J}$.

Solution: The frequency of vibration of CO molecule is : (eq. 4)

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Given: $k = 1870 \text{ Nm}^{-1}$; $\mu = 1.14 \times 10^{-26} \text{ kg}$; $h = 6.63 \times 10^{-34} \text{ Js}$

Substituting the values in above equation we get

$$\omega_{osc} = \frac{1}{2 \times 3.1} \sqrt{\frac{1870}{1.14 \times 10^{-26}}} = 6.45 \times 10^{13} \text{ s}^{-1}$$

The vibrational energy of diatomic molecule is given by

$$E_v = \left(v + \frac{1}{2} \right) h c \omega_{osc}, v = 0, 1, 2, 3, \dots,$$

The lowest level correspond to $v = 0$. $\therefore E_v = \frac{1}{2} h c \omega_{osc}$

Substituting the values we get $E_v = \frac{1}{2} (6.63 \times 10^{-34}) (6.45 \times 10^{13})$

$$\begin{aligned} &= 21.4 \times 10^{-21} \text{ J} \\ &= 21.4 \times 10^{-21} / 1.60 \times 10^{-19} \text{ eV} \\ &= 0.134 \text{ eV} \end{aligned}$$

- 2) The force constant of the bond in CO molecule is 1870 Nm^{-1} . Calculate the frequency of vibration of the molecule and the spacing between its vibrational energy levels. Given that the reduced mass of CO = $1.14 \times 10^{-26} \text{ kg}$, $h = 6.63 \times 10^{-34} \text{ Js}$ and $1 \text{ eV} = 1.60 \times 10^{-19} \text{ s}^{-1}$

Solution: As we calculated in problem 1. The frequency of the CO molecule is:

$$\omega_{osc} = 6.5 \times 10^{13} \text{ s}^{-1}.$$

The separation between two successive vibrational energy levels is

$$\begin{aligned} \Delta E &= E_{v+1} - E_v \\ &= h \omega_{osc} [v + 3/2] - h \omega_{osc} [v + 1/2] \\ &= h \omega_{osc} \\ &= (6.63 \times 10^{-34} \text{ Js}) \times (6.45 \times 10^{13} \text{ s}^{-1}) \\ &= 42.8 \times 10^{-21} \text{ J} / 1.60 \times 10^{-19} \text{ J/eV}. \\ &= 0.2675 \text{ eV}. \end{aligned}$$

- 3) Assume that H_2 molecule behave like a harmonic oscillator with a force constant $k = 573 \text{ N/m}$. Find the vibrational quantum number corresponding to its 4.50 eV dissociation energy. Given: mass of hydrogen atom = $1.67 \times 10^{-27} \text{ kg}$, $h = 6.63 \times 10^{-34} \text{ Js}$.

Solution: The frequency of oscillator of the molecule is given by

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

The reduced mass of the H_2 molecule is

$$\mu = \frac{m_H x m_H}{m_H + m_H} = \frac{1}{2} m_H = 0.5 \times 1.67 \times 10^{-27} \text{ kg} = 0.835 \times 10^{-27} \text{ kg}$$

$$\therefore \omega_{osc} = \frac{1}{2 \times 3.14} \sqrt{\frac{573 \text{ N/m}}{0.835 \times 10^{-27} \text{ kg}}} = 1.32 \times 10^{14} \text{ s}^{-1}$$

Vibrational energy of the H₂ molecule is

$$\begin{aligned} E_v &= h \omega_{osc} \left(v + \frac{1}{2} \right) \\ &= (6.63 \times 10^{-34} \text{ Js}) (1.32 \times 10^{14} \text{ s}^{-1}) [v + \frac{1}{2}] \\ &= 8.75 \times 10^{-20} [v + \frac{1}{2}] \text{ J} \\ &= \frac{8.75 \times 10^{-24} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} \left(v + \frac{1}{2} \right) = 0.547 \left(v + \frac{1}{2} \right) \text{ eV} \end{aligned}$$

For E_v = 4.50 eV, we would have

$$4.50 = 0.547 [v + \frac{1}{2}]$$

$$\therefore v + \frac{1}{2} = 0.457 / 0.547 = 8.2$$

$$\therefore v = 8.2 - 0.5 = 7.7 \approx 8.$$

- 4). The force constant of a vibrating HCl molecule is 480 N/m. Find the energy difference between the lowest and the first vibrational level of HCl. Given N_A = 6.023 × 10²³ mol⁻¹, h = 6.63 × 10⁻³⁴ Js, 1eV = 1.60 × 10⁻¹⁹ J.

Solution. The frequency of vibration of the molecule is given by

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

The reduced mass of H³⁵Cl molecule is

$$\mu = \frac{m_H x m_{Cl}}{m_H + m_{Cl}} = \frac{35}{36} m_H = 0.97 \times 1.67 \times 10^{-27} \text{ kg} = 1.61 \times 10^{-27} \text{ kg}$$

$$\omega_{osc} = \frac{1}{2 \times 3.14} \sqrt{\frac{480 \text{ N/m}}{1.61 \times 10^{-27} \text{ kg}}} = 0.87 \times 10^{14} \text{ s}^{-1}$$

Now, the vibrational energy of the HCl molecule is

$$E_v = h \omega_{osc} \left(v + \frac{1}{2} \right)$$

The energy difference between the lowest ($v = 0$) and the first excited ($v = 1$) vibrational levels of HCl molecule is

$$\begin{aligned}\Delta E &= E_{(v=1)} - E_{(v=0)} \\ &= 3/2h\omega_{osc} - 1/2h\omega_{osc} \\ &= h\omega_{osc} \\ &= (6.63 \times 10^{-34} \text{Js}) (0.87 \times 10^{14} \text{s}^{-1}) \\ &= 5.77 \times 10^{-20} \text{ J} \\ &= \frac{5.77 \times 10^{-24} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = 0.36 \text{ eV}\end{aligned}$$

This is the energy required for the molecule to rise to the first excited state.

The thermal energy of a molecule is of the order kT where k is Boltzmann constant. At room temperature (300 K) this energy is equal to

$$\begin{aligned}kT &= (1.38 \times 10^{-23} \text{ J/K}) (300 \text{K}) = 4.14 \times 10^{-21} \text{ J} \\ &= 4.14 \times 10^{-21} \text{ J} / 1.60 \times 10^{-19} \text{ J/eV} = \mathbf{0.026 \text{ eV}}\end{aligned}$$

Thus, at room temperature, collision of molecule can transfer only 0.026 eV of kinetic energy to the internal energy, which is insufficient to excite even $v = 1$ state (the required energy is 0.36 eV). Hence, HCl molecule is not likely to be found vibrating in its first vibrational excited state at room temperature. However, in case of rotational state, the energy difference between $J = 0$ and $J = 1$ levels is only by 0.0026 eV. Hence, at room temperature collision of HCl molecules can transfer sufficient energy to the internal energy to excite many rotational states.

9.6 The Anharmonic Oscillator

Real molecules do not obey exactly the laws of simple harmonic motion. Real bonds, although elastic, are not so homogeneous as to obey Hooke's law. If the bond between atoms is stretched, for instance, there comes a point at which it will break, then the molecule dissociates into atoms. Thus, although for small compressions and expansions, the bond may be taken as perfectly elastic for larger amplitudes. **Fig. 5** shows diagrammatically, the shape of the energy curve for a typical diatomic molecule, together with simple harmonic parabola.

A purely empirical expression which fits this curve to a good approximation was derived by P. M. Morse, and is called the Morse function.

$$E = D_{eq} [1 - \exp\{a(r_{eq} - r)\}]^2 \text{ ----- (9)}$$

where 'a' is a constant for a particular molecule and D_{eq} is the dissociation energy.

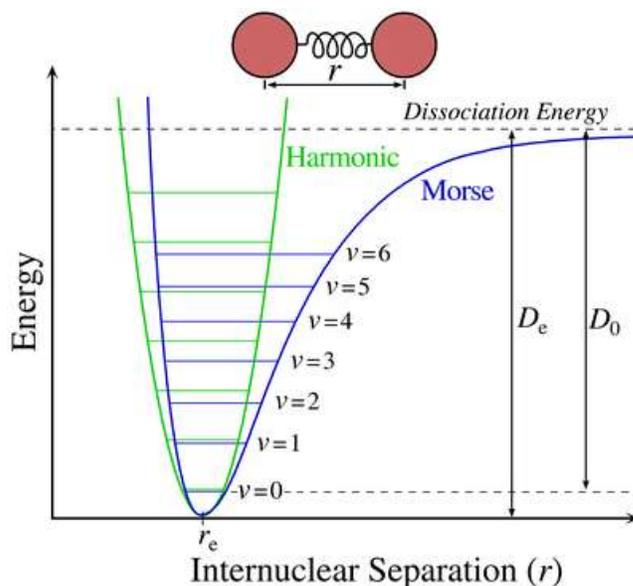


Figure 5: the energy of a diatomic molecule undergoing anharmonic expansions and compressions. The Morse curve

When Eq. (9) is used instead of Eq. (2) in the Schrodinger equation, the pattern of the allowed vibrational energy levels is found to be,

$$\epsilon_v = (v + \frac{1}{2}) \omega - (v + \frac{1}{2})^2 \omega x_e \text{ cm}^{-1} \quad (v = 0, 1, 2, \dots) \text{ ----- (10)}$$

where ω is an oscillation frequency (expressed in wave numbers) and x_e is the corresponding anharmonicity constant which for bond stretching vibrations is always small and positive ($\approx +0.01$), so that the vibrational levels are more closely together with increasing v . Some of these levels are sketched in **Fig. 6**.

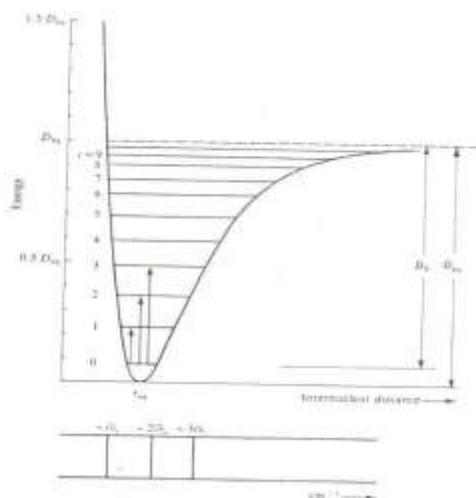


Figure 6: The vibrational energy levels and some transitions between them for a diatomic molecule undergoing anharmonic oscillations.

If we rewrite Eq. (10), for the anharmonic oscillator, then

$$\varepsilon_v = \omega_e \{1 - x_e(v + 1/2)\} (v + 1/2) \text{-----} (11)$$

Compare with the energy levels of the harmonic oscillator (Eq. (6)), we can write

$$\omega_{\text{osc}} = \omega_e \{1 - x_e(v + 1/2)\} \text{-----} (12)$$

Thus, the anharmonic oscillator behaves like the harmonic oscillator but with the oscillation frequency decreases steadily with increasing v . If we consider the hypothetical energy state obtained by putting $v = -1/2$ (at which, according to Eq. 11, $\varepsilon = 0$), the molecule would be at the equilibrium point with zero vibrational energy. Its oscillation frequency (in cm^{-1}) would be,

$$\omega_{\text{osc}} = \omega_e$$

Thus, we see that ω_e may be defined as the (hypothetical) equilibrium oscillation frequency of the anharmonic system, i.e., the frequency for infinitely small vibrations about the equilibrium point.

In the ground state ($v = 0$) we would have

$$\begin{aligned} \omega_0 &= \omega_e(1 - 1/2 x_e) \text{ cm}^{-1} \text{-----} (13) \\ \varepsilon_0 &= 1/2 \omega_e(1 - 1/2 x_e) \text{ cm}^{-1} \end{aligned}$$

We see that the zero-point energy differs slightly from that for the harmonic oscillator. The selection rules for the anharmonic oscillator are found to be,

$$\Delta v = \pm 1, \pm 2, \pm 3 \dots$$

Thus, they are the same as for the harmonic oscillator, with the additional possibility of larger jumps. These, however, are predicted by theory and observed in practice to be of rapidly diminishing probability and normally only the lines of $\Delta v = \pm 1, \pm 2$, and ± 3 , at the most, have observable intensity.

(1) If transition from $v = 0$ to $v = 1$, i.e., $\Delta v = +1$ then

$$\begin{aligned} \Delta \varepsilon &= \varepsilon_{v=1} - \varepsilon_{v=0} \\ &= (1 + 1/2)\omega_e - x_e(1 + 1/2)^2\omega_e - \{1/2\omega_e - (1/2)^2x_e\omega_e\} \\ &= \omega_e(1 - 2x_e) \text{ cm}^{-1} \text{-----} (14a) \end{aligned}$$

(2) If transition from $v = 0$ to $v = 2$, i.e., $\Delta v = +2$ then

$$\begin{aligned} \Delta \varepsilon &= (2 + 1/2)\omega_e - x_e(2 + 1/2)^2\omega_e - \{1/2\omega_e - (1/2)^2x_e\omega_e\} \\ &= 2\omega_e(1 - 3x_e) \text{ cm}^{-1} \text{-----} (14b) \end{aligned}$$

(3) If transition from $v = 0$ to $v = 3$, i.e., $\Delta v = +3$ then

$$\begin{aligned}\Delta\varepsilon &= (3 + \frac{1}{2})\omega_e - \{ \frac{1}{2}\omega_e - (\frac{1}{2})^2x_e\omega_e \} \\ &= 3\omega_e(1 - 4x_e) \text{ cm}^{-1} \text{ ----- (14c)}\end{aligned}$$

These three transitions are shown in **Fig. 6**. Since $x_e \approx 0.01$, the three spectral lines lie very close to ω_e , $2\omega_e$ and $3\omega_e$. The line near ω_e is called the fundamental absorption, while those near $2\omega_e$ and $3\omega_e$ are called the first and second overtones, respectively. The spectrum of HCl, for instance shows a very intense absorption at 2886 cm^{-1} , a weaker one at 5668 cm^{-1} , and a very weak one at 8347 cm^{-1} . If we wish to find the equilibrium frequency of the molecule from these data, we must solve any two of the three equations (Eq 14).

$$\omega_e(1 - 2x_e) = 2886 \text{ cm}^{-1}$$

$$2\omega_e(1 - 3x_e) = 5668 \text{ cm}^{-1}$$

$$3\omega_e(1 - 4x_e) = 8347 \text{ cm}^{-1}$$

9.7 Difference between harmonic and anharmonic oscillators

In case of harmonic oscillator the relation between force and displacement is linear but in the case of anharmonic oscillator relation between force and displacement is not linear as shown in **Fig. 7**. Hence this non-linearity arise the fact that the bond is not capable of exerting a restoring force that is proportional to the displacement

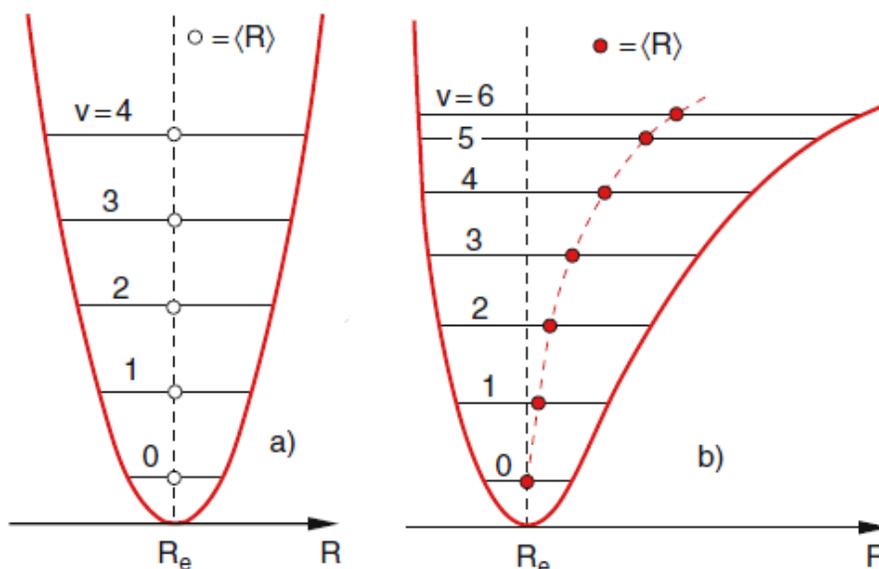


Figure 7: Mean internuclear distance R and rotational constant k for the harmonic (a) and anharmonic (b) potential.

Also harmonic oscillator gives energy levels having constant energy gaps whereas anharmonic oscillator gives increasingly small energy gaps as we go to higher energy levels. Harmonic

oscillator has infinite number of vibrations but anharmonic oscillator only has finite number of bound oscillations.

9.8 The Diatomic Vibrating Rotator

Since the energies of the two motions are so different, we may as a first approximation, consider that a diatomic molecule can execute rotations and vibrations quite independently. This is called the Born-Oppenheimer approximation. Thus, it is assuming that the combined rotational-vibrational energy is simply the sum of the separate energies.

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} \quad (\text{joules}) \text{-----} (15)$$

$$\epsilon_{\text{total}} = \epsilon_{\text{rot}} + \epsilon_{\text{vib}} \quad (\text{cm}^{-1})$$

Taking the separate expressions for ϵ_{rot} and ϵ_{vib} , we have,

$$\begin{aligned} \epsilon_{Jv} &= \epsilon_J + \epsilon_v \\ &= BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + \dots + (v + \frac{1}{2})\omega_e - x_e(v + \frac{1}{2})^2\omega_e \quad \text{cm}^{-1} \text{-----} (16) \end{aligned}$$

Ignore the small centrifugal distortion constants D, H, etc., and hence can write

$$\epsilon_{\text{total}} = \epsilon_{Jv} = B J(J+1) + (v + \frac{1}{2})\omega_e - x_e(v + \frac{1}{2})^2\omega_e \text{-----} (17)$$

The rotational levels are sketched in **Fig. 8.** for the two lowest vibrational levels, $v = 0$ and $v = 1$. It may be shown that the selection rules for the combined motions are the same as those for each separately, therefore we have,

$$\Delta v = \pm 1, \pm 2, \text{ etc. } \Delta J = \pm 1 \text{-----} (18)$$

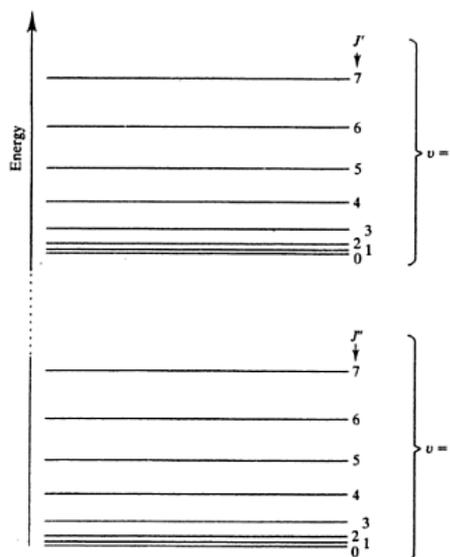


Figure 8: Some of the rotational energy levels for the first two vibrational states of a diatomic molecule.

Strictly speaking we may also have $\Delta v = 0$, but this corresponds to the purely rotational transitions. Note carefully however that, a diatomic molecule, except under very special and rare circumstances, may not have $\Delta J = 0$, in other words a vibrational change must be accompanied by a simultaneous rotational change.

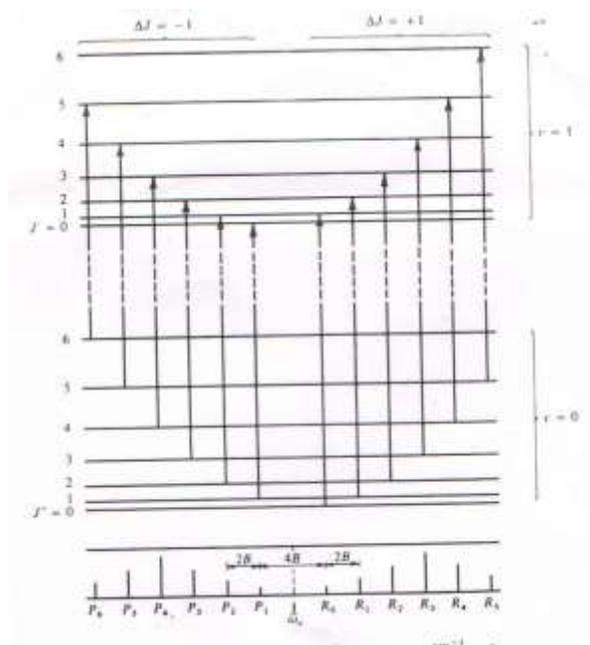


Fig. 9. Figure 9: Some transitions between the rotational-vibrational energy levels of a diatomic molecule, together with the spectrum arising from them.

An analytical expression for the spectrum may be obtained by applying the selection rules to the energy levels. Considering only the $v = 0 \rightarrow v = 1$ transition we have,

$$\begin{aligned} \Delta \varepsilon_{J,v} &= E_{J',v=1} - E_{J'',v=0} \\ &= BJ'(J'+1) + 1/2 \omega_e - 2\frac{1}{4} x_e \omega_e - \{B J''(J''+1) + 1/2 \omega_e - \frac{1}{4} x_e \omega_e\} \\ &= \omega_0 + B(J' - J'')(J' + J'' + 1) \text{ cm}^{-1} \end{aligned}$$

$$1) \quad \Delta J = +1, \text{ that is } J' = J'' + 1 \text{ or } J' - J'' = +1, \text{ hence}$$

$$\Delta \varepsilon_{J,v} = \omega_0 + 2B(J'' + 1) \text{ cm}^{-1} \quad J'' = 0, 1, 2, \dots (19a)$$

$$2) \quad \Delta J = -1, \text{ that is } J'' = J' + 1 \text{ or } J' - J'' = -1, \text{ hence}$$

$$\Delta \varepsilon_{J,v} = \omega_0 - 2B(J' + 1) \text{ cm}^{-1} \quad J' = 0, 1, 2, \dots (19b)$$

These two expressions may be conveniently be combined into,

$$\Delta \varepsilon_{J,v} = \nu_{\text{spect}} = \omega_0 + 2Bm \text{ cm}^{-1} \quad m = \pm 1, \pm 2, \dots (19c)$$

where m is $J'' + 1$ in Eq. (19a) and $J' + 1$ in Eq. (19b) has positive values for $\Delta J = +1$ and negative if $\Delta J = -1$. Note particularly that ' m ' cannot be zero since this would imply values of J' or J'' to be -1 . The frequency ω_0 is usually called the band origin or band centre.

Equation (19c) represents the combined vibration-rotation spectrum. Evidently, it will consist of equally spaced lines (spacing = $2B$) on each side of the band origin ω_0 , but, since $m \neq 0$, the line at ω_0 itself will not appear. Lines to the low-frequency side of ω_0 , corresponding to negative m (that is $\Delta J = -1$) are referred to as the P- branch, while those to the high-frequency side (m positive, $\Delta J = +1$) are called the R- branch.

Lines arising from $\Delta J = -2, -1, 0, +1, +2$

called: O P Q R S branch

The P and R notation, with the lower J (J'') value as a suffix, is illustrated on the diagrammatic spectrum of **Fig. 9**.

9.9 Summary of the unit

If the atoms are pushed close together in a diatomic molecule, the positive charges on the two nuclei repel each other, and the potential energy keeps increasing to higher and higher levels as the atoms get closer and closer. Thus, the atoms are kept from getting too close together.

Similarly, if the atoms move away from each other, the potential energy associated with the molecular bond attempts to bring the atoms back to their equilibrium position. Thus, atoms in diatomic molecule keep vibrating and these vibrational motions are associated with energy called vibrational energy level. Like rotational energy, vibrational energy is also quantized. If enough vibrational energy is put into the system, there reaches a point where the vibrational energy is greater than the potential energy holding the molecule together and the atoms are able to fly apart. This is referred to as *dissociation*. The vibrational motion of diatomic molecule is classified into two types namely harmonic oscillator and anharmonic oscillator.

The harmonic oscillator is only an approximation for diatomic vibrations and it works best only at low quantum number level. The vibration in diatomic molecule deviates from harmonic behavior as move to higher potential energy. Below are the some of the characteristics of harmonic and anharmonic oscillator.

Harmonic oscillator:

Potential Energy	$V(x) = \frac{1}{2} kx^2$
Wave functions	ψ_n : based on Hermite polynomials: $\psi_0 = (a/\pi)^{1/4} \cdot \exp(-ax^2/2)$ $\psi_1 = (4a^3/\pi)^{1/4} \cdot x \cdot \exp(-ax^2/2)$ $\psi_2 = (a/4\pi)^{1/4} \cdot (2ax^2 - 1) \cdot \exp(-ax^2/2)$
Quantum numbers	$n = 0, 1, 2, \dots$
Energy	$E_n = \hbar \sqrt{\frac{k}{\mu}} \left(n + \frac{1}{2} \right) = h\nu_e \left(n + \frac{1}{2} \right)$
Constants and definitions	k = force constant for harmonic oscillator – depends on bond strength $\nu_e = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ = freq. of oscillation $\alpha = \sqrt{k\mu/\hbar^2}$ = constant inside Hermite polynomials

Anharmonic oscillator:

Morse Potential	$V(x) = D_e \left(1 - e^{-a(x-x_e)} \right)^2$
Energy	$E_n = h\nu_e \left(n + \frac{1}{2} \right) - \nu_e X_e \left(n + \frac{1}{2} \right)^2$
Constants and definitions	$X_e = \frac{\hbar^2 \nu_e}{4D_e}$ = anharmonicity constant $a = \left(\frac{k}{2D_e} \right)^{1/2}$ D_e = Dissociation energy (measured from bottom of well to top of plateau) D_0 = Bond energy (measured from bottom vibrational level to top of plateau)

9.10 Key words

Diatomic molecule; Harmonic oscillator; anhrmonic oscillator; Vibrational energy.

9.11 References for further study

- 1) Vibrational/Rotational Spectroscopy of Diatomic Molecules by M Mueller, *Kluwer Academic Publishers*, **2002**.
- 2) Vibrational Spectroscopy: Theory and Applications by D. N. Sathyanarayana, *New Age International*, **2007**.
- 3) Fundamentals of molecular spectroscopy by Colin N Banwell, Elaine M. McCash, *McGraw Hill*, 5th Ed. **2013**.

9.12 Questions for self study:

- 1) Derive the equation for vibrational energy of simple harmonic oscillator.
- 2) Derive the equation for vibrational energy of anharmonic oscillator.
- 3) Write two differences between harmonic and anharmonic oscillators.
- 4) Derive the equation for energy level of the diatomic vibrating rotator.
- 5) What is meant by zero point energy?
- 6) What is force constant?
- 7) Write a selection rule for harmonic and anharmonic oscillator frequencies.

Problems:

- 1) Force constant for H^{19}F molecule is 966 N/m. Find the frequency of vibration of the molecule. ($N_A = 6.023 \times 10^{23}$ /mole) [**Ans.** $1.2 \times 10^{14}\text{s}^{-1}$]
- 2) The simple harmonic force constant for D^{35}Cl is 490.3 N/m. Calculate the frequency (cm^{-1}) of radiation absorbed by DCl. Is this independent of ν ? ($N_A = 6.0^{23} \times 10^{23}\text{mole}^{-1}$, $c = 3.0 \times 10^8$ m/s) [**Ans.** 2097 cm^{-1}]
- 3) The force constant of a vibrating HCl molecule is about 480N/m. Estimate the energy difference between the first vibrational state of HCl ($N_A = 6.0 \times 10^{23}\text{mole}^{-1}$; $h = 6.63 \times 10^{-34}\text{Js}$; $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$) [**Ans.** 0.36 eV]
- 4) In the near-IR spectrum of $^{12}\text{C}^{16}\text{O}$ molecule there is an intense band at 2144 cm^{-1} . Calculate the fundamental vibration frequency, the force constant and the Zero-point energy of the molecule. ($N_A = 6.0 \times 10^{23} \text{ mole}^{-1}$; $h = 6.63 \times 10^{-34}\text{Js}$; $c = 3.0 \times 10^8 \text{ m/s}$; $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$) [**Ans.** $6.43 \times 10^{13}\text{s}^{-1}$; 1860N/m ; 0.133 eV]
- 5) The most intense Vibrational bands of CO and HCl molecules occurs at wave numbers $2.143 \times 10^5\text{m}^{-1}$ and $2.886 \times 10^5\text{m}^{-1}$ respectively. Their reduced masses are $1.14 \times 10^{-26} \text{ kg}$ and $1.61 \times 10^{-27}\text{kg}$ respectively. Find the force constant of CO and HCl molecule. ($c = 3.0 \times 10^8 \text{ m/s}$) [**Ans.** 1858N/m]

UNIT 10**Structure**

- 10.0 Objectives of the unit
- 10.1 Introduction
- 10.2 Vibration-Rotation spectra of diatomic molecule
- 10.3 The vibration-rotation spectrum of carbon monoxide
- 10.4 Isotope Effects
- 10.5 Fundamental and Overtone bands
 - Hot Bands
 - Fermi Resonances
- 10.6 Vibrations of polyatomic molecules
- 10.7 Parallel and perpendicular vibrations
- 10.8 Summary of the unit
- 10.9 Key words
- 10.10 References for further study
- 10.11 Questions for self study

10.0 Objectives of the unit

After studying this unit you are able to

- Interpret the vibration-rotation spectra of diatomic molecule.
- Identify fundamental and overtone bands.
- Explain hot band formation.
- Explain Fermi resonance.
- Identify the number of modes of possible vibrations of poly atomic molecule.
- Explain the differences between parallel and perpendicular vibrations.

10.1 Introduction

A real molecule can simultaneously rotate and vibrate. Since the vibrational frequency is higher than the rotational frequency by one to two orders of magnitude, the molecule undergoes many vibrations (typically 5–100) during one rotational period. This means that the nuclear distance changes periodically during one full rotation.

IR absorption occurs from the stretching and bending of the covalent bonds in molecules. To be accompanied by IR absorption a stretch or bend must change the dipole moment of the molecule. Molecules with symmetric bonds such as N₂, O₂, or F₂ do not absorb in the infrared since bond stretching does not change the dipole moment of the molecule. The two primary modes of vibration are *stretching* and *bending*. Stretching modes are typically of higher energy than bending modes. Stretching modes are often divided into two (a) symmetric and (b) asymmetric stretch; the asymmetric stretch is usually of higher energy.

The energy of the stretch decreases as the mass of the atoms is increased

C-H 3000 cm⁻¹ **C-C** 1200 cm⁻¹ **C-O** 1100 cm⁻¹ **C-Cl** 750 cm⁻¹ **C-I** 500 cm⁻¹

Also the energy of the stretch is related to the hybridization in the order $sp^2 > sp > sp^3$

C-H sp 3300 cm⁻¹ **C-H** sp^2 3100 cm⁻¹ **C-H** sp^3 2900 cm⁻¹

10.2 Vibration-Rotation spectra of diatomic molecule

As discussed for the diatomic vibrating rotator in the unit 8, the rotation-vibration energy of diatomic molecule is approximately the sum of harmonic-oscillator energy and rigid-rotor energy and is given by:

$$E \approx h\nu_e(v+1/2) + h^2J(J+1)/(8\pi^2\mu R_e^2) ; [v = 0,1,2,\dots ; J = 0,1,2,\dots] \text{ ----- (20)}$$

Where v is the vibration quantum number, J is the rotation quantum number γ_e is the fundamental vibration frequency; R_e is the equilibrium bond length and μ is the reduced mass. [$\mu = m_1 \times m_2 / (m_1 + m_2)$].

If ω_e is the fundamental vibration frequency in *wave numbers*, cm^{-1} . Then $\omega_e = \gamma_e / c$, where c is the speed of light. Therefore eq.20 becomes

$$E \approx h\omega_e(v + 1/2) + h^2 J(J+1) / (8\pi^2 \mu R_e^2)$$

$$E \approx \omega_e(v + 1/2) + B_e J(J+1) \text{----- (21)}$$

Units of wave numbers are convenient because infrared spectra are usually recorded in wave numbers. Notice that $\omega_e = 1/\lambda$. And the equilibrium rotation constant or force constant B_e is defined as

$$B_e \equiv h / (8\pi^2 c \mu R_e^2) \text{----- (21a)}$$

The infrared absorptions observed for diatomic molecule are arise from transitions between $v = 0$ and $v = 1$, and various $J'' \rightarrow J'$, with $J' = J'' \pm 1$ as shown in **Fig 1**. [The J value for the initial lower-energy state is denoted J'' .]

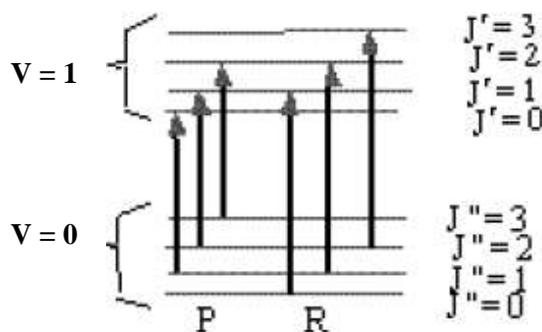


Figure 1: Rotational and vibrational levels of diatomic molecule.

The absorption wave numbers, $\omega = [E(v = 1, J') - E(v = 0, J'')]$. Using equations 20 and 21, we see that absorptions are at the following wavenumbers:

$$\omega \approx \omega_e + B_e [J'(J'+1) - J''(J''+1)] \text{----- (23)}$$

When a molecule absorbs infrared radiation, the vibrational transition is accompanied by rotational transition. The selection rules for absorption of infrared radiation in the rigid-harmonic oscillator approximation are

$$\Delta v = + 1$$

$$\Delta J = \pm 1$$

For the case of $\Delta J = +1$ the eq.(21) becomes

$$E \approx \omega_e (1 + \frac{1}{2}) + B_e (J+1)(J+2) - \omega_e (0 + \frac{1}{2}) - B_e J(J+1)$$

$$E \approx \omega_e + B_e [(J+1)(J+2) - J(J+1)]$$

$$E \approx \omega_e + B_e [J^2 + 2J + J + 2 - J^2 - J]$$

$$E \approx \omega_e + B_e [2J + 2]$$

$$E \approx \omega_e + 2B_e [J + 1] \text{ ----- (24)}$$

{where $J = 0, 1, 2, 3, 4, 5, \dots$ }

Likewise for the case of $\Delta J = -1$ the eq. 21 becomes

$$E \approx \omega_e - 2B_e J \text{ ----- (25)}$$

In both equations (24) and (25) J is the initial rotational quantum number. Typically ω_e is of the order 10^3 cm^{-1} , so the spectrum predicted by equations (24) and (25) for diatomic molecule contains lines at $10^3 \text{ cm}^{-1} \pm \text{integral of } B_e$ as shown in **Fig. 2**.

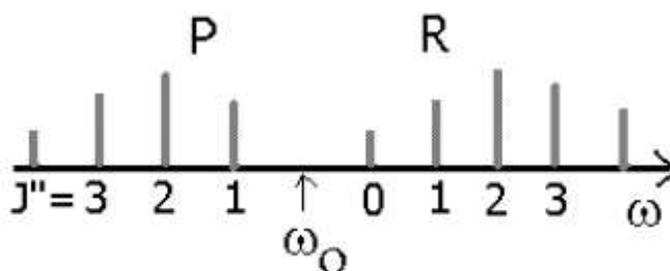


Figure 2: Schematic P and R branches for diatomic molecule.

Absorptions for which $J' = J'' + 1$ are said to belong to the "R" branch; those with $J' = J'' - 1$ are on the "P" branch. Spectrum should look qualitatively as shown in **Fig. 2**

Note: spectrometers may plot ω in increasing order either to the left or to the right. It is higher wave number, not left-right orientation that defines the R branch relative to the P branch. Also there is no line at ω_e because the transition $\Delta J = 0$ is forbidden.

The rotational - vibrational spectrum of HBr(g) is shown in **Fig. 3**.

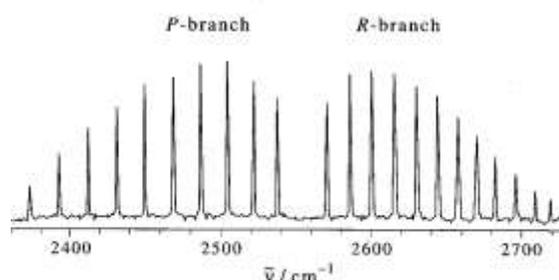


Figure 3: Rotational-Vibrational spectrum of HBr(g) ($0 \rightarrow 1$ vibrational transition).

Solved problems:

- 1) The bond length in $^{12}\text{C}^{14}\text{N}$ is 117 pm and its force constant is 1630 Nm^{-1} . Predict the vibration-rotation spectrum $^{12}\text{C}^{14}\text{N}$.

Solution: Given,

Bond length $R_e = 117 \text{ pm} = 117 \times 10^{-12} \text{ m}$ [1 pico meter is equal to 10^{-12} m or 10^{-10} cm]

$$\gamma = 1630 \text{ Nm}^{-1}$$

First we must calculate the fundamental vibration frequency ω_{osc} (Equation (4) in unit 8), rotational constant B_e (equation 21a). Both quantities require the reduced mass, which is calculated as follows,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{compound is } ^{12}\text{C}^{14}\text{N}, m_1 = 12, m_2 = 14$$

$$\therefore \mu = \frac{12 \times 14}{12 + 14} \times 1.66 \times 10^{-27} \text{ kg} = \frac{168}{28} \times 1.66 \times 10^{-27} \text{ kg}$$

$$\mu = 6.46 \times 1.66 \times 10^{-27} \text{ kg} = 1.07 \times 10^{-26} \text{ kg}$$

$$\omega_{\text{osc}} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{\frac{1}{2}}$$

$$= \frac{1}{2 \times (3.14)^2 (2.99 \times 10^8 \text{ m})} \left(\frac{1630}{1.07 \times 10^{-26}} \right)^{\frac{1}{2}}$$

$$= 2.07 \times 10^5 \text{ m}^{-1}$$

$$= 2.07 \times 10^3 \text{ cm}^{-1}$$

$$B_e = \frac{h}{8\pi^2 c \mu R_e^2}$$

$$= \frac{6.626 \times 10^{-34}}{8 \times (3.14)^2 (2.998 \times 10^8 \text{ m}) (1.17 \times 10^{-26} \text{ kg}) (117 \times 10^{-12} \text{ m})^2}$$

$$= 191 \text{ m}^{-1}$$

$$B_e = 1.91 \text{ cm}^{-1}.$$

The vibration-rotation spectrum will consist of line at $\omega_e \pm 2B_e J$ where $J = 1, 2, 3, \dots$ there will be no line at ω_e and the separation of lines in the P and R branches will be at $2B_e = 3.82 \text{ cm}^{-1}$.

- 2) The line in the R and P branches are customarily labeled by the initial value of the rotational quantum number giving rise to the lines R (0), R(1), R(2)..... , and P(1), P(2)....., given for the $^1\text{H}^{127}\text{I}$ as follows,

Lines	Frequency (cm^{-1})
R(0)	2242.087
R(1)	2254.257
P(1)	2216.723
P(2)	2203.542

Calculate B_0 , B_1 , and R_e ($v = 0$) and R_e ($v = 1$). The reduced mass of the molecule is 1.660×10^{-27} kg.

Solution,

Given $\mu = 1.660 \times 10^{-27}$ kg.

Using eq. (24).

$$\left. \begin{aligned} 2242.087 \text{ cm}^{-1} &= \omega_e + 2B_e \text{ (J = 1)} \\ 2254.257 \text{ cm}^{-1} &= \omega_e + 6B_e - 2B_e \text{ (J = 2)} \end{aligned} \right\} \text{R-branch (Higher frequency)}$$

Similarly using eq. (25)

$$\left. \begin{aligned} 2216.723 \text{ cm}^{-1} &= \omega_e - 2B_e \text{ (J = 1)} \\ 2203.541 \text{ cm}^{-1} &= \omega_e - 2B_e - 6B_e \text{ (J = 2)} \end{aligned} \right\} \text{P-branch (Lower frequency)}$$

If we subtract the first line of the P-branch from the second line of R-branch, we get

$$\begin{aligned} 37.534 \text{ cm}^{-1} &= 6B_e \\ \therefore B_e = B_1 &= 6.256 \text{ cm}^{-1} \end{aligned}$$

Similarly if we subtract the second line of the P branch from the first line of the R-branch, we find

$$\begin{aligned} 38.546 \text{ cm}^{-1} &= 6B_e \\ \therefore B_e = B_0 &= 6.423 \text{ cm}^{-1} \end{aligned}$$

Using equation $B_e = \frac{h}{8\pi^2 c \mu R_e^2}$ we can calculate R_e ($v = 0$) = 162.0 pm and R_e ($v = 1$) 164.1

pm

- 3) The mean of the internuclear distance for H^{35}Cl in the $v = 0$ and $v = 1$ levels is 1.293 \AA . Calculate the wave-number difference between the R(0) and P(1) lines of the fundamental

band for H^{35}Cl . Given: $h = 6.63 \times 10^{-34} \text{ Js}$; $c = 3.0 \times 10^8 \text{ ms}^{-1}$. The reduced mass of HCl molecule is $1.61 \times 10^{-27} \text{ kg}$

Solution: The internuclear distance has been taken same in $v = 1$ and $v = 0$ states. It means that the vibration-rotation interaction has been ignored.

The mean rotational constant for the molecule is

$$B_e = \frac{h}{8\pi^2 c \mu R_e^2}$$

$$= \frac{6.63 \times 10^{-34} \text{ Jc}}{8(3.14)^2 (1.61 \times 10^{-27} \text{ kg})(1.293 \times 10^{-10} \text{ m})^2 (3.0 \times 10^8 \text{ ms}^{-1})} = 1041 \text{ m}^{-1}$$

When the vibration-rotation is ignored, the wave number of R and P lines are given by

$$V_R = R(J) = V_0 + 2B + 2BJ; \quad J = 0, 1, 2, \dots$$

$$V_P = P(J) = V_0 - 2BJ; \quad J = 1, 2, 3, 4, \dots$$

$$\therefore R(0) - P(1) = (V_0 + 2B) - (V_0 - 2B)$$

$$= 4B = 4 \times 1041 \text{ m}^{-1} = 4164 \text{ m}^{-1} = 41.64 \text{ cm}^{-1}$$

10.3 The vibration-rotation spectrum of carbon monoxide

Fig. 4 shows the fundamental vibration-rotation band of carbon monoxide under high resolution. Some lines in the spectra are in the P branches and some are in R branches numbered according to their J'' values. **Table 1** gives the observed wave numbers of the first five lines in each branch. From the table we see that the band centre is at about 2143 cm^{-1} while the average line separation near the centre is 3.83 cm^{-1} . This immediately gives, $2B = 3.83 \text{ cm}^{-1}$, $B = 1.915 \text{ cm}^{-1}$

This is in satisfactory agreement with the value $B = 1.92118 \text{ cm}^{-1}$ derived by microwave studies, and we could, therefore, have obtained quite good values for the rotational constant and hence the moment of inertia and bond length from infrared data alone.

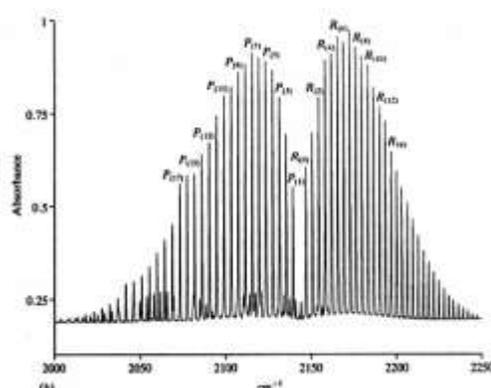


Figure 4: Fundamental bands of CO under high resolution.

Table 1: Part of the infra-red spectrum of CO

Line	ν	Separation, $\Delta\nu$	Line	ν	Separation, $\Delta\nu$
P ₍₁₎	2139.43		R ₍₀₎	2147.08	
P ₍₂₎	2135.55	3.88	R ₍₁₎	2150.86	3.78
P ₍₃₎	2131.63	3.92	R ₍₂₎	2154.59	3.73
P ₍₄₎	2127.68	3.95	R ₍₃₎	2158.31	3.72
P ₍₅₎	2123.70	3.98	R ₍₄₎	2161.97	3.66

10.4 Isotope Effects

The reduced mass of the molecule affects both the vibrational frequency and the rotational constant. For isotopes of the same molecule, the vibrational force constant k and bond distance R_e are independent of the isotope because they depend only on the behavior of the bonding electrons and not on the mass of atom. Thus, if an asterisk distinguishes a molecule of different isotope, we have

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\omega_{osc}^* = \frac{1}{2\pi} \sqrt{\frac{k}{\mu^*}}$$

$$\therefore \frac{\omega}{\omega^*} = \left(\frac{\mu^*}{\mu} \right)^{\frac{1}{2}}$$

Similarly

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

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

$$\therefore \frac{B}{B^*} = \frac{\mu^*}{\mu}$$

Since both vibrational frequency ω_{osc} and the force constant B_e are part of the total vibrational and rotational energy, the H^{35}Cl , H^{37}Cl , D^{35}Cl , and D^{37}Cl each have unique spectra because the substitution of different isotopes changes the reduced mass of the molecule. H atoms have the largest change in isotopic mass of all atoms, a factor of ~ 2 in substituting D (i.e. ^2H) for H (i.e. ^1H). The

study of isotope effects is an important tool in mechanistic organic chemistry. For example, in going from H^{35}Cl to D^{35}Cl the reduced mass increases by a factor of about 2 (precisely 1.9440) so the fundamental vibration frequency should decrease by a factor of about 2.

Problems:

1) The fundamental vibration frequency of HCl occurs at 2886cm^{-1} . Predict the frequency of the the corresponding mode of DCl .

Solution: The difference in frequency arises due to difference in masses of the isotope molecules.

$$\text{We know that, } \omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

The force constant k is same for the both the molecules as it is determined by electronic motion.

If ω^* is the vibrational constant for the heavier isotope, then

$$\therefore \frac{\omega}{\omega^*} = \frac{\gamma}{\gamma^*} = \left(\frac{\mu^*}{\mu}\right)^{\frac{1}{2}} = \rho$$

$$\therefore \omega = \omega^* \rho \text{ or } \omega^* = \omega / \rho$$

$$\rho = \sqrt{\frac{\mu_{\text{DCl}}}{\mu_{\text{HCl}}}} = \sqrt{\frac{2 \times 35 / 2 + 35}{1 \times 35 / 1 + 35}} = \sqrt{\frac{70}{37}} \times \frac{36}{35} = 1.4$$

$$\therefore \omega^* = 2886 / 1.4 = 2061\text{cm}^{-1}$$

2) If the fundamental band of H^1Cl^{35} lies at 2.466μ , calculate the wavelength of the corresponding band of H^2Cl^{37}

Solution: for the above problem we know that

$$\frac{\omega}{\omega^*} = \frac{\gamma}{\gamma^*} = \left(\frac{\mu^*}{\mu}\right)^{\frac{1}{2}} = \rho$$

$$\text{and } \omega = \omega^* \rho \text{ or } \omega^* = \omega / \rho$$

$$1/\lambda = 1/\lambda^* \rho \quad (\text{since wave number } 1/\lambda = \omega)$$

$$\therefore \lambda = \lambda^* \rho$$

$$\rho = \sqrt{\frac{\mu_{\text{DCl}^{37}}}{\mu_{\text{HCl}}}} = \sqrt{\frac{2 \times 37 / 2 + 37}{1 \times 35 / 1 + 35}} = \sqrt{\frac{74}{39}} \times \frac{36}{35} = 1.4$$

$$\therefore \lambda^* = 3.46\mu \times 1.4 = 4.84\mu$$

10.5 Fundamental and Overtone bands

Fundamental vibrational frequencies of a molecule corresponds to transition from $v = 0$ to $v = 1$. For a non-linear molecule there will be $3N-6$ (where N is the number of atoms) number vibrations. For linear molecules, there will be $3N-5$ number of vibrations, because a linear molecule has one less rotational degrees of freedom. **Fig. 5** shows a diagram for a vibrating diatomic molecule. The levels denoted by vibrational quantum numbers v represent the potential energy for the harmonic oscillator. The transition $0 \rightarrow 1$ is called fundamental transition or bands, transitions $0 \rightarrow n$ ($n > 1$) are called overtones transitions or bands, and transitions $1 \rightarrow n$ ($n < 1$) are called hot transitions or hot bands.

Overtone

Overtone occurs when a vibrational mode is excited from $v = 0$ to $v = 2$, which is called the first overtone, or $v = 0$ to $v = 3$, the second overtone. The fundamental transitions, $v = \pm 1$, are the most commonly occurring, and the probability of overtones rapidly decreases as $v = \pm n$ increases. Based on the harmonic oscillator approximation, the energy of the overtone transition will be about n times the fundamental associated with that particular transition. The anharmonic oscillator calculations show that the overtones are usually less than a multiple of the fundamental frequency. Overtones are generally not detected in larger molecules.

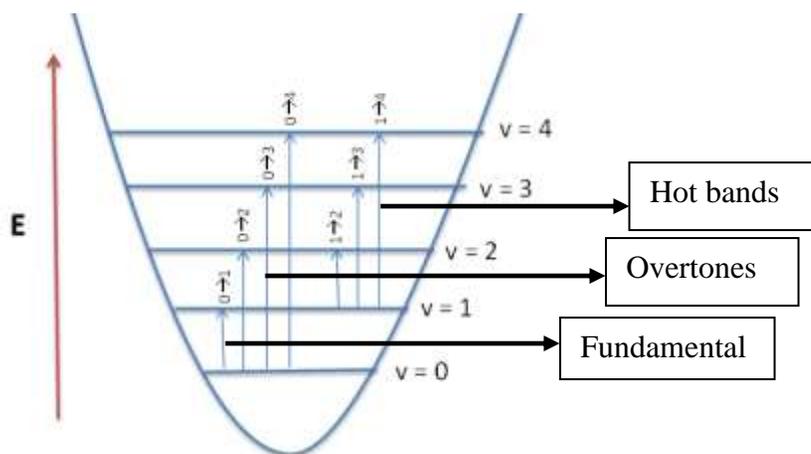


Figure 5: Fundamental and overtone vibrating frequencies of diatomic molecule.

Hot Bands

Hot bands are observed when an already excited vibration is further excited. For example an v^1 to v^2 transition corresponds to a hot band in the IR spectrum. *These transitions are temperature*

dependent, with lower signal intensity at lower temperature, and higher signal intensity at higher temperature. This is because at room temperature only the ground state is highly populated ($kT \sim 200 \text{ cm}^{-1}$), based on the Boltzmann distribution. The Maxwell-Boltzmann distribution law states that if molecules in thermal equilibrium occupy two states of energy ϵ_j and ϵ_i , the relative populations of molecules occupying these states will be,

$$\frac{n_j}{n_i} = \frac{e^{-\frac{E_j}{RT}}}{e^{-\frac{E_i}{RT}}} = e^{-\Delta E/RT}$$

where, k is the Boltzmann constant and T is the temperature in Kelvin.

In the harmonic oscillator model, hot bands are not easily distinguished from fundamental transitions because the energy levels are equally spaced. Because the spacing between energy levels in the anharmonic oscillator decreases with increasing vibrational levels, the hot bands occur at lower frequencies than the fundamentals. Also, the transition moment integrals are slightly different since the ground state will not necessarily be totally symmetric since it is not in $v = 0$.

Fermi Resonances

Fermi resonance results in the splitting of two vibrational bands that have nearly the same energy and symmetry in both IR and Raman spectroscopies. The two bands are usually fundamental vibrations. The wave functions for the two resonant vibrations mix according to the harmonic oscillator approximation, and the result is a shift in frequency and a change in intensity in the spectrum **Fig 6**. As a result, two strong bands are observed in the spectrum, instead of the expected strong and weak bands. It is not possible to determine the contribution from each vibration because of the resulting mixed wave function. If the symmetry requirements are fulfilled and the energies of the two states are similar, mixing occurs, and the resulting modes can be described by a linear combination of the two interacting modes. The effect of this interaction is to increase the splitting between the energy levels. The splitting will be larger if the original energy difference is small and the coupling energy is large. The mixing of the two states also equalized the intensities of the vibrations which allow a weak overtone or combination band to show significant intensity from the fundamental with which it has Fermi resonance with.

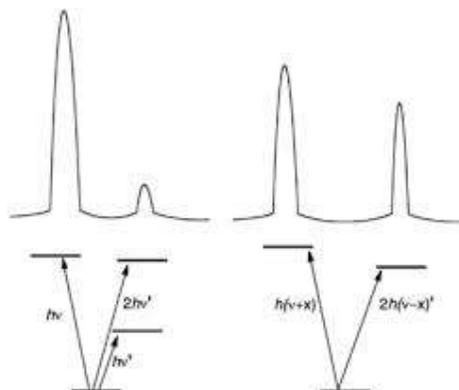


Figure 6: intensity and frequency shifts due to Fermi resonance.

10.6 Vibrations of polyatomic molecules

Consider a molecule containing N atoms; we can refer to the position of each atom by specifying three coordinates (e.g., the x , y , and z Cartesian coordinates). Thus the total number of coordinate values is $3N$ and we say that the molecule has $3N$ *degrees of freedom* since each coordinate value may be specified quite independently of the others. However, once all $3N$ coordinates have been fixed the bond distances and bond angles of the molecule are also fixed and no further arbitrary specifications can be made.

Now the molecule is free to move in three-dimensional space as a whole, without change of shape. We can refer to such movement by noting the position of its centre of gravity at any instant, to do this requires a statement of three coordinate values. This translational movement uses three of the $3N$ degrees of freedom leaving $(3N - 3)$. In general, also, the rotation of a non-linear molecule can be resolved into components about three perpendicular axes. Specification of these axes also requires three degrees of freedom, and the molecule is left with $(3N - 6)$ degrees of freedom. The only other motion allowed to it is internal vibration, so we immediately that a non-linear N -atomic molecule can have $(3N - 6)$ different internal vibrations.

Non-linear: $(3N - 6)$ fundamental vibrations

If, on the other hand, the molecule is linear, there is no rotation about the bond axis. Hence, only two degrees of rotational freedom are required, leaving $(3N - 5)$ degrees of vibrational freedom (one more than in the case of a non-linear molecule).

Linear: $(3N - 5)$ fundamental vibrations

In both cases, since an N-atomic molecule has (N-1) bonds (for acyclic molecules) between atoms, (N- 1) of the vibrations are bond-stretching motions and the other (2N – 5) (non-linear) or (2N- 4) (linear) are bending motions.

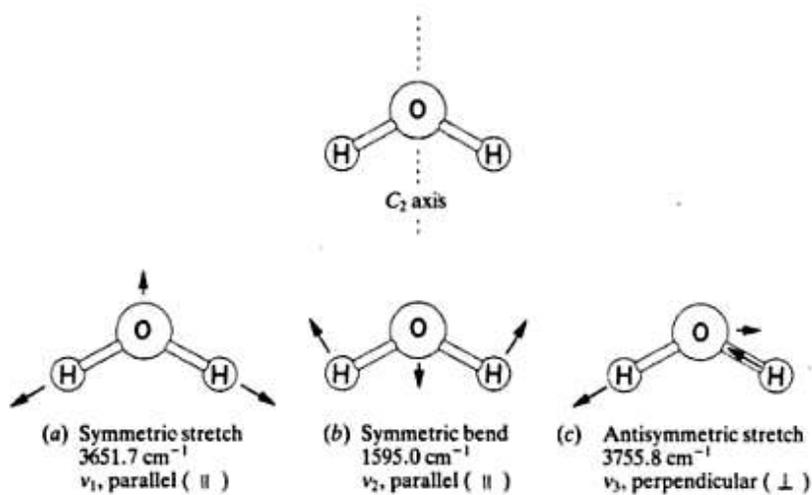


Figure 7: The three fundamental vibrations of H_2O molecule.

Let us look briefly at examples of these rules. First, we see that for a diatomic molecule, $N = 2$, $(3N - 5) = 1$ and thus can be only one fundamental vibration. Note, however, that the $(3N - 5)$ rule says nothing about the presence, absence or intensity of overtone vibrations.

Consider H_2O , this (**Fig. 7**) is non-linear and triatomic. Hence $(3N - 6) = 3$ allowed vibrational modes, the arrows attached to each atom showing the direction of its motion during half of the vibration. Each motion is described as stretching or bending depending on the nature of the change in molecular shape.

These three vibrational motions are also referred to as the normal modes of vibration (or normal vibrations) of the molecule. In general, a normal vibration is defined as a molecular motion in which all the atoms oscillate with the same frequency and pass through their equilibrium positions simultaneously. Further, each motion is labelled either symmetric or antisymmetric.

For linear triatomic molecules, $(3N - 5) = 4$, and we would expect four vibrational modes instead of the three shown in **Fig. 8**. However, ν_2 consists of two vibrations-one in the plane of the paper and the other in which the oxygen atoms move simultaneously into and out of the plane. The two sorts of motion are identical in all respects except direction and are termed degenerate. They must be considered as separate motions.

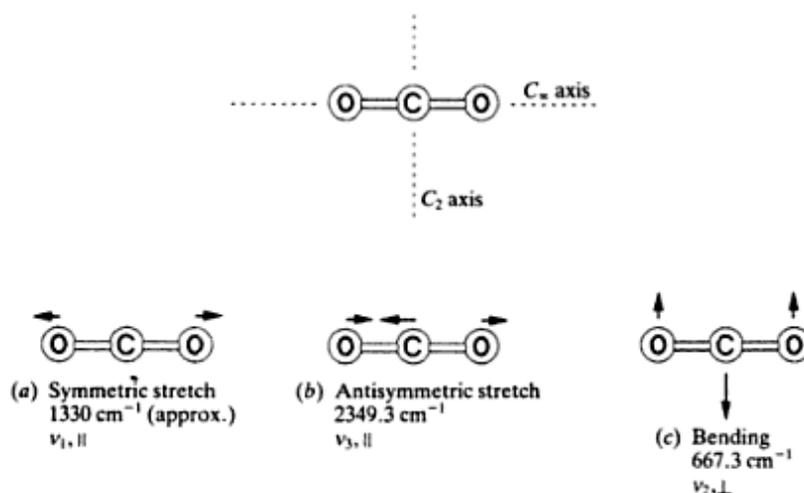


Figure 8: The fundamental vibrations of the carbon dioxide molecule.

10.7 Parallel and perpendicular vibrations:

We know that for a vibration to be infrared active there must be a change in the dipole moment during the vibration. If the molecule possesses some degree of symmetry, the direction of the dipole moment change may coincide with one or more of the principal axes of the molecule. The nature of the dipole moment change for the three vibrations of an angular XY_2 molecule is shown in **Fig. 9**. It shows that the dipole moment change for the symmetric stretching and bending vibrations occurs parallel to the two-fold rotation-axis and for the asymmetric stretching mode, the dipole moment change occurs perpendicular to the symmetry axis. The symmetric stretching and bending vibrations are classified as parallel vibrations and the asymmetric stretching mode as a perpendicular vibration. Similarly, for a linear XY_2 molecule, the stretching vibrations are classified as parallel vibrations and the bending mode as a perpendicular vibration as shown in **Fig. 10**

A vibration is classified as a parallel or perpendicular type usually denoted by the symbol \parallel or \perp , respectively depending on, as stated above, whether the dipole moment change is parallel or perpendicular to the principal rotational axis of symmetry of the molecule. Every band, either a fundamental or an overtone, may be classified as belonging to the parallel or perpendicular type. The selection rules for rotational transitions of a vibrating polyatomic molecule depend rather surprisingly on whether it is a parallel or perpendicular vibration. Thus, the selection rules for the rotational structure on a vibrational band depend on the orientation of the vibrational transition

moment within the molecule. The selection rules and the energies for rotational transitions depend on the rotator type to which the molecule belongs.

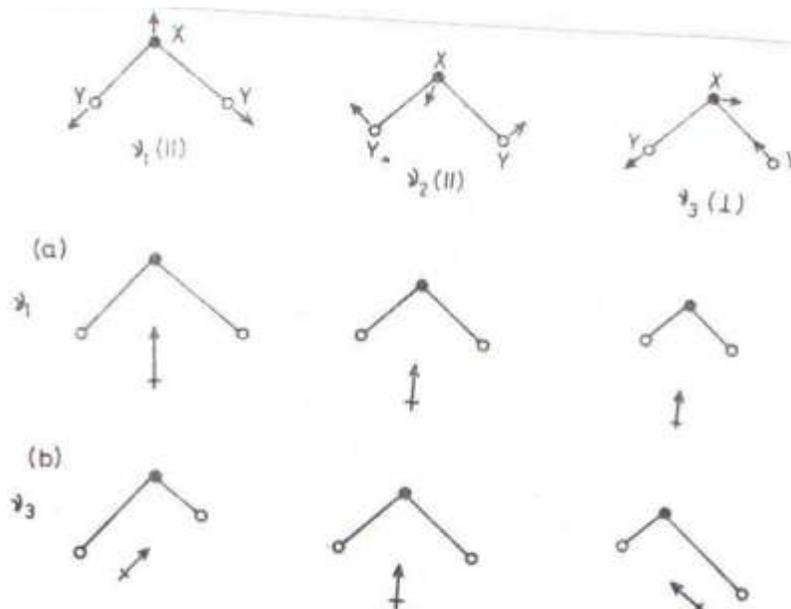


Figure 9: Change in the dipole moment during vibrations of a bent triatomic molecule, (a) parallel vibration and (b) perpendicular vibration.

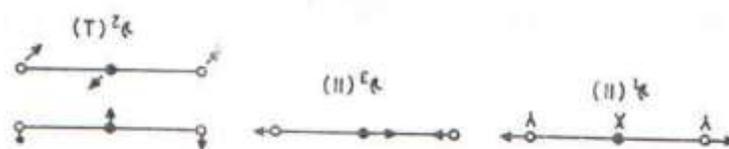


Figure 10: Dipole moment change during the vibrations of a linear triatomic molecule

10.8 Summary of the Unit

The spacing between vibrational energy levels decreases with increasing v , but stays finite up to the dissociation energy. This means that only a finite number of vibrational levels fit into the potential well of a bound molecular state. This is in contrast to the infinite number of electronic states in an atom. Here the distance between Rydberg levels converges with $n \rightarrow \infty$ towards zero.

One has to distinguish between the experimentally determined dissociation energy E_D^{ep} , where the molecule is dissociated from its lowest vibration level, and the binding energy E_B of the potential well, which is measured from the minimum of the potential. The difference is calculated by the equation $E_D^{\text{ep}} = E_B - \frac{1}{2}h\omega$.

The above equation holds good for rotation of a non vibrating molecule and the vibration of a nonrotating molecule. A real molecule can simultaneously rotate and vibrate. Since the vibrational frequency is higher than the rotational frequency by one or two order of magnitude. Therefore, the molecule undergoes many vibrations during one rotational period. This means that the nuclear distance changes periodically during the full rotation. Since the total angular momentum $J = I \times \omega$ of a freely rotating molecule has to be constant in time, but the moment of inertia I is periodically changes. Hence the rotational frequency ω has to change accordingly with a period T_{vib} .

Because the total energy $E = E_{\text{rot}} + E_{\text{vib}} + E_{\text{pot}}$ has to be constant, there is a periodic exchange of rotational, vibrational and potential energy in the vibrating rotor. All allowed transitions of $J'' \rightarrow J'$ between the rotational levels in a given vibrational level form the lower state to the upper state form a *band*. In vibrational-rotational spectra, a band consists of many rotational lines. Transitions with $J = 0$ form the **Q-branch**, those with $J = +1$ the **R-branch** and with $J = -1$ the **P-branch**. Q-branches are only present in transitions where the electronic angular momentum changes by $1h$, in order to compensate for the spin of the absorbed or emitted photon. The total system of all vibrational bands of this electronic transition is called a *band system*. The total number of lines in such a band system depends not only on the transition probabilities but also on the number of populated levels in the lower or upper electronic state.

10.9 Key words:

Isotope effect; Fundamental bands; Overtones; Hot bands; Fermi resonance; stretching vibration; bending vibration.

10.10 References for further study:

- 1) Vibrational/Rotational Spectroscopy of Diatomic Molecules by M Mueller, *Kluwer Academic Publishers*, 2002.
- 2) Vibrational Spectroscopy: Theory and Applications by D. N. Sathyanarayana, *New Age International*, 2007.
- 3) Fundamentals of molecular spectroscopy by Colin N Banwell, Elaine M. McCash, *McGraw Hill*, 5th Ed. 2013.

10.10 Question for self study:

- 1) Derive the expression for the calculation of frequency for the vibartional- rotational spectra of diatomic molecule.

- 2) Derive the expression for isotope effect in vibrational- rotational spectra of diatomic molecule.
- 3) Write a note on Fundamental and overtone bands.
- 4) What are hot bands? Explain their formation in vibration- rotational spectra.
- 5) Write a note on Fermi resonance.
- 6) Write a note on the number of modes of possible vibrations of poly atomic molecule.
- 7) Explain the differences between parallel and perpendicular vibrations.

Problems:

- 1) Calculate the ratio of the vibrational frequencies of hydrogen iodide (H^{127}I) molecule to deuterated hydrogen iodide (D^{127}I) molecule. [Ans. 1.41]
- 2) The fundamental band for D^{35}Cl is centred at 2011.00 cm^{-1} . Assume that the internuclear distance is constant at 1.288 \AA . Calculate the wave numbers of the first two lines of each of the P and R branches of D^{35}Cl . Given: $h = 6.63 \times 10^{-34}\text{ Js}$, $c = 3.0 \times 10^8\text{ m/s}$, $N_A = 6.023 \times 10^{23}\text{ mol}^{-1}$. [Ans. P (1), P(2), R (0) and R (1) are 2000.24 cm^{-1} ; 1989.48 cm^{-1} , 2021.76 cm^{-1} and 2032.52 cm^{-1} respectively.]
- 3) Assume the following data for the molecule $^1\text{H}^{35}\text{Cl}$.
Bond length: 127.5 ; bond force constant 516.3 N/m ; atomic masses $^1\text{H} = 1.673 \times 10^{-27}\text{ kg}$; $^{35}\text{Cl} = 58.066 \times 10^{-27}\text{ kg}$.
Do the following, giving answers in cm^{-1}
 - a) Calculate the zero-point energy and the energy of the fundamental vibration
 - b) Calculate the rotational constant B.
 - c) Calculate the wave numbers of the lines P (1), P(2), P(3), R(0), R(1) and R(2).

UNIT 11**Structure:**

- 11.0 Objectives of the unit
- 11.1 Introduction
- 11.2 Intensity of Absorption band
- 11.3 Types of Absorption
 - Stretching vibrations
 - Bending or deformation vibrations
- 11.4 Interpretation of IR spectra
 - Group frequency region
 - Finger print region
- 11.5 Applications of IR spectra for simple molecules
 - Linear XY_2 type molecule (CO_2)
- 11.6 Factors affecting the group frequency
 - Electrical effects
 - Conjugation
 - Resonance
 - Inductive effect
- 11.7 Hydrogen bonding
- 11.8 Steric effect
- 11.9 Effect of ring strain
- 11.10 Summary of the unit
- 11.11 Key words
- 11.12 References for further study
- 11.13 Questions for self study

11.0 Objectives of the unit

After studying this unit you are able to

- Predict the intensity of IR absorption bands by calculation.
- Identify the types of Absorption.
- Interpret the IR spectrum of the given compound.
- Recognize the group frequency region and finger print region in IR spectra.
- Identify and explain factors affecting the group frequency.

11.1 Introduction

The intensity of an absorption in the IR spectrum is related to the change in dipole that occurs during the vibration. Consequently, vibrations that produce a large change in dipole (e.g. C=O stretch) result in a more intense absorption than those that result in a relatively modest change in dipole (e.g. C=C). Vibrations that do not result in a change in dipole moment (e.g., a symmetrical alkyne C triple bond C stretch) will show little or no absorption for this vibration.

11.2 Intensity of Absorption band

The intensity of an absorption band depends on the change in the dipole moment of the bond and the number of the specific bonds present. The bond dipole results from two things: the bond length and the charge difference between the two atoms. When the molecule absorbs a photon, it stretches and the bond length changes. So that only leaves the charge difference, which can be derived from the electronegativity values of the atoms involved. If we have two different atoms, there will be an electronegativity difference and a photon will be absorbed. If there is no electronegativity difference, such as in an O₂ or an N₂ molecule, then a photon will not be absorbed, and the molecule will not be excited to a higher vibrational state. On the other hand, the bigger the electronegativity difference, the more intense the absorption is. Additionally, the number of the specific bond also determines the intensity of a peak. For example, if you compare the IR spectra of methane to that of octane, the octane molecule will have a much more intense C-H peak because it has many more C-H bonds than methane.

Another factor that determines the peak intensity in infrared spectra is the concentration of molecules in the sample. The equation that relates concentration to absorbance is Beer's law,

$$A = \epsilon lc$$

Where A = absorbance, ϵ = absorptivity, l = path length, c = concentration

E.g. C=C stretching vibration in 2-methyl-but-2-ene has molar absorptivity of only about 5. Similarly C=N, C-C and C-H stretching vibrations tend to give weak absorption bands. On the other hand, carbonyl and other polar groupings like Si-O, C-Cl or C-F tend to give very intense infrared bands with absorptivity in the range 100 to 1000.

11.3 Types of Absorption

Normal modes of vibrations are of two types (1) stretching and (2) bending vibrations.

(1) *Stretching vibrations:*

In this type of vibration, the atom moves essentially along the bond axis, so that the bond length increases at regular intervals, but the atom remain in the same bond axis. Such a mode of vibration does not cause any dipole change in the symmetrical molecule such as O=C=O, and therefore is IR inactive. Stretching vibrations are of two types.

(a) *Symmetrical stretching:* In this type of stretching, with respect to a particular atom, other two atoms in a molecule move in the same direction. E.g. In the case of methylene group (H-C-H), the two hydrogen atoms move away from the central carbon atom without change in the bond angle (**Fig. 1a**)

(b) *Asymmetric stretching:* In this type of stretching one atom move away from the central atom while other atom move towards the central atom. E.g. In methylene group one hydrogen atom approaches the carbon atom while the other hydrogen atom moves away from the carbon atom (**Fig. 1b**).

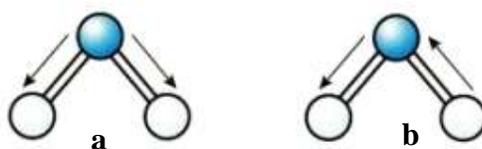


Figure: 1a) Symmetric stretching **b)** Asymmetric stretching.

(2) *Bending or deformation vibrations*

Such vibrations may consist of a change in bond angle between bonds with a common atom or movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with respect to one another. These are of four types (a) Scissoring (b) Rocking (c) Wagging (d) Twisting.

(a) *Scissoring:* The two atoms concerned to an atom move towards and away from each other with deformation of valence angle (**Figure 2a**).

- (b) *Rocking*: The structural units swing back and forth in the plane of the molecule (**Figure 2b**).
- (c) *Wagging*: The structural units swing back and forth out of the plane of the molecule (**figure 2c**).
- (d) *Twisting*: The structural units rotate about the bond which joins it to the remainder of the molecule (**Figure 2d**).

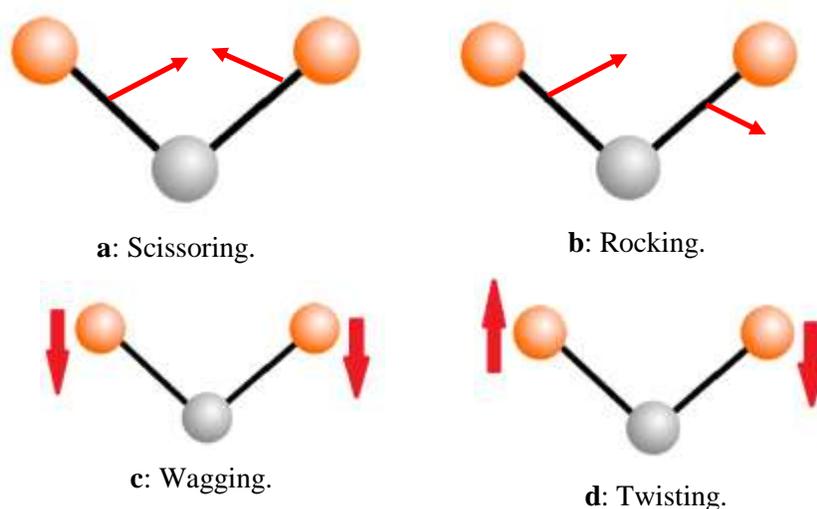


Figure 2: Different bending vibrational motion of polyatomic molecule

11.4 Interpretation of IR spectra:

The band positions of IR spectra are presented as wave number (ν) whose unit is the reciprocal of centimetres (cm^{-1}). IR spectroscopy spans a part of the electromagnetic spectrum in the frequency range of $13,000$ to 10 cm^{-1} . The energy in the range of 100 to 10 cm^{-1} is absorbed and converted into molecular rotation while that in the range $13,000 \text{ cm}^{-1}$ to 100 cm^{-1} is absorbed and converted into molecular vibration. Both these absorption processes are quantized. However, while the rotational spectra of compound consist of discrete lines, the vibrational spectra contain bands rather than discrete bands because each vibrational energy change is accompanied by a number of rotational energy changes.

The IR spectral range is usually divided into three regions: near IR, mid IR and far IR as shown in **Table 1**. In IR, we shall confine ourselves to the mid IR region that is between $4000 - 400 \text{ cm}^{-1}$, which is the most frequently used IR region. Most commercial instruments are designed to operate in this range and hence are most easily available.

Table 1: Infrared spectral ranges

	Near IR	Mid IR	Far IR
Wave number	13,000 – 4,000 cm^{-1}	4,000 – 400 cm^{-1}	400 – 10 cm^{-1}
Wave length	0.78 – 2.5 μm	2.5 – 50 μm	50 - 1000 μm

The IR region ($4000 - 400 \text{ cm}^{-1}$) is of great importance in studying the organic compounds. Since IR spectra contain large number of bands, no two compounds will have the same IR spectrum (except optical isomers). Thus, IR spectra may be regarded as the finger print of the molecule. The fundamental IR region is conveniently divided into (i) group frequency region ($4000 - 1250 \text{ cm}^{-1}$) and (ii) finger print region ($1250 - 400 \text{ cm}^{-1}$).

(i) Group frequency region: In this region absorption bands tend to be characteristic of specific groups of atoms and relatively independent of the composition of the rest of the molecule. Thus, group frequency region is extremely useful for diagnosing the presence or absence of certain functional groups. Further, the region from $4000 - 2500 \text{ cm}^{-1}$ is restricted to hydrogen stretching vibrations, the regions from $2500 - 1600 \text{ cm}^{-1}$ emphasizes double and triple bond stretching vibrations and the regions from $1600 - 1250 \text{ cm}^{-1}$ contains only hydrogen bending vibrations. The characteristic stretching frequencies of some molecular groups are shown in **Table 2**.

(ii) Finger print region: In this region the vibrational frequencies are profoundly affected by the molecular structure as a whole, and therefore bands in this region are considered specific for a particular molecule rather than for a particular functional group. The uniqueness of a given molecule's spectrum in this region justifies calling this as the finger print region.

Table 2: Characteristic stretching frequencies of some molecular groups

Group	Approximate frequency (cm^{-1})	Group	Approximate frequency (cm^{-1})
-OH	3600	$>\text{C}=\text{C}<$	1650
-NH ₂	3400	$>\text{C}=\text{N}<$	1600
$\equiv\text{CH}$	3300	C-C	
$=\text{CH}_2$	3030	C-N	1200 – 1000
-CH ₃	2970	C-O	
	2870	$>\text{C}=\text{S}$	1100
	1460	C-F	1050

	1375	C-Cl	725
-CH ₂	2930	C-Br	650
	2860	C-I	550
	1470		
-SH	2580		
-C≡N	2250		
-C≡C-	2220		
>C=O	1759 - 1600		

In the table we see that, the vibrations of light atoms in the terminal groups (e.g. -CH₃, -OH, -C≡N, >C=O, etc.) are of high frequency, while those of heavy atoms (e.g. C-Cl, C-Br, metal-metal etc.) are low in frequency. Their frequencies and consequently their spectra are highly characteristic of the group.

An example of the application of the group frequency data is shown in the **Fig. 3**. This is the spectrum of thioacetic acid, in which one of the oxygen atoms of acetic acid has been replaced by sulphur atom. The question might be asked – is the molecule CH₃COSH or CH₃CSOH? The IR spectrum gives a very clear answer. It shows a very sharp absorption band at about 1730 cm⁻¹, and one at about 2600 cm⁻¹, and these are consistent with the presence of C=O and SH groups, respectively. Also, there is no strong absorption band at 1100 cm⁻¹, thus indicating the absence of C=S.

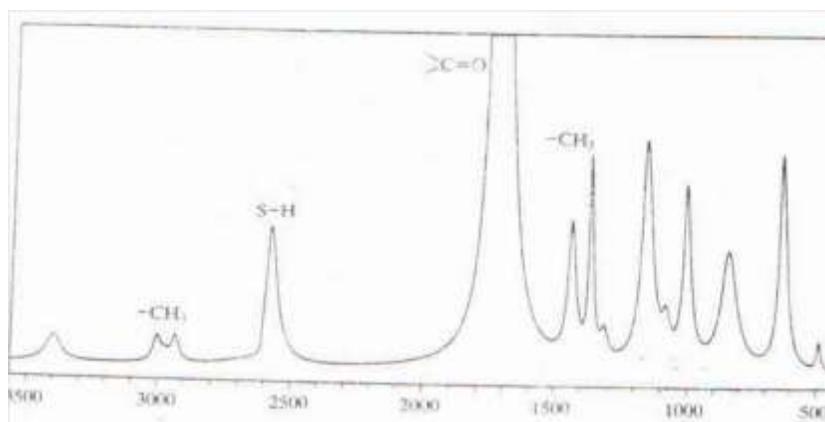


Figure 3: Part of the IR spectrum of thioacetic acid, CH₃COSH.

11.5 Applications of IR spectra for simple molecules:

E.g. Linear XY_2 type molecule (CO_2)

The linear CO_2 molecule will have $(3N - 5) = 4$ fundamental modes of vibration, out of which $(N - 1) = 2$ are stretching modes and $(2N - 4) = 2$ are bending modes. To decide whether all the four modes are IR - active and whether degeneracy exists, it is helpful to diagram the vibrational modes as shown in the **Fig. 4**.

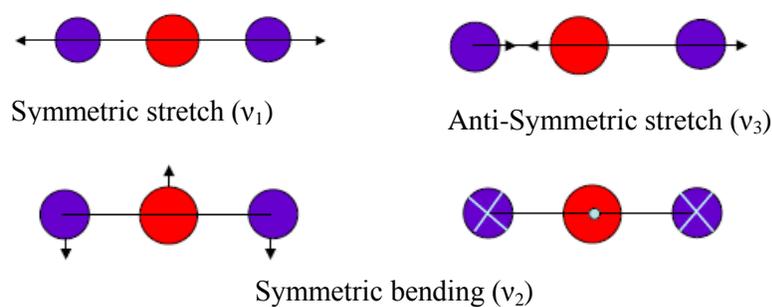


Figure 4: The fundamental vibrations of CO_2 molecule.

Of the four modes of vibrations, symmetrically stretching mode (v_1) involves no change in dipole moment and will thus IR-inactive. On the other hand, this vibration involves a change in polarisability (since ease of displacing bonding electrons will change during the vibration), making this frequency Raman-active. In practice the Raman band appears at 1388 cm^{-1} .

The asymmetrically stretching mode (v_2) will be IR-active since the dipole changes during this vibration. But the polarisability change produced at each atom will be exactly nullified by the asymmetrical displacement of the atom across the symmetry centre and hence the net effect on the polarisability is zero. In practice, IR band for this mode appears at 2349 cm^{-1} .

The frequencies δ_3 and δ_4 are degenerate or occur at the same frequency, and these modes will be IR-active. In practice, δ_3 and δ_4 appear in the IR at 667 cm^{-1} .

11.6 Factors affecting the group frequency:

Electrical effects

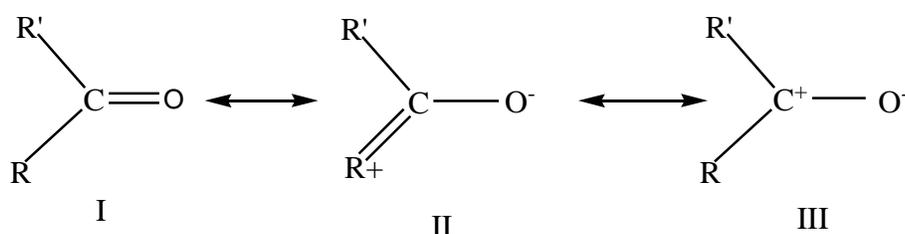
We know that the probable frequency or wave number of absorption can be calculated by the application of Hooke's law. It has been found that the calculated value of frequency of absorption for a particular bond is never exactly equal to its experimental value. The difference arises from the fact that, vibration of each group is influenced by the structure of the molecule in the immediate neighbourhood of the bond. If a particular vibration is absolutely free from any influence, then the infrared spectrum would tell us whether a certain group is not present in the molecule. The value of absorption frequency is also shifted since the force constant of a bond

changes with its electronic structure. There are many factors which are responsible for vibrational shifts and one factor cannot be isolated from another. Following are some of the factors responsible for shifting the vibrational frequencies from the normal values:

1. Conjugation: Conjugation refers to alternate multiple and single bonds, compared with isolated multiple bonds. Hybridization occurs with a result that the multiple bonds transfer some of their π -electron character to the intervening single bond. As a result of conjugation, C=C stretching frequency are shifted to lower frequencies by about $20 - 40 \text{ cm}^{-1}$, compared to isolated double bonds, similarly the C-C stretching frequencies are shifted to higher frequencies. A splitting of absorption bands also results corresponding to in-plane and out-of-plane stretching of alternate C=C bonds. Conjugation can also occur between groups such as C=C and C=O, with the result that both bands are shifted to lower frequencies. An increase in intensity also occurs, which may be visualized as being due to a resonance contribution of the type,



2. Resonance: Resonance refers to the quantum mechanical phenomenon where by a molecular structure is stabilized by contributions from several hypothetical stationary states in such a way that the total energy of the system is minimised. The concept of resonance can be used, for example to explain the effect of adjacent groups on the carbonyl stretching frequency.



Where R' is being varied. The effect of R' can be understood if we consider the contribution of three simple resonance structures, I, II and III.

The **Table 3** shows the frequency of absorption of the carbonyl stretch for five different carbonyl compounds.

Table 3: Effect of adjacent groups on the C=O stretching frequency

Group	Formula	C=O absorption frequency (cm ⁻¹)
Acids	RCOOH	1650
Amides	RCONH ₂	1670
Ketones	RCOR'	1700
Esters	RCOOR''	1735
Acid chlorides	RCOCl	1800

The actual contribution of any particular structure (I, II or III) will depend on the ability of groups R and R' to attract or repel electrons, which in turn depends on the relative electronegativities of R and R'. If the contribution of structure I is significantly greater than that of structures II and III, a normal carbonyl stretching frequency of around 1700 cm⁻¹ is to be expected like that observed with most dialkyl ketones (e.g. acetone and diethyl ketone). If on the other hand, structure II is a significant factor in the electron distribution within the carbonyl group, we can expect a shift of the observed band position to lower frequencies as a result of the increased single bond character of C=O bond system. Structure II becomes important when R is a basic (electron donating) group, and this is the case in acids and amides where R is hydroxyl or amido (**Table 3**). Conversely, groups like OR or Cl, structure III becomes significant and the observed band position shift to higher frequencies. This is due to highly electrostatic nature of C⁺-O⁻ bond which increases the strength of the bond. Thus, the concept of resonance qualitatively explains the effects of shifts in C=O stretching frequency.

3. Inductive effect: The ability of an atom or group of atoms to attract or repel electrons is responsible for inductive effect. Consider a saturated aliphatic ketone, say acetone (CH₃-CO-CH₃), in which C=O stretching absorption takes place at about 1715 cm⁻¹. This absorption frequency undergoes changes as a result of change in the environment of the carbonyl group.

A halogen atom on a carbon atom α- to the ketone functional group increases the vibrational frequency of absorption. E.g. α-chloroacetone (CH₂-CO-CH₂Cl) gives C=O absorption at 1725 cm⁻¹. This halogen effect is observed only when H-X (H-halogen) bond can become coplanar with the C=O bond. E.g. α, α-dichloroacetone (CH₃COCHCl₂) still shows C=O absorption at 1725 cm⁻¹, α, α'-dichloroacetone (ClCH₂COCH₂Cl), however shows twice the effect and absorbs at 1740 cm⁻¹.

The introduction of halogen atom (an electronegative atom) causes negative inductive effect which results in shortening or strengthening of the bond. Consequently, the force constant increases and so frequency of absorption also increases. When alkyl group is attached to the α -position of the C=O group, it exerts a positive inductive effect and causes the wave number of absorption to decrease (as force constant decreases as a result of lengthening or weakening of bond). E.g. C=O stretching absorption of HCHO occurs at 1735 cm^{-1} and that of CH_3CHO at 1730 cm^{-1} .

In acetone, CH_3COCH_3 the C=O group is flanked by two $-\text{CH}_3$ groups. Thus, two positive inductive methyl group make C=O bond strength weak to a greater extent than that of acetaldehyde (CH_3CHO) where only one $-\text{CH}_3$ group is present. Hence C=O absorption occurs at lower wave number than ketone.

11.7 Hydrogen bonding

Hydrogen bonding is a special type of interaction between a proton donor group XH and a proton acceptor atom whereby the hydrogen atom serves as a bridge between the two electronegative atoms. In IR studies, X is usually oxygen or nitrogen, although it may be fluorine.

The effect of hydrogen bonding on IR spectra causes both shifts and broadens the XH stretching band. The shift in frequency to lower energy, because the hydrogen bonding association will tend to weaken the X-H bond. The broadening is generally due to the random degree of association between various molecules.

Among the two types of hydrogen bonding, intermolecular hydrogen bonding (between different molecules) is more important. The essential difference between intermolecular and intramolecular hydrogen bonding is that, the spectral shifts for intermolecular hydrogen bonding show a strong concentration dependence, whereas spectral shifts for intramolecular hydrogen bonding are independent of concentration.

Fig. 5 shows the absorption spectra in the region of O-H stretch for three different concentrations of n-butanol in carbon tetrachloride. To explain the change in spectra, we may assume that equilibria are set up between monomers, dimers, trimers and other polymeric species. Thus, at low concentrations of alcohols, we may assume that mainly monomer is present, giving a sharp absorption band at about 3623 cm^{-1} (almost free OH stretching frequency). At higher concentrations, higher portions of the associated species form, with the result that their absorption maxima shift to lower frequency and broaden considerably.

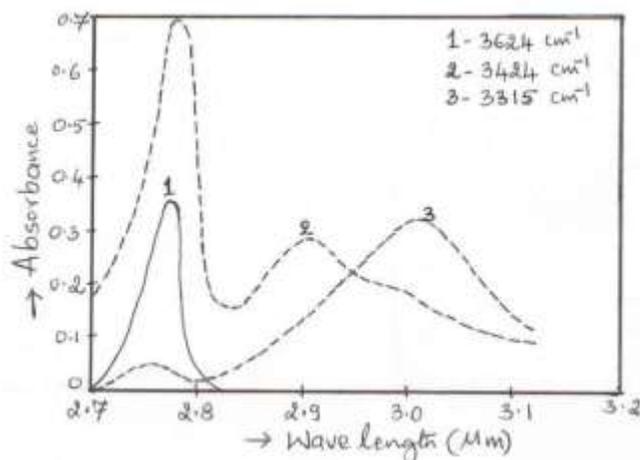
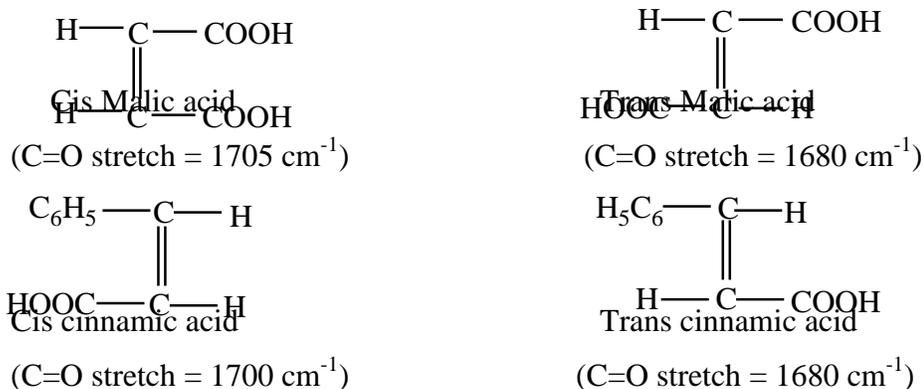


Figure 5: IR absorption spectra of n-butanol in different concentrations of carbon.

11.8 Steric effect

Cis – Trans isomers of an acid show differences in the characteristic C=O stretching frequency.

E.g.

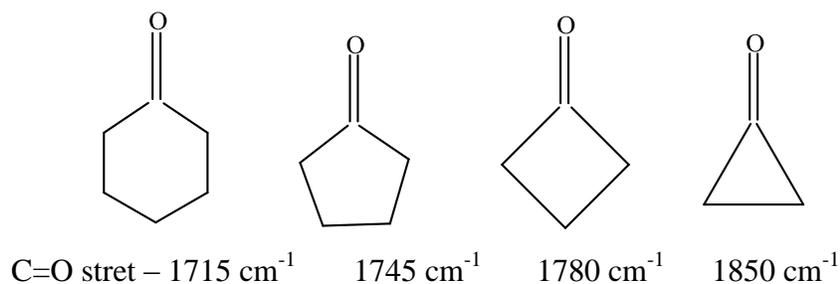


It is well evident from the above examples that, C=O stretching absorption for Cis acids appear at higher wave number than for Trans form of the acids. Because of steric effect (two bulkier groups remains at the same side of the double bond, C=C) in cis form. So, C=O part of –COOH group remain outside the plain of the double bond. Hence, conjugation between C=O and C-C decreases and the frequency of absorption increases.

11.9 Effect of ring strain

Ring strain in cyclic compounds causes a comparatively large shift of the C=O stretching frequency to a higher value. This provides a dependable test to distinguish clearly between three, four, five and larger member ring ketones. Six membered ring ketones show the normal frequency found for the open compounds. Two explanations have been advanced to explain this influence of strain on C=O stretching frequency. The C-CO-C bond angle is reduced below the

normal (120° in acyclic and six membered ring ketones) in strained rings. This leads to an increase in the 's' character in the C=O bond which is therefore strengthened and consequently C=O stretching frequency is increased. Normal acyclic ketones can be recognised by a strong bond at 1720 cm^{-1} . Branching at the α -carbon atom leads to an increase in the C-CO-C bond angle leading to a decrease in the frequency of absorption from the normal value of 1720 cm^{-1} to, for e.g. 1698 cm^{-1} in di-*t*-butylketone. Conversely as the C-CO-C bond angle is decreased, the absorption frequency rises in the case of cyclopentane and cyclobutane in comparison to cyclohexane.



11.10 Summary of the unit:

The covalent bonds of molecules are not rigid, but are more like stiff springs that can be stretched and bent. At ordinary temperatures these bonds vibrate in a variety of ways, and the vibrational energies of molecules may be assigned to quantum levels in the same manner as are their electronic states. Transitions between vibrational energy states may be induced by absorption of infrared radiation, having photons of the appropriate energy. It requires more energy to stretch (or compress) a bond than to bend it, and as might be expected, the energy or frequency that characterizes the stretching vibration of a given bond is proportional to the bond dissociation energy. The force constant (k) is proportional to the strength of the covalent bond linking m_1 and m_2 . In the analogy of a spring, it corresponds to the spring's stiffness. For example, a C=N double bond is about twice as strong as a C-N single bond, and the C≡N triple bond is similarly stronger than the double bond. The infrared stretching frequencies of these groups vary in the same order, ranging from 1100 cm^{-1} for C-N, to 1660 cm^{-1} for C=N, to 2220 cm^{-1} for C≡N.

An important observation is that many functional group absorb infrared radiation at about the same wavenumber, regardless of the structure of the rest of the molecule. For example, C-H stretching vibrations usually appear between 3200 and 2800 cm^{-1} and carbonyl(C=O) stretching vibrations usually appear between 1800 and 1600 cm^{-1} . This makes these bands diagnostic

markers for the presence of a functional group in a sample. These types of infrared bands are called group frequencies because they tell us about the presence or absence of specific functional groups in a sample.

11.11 Key words

Intensity of Absorption band; stretching vibrations; Deformation vibrations; Group frequency region; Finger print region; Conjugation; Steric effect; Hydrogen bonding.

11.12 References for further study

- 1) Vibrational/Rotational Spectroscopy of Diatomic Molecules by M Mueller, *Kluwer Academic Publishers*, **2002**.
- 2) Vibrational Spectroscopy: Theory and Applications by D. N. Sathyanarayana, *New Age International*, **2007**.
- 3) Fundamentals of molecular spectroscopy by Colin N Banwell, Elaine M. McCash, *McGraw Hill*, 5th Ed. **2013**.
- 4) Infrared Spectral Interpretation by Brian Smith, *CRC Press*, **1999**.
- 5) Infrared Spectroscopy: Fundamentals and Applications by Barbara Atuart, *John Wiley&Sons, Ltd.* **2004**.

11.13 Questions for self study:

- 1) Explain briefly how to predict the intensity of IR absorption bands
- 2) Write the different types of Absorption occurs in IR spectroscopy?
- 3) Write notes with example on
 - (1) Symmetrical stretching
 - (2) Asymmetric stretching
 - (3) Scissoring
 - (4) Rocking
 - (5) Wagging
 - (6) Twisting
- 4) What is meant by?
 - a) Group frequency region
 - b) Finger print region
- 5) Calculate the number of modes of vibrations for Linear XY_2 type molecule with (CO_2) molecule and explain their IR activity.

-
- 6) What are the group frequency regions in IR spectra for following functional groups?
a) C=C; b) C≡C; c) -OH; b) CO-NH₂; e) C=NH; f) C≡N;
- 7) Identify and explain following factors affecting the group frequency.
- i) Electrical effects
 - ii) Conjugation
 - iii) Resonance
 - iv) Inductive effect
- 8) Explain hydrogen bonding and steric effects on IR absorption with example
- 9) Discuss in detail the effect of ring strain on IR absorption.

UNIT 12**Structure**

- 12.0 Objectives of the unit
- 12.1 Introduction
- 12.2 Raman and Rayleigh scattering
- 12.3 Polarization of Raman lines
- 12.4 Polarisability Ellipsoid
- 12.5 Depolarization Factor
- 12.6 Theories of Raman Spectra
 - Quantum Theory of Raman Effect
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 - Mutual Exclusion Rule
 - Mutually allowed Transition
 - Mutually forbidden Transition
- 12.10 Comparison of IR and Raman spectra
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- 12.15 Questions for self study

12.0 Objectives of the unit

After studying this unit you are able to

- Explain Raman and Rayleigh scattering.
- Identify Stokes and anti-Stokes lines
- Give a reason for polarization of Raman lines
- Predict the condition for Polarisability Ellipsoid
- Recognize the depolarization Factor
- Explain the theories of Raman Spectra
- Identify difference between rotation Raman spectra and vibration Raman spectra
- Compare the IR and Raman spectra
- Explain the advantages of Raman spectroscopy.

12.1 Introduction:

Information concerning the vibration and rotational states of polyatomic molecules can be obtained by two different experimental techniques, namely infrared absorption spectroscopy and the Raman effect. We shall now focus our attention on the study of molecular vibrations by Raman spectroscopy. The theory of molecular vibrations is the same for infrared as well as Raman spectroscopy. Light incident upon a molecule can interact with the molecule either by absorption of light or by scattering phenomena. We have already discussed the light absorption phenomena in infrared spectroscopy. We shall now deal with the other process. Consider a substance is gas, liquid or a solid state and irradiated by an intense monochromatic light, usually in the visible region of frequency ν_0 . The frequency of the exciting light must be away from all the electronic transition frequencies of the sample. Otherwise it may lead to some other phenomenon. Almost the whole of the incident radiation will pass through the sample unaffected, but a very small part of it will be scattered by the molecules in all directions, except in the direction of the incident beam. It is found that a very high proportion of the scattered light has the same frequency (ν_0) as that of the incident beam. This phenomenon was discovered in 1871 by Rayleigh is known as the Rayleigh scattering or elastic scattering. Rayleigh established that the intensity of the scattered radiation is proportional to the fourth power of the frequency of the incident radiation.

12.2 Raman and Rayleigh Scattering

When a beam of monochromatic radiation is passed through a transparent medium (substance), the molecule present in the medium scatters the radiation beam in all directions.

A fraction of radiation is scattered at right angle to the direction of the incident beam by the molecules (**Fig. 1**). A fraction of radiation aggregates of molecules present in the path of the beam and the frequency of the scattered radiation is generally the same as that of the incident radiation. This type of scattering is known as Rayleigh scattering. In 1928, Sir C.V. Raman discovered experimentally that when monochromatic light of frequency ν_0 is incident upon a sample, the scattered light shows in addition to the Rayleigh scattering line, a spectrum of frequencies shifted from the frequency ν_0 of the incident light beam. By measuring the displacement of the scattered lines from the Rayleigh line at the left and at the right, the shifted frequencies (ν_r) characteristic of the molecule is obtained. This set of shifted frequencies constitutes the Raman spectrum of the sample.

The radiation scattered at right angles has not only the original frequency but also some other frequencies which are generally lower and occasionally higher than that of the incident radiation. This type of scattering is known as Raman scattering.

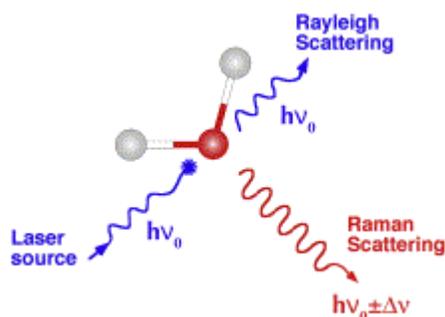


Figure 1: A simple layout of light scattering processes with a simple molecule.

In Raman scattering some of the energy of the incident light may be used up in exciting a molecule to a higher vibrational or rotational energy levels, and the radiation emitted (scattered) by the molecule will be correspondingly lower frequency and energy are called *Stokes lines*. Alternatively, since some of the molecules encountered by the incident radiation will already be in the higher vibrational or rotational energy states, the molecule may contribute this extra energy to the scattered photon, resulting in emitted radiation with higher frequency and energy than that of the incident radiation called an *anti-Stokes line* (**Fig 2**).

In practice, the anti-Stokes lines are much weaker than the Stokes lines and are generally ignored since they furnish the same information as the Stokes lines.

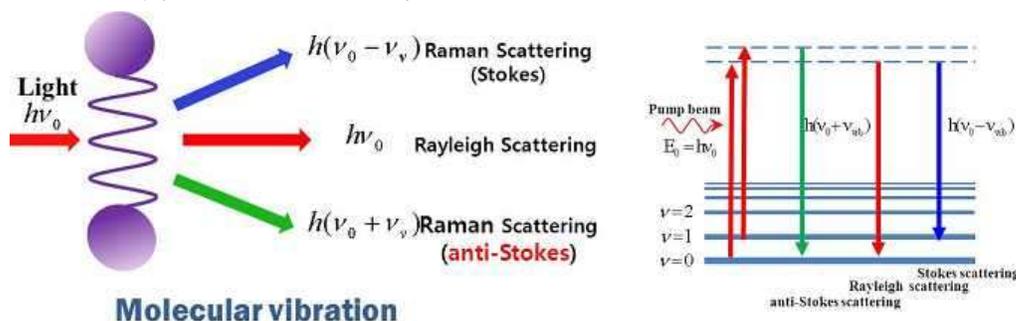


Figure 2: Origin of Stokes and anti-Stokes line in Raman effect:

For a particular mode of vibration to appear in the Raman spectrum, i.e. to be Raman active, the molecules polarisability must change during the course of this vibration. The polarisability of a molecule is the ability of the molecule to be polarized under the action of electric field such as the alternating field of a light wave, and it can be defined in terms of the dipole moment μ produced by the electric field E .

$$\mu = \alpha E$$

Where α is the polarisability. The polarisability is thus a measure of the efficiency with which a varying electric field will induce a dipole moment in a molecule.

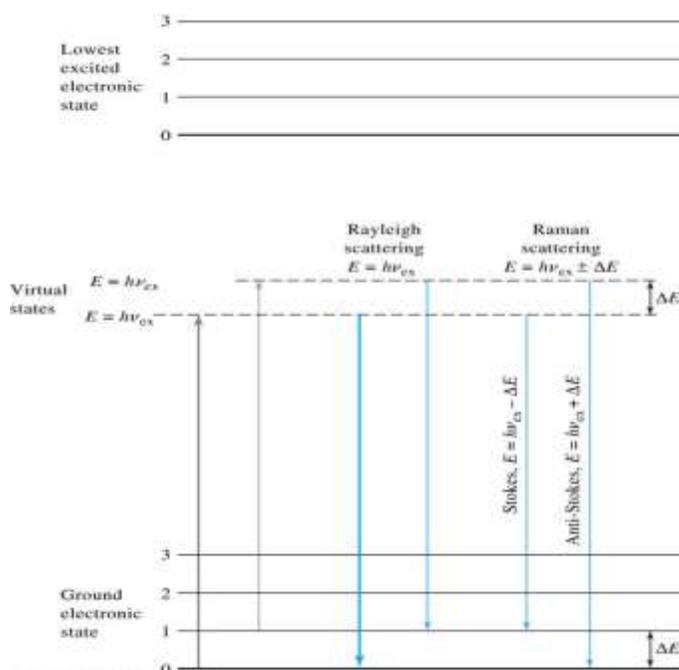


Figure 3: Energy levels involved in Raman and Rayleigh scattering process.

12.3 Polarization of Raman lines

When a molecule is put into a static electric field, it suffers from distortion, the positively charged nuclei being attracted towards the negative pole of the field, the electrons to the positive pole. This separation of charge centers causes induced electric dipole moments to be set up in the molecule, and the molecule is said to be polarized. The size of the induced dipole μ depends both on the magnitude of the applied field E , and on the ease with which the molecule can be distorted. Therefore we can write,

$$\mu = \alpha E$$

where α is the polarisability of the molecule. Consider the diatomic molecule H_2 , which we show placed in an electric field in end-on and side way orientation (**Fig. 4a** and **Fig.4b**).

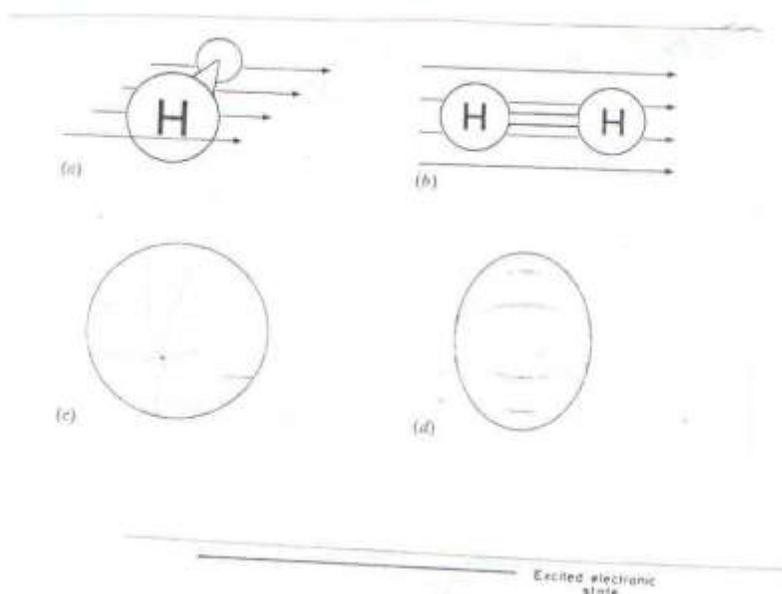


Figure 4: H_2 molecule in an electric field and its polarisability ellipsoid, seen along and across the bond axis.

The electrons forming the bond are more easily displaced by the field along the bond axis (**Fig. 4b**) than that across the bond axis (**Fig. 4a**) and the polarisability is thus said to be anisotropic (the molecule has different polarisability in different directions). This fact may be confirmed experimentally by the study of the intensity of lines in the Raman spectrum of H_2 . It was found that the induced dipole moment for a given field applied along the axis is approximately twice as large as that induced by the same field applied across the axis.

12.4 Polarisability Ellipsoid

The polarisability of a molecule in various directions is conventionally represented by drawing a polarisability ellipsoid. Polarisability ellipsoid is defined as a three dimensional surface whose distance from the electrical centre of the molecule (in H_2 this is also the centre of gravity molecule) is proportional to $\frac{1}{\sqrt{a_i}}$, where a_i is the polarisability along the line joining the point 'i' on the ellipsoid with the electrical centre. Thus, where the polarisability is greatest, the axis of the ellipsoid is least and vice versa. For H_2 its general shape is that of the squashed sphere like a tangerine, and we have drawn this in two orientations (Fig. 4c and Fig. 4d). In Fig. 4c we have looking down on the top of the tangerine just off its axis and in Fig. 3.13d we look at the side ways. If the field is applied along the bond axis (Fig. 4c) the polarisability is greater, and thus the cross section of the ellipsoid is less.

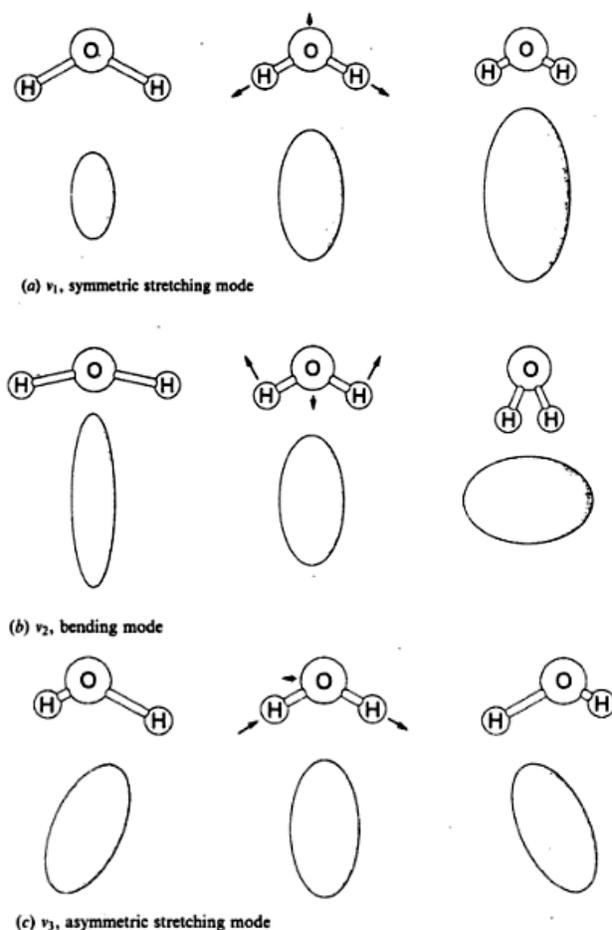


Figure 5: The change in size, shape or direction of the polarisability ellipsoid of the H_2O molecule during each of its three vibrational modes. The centre column shows the equilibrium position of the molecule, while to right and left is the extremes of each vibration.

Fig. 5. illustrate in (a), (b), and (c), respectively, the three fundamental modes ν_1 , ν_2 , and ν_3 , sketching for each mode the equilibrium configuration in the centre with the extreme positions to right and left of H_2O molecule. The approximate shapes of the corresponding polarisability ellipsoids are also shown. During the symmetric stretch in **Fig. 5a**, the molecule as a whole increases and decreases in size, when a bond is stretched, the electrons forming it are less firmly held by the nuclei and so the bond becomes more polarisable. Thus, the polarisability ellipsoid of H_2O may be expected to decrease in size while the bonds stretch, and to increase while they compress, but to maintain an approximately constant shape. On the other hand, while undergoing the bending motion (**Fig. 5b**), it is the shape of the ellipsoid which changes most, thus if we imagine vibrations of very large amplitude, at one extreme (on the left), the molecule approaches the linear configuration with a horizontal axis, while at the other extreme (on the right), it approximates to a diatomic molecule (if the two H atoms are almost coincidental) with a vertical axis. Finally, in **Fig. 5c**, we have the asymmetric stretching motion, ν_3 , where both the size and shape remain approximately constant, but the direction of the major axis changes markedly. Thus, all three vibrations involve obvious changes in at least one aspect of the polarisability ellipsoid, and all are Raman active.

12.5 Depolarization Factor

Most spectroscopic lines are characterized by two basic quantities, the frequency and intensity. Raman lines are further characterized by a third basic quantity, the degree of polarization or polarization ratio. In other words, Raman lines possess the interesting and valuable property of being polarized, which means that Raman emission has a greater intensity in one plane of vibration than in another. Measurement of polarization of a Raman line gives useful extra information, since the degree of polarization is directly related to the symmetry of molecular vibrations from which the line originates.

In defining the depolarization factor, two cases must be considered, depending upon whether natural (unpolarized) incident light (e.g. radiation from the mercury arc) or plane polarized incident light (e.g. Helium-Neon laser source) is being used. When Raman spectra are excited by plane-polarized radiation, the scattered radiation is found to be polarized to various degrees depending on the type of vibration responsible for the scattering. The nature of this effect is illustrated in the **Fig. 6**.

The radiation from a laser source is shown being polarized in the YZ plane. Part of the resulting scattered radiation is as being polarized parallel to the original beam, i.e., in the XZ plane. The intensity of this radiation is symbolized as I_{\parallel} . The remainder of the scattered beam is polarized in the XY plane, which is perpendicular to the polarization of the original beam. The intensity of this radiation is denoted as I_{\perp} . *The depolarization factor is defined as the intensity of the scattered light polarized perpendicular to the XZ plane to that polarized parallel to the XZ plane.*

$$\text{Therefore, } p = \frac{I_{\perp}}{I_{\parallel}}$$

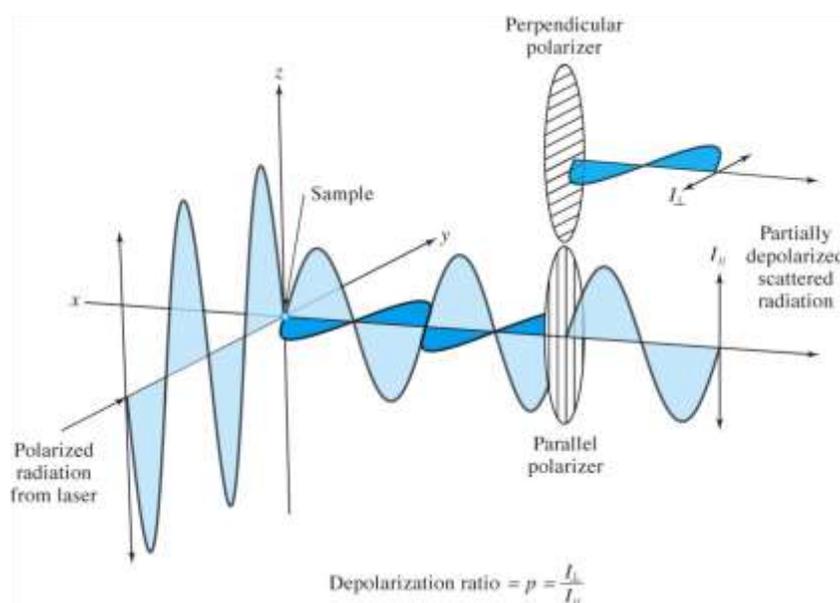


Figure 6: Raman scattered radiation using unpolarized light showing polarized component.

Experimentally, the depolarization ratio is readily obtained by inserting a Polaroid sheet between the sample and the monochromator. The depolarization ratio is dependent upon the symmetry of the vibrations responsible for scattering.

E.g. In CCl_4 , the peak at 459 cm^{-1} (**Fig. 7**) arises from a totally symmetric breathing vibration involving the simultaneous movement of the four tetrahedrally arranged chlorine atoms toward and away from the central carbon atom.

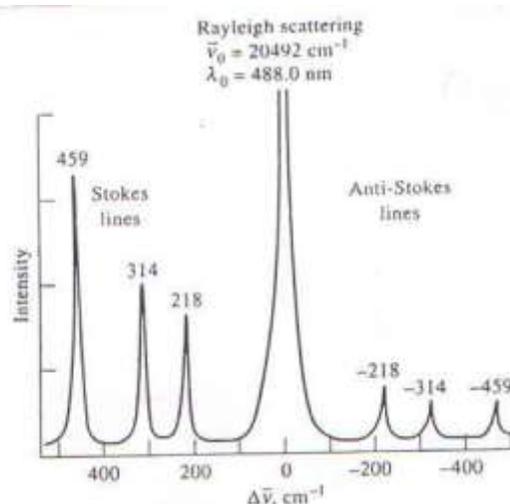


Figure 7: Raman spectrum of CCl₄ using argon ion laser.

The depolarization ratio is 0.005, indicating minimal depolarization (the 459 cm^{-1} line is thus said to be polarized). In contrast, the CCl₄ peaks at 218 cm^{-1} and 314 cm^{-1} , which arise from non-symmetrical vibrations have depolarization ratio of about 0.75. From scattering theory, it is possible to demonstrate that the maximum depolarization for non-symmetric vibration is $6/7$, whereas for symmetric vibrations, the ratio is always significantly less than this number. The depolarization ratio is thus useful in correlating Raman line with modes of vibration.

12.6 Theories of Raman Spectra

Quantum Theory of Raman Effect

The occurrence of Raman scattering may be most easily understood in terms of the quantum theory of radiation. This treats radiation of frequency ' ν ' as consisting of a stream of particles (called photons) having energy $h\nu$ where h is Planck's constant. Photons can be imagined to undergo collisions with molecules and, if the collision is perfectly elastic, they will be deflected unchanged. A detector placed to collect energy at right angles to an incident beam will thus receive photons of energy $h\nu$, i.e., radiation of frequency ' ν '. Elastic scattering can be likened to a ball bearing striking a rigid table, and the ball bearing bounces off the table without any loss of energy.

However, it may happen that energy is exchanged between photon and molecule during the collision; such collisions are called 'inelastic'. The molecule can gain or lose amounts of energy only in accordance with the quantal laws, i.e., its energy change, ΔE joules, must be the difference in energy between two of its allowed states. That is to say, ΔE must represent a

change in the vibrational and/or rotational energy of the molecule. If the molecule gains energy ΔE , the photon will be scattered with energy $(h\nu - \Delta E)$ and the equivalent radiation will have a frequency $(\nu - \Delta E/h)$. Conversely, if the molecule loses energy ΔE , the scattered frequency will be $(\nu + \Delta E/h)$. Radiation scattered with a frequency lower than that of the incident beam is referred to as Stokes radiation, while that at higher frequency is called anti-Stokes radiation. Since the former is accompanied by an increase in molecular energy (which can always occur, subject to certain selection rules) while the latter involves a decrease (which can only occur if the molecule is originally in an excited vibrational or rotational state). Stokes radiation is generally more intense than anti-Stokes radiation.

Classical Theory of the Raman Effect

When a molecule is put into an electric field of strength E , it suffers from distortion, the positively charged nuclei being attracted toward the negative pole of the field, the electrons to the positive pole. The separation of charge centres causes an induced electric dipole moment (μ) to be set up in the molecule, and the molecule is said to be polarized. If α is the polarisability of the molecule, the magnitude of the induced dipole moment is given by,

$$\mu = \alpha E \text{ -----(1)}$$

When electromagnetic radiation of frequency ν falls on the molecule, the electric field (E) experienced by each molecule varies with time (t) according to the equation,

$$E = E_0 \sin 2\pi \nu t \text{ ----- (2)}$$

where E_0 is the amplitude of electric field. Hence, Eq. (1) becomes

$$\mu = \alpha E = \alpha E_0 \sin 2\pi \nu t \text{ -----(3)}$$

Thus, the electromagnetic radiation induces a varying electric dipole moment which then permits emission of light identical in frequency with that of the incident radiation. This is Rayleigh scattering.

In addition, the molecule undergoes some internal motion such as vibration or rotation, which changes the polarisability periodically, then the oscillating dipole will have superimposed upon the vibrational or rotational motions. E.g. a vibrational frequency ν_v which changes the polarisability, then we can write,

$$\alpha = \alpha_0 + \beta \sin 2\pi \nu_v t \text{ -----(4)}$$

where α_0 is the equilibrium polarisability and β represents the rate of change of polarisability with the vibration, then Eq. (1) can be written as,

$$\mu = \alpha E = (\alpha_0 + \beta \sin 2\pi \nu_v t) E_0 \sin 2\pi \nu t \text{-----(5)}$$

Expanding Eq. (5) and using trigonometric relation,

$$\sin A \sin B = \frac{1}{2} \{ \cos (A - B) - \cos (A + B) \}$$

Then we have,

$$\mu = \alpha_0 E_0 \sin 2\pi \nu t + \frac{1}{2} \beta E_0 \{ \cos 2\pi (\nu - \nu_v) t - \cos 2\pi (\nu + \nu_v) t \text{-----(6)}$$

The first term on the right hand side of Eq. (6) contains only one frequency factor ν which that of the incident radiation. This term is interpreted in terms of Rayleigh scattering. The second term on the right hand side contains, in addition to the incident frequency ν , the frequencies $(\nu \pm \nu_v)$. Thus, the induced dipole moments can also oscillate with the two frequencies $(\nu + \nu_v)$ and $(\nu - \nu_v)$. These two frequencies are interpreted as the vibrational Raman frequencies. The $(\nu - \nu_v)$ and $(\nu + \nu_v)$ frequencies are known as the Stokes and anti-Stokes lines, respectively.

It should be noted that, if the vibration does not alter the polarisability of the molecule then $\beta = 0$ and the dipole oscillates only at the frequency of the incident radiation. The same is true for rotation. Thus, we have the general rule, in order to be Raman active, molecular rotation or vibration must cause some change in a component of the molecular polarisability. A change in polarisability is, of course, reflected by a change in either the magnitude or direction of the polarisability ellipsoid.

12.7 Rotation Raman Spectra

Pure rotational Raman spectra give information about internuclear distances, angles, molecular symmetry and nuclear statistics. However, in general, it is necessary to use the spectrometer of very high resolving power. In addition, since the lines are very close to the exciting line, experimental observation becomes difficult owing to the breadth of the corresponding Rayleigh radiation.

The criterion for the occurrence of a pure rotational Raman spectrum is that during the rotation, the polarisability in a fixed direction should change. In other words the molecule should have a non-spherical polarization ellipsoid. That is the polarisability in a fixed direction changes during the rotation of the molecule about an axis perpendicular to the internuclear axis.

The selection rule for pure rotation Raman changes is $\Delta J = 0, \pm 1, \pm 2$.

For linear molecules the selection rule is $\Delta J = 0, \pm 2$

If $\Delta J = 0$, no Raman shift – Rayleigh scattering

$\Delta J = +2$, Stokes line

$\Delta J = -2$, anti-Stokes line

Since the rotational quanta are quite small, the molecules can occupy a number of rotational levels initially even at ordinary temperatures. Hence, several rotational-Raman lines with $J = 0, 1, 2, \dots$ up to 10 or more will be observed.

Energy levels for a rotational level is given by

$$E_r = \frac{h^2}{8\pi^2 I} J(J + 1) \text{-----(7)}$$

For Stokes transition, i.e. $\Delta J = +2$, (low frequency side), then

$$\Delta\nu = \frac{h^2}{8\pi^2 I c} \{(J + 2)(J + 3) - J(J + 1)\}$$

$$\text{Or } \Delta\nu = 2B (2J + 3) \text{ where } B = \frac{h^2}{8\pi^2 I c} \text{----- (8)}$$

For anti-Stokes transition, i.e. $\Delta J = -2$, (high frequency side), then

$$\Delta\nu = - 2B (2J + 3) \text{----- (9)}$$

Thus for Stokes and anti-Stokes lines we have

$$\begin{aligned} \Delta\nu &= \pm 2B (2J + 3) \text{ where } J = 0, 1, 2, 3, \dots \text{(10)} \\ &= \pm 6B, \pm 10B, \pm 14B, \pm 18B, \dots \end{aligned}$$

When the value of $J = 0$, it is seen immediately that the separation of the first line from the exciting line is $6B \text{ cm}^{-1}$, while the separation between the successive lines is $4B \text{ cm}^{-1}$. The negative sign refers to anti-Stokes lines, the positive sign refers to Stokes lines and ν_{ex} is the wave number of the exciting radiation. The allowed transitions and Raman spectrum arising are shown schematically in the **Fig. 8**. Each transition is labelled according to its lower J value and the relative intensities of the lines.

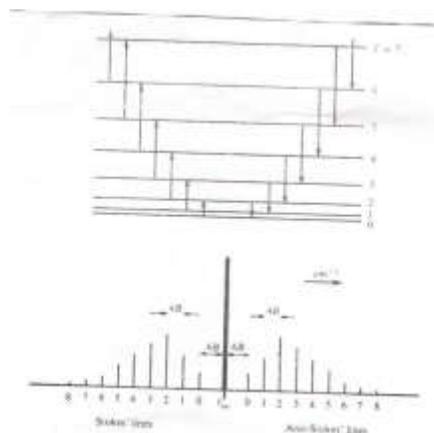


Figure 8: The rotational energy levels of a diatomic molecule and the rotational Raman spectrum arising from transitions between them. Spectral lines are numbered according to their lower J values.

12.8 Vibration Raman Spectra

All diatomic molecules are capable of yielding vibration-Raman spectra, since polarisability must alter during the vibration along the bond.

If a diatomic molecule may be treated as a simple harmonic vibrator, then

$$E_v = \left(v + \frac{1}{2}\right) hc\omega \text{-----} (11)$$

Where v = vibrational quantum number which can take the values 0, 1, 2, and ω = vibrational frequency in cm^{-1} .

The selection rule for the transition is $\Delta v = \pm 1$. Raman vibration occurs only from one level to the next upper level (Stokes) or to the next lower level (anti-Stokes). Most molecules at room temperature occupy the lowest vibrational state. That is $v = 0$ and hence mainly Stokes transitions is predominant. If some molecules are already in $v = 1$ level, then $v = 1 \rightarrow 2$ (Stokes) and $v = 1 \rightarrow 0$ (anti-Stokes) lines are possible. In either case the intensities of the resulting lines must be low because of the less number of molecules involved. Thus, at ordinary temperature Raman spectra consists mainly of Stokes lines due to $v = 0 \rightarrow 1$ transition (since the majority of the molecules are in $v = 0$ level at room temperature).

At high temperature, the intensity of anti-Stokes lines should increase, because the number of molecules that are initially at higher levels should increase.

Vibrational energy of a diatomic molecule acting as an anharmonic oscillator is given by the equation,

$$E_v = \left(v + \frac{1}{2}\right) hc\omega - \left(v + \frac{1}{2}\right)^2 hc\alpha\omega \text{-----} (12)$$

where α = anharmonicity constant and ω = vibrational frequency (cm^{-1})

For a Stokes transition, $v = 0 \rightarrow 1$

$$\begin{aligned} \text{For } v = 1, E' &= (1 + 1/2)hc\omega - (1 + 1/2)^2 hc\alpha\omega \\ &= 3/2 hc\omega - 9/4 hc\alpha\omega \end{aligned}$$

$$\text{For } v = 0, E'' = 1/2hc\omega - 1/4 hc\alpha\omega$$

$$\text{Then, } E' - E'' = (1 - 2\alpha) hc\omega \text{-----}(13)$$

But from pure vibration spectra, $\nu_1 = (1 - 2\alpha) \omega$

Where ν_1 is the fundamental band of vibration spectra. Thus the Raman shift is identical with the vibration bands. For unsymmetrical molecules both IR and Raman spectra are active. For symmetric molecules only Raman spectra are active as $\mu = 0$.

12.9 Correlation between Raman and IR Spectra

Infrared and Raman spectra tend to be complementary to each other because of their differing requirements for activity. A change in polarisability must occur in order for a vibrational mode to be Raman active, but a change in dipole moment is necessary for a vibrational mode to be IR active. The practical manifestation of these requirements can be summarized with one absolute Rule and two additional generalizations.

Mutual Exclusion Rule

This absolute rule says that for all molecules with a centre of symmetry says that, transitions that are allowed in the infrared are forbidden in the Raman spectrum, and conversely that are allowed in the Raman spectrum are forbidden in the infrared.

E.g. O₂ molecule has only one fundamental mode of vibration $(3N - 5) = 1$ and this will be IR inactive since no change in dipole moment occurs during the vibration. On the other hand, this vibration will be Raman active since there will be a change in polarisability during the vibration. That is, there will be a change in the ease of displacement of electrons during the stretch.

Mutually allowed Transition

It is generally true that for all molecules that do not have a centre of symmetry, the transition will be both IR and Raman-active. Since most molecules (and most functional groups) have no centre of symmetry, there is often some correlation between Raman and IR spectra.

For e.g. In the IR and Raman spectra of pentene-2, the characteristic C-H stretching and bending vibrations, found in the region of 3000 and 1400 cm⁻¹ respectively, show both type of spectra.

Mutually forbidden Transition

Although the previous two statements cover the great majority of molecules and transitions, *there are few cases where transitions are forbidden in both the Raman effect and the infrared.*

For e.g. the twisting mode of vibration of the planar ethylene molecule. Since ethylene is planar and symmetrical, it has no permanent dipole moment and no change in dipole moment occurs with the twisting mode making this mode IR inactive. Furthermore, no change in polarisability occurs during this twisting mode because of small amplitude of vibration. No change in the ease of displacing electrons will occur, and thus, this mode is also Raman-inactive.

12.10 Comparison of IR and Raman spectra:

Raman	Infrared
<p>1) It is due to scattering of light by the vibrating molecules.</p> <p>2) Changes of polarisability of molecule will decide whether the Raman spectrum will be observed or not.</p> <p>3) It can be observed in uv/vis region which is more convenient.</p> <p>4) Source is monochromatic and is in uv/vis region.</p> <p>5) Optical system made up of quartz/glass.</p> <p>6) Water can be used as solvent.</p> <p>7) Homonuclear diatomic molecules can be studied.</p> <p>8) Lower frequency that can be studied is 100 cm^{-1} or even less if LASER is used.</p> <p>9) Frequency separation in rotation Raman is 4 cm^{-1}.</p> <p>10) Solutions should be sufficiently concentrated in order to increase the intensity of Raman lines.</p> <p>11) Method is most accurate but relatively less sensitive.</p> <p>12) Sample must be pure, colourless and clear, otherwise absorption and background noise will increase.</p>	<p>1) It is the result of absorption of light by vibrating molecules.</p> <p>2) The changes in dipole moment values decide the activity of the molecule in IR.</p> <p>3) It is observed in IR region only.</p> <p>4) Source employed is polychromatic, and is in IR region.</p> <p>5) Optical system is made of NaCl, KBr, prisms and front reflecting mirrors.</p> <p>6) Water cannot be used as solvent.</p> <p>7) Homonuclear diatomic molecules cannot be studied.</p> <p>8) Lower frequency that can be studied is usually 400 cm^{-1} and can be 200 cm^{-1} with advanced instruments.</p> <p>9) Frequency separation in vibration-rotation spectra is 2 cm^{-1}.</p> <p>10) Dilute solutions are usually preferred.</p> <p>11) Method is accurate as well as sensitive.</p> <p>12) This condition is not critical.</p>

12.11 Advantages of Raman spectroscopy with respect to IR spectroscopy

1. Water is an excellent solvent whereas water cannot be used in IR studies.
2. Glass cells can be used in Raman spectroscopy whereas salt cells which are difficult to handle must be used in IR.

3. Raman spectra are usually simpler than the corresponding IR spectra primarily because overtone and combination effects are relatively small compared with the principal Raman frequencies. The overlapping bands are much less common in Raman spectroscopy.
4. Totally symmetric modes of vibrations can be studied by Raman effect whereas they are not observed in IR spectroscopy.
5. The polarization of Raman spectra adds a valuable extra dimension to the information.
6. Raman studies provide information for the calculation of chemical equilibrium constants and other thermodynamic parameters.
7. The intensity of a Raman line is directly proportional to concentration whereas there is a logarithmic (Beer's law) relationship for conventional spectrophotometry. Thus, quantitative analysis is often more convenient in Raman spectroscopy.

12.12 Summary of the unit

The theory of Raman scattering shows that, the phenomenon results from the same type of quantized vibrational changes that are associated with infrared absorption. Thus, the difference in wavelength between the incident and scattered visible radiation corresponds to wavelengths in the mid-infrared region. The Raman scattering spectrum and infrared absorption spectrum for a given species often resemble one another quite closely. The important advantage of Raman spectra over infrared lies in the fact that water does not cause interference; indeed, Raman spectra can be obtained from aqueous solutions. In addition, glass or quartz cells can be employed, thus avoiding the inconvenience of working with sodium chloride or other atmospherically unstable window materials.

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

12.13 Key words

Raman scattering; Rayleigh scattering; Polarization of Raman lines; Polarizability ellipsoid; Depolarization factor; Quantum theory of Raman effect; Classical theory of the Raman effect; Rotation Raman spectra; Vibration Raman spectra; Mutual exclusion rule; Mutually allowed transition; Mutually forbidden transition.

12.14 References for further study

- 1) Vibrational/Rotational Spectroscopy of Diatomic Molecules by M Mueller, *Kluwer Academic Publishers*, **2002**.
- 2) Vibrational Spectroscopy: Theory and Applications by D. N. Sathyanarayana, *New Age International*, **2007**.
- 3) Fundamentals of molecular spectroscopy by Colin N Banwell, Elaine M. McCash, *McGraw Hill*, 5th Ed. **2013**.

12.15 Questions for self study

- 1) What are Raman and Rayleigh scattering?
- 2) Write notes on Stokes and anti-Stokes lines.
- 3) What is meant by polarization of Raman lines explain in detail?
- 4) Discuss briefly the condition for polarisability ellipsoid
- 5) Write note on depolarization Factor
- 6) Derive the theories of Raman Spectra
- 7) Explain rotation Raman spectra and vibration Raman spectra
- 8) Distinguish between IR and Raman spectra
- 9) Explain the advantages of Raman spectroscopy

Structure**Unit- 13.0**

- 13.0 Objectives of the unit
- 13.1 Introduction
- 13.2 The Nuclear Spin
- 13.3 Spin active nuclei
- 13.4 Orientation of spinning nuclear magnets
- 13.5 Resonance and relaxation phenomenon
- 13.6 Relaxation process
 - Spin-lattice relaxation:
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- 13.12 Factors affecting chemical shift
 - a) Electronegativity- Inductive effect
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 - i) Acetylenic protons
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 - c) Hydrogen bonding
 - d) van der Waals deshielding
- 13.13 Instrumentation
 - a) Continuous Wave (CW) NMR instruments
 - b) Fourier Transform (FT) NMR instruments:
- 13.14 Summary of the unit
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13.0 Objectives of this unit

After studying this unit you are able to

- State the type of nuclei that show the phenomenon of NMR.
- Explain the basic principle of NMR.
- Draw a schematic diagram of NMR spectrometer.
- Describe the relaxation phenomenon and its mechanism.
- Define and explain chemical shift and state the factors affecting it.
- Explain the process of spin-spin splitting.

13.1 Introduction

Block, Hansen and Packard at Stanford University in 1946 first detected a signal of the proton from water. Purcell, Torrey and Pound at Harvard University also observed a signal from the protons from paraffin wax. Since then, the advances in the Nuclear Magnetic Resonance (NMR) spectroscopy technique have widespread applications in various branches of science. Nuclear Magnetic Resonance spectroscopy involves transition of a nucleus from one spin state to another with the absorption of electromagnetic radiation in the radio frequency range by spin active nuclei placed in a strong magnetic field. Hence the phenomenon of magnetic resonance results from the interaction of the magnetic moment of an atomic nucleus (μ) with an external magnetic field. The cause of this magnetic moment is the quantum mechanical angular momentum (spin angular momentum) of all nuclei

A nucleus in an atom is made up of positively charged protons and neutral (no charge) neutrons, which are collectively called nucleons. Therefore nucleus is a positively charged. Like an electron nucleus also spin in its own axis. Since the nucleus has a charge, the spinning motion will generate a magnetic field, and therefore spinning nucleus behaves like a small bar magnet. The axis of nuclear magnet is always parallel to the axis of nuclear spin as shown in figure 1. When the frequency of the rotating magnetic field and that of the precessing nucleus become equal, they are said to be in resonance and absorption or emission of energy by the nucleus occurs. A plot of the peak intensities versus the frequencies of absorption (expressed in δ) constitutes an NMR spectrum. The ^1H nucleus is invariably present in the majority of the organic compounds and also highly abundance in nature. Hence it is commonly studied in NMR spectroscopy.

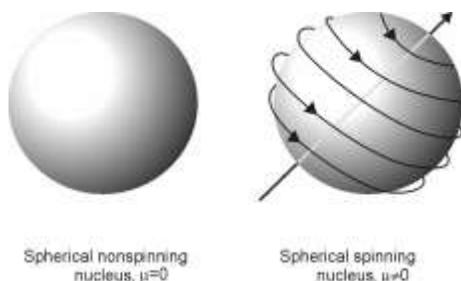


Figure 1: The axis of nuclear magnet is parallel to the axis of nuclear spin

The Nuclear Magnetic Resonance is also referred as Proton Magnetic Resonance (PMR). The NMR spectrum not only provides information about the number of different types of protons but also gives the information regarding the nature of the environment of each of them in a molecule. Despite their low natural abundance, ^{13}C , ^{15}N , ^{19}F , ^{31}P are also an important nucleus and they are present in biomolecules and can be studied in NMR spectroscopy only one at a time and extract valuable information about structure of the molecule they are present.

13.2 The Nuclear Spin

The nucleus is a small charged particle built up by neutron and protons. Nucleus is spinning around its own axis thus representing an electric current. Due to this current the atomic nucleus behaves as a small electromagnet. Therefore each nucleus has an angular momentum. The total angular momentum of a particular nucleus is the resultant of the individual momenta of the constituent protons and neutrons. The total angular momentum of a nucleus in its ground state is called as nuclear spin.

It has been found that all even-even nuclei ie, even number of protons and even number of neutrons have a nuclear spin $I = 0$ in the ground state.

Odd-odd nuclei ie, odd number of neutrons and odd number of protons all have integral nuclear spin other than zero.

All odd-even nuclei ie, odd number of neutrons/protons and even number of protons/neutrons

have half odd integral spin lying between $\frac{h}{4\pi}$ and $\frac{9h}{4\pi}$.

13.3 Spin active nuclei

The fundamental property of an atomic nucleus to exhibit NMR phenomenon is the nuclear spin I . The nuclei having a nuclear spin I not equal to zero are called spin- active nuclei. For example ^1H , ^{13}C , ^{19}F , ^{31}P have nuclear spin or angular momentum equal to $\frac{1}{2}$ and are spin active, whereas

^{12}C , ^{16}O , ^{32}S etc. have $I = 0$ and are not spin active. The actual value of I depends on the mass number and atomic number of that nucleus, as shown in below table

Mass Number	Atomic or number	Nuclear spin
Odd	Even or odd	$\frac{1}{2}, 3/2, 5/2, \dots$
Even	even	0
Even	odd	1,2,3,4.....

Spin-active nuclei have permanent magnetic moments and quantized nuclear spin state which is equal to $(2I + 1)$ where I is the nuclear spin also called angular momentum of that nucleus. The spin active nucleus is spinning about an axis and this generates a magnetic field around them and thus behaves as spinning nuclear magnets. This is the fundamental requirement for nucleus to show NMR spectra.

13.4 Orientation of spinning nuclear magnets

The nuclear magnet spin are random in their atomic or molecular environment (Figure 2a). When this atom or molecule is placed in a strong uniform external magnetic field H_0 , this random nuclear magnet spin align either with or against the applied field (Figure 2b), this giving rise to two separate energy state.

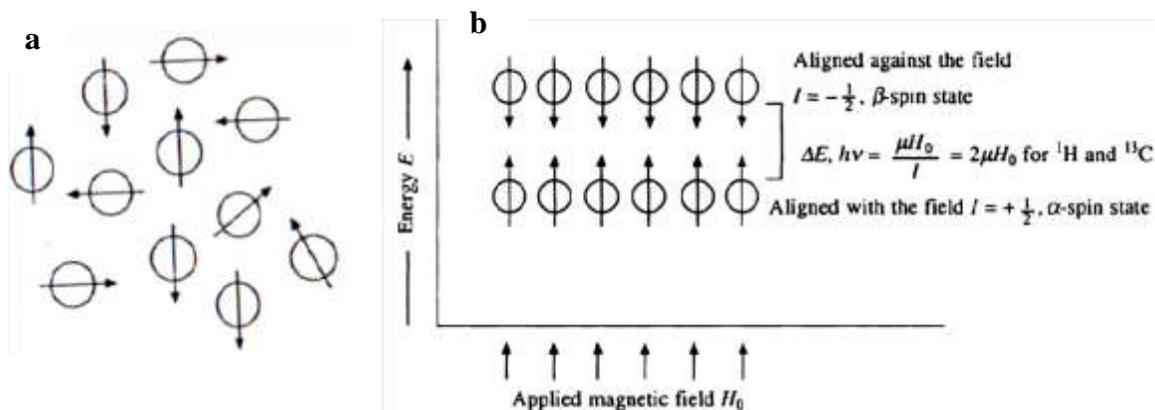


Figure 2: a) Orientation of nuclear magnetic dipoles in the absence of an external magnetic field
b) Orientation of nuclear magnetic dipoles in an external magnetic field H_0

The nuclei in an external applied field H_0 are precessing in two orientations. The nuclear magnet spin aligned with the external magnetic field are lower energy state and they are said to parallel with the external magnet filed. The nuclear magnet spin aligned against the external magnetic field are higher energy state and they are said to be antiparallel with the external magnetic field. Hence parallel orientation is more stable by a small amount of energy and the energy difference

between the two states corresponds to the frequency of radio waves and directly proportional to the strength of external applied magnetic field.

The following fundamental NMR equation correlates the electromagnetic frequency ν for the transition in a given field H_0

$$\nu = \frac{\xi H_0}{2\pi} \text{----- (1)}$$

$$\text{or } \nu \propto H_0$$

where, ξ is magnetogyric ratio (or gyromagnetic ratio) which is a fundamental nuclear constant, the magnetic moment μ of a spinning nucleus behaving like a tiny bar magnet is directly proportional to its spin number I . It has been shown that

$$\xi = \frac{2\pi\mu}{hI} \text{----- (2)}$$

Where h is Planck's constant and ξ the magnetogyric ratio, is the proportionality constant between μ and I .

From equation 1 and 2

$$\nu = \frac{\xi H_0}{2\pi} = \frac{2\pi\mu}{hI} = \frac{H_0}{2\pi} = \frac{\mu H_0}{hI}$$

$$h\nu = \Delta E = \frac{\mu H_0}{I} \text{----- (3)}$$

13.5 Resonance and relaxation phenomenon

As mentioned in the equation 3, energy difference between them is equal to

$$\Delta E = \frac{\mu H_0}{I}$$

Where I = nuclear spin

μ = magnetic moment

For ^1H and ^{13}C , $I = \frac{1}{2}$, hence

$$\text{Hence, } E = 2\mu H_0$$

$$\text{or } \nu = \frac{2\mu H_0}{h}$$

Therefore if the energy equal to $2\mu H_0$ is supplied to a system, a nucleus undergoes transition from one spin state to another. The energy required for this transition can be supplied by electromagnetic radiation in the radio-frequency range. And equation 3 also shows that the

energy required for a transition ΔE is directly proportional to the strength of the applied magnetic field (because μ/I is constant for a given nucleus). This is shown graphically in the figure 3. The stronger the field, greater will be the tendency of the nuclear magnetic dipoles to remain aligned with it and higher will be the energy required for a transition.

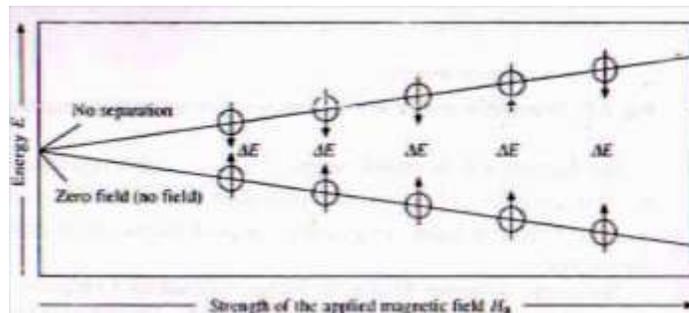


Figure 3: relationship between the transition energy ΔE and the applied magnetic field H_0

i) Process of absorption of energy

If the axis of the nuclear magnet is not oriented exactly parallel or anti-parallel to H_0 , they experience a torque (certain force) which forces them into precession about the axis of the external field. Since the nucleus is spinning, the effect is that its rotational axis draws out a circle perpendicular to the applied magnetic field.

This motion is referred to as Larmor precession and it occurs at the Larmor frequency, ν , which is directly proportional to the strength of applied magnetic field. The Larmor frequency is given by

$$\omega_0 = \zeta H_0$$

we know that

$$\zeta H_0 = 2\pi\nu$$

$$\therefore \omega_0 = 2\pi\nu$$

It is exactly equal to the frequency of electromagnetic radiation necessary to induce a transition from one nuclear spin state to another and is called precessional frequency. The transition from one spin state to the other is called *flipping of the precessing nucleus*. This change can be brought about through the application of electromagnetic radiation whose magnetic vector component H_1 is rotating in a plane perpendicular to the applied magnetic field H_0 . The energy required for resonance depends on B_0 and on the nuclei brought into resonance. These frequencies are in the radio-frequency region of the electromagnetic spectrum. When the frequency of the rotating magnetic field and the precessional frequency of the nucleus become

equal, they are said to be in resonance, and absorption or emission of energy by the nucleus can occur. In the ordinary conditions under the influence of external magnetic field, there is a slight excess of nuclei in the lower spin, i.e., the nuclei take up Boltzmann distribution (Boltzmann factor is about 0.001%). Hence collection of nuclei continually absorbs radio-frequency radiation and the excess of nuclei originally in lower energy state jump to higher energy. When the population of the nuclei between the two spin states becomes equal, there will be no NMR effect. Such a phenomenon is known as *saturation*.

13.6 Relaxation process

After irradiation ceases, not only the population of the states revert to a Boltzmann distribution, but also the individual nuclear magnetic moments begin to lose their phase coherence and return to a random arrangement around the Z-axis. This process is called “*relaxation process*”. There are two types of relaxation process:

Spin-lattice relaxation also called Longitudinal relaxation, denoted by T_1 &

Spin-spin relaxation also called Transverse relaxation, denoted by T_2

Spin-lattice relaxation:

In an NMR experiment the sample in which nuclei are held is called the *lattice*. Nuclei in the lattice are in vibrational and rotational motion, which can produce oscillatory magnetic fields with the same frequency and phase as that of the exciting nucleus. Thus exciting nucleus can lose its energy by passing to the surrounding environment (lattice) and return to lower spin state. This mechanism is known as spin-lattice relaxation. The absorbed energy is lost through vibrational and rotational motion to the lattice. The spin-lattice relaxation follows the first order decay process, and time taken for this process is denoted by T_1 . It is a slower process compared to spin-spin relaxation.

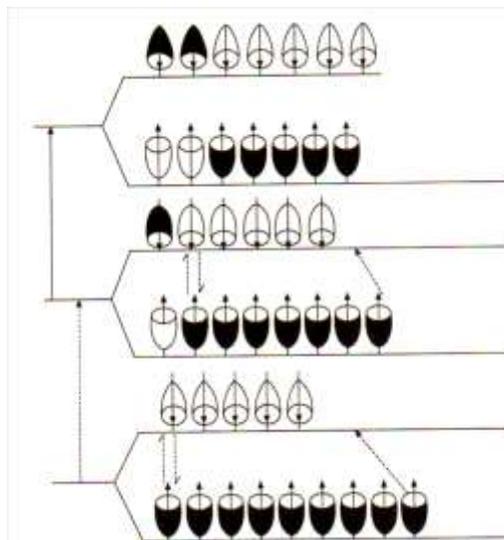


Figure 4: Distribution of nuclei between lower and higher energy states.

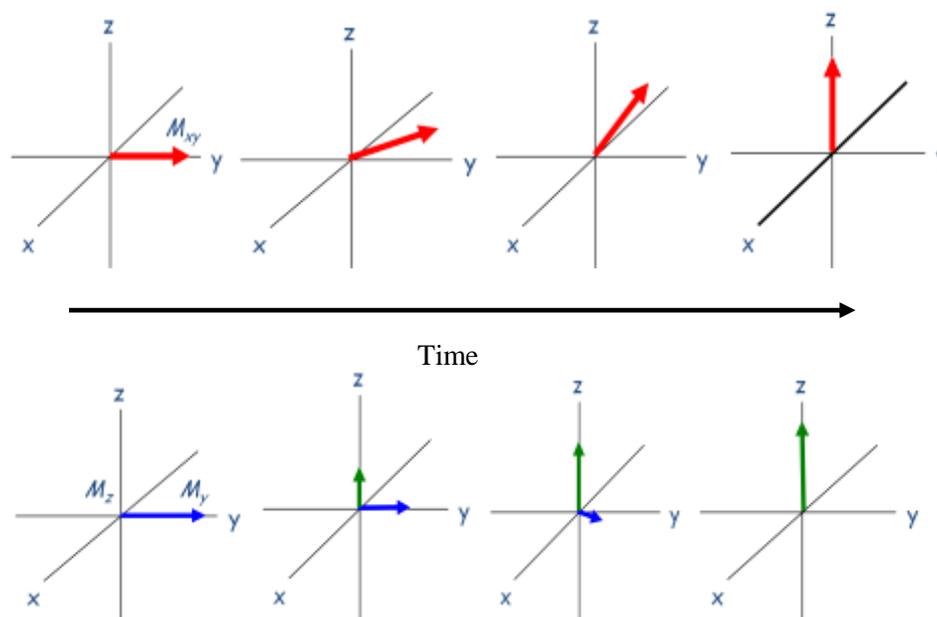


Figure 5: Decay of magnetization along the z-axis of the excited nuclei due to Spin-lattice relaxation.

Spin-lattice relaxation is also defined as the process whereby the z-component of magnetization (M_z) returns to its equilibrium value (M_{z0}) as shown in figure 5. This is also termed longitudinal relaxation because the decay of magnetization occurs along the longitude (z-axis) of the NMR experiment.

Spin-Spin relaxation:

The nucleus in higher energy (excited state) level can undergo relaxation by transferring its energy (net magnetization) to another nucleus which will then excite to higher energy state. This type of relaxation mechanism is called Spin-spin relaxation. This process helps to destroy the phase coherence and leads to transverse relaxation.

There are three main ways for spin-relaxation mechanism to induce. They are,

- dipole-dipole interaction between the same types of nuclei having the same Larmor frequency thereby generate magnetic field of correct frequency for relaxation.
- Generation of slightly different magnetic fields due to the magnetic field of nuclei whose motion is slightly slow. Hence the z-components of these fields produced a different magnetic fields lead to different Larmor frequency. This difference in frequencies causes the magnetization vector to fan out and leads to transverse relaxation. This process is particularly important in viscous liquids or solids, where movement of nuclei is restricted.

c) the third way is very similar to the second except that the slightly different magnetic fields experienced by the observed nuclei are the result of inhomogeneities in the magnetic field of the spectrometer.

Since spin-spin relaxation involves an excited spin state, exchange spins with an adjacent spin active nucleus, the rate of relaxation is fast

and is denoted by T_2 . Like spin-lattice relaxation (T_1), T_2 also follows the first order decay process. There is no net loss of energy and this relaxation process shortens the life time of an individual nucleus in the higher spin state but does not contribute to the maintenance of required excess of nuclei in a lower spin state.

13.7 Relaxation effect and broadening of signals

The time taken for a certain group of nucleus to lose a fraction of their excess energy is known as *relaxation time* for that nucleus. Spin-lattice relaxation (T_1) is slower and spin-spin relaxation (T_2) faster therefore T_2 must be less than T_1 and T_2 may be equal to T_1 but it never greater than T_1 . For many particle purpose it is considered that $T_1 = T_2$. The spectral line width is inversely proportional to the life time of the excited state. The shorter the lifetime of the excited state greater is the line width. All NMR signals have a natural line-width which is depending on the relaxation time, long relaxation times gives rise to sharp spectral lines whereas short relaxation times leads to broadening of spectral line (Figure 7). This arise because the life time of nuclei in the excited state is decreased which causes

uncertainty in the determination of energy difference. An efficient relaxation process involves shorter T_1 time and results in broadening of the absorption peak. Both spin-spin relaxation and

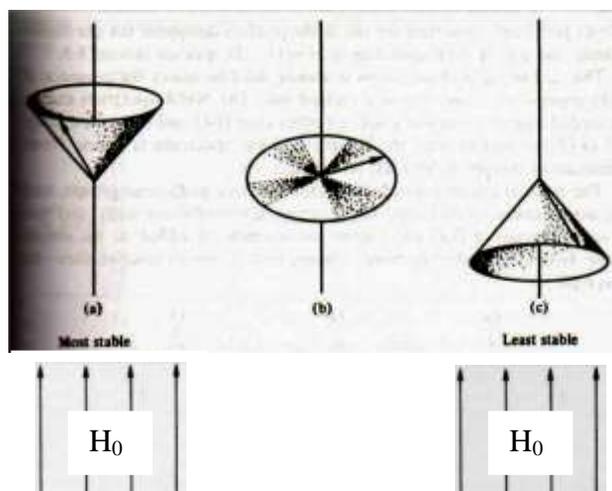


Figure 6: Precession modes for a nucleus in spin-spin relaxation

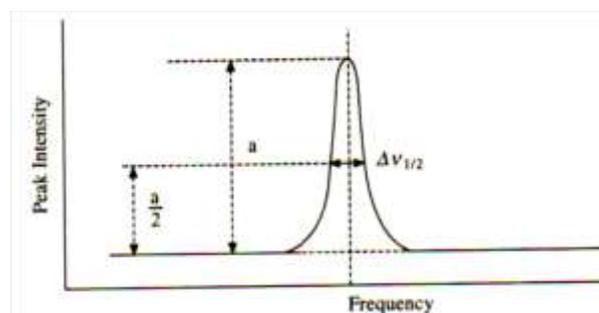


Figure 7: Ideal NMR signal

spin-lattice relaxation contributes to the width of a spectral line. Solid and viscous liquids usually provide properly oriented nuclei in lower spin state which may exchange spins in higher spin states hence reduces the spin-spin relaxation time. Therefore solids and viscous samples generally exhibit very broad spectral lines. In case of liquids, the molecules are moving around relatively freely and therefore the relaxation processes are not as efficient.

13.8 Spin Exchange

Spin exchange is the exchange of spin state between two spins. For example, for two spins, A and B, A has up spin and B has down spin. Spin exchange between A and B can be represented with the following equation. $A (\uparrow) + B (\downarrow) \rightleftharpoons A (\downarrow) + B (\uparrow)$. The bidirectional arrow indicates that the exchange reaction is reversible. The energy difference between the upper and lower energy states of A and of B must be the same for spin exchange to occur. On a microscopic scale, the spin in the upper energy state (B) is emitting a photon which is being absorbed by the spin in the lower energy state (A). Therefore, B ends up in the lower energy state and A in the upper state. Spin exchange will not affect T_1 but will affect T_2 because the distribution of spins between the upper and lower states is not changed. T_2 will be affected because phase coherence of the transverse magnetization is lost during exchange.

Another form of exchange is called chemical exchange. In chemical exchange, the A and B nuclei are from different molecules. For example the chemical exchange between water and ethanol. $\text{CH}_3\text{CH}_2\text{OH}_A + \text{HOH}_B \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH}_B + \text{HOH}_A$. Here the B hydrogen of water ends up on ethanol, and the A hydrogen on ethanol ends up on water in the forward reaction. Chemical exchange will affect both T_1 and T_2 . T_1 is affected because energy transferred from one nucleus to another. For example, if there are more nuclei in the upper state of A, and a normal Boltzmann distribution in B, exchange will force the excess energy from A into B. The effect will make T_1 appear smaller. T_2 is affected because phase coherence of the transverse magnetization is not preserved during chemical exchange.

13.9 Sample Handling

Normally about 0.4 ml of a neat liquid or 10-50mg of a liquid or solid dissolved in 0.4ml of a deuterated solvent is used. The sample is contained in a glass tube with 5mm outside diameter and about 15cm length. The ideal solvent should be contained no protons, low boiling, nonpolar and inert. Deuterated chloroform CD_3Cl (chloroform-d); Hexadeuteroacetone CD_3COCD_3

(acetone-d₆); Hexadeuterobezene C₆D₆ (Benzene-d₆); Deutero water (D₂O); Deutero methanol (MD₄-OD) etc... are used as a solvent.

13.10 Shielding and deshielding effect

Under the influence of the applied magnetic field, electrons surrounding a nucleus start to circulate perpendicular to the applied magnetic field H_0 , and they generate a secondary magnetic field called induced magnetic field (σH_0). This induced magnetic field by surrounding electrons can either oppose or reinforce the applied magnetic field in the region of the nucleus. If the induced field

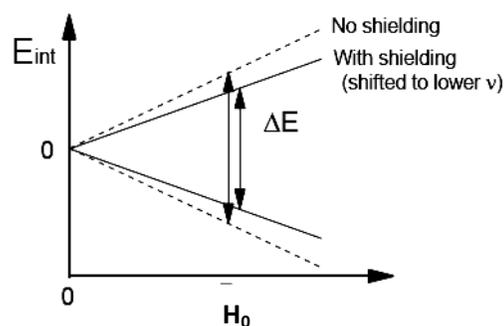


Figure 8: The shielding effect

opposes the applied magnetic field, the nucleus experiences a weaker magnetic field than the applied magnetic field H_0 (Figure 8) and is called *shielding or diamagnetic shielding* and its effect is called shielding effect. Otherwise if induced magnetic field reinforces the applied magnetic field, then the nucleus experienced greater magnetic field than the applied magnetic field. Such a nucleus is said to be deshielded and the effect is said to be deshielding effect.

$$H_{\text{eff}} = H_0 - \sigma H_0 \text{ (where } \sigma \text{ is shielding constant)}$$

13.11 Chemical shift

NMR experiment spectrum is reported as a function of resonance frequency of each proton with respect to relative absorption height. It is obvious that each group of protons have different resonance frequency, this difference is due to the shielding or deshielding effect hence they have different absorption position in NMR spectra. Therefore the resonance frequency of particular proton is compared with methyl proton of the reference compound under the similar experimental conditions. In practice Trimethylsilylchloride is used as reference compound.

The chemical shift of a nucleus (eg: ¹H, ¹³C) in a molecule is a measure of relative difference between the resonance frequency of proton understudy to that of reference compound in a same external magnetic field. Chemical shift is denoted by the symbol δ and represented by units ppm (ie, parts per millennium). The higher the chemical shift of a nucleus means shielded and vice versa. Hence, Chemical shift (δ) = $\gamma_S - \gamma_{(\text{TMS})}$ Hz ----- (4)

Since resonance frequency of a proton is dependent on the operating magnetic field strength of the instrument, same proton will have different resonance frequency studied under instrument having different magnetic field strength. This will show the different chemical shift for same proton. Therefore in order to represent chemical shift is an independent of the operating frequency and magnetic strength of the instrument the equation 4 is divided by the operating radio-frequency of the instrument. This operation makes chemical shift of a proton is independent of the operating frequency and represented on a scale called δ scale or ppm (ie, parts per million) scale with 0-12 unit as represented in the figure 9.

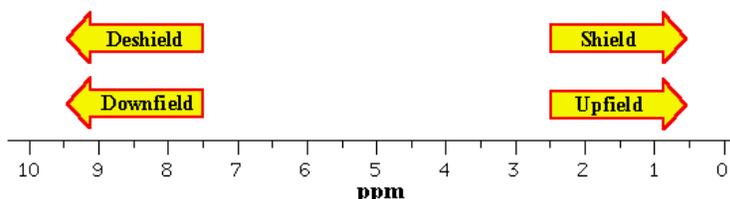


Figure 9: δ or ppm scale used to represent the proton absorption in NMR

Therefore chemical shift $\delta = \frac{\gamma_S - \gamma_{(TMS)} Hz}{Operating\ frequency (MHz)}$

Where γ_S is the resonance frequency of the proton under study and $\gamma_{(TMS)}$ is the resonance frequency of the reference compound.

For example, if the observed shift from TMS is 200 Hz and the operating frequency of the instrument is 100 MHz, then the chemical shift (δ) is given by the following expression

$$\delta = \frac{200 Hz}{100 \times 10^6 Hz} = 2.0 \times 10^{-6}$$

If this frequency ratio is multiplied by 10^6 in order to obtain an easily handled number then the chemical shift δ is expressed as parts per million of the operating frequency.

$$\text{Thus, } \delta = \frac{200 Hz}{100 \times 10^6 Hz} \times 10^6 = 2.0 ppm$$

13.13 Factors affecting chemical shift:

Any factor which is responsible for shielding or deshielding of a proton will generally affect its chemical shift. The following factors are majorly affecting the chemical shifts in NMR experiment,

- a) electronegativity- Inductive effect
- b) Anisotropic effects
- c) Hydrogen bonding and
- d) van der Waals deshielding.

a) *Electronegativity- Inductive effect:*

As already mentioned the degree of shielding depends on the electron density around the proton. The higher the electron density around the proton will increase the shielding effect hence corresponding proton appears at lower δ value (also called up field). This is because an electronegative atom withdraws the electron density around neighboring proton due to $-I$ effect hence proton is deshielded and appears at higher δ value (also called down field). The deshielding effect is increasing as the electronegativity of the atom increases. For example the chemical shift values of the methyl proton in following methyl halides are listed in below table are in accordance with the electronegativity of the halogen attached to it.

Methyl halide	Electronegative value of halide	Chemical shift (δ) value
$\text{CH}_3\text{-F}$	4.0	4.26
$\text{CH}_3\text{-Cl}$	3.0	3.05
$\text{CH}_3\text{-Br}$	2.8	2.68
$\text{CH}_3\text{-I}$	2.5	2.16

Similarly the chemical shifts of methyl protons attached to carbon, nitrogen, and oxygen (ex, CH_3 ($\delta \approx 0.9$); $\text{N}(\text{CH}_3)_3$ ($\delta \approx 2.2$); $\text{CH}_3\text{-O-CH}_3$ ($\delta \approx 3.5$)) are in the order of electronegativity of C, N and O. As the number of electronegativity atoms attached to the carbon atom increases, the concerned protons are more and more deshielded because of less electron density around the proton and hence appears at a down field (ie, higher δ value) for example, CH_4 , CH_3Cl , CH_2Cl_2 and CHCl_3 protons appear at $\delta \approx 0.33$; $\delta \approx 3.05$; $\delta \approx 5.28$ and $\delta \approx 7.24$ respectively. Also the distance from the electronegative atom increases, its deshielding effect on the proton decreases therefore proton signal appears at a relatively up field (ie, lower δ value). For example, methyl

group protons in the compound $\text{CH}_3\text{-Cl}$ appears at $\delta \approx 3.05$ whereas the methyl protons in the compound $\text{CH}_3\text{-CH}_2\text{-Cl}$ appears at $\delta \approx 1.48$.

b) Anisotropic effect:

The word "**anisotropic**" means non-uniform and magnetic anisotropy means that there is a non-uniform magnetic field. In some cases (ex, acetylenic, olifinic, aldehydic and aromatic protons) the chemical shifts of the protons are appears extremely down field or up filed and the reason for this cannot be explained only on the basis of electronegativity. *Electrons in π systems interact with the applied field which induces a magnetic field that causes the anisotropy. As a result, the nearby protons will experience 3 fields: the applied field, the shielding field of the valence electrons and the field due to the π system. Depending on the orientation of the proton in this third field, it can be either shielded (smaller δ) or deshielded (larger δ). This effect is called anisotropic effect.*

v) Acetylenic protons:

Under the influence of applied magnetic field the π electron cloud of triple bond generate an induced magnetic field in cylindrical form, which opposes the applied field in parallel direction and reinforces the applied field in perpendicular direction. Since acetylene is a linear molecule, it is aligned parallel to applied magnetic field and the acetylenic proton fall in this cylindrically induced magnetic field as shown in figure 10. Therefore acetylene proton is additionally shielded and experiences relatively less of the applied magnetic field. That's why its signals are appears at more up field than the expected from the electronegativity of the acetylenic carbon.

vi) Olifinic protons:

In an olifine circulation of π electrons of the olifinic double bond under the influence of external applied magnetic field generates an induced magnetic field which is opposes the applied field in

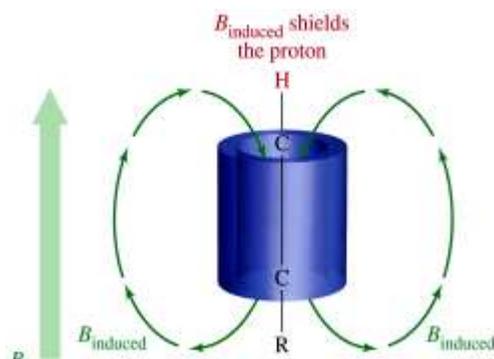


Figure 10: Shielding of acetylenic protons, the molecule is aligned parallel to applied magnetic field and the acetylenic proton fall in this cylindrically induced magnetic field as shown in figure 10. Therefore acetylene proton is additionally shielded and experiences relatively less of the applied magnetic field.

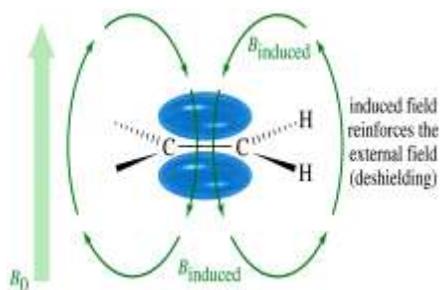


Figure 11: Deshielding of olifinic protons, the molecule is aligned parallel to applied magnetic field and the olifinic proton fall in this induced magnetic field as shown in figure 11. Therefore olifinic proton is additionally deshielded and experiences relatively more of the applied magnetic field.

parallel direction and reinforces the applied field in perpendicular direction. cylidrically induced magnetic field. This is because the olifines are not linear molecules and they are oriented perpendicular to the applied magnetic field as shown in figure 11. Thus the olifinc protons are fall in the induced magnetic field which reinforces the applied magnetic field. Hence they are deshielded and appears at more down field than the expected from the electronegativity of the olifinic carbon.

vii) *Aldehydic protons:*

The circulation of π electrons generates an induced magnetic field which is opposes the applied field in parallel direction and reinforces the applied field in perpendicular direction. Similar to olifinic double bond aldehyde group is oriented perpendicular to the applied magnetic field. Hence the aldehydic proton falls in the region in which the induced magnetic field which reinforces the applied magnetic field as shown in figure 12. Hence aldehydic proton is more deshielded and appears at more down field ($\delta \approx 9.5$) due to the combined effects of the high electronegativity of the oxygen and anisotropic effects produced by the π electrons of the carbonyl group.

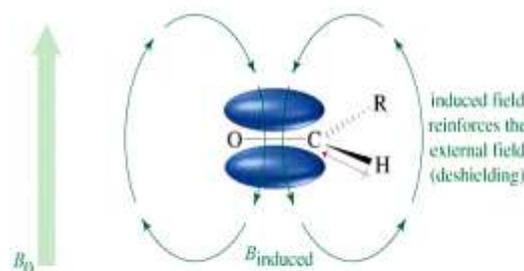


Figure 12: Deshielding of aldehydic proton

viii) *Aromatic protons:*

Aromatic ring contain delocalized $4n+2$ cyclic π electrons clouds. This cyclic π electron cloud produces a ring current when a magnetic field is applied perpendicular to the plane of the aromatic ring. This induced magnetic field which is in the same direction of the applied magnetic field. Outside the ring, induced magnetic field reinforces the applied magnetic field but inside the ring it is opposes the applied magnetic field as shown in figure 13. The aromatic protons are fall on the highly deshielded region and hence appear at lower field. This is also called ring current effect.

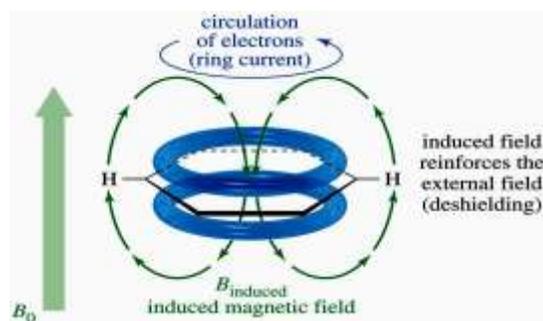
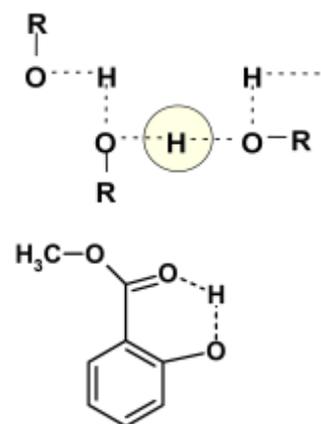


Figure 13: Deshielding of aromatic proton

The σ electrons of the C-C bond also produces magnetic anisotropic effect but this effect is less powerful when compare to anisotropic effect produced by circulating π electrons, also axis of the C-C bond is the axis of the deshielding cone . The protons in the tertiary protons falls in the three deshielding cones of C-C bonds, secondary protons are fall in the two deshielding cones of C-C bonds and primary protons are fall in the only one deshielding cone. Therefore the protons in the sequence RCH_3 , R_2CH_2 and R_3CH are appears progressively down field.

c) Hydrogen bonding:

Hydrogen bond is formed between the hydrogen atom and the hielectronegativity atom like N, O, S, F etc..... Hence protons falls on lower field (down field) than the non-hydrogen bonded protons due to high electronegativity of the atom to which the proton is hydrogen bonded. The electron density around it is decreased as compared to that around the non-hydrogen bonded proton. The down field shift of the absorption depends on the strength of the hydrogen bonding. The stronger the hydrogen bonding corresponding protons appears at more down field.



Intermolecular and intramolecular hydrogen bondings can easily distinguished by NMR spectroscopy because intramolecular hydrogen bonded proton shows no shift in absorption position on changing the concentration of the sample where as absorption position of intermolecular hydrogen bonded proton is concentration dependent.

d) van der Waals deshielding:

In crowded molecular some protons are sterically hindered position resulting in van der Waals repulsion. In such case electron cloud of a bulky group will tend to repel the electron cloud surrounding the proton. Thus proton will be deshielded and will fall slightly down field than expected in the absence of this effect. Study of this effect has been successfully used to get information about the conformational structure of both aromatic and non aromatic compounds.

13.13 Instrumentation

The schematic diagram of NMR spectrometer containing the following components in it as represented in figure 14.

i) *A strong magnet with homogeneous field:* the NMR instrument consists of a very strong magnet which is either permanent magnet/electromagnet or iron magnet/ superconducting magnet. The strength of the magnetic field can be varied continuously and precisely over a relatively narrow range with the help of the sweep generator.

ii) *A radio-frequency oscillator:* The sample is inserted into the centre of the magnetic field and the sample is surrounded by RF coils which generate RF radiation which can be finely tuned with the help of controller to desirable frequency.

iii) *A radio-frequency receiver and detector:* Signals are detected by either the same coil or another coil depending upon the manufacturer's design.

iv) *A recorder, calibrator and integrator.*

v) *A sample holder:* It spins the sample

to keep the sample in the uniform magnetic field around the whole sample.

The sample under investigation (around 0.5ml) is taken in a glass tube of 5mm diameter volume, and placed in the sample holder. Then the sample is irradiated with a beam of constant radio frequency obtained from RF oscillator. The magnetic field strength is varied with the help of the sweep generator which

consequently varies the ΔE value. When the ΔE equal to the energy of incident RF radiation. Absorption of the RF frequency takes place and transition nuclear spin of the proton from lower energy state to higher

energy spin state occurs. This causes a flow of tiny electric current in the coil of the RF receiver. The tiny current is amplified and recorded as a signal on the chart paper by the recorder. The NMR spectrum is recorded as a plot of a series of peaks (signals) corresponding to different applied field strengths against their intensity as shown in figure 15 of ethyl chloride molecule.

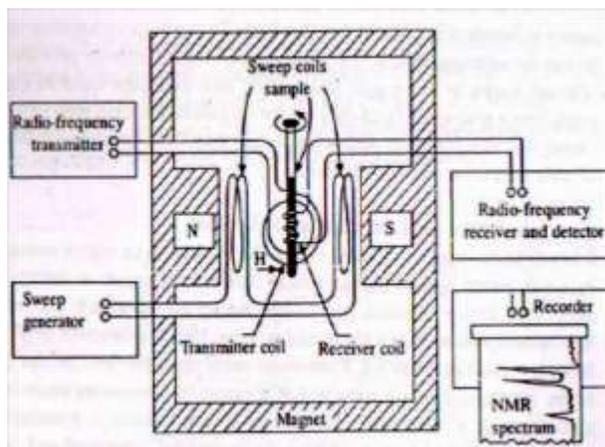


Figure 14: Schematic diagram of NMR spectrometer

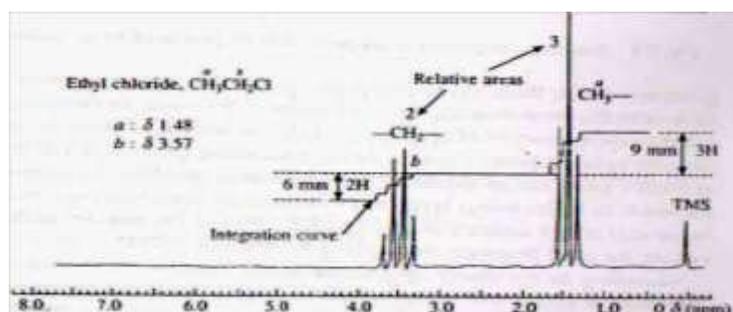


Figure 15: NMR spectrum of ethyl chloride in CDCl_3 at 60MHz

Each peak represents a set of protons and area under the peaks is directly proportional to the number of protons present in that set.

There are two general types of NMR instrument namely continuous wave NMR instrument and Fourier transform (FT) NMR instrument. Early days NMR experiments were conducted with continuous wave NMR instruments, and in 1970 the first Fourier transform instruments became available. FT type instrument is now dominates in the market.

a) *Continuous Wave (CW) NMR instruments* The CW spectrometers use a technique similar to that of classical optical spectrometers: a slow scan of radio frequency (at fixed magnetic field) or of the magnetic field (at fixed radio frequency) over a domain corresponding to the resonance of the nuclei being studied. The signal generated by the absorption of energy is detected, amplified, and recorded. The limitations of the CW spectrometers are low sensitivity and long analysis time.

b) *Fourier Transform (FT) NMR instruments:* The magnitude of the energy changes involved in NMR spectroscopy is very small. This means that, sensitivity can be a limitation when looking at very low concentrations. One way to increase sensitivity would be to record many spectra, and then add them together. As noise is random, it adds as the square root of the number of spectra recorded. For example, if one hundred spectra of a compound were recorded and summed, then the noise would increase by a factor of ten, but the signal would increase in magnitude by a factor of one hundred giving large increase insensitivity. However, if this is done using a continuous wave instrument, the time needed to collect the spectra is very large (one scan takes two to eight minutes). In FT-NMR, all frequencies in a spectral width are irradiated simultaneously with a radio frequency pulse. A single oscillator (transmitter) is used to generate a pulse of electromagnetic radiation of frequency ω_0 but with the pulse truncated after only a limited number of cycles (corresponding to a pulse duration τ) this pulse has simultaneous rectangular and sinusoidal characteristics. It can be proven that the frequencies contained within this pulse are within the range $\pm 1/\tau$ of the main transmitter frequency ω_0 . For example a 5 μ s pulse would generate a range of frequencies of $\omega_0 \pm 1/0.000005$ Hz (i.e. $\omega_0 \pm 200,000$ Hz).

13.14 Summary of the unit

The principle behind NMR is that many nuclei have spin and are electrically charged. If they are placed in an external magnetic field, energy transfer is possible between the base energy to a higher energy level. The energy transfer takes place at a wavelength that corresponds to radio

frequencies and when the spin returns to its base level, energy is emitted at the same frequency. In most spectroscopic techniques, how the energy absorbed by the sample is released is not a primary concern. In NMR, where the energy goes, and particularly *how fast it "gets there"* are of prime importance. The NMR process is an absorption process. Nuclei in the excited state must also be able to "relax" and return to the ground state. The timescale for this relaxation is crucial to the NMR experiment. For example, relaxation of electrons to the ground state in uv-visible spectroscopy is a very fast process, in the order of pico-seconds. In NMR, the excited state of the nucleus can persist for minutes. Because the transition energy between spin levels is so small, attaining equilibrium occurs on a much longer timescale. The timescale for relaxation will dictate the how the NMR experiment is executed and consequently, how successful the experiment is. The signal that matches this transfer is measured in many ways and processed in order to yield an NMR spectrum for the nucleus concerned. The precise resonant frequency of the energy transition is dependent on the effective magnetic field at the nucleus. This field is affected by electron shielding which is in turn dependent on the chemical environment. As a result, information about the nucleus' chemical environment can be derived from its resonant frequency. In general, the more electronegative the nucleus is, the higher the resonant frequency.

NMR spectroscopy became a powerful tool for chemists because of the NMR chemical shift. Beyond distinguishing one nucleus from another, it can in fact reveal information regarding the chemical surroundings of a nucleus. The area under the peak also corresponds to the relative number of each type of proton. Modern NMR spectroscopy goes even beyond NMR chemical shifts caused by chemical inequivalency. Also NMR chemical shift is known to be very sensitive to intra- and intermolecular factors. These effects can be vividly seen in gas-phase NMR spectroscopy of small molecules. Hence the chemical shift is used to identify functional groups and to aid in determining structural arrangements of groups. These applications are based upon empirical correlations between structure and shift.

13.15 Key words

Nuclear Spin; Spin active nuclei; Spin resonance; Spin relaxation; Spin Exchange; Shielding ; Deshielding; Anisotropic effect; Continuous Wave (CW); Fourier Transform (FT).

13.16 References for the further study

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13. 17 Question for self study

- 1) Explain the principle of NMR and obtain the resonance condition.
- 2) List the basic requirements of a typical NMR spectrometer.
- 3) Distinguish between spin lattice and spin-spin relaxations.
- 4) Why spinning of the sample is needed in high resolution NMR spectral study?
- 5) What is meant by the term chemical shift?
- 6) Write with examples the shielding and the deshielding effects involved in NMR spectroscopy.
- 7) Describe with example various factors affect the magnitude of the chemical shift.
- 8) How many signals are expected in each of the following compounds?
 - a) Propane b) Isobutane c) Etanol d) cyclobutane e) Ethylmethyl ether f) Ethyl acetate g) Butanal h) Glycol i) α -alanine j) caprolactum.
- 9) Describe briefly the difference in the position of absorption as noted in the case acetylene and benzene.
- 10) Explain the term spin-spin coupling, why does a peak for a particular set of protons split in to a multiplet? Give example.
- 11) Write a brief notes on following:
 - i) Reference compound in NMR ii) Solvents used in NMR
- 12) Write the possible isomers corresponding to the following molecular formulae and draw their NMR structures (only number of peaks and not multiplicity)
 - i) C_4H_{10} ii) C_2H_6O iii) C_4H_8O iv) $C_4H_6O_2$ v) $C_4H_8O_2$.
- 13) Which of the following atoms does not exhibit nuclear magnetic resonance?
 ^{12}C ; ^{16}O ; ^{14}N ; 2H ; ^{15}N ; ^{19}F ; ^{13}C ;

Structure**Unit- 14.0**

- 14.0 Objectives of the unit
- 14.1 Introduction
- 14.2 Equivalent and Nonequivalent protons
- 14.3 Spin-Spin splitting or Spin-Spin coupling
- 14.4 Origin of Spin-Spin Splitting
- 14.5 Multiplicity-number of component peaks in multiplet
- 14.6 Relative intensities of component peaks of a multiplet
- 14.7** Coupling constant (J Value):
- 14.8 Causes of splitting of NMR signal
- 14.9 *First order splitting*
 - a) *Geminal proton-proton coupling ($^2J_{HH}$)*
 - b) *Vicinal proton-proton coupling ($^3J_{HH}$)*
- 14.10 Non-first order splitting
- 14.11 Consequences of non-first order splitting
- 14.12 Spin-Spin coupling of protons with other nuclei
 - a) *D-H coupling:*
 - b) *$^{14}\text{N-H}$ coupling*
 - c) *$^{19}\text{F-H}$ coupling*
 - d) *$^{13}\text{C-H}$ coupling*
 - e) *$^{31}\text{P-H}$ coupling*
- 14.14 Summary of the unit
- 14. 14 Key words
- 14. 15 References for the further study
- 14.16 Question for self study

14.0 Objectives of the unit

After studying this unit you are able to learn

- Distinguish the Equivalent and Nonequivalent protons
- Explain the phenomenon of Spin-Spin splitting
- Identify the number of component peaks in multiplet for a particular proton in compound.
- Explain the significance of Coupling constant
- Identify the First order splitting and Non-first order splitting
- Difference ate between Geminal proton-proton and Vicinal proton-proton coupling
- Recognize Spin-Spin coupling of protons with other nuclei

14.1 Introduction

We are all experience in your child wood that when two magnets are brought together they attract, just like when neighboring nuclei are close enough they can either interact or couple. Protons have a magnetic field associated with them and when they are placed in a magnetic field approximately half of the protons become aligned with the field and half become aligned against the field. It is the transition between these two states that we observe in NMR. In the simplest case we expect to see a single peak for each type of equivalent protons in a molecule. But what happens if a proton (H_A) is near another nonequivalent proton (H_B).

Half of the molecules of the H_A proton will be adjacent to an H_B aligned with the field and in the other half of the H_A proton will be adjacent to an H_B aligned against the field. Thus, half of the H_A 's in the sample will feel a slightly larger magnetic field than they would in the absence of H_B and half will feel a slightly smaller magnetic field. Thus, we will observe two absorptions for the H_A proton (also observe the same thing for H_B). This splitting of the H_A resonance into two peaks is termed "spin-spin coupling" or "spin-spin splitting" and the distance between the two peaks is called the "coupling constant" usually represented by the symbol J . The spin-spin coupling is transmitted through the electrons in the bonds and so depends on the bonding relationship between the two hydrogens. Remember that only non-equivalent neighboring protons can couple. There are distinct patterns seen when splitting occurs, and the pattern tells us the number of neighboring protons on a carbon atom.

14.2 Equivalent and Nonequivalent protons

Protons with same chemical environment absorb at the same field strength whereas protons with different chemical environment absorb at different field strength. The protons with same

chemical environment are said to be chemically equivalent and called as chemically equivalent protons and they occupy chemically equivalent positions, (ie same chemical shift). The very simple method to identify the chemical equivalence of two or more protons is as follows.

Just imagine of replacement of each proton in turn on the carbon atom by some other atom Z. if the replacement results in only one product then protons are said to be chemical equivalence protons and have *same chemical shift*. On the other hand if the replacement results in *enantiomeric products* then protons are said to be *chemical nonequivalence protons* and have *different chemical shift*.

For example, the replacement of a each protons of methyl group by Z in ethyl chloride ($\text{CH}_3\text{-CH}_2\text{-Cl}$) molecule give same product where as replacement of methylene protons by Z in ethyl chloride molecule gives enantiomers ie, different products As shown in figure 1.

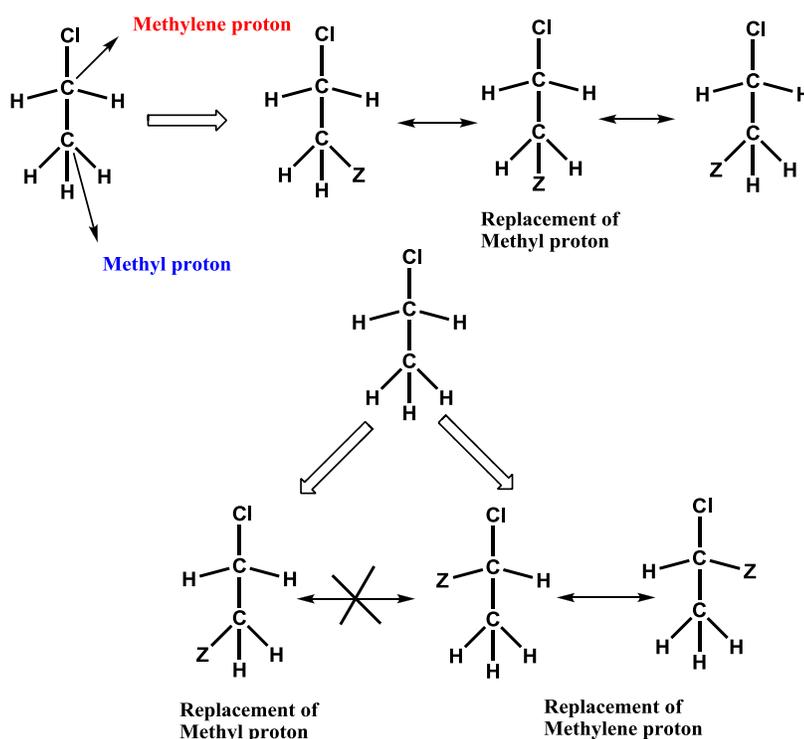


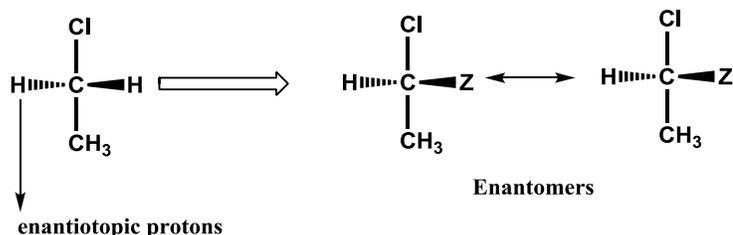
Figure 1: schematic identification of chemically equivalent and nonequivalent protons

Hence we can easily judge that methyl protons and methylene protons in ethylchloride molecules are chemically nonequivalent protons and appear at different δ value (ie, shows different chemical shift).

Also replacement of either of two methylene protons of ethylchloride by Z gives enantiomeric products as shown in figure 2. Such a pair of protons is called enantiotopic protons and have the

same chemical shift and exhibit only one NMR signal (ie, they are also chemically equivalent protons).

On the other hand pair of protons whose replacement gives a pair of



diastereomers are called diastereotopic protons. These protons do not have the same chemical shift and show different NMR signals. Therefore these are nonequivalent protons. For example, replacement of either protons of 2-bromopropene by Z gives diastereomeric products as shown in figure 3.

Similarly in 1,2-dichloropropane the two protons on C-1 are diastereotopic hence are nonequivalent and show separate NMR signals.

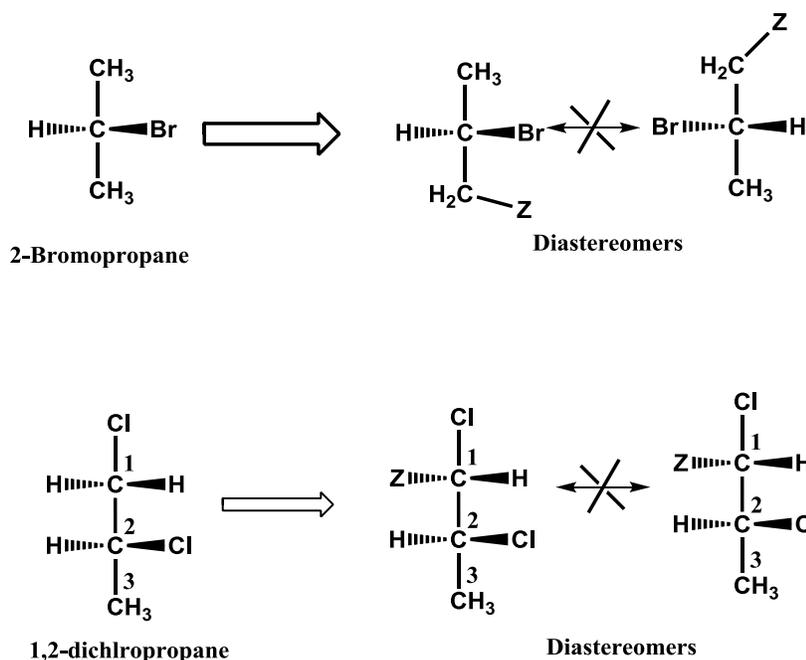


Figure 3: Diastereotopic protons; they have different chemical shift in NMR

14.3 Spin-Spin splitting or Spin-Spin coupling

In the NMR spectra it has been found that in only few cases one kind of proton is appears as a single peak (also called singlet) and in most cases, instead of single peak, a group of speaks (also called multiplet) is observed for a one kind of protons. This is called the splitting of NMR signal due to Spin-Spin coupling of the neighboring protons. For example ethylbromide ($\text{CH}_3\text{-CH}_2\text{-Br}$)

has two kinds of protons and two signals. One of which is split into three peaks (called triplet) and the other into four peaks (called quartet) as shown in figure 4.

14.4 Origin of Spin-Spin Splitting

The splitting of chemical shift peaks occurs as the magnetic moment of a nucleus interacts with the magnetic moments of immediately adjacent nuclei. The magnetic field created by a spinning nucleus affects the distribution of electrons in its bonds to other nuclei. This change in electron distribution then produces changes in the magnetic field of adjacent nuclei and causes splitting of energy levels and hence multiple transitions occur. Thus the signal is split into a group of peaks and called spin-spin splitting or spin-spin coupling. *The phenomenon of multiplicity of a NMR signal due to the interaction of the proton magnetic field with neighboring*

bonding electrons is called Spin-Spin splitting or Spin-Spin coupling. The spin orientations i.e., alignments of the methine, methylene (-CH₂-) and methyl (-CH₃) protons are shown in figure 6. The two spin orientation of the methane proton shall effect the absorption position of the vicinal protons in two ways, thus the signal of the methane is split into peaks (called doublet) with intensity ratio 1:1 because the probability of the two spin orientations is equal.

Similarly there are three different spin alignments possible for the methylene protons and there are four different spin orientations possible for the methyl proton as shown in figure 6. Therefore methylene protons affect the absorbance of the vicinal proton in three ways resulting split into three peaks (also called triplet) with intensity ration of 1:2:1 and methyl protons affect the

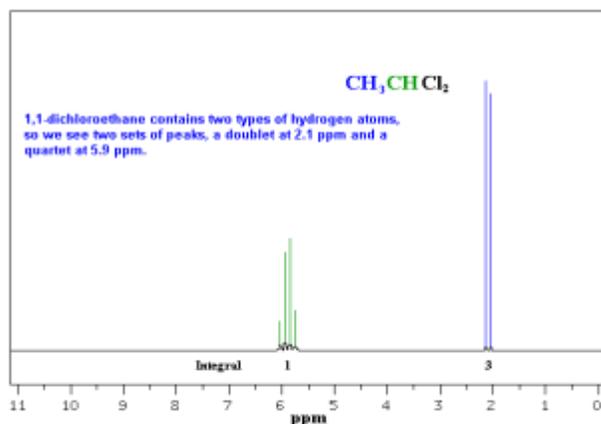


Figure 4: NMR spectra of Ethylbromide

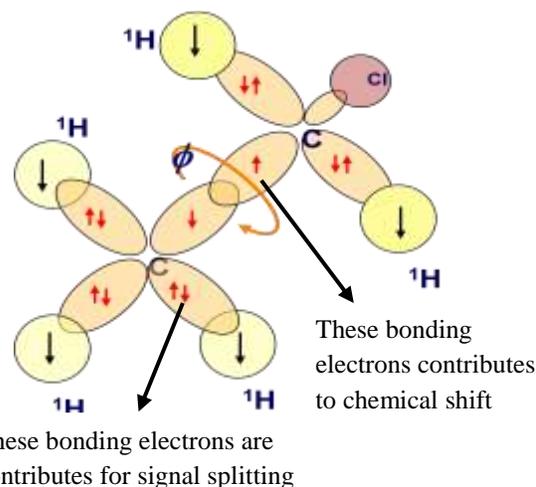


Figure 5: Interaction neighboring bonding electrons with proton magnetic field to cause a spin-spin splitting

absorption of the vicinal protons in four ways and split the signal in to four peaks (also called quartet) with intensity ration 1:3:3:1. The abbreviation for multiplets observed in NMR spectra is as follows: *s* (singlet); *d* (doublet); *t* (triplet); *q* (quartet) and beyond that the splitting is generally called as *m* (multiplet).

14.5 Multiplicity-number of component peaks in multiplet

The spin-spin splitting is observed only between nonequivalent (ie, different chemical shifts) neighboring protons. Though the equivalent protons (same chemical shift) protons also do spin-spin couple with one another, splitting is not observed. In general the number of peaks in a multiplet is equal to $n+1$, where n is the number of equivalent protons causing the splitting as shown in figure 6.

For example; in $\text{CH}_3\text{-CH}_2\text{-Cl}$ molecule, three methyl protons are equivalent but they are non equivalent to the methylene protons.

Therefore three methyl protons have spin-spin coupling with methylene protons and split their signal in to $3+1 = 4$ peaks ie, methylene protons appears as a quartet. Similarly the two methylene protons have spin-

spin coupling with methyl protons and split their signal in to $2+ 1= 3$ peak ie, methyl protons appears as a triplet. On the other hand, the protons of both the methyl groups in $\text{CH}_3\text{-CH}_3$ are equivalent. Hence they do not split their signal and all the six protons appear as a single peak.

If the protons responsible for spin-spin splitting are nonequivalent, then the number of peaks (lines) for a particular multiplet will be equal to $(n+1)(n'+1)(n''+1)$ where n , n' and n'' are the number of different kind of protons.

For example: in 1,1-dibromo-3,3-dichloropropane molecule there are three kinds of protons. The methylene protons *b* have two kinds of vicinal protons ie, *a* and *c*. Hence the signal for the methylene protons ($-\text{CH}_2-$) appears as a multiplet consisting of $(n+1)(n'+1) = (1+1)(1+1) = 4$ lines.

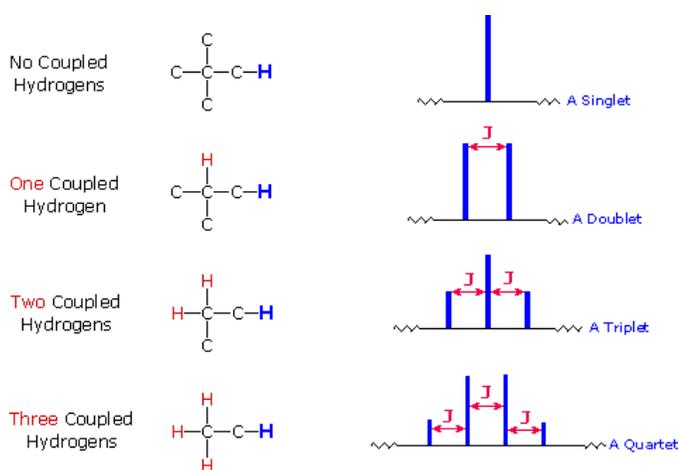


Figure 6: spin multiplicity obtained for different groups in NMR spectra

14.6 Relative intensities of component peaks of a multiplet

The relative intensities of the component peaks of a multiplet depends on the number of equivalent protons causing the splitting (ie, n) and are given by the numerical co-efficients of the term in the expansion of $(x + 1)^n$ to the desired value of n .

If $n = 1$, then $(x + 1)^1 = x + 1$. Thus the peaks of a doublet have relative intensities 1:1.

If $n = 2$, then $(x + 1)^2 = x^2 + 2x + 1$. Thus the peaks of a triplet have relative intensities 1:2:1

If $n = 3$, then $(x + 1)^3 = x^3 + 3x^2 + 3x + 1$. Thus the peaks of a quartet have relative intensities 1:3:3:1

The relative intensities of component peaks of any $(n + 1)$ multiplet can be calculated with the help of Pascal's triangle as shown in figure 7.

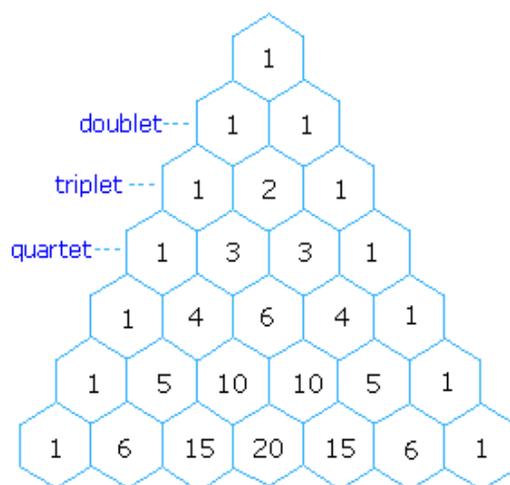


Figure 7: Calculation spin multiplicity using Pascal's triangle

14.7 Coupling constant (J Value)

Coupling constant is the strength of the spin-spin splitting interaction and the distance between the split lines and denoted by symbol J . The distance between the splitting lines within a multiplet is depends on the coupled nuclei and is equal or different. The coupling constants reflect the bonding environments of the coupled nuclei.

14.8 Causes of splitting of NMR signal

If an atom under examination is perturbed or influenced by a nearby nuclear spin (or set of spins), the observed nucleus responds to such influences, and its response is manifested in its resonance signal. This spin-coupling is transmitted through the connecting bonds, and it functions in both directions. Thus, when the perturbing nucleus becomes the observed nucleus, it also exhibits signal splitting with the same J .

For spin-coupling to be observed, the sets of interacting nuclei must be bonded in relatively close proximity (e.g. vicinal and geminal locations), or be oriented in certain optimal and rigid configurations. Some spectroscopists place a number before the symbol J to designate the number of bonds linking the coupled nuclei. According to this terminology, geminal constant is represented by symbol 2J and a vicinal coupling constant is represented by symbol 3J .



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14.9 First order splitting

The simple splitting pattern resulting from the coupling of protons having large difference in chemical shift ($\Delta\gamma$) compared to the coupling constant J (ie, $\Delta\gamma/J > 6$) is called first order splitting. The splitting patterns shown in figure 8 display the ideal or "**First-Order**" arrangement of lines

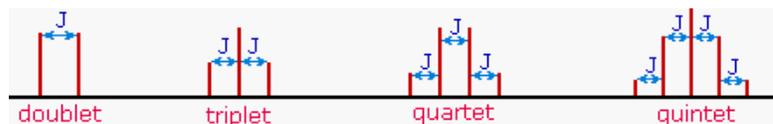


Figure 8: Type of first order splitting observed in NMR

Conditions for first order splitting

The following conditions (rules) govern the appearance of first order splitting.

- i) Equivalent protons do not interact with one another to give multiple absorption peaks
- ii) Coupling is seldom observed at distances greater than three bond lengths unless there is ring strain in a small ring or bridged systems or delocalization as in aromatic and unsaturated systems.
- iii) The multiplicity of a signal is determined by the number (n) of magnetically equivalent protons on the neighboring atoms and is given by the quantity $n + 1$.
- iv) If the protons on atom B are affected by protons on atoms A and C which are nonequivalent, the multiplicity of B is equal to $(n_A + 1)(n_C + 1)$, where n_A and n_C are the number of equivalent protons on A and C, respectively.
- v) The approximate relative areas of a multiplet are symmetric around the midpoint of the band.

The first order splitting rules are applicable only if the following conditions are satisfied.

- a) The chemical shift difference between the interacting nuclei must be large compared with the coupling constant (ie, $\Delta\gamma/J > 6$)

b) Each nucleus of one group must interact equally with each and every nucleus of the second group.

The coupling constant is classified as follows:

c) *Geminal proton-proton coupling* (${}^2J_{HH}$)

Geminal coupling occurs through two bonds as shown in figure 9. Two protons having geminal coupling are not chemically

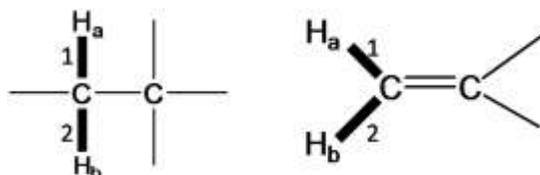


Figure 9: Geminal coupling

equivalent. This coupling ranges from -20 to 40 Hz. ${}^2J_{HH}$ depends on

- i) Hybridization of carbon atom
- ii) The bond angle and
- iii) The substituent such as electronegative atoms.

When S-character is increased, geminal coupling constant is increased in the order ${}^2J_{sp} > {}^2J_{sp^2} > {}^2J_{sp^3}$. The change in bond angle of H-C-H gives rise to change in ${}^2J_{HH}$ value and in the cyclic systems it depends on the ring strain. Hence size of the ring can be determined by measuring geminal coupling constant. When bond angle is decreased, ring size is decreased so that geminal coupling constant is more positive. Also if an atom is replaced by an electronegative atom, geminal coupling constant moves to positive value.

d) *Vicinal proton-proton coupling* (${}^3J_{HH}$)

Vicinal coupling occurs through three bonds as shown in figure 10. Vicinal coupling provides most useful information of dihedral angle, leading to stereochemistry and conformation of molecules.

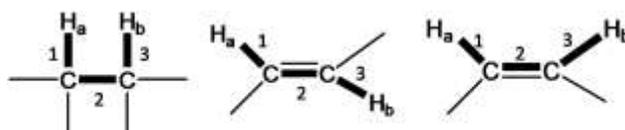


Figure 10: Vicinal coupling protons

Vicinal coupling constant always has the positive value and is affected by the following factors:

- i) Dihedral angle (H-C-C-H),
- ii) The valence angle (H-C-C)
- iii) The bond length of carbon-carbon, and
- iv) The effects of electronegative atoms.

Vicinal coupling constant depending on the dihedral angle is calculated by the Karplus equation.

$${}^3J = 7.0 - 0.5\cos\phi + 4.5\cos^2\phi$$

When Φ is the 90° , vicinal coupling constant is zero.

When $\Phi=180^\circ$ and $\Phi = 0^\circ$, vicinal coupling constant ranges from 8 to 15 Hz.

When $\Phi = 60^\circ$ vicinal coupling constant ranges from 2 to 5 Hz at

Therefore $\Phi = 0^\circ$ and $\Phi = 180^\circ$ means that the coupled protons have cis and trans configuration, respectively as shown in figure 11.

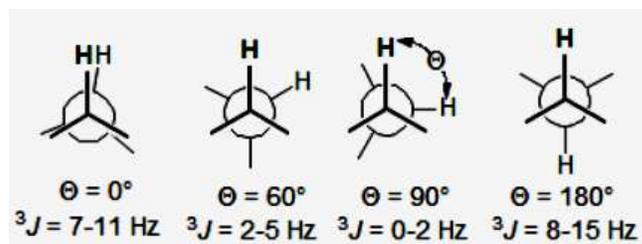


Figure 11: The dihedral angle dependent vicinal coupling constants in NMR

The valence angle also causes change of $^3J_{HH}$ value. We know that valence angle is related with ring size (figure 12). Typically, when the valence angle decreases, the coupling constant reduces. The distance between the carbon atoms gives influences to vicinal coupling constant

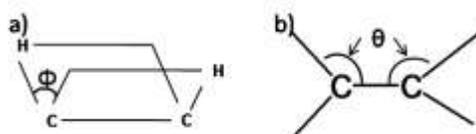


Figure 12: a) Dihedral angle and b) valence

The coupling constant increases with the decrease of bond length. Electronegative atoms affect vicinal coupling constants so that electronegative atoms decrease the vicinal coupling constants.

14.10 Non-first order splitting

When the chemical shifts of the interacting nuclei is approximately the same magnitude as the coupling constant (J). In such cases the first order splitting rules are no longer applicable (as shown in figure 13). The pattern of splitting in the multiplet becomes distorted and the bands are not symmetrical. Such spectra are more

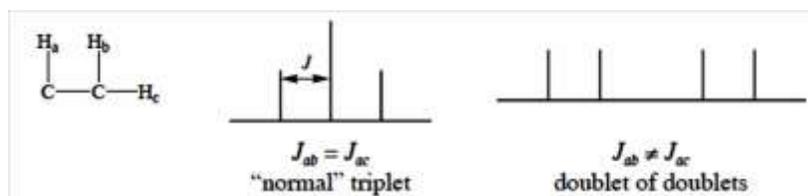


Figure 13: Second order splitting observed in NMR

complex and are known as second order spectra or No-first order spectra. Nuclei which give rise to second order spectra are said to be strongly coupled.

For example: Normal splitting patterns occur when coupling constants of neighboring protons CH of $-\text{CH}-\text{CH}_2-$ are equal i.e., ($J_{ab} = J_{ac}$) and is a triplet. If $J_{ab} \neq J_{ac}$, then more complex patterns arise.

Second order spectra may be recognized by the following features:

- Often more lines are present than are predicted by $(2n + 1)$ rule used for first order spectra.
- Even in the case of only two different groups of coupling nuclei, the lines of a particular multiplet are not equally spread.
- The relative intensities of the peaks of a multiplet are not given by coefficients of the terms in binomial expression of $(x + 1)^n$.
- The chemical shifts and coupling constant both cannot be measured directly from the spectrum. However they can be analyzed by quantum mechanical calculations.

14.11 Consequences of non-first order splitting

If a given nucleus is spin-coupled to two or more sets of neighboring nuclei by different J values, the $n+1$ rule does not predict the entire splitting pattern. Instead, the splitting due to one J set is added to that expected from the other J sets. Then there may be fortuitous coincidence of some lines if a smaller J is a factor of a larger J .

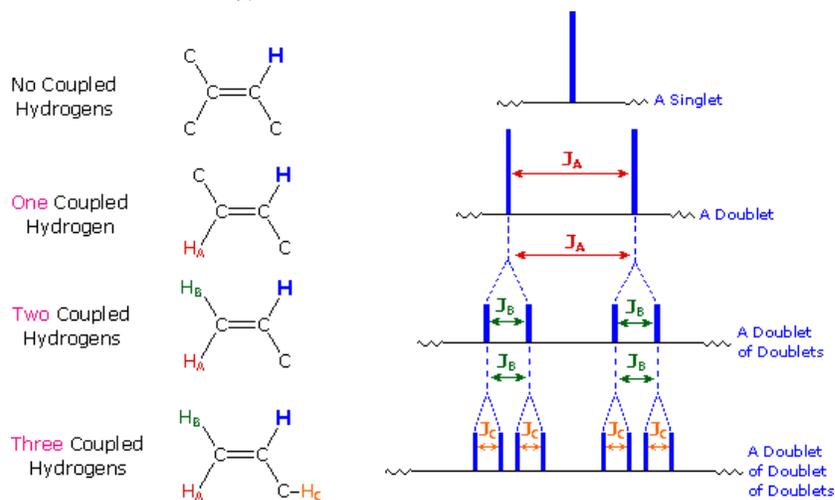


Figure 14: Different kind of second order splitting observed in NMR

The situation of protons with close chemical shifts coupled to each other is more complex. Even only two protons are coupled to each other, the pattern still appears as two doublets but the

intensities are no longer 1:1 and the chemical shifts are not the centers of the doublets as shown in figure 15.

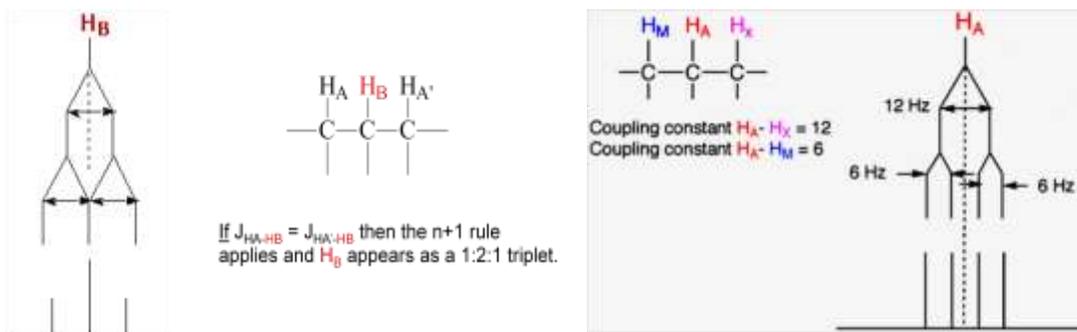


Figure 15: Complex splitting pattern for protons coupled to each other with close chemical shifts

Example of such complex splitting pattern is illustrated in figure 16. The vinyl protons H_x , H_m and H_a in (2-chloroethoxy) ethene compounds have nearly same chemical shift in NMR but due to second order splitting their multiplicity does not follow n+1 rule. H_a proton which would appear triplet will show 4 peaks with all peaks having same height. This kind of splitting is called as doublet of doublet. Since H_x and H_m protons have cis and trans relation with H_a proton respectively, they coupled with H_a individually and produce doublet peak for each proton. This is because the cis and trans protons even in the same carbon atom have slightly different chemical shift.

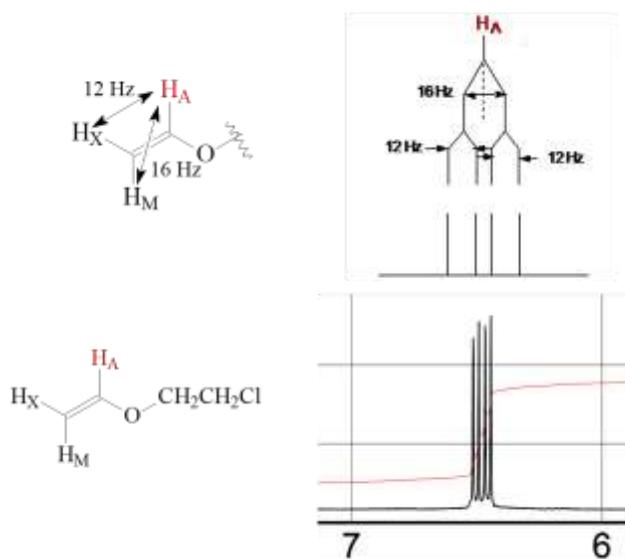


Figure 16: *Cis* and *Trans* coupling in a Carbon-Carbon Double Bond follows non-first order coupling

The separation between the lines of each doublet is still the coupling constant J . The chemical shifts are closer to the larger peaks of each doublet and can be calculated using a simple equation as shown below.

Structural Type	J (Hz)	Structural Type	J (Hz)
	0 (unless in a rigid ideal orientation)		12 to 18
	6 to 8		7 to 12
	5 to 7		0.5 to 3
	2 to 12 (depends on dihedral angle and the nature of X and Y)		3 to 11 (depends on dihedral angle)
	0.5 to 3		2 to 3
	12 to 15 (must be diastereotopic)		o 6 to 9 m 1 to 3 p 0 to 1

14.12 Spin-Spin coupling of protons with other nuclei

Any nucleus which has $I > 0$ is capable of exhibiting a NMR spectrum. Different nuclei (eg. ^1H ; ^2D ; ^{13}C ; ^{19}F etc....) require different oscillator frequencies for exhibiting NMR in a given magnetic fields. For example, in a magnetic field of 14,092 gauss, ^1H ; ^2D ; ^{13}C and ^{19}F , nuclei resonate at 60.000; 9.211; 15.085 and 56.446 MHz respectively. Thus under a given set of conditions for NMR of a particular nucleus, signals due to other nuclei are not observed on the spectrum. Proton may couple with any nucleus (having $I > 0$) to which it is covalently bonded.

Nuclei with $I \geq 1$ have an electric quadrupole moment, the magnitude of which is a measure of the nonspherical nature of the electric charge distribution within the nucleus. *The NMR signals for protons attached to a nucleus which has an electric quadrupole moment are broadened hence splitting is not observed.* The greater the magnitude of the electric quadrupole moment, the more is the broadening of the signals.

a) H-D coupling:

The signals of protons coupled with deuterons, which have only small quadrupole moment, are not appreciably broadened. The coupling constant for a proton with deuteron (J_{HD}) in the molecule type $-\text{CHD}-$ is $\approx 2\text{Hz}$ and in the molecule type $-\text{CH}-\text{CD}-$ is less than 1Hz

b) N-H coupling:

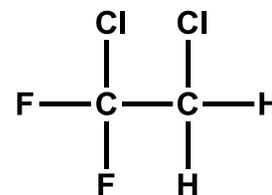
The N-H group should display splitting, since ^{14}N has a nuclear spin $I = 1$. However the proton signals coupled with nitrogen nucleus are always broadened because of the intermediate value for its electric quadrupole moment. The quadrupole moment of nitrogen can effectively provide the vectors orientation necessary for excited protons to relax quickly (ie, T_1 is very short) and hence ^{14}N spin-splitting of the proton resonance is not resolved. ^{14}N -coupling is only observed when the nitrogen atom is quaternary. In all other cases, any coupling is lost by exchange broadening or quadrupole broadening. Two bands ie, $^{14}\text{N-CH}_2$ - are not observed even when the nitrogen is quaternary because the coupling is vanishingly small.

c) *F-H coupling:*

Protons do not couple with halogen atoms (except fluorine) on the adjacent atoms or on the same atom because the very large quadrupole moments of the halogen atoms cause spin-spin decoupling of adjacent protons.

^{19}F nucleus as $I = \frac{1}{2}$ and does not have electric quadrupole moment, thus ^{19}F nuclei can efficiently couple with each other as well as with protons. Hence splitting of their signals occurs ($J_{\text{HCF}} \approx 60\text{Hz}$; $J_{\text{HCCF}} \approx 20\text{Hz}$).

For example in 1,2-dichloro-1,1-difluoroethane, the coupling of two equivalent protons with fluorine nuclei gives a triplet in the spectrum. Appear of triplet in the NMR spectra of 1,2-dichloro-1,1-difluoroethane is rather surprising but it is easily understandable because different nuclei require different radio frequency for



exhibiting NMR in a given magnetic field. Thus under the PMR conditions another triplet due to two fluorine atoms is not observed. Similarly in the ^{19}F NMR spectrum of 1,2-dichloro-1,1-difluoroethane only a triplet due to two fluorine atoms will be observed and triplet due to the protons will not be observed.

d) $^{13}\text{C-H}$ coupling:

^{13}C gives rise to observable $^{13}\text{C-H}$ coupling ($J^{13}\text{C-H} \approx 100\text{-}250\text{ Hz}$; $(J^{13}\text{CCH}) \approx 40\text{ Hz}$, especially in spectra recorded at amplitude. Peak resulting from coupling with ^{13}C are called ^{13}C satellite peaks. These weak peaks appear symmetrically on the either side of the much stronger signals of $^{12}\text{C-H}$ group.

For example: the spectrum of chloroform exhibits an intense singlet due to the absorption of uncoupled hydrogen in $^{12}\text{CHCl}_3$ and two weak outer bands (satellites) for the absorption of

coupled hydrogen in $^{13}\text{CHCl}_3$ as shown in figure 18. The relative intensity of the coupled ^{13}CH peaks is directly proportional to the ratio of $^{13}\text{C}/^{12}\text{C}$. The ^{13}C - ^1H coupling constant has been used to determine the percent of s-character of a carbon-hydrogen bond (ie, hybridization of carbon atom), particularly in strained, small ring compounds.

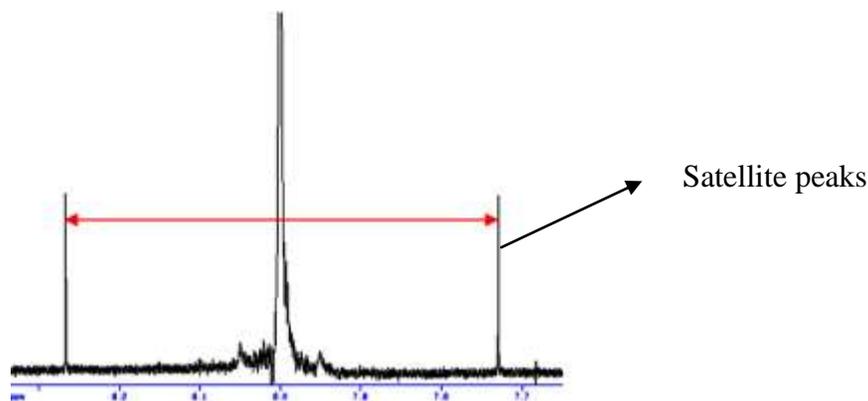


Figure 17: ^1H Signal of CHCl_3 showing ^{13}C coupling

The couplings due to ^{13}C - ^1H vary in size with hybridization as shown in the below table.

Type of hybridization	$J^{13}\text{C}-^1\text{H}$
sp^3	125
sp^2	170
sp	250

e) ^{31}P -H coupling:

Phosphorus is another heteroatom of major coupling importance. Like ^{19}F , ^{31}P has a nuclear spin $I = \frac{1}{2}$ and a 100% natural abundance. Hydrogen couples with phosphorus and consequently P-H absorptions are doublets with $J_{\text{P-H}} = 200$ to 700 Hz

^{31}P shows an interesting peculiar feature the size of the couplings normally decreases dramatically with the number of the intervening bonds.

14.13 Summary of the unit

Electrons are negatively charged particles that surround nuclei in a molecule. We know that moving charged particles will generate a magnetic field. Electrons around nuclei in a molecule generate their own magnetic field, the lines of force (magnetic moment) generated by this magnetic field will run in the opposite direction as the lines of force generated by the external magnetic field \mathbf{H}_0 . In fact, the electron's magnetic field runs *anti-parallel* to the external

magnetic field. When this happens, the electron-generated magnetic moment will run in opposition to the magnetic moment of the external magnetic field. This has the effect of reducing the net magnetic moment affecting the proton. This requires that the external magnetic field be greater or higher in order to overcome this opposition so that an NMR signal may be generated. This electronic magnetic field effect will cause protons with different chemical environments to yield resonance frequencies perturbed from the frequency defined by the applied external field H_0 . The Larmor frequency can be re-written to include the electronic effect:

$$\omega_0 = \gamma(H_0 - S)$$

where S represents the change in magnet field caused by the opposing electron magnetic moment.

All electrons making up the sigma bonding around the nuclei will generate a magnetic field that will be anti-parallel to the external magnetic field's lines of force. This causes the NMR signal generation to occur at a higher external magnetic field setting. There for the NMR signal is shifted to upfield, and the protons are said to be electronically shielded. The word shielded is used because the electronic magnetic moment actively shields the proton from the external magnetic field such that the effect of the external field is not as great as it could be if the proton was "naked".

Sigma electrons always shield spinning nuclei like protons and cause the NMR signal to be at a lower than expected resonance frequency. However if these sigma electrons can be diverted or shifted away from the proton nucleus, then the electronic shield they generate will be partially stripped away. This occurs when highly electronegative atoms like halogen, sulfur, oxygen, or nitrogen atoms are near these sigma electrons. The highly electronegative atoms attract these sigma electrons toward themselves and away from the proton nucleus. This is called an inductive effect, and it has the effect of stripping away part of the electronic shielding. As expected this phenomenon is called deshielding. If proton nuclei are deshielded then the NMR signal is generated at a higher resonance frequency. The deshielding is said to shift the signals downfield. Nearby oxygen, nitrogen, or halogen atoms attached to the same carbon or adjacent to such carbon atoms will cause an NMR signal to be generated further downfield.

π -electrons also generate magnetic fields just like the sigma-electrons, but unlike the sigma electrons which always shield spinning nuclei, π -electrons can both shield or deshield proton nuclei depending upon whether the magnetic lines of force (magnetic moments) generated by the

π -electron's are parallel (deshield) or anti-parallel (shield) to the applied magnetic field. In general, π -electrons deshield the protons that are attached to the sp^2 hybridized carbons. Thus, olefins and aromatics resonate downfield from protons sigma bonded to sp^3 hybridized carbons

The following general rules summarize important requirements and characteristics for spin 1/2 nuclei

- 1) Nuclei having the same chemical shift (called **isochronous**) do not exhibit spin-splitting. They may actually be spin-coupled, but the splitting cannot be observed directly.
- 2) Nuclei separated by three or fewer bonds (e.g. vicinal and geminal nuclei) will usually be spin-coupled and will show mutual spin-splitting of the resonance signals (same J's), provided they have different chemical shifts. Longer-range coupling may be observed in molecules having rigid configurations of atoms.
- 3) The magnitude of the observed spin-splitting depends on many factors and is given by the coupling constant J (units of Hz). J is the same for both partners in a spin-splitting interaction and is independent of the external magnetic field strength.
- 4) The splitting pattern of a given nucleus (or set of equivalent nuclei) can be predicted by the *n+1 rule*, where n is the number of neighboring spin-coupled nuclei with the same (or very similar) Js. If there are 2 neighboring, spin-coupled, nuclei the observed signal is a triplet ($2 + 1 = 3$); if there are three spin-coupled neighbors the signal is a quartet ($3 + 1 = 4$). In all cases the central line(s) of the splitting pattern are stronger than those on the periphery. The intensity ratio of these lines is given by the numbers in Pascal's triangle. Thus a doublet has 1:1 or equal intensities, a triplet has an intensity ratio of 1:2:1, a quartet 1:3:3:1 etc.

Lastly unlike PMR spectra, NMR spectra of nuclei which have large electric quadrupole moments have very broad bands rather than sharp peaks. The spread in resonance frequencies of other nuclei and the magnitude of the coupling constant are very large when compared with corresponding values for PMR spectra. Similar to PMR spectroscopy, NMR spectra of other nuclei also provide structural information about compounds.

14.14: Key words

Equivalent and Nonequivalent protons; Spin-Spin splitting; Coupling constant; First order splitting; Geminal proton-proton coupling; Vicinal proton-proton coupling; Non-first order splitting; Hetero nuclear coupling.

14.15 References for the further study

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14.16 Question for self study

- 1) Write a detailed note on spin-spin coupling
- 2) Describe what is coupling constant?
- 3) What is first order splitting?
- 4) How do you distinguish Cis and Trans isomers with the help of NMR spectroscopy?
- 5) Write a note on, a) Geminal proton-proton coupling ($^2J_{HH}$) b) Vicinal proton-proton coupling ($^3J_{HH}$)
- 6) Explain with example Equivalent and Nonequivalent protons in a molecule?
- 7) Write two differences between Equivalent and Nonequivalent protons.
- 8) Identify how Equivalent and Nonequivalent groups of protons present in the following compounds?
 - a) Trimethyl silane
 - b) 3-methoxy-4-pentyne-2one
 - c) cyclohexane
 - d) methyl tertiary butyl ether
 - e) N,N-dimethyl acetamide
 - f) diethyl succinate
 - g) dibromo ethylacetate
 - h) – phenyl ethanol.
- 9) What is second order coupling?
- 10) Write a general rules governing in spi-spin splitting
- 11) Write a note on Spin-Spin coupling of protons with other nuclei

UNIT-15**Structure**

- 15.0 Objectives of the unit
- 15.1 Introduction
- 15.2 Basic Principle
- 15.3 Mass spectrometer
 - a) *Sample inlet*
 - b) *Ion source*
 - c) *Mass analyzer*
 - d) *Detector and data system*
- 15.4 Mass spectrum
 - i) *Base peak*
 - ii) *Molecular ion*
 - iii) *Doubly charged ions*
 - iv) *Fragment ion:*
 - v) *Metastable ion*
- 15.5 Even electron rule
- 15.6 Nitrogen rule
- 15.7 Common ionization method used in mass spectrometry
- 15.8 Electron Impact Ionization
- 15.9 Chemical Ionization
- 15.10 Electrospray Ionization Method
- 15.11 FAB
- 15.12 Matrix Assisted Laser Desorption (MALDI)
- 15.13 Factors governing general fragmentation process
- 15.14 Summary of the unit
- 15. 15 Key words
- 15. 16 References for the further study
- 15.17 Question for self study

15.0 Objectives of the units

- After studying this unit you are able to
- Explain the basic principle of mass spectrometry
- Explain the differences between various ionization techniques used mass spectrometry
- Identify the base pea, molecular ion peak and metastable ion peak

15.1 Introduction

Mass spectrometry is an analytical technique used to the study the molecular weight determination, structural characterization, gas phase of ionized molecules, gas phase reactivity study and both qualitative and quantitative analysis of components in a mixture. Mass spectrometry consists of weighing ions in the gas phase. The instrument used for mass spectrometry is considered as a sophisticated balance which determines the masses of individual atoms and molecules with high precision. Depending on the chemical and physical properties of sample to be analyzed, different ionization techniques have been used. themolabile is the main factors to choose which ionization technique to be used. For relatively not volatile samples ionization such as Electron Impact and/or Chemical Ionization techniques are effectively used. For samples that are thermolabile such as peptides, proteins and other samples of biological interest, soft ionization techniques are employed. Electrospray (ESI) and Matrix Assisted Laser Desorption (MALDI) are among the mostsoft ionization techniques used in mass spectrometry. The name given to a particular mass spec technique is usually pointing to the ionization method being used.

In mass spectrometry method atomic and molecular masses are assigned relative to the mass of the carbon isotope, ^{12}C , whose atomic weight is defined as exactly 12. The actual mass of ^{12}C is 12 daltons, with one dalton is equal to 1.661×10^{-24} g. The mass of a molecule or an ion can be presented in daltons (Da) or kilodaltons (kDa).

15.2 Basic Principle

The first step in the mass spectrometric analysis of compounds is the production of gas phase ions of the compound, basically by electron ionization. This molecular ion undergoes fragmentation. Each primary product ion derived from the molecular ion, in turn, undergoes fragmentation, and so on. The ions are separated in the mass spectrometer according to their mass-to-charge ratio, and are detected in proportion to their abundance. A mass spectrum of the molecule is thus produced. It displays the result in the form of a plot of ion abundance versus

mass-to-charge ratio. Ions provide information concerning the nature and the structure of their precursor molecule. In the spectrum of a pure compound, the molecular ion, if present, appears at the highest value of m/z (followed by ions containing heavier isotopes) and gives the molecular mass of the compound.

A mass spectrometer generates multiple ions from the sample under investigation, it then separates them according to their specific mass-to-charge ratio (m/z), and then records the relative abundance of each ion type

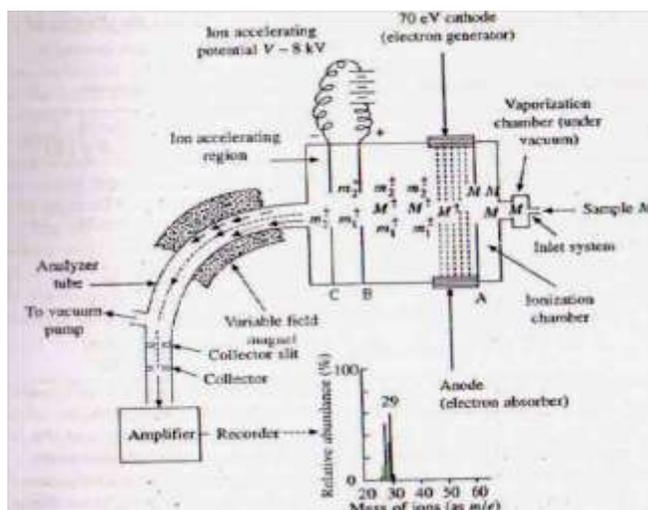
15.3 Mass spectrometer

Mass spectrometer consists of five components, namely

- 1) Sample inlet
- 2) Ion source
- 3) Mass analyzer
- 4) Detector and
- 5) Detector and data system

Sample inlet:

The sample under investigation is introduced to the spectrometer through the sample inlet. This component is partially evacuated and supplies a stream of sample molecule to the ion source component where the sample undergoes ionization. The solid and liquid samples are slightly heated using electric coil in order to produce vapors of pressure at least 10^{-2} torr, in case of gaseous sample it is directly injected. The sample inlet is connected to ionization chamber through reservoir with small pinhole called molecular leak. The ion source system is kept at very low pressure hence the samples move towards it through the molecular leak which provides a steady flow of molecule.



Schematic representation of a mass spectrometer

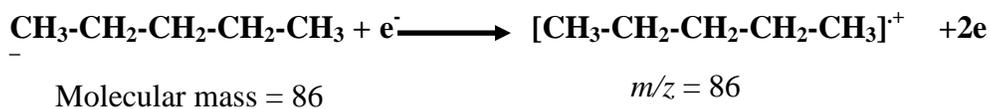
Ion source:

The sample molecules entering the ion source unit are then ionized using different ionization methods which we discuss later in this unit. The most commonly used method in most of the mass spectra is Electron ionization (EI). In this method the stream of molecules entering the unit is exposed to rapidly moving energetic electron shot out from electron gun. The electron gun consists of carbonized tungsten filament heated to several thousand degrees Celsius so that electrons are emitted from the filament. These electrons are travels towards the anode kept opposite to the filament and collision with the molecules (which are moving perpendicularly) takes place.

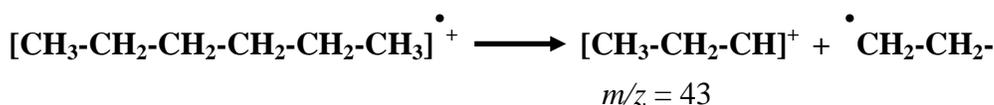
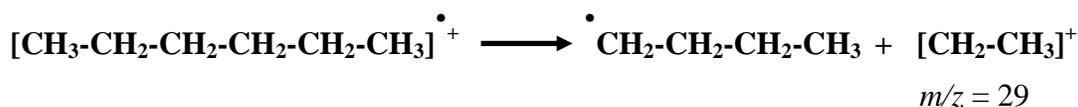
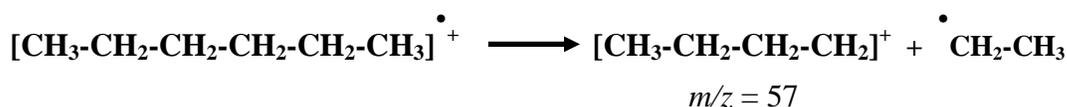
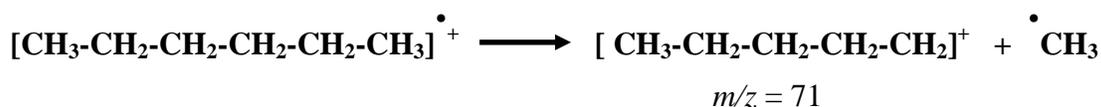
The energy needed to remove the outermost electron of most of the organic compound in gaseous state lies within the range 8 to 15 eV. The electron emitted from the electron gun has energy approximately in this range. Generally an electron beam with energy 70 eV is used. This results in fragmentation of the molecule therefore helpful in determining the structure of the compound. The collision between electron and molecule strips electron from the molecule thereby converting it in to cation which may undergo fragmentation depending on its stability and the energy of the electron.



For example, the collision between electron and hexane molecule first result in molecular radical ion with relative molecular mass 86.



This molecular ion undergoes further fragmentation forming different cation and radicals with different masses.



Here m/z corresponds to mass-to charge ratio and it has the value of m (molecular weight). Fragmentation produced in mass spectra is reproducible and the pattern of fragmentation is dependent on the structure of the compound and hence it is an indicative of the structure.

Mass analyzer:

The ions of the sample formed in ion source are then pushed to the mass analyzer by applying electric field through metal grid. There are two kinds of grid, one is positively charged and called repeller plate. It pushes the positive ions towards a series of negatively charged grid called accelerator plates. A large potential difference is applied across the accelerating plates which accelerate the positively charged ions. These ions emerge out as a beam from the accelerating plates and are allowed to move in to the mass analyzer.

Only few samples are ionized completely in ionization chamber and most of the samples molecules remains unionized. These unionized samples are removed by applying vacuum. Along with positive ions some negative ions are also produced due to electron capture by the molecules in the ion source. These are attracted by positively charged grid and discharged.

The beams of ions coming out of the ion source unit are passes through curved path under the influence of magnetic field.

Suppose an ion of mass 'm' moving with velocity 'v',

Then the kinetic energy of the ion is equal to $\frac{1}{2} mv^2$.

This energy is acquired due to the accelerating potential 'V'. We know that the ion with charge 'Z' in electrostatic field of 'V' acquires potential energy ZV which is equal to the kinetic energy of the ion.

$$\text{Hence, } ZV = \frac{1}{2} mv^2$$

$$\therefore v^2 = \frac{2ZV}{m} \text{ ----- (1)}$$

Since ion is moved in circular path under the influence of magnetic field, therefore the centrifugal force equal to centripetal force.

If the radius of the circular path is 'r' then the centrifugal force is mv^2/r . In presence of the magnetic field B, the centripetal force is ZBV. Therefore

$$\frac{mv^2}{r} = ZBV$$

$$v = \frac{ZBV}{m}$$

$$\text{or } v^2 = \left[\frac{ZBV}{m} \right]^2 \text{ ----- (2)}$$

Substitute equation (1) in equation (2) we get

$$\frac{2ZV}{m} = \left[\frac{ZBV}{m} \right]^2$$

$$\frac{m}{z} = \frac{B^2 r^2}{2V} \text{ -----(3)}$$

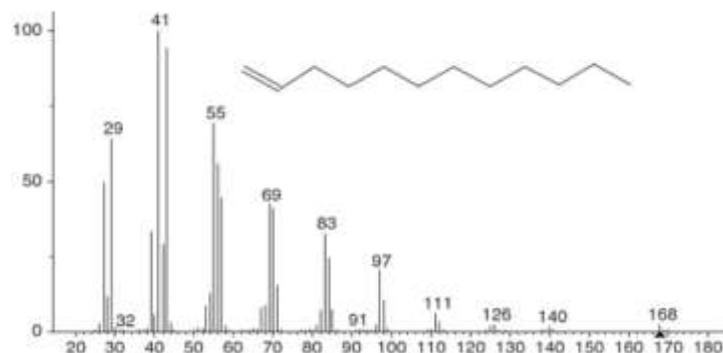
Equation 3 tell us that the mass to charge ratio (m/z) of the ion that follows circular path of definite radius r depends on the square of the magnetic field strengths (B) and inversely proportional to the accelerating potential V . In a mass spectrometer the radius of the circular path is constant therefore for a particular magnetic deflection, ion which follows this circular path can only enter to the detector unit. By varying the magnetic field strength or accelerating potential, ions with different m/z value can be detected.

Detector and data system:

The analyzer successively leads the positive ions to the detector unit. Each of these ions with particular m/z value produces the electric current by striking the counter. The amount of current produced is proportional to the number of ions striking the counter, therefore amount of current produced by each type of ion is equal to the relative abundance of that ion with particular m/z value. The current produced when positive ion strike the counter is amplified using electric amplifier. The amplified current corresponding to each type of ions is then reaches detector which is made up of lead-doped galss coated with lead oxide. The data system store and display the output of the detector both in tabular and graph form with the aid of computer.

15.4 Mass spectrum

Mass spectrum of a compound is the plot of mass- to- charge (m/z) values along x-axis and the corresponding ion abundance (intensity) along the y-axis as shown in figure below.



vi) *Base peak*

The most intense peak (tallest peak) in the mass spectra which representing the most abundant ion is called base peak. Generally base peak is assigned as relative intensity of 100% and the intensities of other peaks are expressed as relative percentage of base peak.

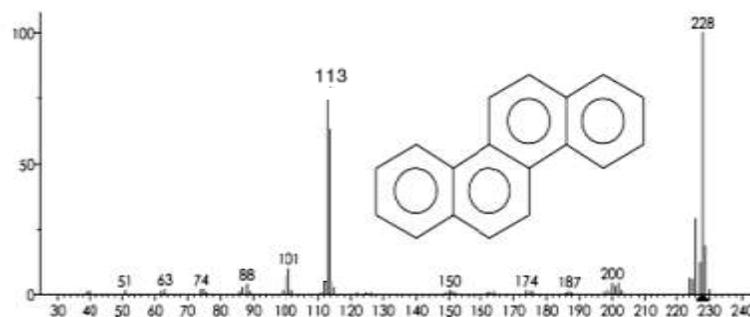
vii) *Molecular ion*

The ion formed from a molecule by the removal of one electron of lowest ionization potential is called as molecular ion. The energy required to remove an electron varies in the order: lone pair $<$ conjugated $\pi <$ non-conjugated $\pi <$ σ .

viii) *Doubly charged ions*

The molecular ions that become doubly charged during the ionization process, will generate a peak in the mass spectrum at an m/z value equal to one-half the molecular weight of the compound and are called doubly charged ions. These ions are insignificant in the mass spectra of compounds. However doubly charged ions are sometimes useful in data interpretation.

Ex: The mass spectrum of chrysene (mol.wt 226) exhibits a relatively intense peak at m/z 113 for the doubly charged molecular ion as shown below.



ix) *Fragment ion*

The ions produced from the molecular ion by cleavage of bonds are called fragment ions. They have lower masses and used as a building blocks to reconstruct the molecular structure. Fragmentation of molecular ions may occur by cleavage of bonds in two ways, heterolytic or hemolytic.

x) *Metastable ion*

Some fragment ions, undergo secondary fragmentations in the analyzer tube of the mass spectrometer. The resulting signals or peaks represent neither the m/z of the first ion nor that of the second ion, are called metastable ion. The peaks corresponding to metastable ion are called “metastable ion” peaks. The metastable ions give valuable information about fragmentation patterns of molecular ions.

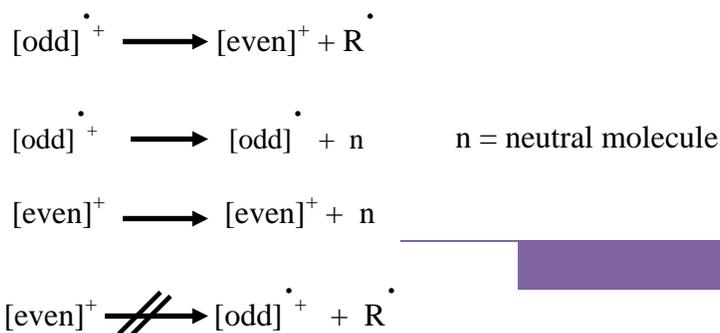
Origen of metastable ions

The term ‘metastable’ has been applied to those ions in a mass spectrometer that have just sufficient energy to fragment some time after leaving the ion source but before arriving at the detector. The excess of internal energy imparted to these ions during ionization is sufficient to give them decomposition occurs during the ion flight-time. The product ions from such ‘in-flight’ fragmentation have kinetic energy less than the originally imparted to the precursor metastable ion when it left the ion source. This is because the initially imparted momentum is shared between the products of decomposition. This reduced momentum leads to the products of metastable ions having an apparent mass different from the corresponding ‘normal’ product ions formed in the ion source.

15.5 Even electron rule

Odd-electron ions such as molecular ions and fragment ions formed by rearrangement may eliminate either a radical or an even-electron neutral species, but even-electron ions such as protonated molecules or fragments formed by single bond cleavage will not usually lose a radical to form an odd-electron cation. In other words the successive loss of radical is forbidden.

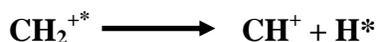
The even-electron rule serves as reliable guideline rather than a strict rule for the fragmentation of ions for the interpretation of mass spectra. The even-electron-rule can be summarized in the following scheme.



Ex: According to the even-electron rule the molecular ion of methane should undergo the following dissociations.



The CH_2^{+*} fragment ion decomposes further in a way identical to the molecular ion of carbene.



Loss of a radical from a radical ion creates an even-electron fragment ion CH_3^+ which preferably undergoes subsequent loss of molecule. But loss of H^* from CH_3^+ should not occur.



15.6 Nitrogen rule

Nitrogen rules state that, if the molecular mass of an unknown compound is an odd number, then the compound contains an odd number of nitrogens in its molecular formula. Or if the molecular mass is an even number, then the compound contains zero or an even number of nitrogens in its molecular formula.

Nitrogen rule holds for all compounds containing C, H, N, O, S, P, B, Si, As, Alkaline earths, Halogens. The nitrogen rule is based on the fact that, most of the elements present in organic compounds, there is a correspondence between the mass number and their valency. i.e., both are even numbered or both are odd numbered. But nitrogen is an exception having mass number 14 (even number) and its valency is 3 (odd number) this is the basis for nitrogen rule.

Ex: The molecular ion for aminoethane (ethylamine), $[\text{CH}_3\text{CH}_2\text{NH}_2]^+$, is $m/z = 45$ amu, an odd number and contains one nitrogen atom.

The molecular ion for 1,2-diaminoethane, $[\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2]^+$, is $m/z = 60$ amu, an even number and contains two nitrogen atoms.

15.7 Common ionization method used in mass spectrometry

The following methods are generally used for the production of ions from organic molecules.

- i) EI = Electron Impact.
- ii) CI = Chemical Ionization.
- iii) FAB = Fast Atom Bombardment.
- iv) LDMS = Laser Desorption Mass Spec.
- v) PDMS = Plasma Desorption Mass Spec.
- vi) ESMS = Electrospray Mass Spec.

15.8 Electron Impact Ionization

Electron ionization (EI) is widely used in mass spectrometry for relatively volatile samples that are insensitive to heat and have relatively low molecular weight. The spectra, usually containing many fragment-ion peaks, are useful for structural characterization and identification. Small impurities in the sample are easy to detect. The molecular weight range is 50 to 800 Da. In rare cases it is possible to analyze samples of higher molecular weight. Accuracy of the mass measurement at low resolving power is ± 0.1 Dalton and in the high resolution mode, ± 5 ppm.



EI mass spectra, in most of cases, contain intense fragment ion peaks and much less intense molecular ion peak. When the molecular ion peak is not observed in the mass spectrum, chemical ionization can be used in order to get molecular ion information.

15.9 Chemical Ionization

Chemical Ionization (CI) is especially useful technique when no molecular ion is observed in EI mass spectrum, and also in the case of confirming the mass to charge ratio of the molecular ion. Chemical ionization technique uses virtually the same ion source device as in electron impact, except, CI uses tight ion source, and reagent gas. Reagent gas (e.g. ammonia) is first subjected to electron impact. Sample ions are formed by the interaction of reagent gas ions and sample molecules. This phenomenon is called ion-molecule reactions. Reagent gas molecules are present in the ratio of about 100:1 with respect to sample molecules. Positive ions and negative ions are formed in the CI process. Depending on the setup of the instrument (source voltages, detector, etc...) only positive ions or only negative ions are recorded.

In CI, ion molecule reactions occur between ionized reagent gas molecules (G) and volatile analyte neutral molecules (M) to produce analyte ions. Pseudo-molecular ion MH^{+} (positive ion mode) or $[M-H]^{-}$ (negative ion mode) are often observed. Unlike molecular ions obtained in EI method, MH^{+} and $[M-H]^{-}$ detection occurs in high yield and less fragment ions are observed.

Positive ion mode:

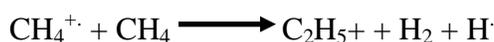
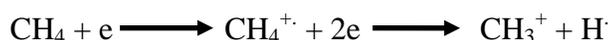


Negative ion mode:

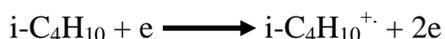


The main reagent gases used in CI are: Ammonia, Methane, and Isobutane. The predominant reactant ions formed are given in the mechanisms shown below. Choice of reagent gas affects the extent of fragmentation of the quasi-molecular ion.

Methane (positive ion chemical ionization):



Isobutane (positive ion chemical ionization):



Ammonia (positive ion chemical ionization):



Two factors determine the choice of the reagent gas to be used:

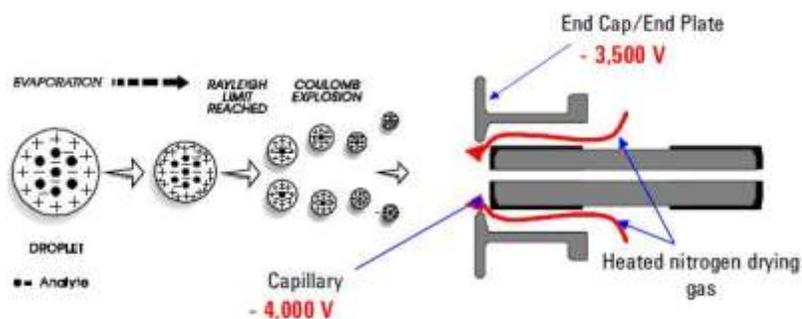
1. Proton affinity PA
2. Energy transfer

NH₃ (ammonia) is the most used reagent gas in CI because of the low energy transfer of NH₄⁺ compare to CH₅⁺ for example. With NH₃ as reagent gas, usually MH⁺ and MNH₄⁺ (17 mass units difference) are observed.

15.10 Electrospray Ionization Method

It uses an electrical stress between the ESI probe exit (e.g. capillary) and the counter electrode, which is located few millimeters from the probe. The process results in the generation of highly charged droplets directly from the infused solution. Multiply and/or singly charged analyte

molecules desorb from the sprayed droplets and sampled through the rest of the mass spectrometer.



Electrospray ionization (ESI) allows production of molecular ions directly from samples in solution. It can be used for small and large molecular-weight biopolymers (peptides, proteins, carbohydrates, and DNA fragments), and lipids. It is a continuous ionization method that is suitable for using as an interface with HPLC or capillary electrophoresis. Multiply charged ions are usually produced. ESI should be considered a complement to MALDI. The sample must be soluble, stable in solution, polar, and relatively clean (free of nonvolatile buffers, detergents, salts, etc.).

Advantages of ESI:

- Soft ionization process so intact molecular ions are observed
- ESI allows production of multiply charged ions. This results in the ability of analyzing very high molecular weight species using the most available mass analyzers (e.g. quadrupoles).
- ESI is an atmospheric pressure process. This makes it easy to use and easy to interface with HPLC and CE separation techniques.

15.11 FAB

Fast atom bombardment ionization (FAB or sometimes called liquid secondary ionization MS, LSIMS) is a softer ionization method than EI. It has been recently come into common use in organic spectroscopy.

The analyte is dissolved in a viscous liquid, typically glycerol (matrix material) and ionization is achieved by bombardment of the sample matrix (a metal plate coated with viscous solution of the sample) by a beam of fast moving neutral atoms. The bombarding atoms are usually rare gases,

either Xenon or Argon. In order to achieve a very high kinetic energy, the atoms of the gas are first ionized and these ions are then passed through electric field.

The spectrum often contains peaks from the matrix, which is necessary for ionization, a few fragments and a peak for a protonated or deprotonated sample molecule. FAB is used to obtain the molecular weight of sensitive, nonvolatile compounds. The method is prone to suppression effects by small impurities. The molecular weight range is 100 to 4000 Da. Exact mass measurement is usually done by peak matching. The accuracy of the mass is the same as obtained in EI, CI.

15.12 Matrix Assisted Laser Desorption (MALDI)

Matrix Assisted Laser Desorption (MALDI) mass spectrometry technique was for the study of peptides and proteins. This technique was also used to analyze other type of biomolecules, such as oligosaccharides, glycolipids, nucleotides, and synthetic polymers.

In this technique, samples are cocrystallized with a UV-absorbing substance called matrix. For example for proteins, the matrix of choice is often sinapinic acid. A 337 nm radiation from nitrogen laser is most commonly used to ionize the sample. The laser helps introducing energy into the molecular system in such a way that it preventing the thermal decomposition.

Molecular weights up to few hundreds of daltons could be measured in this technique. Comparison of MALDI and ESI ionization techniques was attempted in the last few years. These two techniques are not competitive but complementary, for high molecular weight species, MALDI leads to the formation of singly charged molecular ions while ESI allows the formation of multiply charged molecular ions.

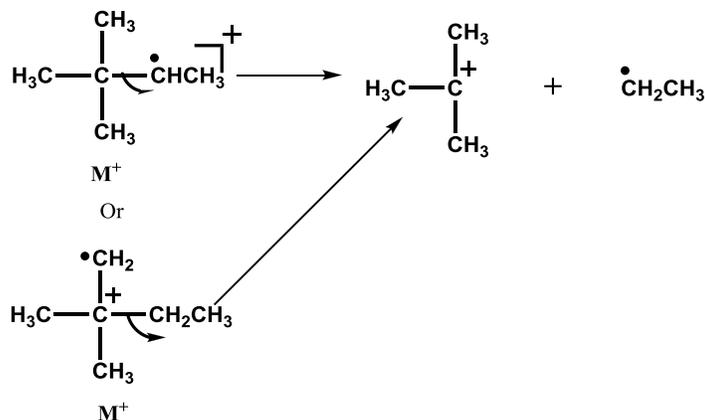
15.13 Factors governing general fragmentation process

The following factors dominate the general modes of fragmentation

- 1) Weak bonds tends to broken
- 2) Stable fragments (ions, radicals and molecules) tends to formed
- 3) Ability of ions to assume cyclic transition states- rearrangements process

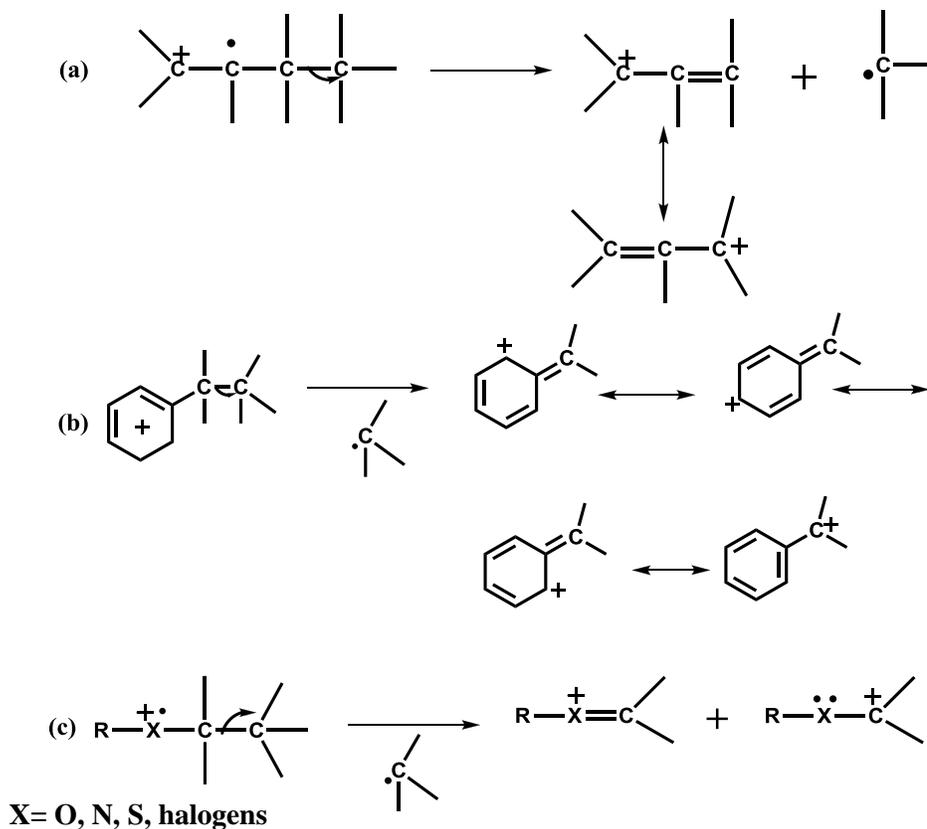
Favorable fragmentation process naturally occurs more frequently and ions thus formed appear as strong peaks in the mass spectrum. General concepts of mechanistic organic chemistry are very useful in predicting and understanding favourable mass spectrometric fragmentation processes.

- i) Fragmentation at branch point is favored in aliphatic carbon skeleton because it gives more stable carbocations. [the relative stabilities of carbocations are tertiary > secondary > primary] For example,

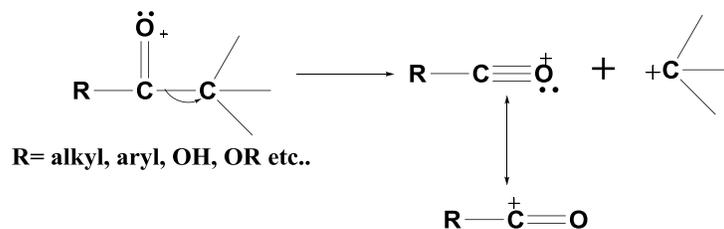


Generally the largest substituent at branch point is eliminated most readily as a radical because a long-chain radical achieves some stability by delocalization of the lone electron.

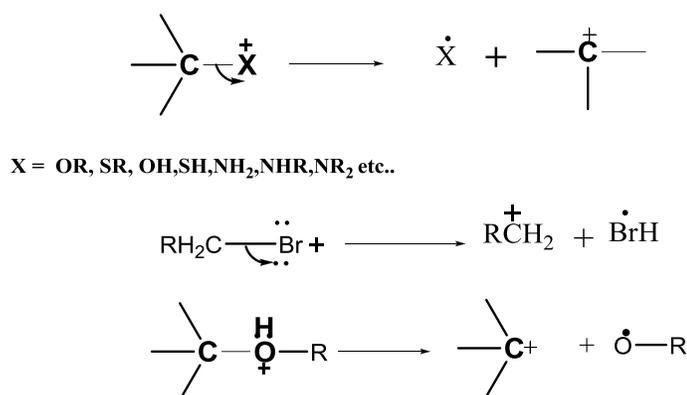
- ii) The cleavage tends to occur β to a) double bonds (allylic cleavage) b) aromatic rings (benzylic cleavage) and c) hetero atoms singly bonded to a carbon atom because it gives resonance-stabilized carbocations.



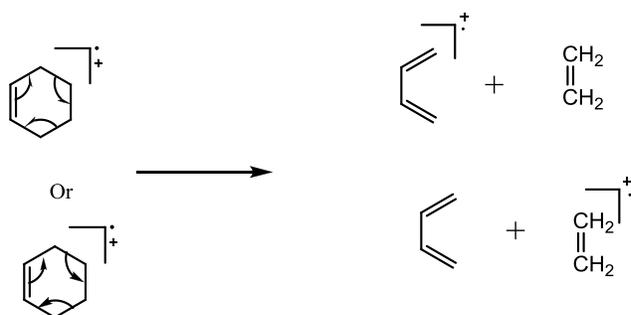
iii) Cleavage bond occurs α to a carbonyl group to give resonance-stabilized acylium cations.



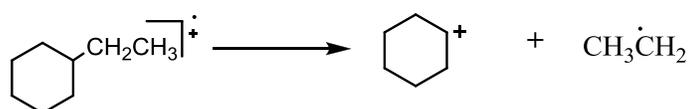
iv) Cleavage also occurs α to heteroatoms singly bonded to a carbon atom. Example in case of ethers, sulphides, thiols, amines and halogen compounds.



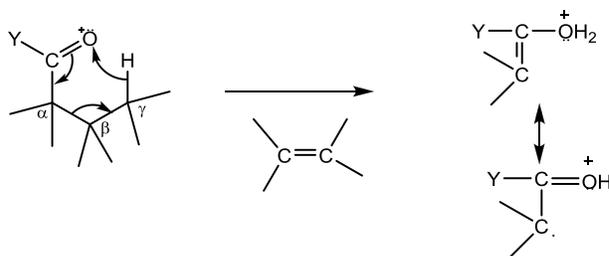
v) Cyclohexene and its derivatives undergo characteristic fragmentation through retro-Diels-Alder reaction in which the charge may be with the diene portion or the ethylenic portion.



In saturated rings, cleavage tends to occur at α bond to lose the side chain. This is just a special case of fragmentation at branch point.



vi) Ions which have ability to assume cyclic transition states, especially six membered tend to undergo fragmentations accompanied by rearrangements. The most important one is the *McLafferty rearrangement*. This involves the migration of a γ -hydrogen accompanied by cleavage of β -bond through a six-membered cyclic transition state to form a radical cation and a neutral molecule. This rearrangement is characteristic of compound containing γ -hydrogen with respect to a multiple bond.



Several other rearrangements occurring during fragmentation process are hydrogen transfer rearrangement, the transfer of an aryl, alkyl or alkoxy groups occurs in very few cases.

15.14 Summary of the unit

Mass spectrometry is an analytical tool used for measuring the molecular mass of a sample. Structural information can be generated using certain types of mass spectrometers, usually those with multiple analysers which are known as tandem mass spectrometers. This is achieved by fragmenting the sample inside the instrument and analysing the products generated. This procedure is useful for the structural elucidation of organic compounds and for peptide or oligonucleotide sequencing. The ionization methods can be split into two groups: 'hard' and 'soft' ionization. Namely, hard ionization – results in the breaking of chemical bonds and the formation of fragment ions. Soft ionization – results in the formation of ions without breaking any chemical bonds. In other words, all covalent interactions are kept intact. Sometimes non-covalent interactions can also be kept intact. Usually the ions formed in MS are positively charged (cations), although negative ions (anions) can also be generated. MS experiment in positive or negative ion mode is dependent on the sample to be analyzed. For example, DNA is negatively charged, so it probably good to run the experiment in negative ion mode. As a general rule if the sample is basic (e.g. a protein), analyze it in positive ion mode, and if it is acidic (e.g. DNA), analyze it in negative ion mode. Hence the choice of ionization method depends on the nature of the sample and the type of information required from the analysis. So-called 'soft

ionization' methods such as matrix-assisted laser desorption ionization (MALDI) and electrospray ionization (ESI) tend to produce mass spectra with little or no fragment-ion content.

15.15 Key words

Ion source; Mass analyzer; Base peak; Molecular ion; Doubly charged ions; Fragment ion; Metastable ion; Even electron rule; Nitrogen rule; FAB; MALDI.

15.16 References for the further study

- 1) Mass Spectrometry: Principles and Applications by Edmond de Hoffmann, Vincent Stroobant; *John Wiley & Sons* **2007**.
- 2) Mass Spectrometry - A Textbook by Jürgen Gross, *Springer-Verlag Berlin Heidelberg* **2002**.
- 3) Tandem Mass Spectrometry by F. W. McLafferty, *John Wiley & Sons Inc* **1983**.
- 4) Introduction to Mass Spectrometry: Instrumentation, Applications, and Strategies for Data Interpretation by J. Throck Watson, O. David Sparkman, *John Wiley & Sons* **2008**.

15.17 Question for self study

- 1) Describe basic principles of mass spectroscopy.
- 2) Describe briefly various parts of mass spectrometry and their functions.
- 3) Write a note on the molecular ion or the parent ion
- 4) Write a note on McLafferty rearrangement.
- 5) Define base peak in mass spectrum. Is it true that molecular ion peak should always be the base peak?
- 7) What are the metastable ions? Explain their utility in confirming a fragmentation of molecule.
- 8) How chemical ionization differ from electron impact phenomenon? How it helps in determining the accurate molecular ion peak.

Structure**Unit- 16.0**

- 16.0 Objectives of the unit
- 16.1 Introduction
- 16.2 Non spherical nucleus
- 16.3 Quadrupolar Nucleus and Quadrupole interaction
- 16.4 Origin of nuclear quadrupole interaction
- 16.5 Conditions for NQR spectroscopy
- 16.6 Similarity and difference between NMR and NQR
- 16.7 Frequencies of transition for axial symmetric systems
 - Nucleus having half integral spins*
 - Nucleus having half integral spins*
- 16.8 Frequencies of transition for non-axial symmetric systems
 - Nucleus having half integral spins*
 - Nucleus having half integral spins*
- 16.9 Intensity of NQR signals
- 16.10 Instrumentation in NQR spectroscopy
- 16.11 Application of NQR spectroscopy
- 16.12 Charge transfer compounds
- 16.13 Halogen quadrupole resonance
- 16.14 Nitrogen quadrupole resonance
- 16.15 Group-III trihalides
- 16.16 Groups-IV halides
- 16.17 Other halides
- 16.18 Quadrupole resonance of Minerals
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- 16.20 Hydrogen bonding
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16.0 Objectives of the unit

After studying this unit you are able to learn

- Identify the shape of prolate and oblatenuclei
- Explain quadrupole interaction and Electric-field gradient
- Explain the necessary conditions for NQR spectroscopy
- Identify the differences and similarity between NMR and NQR
- Calculate the frequencies of transition for axial and non-axial symmetry system.
- Explain the applications of NQR spectroscopy in solving structure of solids.

16.1 Introduction

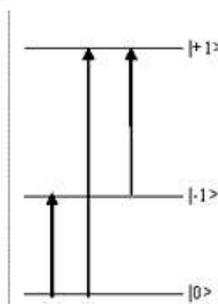
Quadrupole Resonance (QR) is a branch of Magnetic Resonance (MR) spectroscopy involving the investigation of the properties of solid chemical compounds of nucleus having a non spherical charge distribution (quadrupolar elements). Contrary to MR that requires a strong and highly uniform static magnetic field to produce the energy level splitting, the energy levels in QR are induced by the interaction between the nuclear electric quadrupole moment and the gradient of the electrostatic field surrounding the nucleus. The nuclear quadrupole moment is an intrinsic property of the element, the electrostatic distribution is governed by the nature of the chemical bonds of the quadrupolar nucleus within the molecule's structure. As a consequence, the QR spectrum is specific to each molecule and thus provides unique spectra.

Many elements and isotopes exhibit a nuclear quadrupolar moment (ex: ^2H , ^{14}N , ^{17}O , ^{35}Cl , ^{37}Cl , ^{39}K , ...etc). Consider nitrogen ^{14}N , which has spin quantum number $I = 1$, the ^{14}N quadrupole interaction gives rise to three energy levels and hence three QR line frequencies:

$$\nu_{+1} = \frac{3 e^2 Q q}{4 h} \left(1 + \frac{\eta}{3} \right)$$

$$\nu_{-1} = \frac{3 e^2 Q q}{4 h} \left(1 - \frac{\eta}{3} \right)$$

$$\nu_0 = \frac{1 e^2 Q q}{2 h} \eta$$



ν_Q = Quadrupole resonance freq (Hz)
 e = elementary charge (C)
 q = electric field gradient (V/m^2)
 Q = electric quadrupole moment (C/m^2)
 h = Planck's const. ($\text{J}\cdot\text{s}$)
 η = asymmetry parameter

in which Q is the nuclear electric quadrupole moment and η the asymmetry parameter corresponds to the deviation of the electric field gradient tensor from axial symmetry and is specific to the chemical bonding to the nitrogen atom. ^{14}N frequencies range from a few 100 kHz up to 6 MHz. The quantity e^2Qq/h is called the quadrupole coupling constant, and varies from one compound to another. The transitions are induced by one or more pulses at an appropriate radio frequency. Following the first pulse, a decaying signal is observed known as free induction decay (FID); two or more pulses generate echo signals lying midway between each pulse pair.

16.2 Non spherical nucleus

The nucleus has charge, but not dipole moment since it is all positive. But if the nucleus is not spherically symmetric, it will have a quadrupole moment. The nuclear electric quadrupole moment is a parameter which describes the effective shape of the ellipsoid of nuclear charge distribution.

A non-zero quadrupole moment Q indicates that the charge distribution is not spherically symmetric. By convention, the value of Q is taken to be positive if the ellipsoid is *prolate* (like symmetrical egg shape) and negative if it is *oblate*

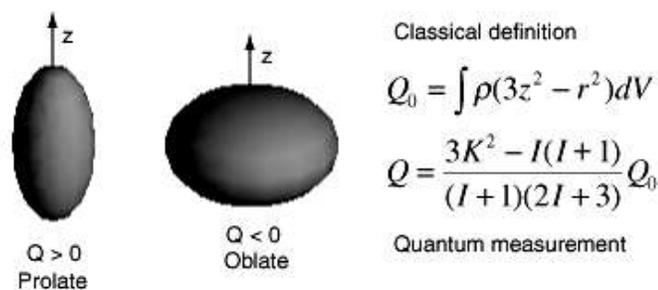


Figure 1: prolate and oblate nuclei

16.3 Quadrupolar Nucleus and Quadrupole interaction

A quadrupolar nucleus is one that has a quantum spin number greater than $1/2$. Such nuclei have a lower symmetry than spin $1/2$ nuclei. The quadrupole moment that varies between nuclei is a measure of this asymmetry. Two atoms bonded together possess an inhomogeneous electric field produced from asymmetry in the electron distribution in the molecule which is declined by the electric-field gradient (EFG) Q at the molecule. Quadrupole nuclei with a half-integer spin

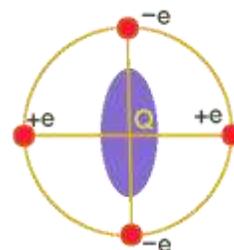


Figure 2: interaction of quadrupole moment with surrounding electric field

larger than $1/2$ possess a quadrupole moment Q , which interacts with the **electric-field gradient (EFG)** generated by their surroundings as shown in figure 2. The coupling of Q (a property of the nucleus) with an EFG (a property of a sample) is called the *quadrupole interaction*. Their energies split upon the application of a magnetic field into multiple levels. By comparison, spin $-1/2$ nuclei split into only two levels. The number of levels is given by $2n + 1$ where n is the spin number. The different splitting patterns can be seen in their coupling with other nuclei.

Even though the charge density inside a nucleus is uniform, the distorted shape gives rise to a charge distribution which is non spherical. Therefore the electric quadrupole moment eQ for distorted nucleus is defined by

$$eQ = \int \rho(x, y, z) r^2 (3 \cos^2 \theta - 1) d\tau \text{ ----- (1)}$$

where e is the charge on the proton, $\rho(x, y, z)$ is the charge density at (x, y, z) , ' r ' is the distance of volume element $d\tau$ from the nucleus and θ is the angle which the radius vector ' r ' makes with the nuclear spin axis. The nuclear quadrupole moment eQ is a measure of the departure from spherical symmetry of the nuclear charge. It is greater than zero for prolate molecules and less than zero for oblate molecule as shown in figure 3.

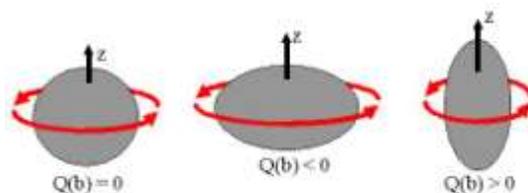


Figure 3: The nuclear quadrupole moment (eQ) of different nuclei

The charges near the nucleus produce an electrostatic potential V at the nucleus. The electric field gradient eQ is defined as the second derivative of V and in general it is a tensor with nine

components. Those components are given by $eQ_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}$, $x_i, x_j = x, y, z$ ----- (2)

If the tensor eq is diagonal to the selected coordinate axes, then terms such as $\frac{\partial^2 V}{\partial x^2 \partial y}$, $\frac{\partial^2 V}{\partial x \partial z}$ etc..... vanish. In such a principal axes system, the eq tensor is traceless,

$$q_{xx} + q_{yy} + q_{zz} = 0 \text{ ----- (3)}$$

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0 \text{ ----- (4)}$$

Hence, out of q_{xx} , q_{yy} and q_{zz} only two are independent. The convention generally followed is that

$$|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$$

The interaction of quadrupole moment with electronic charge vanishes and the field gradient is spherical if $q_{zz} = q_{yy} = q_{xx}$. This leads to generate quadrupole levels. If the field has an axial symmetry then q_{zz} lies along the symmetry axis z , $q_{zz} \neq q_{yy} = q_{xx}$. When $q_{zz} \neq q_{yy} \neq q_{xx}$, to measure the departure of the field gradient from axial symmetry, an asymmetry parameter η is introduced this is defined by

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}} \text{ ----- (5)}$$

In general η varies from 0 to 1, therefore $\eta = 0$ corresponds to axial symmetry where as $\eta = 1$ to

the condition $\frac{\partial^2 V}{\partial x^2} = 0, \frac{\partial^2 V}{\partial y^2} = -\frac{\partial^2 V}{\partial z^2}$.

16.4 Origin of nuclear quadrupole interaction

The nucleus has an electric charge but it interact with electric field. The electric energy of non-spherical nuclei depends on nuclear orientation and this electric interaction has an effect on nuclear orientation.

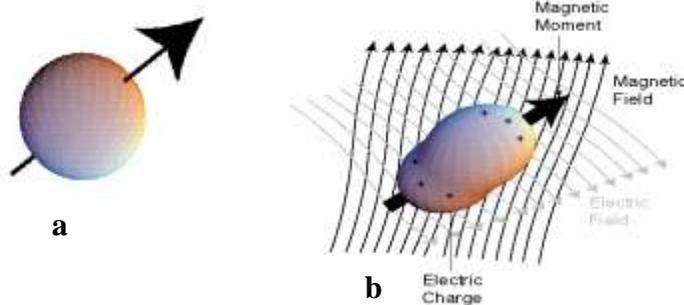


Figure 4: a) Nucleus with spin-1/2 nuclei has no electric interaction relevant for NMR
b) Quadrupolar nuclei with spin $I > \frac{1}{2}$ has Dominant electric interaction

Therefore a quadrupolar nucleus has different nuclear orientations caused by the interaction between the nuclear quadrupole moment of a nucleus and the electric field gradient. These interactions give rise to a set of quantized energy levels.

The nuclear quadrupole resonance (NQR) spectroscopy deals with transition between these quantized energy levels when electromagnetic radiation of proper frequency is allowed to interact with the system. The origin of the energy levels is purely electrical in nature but the transitions are magnetic type since transitions are induced by the interaction between the magnetic component of the radio frequency (RF) field and the magnetic moment of the nucleus.

16.5 Conditions for NQR spectroscopy

1. It is observed only for nuclei with $I > 1/2$. In case of nuclei with $I < 1/2$, the nuclei do not possess eQ so that there is no nuclear quadrupole interaction with eq.
2. NQR is observed in the solid state. In the liquid and gaseous states, because of very fast molecular collision resulting in a fast tumbling motion, the axis of rotation changes continuously so that EFG, q averages to zero. Thus there is no NQR.
3. The quantities e^2Qq , q and η are three most important quantities in NQR spectroscopy. η is a measure of nonsymmetry of EFG.
4. For a better result the nucleus under study must have reasonably large value for the nuclear quadrupole moment and natural abundance. ^{14}N nucleus has special interest because of its different types of bonding in different molecules.
5. The chemical bond associated with the nucleus under study must have an appreciable p character to give a sufficiently large field gradient.

16.6 Similarity and difference between NMR and NQR

Though both NQR and NMR involve the coupling of radio-frequency with a set of nuclear energy levels, differences exist between them. In NMR, the set of nuclear levels are magnetic in origin whereas it is of electrical origin in NQR. In NMR, the splitting between energy levels is proportional to the applied magnetic field and transitions are usually studied by using a fixed frequency oscillator while varying the magnetic field. In NQR as the electric field gradient is a fixed property of the solid, a variable frequency detection system must be used.

16.7 Frequencies of transition for axial symmetric systems

For a system having axial symmetry, the Hamiltonian representation of the interaction between the nuclear quadrupole moment of the nucleus and the electric field gradient leads to the energy eigenvalues given by

$$E_m = \frac{e^2qQ[3m_l^2 - I(I+1)]}{4I(2I-1)} \text{----- (6)}$$

where I is the nuclear spin quantum number $eq = \frac{\partial^2 V}{\partial z^2}$ is the magnitude of the electric field gradient in the direction of the axis of symmetry, eQ is the nuclear quadrupole moment and m_I is the magnetic quantum number which takes the values $(2I + 1)$

$m_I = I, I-1, I-2, \dots, -I$, the states $+m_I$ and $-m_I$ are degenerate as m_I appears as m_I^2 in the expression. The selection rule for magnetic dipole transition is $\Delta m_I = \pm 1$.

Then the frequency of the $(m_I-1) \rightarrow m_I$ transition is given by

$$\gamma = \frac{3e^2qQ}{4I(2I-1)h} (2|m_I| - 1) \text{----- (7)}$$

The expression $\frac{e^2qQ}{h}$ in the equation is called the nuclear quadrupole coupling constant and has unit of frequency. The NQR frequencies of nuclei usually lie in the range of 100 kHz to 1000MHz.

Nucleus having half integral spins:

For nuclei having spin $I = 3/2$ (^{35}Cl , ^{79}Br) equation 7 allows only a single transition of frequency

$$\gamma = \frac{e^2qQ}{2h} \text{----- (8)}$$

For nuclei with spin $I = 5/2$ (^{126}I , ^{121}Sb), there will be three levels and two transitions.

They are $\gamma_1 = \frac{3e^2qQ}{20h}$ and $\gamma_2 = \frac{6e^2qQ}{20h}$ ----- (9)

The energy levels and transitions for these nuclei are illustrated in figure 5. The order of the levels may change depending on the sign of q or Eq .

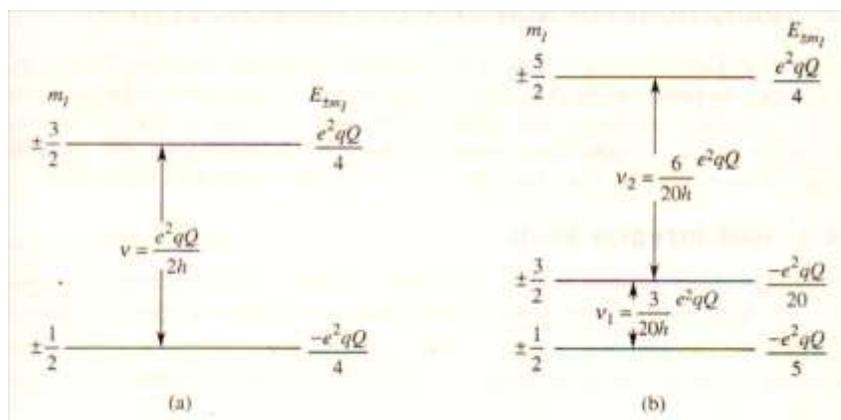


Figure 5: Energy levels and transitions for a) $I = 3/2$ b) $I = 5/2$.

Nucleus having half integral spins:

For integral spins, the energy expression in equation 7 leads to $(I + 1)$ doubly degenerate and one non-degenerate levels. A single resonance line results for nuclei having $I = 1$, (^{14}N , ^6Li) the

frequency of which is given by $\gamma = \frac{3e^2qQ}{4h}$

The energy levels and transition for $I = 1$ case is illustrated in figure 6.

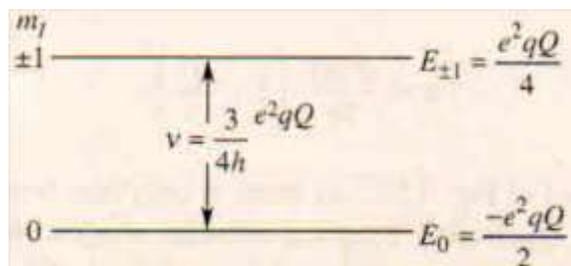


Figure 6: Energy levels and transition for $I = 1$

16.8 Frequencies of transition for non-axial symmetric systems

When the field gradient is not axial (ie, $\eta \neq 0$), the energy levels and transition frequencies are more complex. In large number of system, the nucleus under investigation is situated in axially symmetric position in free molecule, the axial symmetry is destroyed within the crystal lattice due to intermolecular interaction. Even in simple systems, the double bond character of bonds often leads to departure from axial symmetry in the field gradient.

Nucleus having half integral spins:

Formulation of exact solutions beyond $I = 3/2$ will be difficult and will involve complicated expressions. Such systems are handled by using series approximation when η is small or by using numerical methods. For $I = 3/2$ some of the off diagonal matrix elements of the Hamiltonian are not zero and evaluation of the energy eigenvalues gives the secular equation

$$E^2 - 3\left(\frac{e^2qQ}{12}\right)^2 \eta^2 - 9\left(\frac{e^2qQ}{12}\right)^2 = 0 \text{----- (10)}$$

The two roots of this equation are $E_{\pm\frac{3}{2}} = \frac{3e^2qQ}{12} \left(1 + \frac{\eta}{3}\right)^{\frac{1}{2}}$ and

$$E_{\pm\frac{3}{2}} = \frac{-3e^2qQ}{12} \left(1 + \frac{\eta}{3}\right)^{\frac{1}{2}}$$

The selection rule $\Delta m_I = \pm 1$ leads to a single transition having frequency γ given by

$$\gamma = \frac{e^2 q Q}{2h} \left(1 + \frac{\eta}{3}\right)^{\frac{1}{2}} \text{----- (11)}$$

The transition is represented in figure 7. As there is only one frequency, it is not possible to determine both the nuclear quadrupole coupling constant $\frac{e^2 q Q}{h}$ and the symmetry parameter η simultaneously. This difficulty which is unique for $I = 3/2$ systems can be solved by investing the spectrum in the presence of weak magnetic field.

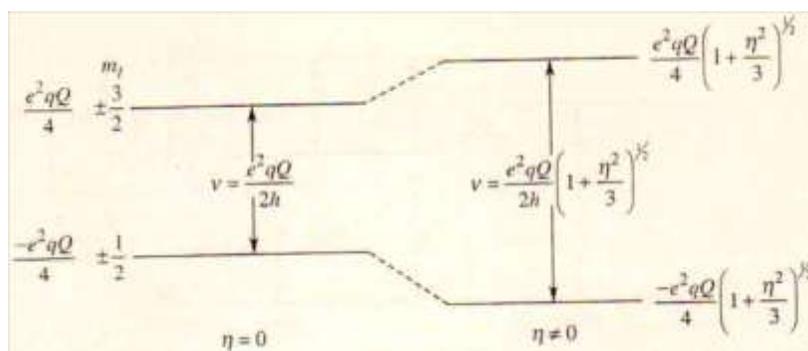


Figure 7: Energy level and transition for $I = 3/2$, $\eta \neq 0$. The one for $\eta = 0$ is given for comparison

Nucleus having half integral spins:

The introduction of symmetry removes the degeneracy in m_I for integer spin system. For nuclei of spin $I = 1$, the energy levels are given by the equation

$$E_0 = -2A_1 \quad \text{where } A_1 = \frac{e^2 q Q}{4}$$

$$E_{\pm 1} = A_1(1 \pm \eta)$$

The energy levels and allowed transition are shown in figure 8. For comparison $I = 1$, $\eta = 0$ case is also included. The frequencies of the three transitions are given by

$$\gamma_0 = \frac{1}{2} \frac{e^2 q Q}{h} \eta$$

$$\gamma_{\pm} = \frac{3}{4} \frac{e^2 q Q}{h} \left(1 \pm \frac{\eta}{3}\right) \text{----- (12)}$$

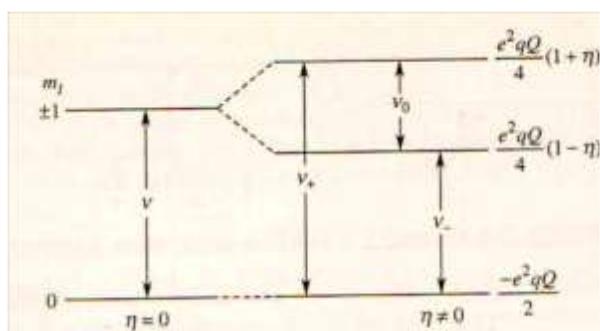


Figure 8: Energy levels and transitions for an $I = 1$

When $\eta = 0$ these frequencies reduces to a single frequency given equation 12. The familiar example for $I = 1$ system is that of ^{14}N . Since the quadrupole coupling constant for nitrogen is of the order of 4MHz, the ν_0 transition can only be observed when η is large.

Energy levels observed for nuclei with different spin in NQR is shown in figure 9.

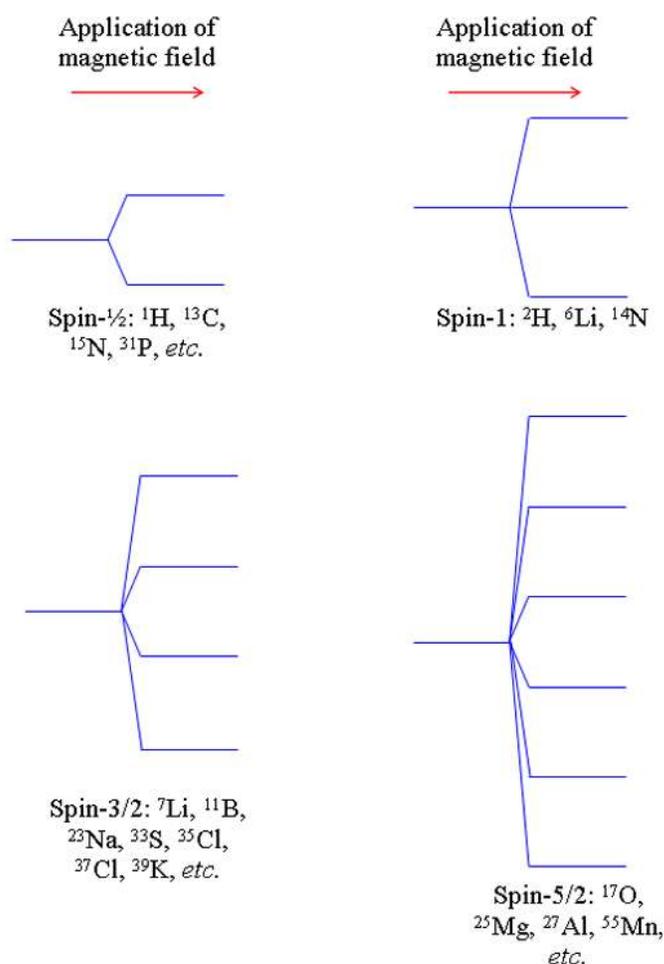


Figure 9: Energy level diagrams for nuclei of different spins

16.9 Intensity of NQR signals

Intensity of NQR line becomes a maximum when the RF field is perpendicular to the symmetry axis and vanishes when it is parallel. Therefore a study of the dependence of the intensity of the quadrupole lines on the direction of the RF field with respect to axes fixed in the crystal helps one to determine the axis of symmetry of the field gradient tensor. The experimental determination of the transition frequencies allows the calculation of quadrupole coupling constant $\frac{e^2 q Q}{h}$ and the symmetry parameter η except for $I = 3/2$.

16.10 Instrumentation in NQR spectroscopy

Nuclear quadrupole resonance (NQR) uses radio-frequency (RF) magnetic fields to induce and detect transitions between sublevels of a nuclear ground state. NMR refers to the situation where the sublevel energy splitting is predominantly due to a nuclear interaction with an applied static magnetic field, while NQR refers to the case where the predominant splitting is due to an interaction with electric field gradients within the material. So-called “pure NQR” refers to the common case when there is no static magnetic field at all.

The NQR line is often broadened by static and dynamic influences to such an extent that it may be difficult to detect the resonance. It can be minimized by cooling the sample and allowing a sample for a more favorable population density. NQR instrumentation has not yet advanced to the level where sensitivity loss due to

- 1) The inherent characteristic of the molecule such as dipole-dipole broadening cannot be avoided.
- 2) Cross coil detection is not possible as in NMR since $\pm m_I$ degeneracy causes a net cancellation of the nuclear induction in a direction perpendicular to the axis of the driving coil.
- 3) Because of the smaller spin lattice relaxation times of quadrupole nuclei, experiments require much larger RF power than magnetic resonance experiments.

To simplify these problems three different methods are generally used for the determination of NQR frequencies:

- i) Super regenerative oscillators
- ii) Regenerative continuous wave oscillators and

iii) Pulsed RF or spin echo method.

In the first two methods an RF oscillator is used to act as exciter of the nuclei and detector. In the third method, separate transmitter and receiver carry out these functions.

Regenerative continuous wave oscillator method is simpler method compare to super regenerative oscillator method. A schematic diagram of Regenerative continuous wave oscillator method is illustrated in figure10.

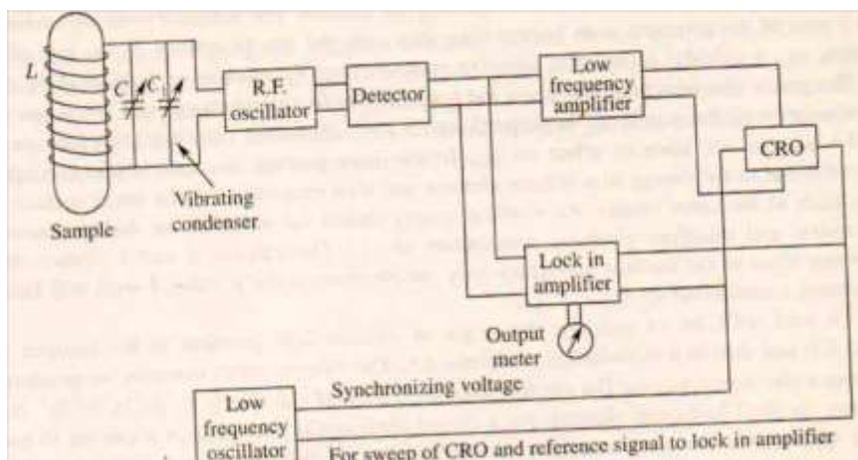


Figure 10: Block diagram of a regenerative continuous wave oscillator-detector arrangement to observe NQR

The sample is placed in the inductance L which is tuned to the transition frequency using the large capacitor C . Changes in frequency over a limited range is affected by changing the capacitance C . Using the LC circuit as the oscillating element with electronic feedback, the voltage level of oscillation becomes a function of nuclear absorption. The applied frequency is modulated about the resonant frequency by varying the small capacitor C_1 sinusoidally. The signal may be presented in an oscilloscope or the derivative of the signal can be recorded by the help of a narrow band lock in the system followed by a recorder.

The NMR signals of quadrupolar nuclear are usually wider than those of spin- $\frac{1}{2}$ nuclei due to rapid quadrupolar relaxation. The line-width increases with the line-width factor that is related to the quadrupole moment of the nucleus, the size and asymmetry of the molecule. For example, deuterium has a small line-width factor of 0.41 fm with a quadrupole moment of 0.286 fm and yields a line-width in HOD of 1.7 Hz while ^{17}O has a line-width factor of 2.1 fm with a quadrupole moment of -2.56 and yields a line-width in H_2^{17}O of 69 Hz. Some nuclei such as ^{197}Au and ^{201}Hg signals are too broad to be observed with a high-resolution NMR spectrometer. The effect of shape and size of the molecule can be demonstrated with ^{14}N -NMR (figure 11).

NH_4^+ is small and highly symmetric yielding a line-width of 0.8 Hz, NH_3 is also small but asymmetric giving a line-width of 16 Hz. Urea is larger and even less symmetric yielding a line-width of 982 Hz.

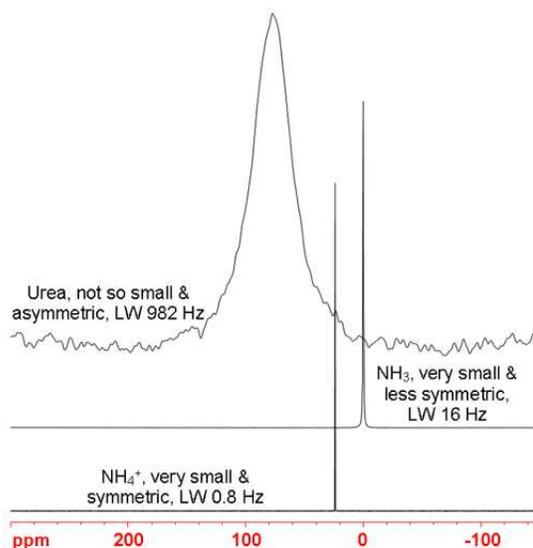


Figure 11: Comparison of line-widths of ^{14}N signals. Larger and less symmetric the molecule, wider the signal is.

16.11 Application of NQR spectroscopy:

1) In silicontetrachloride molecule, all the chlorine atoms are equivalent in the vapour phase and correspond to sp^3 hybridized Si atom. The spin of ^{35}Cl is $3/2$ and is expected to give only one NQR line. This is true in the solid state too if the four chlorine atoms are equivalent. However the NQR of SiCl_4 showed four lines with frequencies 20.273, 20.408, 20.415 and 20.464 MHz. This is because in the solid state, the four chlorine atoms are not crystallographically equivalent. In the solid state, the molecule is subjected to the crystalline environment with different type of intermolecular forces. Thus in crystallographically inequivalent chlorine nuclei. Thus crystallographic inequivalence can be studied by NQR spectroscopy.

2) The EFG at a particular nucleus in an atom or molecule is due to the valence electrons. We know that, the closed shell and s-electrons don not contribute to EFG and only p and d-electrons in a valance shell contribute to EFG. Therefore quadrupole coupling constant q at a particular nucleus is given by the equation

$$q = e \int \psi^* \left[\frac{3 \cos^2 \theta - 1}{r^3} \right] \psi \cdot d\tau$$

Where Ψ is the wave function of the valence electrons, θ is angle between the fixed z-axis in space and the radius vector r (from nucleus to electron). In molecules Ψ is the LCAO function.

Thus the dominant contribution of EFG at the nucleus is due to p-electron and p-type lone pairs. Thus nuclear quadrupole constant for atom q_{atom} or for molecule q_{mole} can be calculated.

16.12 Charge transfer compounds

When an equimolar CCl_4 and p-xylene as well as Br_2 and benzene or CBr_4 and p-xylene are brought together, a charge transfer compound is formed. The studies of frozen solution of this mixture found that the resonance frequencies of the halogens in the complex mixture and in the pure molecule are almost similar. It is clearly for this study that there is a lack of charge transfer between these compounds in the ground state.

16.13 Halogen quadrupole resonance

Nuclear quadrupole resonance of halogen nuclei are the most extensively investigated ones because of their large quadrupole moment values. The charge distribution around the nucleus affects the quadrupole coupling constant of halogen atoms.

16.14 Nitrogen quadrupole resonance

Nitrogen quadrupole resonance is not investigated as extensively as halogen resonance because of its low resonance frequency (2-10 MHz). However, ^{14}N resonance is of interest because of its varied type of bonding structures possible in inorganic, organic and biological compounds. ^{14}N has a spin $I = 1$ and therefore in an axial field we expect only one line whereas we get two or three lines in a field of non-axial symmetry. Experimental measurements give e^2qQ and η . Data from N-chlorodimethylamine was used to check the validity. The ^{14}N quadrupole data in metal cyano complexes are interpreted in terms of π bonding due to the migration of electrons of the central metal atom into the vacant antibonding π molecular orbitals of the cyano groups.

16.15 Group-III trihalides

The halogen spectrum of group -III trihalides consisted of two closely spaced resonances lying well above a third one. NQR data suggest a dimerized molecule with the two metal ions bonded by two halogen bridge bonds as shown in figure.12 with AlBr_3 as an example molecule.

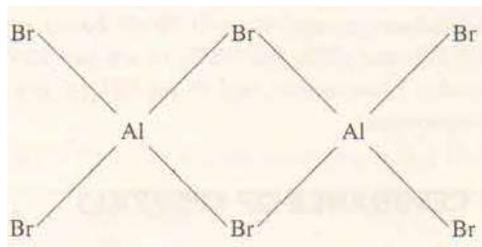


Figure 12: structure of dimerized AlBr_3 molecule.

NQR data of some bridged dimmers are listed in below table 1. The resonance at low frequency is due to the bridged atoms and the high frequency ones are due to the terminal atoms.

Table 1. Observed NOR frequencies of Group-III trihalides

<i>Molecule</i>	<i>Nucleus</i>	<i>Terminal halogen frequency (MHz)</i>	<i>Bridging halogen frequency (MHz)</i>
AlBr ₃	⁷⁹ Br	113.790, 115.450	97.945
ICl ₃	³⁵ Cl	33.413, 34.918	13.740
AuCl ₃	³⁵ Cl	36.116, 33.340	23.285
GaCl ₃	³⁵ Cl	19.084, 20.225	14.667

From the quadrupole resonance of cation and halogen nuclei, it is possible to determine the various angles and the type of hybridization in the molecule. The results showed that the bonds connecting the metal atoms with the bridged halogens are weaker than the others.

16.16 Groups-IV halides

The quadrupole coupling constants of a series of group-IV halides of the type MH₃X where M = C, Si, Ge and X = Cl, Br were determined and the results were interpreted on the basis of percentage of ionic, single bond and double bond character present in M-X bond. It has been found from the studies that the double bond character is greater for SiH₃Cl leading to a larger dipole moment value for GeH₃Cl compare to SiH₃Cl. It is argued that increased π character in Si compounds tends to shorten the Si-X internuclear distance and hence a decrease in the dipole moment. Further, for group-IV tetrahalides, the halogen quadrupole coupling show an increasing ionic character with increasing electronegativity difference between the group-IV metals and the halogen.

In compounds of the type MX₄, MH₃X where M = C, Si, Ge, Sn and X = Cl, Br, I the electronegativity of the central metal atoms is calculated from observed quadrupole coupling constants. Electronegativity difference versus e^2qQ gives a linear relation for each serie. It is found that SiX, X = Cl, Br, I compounds show the smallest coupling constants indicating Si o be most electronegative of these four elements. From such studies, the following electronegativity order is established: C > Ge > Sn > Si.

16.17 Other halides

Interseeting results have been obtained in number of other halides. The NQR spectra of a series of hexahalides of heavier atom are interpreted in terms of the covalency of the metal-ligand bond. The covalent character of paramagnetic halides TiCl₃, VCl₃, and CrBr₃ calculated from

pure quadrupole resonance frequencies agreed with those based on electronegativities. Quadrupole studies on NH_4I_3 , RbI_3 and CsI_3 show that the three iodine atoms are non equivalent.

16.18 Quadrupole resonance of Minerals

The high sensitivity of NQR frequency shifts due to different structures helps the study of fine features of minerals such as degree of distortion in the coordination polyhedrons, the nature of flaws and their distribution throughout the lattice, the dynamics of lattice etc.....X-ray studies will not be able to give accurate results, since the data are only average for both standard and distorted unit cells. Temperature relationships between spin lattice relaxation T_1 and the resonance frequencies give information regarding dynamics of individual functional group of atoms in mineral structures. Thus NQR studies open up new approaches to the study of the features of the chemistry and structure of minerals.

16.19 NQR group frequencies

Halogen NQR frequencies depends to a large extent on the ionic character of M-Cl bond, M is a metal such as Al, Ti, Cr, Cu etc..... depending on the other substituents on M, a spread of NQR frequencies is noticed for a given M-Cl bond. Frequency tables for $\text{M}-^{35}\text{Cl}$ and $\text{C}-^{35}\text{Cl}$ are available which are extremely useful in structure determination. One such table for $\text{C}-^{35}\text{Cl}$ group frequencies is given below table 2.

Table 2. ^{35}Cl NQR group frequencies for C-Cl group.

Group	Frequency range (MHz)	Group	Frequency range (MHz)
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{Cl} \end{array}$	28.8-34.0	$\begin{array}{c} \text{Cl} \\ \\ -\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array}$	37.8-42.0
$\begin{array}{c} \\ -\text{O}-\text{C}-\text{Cl} \\ \end{array}$	29.7-32.7	$\begin{array}{c} \\ -\text{S}-\text{C}-\text{Cl} \\ \end{array}$	33.0-34.6
$\begin{array}{c} \\ -\text{C}-\text{Cl} \\ \end{array}$	31.0-43.0		34.6-40.0
$\begin{array}{c} \\ -\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array}$	34.5-42.5	$\begin{array}{c} \diagup \\ \text{C}-\text{Cl} \end{array}$	36.5-39.5

The use of group frequency table can be illustrated with the spectrum of trichloro acetyl chloride (CCl_3COCl). The ^{35}Cl resonance of the three chlorine nuclei in CCl_3 part is expected to give three lines in the frequency range 38-42 MHz. the observed spectrum showed resonances at 33.7, 40.13, 40.47 and 40.6 MHz. from the table it is obvious that the three lines on the high frequency side are from the three chlorine nuclei in the CCl_3 part and the one at 33.72 MHz is due to

chlorine in COCl group. Similar table for ^{14}N nucleus is also available. Hence NQR frequencies of ions having halides are often used as finger print for their identification. Some of the ions identified in this way are BCl_4^- , AlCl_4^- , PCl_4^+ , PCl_6^- and SbCl_6^-

16.20 Hydrogen bonding

Hydrogen bonds are also detectable by NQR. The quadrupole coupling constant of nuclei in hydrogen containing molecules are found to be greater in vapour state (microwave measurements) than in the solid state (NQR measurements). The ^{35}Cl quadrupole coupling constant in HCl in the solid state is 21% smaller than that in the vapour state. Similarly the ^{14}N quadrupole coupling constant in NH_3 is smaller by 25% in the solid state. In general, a reduction in quadrupole coupling constant is noticed while going from the vapour to the solid state. This is due to the reduction in the field gradient at the nucleus caused by strong intermolecular hydrogen bonding in the solid state. The ^{35}Cl NQR spectrum of sodium tetrachloroaurate dihydrate showed four NQR resonances, one of which is 2.5 MHz lower at 77K. This is attributed to a ^{35}Cl atom which is involved in two hydrogen bonds to two adjacent water molecules. As the temperature is increased, hydrogen bonding gets decreased and the frequency of the NQR lines start shifting. Thus NQR can be used for investigating hydrogen bonding in crystals.

16.21 Summary of the unit

Following points are remember to understand NQR

- Quadrupolar interaction is the interaction of nuclear quadrupolar electric moment and electric field gradient.
- NMR spectrum of quadrupolar nucleus with spin- I contains $2I$ transitions.
- NMR spectrum of quadrupolar nucleus depends on qQ and eQ parameters.
- ST are broadened by 1st and 2nd order quadrupolar interaction and are difficult to observe.
- CT is broadened by 2nd order quadrupolar interaction, which is not completely removed by MAS.
- CT can be selectively excited by using low power rf field.
- Quadrupolar interaction provides information on structure

16.22 Key words

Non spherical nucleus; prolate nucleus; oblate nucleus; Quadrupolar Nucleus; Electric-field gradient; Quadrupole interaction; Charge transfer compounds; nuclear quadrupole interaction.

16.23 References for the further study

1) Spectroscopy in inorganic chemistry. Vol-1. by C. N. Rao, *Academic Press Inc.*

16.24 Question for self study

- 1) Explain i) quadrupole moment of a nucleus and ii) electric field gradient.
- 2) What is electric field gradient tensor? Define asymmetry parameter of a quadrupole nucleus.
- 3) Explain the principle of NQR
- 4) Outline some of the differences between NMR and NQR.
- 5) Explain how NQR spectroscopy helps in studying hydrogen bonding in crystals.
- 6) Write notes on i) nitrogen quadrupole resonance and ii) quadrupole resonance of minerals.
- 7) Write a note on the result of ^{35}Cl resonance on i) group-III halides ii) group-IV halides.
- 8) Define quadrupole coupling constant. Outline a procedure for its determination.
- 9) Account for the appearance of four ^{35}Cl resonances in the NR spectrum of SnCl_4 and GeCl_4 .