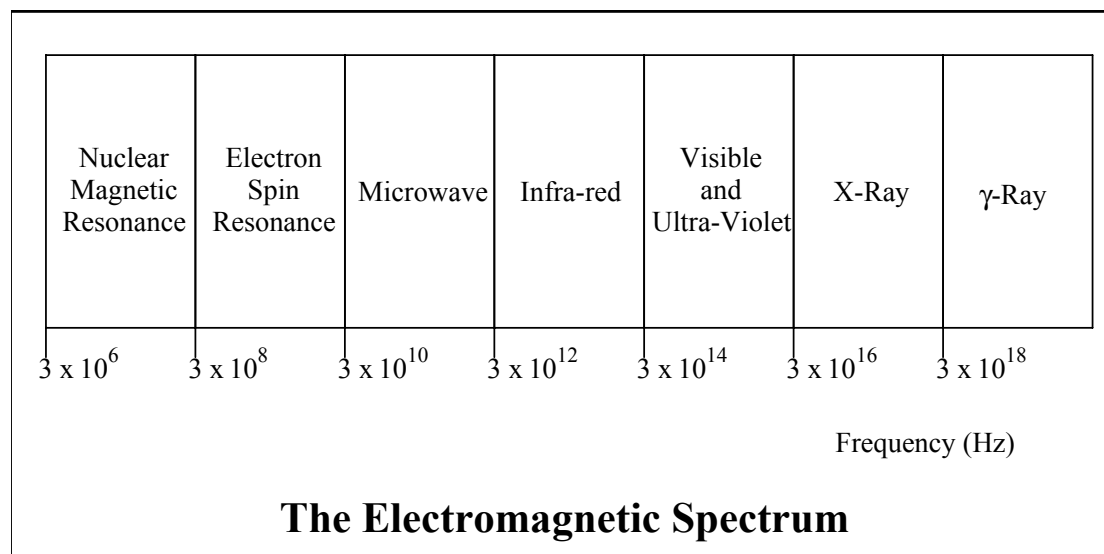


#### **[4] Ultra-Violet / Visible Spectroscopy**

Compounds in solution can absorb light of varying frequencies. In the electromagnetic spectrum these frequencies lie in the ultra-violet and visible regions.



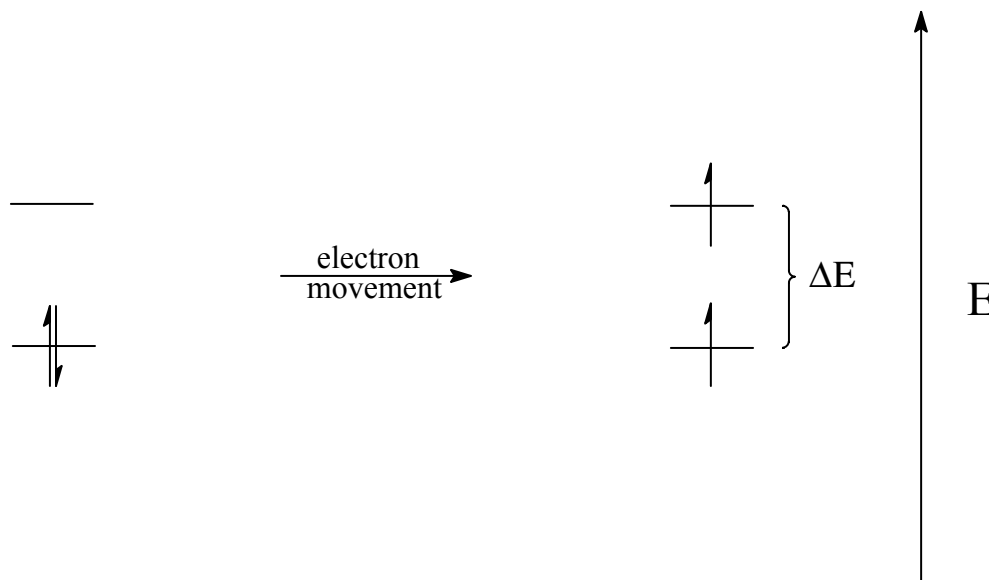
Rotational  $\sim 10 \text{ cm}^{-1}$

Vibrational  $\sim 10^3 \text{ cm}^{-1}$

Electronic  $\sim 10^6 \text{ cm}^{-1}$



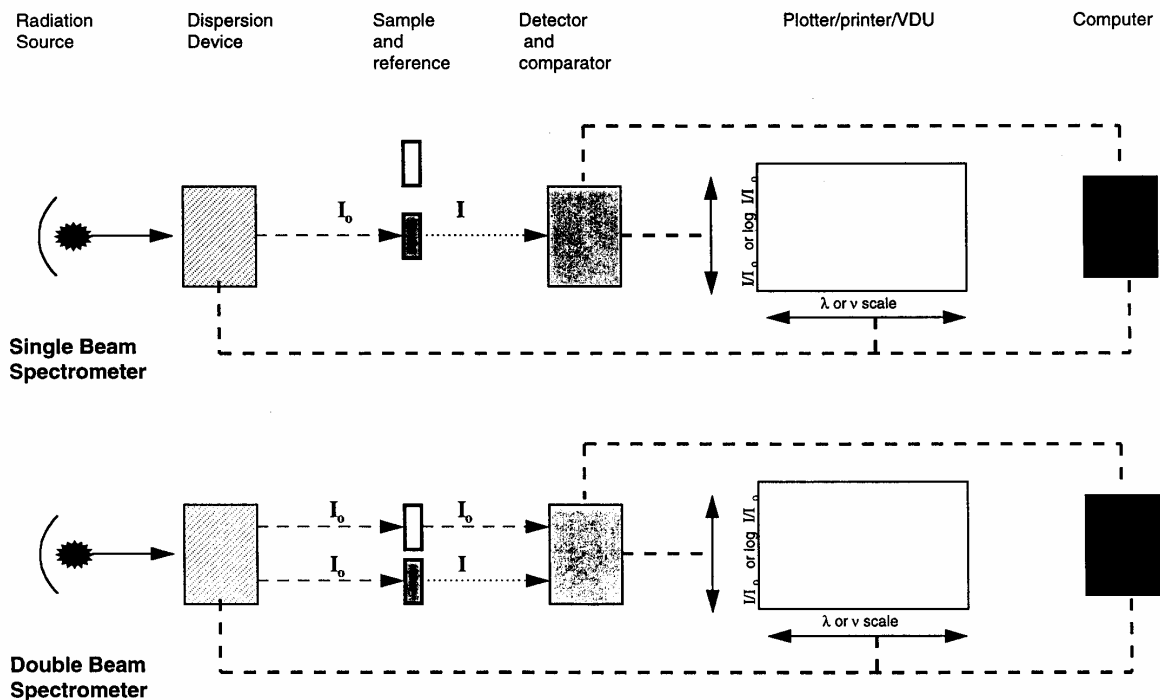
Therefore, if a bond receives some energy (for example from a laser or intense light source) then an electron from the bonding energy level may become excited into the empty antibonding energy level.



The electron has to receive precisely  $\Delta E$  to jump up a level. This also equates to a precise frequency, since:

$$\Delta E = h\nu$$

Therefore, if radiation of such a specific frequency is given to a bond, then this radiation will be absorbed by the bond - we can detect this absorption since the light/radiation coming through our sample which is absorbed will not be recorded and its absence will be noted.



In UV/Vis spectroscopy we irradiate the sample with a sweeping range of frequencies to obtain the spectrum. Since different types of molecules have different values of  $\Delta E$ , we will have a characteristic pattern on our spectrum for each different molecule.

Spectra are plotted as Absorbance (y axis) vs Wavelength (x axis).

### Beer-Lambert Law

$$\log_{10}\left(\frac{I_0}{I}\right) = \epsilon[C]l$$

where:

$I_0$  = Incident light

$I$  = light passing through the sample

$\epsilon$  = molar absorption coefficient ( $L \text{ mol}^{-1} \text{ cm}^{-1}$ )

$C$  = concentration of the solution ( $\text{mol L}^{-1}$ )

$l$  – path length of the cell (in cm)

$A$  = Absorbance

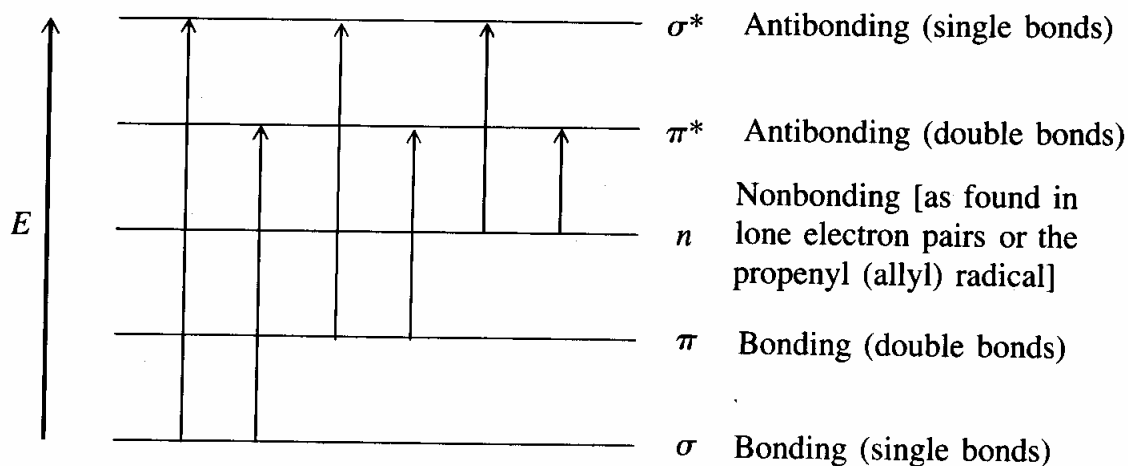
### Transitions

C-C and C-H bonds possess good orbital overlap and  $\Delta E$  for  $\sigma \rightarrow \sigma^*$  is relatively large. Transitions are usually  $< 200 \text{ nm}$ .

Excitation of  $\pi$  electrons require less energy ( $\pi \rightarrow \pi^*$ )

Nonbonding electrons can also be excited into higher states:  $n \rightarrow \sigma^*$  and  $n \rightarrow \pi^*$

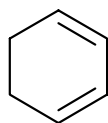
-----  
Various possible electronic transitions in a conjugated molecule.



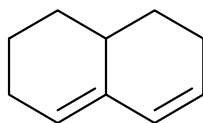
Relates conjugation and substituents (auxochromes) to electronic transitions and can be used to calculate  $\lambda_{\text{max}}$ :

## Fieser-Woodward Rules

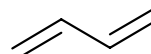
### [1] Parent dienes



Homoannular  
(s-cis)



Heteroannular  
(s-trans)



Open chain diene  
(s-trans)

Parent heteroannular or open chain diene (s-trans) = 214 nm

Parent homoannular diene (s-cis) = 253 nm

Increments:

Additional conjugated double bond = 30 nm

Each exocyclic double bond = 5 nm

### [2] Substituent effects

Substituents on the conjugated chain can shift  $\lambda_{\max}$  bathochromically.

For example:

Each alkyl substituent or ring residue = 5 nm

-OAcyl = 0 nm

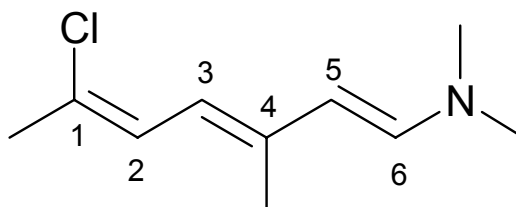
-OR = 6 nm

-NR<sub>2</sub> = 60 nm

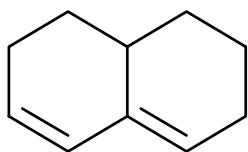
-SR = 30 nm

-Cl or Br = 5 nm

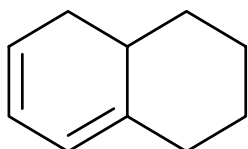
Examples:



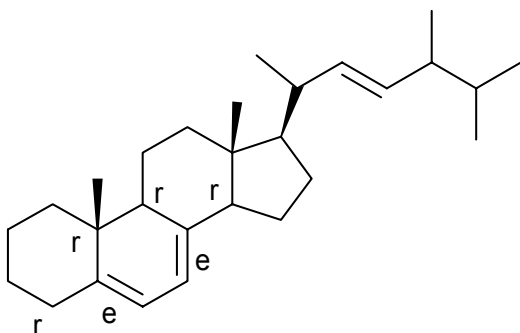
Theoretical  $\lambda_{\max}$  = 214 (standard value for a linear conjugated diene) + 30  
(extended olefin) + 10 (alkyl groups at 1 and 4) + 5 (Cl at 1) + 60 (dialkylamino  
Group at 6) = 319 nm



Theoretical  $\lambda_{\max}$  = 214 (parent diene) + 15 (3 alkyl groups) + 5 (exocyclic double bond) = 234 nm. Observed =  $\lambda_{\max}$  234 nm.

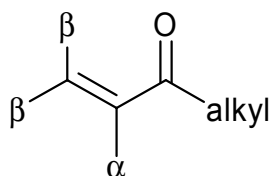


Theoretical  $\lambda_{\max}$  = 253 (parent diene) + 15 (3 alkyl groups) + 5 (exocyclic double bond) = 273 nm. Observed =  $\lambda_{\max}$  275 nm.

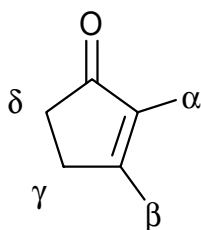


Theoretical  $\lambda_{\max}$  = 253 (parent diene) + 20 (4 ring residues, 'r') + 10 (2 exocyclic double bonds, 'e') = 283 nm. Observed =  $\lambda_{\max}$  282 nm.

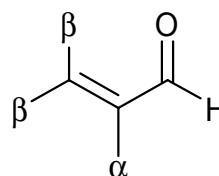
## Conjugated carbonyl compounds



Acyclic or as part  
of a 6-membered or  
larger ring  
215 nm



Cyclopentenone  
214 nm



Aldehydes  
207 nm

Structural feature	each	α	β	γ and higher
Extended conjugation (per double bond)	-	-	30	-
Homodiene component	39	-	-	-
Exocyclic location of double bond	5	-	-	-
Alkyl groups or ring residues		10	12	18
OH		35	30	(δ, +50)
OR		35	30	17 (δ, +50)
SR		-	85	
CH <sub>3</sub> CO <sub>2</sub>		6	6	(δ, +6)
Cl		15	12	
Br		25	30	
NR <sub>2</sub>			95	

With increasing polarity,  $\pi \rightarrow \pi^*$  transitions are shifted to longer wavelength, therefore there needs to be a solvent correction:

Cyclohexane, hexane - 11 nm

Ether – 7nm

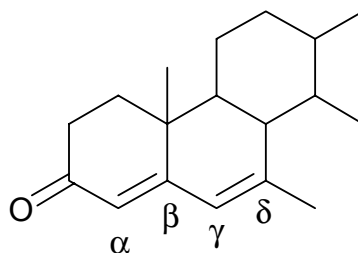
Dioxane – 5 nm

Chloroform – 1 nm

Methanol 0 nm

Water + 8 nm

Example:



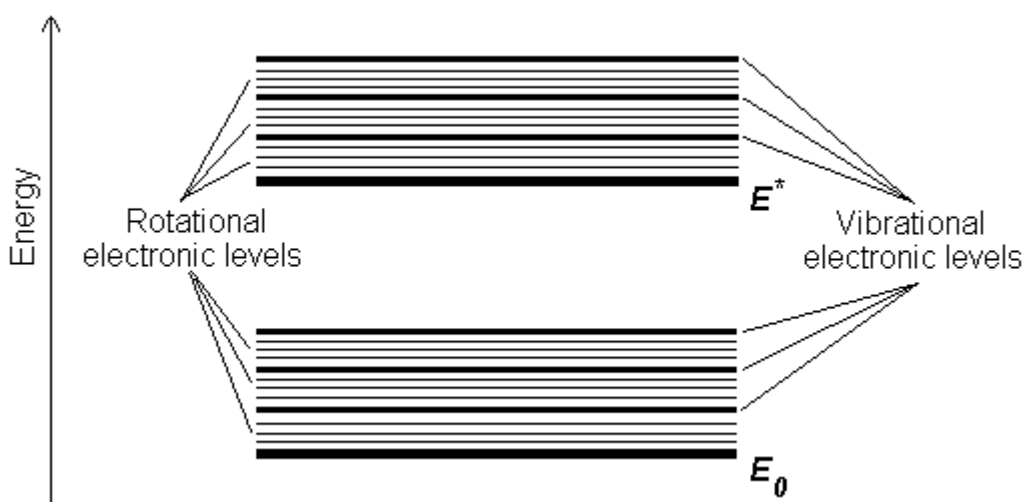
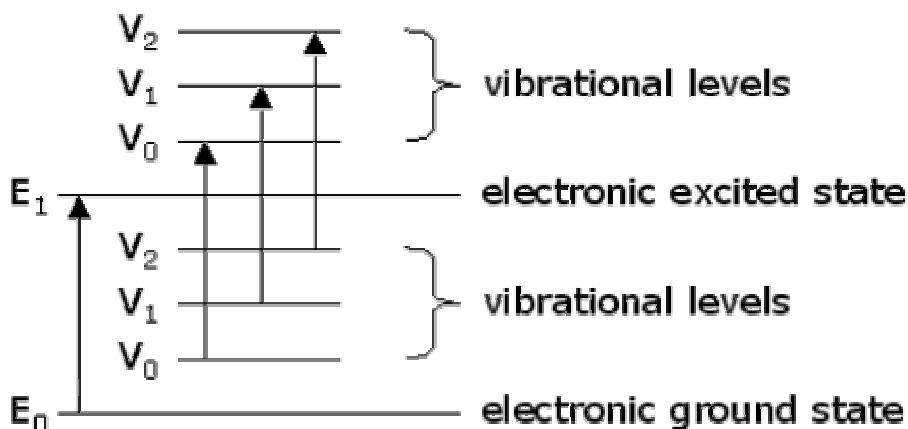
Theoretical  $\lambda_{\max} = 215$  (6-membered base) + 30 (additional double bond) + 5 ( $\alpha, \beta$  olefin is exocyclic) + 12 (ring residue on  $\beta$ ) + 36 (ring residue and alkyl group on  $\delta$ ) = 298 nm.

The above infer that single sharp peaks are observed. However, two features complicate the spectra:

[1] Since the electron distribution is changed, the nuclei are subjected to different forces after the transition and the molecule responds by vibrating. The vibrational structure of electronic transitions merge in liquids and solids (can be resolved for gases) to give a broad band. The vibrational transitions are further complicated by rotational transitions.

UV absorptions are generally broad because vibrational and rotational levels are "superimposed" on top of the electronic levels.

For this reason, the wavelength of maximum absorption ( $\lambda_{\max}$ ) is usually reported.



[2] Enough energy can be absorbed to cause the molecule to break bonds – *photodissociation*.

### Summary

The UV/Vis spectrum gives us a pattern which represents a unique behaviour pattern of our sample. It tells us very little indeed about the precise structure of our molecule. If we knew the structure beforehand we could calculate the theoretical appearance of the sample's spectrum using the Fieser-Woodward Rules, but for the purpose of structure determination this procedure has its limits.

The following definitions are useful in a discussion of UV/Vis spectroscopy:

**Chromophore** Any group of atoms that absorbs light whether or not a color is thereby produced.

**Auxochrome** A group which extends the conjugation of a chromophore by sharing of nonbonding electrons.

**Bathochromic shift** The shift of absorption to a longer wavelength.

**Hypsochromic shift** The shift of absorption to a shorter wavelength.

**Hyperchromic effect** An increase in absorption intensity.

**Hypochromic effect** A decrease in absorption intensity.