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# ORGANIC SPECTROSCOPY - UV BY

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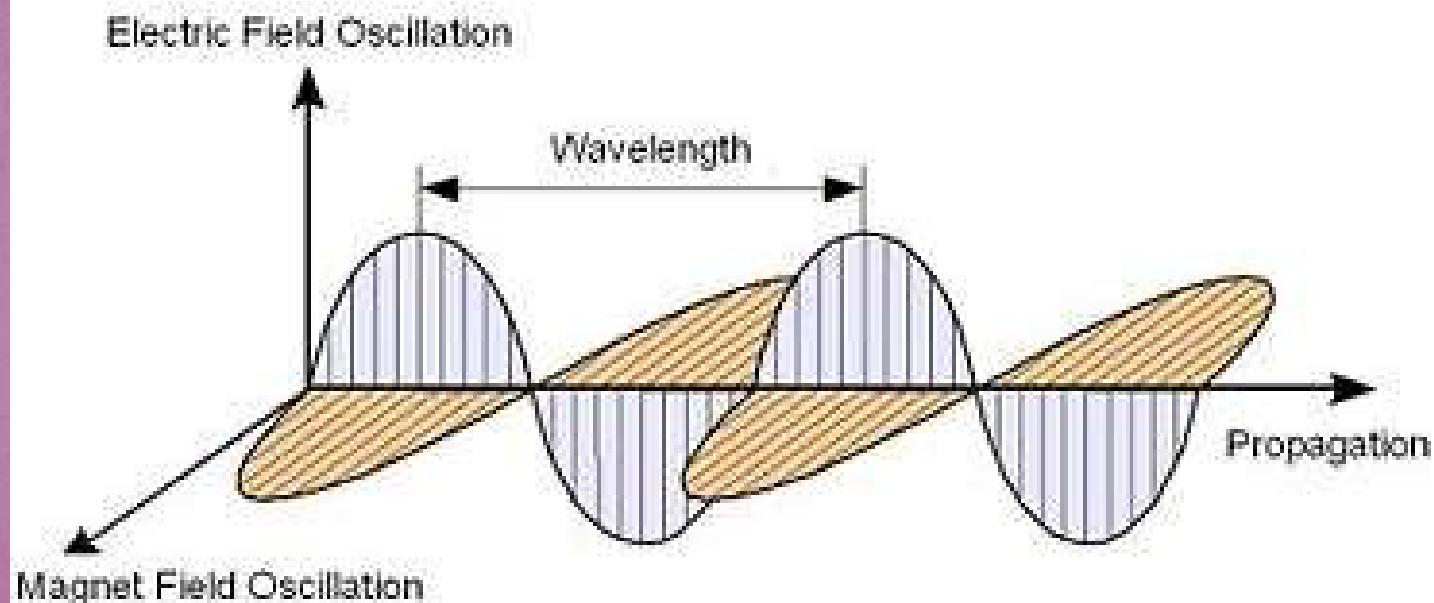


# ELECTROMAGNETIC RADIATION

- Electromagnetic radiation is a type of energy that is transmitted through space at enormous velocities.
- Radiant energy has wave nature and being associated with electric as well as magnetic field, these radiations are called electromagnetic radiation.
- Electromagnetic radiation has its origin in atomic and molecular processes.

- The field may be represented as electric and magnetic vectors oscillating in mutually perpendicular planes.

## Electromagnetic Radiation



## ENERGY OF AN EMR

The energy of an EMR can be given by the following equation:

$$E=h\nu$$

Where E= Energy of radiation

h=Planck's constant

$\nu$ =Frequency of radiation

$$\text{Frequency}(\mu) = c/\lambda$$

Where  $c$  = velocity of light in vacuum

$\lambda$  = wavelength

∴ Hence,  $E = h\mu$

$$E = hc/\lambda$$

Therefore, energy of a radiation depends upon frequency and wavelength of radiation.

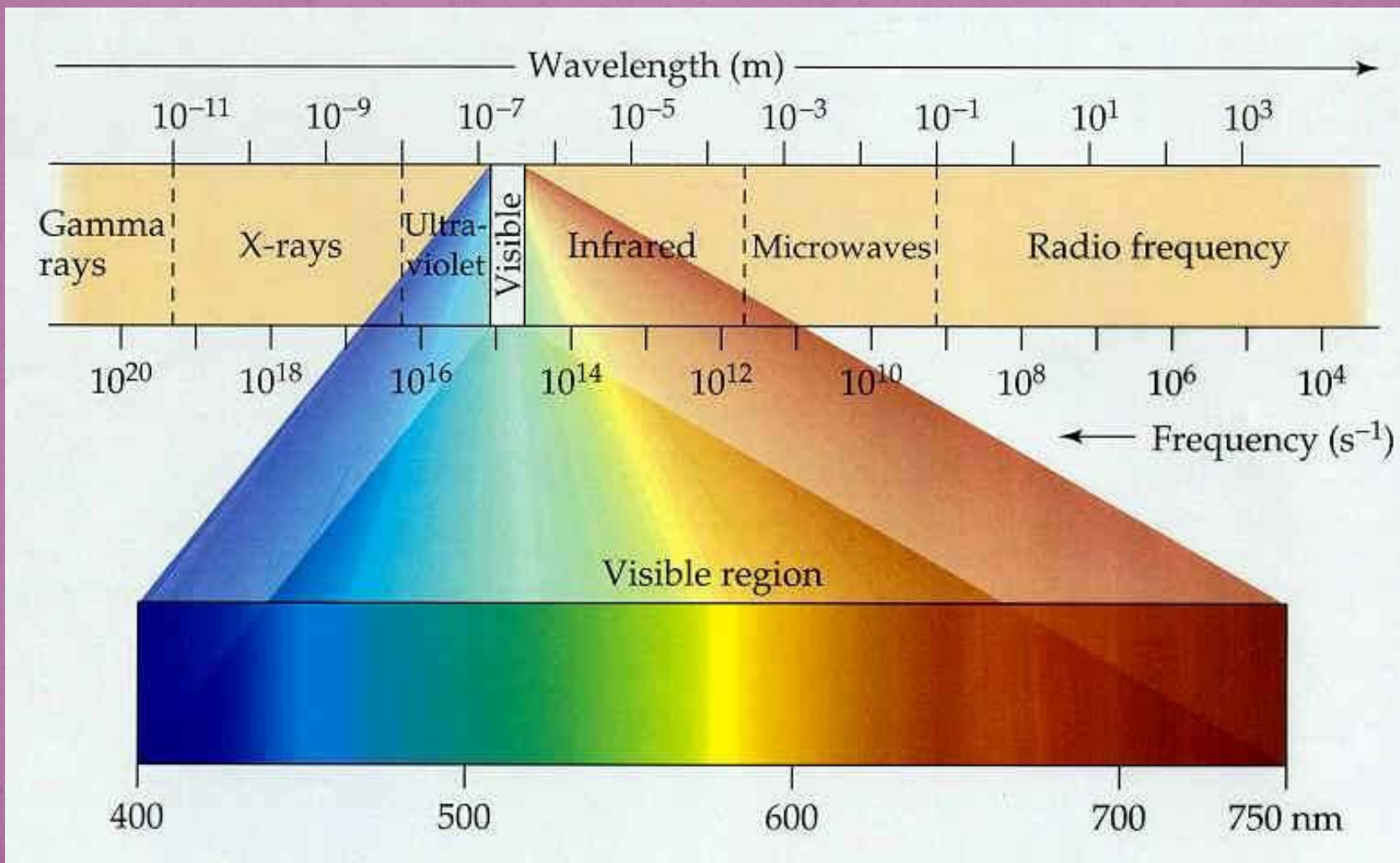


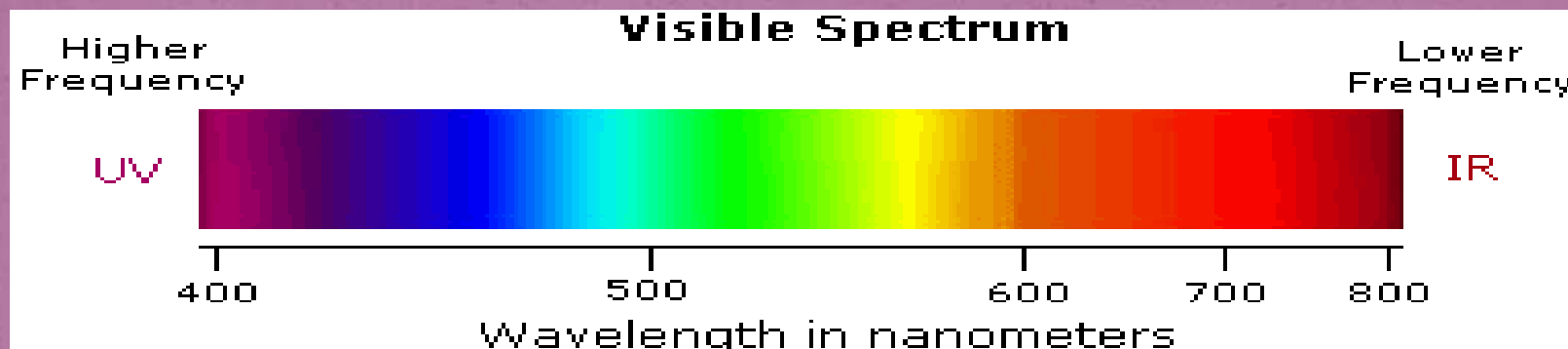
# ELECTROMAGNETIC SPECTRUM

The arrangement obtained by arranging various types of electromagnetic waves or radiations in order of their increasing wavelegth or decreasing frequencies is called electromagneticspectrum.

The electromagnetic spectrum is divided into a number of regions; these are artificial divisions in the sense that they have been defined solely as a result of differences in the instrumentation required for producing and detecting radiation of a given frequency range.

# REGIONS OF ELECTROMAGNETIC SPECTRUM





- ☐ Ultraviolet: 190~400nm
- ☐ Violet: 400 - 420 nm
- ☐ Indigo 420 - 440 nm
- ☐ Blue: 440 - 490 nm
- ☐ Green: 490 - 570 nm
- ☐ Yellow: 570 - 585 nm
- ☐ Orange: 585 - 620 nm
- ☐ Red: 620 - 780 nm



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# spectroscopy

# SPECTROSCOPY

Spectroscopy is the measurement and interpretation of electromagnetic radiation absorbed or emitted when the molecules or atoms or ions of a sample moves from one energy state to another energy state



## TYPES OF SPECTROSCOPY

### 1) Atomic spectroscopy:

Here, the changes in energy takes place at atomic level.

Eg: Atomic absorption spectroscopy, Flame photometry

### 2) Molecular spectroscopy:

Here, the changes in energy takes place at molecular level.

Eg: UV spectroscopy, colorimetry, infra red spectroscopy



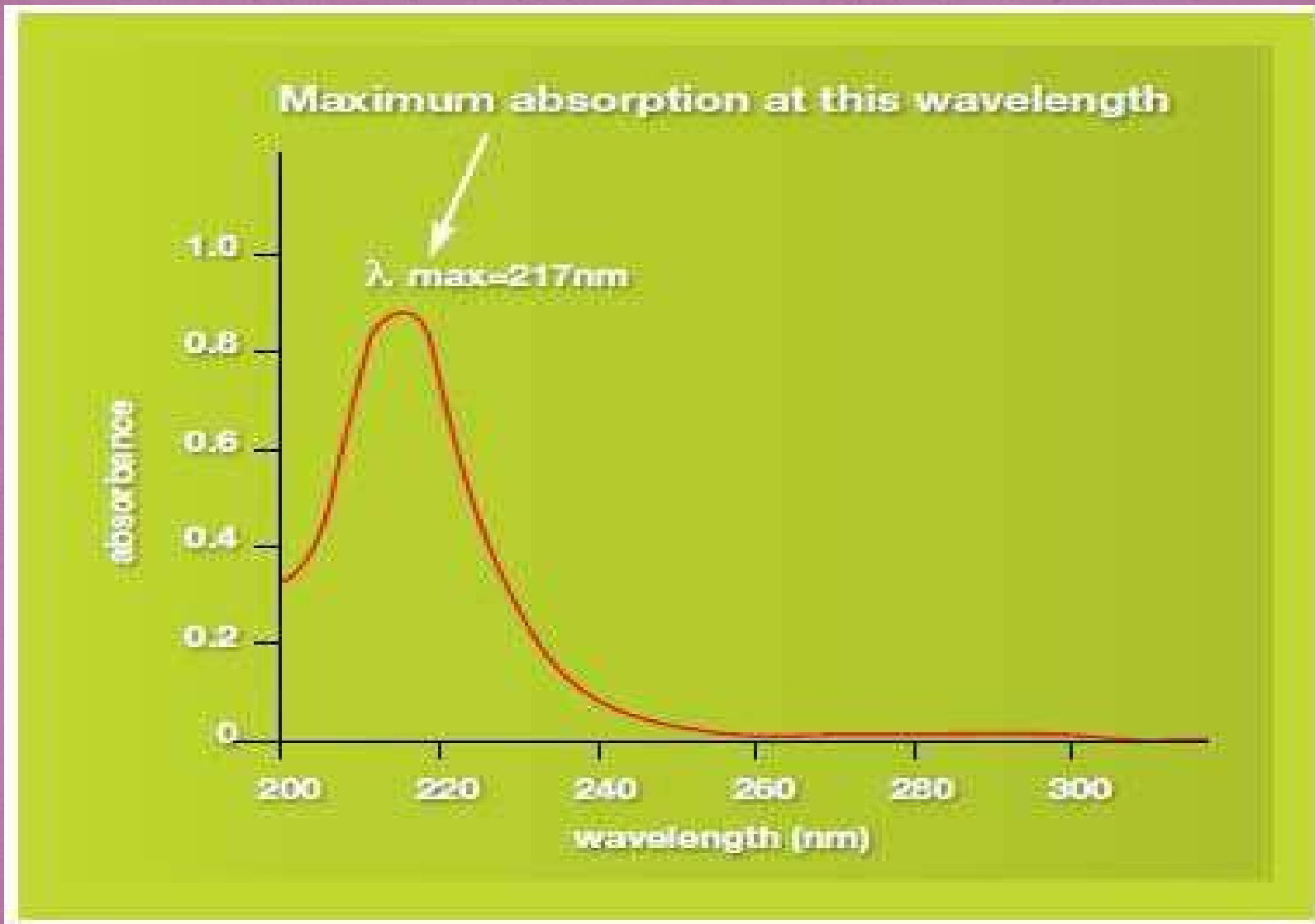
# ABSORPTION SPECTROPHOTOMETRY

Absorption spectrophotometry can be defined as the measurement of absorption of radiant energy by various substances. It involves the measurement of absorptive capacity for radiant energy in the visible, UV and IR regions of the spectrum.



# COLORIMETRY

- $\lambda$ - 400-800nm
- Coloured substance absorbs light of different  $\lambda$  in different manner and hence get an absorption curve
- The  $\lambda$  at which maximum absorption takes place is called as  $\lambda_{\max}$
- $\lambda_{\max}$  is characteristic for every coloured substance
- On plotting a graph of concentration v/s absorbance, we get a calibration curve that is useful in determining the concentration or amount of a drug substance in the given sample solution.

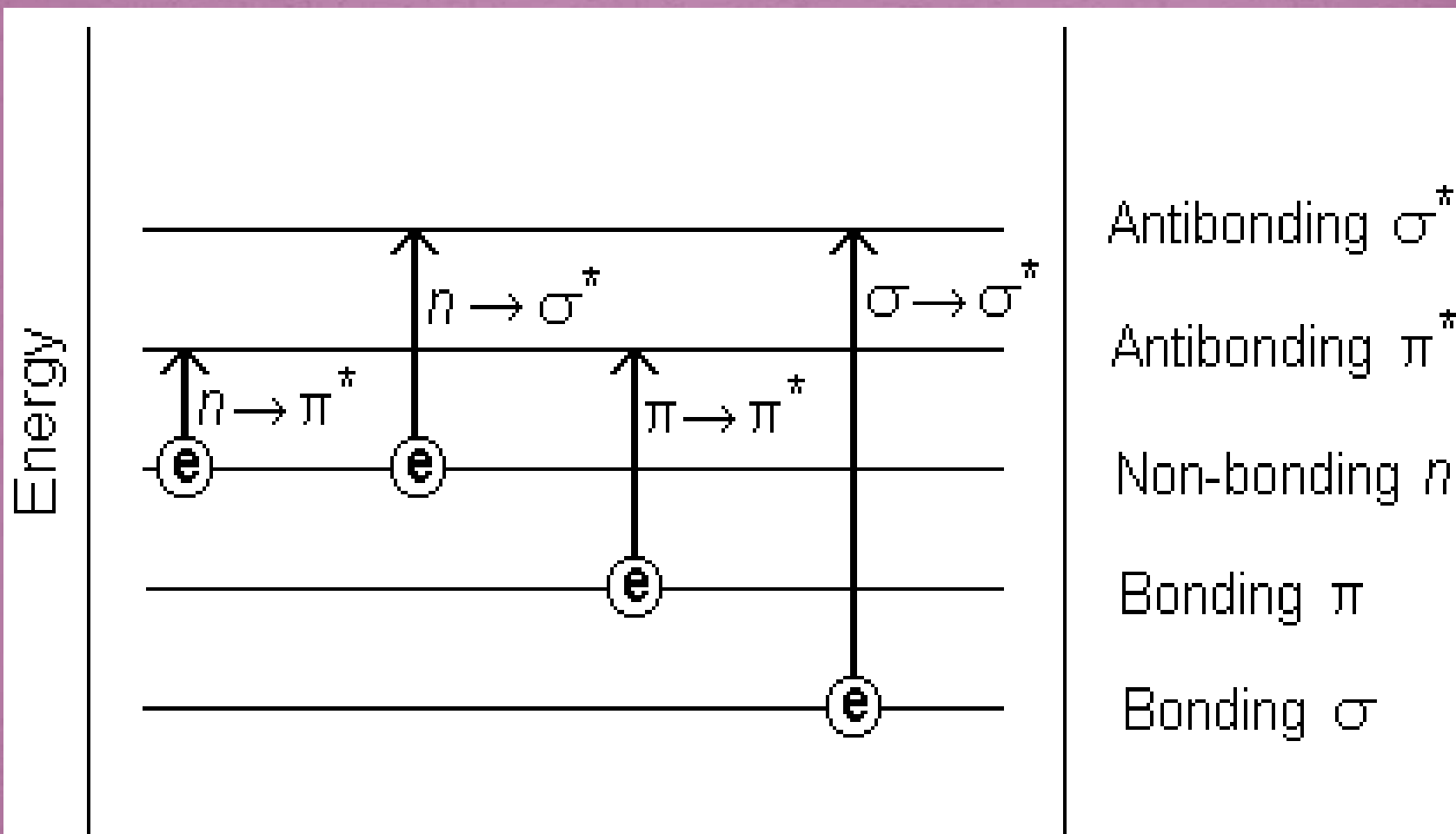




# UV SPECTROSCOPY

- UV spectroscopy is concerned with the study of absorption of uv radiation which ranges from 200-400nm.
- Valence electrons absorb the energy thereby molecules undergoes transition from ground state to excited state.
- This absorption is characteristic and depends on the nature of electrons present.
- Types of electrons
  - σ electrons: in saturated compounds
  - π electrons: in unsaturated compounds
  - n electrons: in non bonded electrons

# ELECTRONIC TRANSITIONS



## 1) $\sigma$ - $\sigma^*$

- $\sigma$  electron from orbital is excited to corresponding anti-bonding orbital  $\sigma^*$ .
- The energy required is large for this transition.
- The organic compounds in which all the valence shell electrons are involved in the formation of  $\sigma$  bond do not show absorption in normal uv region (200-400nm)
- This transition is observed with saturated compounds.



- Eg: Methane( $\text{CH}_4$ ) has C-H bond only and can undergo  $\sigma$ - $\sigma^*$  transition and shows absorption maxima at 122nm.
- The usual spectroscopic technique cannot be used below 200 nm.
- To study this high energy transition, the entire region should be evacuated (Vacuum uv region)
- Here, the excitation occurs with net retention of electronic spin
- This region is less informative

## 2) $\pi$ - $\pi^*$

- $\pi$  electron in a bonding orbital is excited to corresponding anti-bonding orbital  $\pi^*$ .
- Energy required is less when compared to  $n$ - $\sigma^*$
- Compounds containing multiple bonds like alkenes, alkynes, carbonyls, nitriles, aromatic compounds etc undergo  $\pi$ - $\pi^*$  transition.
- Eg: Alkenes generally absorb in the region 170-205nm.



- Absorption usually occurs in the ordinary uv spectrophotometer
- Absorption bands in unconjugated alkenes (170-190nm)
- Absorption bands in carbonyls (180 nm)
- Introduction of alkyl group in olefinic linkage produces bathochromic shift

### 3) $n-\sigma^*$

- Saturated compounds containing one hetero atom with unshared pair of electrons ( $n$ ) like O, N, S and halogens are capable of  $n-\sigma^*$  transition.
- These transition require less energy than  $\sigma-\sigma^*$  transition.
- In saturated alkyl halides, the energy required for transition decrease with increase in the size of halogen atom (or decrease in electronegativity)



- Eg: Methyl chloride has a  $\lambda_{\max}$  of 173nm.  
Methyl iodide has a  $\lambda_{\max}$  of 258nm.
- This type of transition is very sensitive to hydrogen bonding Eg: Alcohol & amines
- Hydrogen bonding shift the uv absorptions to shorter wavelength.

## 4) $n-\pi^*$

- An electron from non-bonding orbital is promoted to anti-bonding  $\pi^*$  orbital.

Compounds containing double bonds involving hetero atoms (C=O, N=O) undergo such type of transitions.

- This transition require minimum energy out of all transitions and shows absorption band at longer wavelength around 300nm.
- Eg: Saturated aldehydes shows both type of transitions ( $n-\pi^*$ ,  $\pi-\pi^*$ ) at {low energy and high energy} around 290 and 180 nm.



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# TERMS USED IN UV- VISIBLE SPECTROSCOPY

# CHROMOPHORE

- Chromophore is defined as the nucleus or any isolated covalently bonded group responsible for the absorption of light radiation.
- Any group which exhibits absorption of electromagnetic radiations in the visible or ultraviolet region.  
 $C=C$  ,  $C=O$  ,  $NO_2$  etc
- Some of the important chromophores are carbonyls, acids, esters, nitrile, ethylenic groups.

# ABSORPTION CHARACTERISTICS OF SOME COMMON CHROMOPHORES

## Chromophores: examples

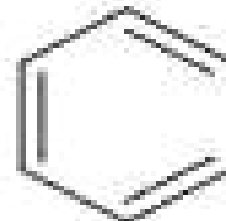
Chromophore	Example	Excitation	$\lambda_{\max}$ , nm	$\epsilon$	Solvent
<b>C=C</b>	<b>Ethene</b>	$\pi \rightarrow \pi^*$	171	15,000	hexane
<b>C<math>\equiv</math>C</b>	<b>1-Hexyne</b>	$\pi \rightarrow \pi^*$	180	10,000	hexane
<b>C=O</b>	<b>Ethanal</b>	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	15 10,000	hexane hexane
<b>N=O</b>	<b>Nitromethane</b>	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	17 5,000	ethanol ethanol
<b>C-X; X=Br X=I</b>	<b>Methyl bromide Methyl iodide</b>	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	200 360	hexane hexane

# AUXOCHROME

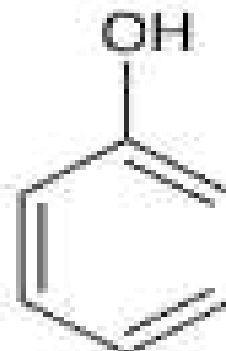
- These are co-ordinatively saturated or un saturated groups which themselves do not absorb radiations, but when present along with a chromophore enhances the absorbing properties of chromophore.
- Also known as colour enhancing group.
- All auxochromes have one or more non-bonding pair of electrons.  
-NH<sub>2</sub>, -OH, -OR, -COOH etc
- It extend the conjugation of a chromophore by sharing the non-bonding electrons.

## AUXOCHROME

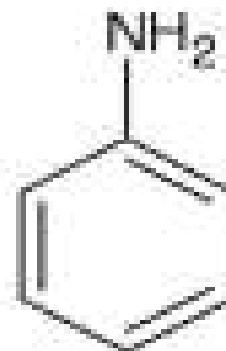
e.g. Benzene  $\lambda_{\text{max}} = 255 \text{ nm}$



Phenol  $\lambda_{\text{max}} = 270 \text{ nm}$



Aniline  $\lambda_{\text{max}} = 280 \text{ nm}$





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# ABSORPTION & INTENSITY SHIFTS

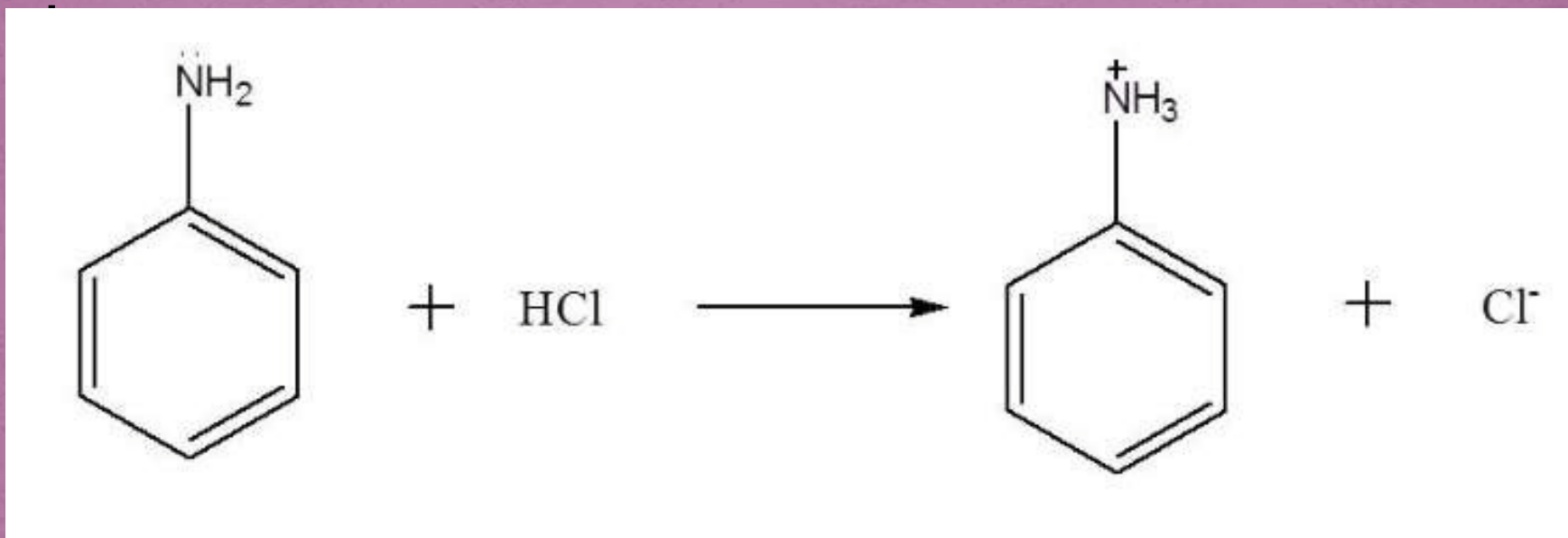
## 1) Bathochromic shift(red shift)

- When the absorption maxima( $\lambda_{\max}$ ) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.
- The effect is due to the presence of auxochrome or by change of solvent.
- Eg: The  $n-\pi^*$  transition for carbonyl compounds experiences bathochromic shift when the polarity of solvent is decreased.

## 2) Hypsochromic shift(blue shift)

- When the absorption maxima ( $\lambda_{\max}$ ) of a compound shifts to a shorter wavelength, it is known as hypsochromic shift or blue shift.
- The effect is due to the presence of a group causes removal of conjugation or by change of solvent.

Eg

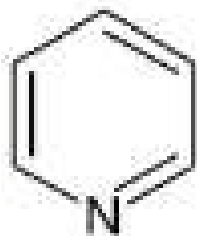


Aniline shows blue shift in acidic medium since it loses conjugation. Aniline(280nm) & Anilinium ion (- 203nm).

### 3) Hyperchromic effect

When the absorption intensity( $\epsilon$ ) of a compound is increased, it is known as hyperchromic shift.

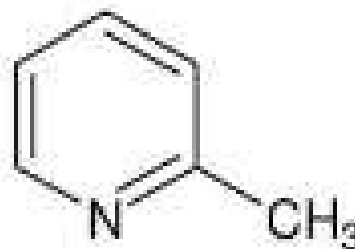
The introduction of auxochrome usually increases absorption intensity.



Pyridine

$$\lambda_{\max} = 257 \text{ nm}$$

$$\epsilon = 2750$$



2-methyl pyridine

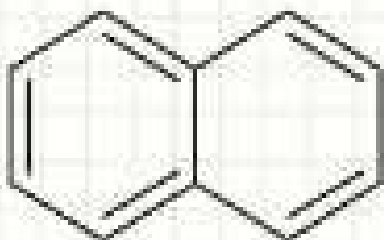
$$\lambda_{\max} = 260 \text{ nm}$$

$$\epsilon = 3560$$

## 4) Hypochromic effect

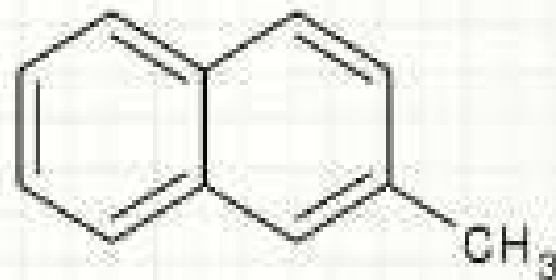
When the absorption intensity ( $\epsilon$ ) of a compound is decreased, it is known as hypochromic shift.

The introduction of a group which distorts the geometry of molecule causes hypochromic effect.



Naphthalene

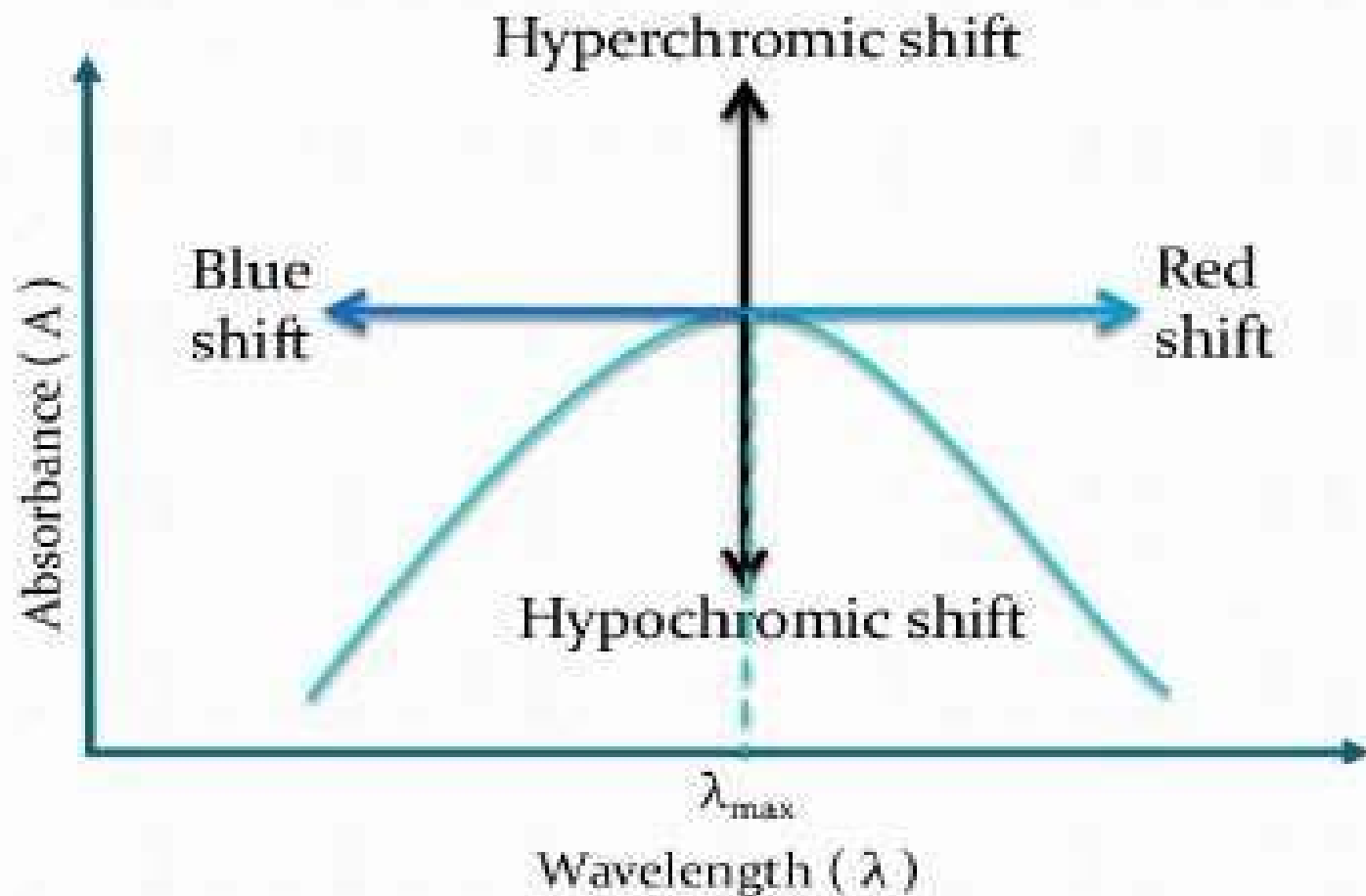
$$\epsilon = 19000$$



2-methyl naphthalene

$$\epsilon = 10250$$

# SHIFTS & EFFECTS





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# ABSORPTION BANDS



## FORMATION OF ABSORPTION BANDS

- The spectrum consist of sharp peaks and each peak will correspond to the promotion of electron from one electronic level to another.
- During promotion, the electron moves from a given vibrational and rotational level within one electronic mode to the other within the next electronic mode.
- Thus, there will be a large no of possible transitions
- Hence, not just one but a large no. of wavelengths which are close enough will be absorbed resulting in the formation of bands

# TYPES OF ABSORPTION BANDS

## 1) K –Band

- ❖ K-Bands originate due to  $\pi$ - $\pi^*$  transition from a compound containing a conjugated system
- ❖ Such type of bands arise in compounds like dienes, polyenes and enones etc.

Compound	Transition	$\lambda_{\max}(\text{nm})$	$\epsilon_{\max}$
Acetophenone	$\pi$ - $\pi^*$	240	13,000
1,3-butadiene	$\pi$ - $\pi^*$	217	21,000

## 2) R-Band

- ❖ R-Band transition originate due to  $n-\pi^*$  transition of a single chromophoric group and having at least one lone pair of electrons on the hetero atom
- ❖ These are less intense with  $\epsilon_{\max}$  value below 100

Compound	Transition	$\lambda_{\max}(\text{nm})$	$\epsilon_{\max}$
Acetone	$n-\pi^*$	270	15
Acetaldehyde	$n-\pi^*$	293	12

### 3) B-Band

- ❖ Such type of bands arise due to  $\pi$ - $\pi^*$  transition in aromatic or hetero-aromatic molecules.
- ❖ Benzene shows absorption peaks between 230-270nm. when a chromophoric group is attached to the benzene ring, the B-Bands are observed at longer wavelengths than the more intense K Bands.

Compound	Transition	$\lambda_{\max}(\text{nm})$	$\epsilon_{\max}$
Benzene	$\pi$ - $\pi^*$	255	215
Phenol	$\pi$ - $\pi^*$	270	1450

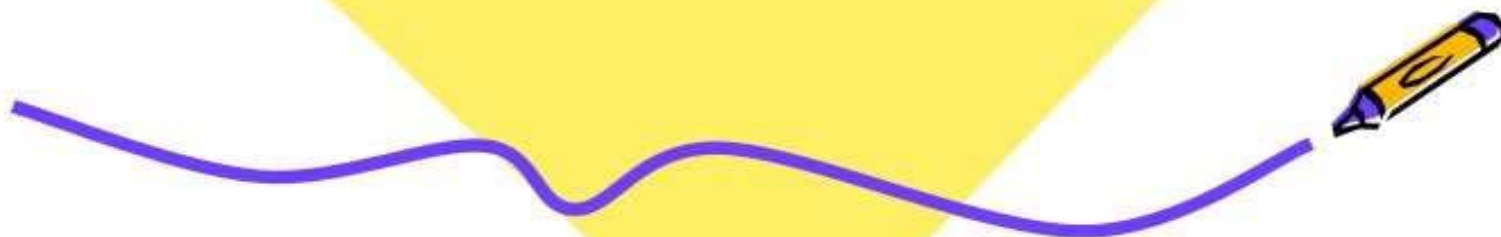
## 4) E-Band

- ❖ E-Band originate due to the electronic transitions in the benzenoid systems of three ethylenic bonds which are in closed cyclic conjugation.
- ❖ These are further characterized as E1 and E2 bands
- ❖ E1 band which appear at shorter wavelength is usually more intense than the E2 band for the same compound which appears at longer wavelength.

Compound	E1 Band	E1 Band	E2 Band	E2 Band
	$\lambda_{\max}(\text{nm})$	$\epsilon_{\max}$	$\lambda_{\max}(\text{nm})$	$\epsilon_{\max}$
Benzene	184	50,000	204	79,000
Napthalene	221	133,000	286	9,300



# The Beer-Lambert Law



## ➤ BEER'S LAW

According to this law, when a beam of monochromatic radiation is passed through a solution of absorbing species, the intensity of beam of monochromatic light decreases exponentially with increase in concentration of absorbing species

$$-dI/dc \propto I$$

## ➤ LAMBERT'S LAW

Lambert's law states that the rate of decrease of intensity of monochromatic light with the thickness of the medium is directly proportional to the intensity of incident light.

$$-dI/dt \propto I$$

# DERIVATION OF BEER-LAMBERT'S LAW

According to beer's law,

$$\frac{-dl}{dc} \propto I$$

The decrease in the intensity of light (I) with concentration(c) is proportional to intensity of incident light(I)

$$\frac{-dl}{dc} = K.I \quad \left\{ \begin{array}{l} \text{removing \&introducing the} \\ \text{constant of proportionality} \\ \text{"K"} \end{array} \right\}$$

$$\frac{-dl}{I} = K.dc \quad \left\{ \text{rearranging terms} \right\}$$

On Integrating the equation,

$$-\int dI/I = K \cdot \int dc$$

$$-\ln I = K \cdot c + b \quad \text{--- 1} \quad \{ b \rightarrow \text{constant of integration} \}$$

When concentration = 0, there is no absorbance, Hence

$I = I_0$  Substituting in equation 1

$$-\ln I_0 = K \cdot 0 + b$$

$$-\ln I_0 = b$$

Substituting the value of  $b$  in equation 1

$$-\ln I = K \cdot c - \ln I_0$$

$$\ln I_0 - \ln I = Kc \quad \{ \text{since } \log A - \log B = \log A/B \}$$

$$\ln \frac{I_0}{I} = Kc$$



$$\frac{I}{I_0} = e^{-kc} \quad \{\text{removing natural log}\}$$

$$\frac{I}{I_0} = e^{-kc} \quad \{\text{making inverse on both sides}\}$$

$$I = I_0 e^{-kc} \quad \text{————— 2 [equation for beer's law]}$$

According to Lambert's law,

$$\frac{-dI}{dt} \propto I$$

This eqn can be simplified by replacing 'c' with 't' in 2

$$I = I_0 e^{-kt} \quad \text{————— 3}$$

Eqn 2 & 3 can be combined to get  $I = I_0 e^{-kct}$

Converting natural log to base 10 &  $K = k \times 0.4343$

$$\frac{I}{I_0} = 10^{-kct} \quad \{\text{rearranging terms}\}$$

$$\frac{I_0}{I} = 10^{kct} \quad \{\text{inverse on both sides}\}$$

Taking log on both sides ,

$$\log \frac{I_0}{I} = Kct \quad \text{—————} \quad 4$$

Here, Transmittance  $T = \frac{I}{I_0}$  , Absorbance,  $A = \frac{\log 1}{T}$



$$A = \log \frac{1}{T}$$

$$A = \log \frac{1}{I/I_0} \quad \{ \text{Since } T = I_0/I \}$$

$$A = \log \frac{I_0}{I} \quad \text{---} \quad \text{5}$$

Using eqn 4 & 5, since  $A = \log I_0/I$  and  $\log I_0/I = Kct$ ,

$$A = Kct$$

Instead of K, we can use  $\epsilon$

**$A = \epsilon c t$  { Mathematical eqn for beer lambert's law }**

For any particular wavelength,

$$A = \epsilon b C$$

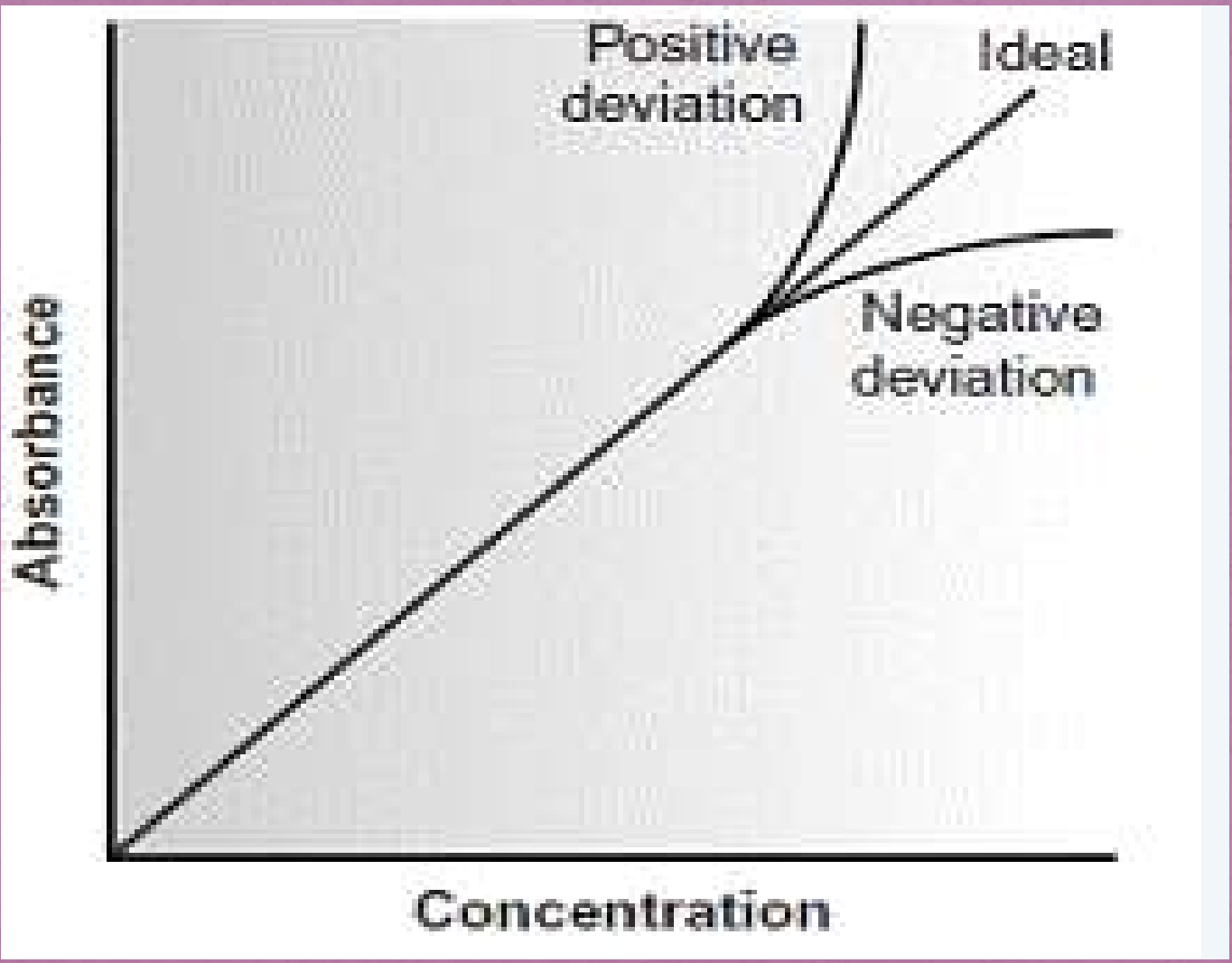
**Absorbance** (points to  $A$ )

**Molar absorptivity**  $\rightarrow$  L/(mol cm) (points to  $\epsilon$ )

**Path length**  $\rightarrow$  cm (points to  $b$ )

**Concentration** Mol/L (points to  $C$ )

# DEVIATIONS FROM BEER-LAMBERT'S LAW



There are 3 types of deviations usually observed

A) The real limitation of the law is that the Beer's law is successful in describing the absorption behaviour of dilute solutions only.

B) CHEMICAL DEVIATIONS:

✓ Association of molecules

This can be explained by taking the examples of methylene blue at small concentration ( $10^{-5}$  molar) and at concentration above  $10^{-5}$  molar.

## ✓ Dissociation of molecules

This can be explained by the fact that dichromate ions possess their maximum absorbance at 450nm which is orange in colour. But upon dilution, it will be dissociated to chromate ions having maximum absorbance at 410nm which is yellow in colour.

- ✓ This law is not valid in case if the absorbing material is coagulated into a small number of large units.
- ✓ This law shows deviation if the absorbing material at the required wavelength contains presence of impurities.

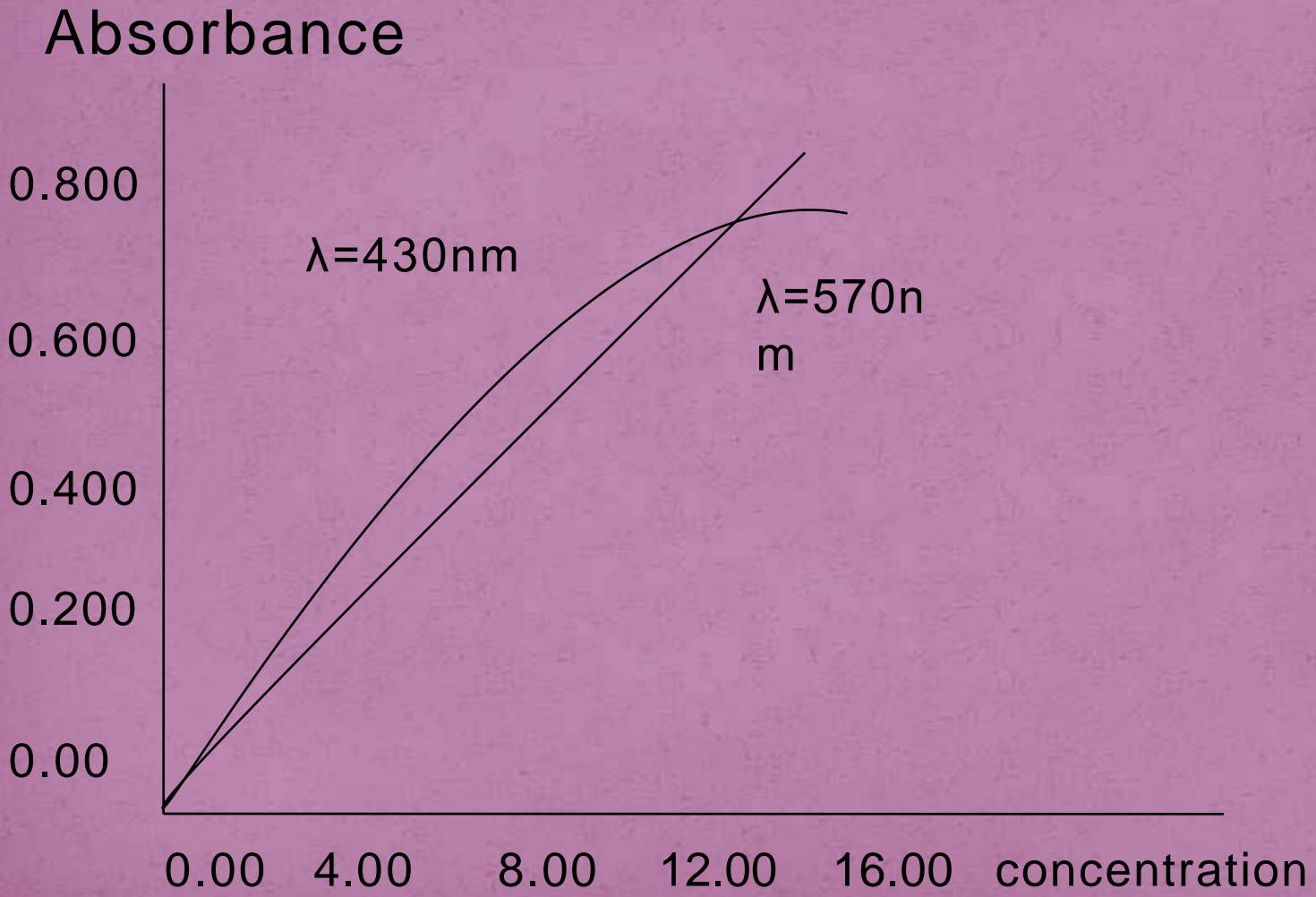
□ This law is not applicable in case of suspension.

### C) INSTRUMENTAL DEVIATIONS:

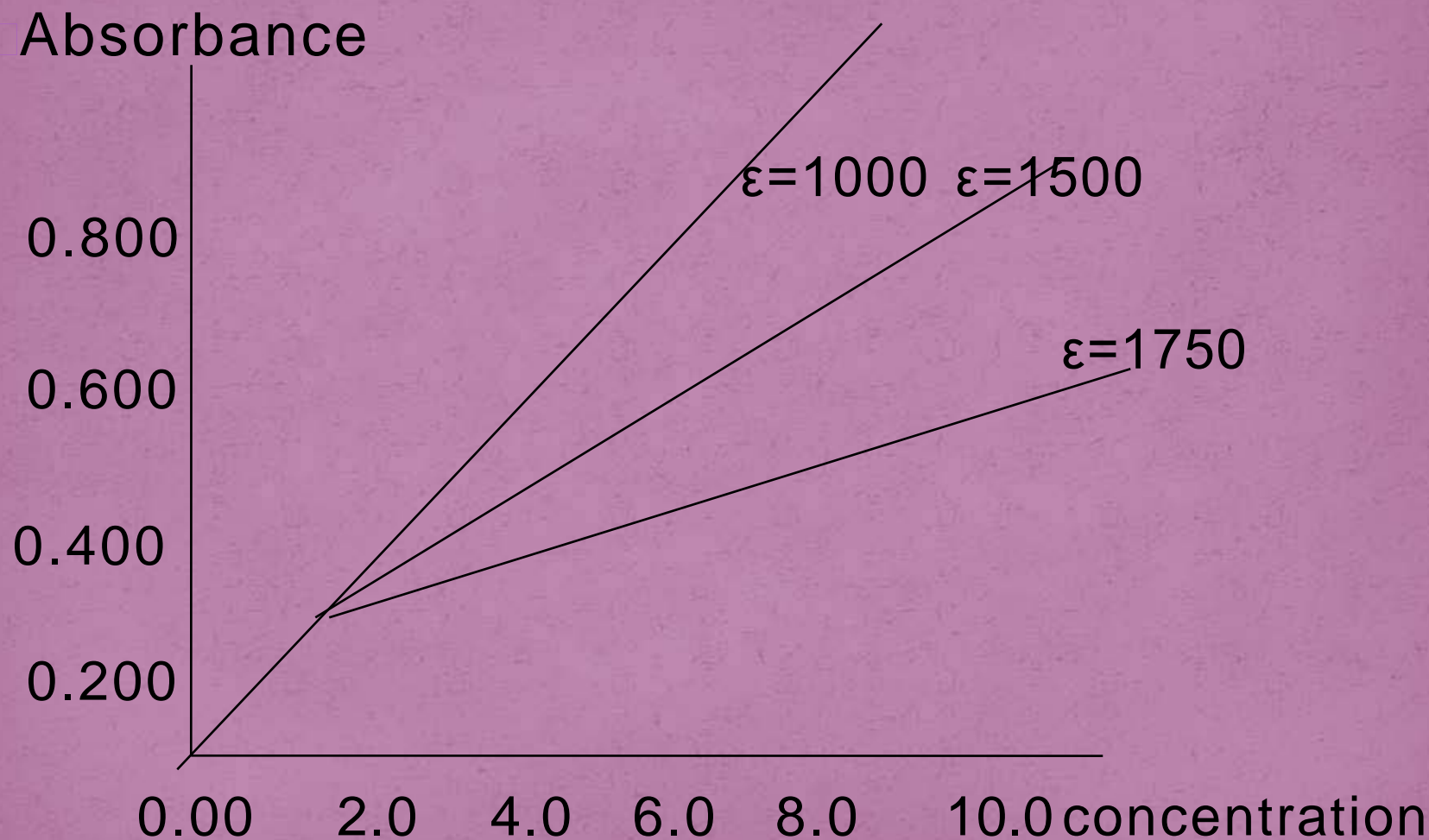
- ✓ Strict adherence of an absorbing system to this law is observed only when the radiation used is monochromatic.
- ✓ Stray radiation, slit width also causes deviation.

Hence, the reasons for the deviation depends on environment such as temperature, pressure, solvent, refractive index of the sample

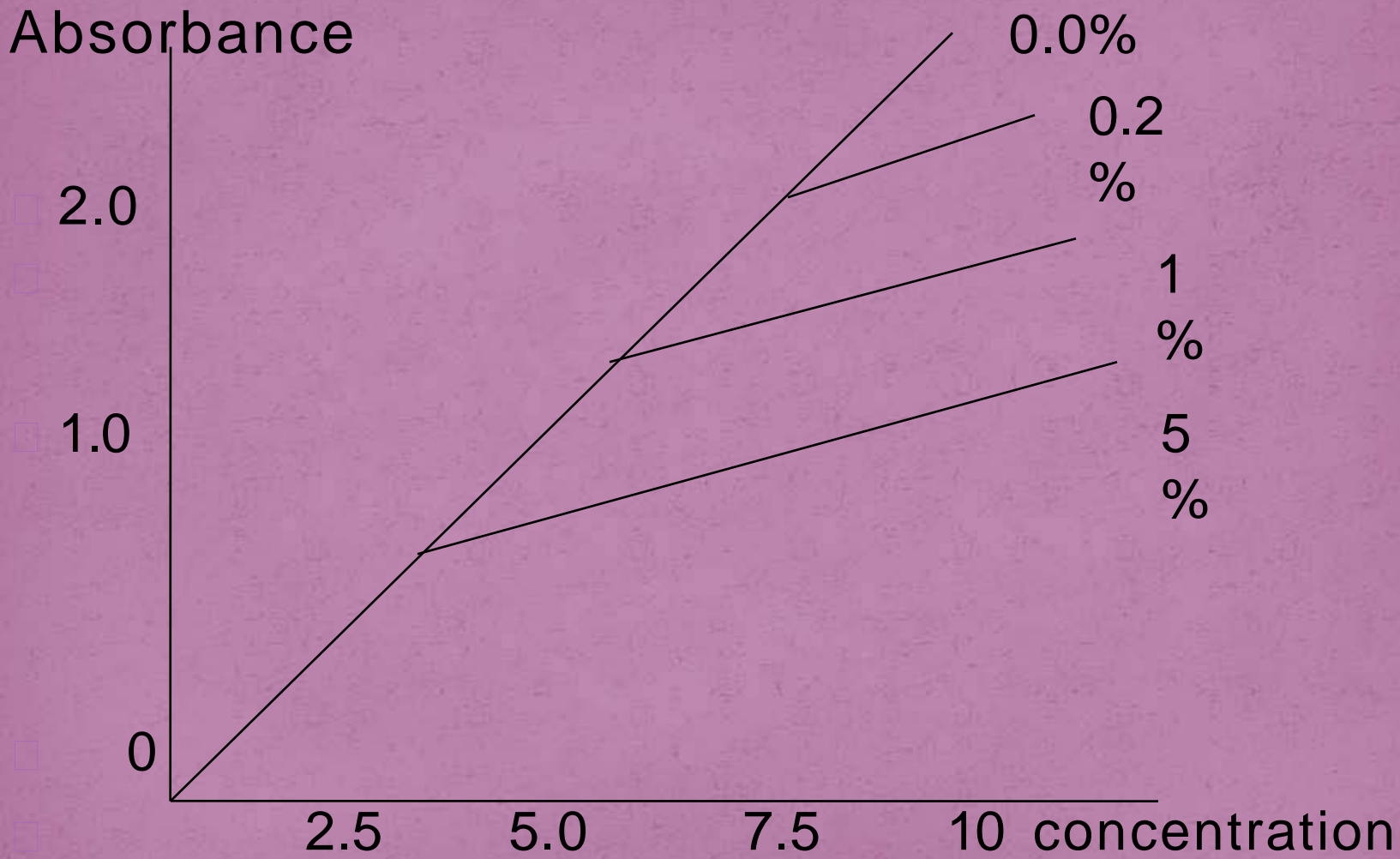
# CHEMICAL DEVIATIONS



## INSTRUMENTAL DEVIATIONS (Polychromatic light)



# INSTRUMENTAL DEVIATIONS (Stray radiation)





## REFERENCE

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