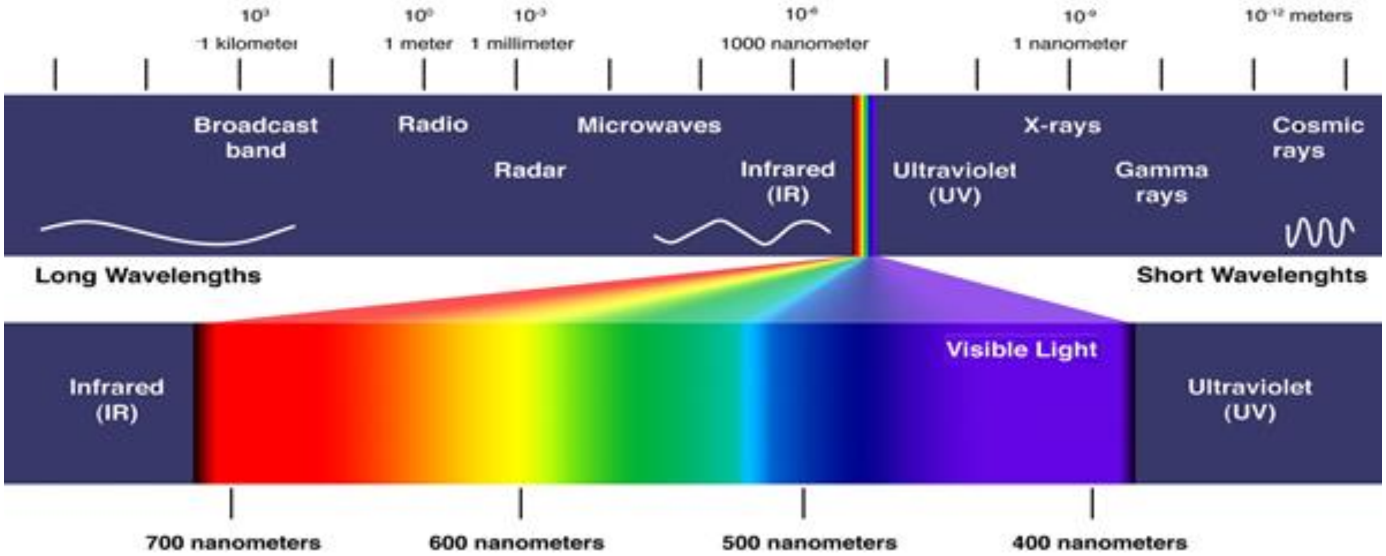
SPECTROSCOPIC METHODS OF ORGANIC MOLECULES



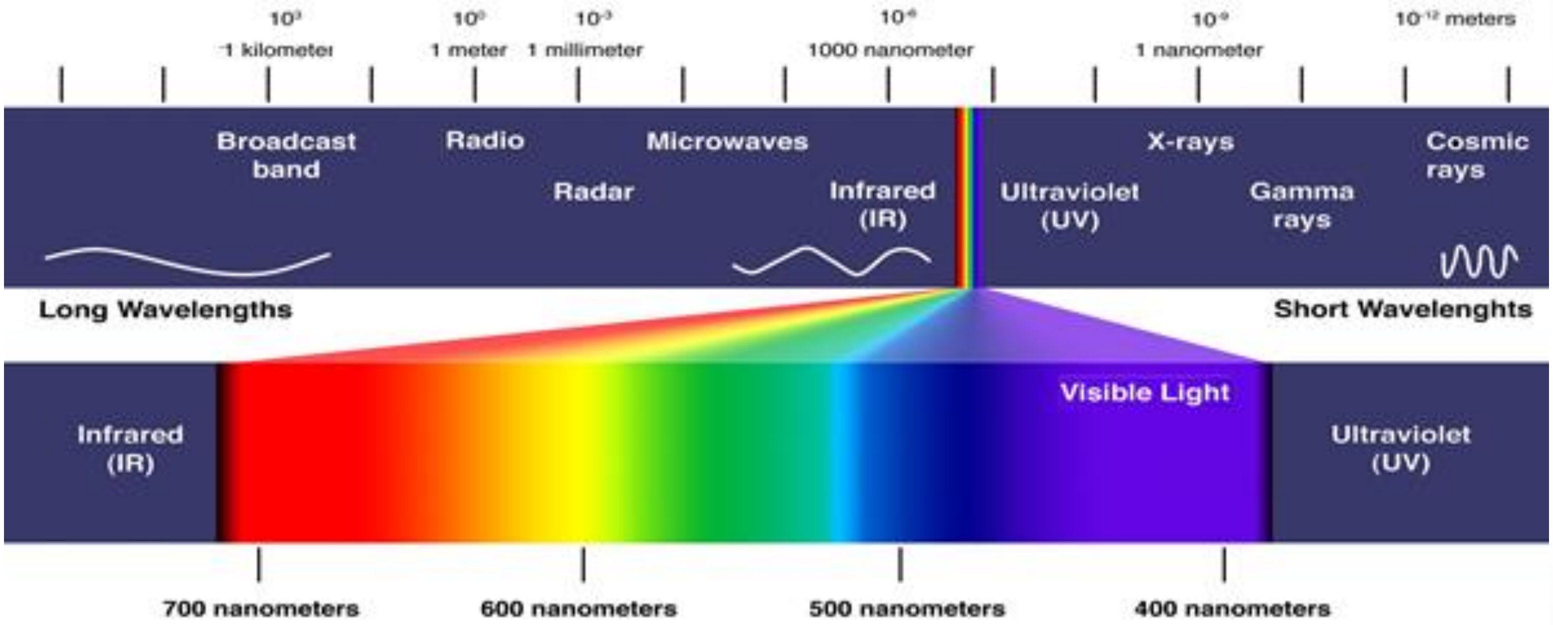
Professor Ioannis P. Gerothanassis

Department of Chemistry, University of Ioannina

FEBRUARY 2018

SPECTROSCOPIC METHODS OF ORGANIC MOLECULES

UV SPECTROSCOPY



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WHAT IS SPECTROSCOPY?

The study of the interaction between ELECTROMAGNETIC (EM) RADIATION and MATTER

https://ashomarconfidential.files.wordpress.com/2012/08/spectroscopy-methods.ppt

SPECTROSCOPIC ANALYSIS

covers

ATOMIC SPECTROSCOPY

MOLECULAR SPECTROSCOPY

https://ashomarconfidential.files.wordpress.com/2012/08/spectroscopy-methods.ppt

To Understand Spectroscopy We Must Understand Electromagnetic Radiation

What is Electromagnetic Radiation?

- is a form of energy that has both Wave and Particle Properties.
- For example: Ultraviolet, visible, infrared, microwave, radio wave.

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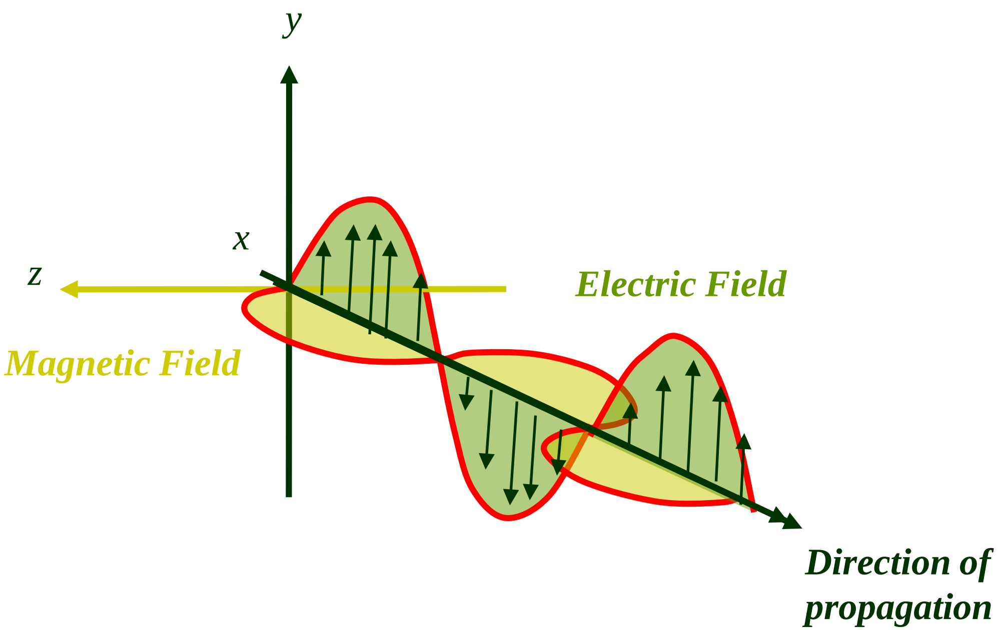
WAVE PROPERTIES

- EM radiation is conveniently modeled as waves consisting of perpendicularly oscillating electric and magnetic fields, as shown below.



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- At 90° to the direction of propagation is an oscillation in the ELECTRIC FIELD.

- At 90° to the direction of propagation and 90° from the electric field oscillation (orthagonal) is the MAGNETIC FIELD oscillation.

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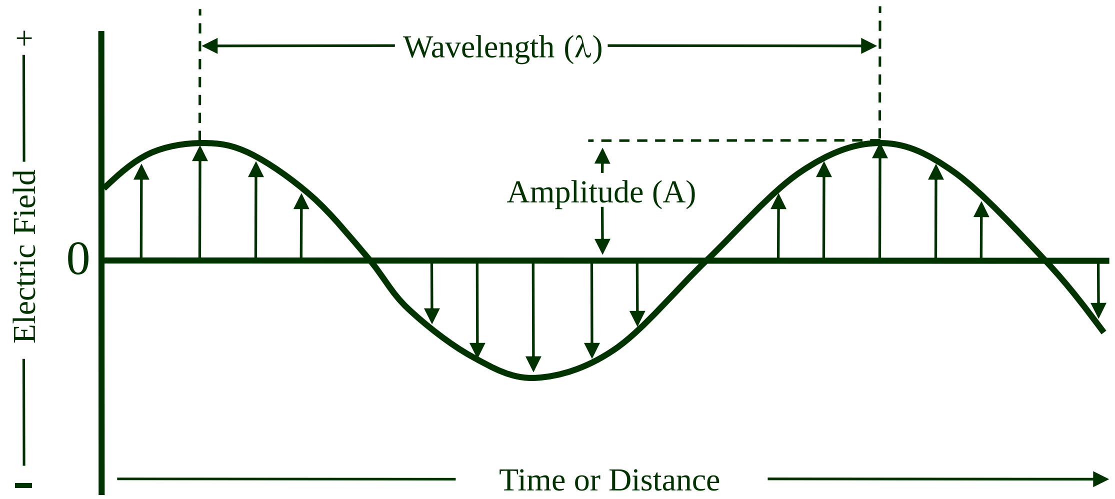
Wave parameters



We Use Symbols to Designate the Various Properties of Waves

- λ is the wavelength of the waves
- ν *is the frequency of the waves*
- *c is the speed of light*

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Definitions:

- ***Period*** **(p)** – the time required for one cycle to pass a fixed point in space.
- ***Frequency*** **(ν)** – the number of cycles which pass a fixed point in space per second.
- ***Amplitude*** **(A)** – The maximum length of the electric vector in the wave (Maximum height of a wave).
- ***Wavelength*** **(λ)** – The distance between two identical adjacent points in a wave (usually maxima or minima).
- ***Wavenumber*** **($\bar{\nu}$)** - The number of waves per cm in units of cm^{-1}.

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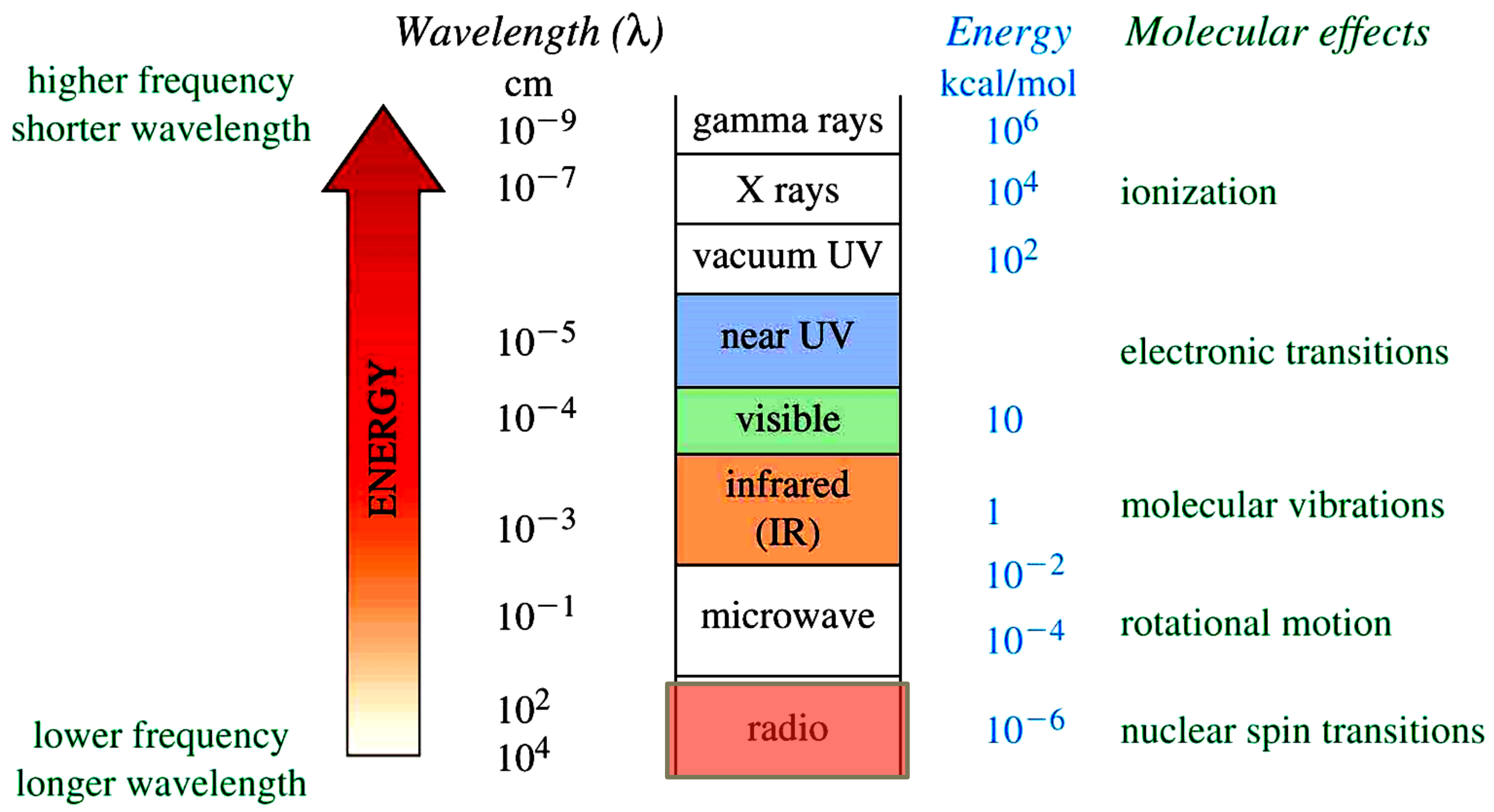
- **Purpose of each Electromagnetic Radiation**

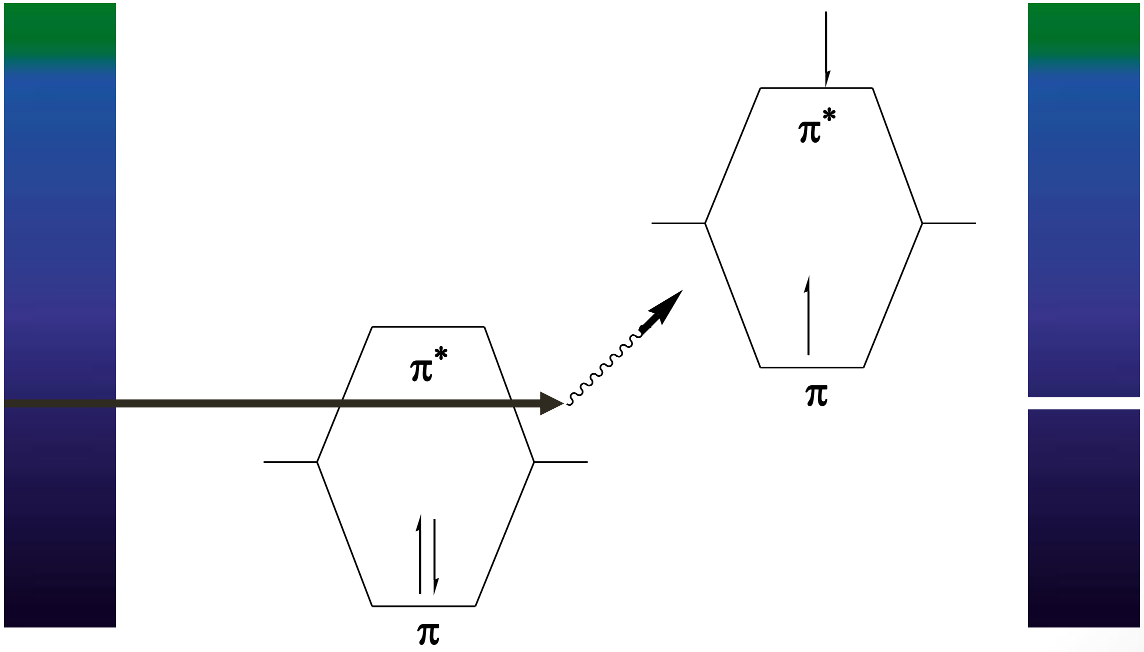


Wavelength (λ) cm		*Energy* kcal/mol	*Molecular effects*
10^{-9}	gamma rays	10^{6}	
10^{-7}	X rays	10^{4}	ionization
	vacuum UV	10^{2}	
10^{-5}	near UV		electronic transitions
10^{-4}	visible	10	
10^{-3}	infrared (IR)	1	molecular vibrations
		10^{-2}	
10^{-1}	microwave	10^{-4}	rotational motion
10^{2} 10^{4}	radio	10^{-6}	nuclear spin transitions

UV Spectroscopy

The Spectroscopic Process

- In UV spectroscopy, the sample is irradiated with the broad spectrum of the UV radiation
- If a particular electronic transition matches the energy of a certain band of UV, it will be absorbed
- The remaining UV light passes through the sample and is observed
- From this residual radiation a spectrum is obtained with "gaps" at these discrete energies – this is called an *absorption spectrum*



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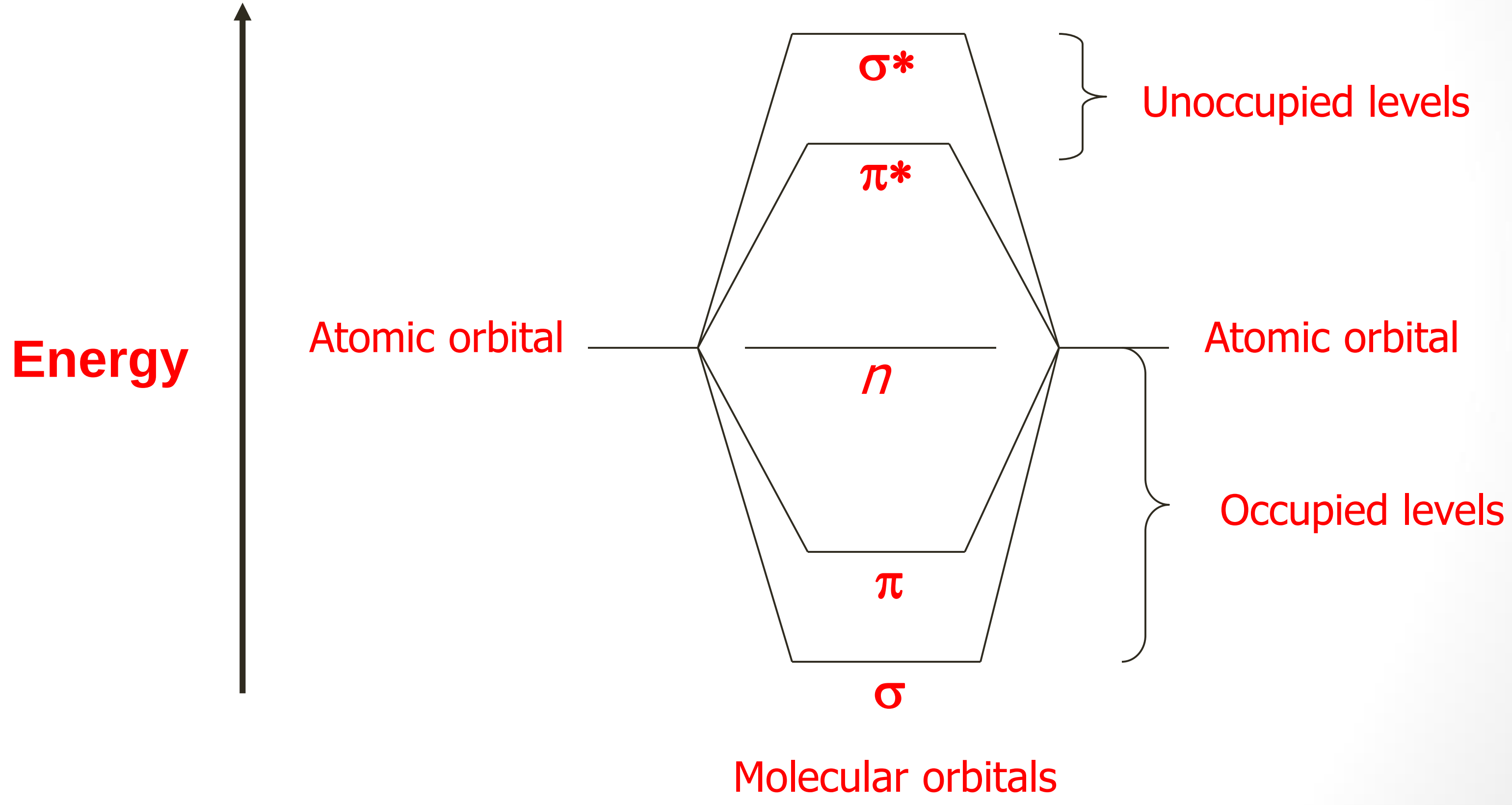
UV Spectroscopy

Observed electronic transitions

- Here is a graphical representation



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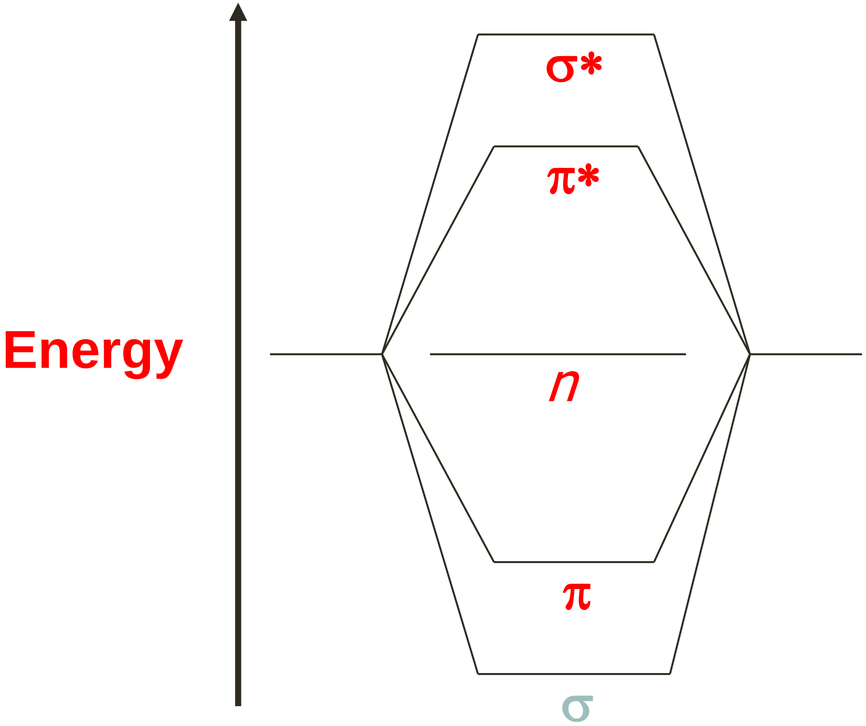
UV Spectroscopy

Observed electronic transitions

- From the molecular orbital diagram, there are several possible electronic transitions that can occur, each of a different relative energy:



$\sigma \longrightarrow \sigma^*$ alkanes

$\sigma \longrightarrow \pi^*$ carbonyls

$\pi \longrightarrow \pi^*$ unsaturated cmpds.

$n \longrightarrow \sigma^*$ O, N, S, halogens

$n \longrightarrow \pi^*$ carbonyls

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UV Spectroscopy

Observed electronic transitions

- Although the UV spectrum extends below 100 nm (high energy), oxygen in the atmosphere is not transparent below 200 nm
- Special equipment to study *vacuum* or *far UV* is required
- Routine organic UV spectra are typically collected from 200-700 nm
- This limits the transitions that can be observed:

$\sigma \longrightarrow \sigma^*$	alkanes	150 nm	
$\sigma \longrightarrow \pi^*$	carbonyls	170 nm	
$\pi \longrightarrow \pi^*$	unsaturated cmpds.	180 nm	**√ - if conjugated!**
$n \longrightarrow \sigma^*$	O, N, S, halogens	190 nm	
$n \longrightarrow \pi^*$	carbonyls	300 nm	√

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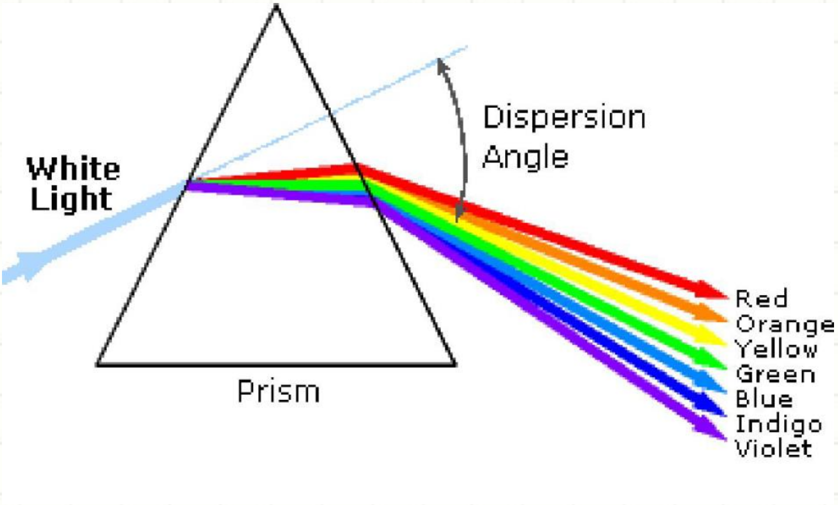
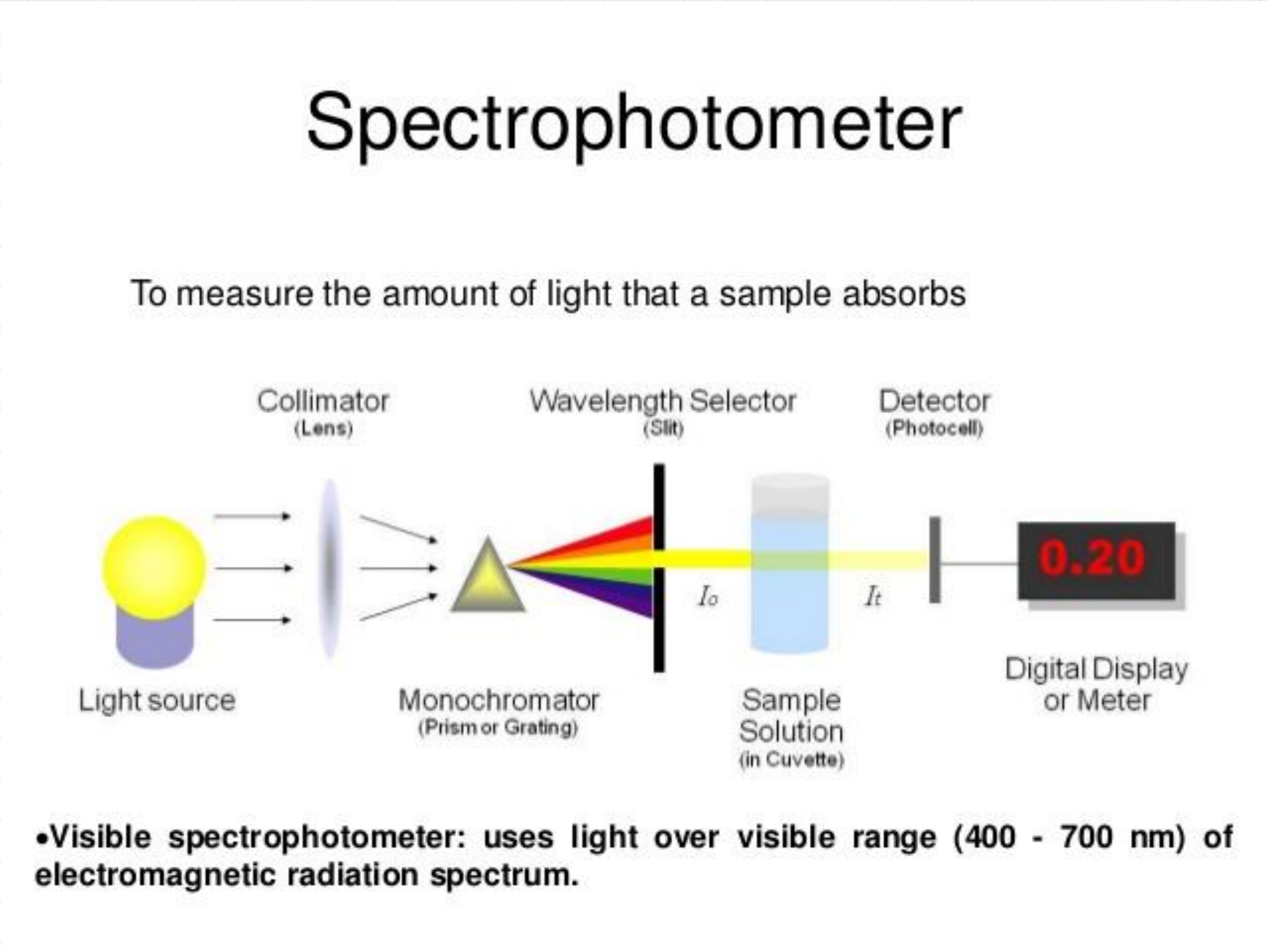
Electromagnetic Radiation



Violet0	400 - 420 nm	Yellow	570 - 585 nm
Indigo	420 - 440 nm	Orange	585 - 620 nm
Blue	440 - 490 nm	Red	620 - 780 nm
Green	490 - 570 nm		

S. Damkondwar, Pune, Maharashtra, India, January, 2013

http://www.slideshare.net/Santachem/uv-visible-spectroscopy-

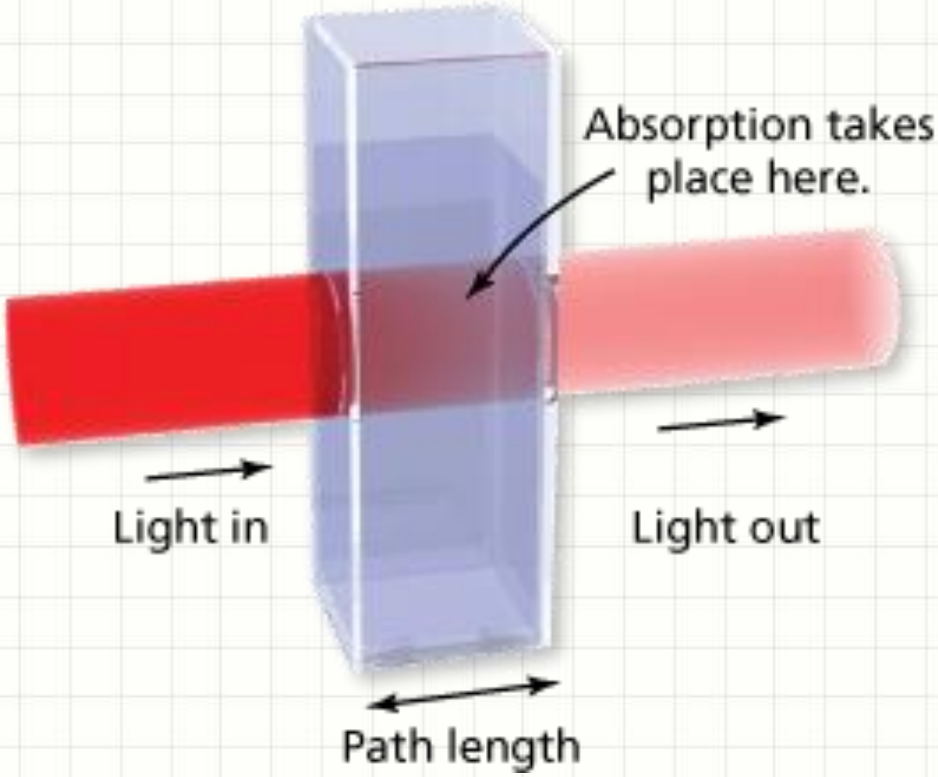


Spectrophotometer

To measure the amount of light that a sample absorbs

- **Visible spectrophotometer: uses light over visible range (400 - 700 nm) of electromagnetic radiation spectrum.**

http://www.slideshare.net/Santachem/uv-visible-spectroscopy



http://www.math.andyou.com/310

http://www.slideshare.net/Santachem/uv-visible-spectroscopy

Absorption: The Beer-Lambert Law

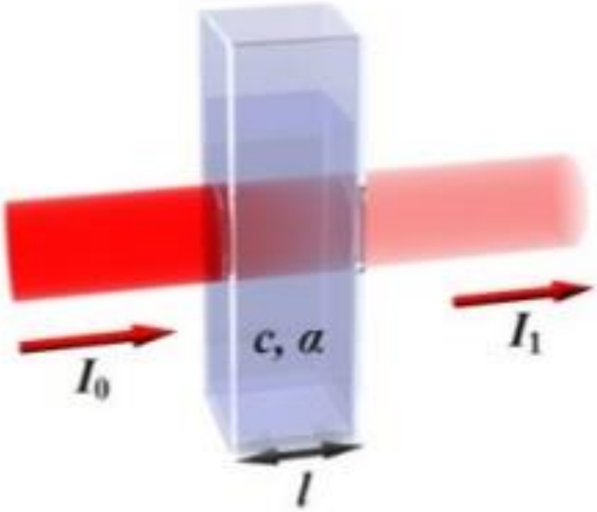
August Beer (1825-1863): Added absorption co-efficient and related to conc. in solution.

Pierre Bouguer

Astronomer: Light is diminished as it passes through the atmosphere.

Johan Lambert

Mathematician, first to prove that π is irrational. No absorption coefficient



$$A = -\log(I_1 / I_0) = \varepsilon c l$$

ϵ: Extinction coefficient

c: Concentration

l: Path length

http://www.slideshare.net/Santachem/uv-visible-spectroscopy

UV Spectroscopy

From an experimental point of view, three other considerations must be made:

- a longer *path length, l,* through the sample will cause more UV light to be absorbed – linear effect
- the greater the *concentration, c,* of the sample, the more UV light will be absorbed – linear effect
- some electronic transitions are more effective at the absorption of photon than others – *molar absorptivity, ε,*
  this may vary by orders of magnitude…

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UV Spectroscopy

The Beer-Lambert Law: $A = \varepsilon c l$

- for most UV spectrometers, l would remain constant (standard cells are typically 1 cm in path length)
- Concentration c is typically varied depending on the strength of absorption observed or expected – typically dilute – sub .001 M
- molar absorptivities ε vary by orders of magnitude:
  - values of 10^4-10^6 are termed *high intensity absorptions*
  - values of 10^3-10^4 are termed *low intensity absorptions*
  - values of 0 to 10^3 are the absorptions of *forbidden transitions*

A is unitless, so the units for ε are cm^{-1} x M^{-1} and are rarely expressed

Since path length and concentration effects can be easily factored out, absorbance simply becomes proportional to ε, and the y-axis is expressed as ε directly or as the logarithm of ε

UV Spectroscopy

Selection Rules

- Not all transitions that are possible are observed

- For an electron to transition, certain quantum mechanical constraints apply – these are called "selection rules"

- For example, an electron cannot change its spin quantum number during a transition – these are "forbidden"
  Other examples include:
  - the number of electrons that can be excited at one time
  - symmetry properties of the molecule
  - symmetry of the electronic states

- To further complicate matters, "forbidden" transitions are sometimes observed (albeit at low intensity) due to other factors

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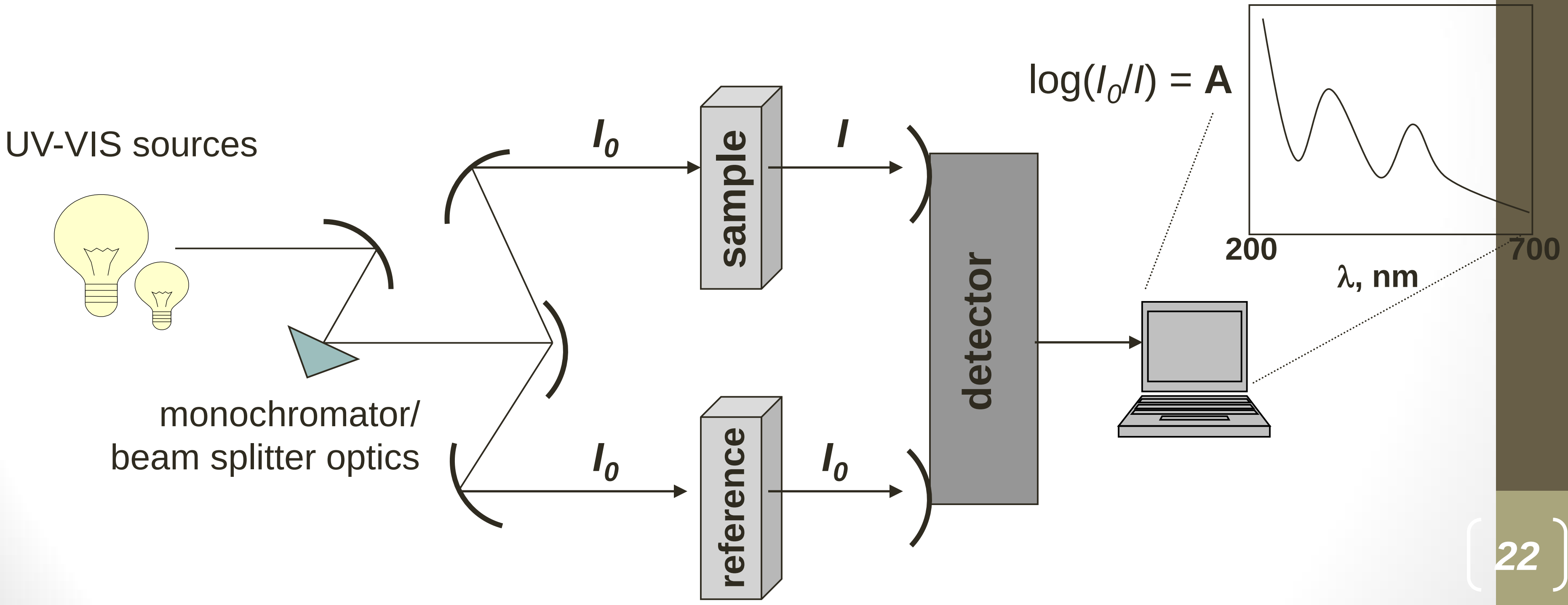
UV Spectroscopy

Instrumentation and Spectra

- Here is a simple schematic that covers most modern UV spectrometers:



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Instrumentation and Spectra,

- Two sources are required to scan the entire UV-VIS band:
  - Deuterium lamp – covers the UV – 200-330
  - Tungsten lamp – covers 330-700

- As with the dispersive IR, the lamps illuminate the entire band of UV or visible light; the monochromator (grating or prism) gradually changes the small bands of radiation sent to the beam splitter

- The beam splitter sends a separate band to a cell containing the sample solution and a reference solution

- The detector measures the difference between the transmitted light through the sample (I) vs. the incident light (I_0) and sends this information to the recorder

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UV Spectroscopy

Instrumentation – Sample Handling

- Solvents must be transparent in the region to be observed; the wavelength where a solvent is no longer transparent is referred to as the cutoff

- Since spectra are only obtained up to 200 nm, solvents typically only need to lack conjugated π systems or carbonyls

Common solvents and cutoffs:

acetonitrile	190
chloroform	240
cyclohexane	195
1,4-dioxane	215
95% ethanol	205
n-hexane	201
methanol	205
isooctane	195
water	190

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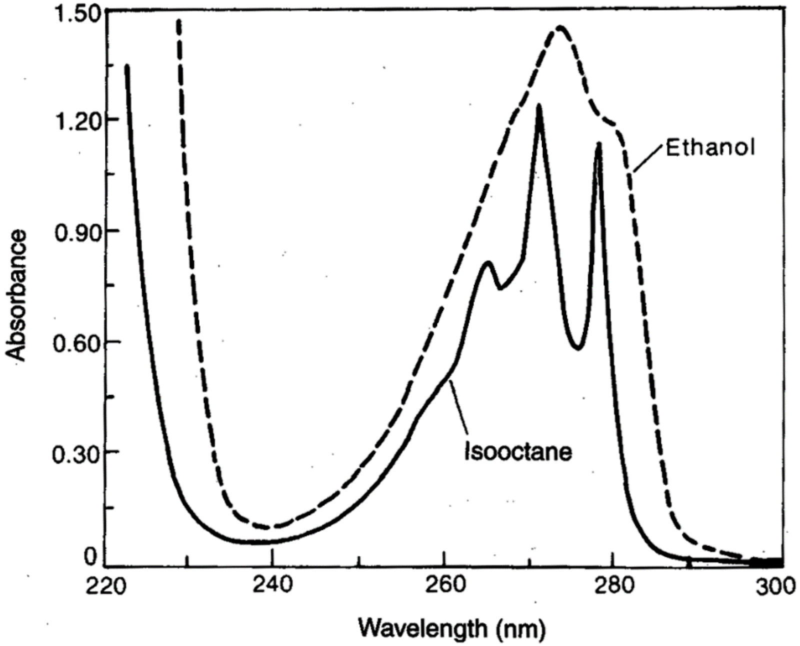
UV Spectroscopy

Instrumentation – Sample Handling

- Additionally solvents must preserve the fine structure (where it is actually observed in UV!) where possible
- H-bonding further complicates the effect of vibrational and rotational energy levels on electronic transitions, dipole-dipole interacts less so
- The more non-polar the solvent, the better (this is not always possible)



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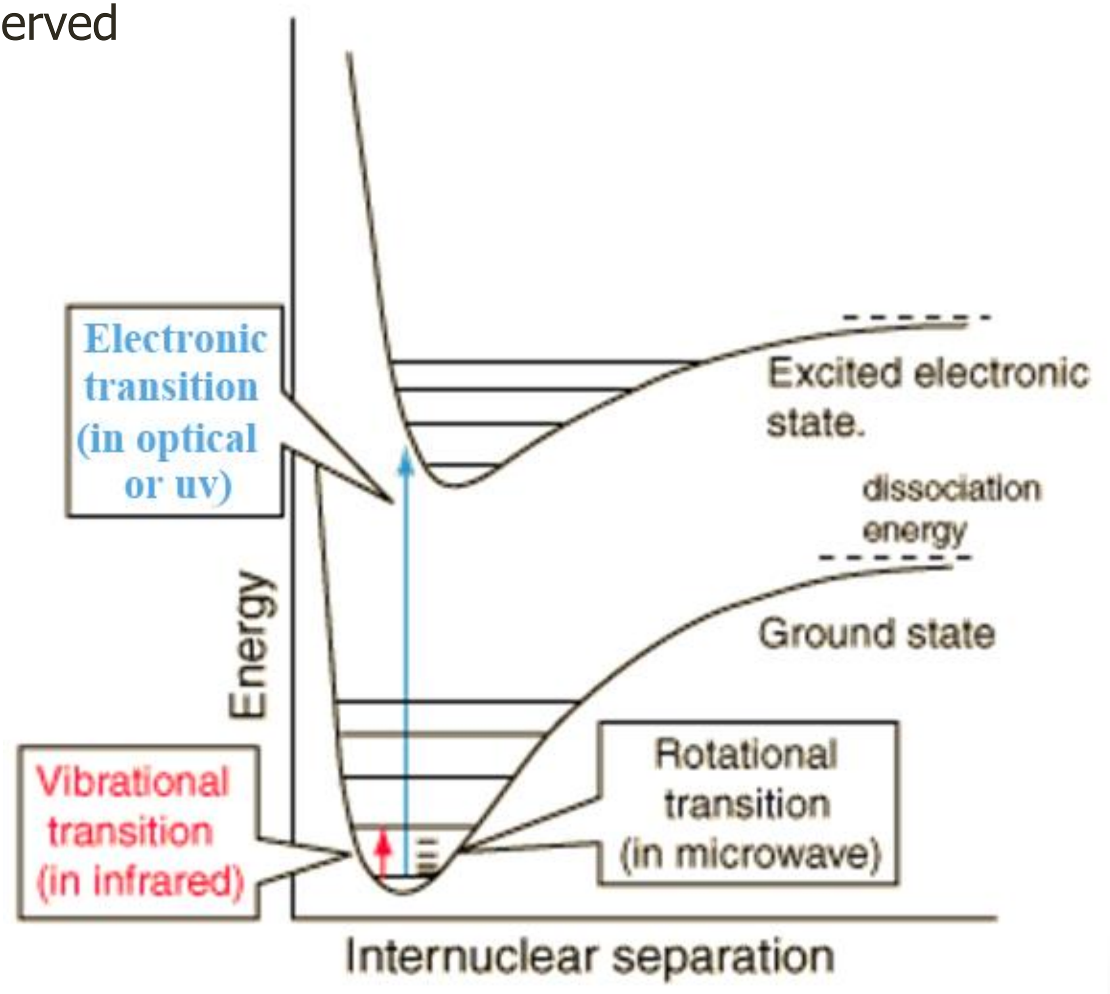
UV Spectroscopy

Band Structure

- When these energy levels are superimposed, the effect can be readily explained – any transition has the possibility of being observed



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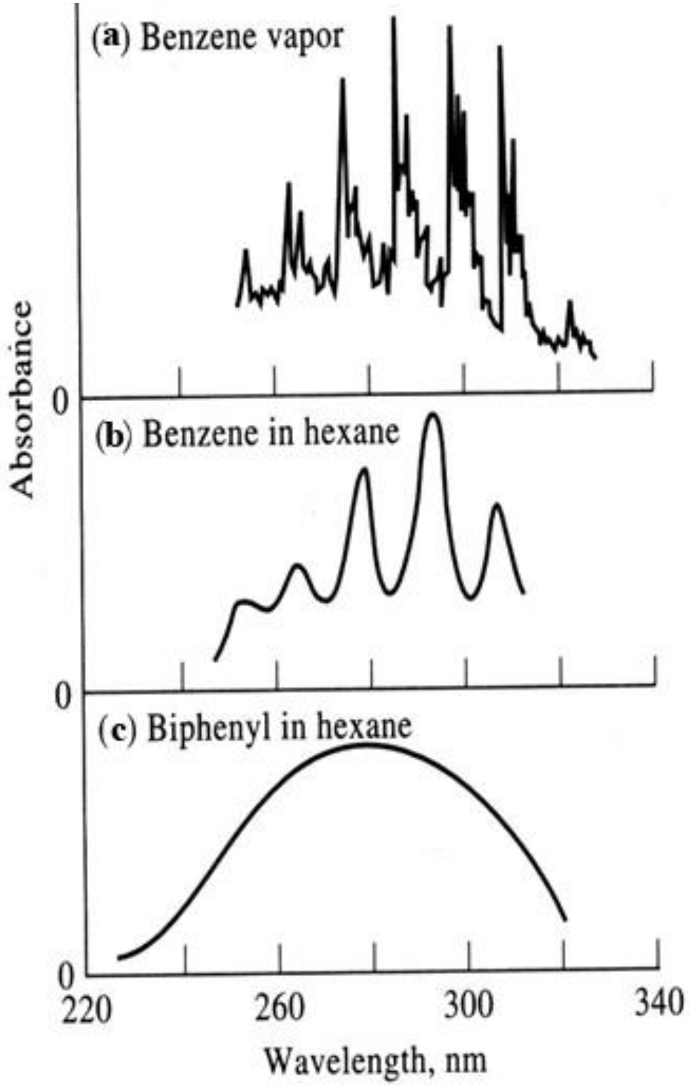
MOLECULAR ABSORPTION SPECTRA

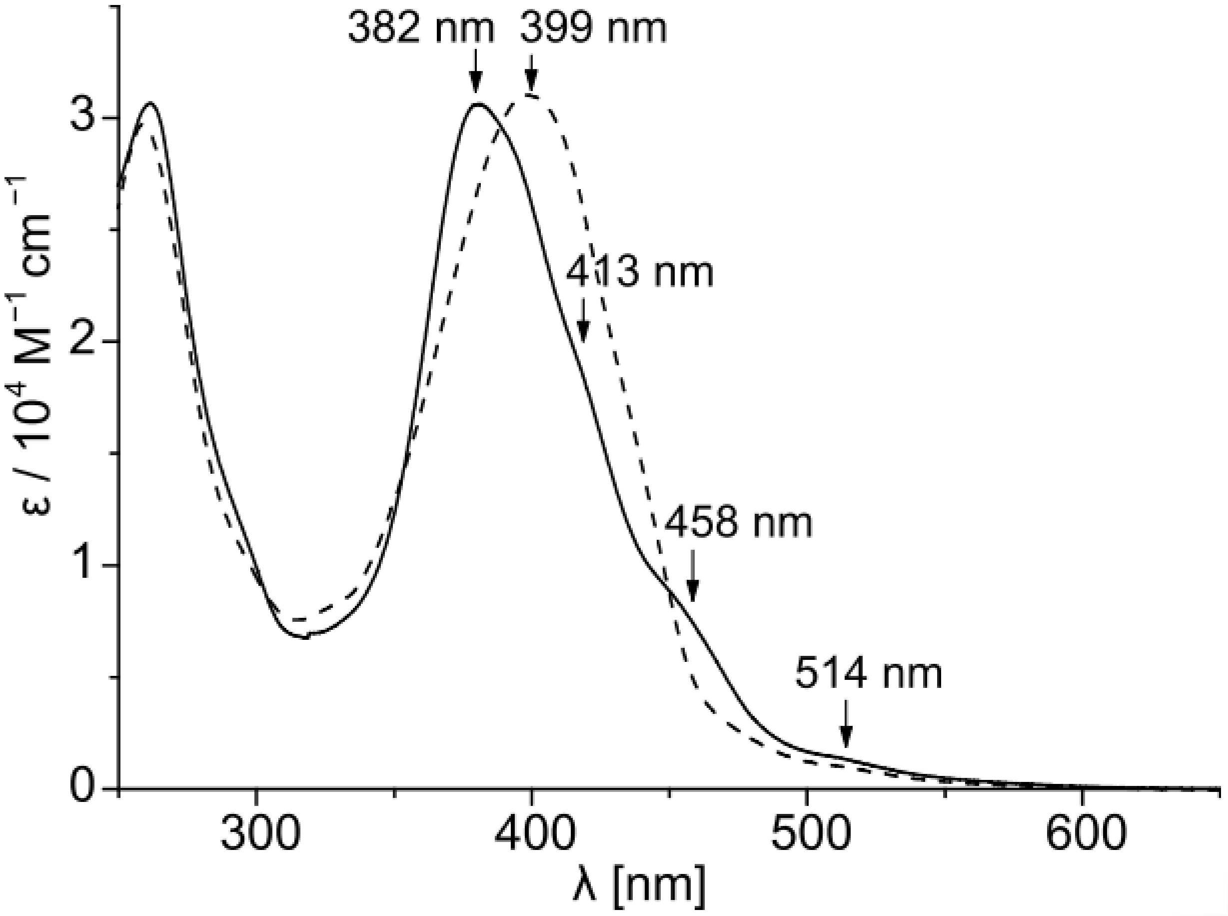


- The sharpness of molecular absorption spectra also depends on the state of the sample.
- Figure (a) shows an *absorption band* due to transitions between electronic-vibrational-rotational states
- Figure (c) shows a *continuous spectra* due to the sample is in the condensed state. In condensed states the spectra broaden due to molecular collisions.

https://ashomarconfidential.files.wordpress.com/2012/08/spectroscopy-methods.ppt

UV Spectroscopy

- Due to the lack of any fine structure, spectra are rarely shown in their raw form, rather, the peak maxima are simply reported as a numerical list of “lamba max” values or λ_{max}



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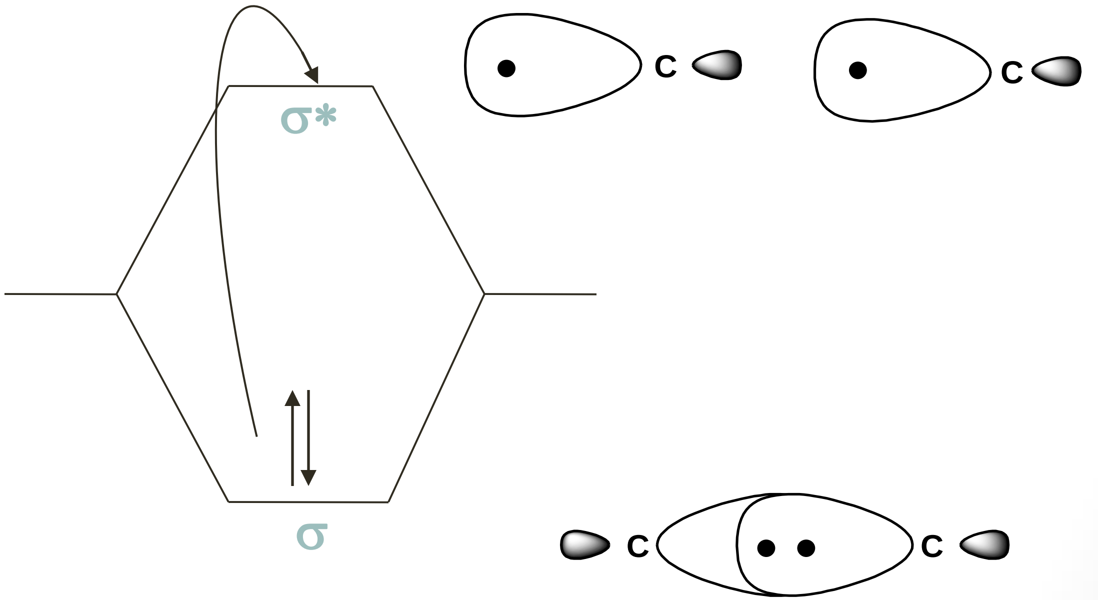
UV Spectroscopy

Chromophores

1. Alkanes – only posses σ-bonds and no lone pairs of electrons, so only the high energy σ → σ* transition is observed in the far UV

   This transition is destructive to the molecule, causing cleavage of the σ-bond



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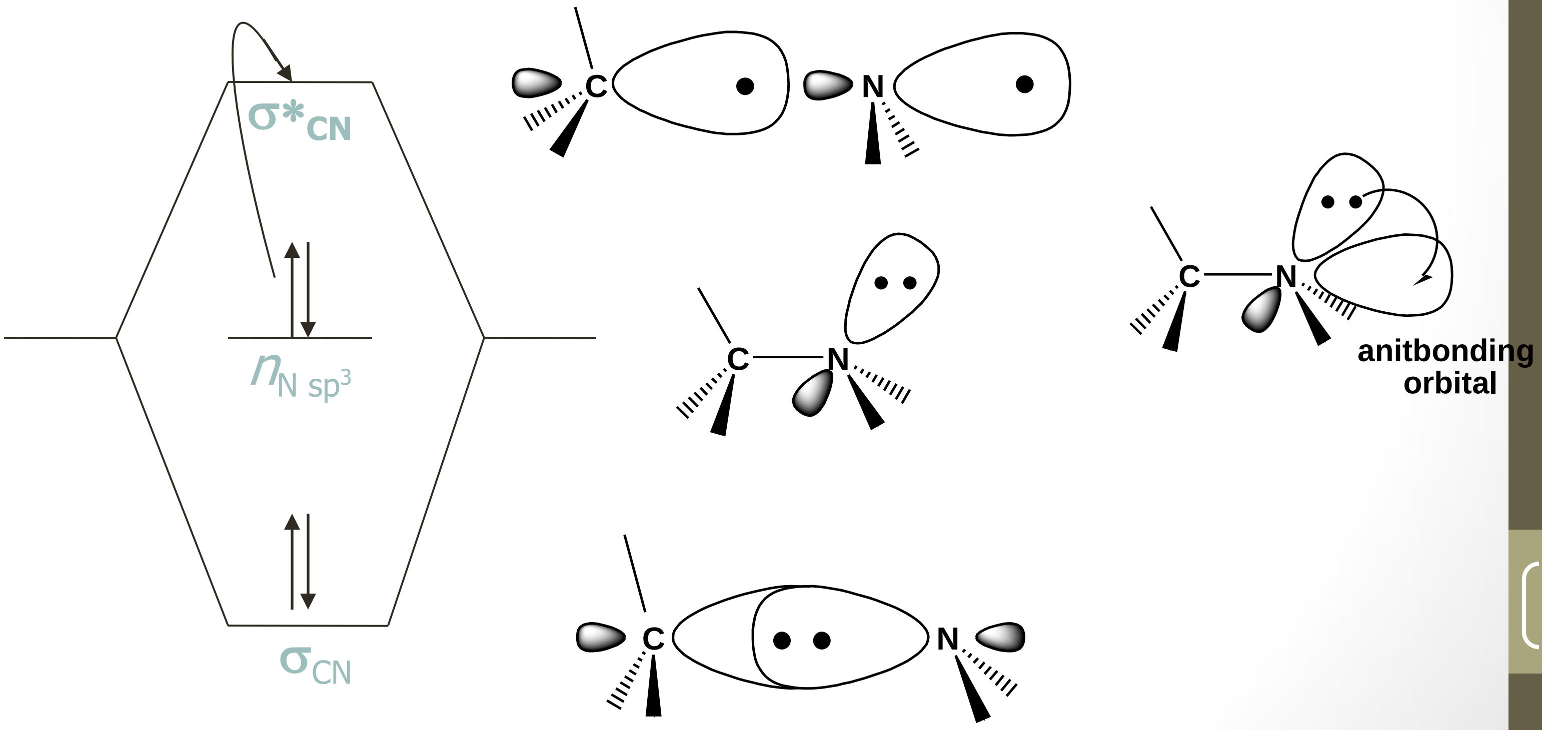
UV Spectroscopy

Chromophores

2. Alcohols, ethers, amines and sulfur compounds – in the cases of simple, aliphatic examples of these compounds the $n \rightarrow \sigma^*$ is the most often observed transition; like the alkane $\sigma \rightarrow \sigma^*$ it is most often at shorter λ than 200 nm

   Note how this transition occurs from the HOMO to the LUMO



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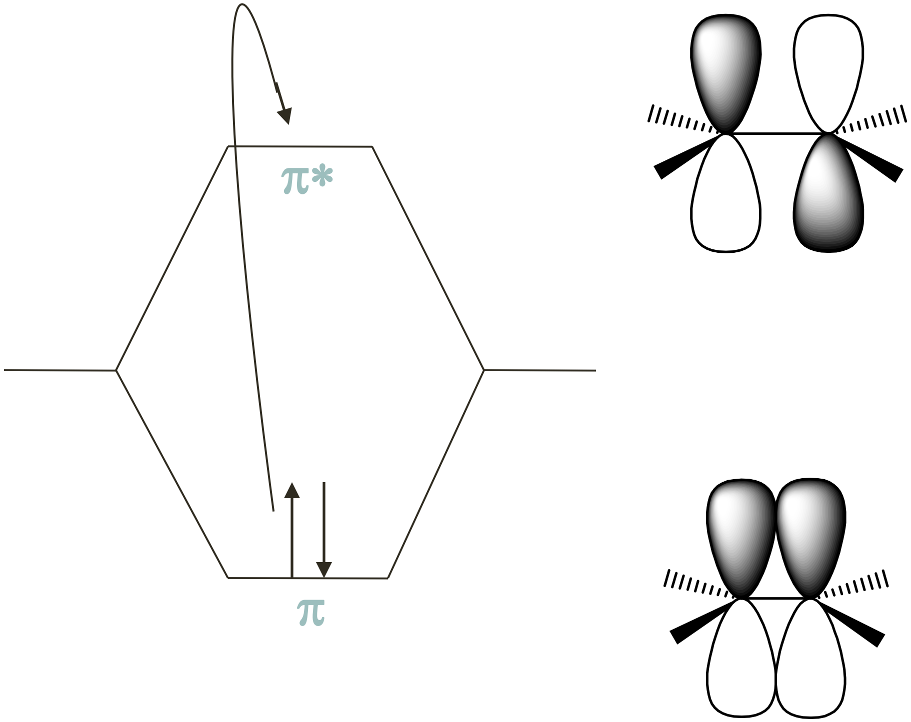
UV Spectroscopy

Chromophores

3. Alkenes and Alkynes – in the case of isolated examples of these compounds the π → π* is observed at 175 and 170 nm, respectively

   Even though this transition is of lower energy than σ → σ*, it is still in the far UV – however, the transition energy is sensitive to substitution



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Chromophores

4. Carbonyls – unsaturated systems incorporating N or O can undergo *n* → π* transitions (~285 nm) in addition to π → π*

   Despite the fact this transition is forbidden by the selection rules (ε = 15), it is the most often observed and studied transition for carbonyls

   This transition is also sensitive to substituents on the carbonyl

   Similar to alkenes and alkynes, non-substituted carbonyls undergo the π → π* transition in the vacuum UV (188 nm, ε = 900); sensitive to substitution effects

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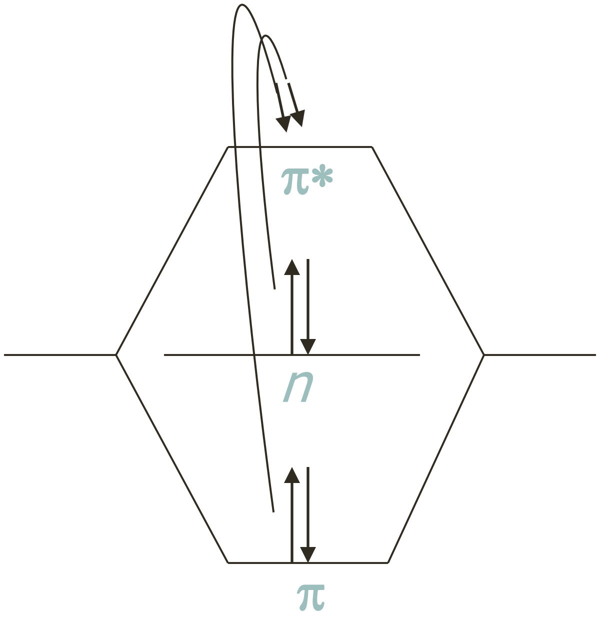
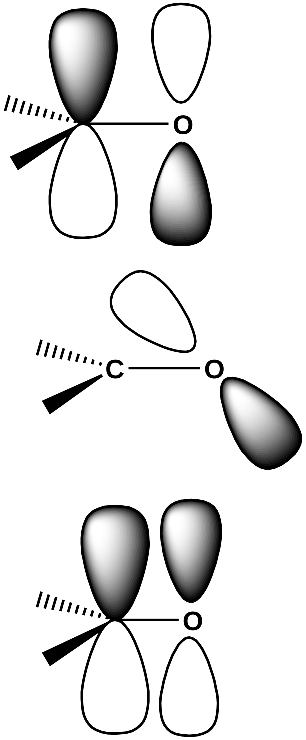
UV Spectroscopy

Chromophores

4. Carbonyls – *n* → π* transitions (~285 nm); π → π* (188 nm)





It has been determined from spectral studies, that carbonyl oxygen more approximates *sp* rather than sp^2 !

σ_{CO} transitions omitted for clarity

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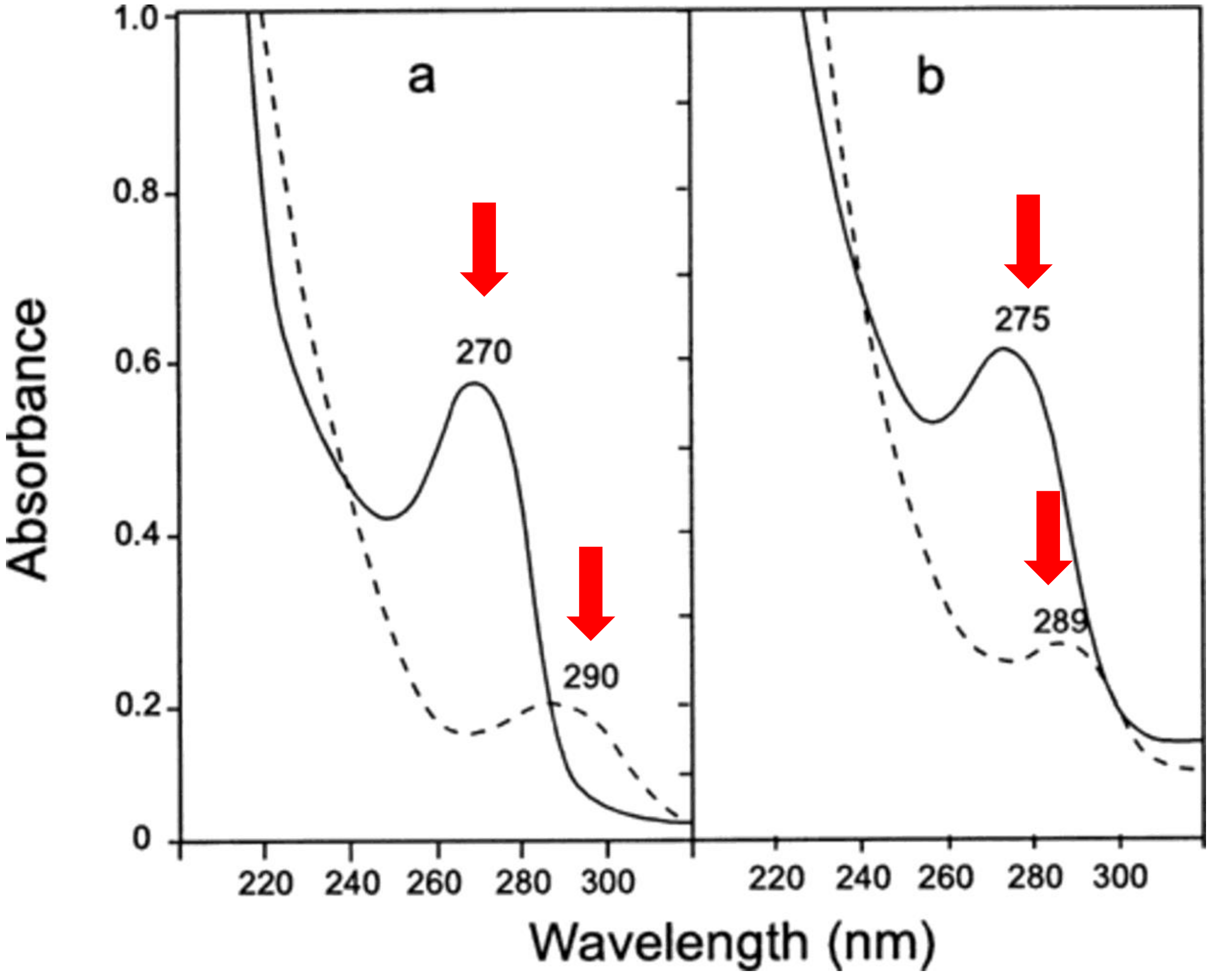
Forbidden *n* → π* transitions



UV Spectroscopy

Chromophores - Substituent Effects

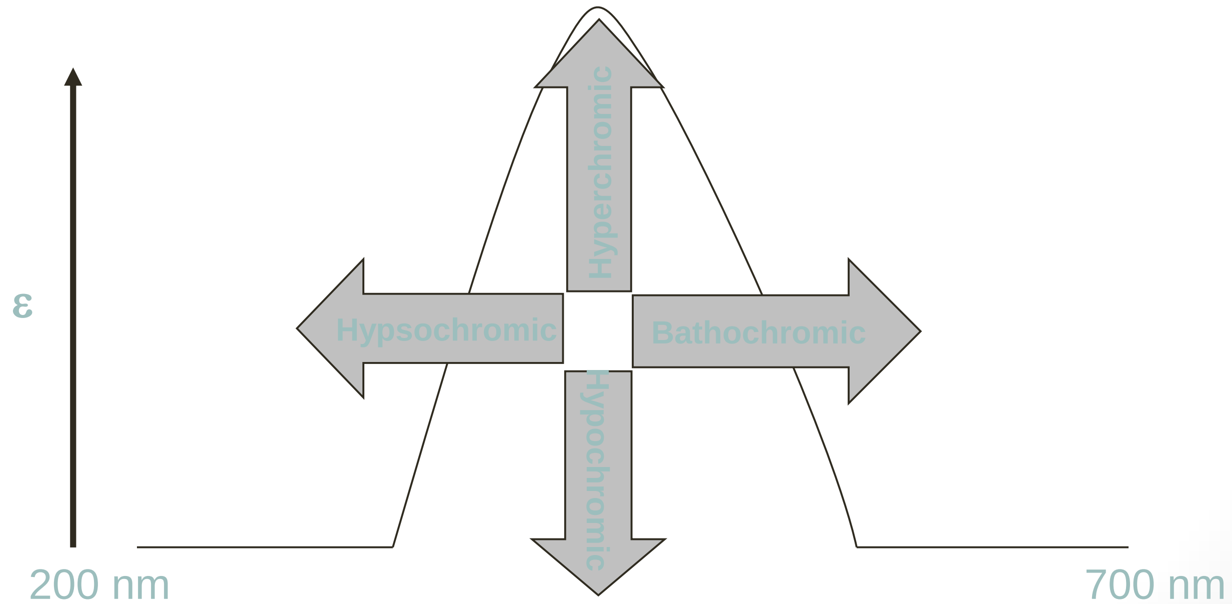
General – Substituents may have any of four effects on a chromophore

i. Bathochromic shift (red shift) – a shift to longer λ; lower energy

ii. Hypsochromic shift (blue shift) – shift to shorter λ; higher energy

iii. Hyperchromic effect – an increase in intensity

iv. Hypochromic effect – a decrease in intensity



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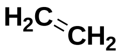
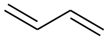
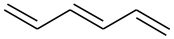
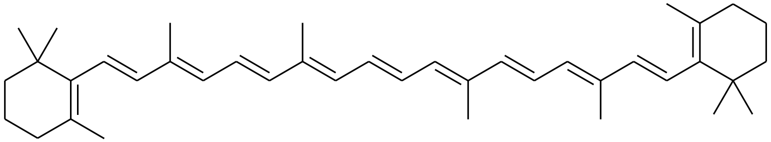
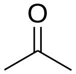
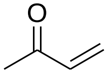
UV Spectroscopy

Chromophores - Substituent Effects

1. Conjugation – most efficient means of bringing about a bathochromic and hyperchromic shift of an unsaturated chromophore:

		λ_{max} nm	ε
		175	15,000
		217	21,000
		258	35,000
 β-carotene		465	125,000
	$n \rightarrow \pi^*$	280	12
	$\pi \rightarrow \pi^*$	189	900
	$n \rightarrow \pi^*$	280	27
	$\pi \rightarrow \pi^*$	213	7,100

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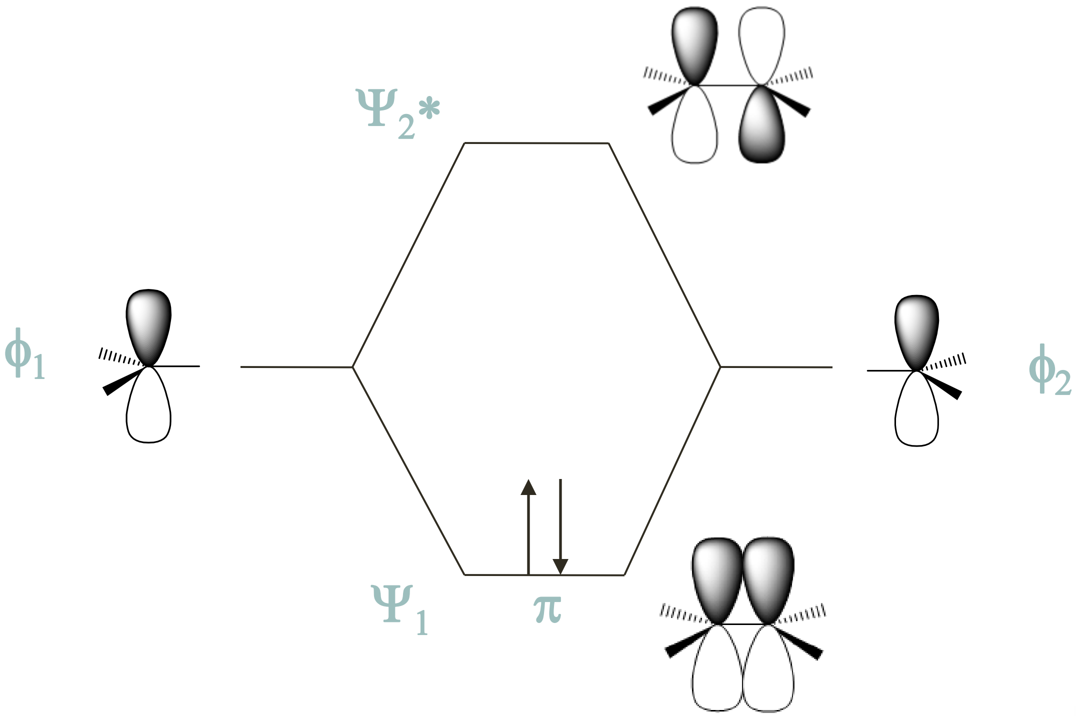
UV Spectroscopy

Chromophores - Substituent Effects

1. Conjugation – Alkenes

   The observed shifts from conjugation imply that an increase in conjugation decreases the energy required for electronic excitation

   From molecular orbital (MO) theory two atomic *p* orbitals, ϕ_1 and ϕ_2 from two sp^2 hybrid carbons combine to form two MOs Ψ_1 and Ψ_2^* in ethylene



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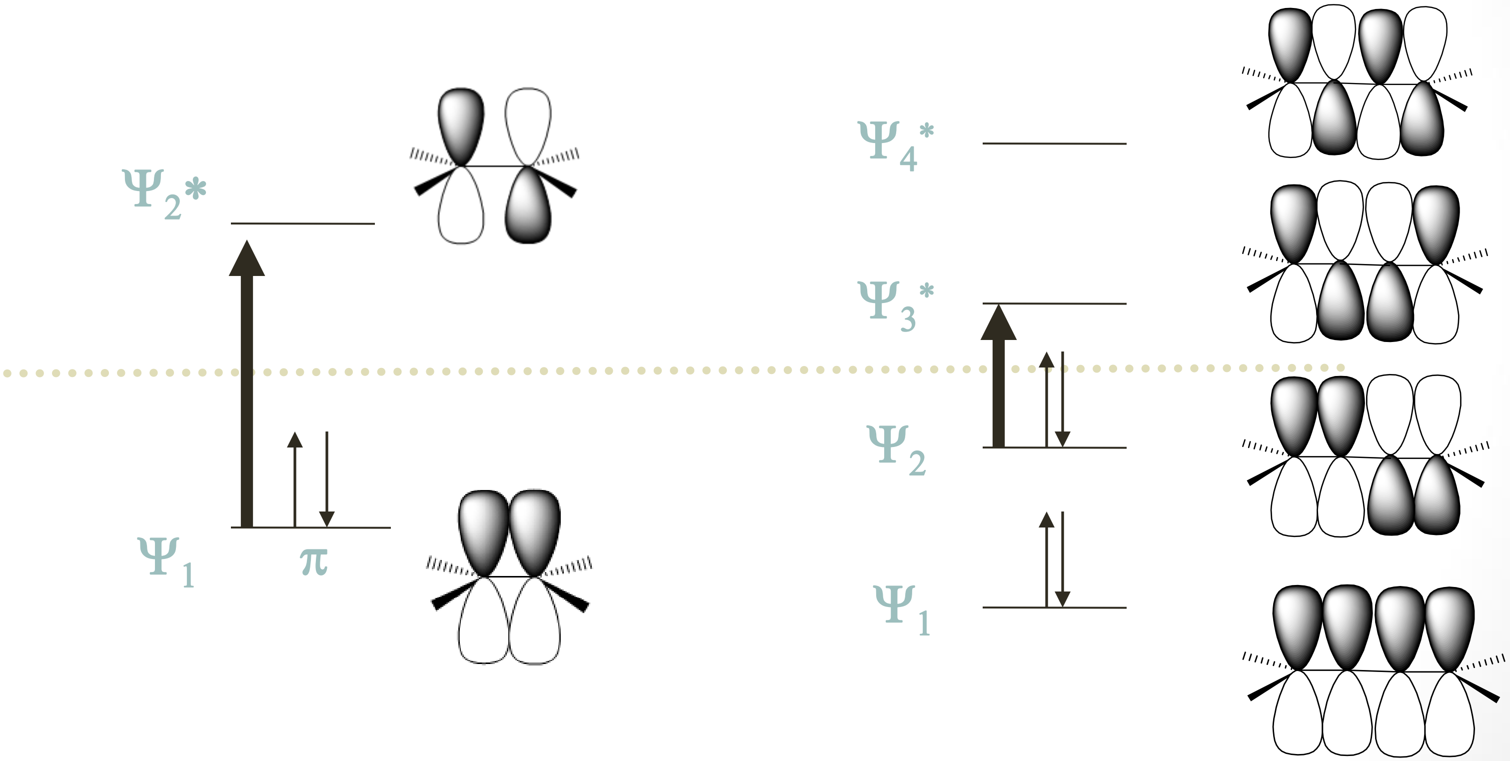
UV Spectroscopy

Chromophores - Substituent Effects

2. Conjugation – Alkenes

   When we consider butadiene, we are now mixing 4 p orbitals giving 4 MOs of an energetically symmetrical distribution compared to ethylene



ΔE for the HOMO → LUMO transition is **reduced**

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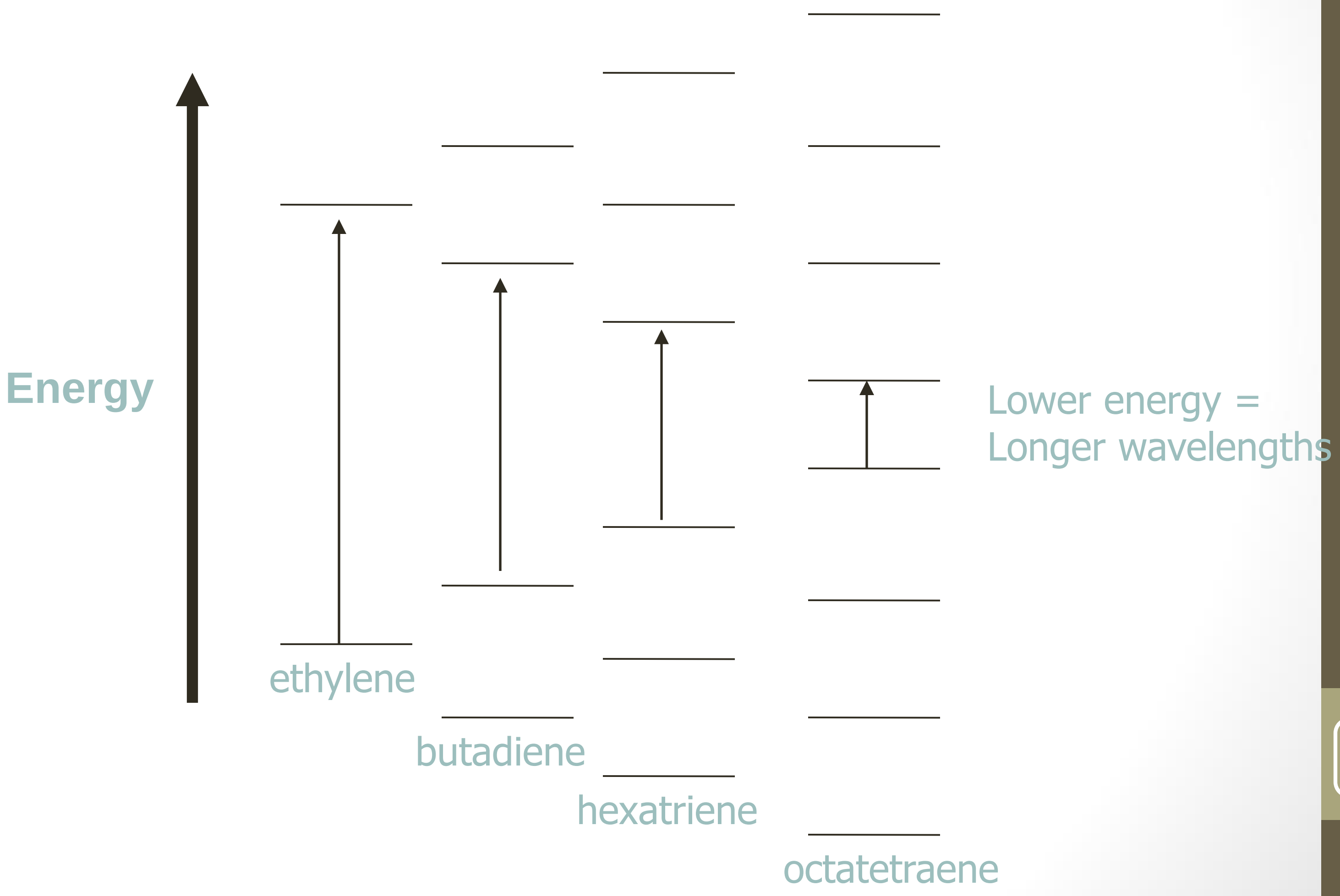
UV Spectroscopy

Chromophores - Substituent Effects

2. Conjugation – Alkenes

   Extending this effect out to longer conjugated systems the energy gap becomes progressively smaller:



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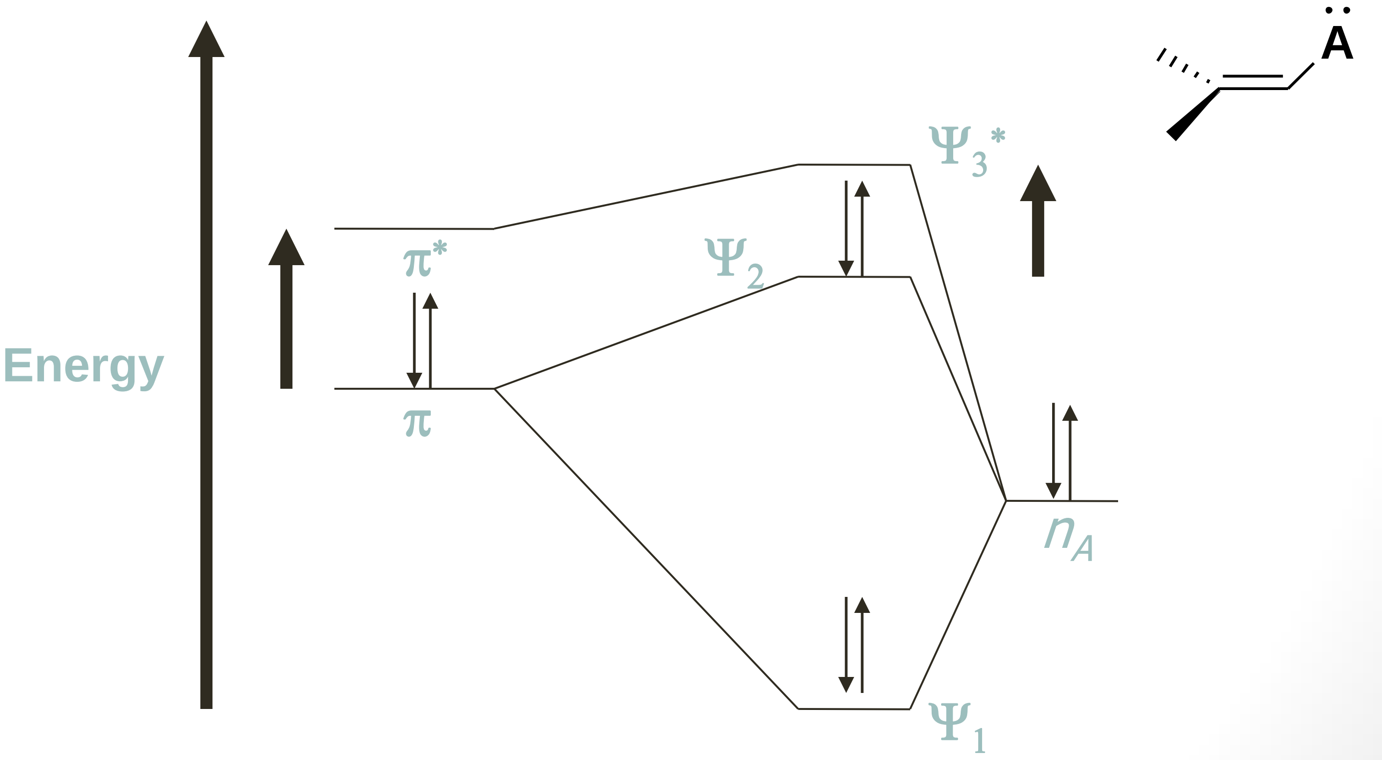
UV Spectroscopy

Chromophores - Substituent Effects

2. Conjugation – Alkenes
   Similarly, the lone pairs of electrons on N, O, S, X can extend conjugated systems – auxochromes
   Here we create 3 MOs – this interaction is not as strong as that of a conjugated π-system



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UV Spectroscopy

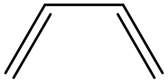
Structure Determination

Dienes

1. General Features

For acyclic butadiene, two conformers are possible – *s-cis* and *s-trans*

s-trans



s-cis

The *s-cis* conformer is at an overall higher potential energy than the *s-trans*; therefore the HOMO electrons of the conjugated system have less of a jump to the LUMO – lower energy, longer wavelength

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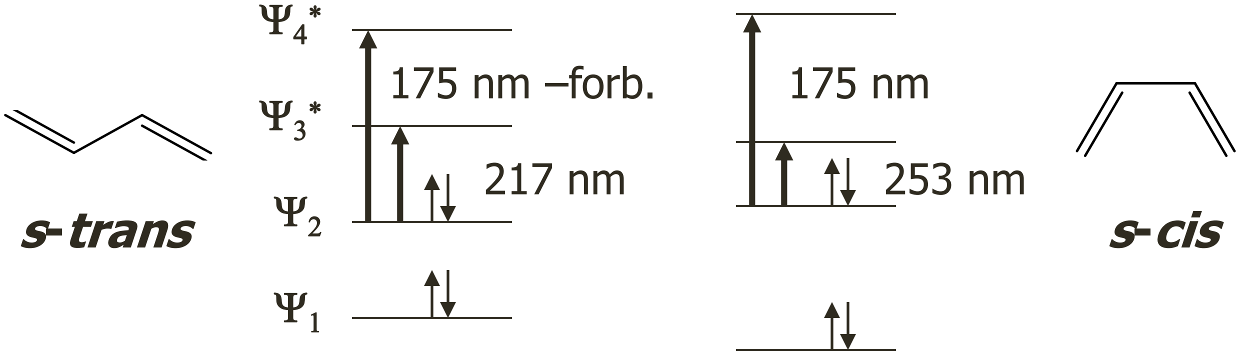
UV Spectroscopy

Structure Determination

Dienes

1. General Features

Two possible $\pi \rightarrow \pi^*$ transitions can occur for butadiene $\Psi_2 \rightarrow \Psi_3^*$ and $\Psi_2 \rightarrow \Psi_4^*$



The $\Psi_2 \rightarrow \Psi_4^*$ transition is not typically observed:

- The energy of this transition places it outside the region typically observed – 175 nm
- For the more favorable *s-trans* conformation, this transition is forbidden

The $\Psi_2 \rightarrow \Psi_3^*$ transition is observed as an intense absorption

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UV Spectroscopy

Structure Determination

Dienes

2. Woodward-Fieser Rules - Dienes

The rules begin with a base value for λ_{max} of the chromophore being observed:

acyclic butadiene = 217 nm

The incremental contribution of substituents is added to this base value from the group tables:

Group	Increment
Extended conjugation	+30
Each exo-cyclic C=C	+5
Alkyl	+5
$-OCOCH_3$	+0
-OR	+6
-SR	+30
-Cl, -Br	+5
$-NR_2$	+60

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UV Spectroscopy

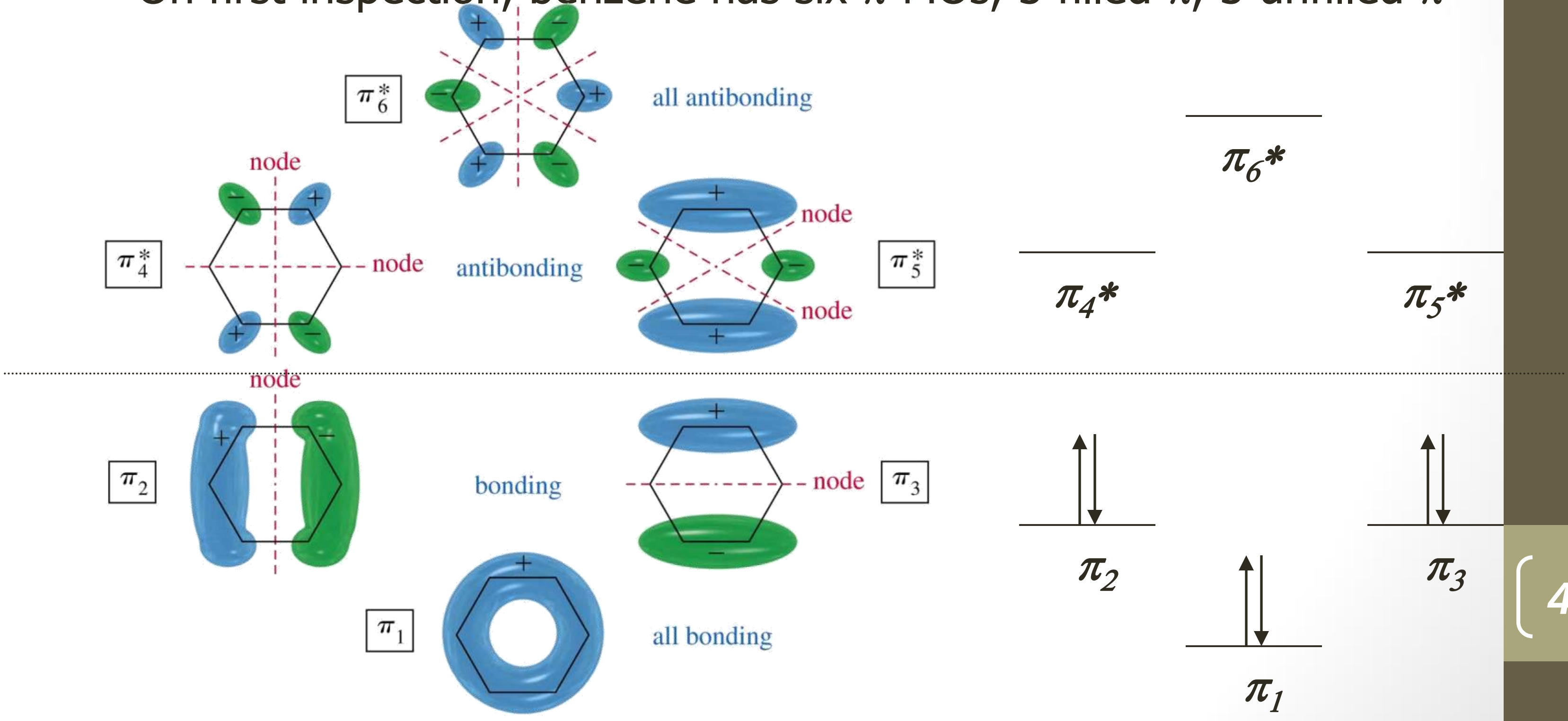
Structure Determination

Aromatic Compounds

1. General Features

Although aromatic rings are among the most widely studied and observed chromophores, the absorptions that arise from the various electronic transitions are complex

On first inspection, benzene has six π-MOs, 3 filled π, 3 unfilled π*



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UV Spectroscopy

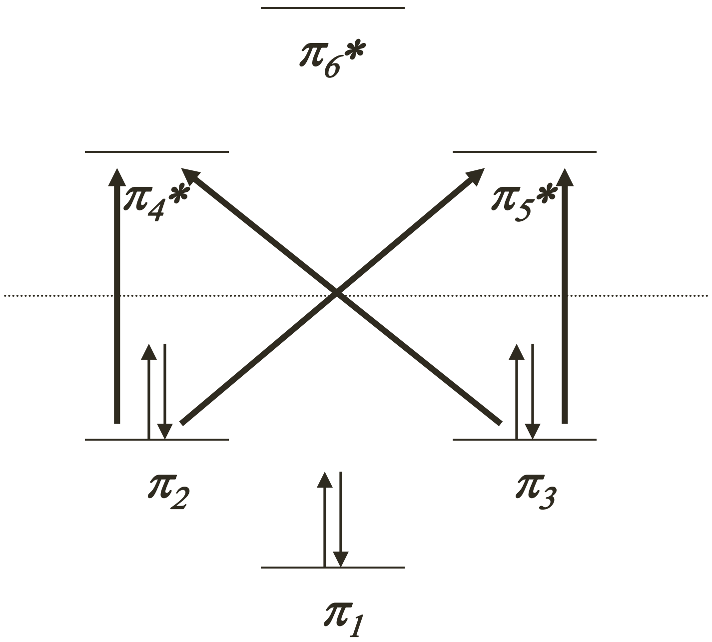
Structure Determination

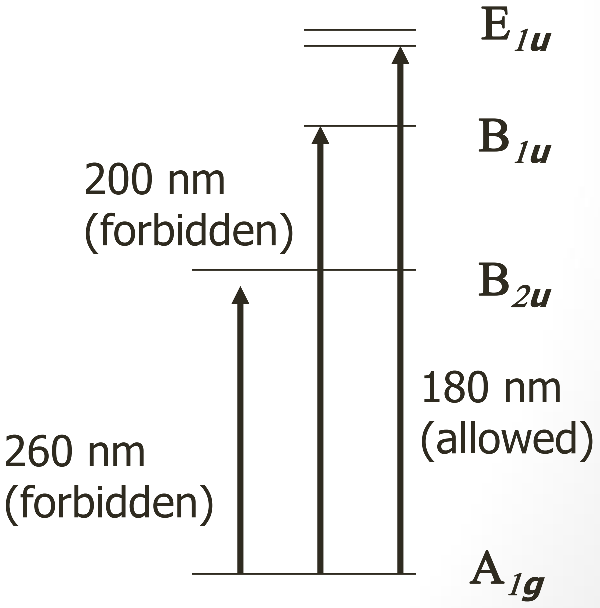
Aromatic Compounds

1. General Features

   One would expect there to be four possible HOMO-LUMO π → π* transitions at observable wavelengths (conjugation)

   Due to symmetry concerns and selection rules, the actual transition energy states of benzene are illustrated at the right:





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UV Spectroscopy

Structure Determination

Aromatic Compounds

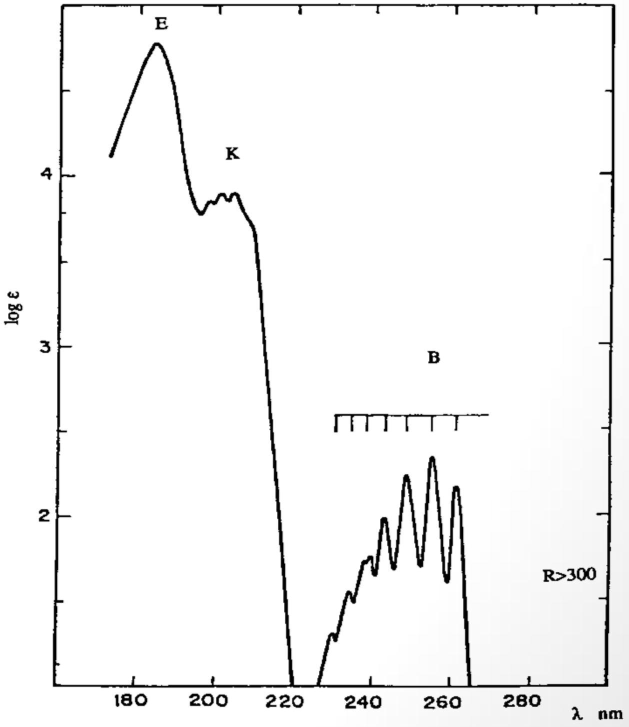
1. General Features

The allowed transition (ε = 47,000) is not in the routine range of UV obs. at 180 nm, and is referred to as the *primary band*

The forbidden transition (ε = 7400) is observed if substituent effects shift it into the obs. region; this is referred to as the *second primary band*

At 260 nm is another forbidden transition (ε = 230), referred to as the *secondary band.*

This transition is fleetingly allowed due to the disruption of symmetry by the vibrational energy states, the overlap of which is observed in what is called *fine structure*



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UV Spectroscopy

Structure Determination

Aromatic Compounds

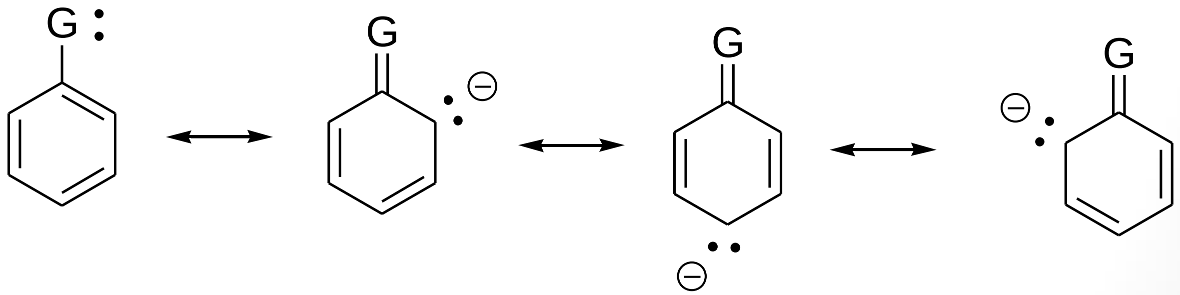
2. Substituent Effects

   a. Substituents with Unshared Electrons

      - If the group attached to the ring bears *n* electrons, they can induce a shift in the primary and secondary absorption bands

      - Non-bonding electrons extend the π-system through resonance – lowering the energy of transition π → π*

      - More available *n*-pairs of electrons give greater shifts



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UV Spectroscopy

Structure Determination

Aromatic Compounds

2. Substituent Effects
   a. Substituents with Unshared Electrons
      - pH can change the nature of the substituent group
      - deprotonation of oxygen gives more available *n*-pairs, *lowering* transition energy
      - protonation of nitrogen eliminates the *n*-pair, *raising* transition energy

	Primary		**Secondary**	
Substituent	λ_{max}	ε	λ_{max}	ε
-H	203.5	7,400	254	204
-OH	211	6,200	270	1,450
$-O^-$	235	9,400	287	2,600
$-NH_2$	230	8,600	280	1,430
$-NH_3^+$	203	7,500	254	169
-C(O)OH	230	11,600	273	970
$-C(O)O^-$	224	8,700	268	560

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UV Spectroscopy

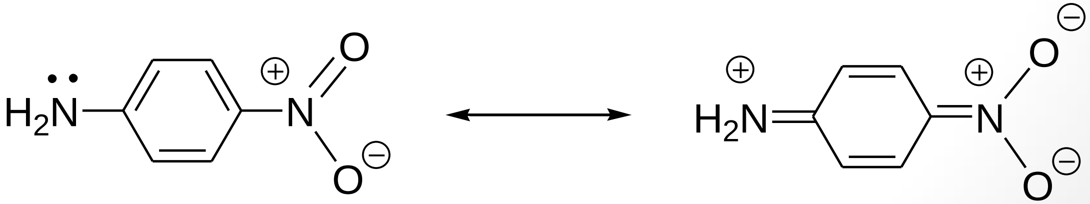
Structure Determination

Aromatic Compounds

2. Substituent Effects

d. Di-substituted and multiple group effects

- With di-substituted aromatics, it is necessary to consider both groups
- If both groups are electron donating or withdrawing, the effect is similar to the effect of the stronger of the two groups as if it were a *mono* - substituted ring
- If one group is electron withdrawing and one group electron donating and they are *para* - to one another, the magnitude of the shift is greater than the sum of both the group effects
- Consider *p* - nitroaniline:



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UV Spectroscopy

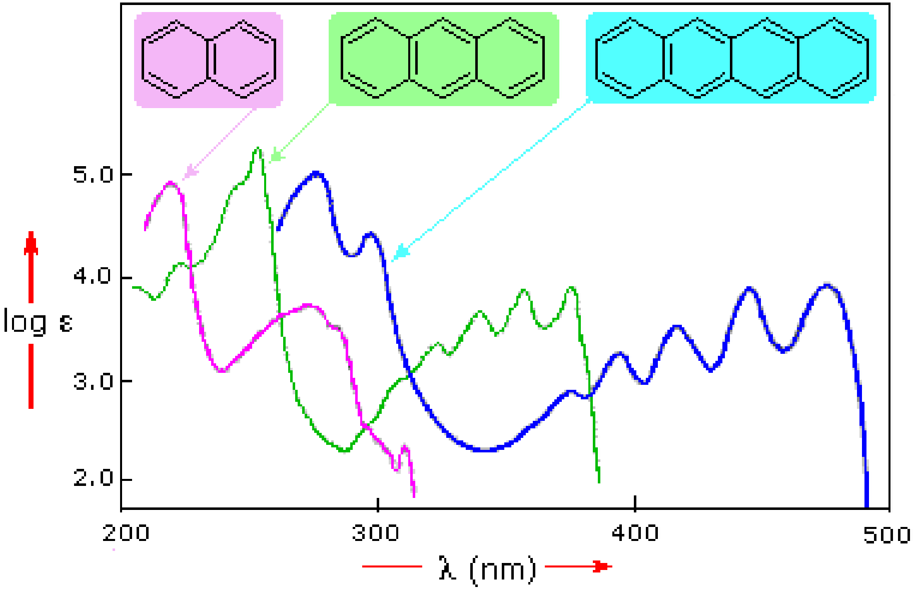
Structure Determination

Aromatic Compounds

2. Substituent Effects

d. Polynuclear aromatics

- When the number of fused aromatic rings increases, the λ for the primary and secondary bands also increase



- For heteroaromatic systems spectra become complex with the addition of the *n* → π* transition and ring size effects and are unique to each case

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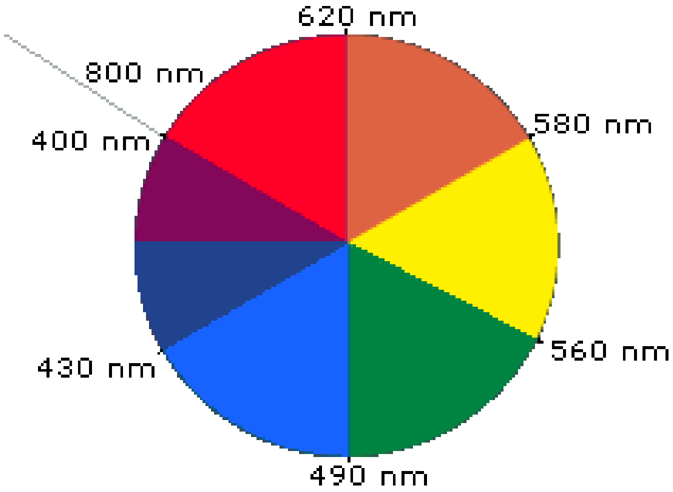
UV Spectroscopy

Visible Spectroscopy

Color

1. General
   - When white (continuum of λ) light passes through, or is reflected by a surface, those ls that are absorbed are removed from the transmitted or reflected light respectively
   - What is "seen" is the complimentary colors (those that are not absorbed)
   - This is the origin of the "color wheel"



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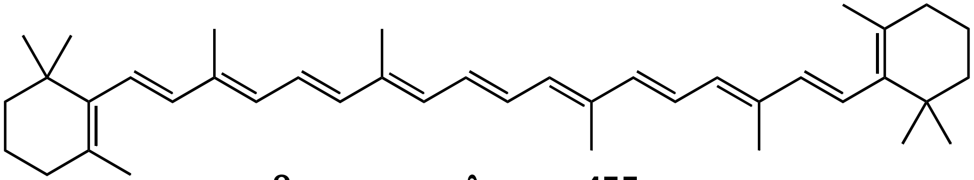
UV Spectroscopy

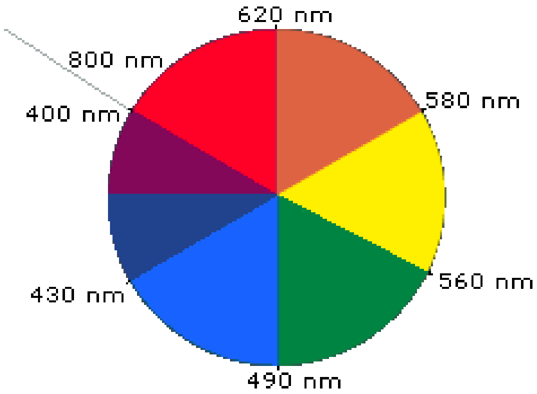
Visible Spectroscopy

Color

1. General
   - Organic compounds that are "colored" are typically those with extensively conjugated systems (typically more than five)
   - Consider β-carotene



β-carotene, λ_{max} = 455 nm



λ_{max} is at 455 – in the far blue region of the spectrum – this is absorbed

The remaining light has the complementary color of orange

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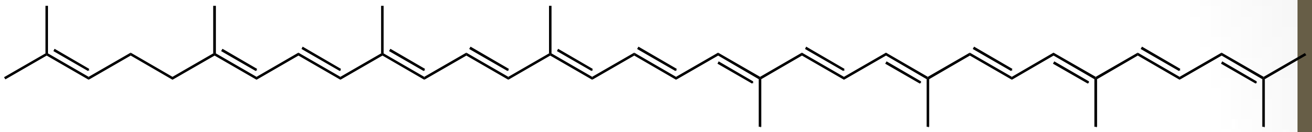
UV Spectroscopy

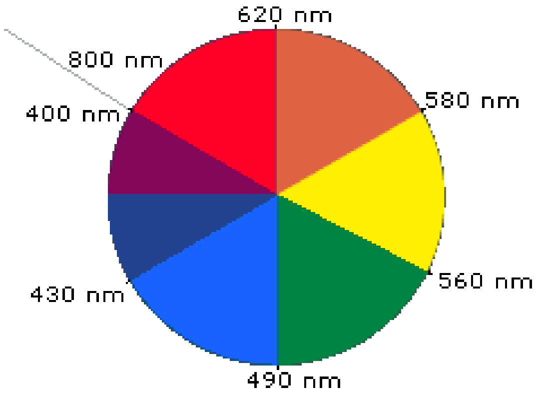
Visible Spectroscopy

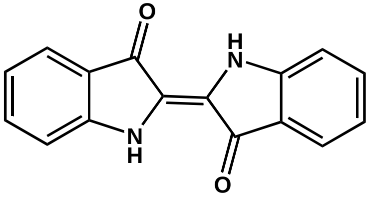
Color

1. General
   - Likewise:



lycopene, λ_{max} = 474 nm





indigo

λ_{max} for lycopene is at 474 – in the near blue region of the spectrum – this is absorbed, the compliment is now red

λ_{max} for indigo is at 602 – in the orange region of the spectrum – this is absorbed, the compliment is now indigo!

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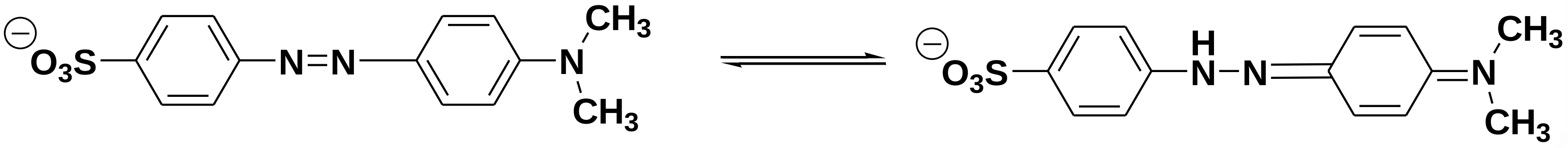
UV Spectroscopy

Visible Spectroscopy

Color

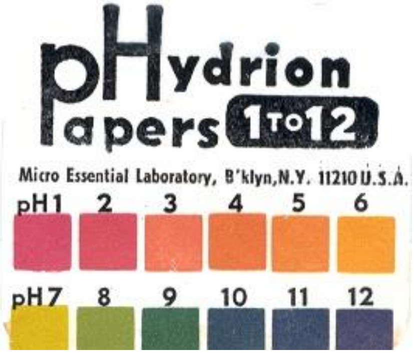
1. General
   - In the chemical sciences these are the acid-base indicators used for the various pH ranges:
   - Remember the effects of pH on aromatic substituents

Methyl Orange



Yellow, pH > 4.4

Red, pH < 3.2



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