UV Spectroscopy

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Spectroscopy

- It is the branch of science that deals with the study of interaction of matter with light.

OR

- It is the branch of science that deals with the study of interaction of electromagnetic radiation with matter.

Electromagnetic Radiation

- Electromagnetic radiation consist of discrete packages of energy which are called as photons.

- A photon consists of an oscillating electric field (E) & an oscillating magnetic field (M) which are perpendicular to each other.

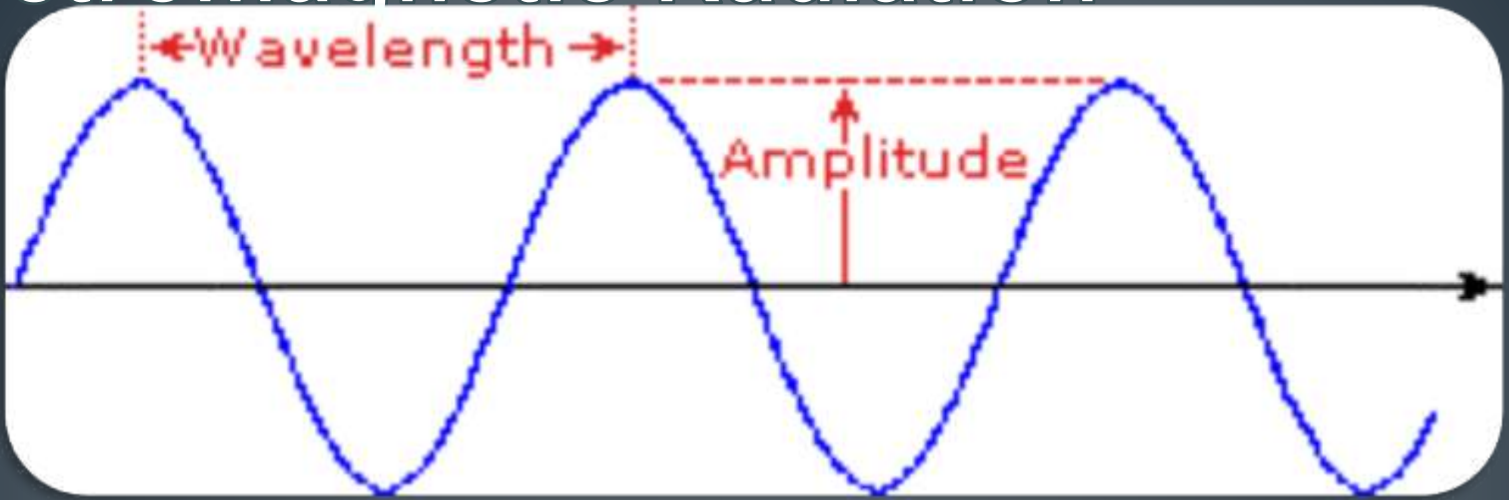
Electromagnetic Radiation

- Frequency (ν):
  - It is defined as the number of times electrical field radiation oscillates in one second.
  - The unit for frequency is Hertz (Hz).

    1 Hz = 1 cycle per second

- Wavelength (λ):
  - It is the distance between two nearest parts of the wave in the same phase i.e. distance between two nearest crest or troughs.

Electromagnetic Radiation



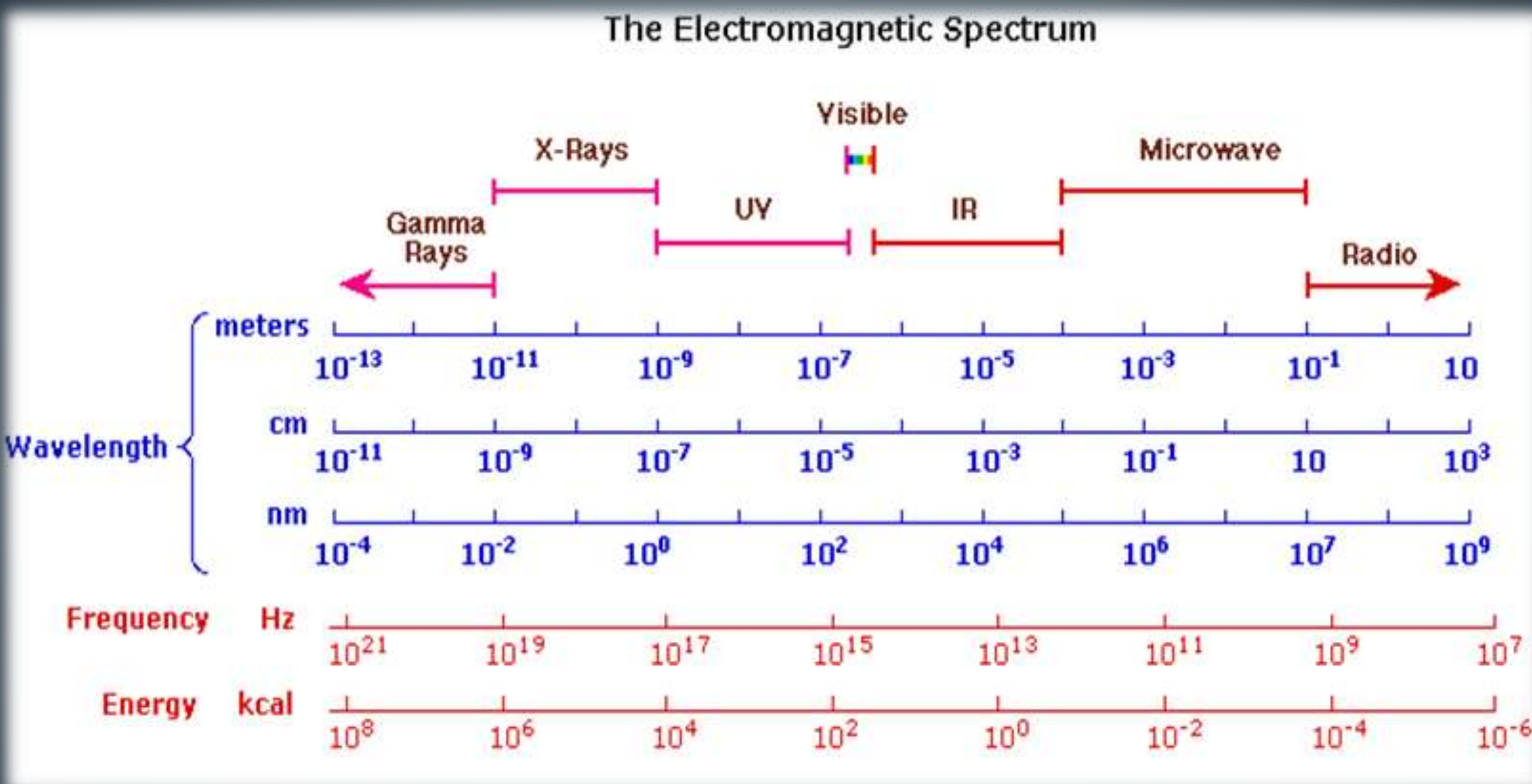
- The relationship between wavelength & frequency can be written as:

$$c = \nu \lambda$$

- As photon is subjected to energy, so

$$E = h \nu = h c / \lambda$$

Electromagnetic Radiation



Electromagnetic Radiation

Violet	400 - 420 nm	Yellow	570 - 585 nm
Indigo	420 - 440 nm	Orange	585 - 620 nm
Blue	440 - 490 nm	Red	620 - 780 nm

Principles of Spectroscopy

- The principle is based on the measurement of spectrum of a sample containing atoms / molecules.
- Spectrum is a graph of intensity of absorbed or emitted radiation by sample verses frequency (ν) or wavelength (λ).
- Spectrometer is an instrument design to measure the spectrum of a compound.

Principles of Spectroscopy

1. Absorption Spectroscopy:

- An analytical technique which concerns with the measurement of absorption of electromagnetic radiation.

- e.g. UV (185 - 400 nm) / Visible (400 - 800 nm) Spectroscopy, IR Spectroscopy (0.76 - 15 μm)

Principles of Spectroscopy

2. Emission Spectroscopy:
   - An analytical technique in which emission (of a particle or radiation) is dispersed according to some property of the emission & the amount of dispersion is measured.
   - e.g. Mass Spectroscopy

Beer –lambert's law

Lambert's Law

- When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation with thickness of the solution is directly proportional to the intensity of the incident light.

- Let I be the intensity of incident radiation.

x be the thickness of the solution.

Then

Lambert's Law

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

So, $$-\frac{dI}{dx} = KI$$

Integrate equation between limit

I = Io at x = 0 and

I = I at x=l,

We get,

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

Lambert's Law

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

$$\log \frac{I}{I_0} = -\frac{K}{2.303} l$$

Where, $\log \frac{I_0}{I} = A$ Absorbance

$$\frac{K}{2.303} = E$$ Absorption coefficient

$$A = E.l$$ Lambert's Law

Beer’s Law

- When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation with thickness of the solution is directly proportional to the intensity of the incident light as well as concentration of the solution.

- Let I be the intensity of incident radiation.

x be the thickness of the solution.

C be the concentration of the solution.

Then

Beer's Law

$$-\frac{dI}{dx}\alpha C.I$$

So, $$-\frac{dI}{dx} = K'C.I$$

Integrate equation between limit

I = Io at x = 0 and

I = I at x=l,

We get,

$$\ln\frac{I}{I_0} = -K'C.l$$

Beer’s Law

$$2.303\log\frac{I_0}{I} = K.C.l$$

$$\log\frac{I_0}{I} = \frac{K}{2.303}C.l$$

Where, $$\log\frac{I_0}{I} = A$$ Absorbance

$$\frac{K}{2.303} = E$$ Molar extinction coefficient

$$A = E.C.l$$ Beer’s Law

Beer's Law

$$A = E.C.l$$

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

From the equation it is seen that the absorbance which is also called as optical density (OD) of a solution in a container of fixed path length is directly proportional to the concentration of a solution.

Principle

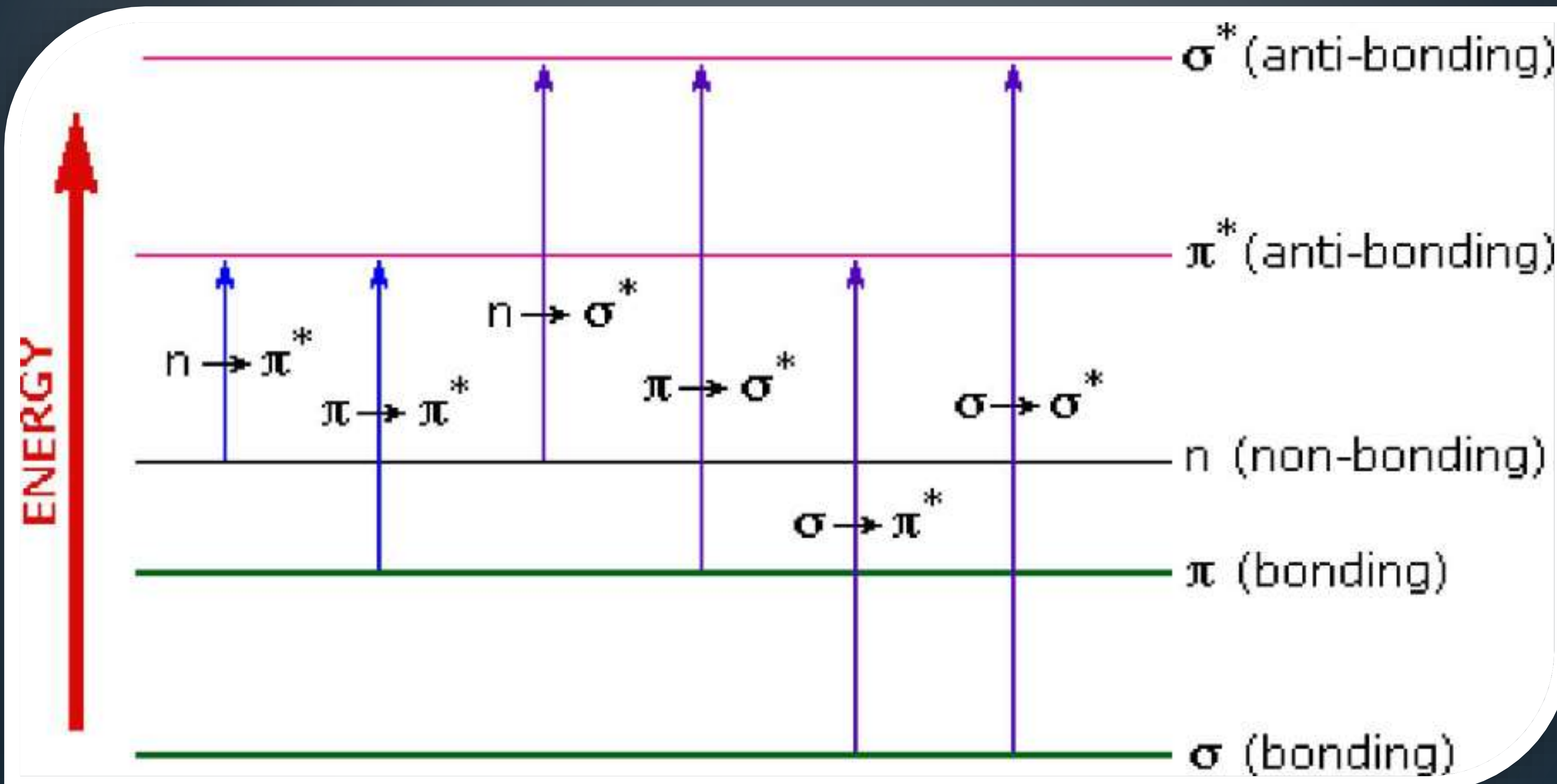
- The UV radiation region extends from 10 nm to 400 nm and the visible radiation region extends from 400 nm to 800 nm.

Near UV Region: 200 nm to 400 nm

Far UV Region: below 200 nm

- Far UV spectroscopy is studied under vacuum condition.
- The common solvent used for preparing sample to be analyzed is either ethyl alcohol or hexane.

The possible electronic transitions can graphically shown as:



The possible electronic transitions are

1. $\sigma \rightarrow \sigma^*$ transition
2. $\pi \rightarrow \pi^*$ transition
3. $n \rightarrow \sigma^*$ transition
4. $n \rightarrow \pi^*$ transition
5. $\sigma \rightarrow \pi^*$ transition
6. $\pi \rightarrow \sigma^*$ transition

1 • σ → σ* transition

- σ electron from orbital is excited to corresponding anti-bonding orbital σ*.
- The energy required is large for this transition.
- e.g. Methane (CH_4) has C-H bond only and can undergo σ → σ* transition and shows absorbance maxima at 125 nm.

2

• π → π* transition

- π electron in a bonding orbital is excited to corresponding anti-bonding orbital π*.

- Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, etc undergo π → π* transitions.

- e.g. Alkenes generally absorb in the region 170 to 205 nm

3

• n → σ* transition

- Saturated compounds containing atoms with lone pair of electrons like O, N, S and halogens are capable of n → σ* transition.

- These transitions usually requires less energy than σ → σ* transitions.

- The number of organic functional groups with n → σ* peaks in UV region is small

4 • n → π* transition

- An electron from non-bonding orbital is promoted to anti-bonding π* orbital.

- Compounds containing double bond involving hetero atoms (C=O, C≡N, N=O) undergo such transitions.

- n → π* transitions require minimum energy and show absorption at longer wavelength around 300 nm.

5 • σ → π* transition

& • π → σ* transition 6

- These electronic transitions are forbidden transitions & are only theoretically possible.

- Thus, n → π* & π → π* electronic transitions show absorption in region above 200 nm which is accessible to UV-visible spectrophotometer.

- The UV spectrum is of only a few broad of

Chromophore

The part of a molecule responsible for imparting color, are called as chromospheres.

OR

The functional groups containing multiple bonds capable of absorbing radiations above 200 nm due to n → π* & π → π* transitions.

e.g. NO_2, N=O, C=O, C=N, C≡N, C=C, C=S, etc

Chromophore

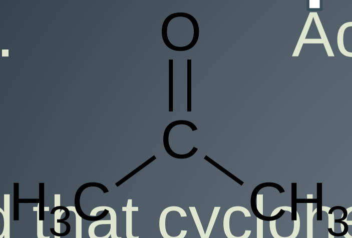
To interpretate UV – visible spectrum following points should be noted:

1. Non-conjugated alkenes show an intense absorption below 200 nm & are therefore inaccessible to UV spectrophotometer.

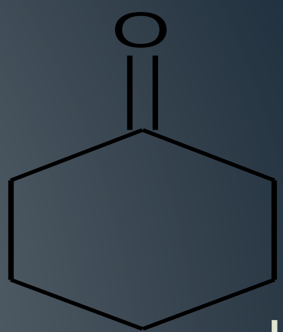
2. Non-conjugated carbonyl group compound give a weak absorption band in the 200 - 300 nm region.

Chromophore

e.g. Acetone which has λ_{max} = 279 nm



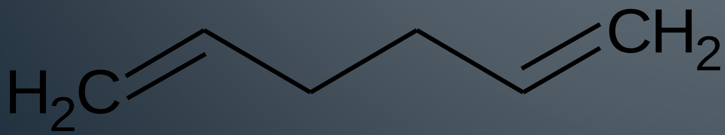
and that cyclohexane has λ_{max} = 291 nm.

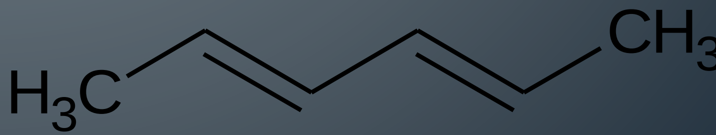


When double bonds are conjugated in a compound λ_{max} is shifted to longer wavelength.

e.g. 1,5 - hexadiene has λ_{max} = 178 nm

2,4 - hexadiene has λ_{max} = 227 nm



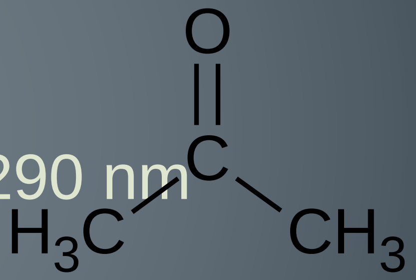


Chromophore

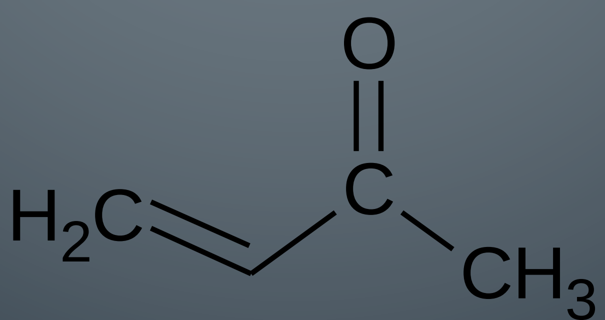
3. Conjugation of C=C and carbonyl group shifts the λ_{max} of both groups to longer wavelength.

e.g. Ethylene has λ_{max} = 171 nm

Acetone has λ_{max} = 279 nm



Crotonaldehyde has λ_{max} = 290 nm



Auxochrome

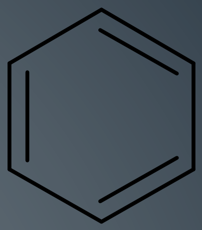
The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light , altering the wavelength or intensity of absorption.

OR

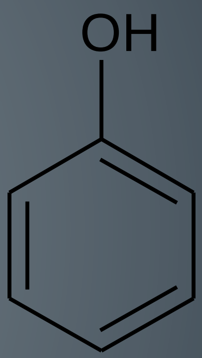
The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.

Auxochrome

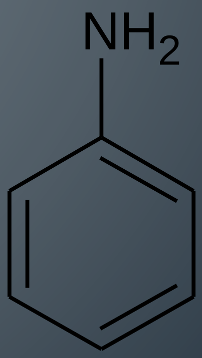
e.g. Benzene λ_{max} = 255 nm



Phenol λ_{max} = 270 nm



Aniline λ_{max} = 280 nm



1. Bathochromic Shift (Red Shift)
2. Hypsochromic Shift (Blue Shift)
3. Hyperchromic Effect
4. Hypochromic Effect

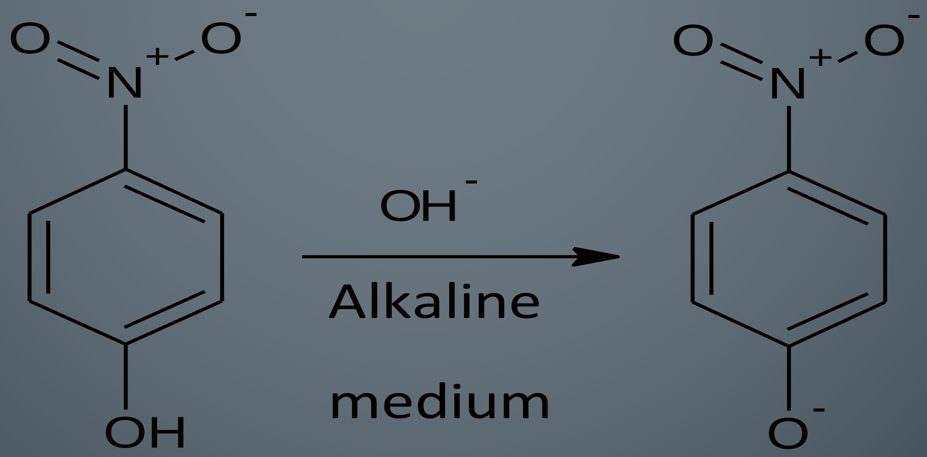
1

• Bathochromic Shift (Red Shift)

- When absorption maxima (λ_{max}) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.
- The effect is due to presence of an auxochrome or by the change of solvent.
- e.g. An auxochrome group like –OH, $-OCH_3$ causes absorption of compound at longer wavelength.

1 • Bathochromic Shift (Red Shift)

- In alkaline medium, p-nitrophenol shows red shift. Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron.



p-nitrophenol

λ_{max} = 255 nm λ_{max} = 265 nm

2 • Hypsochromic Shift (Blue Shift)

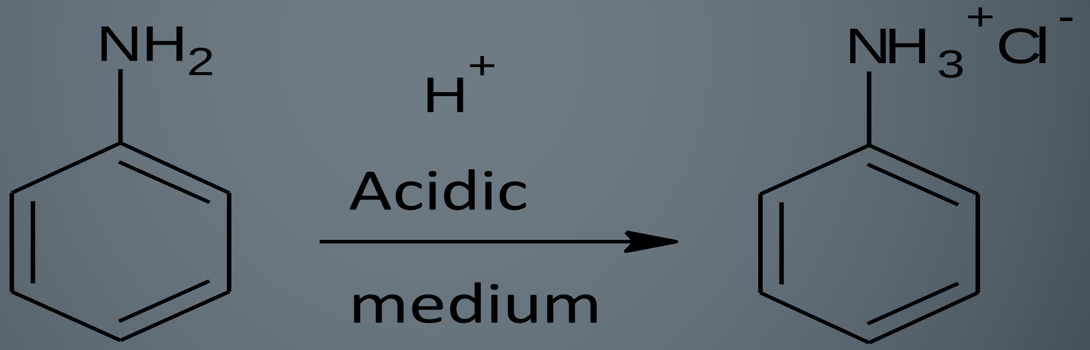
- When absorption maxima (λ_{max}) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift.

- The effect is due to presence of an group causes removal of conjugation or by the change of solvent.

2

• Hypsochromic Shift (Blue Shift)

- Aniline shows blue shift in acidic medium, it loses conjugation.



Aniline

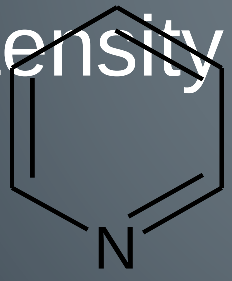
λ_{max} = 280 nm λ_{max} = 265 nm

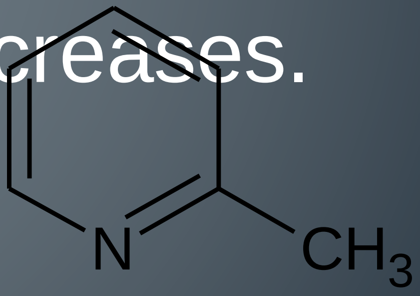
3

• Hyperchromic Effect

- When absorption intensity (ε) of a compound is increased, it is known as hyperchromic shift.

- If auxochrome introduces to the compound, the intensity of absorption increases.





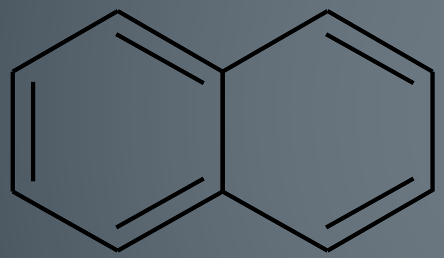
Pyridine

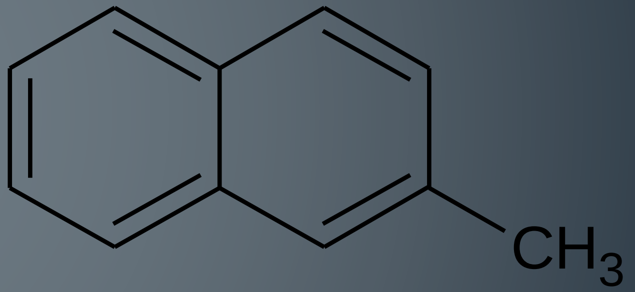
2-methyl pyridine

4

• Hypochromic Effect

- When absorption intensity (ε) of a compound is decreased, it is known as hypochromic shift.





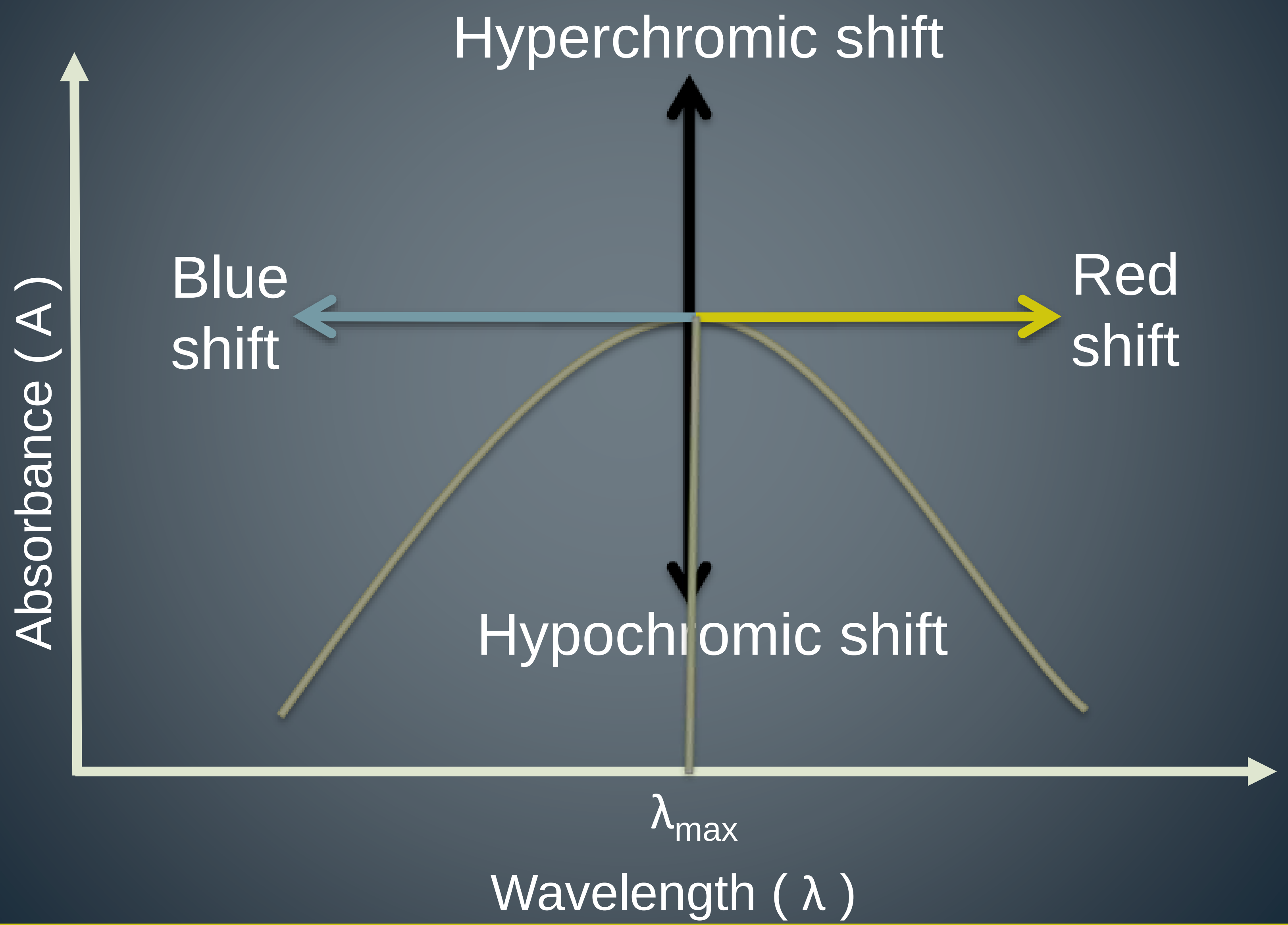
Naphthalene

$\varepsilon = 19000$

2-methyl naphthalene

$\varepsilon = 10250$

Shifts and Effects



Instrumentation

Two types

- 1. Colorimeters
  - Inexpensive and less accurate
  - 400-700nm
- 2. Spectrophotometer
  - Used for wide range of wavelength
  - Highly accurate
  - expensive

Source of light

- Visible spectrum 400-800 nm
- Requirements for source:
  - Should provide continuous radiation from 400-800 nm
  - Adequate intensity
  - Stable and free from fluctuations

Two types of lamps

- 1. Tungsten lamp
  - Most widely used
  - Consist of tungsten filament in vacuum bulb
- 2. Carbon arc lamp
  - High intensity
  - Also provide entire range of visible spectrum

Filters and monochromaters

- Light gives radiation from 400-800nm
- This is called polychromatic light which is of several wavelength
- Hence a filter or monochromater is used to convert polychromatic light into monochromatic lights used

Types of filters and monochromaters

- Filters
  - Absorption filters
  - Interference filter
- Monochromaters
  - Prism type (dispersive type or Littrow type)
  - Grating type (Diffraction grating & transmittance grating)

1. Absorption filters

- Filters are made up of glass, coated with pigment or they are made up of dyed gelatin.
- They absorb unwanted radiation and transmit the rest of the radiation which is required for colorimetry.
- Merits:
  - Simple, cheaper
- Demeits:
  - Less acurate, bandpass is more (+/- 30 nm), intensity is less

2. Interference filter

- Also known as fabry-perot filter
- It has dielectric spacer made up of CaF_2, MgF_2, or SiO.
- Thickness o dielectric spacer film can be ½ ʎ (1st order), 2/2 ʎ (2nd order) , 3/2 ʎ (3rd order).
- Mechanism is constructive interference folloved by this equatuion.

ʎ=2ηb/m

ʎ=wavelength of light

η= dielectric constant of material

B= layer thickness

Interference filter (cont'd…)

- Band pass is +/- 10 nm
- Transmittance is 40%
- Merits :
  - Inexpensive, lower band pass, use of additional filter cut off for undesired wavelength
- Demerits:
  - Peak transmission is low