

SPECTROSCOPY

Molecular spectroscopy may be defined "the study of interaction of electromagnetic radiations with molecules". Molecular emission & absorption provides useful information regarding the molecular structure.

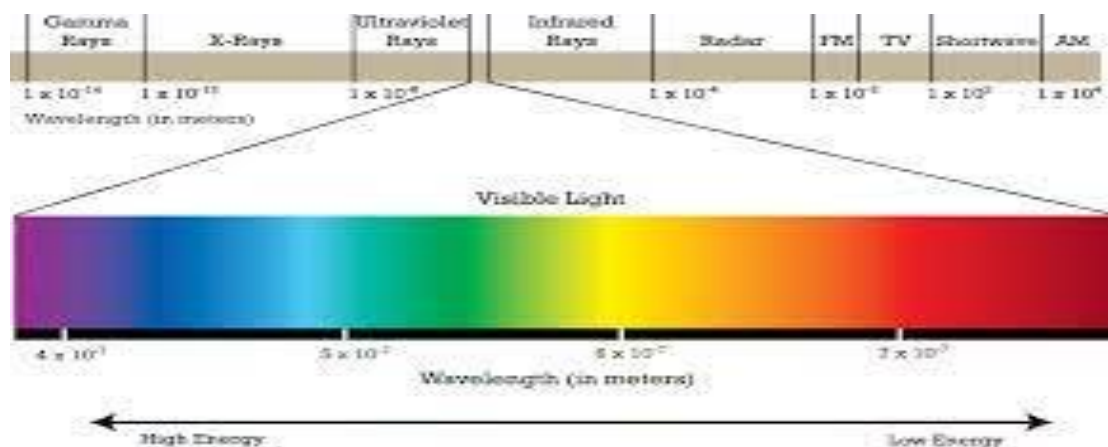
The energy changes within a molecule during emission or absorption of electromagnetic radiation are quantised. The energy changes in a molecule are specified in terms of frequency(ν), wavelength(λ) and wavenumber ($\bar{\nu}$) as:

Planck relation:

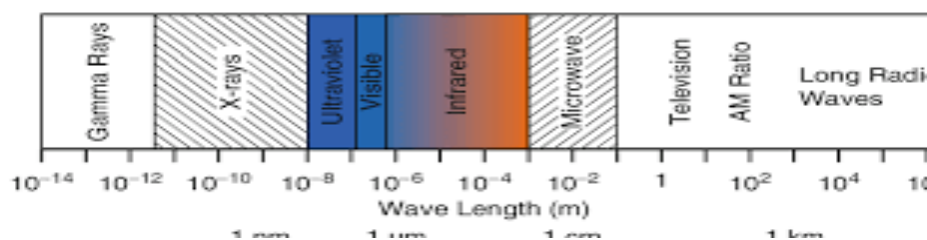
$$E = h\nu = \frac{hc}{\lambda}$$

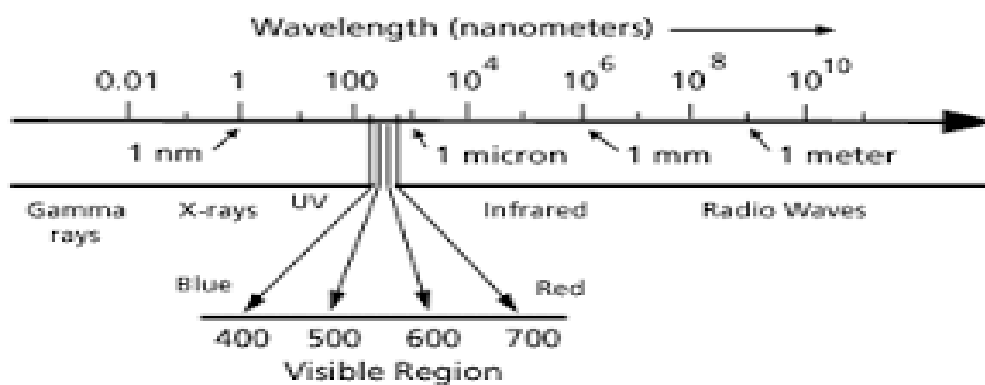
where:

E = energy
h = Plank constant
 ν = frequency
c = speed of light
 λ = wavelength



as, white areas denote atmospheric transparency known as the window





Electromagnetic Spectrum

Types of energy present in molecules:

- (i) *Translational energy* : Is concerned with the overall movement of the molecules along the three axes. It is significant only in gases and to a lesser extent for liquids.
- (ii) *Rotational energy*: Involves the spinning of molecules about the axes passing through their centre of gravity.
- (iii) *Vibrational energy* : Involves change in the distribution of electrons by the promotion of electrons to higher levels on absorption of energy.

Difference between the energy levels for:

- (i) Electronic energy change = $100-10^4$ KJ mol⁻¹
- (ii) Vibrational energy change = $1-100$ KJ mol⁻¹
- (iii) Rotational energy change = $0.01-1$ KJ mol⁻¹

	Microwave	Infrared	Ultra violet & visible
Radiation absorbed	$\nu = 3 \times 10^{10} - 3 \times 10^{12}$ Hz $-\nu = 1 - 100$ cm ⁻¹	$\nu = 3 \times 10^{12} - 3 \times 10^{14}$ Hz $= 100 - 10^4$ cm ⁻¹	$\nu = 3 \times 10^{14} - 3 \times 10^{16}$ Hz $= 10^4 - 10^6$ cm ⁻¹
Effect on the molecule	Change in rotational energy levels of the molecule	Change in the vibrational & rotational energy levels of the molecule	Change in electronic energy levels within the molecule
Information obtained	Calculation of force constant, bond length & bond angle	Detection of functional groups, calculation of bond length, bond angle & Force constant	In qualitative and quantitative analysis

ULTRAVIOLET (UV) & VISIBLE (VIS) SPECTRA:

Absorption of radiation in the UV (wavelength range 200-400nm) & visible (wavelength range 400-750nm) region of the electromagnetic spectrum results in transition between

electronic levels, because the energy changes are relatively large and this corresponds to 100-100,000KJ mol⁻¹.

Origin of absorption bands in UV & Visible spectra:

According to M.O theory, the interaction of atomic orbitals leads to the formation of bonding and antibonding molecular orbitals. Depending upon the nature of the atomic orbitals involved, the bonding orbitals may be of:

- (i) Sigma (σ) type: In which the electron density is concentrated along the inter nuclear axis,
- (ii) Pi (π) type: In which the electron density is concentrated above and below the inter nuclear axis.

Fig depicts the electron density probability cantors for electrons occupying σ and π bonding and σ^* and π^* (antibonding) orbitals while depicts the relative energies of bonding, antibonding and nonbonding (n) molecular orbitals.

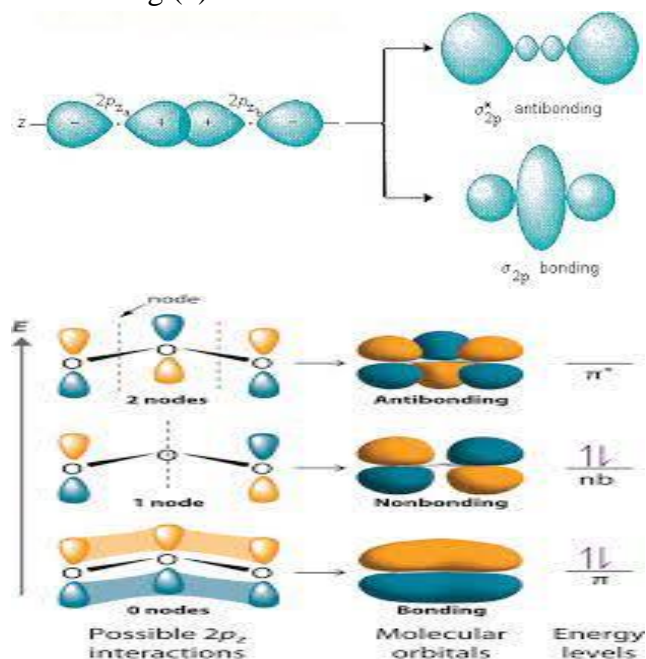


Fig: Shape and relative energies of molecular orbitals

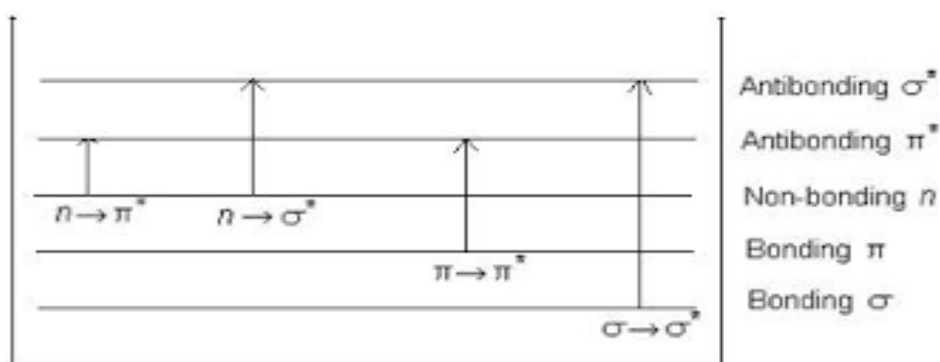


Fig: Relative energies of molecular orbitals and possible transitions between them.

When excitation occurs, an electron from one of the filled σ , π or n molecular orbitals get excited to vacant σ^* and π^* (antibonding) molecular orbitals.

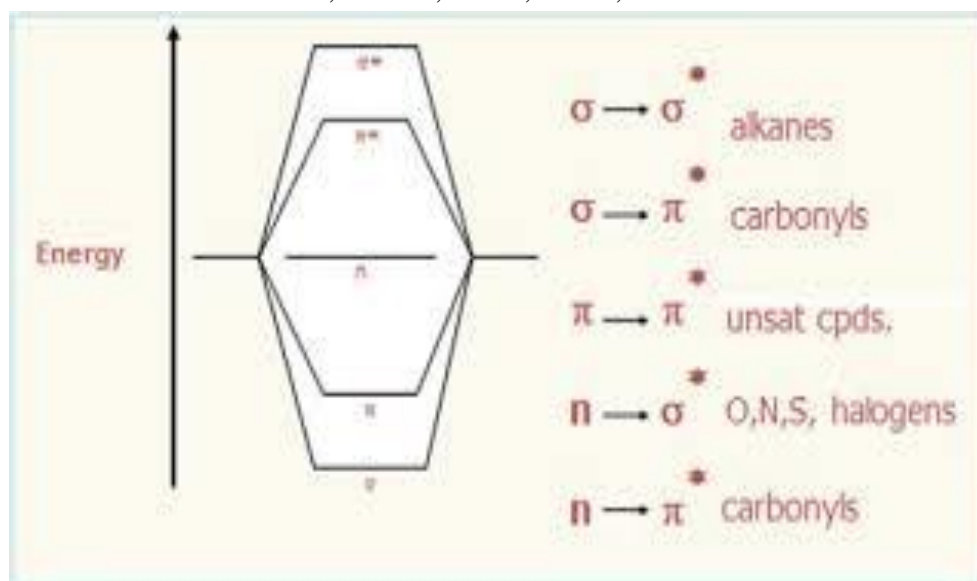
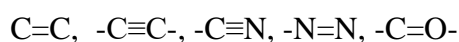
Since σ electrons require a high energy for excitation to σ^* , so order of decreasing energy for the absorption is :



out of the above possible transitions , the last three ones account for the absorption in 200-800nm region of electromagnetic radiation. First three transition much require more energy. So only molecules with n or π electrons give rise to characteristic spectra in the region 200-800 nm of electromagnetic radiation. It may be pointed that alkanes absorb in region below 200 nm.

Chromophores: The molecule having n or π electrons is essentially responsible for absorption, and these fragments, are known as chromophores.

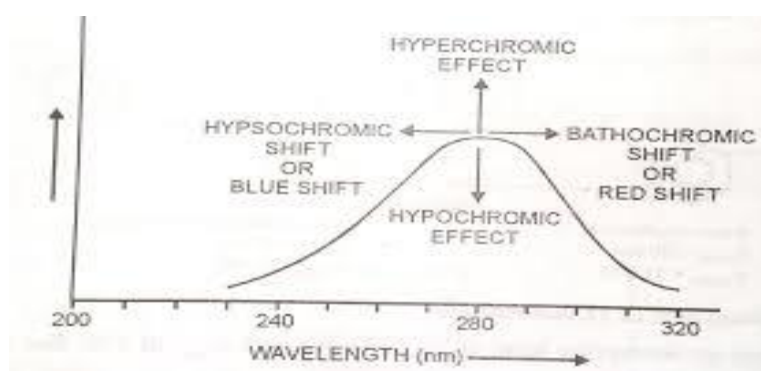
Simple chromophores.



Undergoes $\pi \rightarrow \pi^*$ transitions in the short wavelength regions of UV radiation

UV / visible Spectroscopy

1. **Bathochromic shift** (red shift)
 - lower energy, longer wavelength
 - CONJUGATION.
2. **Hypsochromic shift** (blue shift)
 - higher energy, shorter wavelength.
3. **Hyperchromic effect**
 - increase in intensity
4. **Hypochromic effect**
 - decrease in intensity



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• Bathochromic Shift (Red Shift)

- When absorption maxima (λ_{max}) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.
- The effect is due to presence of an auxochrome or by the change of solvent.
- e.g. An auxochrome group like $-\text{OH}$, $-\text{OCH}_3$ causes absorption of compound at longer wavelength.

Absorption Characteristics of Some Common Chromophores




Chromophore	Example	Solvent	λ_{\max} (nm)	ϵ_{\max}	Type of transition
Alkene	$C_6H_{13}HC=CH_2$	<i>n</i> -Heptane	177	13,000	$\pi \rightarrow \pi^*$
Alkyne	$C_5H_{11}C \equiv C-CH_3$	<i>n</i> -Heptane	178 196 225	10,000 2,000 160	$\pi \rightarrow \pi^*$ — —
Carbonyl	$\begin{array}{c} O \\ \\ CH_3CCH_3 \end{array}$	<i>n</i> -Hexane	186 280	1,000 16	$n \rightarrow \sigma^*$ $n \rightarrow \pi^*$
	$\begin{array}{c} O \\ \\ CH_3CH \end{array}$	<i>n</i> -Hexane	180 293	Large 12	$n \rightarrow \sigma^*$ $n \rightarrow \pi^*$
Carboxyl	$\begin{array}{c} O \\ \\ CH_3COH \end{array}$	Ethanol	204	41	$n \rightarrow \pi^*$
Amido	$\begin{array}{c} O \\ \\ CH_3CNH_2 \end{array}$	Water	214	60	$n \rightarrow \pi^*$
Azo	$H_3CN=NCH_3$	Ethanol	339	5	$n \rightarrow \pi^*$
Nitro	CH_3NO_2	Isooctane	280	22	$n \rightarrow \pi^*$
Nitroso	C_4H_9NO	Ethyl ether	300	100	—
			665	20	$n \rightarrow \pi^*$
Nitrate	$C_2H_5ONO_2$	Dioxane	270	12	$n \rightarrow \pi^*$

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Auxochromes:

Polar groups such as $-OH$, OR , $-NH_2$, $-SH$ AND $-X$ having unshared pair of electrons and may show absorption above 190 nm. Such groups are called auxochromes, when conjugated with **chromophores**.

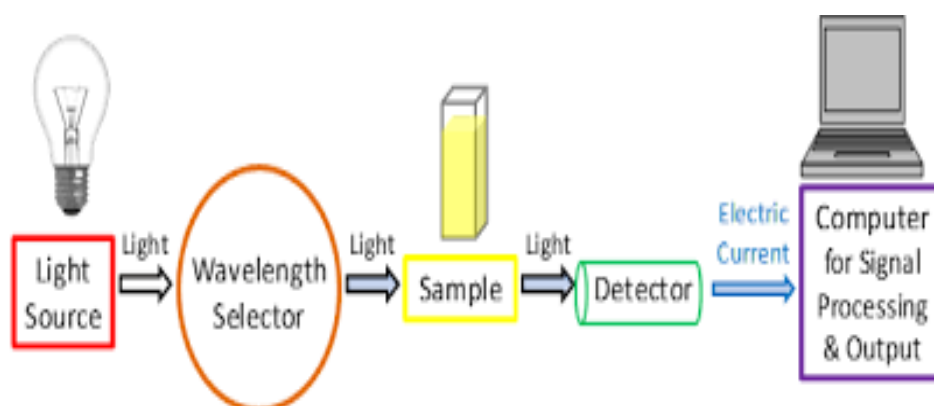
Compounds containing carbon-oxygen double bond also absorb light in the UV region. Ex. Acetone broad absorption peak at 280 nm, corresponding to excitation of an electron from a non bonding to π^* orbita of the C-O double bond. If C-O double bond is conjugated with C-C double bond, then the absorption maxima correspond to $n \rightarrow \pi^*$ excitation and $\pi \rightarrow \pi^*$ excitation. The $n \rightarrow \pi^*$ excitation absorption maxima occurs at a longer wavelength, but is much weaker. For ex. The compound, $CH_2=CH-CO-CH_3$ gives $n \rightarrow \pi^*$ λ_{\max} at 324 nm and $\pi \rightarrow \pi^*$ λ_{\max} at 219 nm.

1.	Benzene		$\lambda_{\text{max}} = 255 \text{ nm}$
	Phenol		$\lambda_{\text{max}} = 270 \text{ nm}$
	Aniline		$\lambda_{\text{max}} = 280 \text{ nm}$
2.	-	$-\text{CH}=\text{CH}-$	$\lambda_{\text{max}} = 190 \text{ nm}$
	-	$-\text{CH}=\text{CH}-\text{NH}_2$	$\lambda_{\text{max}} = 230 \text{ nm}$

• Table: Examples of the effect of auxochrome

Instrumentation:

In visible-UV spectrometer, a beam of light is split into two equal halves. One-half of the beam (the sample beam) is directed through a transparent cell containing a solution of the compound being analysed and one-half (the reference beam) is directed through an identical cell that contains only the solvent. The instrument is so-designed that it can compare the intensities of the two beams at each wavelength of the region. If the compound absorbs light at a particular wavelength, then intensity of the sample beam (I) will be less than that of the reference beam (I_0). The instrument gives output graph – a plot of the wavelength of the entire region versus the absorbance (A) of the light at each wavelength. Where absorbance (A) = $\log(I_0/I)$. Such a graph is known as absorption spectrum.



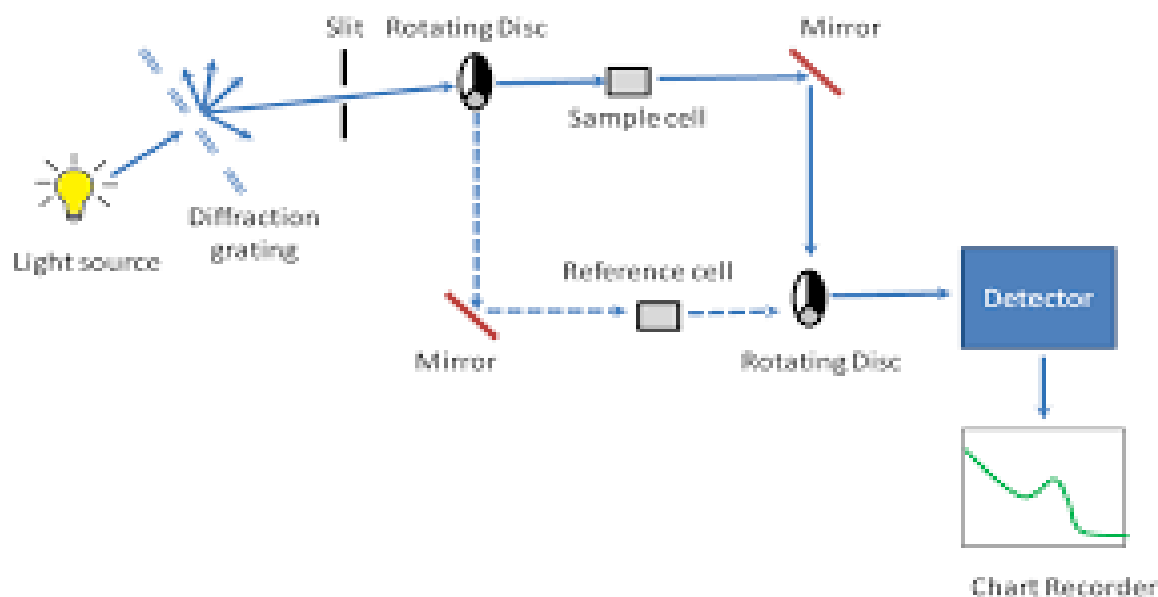
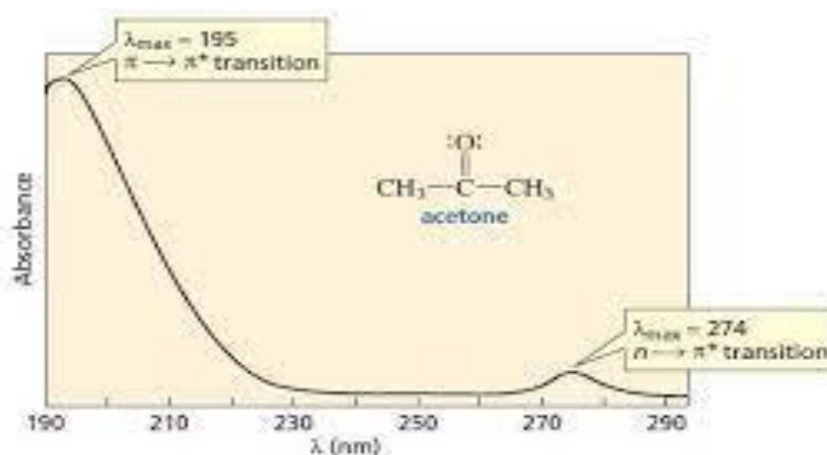


Fig: Schematic diagram for a typical visible-UV spectrometer

Examples of visible-UV spectroscopy:

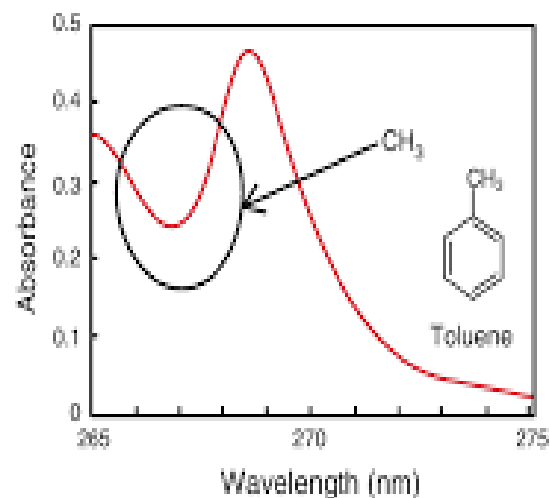
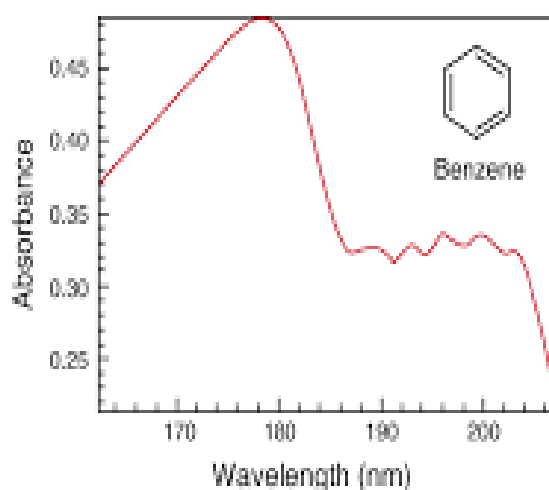
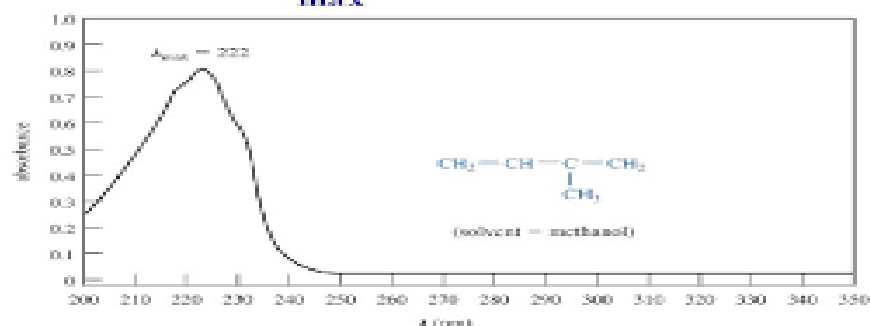
Arenes are organic compounds that contain one or more benzene ring. The electrons in benzene are spread around the hexagonal ring of carbon atom. The large absorptions are caused by electrons moving between $\pi \rightarrow \pi^*$ orbitals. The small peak and troughs are caused by vibration of the molecule. The large peak occur around 250 nm for benzene & 280 nm for naphthalene.

UV-visible absorption spectrum of propanone (CH_3COCH_3) has a peak near 280 nm, corresponding to $n \rightarrow \pi^*$ transition.



UV Spectrum of Isoprene

$$\lambda_{\max} = 222 \text{ nm}$$



Beer-Lambert Law Statement:

The Beer-Lambert law states that: For a given material sample path length and concentration of the sample are directly proportional to the absorbance of the light.

The Beer-Lambert law is expressed as: $A = \epsilon lc$

Where, A = is the amount of light absorbed for a particular wavelength by the sample

ϵ = is the molar extinction coefficient

l = is the distance covered by the light through the solution

c = is the concentration of the absorbing species

What is Beer's Law?

Beer's law was stated by August Beer which states that concentration and absorbance are directly proportional to each other

What is Lambert Law?

Johann Heinrich Lambert stated Lambert law. It states that absorbance and path length are directly proportional.

Beer-Lambert Law Formula: $I = I_0 e^{-\mu(x)}$

Where,

I = Is the intensity

I_0 = The initial intensity

X = The depth in meters

μ = The coefficient of absorption

Infrared IR spectra:

Electromagnetic radiation in the region of the spectrum (3×10^{12} to 3×10^{14}) Hz results in changes of the vibrational energy of molecule. The energy change required for the molecular vibration is of the order of 1 to 100 KJ mol⁻¹. The change in vibrational energy level are accompanied by the rotational levels also.

Requisite for IR spectra: Only those molecules which exhibit change in dipole moment during a vibration can exhibit IR spectra. EX: Homo nuclear diatomic molecules (H₂, O₂, N₂ & Cl₂) do not show change in dipole moment during vibration.

The quantum theory predicts that permitted vibrational energies are governed by the expression:

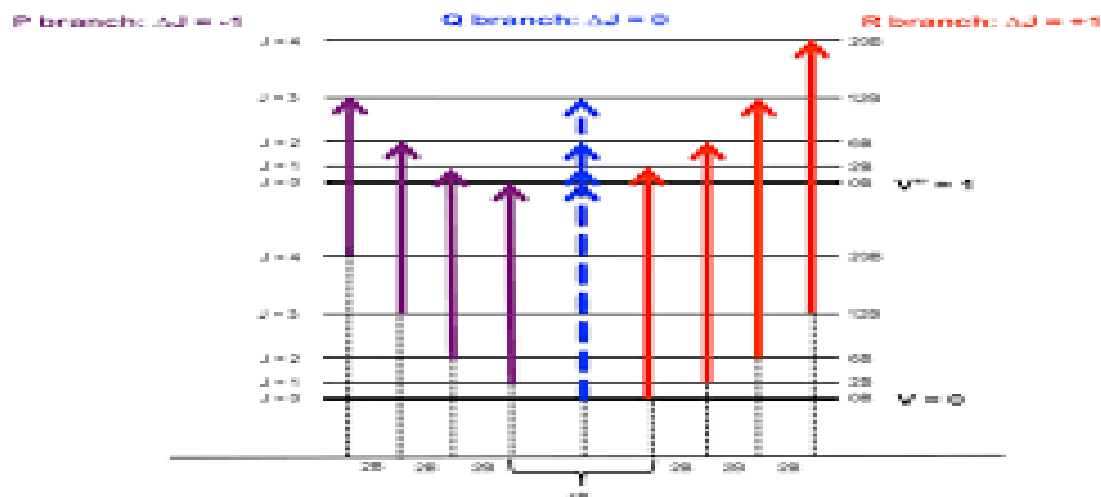
$$E_{\text{vib}} = \left\{ v + \frac{1}{2} \right\} h\nu_0$$

Where, v is the vibrational quantum number, possible values of 0,1,2, etc., & V_0 fundamental frequency. The lowest two energy eves, $v=0$ and $V=1$ possess of $1/2 h\nu_0$ and $3/2 h\nu_0$ And the difference between them is $h\nu_0$. The appropriate frequency of the electromagnetic radiation associated with this energy change, is the fundamental frequency (ν_0). It may be noted that even in the ground vibrational state, the molecule as vibrational energy = $1/2 h\nu_0$.
Vibrational spectra of diatomic spectra: The vibrational motion of diatomic molecule is akin to vibration of simple harmonic oscillator. Whose restoring force (F) is proportional to the displacement x (hooks law)

$$\text{i.e., } F \propto -x$$

$$F = -kx \dots \dots \dots (i)$$

The frequency (V) for the simple harmonic motion is given by:



$$V = 1/2\pi \sqrt{\frac{k}{\mu}} s - 1 \dots\dots\dots(ii)$$

K= force constant and μ reduced mass

In spectroscopy, the unit commonly used is wave number ($\bar{\nu}$) so, dividing eq. (ii) through by velocity (c), we get:

$$\bar{\nu} = \nu/c = 1/2 \pi c \sqrt{k/(\mu)} cm^{-1} \dots\dots\dots(iii)$$

vibration energy is quantized. Permitted vibrational energies can be calculated by using schrodinger equation. Accordingly the energy associated with any vibration state is given by:

$$E = h\nu_0 (V + 1/2) \text{ joules} \dots\dots\dots(iv)$$

V vibrational quantum no ν_0 is fundamental vibration frequency

Suppose there is a transition from lower frequency vibrational level to higher vibrational level then:

$$\begin{aligned} \Delta E_{\text{vib}} &= E^1 - E = (v^1 + 1/2) h\nu - (v + 1/2) h\nu \\ &= (v^1 - v) h\nu = \Delta v \cdot h\nu \dots\dots\dots(v) \end{aligned}$$

For transition between adjacent vibrational energy levels, we get by applying selection rule, $\Delta v = \pm 1$

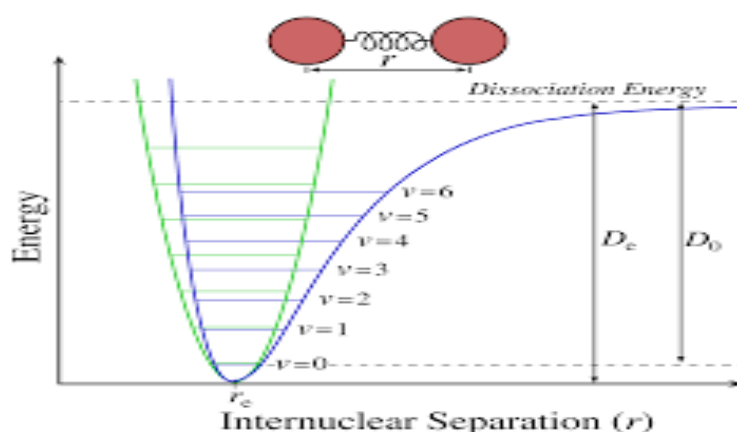
$$\text{Eq. (v) becomes: } \Delta E = h\nu \dots\dots\dots(vi)$$

From eq. (iv) & (v) we get,

$$h\nu_0 = h\nu$$

$$\nu = \nu_0 \dots\dots\dots(vii)$$

Selection rule for a harmonic vibrational transition: From the solution of Schrodinger eq, we get $\Delta v = \pm 1$ i.e., the increase or decrease in the vibrational quantum number is by one unit only. The energy difference between two vibrational eves involved in a transition would always be equal to spacing ($h \nu_0$).



The instrument used to record the spectra of molecules , is called a spectrometer. The exact design of the instrument varies according to the spectra region examined, but the basic features of all spectrometers are similar. A generalised schematic representation of spectrometer is shown in Fig.

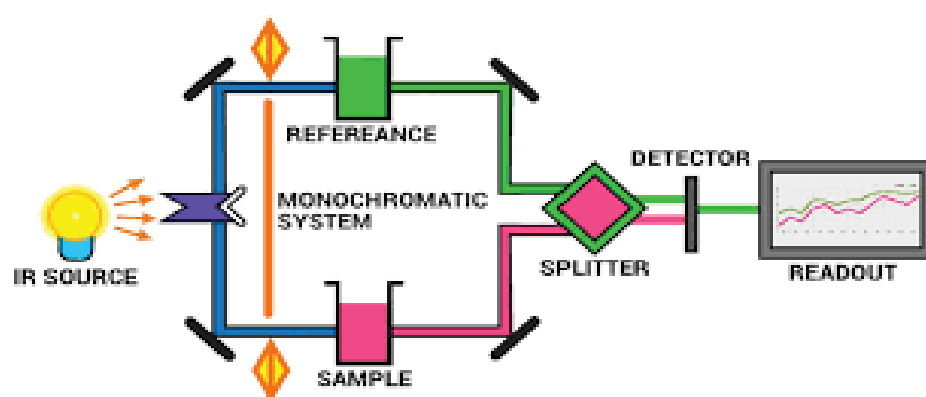
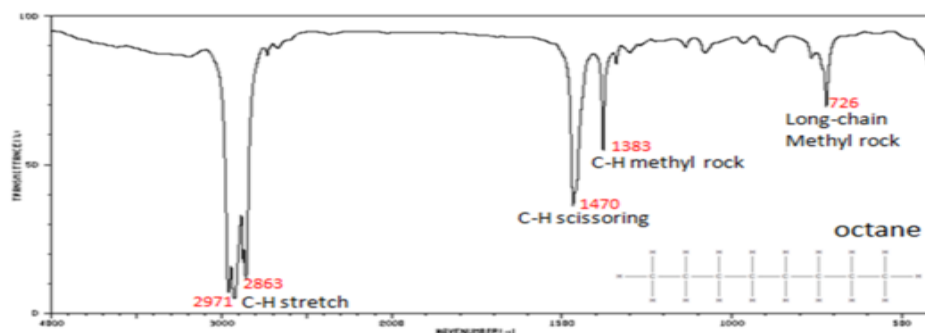


Fig: IR instrumentation

Applications for IR spectroscopy:

Characteristic infrared absorption frequencies for different groups:

Bond	Type of compound	Frequency (cm ⁻¹)
C-H	Aliphatic	2,800-3,000
C-H	Aromatic (Ar-H)	3,000-3,300
C-H	Cycloalkane	2,920-3,100
C-H	Olefinic	3000-3,100
C-H	acetylenic	3,300
C-C	Open chain aliphatic	750-11,00
C-C	Aromatic	1400-1600
C-C	Olefin	1,620-1,670
C-C	Acetylene	2,100-2,250
C=O	Aldehyde (aliphatic)	1,720-1,740
C=O	Aldehyde (Aromatic)	1495-1,715
C=O	Ketone (Aliphatic)	1,705-1,720
C=O	Ketone (Aromatic)	1,720-1,740
C=O	Esters (Aliphatic)	1,725-1,745
C=O	Esters (Aromatic)	11,230-1,260
C=O	Acids	1,650
C=O	Amides	1,790-1,800
O-H	Acid chloride	3,045
O-H	Primary alcohol	3,630
O-H	Secondary alcohol	3,620
O-H	Tertiary alcohol	3,600
N-H	Phenols	3,500
N-H	Primary amines	3,450
C-N	Secondary amine	1,180-1,360
C=N	Amines	1,650
-NO ₂	Nitro compound	1,565-1,585
C-Cl	-----	600-700
C-Br	-----	500-600
C-F	-----	1,000-1,350



- C–H stretch from 3000–2850 cm^{-1}
- C–H bend or scissoring from 1470–1450 cm^{-1}
- C–H rock, methyl from 1370–1350 cm^{-1}
- C–H rock, methyl, seen only in long chain alkanes, from 725–720 cm^{-1}

Figure. shows the IR spectrum of octane. dipole moment with respect to distance for the C–H stretching is greater than that for others shown, which is why the C–H stretch band is the more intense.

In aromatic compounds, each band in the spectrum can be assigned:

C–H stretch from 3100–3000 cm^{-1}

overtones, weak, from 2000–1665 cm^{-1}

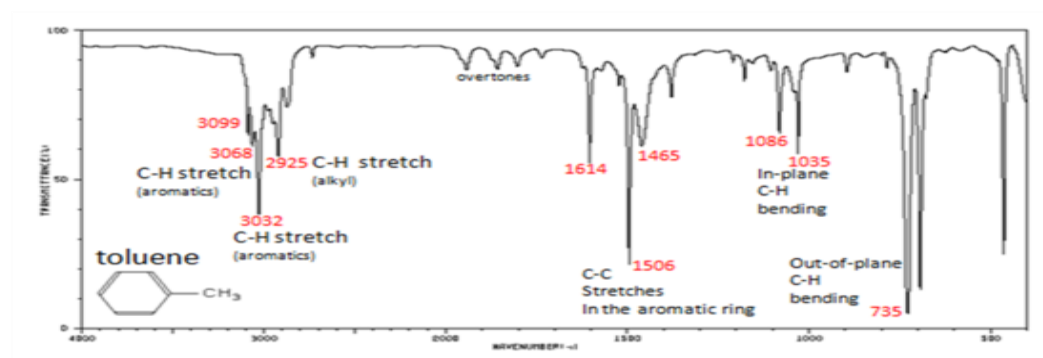
C–C stretch (in-ring) from 1600–1585 cm^{-1}

C–C stretch (in-ring) from 1500–1400 cm^{-1}

C–H "oop" from 900–675 cm^{-1}

Note that this is at slightly higher frequency than is the –C–H stretch in alkanes. This is a very useful tool for interpreting IR spectra. Only alkenes and aromatics show a C–H stretch slightly higher than 3000 cm^{-1} .

Figure . shows the spectrum of toluene.



If a compound is suspected to be an aldehyde, a peak always appears around 2720 cm^{-1} which often appears as a shoulder-type peak just to the right of the alkyl C–H stretches.

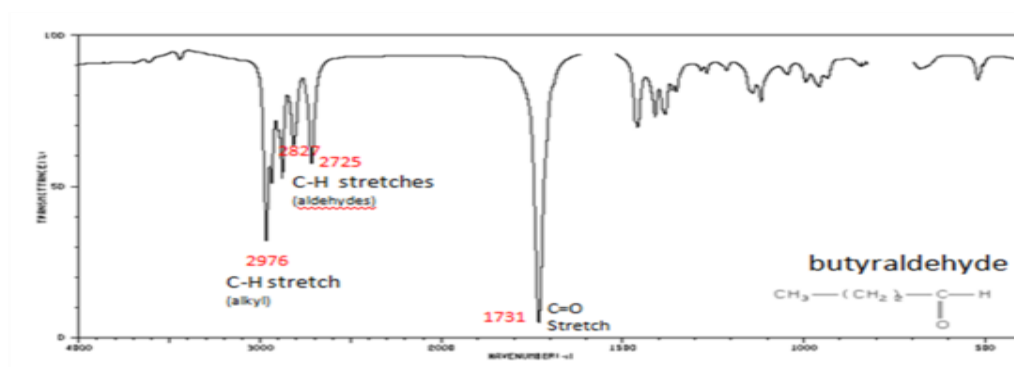
H–C=O stretch 2830–2695 cm^{-1}

C=O stretch:

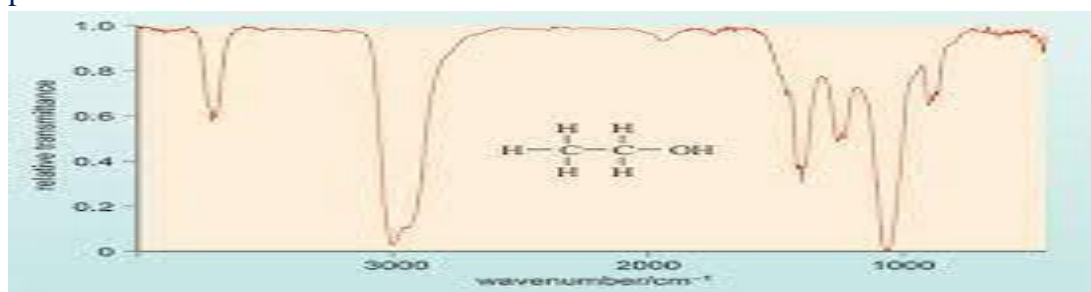
aliphatic aldehydes 1740–1720 cm^{-1}

alpha, beta-unsaturated aldehydes 1710–1685 cm^{-1}

Figure. shows the spectrum of butyraldehyde.

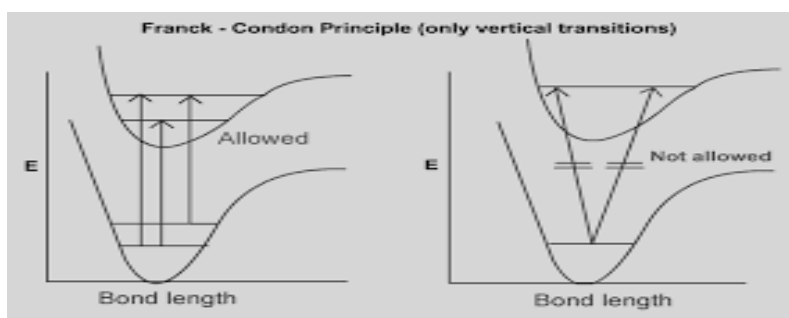


Ethanol (CH₃CH₂OH) spectrum is shown in Fig. with three characteristic peaks



Franck-Condon principle:

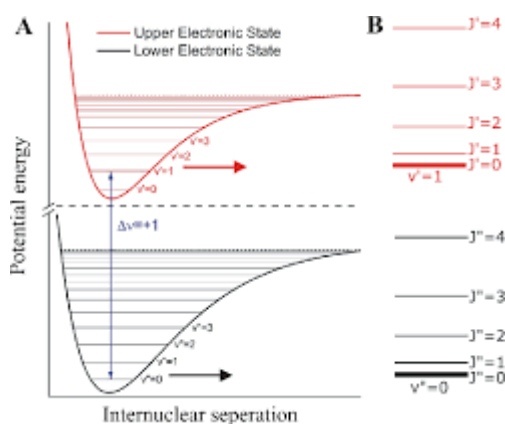
According to it *since electrons move much more rapidly than nuclei, so it as a good approximation to assume that in an electronic transition, the nuclei do not change their positions*. Therefore, an electronic transition may be represented by a vertical line (Fig.A) shows the potential energy curves for the ground state and first excited state of a diatomic molecule XY. The molecule has a different electronic structure in the excited state, and the potential energy of the excited state is higher. The equilibrium inter nuclear separation in the excited state is higher than that of ground state. This is because the excited state has antibonding electrons and therefore weaker bonding, which in turn lowers the dissociation energy for the excited state.



(Fig-A): Potential energy curves for the ground state and first excited state of molecule XY

When the molecule in the ground state absorbs radiation, it is most likely to be at its equilibrium internuclear separation. According to the Franck-Condon principle, the most probable transition is $0 \rightarrow 2$, because the excited molecule in the $v=2$ state does not have much internuclear kinetic energy and has probability at the equilibrium distance of the vibrational zero point level of the ground electronic state. It may be pointed out that transitions to other vibrational levels of the excited state do occur, but with lower probability as indicated by the absorption spectrum of molecule XY in (Fig.B).

If the minimum potential energy of the excited state is at a greater internuclear distance, the absorption of radiation by the ground state will produce excited molecules with enough energy to dissociate, as shown (Fig.a). Since variable amounts of energy may lead to dissociation, so a continuous spectrum is produced. As shown in (Fig.b). There is some probability of excitation to levels $v=3, 4$ & 5 and hence, some lines also appear in the absorption spectrum.



(Fig- B) : Absorption spectrum of diatomic molecule XY.