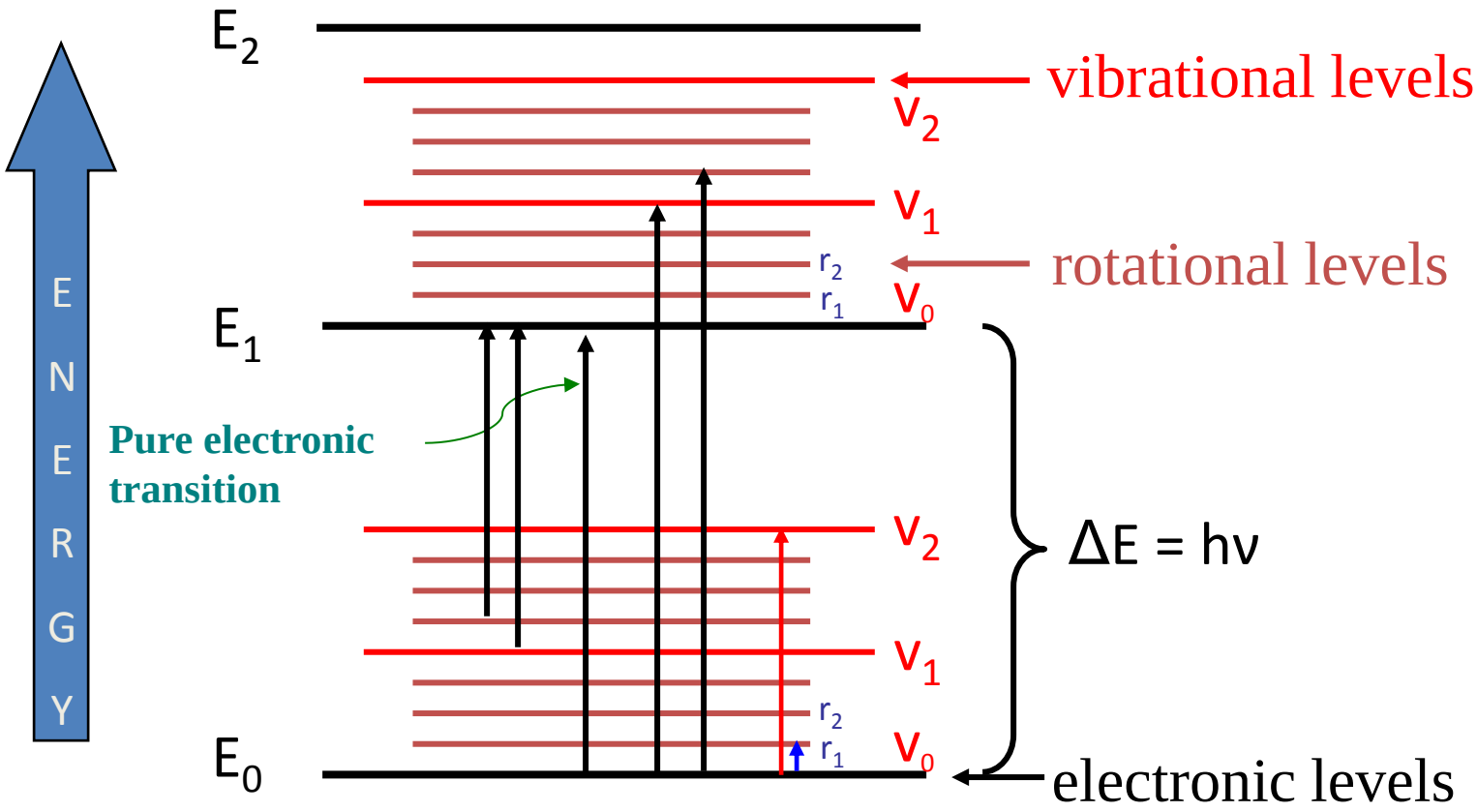
ULTRAVIOLET-VISIBLE SPECTROSCOPY

WHAT HAPPENS WHEN A MOLECULE ABSORBS UV-VISIBLE RADIATION?

- When a molecule absorbs light having sufficient energy (e.g. UV-Vis radiation) to cause an electronic transitions, additional vibration and rotation transitions also occur

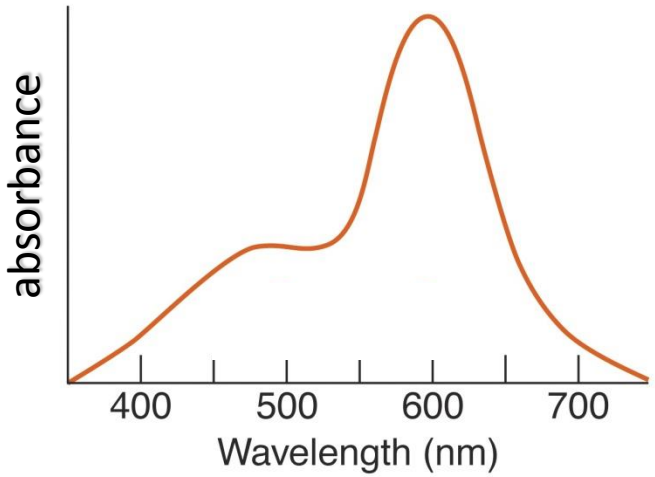
- Molecule can absorb one photon of just the right energy to cause the following simultaneous changes:



1. **A transition from the ground electronic state E_0 to the E_1 excited electronic state**
2. **A change in the vibrational energy from the ground vibrational state of E_0 to an excited vibrational state of E_1**
3. **A transition from one rotational state of E_0 to a different rotational state of E_1**
4. **All the above transitions are quantized which means that they required certain exact amount of energy**
5. **Thus, total energy absorbed = $E_{elec} + E_{vib} + E_{rot}$**

$$\Delta E_{elec} >> \Delta E_{vib} >> \Delta E_{rot}$$

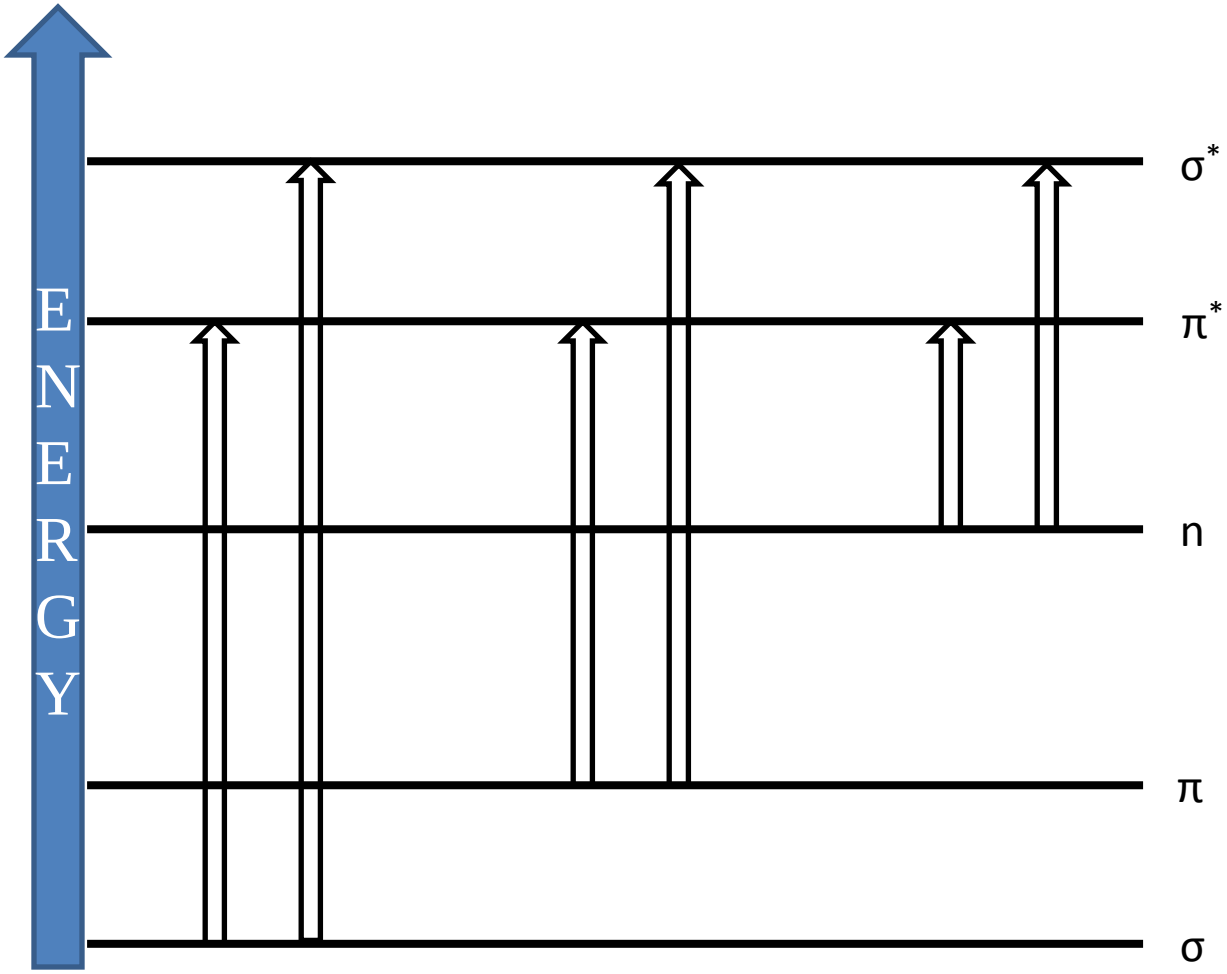
As a result, a large numbers of photons of certain wavelengths are absorbed by a molecule. These individual wavelengths are too numerous and too close to each other and a spectrum of broad bands of absorbed wavelengths are obtained



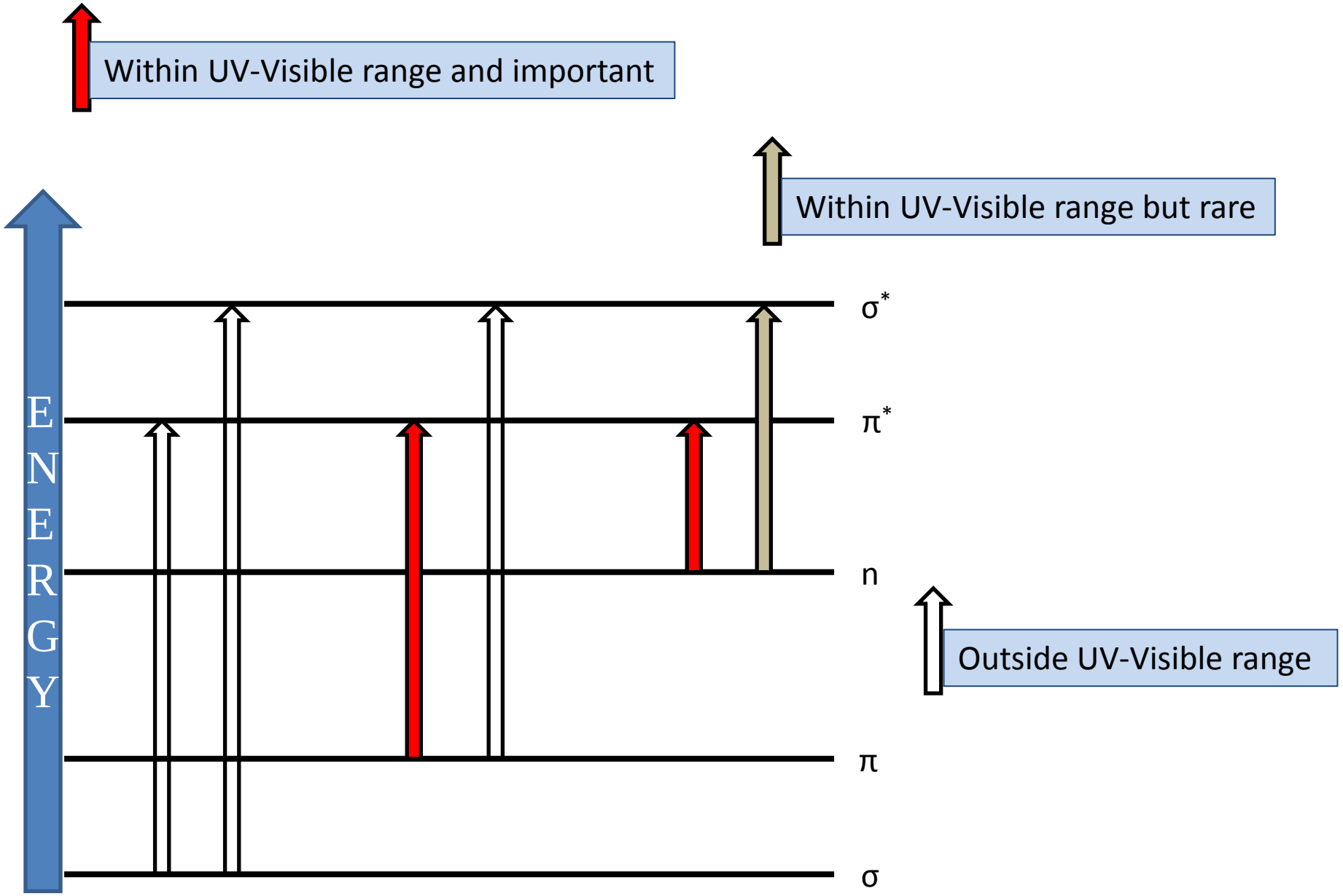
Spectrum (a graph that shows how absorbance varies with wavelength)

ELECTRONIC TRANSITIONS

Possible Electronic Transitions



Important Electronic Transitions



CHROMOPHORE

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

CHROMOPHORE

The functional groups containing multiple bonds capable of absorbing radiations.

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

CHROMOPHORE

Chromophore	Example	Excitation	λ_{max}, nm	ε	Solvent
C=C	Ethene	π --> π*	171	15,000	hexane
C≡C	1-Hexyne	π --> π*	180	10,000	hexane
C=O	Ethanal	n --> π* π --> π*	290 180	15 10,000	hexane hexane
N=O	Nitromethane	n --> π* π --> π*	275 200	17 5,000	ethanol ethanol
C-X X=Br X=I	Methyl bromide Methyl Iodide	n --> σ* n --> σ*	205 255	200 360	hexane hexane

AUXOCHROME

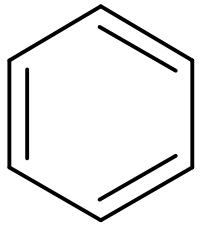
The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light , altering the wavelength or intensity of absorption.

OR

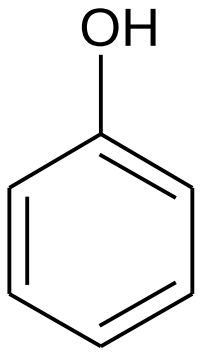
The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.

AUXOCHROME

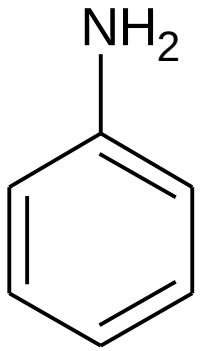
Benzene λ_{max} = 255 nm

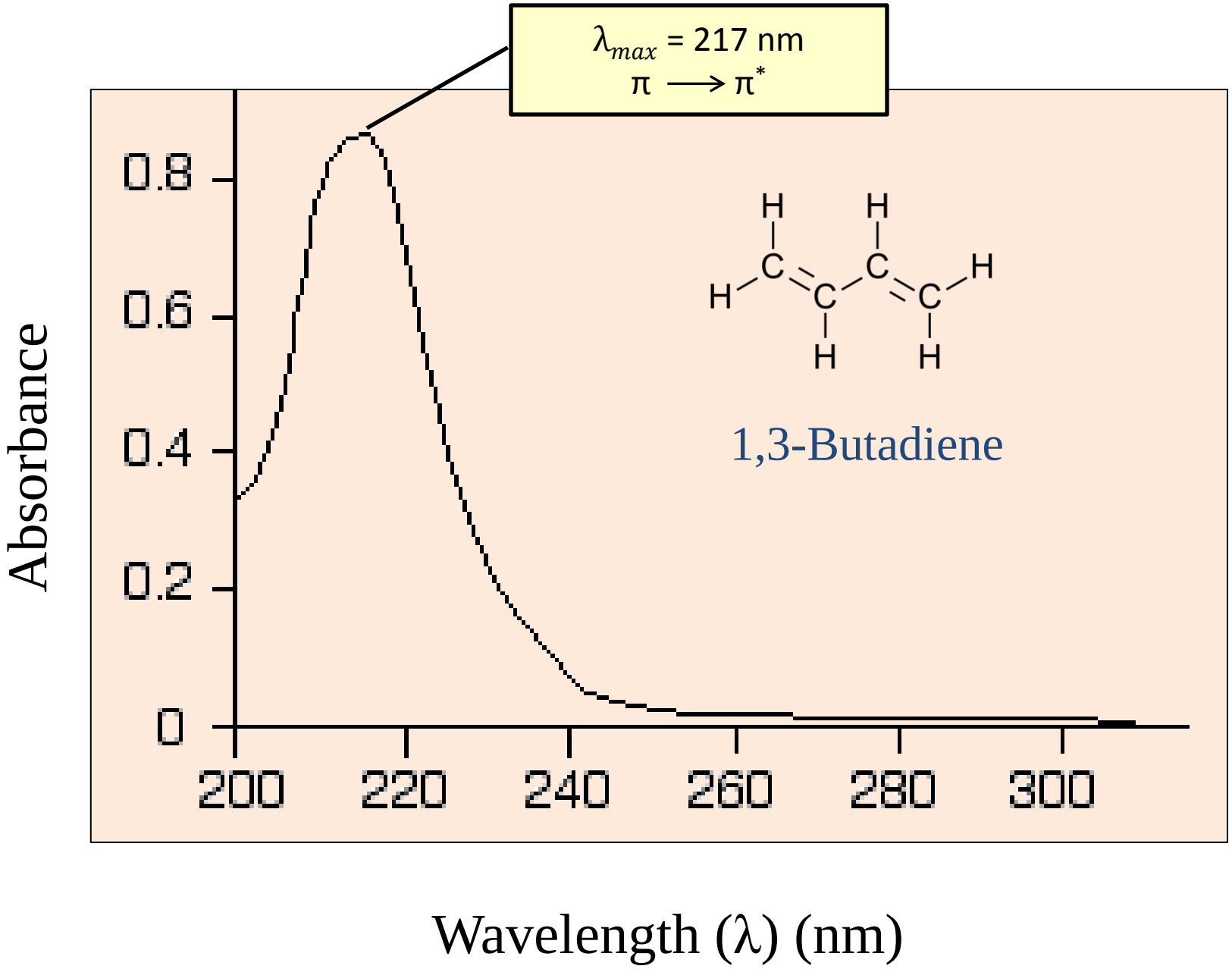


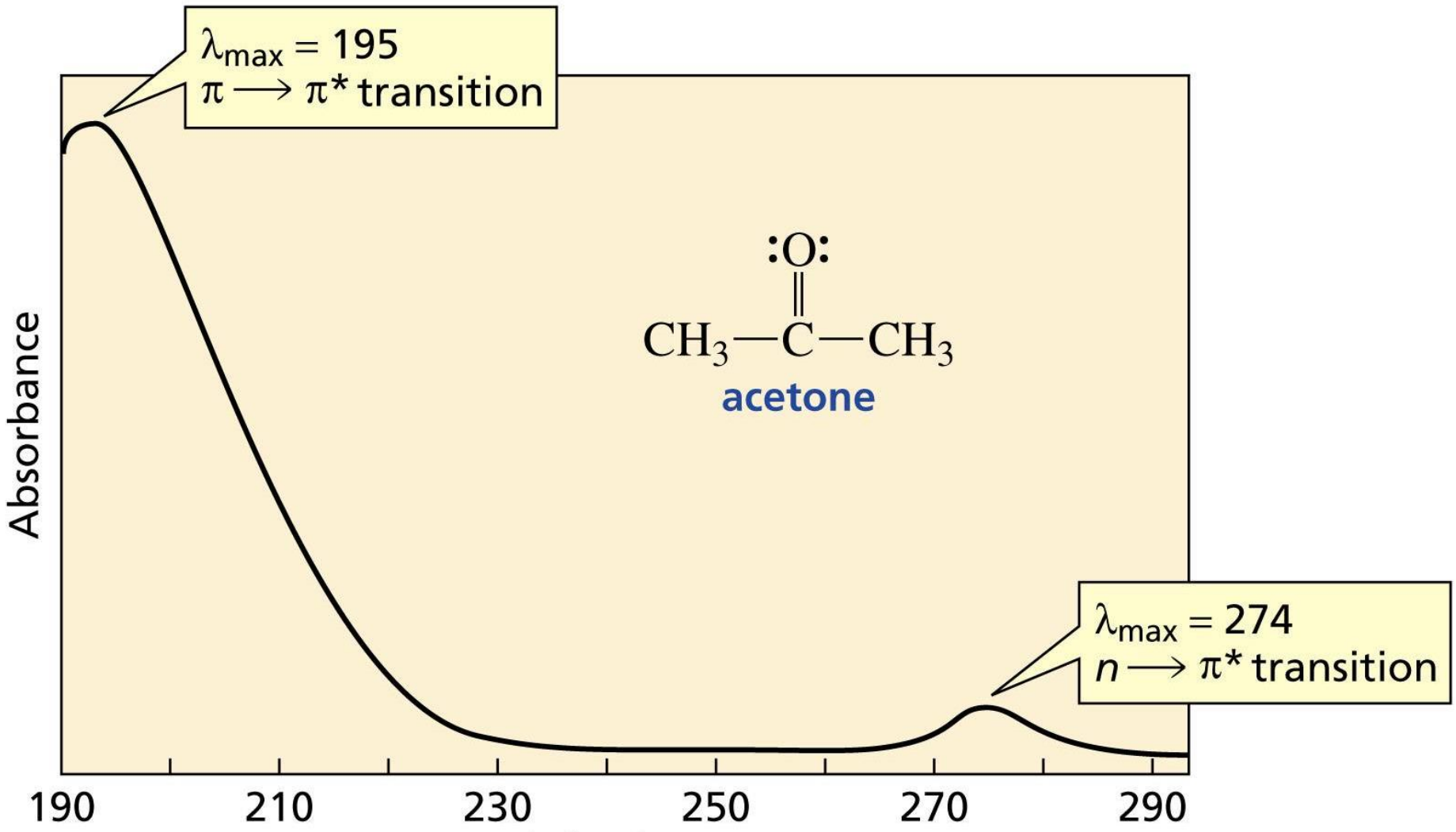
Phenol λ_{max} = 270 nm



Aniline λ_{max} = 280 nm




λ_{max} = 217 nm
$\pi \longrightarrow \pi^*$
1,3-Butadiene
Absorbance
0
0.2
0.4
0.6
0.8
200
220
240
260
280
300
Wavelength (λ) (nm)


λmax = 195
π ⟶ π* transition
:O:
CH3—C—CH3
acetone
λmax = 274
n ⟶ π* transition
Absorbance
190
210
230
250
270
290
Wavelength (λ) (nm)

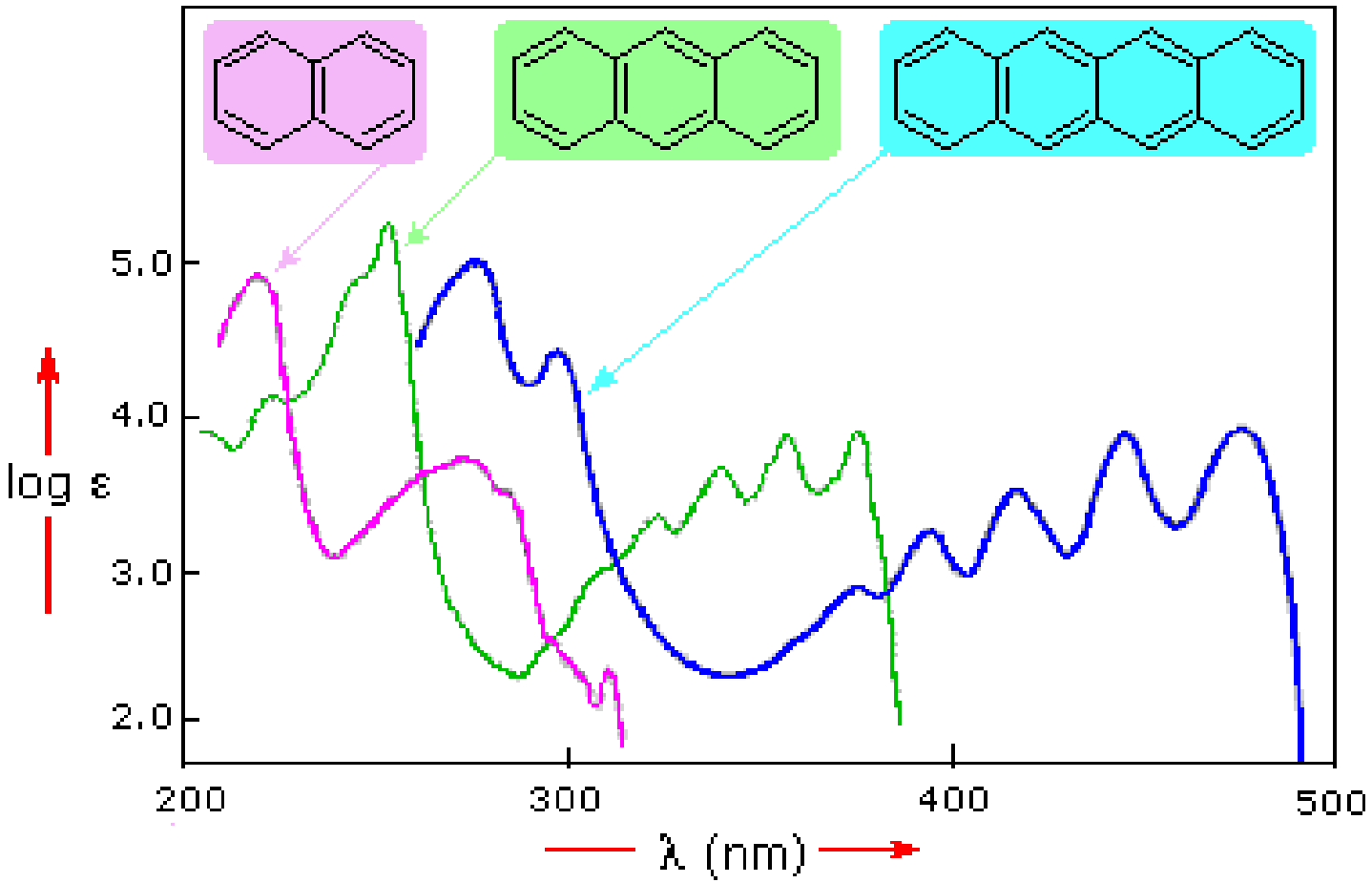
EFFECT OF CONJUGATION

Effect of Conjugation

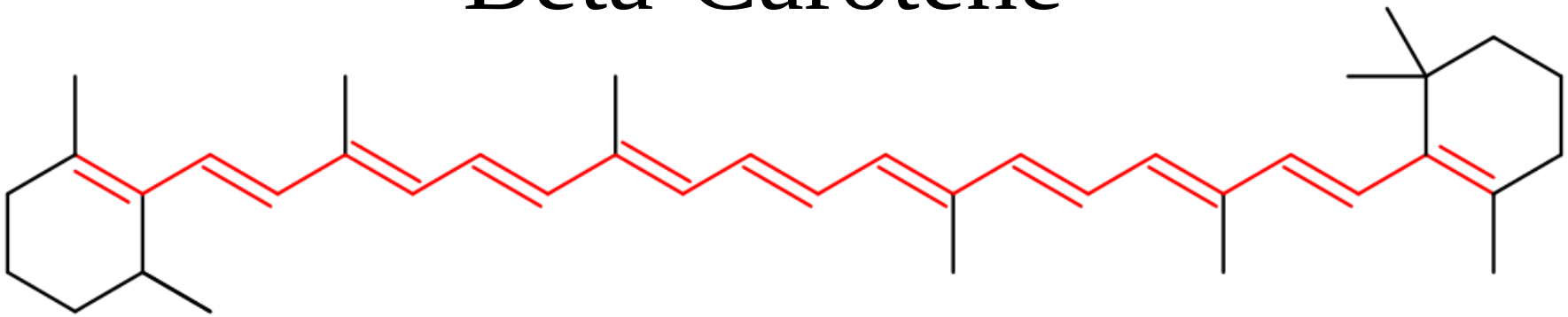
$CH_2=CH_2$	$CH_2=CH-CH=CH_2$	$CH_2=CH-CH=CH-CH=CH_2$
Ethene	1,3-Butadiene	1,3,5-Hexatriene

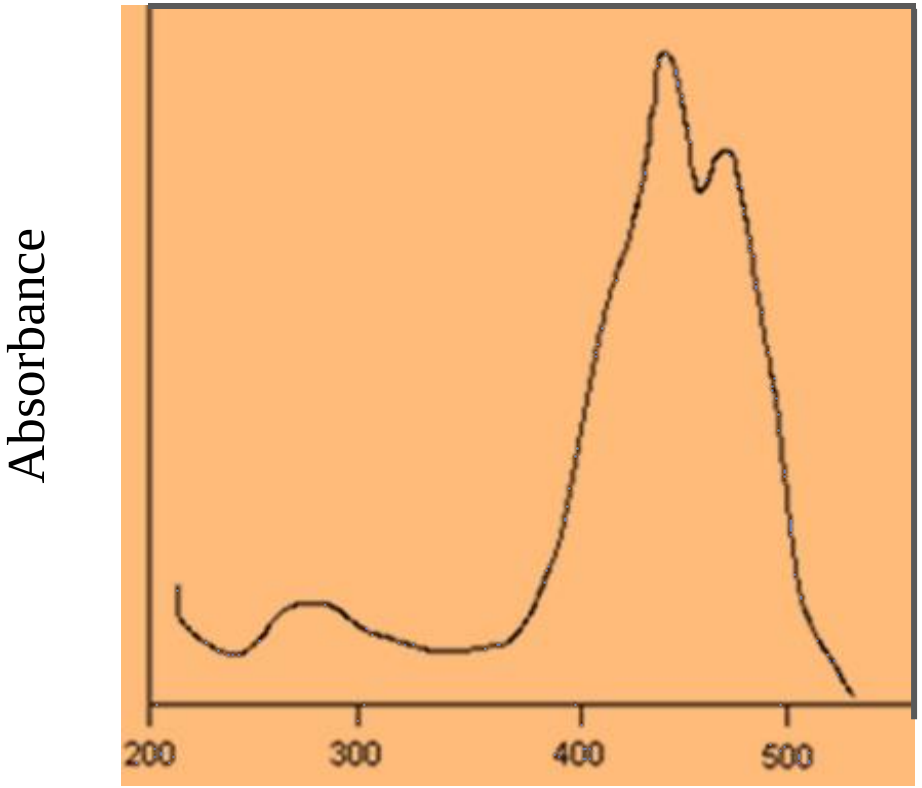
Molecule	**λ_{max} (nm)**
$CH_2=CH_2$	171
$CH_2=CH-CH=CH_2$	217
$CH_2=CH-CH=CH-CH=CH_2$	258

Effect of Conjugation

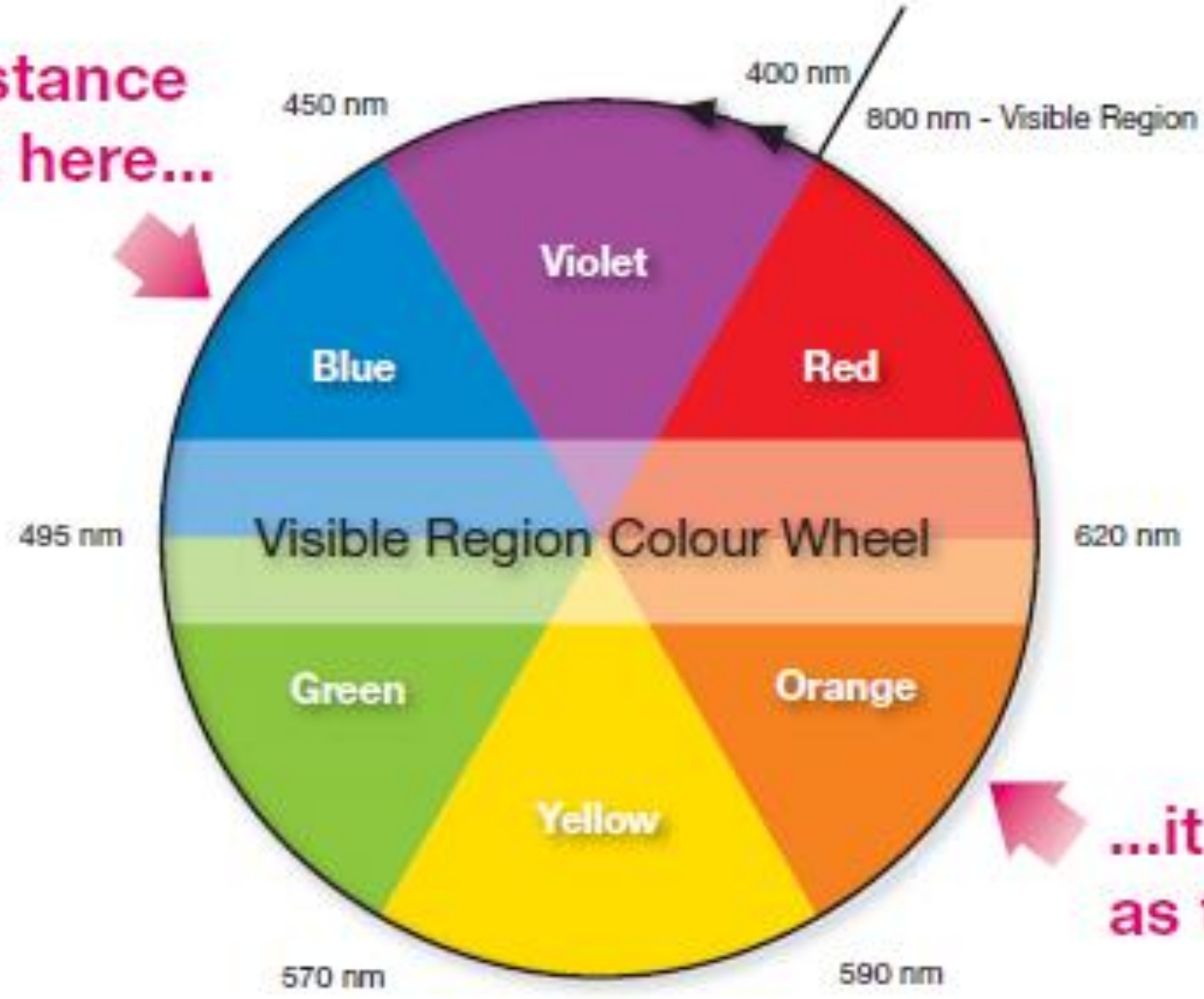


Beta-Carotene

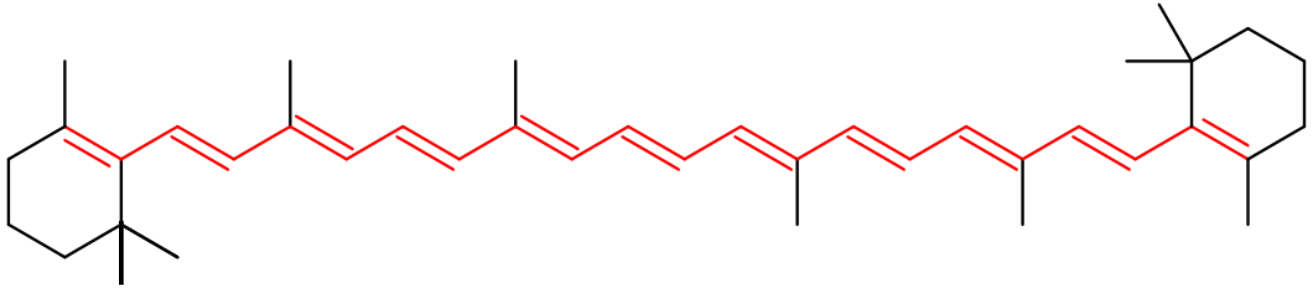




If a substance absorbs here...



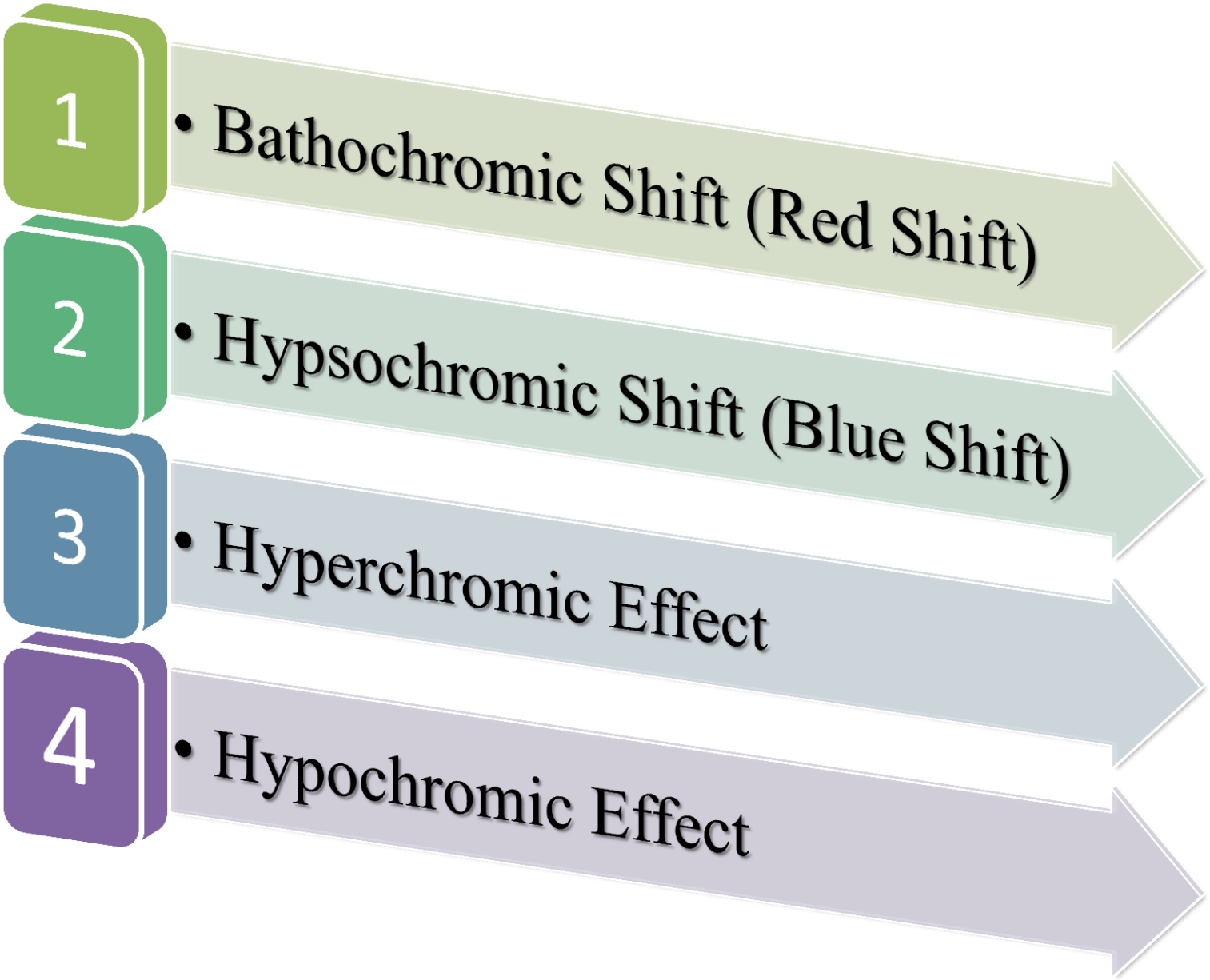
...it appears as this colour



B- Carotene

Lycopene

Absorption & Intensity Shifts


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.

2 • Hypsochromic Shift (Blue Shift)

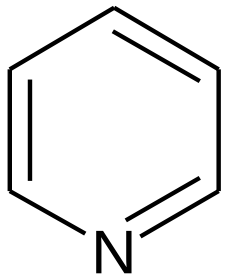
- When absorption maxima (λ_{max}) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift.

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

3 • Hyperchromic Effect

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

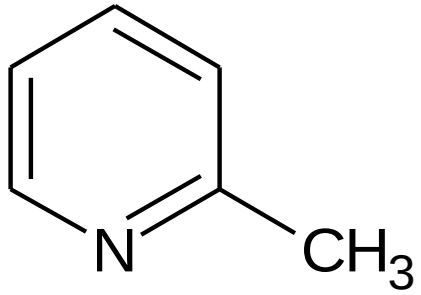
- If auxochrome introduces to the compound, the intensity of absorption increases.



Pyridine

λ_{max} = 257 nm

ε = 2750



2-methyl pyridine

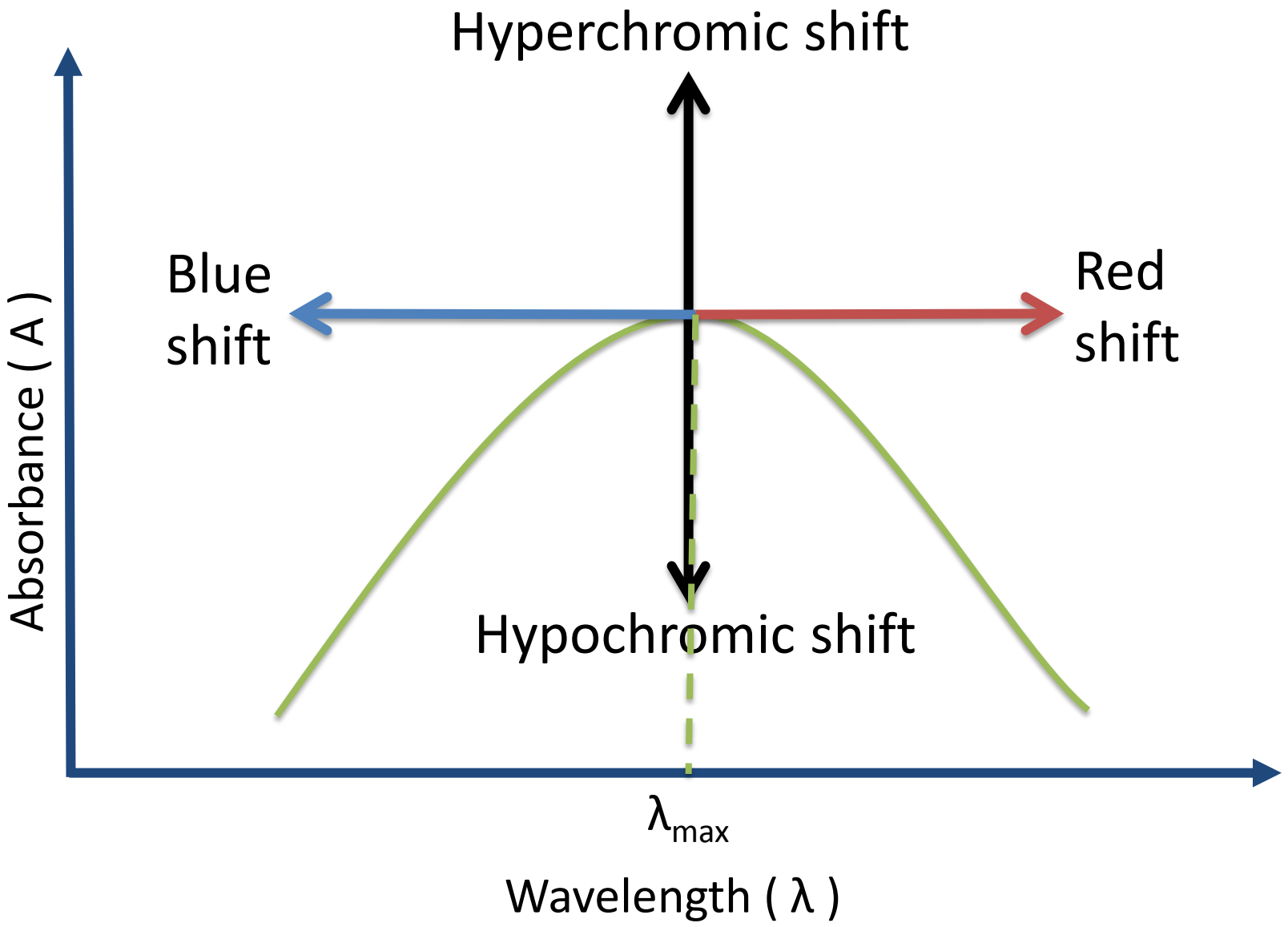
λ_{max} = 260 nm

ε = 3560

4 • Hypochromic Effect

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

Shifts and Effects

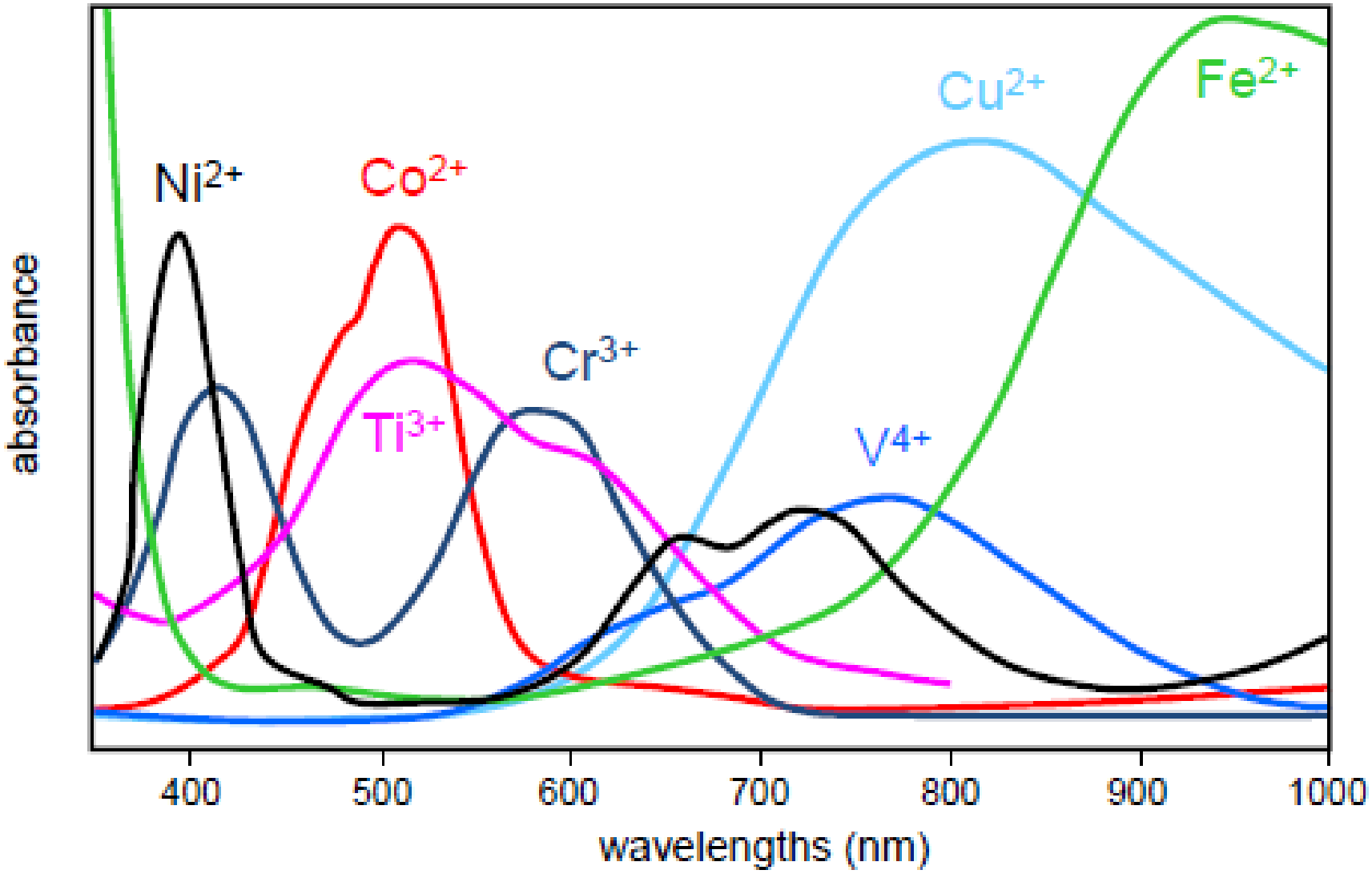


ULTRAVIOLET-VISIBLE SPECTROSCOPY OF INORGANIC COMPOUNDS

Compounds of Transition metal complexes solution

$[Fe(H_2O)_6]^{3+}$ $[Ni(H_2O)_6]^{2+}$ $[Zn(H_2O)_6]^{2+}$

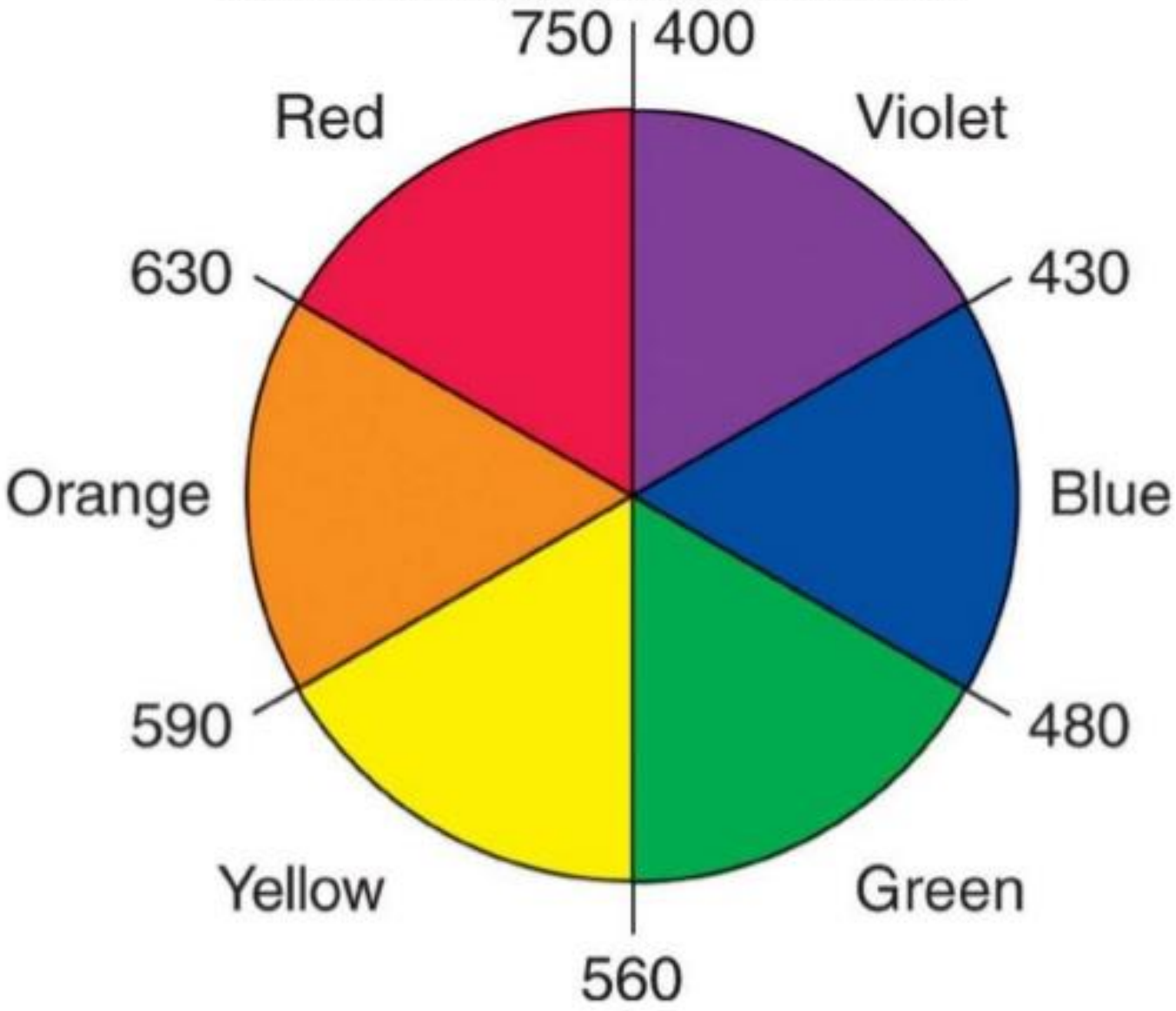
$[Co(H_2O)_6]^{2+}$ $[Cu(H_2O)_6]^{2+}$


absorbance
Ni2+
Co2+
Cr3+
Ti3+
V4+
Cu2+
Fe2+
400
500
600
700
800
900
1000
wavelengths (nm)

Spectrochemical Series

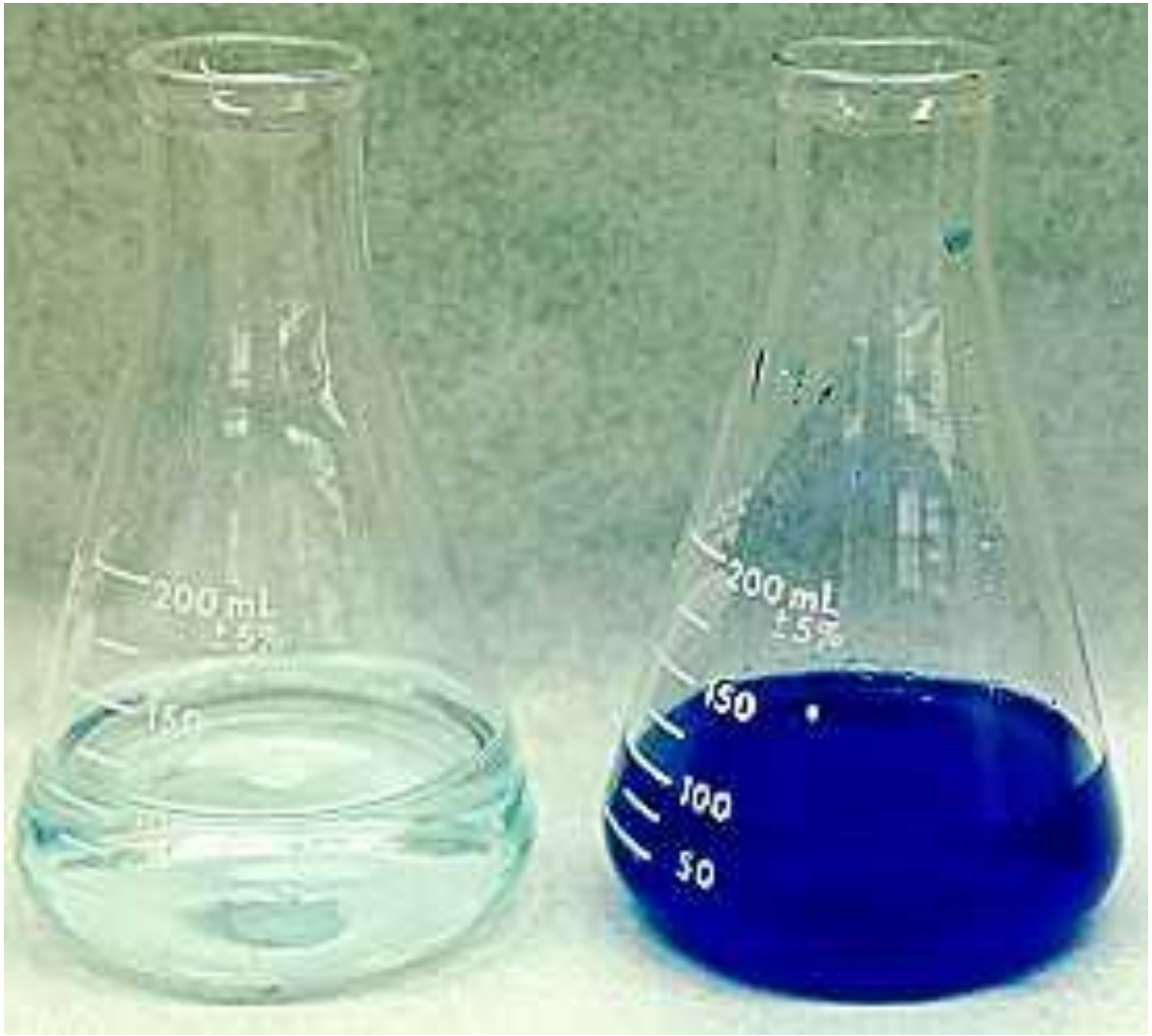
I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^-, F^- < urea, OH^- < ox, O^{2-} < H_2O < NCS^- < py, NH_3 < en < bpy, phen < NO_2^- < CH_3^-, $C_6H_5^-$ < CN^- < CO.

An artist's wheel



Absorbed color and observed colors

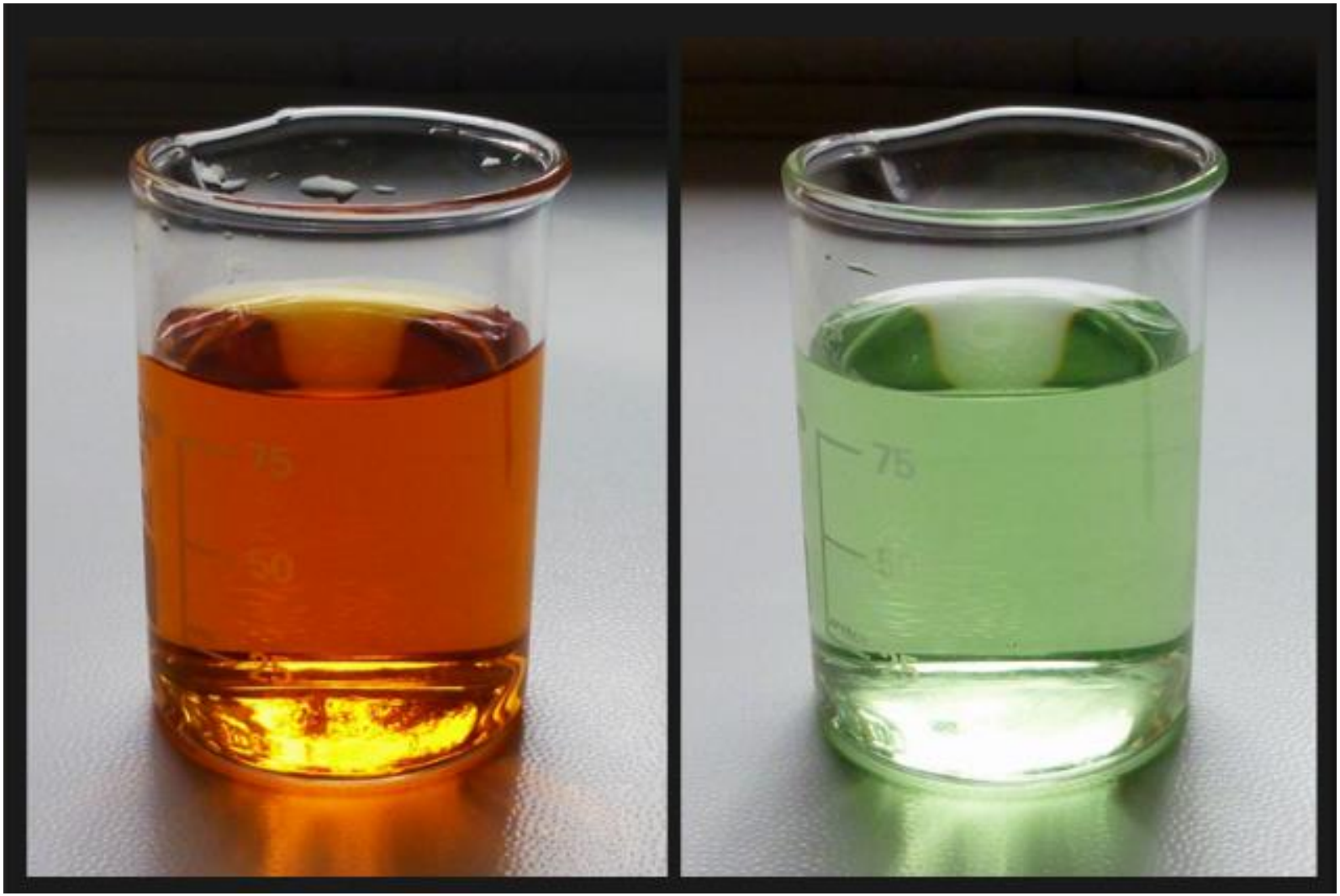
Absorbed Color	λ (nm)	Observed Color	λ (nm)
Violet	400	Green-yellow	560
Blue	450	Yellow	600
Blue-green	490	Red	620
Yellow-green	570	Violet	410
Yellow	580	Dark blue	430
Orange	600	Blue	450
Red	650	Green	520



$Cu[(H_2O)6]^{2+}$ $Cu[(NH_3)]^{2+}$

$[Ni(NH_3)_6]^{2+}$

$[NiCl_4]^{2-}$



$Fe[(H_2O)6]^{3+}$ $Fe[(H_2O)6]^{2+}$

FIVE BASIC OPTICAL INSTRUMENT COMPONENTS

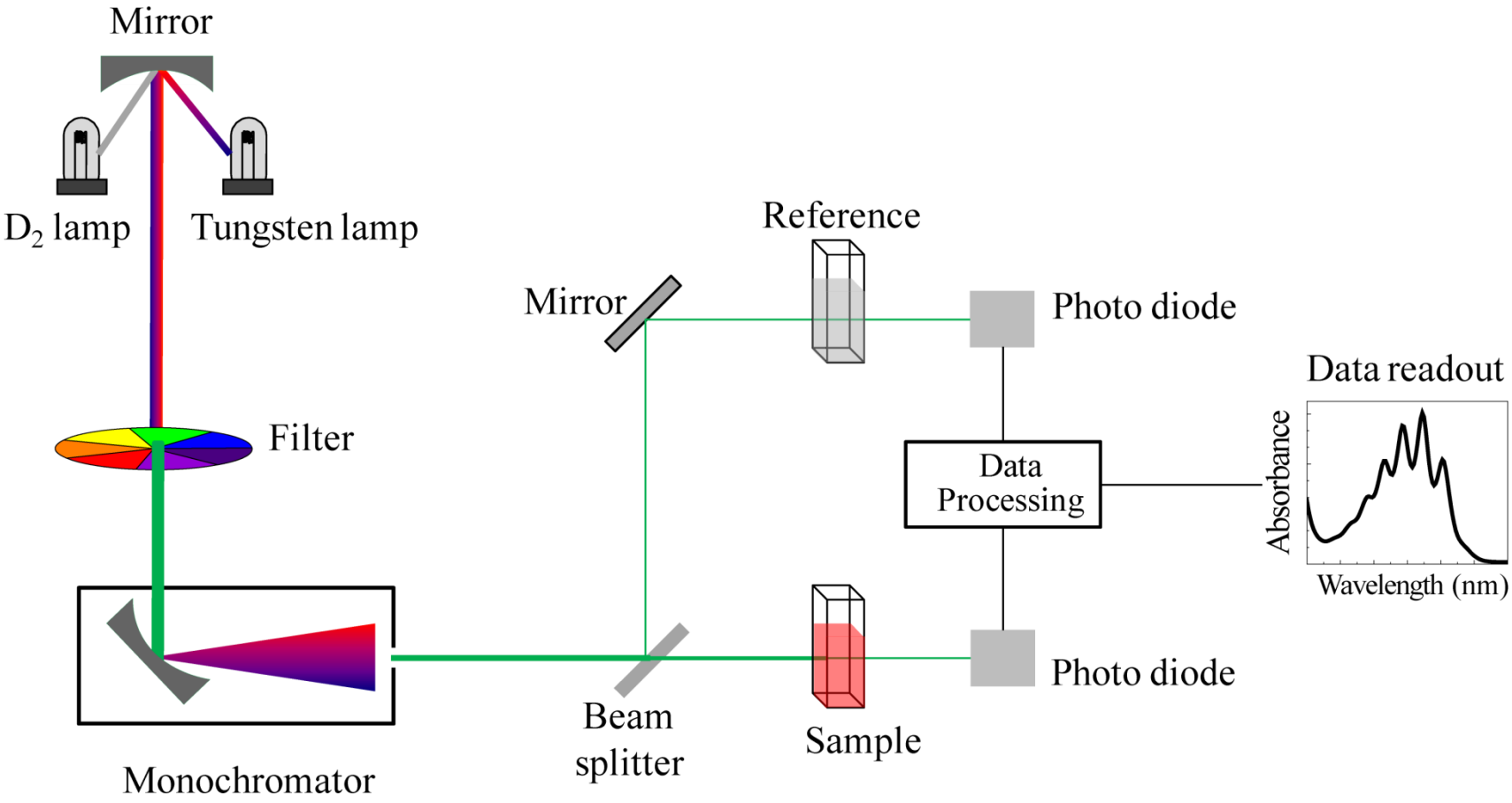
1)**Source** - A stable source of radiant energy at the desired wavelength (or λ range).

2)**Sample Holder** - A transparent container used to hold the sample (cells, cuvettes, etc.).

3)**Wavelength Selector** - A device that isolates a restricted region of the EM spectrum used for measurement (monochromators, prisms, & filters).

4) **Detector** - Converts the radiant energy into a useable signal (usually electrical).

5)**Signal Processor & Readout** - Amplifies or attenuates the transduced signal and sends it to a readout device such as a meter, digital readout, chart recorder, computer, etc.


Mirror
D2 lamp
Tungsten lamp
Filter
Monochromator
Mirror
Beam splitter
Reference
Sample
Photo diode
Photo diode
Data Processing
Data readout
Absorbance
Wavelength (nm)