

Spectroscopy

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Reference Books:

1. Fundamentals of Molecular Spectroscopy, 4th Edition, by **Colin N. Banwell** and Elaine M. McCash
2. Introduction to Spectroscopy, 5th Edition, **Donald L. Pavia**, Gary M. Lampman, George S. Kriz
3. Organic Spectroscopy By **William Kemp**
4. Spectroscopy Of Organic Compounds By **P S Kalsi**
5. Elementary Organic Spectroscopy By **Y R Sharma**

Why is Chemistry Important?

Chemistry impacts on our everyday lives through:



Why is Spectroscopy Important?

- Atoms and molecules have unique **spectra**.
- Spectra can be used to **detect, identify and quantify** information about the atoms and molecules.

Definition of Spectroscopy:

It is a branch of science which deals with interaction of **matter** with **light** or **electromagnetic radiation**.

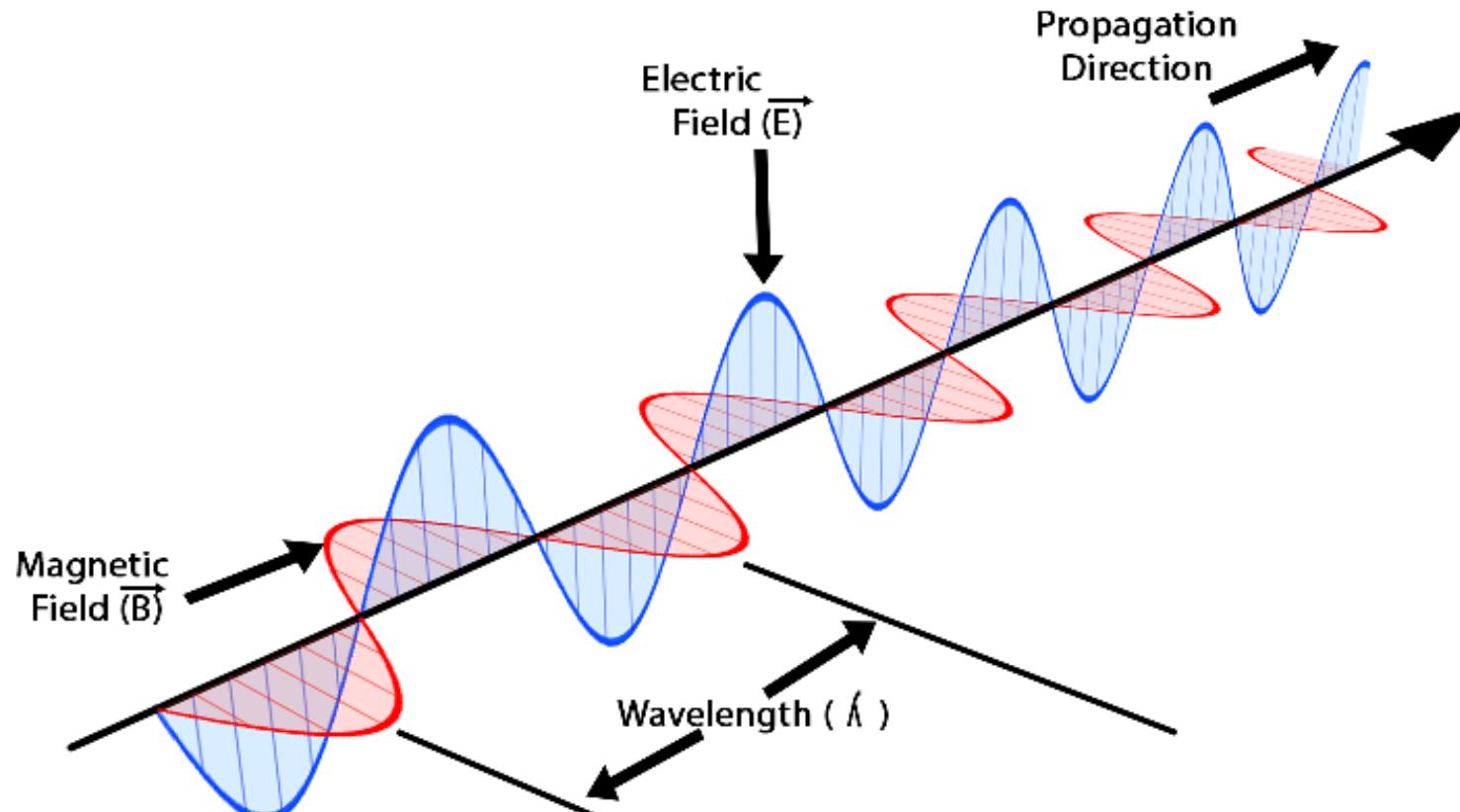
OR

It is a branch of science in which **electromagnetic radiation** of particular wavelength or range of wavelength is used for qualitative and quantitative analysis of **matter**.

Matter – Anything which occupy space in universe and having mass.

Electromagnetic Radiation

Definition: Wave produced by motion of electrically charged particle (photon).



- Consists of two components - Electric and Magnetic.
- It can be described as a simple harmonic wave of sinusoidal character.

Terms and definitions

Wave length (λ): The distance between two identical adjacent points in a wave (or) distance between two adjacent crests (maxima) or troughs (minima) in a wave (Units – **meter**).

Frequency (v): Number of waves that passes a given point per second (Units – **Hz**).

Wave number (ν): Number of waves present in one meter distance of a wave (Units – **meter⁻¹**).

Amplitude (A): Distance from rest position to crest (maxima) or trough (minima).

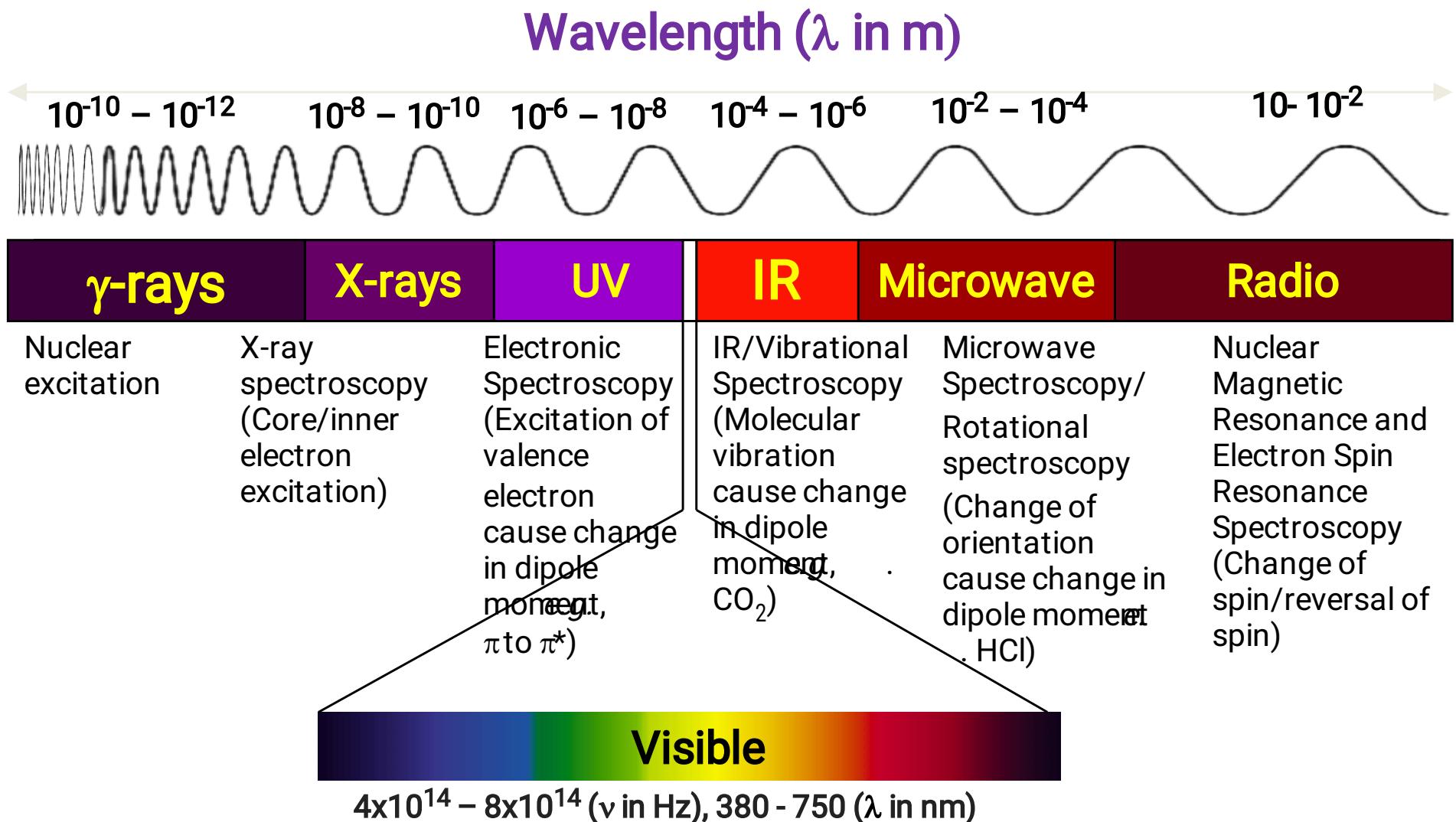
$$v \propto 1/\lambda$$

$$v = c/\lambda$$

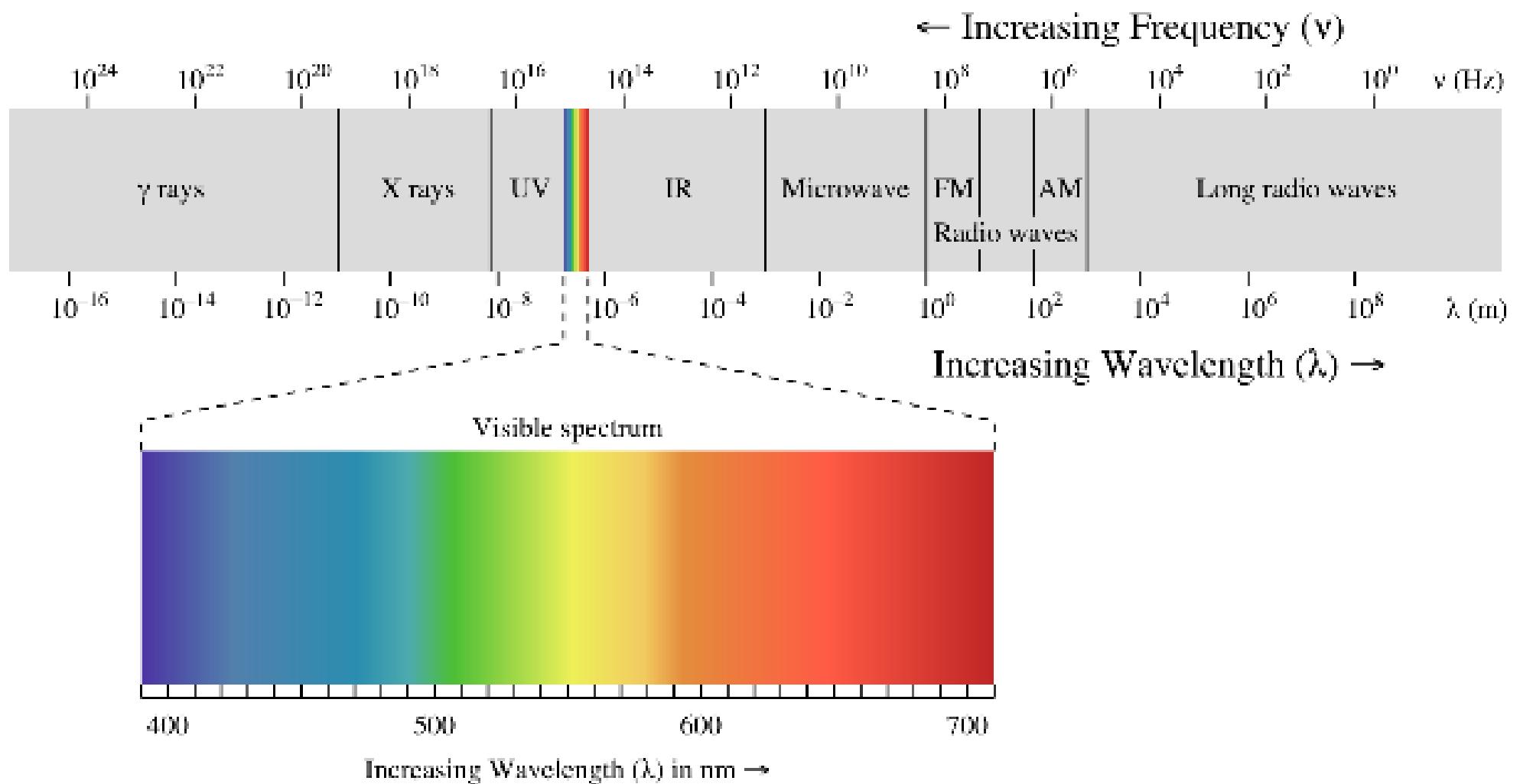
$$v = c\nu$$

Electromagnetic spectrum

- The entire distribution of electromagnetic radiation according to wavelength.

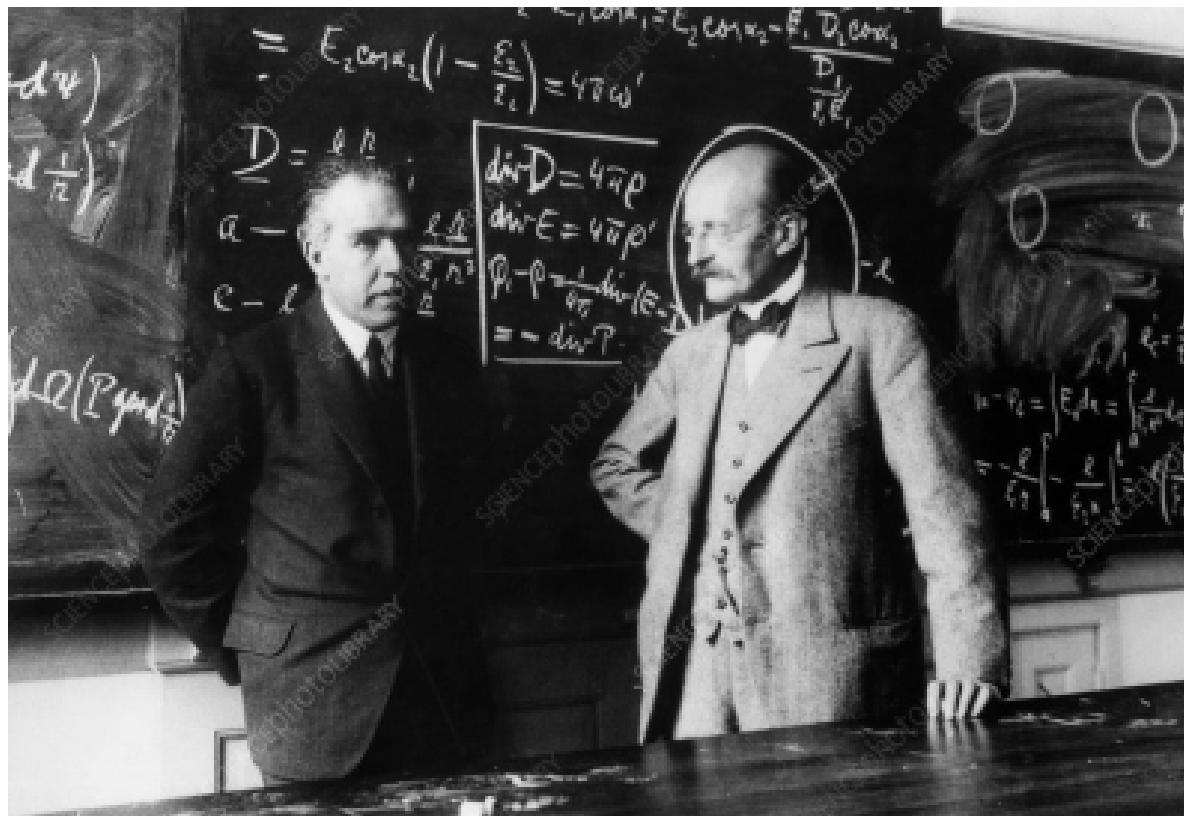


Electromagnetic spectrum



Quantization of Energy

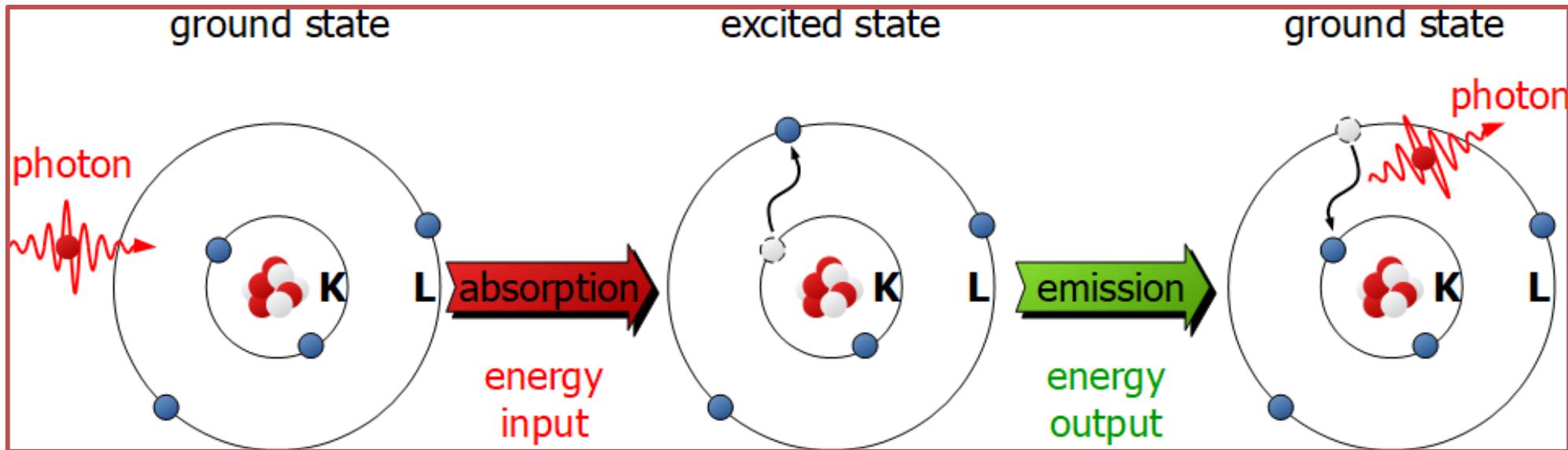
N. Bohr
Nobel Prize
On 1921



M. Plank
Nobel Prize
On 1918

Historical portrait of the Danish physicist Niels Henrik David Bohr (1885-1962) with the German physicist Max Planck (1858-1947). Planck proposed in 1900 that radiation is emitted or absorbed in discrete packets (quanta). Bohr's 1913 model of the hydrogen atom used quantized energy levels for electrons orbiting the nucleus. Bohr received the Nobel Prize for Physics in 1922, as Planck had in 1918. Photographed in 1930.

- ❖ Max Planck and Albert Einstein (Nobel price 1921) explained the photoelectric effect by assuming that light was actually a stream of little particles, or packets of energy known as photons or quanta.



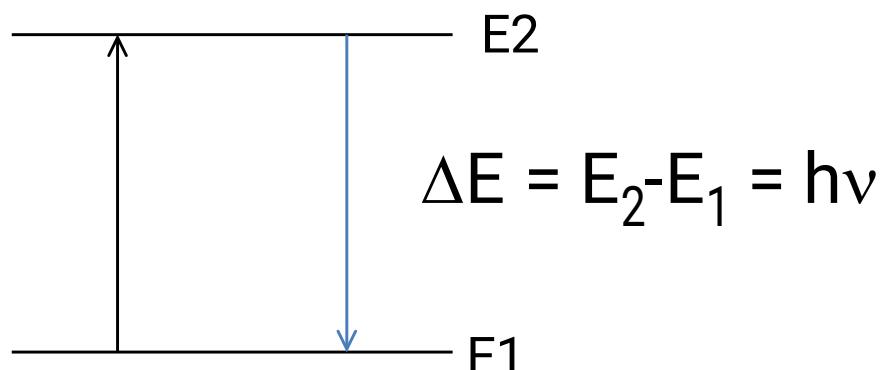
Energy of a Photon $E \propto \nu$

$$E = h\nu$$

$$E = hc/\lambda$$

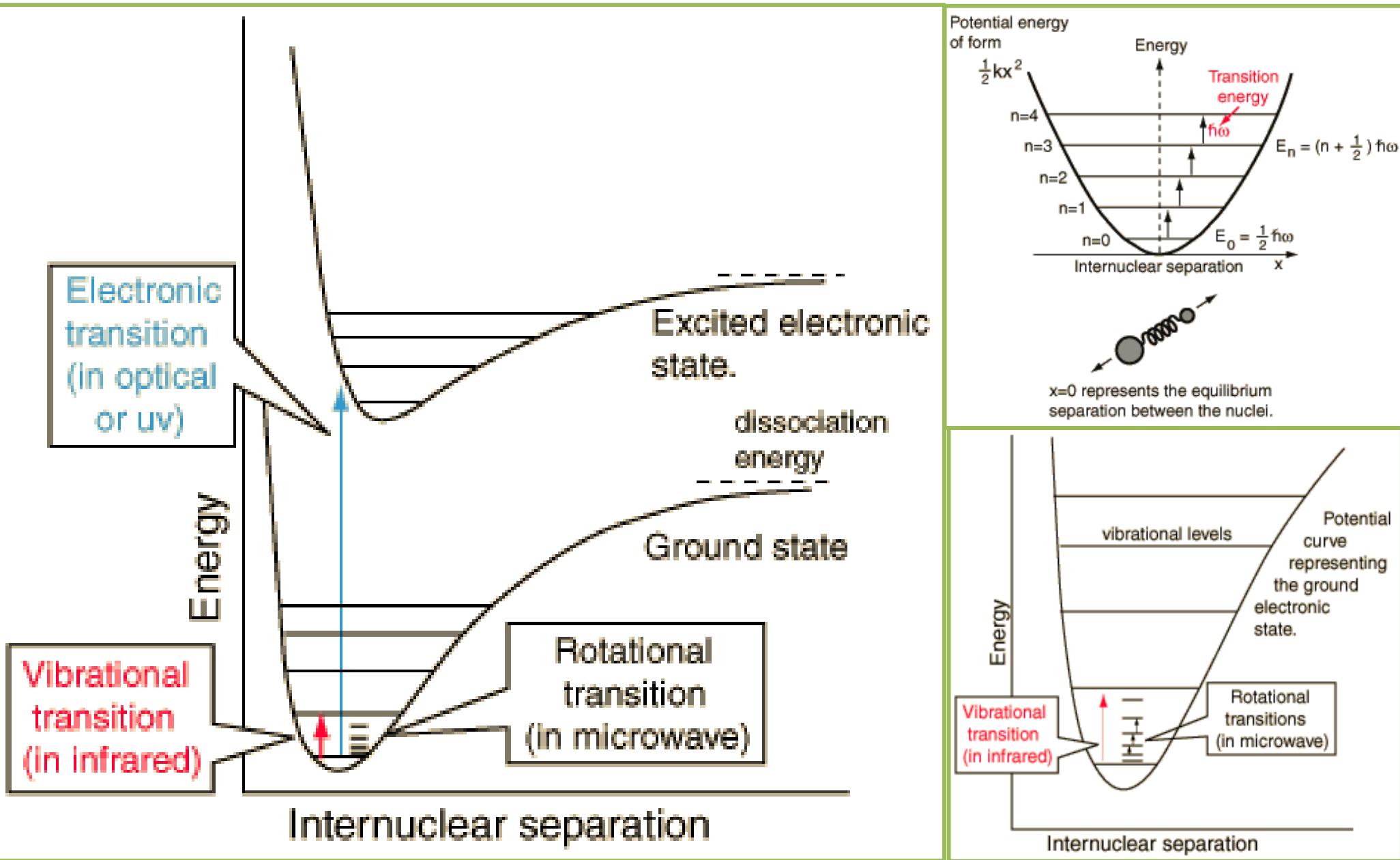
Where, $h = 6.626 \times 10^{-34}$ J. sec;

$$c = 3 \times 10^8 \text{ m/sec}$$

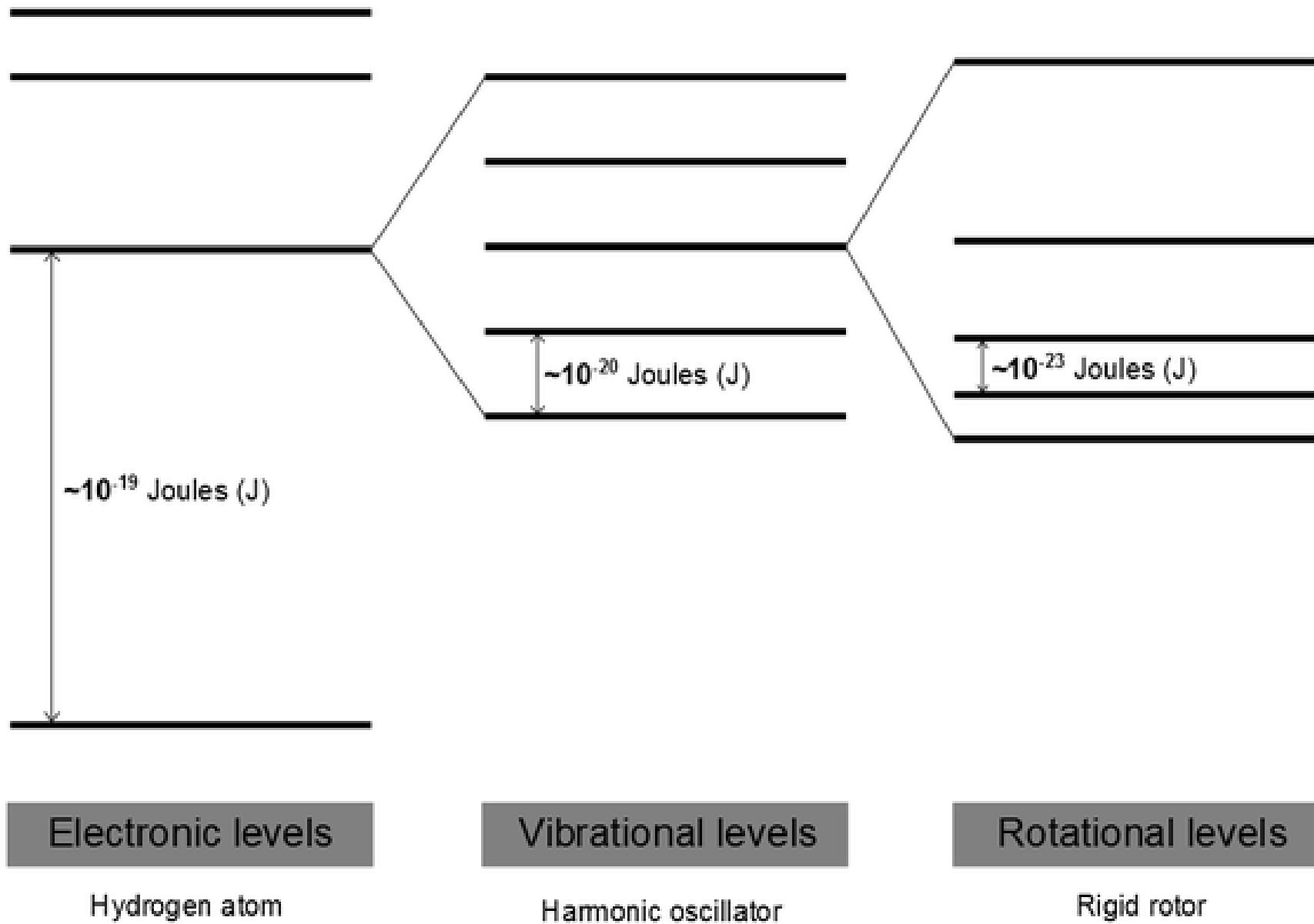


Molecular Transitions

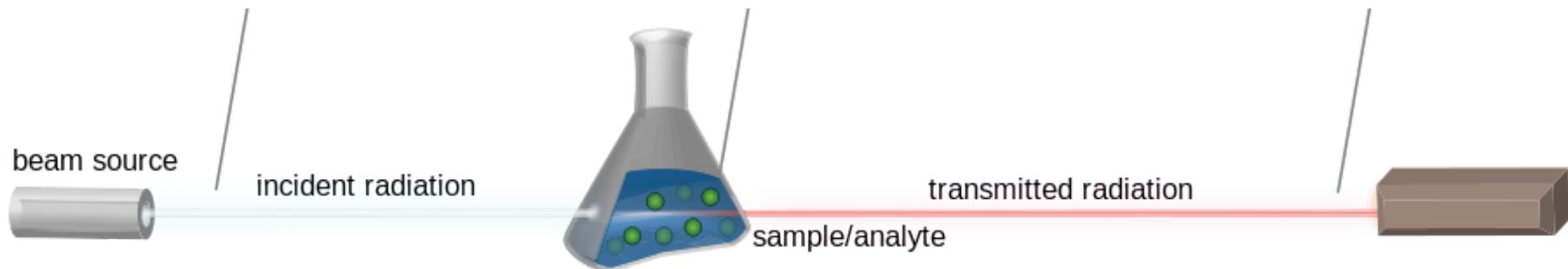
- ❖ Electronic, vibrational and rotational transitions.



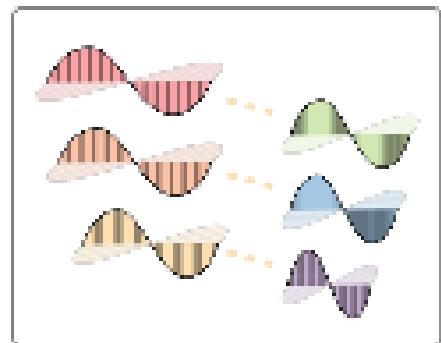
Molecular Transitions



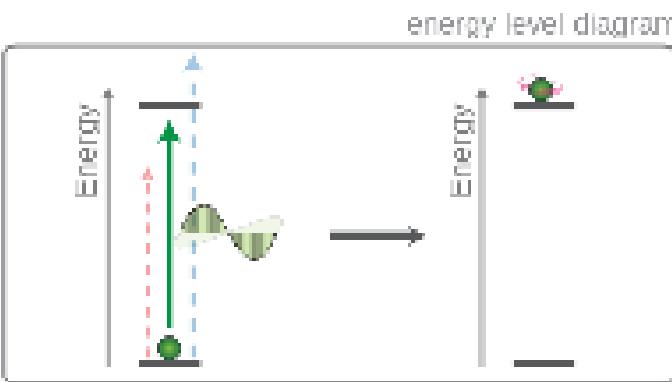
- When electromagnetic radiation is passed through the substance under analysis, then radiations of **certain wavelength** are absorbed by the substance depending on the structure of the compound.



Emission



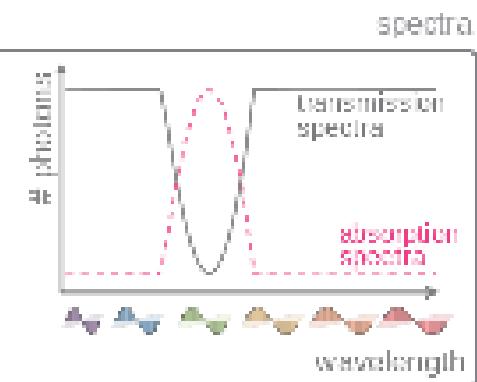
Absorption



Transmission

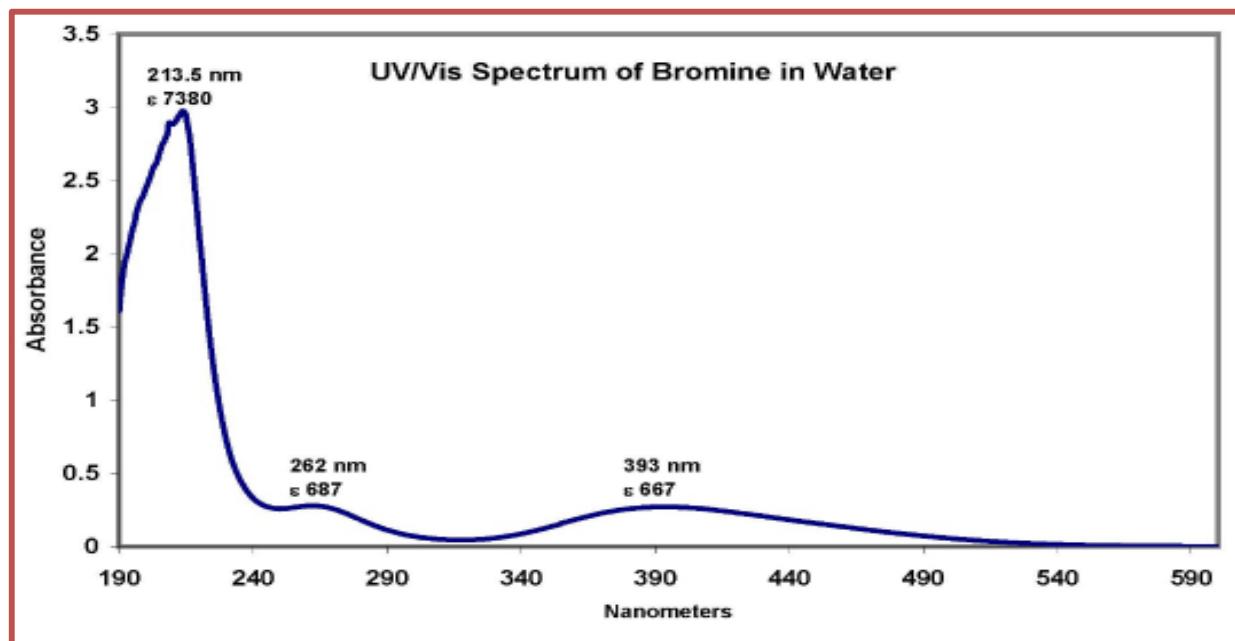


Detection

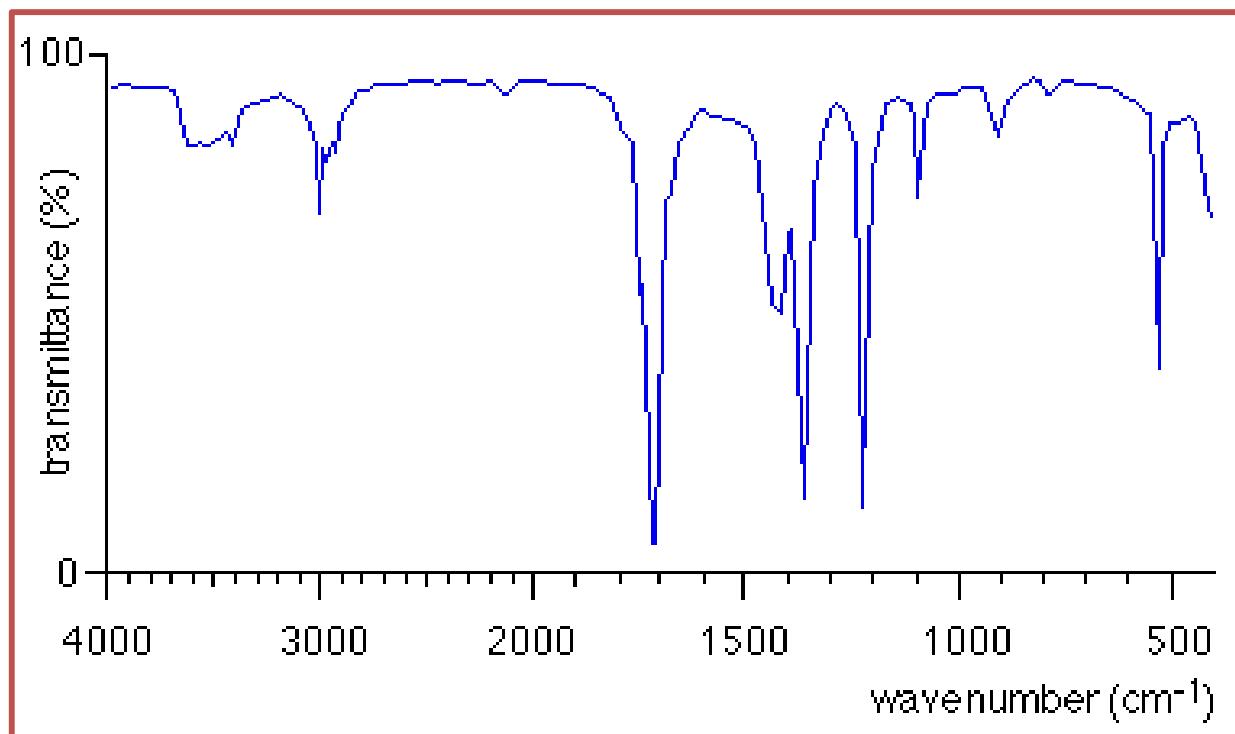


Representation of spectra

UV-Visible Spectrum



IR Spectrum of Acetone



Factors affecting on spectra: Width of spectral lines

- ❖ **Collision broadening:** Molecular interactions are more severe in liquids than in gas (Gas phase spectra are sharper than those of the corresponding liquids). In case of solids, the spectral lines are sharper but show evidence of interactions by splitting of lines.

- ❖ **Doppler effect:** Atoms or molecules in gases and liquids are in continuous motions with different velocities in different directions from the detector which causes Doppler effect (More in gases than in liquids)

Factors affecting on spectra: Intensity of spectral lines

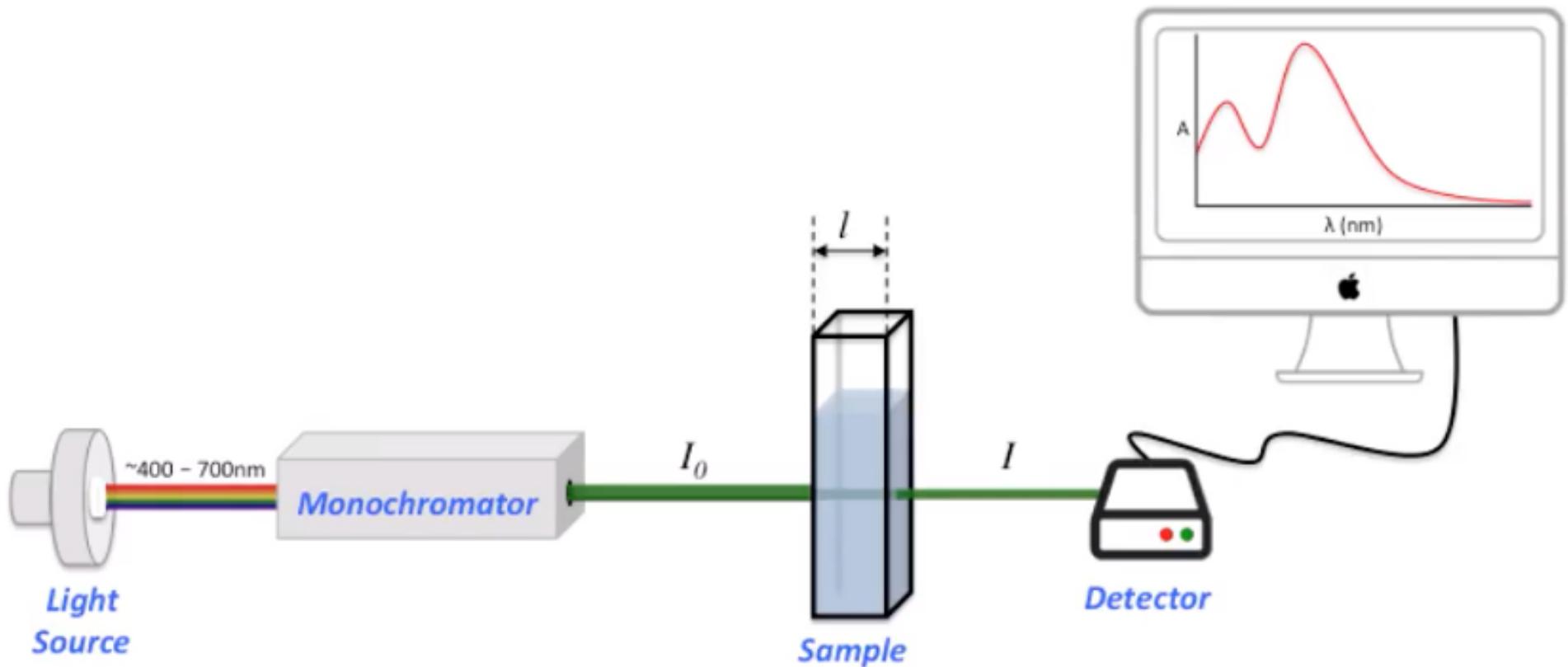
- ❖ **Transition probability:** As the probability increases intensity increases.
- ❖ **Population of states:**

Boltzmann's distribution law

$$N_{\text{upper}}/N_{\text{lower}} = e^{(-\Delta E/KT)}$$

Where, K = Boltzmann's constant (1.38×10^{-23} J/K)

- ❖ Concentration or Path length of the sample: Can be explained by the absorption laws



Absorption laws

Lambert's Law : Solid Sample (Absorbance \propto Path length)

Beer's Law : Solution (Absorbance \propto Concentration)

- ❖ **Beer–Lambert law:** Combines the two laws ($A \propto cl$)

Beer–Lambert law: The law states that when a beam of monochromatic radiation on UV-visible range is passed through absorbing medium, “the rate of decrease of intensity of radiation is proportional to the intensity of radiation as well as the concentration of the solution”.

$$A = \epsilon Cl \quad (\epsilon \text{ molar absorption coefficient})$$

Transmittance (T): It is a measure of the fraction of light that passes through the sample. It is the ratio between I_t and I_o .

$$T = \frac{I_t}{I_o}$$

$$\%T = T \times 100$$

Absorbance (A): Amount of light absorbed by the sample

$$A = -\log(T) \text{ or } \log(1/T) \text{ or } -\log\left(\frac{I_t}{I_o}\right) \text{ or } \log\left(\frac{I_o}{I_t}\right)$$

or

$$A = 2 - \log(\%T)$$

Derivation: Mathematically, the law is expressed as,

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

$$\Rightarrow -\frac{dI}{dx} = kIc$$

$$\Rightarrow \int_{I_o}^{I_t} \frac{dI}{I} = - \int_{x=0}^{x=l} kc \, dx$$

Where,

c = Concentration of the solution (mol/lit)

k = Proportionality constant

l = Path length

$$\text{Since, } \ln \frac{I_t}{I_o} = 2.303 \log \frac{I_t}{I_o}$$

$$\Rightarrow \ln \frac{I_t}{I_o} = -k' cl \quad \text{or} \quad \log \frac{I_t}{I_o} = -\frac{k'}{2.303} cl$$

$$I_t/I_o = e^{-kCl} \Rightarrow I_t = I_o 10^{-\varepsilon cl}$$

$$\Rightarrow I_t = I_o 10^{-\varepsilon l}$$

Here, $\varepsilon = \frac{k}{2.303}$ where ε is known as **molar extinction coefficient or molar absorptivity** of the absorbing medium (units: lit/mol.cm).

$$\frac{I_t}{I_o} = 10^{-A} \quad \text{or} \quad \log \frac{I_o}{I_t} = A$$

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

Here, **A** is known as **Absorbance** And **T** is called **Transmittance** which is equal to $\frac{I_t}{I_o}$.

We know,

$$T = \frac{I_t}{I_o}; \quad \text{Then, } \%T = 100T$$

$$\text{Absorbance, } A = \log \frac{I_o}{I_t} = \log \frac{1}{T}; \Rightarrow A = \log \frac{100}{T\%}$$

$$\Rightarrow A = 2 - \log T\%$$

Problems:

$$A = \epsilon cl = \log \frac{I_o}{I_t} = \log \frac{1}{T} = 2 - \log(\%T)$$

1. The molar absorption coefficient of tyrosine in water is $1280 \text{ M}^{-1} \text{ cm}^{-1}$ at 280 nm. Calculate the concentration of a tyrosine solution in water if the absorbance of the solution is 0.34 in a 1 cm path length cell.
2. Calculate absorbance of a radiation in a photo-absorption technique if 60% of it has been absorbed by the sample.
3. There is a substance in a solution (4 g/liter). The length of cuvette is 2 cm and only 50% of the certain light beam is transmitted. What is the extinction coefficient?
4. The absorption coefficient of a glycogen-iodine complex is 0.20 mol/lit at light of 450 nm. What is the concentration when the transmission is 40 % in a cuvette of 2 cm?

Answers:

1. $A = \epsilon cl$

$\epsilon = 1280 \text{ M}^{-1}\text{cm}^{-1}$; $A = 0.34$; $l = 1 \text{ cm}$

c = ?

$$c = A / \epsilon l = 0.34 / (1280 \times 1) = 2.83 \times 10^{-3} \text{ M (mole/Lit)}$$

2. $A = -\log(T) = \log\left(\frac{I_0}{I_t}\right)$

60% is absorbed by the sample, transmitted = 40%

$$A = \log(1/0.4) = \log 10 - \log 4 = 1 - 0.6020 = 0.398$$

3. $\epsilon cl = \log\left(\frac{I_0}{I_t}\right); \epsilon = ?$

$c = 4 \text{ g/lit}$; $l = 2 \text{ cm}$; 50% of light beam is transmitted

$$8\epsilon = \log(1/0.5)$$

$$\epsilon = (\log 10 - \log 5)/8 = (1 - 0.6989)/8 = 0.0376$$

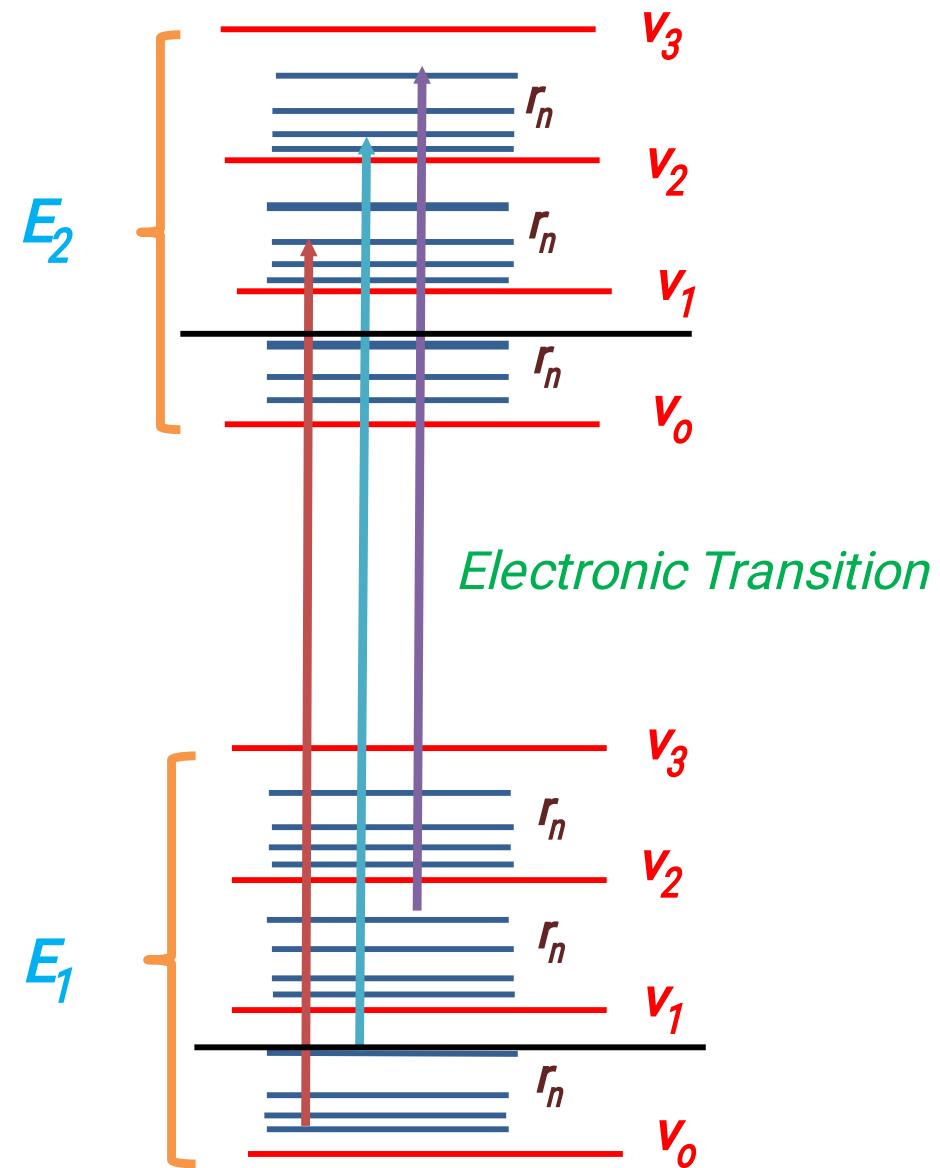
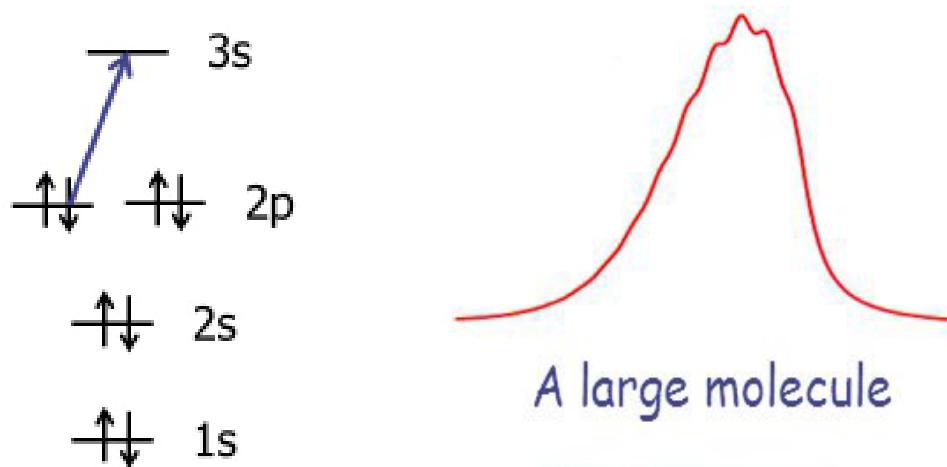
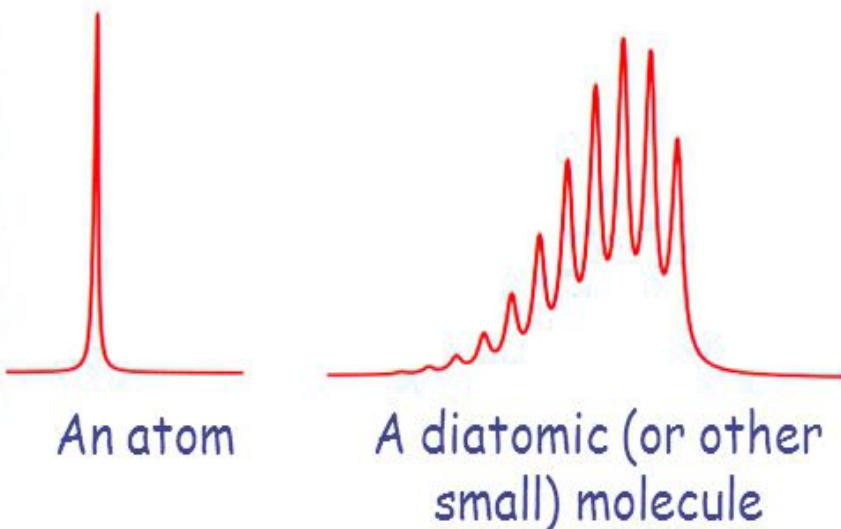
4. $\epsilon cl = \log\left(\frac{I_0}{I_t}\right); c = ?$

$\epsilon = 0.2 \text{ mole/lit}$; $l = 2 \text{ cm}$; 40% of light beam is transmitted

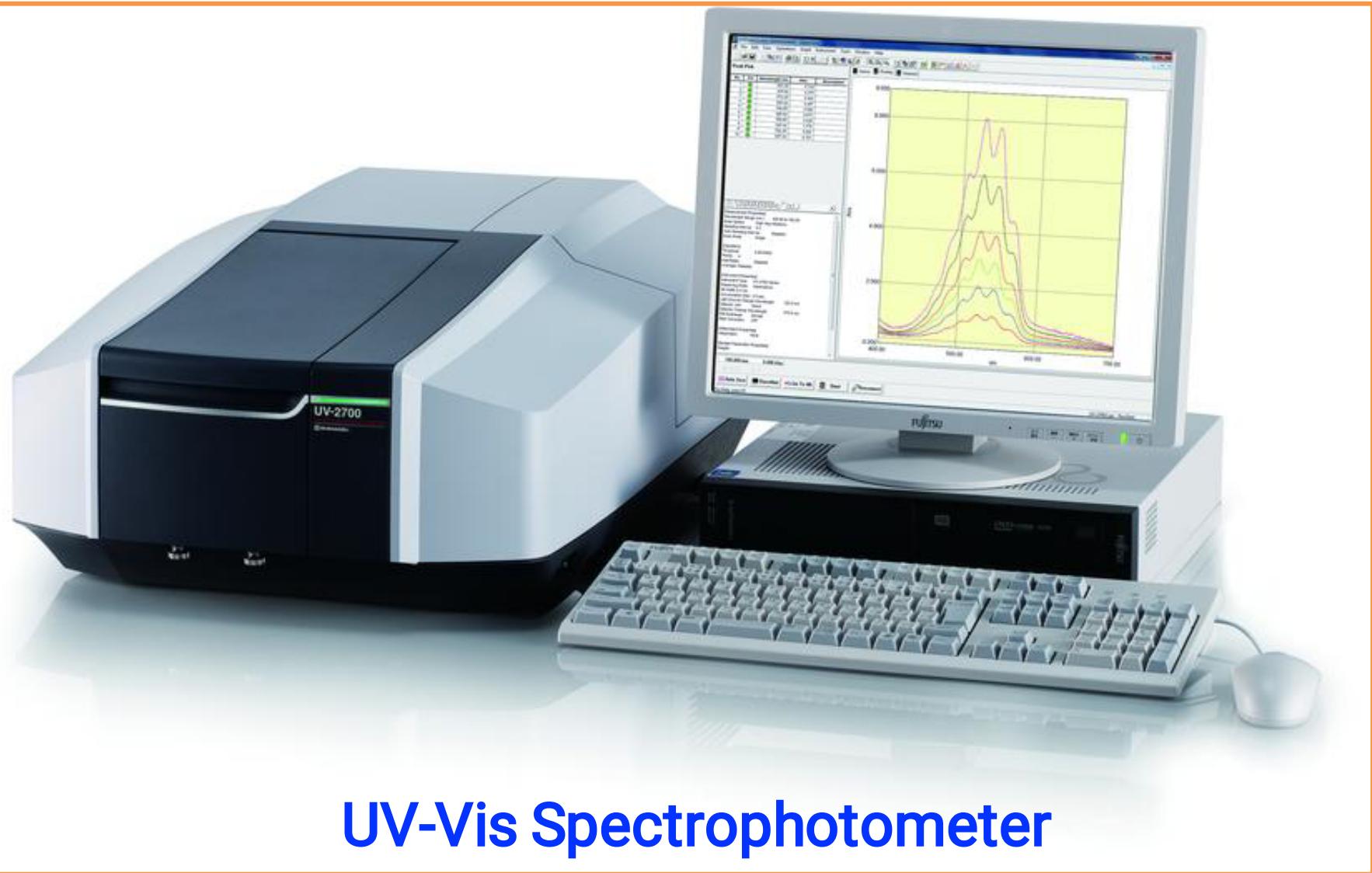
$$0.4 c = \log(1/0.4)$$

$$c = (\log 10 - \log 4)/0.4 = (1 - 0.6020)/0.4 = 0.995 \text{ mol/lit}$$

Absorption peaks broadens from atom to polyatomic molecules



UV-Visible/Electronic Spectroscopy



UV-Vis Spectrophotometer

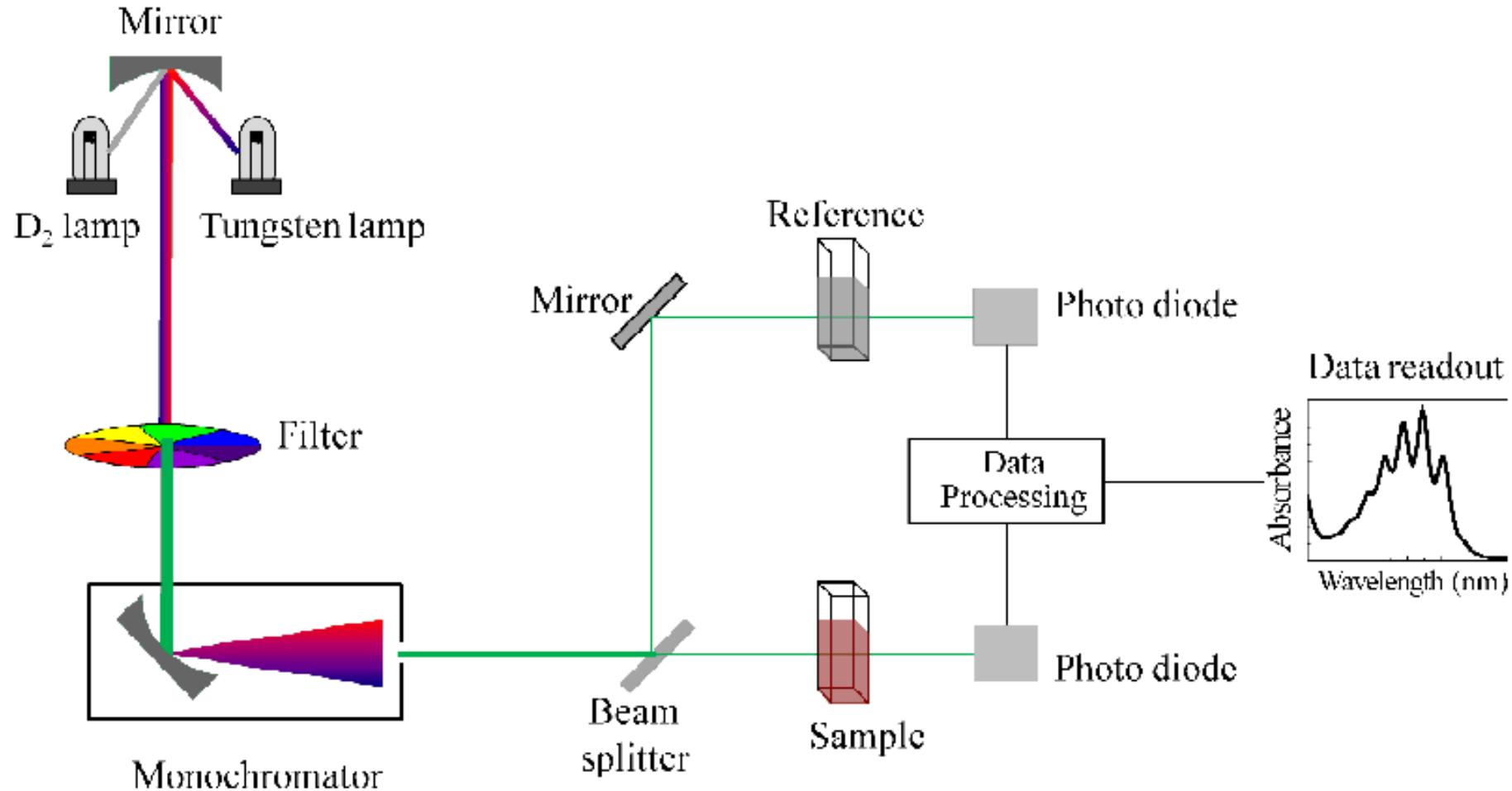
Why UV-Visible/Electronic Spectroscopy?

- ❖ Useful to detect the presence of chromophores like dienes, aromatics, polyenes, and conjugated ketones etc.

UV-Visible radiation

- ❖ Wave length: 10-780 nm
 - Visible: 400 – 780 nm
 - Near UV: 250 – 400 nm
 - Far UV: 190 – 250 nm
 - Vacuum UV: < 190 nm
- The vacuum UV is named because the molecules of air (e.g. O₂, N₂) absorb radiation in this region, and thus this region is accessible only with special vacuum equipment's.

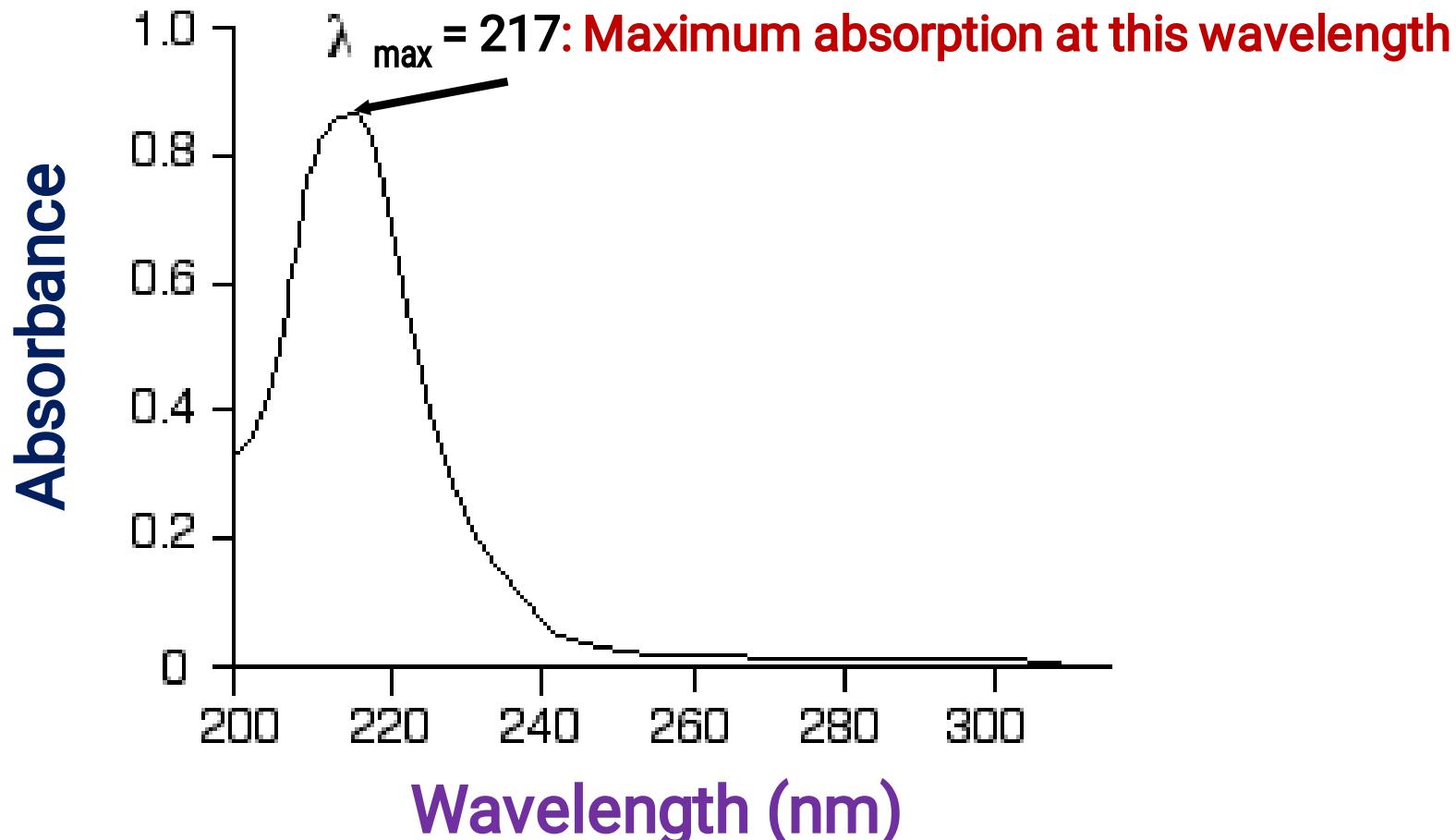
Schematic of UV-Vis Spectrophotometer



Double beam spectrophotometer

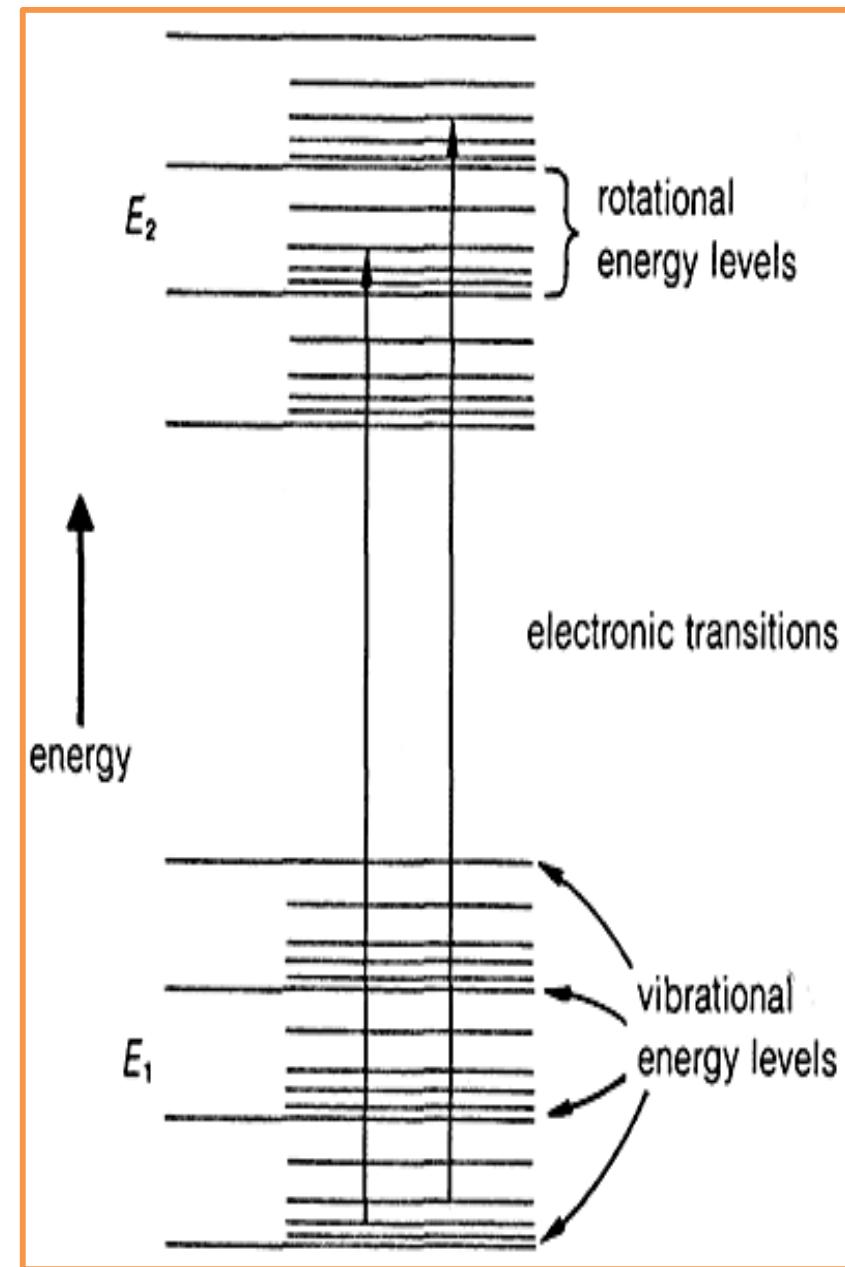
Plot of Electronic Spectra

The UV-Vis spectra is observed as a plot of **intensity of absorbed (or absorbance) radiation against the wavelength of the radiation.**



Born-Oppenheimer approximation

- Born-Oppenheimer (BO) approximation is the assumption that the motion of atomic nuclei and electrons in a molecule can be treated separately. Because electrons are much lighter than the nuclei ($m_e/m_H \approx 1/1836$). Their motion is much faster than the vibrational and rotational motions of the nuclei within the molecule.
- The approach is named after Max Born and J. Robert Oppenheimer who proposed it in 1927.
- BO approximation means considering molecular energy as a sum of independent terms (vibrational and rotational energies are treated separately).



Total energy of a molecule

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$

(These energies are completely independent to each others, can represent in terms of Joules or cm^{-1})

$$E_{\text{ele}} (10^{5-6} \text{ cm}^{-1}) \ggg E_{\text{vib}} (10^3 \text{ cm}^{-1}) > E_{\text{rot}} (1-10 \text{ cm}^{-1})$$

Electronic spectra of diatomic molecules

Rotational spectra: Molecules with permanent dipole moment.

Vibrational spectra: Molecules with change in dipole moment on vibration

Electronic spectra: All molecules gives electronic spectra

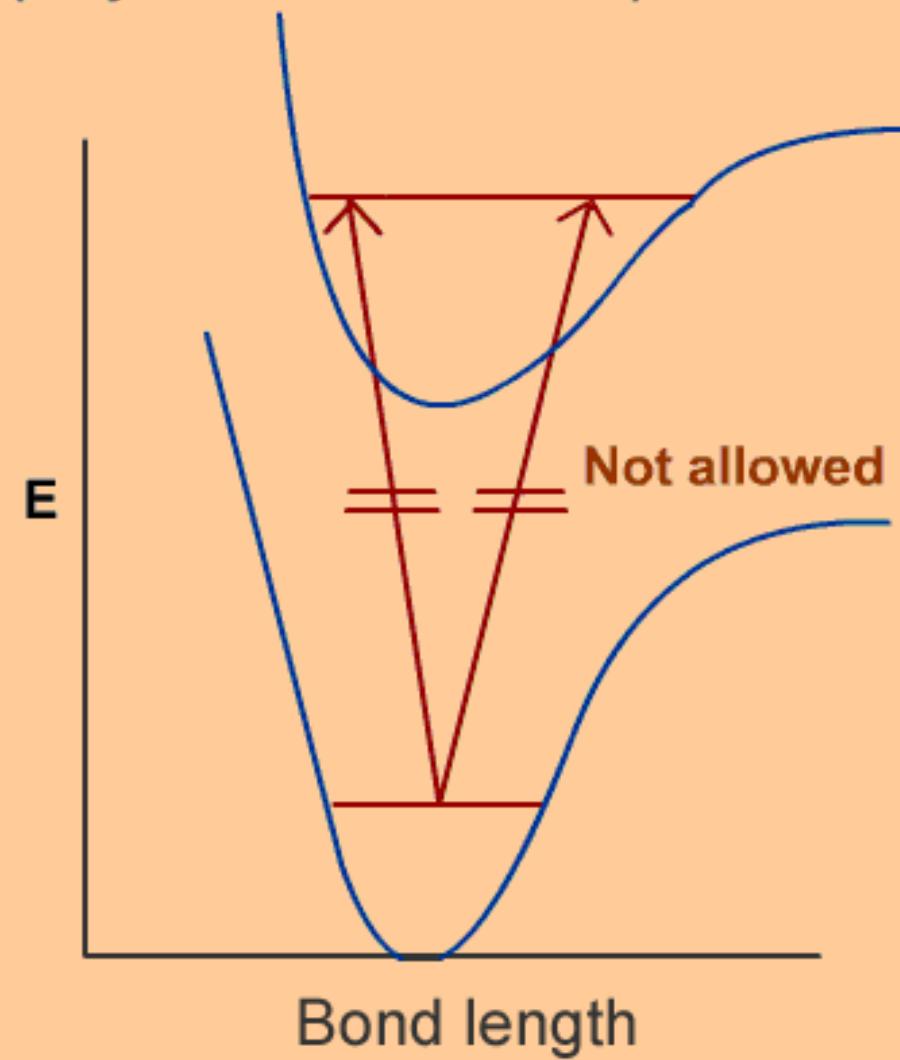
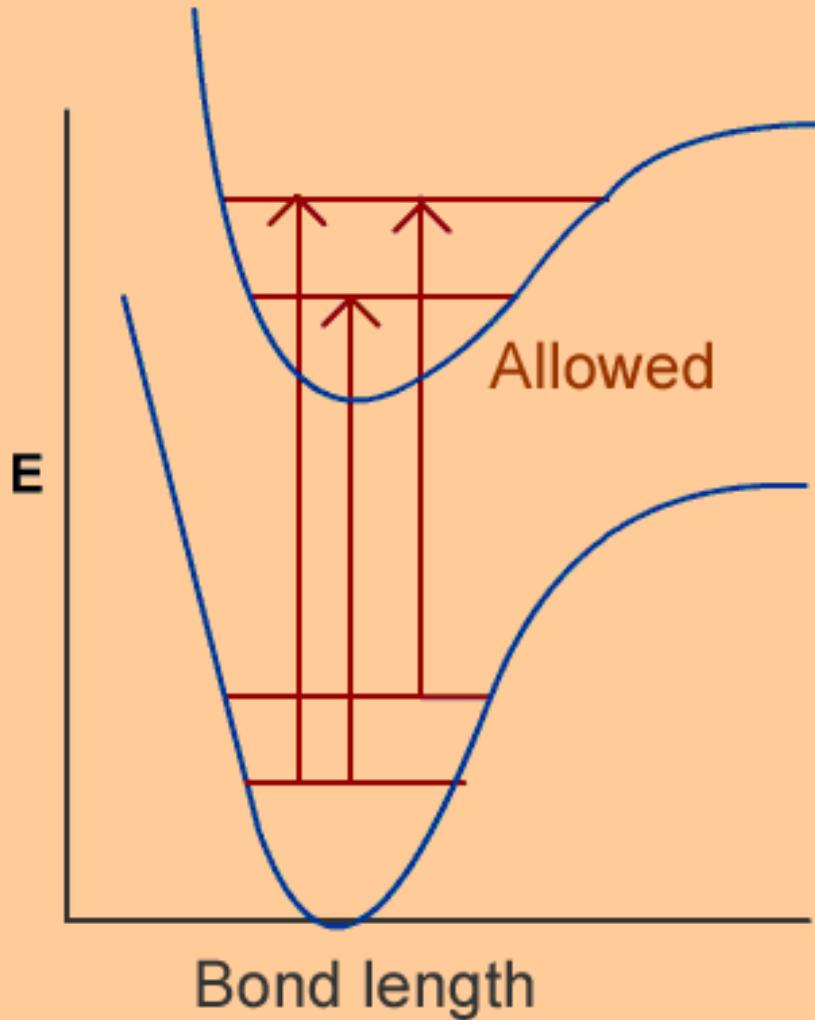
Change in electron distribution in a molecule are always accompanied by a dipole change.

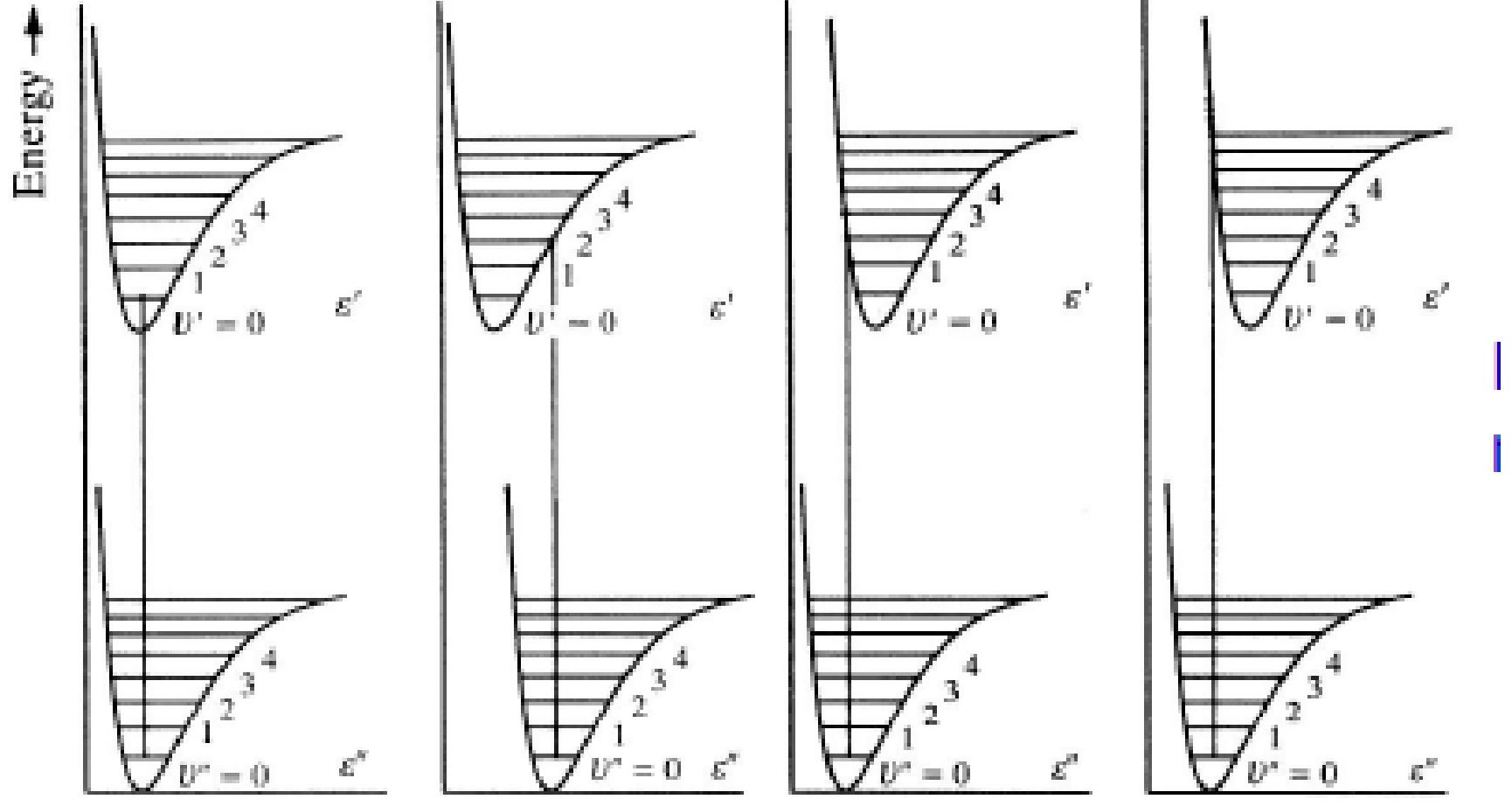
Frank-Condon Principle

- ❖ This principle is the establishment of Born-Oppenheimer Approximation.
- ❖ An electronic transition is very fast compared to the nuclear motion.
- ❖ During an electronic transition the vibrating molecule does not change its inter-nuclear distance (little change in the geometry of the molecule).

- All transitions are represented by vertical lines

Franck - Condon Principle (only vertical transitions)





Same

0.0 1.0 2.0 3.0

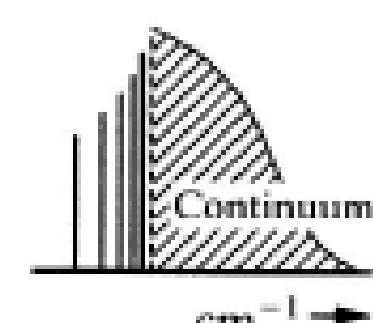
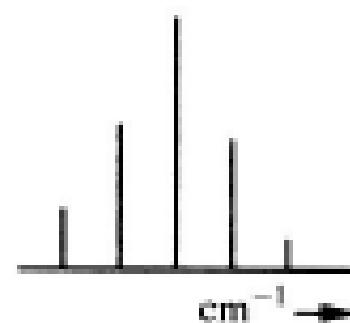
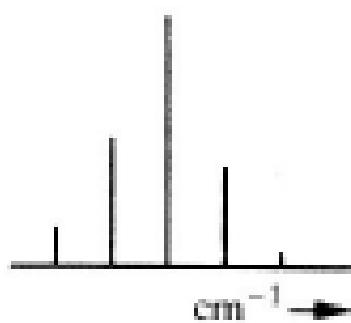
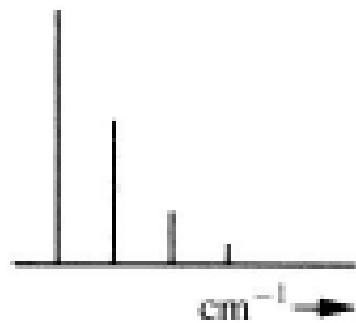
Smaller

0.0 1.0 2.0 3.0 4.0

Bigger

0.01 0.2 0.3 0.4 0

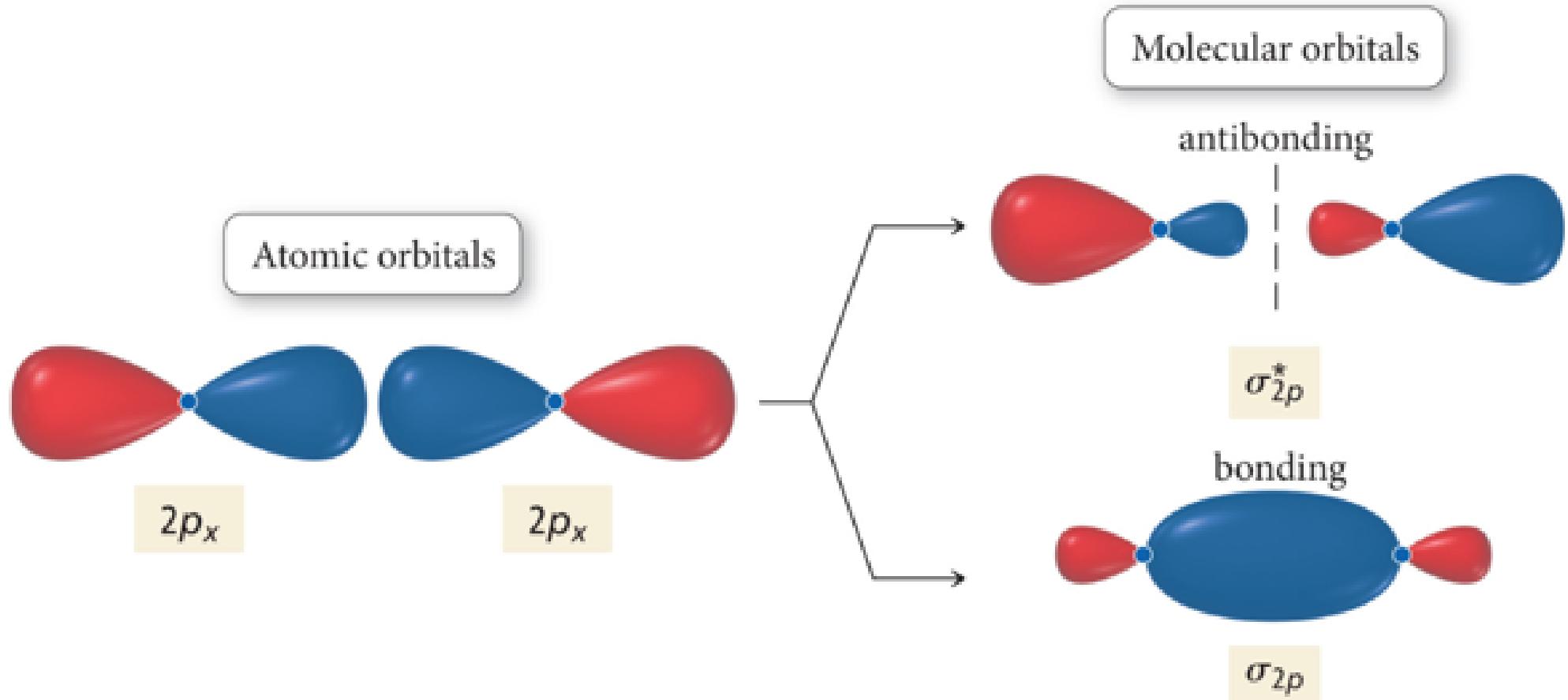
Much bigger



Special Feature

- Number of Transitions
- Energy of Transitions
- Intensity of Transitions

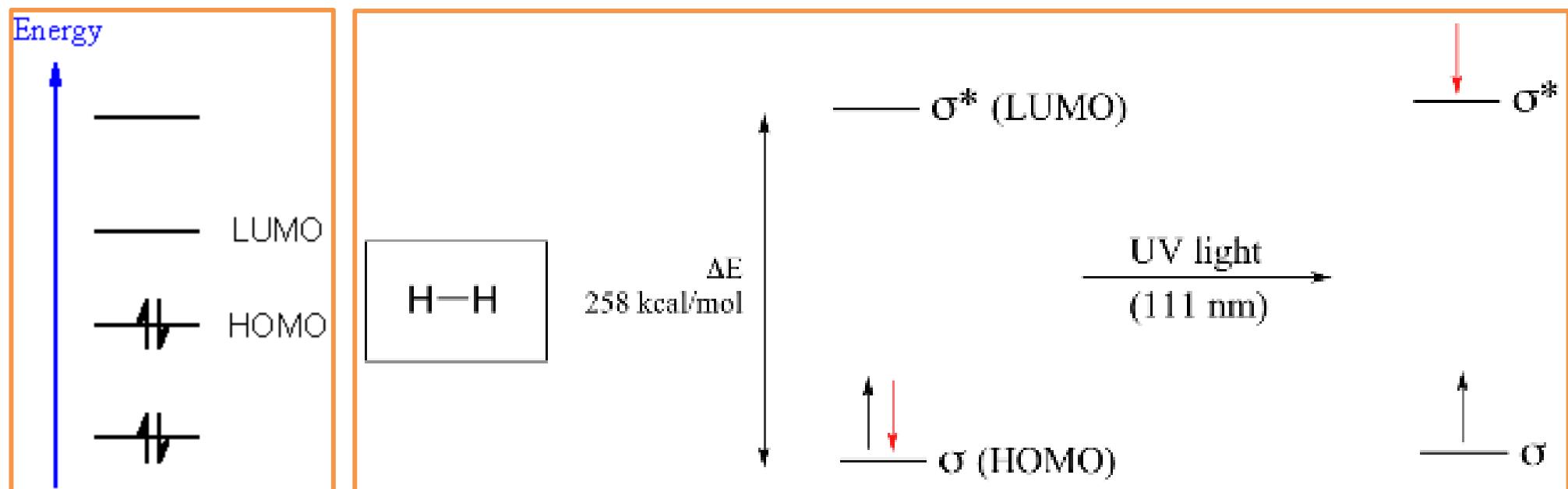
Electronic Transitions



Electronic Transitions

Generally the most probable transition is from:

HOMO LUMO 



The energy differences between electronic levels in most molecules vary from 125 to 650 kJ/mole.

Types of Electronic Transitions

Four types of electronic transitions are possible:

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \\ \rightarrow \pi^*$$

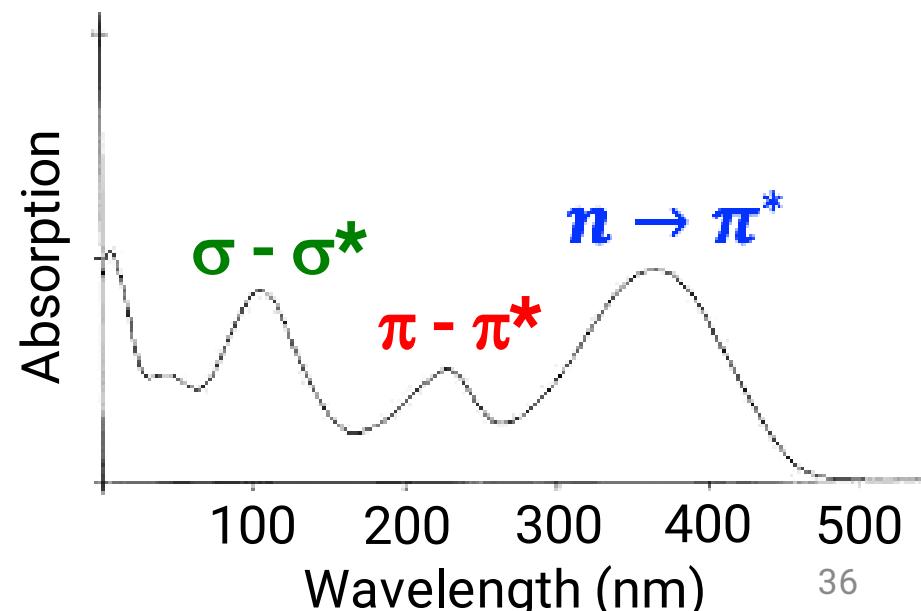
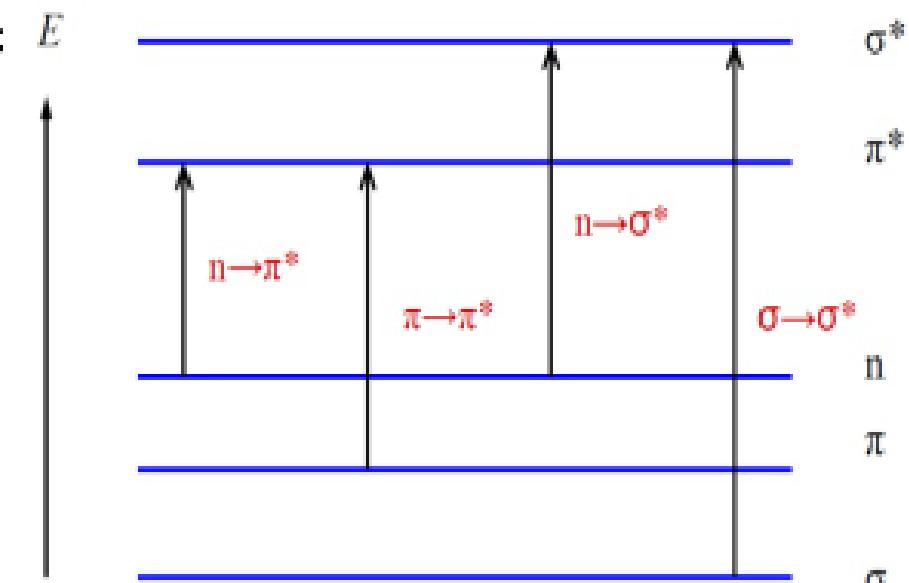
→ Energy decreasing order

$\sigma \rightarrow \sigma^*$ Transition

$n \rightarrow \sigma^*$ Transition

$\pi \rightarrow \pi^*$ Transition

$n \rightarrow \pi^*$ Transition

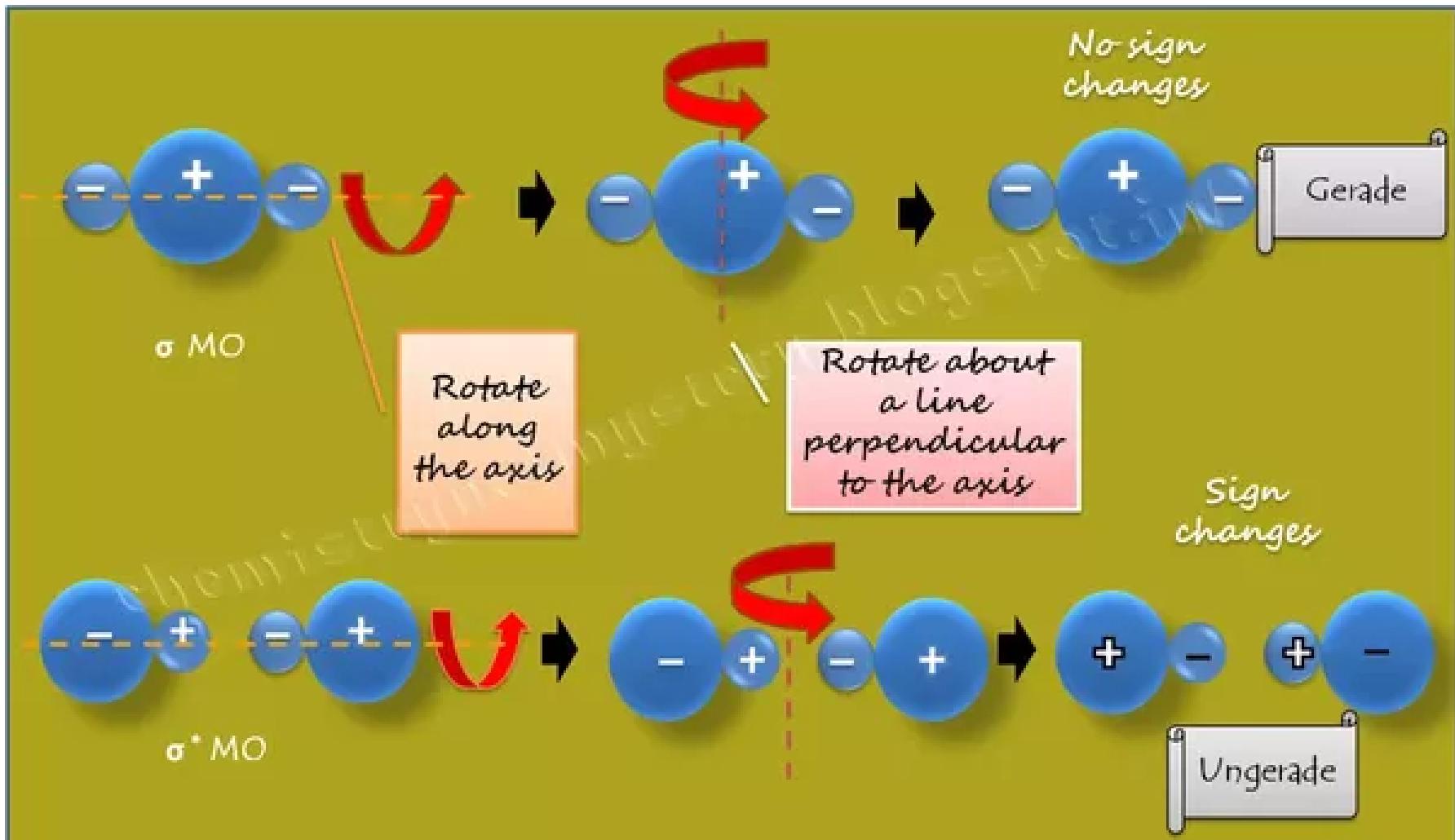


Selection Rules of Electronic Transitions

- **Spin selection rules ($\Delta S = 0$):** There should be **no change in spin orientation** i.e. no spin inversion takes place during electronic transition. Thus $S \rightarrow S$, $T \rightarrow T$ are allowed, but $S \rightarrow T$ and $T \rightarrow S$ are **forbidon transitions**.
- **Laporte (orbital) selection rule ($\Delta l = \pm 1$):** If the molecule has a centre of symmetry, transition within a given set of p- or d-orbitals (i.e. those which only involve a redistribution of electrons within a given subshell) are **forbidden**.
- There must be a change in the parity (symmetry), i.e. transition can occur only between states of opposite parity.

- ❖ Laporte allowed transitions: $g \rightarrow u, u \rightarrow g$
- ❖ Laporte forbidden transitions: $g \rightarrow g, u \rightarrow u$
(g stands for gerade – compound with a center of symmetry. u stands for ungerade – compound without a center of symmetry)

Thus, $s \rightarrow p, p \rightarrow d$ are allowed, but $s \rightarrow s, p \rightarrow p$ are forbidden



- $h\nu = \Delta E$ transition energy (photon matches energy gap between ground and excited state).
- $\Delta\mu \neq 0$ transitions which give no change in dipole moment are forbidden and hence will have almost zero intensity.

$\sigma \rightarrow \sigma^*$ Transition

- ❖ High energy transitions ($<< 200$ nm)
- ❖ Compounds with single bond show $\sigma \rightarrow \sigma^*$ Transitions.
- ❖ Saturated hydrocarbons shows this type of transitions.
 - e.g. Cyclopropane, λ_{\max} 190 nm.
 - Cyclohexane, λ_{\max} 153 nm (vacuum UV)
- ❖ Colourless, since not absorbed light in visible region.

$n \rightarrow \sigma^*$ Transition

- Appear in the **near UV or Visible region.**
- Compounds containing **non-bonding or lone-pair electrons** show this type of transition.

e.g. Water $\lambda_{max} 167\text{ nm}$

MeOH $\lambda_{max} 174\text{ nm}$

MeCl $\lambda_{max} 169\text{ nm}$

NEt₃ $\lambda_{max} 227\text{ nm}$

- In case of saturated alkyl halides, as the electronegativity increases λ_{max} values decrease.

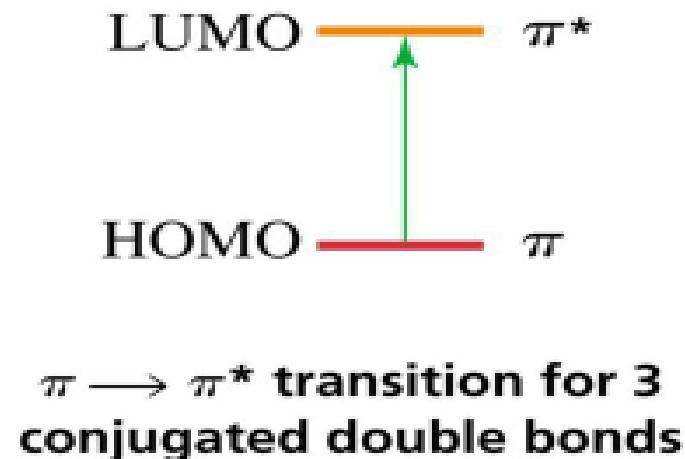
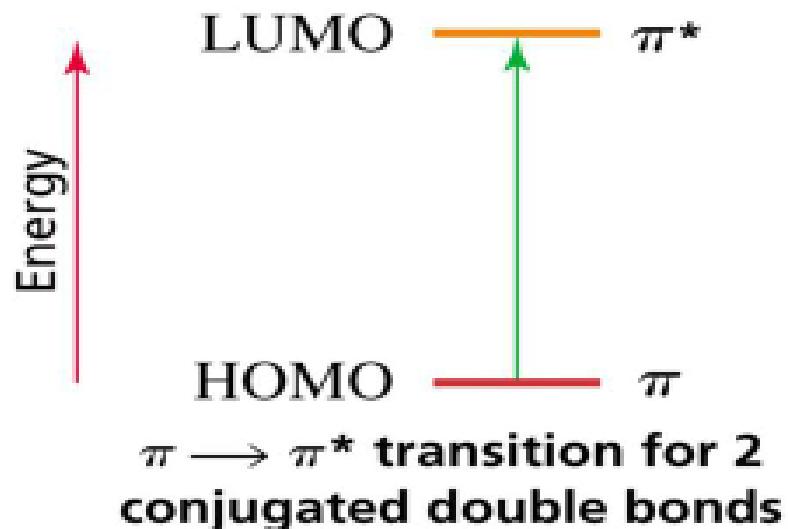
MeCl $\lambda_{max} 169 \text{ nm}$

MeI $\lambda_{max} 258 \text{ nm}$

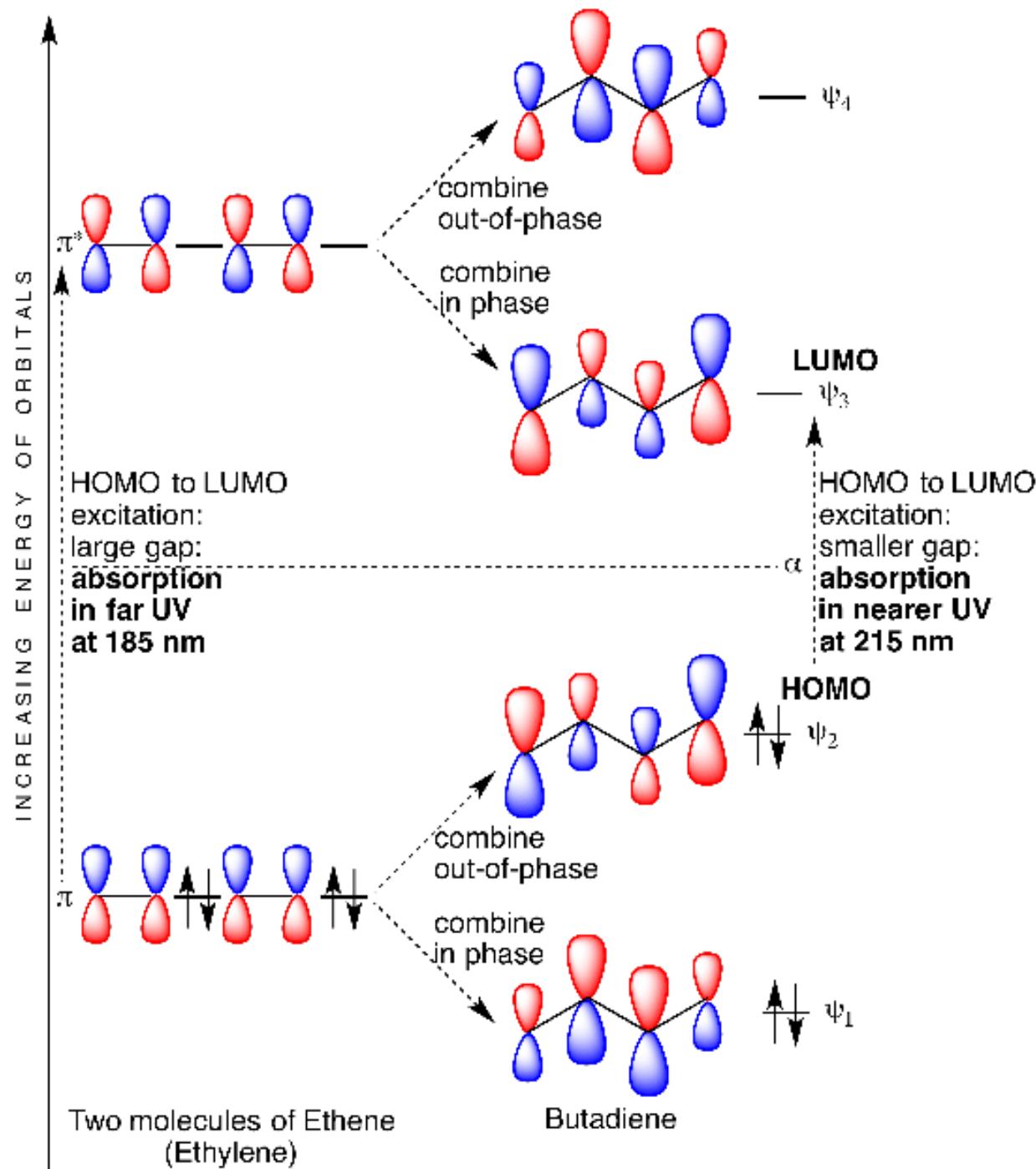
- Since, nonbonding electrons are more difficult to excite in case of more electronegative atom.

$\pi \rightarrow \pi^*$ Transition

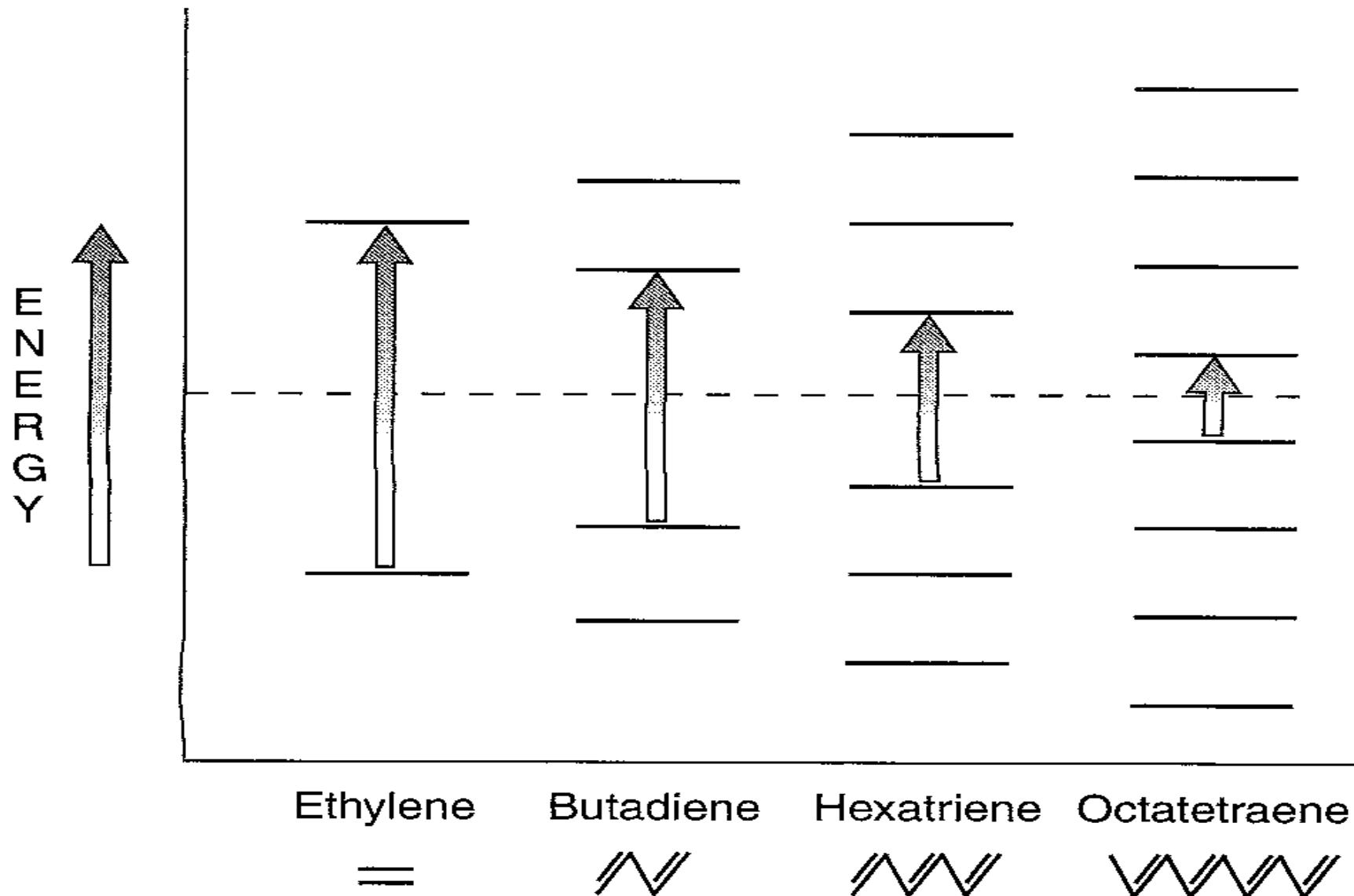
- Compounds containing **double, triple bonds and aromatic rings** show this type of transition.
e.g. Alkenes, Alkynes, Carbonyls, Cyanides, Azo compounds etc.
 - This is usually a **symmetry allowed and high intensity** transition.
- **Conjugation makes the electronic transitions easier (lowers the ΔE and increase in λ_{max})**.

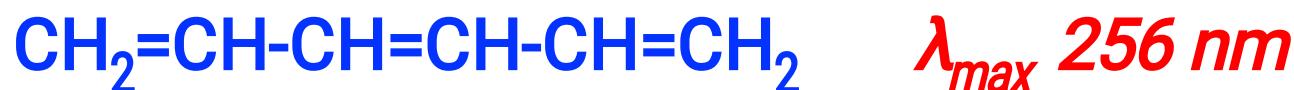


Effect of conjugation



Conjugation lower the energy between HOMO and LUMO or increases the wavelength of absorption





Problems:

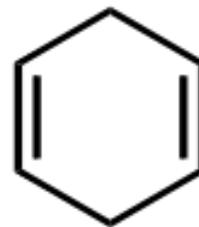
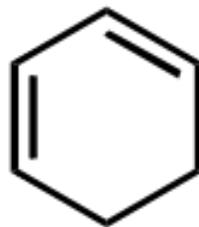
Q1. Ethylene λ_{max} value is 171 nm. What could be the λ_{max} value of 3-hexene (decreases or increases)?

Ans. Increases because of + Inductive effect.

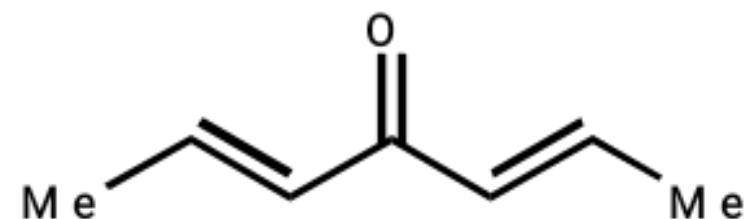
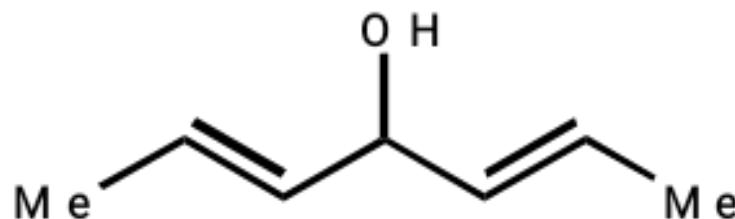


Q2. Out of the given set of compounds, find out the one which absorbs at the longest wavelength?

(i)



(ii)



$n \rightarrow \pi^*$ Transition

- The excitation of an electron on a **nonbonding (lone pairs) orbital**, such as unshared pair electrons on O, N, S to an **antibonding, π^* orbital**.
- Usually in an double bond with hetero atoms, such as C=O, C=S, N=O etc show this transition.
e.g. Saturated aldehydes and ketones : λ_{max} 185-300 nm
- A **symmetry forbidden and low intensity transition**.

- In carbonyl compounds, two types of transitions take place, they are:

High energy transitions: $n \rightarrow \sigma^*$ Transition (Intense)

$\pi \rightarrow \pi^*$ Transition (Intense)

Low Energy Transition: $n \rightarrow \pi^*$ Transition (Weak)

Problems:

Q1. Assign types of electronic transitions for the following compounds.

Acetaldehyde, Benzene, Cyclohexane, Ethanol, Heptane, Aniline, Butadiene.

Ans.

Q2. Acetaldehyde is having absorption peak at 160nm , 180 nm and 292nm . What type of transition is responsible for each of these absorption?

Ans.

Transition Probability

Transition probability: Probability of a particular transition taking place.

As transition probability increases, intensity of transition increase (High ϵ_{max} value).

Depends on:

- Energy of the transition/incident light.
- Orientation of the molecule/material.
- Symmetry of the initial and final states.
- Angular momentum (spin).

Allowed Transitions

- The transition whose ϵ_{max} value is more than 10^4 are allowed transitions.

$\pi \rightarrow \pi^*$ Transition is allowed.

$n \rightarrow \pi^*$ Transition is forbidden.

e.g. Benzophenone, there are two transitions.

252 nm ϵ_{max} 20000 (allowed)

325 nm ϵ_{max} 180 (forbidden)

Chromophore

- Chromophore is a region/group in the molecule, which is responsible for the absorption of the UV-Visible radiation.
- Responsible for imparting color to the compound (some times).
- Chromophore are groups containing either π electrons or both π & n electrons
 - e.g. C=O, C=C, NO₂, -COOH, -N=N-, C≡C etc.

Auxochrome

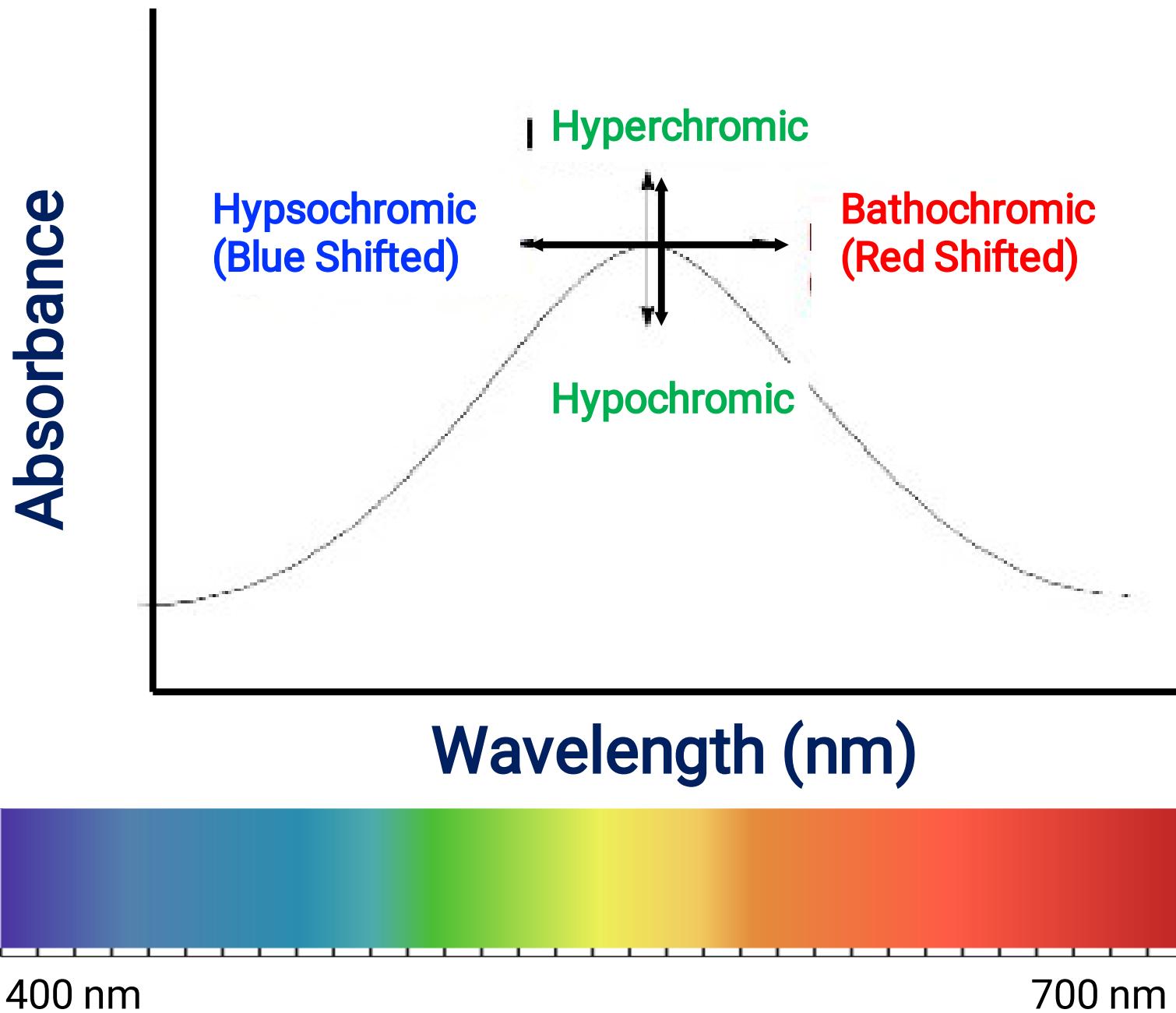
- A functional group that attached to the chromophore which **modifies the ability of the chromophore** to absorb light, altering the wavelength or intensity of the absorption.
- Saturated group containing unshared electrons attached to a chromophore: **changes both intensity and λ_{\max}**

e.g. OH, NH₂, -SH, -Cl, OR, NHR₂ etc.

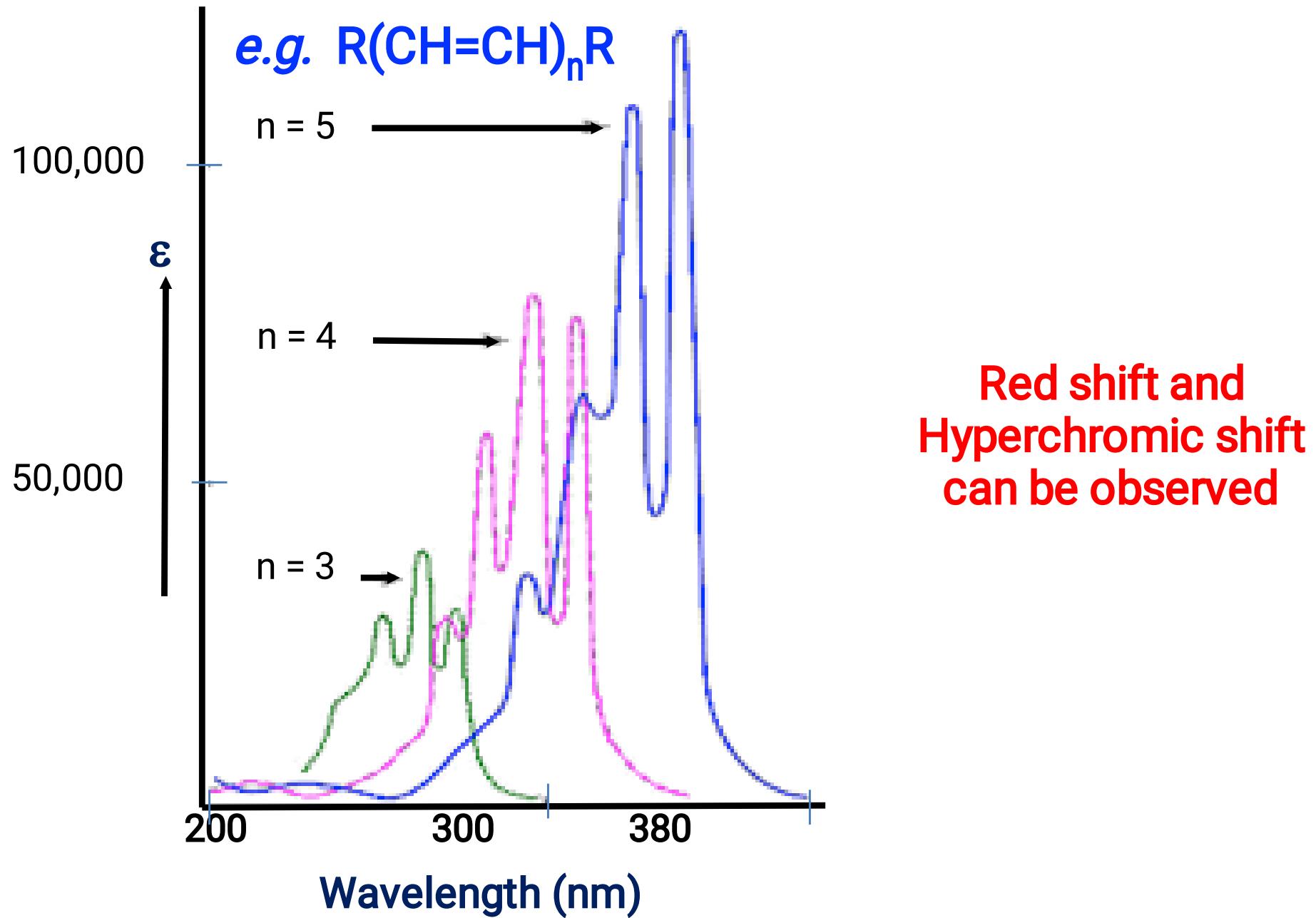
- Auxochromes has ability to extend conjugation of chromophores by sharing its nonbonding electrons

e.g. Benzene absorbs at 255 nm
Aniline absorbs at 280 nm (**moves to longer λ_{\max}**)

Absorption and intensity shift

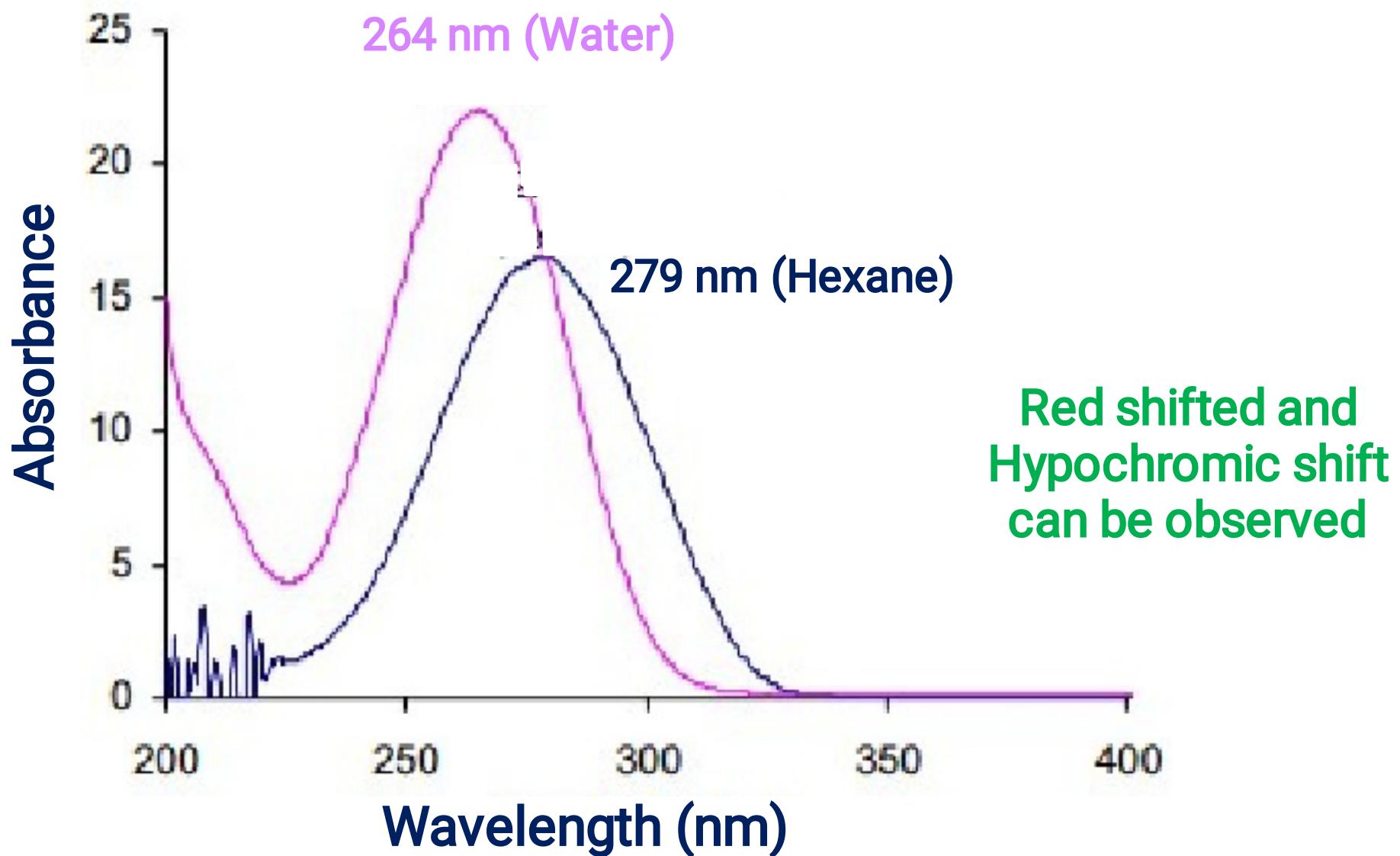


Examples 1.



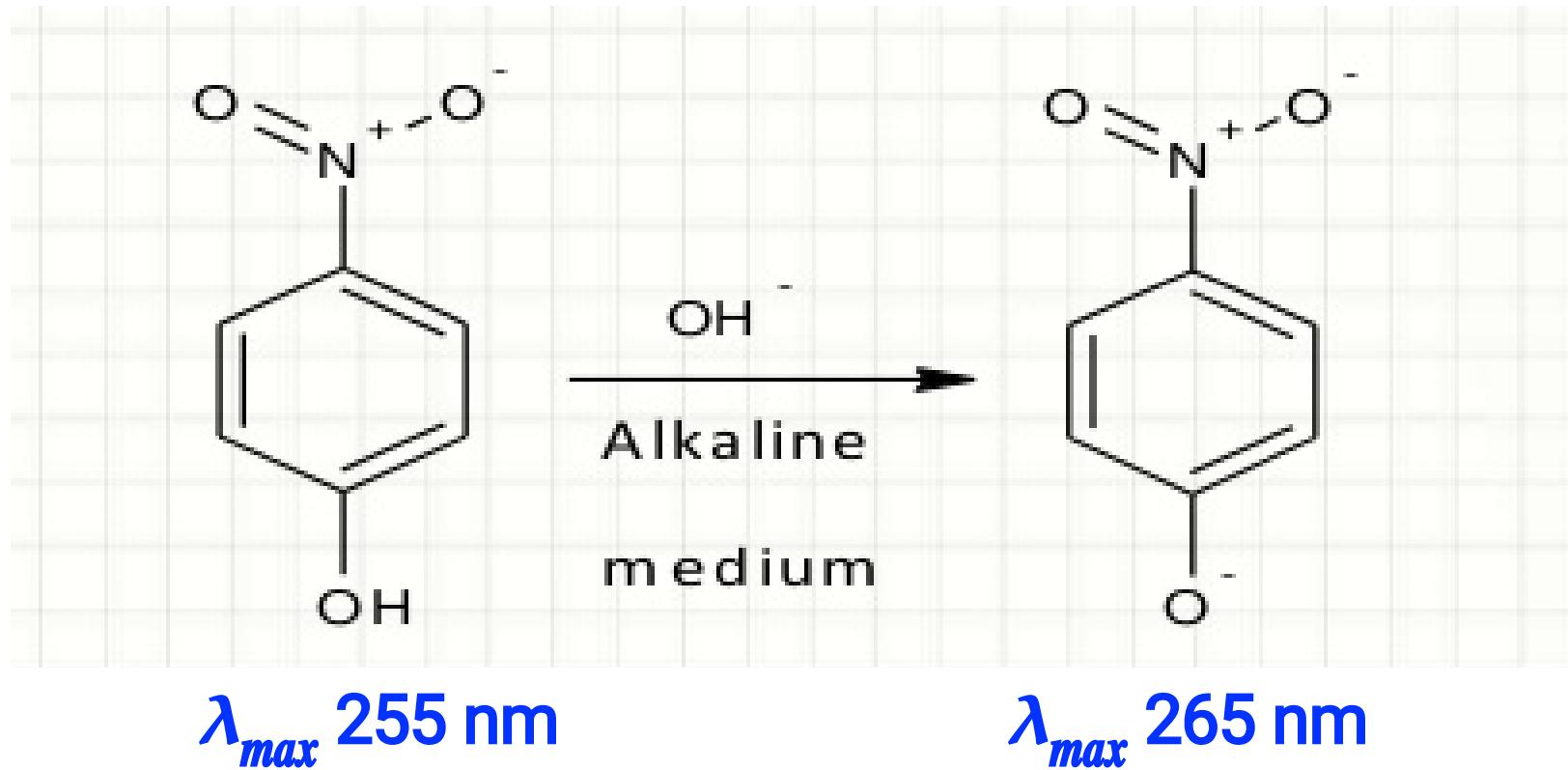
Examples 2.

UV-Vis. spectra of acetone in hexane and in water



Examples 3.

4-Nitrophenol in alkaline medium

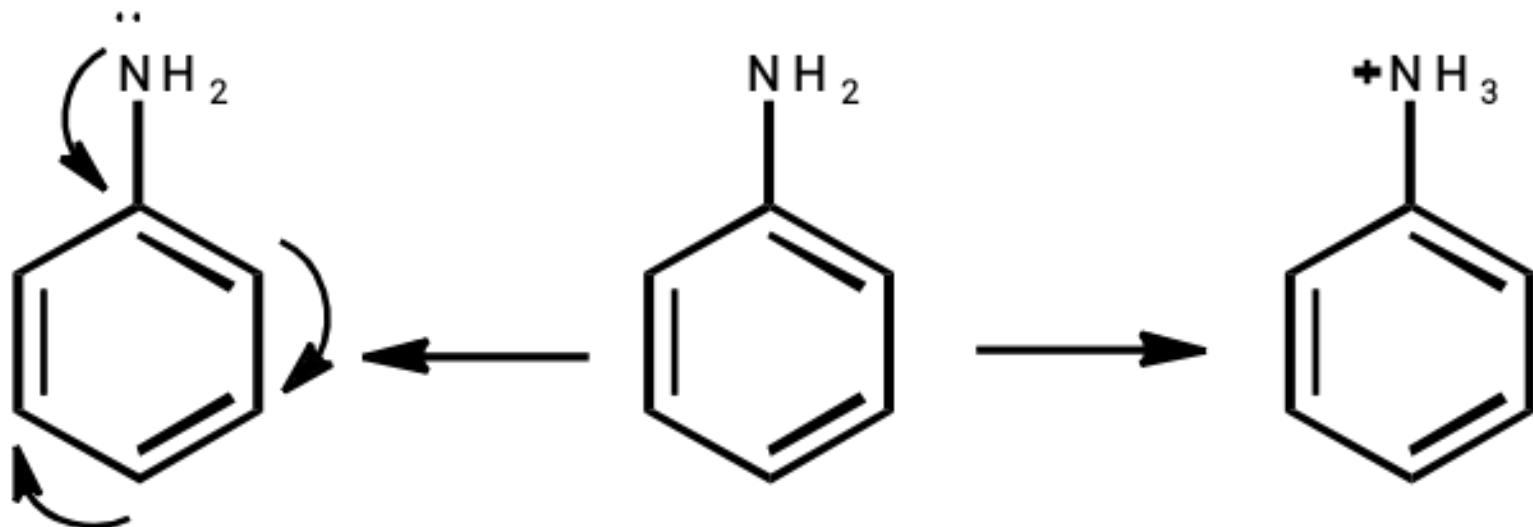


Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron

Bathochromic shift (Red shift)

Examples 4.

Aniline in acidic medium (protonation)

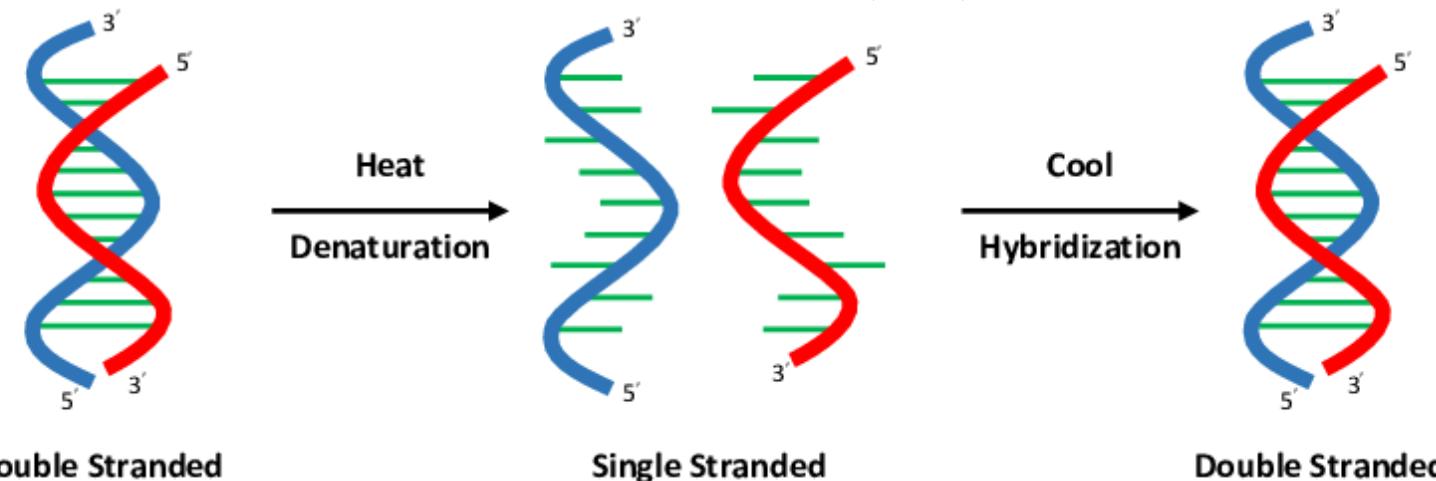
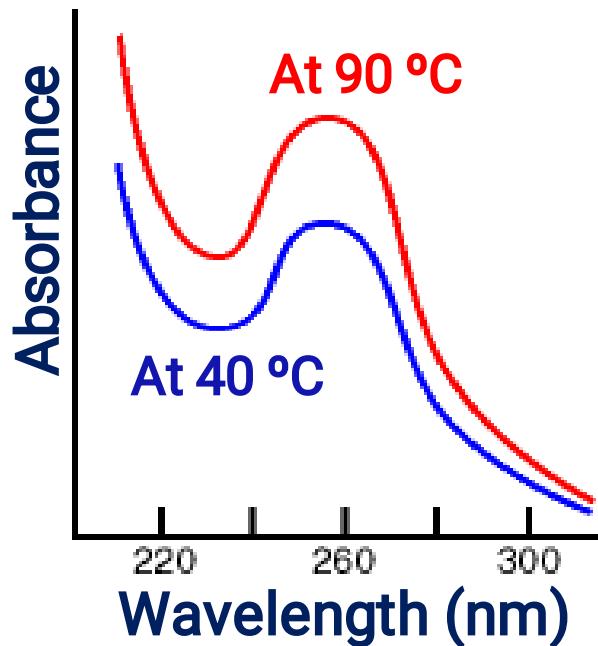


Lone pair of electron involve
in conjugation (280 nm)

No conjugation (203 nm)

Hypsochromic shift (Blue shift)

Examples 5. DNA at different temperatures



Double strand DNA absorbed less strongly than denatured DNA due to the stacking interactions between the bases. On denaturation, the bases are exposed thereby showing increased interaction.

Hyperchromic shift

Examples 6.

Pyridine: $\lambda_{max} = 257 \text{ nm}$, $\epsilon_{max}: 2750$

2-Methylpyridine: $\lambda_{max} = 260 \text{ nm}$, $\epsilon_{max}: 3560$

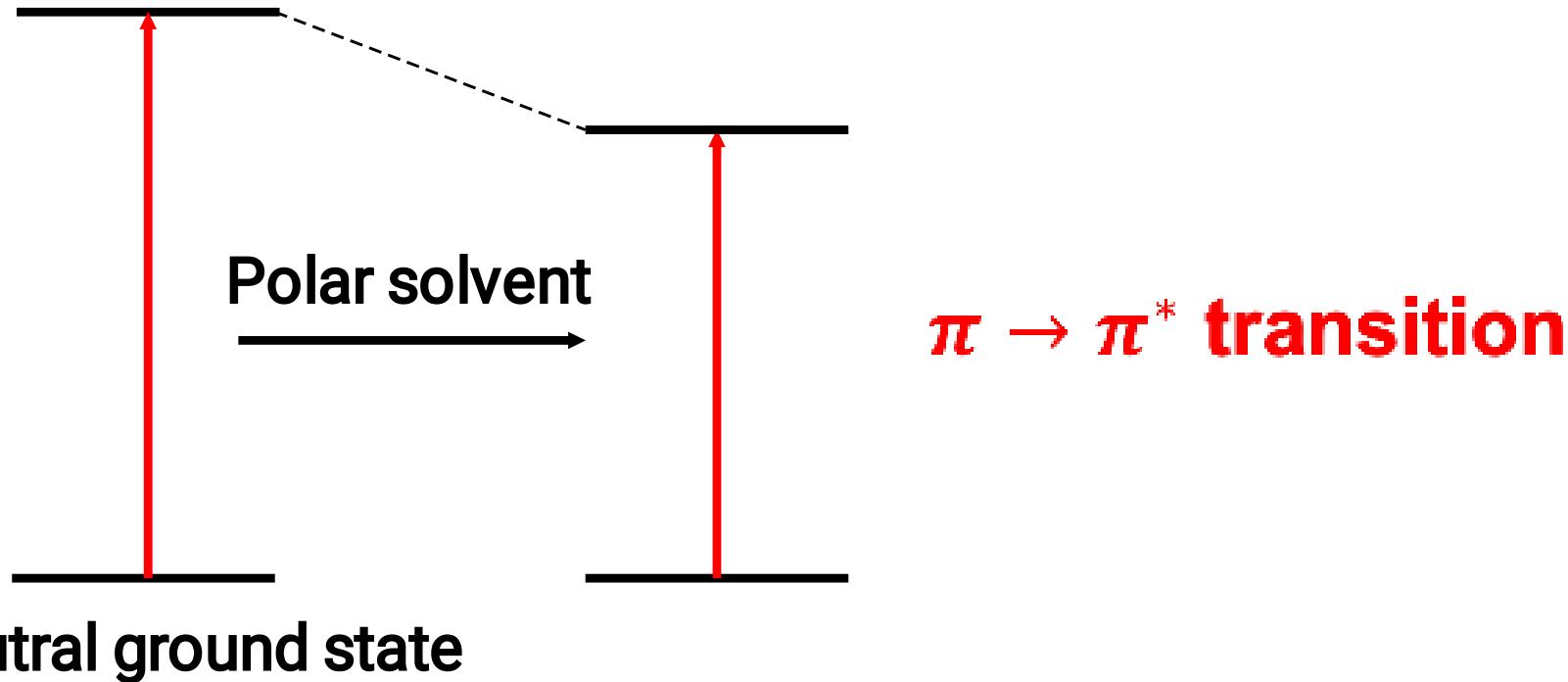
Examples 7.

Biphenyl: $\lambda_{max} = 250 \text{ nm}$; $\epsilon_{max}: 19000$

2-Methylbiphenyl: $\lambda_{max} = 237 \text{ nm}$; $\epsilon_{max}: 10250$

Effect of Solvent

Polar excited state

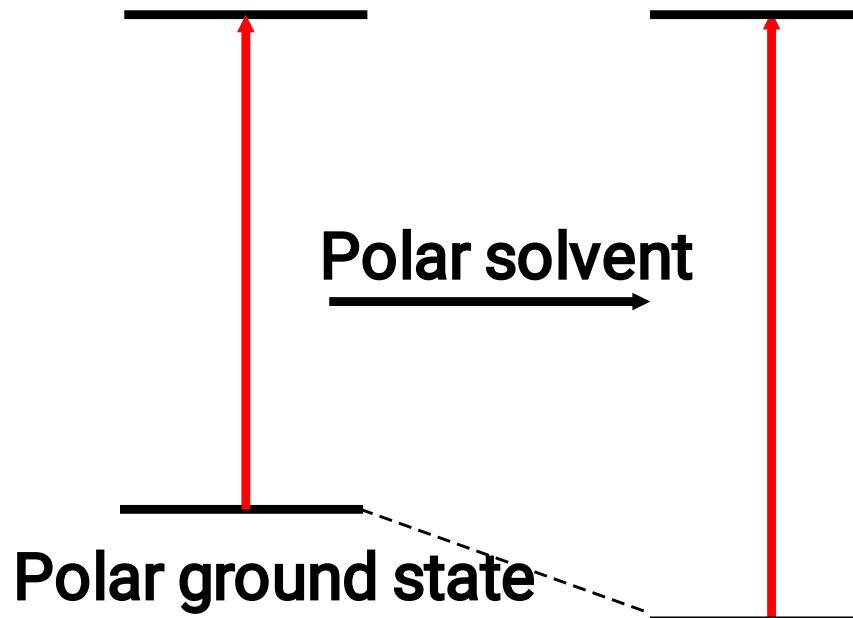


Neutral ground state

- Polar solvent will only interact with the polar excited state and stabilize it. Hence, absorption shifts to longer wavelength.

Effect of Solvent

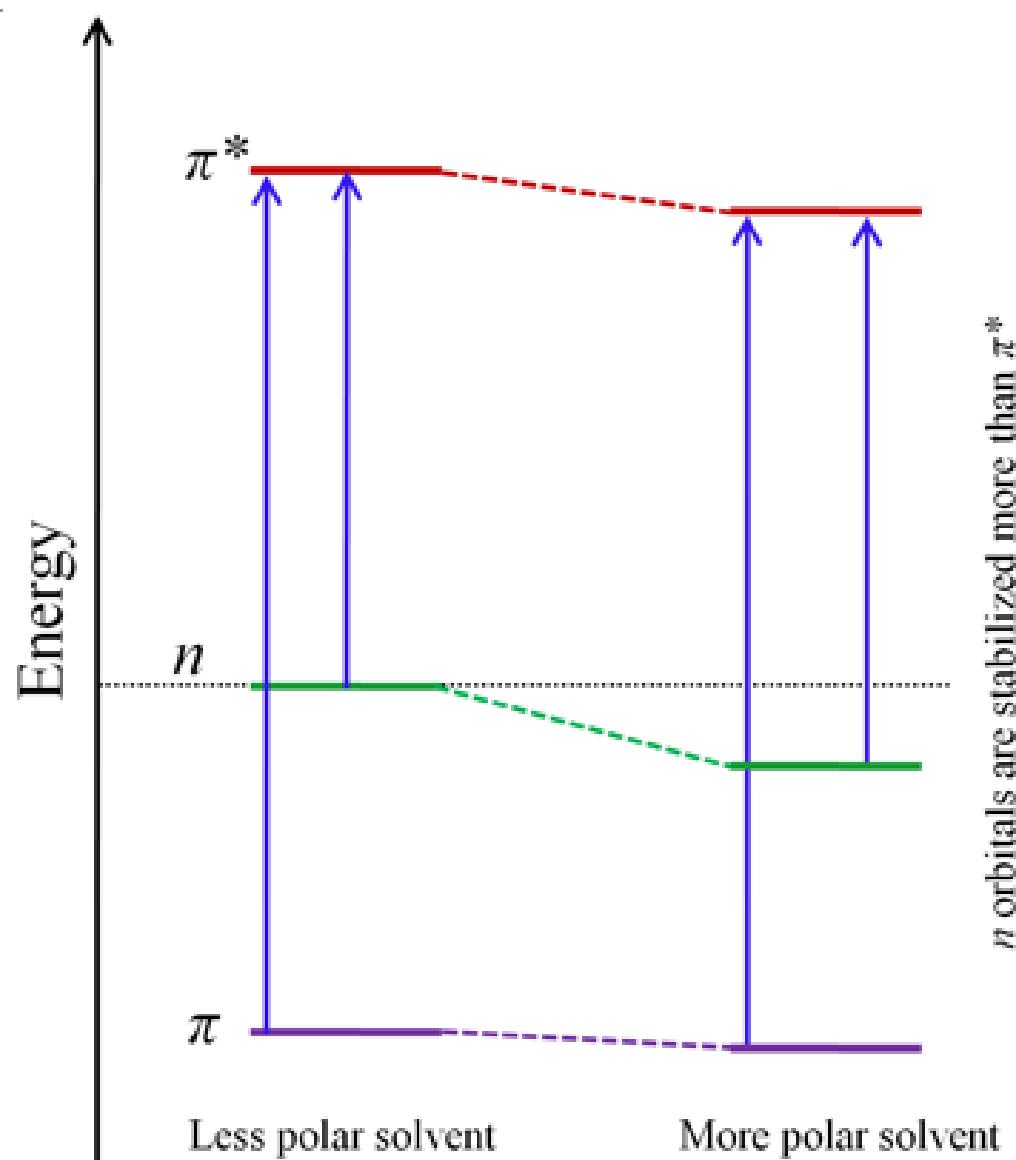
Neutral excited state



$n \rightarrow \sigma^*$ transition

- The ground state lower its energy due to solvation with polar solvents. Hence, the absorption shifts to shorter wavelength.

Effect of Solvent



As the solvent polarity increases:

$\pi \rightarrow \pi^*$ band shifts to

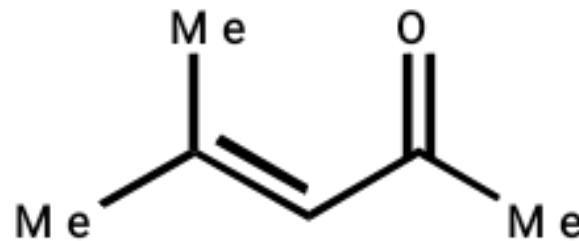
Longer λ_{max}

$n \rightarrow \pi^*$ band shifts to

Shorter λ_{max}

Example.

Influence of solvent on the UV λ_{\max} and ϵ_{\max} of the
 $n \quad \pi^* \text{ and } \pi \quad \pi^* \text{ excitation of 4-methylpent-3-en- 2-one.}$



Solvent	$\pi \longrightarrow \pi^*$	$n \longrightarrow \pi^*$
<i>n</i> -hexane	230(12,600)	327(98)
ether	230(12,600)	326(96)
ethanol	237(12,600)	315(78)
water	245(10,000)	305(60)

Solvent selection

- Should not absorb in UV region
- Solvents should not contain conjugated systems: most preferred
- Solvent should not interact with solute (Non polar solvent - does not form H-bonding).

Common solvents used in UV-Vis. spectroscopy

Solvent	Minimum wavelength for 1 cm cell, nm
Water	190
Cyclohexane	195
Hexane	200
Methanol	200
Ethanol	200
Ether	215
Methylenedichloride	220
Chloroform	240

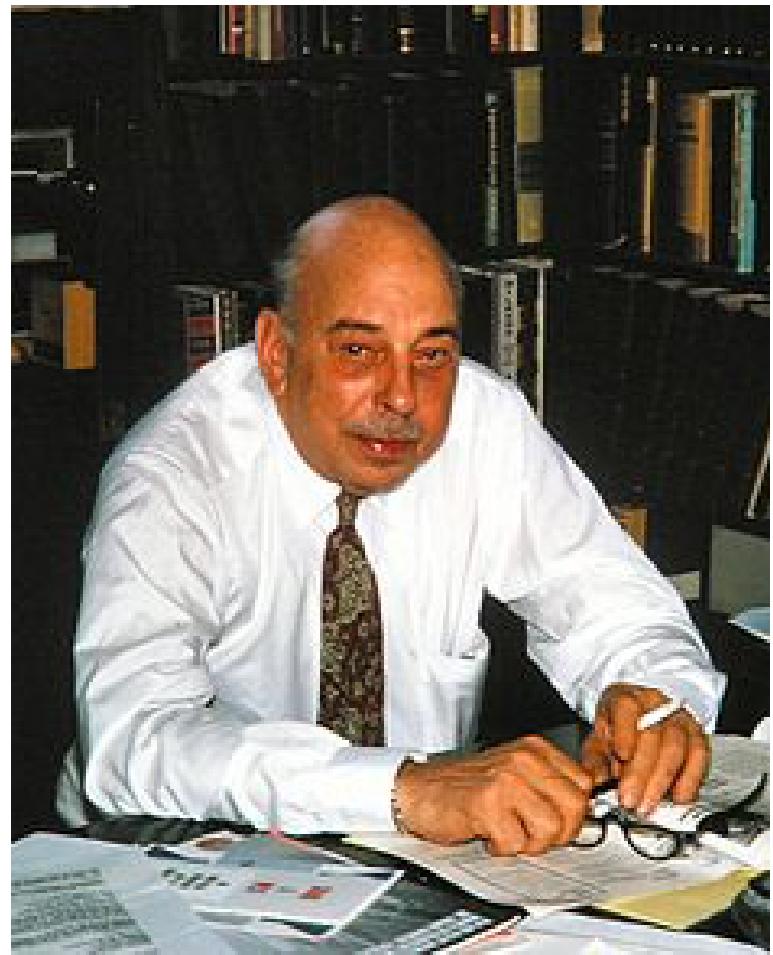
Woodward-Fieser Rule

Calculation of λ_{max} Values

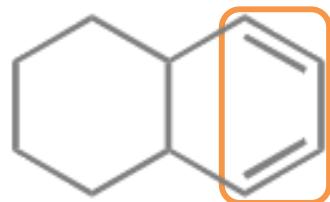
Applicable for the low energy transition ($\pi \rightarrow \pi^*$)



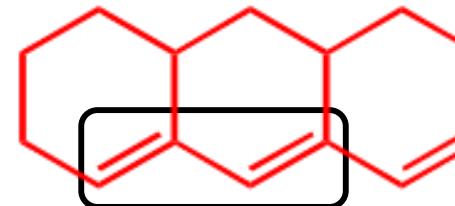
Robert Burns Woodward
Nobel Prize in Chemistry in 1965



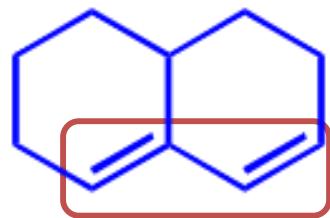
Louis Frederick Fieser



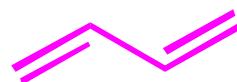
Homoannular diene
(Cisoid or *S*-cis)



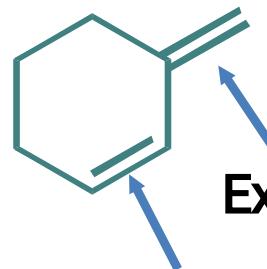
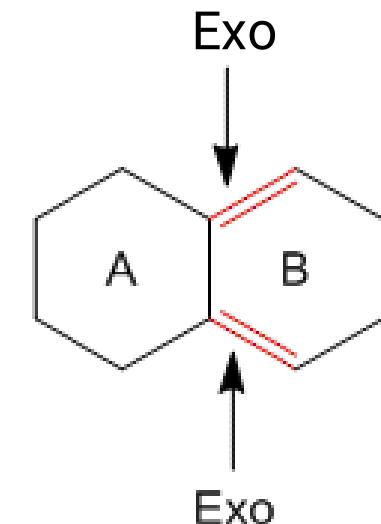
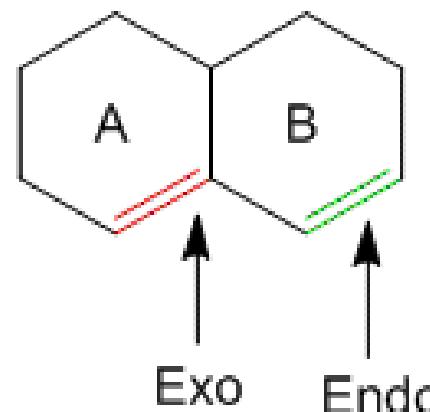
Extended conjugation



Heteroannular diene
(Transoid or *S*-trans)

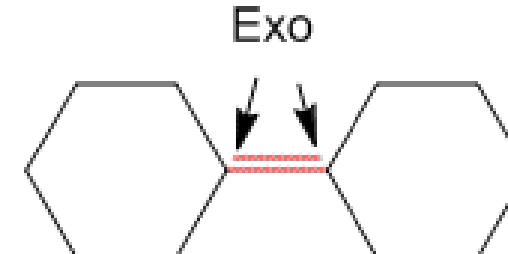


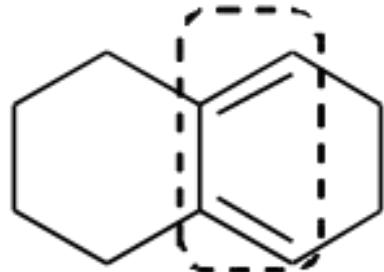
Acyclic



Exocyclic double bond

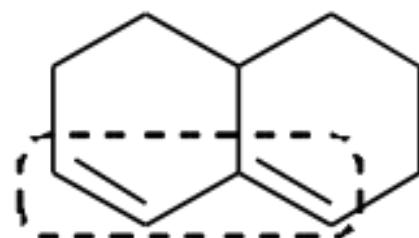
Endocyclic double bond





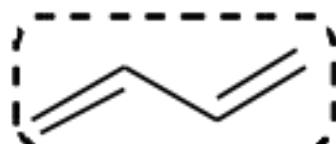
Homoannular Diene
(cisoid or *s*-cis)

Base value (λ_{\max}) = 253 nm



Heteroannular Diene
(transoid or *s*-trans)

Base value (λ_{\max}) = 214 nm



A cyclic

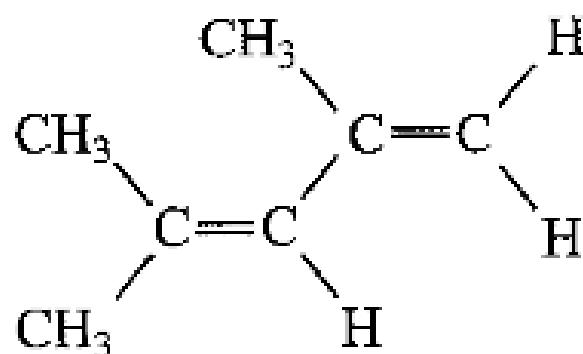
Base value (λ_{\max}) = 214 nm

Empirical rules for dienes

	λ_{\max}
Parent value:	
Homoannular diene	253
Heteroannular diene	214
Increments for:	
Each double bond extending conjugation	30
Each Alkyl Residue or ring residue	5
Exocyclic double bond	5
Polar groupings:	
-OR	6
-SR	30
-Cl, -Br	5
-NR ₂	60
-OCOCH ₃	0

Problems

Q1.

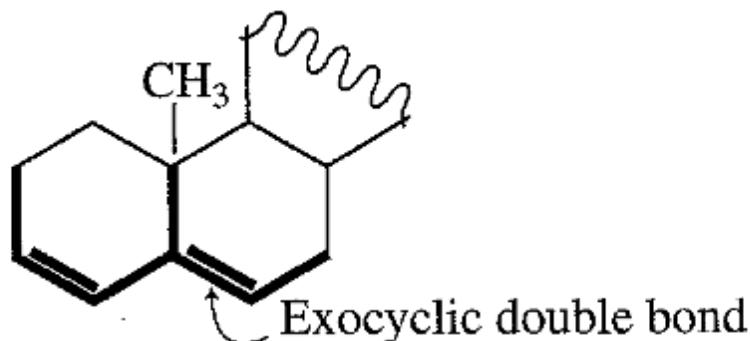


Transoid:

214 nm

$$\text{Alkyl groups: } 3 \times 5 = \frac{15}{229 \text{ nm}}$$

Q2.



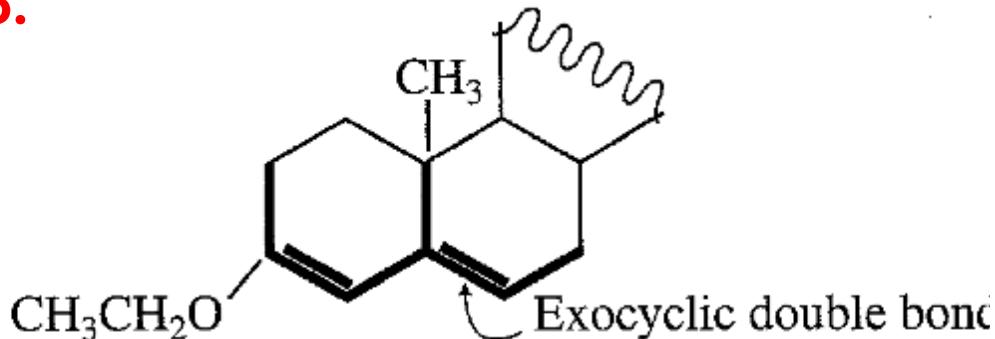
Transoid:

214 nm

$$\text{Ring residues: } 3 \times 5 = 15$$

$$\text{Exocyclic double bond: } \frac{5}{234 \text{ nm}}$$

Q3.



Transoid:

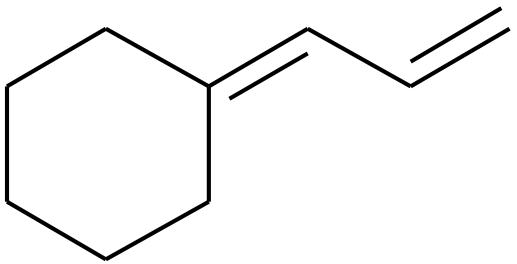
214 nm

$$\text{Ring residues: } 3 \times 5 = 15$$

$$\text{Exocyclic double bond: } 5$$

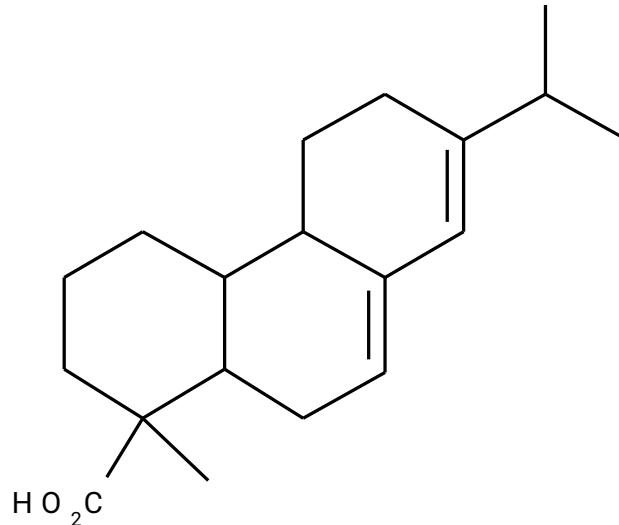
$$-\text{OR: } \frac{6}{240 \text{ nm}}$$

Q4.



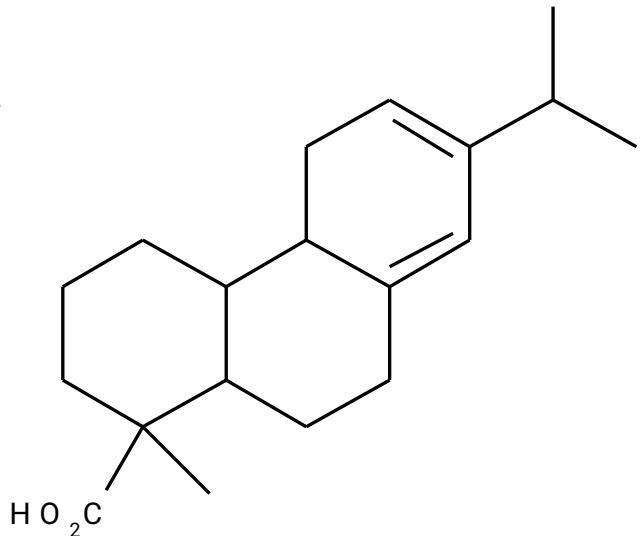
Base value : 214
Alkyl substitutions (2) : 10
Exocyclic double bond : 5
Total : 229

Q5.



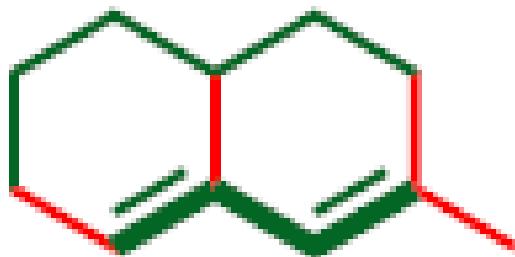
Base value : 214
4 x alkyl subst. : 20
exo DB : 5
total : 239

Q6.



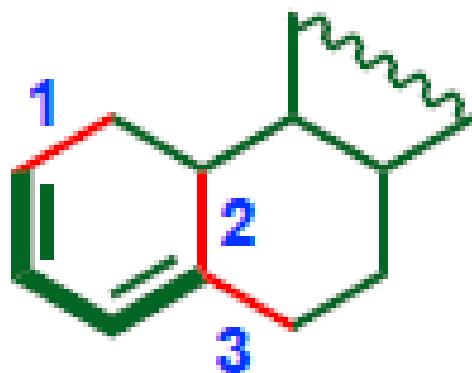
Base value : 253
4 x alkyl subst. : 20
exo DB : 5 **total : 278**

Q8.



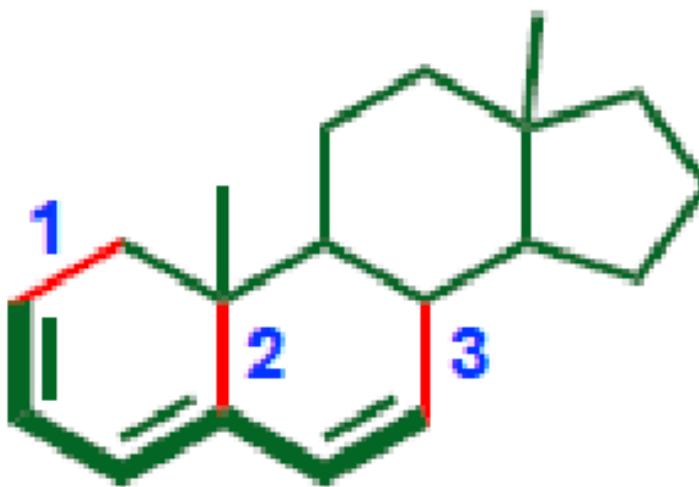
Transoid (base):	214 nm
3 Ring residues:	+15
1 Alkyl substituent:	+ 5
1 Exocyclic C=C:	+ 5
Total:	239 nm

Q9.



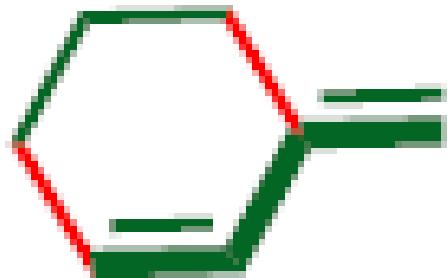
Cisoid (base):	253 nm
3 ring residues:	+15
1 exocyclic C=C:	+ 5
Total:	273 nm
Observed:	275 nm

Q10.



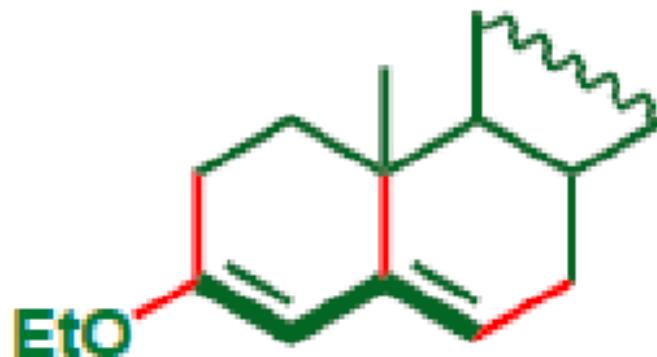
Cisoid (base):	253 nm
3 Ring residues:	+15
1 Exocyclic C=C:	+ 5
Double-bond Extending Conjugation:	<u>+30</u>
Total:	303 nm
Observed:	304 nm

Q11.

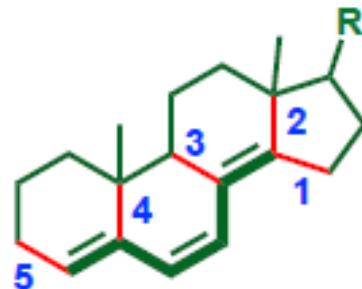


Base value:	214 nm
2 Ring residue	+10
Exocyclic C=C:	+ 5
<hr/>	<hr/>
Total:	229 nm
Observed:	230 nm

Q12.

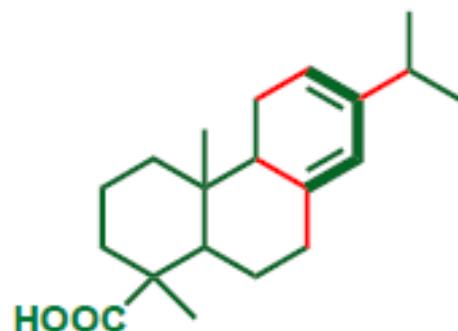


Transoid (base):	214 nm
3 ring residues:	+15
1 exocyclic C=C:	+ 5
-OR:	+ 6
Total:	240 nm



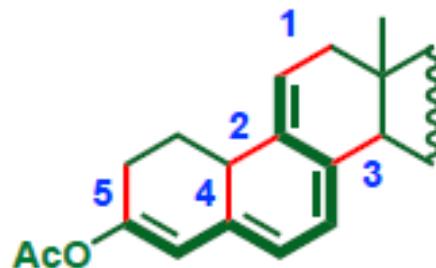
Transoid (base):
5 ring residues:
1 DEC:
3 exocyclic C=C
Total:
Observed:

214 nm	+25
+25	+30
+30	+15
<hr/>	
284 nm	
283 nm	



Cisoid (base):
3 ring residues:
1 Alkyl subs:
1 exocyclic C=C
Total:
Observed:

253 nm	+15
+15	+5
+5	+5
<hr/>	
278 nm	
275 nm	

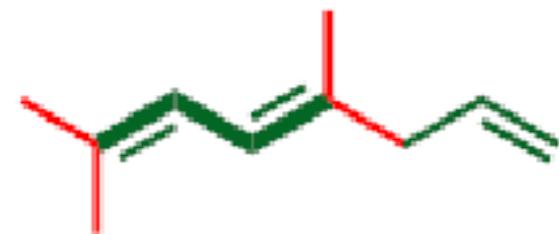


Cisoid (base):
5 ring residues:
2 DEC:
3 exocyclic C=C
Total:
Observed:

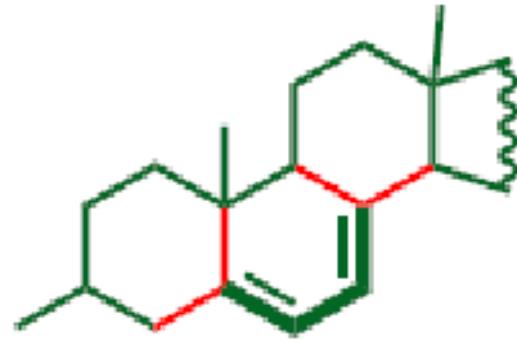
253 nm	+25
+25	+60
+60	+15
<hr/>	
353 nm	
355 nm	



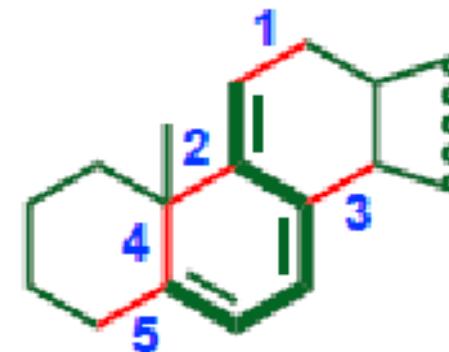
Base value: 214 nm
3 Alkyl grs: +15
Total: 229 nm
Observed: 232 nm



Base value: 214 nm
4 Alkyl grs: +20
Total: 234 nm
Observed: 235 nm



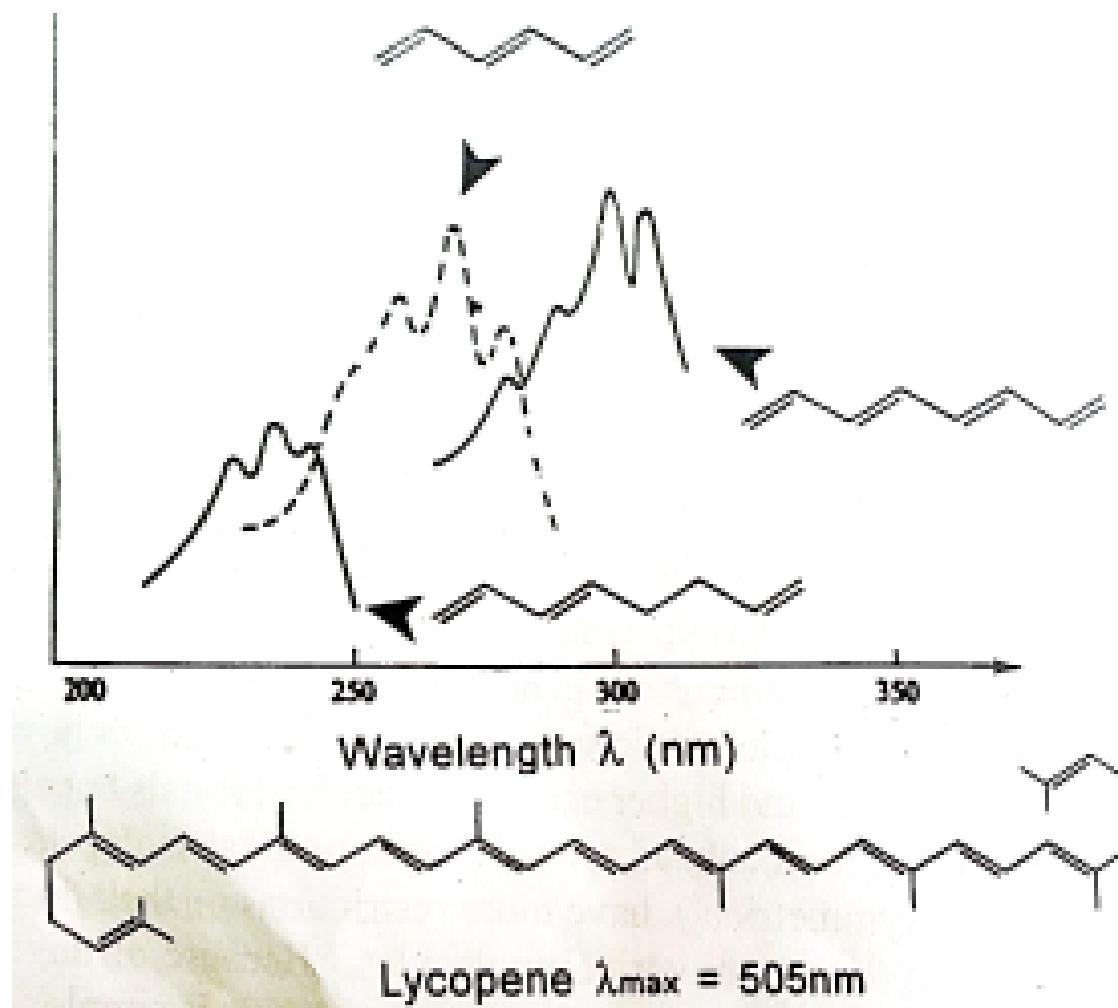
Base value:	253 nm
4 Ring residues:	+20
2 Exocyclic C=C:	+10
Total:	283 nm
Observed:	282 nm



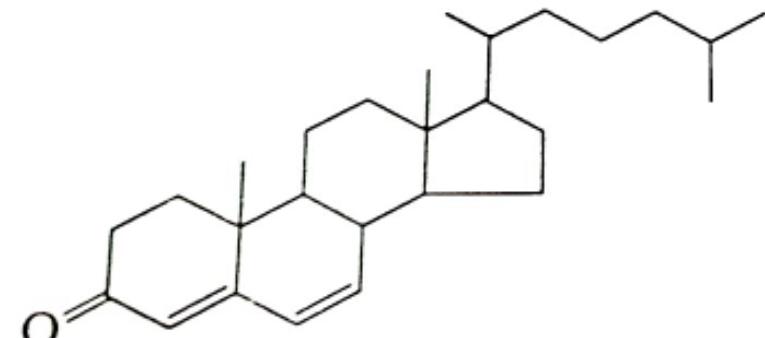
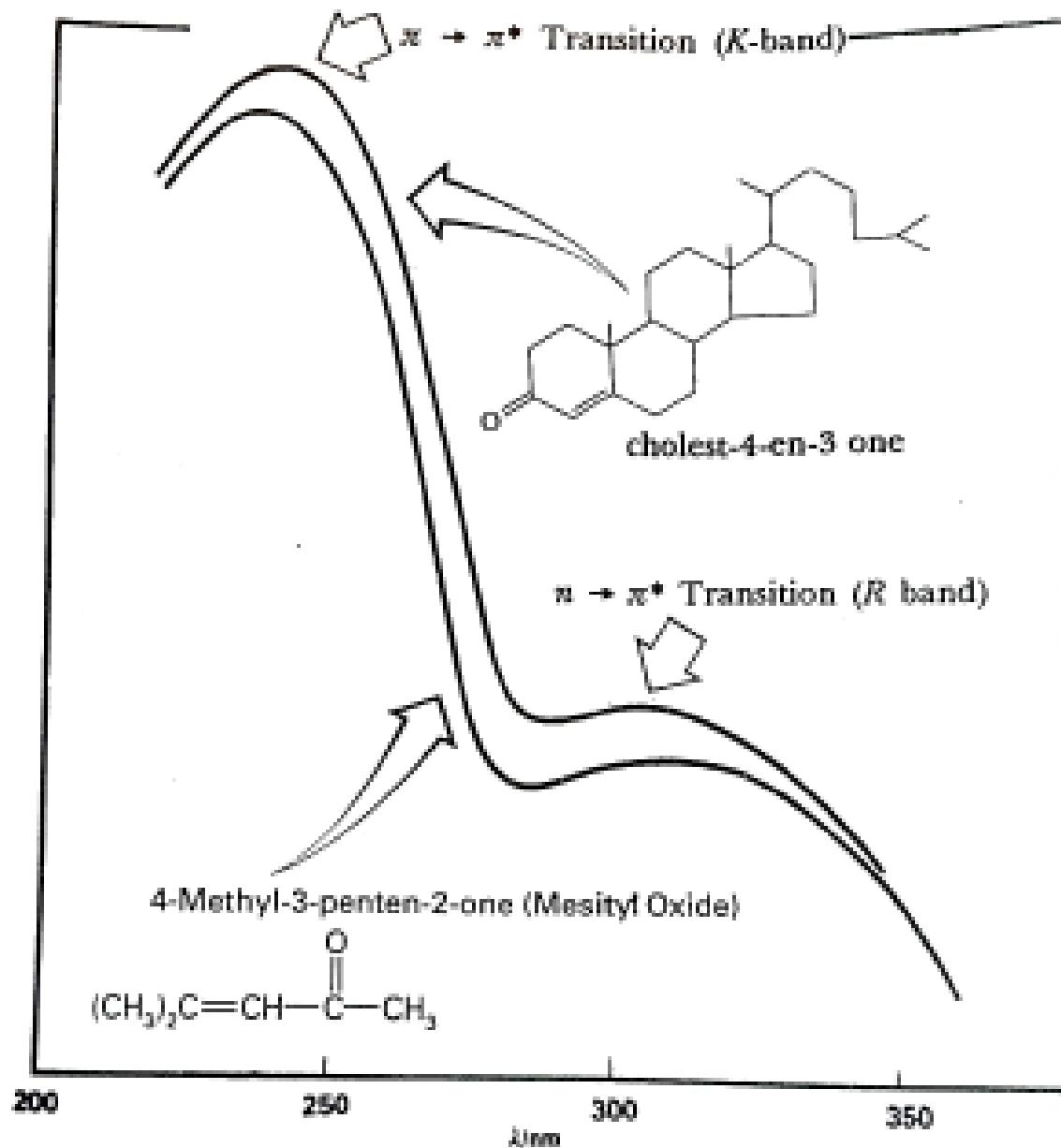
Base value:	253 nm
5 Ring residues:	+25
3 Exocyclic C=C:	+15
DEC:	+30
Total	323 nm
Observed:	325 nm

Application of UV-Visible Spectroscopy

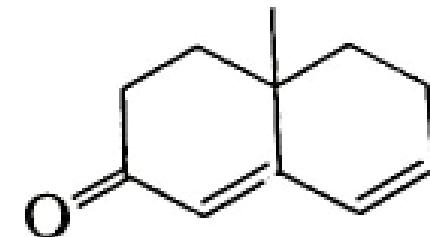
1. **Detection of Conjugation:** Addition of unsaturation (double or triple bond) shifts the absorption to longer wave length.
 - The compound with sufficient conjugation becomes colored (e.g. **Lycopene** – gives red colour to tomatoes - 11 conjugated double bonds).



2. Distinction in Conjugated & Non Conjugated Isomers: It can differentiate conjugated dienes from non-conjugated dienes; α,β -unsaturated ketones from β,γ -unsaturated ketones.

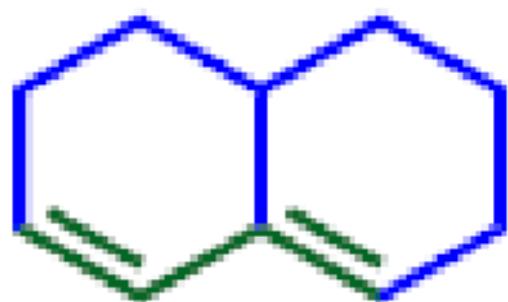


$$\lambda_{\max} = 284\text{nm}$$



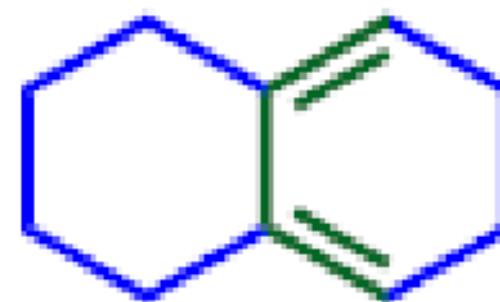
$$\lambda_{\max} = 283\text{nm}$$

3.Detection of Geometrical Isomers:



$\lambda_{\text{max}} = 234 \text{ nm}$

$\epsilon_{\text{max}} = 12000-28000$



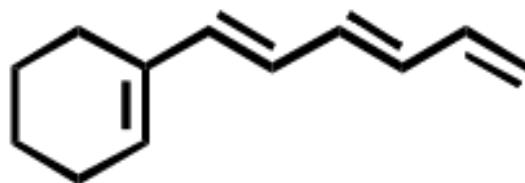
$\lambda_{\text{max}} = 273 \text{ nm}$

$\epsilon_{\text{max}} = 5000-15000$

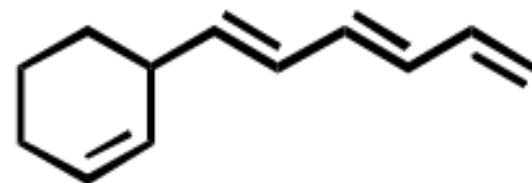
Some Important Examples

Question.

How can you distinguish the following isomers (A & B) using λ_{\max} ?



A



B

Ans.

Compound A: Base value (transoid) = 214 nm

2-extended conjugation = $2 \times 30 = 60$ nm

λ_{\max} : 274 nm

Compound B: Base value (transoid) = 214 nm

1-extended conjugation = 30 nm

1-ring residue = 5 nm

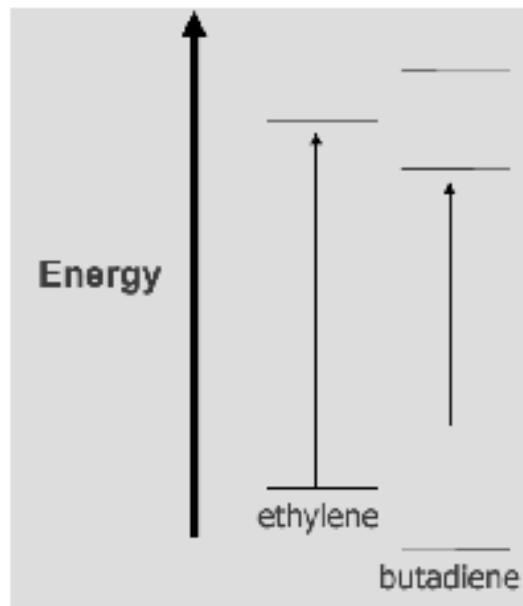
λ_{\max} : 249 nm

Question.

'With increase in conjugation, λ_{\max} for the $\pi \rightarrow \pi^*$ transition increases'. Using energy level diagram explain this observation with reference to ethylene and 1,3-butadiene. (3 Marks)

Ans.

Ans: Conjugation in alkenes: The observed shifts from conjugation imply that an increase in conjugation decreases the energy required for electronic excitation. Extending this effect out to longer conjugated systems the energy gap becomes progressively smaller. (1+1 marks)



(1 mark)

Question.

When a beam of light (5000 Å) was allowed to pass through a solution in 4 mm quartz cuvette, the intensity of transmitted light was reduced to 20 % of its initial intensity. What will be the percentage of absorption when the concentration was doubled and the solution was taken in 2 mm quartz cuvette? (2 marks)

Ans.

$$A = \epsilon cl \text{ (from Beer - Lambert's law)}$$

$$I_1 = 4 \text{ mm}, A_1 = (100 - 20) \% = 80 \% = 0.8, c_1 = x$$

$$I_2 = 2 \text{ mm}, A_2 = ?, c_2 = 2x,$$

As the solution is same assume that molar absorption coefficient (ϵ) remains same.

$$A_1/A_2 = c_1 I_1 / c_2 I_2$$

$$A_2 = c_2 I_2 / c_1 I_1 * A_1$$

$$A_2 = 0.8 = 80\%$$

i.e. in both the cases the % absorption remains unchanged.

Question.

The absorption maximum of aniline is observed to be at 230 nm. However, the absorption maximum shifts to 203 nm in acidic conditions. Explain. (2 marks)

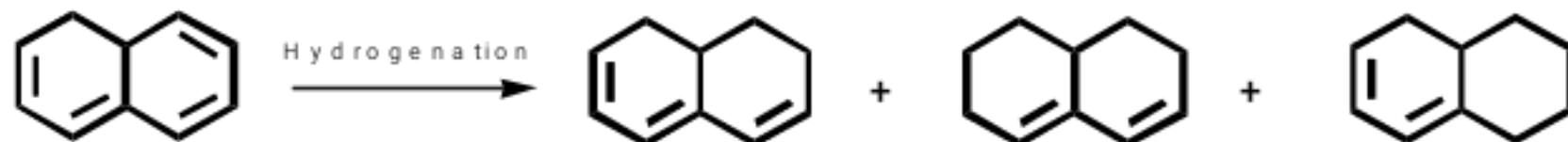
Ans.

Answer: When the absorption spectrum of Aniline is recorded in the acidic condition a hypsochromic shift is observed due to the formation of anilinium cation. In aniline the lone pair of electron on Nitrogen atom can participate in conjugation with the benzene ring, whereas when it is acidified the lone pair is no more available for conjugation with the ring. (if structure showing conversion of aniline to anilinium cation is drawn provide 1 mark).

Question.

The partial hydrogenation of the following tetraene gave three products, which are separated by gas chromatography. How Woodward-Fieser Rules (λ_{\max}) can be used to distinguish the products?

(3 marks)



Ans.

Answer: Product 1: (base value: 253 nm) + 15 nm (3-alkyl substituents, 3x5) + 30 nm (1-extended conjugation) + 5 nm (1-exocyclic double bond). Total = 303 nm. (1 mark)

Product 2: (base value: 214 nm) + 15 nm (3-alkyl substituents, 3x5) + 5 nm (1-exocyclic double bond). Total = 234 nm. (1 mark)

Product 3: (base value: 253 nm) + 15 nm (3-alkyl substituents, 3x5) + 5 nm (1-exocyclic double bond). Total = 273 nm. (1 mark)