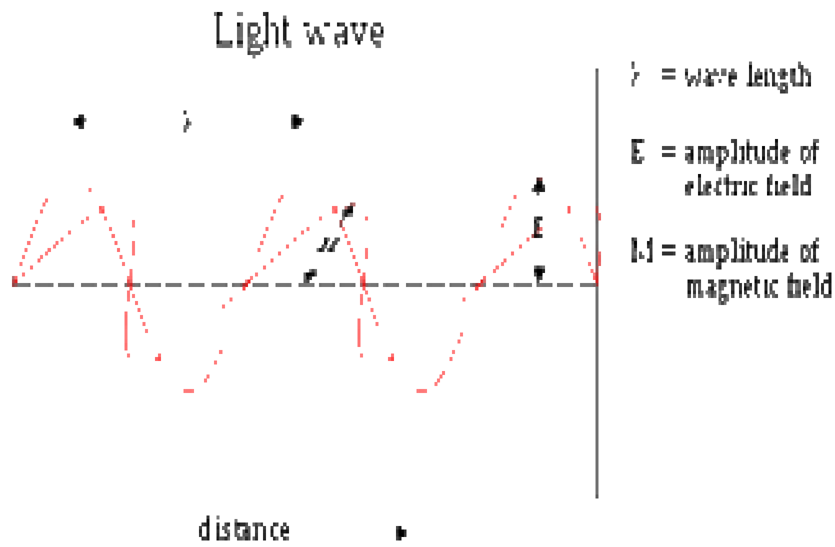
CHEM 308

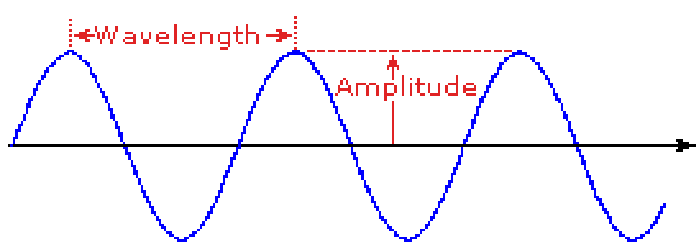
INSTRUMENTAL ANALYSIS

Spectroscopic Tehniques

- Ultraviolet and Visible (UV/Vis) Spectrophotometry
- Fluorescence and Phosphorescence Spectrophotometry
- Atomic Spectrometry (Emission and Absorption)
- Infrared (IR) Spectrophotometry
- Raman Spectroscopy
- X-Ray Spectroscopy
- Radiochemical Techniques
- Nuclear Magnetic Resonance (NMR) Spectroscopy
- Electron Spin Resonance (ESR) Spectroscopy



Electromagnetic radiation is commonly treated as a <u>wave</u> phenomenon, characterized by a wavelength (λ) or frequency (ν).



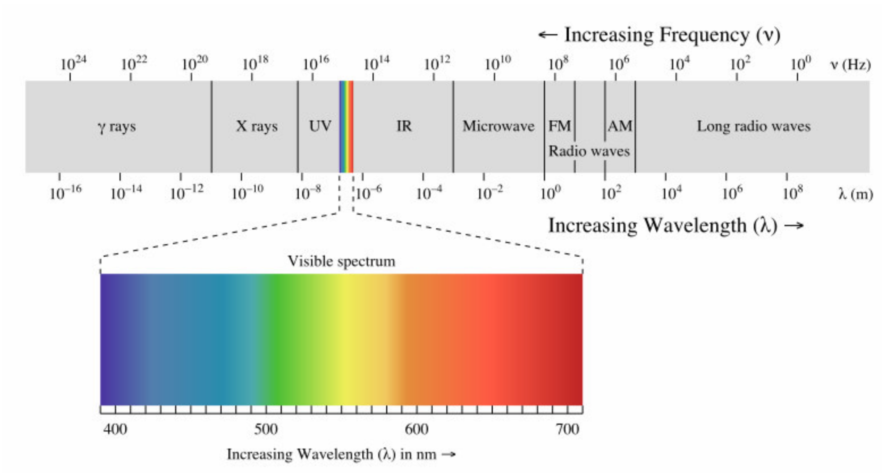
Wavelength is defined as the distance between adjacent peaks (or troughs), and may be designated in meters, centimeters or nanometers (10^{-9} meters).

Frequency is the number of wave cycles that travel past a fixed point per unit of time, and is usually given in cycles per second, or hertz (Hz).

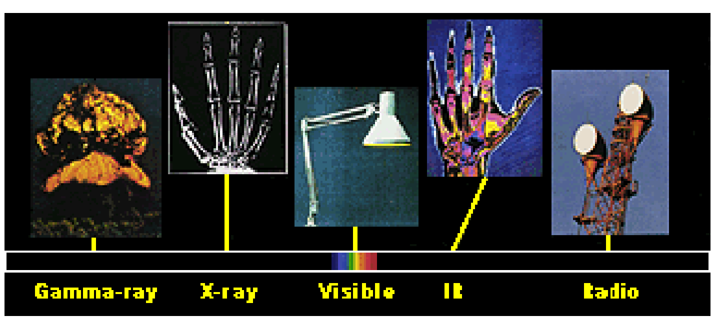
The energy associated with a given segment of the spectrum is proportional to its frequency.

$\upsilon = c/\lambda$ υ=frequency, λ=wavelength, c=velocity of light ($c=3\cdot10^{10}$ cm/sec)

$\Delta E = h\upsilon$ E=energy, υ=frequency, h=Planck's constant ($h=6.6\cdot10^{-27}$ erg sec)



A Radio Wave is not a Gamma-Ray, a Microwave is not an X-ray ... or is it?

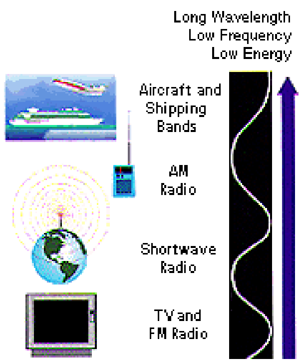


Radio waves, visible light, X-rays, and all the other parts of the electromagnetic spectrum are fundamentally the same thing, electromagnetic radiation.

imagine.gsfc.nasa.gov/docs/science/know_l1/emspectrum.html

Different types of radiation in the EM spectrum,

in order from lowest energy to highest:



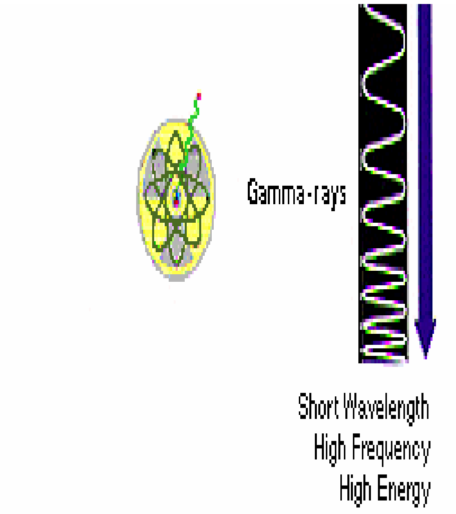
- **RADIO:**
  This is the same kind of energy that radio stations emit into the air for your boom box to capture and turn into your favorite Mozart, Madonna, or Coolio tunes. But radio waves are also emitted by other things ... such as stars and gases in space. You may not be able to dance to what these objects emit, but you can use it to learn what they are made of.

imagine.gsfc.nasa.gov/docs/science/know_l1/emspectrum.html

Microwaves

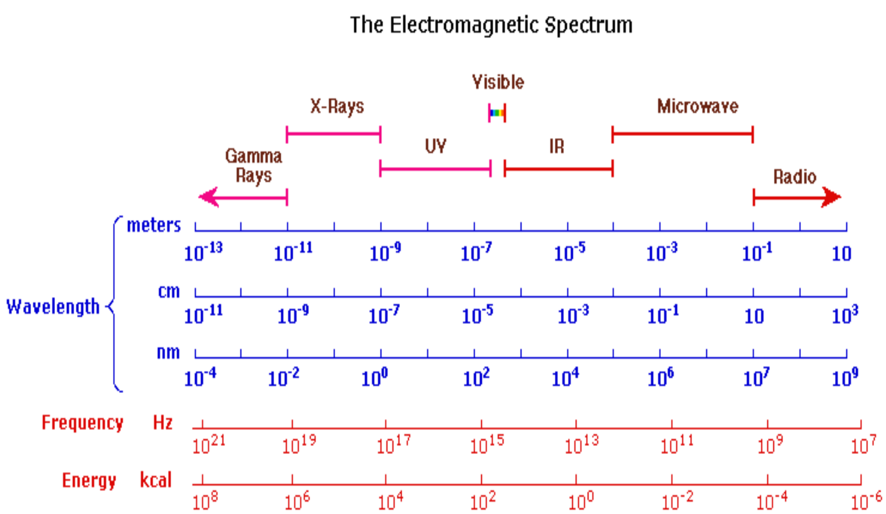
- They will cook your popcorn in just a few minutes! In space, microwaves are used by astronomers to learn about the structure of nearby galaxies, including our own Milky Way!

imagine.gsfc.nasa.gov/docs/science/know_l1/emspectrum.html



- Gamma-rays: radioactive materials (some natural and others made by man in things like nuclear power plants) can emit gamma-rays. Big particle accelerators that scientists use to help them understand what matter is made of can sometimes generate gamma-rays. But the biggest gamma-ray generator of all is the Universe! It makes gamma radiation in all kinds of ways.

imagine.gsfc.nasa.gov/docs/science/know_l1/emspectrum.html



colour region	wavelength (nm)
violet	380 - 435
blue	435 - 500
cyan	500 - 520
green	520 - 565
yellow	565 - 590
orange	590 - 625
red	625 - 740

Spectroscopy Using UV and V Light

- Molecular :
- *a-Absorption*
- *b-Emission (Luminescence= Fluorescence+ Phosphoresence)*

- Atomic :
- *a-Absorption*
- *b-Emission (Flame photometry,atomic emission spectrometry)*
- *c-Emission (Atomic Fluoresence spectrometry)*

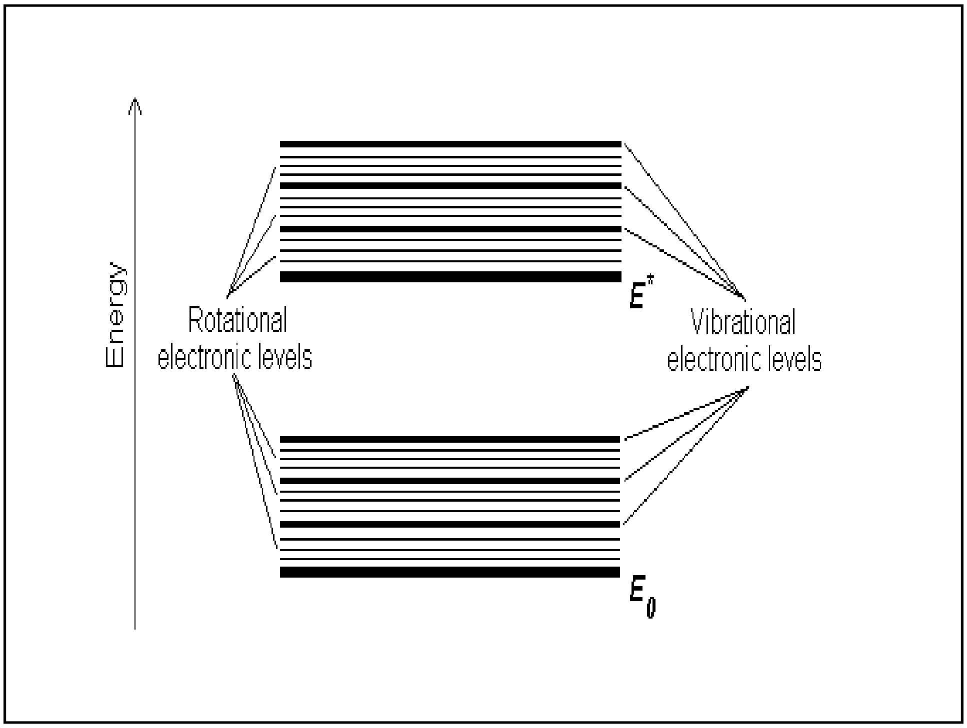
UV/Vis spectroscopy is routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds.

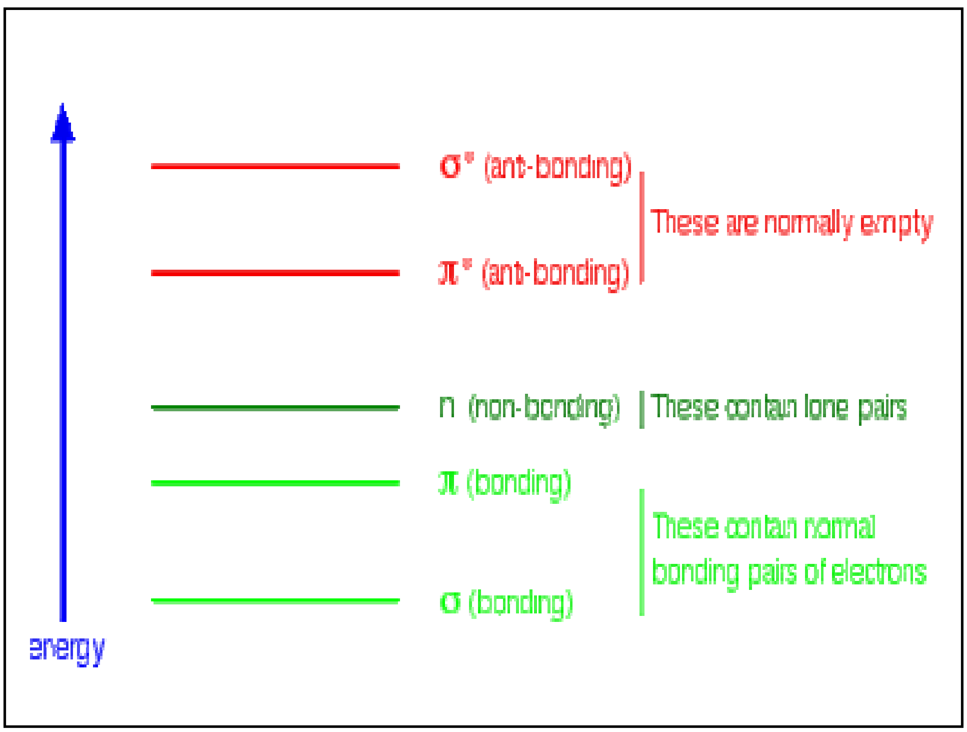
Absorption spectroscopy carried out in UV-V region is sometimes called "electronic spectroscopy".

a **molecular energy state** is the sum of an electronic, vibrational, rotational, nuclear and translational component

$$E = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational} + E_{nuclear}$$

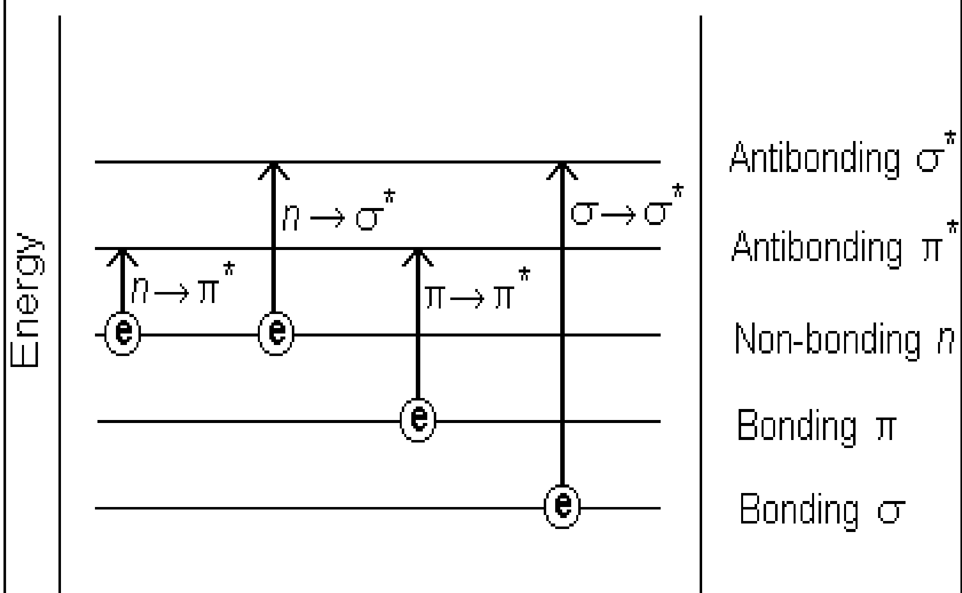
The molecular energy levels are labelled by the molecular term symbols.


Energy
Rotational
electronic levels
Vibrational
electronic levels
E*
E0


σ* (anti-bonding)
π* (anti-bonding)
These are normally empty
n (non-bonding)
These contain lone pairs
π (bonding)
σ (bonding)
These contain normal
bonding pairs of electrons
energy

The following molecular electronic transitions exist:

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



σ → σ * Transitions

(λ<200 nm)

The energy required is large.
Methane (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-V spectra
(200 - 700 nm)

n → σ* Transitions

Saturated compounds containing atoms with lone pairs (non-bonding electrons).

They can be initiated by light whose wavelength is in the range 150 - 250 nm.

The number of organic functional groups with n → σ* peaks in the UV region is small.

$n \rightarrow \pi^*$

$\pi \rightarrow \pi^*$

Transitions

Most absorption spectroscopy of organic compounds is based on these transitions.

This is because the absorption peaks for 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 π electrons.

Molar absorbtivities from $n \rightarrow \pi^*$

are relatively low, 10 to100 L mol^{-1} cm^{-1} .

$\pi \rightarrow \pi^*$ normally give molar absorbtivities

between 1000 and 10,000 L mol^{-1} cm^{-1} .

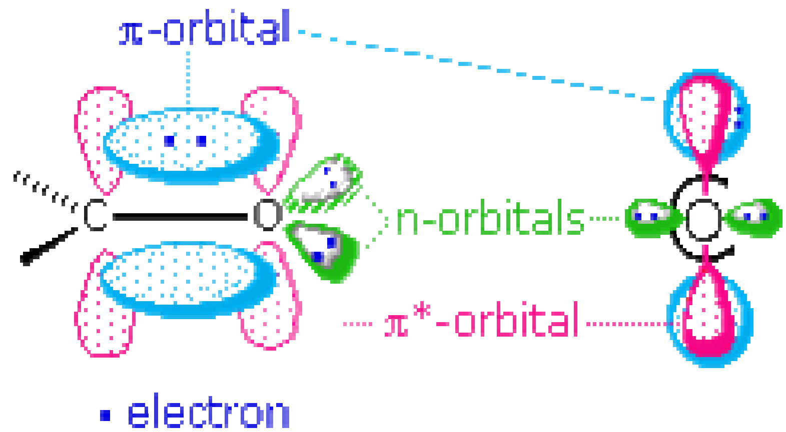
Molar absoptivities ,ε, may be very large for strongly absorbing chromophores (>10,000) and very small if absorption is weak (10 to 100).

The magnitude of ε reflects both the size of the chromophore and the probability that light of a given wavelength will be absorbed when it strikes the chromophore.

$$\varepsilon = 0.87 \cdot 10^{20} \times P \times a$$

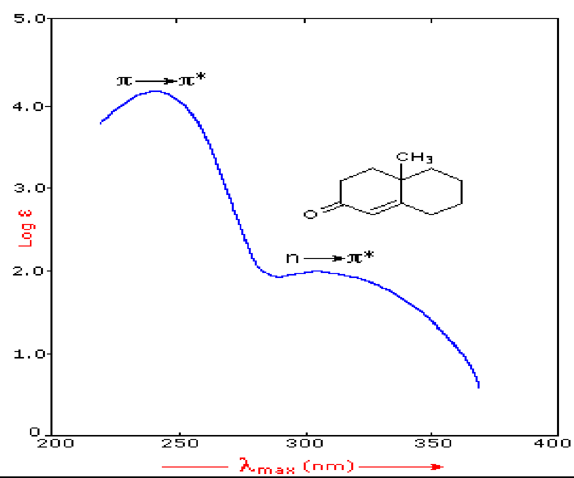
P is the transition probability (0 to 1)

a is the chromophore area in cm^2



The π —> π* absorption located at 242 nm is very strong, with an ε = 18,000.

The weak n —> π* absorption near 300 nm has an ε = 100.

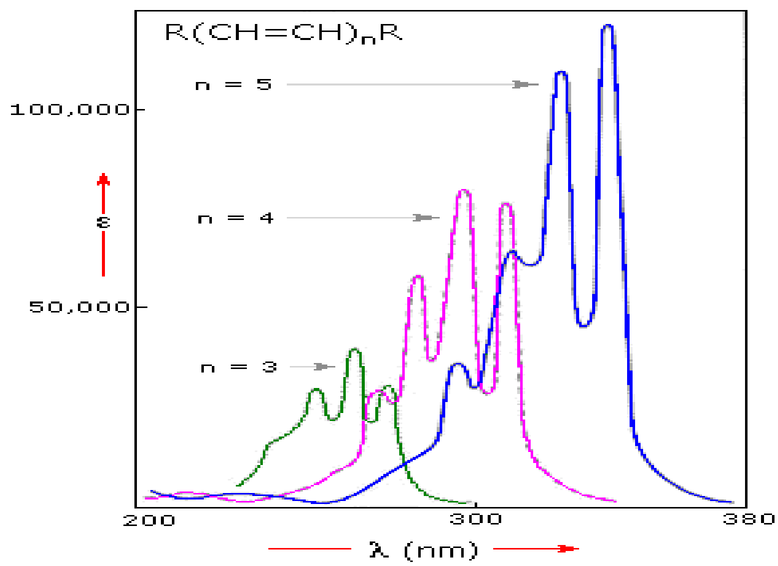


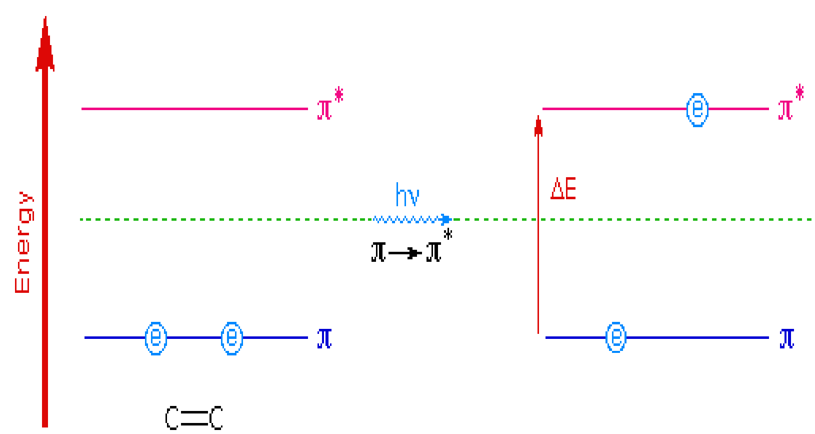
Chromo-phore		Excitation	λ_{max}, nm	ε	Solvent
C=C		$\pi \rightarrow \pi^*$	171	15,000	hexane
C≡C		$\pi \rightarrow \pi^*$	180	10,000	hexane
C=O		$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	15 10,000	hexane hexane
N=O		$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	17 5,000	ethanol ethanol
X=Br X=I		$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	200 360	hexane hexane

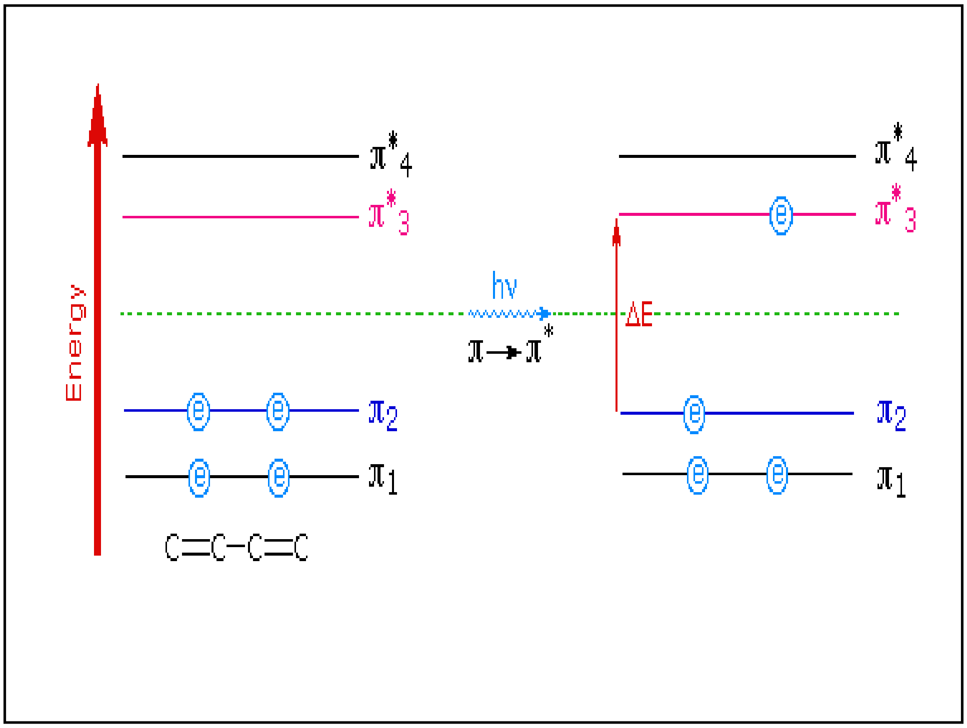
Terminology for Absorption Shifts

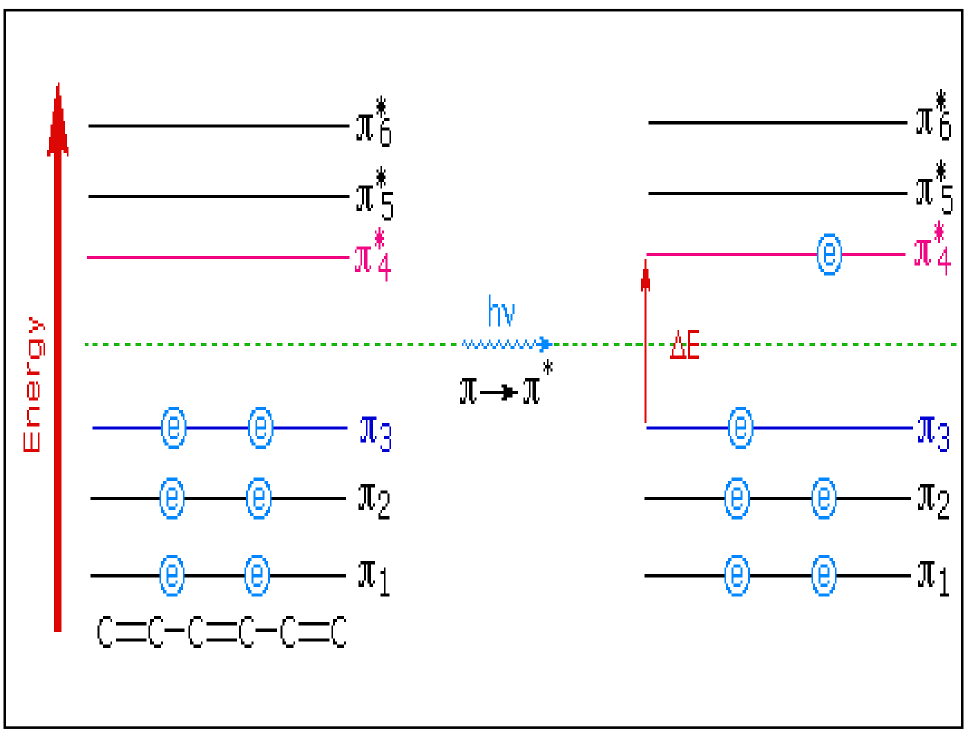
Nature of Shift	Descriptive Term
To Longer Wavelength	Bathochromic
To Shorter Wavelength	Hypsochromic
To Greater Absorbance	Hyperchromic
To Lower Absorbance	Hypochromic

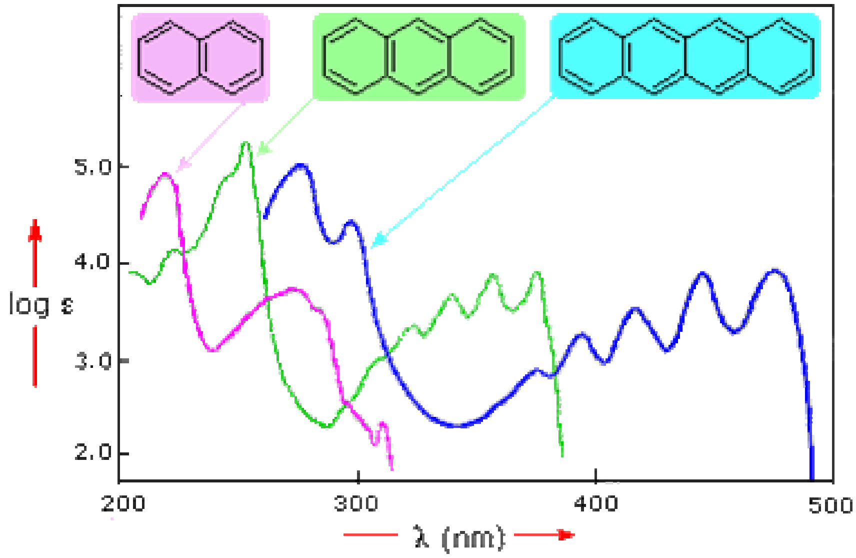
The Importance of Conjugation






Energy
π*4
π*3
hν
π→π*
ΔE
π2
π1
C=C-C=C
π*4
π*3
π2
π1


Energy
π*6
π*5
π*4
hν
π→π*
ΔE
π3
π2
π1
C=C-C=C-C=C
π*6
π*5
π*4
π3
π2
π1



Electronic transitions also have so-called **bands** associated with them.

R-band from the German *radikalartig* or radical-like,

K-band from the German *Konjugierte* or conjugated,

B-band from benzoic and

E-band from ethylenic