Visible, Ultra-Violet Spectroscopy

Electronic transitions in molecules

Energy levels of molecules

Total Energy

$$E_T = E_{elec} + E_v + E_{rot}$$

Any transition leading to an energy change

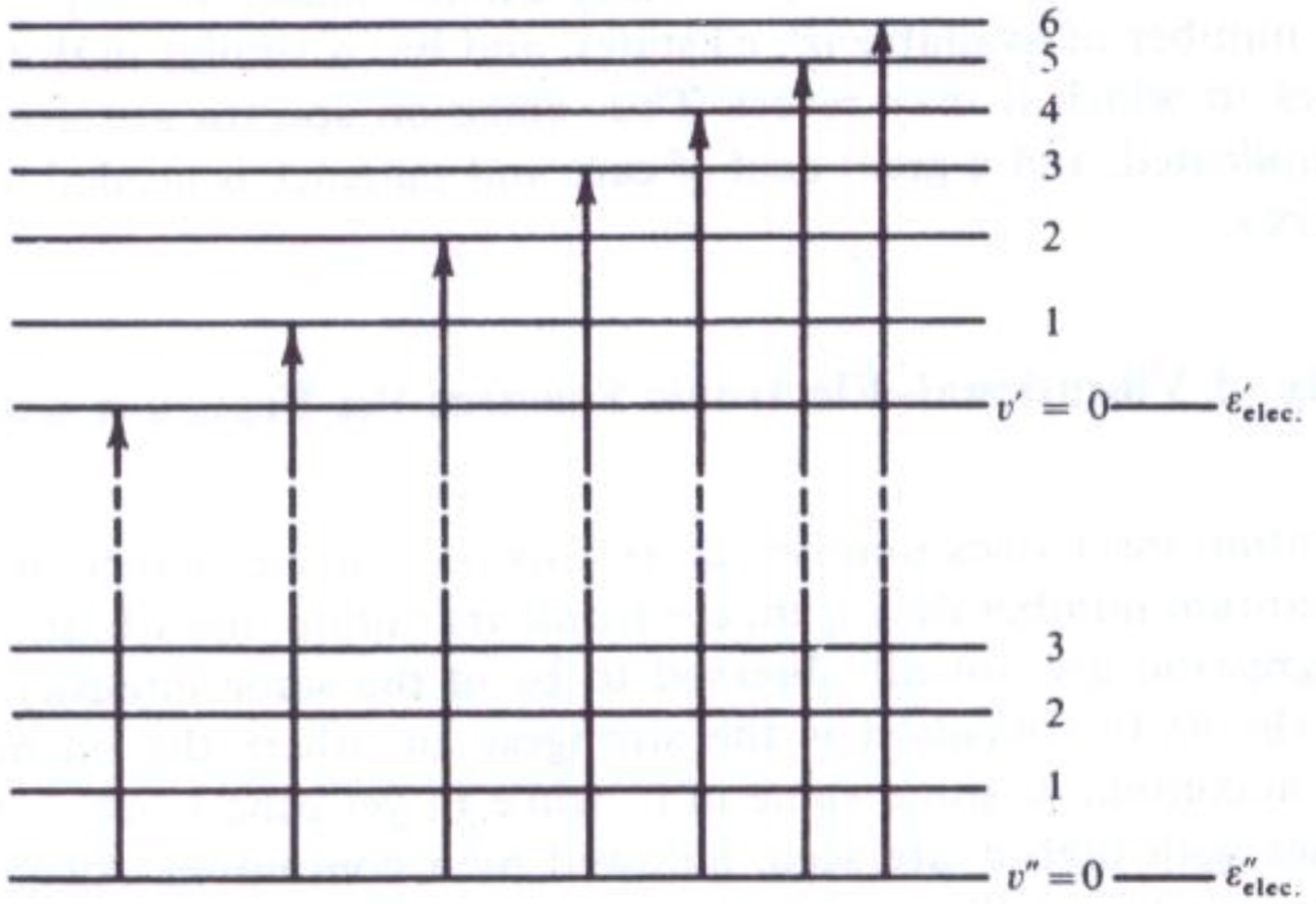
$$\Delta E_T = \Delta E_{elec} + \Delta E_v + \Delta_{rot}$$

This is Born-Oppenheimer approximation.

Each of the degree of freedom can be independently considered.

Frank-Condon Principle

- No selection criteria for electronic transition with regards to vibrational states.
- Electronic transitions take place so quickly
  - Vibrational mode change is seldom associated.
  - Most probable transition is from zero to zero vibrational state.

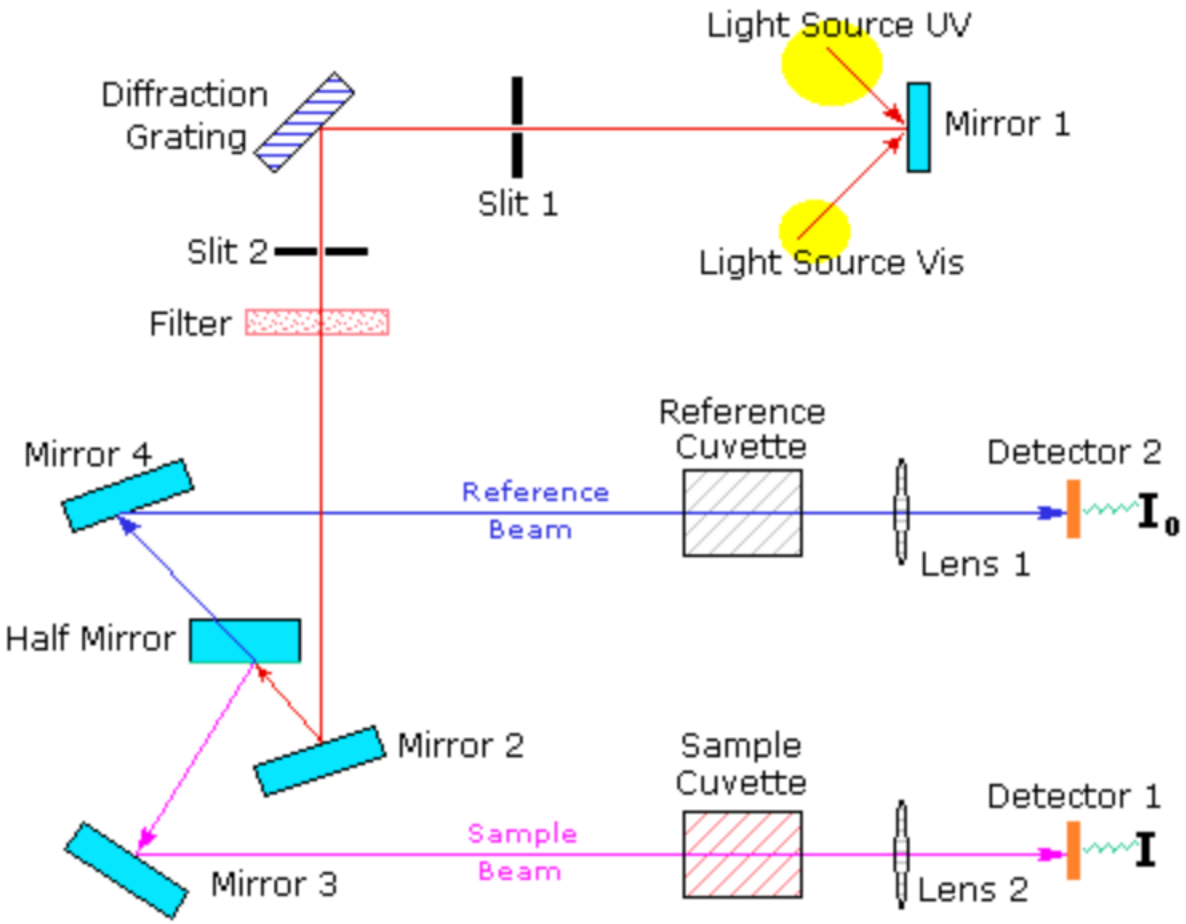


UV-Visible region

- 200 – 400 nm – UV
- 400 – 800 nm – Visible

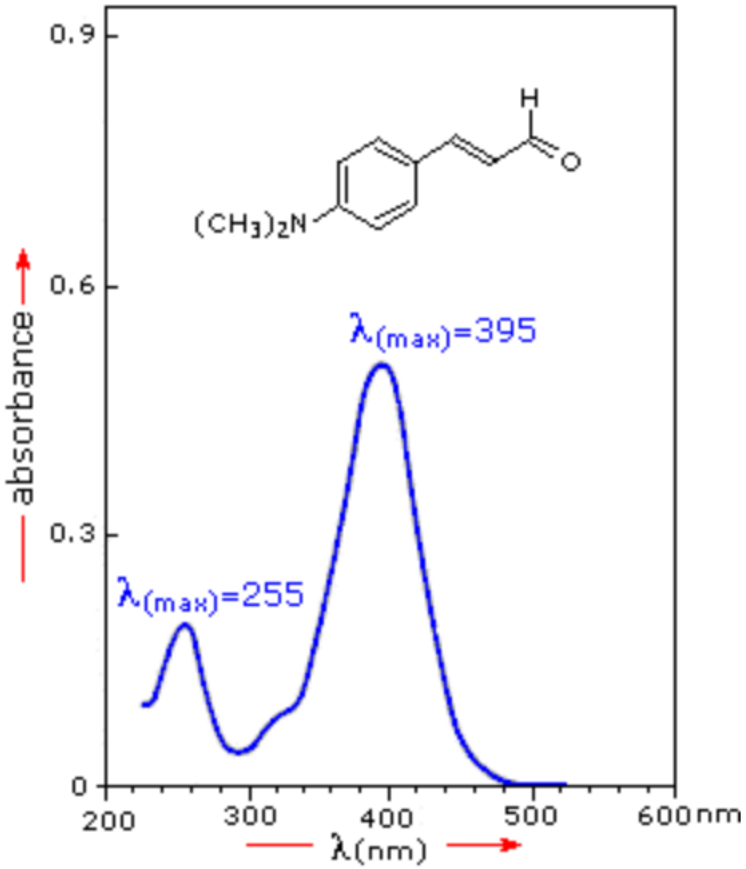
Remember, $A = \log I/I_0$

Molar Absorptivity = A/cl



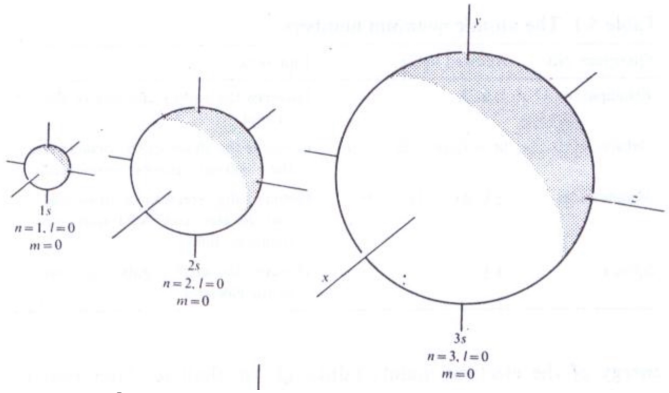
A typical measurement

- 0.249 g of aldehyde
- In ethanol
- Can we estimate the absorptivity at 395 and 255
- $\epsilon > 10000$ are strong absorbers and $\epsilon < 100$ are weak absorbers



Molecular Orbital Theory

Electrons in a Atom



- ψ – a complex valued function such that $|\psi^*\psi|$ (r) gives the probability to find an electron at r.
- ψ for any atom requires only three integers to uniquely define its shape.
- n – principle quantum number $\psi_n(r) = f(r)e^{-r/na_0}$

  The probability to find an electron dies exponentially with r

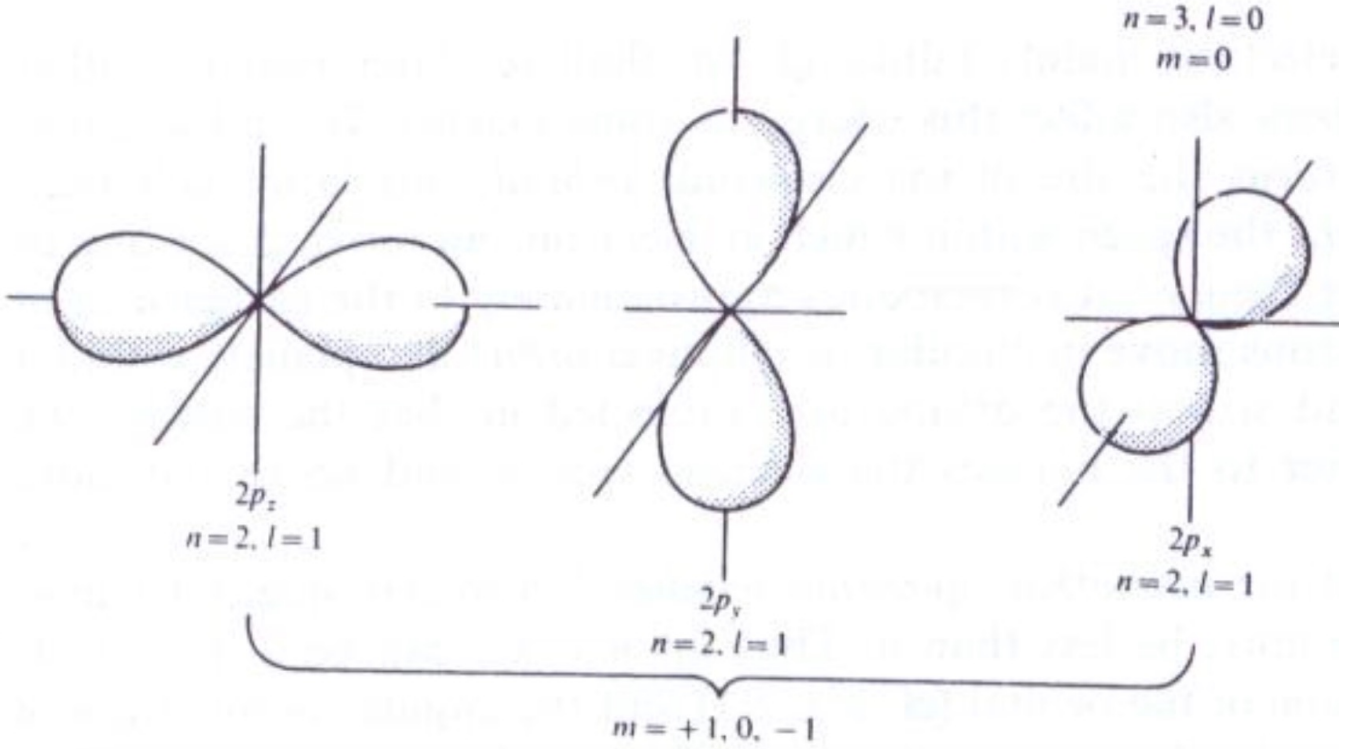
  This fall is modulated by n. For larger n, the electrons fall slowly.

  The region in space where electron spends >95% of time is called orbital.

Orbital Angular Momentum

Solutions to the spherically symmetric potential well also have solutions with angular nodes!

Ie, the electrons chose to stay away from certain angles



The situation where

L – number of angular nodes

L = 1.

Has three degenerate ways

Designated by m = 0, ± 1

Higher order wavefunctions

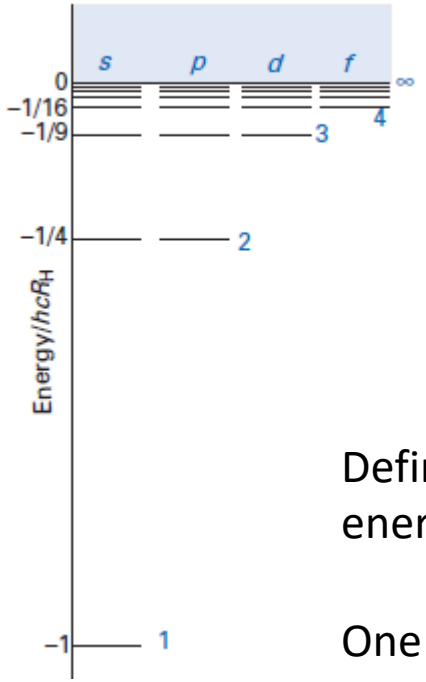
- When l = 1, you have two lobes separated by a node
- When l =2, the wavefunction has two nodes.
  - This gives 5 possible ways to distribute them in 3D space.
  - We call these D-diffused orbitals.
- When l = 3, we have three nodes
  - There 7 different m-values.

Energy levels in a molecule

Energy levels in an atom

$$E_n = -\left(\frac{\mu e^4}{32\pi^2\epsilon^2\hbar^2}\right)\frac{1}{n^2}$$

For n = 1,2,……



Another way to write the same:

$$E_n = -\frac{hcR_H}{n^2} \text{ where } R_H = \frac{\mu e^4}{8\epsilon^2 h^3 c}$$

R_H is called as Rydberg constant

Initial State	Final State	Series
2,3,..	1	Lyman
3,4,…	2	Balmer
4,5,…	3	Paschen
5,6,…	4	Brackett

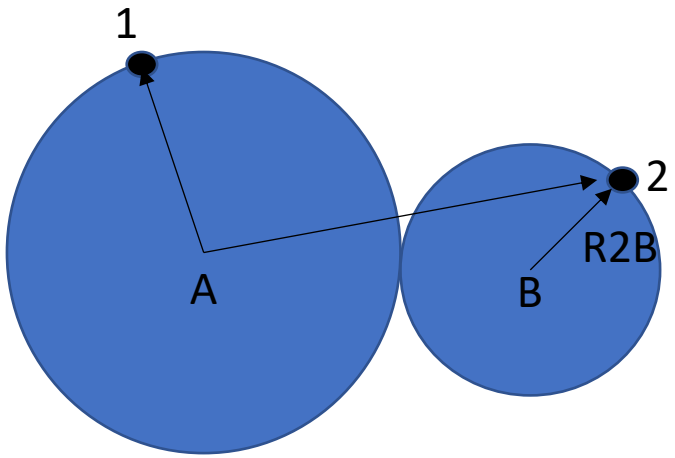
Defined in this fashion, since the expression of light energy $\mathrm{E} = \mathrm{h}c\bar{\nu}$ can be compared with atomic energy lines.

One can then expect light emission/absorption such that

$$\bar{\nu} = \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)R_H$$

Electrons in a molecule

- Biggest difference: Electrons in a shared potential of the atomic cores as well as other electrons



Hamiltonian of the Hydrogen molecule:

$$H = -\frac{h^2}{8\pi^2 m}\left[\nabla_1^2 + \nabla_2^2\right] + \frac{e^2}{R} - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}} - \frac{e^2}{r_{1B}} + \frac{e^2}{r_{12}}$$

If ϕ_A is the 1S atomic orbital of Atom A
And ϕ_B is the 1S atomic orbital of Atom B,

A trial solution to Schrodinger's equation can be obtained by a linear combination of atomic orbitals

One solution is a direct linear combination of atomic orbitals

$$\psi^1 = c_1\phi_A + c_2\phi_B$$

A second solution can be obtained by

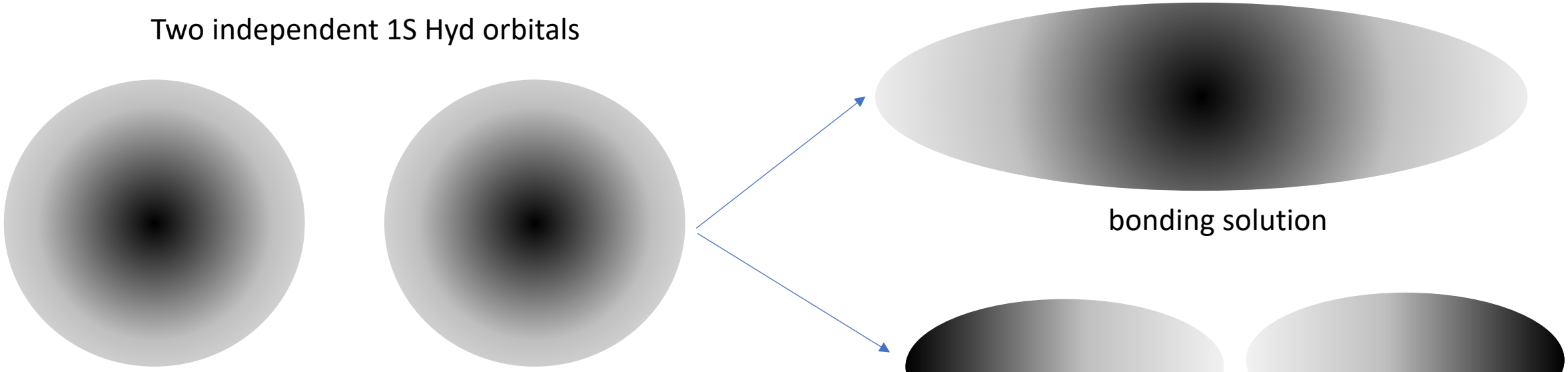
$$\psi^2 = c_3\phi_A - c_4\phi_B$$

.

In the bonding case, the wavefunctions add up with the probability at the regions of overlap higher than other regions.

In the anti-bonding case, the wavefunctions cancel each other with the probability at overlap the lowest.

Two independent 1S Hyd orbitals

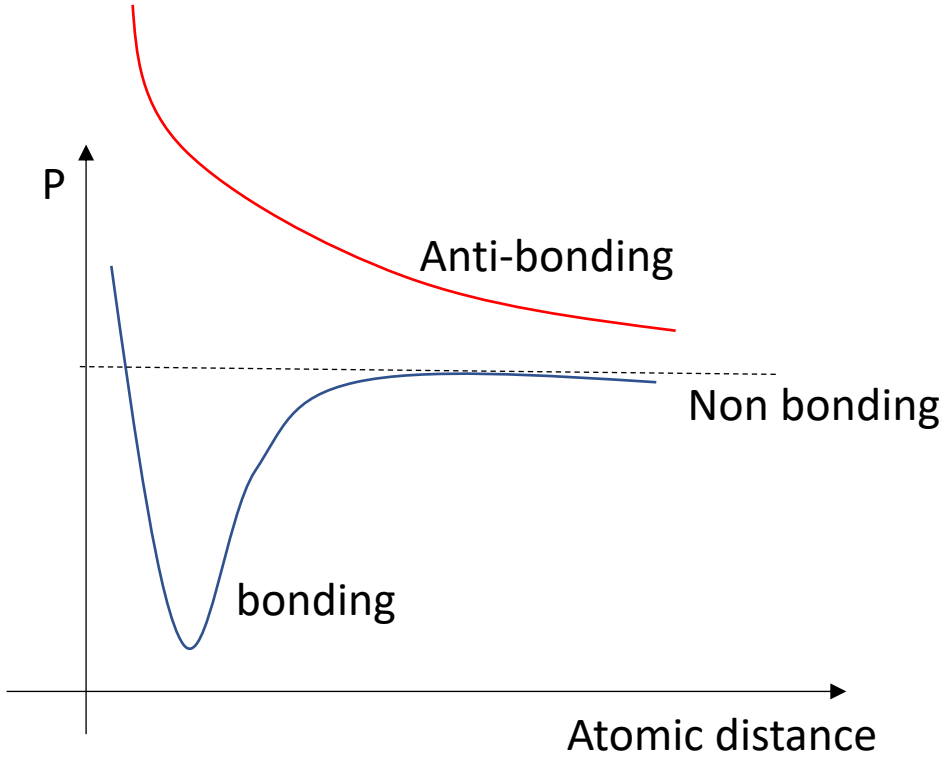


bonding solution

Antibonding solution

Centered on two atoms.

Bond Energetics



As two atoms are brought together, the coulombic attraction due to bonding allows for the total energy to reduce.

-> This leads to a dip in potential energy with a minima at a distance called as the bond length

-> This curve denotes the bonding curve which typically goes as $\psi = c_1\phi_A + c_2\phi_B$

-> The anti-bonding orbital, in which the contributions of the two atoms are added out-of-phase, has energies much higher than the bonding ones.

-> There is no energetic minimum for the non-bonding case.

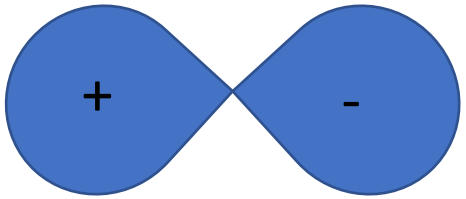
During bonding, there is mixing of atomic orbitals!

Hydrogen is among the simplest of molecules.

What happens, when there is mixing between orbitals, which are not spherically symmetric ?

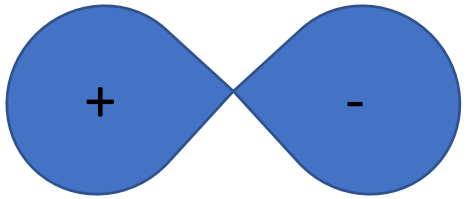
Interestingly, the difference will lead to bonding scenario and the summation will lead to anti-bonding scenario

Consider an electron in p orbital



Px orbital

Mixing with another px

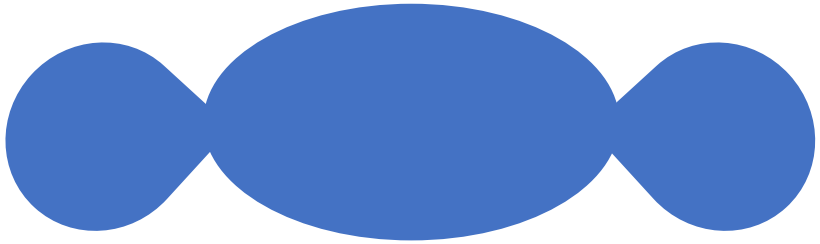


Px orbital

one option:

$$\psi_{2p} = \psi_{2p}^{A} - \psi_{2p}^{B}$$

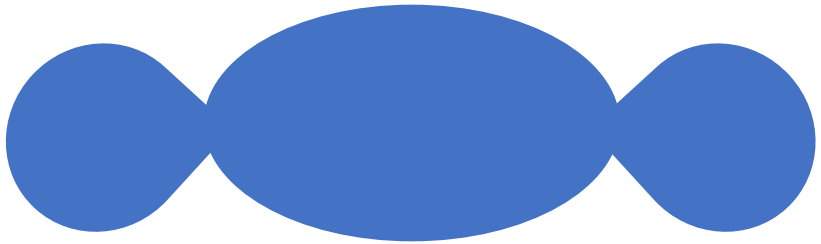
One sort of bonding is obtained when the orbitals overlap in an 'end on' mode



Such bonds are called as sigma bonds

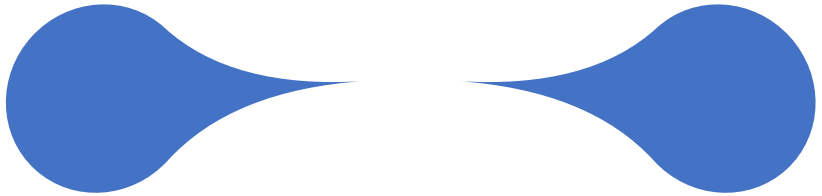
Sigma Bonding orbitals

$$\psi_{2p} = \psi_{2p}^{A} - \psi_{2p}^{B}$$

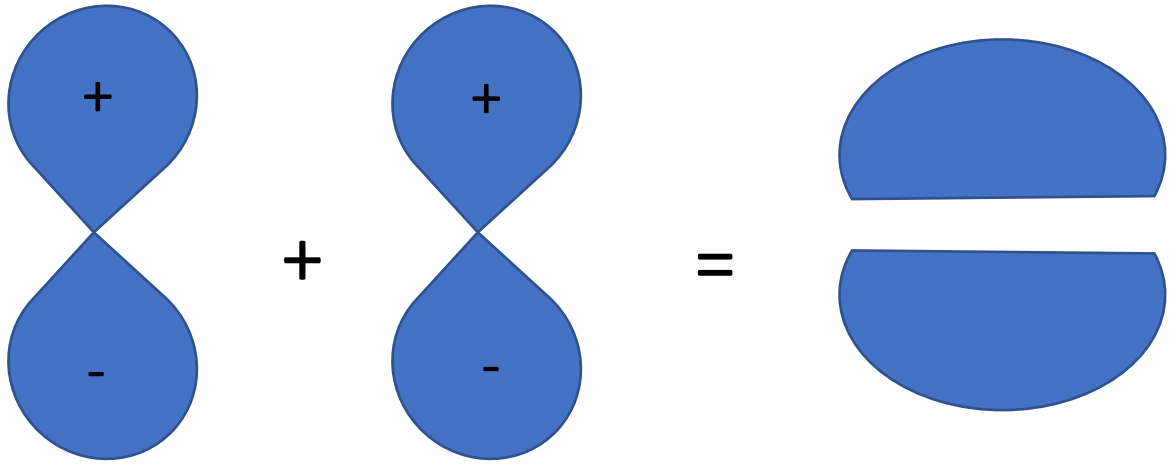


Sigma anti-bonding orbitals

$$\psi_{2p} = \psi_{2p}^{A} + \psi_{2p}^{B}$$



Mixing of two p-orbitals in sideways



$$\psi_{2p} = \psi_{2p}^{A} + \psi_{2p}^{B}$$

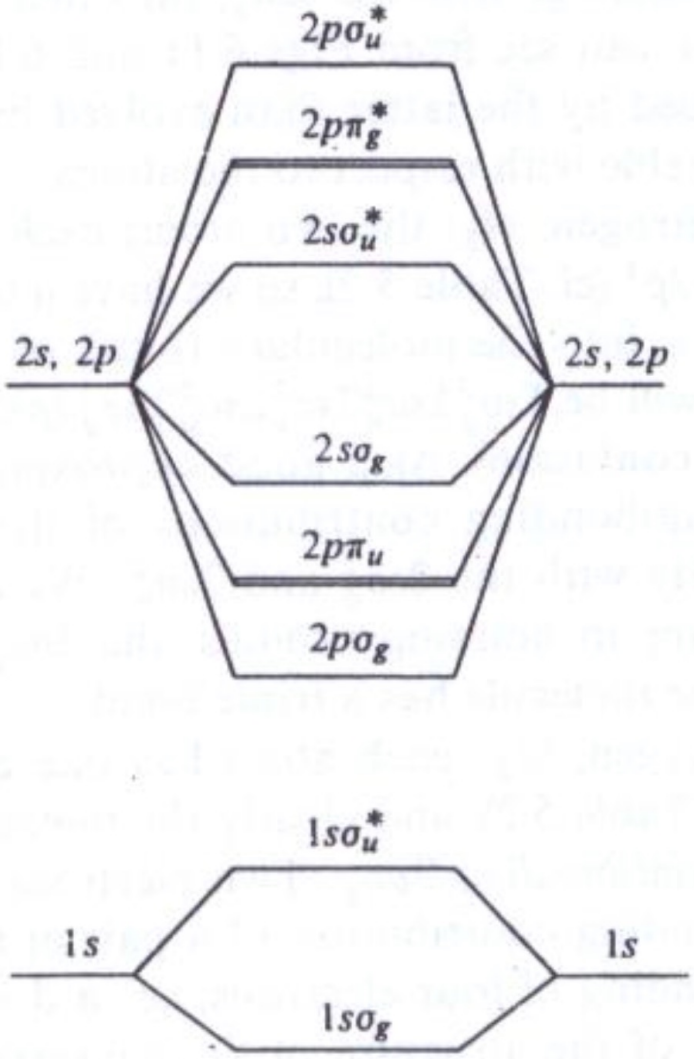
Such an overlap/mixing is called as Pi bonding

Remember, for each of the bonding orbital, there exists an equivalent anti-bonding orbital.

For σ bonds, you have an anti-bonding orbital called as σ^* bonds

For π bonds, you have an anti-bonding orbital called as π^* bonds.

Case of a diatomic molecule

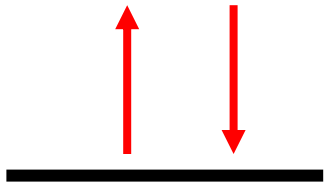


For H_2 , has 2 electrons.

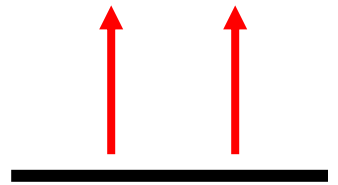
Both these electrons will sit in the 1sσ state.
This is the ground state of the hydrogen molecule.

Pauli's exclusion says, no two electrons with same spin can be in the same energy.

So, the ground state of the hydrogen atom is a spin singlet.



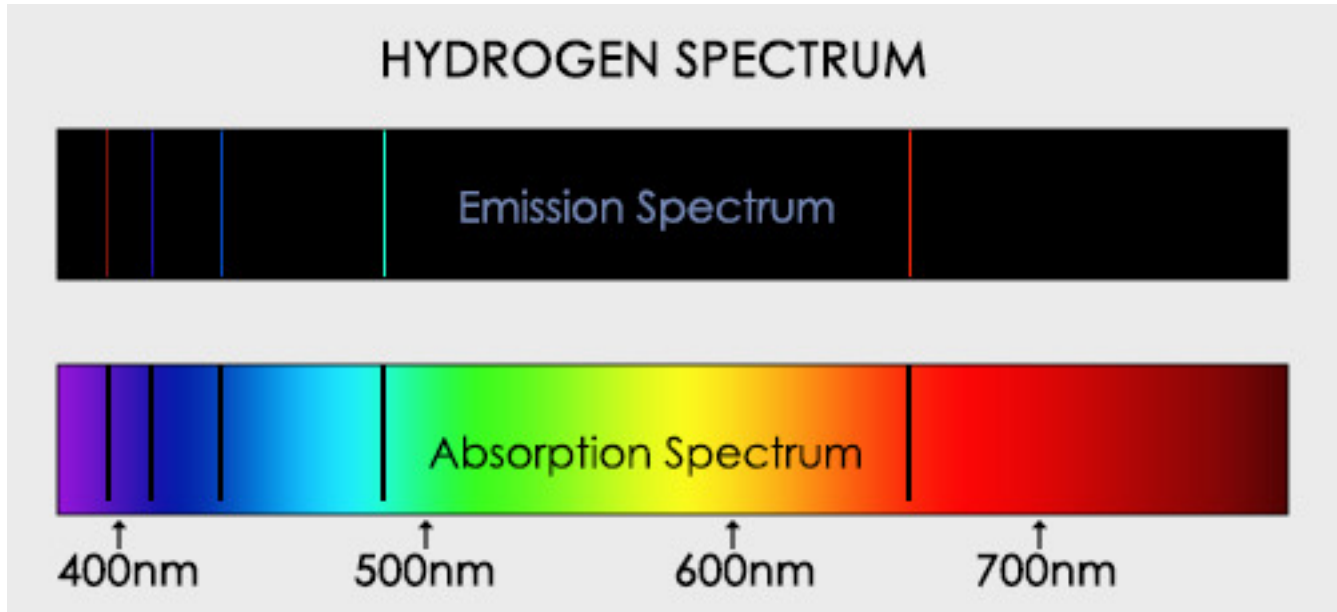
Spin singlet



Spin triplet

In a diatomic molecule, a huge collection of excitation is possible with discrete energies

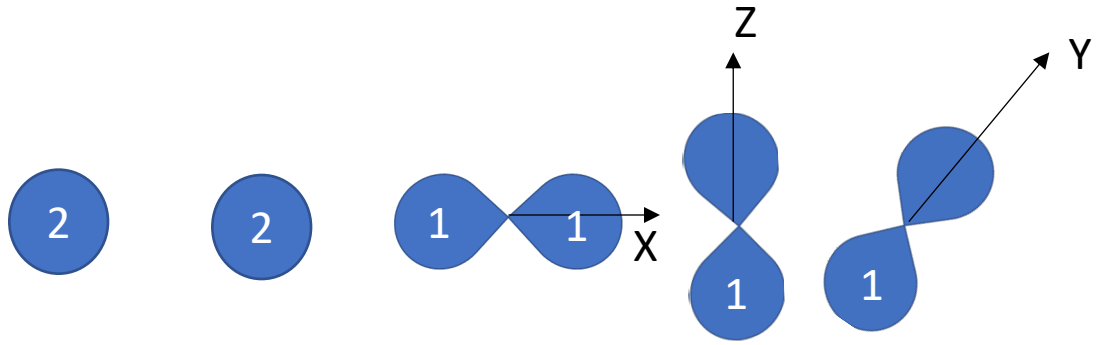
Homework: Why He_2 molecule doesn't form ?


HYDROGEN SPECTRUM
Emission Spectrum
Absorption Spectrum
400nm
500nm
600nm
700nm

Poly-atomic molecules

Example: Say water.

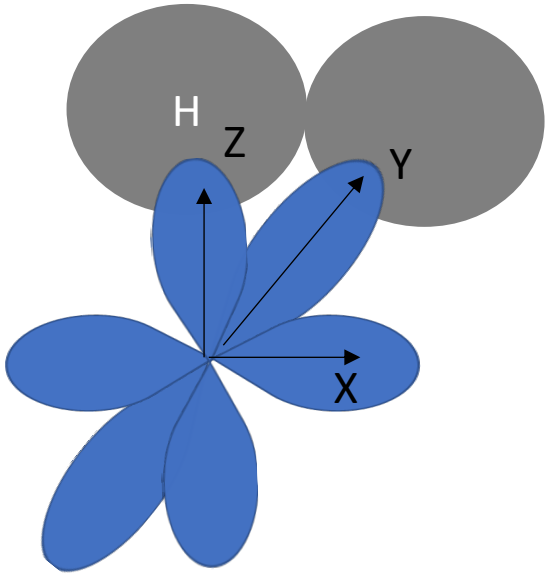
Oxygen has electronic configuration:



1S2,2S2,2P4

Hydrogen with 1S orbitals can overall with any orbitals in an end-on way due to spherical symmetry.

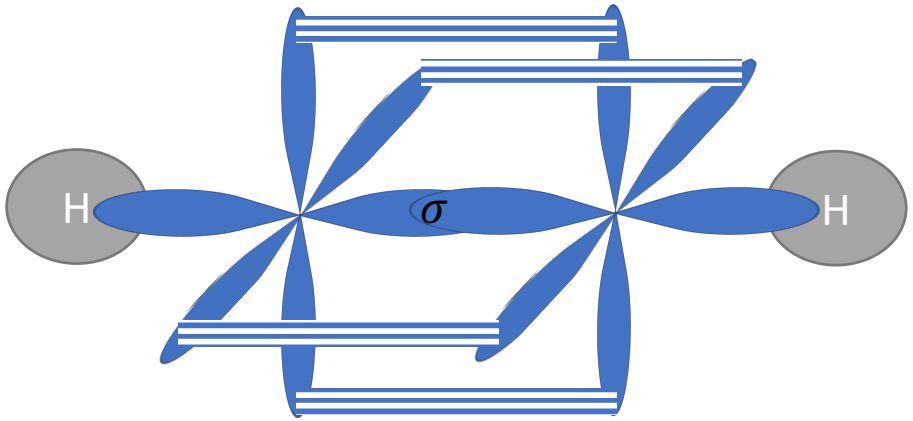
So water forms two hydrogen molecular sigma bonds with px and pz orbitals.



If PY and PZ orbitals are orthonormal,

What is the angle between the water bonds ?

Bonding picture of Acetylene



Atomic orbitals of certain atoms are special.

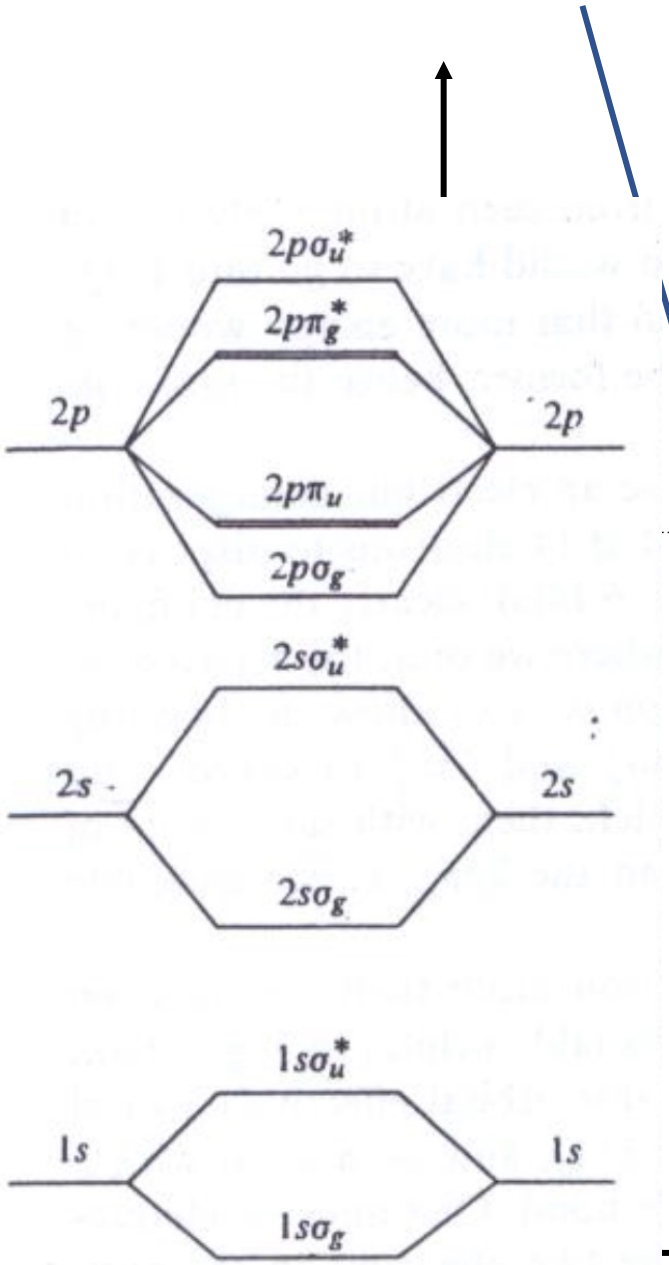
For instance, those in carbon hybridize within the atom. The valence of carbon has 2S2, and 2P2 electrons.

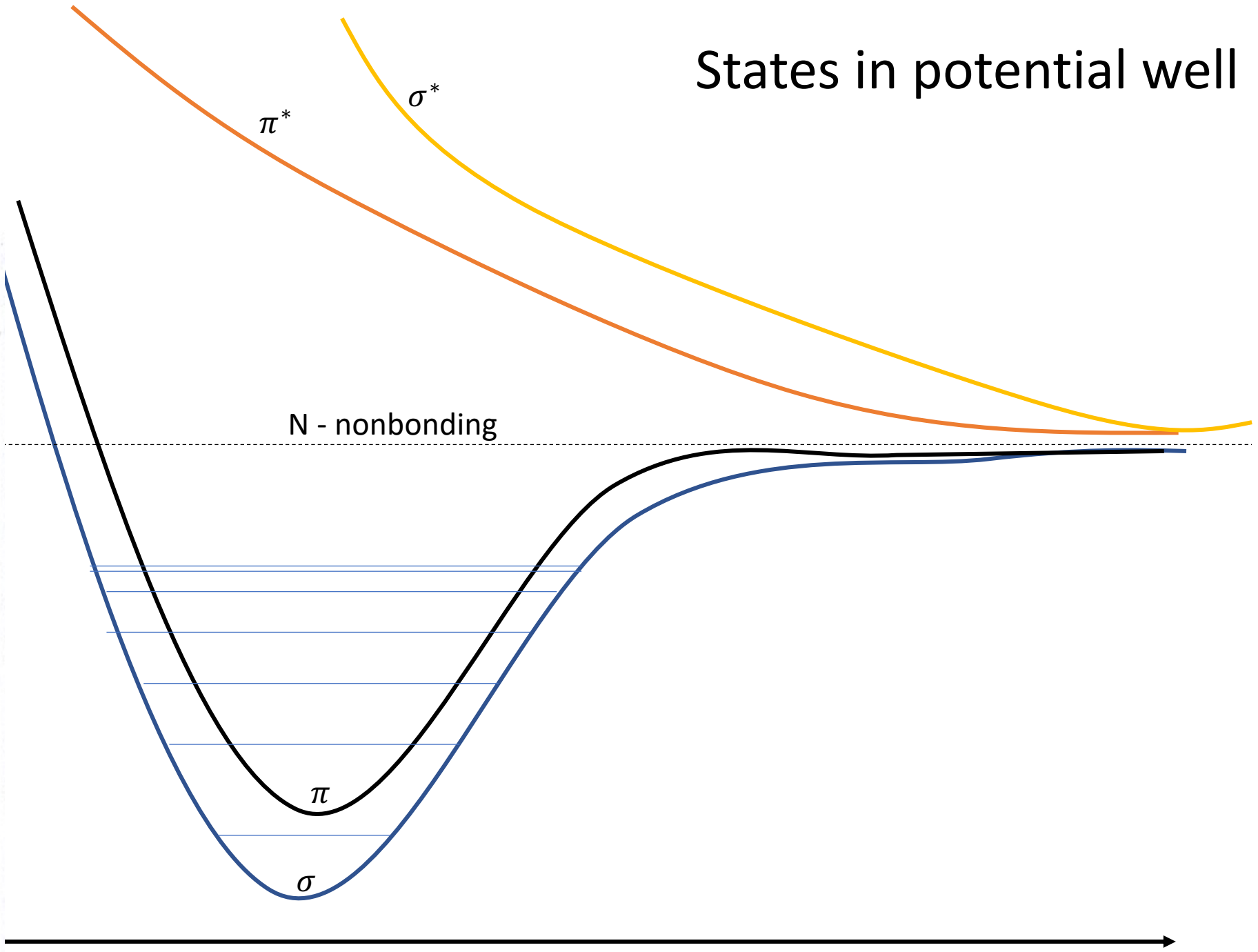
In this example of Acetylene, the S orbitals and 1P orbital of carbon hybridize (mix together) forming two SP orbitals.

They form bond with hydrogen and another carbon atom as shown in the figure.

Free py and pz orbitals of carbon overlap forming the pi bonds.

States in potential well



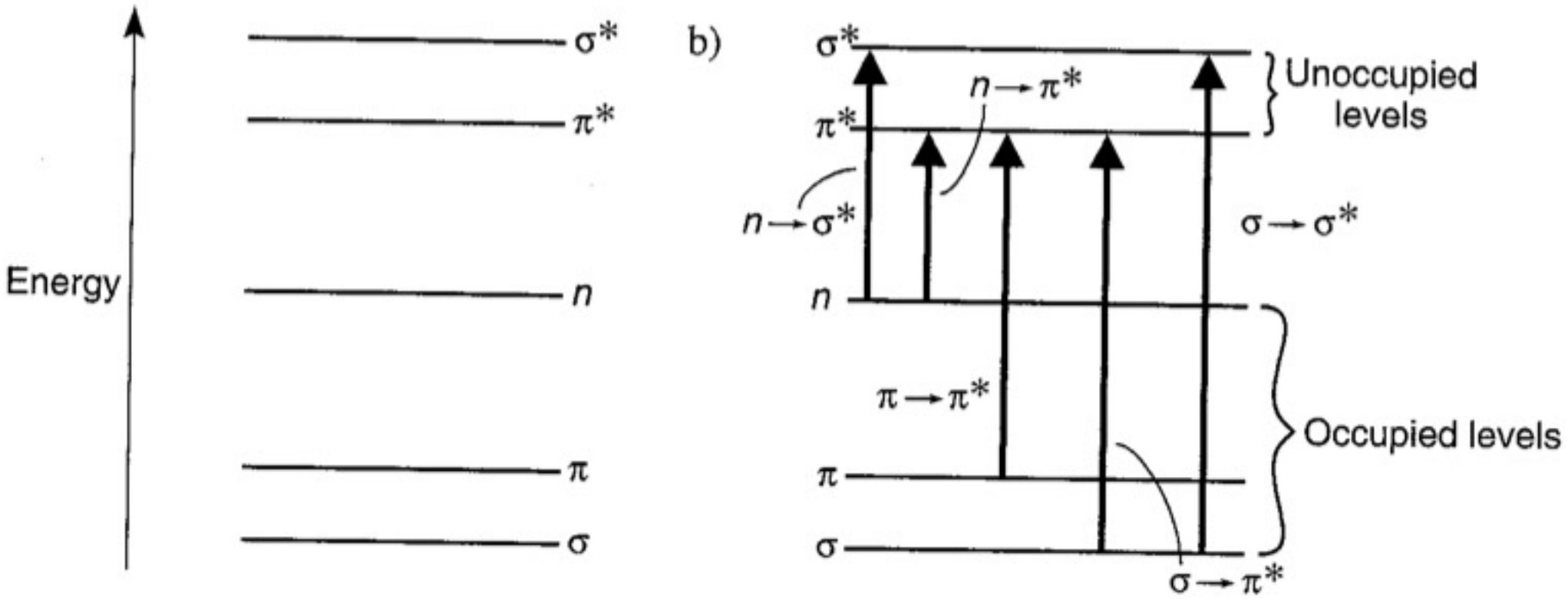


Types of electrons in molecule

- Sigma bonded electrons as in C-C, C-H, O-H etc.
- Pi electrons in C=C, $C \equiv C$, C=N etc.
- Atoms to the right of C in the periodic table O, N and halogens have unbonded valence electrons.

Energies and excitation with high energy radiations

Typical energy difference: 150 – 600 kJ/mol



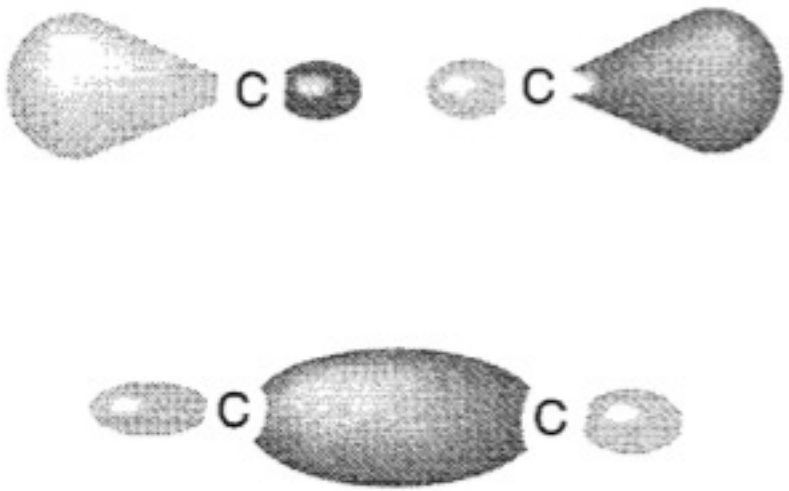
Before the interaction with light, electrons in a molecule are either in the bonding orbitals (σ, π) or non-bonded (atom localized). Anti-bonding states are un-occupied energy levels.

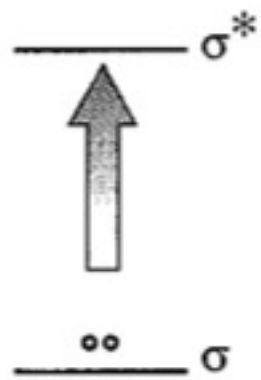
The high energy excitations have very small interaction time: ~10^{-15} s. Thus, they do not interact with much slower nuclear motion (~10^{-13}s)

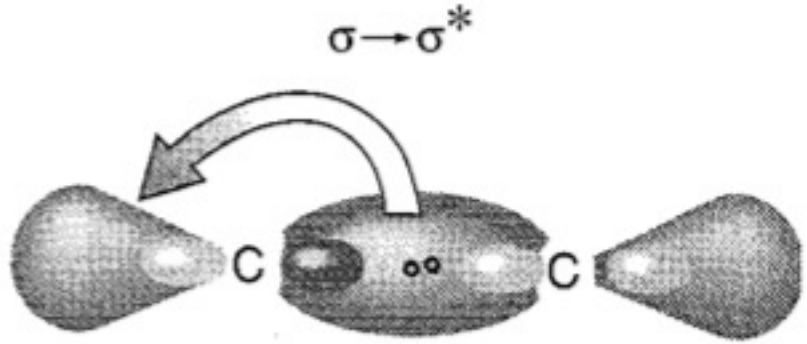
Selection Rules for Transition:

1. No change in electron spin state is allowed. An singlet state to remain singlet and a triplet a triplet
2. $\sigma \rightarrow \pi^*$ transitions and $\pi \rightarrow \sigma^*$ transitions are forbidden
3. $n \rightarrow \pi^*$ are also symmetry forbidden, but can sometimes be seen
4. $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ are commonly observed.

Possible transitions in Alkanes: (Say Ethane CH3-CH3)







Only possible transitions are high energy $\sigma \rightarrow \sigma^*$ requiring about 135 nm

If we introduce an atom containing non-bonded electrons like N

Consider a molecule such as $CH_3 - NH_2$

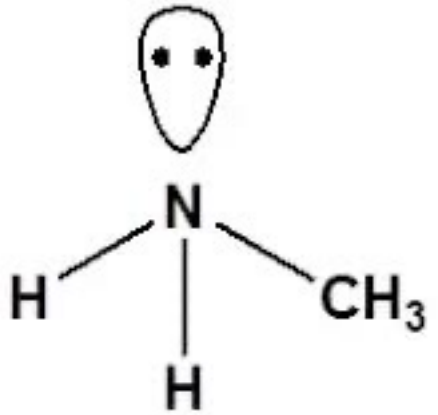
Two different absorption peaks are observed:

1. $\sigma \rightarrow \sigma^*$ at 170 nm
2. $n \rightarrow \sigma^*$ at 213 nm

Two observations here:

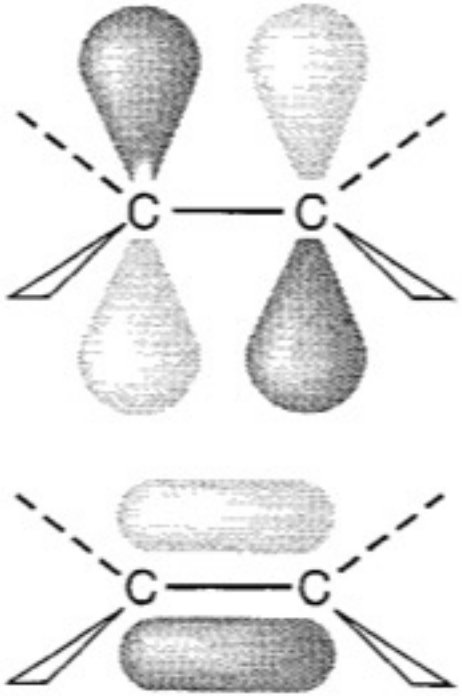
Inclusion of another atomic cluster

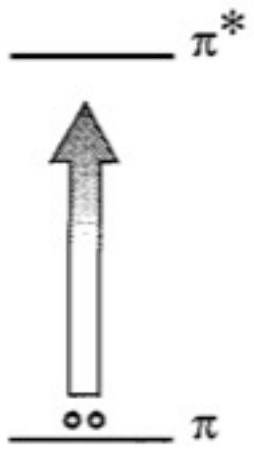
- changed the sigma transition energies
- Increased the lowest energy transition

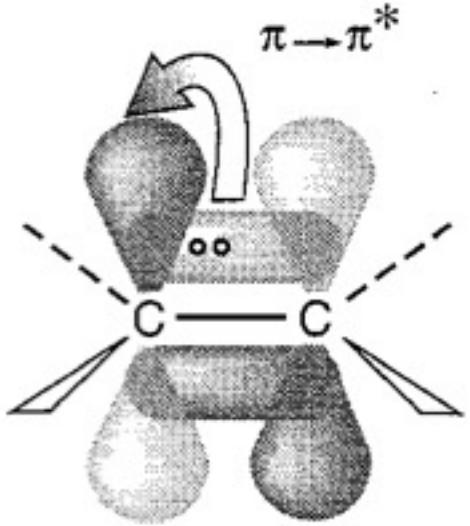


Methylamine

Transitions in molecules with π - bonding







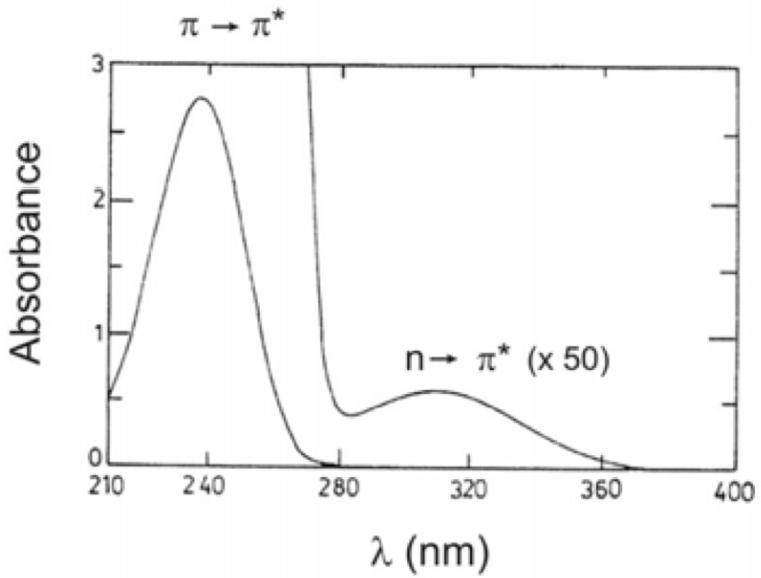
These transitions though also a bit high in energy, is also accessible under deep UV illuminations in certain molecules

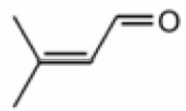
Carbonyl compounds

Molecules having oxygen/nitrogen

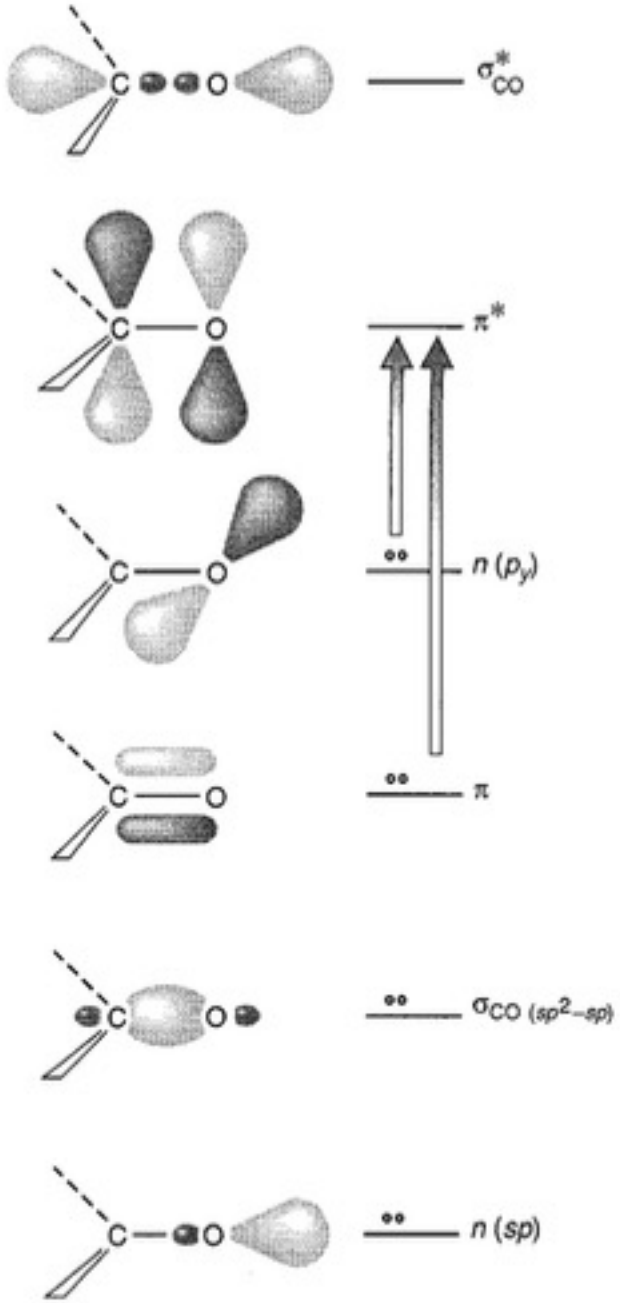
Have unbonded electrons, which can undergo $n \rightarrow \pi^*$ such transitions have absorption peaks around 380 – 300 nm

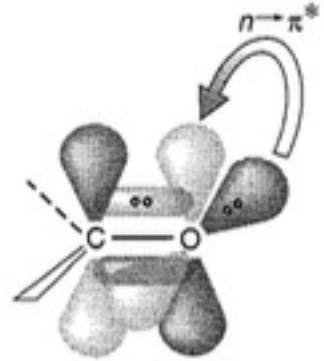
Existence of π bonded electrons also allow for $\pi \rightarrow \pi^*$

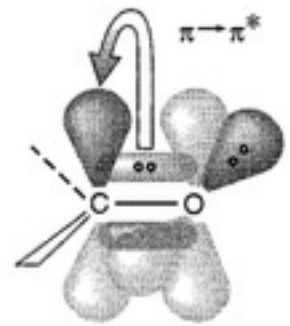




methanol





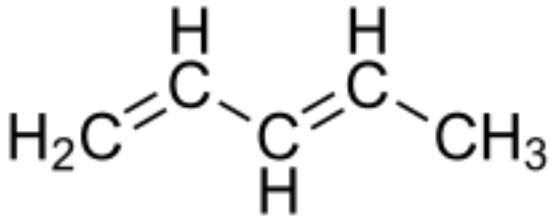


Chromophore	*Compound*	*Transition*	λ_{max} (nm)	ε
C–H	CH_4	σ→σ*	122	
C–C	C_2H_6	σ→σ*	135	
C=C	C_2H_4	π→π*	103	15000
			174	5500
C=C=C	C_3H_4	π→π*	170	4000
			227	630
C≡C	R–C≡C–R´	π→π*	178	10000
			196	2000
			223	160
C–O	R–O–R	*n*→σ*	180	500
C–O	R–O–R´	*n*→σ*	180	3000
C–N	Amino	*n*→σ*	190-200	2500-4000
C–S	R–S–H	*n*→σ*	195	1800
C–S	R–S–R	*n*→σ*	235	180
C=O	Aldehyde/Ketone	*n*→σ*	166	16000
		π→π*	189	900
		n→π*	270	10-20
C=O	Carboxylic acid	*n*→π*	200	50
C=O	Carboxylate	*n*→π*	210	150
C=O	Ester	*n*→π*	210	50
C=O	Amide	*n*→π*	205	200
C=N	$(NH_2)_2C=NH$	*n*→π*	265	15
C≡N	$CH_3C≡N$	π→π*	<170	
N=N	Me–N=N–Me	*n*→π*	350-370	15
N=O	Me_3NO	*n*→π*	300	100
			665	120
N=O	Me_3NO_2	*n*→π*	276	27
C=C=O	$Et_2C=C=O$	π→π*	227	360
		n→π*	375	20
C–Cl		*n*→σ*	173	200
C–Br		*n*→σ*	208	300
C–I		*n*→σ*	259	400

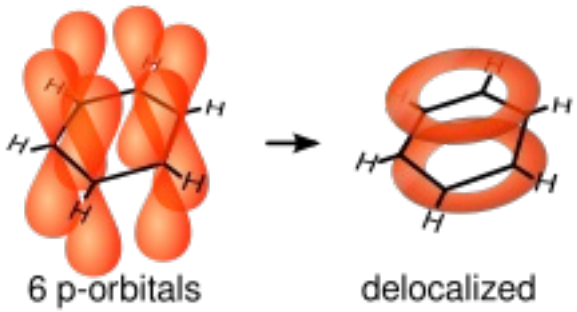
Common molecules and their absorption peak position with Stength

Chromophore	System	λ_{max} (nm)	ε_{max}
Aldehyde	—CHO	210	strong
		280-300	11-18
Amine	—NH_2	195	2800
Bromide	—Br	208	300
Carbonyl	>C=O	195	1000
		270-285	18-30
Carboxyl	—COOH	200-210	50-70
Disulfide	—S—S—	194	5500
		255	400
Ester	—COOR	205	50
Ether	—O—	185	1000
Ethylene	—C=C—	190	8000
Iodide	—I	260	400
Nitrate	—ONO_2	270 (shoulder)	12
Nitrile	—C≡N	160	-
Nitrite	—ONO	220-230	1000-2000
		300-400	10
Nitro	—NO_2	210	strong
Nitroso	—NO	302	100
Sulfoxide	>S=O	210	1500
Benzene		184	46700
		204	6900
		255	170
Diphenyl		246	20,000

Effect of conjugation



Penta 1-3- diene



Delocalized orbitals of Benzene

Collection of delocalized p-orbitals leads to strong $\pi \rightarrow \pi^*$ transitions with low energy excitations.

When interfaced with non-bonded electrons (O,N), strong absorbers in visible region are observed.

Chromophore:

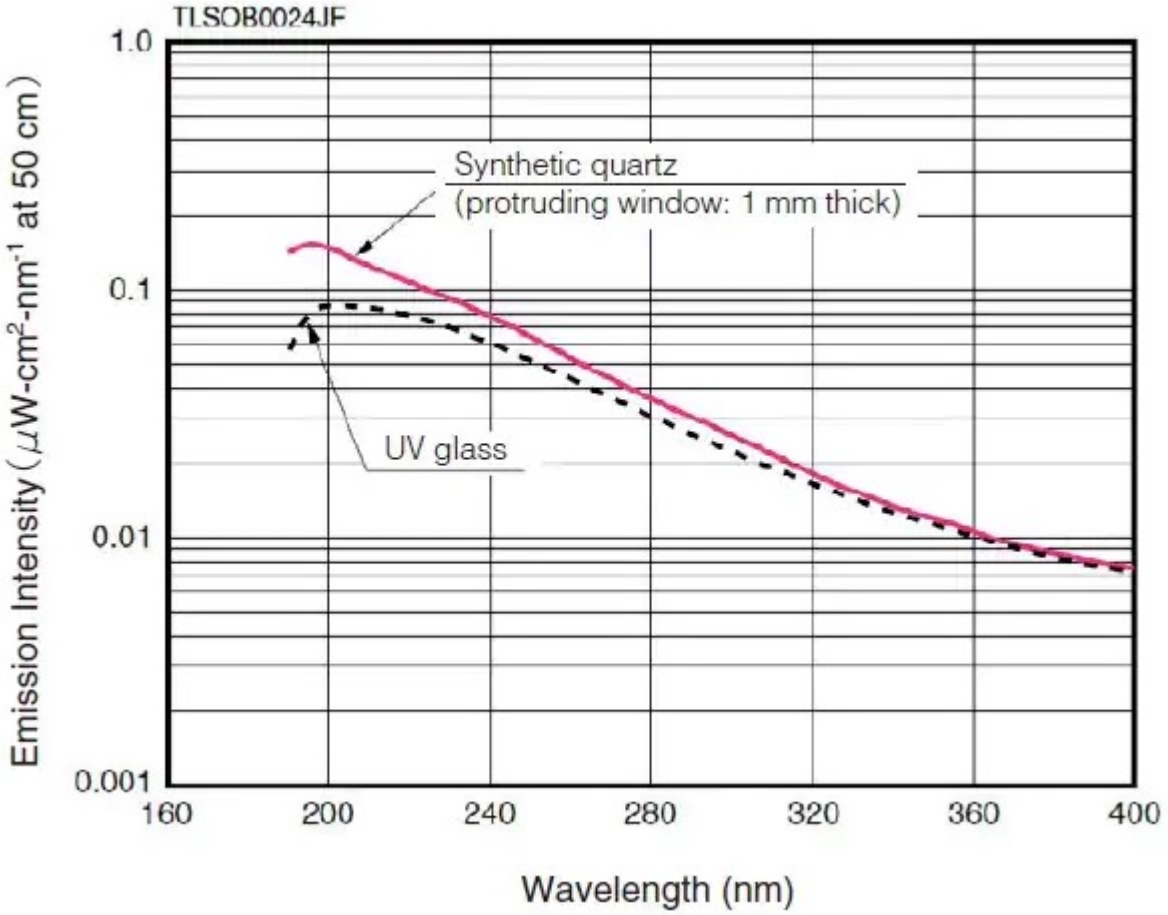
The group of atoms which decide the absorption behavior of bonded electrons is called as Chromophore. Such chromophores typically used in dyes are made of such cyclic conjugated molecules.

Image courtesy: Wikipedia

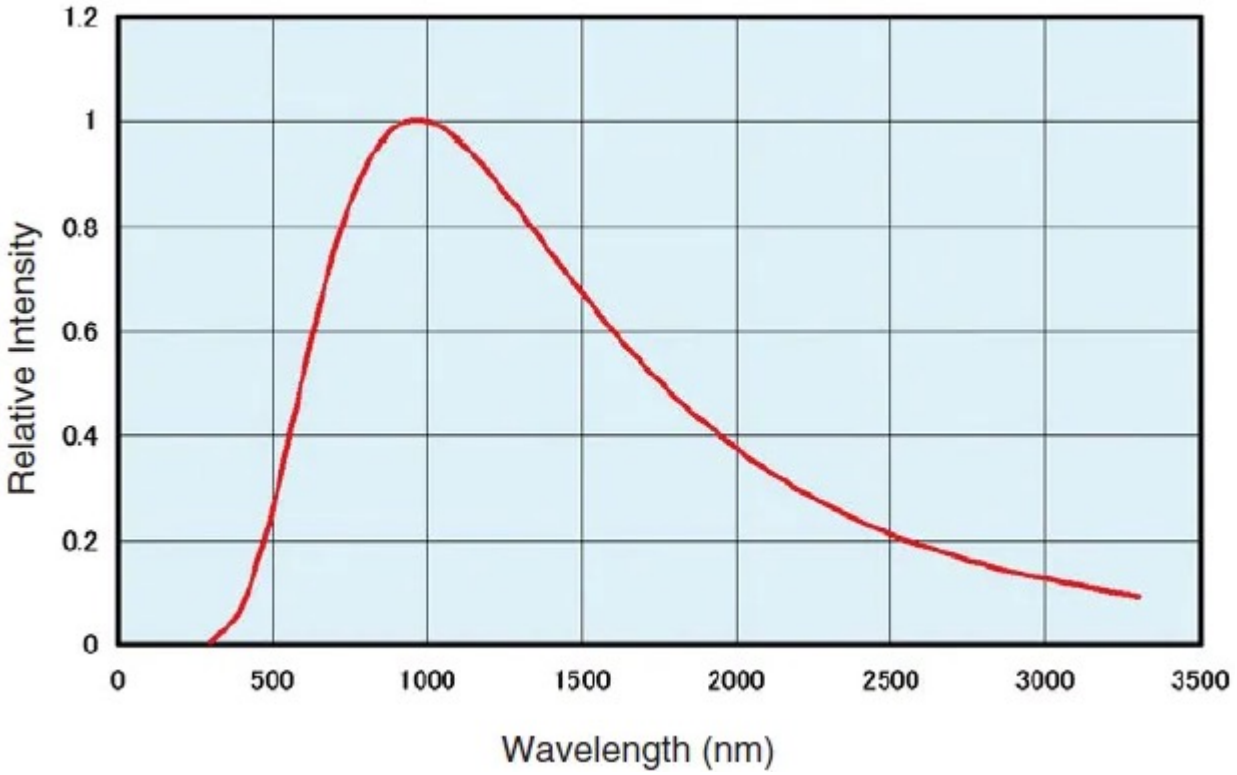
Instrumentation

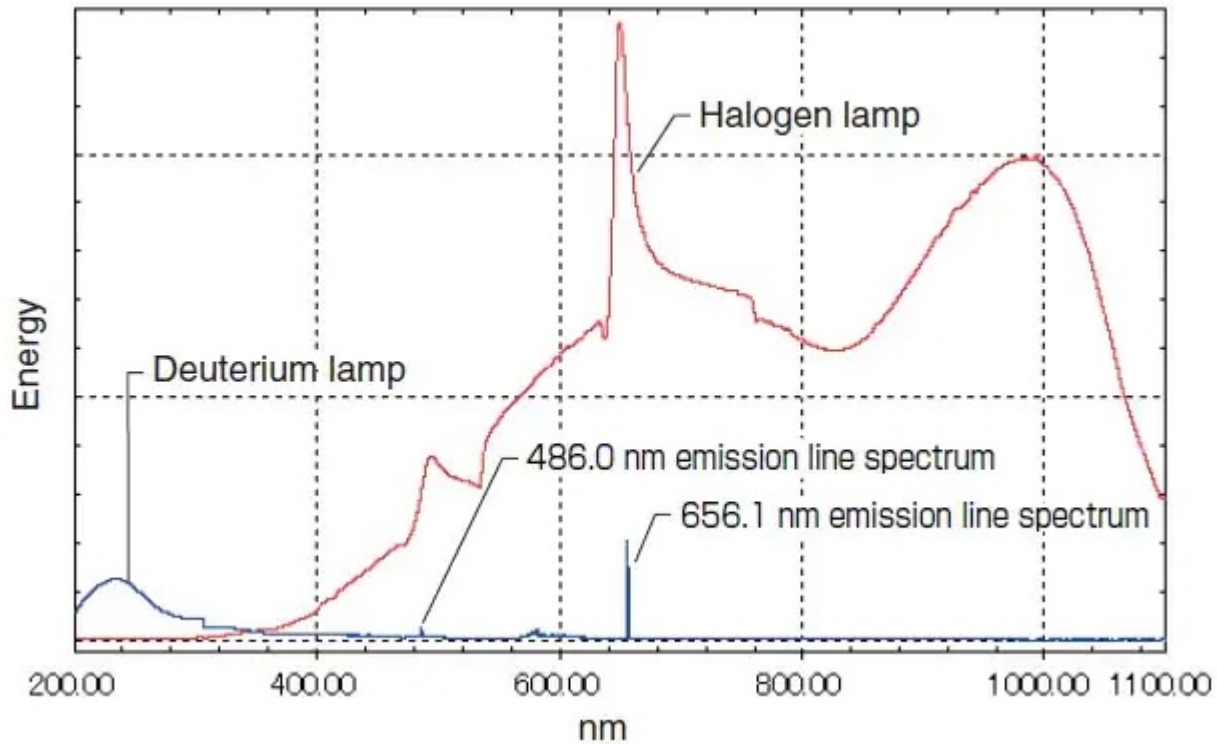
UV light source:

Typically used element is Deuterium arc source



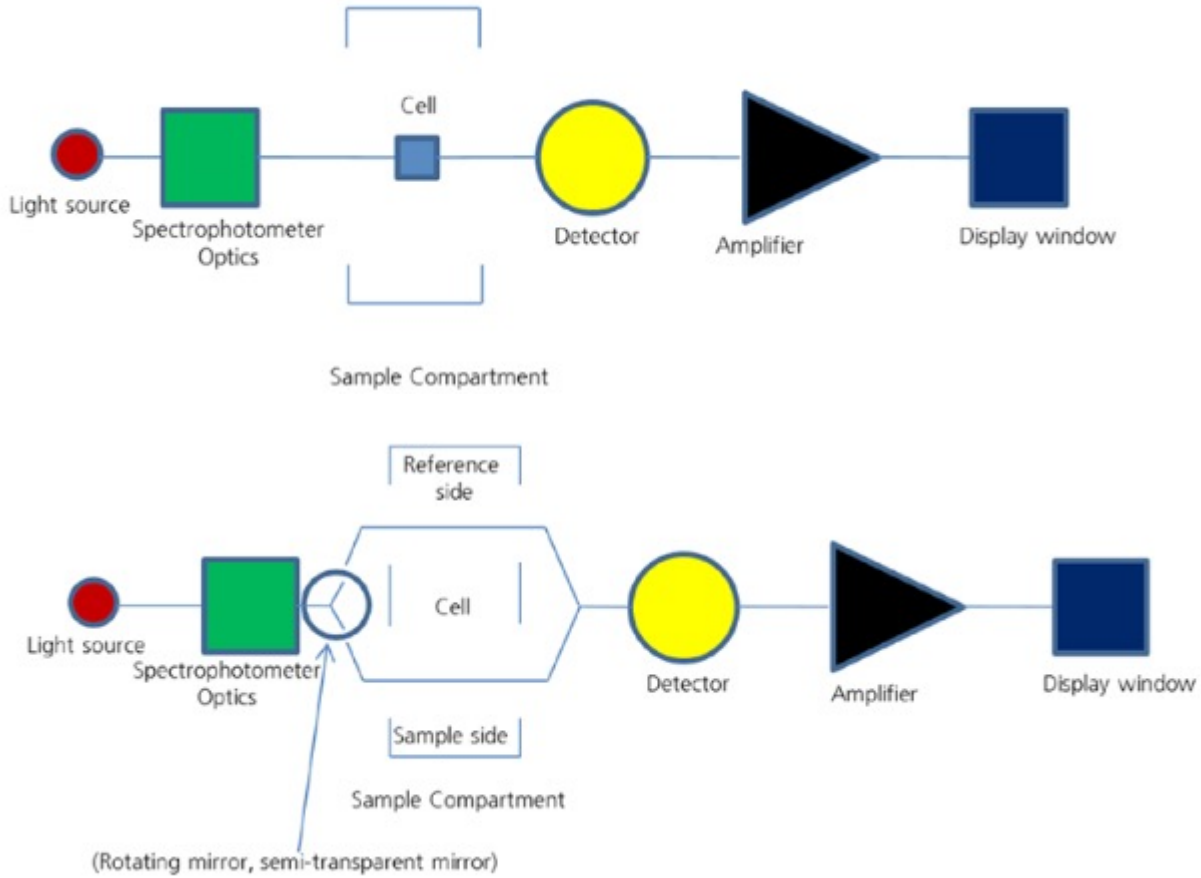
Visible-IR light source: Tungsten halogen lamp





Light source is switch at around 300 – 350 nm where the light intensity of the two sources are approximately equal.

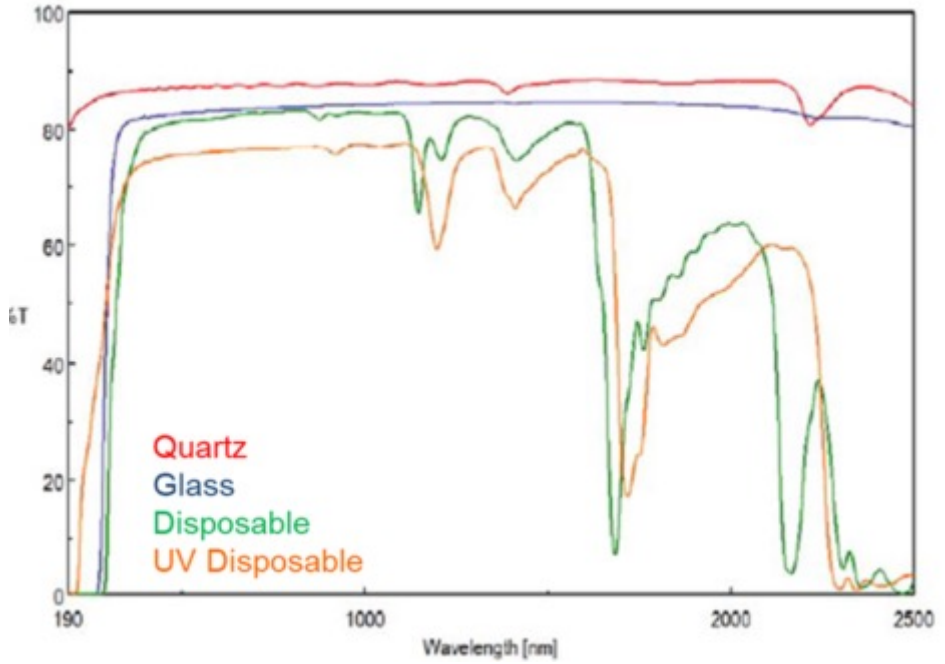
General spectrometer setup:



Sample holders:

Cuvettes:

Cuvettes transparency



Cuvette volumes: macro cells – 2.5 – 4 ml
micro cells – 250 – 1000 μL

Other custom sizes and volumes can also be designed as necessary.

Influence of Solvents:

An ideal solvent does not interfere not absorb in the region of interest.

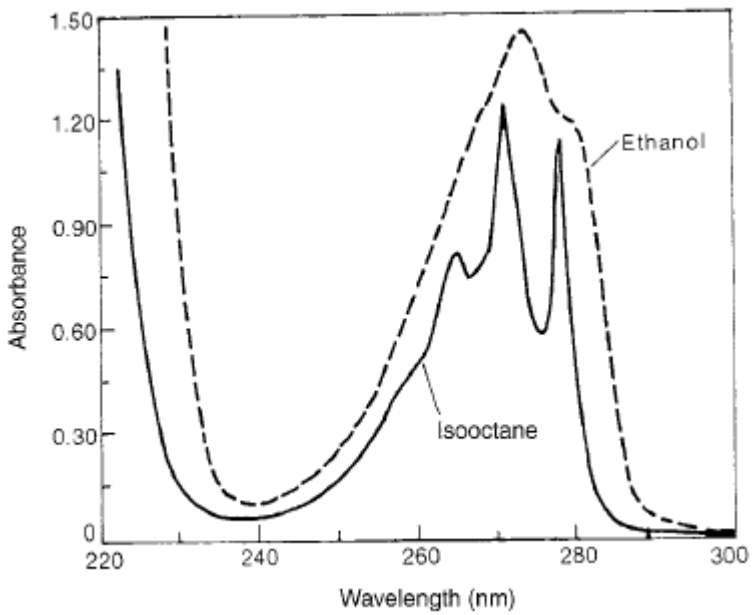
Given below is a list of commonly used solvents and their UV cut-offs

SOLVENT CUTOFFS

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

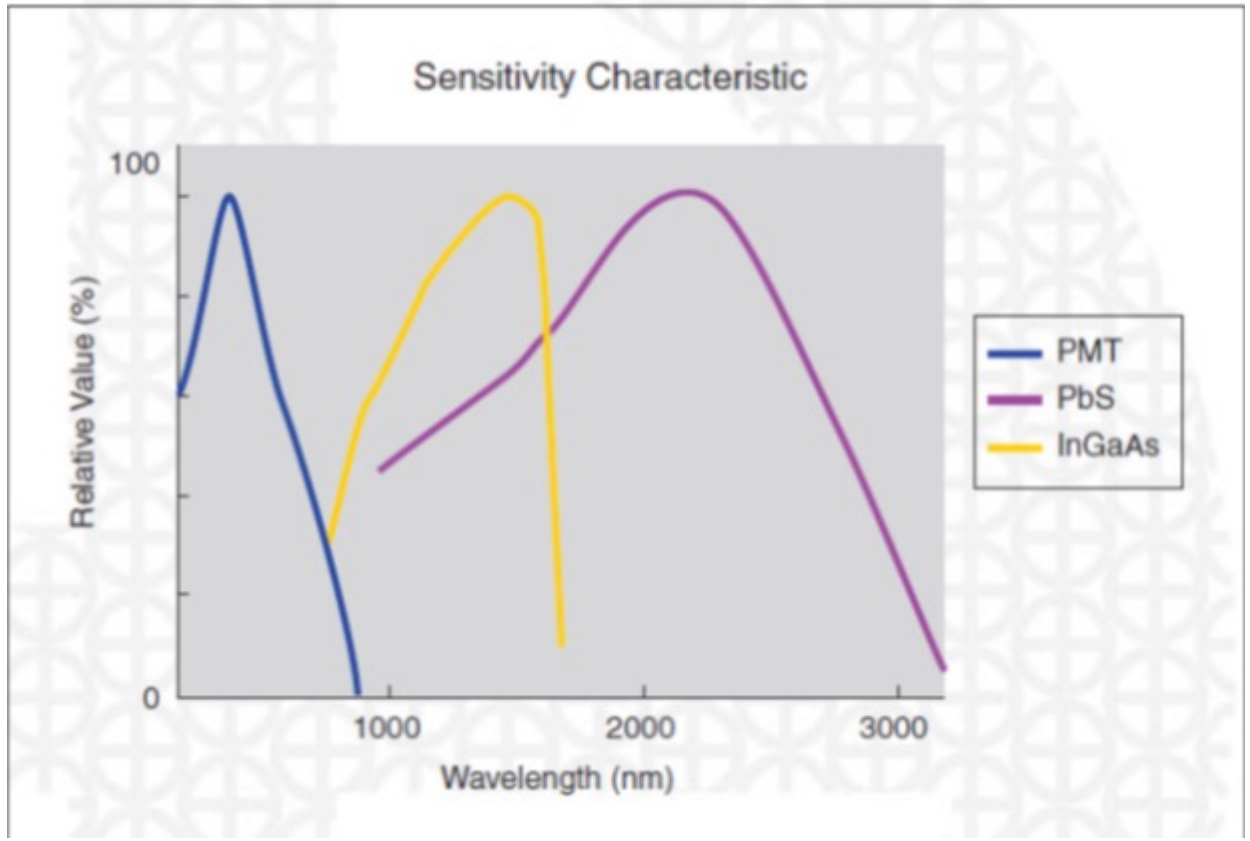
While water starts absorbing below 190 nm, ethanol absorbs below 205 and such as shown.

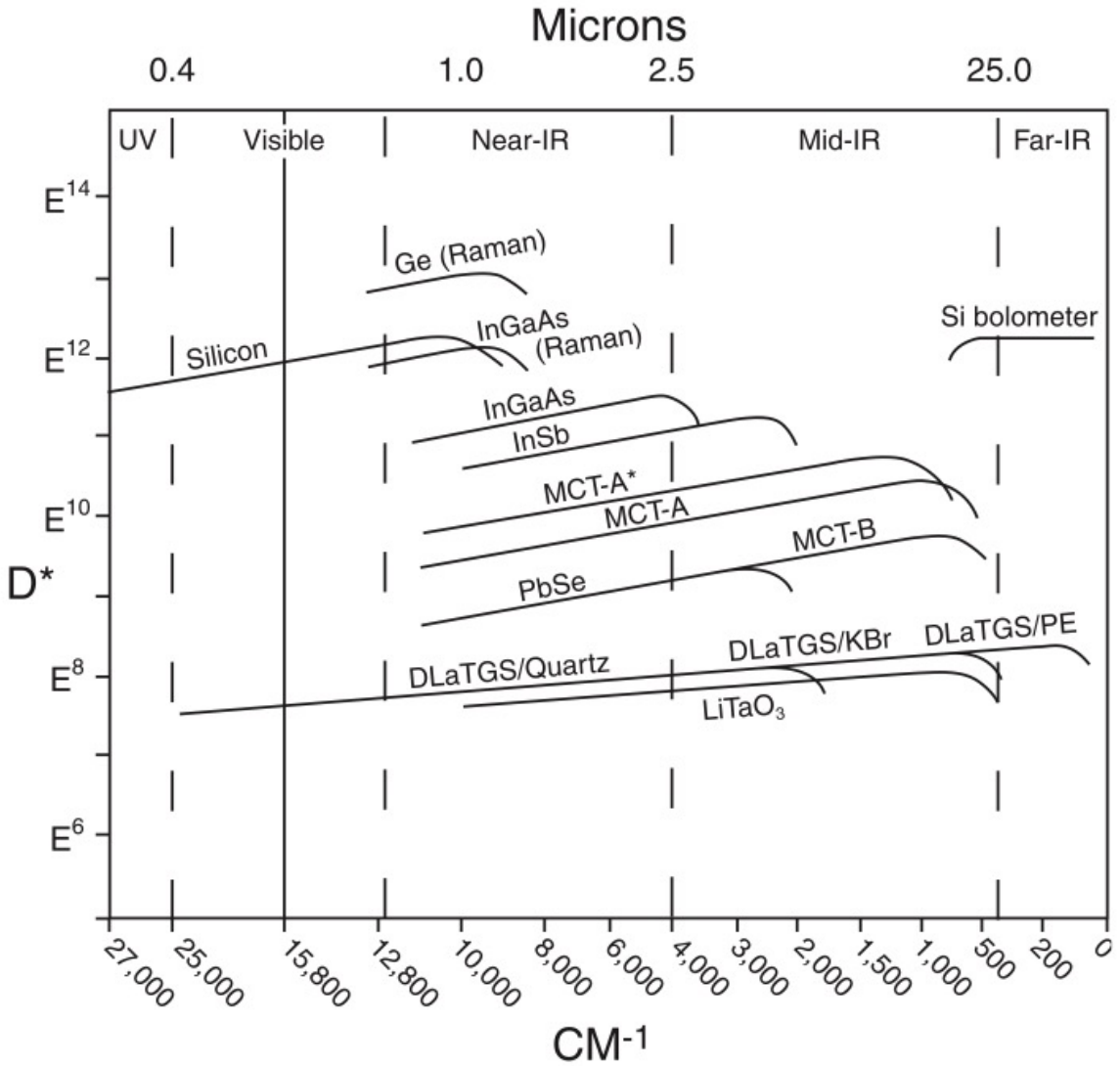
This can hide several characteristic peaks occurring in the region.



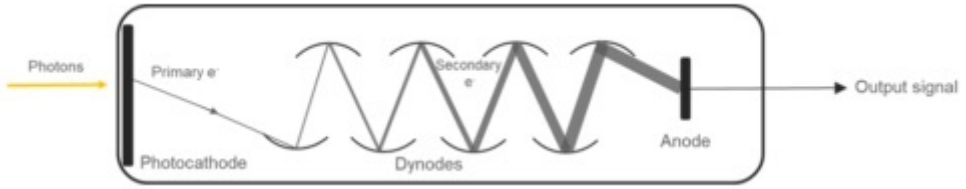
Polar molecules form hydrogen bond with the solute. This obstructs independent absorption smearing sharp features

Detector set for spectroscopic applications





Operation of a Photo-multiplier Tube



A primary detector finds the photons and generates photo dependent electrons.

The electrons are subsequently accelerated by several collisions in dynodes

Finally, a large avalanche of electrons are generated from a single photo generated electron.

Pro: Highly sensitive. Can be extended to single photon detection.

Con: Susceptible to noises. Stray electrons are also multiplied.
Large jitter, turn around time for generation of electric pulses to a single photon input.
The detector is down for a significant portion of time. Limiting photo detection bandwidth