- Spectroscopy is an analytical technique arising from the interaction of a species with electromagnetic radiation- the electromagnetic radiation absorbed, emitted or scattered by the molecule is analyzed.

- **Spectroscopy** is the study of spectra, that is, the dependence of physical quantities on frequency. It is the study of the interaction of the electromagnetic radiations and matter.

- It is often used in physical and analytical chemistry for the identification of substances, through the spectrum emitted or absorbed. A device for recording a spectrum is a **spectrometer**.

- Spectroscopy can be classified according to the physical quantity which is measured or calculated or the measurement process. Spectroscopy is also heavily used in astronomy.

MEASUREMENT PROCESS

Different types of spectroscopy use different measurement processes:

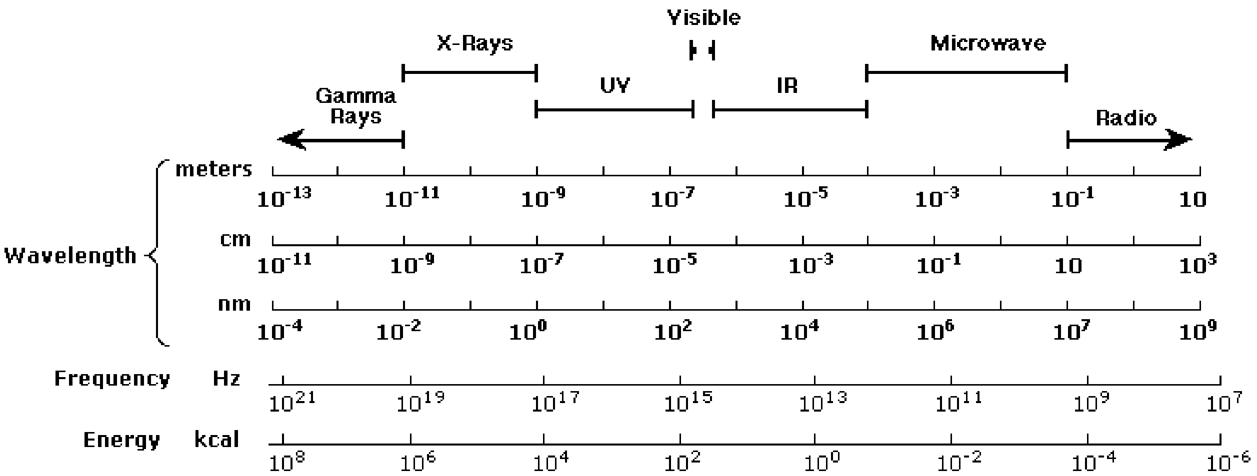
Three main types of spectroscopy

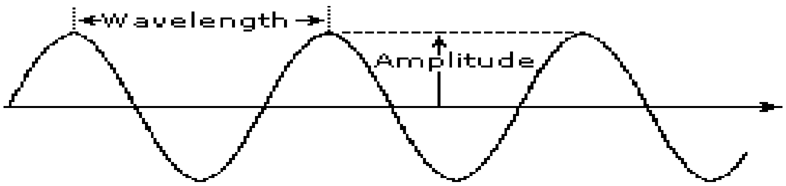
- **Absorption spectroscopy** uses the range of electromagnetic spectra in which a substance absorbs. In atomic absorption spectroscopy, the sample is atomized and then light of a particular frequency is passed through the vapour. After calibration, the amount of absorption can be related to the concentrations of various metal ions through the Beer-Lambert law.
- **Emission spectroscopy** uses the range of electromagnetic spectra in which a substance radiates. The substance first absorbs energy and then radiates this energy as light. This energy can be from a variety of sources, including collision (either due to high temperatures or otherwise), chemical reactions, and light.
- **Scattering spectroscopy** measures certain physical properties by measuring the amount of light that a substance scatters at cetain wavelengths, incident angles, and polarization angles. Scattering spectroscopy differs from emission spectroscopy due to the fact that the scattering process is much faster than the absorption/emission process. One of the most useful applications of light scattering spectroscopy is Raman spectroscopy.

THE ELECTROMAGNETIC SPECTRUM

The visible spectrum constitutes but a small part of the total radiation spectrum. Most of the radiation that surrounds us cannot be seen, but can be detected by dedicated sensing instruments. This **electromagnetic spectrum** ranges from very short wavelengths (including gamma and x-rays) to very long wavelengths (including microwaves and broadcast radio waves). The following chart displays many of the important regions of this spectrum, and demonstrates the inverse relationship between wavelength and frequency

The Electromagnetic Spectrum





UV – Visible spectroscopy:

Many atoms emit or absorb visible light. In order to obtain a fine line spectrum, the atoms must be in a gas phase. This means that the substance has to be vaporised. Spectrum is studied in absorption or emission.

All atoms absorb in the UV region because photons are energetic enough to excite outer electrons. If the frequency is high enough, Photoionisation takes place.

Ultraviolet-Visible spectrum

An ultraviolet-visible spectrum is essentially a graph (or plot) of light absorbance vs. wavelength in a range of ultraviolet and/or visible regions. Such a spectrum can often be produced by a more sophisticated **spectrophotometer**. Similarly, for a given material of species, a standard graph of extinction coefficient ε vs. wavelength may be made or used if one is already available. Such a standard graph would be effectively "concentration-corrected" and thus

THE ABSORPTION LAWS

Lambert's Law

When a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiartion with thickness of absorbing medium is proportional to the intensity of the incident radiation. Mathemetically this law can be represented as

$$-\frac{dI}{dx} = kI$$

Where

- I is the intensity of radiation after passing through a thickness x of the medium
- dI is the infinitesimally small decrease in the intensity of radiation on passing through infinitesimally small thickness, dx of the medium
- -dI/dx is the rate of decrease of intensity of radiation with thickness of the absorbing medium
- k is the proportionality constant or absorption coefficient.

If I_o is the intensity of radiation before entering the absorption medium (x = o)

Then I, the intensity of radiation after passing through any thickness, say x of the medium can be calculated as :

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_{x=0}^{x=x} k\,dx$$

or

$$\ln \frac{I}{I_0} = -kx \quad \text{or} \quad \frac{I}{I_0} = e^{-kx}$$

$$I = I_0\, e^{-kx}$$

The intensity of the radiation absorbed, I_{abs} is given by :

$$I_{abs} = I_0 - I = I_0(1 - e^{-kx})$$

The above Lambert's law equation can also be written by changing the natural logarithm to the base 10.

$$I = I_0\, 10^{-ax}$$

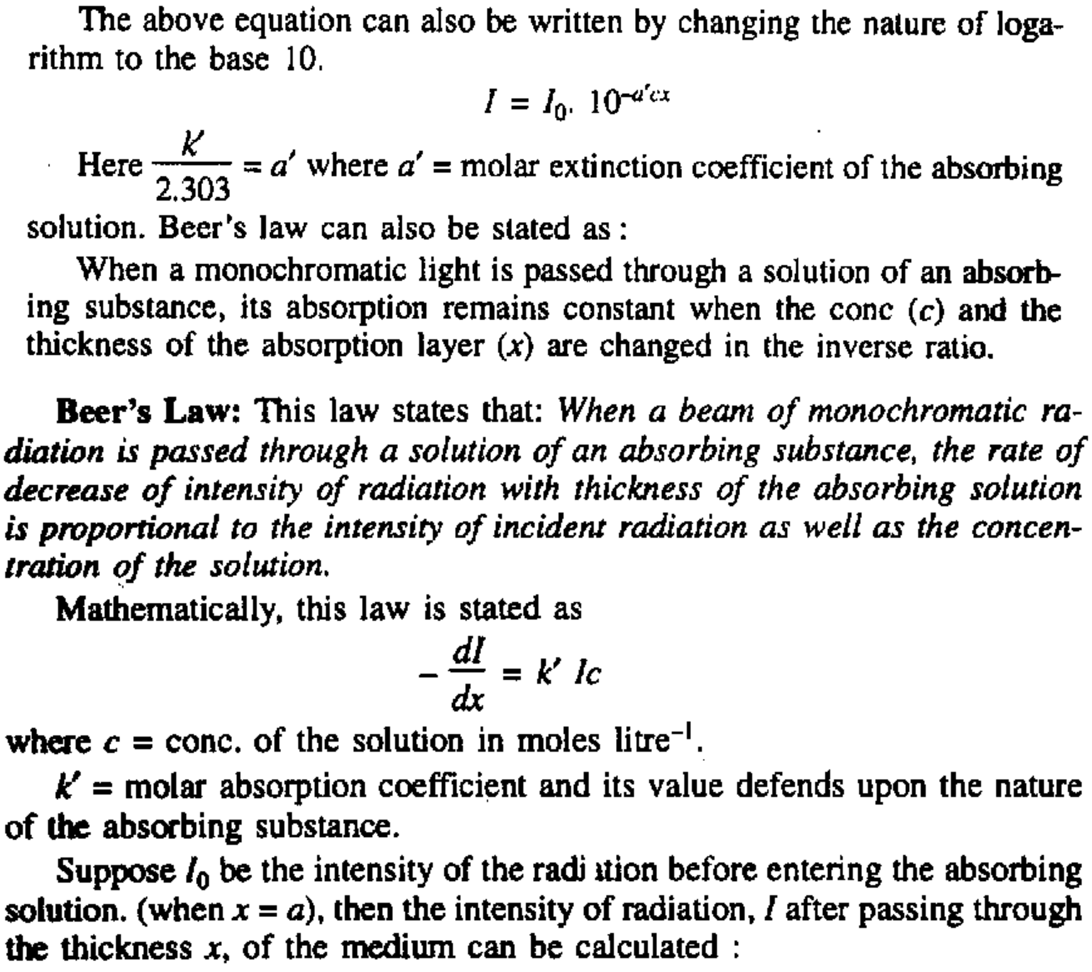
where a = extinction coefficient of the absorbing medium

$$\left(a = \frac{k}{2.303}\right)$$

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_{x=0}^{x=x} K'\, c\,dx$$

or

$$I = I_0 e^{-K'cx}$$



The above equation can also be written by changing the nature of logarithm to the base 10.

$$I = I_0 . 10^{-a'cx}$$

Here $\frac{k'}{2.303} = a'$ where a' = molar extinction coefficient of the absorbing solution. Beer's law can also be stated as :

When a monochromatic light is passed through a solution of an absorbing substance, its absorption remains constant when the conc (c) and the thickness of the absorption layer (x) are changed in the inverse ratio.

Beer's Law: This law states that: *When a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the concentration of the solution.*

Mathematically, this law is stated as

$$-\frac{dI}{dx} = k' Ic$$

where c = conc. of the solution in moles litre^{-1}.

k' = molar absorption coefficient and its value defends upon the nature of the absorbing substance.

Suppose I_0 be the intensity of the radiation before entering the absorbing solution. (when $x = a$), then the intensity of radiation, I after passing through the thickness x, of the medium can be calculated :

BEER-LAMBERT LAW

The method is used in a quantitative way to determine concentrations of an absorbing species in solution, using the Beer-Lambert law:

$$A = -\log_{10}(I/I_0) = \epsilon \cdot c \cdot L$$

,

where A is the measured absorbance, I_0 is the intensity of the incident light at a given wavelength, I is the transmitted intensity, L the pathlength through the sample, and c the concentration of the absorbing species. For each species and wavelength, ε is a constant known as the extinction coefficient.

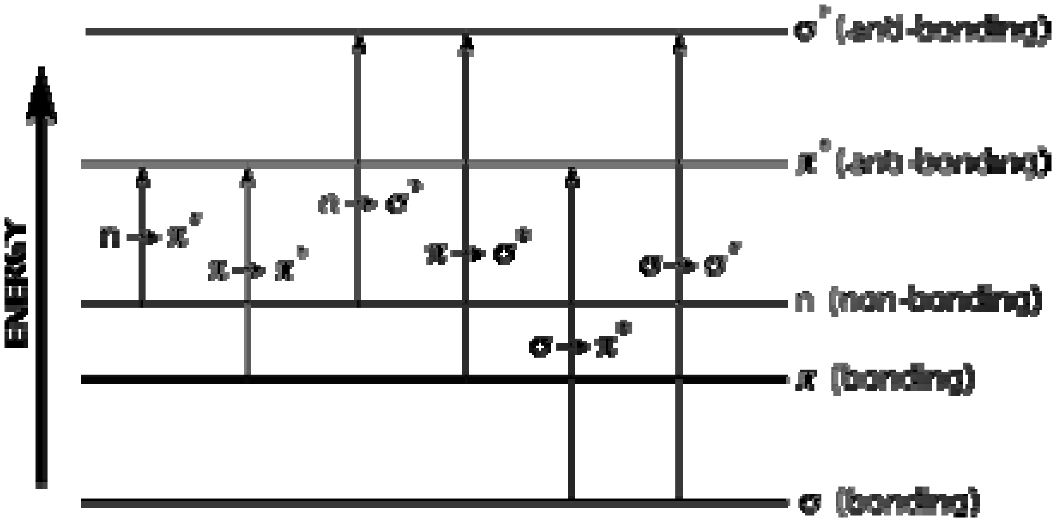
The absorbance A and extinction ε are sometimes defined in terms of the natural logarithm instead of the base-10 logarithm.

TRANSITIONS

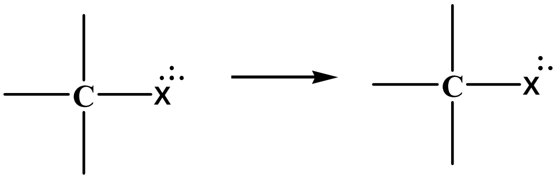
According to the molecular orbital theory when a molecule is excited by the absorption of energy (UV or visible), its electrons are promoted from a bonding to anti bonding orbital.

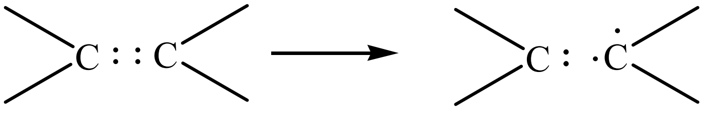
- The anti bonding orbital which is associated with the excitation of the σ electron is called σ^* anti bonding orbital **σ to σ^***
    - So σ to σ^* transition takes place when the σ electron is promoted to the anti bonding σ orbital
- When a non-bonding electron gets promoted to an anti bonding σ^* orbital **n to σ^***
- The **π to π^*** transitions represent the promotion of the π electron to the anti bonding π orbital i.e. π^*

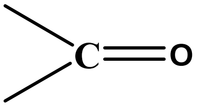
σ to σ^* > n to ó* > π to π^*> n to π^*



- **σ to σ^*** this is a high-energy process since σ bonds are in general very strong. The organic compounds in which all the valence shell electrons are involved in the formation of sigma bonds do not show absorption in the UV region
- **n to σ^*** transition takes place in saturated compounds containing one hetro atom with unshared pair of electrons.
- **π to π^*** this type of transitions occur in the unsaturated center of the molecule i.e. in compounds containing double or triple bonds and also in aromatics
- **n to π^*** in this type of transition an electron of unshared electron pair on ro atom gets excited to π^* anti-bonding orbital. Saturated aldehydes show both types of transitions i.e. low energy **n to π^*** and high energy **π to π^*** occurring around 290 mμ and 180 mμ respectively.







CHROMOPHORE

This is defined as any isolated covalently bonded group that shows a characteristic absorption in the UV or visible region.

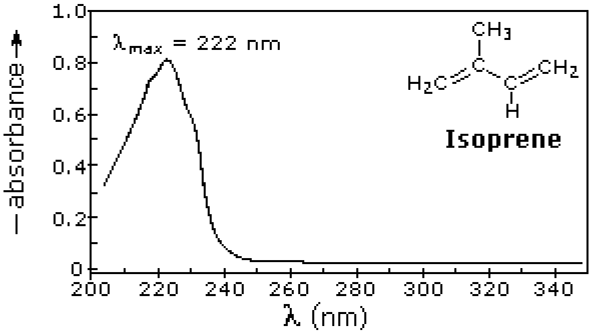
Chromophore	Example	Excitation	λ_{max} nm	ε molar absorptivity	solvent
C=C	Ethene	π –> π*	171	15,000	hexane
C≡C	1-Hexyne	π –> π*	180	10,000	hexane
C=O	Ethanal	n –> π* π –> π*	290 180	15 10,000	hexane hexane
N=O	Nitromethane	n –> π* π –> π*	275 200	17 5,000	ethanol ethanol
C-X X = Br, I	Methyl bromide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

AUXOCHROME

An auxochrome is defined as any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum. Some common auxochromic groups are –OH, -OR, $-NH_2$, -NHR, $-NR_2$, -SH

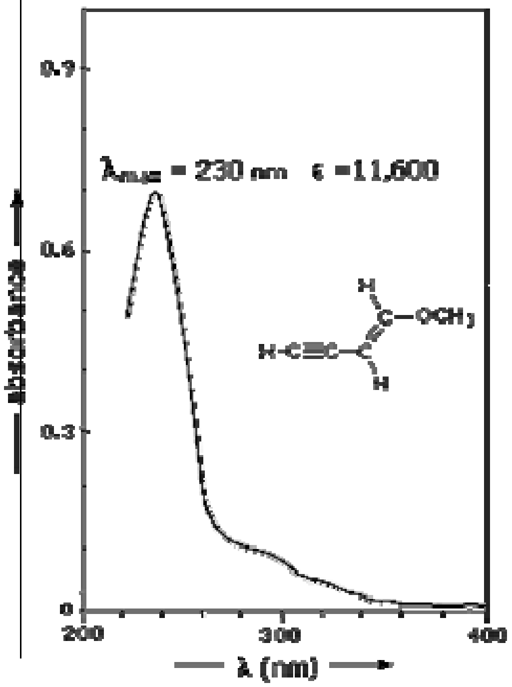
THE IMPORTANCE OF CONJUGATION

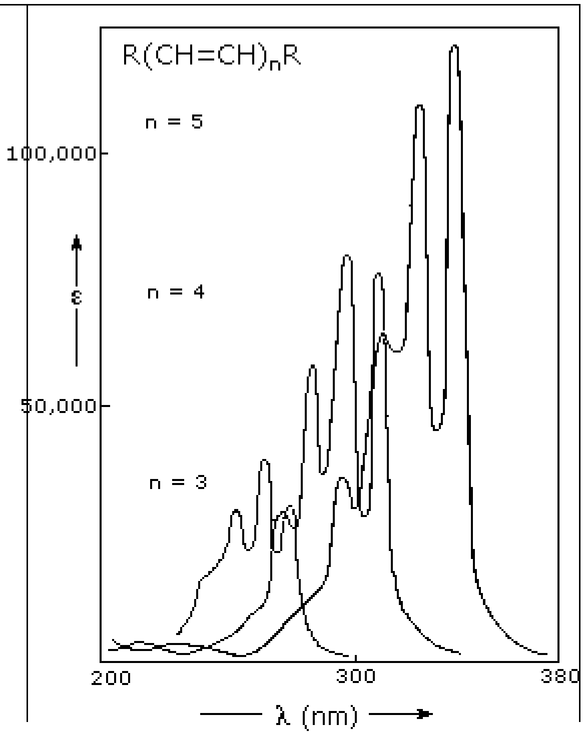
A comparison of the absorption spectrum of 1-pentene, λ_{max} = 178 nm, with that of isoprene clearly demonstrates the importance of chromophore conjugation.



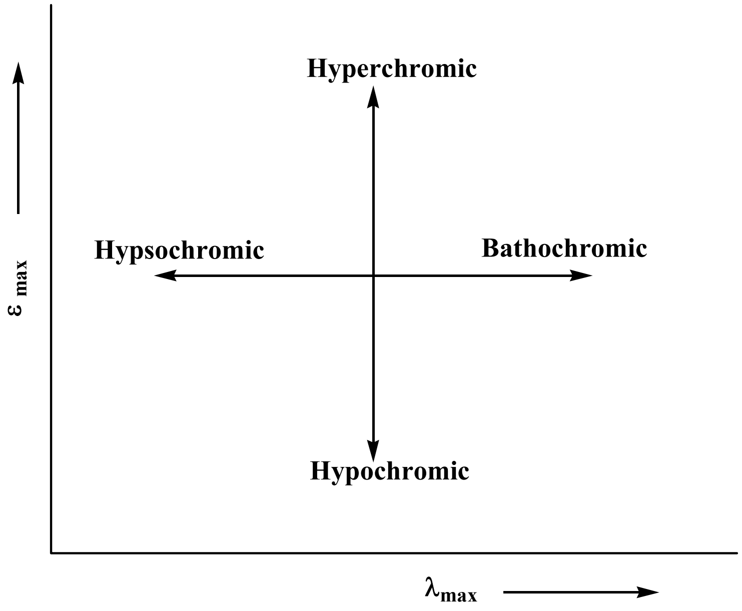
Further evidence of this effect is shown below. The spectrum on the left illustrates that conjugation of double and triple bonds also shifts the absorption maximum to longer wavelengths. From the polyene spectra displayed on the right, it is clear that each additional double bond in the conjugated pi-electron system shifts the absorption maximum about 30 nm in the same direction. Also, the molar absorptivity (ε) roughly doubles with each new conjugated double bond. Spectroscopists' use the terms defined in the table on the right when describing shifts in absorption. Thus, extending conjugation generally results in bathochromic and hyperchromic shifts in absorption.

The appearance of several absorption peaks or shoulders for a given chromophore is common for highly conjugated systems, and is often solvent dependent. This fine structure reflects not only the different conformations such systems may assume, but also electronic transitions between the different vibrational energy levels possible for each electronic state. Vibrational fine structure of this kind is most pronounced in vapor phase spectra, and is increasingly broadened and obscured in solution as the solvent is changed from hexane to methanol.





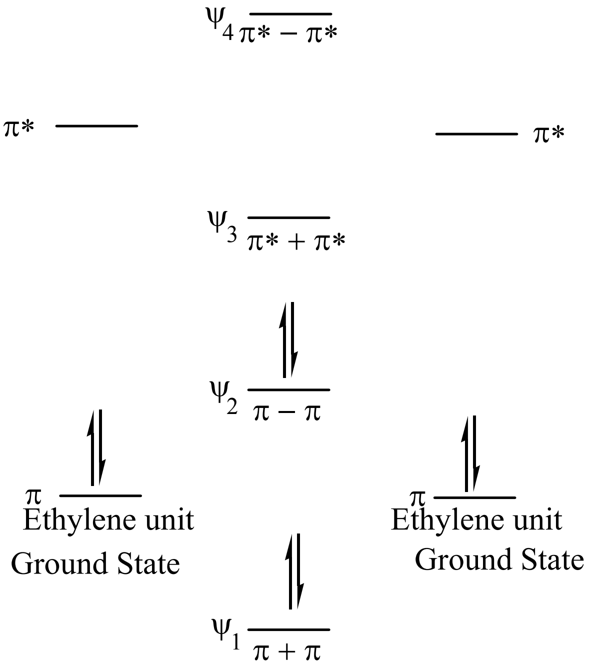
Terminology for Absorption Shifts	
Nature of Shift	**Descriptive Term**
To Longer Wavelength	Bathochromic
To Shorter Wavelength	Hypsochromic
To Greater Absorbance	Hyperchromic
To Lower Absorbance	Hypochromic



CONJUGATED DIENES

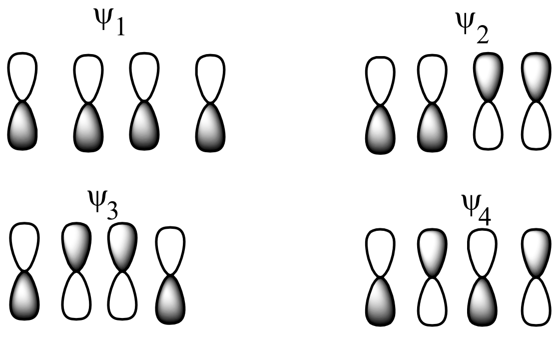
- The wavelength is shifted to higher value (Bathochromic shift) if two or more chromophoric groups are present in conjugation in a molecule.

Ethylene	1 double bond	170mµ
Butadiene	2 conjugated double bonds	217mµ



- The two π bonding orbitals from each ethylene unit interact or mix up to give rise to two new bonding orbitals
  - $\pi + \pi = \pi_1$ or ψ_1 having higher energy. The energy of ψ_1 is less than any one of the two combining atomic orbitals.
  - $\pi - \pi = \pi_2$ or ψ_2 having lower energy
- The two π^* anti bonding orbitals from each ethylene unit interact or mix up to give rise to two new bonding orbitals
  - $\pi^* + \pi^* = \pi^*_1$ or ψ_3 having lower energy.
  - $\pi^* - \pi^* = \pi^*_2$ or ψ_4 having higher energy

thus the four states can be represented as



WOODWARD-FIESER RULE for calculating Absorption Maximum in Dienes

Woodward formulated certain empirical rules for calculating the λ_{max} in case of dienes. Fieser later modified the rules. According to these rules, each type of diene has a certain fixed basic value and the value of the absorption (λ_{max} depends upon

1. The number of alkyl substituents or ring residues on the double bond.
2. The number of double bonds which extend conjugation
3. The presence of polar groups such as –Cl, -Br, -OR, -SR etc.

Transition Involved π-π^*	Absorption
Parent value for Butadiene or a cyclic conjugated diene	217mμ
Increment for each substituent	
Alkyl Substituent or ring residue	5 mμ
Exocyclic double bonds	5 mμ
Double bond extended conjugation	30 mμ
Auxochrome	
-OR	+6 mμ
-SR	+30 mμ
-Cl, -Br	+5 mμ
-NR_2	+60 mμ
$OCOCH_3$	0

e.g.

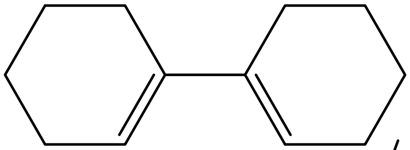
1

CH_3-CH=CH-CH=CH-CH_3

Basic Value	217 mμ
2 alkyl substituents (2 x 5)	10 mμ
Calculated value	**227 mμ**
Observed value	227

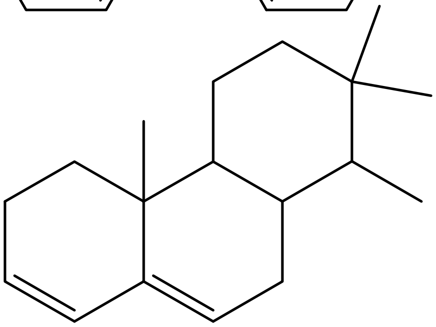
2

Basic Value	215 mμ
4 ring residues (4 x 5)	20 mμ
Calculated value	**235 mμ**
Observed value	234mμ



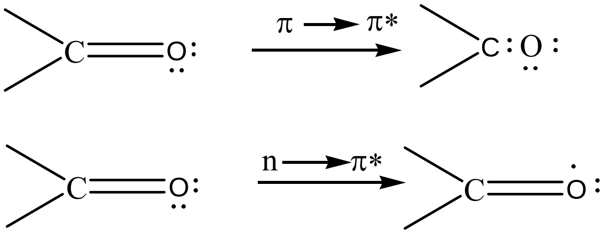
3

Basic Value	253 mμ
4 ring residues (4 x 5)	20 mμ
2 exocyclic double bonds(2 x 5)	10mμ
1 double bond extending conjugation	30mμ
Calculated value	**313 mμ**
Observed value	312mμ

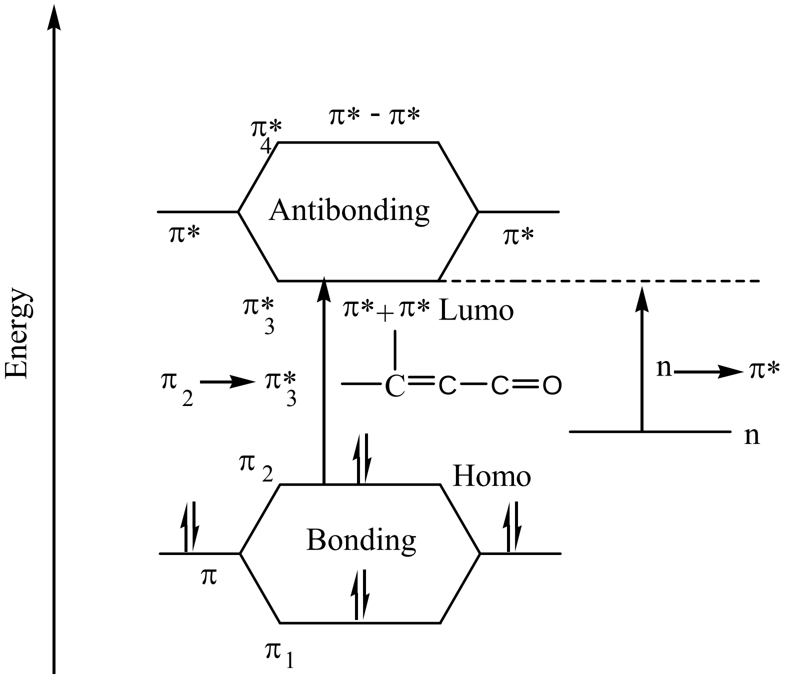


α, β Unsaturated Carbonyl Compounds

For a carbonyl compound two types of transitions occur



The first transition involves the promotion of one of the π electron to an antibonding π^* orbital. This is very intense and corresponds to shorter wavelength. The second transition is an **n – π*** involving the promotion of one of the non-bonding paired electron to the π^*_3 orbital. This is less intense and corresponds to the longer wavelength.



In α,β unsaturated carbonyl compounds the double bond and the carbonyl groups are in conjugation. The spectra of such compounds are simple summation of ethylene and carbonyl chromophores. A bathochromic shift is observed if two chromophoric groups are conjugated as the π electron cloud is spread over at least four carbon atoms. There is a **π – π*** transition due to the ethylene unit.

In α,β unsaturated carbonyl compounds where ethylene and carbonyl groups are conjugated, both **π – π*** and **n – π*** transitions show bathochromic shifts.

WOODWARD-FIESER RULE for calculating Absorption Maximum in α,β unsaturated carbonyl compounds

1. The nasic value of α,β unsaturated ketone is taken as 215mμ. The α,β unsaturated ketone may be cyclic or six membered.
   - For a compound = CH-COX, a basic value is 215 mμ, if X is alkyl group
   - If X =H, the basic value becomes 207mμ.
   - The basic value becomes 193mμ if X is OH or OR.

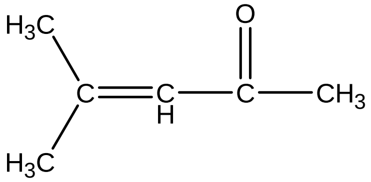
2. If the double bond and the carbonyl group are contained in a fivemembered ring, then for such compounds the basic value becomes 202mμ.

	Structure	Increment
1	For each exocyclic double bond	+ 5mμ
2	For each exocyclic double bond in 5 or 7 membered ring except cyclopenta-2-enone	+ 5mμ
3	For each alkyl substituent or ring residue at the	
	α position	+ 10 mμ
	β position	+12 mμ
	Γ or δ or higher position	+ 18 mμ
4	For each double bond extending conjugation	+ 30 mμ
5	For Homoannular conjugated diene	+ 39 mμ

Chromophoric increments in **mμ** for position wrt the carbonyl group				
Group	**α**	**β**	**γ**	**δ or higher**
-OH	+35	+30	-	-50
-Oac	+6	+6	+6	+6
-Cl	+15	+12	-	-
-Br	+25	+35	-	-
-OR	+35	+30	+17	31
-SR	-	+85	-	-
NR_2	-	+95	-	-

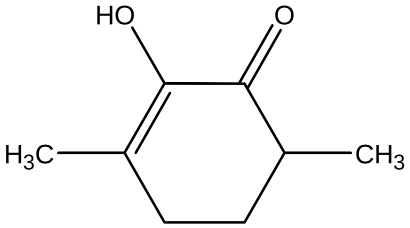
1

Basic Value	215 mμ
2β alkyl substituents (2 x 12)	24 mμ
Calculated value	**239 mμ**
Observed value	237mμ



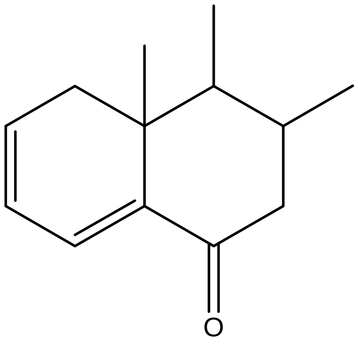
2

Basic Value	215 mμ
OH at α position	35 mμ
2β substituents (one alkyl, one ring residue)	24mμ
Calculated value	**274 mμ**
Observed value	275mμ

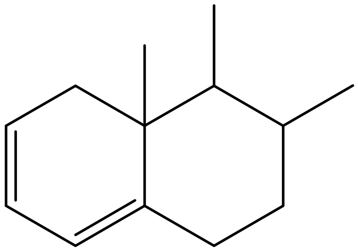


3

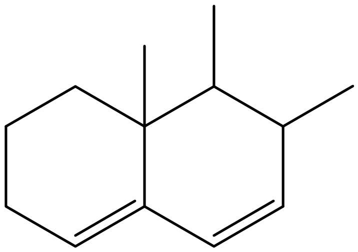
Basic Value	215 mμ
α ring residue	10mμ
δ ring residue	18mμ
1 exocyclic double bond	5mμ
Homoannular conjugated diene	39 mμ
I double bond extending conjugation	30 mμ
Calculated value	**317 mμ**
Observed value	319mμ



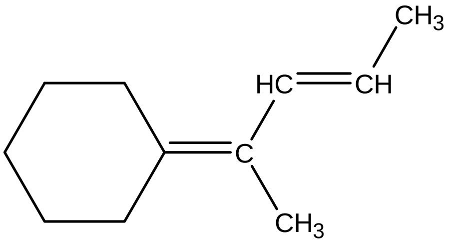
Basic Value	253 mμ
3 ring residues (3 x 5)	15 mμ
1 endo cyclic double bonds (1 x 5)	5mμ
Calculated value	**273 mμ**
Observed value	274 mμ

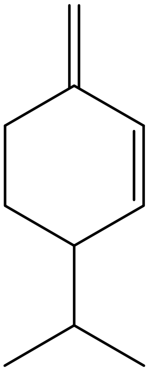


Basic Value	215 mμ
3 ring residues (3 x 5)	15 mμ
1 exocyclic double bonds(1 x 5)	5mμ
Calculated value	**235 mμ**
Observed value	235 mμ

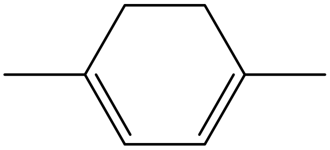


Basic Value	217 mμ
2 Alkyl substituents	10 mμ
2 ring residues (2 x 5)	10 mμ
1 exocyclic double bonds	5 mμ
Calculated value	**242 mμ**
Observed value	242 mμ





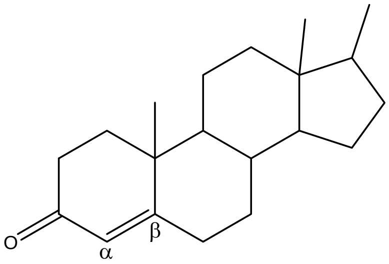
232



273

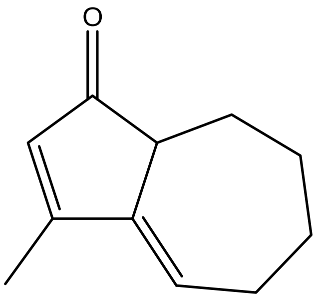
Unsaturated Ketones

Basic Value	215 mμ
2 β ring residues (2 x 12)	24 mμ
1 exocyclic double bond	5mμ
Calculated value	**244 mμ**
Observed value	241 mμ

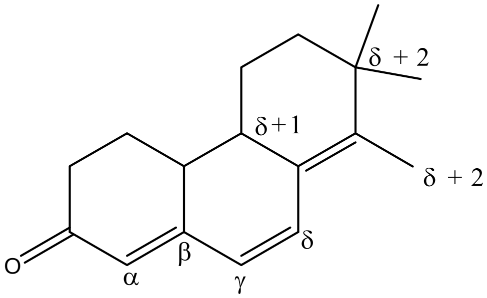


α,β-unsaturated cyclopentanone system

Basic Value	202 mμ
1 β alkyl substitution	12 mμ
1 exocyclic double bond	5 mμ
I double bond extending conjugation	30 mμ
1 γ ring residue	18 mμ
1 δ ring residue	18mμ
Calculated value	**285 mμ**
Observed value	287 mμ



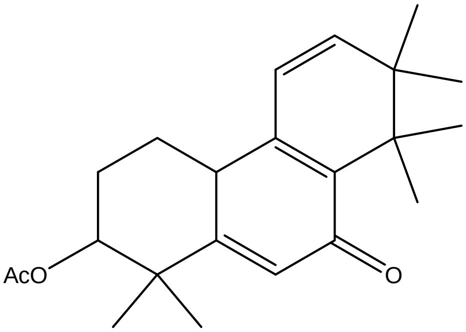
Basic Value	215 mμ
1 β ring residue	12 mμ
1 (δ + 1) ring residue	18mμ
2 (δ + 2) ring residue	36mμ
2 double bond extending conjugation	60 mμ
2 exocyclic double bond	10 mμ
Calculated value	**351 mμ**
Observed value	354 mμ



In case there is cross conjugation in a compound, i.e. the carbonyl group has a α,β-unsaturation on either sidethen the value of absorption maximum is estimated by considering the most highly substituted conjugated system

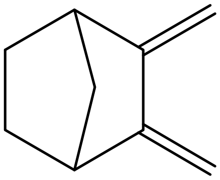
In ring B, the carbonyl is conjugated on either sideBut the conjugated system is highly substituted towards ring C

Basic Value	215 mμ
1 α ring residue	10 mμ
1 β ring residue	12 mμ
1 δ ring residue	18mμ
I double bond extending conjugation	30 mμ
Homoannular conjugated diene	39 mμ
Calculated value	**324 mμ**
Observed value	327 mμ



Bicyclic rings

Basic Value	217 mμ
2 ring residues (2 x 5)	10 mμ
2 exocyclic double bond	10 mμ
1 bicyclic system (strain Correction)	15 mμ
Calculated value	**252 mμ**
Observed value	254 mμ



Observed Basic Value	217 mμ
2 ring residues (2 x 5)	10 mμ
1 exocyclic double bond	5 mμ
1 bicyclic system (strain Correction)	15 mμ
Calculated value	**247 mμ**
Observed value	247 mμ