* INTRODUCTION

The transitions of electrons from one energy level to another results in emission or absorption of radiation and energy difference gives spectral lines in different regions, giving rise to atomic spectra, which gives useful information about atomic structure. Similarly, molecular spectra gives information about molecular structure.

* definition
→ structure of.
It deals with study of compound by studying interaction of em radiation with matter.

* TYPES OF ENERGY PRESENT IN MOLECULES.

i) Translational energy : The energy associated with overall movement molecules along three axes. (E_{trans})

ii) Rotational energy : The energy associated with spinning of molecules along the axes passing through centre of gravity. (E_{rot})

iii) Vibrational energy : The energy associated with the vibrations within the molecule (E_{vib}).

iv) Electronic energy : The energy associated with change in distribution of electrons by promotion of electrons to higher level on absorption of energy. (E_{elec}).

* TYPES OF SPECTRA

i) Emission spectra
ii) Absorption spectra

i) Emission spectra : Molecules gives emission spectra when they are subjected to intense heat. The energy of excitation is obtained from these sources when molecule returns to lower or ground state, energy is emitted in form of em radiation or photon and corresponding frequency is recorded as emission spectra.

$$\nu = \frac{E_2 - E_1}{h} = \frac{\Delta E}{h}.$$

ii) **Absorption spectra:** when a substance is irradiated with electromagnetic radiation, then energy of photon may be transferred to molecules, resulting in their excitation. When they returns to ground state, energy is again emitted. This process is called absorption and corresponding spectra is called absorption spectra. Energy absorption occurs only when the energy of incident electromagnetic radiation is exactly equal to the difference in b/w that of excited and lower energy level.

Three types of absorption spectra are:

i) Microwave

ii) Infrared

iii) Ultraviolet. and visible.

	Infrared	Ultraviolet and visible
radiations absorbed	$\nu = 3 \times 10^{12} - 3 \times 10^{14}$ Hz $\bar{\nu} = 100 - 10^4$ cm^{-1} $\lambda = 0.01$ cm $- 1000$ nm $E = 1 - 100$ KJ/mol	$\nu = 3 \times 10^{14} - 3 \times 10^{16}$ Hz $\bar{\nu} = 10^4 - 10^6$ cm^{-1} $\lambda = 1000$ nm $-$ 1nm $E = 100 - 10^4$ kJ/mol
Effect on molecule	Changes in vibration and rotational energy levels only.	changes in electronic energy levels.
Information obtained.	Detection of functional group, bond length, bond angle etc, in quantitative Analysis.	In qualitative and quantitative analysis.

* **REPRESENTATION OF ABSORPTION SPECTRUM:**

when em radiation interacts with the molecules, some of the wavelengths are absorbed while others are transmitted.

So, (i) Absorbance (A) vs $\lambda, \nu, \bar{\nu}$ curve

(ii) Transmittance (/-T) vs $\lambda, \nu, \bar{\nu}$ curve.
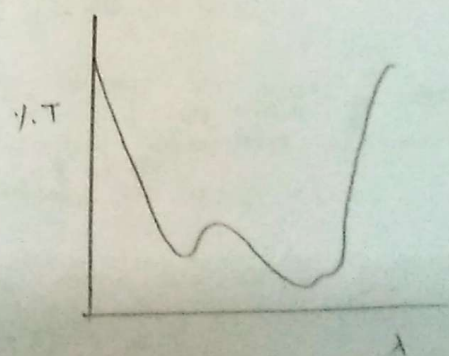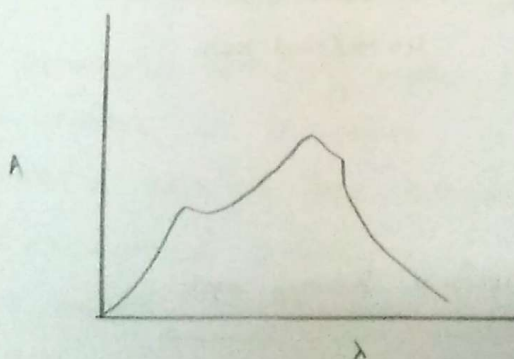
* Infra-red spectra.

Electromagnetic radiations in the IR region of spectrum changes the vibrational energy of molecules. The change in vibrational energy levels is accompanied with transitions in rotational levels also. So, along with each line in vibrational structure, rotational fine structure is also present. So, this spectrum is called vibrational-rotational spectrum.

* Requisite for IR spectra : All molecules cannot interact with IR rad. Only those molecules whose dipole moment changes during vibrations can exhibit IR spectra. or all homonuclear diatomic molecules cannot exhibit IR spectra.

The permitted vibrational energies are given by :

$$E_{vib} = \left(v + \tfrac{1}{2}\right) h\nu_0 \qquad , v = 0,1,\cdots$$

where v is vibrational quantum number and ν_0 = fundamental frequency

For two lowest vibrational energy levels, $v=0$ and $v=1$ and they possess energies $E_{vib} = \tfrac{1}{2} h\nu_0$ and $\tfrac{3}{2} h\nu_0$. So, energy diff b/w them ($v=0 \rightarrow v=1$ transition) is $h\nu_0$. The appropriate frequency of em rad associated with this energy difference is called fundamental frequency. The ground vibrational energy is $\tfrac{1}{2} h\nu_0$ and not zero. this is called zero point energy, which signifies that even in ground state, molecule must always vibrate, it can never be at rest.

* VIBRATIONAL SPECTRA FOR DIATOMIC MOLECULE : The vibrations of a diatomic molecule are similar to vibrations of simple harmonic oscillator, for which, $f \alpha -x$

$$f = -kx.$$

The frequency of simple harmonic oscillations is given by:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \; s^{-1} \qquad \text{where} \quad k = \text{force const.}$$
$$\mu = \text{reduced mass.}$$

In terms of wave no.,

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}.$$

The energy associated with each vibrational energy state,

$$E_{vib} = (v + \tfrac{1}{2}) h\nu$$

Suppose, there is a transition from lower state (v) to higher state (v').

$$\therefore \quad \Delta E_{vib} = \left(v' + \frac{1}{2}\right)h\nu_o - \left(v + \frac{1}{2}\right)h\nu$$

$$= (v' - v)\, h\nu = \Delta v \cdot h\nu.$$

By selection rule, $\Delta v = \pm 1$ (for transitions b/w adjacent vibrational energy levels)

$$\therefore \quad \Delta E_1 = h\nu$$

$$\therefore \quad h\nu_o = h\nu \qquad \text{(from ①)}$$

$$\boxed{\nu_o = \nu}$$

The frequency absorbed infrared radiation is equal to the fundamental frequency of molecules.

SELECTION RULE FOR HARMONIC VIBRATIONAL TRANSITION

$\Delta v = \pm 1$ ie. the increase or decrease in vibrational quantum no. is by one unit only.
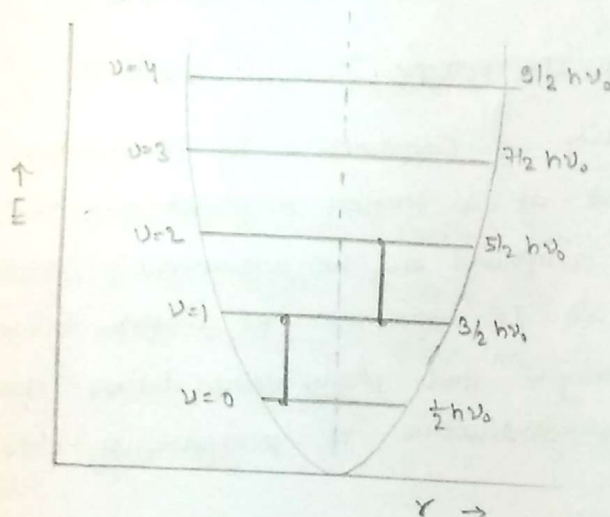
Fig 7 :
Allowed vibrational energy levels and transitions b/w them.

* IR SPECTRA OF POLYATOMIC MOLECULES.

for polyatomic molecules, the bonds can vibrate in more than one ways. These are known as vibrational modes and each vibration is associated with a fundamental frequency.

for CO_2 (linear molecule), three fundamental frequencies are:

i) ν_1 the symmetrical stretching mode involves no change in dipole moment & hence is inactive in IR region, so no corresponding absorption of energy both bonds a and b are elongated or shortened to same extent.

ii) ν_2, the asymmetrical stretching mode involves change in bond length (∴ change in dipole moment). one of bonds is shortened while other is elongated.
$\nu = 2349\ cm^{-1}$

iii) ν_3, the bending mode involves change in bond angle (∴ change in dipole moment). So, $\nu_3 = 667$ cm⁻¹.
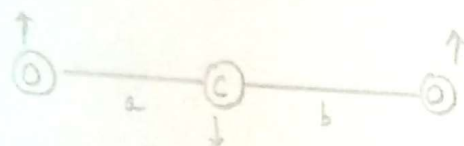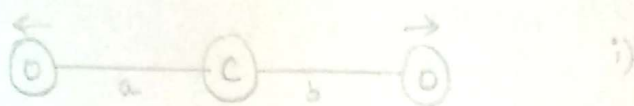
IR spectra becomes more complex from diatomic, ... to polyatomic molecules due to increased no. of vibrational modes :

i) For linear molecules, vibrational modes = $3n-5$

ii) for non linear molecules, vibrational modes = $3n-6$

where n = no. of atoms in a molecule.

* APPLICATIONS FOR IR-SPECTROSCOPY :

i) to establish identity of compounds : The IR spectrum of a compound is compared to that of a known compound and on basis of resemblance, nature of compound can be determined. Particular groups absorbs certain wavelength in IR -spectrum, no matter to which compound it belongs, eg. Benzaldehyde and phenylmethyl ketones show absorption peak at 1700 cm⁻¹. This is indicative of presence of $C=O$ group.

ii) In detecting impurities in sample : IR spectrum of impure substance have extra absorption Bands peaks. By comparision IR spectrum of pure compound, presence of impurity can be detected.

iii) To ascertain hydrogen bonding in a molecule : A series of IR spectra of same compound at diff. dilutions are recorded. As dilution ↑, absorption bands for intermolecular H-bonding diminishes and that for intramolecular H-bonding remains unchanged.

iv) Provides information about bond angle, bond lengths, dipole moment.

v) Distinguishing position isomers of same compound.

vi) For Quantitative analysis for mixture of compounds.

ULTRA-VIOLET (UV) AND VISIBLE (VIS) SPECTRA

[Absor]ption of radiation from UV and vis regions of electromagnetic spectrum
(200-400nm)   (400-750 nm)

[resul]ts in transitions between electronic levels, because energy changes are [rel]atively large and corresponds to $100-100000$ kJmol^{-1}. Every molecule can [und]ergo electronic transitions. The large energy changes involved in electronic [tra]nsitions also cause simultaneous change in vibrational & rotational energies. [Thi]s is because $E_{elec} > E_{vib} > E_{rot}$.

TRANSITIONS INVOLVING π, σ and n electrons.

[Abs]orption of ultraviolet and visible radiation in organic molecules [occ]urs due to excitation of electrons from bonding or non-bonding [orb]itals (ground state) to antibonding molecular b orbitals (excited state) which [are] usually empty when molecule is in ground state.

[An] antibonding orbital associated with σe- is σ* and π e- is π*. However, [no]n-bonding e-(n) are not associated to any kind of antibonding molecular orbit[al]

[Four] types of electronic transitions are possible:

σ→σ* Transitions

[An] electron in a bonding σ orbital is excited to corresponding antibonding [or]bital. The energy required is large. because σ e- are highly stable [as] they are involved in bond formation. These transitions are shown only [by] those compounds al in which all e's are involved in σ-bond formation. [eg.] Saturated hydrocarbons like CH$_4$.

n → σ* transitions.

[An] electron in non-bonding orbital is excited to antibonding σ* orbital. [S]aturated compounds containing atoms with lone pairs are capable of [n] → σ* transitions. eg: alcohols, amines etc. eg. CH$_3$-ṄH$_2$
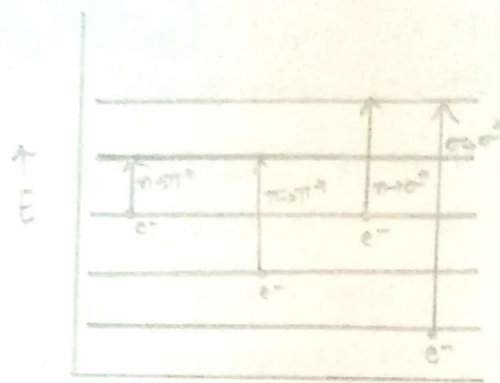
n→ π* transitions.

[An] e- in non-bonding orbital is excited to antibonding π* orbitals. [Al]l organic compounds containing double bond b/w C and heteroatom (O,S,N) show [thi]s transition. eg CH$_2$=CH-CH=CH-CH=Ö:
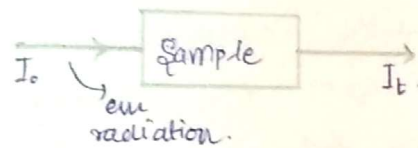
π → π* transitions.
An e- in bonding π orbital is excited to corresponding π* orbital. All unsaturated compounds (alkenes, alkynes) etc. Show this transition.

Antibonding σ^* } empty
Antibonding π^* } empty

non-bonding n } lone pairs

Bonding π } Bonding pair
Bonding σ } of e^-.

* ABSORBANCE AND TRANSMITTANCE

$$I_o \xrightarrow{\text{em}^\text{n} \ \text{radiation}} \boxed{\text{Sample}} \xrightarrow{} I_t.$$

Transmittance is defined as the ratio of intensity of transmitted light to that of incident light.

$$T = I_t/I_o$$

Absorbance, $A = -\log T = -\log\left(I_t/I_o\right)$

* Absorbance is an additive property.
* Transmittance is an multiplicative property.

* LAMBART'S LAW :

It states that the rate at which the intensity of incident light decreases with thickness of absorbing medium is directly proportional to the intensity of incident light.

i.e. $-\dfrac{dI}{dx} \propto I$ or $-\dfrac{dI}{dx} = kI$ or $-\dfrac{dI}{I} = kdx$.

Integrating both sides with proper limits,

$$-\int_{I_o}^{I_t} \dfrac{dI}{I} = k\int_0^l dx \quad \Rightarrow \quad -[\ln I]_{I_o}^{I_t} = k[x]_0^l$$

$$\Rightarrow -\left[\ln \dfrac{I_t}{I_o}\right] = kl \quad \text{or} \quad \ln \dfrac{I_t}{I_o} = -kl \quad \text{or} \quad 2.303 \log \dfrac{I_t}{I_o} = -kl$$

$$\Rightarrow -\log \dfrac{I_t}{I_o} = +\dfrac{k}{2.303}l \quad \Rightarrow \quad I_t = I_o\, e^{-\frac{k}{2.303}l}$$

$$\Rightarrow \boxed{I_t = I_o\, e^{-\epsilon l}}$$

$$\Rightarrow \boxed{A = \epsilon l} \quad \text{where } \epsilon = \dfrac{k}{2.303}.$$

* LAMBERT- BEER'S LAW: The rate at which intensity of incident light ↓ with thickness of absorbing media is directly proportional to the intensity of incident radiation and concentration of solution.

ie. $-\frac{dI}{dx} \propto I$ and $-\frac{dI}{dx} \propto c$ ∴ $-\frac{dI}{dx} \propto Ic$

$-\frac{dI}{dx} = KIc$ ∴ $-\frac{dI}{I} = kcdx$ ⇒ $-\int_{I_o}^{I_t}\frac{dI}{I} = kc\int_0^l dx$

$-\left(\ln\frac{I_t}{I_o}\right) = kcl$ ∴ $-2.303 \log\frac{I_t}{I_o} = kcl$

⇒ $-\log\frac{I_t}{I_o} = \frac{k}{2303}cl$ ⇒ $\boxed{A = \mathcal{E}cl}$

A is absorbance or optical density and has no units.

* definition of $\mathcal{E}$: The molar absorptivity or molar extinction coefficient of a chemical species at a particular wavelength is a measure of how strongly the species absorbs light at that wavelength. units → $Lmol^{-1}cm^{-1}$.

* LIMITATIONS

i) when polychromatic beam of light is used.

ii) when highly concentrated solution is used.

iii) when diff. forms of compounds (keto, enol) exists in the solution.

iv) when complex formation takes place.

v) when medium is heterogeneous.

vi) when fluoroscent compounds are used.

* chromophores

Functional groups which absorbs radiation in UV and vis region, irrespective of the fact that whether it imparts colour to the compound or not, are termed as chromophores.

eg: $\overset{\lambda_{max}}{\underset{(175)}{>C=C<}}$, $\overset{}{\underset{(170)}{>C\equiv C<}}$, $\overset{}{\underset{(190)}{>C=O}}$, $\overset{}{\underset{(165)}{-C\equiv N-}}$

$\underset{(\pi\to\pi^*)}{}$ $\underset{(\pi\to\pi^*)}{}$ $\underset{(\pi\to\pi^*)}{}$ $\underset{(n\to\pi^*)}{}$
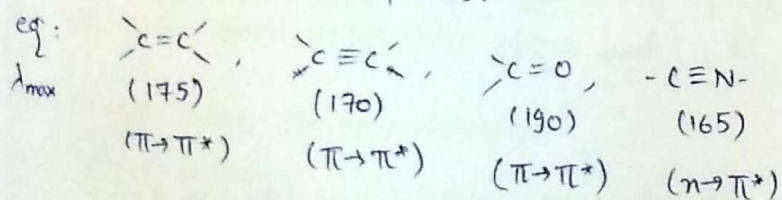
Chromophores can be of two groups:-
i) $\pi\to\pi^*$ (transitions taking place)
ii) $n\to\pi^*$
$\pi\to\pi^*$ (transitions taking place).

AUXOCHROMES : Groups which themselves do not show any characteristic absorption above 200 nm, but when attached with chromophore, cause shift of absorption (max) towards longer wavelength ie. it causes Bathochromic effect.

eg. $-NH_2$, $-NR_2$, $-SH$, $-OR$, $-SR$ etc.

The absorption band can be affected by :

i) Bathochromic effect or red shift.

ii) Hypsochromic shift or blue shift

iii) Hyperchromic shif effect.

iv) Hypochromic effect.

i) Bathochromic eff shift or red shift :

The shift of maximum absorbance towards longer wavelength is called bathochromic shift. This can be achieved by

i) attaching an auxochrome to a carbon-carbon double bond or benzene ring.

ii) decreasing polarity of solvent.

iii) conjugation of two chromophores.

eg.

λ_{max} = 256 nm   280nm
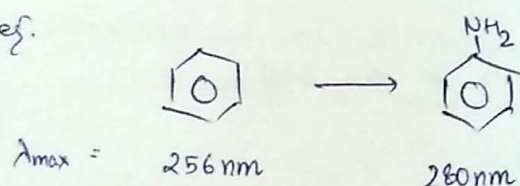
[due to fact that $-NH_2$ is in conjugation with ring].

These factors bring out ↓ in energy diff. b/w orbitals involved in transitions.

ii) Hypsochromic or blue shift.

The shift of maximum absorbance towards shorter wavelength. This can be achieved by :

i) Attaching auxochrom to $C=O$ group. For Acetaldehyde, λ_{max} = 293 nm but when H is replaced by Cl, λ_{max} = 235.

ii) Increasing polarity of solvent.

eg: $n \to \pi^*$ transition of Acetone in hexane occurs at 279 nm & 264 nm in water.

iii) Hyperchromic shift : change (increase) in intensity of absorption without change in λ_{max}.

iv) Hypochromic shift : change (decrease) in intensity of absorption without change in λ_{max}.

λ_{max} : The wavelength that corresponds to maximum absorbance.
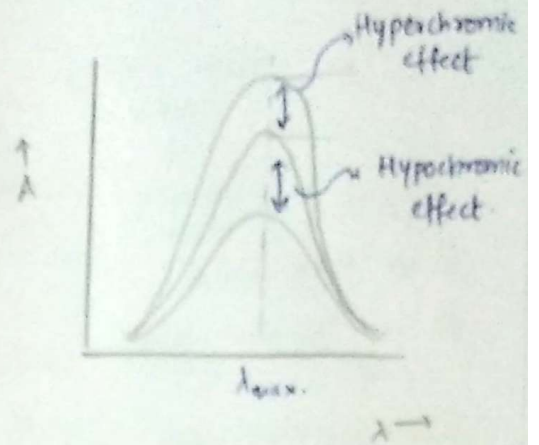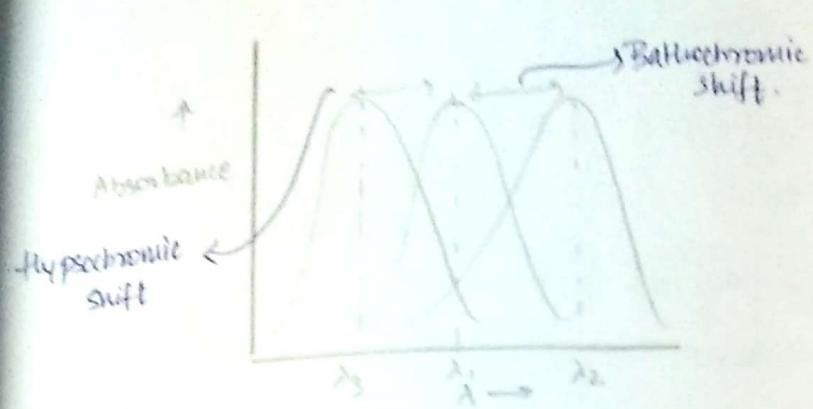
* Spectrophotometer : A device used to measure the intensity or amount of light absorbed by a substance when some kind of radiations are passed through it.
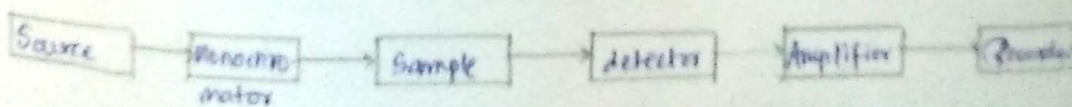
i) IR spectrophotometer :
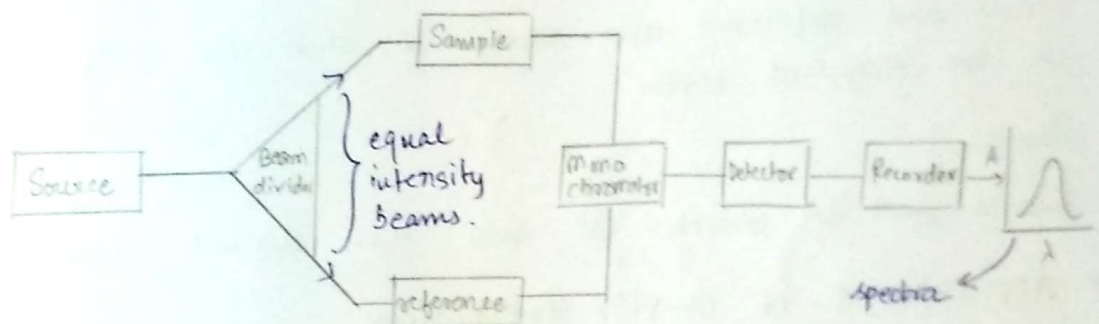
Source is electrically heated Nernst filament (oxides of Zr, cerium, thorium) or global red (silicon carbide-red). Temperature maintained is 1000°C.

Sample and reference cells cannot be made of quartz and glass as they absorb in IR range. and gives wrong results. Alkylhalides such as KBr should be used in case of solids. In case of liquids, 'IR' inactive sol^n such as nujol (a transparent hydrocarbon) are used. Cell can also be used.

ii) UV-vis spectrophotometer

(a) Single Beam spectrophotometer.
   (Block Diagram).

b) double-beam spectrophotometer.

for UV: H_2/D_2 lamps

for vis: Tungston lamps.
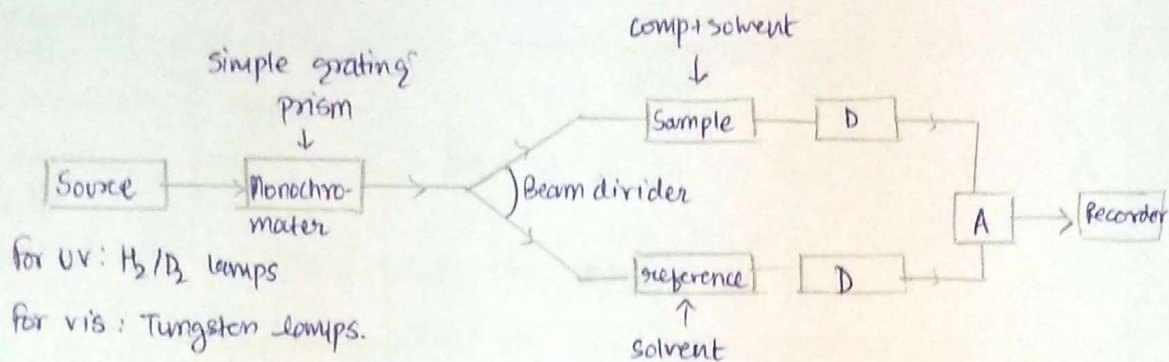
Beam divider are rotating mirrors which divides incident light without change in intensity.

D is a detector (photo-voltaic cells which detects signal in form of quanta and converts it into some measurable quantity ie voltage).

A is an amplifier which amplifies the signal.

Sample and reference cells should be such that they dos not absorb in the required region.

Sample !

Quartz does not absorbs UV and glass doesn't absorb visible.

* APPLICATIONS OF UV-VIS. SPECTROSCOPY.

i) detection of conjugation : Compounds without conjugation absorbs in λ range below 200 nm.

ii) Extent of conjugation : more the double bond, more is the λ_{max}.

extent of conjugation $\propto \lambda_{max}$
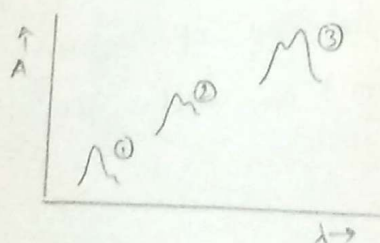
extent of conjugation in
① < ② < ③.

iii) Detection of presence of Auxochrome & chromophore

iv) in qualitative analysis and quantitative Analysis.
(Lambert's-Beer law).
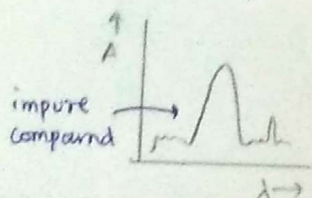
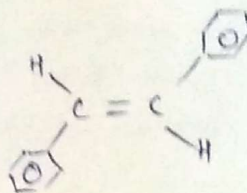If compound is pure, we will get a single-well-resolved peak.

iv). It can differentiate b/w geometrical isomers.
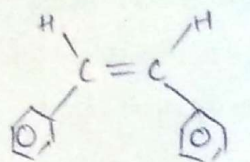
cis alkene   trans alkene.

↳ absorbs at shorter wavelength than trans alkene.

cis-alkene : loss of coplanarity, more steric hinderence results in an ↑ in energy reqd. for most favourite transition and hence λ_{max} is less.
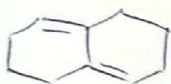
* WOODWARD FIESER'S RULE

used to find λ_{max}.

* Some common terminologies.

i) Homoannular diene : If two double bonds present inside the same
   same   two double-bond   ring, then it is a Homoannular diene.

      Base value : 253 nm

ii) Heteroannular diene : If two double bonds are present inside the in
    different   two double bonds   different rings, then it is called Heteroannular.

     Base value : 217 nm / 215 m (Both can be used). / 214
                                                    ‿‿‿‿‿
                                            doubt (needed to be resolved).

iii) Exocyclic double bonds : The double bond present outside the ring such
     outside   that one of the doubly-bonded carbon is
                              included in the ring.

Exocyclic double bond for A-
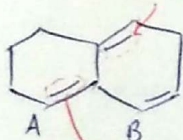
A   B
exocyclic double
bond for ringB

eg : There are two rings A and B, forming A, no. of exocyclic bonds = 1 and for ring B = 1. So, total no. of exocyclic double bonds = 2.
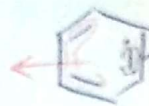
Base value for each exocyclic double bond = 5. nm

iv) double-bond extending conjugation : If extra double bonds are present, in addition with di-ene and if this extra double bond is in conjugation with di-ene, then the extra double bonds are called double-bond extending Conjugation. Base value for each = 30 nm

for understanding, take an example:

these two → [ring structure] ← As it is an extra double bond which is in conjugation with other double bonds.

these two double-bonds are in conjugation.

∴ no. of double bond extending conjugation = 1

So, for λ_{max}, 30 nm (its base value) will be added.

* **Ring-residue** : Firstly, note all the carbons which are there in conjugation. Then, these bonds which are attached to conjugated carbons and are present inside ring but are not involved in conjugation are called ring-residue.

eg.
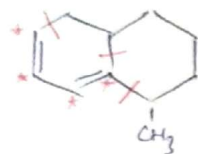
Star marked are carbons involved in conjugation. Now, note the bonds attached to these conjugated carbons which are not involved in conjugation. Let these are marked by '|'.

So, no. of ring residues = 3

Base value for each ring residue = 5 nm.

* **Other increments**.

Only those substituents are added to calculate λ_{max} which are attached to conjugated carbons.

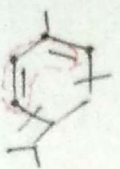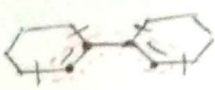| Alkyl substituents	5 nm	→ Base values.
—X	5 nm	
—OH	6 nm	
—OR	6 nm	
—NH₂	30 nm	
—NR₂	60 nm.	

NOTE: If in a structure, both homo annular and heteroannular diene are present, then base value of homoannular diene is used.

RULES FOR FINDING λ_{max}.

* Mark or star all the conjugated carbons
* Add Base value for homo/heteroannular diene.
* Add Base values for exocyclic double bond
* Add Base values for ring residues.
* Add Base values for double bond extending conjugation
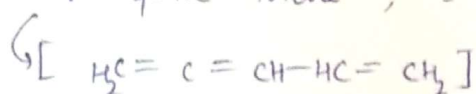* Add Base values for increments.

Scanned by CamScanner

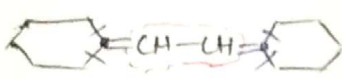SOME QUESTIONS :

i)

λ_{max} = 253 (homoannular diene) + 5×2 (2 ring residues) + 5 (one alkyl gp.)

= 253 + 15

= 268

ii)

λ_{max} = 217 (Heteroannular) + 4×5 (4 ring residues)

= 237 nm.

NOTE : For Acyclic conjugated diene, Base value = 217 nm

cyclic conjugated diene , Base value = 217 nm.

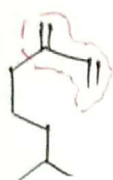Alicyclic Triene , = 245 nm.

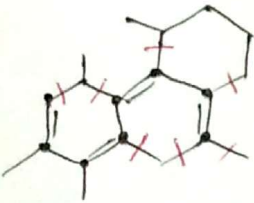$[\,H_2C = C = CH-HC = CH_2\,]$

iii)

λ_{max} = 217 + 2×5 (exocyclic bonds) + 4×5 (ring residue)

= 247 nm.

iv)

(wrong ques).

v)

λ_{max} = 217 (alicyclic) + 5×1 (alkyl) = 222.

vi)

λ_{max} = 217 (Acyclic) + 1×5 (alkyl) = 222.

vii)

$CH_2 = CH - CH = CH_2$

217.

viii)

λ_{max} = 253 (homoannular) + 30×2 (2-double bond extending conjugation)

+ 6×5 (6 ring residues)

+ 4×5 (4 exocyclic bonds)

+ 3 Alkyl gps (3×5)

= _____.

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