

Spectroscopy

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Syllabus

Introduction

UV-Vis spectroscopy: Beer Lambert's law, Types of transition, Concept of auxochrome and chromophore, factors affecting , Woodward-Fieser rules for calculation of λ_{max} in diene systems.

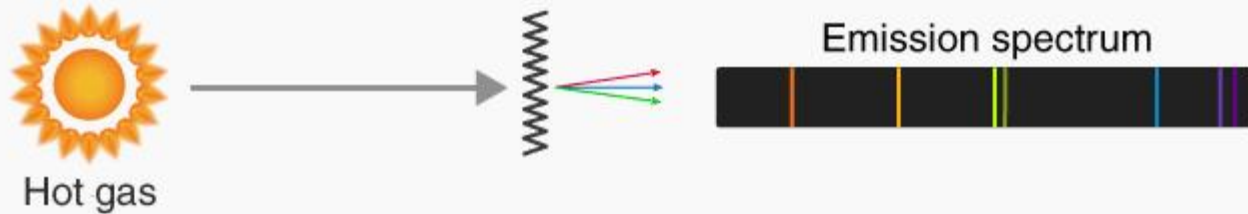
IR spectroscopy: Introduction, types of vibration, selection rules, Hooke's law, problem, identification of functional groups like C-C, C=C, -OH, -NH₂ and -C=O.

NMR spectroscopy: Basics of NMR spectroscopy, chemical shift, Shielding and de-shielding effect, Factors affecting chemical shift,

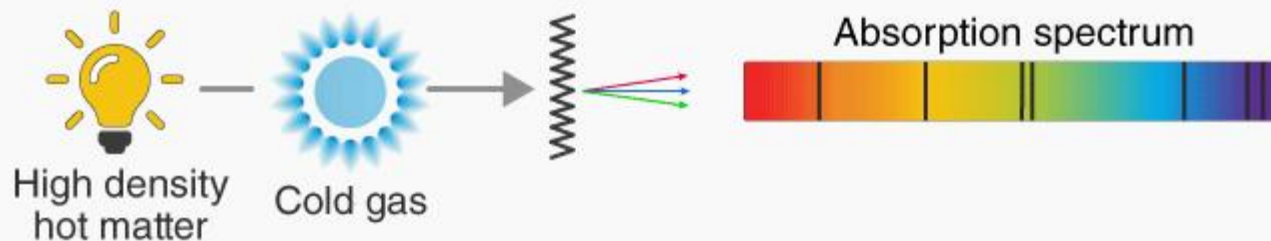
Structural elucidation of simple compounds

Absorption Spectrum and Emission Spectrum

(a) Emission Spectra



(b) Absorption Spectra



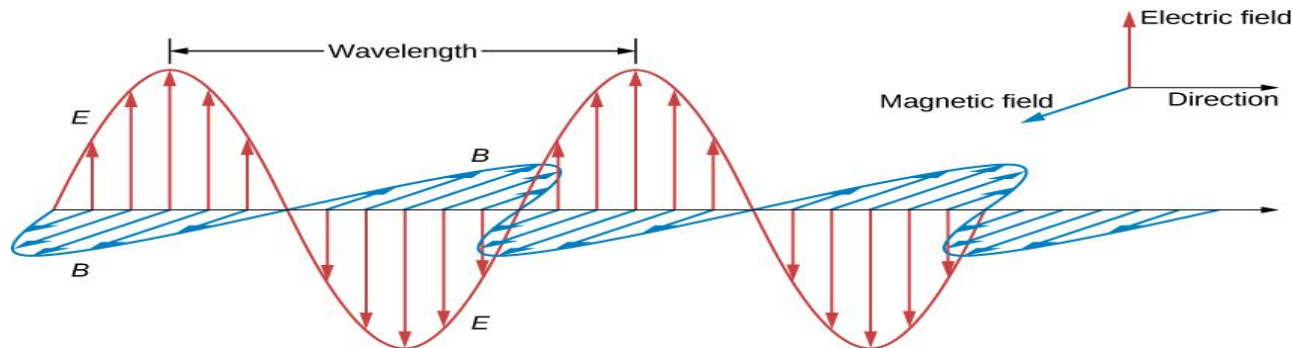
The difference between **absorption** and **emission spectra** are that **absorption** lines are where light has been **absorbed** by the atom thus you see a dip in the **spectrum** whereas **emission spectra** have spikes in the **spectra** due to atoms releasing photons at those wavelengths.

Electromagnetic Radiation

Radiation is a form of energy which has both magnetic and electrical properties, hence called electromagnetic radiation. The electromagnetic radiation covers a long range of radiations which are described or characterized by either wavelength or frequency.

Characteristics

1. Produced by the oscillation of Electric charge and magnetic field residing on the atom, which are mutually perpendicular to each other and are coplanar.
2. Characterized by their wavelength or frequency or wave number.
3. Energy carried by electromagnetic radiation is directly proportional to its frequency. Emission or absorption is quantised and each quantum of radiation is called a photon.
4. All type of radiation travel with the same velocity and no medium is required. They can travel through vacuum.
5. A group of electromagnetic radiation can be split up into various components for analysis.



Electromagnetic Radiation

Wavelength (λ) is defined as the distance between the successive peaks, which is measured in the unit nanometers (nm).

Wave number ($\bar{\nu}$) is the reciprocal of wave length, which is measured in the unit cm^{-1} .

Frequency (ν) of radiation is defined as the number of successive peaks passing a given point in 1 second, which is measured in the unit cycles per sec or Hertz (Hz). $1 \text{ Hz} = 1 \text{ cycle sec}^{-1}$.

The relationship between these is:

➤ $\nu \propto \frac{1}{\lambda}$

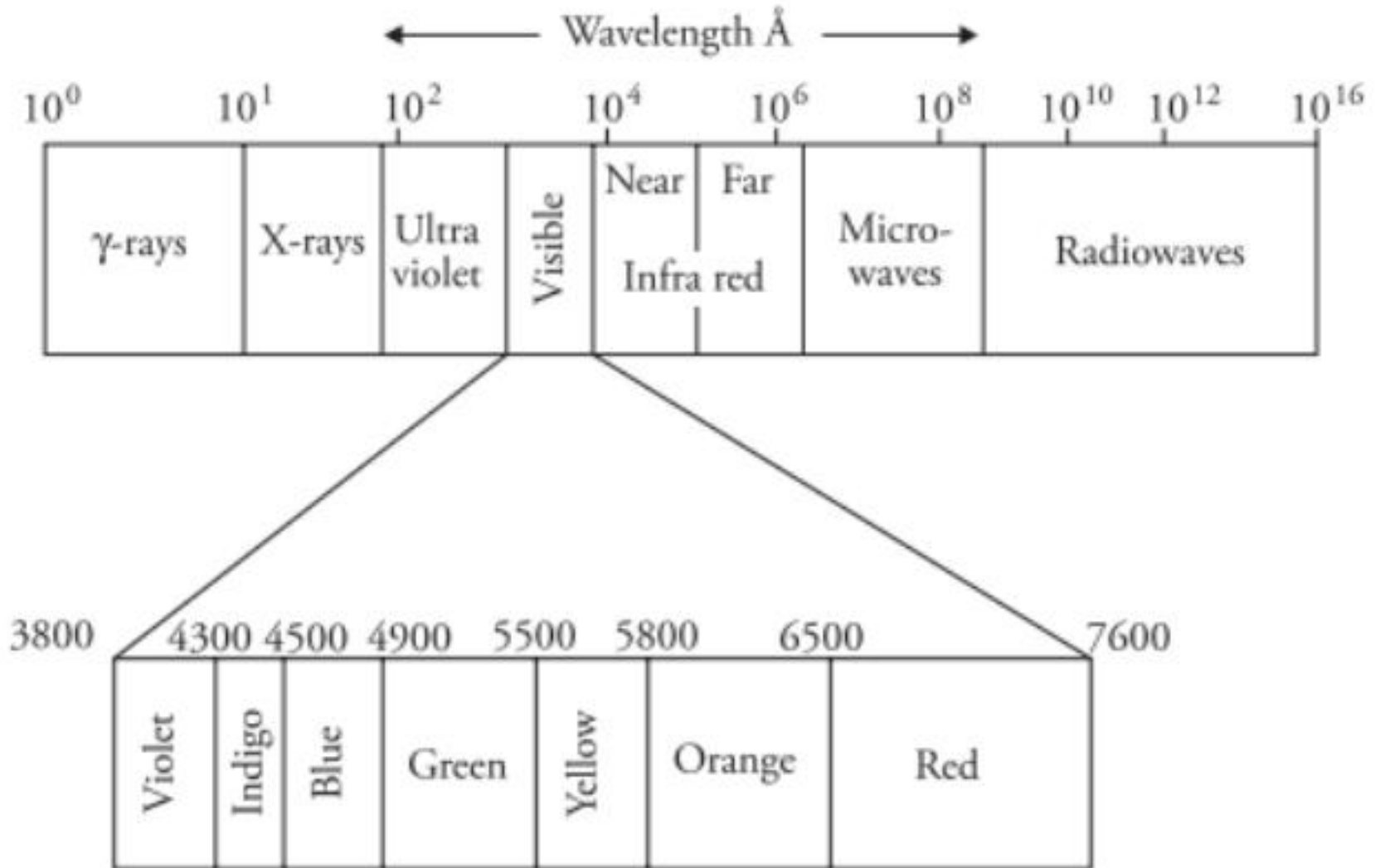
➤ But, the energy (E) is directly proportional to the frequency and inversely proportional to wavelength.

$$\text{i.e. } E = h\nu = \frac{hc}{\lambda}$$

$$\begin{aligned} h &= 6.626 \times 10^{-27} \text{ erg sec} \\ c &= 2.998 \times 10^{10} \text{ cm sec}^{-1} \end{aligned}$$

➤ Where, h is a Plank's constant and c is the speed of light

Electro-Magnetic Spectrum



Visible Spectrum

Interaction of Radiation with Matter

- ✓ Radiation could either be absorbed or transmitted.
- ✓ *The interaction of radiation involves energy transition between the different energy levels of atoms or molecules.*
- ✓ *The other types of interactions are reflection, refraction and diffraction, are often related to the bulky properties of materials.*
- ✓ The internal energy of a molecule is due to the energy associated with:
 - *The electrons*
 - *Vibrations between atoms*
 - *The rotation of various groups of atoms within a molecule*
- ✓ The energy levels can be altered by the absorption or emission of radiant energy.
- ✓ A study of the wavelength or frequency of radiation absorbed or emitted by an atom or molecule will give information about its identity. This technique is known as qualitative spectroscopy.

Types of spectroscopy

Based on the nature of the radiation that is being absorbed or emitted, there are different types of spectroscopy.

- **Ultraviolet/visible spectroscopy**
- **Infra-red (IR) spectroscopy**
- **Nuclear Magnetic Resonance (NMR) spectroscopy**
- Mass spectroscopy
- Flame Photometry
- Atomic Absorption Spectroscopy
- Raman spectroscopy
- X- ray spectroscopy
- Fluorescence spectroscopy
- Mossbauer spectroscopy

UV-visible Spectroscopy

UV-visible Spectroscopy

It is also known as **Electronic Spectroscopy** since it involves the promotion of electrons (σ , π , n electrons) from the ground to the higher energy states.

- ✓ It is useful to measure the number of conjugated double bonds and also aromatic conjugation within various molecules.
- ✓ Distinguishes between conjugated and non-conjugated systems.
- ✓ Distinguishes homoannular and hetero annular conjugated dienes.

Since the energy levels of a molecule are quantized, the energy required to bring about the excitation is a fixed quantity.

The UV-Vis spectral region

- This region of the spectrum is conventionally divided into three sub-domains termed
UV (185–400 nm),
Visible (400–700 nm) and
Near Infrared (NIR) (700–1100 nm).
- Most commercial spectrophotometers cover the spectral range of 185 to 900 nm.
- The lower limit of the instrument depends upon the nature of the optical components used and of the presence, or not, along the optical pathway of air, knowing that oxygen and water vapour absorb intensely below 190 nm.
- Some instruments, on condition that they are operating in a vacuum, can attain 150nm with samples in the gaseous state. This is the domain of *vacuum or far ultraviolet*.
- The long-wavelength limit is usually determined by the wavelength response of the detector in the spectrometer. High-end commercial UV-Vis spectrophotometers extend the measurable spectral range into the near infrared region as far as 3300 nm.

The origin of the absorptions

- The origin of absorption is the interaction of photons from a source with ions or molecules of the sample.
- When a molecule absorbs a photon from the UV-Vis region, the corresponding energy is captured by one (or several) of its outermost electrons.
- As a consequence there occurs a modification of its electronic energy E_{elec} , a component of the total mechanical energy of the molecule along with its energy of rotation E_{rot} and its energy of vibration E_{vib} .
- A modification of E_{elec} will result in alterations for both E_{rot} and E_{vib} resulting in a vast collection of possible transitions obtained in all three cases, and since the polarities of the bonds within the molecules will be disturbed their spectra are given the generic name of *charge transfer spectra*.

$$\Delta E_{\text{tot}} = \Delta E_{\text{rot}} + \Delta E_{\text{vib}} + \Delta E'_{\text{elec}}$$

with $\Delta E_{\text{elec}} > \Delta E_{\text{vib}} > \Delta E_{\text{rot}}$.

Beer-Lambert's Law

It states that when a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease in intensity of incident radiation with thickness of absorbing solution is directly proportional to the product of the intensity of incident radiation and concentration of the solution.

$$-\frac{dI}{dx} \propto IC$$

$$-\frac{dI}{dx} = kIC$$

$$\frac{dI}{I} = -kCdx$$

$$\int_{I_0}^I \frac{dI}{I} = -kC \int_0^x dx$$

$$\ln \frac{I}{I_0} = -kCx$$

$$2.303 \log \frac{I}{I_0} = -kCx$$

$\frac{I}{I_0}$ is called Transmittance

$$\log \frac{I}{I_0} = -\frac{kCx}{2.303}$$

$$\log \frac{I_0}{I} = \frac{k}{2.303} Cx$$

$$\log \frac{I_0}{I} = \epsilon Cx$$

ϵ is called **molar absorption coefficient** or **molar absorptivity** or **molar extinction coefficient**

$\log \frac{I_0}{I}$ is called *absorbance* or *optical density* (A)

$$A = \epsilon C x$$

If concentration and thickness of absorbing solution becomes unity, i.e., $C = 1 \text{ mol/L}$ and $x = 1 \text{ cm}$, then

$$A = \epsilon$$

Thus, molar absorption coefficient (ϵ) can be defined as the absorbance (A) of an absorbing solution of unit concentration and unit path length. It depends on the frequency of incident radiation and is the largest when absorption of radiation takes place to a greater extent. Its unit is $\text{Conc}^{-1} \text{ length}^{-1}$

$$A = \log \frac{I_0}{I} = -\log \frac{I}{I_0}$$

$$A = -\log T \quad \text{where, } T \text{ is the transmittance}$$

$$\frac{I_0}{I} = 10^{\epsilon C x}$$

$\frac{I_0}{I}$ is called *opacity*

Example For a solution of camphor in hexane in a 5-cm cell, the absorbance A was found to be 2.52 at 295 nm with $\varepsilon_{\text{max}} = 14$. What is the concentration of camphor?

Solution

$$A = \varepsilon c \ell$$

$$A = 2.52 \quad c = ? \quad \varepsilon = 14 \quad \ell = 5 \text{ cm}$$

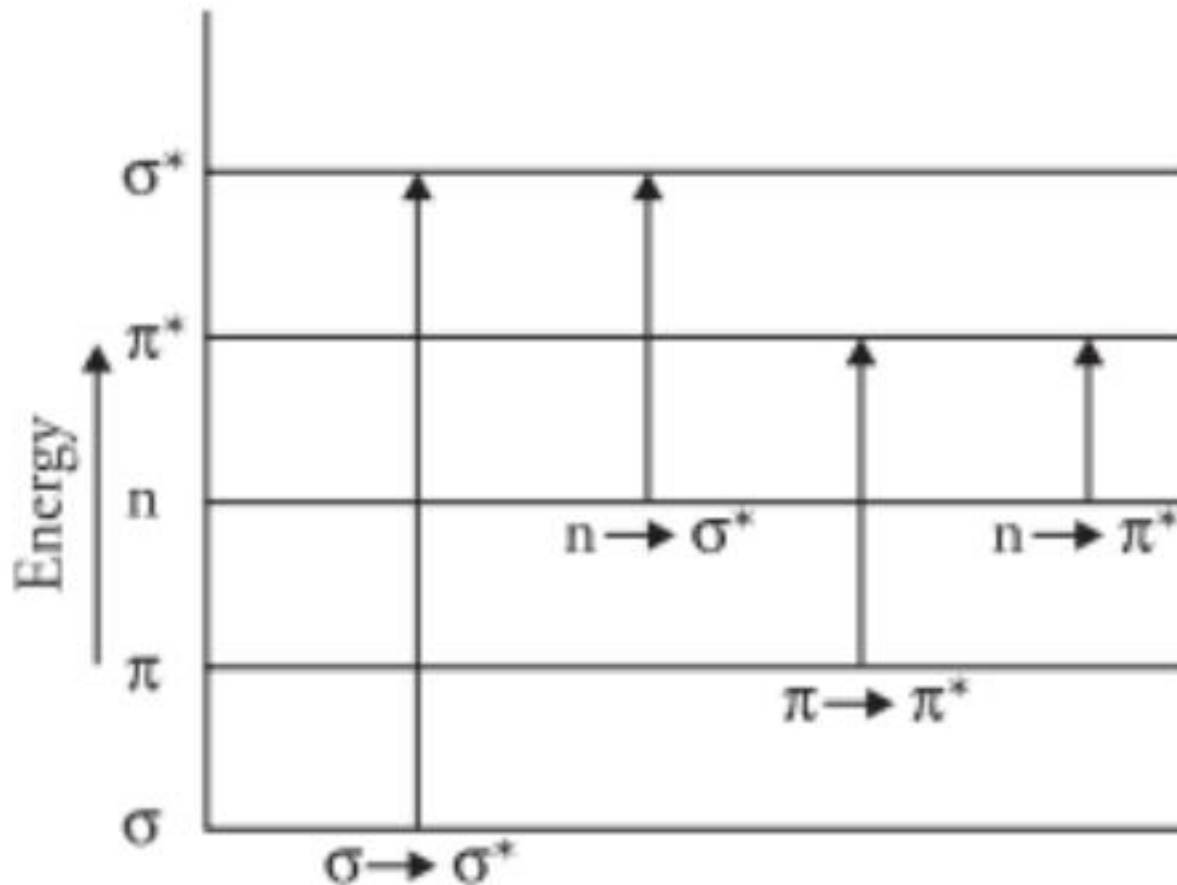
$$\therefore 2.52 = 14 \times c \times 5$$

$$c = \frac{2.52}{14 \times 5} = 3.6 \times 10^{-2} \text{ mol/L}$$

Types of Electronic Transitions

When a molecule absorbs ultraviolet or visible light, its electrons are promoted from the ground state to a higher energy state. The electrons in the bonding molecular orbitals, for example, σ orbital, π orbital or non-bonding orbitals are promoted to anti-bonding molecular orbitals like σ^* and π^* (asterick * designates the anti-bonding orbital).

The following types of electronic transitions are possible.



$\sigma \rightarrow \sigma^*$ transitions The σ bonded electrons are held firmly in the molecule. Hence, the transitions from σ to σ^* require large amount of energy. These transitions require high energy radiations and therefore, occur in the far ultraviolet region (~ 150 nm; high energy). Since oxygen of air absorbs strongly in this region, air has to be evacuated (vacuum ultraviolet spectroscopy). $\sigma \rightarrow \sigma^*$ transitions occur in hydrocarbons like methane, propane and are less informative.

$n \rightarrow \sigma^*$ transitions This type of transitions occur in saturated compounds with one hetero atom having unshared pairs of electrons (n electrons) like alcohols, ethers, amines, ketones, aldehydes, etc. The energy required for these transitions is lesser than the energy required for $\sigma \rightarrow \sigma^*$ transitions, for example, water absorbs at 167 nm, methyl alcohol at 174 nm and methyl chloride absorbs at 169 nm.

$\pi \rightarrow \pi^*$ transitions These transitions take place in compounds containing double and triple bonds. The excitation of π electrons requires lesser energy; hence they occur at longer wavelength. In unconjugated alkenes, absorption bands appear around 170–190 nm.

$n \rightarrow \pi^*$ transitions In these transitions, the electrons of the unshared electron pair on the hetero atom is excited to π^* anti-bonding orbital. As non-bonding electrons are loosely held, these require least energy and occur at larger wavelengths. They occur in unsaturated compounds with hetero atoms having unshared pairs of electrons like $C = O$, $C = S$.

The relative energies required for the various transitions follow the order.



Chromophore

It is defined as any isolated covalently bonded group that shows a characteristic absorption in the UV-Vis region.

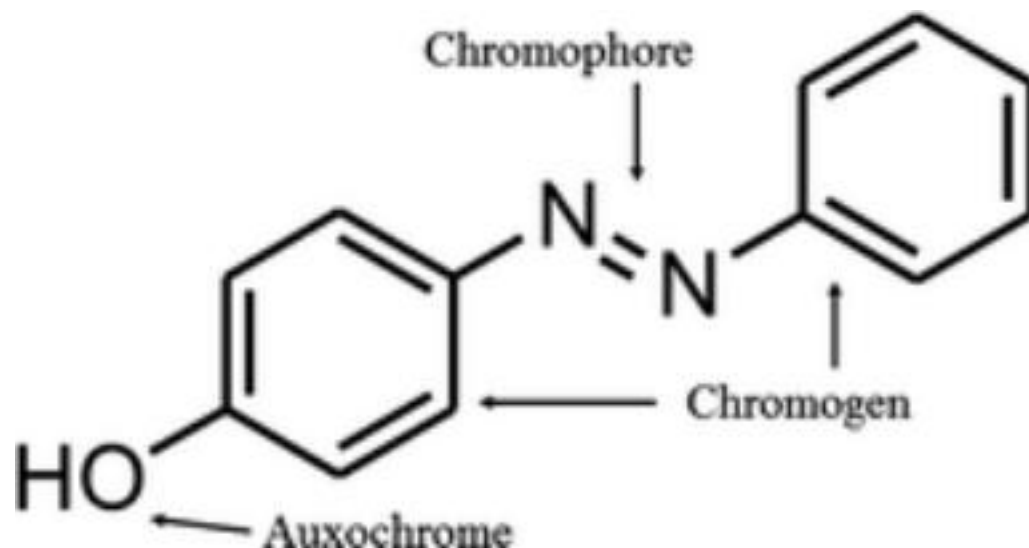
The functional groups of organic compounds (ketones, amines, nitrogen derivatives, etc.), responsible for absorption in UV/Vis are called *chromophores*. A species formed from a carbon skeleton transparent in the near UV on which are attached one or several chromophores constitutes a *chromogene*.

Name	Chromophore	λ_{\max} (nm)	ϵ_{\max} (Lmol ⁻¹ cm ⁻¹)
Amine	-NH ₂	195	3000
Oxime	=NOH	190	5000
Nitro	-NO ₂	210	3000
Nitrite	-ONO	230	1500
Nitrate	-ONO ₂	270	12
Nitroso	-N=O	300	100

Chromophore	Excitation	λ_{max} , nm	Solvent
C=C	$\pi \rightarrow \pi^*$	171	hexane
C=O	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	hexane hexane
N=O	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	ethanol ethanol
C-X X=Br, I	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	hexane hexane

Auxochrome

An auxochrome can be defined as any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the longer wavelength of the spectrum. $-OH$, $-OR$, $-NH_2$, $-NHR$, $-SH$ etc. are the examples of auxochromic groups.



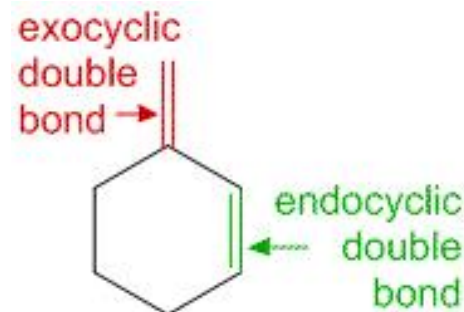
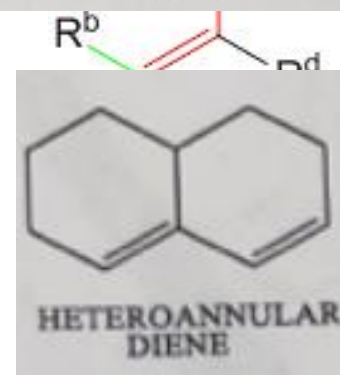
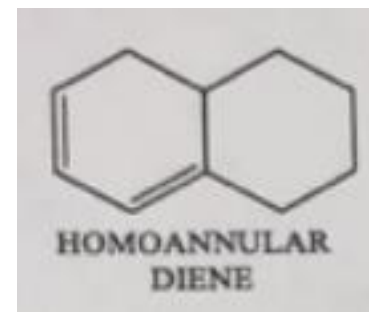
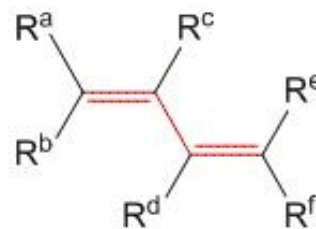
Woodward-Fieser rules for prediction of λ_{max}

The base value for:

- Butadiene system or acyclic conjugated diene = 217 nm.
- Homoannular conjugated diene (conjugated double bond in same ring) = 253 nm.
- Heteroannular conjugated diene (conjugated double bond in different rings) = 215 nm.

Increment for each substituent:

- Double bonds extending conjugation = + 30 nm
- Exocyclic double bond = + 5 nm
- Each alkyl substituent or ring residue = + 5 nm

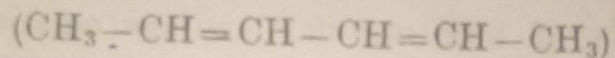


Substituent/Auxochrome effect:

-OCOR or -OCOAr	+ 0 nm
Simple alkyl substituents or ring residue	+ 5 nm
Halogen (-Cl, -Br)	+ 5 nm
OR (R=Alkyl)	+ 6 nm
SR (R=Alkyl)	+ 30 nm
NR ₂ (R=Alkyl)	+ 60 nm

Example 1. Calculate the absorption maximum in the ultra-violet spectrum of 2, 4 Hexadiene.

The basic unit in 2, 4 hexadiene



is butadiene. There are two alkyl substituents (one on each double bond) on it. Thus,

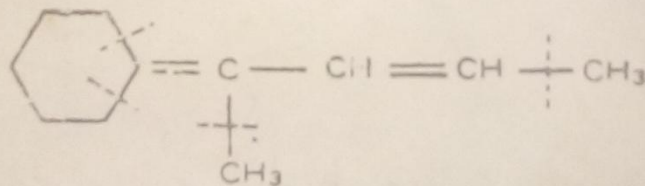
$$\text{Basic value} = 217 \text{ m}\mu$$

$$2\text{-alkyl substituents } (2 \times 5) = 10 \text{ m}\mu$$

$$\text{Calculated value} = \underline{227 \text{ m}\mu}.$$

The observed value* is also found to be 227 mμ.

Example 2. Calculate the absorption maximum in the UV spectrum of



It is a butadiene system. There are two alkyl substituents and two ring residues on the double bonds. Moreover, there is an exo-cyclic double bond.

The value of absorption maximum is calculated as follows :

$$\text{Basic value} = 217 \text{ m}\mu$$

$$2\text{-alkyl substituents } (2 \times 5) = 10 \text{ m}\mu$$

$$2\text{-Ring residues } (2 \times 5) = 10 \text{ m}\mu$$

$$1\text{-Exocyclic double bond} = \underline{5 \text{ m}\mu}$$

$$\text{Calculated value} = \underline{242 \text{ m}\mu}$$

The observed value is also found to be 242 mμ.

Example 3. Calculate λ_{max} for

It is an example of heteroannular diene



and there are four ring residues on the double bonds. Thus,