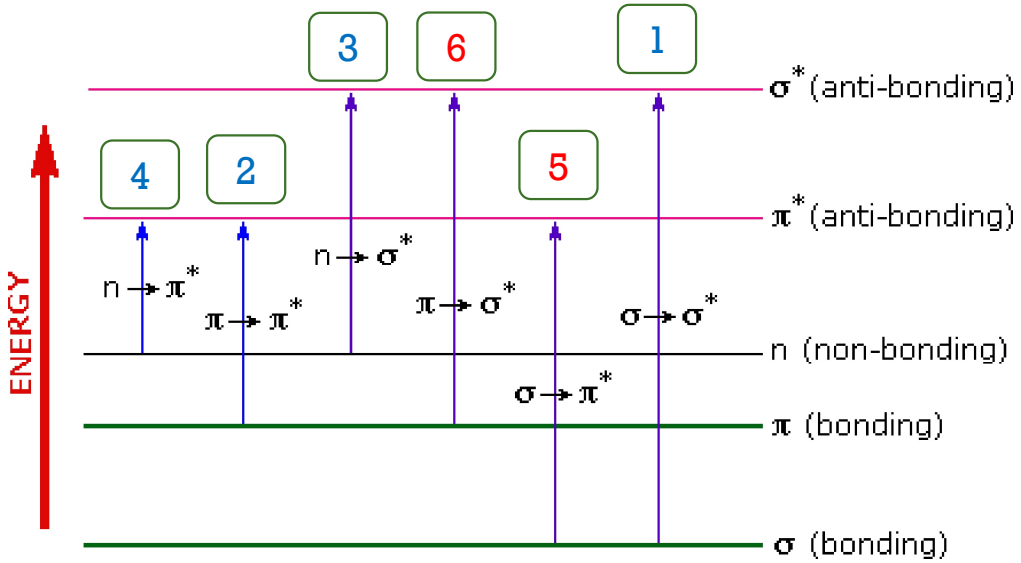
MOLECULAR TRANSITIONS

- $\sigma \rightarrow \sigma^*$ transition
- $\pi \rightarrow \pi^*$ transition
- $n \rightarrow \sigma^*$ transition
- $n \rightarrow \pi^*$ transition
- $\sigma \rightarrow \pi^*$ transition
- $\pi \rightarrow \sigma^*$ transition



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

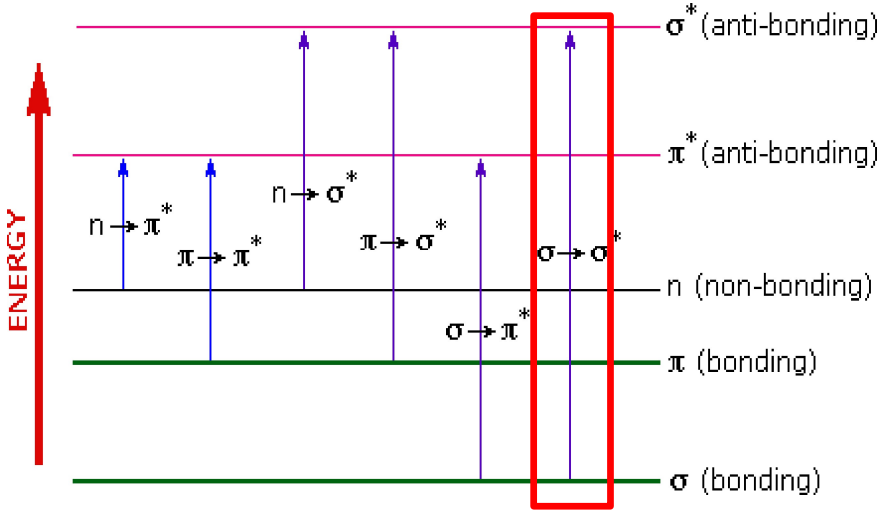
High energy (E)
Low wavelength (λ)

σ → σ* transition

- An electron in a bonding σ orbital is excited to the corresponding antibonding orbital. The energy required is large.

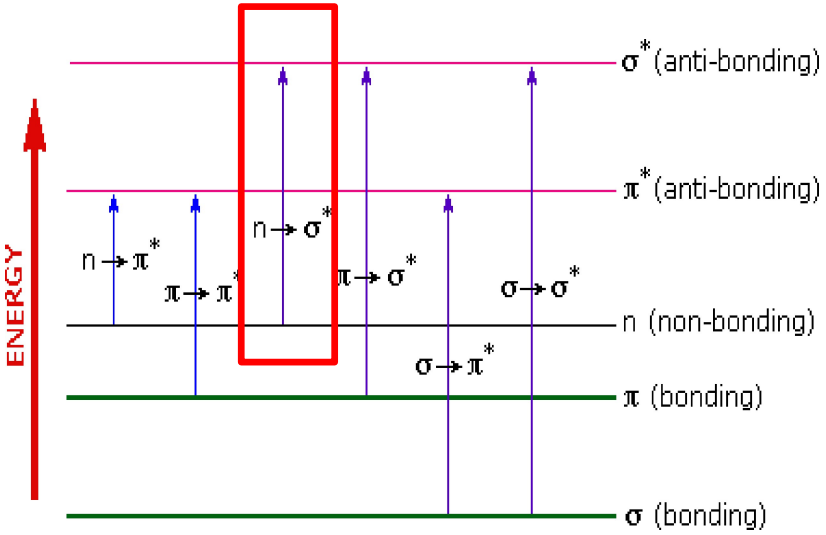
- For example, methane (CH_4) (which has only C-H bonds, and can only undergo σ → σ* transitions) shows an absorbance maximum at 125 nm.

- Absorption maxima due to σ → σ* transitions are not seen in typical UV-VIS spectra (200 - 700 nm)



$n \rightarrow \sigma^*$ transition

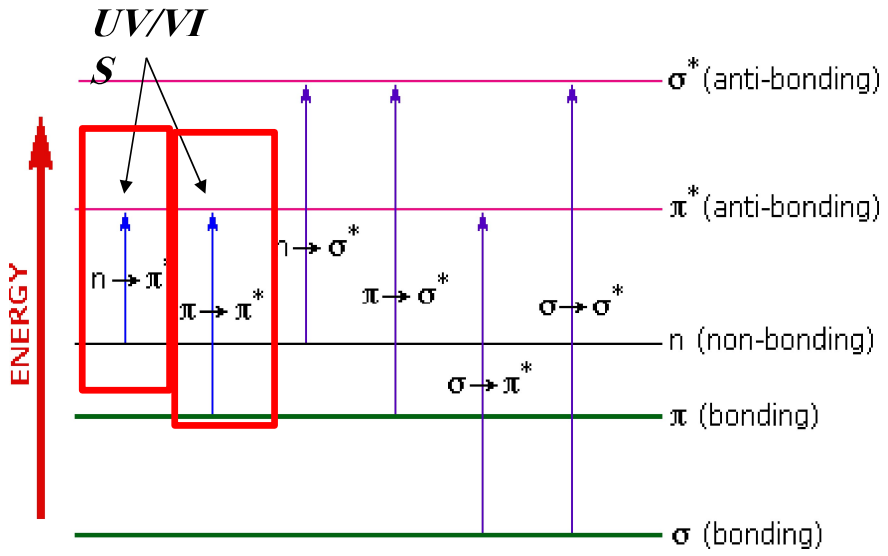
- Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of $n \rightarrow \sigma^*$ transitions.
- These transitions usually need less energy than $\sigma \rightarrow \sigma^*$ transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm.
- The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in the UV region is small.



n → π* transition

π → π* transition

- Most absorption spectroscopy of organic compounds is based on transitions of *n* or p electrons to the p* excited state.
- These transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm).
- These transitions need an unsaturated group in the molecule to provide the p electrons.



- $n \rightarrow \pi^*$ have low (∈) (10-100 $L.mol^{-1}.cm^{-1}$)
- $\pi \rightarrow \pi^*$ have high (∈) (1000-10000 $L.mol^{-1}.cm^{-1}$)
- With highly polar solvent, ($n \rightarrow \pi^*$) are shifted to lower (λ) (*blue shift*), due to unpaired electrons.
- With highly polar solvent, ($\pi \rightarrow \pi^*$) are shifted to higher (λ) (*red shift*), because of the attractive polarisation forces between solvent and absorbent.

($\pi \rightarrow \pi^*$) TRANSITION IS THE MOST CONVENIENT AND USEFUL TRANSITION IN UV-VIS SPECTROSCOPY. WHY?

π–π^* transition is the most frequently used transition for the following reasons:

- The ϵ for the π–π^* transition is high allowing sensitive determinations.
- The energy required is moderate, far less than dissociation energy.
- In presence of the most convenient solvent (water), the energy required for a π–π^* transition is usually smaller.

Chromophore	Excitation	λ_{max}, nm	Solvent
C=C	$\pi \rightarrow \pi^*$	171	hexane
C=O	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	hexane hexane
N=O	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	ethanol ethanol
C-X X=Br, I	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	hexane hexane

Factors influencing uv-vis absorption

- Type of solvent
- pH of the solution
- Temperature
- Concentration
- Conjugation

- This depends on the nature of the interaction of the particular solvent with the environment of the chromophore in the molecule under study.
- It is usually observed that ethanol solutions give absorption maxima at longer λ than hexane solutions.
- Changes in the polarity of the solvent can influence shifts to longer or shorter λ, by changing in the energy gap between these electronic states.
- **Non-polar solvents** (saturated hydrocarbons) **do not** interact with solute molecules either in the ground or excited state.

Factors influencing uv-vis absorption

- Type of solvent
- pH of the solution
- Temperature
- Concentration
- Conjugation

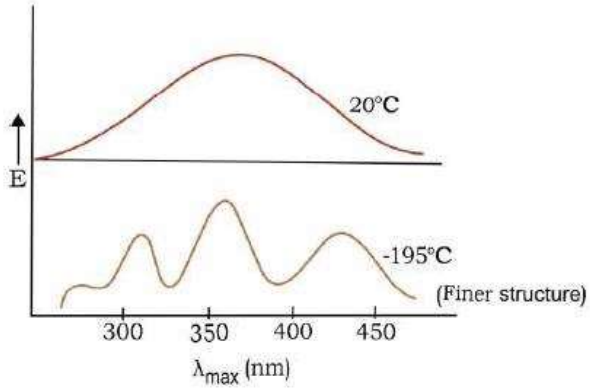
- The buffer though needs to be transparent over the wavelength range of the measurements. If the buffer absorbs radiation, absorbance readings attributed to the analyte may be higher than they should because the buffer and analyte absorptions will add together at each wavelength.
- If the optimum pH buffer solution is suitable with analyte, The absorbance spectra will show clear peak of the analyte, and vice versa.

Factors influencing uv-vis absorption

- Type of solvent
- pH of the solution
- Temperature
- Concentration
- Conjugation

- To get more accurate results, the spectrum needs to taken at a specified or constant temperature.

1. Band sharpness increases with decreasing temperature.
2. Position of absorption maximum does not move or moves very little towards the longer wavelength side, with decreasing temperature.
3. The total absorption intensity is approximately independent of the temperature.



Factors influencing uv-vis absorption

- Type of solvent
- pH of the solution
- Temperature
- Concentration
- Conjugation

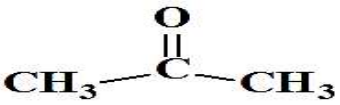
- Sample concentration is proportional to the intensity of the absorption.
- At high concentrations however, molecular interactions can take place causing changes to the position and shape of absorption bands.
- Such an outcome can affect the linearity of the relationship between sample concentration and absorbance.
- Higher the concentration of the analyte show higher absorbance they probably don't follow Beer-Lambert's law.
- Optimum concentration of analyte will be use , the absorbance will below then (0.8) .

Factors influencing uv-vis absorption

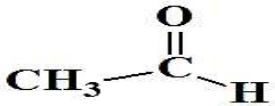
- Type of solvent
- pH of the solution
- Temperature
- Concentration
- Conjugation

- Wavelength of UV radiation that causes $\pi \rightarrow \pi^*$ excitation in a conjugated molecule ultimately depends on the nature of the conjugated system
- Degree of conjugation has a significant influence on the wavelength and molar absorptivity.

Name	Structure	λ_{max} (nm)
2-Methyl-1,3-butadiene	$H_2C{=}C(CH_3){-}CH{=}CH_2$	220
1,3-Cyclohexadiene		256
1,3,5-Hexatriene	$H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2$	258
1,3,5,7-Octatetraene	$H_2C{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH_2$	290
3-Buten-2-one	$H_2C{=}CH{-}C(=O){-}CH_3$	219
Benzene		203



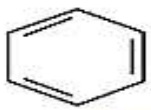
$\varepsilon = 19$



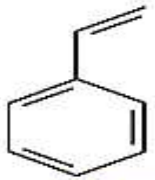
$\varepsilon = 12$

$\varepsilon = 20,900$

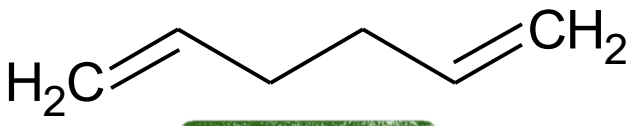
$\varepsilon = 4,580$



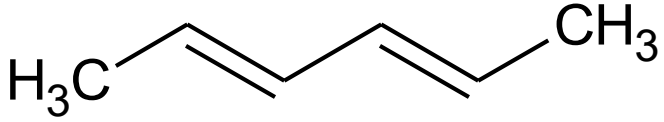
$\varepsilon = 8,000$



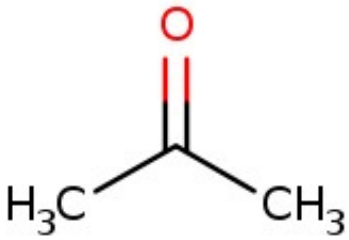
$\varepsilon = 12,000$

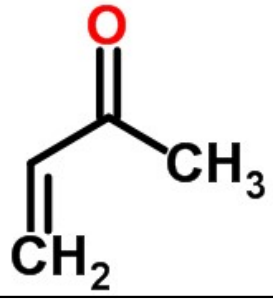


λ_{max}= 178 nm



λ_{max}= 227 nm





n → π*	λ_{max}= 274 nm (ϵ_{max}= 13.6)	λ_{max}= 331 nm (ϵ_{max}= 25)
π → π*	λ_{max}= 195 nm (ϵ_{max}= 9000)	λ_{max}= 203 nm (ϵ_{max}= 9600)

MORE conjugated double bonds MEANS LESS (*E*)is required for the electronic transition, and therefore LONGER λ at which the electronic transition occurs.

Important Notes

1. The most useful region for UV spectroscopy is at wavelengths longer than 200 nm.
2. Transitions in the non-useful 100-200 nm range include $\pi \rightarrow \pi^*$ for isolated double bonds and $\sigma \rightarrow \sigma^*$ for ordinary carbon-carbon bonds.
3. Useful transitions (200-400 nm) include $\pi \rightarrow \pi^*$ for conjugated double bonds, and some $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transitions.
4. Alkenes and nonconjugated dienes typically have absorption maxima below 200 nm, such as ethene at 171 nm and 1,4-pentadiene at 178 nm.
5. Compounds with conjugated multiple bonds have absorption maxima at wavelengths longer than 200 nm.
6. Less energy is needed to promote a π electron in 1,3-butadiene (conjugated) than in ethylene (non-conjugated).
7. The energy gap between the HOMO and LUMO is smaller for conjugated double bonds.
8. Resonance stabilization of the excited state is a factor that decreases the excited state's energy.

Applications in Pharmaceutical Analysis:

- **Quality Control & Purity**: Verifies drug identity and purity by detecting impurities and confirming API (Active Pharmaceutical Ingredient) levels.
- **Concentration Determination**: Quantifies drug amounts in raw materials and finished products, ensuring correct dosage.
- **Drug Development**: Used to characterize compounds, study reaction kinetics, and determine dissociation constants (pKa).
- **Dissolution Testing**: Measures drug release rates from tablets or capsules, a critical step in formulation.
- **Stability Studies**: Monitors degradation of drugs over time to assess shelf life.
- **Pharmacokinetic Studies**: Measures drug levels in biological fluids (like blood) during clinical trials to understand absorption, distribution, metabolism, and excretion.
- **Raw Material Testing**: Ensures quality of starting materials and intermediates used in manufacturing.
- **Impurity Profiling**: Identifies and quantifies impurities, crucial for safety and regulatory compliance.
- **Simultaneous Analysis**: Can analyze multiple drugs in a single mixture (e.g., combined tablets) using methods like the simultaneous equation method.