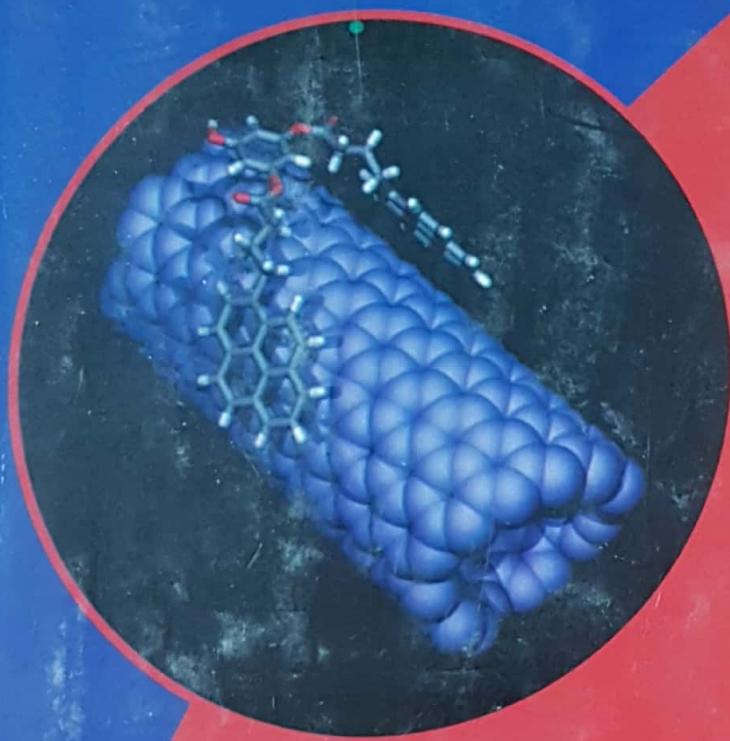


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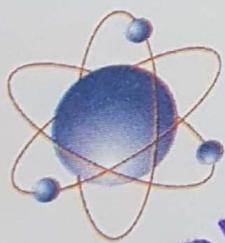
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CHAPTER

1

Spectroscopy and its Applications

1.1 INTRODUCTION TO SPECTROSCOPY

Light is supposed to travel in the form of waves. Visible light is a form of energy. It has been explained by (i) the corpuscular theory and (ii) by Wave theory.

According to wave theory, light travel in the form of wave. Like visible light, there are different forms of electromagnetic radiations such as Ultra-violet, Infra-red, X-rays, Radiowaves etc.

1.2 ELECTROMAGNETIC RADIATION

1. This is a form of energy that is transmitted through space at an enormous velocity (*i.e. velocity of light* 3×10^8 m/sec).
2. Electromagnetic radiation has dual character *i.e.* wave as well as particle behaviour.
3. The electromagnetic radiation consists of electric and magnetic field, which are perpendicular to each other and are perpendicular to the direction of propagation of wave.
4. The electromagnetic radiation does not require any medium for its propagation.

All the types of electromagnetic radiations possess energy.

A wave is actually a type of disturbance which originates from the vibrating source. It travels as a continuous sequence of alternating crests and troughs. Waves of visible light and those of other energy radiations have the following features :

1. Wavelength

It is the distance between adjacent crests or troughs in a particular wave. It is denoted by λ (Lambda). Visible light constitutes waves ranging from 3800 Å (Violet) to 7600 Å (Red). Different colours of light have different wavelengths.

Different units and relationships in these units in which wavelength can be expressed are :

$$1 \text{ \AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$$

$$1 \mu\text{m} = 10^{-4} \text{ cm} = 10^{-6} \text{ m}$$

$$1 \text{ m}\mu\text{m} = 10^{-7} \text{ cm} = 10^{-9} \text{ m}$$

$$1 \text{ nm} = 10^{-7} \text{ cm} = 10^{-9} \text{ m}$$

2. Wave Number

It is defined as total number of waves which can pass through a space of 1 cm. It is represented as \bar{v}

$$\bar{v} = \frac{1}{\lambda \text{ in cm}}$$

The unit of \bar{v} is cm^{-1} .

3. Frequency

It is defined as number of waves which can pass through a point in 1 second. It is denoted by v .

$$v \propto \frac{1}{\lambda}$$

$$v = \frac{c}{\lambda} \quad c = \text{velocity of light i.e. } 3 \times 10^{10} \text{ cm/sec}$$

Units of v are cycles/sec or hertz (Hz).

1.3 DIFFERENT TYPES OF SPECTROSCOPIES

U.V., visible, IR, NMR etc. are different types of spectroscopies because different wavelengths of the electromagnetic radiations are absorbed.

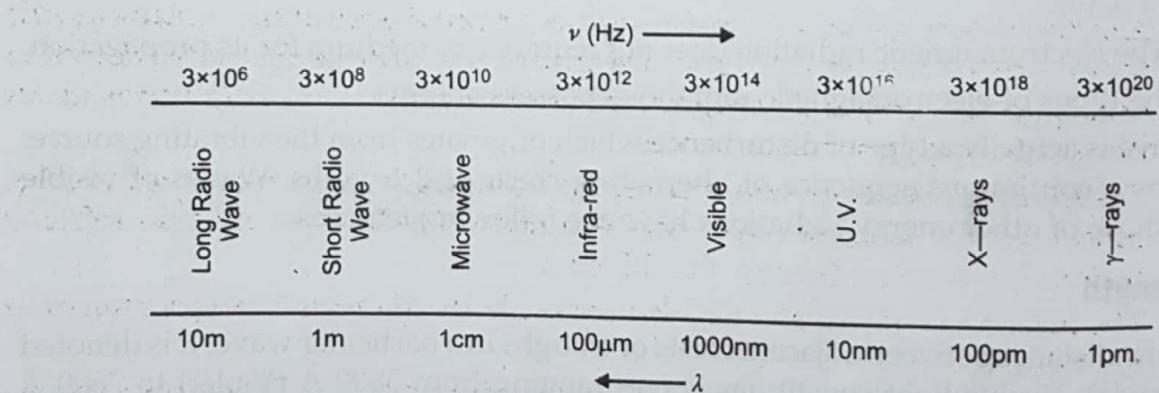


Fig. 1.1 Electromagnetic Spectrum

The visible light represents only small part of entire electromagnetic spectrum.

The complete electromagnetic spectrum gives the arrangement of various types of electromagnetic radiations in order of their increasing frequency and increasing wavelength as shown above in Fig. 1.1.

The arrangement of all types of electromagnetic radiations in order of their increasing wavelengths or decreasing frequencies is called **complete electromagnetic spectrum**.

1.4 ABSORPTION OF CHARACTERISTIC WAVELENGTHS

If light is passed through sample, some of wavelengths are absorbed while others belonging to that light source remain unaffected. A molecule can absorb a radiation of a particular wavelength which is sufficient enough to provide energy ($h\nu$) to molecule which is equal to difference in the energy (ΔE) between the ground state molecular orbital (E_1) and excited state molecular orbital (E_2). Thus, the wavelengths absorbed are measured with the help of a spectrometer. If we plot the change in absorption against wavelength, we get certain absorption bands which are highly characteristic of a compound. This is called spectrum. Different compounds will absorb different wavelength, because different compounds require different amount of energy for the excitation of the molecule from the ground state to higher energy state.

This technique provides an excellent tool to ascertain the molecular structure of an unknown compound.

If electromagnetic radiation (of certain wavelength, depending on the type of spectroscopy that we want to study) is passed through the substance under analysis for some time, then radiations of certain wavelength are absorbed by the substance. The wavelengths which are absorbed characterises **some particular functional groups present in the compound**. This dark pattern of lines which corresponds to the wavelength absorbed is called **absorption spectrum**. After absorption, the transmitted light is analysed by the spectrometer relative to the incident light of a given wavelength or frequency.

In an electromagnetic spectrum we may note that :

- (i) **Visible and ultraviolet radiations.** Cover the wavelength range from 200-500 m μ . The absorption of radiation in this region by the molecule causes excitation of π electrons in a conjugated or unconjugated diene system.

Also the carbonyl group of an aldehyde or ketone absorb at some characteristic wavelengths. Thus, an U.V. or visible spectrum is quite useful for the detection of **conjugation, carbonyl group** etc. and may not provide any information about the remaining part of the molecule.

- (ii) **The Infrared radiations** which cover the wavelength range from 0.8 μ to 2.5 μ constitute near Infrared region and that from 15 to 25 μ is called far infrared region. The most useful region is 2.5-15 μ .

The absorption of radiation by the molecule in this region causes molecular vibrations.

The absorption of higher wavelength in the Infrared region (Finger print region) are most characteristics of a compound and are helpful in distinguishing a compound from the other.

- (iii) **NMR spectroscopy** provides a complete insight into environment and the arrangement of atoms within a molecule. **Radiowaves** are used for this purpose. A sample under investigation is placed in strong magnetic field and irradiated with radiowaves. Depending upon the strength of the magnetic field employed, radiations of definite wavelength will bring the nucleus into specific orientation with respect to the applied magnetic field.

1.5 WHAT IS A SPECTRUM ?

This is a graph plotted between the parameters along X and Y-axis.

e.g. In case of U.V. spectroscopy the spectrum is actually a plot between λ_{max} value (i.e. λ of the light absorbed by the sample) along X-axis and intensity along Y-axis.

In case of NMR, it is actually a plot between magnetic field/chemical shift δ vs intensity.

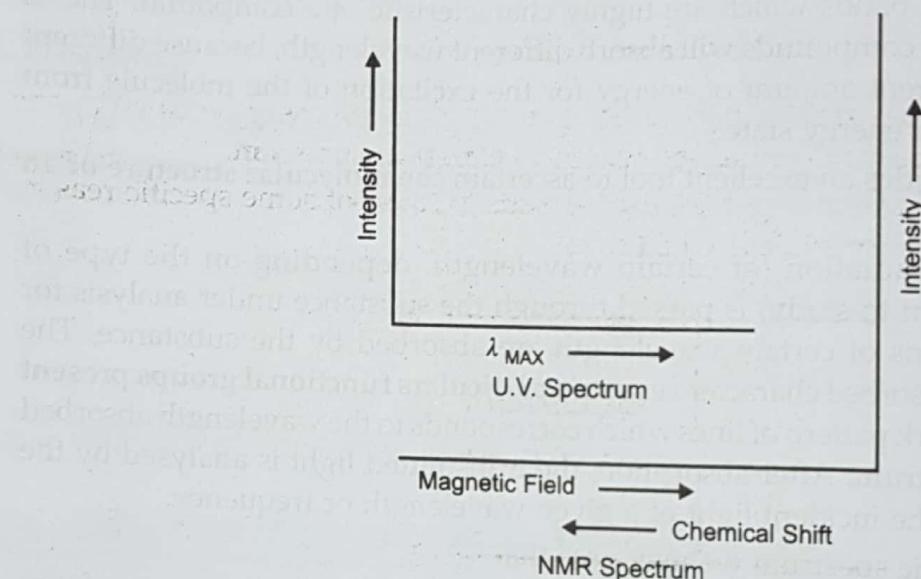


Fig. 1.2 Spectra

Energy of a molecule can change not only as a result of electronic transition but also because it can undergo change of rotational and vibrational state. The rotational and vibrational change does not take place in case of atoms. How vibrational and rotational changes are taking place in a molecule will be made clear later in the chapter.

1.6 ATOMIC AND MOLECULAR SPECTROSCOPY

Atomic spectrum arises from the transition from lower energy level of atom to higher energy level of the atom. It gives the information about electronic structure of the atom. Molecular spectrum on the other hand arises because of transition between molecular energy levels. This is more complicated but gives more detailed information.

1.7 ABSORPTION AND EMISSION SPECTRA

According to quantum theory, the energy levels of all the molecules possess definite amount of energy i.e. quantized. When any electromagnetic radiation falls on a molecule in the ground state, the molecule undergoes a transition from lower energy level to highest energy level, with the absorption of a photon of energy $h\nu$.

The spectrum is thus called **absorption spectrum**.

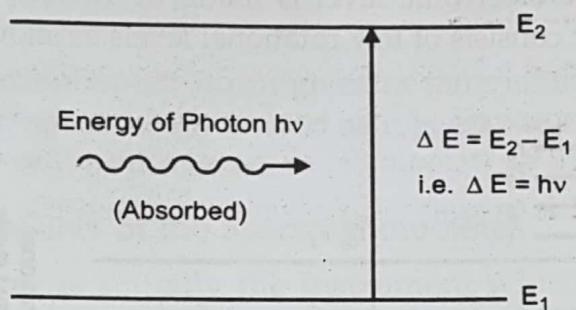


Fig. 1.3 Absorption of Energy

If a molecule is present in the excited state, then the radiation energy emitted by the molecule while coming back to ground state leads to **emission spectrum**.

The molecule may have attained the excited state because of some specific reason. The energy emitted by the molecule is equal to hv .

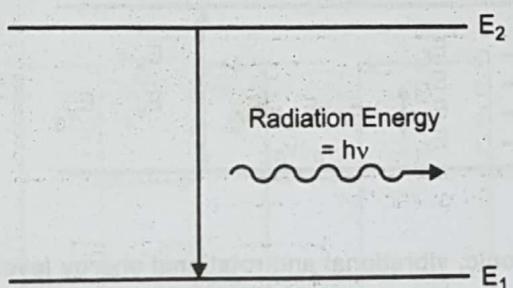


Fig. 1.4 Emission of Energy

$$\Delta E = E_2 - E_1 = hv$$

h = Planck's constant (6.6×10^{-34} J sec or 6.6×10^{-27} erg sec)

v = Frequency of electromagnetic radiation

Absorption by a Molecule

When an atom absorbs energy, it leads to excitation of electrons from lower to higher energy levels. But if a molecule absorbs energy it may lead to vibrational, rotational or electronic transitions depending upon the amount of energy absorbed.

Actually one molecule has large number of energy levels. So definite amount of energy is required to bring the transitions between two energy levels. Some transitions require large energy while others require small energy.

High energy UV/visible radiations are required to bring electronic transitions. While low energy, IR radiations have sufficient energy to bring about vibrational transitions, for rotational transitions least amount of energy is required which is provided by the microwave radiations.

i.e.

$$E_e > E_v > E_r$$

E_e = Electronic energy

E_v = Vibrational energy

E_r = Rotational energy

In a molecule one electronic level is made up of few vibrational levels. Each vibrational level further consists of few rotational levels as shown :

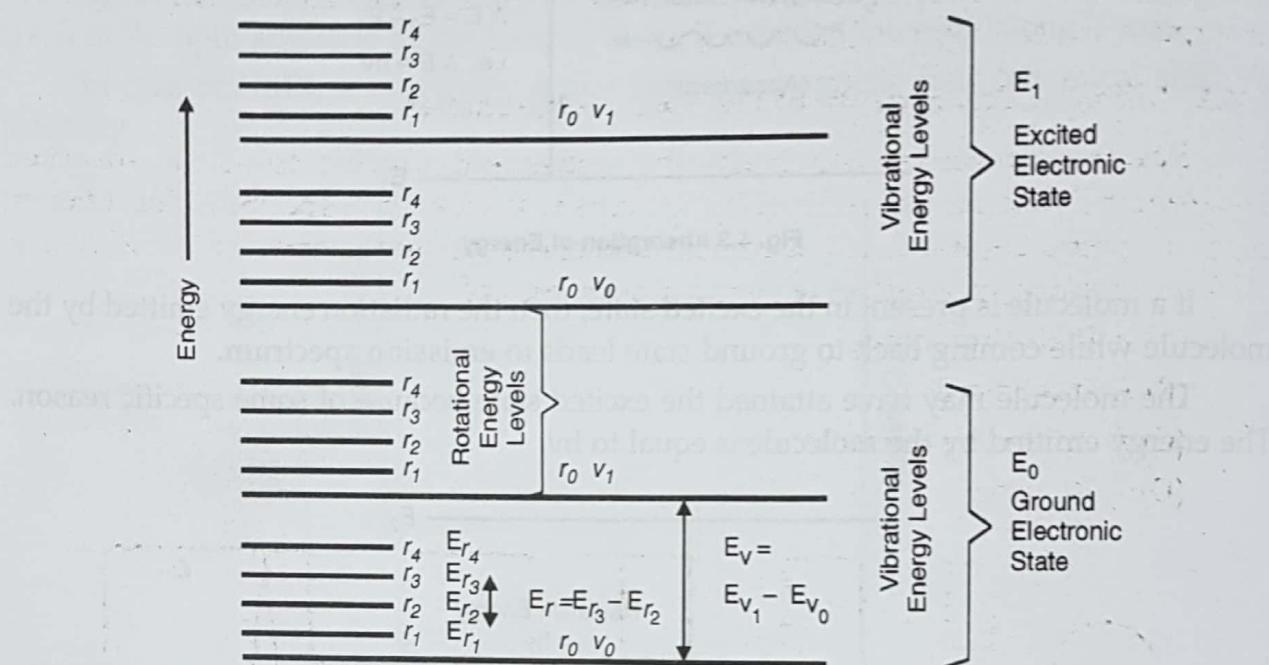


Fig. 1.5 Electronic, vibrational and rotational energy levels of a molecule

$r_0, r_1, r_2 \dots$ are different rotational energy levels

V_0, V_1, \dots etc. are different vibrational energy levels

E_0, E_1, \dots etc. are different electronic energy levels

E_e = Energy of electronic level

E_v = Energy of vibrational level

E_r = Energy of rotational level

ΔE_e = Difference of energy between two electronic levels

ΔE_v = Difference of energy between two vibrational levels

ΔE_r = Difference of energy between two rotational levels

All the energy levels are called molecular energy levels.

According to Born Oppenheimer approximation,

$$E_{\text{molecule}} = E_e + E_v + E_r$$

E_{molecule} is energy of the molecule.

As it is clear that if molecule absorbs energy and shows electronic transition, it will automatically undergo vibrational and rotational energy level changes, as $E_e > E_v > E_r$.

If a molecule absorbs energy, type of transition shown by the molecule depend on the amount of energy absorbed by it. Low energy radiation may cause a rotational or vibrational change. Higher energy radiations are responsible for the electronic transition.

1.8 EXPERIMENTAL TECHNIQUE

Absorption and emission spectroscopy gives the same information about the sample. But generally absorption spectroscopy is used as it is easy to read than emission. Here absorption spectroscopy will be discussed.

1.8.1 Different Components of the Spectrophotometer

Spectrophotometer is actually the instrument which records the absorbed wavelength by the sample and display the facts in the form of a **spectrum**. For different types of spectroscopies, of course construction of the spectrophotometer is different. But all the absorption spectrophotometers mainly consist of :

- (A) A Radiation source
- (B) A Sample cell
- (C) A dispersing element
- (D) A Recorder

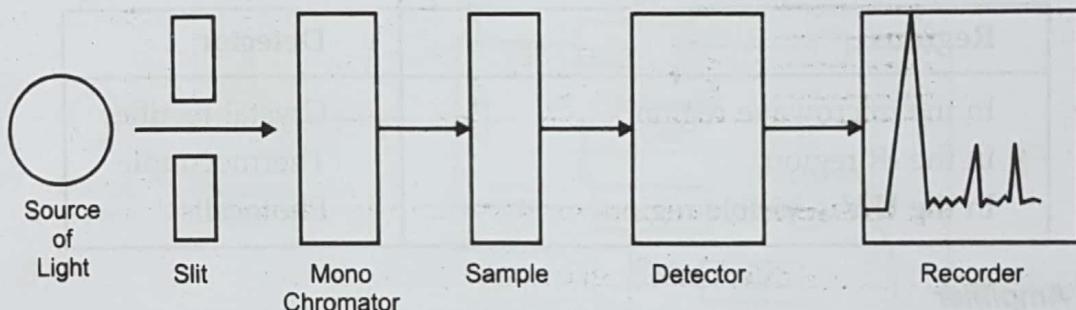


Fig. 1.6 Important Components of U.V.—Visible Spectrophotometer (Single beam Spectrophotometer)

Radiation from source is focussed through the sample after passing through monochromator. Now the radiation passes onto detector followed by signal amplifier and the recorder.

The individual components for various type of spectrophotometers for different types of spectroscopies are discussed here :

1. Radiation Source

In the microwave region, the Klystron value (magnetron) is that source of radiation. The Klystron is a specially devised electron tube in which the electrons on their way towards the plate generates electromagnetic radiations of suitable frequency, it acts as its own monochromator.

In the infrared region the source of heat radiation is Nernst glower. Its filament consists of mixture of oxides of Cesium and Thorium, which are kept at high temperature electrically. For the far infrared region Wetsbach lamp or strongly heated glass is used.

In the visible—U.V. region incandescent lamps or many types of discharge tubes such as hydrogen deuterium lamps and mercury arcs are used.

The Sample Container

The sample is placed in sample container, the material of which should be chemically inert. In the visible/U.V. region container of quartz is used. In the infrared region, NaCl

and KBr is used. For the study of aqueous solutions AgCl is used. The length of the sample container is 0.01-0.1 mm for solid and liquid samples. Gas samples are usually contained in cells either 5 or 10 cm long.

Dispersing Unit

This is also called as **monochromator**. A radiation which consists of waves of one wavelength is called monochromatic light. A device (which converts polychromatic light to monochromatic light is called monochromator) by means of which the radiations can be separated in space according to wavelength after it has passed the sample is known as monochromator. Its principal part is a dispersing element i.e. a **prism or a grating unit**.

Detector

The radiation emitted by the sample is analysed with respect to intensity of radiation and wavelength.

The radiation energy is measured by changing it to electrical energy. This conversion is done by the **detector**.

Regions	Detector
In the microwave region	Crystal rectifier
In the IR region	Thermocouple
In the U.V.-visible region	Photocells

Signal Amplifier

Amplification of the electrical signal is done by amplifier. The beam of signal is chopped by a shutter that rotates, so that alternating signals are obtained from the detector. Because it is easy to amplify the alternating signals.

Recorder

When sample cell is empty, the detector output will be constant over the range of frequencies covered by the instrument. But when the sample is present in the instrument and if it has only two possible energy levels as E_1 and E_2 , the detector output will show a sudden fall at the frequency given by

$$\nu = \frac{E_2 - E_1}{h}$$

The question arises why this downfall is there. This is so because at this ν , some energy is absorbed by the sample and it does not reach the detector. On a paper, record is taken by the machine in the form of a graph between detector output on left hand and % of energy absorbed by the sample on right hand side.

This is shown in the Fig. 1.7.

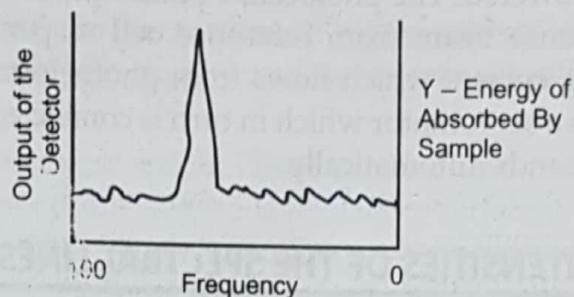


Fig. 1.7 Record Taken by the Recorder

1.8.2 Double Beam Spectrophotometer

Spectrophotometer can be single beam (as shown in fig. 1.6 or double beam spectrophotometer). Mostly spectrophotometers are double beam instruments.

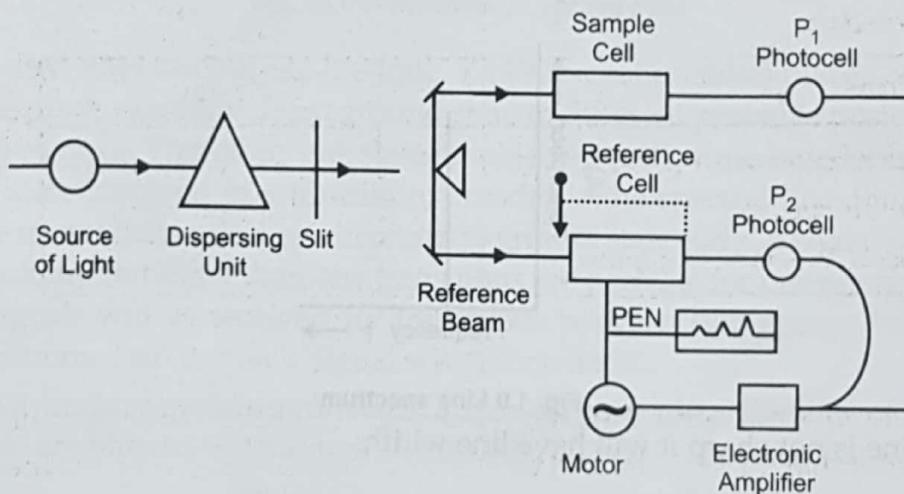


Fig. 1.8 Double Beam Spectrophotometer

The incident radiation is dispersed with the help of rotating prism. Different wavelengths of the light are separated by prism and then selected by slits such that rotation of prism causes series of continuously increasing wavelengths to pass through the slits. The selected beam is monochromatic which is divided into two beams of equal intensity.

One beam of monochromatic light is passed through sample cell having sample dissolved in a suitable solvent and the other beam is passed through the reference cell having only solvent (same as in which sample is dissolved). Each absorbance/transmittance measurement on the sample is accompanied by a simultaneous measurement on the pure solvent. The intensity of the respective transmitted beams are then compared over the whole wavelength range of instrument. (The spectrophotometer electronically subtracts the absorption of solvent in reference beam from the absorption of the sample). Hence the effects due to absorption of light by the solvent are minimised. In this way, the absorbance or transmittance characteristic of the compound alone can be measured. The signal for the intensity of absorbance versus corresponding wavelength is automatically recorded on the graph. The spectrum is usually plotted as A (absorbance) against λ (wavelength). When light actually passes through the sample, it absorbs light

and intensity of light is lowered. The photocells P_1 and P_2 will receive a weak beam from sample cell and an intense beam from reference cell respectively. This results into generation of alternating current which flows from photoelectric cells to amplifier. The amplifier is connected to a servomotor which in turn is connected to Pen-recorder. Thus it records the absorption bands automatically.

1.9 WIDTHS AND INTENSITIES OF THE SPECTRAL LINES

In the spectra, the spectral lines or different signals are not sharp but these have some finite width. In any molecular spectroscopy, the two important features of spectral lines are (i) How sharp/broad are the lines i.e. line width ? (ii) How strong is the line i.e. intensity of line ?

1.9.1 Line Width

If the signal is sharp there won't be any width i.e.

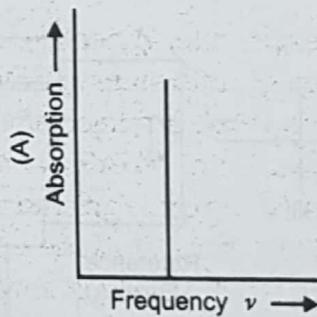


Fig. 1.9 Line spectrum

But if line is not sharp it will have line width.

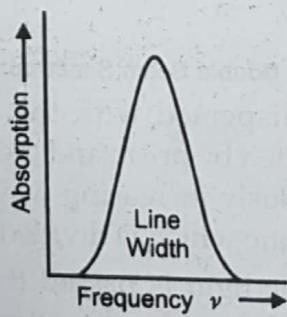


Fig. 1.10 Band spectrum

There may be different reasons for this :

1. Collision broadening

In the solid phase spectra i.e. when the sample is in the solid form, spectra are often sharp because motion of the particles are limited. Molecular interactions take place more in liquids than in gases. Molecules collide frequently with each other or with the walls of container which causes some deformations of the particles and hence line broadening takes place while spectra show intense peaks with negligible line widths in case of solids.

1.10 UV-VISIBLE SPECTROSCOPY

1.10.1 Principle

Ultraviolet spectroscopy is also called electronic spectroscopy because it involves transition of different types of electrons (n , π and σ) present in the sample molecule from ground state to excited state i.e. from lower energy to higher energy molecular orbitals.

where n stands for non-bonding electrons i.e. lone pairs of electrons

π stands for π electrons i.e. electrons involved in the formation of π bond.

σ stands for σ electrons i.e. electrons involved in the formation of σ bond.

According to molecular orbital theory, when a molecule is excited by the absorption of energy of radiation (in the range of U.V. or visible light) its electrons are promoted from the bonding (low energy molecular orbital) to antibonding molecular orbital (high energy molecular orbital).

The antibonding molecular orbital which is associated with the excitation of σ electrons is called σ^* antibonding molecular orbital. So for σ electrons the σ to σ^* transition takes place i.e. transition from σ bonding molecular orbital to σ^* antibonding molecular orbital will take place ($\sigma \rightarrow \sigma^*$).

If the molecule has π bond, then likewise for π electrons, molecular orbital of low energy is known as π bonding molecular orbital and of high energy is known as π antibonding molecular orbital (π^*). So π e will occupy π bonding molecular orbital i.e.

ground state. On absorption of energy the π e will get excited to higher energy orbital i.e. π^* or π antibonding molecular orbital ($\pi \rightarrow \pi^*$).

If the molecule has n electrons also the possible transitions for n electrons, which will occupy n molecular orbital (i.e. non-bonding molecular orbital) in the ground state may be n to σ^* and for n to π^* . ($n \rightarrow \sigma^*$) and/or ($n \rightarrow \pi^*$) or ($n \rightarrow \sigma^*$).

Transitions from bonding σ and π to antibonding π^* and σ^* respectively, i.e.

$\sigma \rightarrow \pi^*$ and π to σ^* can also take place. But according to selection rule, these transitions are forbidden and are of very weak intensity.

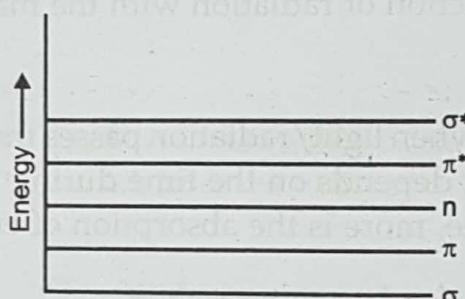


Fig. 1.12 Different Electronic Energy Levels

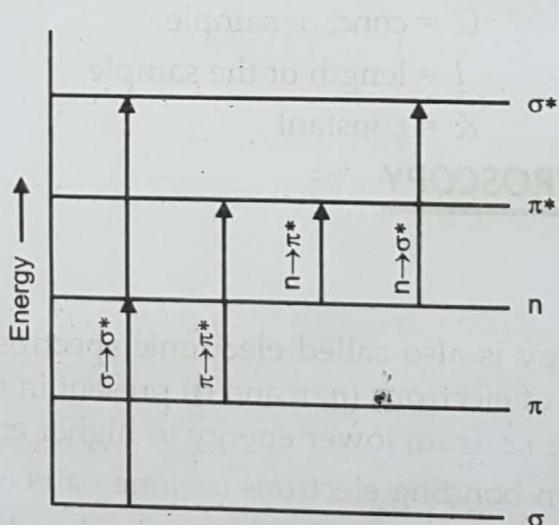


Fig. 1.13 Different Electronic Transitions

The different transitions obey the following trend of energy requirement.

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

When an electromagnetic radiation in U.V. region (200-400 nm) or visible region (400-800 nm) passes through the sample compound having multiple bond in its structure, a part of the incident light is absorbed. This absorption imparts energy which leads to different transitions of valence electrons in the sample molecule. Since sigma electrons are tightly held and higher amount of energy is required to excite σ electrons, so it is outside the range of usual spectrophotometers.

1.10.2 Different Types of Transitions

Let us now consider the various types of transitions possible in U.V. spectroscopy :

1. $\sigma \rightarrow \sigma^*$ transitions

It is a high energy process, since σ bonds are very strong. The organic compound in which all the valence shell electrons are σ electrons do not show absorption in the normal U.V. region i.e. 180-400 nm e.g. of $\sigma \rightarrow \sigma^*$ is methane i.e. a saturated hydrocarbon.

This transition requires high energy i.e. short wavelength. The usual spectroscopic technique cannot be used below 200 nm since oxygen present in air begins to absorb strongly in this region. To study such a transition, the entire path length must be evacuated. The region below 200 nm is called vacuum U.V. region. This region is less informative.

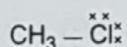
2. $n \rightarrow \sigma^*$ transitions

This type of transition takes place in saturated hydrocarbons having one hetero atom with lone pair of electrons e.g. halides, alcohols, ethers, amines etc.

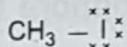
$n \rightarrow \sigma^*$ transitions require less energy than $\sigma \rightarrow \sigma^*$ transitions but majority of compounds in this class show no absorption in the near U.V. region.

Effect of the size of Halogen Atom

In saturated alkyl halides energy requirement for $n \rightarrow \sigma^*$ transition decreases with increase in size of the halogen atom because it leads to decrease in electronegativity.



λ value for $n \rightarrow \sigma^*$ = 172—175 nm



λ for $n \rightarrow \sigma^*$ = 258 nm

Due to more electronegativity of Cl than I n electrons of Cl are difficult and excite hence more energy or shorter wavelength is required.

Similarly amines absorb at higher wavelength as compare to alcohol.

Effect of H bonding

Alcohols and amines can show H-bonding with the solvent molecules. This takes place due to presence of lone pair of electrons on hetero atoms. As n electrons of the sample molecule are involved in hydrogen bonding, more energy is required for their transition to higher energy molecular orbital. Hence H-bonding shifts the ultra-violet absorptions to shorter wavelength.

3. $\pi \rightarrow \pi^*$ transitions

Unsaturated molecules show this type of transition. For example alkene, alkyne, carbonyl compounds, aromatics etc. This transition requires still less energy as compared to $n \rightarrow \sigma^*$ transition and hence absorption of longer wavelength takes place. Absorption occurs within the range of ultraviolet spectrophotometer.

4. $n \rightarrow \pi^*$ transitions

An electron of unshared electron pair on the hetero atom gets excited to π^* orbital. This type of transition requires least amount of energy and hence absorption of highest value of λ takes place. Examples of the molecules showing $n \rightarrow \pi^*$ transitions are carbonyls i.e. Aldehydes, Ketones, Carboxylic acids, Esters etc.

Saturated aldehydes show both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions at around 290 nm and 180 nm respectively. Absorption occurring at smaller wavelength is usually intense. Extinction coefficient of $n \rightarrow \pi^*$ is quite low as compare to $\pi \rightarrow \pi^*$. In addition to these two, $n \rightarrow \sigma^*$ transition also takes place in case of carbonyl compounds.

It can be summed up as that in carbonyl compounds two types of transition [(i) and (ii)] take place.

(i) **High Energy Transitions**, which include $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions. The signal for both the transitions are intense.

(ii) **Low Energy Transitions**. $n \rightarrow \pi^*$ transition requires less energy and signal is a weak bond.

1.10.3 Allowed and Forbidden Transitions

Allowed Transitions. The transitions having ϵ_{\max} (extinction coefficient) value more than 10^4 are called allowed transitions. These generally arise due to $\pi \rightarrow \pi^*$ transitions e.g. In 1, 3-Butadiene, $\pi \rightarrow \pi^*$ at 217 nm with $\epsilon_{\max} = 21,000$ is allowed transition.

Forbidden Transitions. The transitions having ϵ_{\max} value in the range of 10-1000 are called forbidden transitions e.g. $n \rightarrow \pi^*$ transitions in carbonyls at 300 nm with ϵ_{\max} value less than 100. So it is a forbidden transition and probability of this transition is low.

1.10.4 The Chromophore Concept

Chromophore is defined as any isolated covalently bonded group that shows a characteristic absorption in the ultraviolet or visible region.

The absorption occurs irrespective of the fact whether colour is produced or not.

There are two types of chromophore :

- In which π electrons are present and hence $\pi \rightarrow \pi^*$ transitions are shown e.g. ethylene, acetylene, Benzene etc.
- Those which have both n and π electrons so that these show $n \rightarrow \pi^*$ transitions in addition to $\pi \rightarrow \pi^*$ transitions.

Examples are carbonyls ($>\text{C=O}$) nitriles, ($\text{R}-\text{C}\equiv\text{N}$) etc.

1.10.5 Auxochrome

An auxochrome is a colour enhancing group. It does not itself act as a chromophore, but when it is bonded to a chromophore, it increases the absorption value in terms of λ and intensity, because a new chromophore is formed due to this combination. Examples of auxochrome are $-\ddot{\text{O}}\text{H}$, $-\ddot{\text{O}}\text{R}$, $-\text{NH}_2$, $-\text{NRH}$, $-\text{NR}_2$, $-\text{SH}$ etc. All the auxochromes have n electrons. The effect of the auxochrome (i.e. increase in λ value) is due to its ability to extend the conjugation of the chromophore by the non-bonding electrons. Thus a new chromophore results which has a different higher value of absorption maxima as well as intensity.

For example, benzene shows λ_{\max} at 255 nm whereas aniline shows absorption at 280 nm.

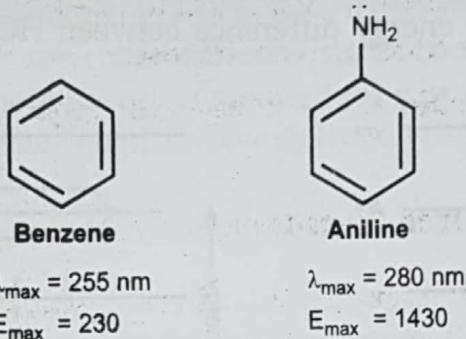
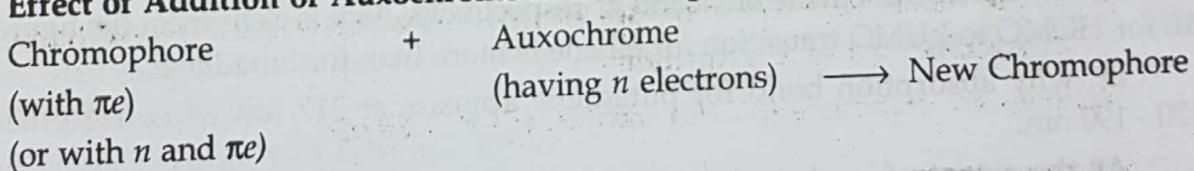


Fig. 1.14 Effect of auxochrome ($-\text{NH}_2$) on chromophore 

Benzene is a chromophore whereas $-\text{NH}_2$ group is an auxochrome, which when gets attached to benzene, it forms aniline i.e. a new chromophore where n electrons on N of $-\text{NH}_2$ group will enter into conjugation with the chromophore and hence extends the conjugation with π electrons of benzene. This results into increase in absorption maxima (λ_{\max}). This is so because extended conjugation reduces energy difference between the ground state and the excited states. This results into shift of absorption to longer wavelength with simultaneous increase in intensity of the absorption band.

Effect of Addition of Auxochrome to Chromophore can be summarized as :



λ_{\max} of chromophore

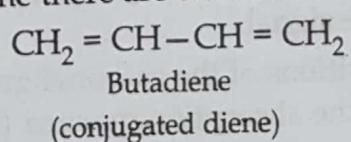
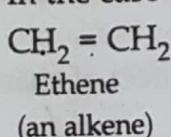
λ_{\max} of new chromophore $> \lambda_{\max}$ of chromophore because of extended conjugation

1.10.6 Effect of conjugation on the λ_{\max} value

Normally the absorption of U.V. visible light results in excitation from ground state to higher energy state. The higher energy states are called high energy molecular orbital or antibonding molecular orbital. The highly probable transition on the absorption of quantized energy is from HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital).

In an alkene the most probable transition occurs from $\pi \rightarrow \pi^*$ at 170-190 nm.

In the case of conjugated diene there are two π bonds as shown.



In case of butadiene as there are two π bonds, the π orbitals of separate alkene groups combine to form new orbitals i.e. two bonding molecular orbitals π_1 and π_2 (where $\pi_1 = \pi + \pi$ and $\pi_2 = \pi - \pi$) and two antibonding molecular orbitals π_3^* and π_4^* (where $\pi_3^* = \pi^* + \pi^*$ and $\pi_4^* = \pi^* - \pi^*$). Thus, the energy difference between HOMO and LUMO decreases. How?

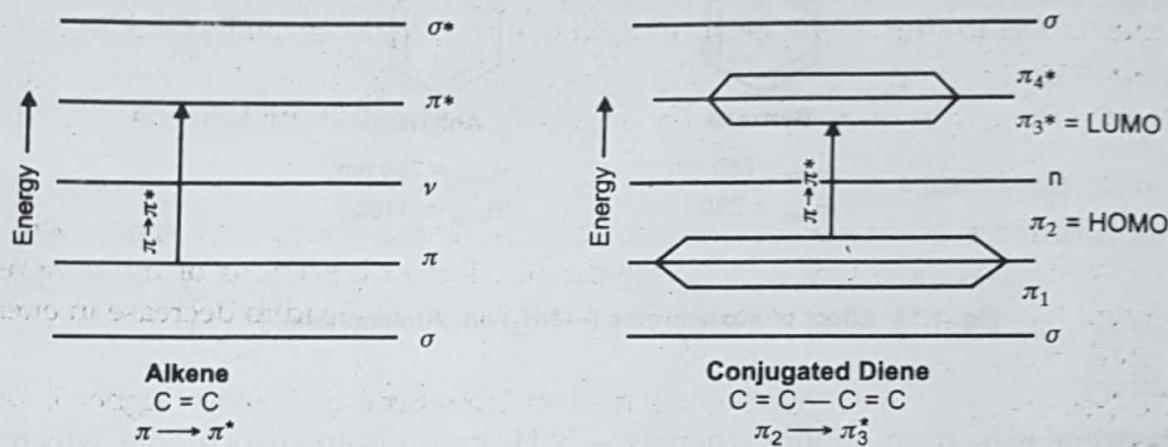


Fig. 1.15 The effect of conjugation on the electronic transition in conjugated diene

As butadiene has four π electrons, these four π electrons will occupy the ground state i.e. π_1 and π_2 . On absorption of energy the excitation of π electrons will take place from HOMO to LUMO. HOMO is π_2 as Energy of π_2 is more than that of π_1 . LUMO is π_3^* because out of two unoccupied molecular orbitals π_3^* is of lower energy hence it will be lowest unoccupied molecular orbital. Hence HOMO to LUMO transition results into $\pi_2 \rightarrow \pi_3^*$ transition.

Thus, energy difference between HOMO and LUMO ($\pi_2 \rightarrow \pi_3^*$) decreases as compare to that in case of alkene, where energy difference between π and π^* is more. Because HOMO and LUMO for ethene are π and π^* respectively. As it is clear from the figure that ΔE for HOMO to LUMO transition for ethene is more than for butadiene.

i.e. why absorption bond for butadiene appears at 217 nm while for ethene at 170 - 190 nm.

As the extent of conjugation increases, the energy difference between HOMO and LUMO decreases and absorption wavelength increases. So it can be interpreted that the wavelength of absorption increases with the increase in conjugation.

1.10.7 Solvent Effect (Polarity of the Solvent) on λ_{\max} value

A solvent used for a particular type of spectroscopy should be so which does not absorb in the specified region. For spectral analysis, a dilute solution of the sample is prepared in the solvent. 95% ethanol is usually used as a solvent in U.V-visible spectroscopy. For other examples are water and cyclohexane.

By changing the polarity of the solvent, the intensity and λ_{\max} of the signal is shifted for the polar samples. For the non-polar samples, no appreciable effect is detected in the λ_{\max} and intensity value of the signal.

Let us consider few transitions of the carbonyl group and see the effect of changing the polarity of the solvent on the absorption maxima (λ_{\max}) value.

(i) $n \rightarrow \pi^*$ transitions

In the carbonyl compounds, if we consider n electrons, the ground state is more polar as compare to excited state. The hydrogen bonding with the solvent molecules takes place to less extent with the carbonyl group in the excited state and more in the ground state. Hence if polarity of the solvent is increased, the H-bonding shown by carbonyl in ground state increases. So more energy is required for $n \rightarrow \pi^*$ transition and hence the absorption moves to shorter wavelength i.e. blue shift or Hypsochromic effect (as explained in the next topic).

For example λ_{max} of acetone is 279 nm in hexane but 264 nm in water.

(ii) $\pi \rightarrow \pi^*$ transitions

If we consider the π electrons of the carbonyl group, the ground state is less polar and excited state is more polar. So, more dipole-dipole interactions of the sample with solvent will take place in the excited state and hence it will lead to decrease in energy of the excited state i.e. π^* .

So less energy is required for the $\pi \rightarrow \pi^*$ transitions and hence higher λ value is absorbed.

If the polarity of the solvent is increased, it will lead to decrease in energy of π^* molecular orbital and hence will raise the λ_{max} value.

Conclusion. With the increase in polarity of the solvent, the $\pi \rightarrow \pi^*$ of the carbonyl group will show higher value of λ_{max} and $n \rightarrow \pi^*$ transition will show absorption at lower value of λ_{max} .

1.10.8 Absorption and Intensity Shifts

(a) Bathochromic Effect/Red Shift

It is the effect by virtue of which the absorption maximum is shifted towards longer wavelength due to presence of an auxochrome or by change of solvent. This shift is called Red Shift.

Factors Causing Bathochromic Effect

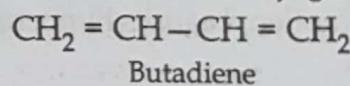
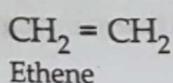
- (i) Presence of auxochrome (as explained earlier)
- (ii) Nature of solvent (as explained earlier)
- (iii) Extension in conjugation (as explained earlier)

(b) Hypsochromic Effect or Shift/Blue Shift

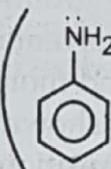
It is the effect by virtue of which the absorption maxima is shifted towards the shorter wavelength. This is called Blue shift. Removal of conjugation or changes in polarity of the solvent, are the two factors responsible for blue shift :

1. Removal of Conjugation

Butadiene shows absorption maxima at 270 nm but ethene shows at 180-190 nm. This blue shift in ethene is because of removal of conjugation.



2. Polarity of Solvent

If aniline  ANILINE ($\lambda_{\text{max}} = 280 \text{ nm}$) is taken in acidic solvent, the lone pair of electron present on N will not show conjugation with π -bond system of benzene ring. Hence a blue shift is caused which will lead the absorption to lower wavelength. (Blue Shift)

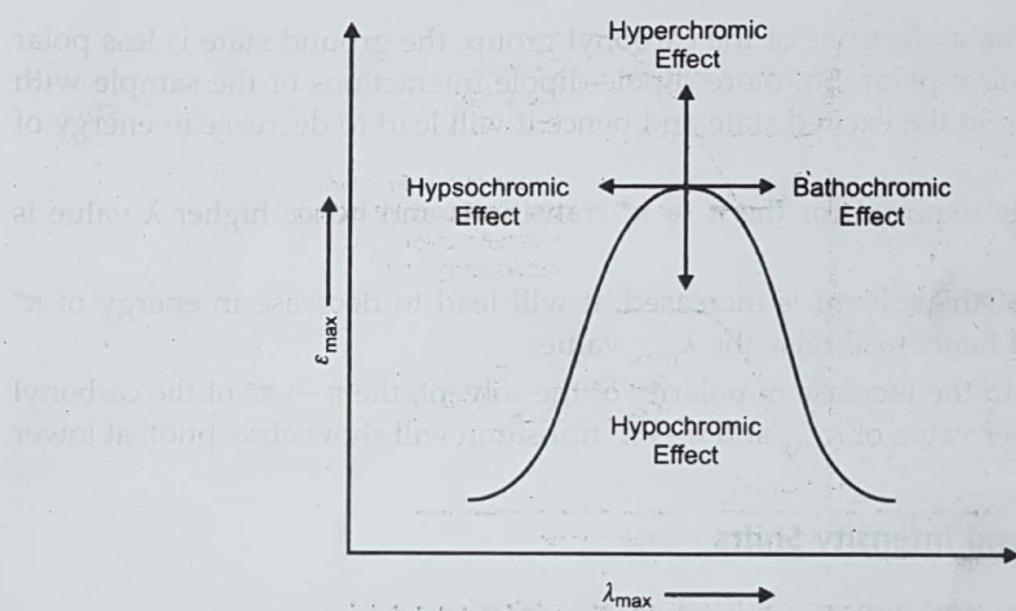


Fig. 1.16 Absorption and Intensity Shifts

The n electrons on N in aniline, if taken in acidic solvent will form a bond with H^+ from solvent and will form $\text{C}_6\text{H}_5\text{NH}_3^+$ and hence no longer available for extension of conjugation.

3. Hyperchromic Effect or Shift

It is the effect by virtue of which intensity of the absorption maximum increases. Introduction of an auxochrome increases the value of the intensity of the wavelength absorbed.

4. Hypochromic Effect or Shift

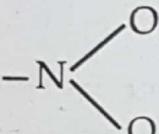
It is the effect by virtue of which the intensity of the absorption maxima decreases. This effect or shift is called Hypochromic effect or shift. The introduction of the group which distort the geometry of the molecule cause hypochromic effect. For example $\epsilon_{\text{max}}/\text{intensity}$ for biphenyl and 2-methyl biphenyl is 19000 and 10250 respectively. The substitution of methyl group in biphenyl causes hypochromic shift due to distortion caused by it.

1.10.11 Applications of Ultraviolet-Visible Spectroscopy

1. Detection of Functional Group

This technique is very useful in detecting the presence or absence of the chromophore. The absence of a band at a particular wavelength may be regarded as evidence for the absence of a particular group in the compound.

Table 1.1 λ_{\max} absorbed by different chromophores

Chromophore	Example	Type of Excitation	λ_{\max} (nm)
$>\text{C}=\text{C}<$	$\text{CH}_2 = \text{CH}_2$	$\pi \rightarrow \pi^*$	171
$-\text{C}\equiv\text{C}-$	$\text{HC}\equiv\text{CH}$	$\pi \rightarrow \pi^*$	173
$>\text{C}=\ddot{\text{O}}:$	$(\text{CH}_3)_2\text{CO}$	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	189 279
	CH_3NO_2	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	201 274

2. Extent of Conjugation

λ_{\max} value increases with increase of conjugation. It is found that the absorption occurs at 420 nm if eight double bonds are present in a conjugated system. Such as alkene will appear coloured to human eye.

3. Distinction between Conjugated and Non-conjugated Compounds

The following isomers can be easily distinguished :

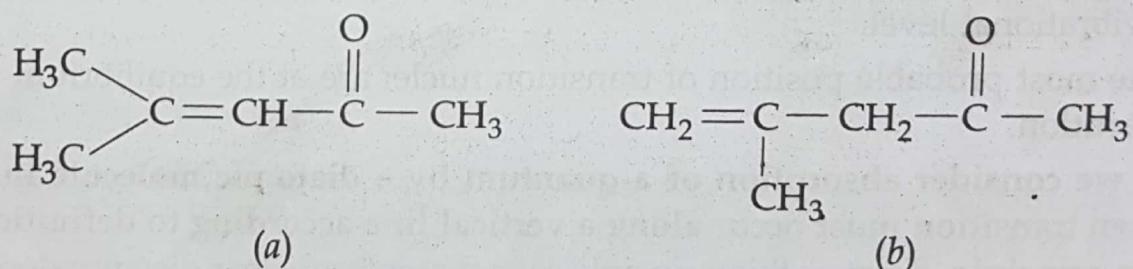


Fig. 1.18 (a) Conjugated and non-conjugated (b) dienes.

$n \rightarrow \pi^*$ transitions for (a) will appear at longer wavelength as compared to $n \rightarrow \pi^*$ transitions for (b) because of conjugation present in (a).

A bathochromic and hyperchromic shift can be seen while comparing the spectrum of conjugated trienes and conjugated dienes.

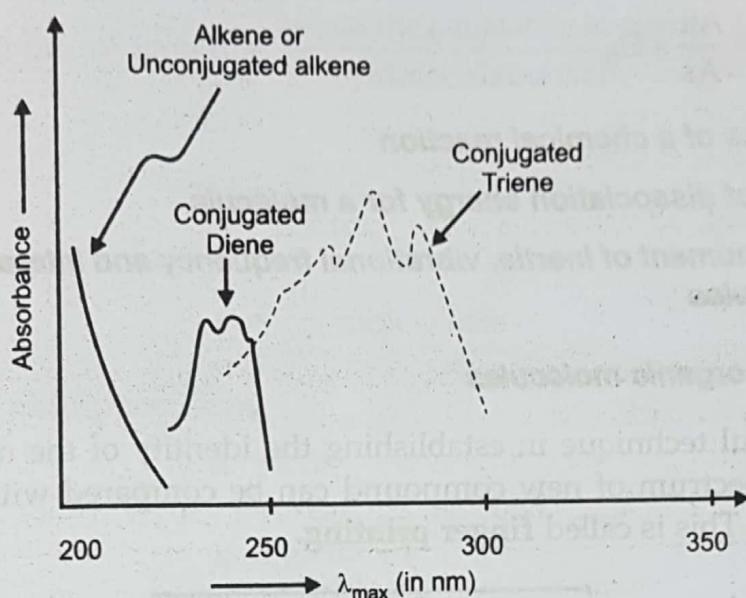


Fig. 1.19 Absorption in conjugated and unconjugated systems

4. Distinction between cis and trans isomers

The cis isomers show smaller value of λ_{max} as compare to trans isomers.

5. Detection of Impurities

U.V. visible spectroscopy is very useful technique in the detection of impurities. **Benzene is a common impurity in cyclohexane.** It can be easily detected as cyclohexane shows absorption at 255 nm while benzene shows at 204 nm.

6. Control of Purification

The process of purification should be continued till the compound which is being purified, stops showing signals of impurity. When there is no signal for impurity, purification is complete.

7. Detection of Unknown concentration (if absorbance is given)

For a particular spectrophotometer ϵ and x values are the same with every sample. Now if there is a sample i.e. unknown and a standard (i.e. sample of known concentration and absorbance).

$$\underline{\epsilon} = \frac{A_s}{C_s x}, C_s = \text{conc. of standard i.e. sample of known concentration}$$

$$\epsilon = \frac{A_\mu}{C_\mu x}, C_\mu = \text{conc. of unknown i.e. sample}$$

$$\frac{A_s}{C_s x} = \frac{A_\mu}{C_\mu x}$$

$$C_\mu = \frac{A_\mu}{A_s} \times C_s$$

8. Study of kinetics of a chemical reaction

9. Determination of dissociation energy for a molecule

10. Calculation of moment of Inertia, vibrational frequency and interatomic distances of diatomic molecules

11. Identification of organic molecules

It is very useful technique in establishing the identity of the new and unknown compounds. The spectrum of new compound can be compared with spectrum of the known compounds. This is called **finger printing**.

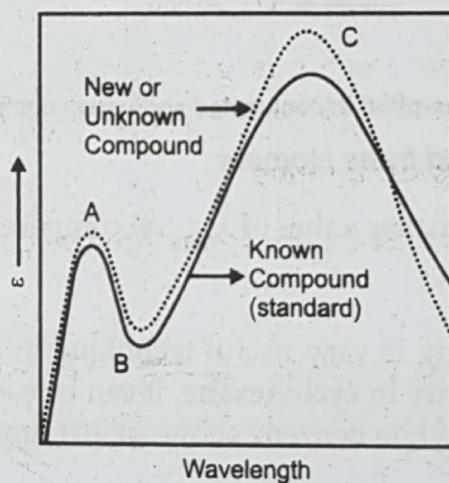


Fig. 1.20 Isobestic Points

The points A, B and C marked in the figure above where the λ_{max} value is same for the two compounds are called **Isobestic Points**.

12. o-p Hydrogens

The study of electronic band spectra has led to the important discovery that hydrogen exist in two forms, i.e. ortho and para. It has been established that ortho and para form exist in the ratio of 3 : 1 by comparing the intensities of the two kinds of lines.

13. Determination of Molecular weight

If we have 1% solution of a compound in 1 cm thick cell, then its molecular weight (M) can be determined.

1% solution means :

1 gm/100 ml of solution

or 10 gm/1000 ml of solution

hence Concentration = 10 gm/litre

As concentration is in moles/litre, then

$$n \text{ (no. of moles)} = \frac{\text{wt. of the substance in grams}}{\text{Molecular weight}}$$

$$n = \frac{W}{M}$$

$$n = \frac{10}{M} \text{ moles/litre}$$

According to absorption laws,

$$A = \epsilon cx$$

$$A = \epsilon \times \frac{10}{M} \times 1$$

If ϵ of the spectrophotometer is given and A can be studied from the spectrophotometer. The value of M (Molecular weight) can be calculated.

14. Preference over two Tautomeric forms

If a molecule exists in two tautomeric forms, preference of one over the other can be detected by U.V. spectroscopy.

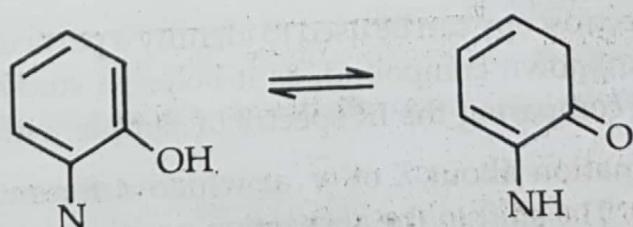
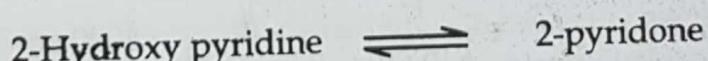


Fig. 1.21 Tautomers

The spectra of these two compounds were found to favour 2-pyridone which is α, β -unsaturated ketone and equilibrium is shifted to right.

15. Distinction between axial and equatorial conformations

16. Other Physiochemical Studies

U.V. visible spectrophotometry has been useful in determination of dissociation constant of acids and bases, heats of formation of molecular addition compounds and complexes in solution and empirical formulae of complexes in solutions.

1.11 INFRARED SPECTROSCOPY

1.11.1 Introduction

The infrared region extends from $0.8\text{ }\mu$ to $200\text{ }\mu$ in wavelength (or 12500 to 50 cm^{-1} in wave number). The region from $0.8\text{ }\mu$ to $2.5\text{ }\mu$ is called near infrared region and from $15\text{ }\mu$ to $200\text{ }\mu$ is called far Infrared region. The ordinary Infrared region extends from 2.5 to 15μ (4000 – 6670 m^{-1}). This is most important region for an organic chemist.

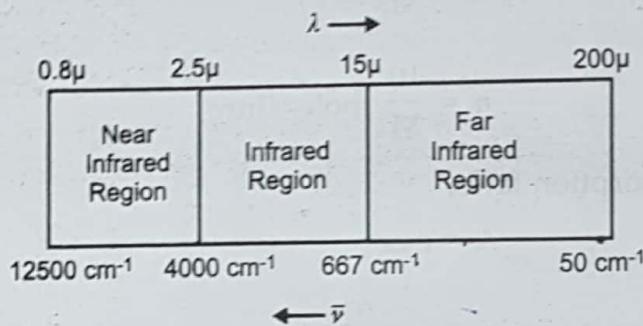


Fig. 1.22 Infrared Regions

The absorption of Infrared radiation can be expressed either in terms of wavelength (λ) or wave number ($\bar{\nu} = \frac{1}{\lambda}$).

$$10^4 \mu = 1 \text{ cm}$$

(μ represents microns)

$$\text{If } \lambda = 2.5 \mu = 2.5 \times 10^{-4} \text{ cm}$$

$$\bar{\nu} = \frac{1}{\lambda \text{ in cm}} = \frac{1}{2.5 \times 10^{-4}} = 4000 \text{ cm}^{-1}$$

Infrared (IR) spectroscopy can be used to identify a particular compound or to predict the structure of an unknown compound, as it helps in studying the presence of many functional groups by comparing the IR spectra of sample with the standard chart/table.

The latter has information about λ or $\bar{\nu}$ at which different functional groups show absorption of IR light. The shift in the absorption position w.r.t. expected value, helps in predicting the factor responsible for this shift. Hence this technique is very informative. The region below 1500 cm^{-1} of IR is called **Finger Print Region**. Identification of unknown compounds is done in this region. No two compounds can have same pattern of peaks in finger print region. Some molecules containing the same functional group show similar absorption above 1500 cm^{-1} , but their spectra differ in finger print region.

1.11.2 Selection Rule (Which type of molecules are IR active)

Electric dipole moment of molecule must change when the atoms are displaced relative to one another or when molecule vibrates. Such vibrations are infrared active. It is very important to note here that molecule need not have a permanent dipole moment. But change of dipole moment during vibration is required. (Molecule may even have zero dipole moment but during vibration it must change the dipole moment). There are

some vibrations which do not affect the molecule's dipole moment e.g. stretching motion (a vibration) of a homonuclear diatomic molecule), so they neither absorb nor generate radiation, such vibrations are said to be infrared inactive. Homonuclear diatomic molecules are IR inactive as their dipole moment remains zero. But heteronuclear diatomic molecules show the change in dipole moment and hence are IR active.

1.11.3 Why molecules absorb IR radiation ?

During vibration of a molecule, if there occurs a change in dipole moment, it generates oscillating electrical field. If this molecule is exposed to IR radiation, and frequency of this oscillating electric field matches (or is equal to) the frequency of fluctuating electric field of IR radiation, there occurs resonance and hence energy can be transferred from IR radiation to the molecule (absorption IR spectrum) or vice versa (emission IR spectrum). Infra-red inactive molecules do not show IR spectrum.

Result of Absorption of IR Light

The extent of absorption depends on the wavelength/frequency of IR radiation passing through the molecule and structure of the molecule. **The gain in energy leads to variety of vibrations in the molecules.** Hence corresponding to each absorption, there appears a signal in the spectrum. Every signal refers to a particular vibration shown by a particular functional group. This is called **IR spectrum**.

1.11.4 Simple Harmonic Oscillator

1.11.4.1 Introduction

Vibrations in a simple Heteronuclear diatomic molecule are the same as vibrations in simple harmonic oscillator. Hence a vibrating simple diatomic molecule can be considered as a simple harmonic oscillator which obeys Hooke's law.

According to Hooke's law, restoring force is proportional to extent of displacement from the position when the masses are stretched or compressed away from the resting position.

$$\text{i.e.} \quad \text{Restoring force} = -Kx$$

where K is constant of proportionality i.e. force constant. It is restoring force per unit displacement from the resting position. The negative sign indicates that restoring force tends to pull the spring back to its original position.

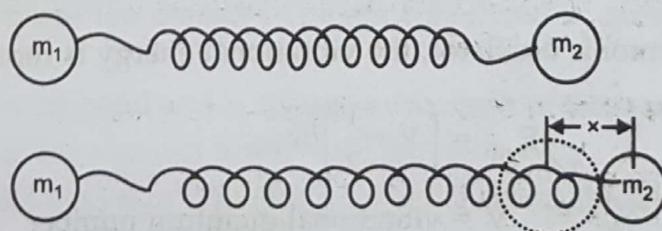


Fig. 1.23 A Simple Harmonic Oscillator

When the spring is compressed, it exerts a force to expand, when it is stretched, exerts a force to pull back.

As diatomic molecule behaves as simple harmonic oscillator, each chemical bond acts as a spring, connected to two atoms of masses m_1 and m_2 . So the above fig. 1.23. can represent vibration in diatomic molecule. A set of masses (atoms) that are connected to spring (chemical bond), tends to settle into specific motion, when disturbed. The masses (atoms) vibrate with frequency that depends on the masses (mass of atoms) and strength of spring (chemical bond). Such vibrations which occur at particular frequencies are measured in infrared spectra.

For simple harmonic motion of spring (diatomic molecule), frequency of vibration is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (\text{Hooke's Law})$$

This equation helps in interpreting/studying the nature of vibrational-rotational spectra.

1.11.4.2 Selection Rule

For simple harmonic oscillator $\Delta V = \pm 1$ (+ sign is for absorption and - sign is for emission). But it is reduced to $\Delta V = +1$, because vibrational spectrum is studied for absorption only. Selection rule for rotational transitions is $\Delta J = \pm 1$ during the vibrational transition of a diatomic molecule. [The selection rule may allow $\Delta J = 0$ if the molecule also possesses angular momentum about its axis].

1.11.4.3 Vibration Energy for Simple Harmonic Oscillator (SHO)

1.11.5 Hooke's Law or Vibrational Frequency

(3)

The value of stretching vibrational frequency (ν) of a bond can be calculated theoretically by using Hooke's law. It is represented as :

$$\frac{\nu}{c} = \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \text{ where}$$

or $\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ = reduced mass

where m_1 and m_2 are the masses of atoms concerned in grams or kilograms in a particular bond.

K = force constant of bond and is related to strength of the bond.

For a single bond, the value of $K = 5 \times 10^5 \text{ gm/sec}^2$.

It becomes double than this value for double bond and three times than this value for a triple bond.

c = velocity of light = $3 \times 10^{10} \text{ cm/sec}$.

With the increase in bond strength, (K) stretching vibrational frequency (ν) increases and with increase of reduced mass, value of ν decreases.

- (i) C-C stretching vibration is expected to absorb less frequency as compare to C=C, because $K_{C-C} < K_{C=C}$.
- (ii) In case of O-H functional group, stretching vibration takes place at higher frequency as compare to C-C. This is so because $\nu \propto \frac{1}{\mu}$ as $\mu_{O-H} < \mu_{C-C}$.

1.11.6 Vibrations shown by a Polyatomic Molecule (Basic Principle)

Absorption in IR region is because of change in vibrational and rotational levels because a single change in vibrational energy is accompanied by large no. of rotational energy changes. So, absorption of IR radiation brings predominant changes in the vibrational energy. Atoms in the molecule are not held rigidly. It can be visualized as balls tied with springs where balls are atoms and springs are bonds. To explain vibrations in molecules let us take example of AX_2 types of groups. When IR light passes through the sample, molecule shows two types of vibrations :

- I. Stretching
- II. Bending

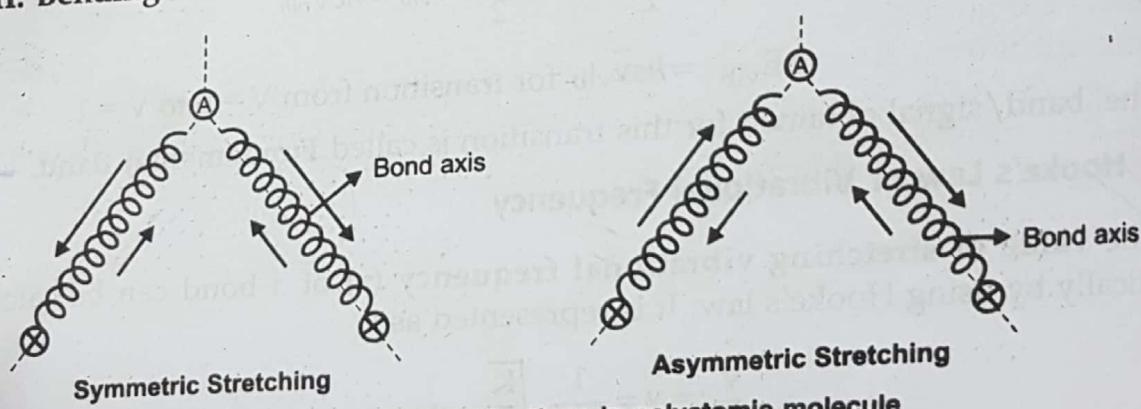


Fig. 1.25 Stretching vibrations in polyatomic molecule

I. Stretching

When distance between two atoms is increasing or decreasing but atoms remain in same bond axis i.e. no change in the bond angle.

Stretching vibration is of two types :

- Symmetric. Movement of atoms w.r.t. particular atom is in the same direction.
- Asymmetric. One atom approaches the central atom while the other departs from it.

II. Bending

Position of atoms changes w.r.t. original bond axis i.e. bond angle changes but internuclear distance does not change. There are four types of bending vibrations.

- Scissoring. When two atoms approach each other.

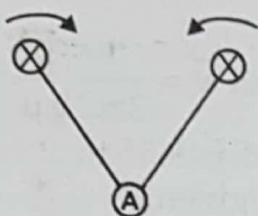


Fig. 1.26 (a) Scissoring

(b) **Rocking.** When the atoms is in the same direction.

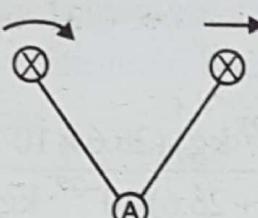


Fig. 1.26 (b) Rocking

(c) **Wagging.** When two atoms move above or below the plane w.r.t. central atom.

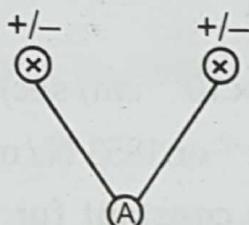


Fig. 1.26 (c) Wagging

(d) **Twisting.** One of the atom move up and other moves below the plane w.r.t. central atom.

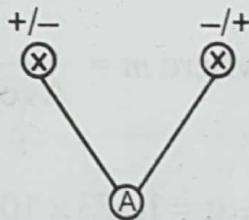


Fig. 1.26 (d) Twisting

[positive sign (+) represents motion from the page towards the reader and negative sign (-) represents motion away from the reader].

Examples of AX_2 groups are $-\text{CH}_2-$, $-\text{NO}_2-$, $-\text{NH}_2$ etc.

These vibrations are called **Fundamental vibrations**. Sometimes **overtones** also appear in addition to fundamental transitions or fundamental vibrations. **Beats** are also observed sometimes which arise due to combination or different frequencies. **For a particular bond, stretching vibration appears at higher frequency as compared to bending vibration hence**, in the IR spectrum absorption band appearing for stretching vibration is at higher frequency as compare to band appearing for bending vibration.

fundamental ones.

1.11.8 Factors affecting Wave Number Value (\bar{v}) or Vibrational Frequency

1. **Electronic Effect.** Electronic effects include inductive effect, mesomeric effects, field effects etc. Under the influence of electronic effects, force constant or the bond strength changes and its absorption frequency shifts from normal value. The introduction of a group which results into $+I$ effect, causes lengthening/

weakening of the bond hence the value of k (force constant) is lowered and wave number of absorption decreases for carbonyl group ($>\text{C}=\text{O}$ group)

e.g. \bar{v} formaldehyde (HCHO) = 1750 cm^{-1}

\bar{v} of acetaldehyde (CH_3CHO) = 1745 cm^{-1}

\bar{v} of acetone (CH_3COCH_3) = 1715 cm^{-1}

This decrease in the wave number is because of introduction of an alkyl group ($-\text{CH}_3$) with +I effect, which results into lowering the value of K and hence value of \bar{v} decreases. The **introduction of an electronegative atom / group** results into **-I effect i.e.** electron with drawing inductive effect which results into **increase of bond order** and hence value of K (Force constant) increases.

Hence \bar{v} also increases as :

e.g. \bar{v} value for acetone CH_3COCH_3 is 1715 cm^{-1}

\bar{v} value of chloroacetone $\text{ClCH}_2\text{COCH}_3$ is 1725 cm^{-1}

\bar{v} value of dichloroacetone $\text{Cl}_2\text{CHCOCH}_3$ is 1740 cm^{-1}

\bar{v} value of tetrachloroacetone $\text{Cl}_2\text{CHCOCHCl}_2$ is 1750 cm^{-1} and 1778 cm^{-1} .

This increase in value of \bar{v} is because of addition of - Cl or electromagnetics atom, which has - I effects.

2. Effect of Conjugation. Conjugation lowers the absorption frequency of C=O bond.

3. Hydrogen-bonding. Infrared technique is used to distinguish between two types of H-bonds i.e. **intermolecular** and **intramolecular** H-bond. H-bond results into (i) shift of \bar{v} for the O—H bond, towards lower value from the normal value. (ii) **Intermolecular H-Bond results into formation of a broad band at lower \bar{v} value** and intramolecular H-Bond results into a sharp band at lower \bar{v} value than the \bar{v} value at which non-hydrogen bonded O—H group (free – OH group) will show its signal.

Dilution reduces the intermolecular H-bond but has no effect on intramolecular H-bond, so if the sample is analysed after the dilution and if it shows diminishing of the band (that was at lower \bar{v} value and was expected due to H-bonding), it results that band at lower \bar{v} value was because of intermolecular H-bond. But if after dilution, sample does not show any effect on the band appearing at low \bar{v} value, it results that band is because of intra molecular H-bond. This is so because dilution reduces intermolecular H-bond but it has no effect on intramolecular H-bond.

4. Coupled Vibrations. Coupled vibrations also affect the expected value of \bar{v} .

The actual value of \bar{v} varies from the expected value.

1.11.9 Applications of Infrared Spectroscopy

Infrared spectroscopy gives more information than electronic spectroscopy. In IR spectroscopy all the functional groups absorb characteristically within a definite range. The shift in the absorption position (\bar{v}) change with change in structure of sample molecule.

The particular position of the band not only tells us about the type of functional group present but also tells us about the environment of the sample molecule. (If the spectrum has a strong band between $1900\text{-}1600\text{ cm}^{-1}$ the presence of $\text{C}=\text{O}$ group may be there)

Aldehydes can be recognised from its characteristic C-H stretching at 2820 cm^{-1} (sym) and 2720 cm^{-1} (asym), ester can be recognized from C-O stretching at 1240 cm^{-1} and amides show absorption for N-H stretching at 3400 cm^{-1} , 3500 cm^{-1} in addition to their bands for $\text{C}=\text{O}$ at particular range.

In case of alcohol there may be two bands for $-\text{OH}$ group. One for free $-\text{OH}$ group and other for $-\text{OH}$ group showing hydrogen bonding. So overall a very useful technique.

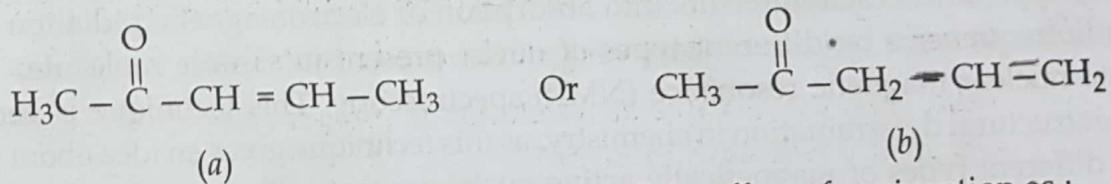
The application of IR spectroscopy can be explained as :

1. Structural Determination

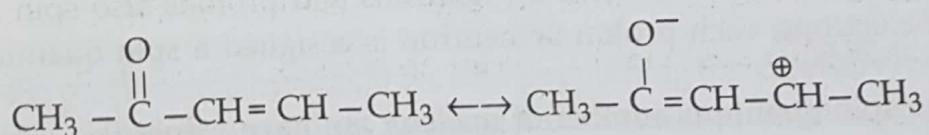
This is a very useful technique to determine different aspect of the structure of the sample molecule.

(i) **Detection of functional groups present in the sample.** By comparing the \bar{v} of the signals appearing in IR spectrum of the sample w.r.t. standard chart, different functional groups can be confirmed.

(ii) **Detection of Conjugation.** It is a very useful technique in detection of conjugation. For example molecular formula of a sample molecule is $\text{C}_5\text{H}_8\text{O}$. Its structural formulae can be :



But if the structural formula is (a), there will be effect of conjugation as :



Conjugation will result into decrease in value of K i.e. bond constant/force constant between C and O. It will result into decrease in value of \bar{v} for $\text{C}=\text{O}$ less than expected. It means the sample molecule $\text{C}_5\text{H}_8\text{O}$ has structural formula (a), Otherwise (b).

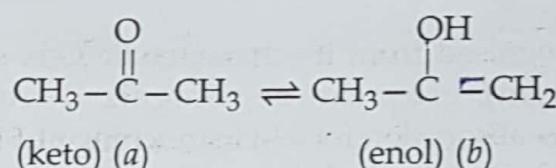
(iii) **Detection of axial and equatorial $-\text{OH}$ group.** The Number of axial and equatorial $-\text{OH}$ groups attached to the sample molecule can be detected

$\bar{v}_{\text{axial}} > \bar{v}_{\text{equatorial}}$. Hence distinction can be made between axial and equatorial $-\text{OH}$ group attached.

(iv) **Distinction between Inter and Intra molecular hydrogen bonding.** As explained in the factor affecting \bar{v} .

(v) **Helpful in studying the Keto-enol Tautomers**

Keto-enol tautomers can be distinguished from each other by using IR-Spectroscopy e.g.



(a) form is keto form, it is different from enol form (b) by the fact that $>\text{C}=\text{O}$ group is present but in case of enol, $>\text{C}=\text{O}$ group is absent by instead, $-\text{OH}$ group and $>\text{C}=\text{C}<$ groups are present. Hence the two forms can be distinguished from each other.

2. Bond distance and Bond Angle

The force constant responsible for the absorption peaks can be used to calculate bond distance and bond angle in some simple cases.

1.12 MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance involves interaction of oscillating magnetic field of an electromagnetic radiation with magnetic field of the nucleus (magnetic), when these (electromagnetic radiation and nucleus) are placed in an external static magnetic field. This type of interaction results into absorption of electromagnetic radiation of different radiofrequencies by different types of nuclei present in sample molecule. This results into nuclear magnetic resonance (NMR) spectroscopy. This technique is very useful in the structural determination in chemistry, as this technique gives an idea about the number of different types of magnetically active nuclei present in the sample molecule.

Like electrons, particles of nucleus i.e. neutrons and protons also spin about their own axis. Like electrons, each proton or neutron is assigned a spin quantum number

equal to $\frac{1}{2}$. The spin quantum number of nucleus can have values $0, \frac{1}{2}, 1, 1\frac{1}{2}, 2$ etc.

depending on number of neutrons and protons having parallel and antiparallel spins. The spin quantum number of nucleus is represented as I. It has been found that

- (i) For nuclei in which sum of protons and neutrons is even as well as number of each of them is even, $I = 0$. For example $I = 0$ for ${}^4_2\text{He}$, ${}^{12}_6\text{C}$, ${}^{16}_8\text{O}$, ${}^{32}_{16}\text{S}$ etc.

Assignment - 8

Q 2

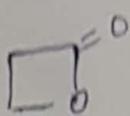
Answer :-



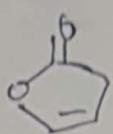
1650 cm^{-1}



1775 cm^{-1}



1840 cm^{-1}



1800 cm^{-1}

Q 6 Answer :- $200 - 380 \text{ nm}$ UV region
and beyond 380 nm , up to 800 nm is
visible region.

Q 7 Answer $\pi \rightarrow \pi^*$ transition at 210 nm (11,500); Allowed
 $n \rightarrow \pi^*$ transition at 315 nm . (15); forbidden

Q 8 Answer In $(\text{CH}_3)_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}=\text{CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$, there is extention
in conjugation because of which, the ΔE decreases,
and λ_{abs} increases in comparison to $\text{CH}_2=\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}=\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{CH}_3$.
In later there is no conjugation.

Q 9 Answer! - Presence of methyl group
distorts the geometry of the molecule.

Molecules, $-\text{CH}_3$ gp has Electron
releasing inductive effect + I effect
which decreases conjugation, so
it causes hypsochromic shift