Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Second Year)

Subject: Chemistry

Course Code: CHC103

Course Title: Physical and Organic Chemistry (Section B)

Unit: UV-Visible Spectroscopy in Organic Chemistry

Module Name: UV Spectroscopy- Important terms

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Notes

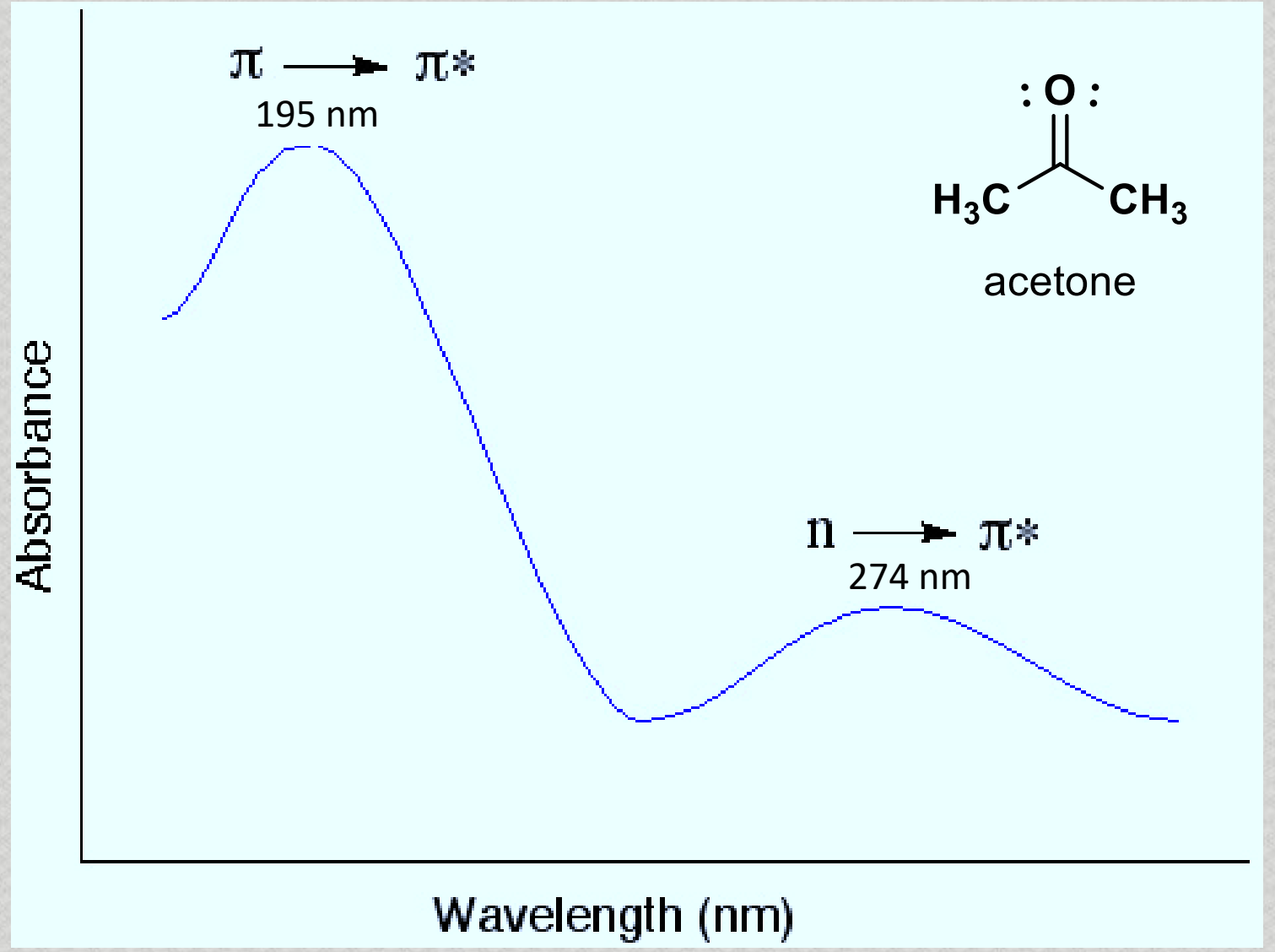
Introduction

- Spectroscopy deals with interaction of electromagnetic radiation with matter.
- The UV region corresponds to radiation whose wavelengths fall in 200 – 400 nm while the visible region corresponds to 400 – 800 nm of the electromagnetic spectrum.
- Each molecule has a specific λ_{max} depending on its structure which relates to the position and degree of substitution of certain functional groups present in the molecule.
- Some Important terminology in UV-Vis Spectroscopy is discussed further.

Maximum absorption (λ_{max})

- ✓For any molecule, the wavelength along the absorption spectrum where it has maximum photon absorption is referred to as the λ_{max} of the molecule.
- ✓A molecule containing multiple functional groups or bonds will absorb UV-Vis radiations having characteristic $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ electronic transitions.
- ✓The one with highest intensity of absorption will be referred to as the λ_{max} of the molecule .

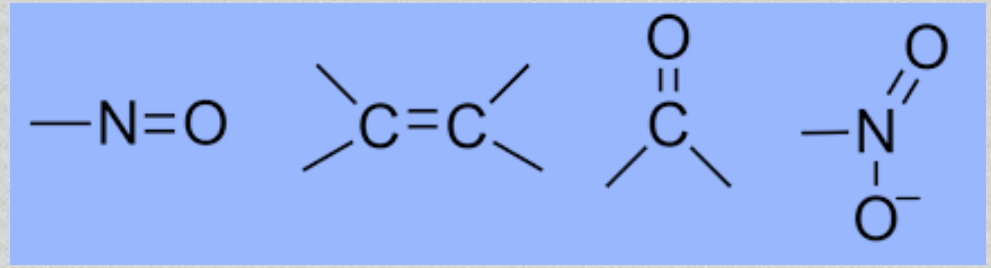
λ_{max}

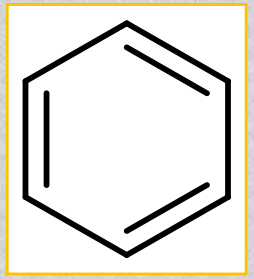

π → π*
195 nm
: O :
H3C
CH3
acetone
Absorbance
n → π*
274 nm
Wavelength (nm)

Chromophores (color bearing)

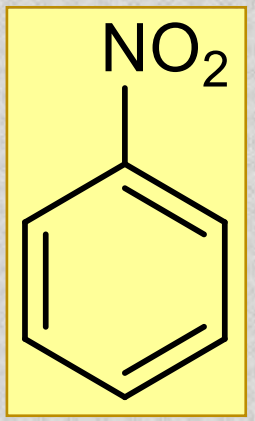
- ✓Part of the molecule responsible for imparting color.
- ✓The functional group containing multiple bonds capable of absorbing radiation having characteristic $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ electronic transitions above 200 nm is called a chromophore.
- ✓Structural or electronic changes in the chromophore can be quantified and used to predict shifts in the observed electronic transitions.

Chromophores examples

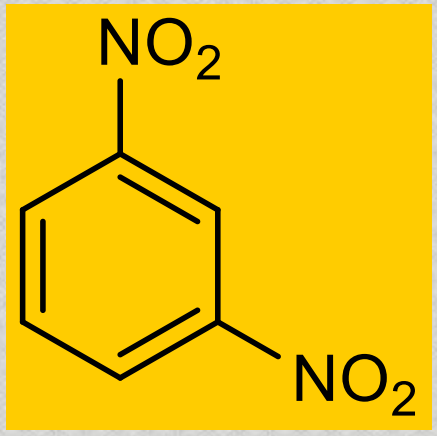




Benzene



Nitrobenzene



m-dinitrobenzene

Auxochromes (Auxanein=increase)

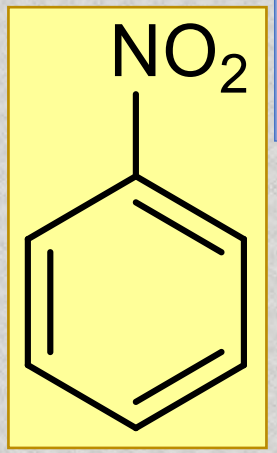
- ✓Does not impart color to the molecule.
- ✓The functional group(s) not capable of producing colour but when attached to a chromophore intensifies the colour is called a auxochrome.
- ✓An auxochrome should be directly attached to the chromophore for the necessary change in absorption.

Auxochromes examples

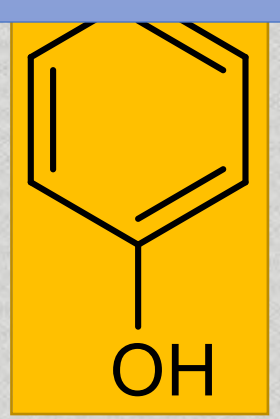
—OH —NHR —Cl —Br

$—CH_3$ $—NO_2$ $—NR_2$ —COOH

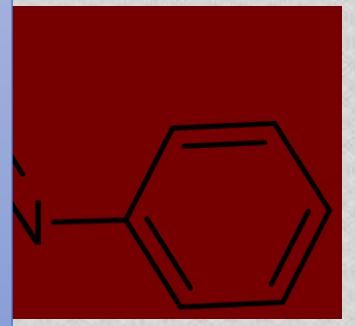
$—NH_2$ $—SO_3H$



Nitrobenzene



p-hydroxy nitrobenzene

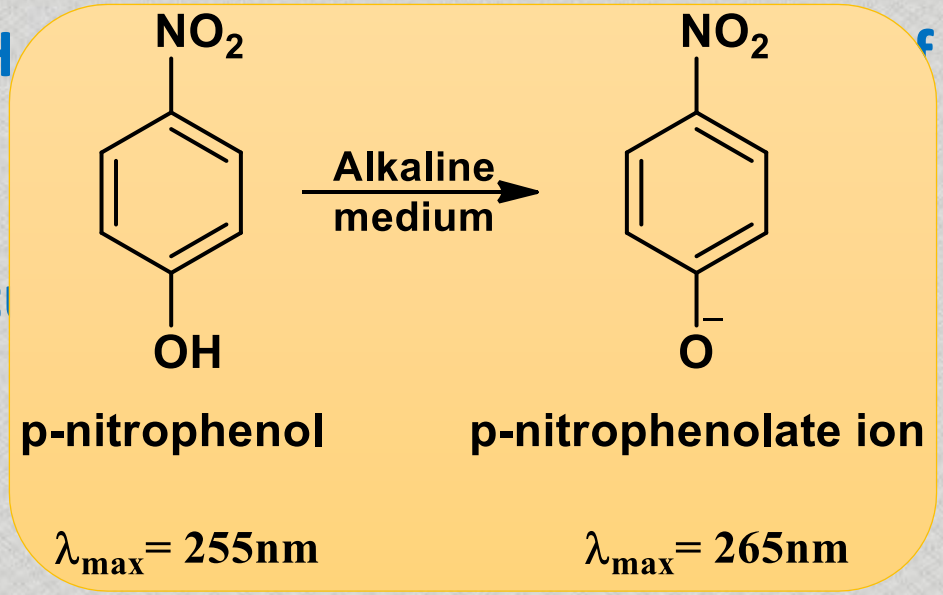


Azobenzene

p-hydroxy azobenzene

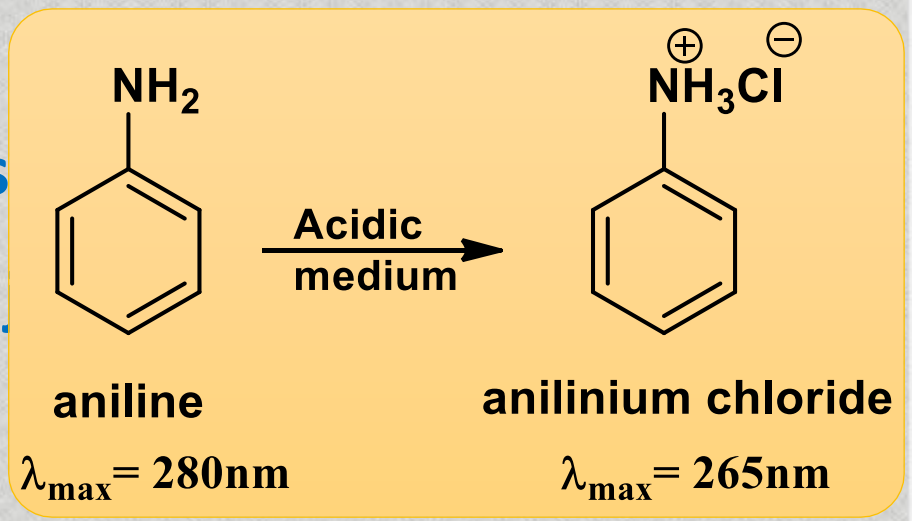
Bathochromic Shift

- ✓The shift of the absorption maxima (λ_{max}) of a compound to a longer wavelength caused by either substitution on chromophore (by an auxochrome) or change in solvent.
- ✓E.g. An auxochrome group like –OH
  compound at longer wavelength.
- ✓Also extended conjugation in a molec
  by absorption at a longer wavelength.
- ✓Also called the **Red Shift**



Hypsochromic Shift

- ✓The shift of the absorption maxima (λ_{max}) of a compound to a shorter wavelength caused by either substitution on chromophore (causing removal of conjugation) or change in solvent.
- ✓E.g. Aniline when protonated, causes shorter wavelength due to loss of con
- ✓Also called the **Blue Shift.**

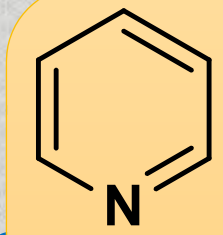


Intensity of absorption (ε)

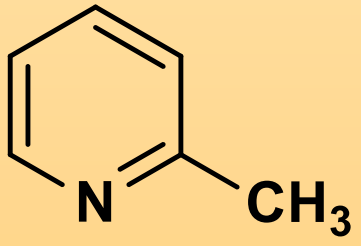
- ✓Intensity of absorption generally relates to the molar absorptivity of a substance (ε) of a substance which is a proportionality constant.
- ✓The molar absorptivity of a substance (ε) of a substance can be defined as the absorbance observed at 1M concentration of that substance at a particular wavelength.
- ✓It has the units $L.mol^{-1}.cm^{-1}$

Hyperchromic Shift

- ✓When absorption intensity (ε) of a compound is increased due to substitution or change in solvent it is referred to as hyperchromic shift.
- ✓Usually an auxochrome intensifies the color of a chromophore and results in a hyperchromic shift
- ✓Also, Bathochromic shift is a hyperchromic shift.



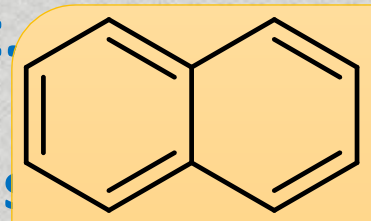
pyridine
ε= 2750



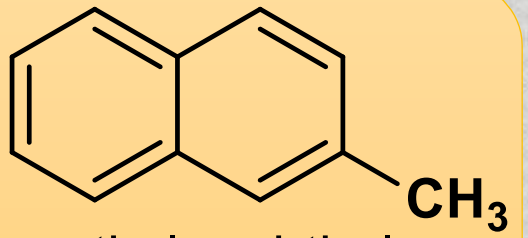
2-methylpyridine
ε= 3560

Hypochromic Shift

- ✓When absorption intensity (ε) of a compound is decreased due to substitution or change in solvent it is referred to as hypochromic shift.
- ✓Usually removal of conjugation or substitution on chromophore, results in a hyperchromic shift.
- ✓Also, Hypsochromic shift is hypochromic shift.



naphthalene
ε= 19000



2-methylnaphthalene
ε= 10250

Effects and Shifts