UCB008 - APPLIED CHEMISTRY

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

SCBC-TIET

Molecular Spectroscopy Series

Lecture - V

UV-Visible Spectroscopy – Absorption and Intensity Shifts

by

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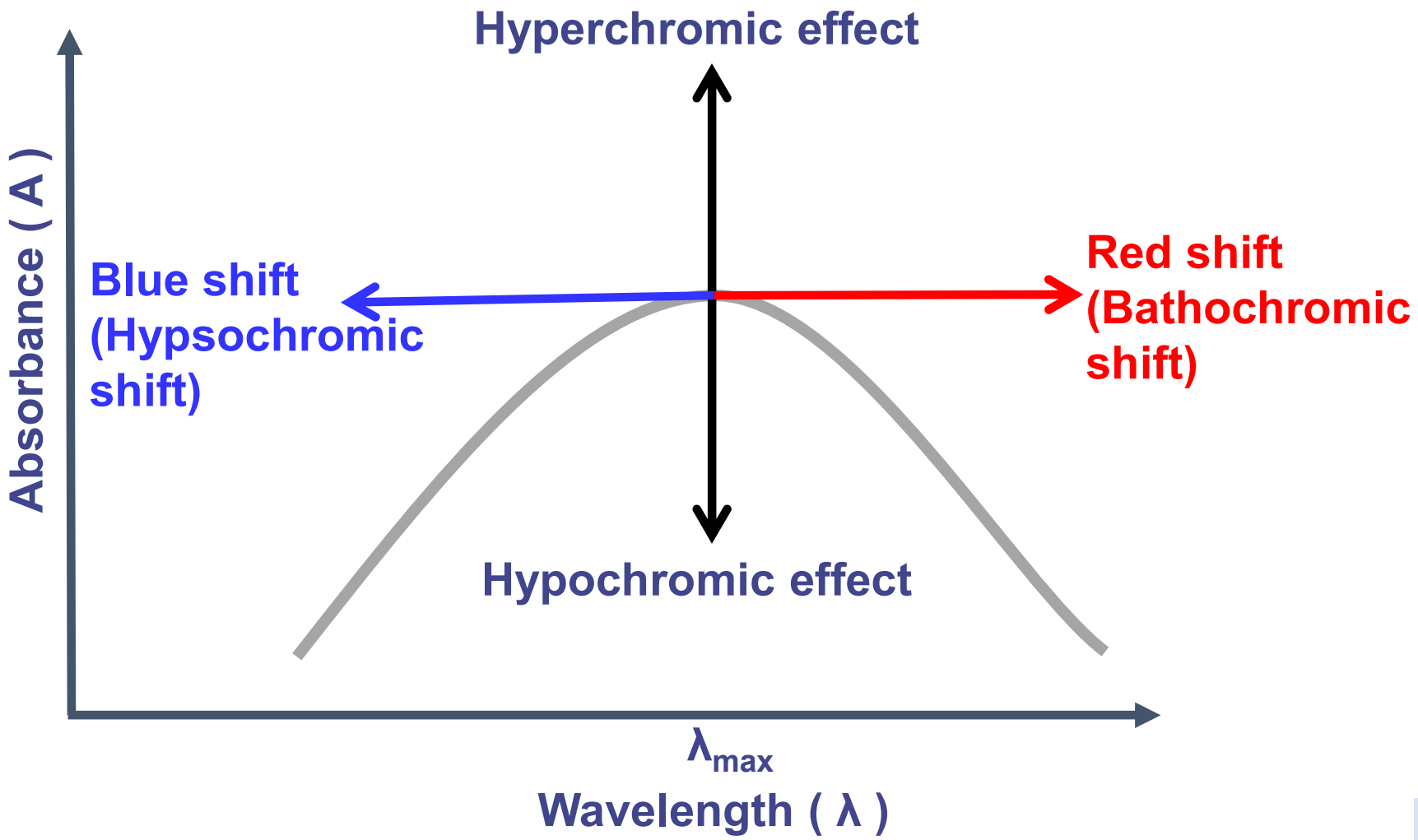
Learning Outcomes

At the end of this session participants should be able to:

- Distinguish between various shifts and effects associated with UV-visible spectroscopy

Shifts and Effects



Bathochromic Shift (Red Shift)

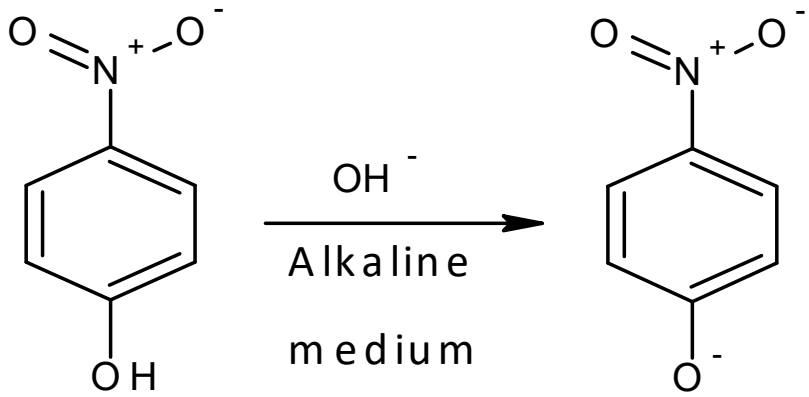
- When absorption maximum (ε_{max}) is shifted towards longer wavelength, it is known as bathochromic shift or red shift.

- The effect is due to presence of an auxochrome or by the change of solvent.

- For example, an auxochrome group like –OH, $-OCH_3$ causes absorption of compound at longer wavelength.

Bathochromic Shift (Red Shift)

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

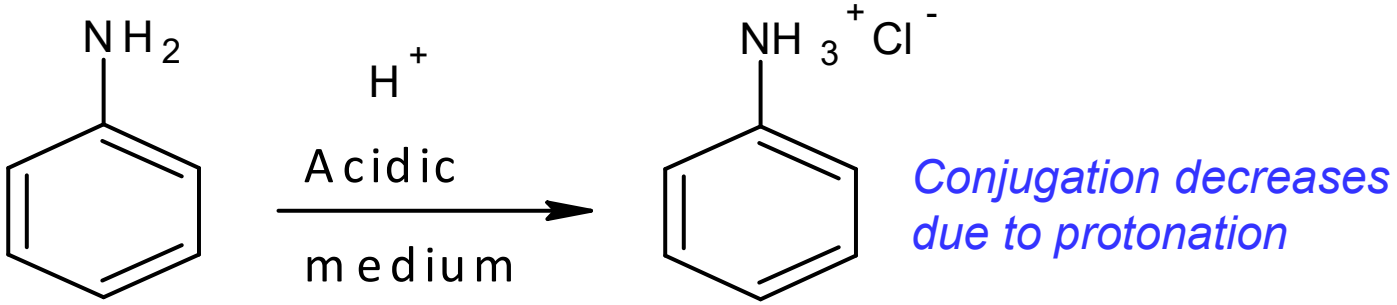


λ_{max} = 255 nm p-nitrophenol

λ_{max} = 265 nm p-nitro-phenoxide

Hypsochromic Shift (Blue Shift)

- When absorption maximum (ε_{max}) is shifted towards shorter wavelength, it is known as Hypsochromic shift or blue shift.
- The effect is due to removal of conjugation or by the change of solvent.
- Aniline shows blue shift in acidic medium because it loses conjugation.

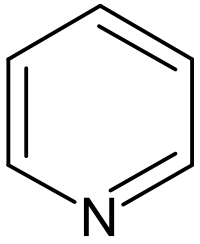


λ_{max} = 280 nm
Aniline

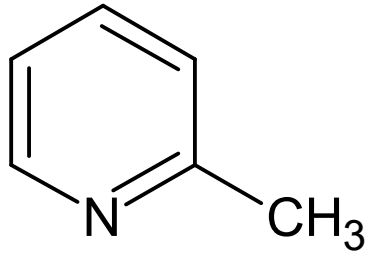
λ_{max} = 265 nm
Anilinium chloride

Hyperchromic effect

- When intensity of absorption maximum (e_{max}) of a compound increases, it is known as **hyperchromic effect**.



A = ε c x



λ_{max} = 257 nm
ε = 2750
Pyridine

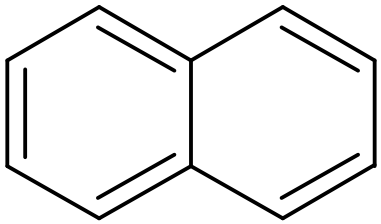
λ_{max} = 260 nm
ε = 3560
2-methyl pyridine

- Inclusion of an auxochrome also increases intensity of absorption.

Sharma YR, Elementary Organic Spectroscopy, S. Chand & Co.

Hypochromic effect

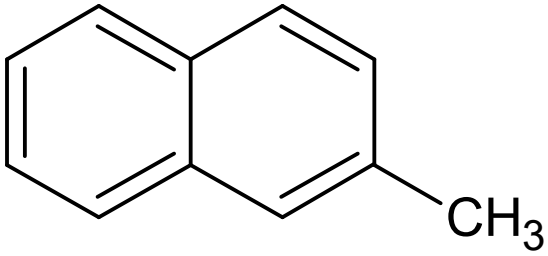
- When intensity of absorption maximum (ε_{max}) of a compound decreases, it is known as **hypochromic effect**.



ε = 19000

λ_{max} = 250 nm

Naphthalene



ε = 10250

λ_{max} = 237 nm

2-methyl naphthalene

- ε_{max} decreases due to the distortion caused by the methyl group.

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In the next session…..

- Understand the effect of conjugation on λ_{max}
- Colour in organic compounds