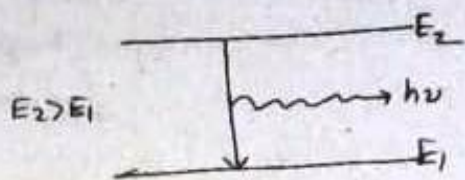
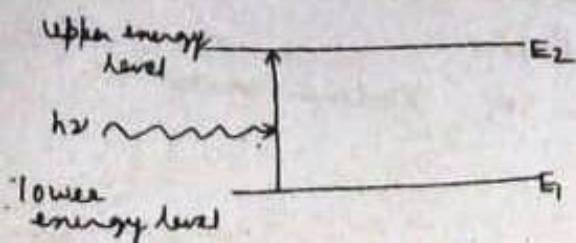


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• Sem V

Q What do you understand by absorption spectra and emission spectra?

Ans →



Emission Spectra →

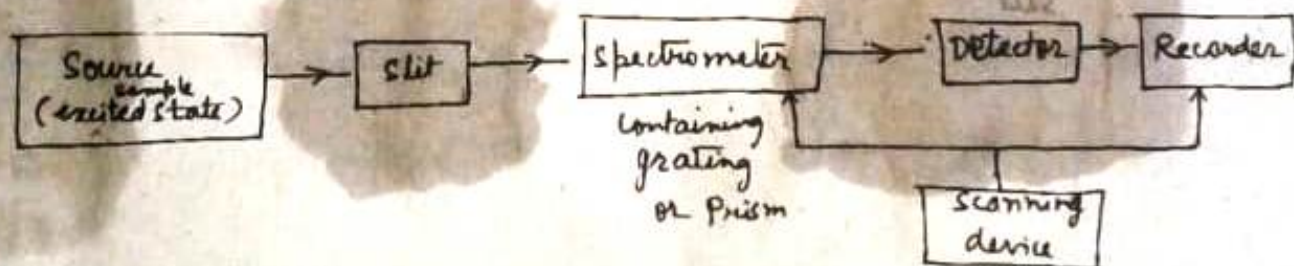
Absorption of radiation

Emission of radiation

When radiation is absorbed by a particle (sample), it goes to higher energy level, this is called excited state of energy. The excited state is unstable state hence after sometime, it comes back to its ground state. In the process of coming back to ground state the absorbed energy is emitted. This emitted energy is captured by spectrometer in the form of line in case of atoms and in the form of collection of lines (called as band) in case of molecules.

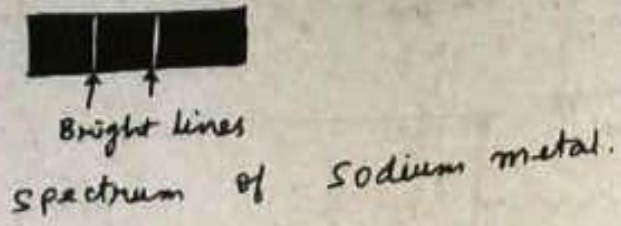
Thus spectra formed is called emission spectra.

The block diagram for emission spectra can be given as



Absorption spectra are more useful in the study of structure of molecule. Depending upon the radiation used, it may have called as IR, UV, NMR etc. Spectroscopy.

emission spectrum obtained contains bright lines in dark background.



Absorption spectra →

If radiation is passed through a substance, then some part is absorbed by the substance (sample) and rest part is transmitted. The transmitted part of the radiation is passed through spectrometer and a spectrum is obtained. This spectrum contains ^{all} the radiations except those are absorbed by the sample.

Absorption spectrum contains dark lines in bright background. eg. spectrum of sodium metal seems to be



The block diagram for absorption spectra can be given as



Q Write a note on chromophore:

Ans → Chromophore may be defined as an isolated group with covalent bond which exhibits a characteristic absorption in UV or in the visible region.

Chromo means colour hence originally chromophores were considered as any molecular system which gives a colour, but it has been found that colour is observed due to absorption of light but in chromophore absorption occurs irrespective of fact whether colour is produced or not.

There are two types of chromophores:

- a) Groups containing π electrons which undergo $\pi \rightarrow \pi^*$ transition eg ethylene, acetylene etc.
- b) Groups containing both π electrons and non-bonding electrons which undergo $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition eg carbonyls, nitriles, nitro, azo compounds

There are no set of rules for identification of chromophore.

However following facts may be considered:

- i) For ϵ_{max} value between 10,000 to 1,000 shows an aromatic system.
- ii) For ϵ_{max} value between 20,000 to 10,000 shows α, β -unsaturated ketones
- iii) For ϵ_{max} value between 100 to 10 shows $n \rightarrow \pi^*$ transition for carbonyl group.

Q Write a note on auxochrome.

Ans → Auxochrome may be defined as any group which does not itself act as chromophore but whose presence brings about a shift of absorption band towards the longer wavelength of the spectrum called as red shift or bathochromic shift.

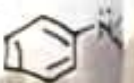
The absorption of radiation at relatively longer wavelengths may be attributed to the combination of a chromophore and an auxochrome. The combination behaves like another chromophore. Actually auxochromic group is colour enhancing group. Auxochromic groups do not exhibit absorption above 200 m μ .

Common auxochromic groups are $-OH$, $-OR$, $-NH_2$, $-NHR$, $-NR_2$, $-SH$ etc.

eg The value of λ_{max} for benzene is 255 m μ



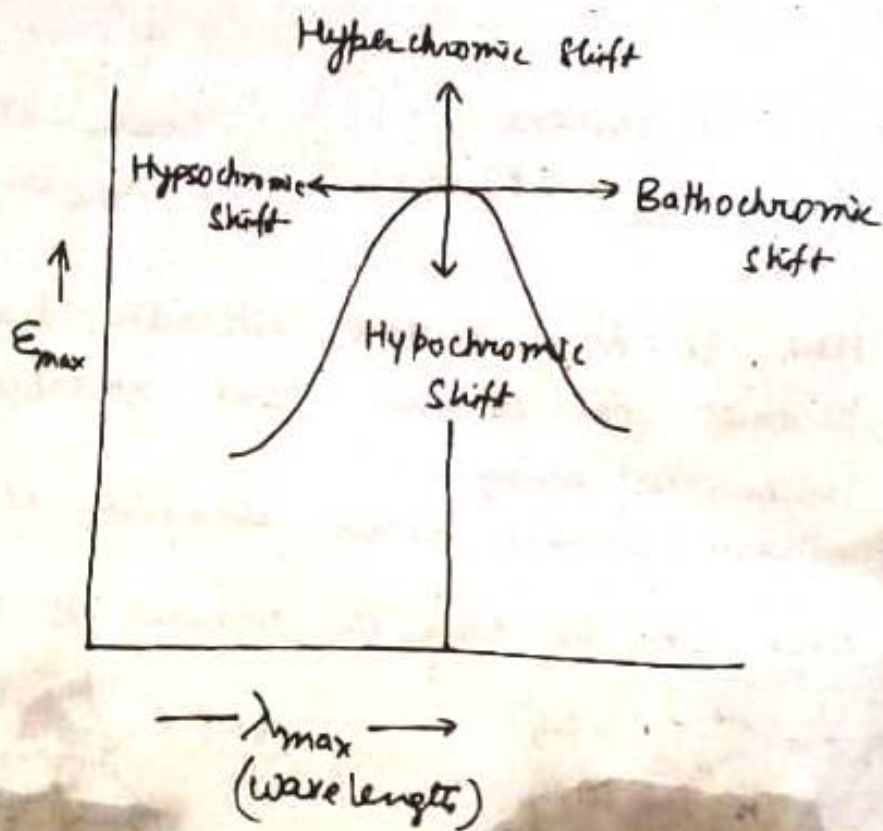
whereas value of λ_{max} for aniline is 280 m μ



Thus, here, $-NH_2$ group acts as auxochrome.

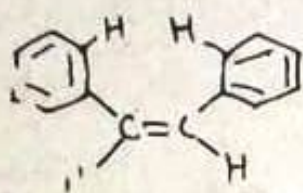
Actually auxochromic group contains non-bonding electrons which causes conjugation of chromophore in enhanced way.

Absorption and shift of intensity



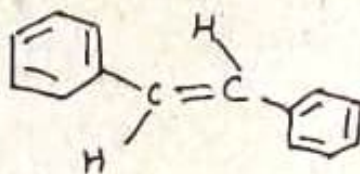
Q How can you distinguish between cis- and trans-isomer with the help of UV spectroscopy?

Ans → The results of absorption indicate that cis-form absorbs at different wavelength as compared to its corresponding trans-form. eg. 1,2-Diphenyl ethene (stilbene)



cis-stilbene

$$\lambda_{\text{max}} = 283 \text{ nm}$$



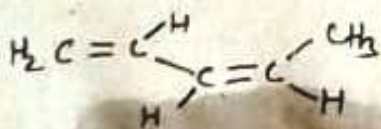
Trans-stilbene

$$\lambda_{\text{max}} = 295.5 \text{ nm}$$

Here cis-form suffers distortion due to steric hindrance becomes non-coplanar and absorption takes place at lower wavelength.

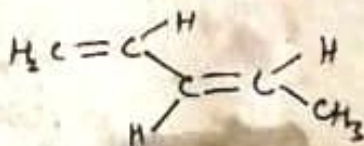
Trans isomers shows absorption at higher wave length.

Now let us take the example of Pent-1,3-diene.



cis-isomer

$$\lambda_{\text{max}} = 211 \text{ nm}$$



trans-isomer

$$\lambda_{\text{max}} = 215 \text{ nm}$$

Here also we see that trans-isomer absorbs at higher wave length in comparison to cis-isomer.

Q write a note on finger print region and its significance. 7

Ans → The spectral region 667 cm^{-1} to 4000 cm^{-1} is called mid IR region. This region is divided into two parts

- a) 910 cm^{-1} - 1430 cm^{-1}
- b) 1430 cm^{-1} - 4000 cm^{-1}

The region 910 cm^{-1} - 1430 cm^{-1} contains many absorption caused by bending vibrations in a molecule as compared to stretching vibrations. This region of spectrum is relatively rich in absorption bands and shoulders. Hence, it is called finger print region.

However molecules having similar groups show almost identical spectra in the region 1430 cm^{-1} - 4000 cm^{-1} but there is always notable differences in the finger print region.

Some scientists consider that finger print region is sub-divided into three regions

- a) 1500 cm^{-1} - 1350 cm^{-1}
- b) 1350 cm^{-1} - 1000 cm^{-1}
- c) 1000 cm^{-1} and below

a) 1500 cm^{-1} - 1350 cm^{-1} → -NO_2 gr - 1350 cm^{-1}

Gem dimethyl - 1380 cm^{-1}

t-butyl gr - 1380 cm^{-1} (m) & 1365 cm^{-1} (s)

b) 1350 cm^{-1} - 1000 cm^{-1} → 1° alcohol - 1350 - 1260 cm^{-1} ← 1057 cm^{-1} (b, m, s)

phenol - 1280 cm^{-1}

ester - 1300 - 1050 cm^{-1} (s)

ether - 1150 - 1070 cm^{-1}

c) 1000 cm^{-1} & below → cis & trans alkene - 970 - 960 cm^{-1}

Q DISCUSS IR absorption positions of O and N containing functional groups.

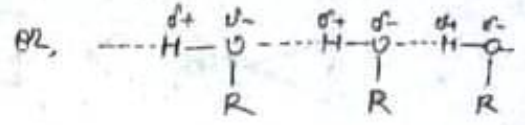
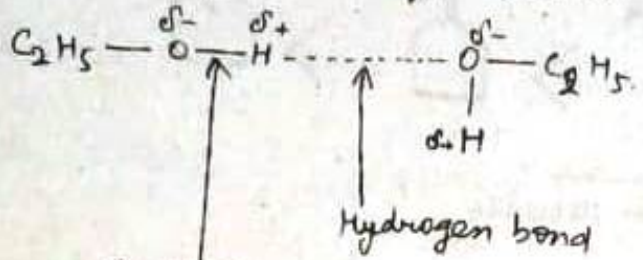
Ans → Characteristic absorption frequencies of functional group are as follows: -

| Type of vibration | Class of compound | Frequency (cm^{-1}) | Intensity |
|-------------------|-------------------------------------|--------------------------------|--------------------|
| C-H str. | alkane | 2960-2850 | s (sharp) |
| C-H str. | alkene | 3100-3010 | s |
| C-H str. | alkyne | ~3300 | s |
| C-H str. | aromatic | 3150-3020 | s |
| C-H str. | aldehyde | ~2820 | w (weak) |
| C=C " | alkene | 1675-1600 | m, w (medium weak) |
| C=C " | aromatic | 1600-1450 | m, w |
| C≡C " | Alkyne | 2260-2100 | s |
| C=O " | ketone | 1725-1705 | s |
| C=O " | aldehyde | 1740-1720 | s |
| C=O " | Carboxylic acid | 1725-1700 | s |
| C=O " | ester | 1750-1730 | s |
| O-H " | alcohol, Phenol | 3650-3580 | s, |
| O-H " | alcohol, Phenol (H-bond) | 3550-3200 | b s |
| O-H " | Carboxylic acid | 2700-2500 | b (broad) |
| N-H " | 1° amine, amides (Free) (two bands) | ~3500 | m |
| N-H " | 1° amine, amide (H-bonded) | ~3400 | m |
| N-H " | 2° amine amide | ~3500-3300 | |
| C≡N " | Nitrile | 2260-2220 | m |

Q Discuss the effect of H-bonding in IR spectra

Ans → Due to Hydrogen bonding, the value of force constant decreases because of attraction and hence the shift to absorption goes towards lower wave number

eg. H-bonding in ethyl alcohol



Bond is weakened due to attraction by H-bond.

Following changes may be observed due to H-bonding.

i) Intermolecular H-bonding gives broader band while intra-molecular H-bonding gives sharp and well defined bands.

The appearance of broad band in hydrogen bonded molecule is due to existence of dimer, trimer, etc due to association.

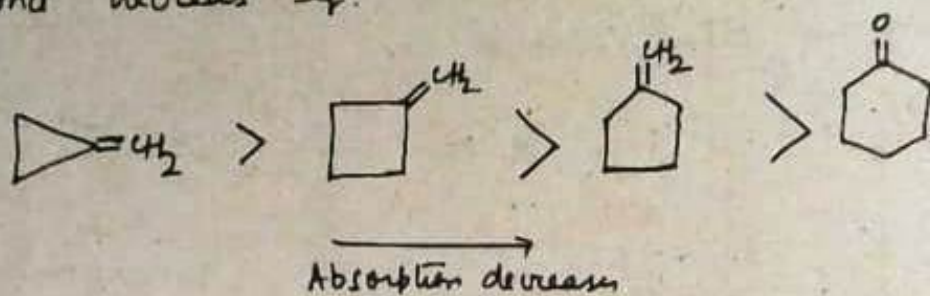
Stronger the H-bonding, more broadening of the band occurring at much lower wave number

eg alcohol in vapour state (isolated) gives absorption at 3600 cm⁻¹, whereas in associated form it gives absorption at 3200 cm⁻¹.

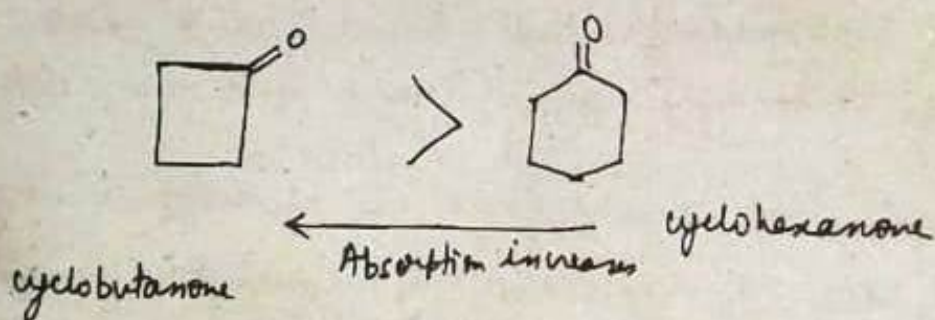
ii) The absorption band in the intermolecular H-bonding depends upon concentration whereas in case of intramolecular H-bonding does not depend upon concentration because it takes place with only single molecule. This fact can be utilised to differentiate between two types of H-bond.

Q Discuss the effect of ring size in IR spectra.

Ans → As the size of ring increases, the C=C stretching frequency in exocyclic olefinic double bond decreases eg.



Similarly, in cyclic ketones $\nu_{C=O}$ absorption increases as the size of the ring decreases (ring strain increases)



Q. How propanal (CH_3CH_2CHO) and propanone (CH_3COCH_3) are distinguished by IR spectra?

Ans → In propanal, $\nu_{C=O}$ stretching at 1720 cm^{-1} and ν_{C-H} stretching at $\sim 2720\text{ cm}^{-1}$ is obtained but in propanone, ν_{C-H} stretching at $\sim 2720\text{ cm}^{-1}$ is missing only $\nu_{C=O}$ stretching at 1720 cm^{-1} is observed.

Q Discuss the effect of hybridisation of Carbon on the stretching frequency of C-H bond.

Ans → As the s-character of hybridised Carbon increases, the force constant (k) for C-H bond increases and therefore, stretching frequency increases.

| | | | |
|---------------------|------------------------|------------------------|----------------|
| | C-H | =C-H | ≡C-H |
| hybridisation → | sp^3 | sp^2 | sp |
| ν_{C-H} value → | (2950-2850 cm^{-1}) | (3000-3100 cm^{-1}) | 3300 cm^{-1} |
| s-character → | 25% | 33.3% | 50% |