Spectroscopy

Spectroscopy: The identification & structural characteristics of atoms, ions or molecules by their internal energy changes after analysing emmition or absorption spectrum is called as spectroscopy.

Instrument which is used to measure the amount of radient energy absorbed at each wavelength is called as spectrophotometer.

Spectrophotometer containing photoelectric cell which is used to measure the intensity of absorbed radient energy at each wavelength is called as spectrophotometer

Radiation	Wavelength	molecular rearrangement
cosmic ray	5×10^{-5} nm	Nuclear transition
γ-rays	10^{-3} to 0.01 nm	Nuclear Transition
x-ray	0.01 to 4 nm	— " —
Far UV	4 to 200 nm	Electronic Transition

Near UV	200 to 400 nm	Electronic Transition
visible	400 to 800 nm	— " —
Near IR	0.5 μ to 2.5 μ ($20,000\ cm^{-1} - 4000\ cm^{-1}$)	molecular vibration
Vibrational IR	2.5 μ to 15 μ ($4000\ cm^{-1} - 667\ cm^{-1}$)	molecular vibration
far IR	15 μ to 200 μ ($667\ cm^{-1} - 50\ cm^{-1}$)	rotational Transition
Microwave	10^{-3} m	— " —
Radar	10^{-2} m	— " —
Television	1 m	Nuclear spin Transition
Radio	10^{2} m	Nuclear spin Transition.

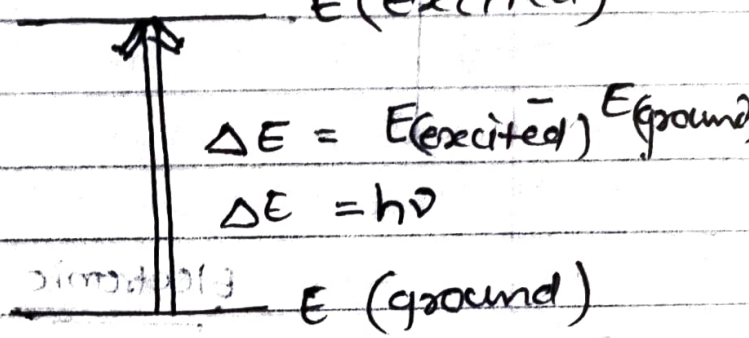
$$E = h\nu$$

$$\therefore \nu = \frac{c}{\lambda}$$

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

$$\boxed{E \propto \frac{1}{\lambda}}$$ (wavelength)

The strength of electronic spectroscopy lies in its ability to measure the extent of multiple bond or aromatic conjugation within molecules. The non bonding electrons on oxygen, nitrogen & sulphur may also be involved in extending the conjugation of multiple-bond systems.



The excitation process.

Increasing energy

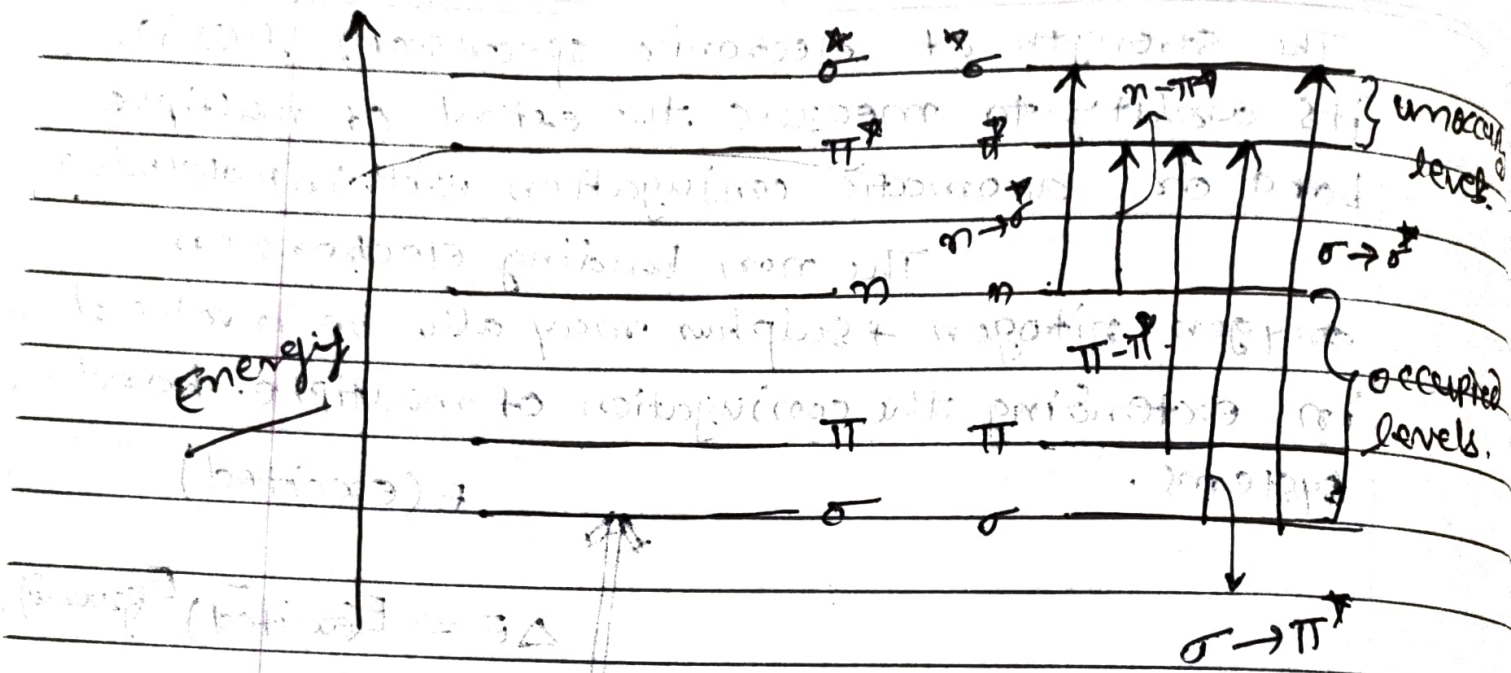
$\sigma \rightarrow \sigma^*$ In alkane

$\sigma \rightarrow \pi^*$ In carbonyl comp.

$\pi \rightarrow \pi^*$ In alkene, carbonyl comp. alkynes, azo comp. & so on.

$n \rightarrow \sigma^*$ In oxygen, nitrogen, sulfur & halogen compounds.

$n \rightarrow \pi^*$ In carbonyl compounds.



Electronic energy levels and Transitions.

one important selection rule state that transitions that involve a change in the spin quantum number of an electron during the transition are not allowed to take place; they are called "forbidden" Transitions (ε_{max} is less than 100) eg. ($n \rightarrow \pi^*$)

The intensity of the absorption tends to be much lower than for transition that are allowed by the selection rule

eg. $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $\sigma \rightarrow \sigma^*$ etc.

Not all transitions from filled to unfilled orbital are allowed.

where a transition is 'forbidden' the

probability of that transition occuring is low, and correspondingly the intensity of the associated absorption band is also low.

In alkane, the only transition available is the promotion of an electron from low-lying σ- orbital to high energy σ^* antibonding orbital. This is high-energy process and requires very short wavelength ultraviolet light (around 150 nm). This type of transition is classed as $\sigma \rightarrow \sigma^*$ (sigma to sigma star)

In simple alkenes, several transition are available, but the lowest energy transition is the most important. This is the $\pi \rightarrow \pi^*$ transition, which is responsible for the absorption band around 170-190 nm in unconjugated alkenes.

In saturated aliphatic ketones, the lowest energy transition involves the non bonding electrons on oxygen, one of which can be promoted to the relatively low-lying π^* orbital, This is the $n \rightarrow \pi^*$ transition is forbidden in symmetry terms & therefore the intensity is low, although the wavelength is long (around 280 nm)

Two other transition available are $n \rightarrow \sigma^*$ and $\pi \rightarrow \sigma^*$ and $\pi \rightarrow \sigma^*$

these are both allowed transitions and give rise to strong absorption band, but the energy involved is higher than for $n \rightarrow \pi^*$, therefore the wavelength of the absorption is shorter (around 185 for $n \rightarrow \sigma^*$) & around 160 for $\pi \rightarrow \pi^*$).
The most intense band for these comp. is always due to the $\pi \rightarrow \pi^*$ transition.

Laws of Light Absorption - BEER'S AND LAMBERT'S LAWS.

These two early empirical laws govern the absorption of light by molecules.

Beer's law relates the absorption to the concentration of absorbing solute, & Lambert's law relates the total absorption to the optical path length.

They are most conveniently used as the combined Beer-Lambert Law.

$$\log\left(\frac{I_0}{I}\right) = \epsilon c l \text{ or } \epsilon = A/cl$$

Where I_0 is the intensity of the incident light (or the light intensity passing through a reference cell),

I is the light transmitted through the sample solution

$\log(I_0/I)$ is the absorbance (A) of the solution (formerly called the optical density, OD)

c is the concentration of solute (in $mol\,dm^{-3}$)

l is the path length of the sample (in cm)

ϵ is the molar absorptivity (formerly called the molecular extinction coefficient)

conjugated system and Transition Energies

In conjugated diene the π-orbitals of the seprate alkene groups combine to give new orbitals i.e, the two new bonding orbitals which are designated $\bullet\pi_1$ & π_2 and two anti-bonding orbitals which are designated π_3^* & π_4^*. The relative energy of these new orbitals, and it is apparent that now the $\pi_2 - \pi_3^*$ transition of conjugated diene is of very low energy than $\pi \rightarrow \pi^*$ transition on an unconjugated alkene.

e.g. butadiene (λ_{max} 217 nm) is bathochromically shifted relative to $\pi \rightarrow \pi^*$ transition of ethylene λ_{max} 171 nm.

* Designation of Bands :-

In the $\pi \rightarrow \pi^*$ transition a compound with conjugated π-system is usually intense ($\epsilon_{max} > 10,000$) & is frequently called as K-band (German Konjugierte)

e.g. Benzene :- 184, 204, 256
↓
K-band.

The $n \rightarrow \pi^*$ transition (R-band German-Radikal) ($\epsilon_{max} < 100$) forbidden.

The B-Band i.e. benzenoid bands are characteristic of aromatic and heteroaromatic compound.

In benzene the B band at 256 nm.

E-Band i.e. ethylenic bands are characteristic of aromatic system like B-bands.

e.g. In benzene E-band at 184.

chromophore :-

The characteristic energy of a transition and the wavelength of radiation absorbed are properties of a group of atom rather than of electrons themselves. The group of atoms producing such an absorption is called a chromophore.

* chromophore is covalently double or Triple bonded group.

e.g. $-C\equiv C-$, $>C=O$, $-N=O$, etc.

$R-C\equiv N$	160	$\pi \to \pi^*$	
$R-N=N-R$	340	R-CHO	290
$R-NO_2$	271		190 $\pi \to \pi^*$

Auxochrome :-

Substituent that increase the intensity of the absorption and possibly the wavelength are called auxochromes.

A Auxochrome are covalently single bonded group.

e.g. $-CH_3$, $-OH$, $-OCH_3$, $-Cl$, $-NH_2$ etc.

class	Transition	λ_{max}
R-OH	$n \to \sigma^*$	180
R-OR	— " —	180
$R-NH_2$	— " —	190
R-SH	— " —	210

Four kinds of effects on the absorption

1) Bathochromic shift (red shift) :-
a shift to lower energy or longer wavelength.

2) Hypsochromic shift (blue shift)
a shift to higher energy or shorter wavelength.

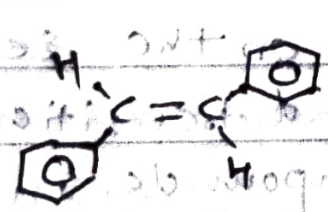
3) Hyperchromic effect :-
an increase in intensity.

4) Hypochromic effect :-
a decrease in intensity.

☆ Effect of Geometrical Isomerism - steric effect

In compounds where geometrical isomerism is possible e.g. in stilbene, the E-isomer (trans-stilbene) absorbs at a longer wavelength with greater intensity than Z-isomer (cis-stilbene) due to steric effect

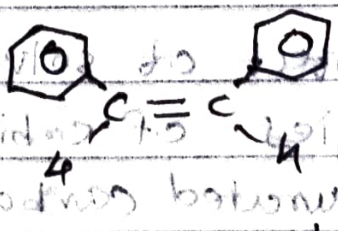
Coplanarity is needed for the most effective overlap of the π-orbitals and increased ease of the $\pi \rightarrow \pi^*$ transition. The Z-isomer is forced into a nonplanar conformation due to steric effect.



trans-stilbene

$\lambda max = 295\ nm$

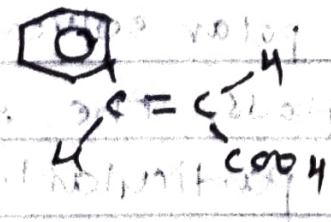
$\epsilon = 27,000$



cis-stilbene

$\lambda max = 280\ nm$

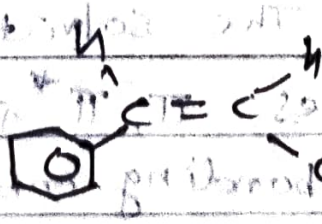
$\epsilon = 13,500$



Trans cinnamic acid

$\lambda max =$

$\epsilon max =$

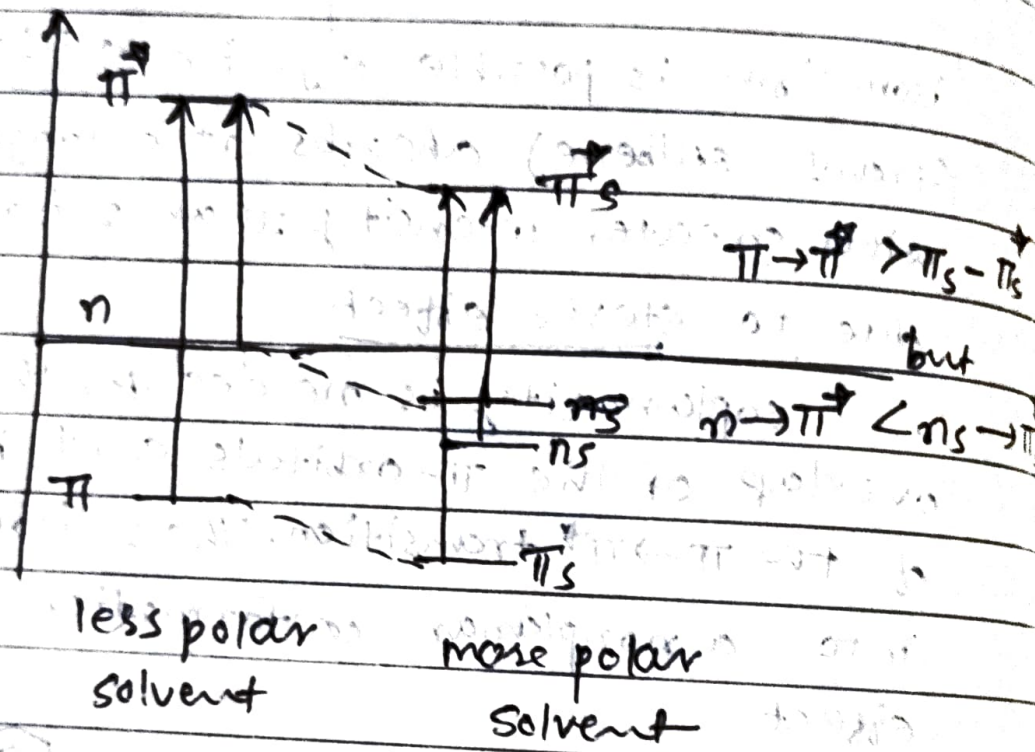


cis cinnamic acid

$\lambda max =$

$\epsilon max =$

★ SOLVENT EFFECTS :→



Effect of solvention on the relative energies of orbitals and transition in α,β-unsaturated carbonyl compounds. In more polar solvents $\pi \rightarrow \pi^*$ absorption moves to longer λ, $n \rightarrow \pi^*$ moves to shorter λ.

The solvation by a polar solvent stabilises π, π* & n orbitals, The stabilisation of nonbonding orbitals is particularly pronounced with hydrogen-bonding solvents (such as water or ethanol) & π* orbitals are more stabilised by solvation than π-orbitals, because π* orbitals are the more polar. The net result is the energy of transition $\pi \rightarrow \pi^*$ becomes

less solvation (red shift) while the energy of transition, $n \rightarrow \pi^*$ becomes greater (blueshift).

THE WOODWARD - FIESER RULES FOR DIENES:→

Empirical Rules for diene

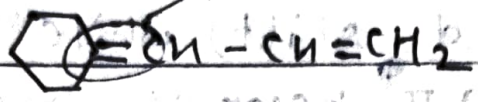
	Homoannular (cisoid)	Heteroannular (transoid)
parent	$\lambda = 253$	$\lambda = 214$ nm
Increments for:		
Double-bond-extending conjugation	30	30
Alkyl substituent or ring residue	5	5
Exocyclic d.b.	5	5
polar groupings:		
$-OCOCH_3$	0	0
$-OR$	6	6
$-Cl, -Br$	5	5
$-NR_2$	60	60
$-SR$	30	30

Homoannular Diene

Heteroannular Diene

λ_{max} 253 λ_{max} 214 nm

exocyclic double bond

1)  Base value = 214 nm

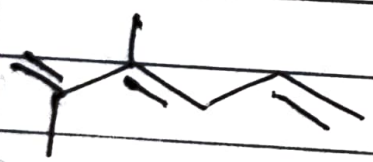
one exocyclic d.b. + 5

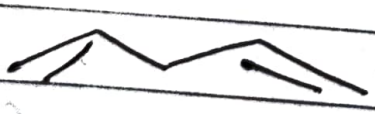
Two ring residue + 10 nm

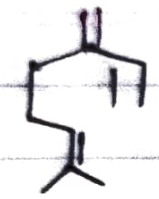
2 x's

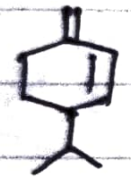
$\lambda_{max.}$ = 229 nm

2) 

3) 

4) 

5) 

6) 

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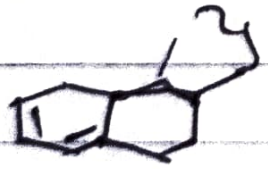
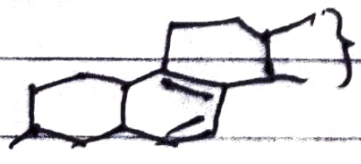
9) 

10) 

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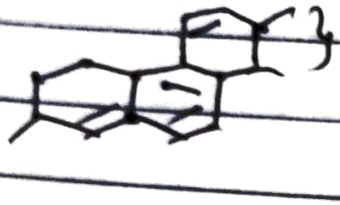
12) 

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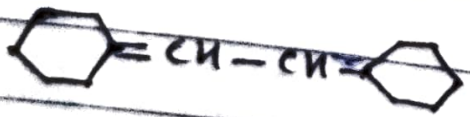
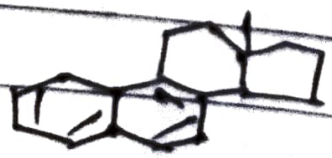
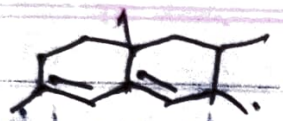
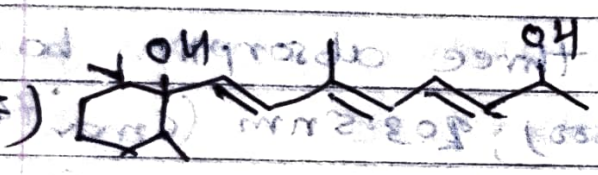
14) 

15) 

16) 

17) 

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