# Ultraviolet – visible spectroscopy

- تتراوح موجات الأشعة المرئية والفوق بنفسجية من (10-800 nm) بشكل عام حيث تحتل الأشعة فوق البنفسجية المهمة طول موجة حوالي (200-400 nm) بينما يقع مجال الأشعة المرئية مابين طول موجة تقدرمن (400-800 nm) وأما بالنسبة للمنطقة الواقعة بين ( 10-200 nm) نانومتر فتسمى بمنطقة الأشعة فوق البنفسجية البعيدة وهي منطقة غير مهمة في دارسة تركيب الجزيئات العضوية

# NOT:

- عندما نسلط الأشعة الفوق بنفسجية أو المرئية على الجزيئات العضوية ستحدث لدينا تغيرات في الطاقة الكامنة تنتقل فيها الجزيئات من الحالة المستقرة إلى الحالة المثارة نتيجة لترقية الألكترونات بسبب اكتسابها طاقة عالية من الضوء تسبب اظطرابا للألكترونات بتردد معين نتيجة لأمتصاص الطاقة من قبل جزيئات المادة العضوية.
- " أن كمية الطاقة الممتصة تتناسب عكسياً مع طول موجة الشعاع

# Nature of Electronic Transitions

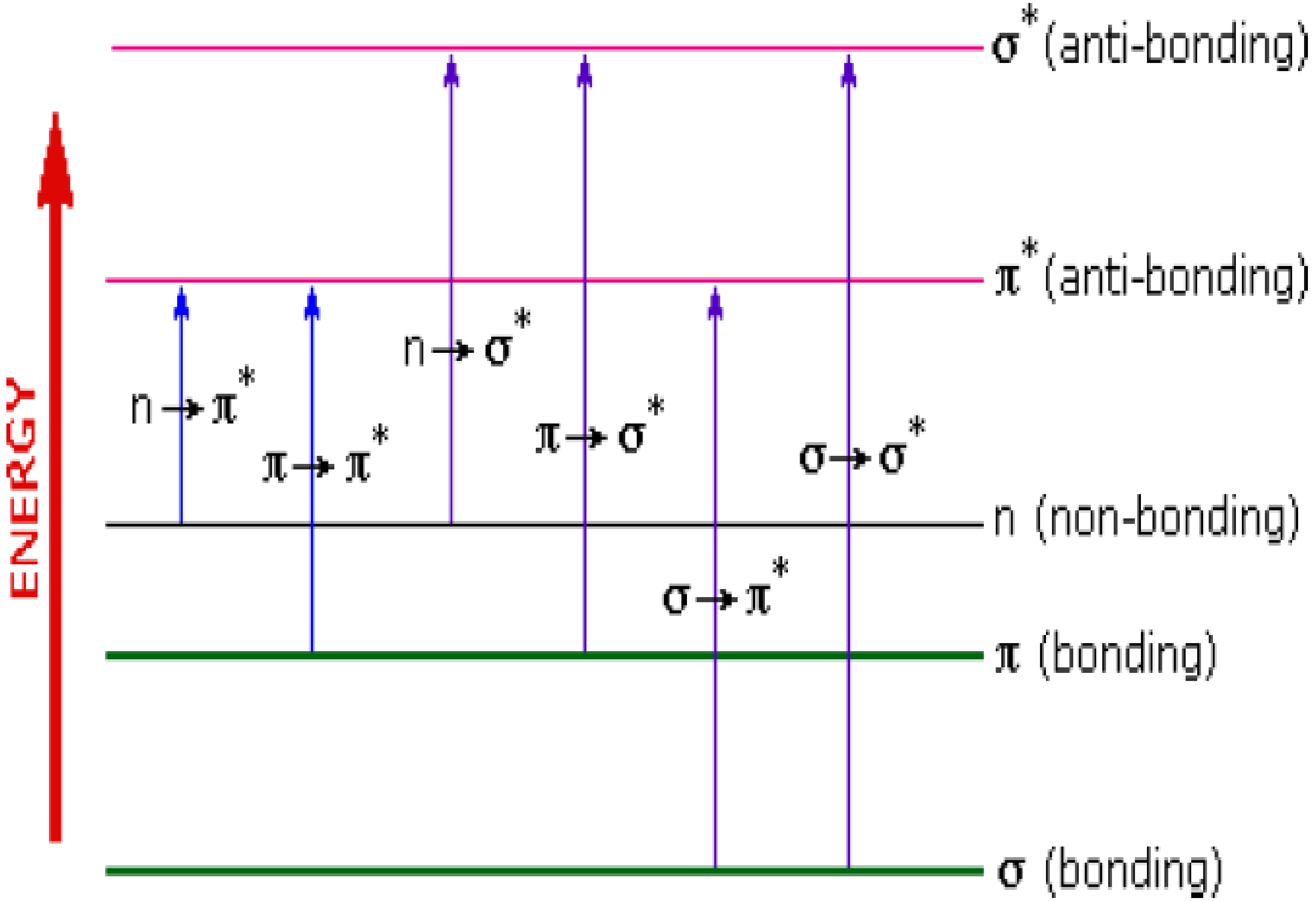
- The total energy of a molecule is the sum of its electronic, its vibrational energy and its rotational energy.
- Energy absorbed in the UV region produces changes in the electronic energy of the molecule. As a molecule absorbs energy, an electron is promoted from an occupied molecular orbital (usually a non-bonding n or bonding π orbital) to an unoccupied molecular orbital (an antibonding $\pi^*$ or $\sigma^*$ orbital) of greater potential energy

# Nature of Electronic Transitions

- For most molecules, the lowest-energy occupied molecular orbitals are σ orbitals, which correspond to σ bonds.
- The π orbitals lie at relatively higher energy levels than σ orbitals and the non-bonding orbitals that hold unshared pairs of electrons lie even at higher energies.
- The antibonding orbitals ($\pi^*$ and $\sigma^*$ ) are orbitals of highest energy.

# Nature of Electronic Transitions

- The saturated aliphatic hydrocarbons (alkanes) exhibit only σ to $\sigma^*$ transitions but depending on the functional groups the organic molecules may undergo several possible transitions which can be placed in the increasing order of their energies



ENERGY
σ* (anti-bonding)
π* (anti-bonding)
n (non-bonding)
π (bonding)
σ (bonding)
n → π*
π → π*
n → σ*
π → σ*
σ → σ*
σ → π*

Increasing energy ↑

| | |
|---|---|
| $\sigma \longrightarrow \sigma^*$ | In alkanes |
| $\sigma \longrightarrow \pi^*$ | In carbonyl compounds |
| $\pi \longrightarrow \pi^*$ | In alkenes, carbonyl compounds, alkynes, azo compounds, and so on |
| $n \longrightarrow \sigma^*$ | In oxygen, nitrogen, sulfur, and halogen compounds |
| $n \longrightarrow \pi^*$ | In carbonyl compounds |

# Solvent Effects

- The chose of the solvent to be used in ultraviolet spectroscopy is quite important .
- Should be not absorb ultraviolet radiation in the same region as the substance whose spectrum is being determined.
- Do not containing conjugated system.
- Effect on the fine structure of an absorption band.
- The non polar solvent dose not hydrogen bond with the solute, and the spectrum of the solute closely approximates the spectrum that would be produced in the gaseous state.
- In polar solvent the hydrogen bonding forms a solute – solvent complex and the fine structure may be disappear.

# Solvent Effects

- Polar solvent shift the transitions of $n \rightarrow \pi *$ type to shorter wavelengths on other hand polar solvent shift the transition of $\pi \rightarrow \pi *$type to longer wavelengths.

| | | | |
|---|---|---|---|
| Acetonitrile | 190nm | n-Hexane | 201nm |
| Chloroform | 240 | Methanol | 205 |
| Cyclohexane | 195 | Isooctane | 195 |
| 1,4Dioxane | 215 | Water | 190 |
| 95%Ethanol | 205 | Trimethyl phosphate | 210 |

يفضل المذيب غير القطبي حتى لا يكون رابطة هيدروجينية مع المذاب عكس المذيب القطبي الذي يكون رابطة هيدروجينية مع المذاب ويؤدي الى ظهور طيف غير واضح او غير دقيق.

ان اختيار المذيب في طيف الاشعة فوق البنفسجية مهم جدا ومن شروط المذيب ان لا يمتص في نفس المنطقة UV التي تمتص فيها المادة ويفضل المذيب الذي ليس له اواصر مزدوجة متعاقبة حتى يكون شفاف .

# What is Chromophore

- Although the absorption of ultraviolet result from the excitation of electrons from ground to excited state, the nuclei that the electrons hold together in bonds play an important role in determining which wavelengths of radiation are absorbed.
- The nuclei determine the strength with which the electrons are bond and influence the energy spacing between ground and excited states.
- Hence the characteristic energy of a transition and the wavelength of radiation absorbed are properties of a group rather than of electrons themselves.
- The group of atoms producing such an absorption is called a **Chromophore**.

# What is Chromophore

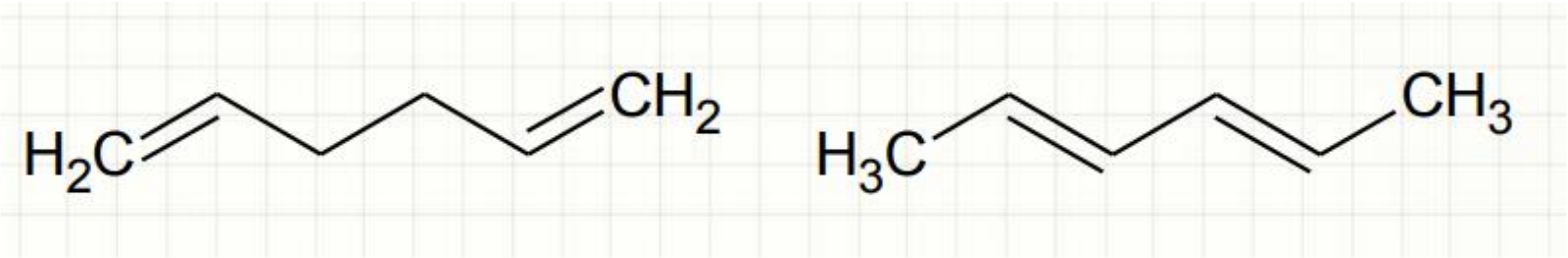
- The part of a molecule responsible for imparting color, are called as chromospheres.
- The functional groups containing multiple bonds capable of absorbing radiations above 200 nm due to n → π* & π → π* transitions.
- e.g. NO2 , N=O, C=O, C=N, C≡N, C=C, C=S, etc

# What is Chromophore

- Non-conjugated alkenes show an intense absorption below 200 nm & are therefore inaccessible to UV spectrophotometer.
- Non-conjugated carbonyl group compound give a weak absorption band in the 200 - 300 nm region.

# What is Chromophore

- When double bonds are conjugated in a compound λmax is shifted to longer wavelength. e.g. 1,5 - hexadiene has λmax = 178 nm 2,4 - hexadiene has λmax = 227 nm

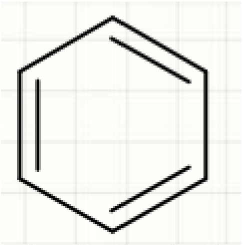


# Auxochrome

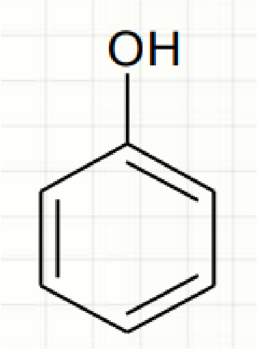
- The substituents that themselves do not absorb ultraviolet radiations but their presence shifts the absorption maximum to longer wavelength are called auxochromes. The substituents like methyl, hydroxyl, alkoxy, halogen, amino group etc.
- The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light , altering the wavelength or intensity of absorption.
- 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 λmax = 255 nm.



- Phenol λmax = 270 nm.



- Aniline λmax = 280 nm.