UV-VIS spectroscopy
or
Electronic Spectroscopy
(Part-I)

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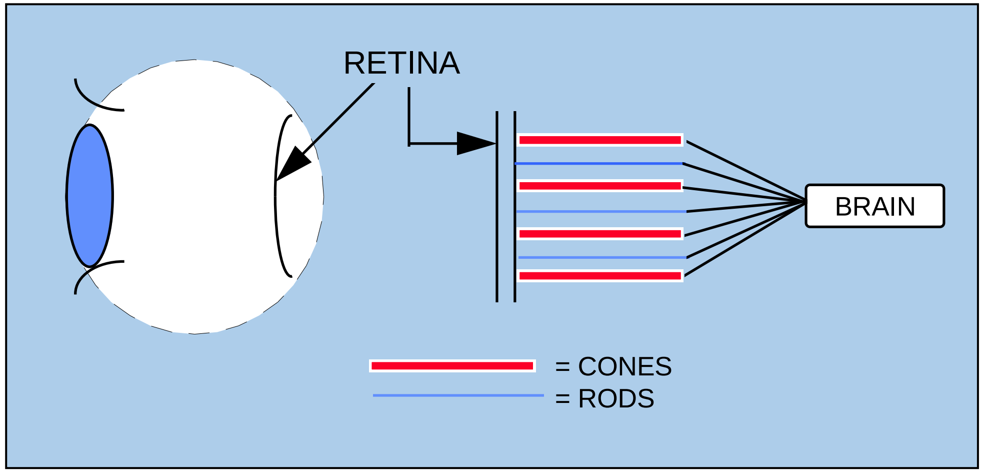
VISIBLE SPECTROSCOPY

WHAT IS COLOUR?

Colour is a sensation which occurs when light enters the eye and focuses on the retina at the back of the eye. The light actually initiates a photochemical reaction in the nerve cells attached to the retina. These transmit impulses to the brain and stimulate our sense of colour

CONES - Give three types of colours; red, blue and green

RODS - Give grey/black and also used for night vision.

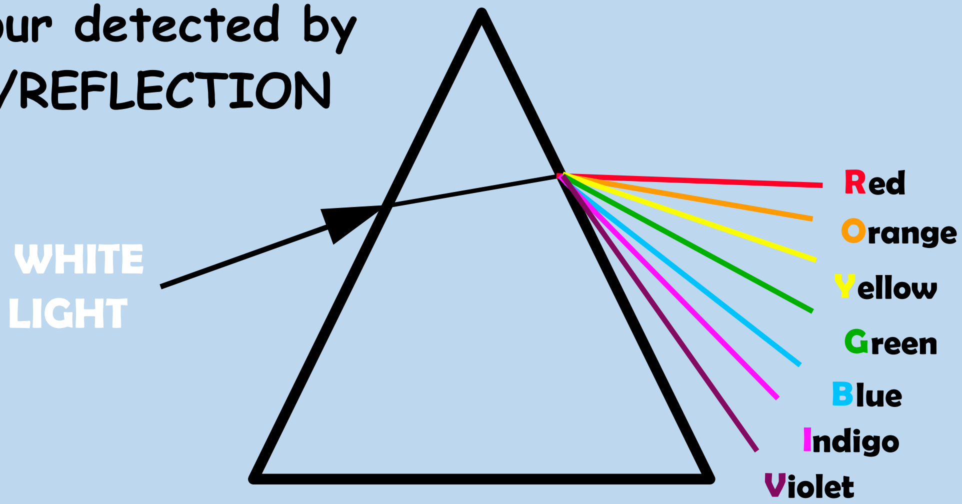


All the colours we actually sense are made up of these three colours together with white , grey and black.

VISIBLE SPECTROSCOPY

- Sunlight is white light composed of a range of colours covering a wavelengths from 380 to 750nm.

When white light falls on an object the colour detected by the eye will depend upon the ABSORPTION/REFLECTION properties of the material in the object;



- If the material completely REFLECTS all light it appears WHITE
- If the material absorbs a constant fraction of the light across the spectrum it appears GREY.
- If the material completely ABSORBS all the light it appears BLACK

VISIBLE SPECTROSCOPY

When a sample only absorbs light of a single wavelength the eye sees COMPLEMENTARY colours.

Wavelength Range Absorbed	Colour Absorbed	Colour Seen By Eye
380 - 430	Violet	Yellow - Green
430 - 480	Blue	Yellow
480 - 490	Green - Blue	Orange
490 - 500	Blue - Green	Red
500 - 560	Green	Purple
560 - 580	Yellow - Green	Violet
580 - 590	Yellow	Blue
590 - 610	Orange	Green - Blue
610 - 750	Red	Blue - Green

LOW Energy **High energy**

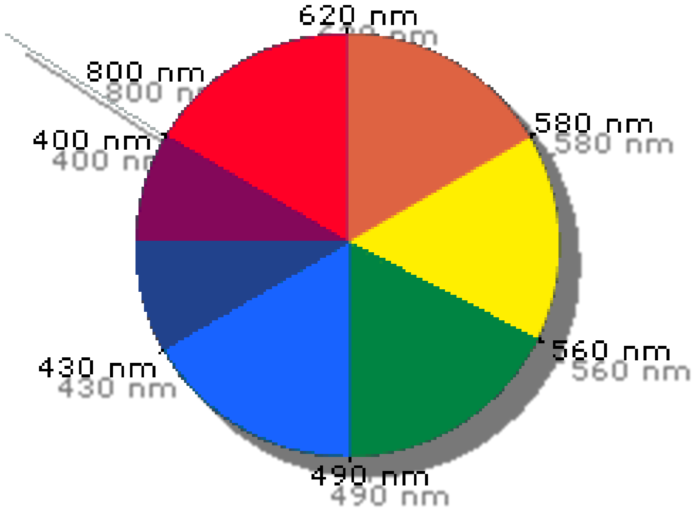
UV Spectroscopy

Visible Spectroscopy

A. Color

1. General

- When white (band of λ) light passes through, or is reflected by a surface, those wavelengths 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"

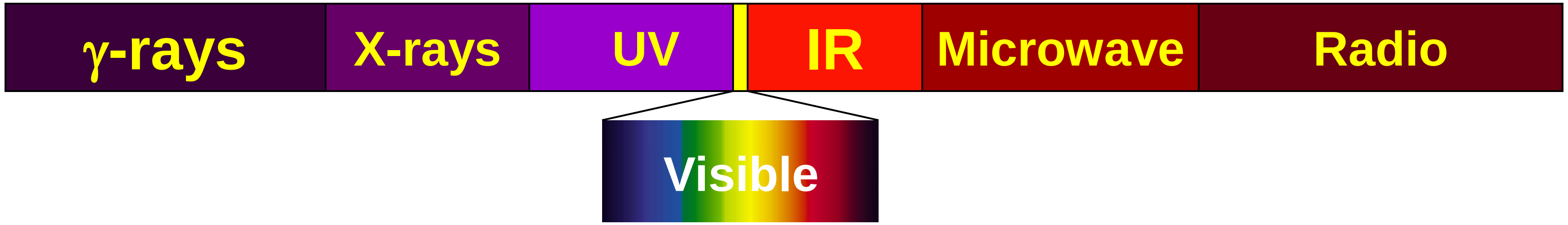


UV radiation and Electronic Excitations

The difference in energy between molecular bonding, non-bonding and anti-bonding orbitals ranges from 125-650 kJ/mole

This energy corresponds to EM radiation in the ultraviolet (UV) region, 100-350 nm, and visible (VIS) regions 350-700 nm of the spectrum

For comparison, recall the EM spectrum:



Using IR we observed vibrational transitions with energies of 8-40 kJ/mol at wavelengths of 2500-15,000 nm

For purposes of our discussion, we will refer to UV and VIS spectroscopy as UV

UV / VISIBLE SPECTROSCOPY

UV Radiation – Wavelength range: 220 - 380nm

VISIBLE Radiation – Wavelength range: 380 - 780nm

Substances can absorb varying amounts of UV and/or Visible radiation at particular wavelengths – Coloured compounds absorb energy in both UV and visible region of the electromagnetic spectrum.

Substances can be liquids or solids and measurements are made with instruments called SPECTROPHOTOMETERS

Modern instruments can be coupled to microscopes which allow solid samples and very small samples of solids and liquids to be analysed both qualitatively and quantitatively.

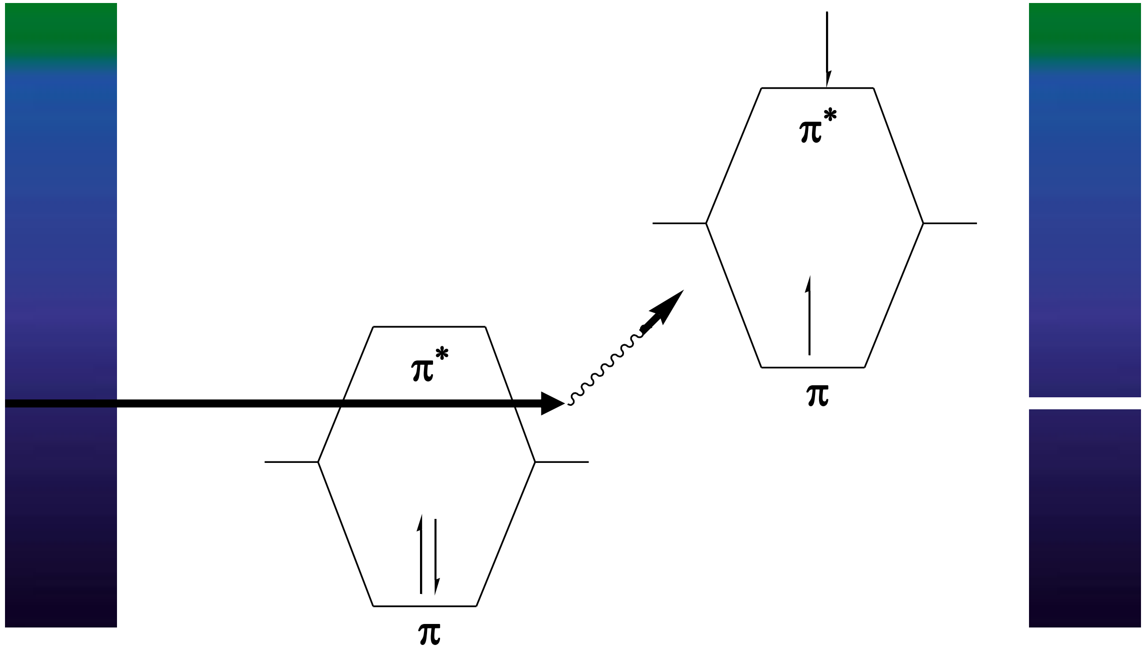
The Spectroscopic Process

In UV spectroscopy, the sample is irradiated with the broad spectrum of the UV radiation

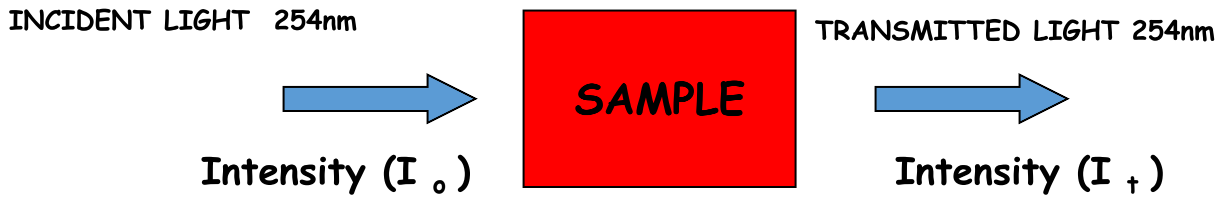
If a particular electronic transition matches the energy of a certain band of UV, it will be absorbed

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*



UV / VISIBLE SPECTROSCOPY :The THEORY



INCIDENT LIGHT 254nm

Intensity (I_o)

SAMPLE

TRANSMITTED LIGHT 254nm

Intensity (I_t)

- **If a particular wavelength of UV or Visible radiation can be isolated from the source and passed through a sample which can ABSORB some of the radiation then the TRANSMITTED light intensity (It) will be less than the INCIDENT light intensity (Io)**
- **The amount of light transmitted with respect to the incident light is called TRANSMITTANCE (T) ie.,**

$$T = \frac{I_t}{I_o}$$

- **Sample can absorb all or none of the incident light and therefore**
- **transmittance is often mentioned as percentage eg.,**

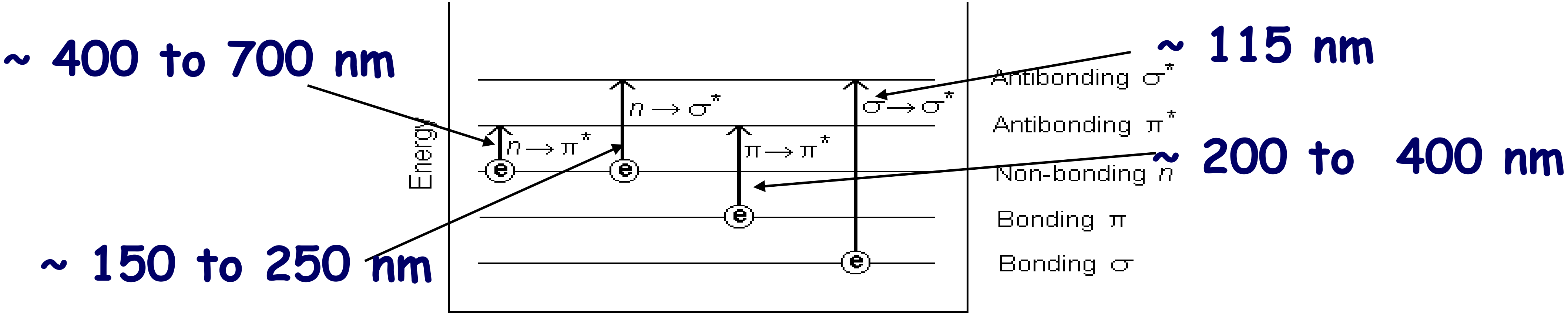
$$\% T = \frac{I_t}{I_o} \times 100$$

Absorption: Physical Basis

Absorption occurs when the energy contained in a photon is absorbed by an electron resulting in a transition to an excited state

Since photon and electron energy levels are quantized, we can only get specific allowed transitions

$E=h\nu$



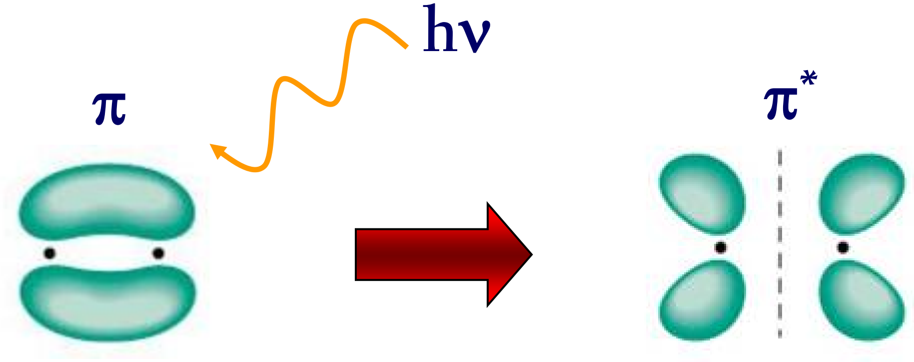
~ 400 to 700 nm

~ 150 to 250 nm

~ 115 nm

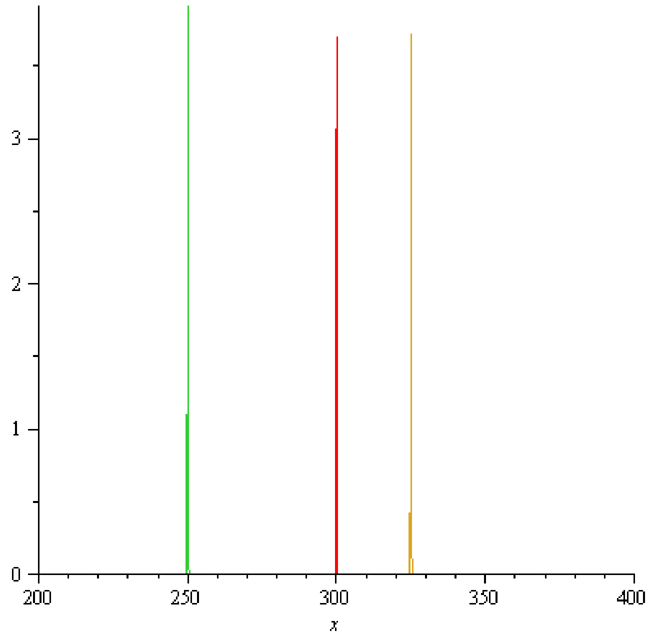
~ 200 to 400 nm

Absorption: Lineshape



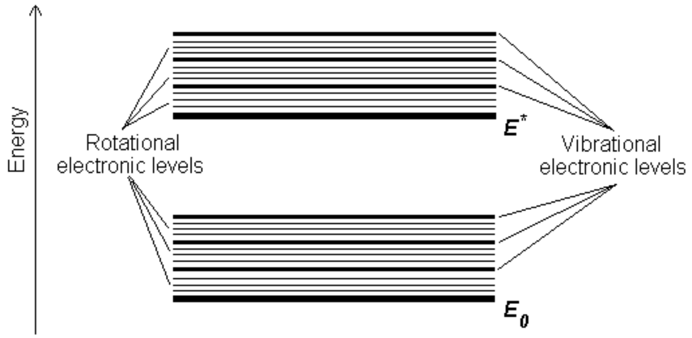
- So, our absorption spectrum should probably look like this:

- But they don't…

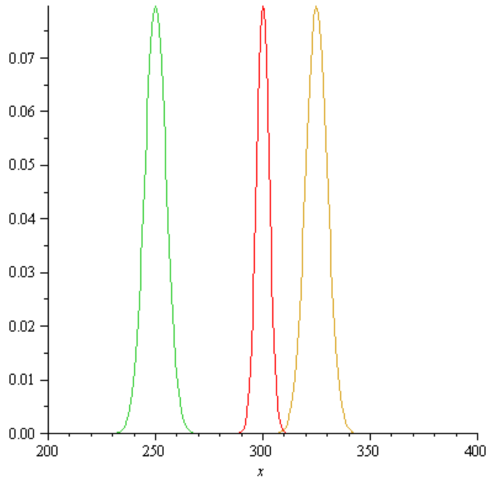


Absorption: Lineshape

- This is because molecules are always rotating and vibrating. Each rotational or vibrational state slightly changes the energy of the transition.

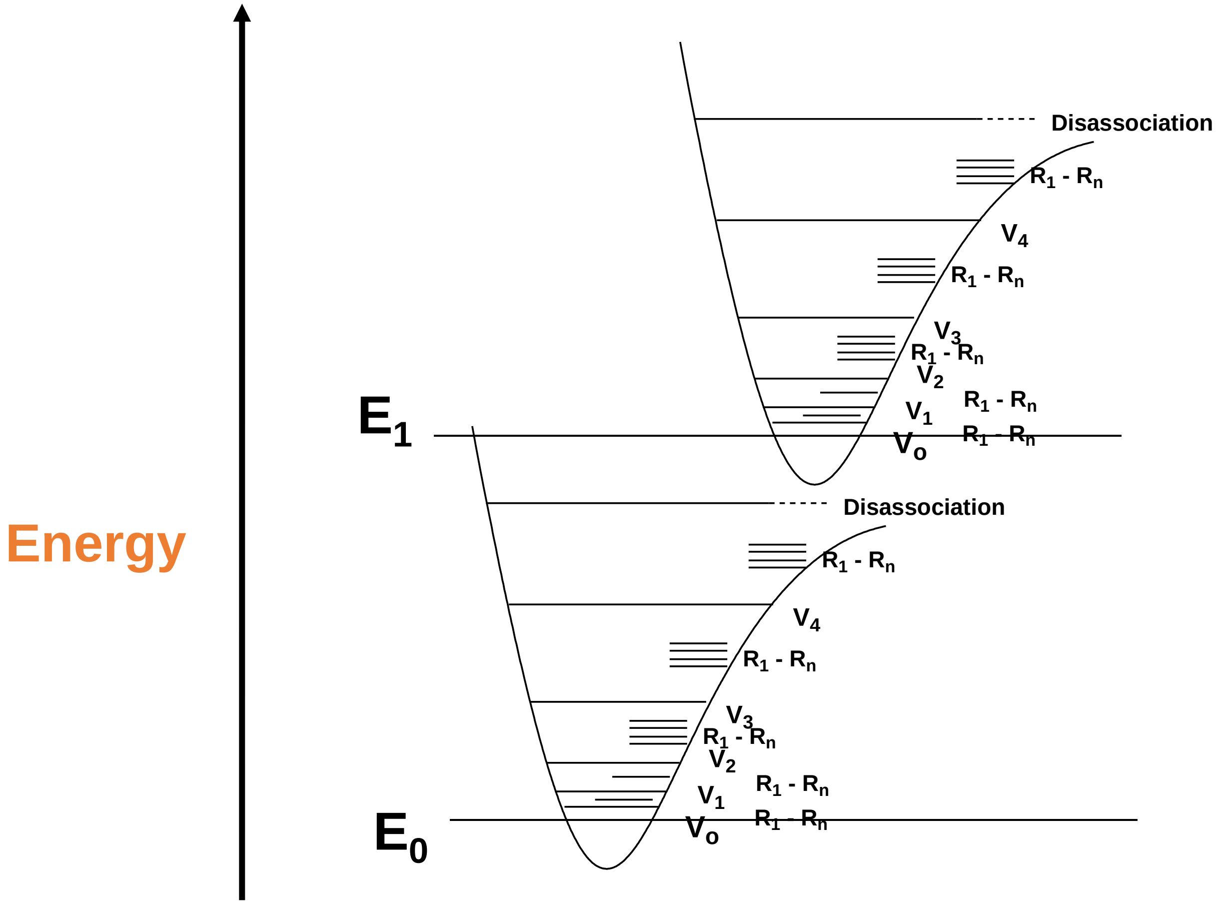


- Distrubtion of these states is… a random walk.
- So the lineshape of our absorption spectra is… normally distributed

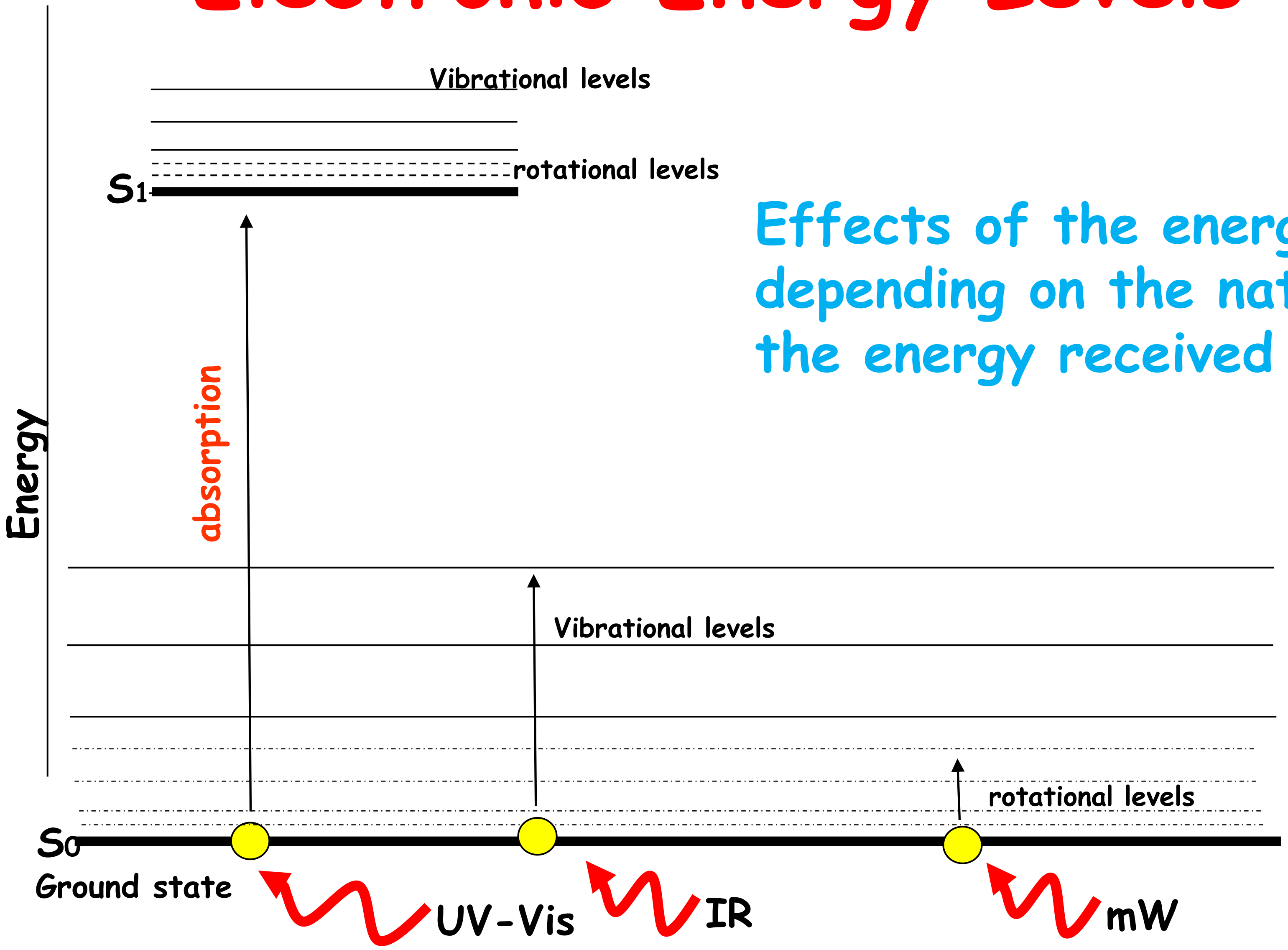


Band Structure

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



Electronic Energy Levels



Effects of the energy levels depending on the nature of the energy received

THE LAWS OF SPECTROPHOTOMETRY

Whenever a UV light falls on a substance, the consequences are controlled by two very important basic laws

LAMBERTS LAW : ABSORBANCE (A) is proportional to the PATHLENGTH (l) of the absorbing medium.
BEERS LAW : ABSORBANCE (A) is proportional to the CONCENTRATION (c) of the sample.

Absorbance (A) is the ratio of intensity of incident radiation (I_o) to the intensity of transmitted radiation (I_t)

$$\log(I_0/I_t) = A$$

The combined BEER- LAMBERT LAW says that ABSORBANCE (A) proportional to c x l

$$\log_{10}(I_0/I_t) \propto cl \quad ; \log_{10}(I_0/I_t) = \varepsilon\, cl$$

The constant ε is called the molar extinction coefficient, $\log_{10} I_0/I = \varepsilon\, Cl$
concentration (c) - Moles litre^{-1} , path length (l) - cm,
ε, Molar extinction coefficient or molar absorptivity , is a constant for a particular organic compound at a given wave length. Molar absorptivity is most commonly replaced as ε_{max} molar absorptivity at an absorption band maximum.

$$\varepsilon_{max} = 0.87 \times 10^{20}\, P.a$$

P= Transition probability. a= Target area of the absorbing system known as chromophore

Allowed transitions have ε values greater than 10000, but for forbidden transitions ε is less than 1000.

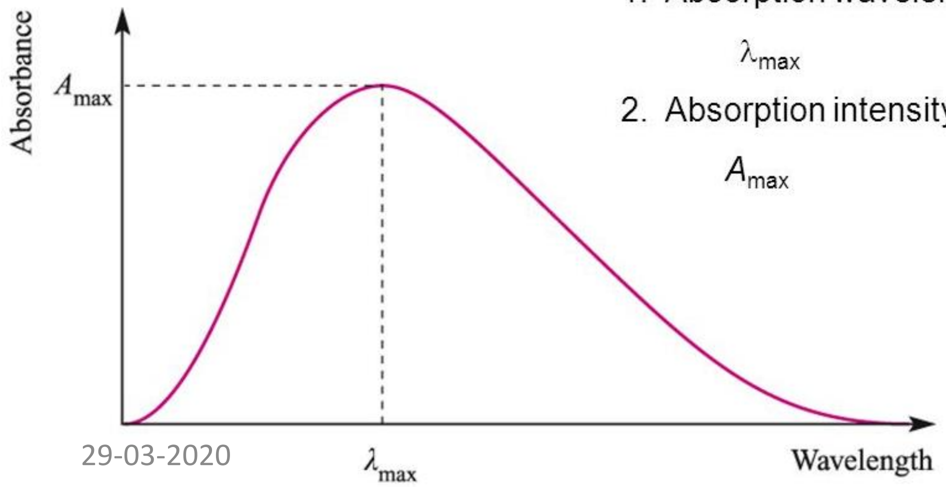
The Spectrum

From the spectrometers point of view, absorbance is the inverse of transmittance:

$$A = \log_{10} (I_0/I)$$

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

i. a longer *path length, l* through the sample will cause more UV light to be absorbed – linear effect
ii. the greater the *concentration, c* of the sample, the more UV light will be absorbed – linear effect
iii. some electronic transitions are more effective at the absorption of photon than others – *molar absorptivity*



The two main properties of an absorbance peak are:

1. Absorption wavelength

   λ_{max}

2. Absorption intensity

   A_{max}

These effects are combined into the Beer-Lambert Law $A = \varepsilon c l$

i. for most UV spectrometers, *l* would remain constant (standard cells are typically 1 cm in path length)

ii. concentration is typically varied depending on the strength of absorption observed or expected – typically dilute – sub .001 M

iii. molar absorptivities 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*

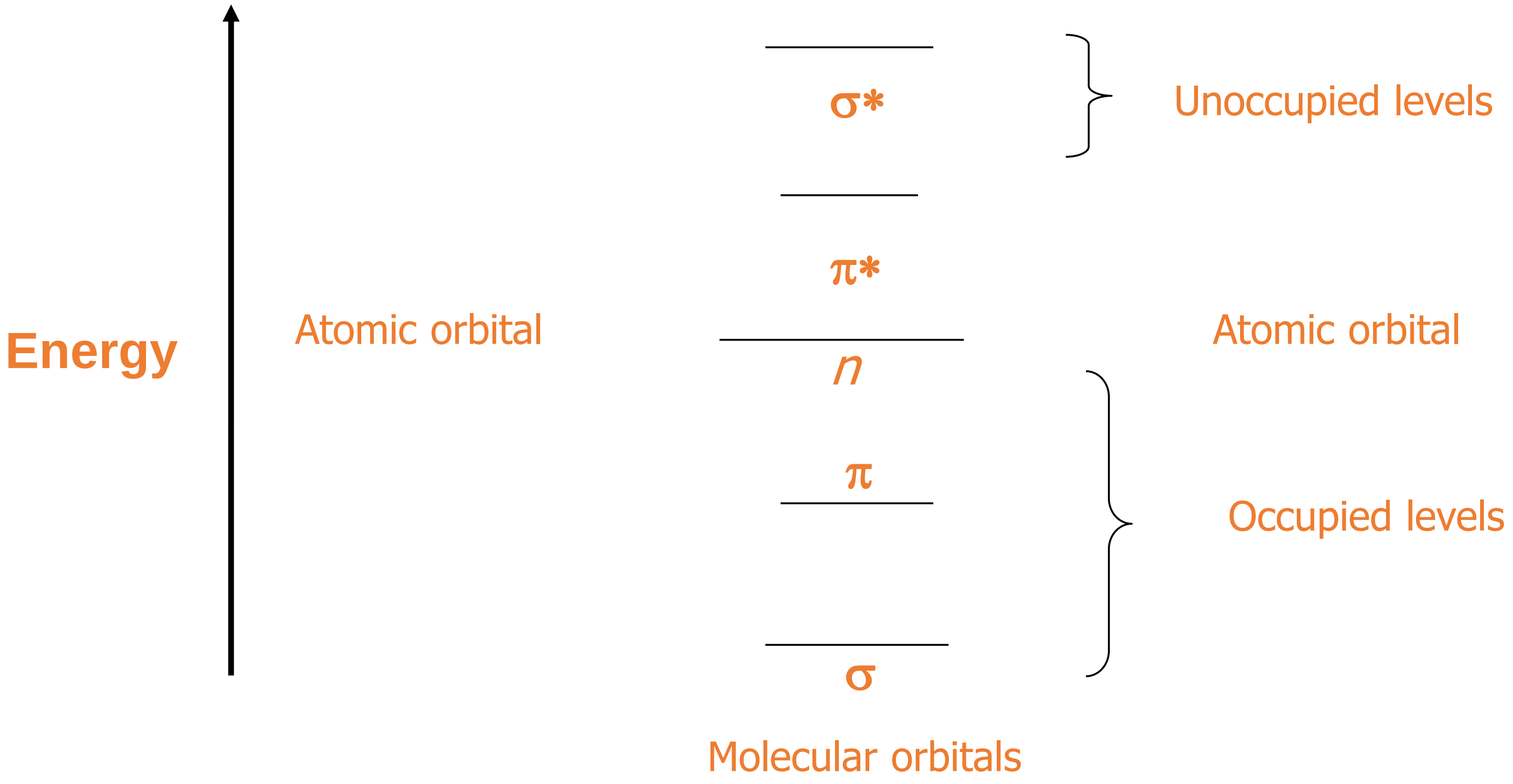
A is unitless, so the units for ε are $cm^{-1} \cdot M^{-1}$ and are rarely expressed

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

Observed electronic transitions

1. The lowest energy transition (and most often obs. by UV) is typically that of an electron in the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO)
2. For any bond (pair of electrons) in a molecule, the molecular orbitals are a mixture of the two contributing atomic orbitals; for every bonding orbital "created" from this mixing (σ, π), there is a corresponding anti-bonding orbital of symmetrically higher energy (σ^*, π^*)
3. The lowest energy occupied orbitals are typically the σ; likewise, the corresponding anti-bonding σ^* orbital is of the highest energy
4. π-orbitals are of somewhat higher energy, and their complementary anti-bonding orbital somewhat lower in energy than σ^*.
5. Unshared pairs lie at the energy of the original atomic orbital, most often this energy is higher than π or σ (since no bond is formed, there is no benefit in energy)

Observed electronic transitions



Energy

Atomic orbital

σ*

π*

n

π

σ

Molecular orbitals

Unoccupied levels

Atomic orbital

Occupied levels

Types of electronic transitions

Energy order $\sigma \rightarrow \sigma^* > \pi \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$

1. $\sigma \rightarrow \sigma^*$: Saturated molecules containing electrons only in σ M.O. Very high energy transitions. Generally occurs below 150 nm. Helps to study bond energy.

NB: Below 200 nm oxygen starts absorbing. Whole system needs to be evacuated. Below 200 nm is known as vacuum UV region.

2. $\pi \rightarrow \sigma^*$: Below 180 nm. Very less studied

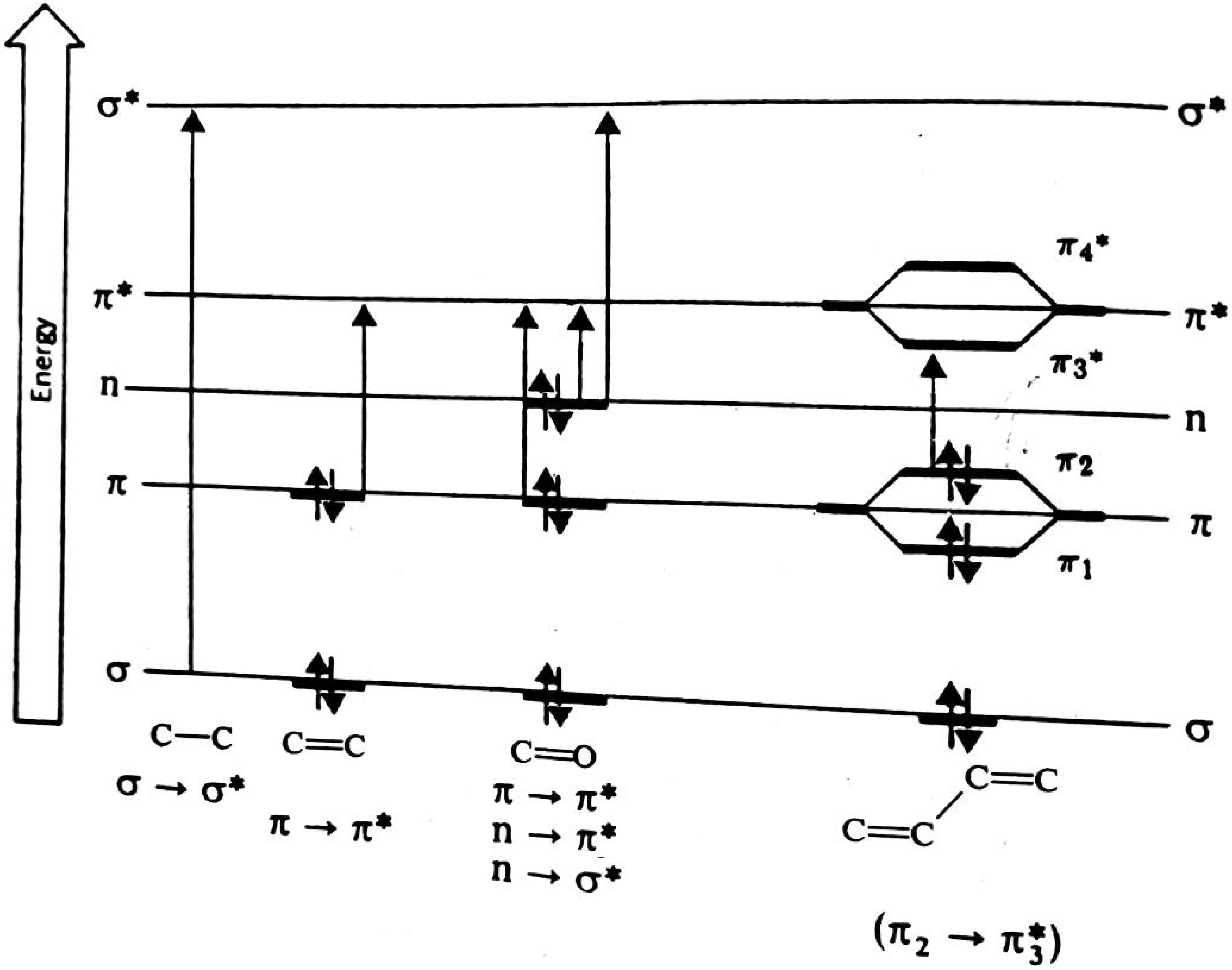
3. $n \rightarrow \sigma^*$: Chromospheres having electrons in Non Bonding and σ M.O. Saturated organic compounds with lone pairs.

Group	Wavelength	Due to increased size & polarizability amines absorb at high values than alcohols
ROH	174 nm	
R NH_2	215 nm	
RSH	193 nm	
RCl	169 nm	Increased size & low electronegativity of heteroatoms decrease the energy gap
RI	259 nm	

4. $\pi \rightarrow \pi^*$: Electron only in π M.O. Ex Alkenes, alkynes, carbonyls, cyanides, azo etc

5. $n \rightarrow \pi^*$: Transition of non bonding electrons on hetero atoms to vacant π^* M.O.

This is symmetry forbidden transition, hence of very low intensity.


Energy
σ*
π*
n
π
σ
σ*
π*
n
π
σ
π4*
π3*
π2
π1
C—C
σ → σ*
C═C
π → π*
C═O
π → π*
n → π*
n → σ*
C═C
C═C
(π2 → π3*)

Observed electronic transitions

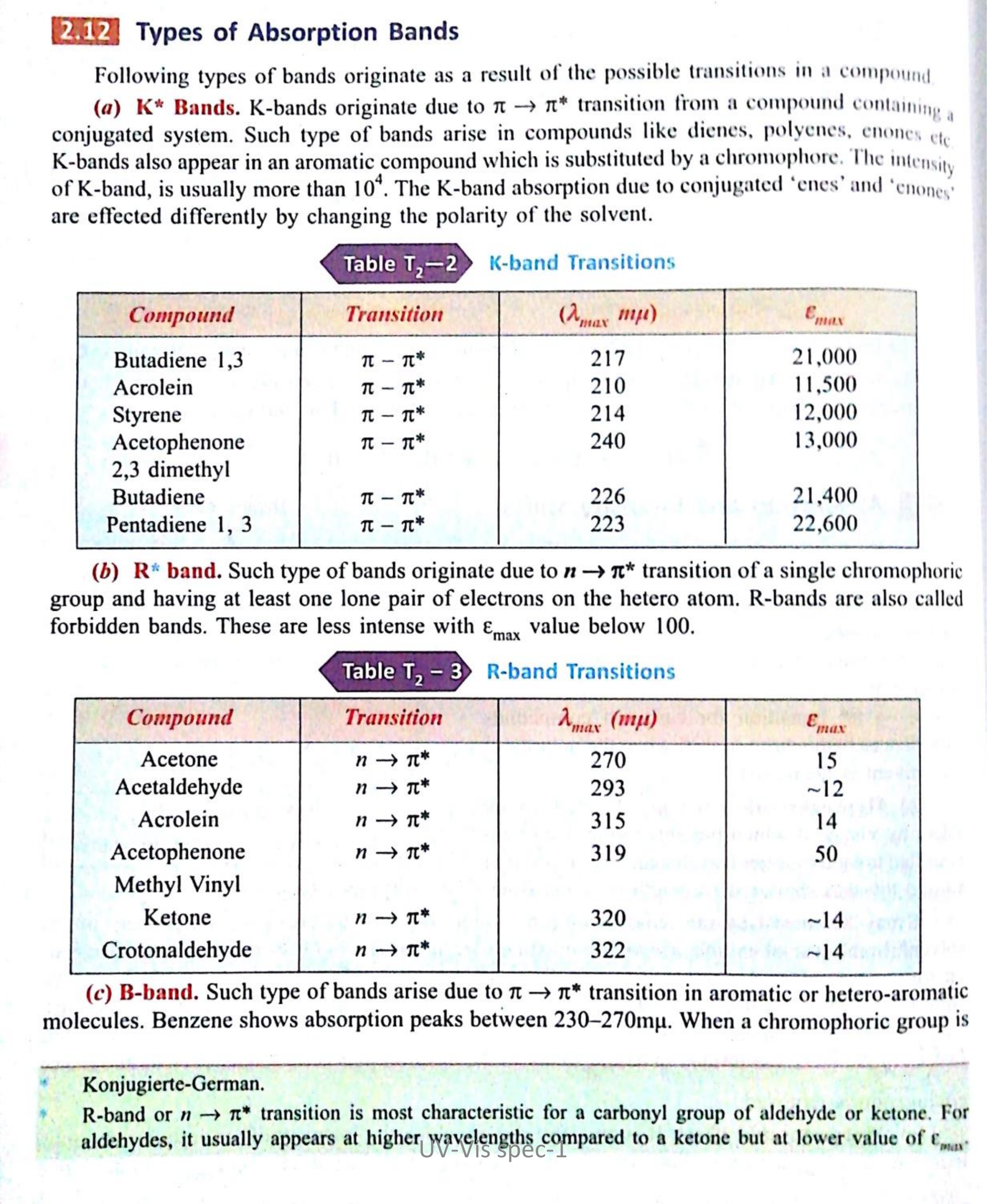
Although UV spectrum extends below 100 nm, atmospheric oxygen is not transparent below 200 nm

Special equipment required 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 compds.	180 nm
$n \longrightarrow \sigma^*$	O, N, S, halogens	190 nm
$n \longrightarrow \pi^*$	carbonyls	300 nm



2.12 Types of Absorption Bands

Following types of bands originate as a result of the possible transitions in a compound.

(*a*) K* Bands. K-bands originate due to π → π* transition from a compound containing a conjugated system. Such type of bands arise in compounds like dienes, polyenes, enones etc. K-bands also appear in an aromatic compound which is substituted by a chromophore. The intensity of K-band, is usually more than 10^4. The K-band absorption due to conjugated 'enes' and 'enones' are effected differently by changing the polarity of the solvent.

Table T$_2$—2 K-band Transitions

Compound	*Transition*	(λ_{max} *mμ*)	ε_{max}
Butadiene 1,3	π – π*	217	21,000
Acrolein	π – π*	210	11,500
Styrene	π – π*	214	12,000
Acetophenone	π – π*	240	13,000
2,3 dimethyl Butadiene	π – π*	226	21,400
Pentadiene 1, 3	π – π*	223	22,600

(*b*) R* band. Such type of bands originate due to *n* → π* transition of a single chromophoric group and having at least one lone pair of electrons on the hetero atom. R-bands are also called forbidden bands. These are less intense with ε_{max} value below 100.

Table T$_2$ – 3 R-band Transitions

Compound	*Transition*	λ_{max} (*mμ*)	ε_{max}
Acetone	*n* → π*	270	15
Acetaldehyde	*n* → π*	293	~12
Acrolein	*n* → π*	315	14
Acetophenone	*n* → π*	319	50
Methyl Vinyl Ketone	*n* → π*	320	~14
Crotonaldehyde	*n* → π*	322	~14

(*c*) B-band. Such type of bands arise due to π → π* transition in aromatic or hetero-aromatic molecules. Benzene shows absorption peaks between 230–270mμ. When a chromophoric group is

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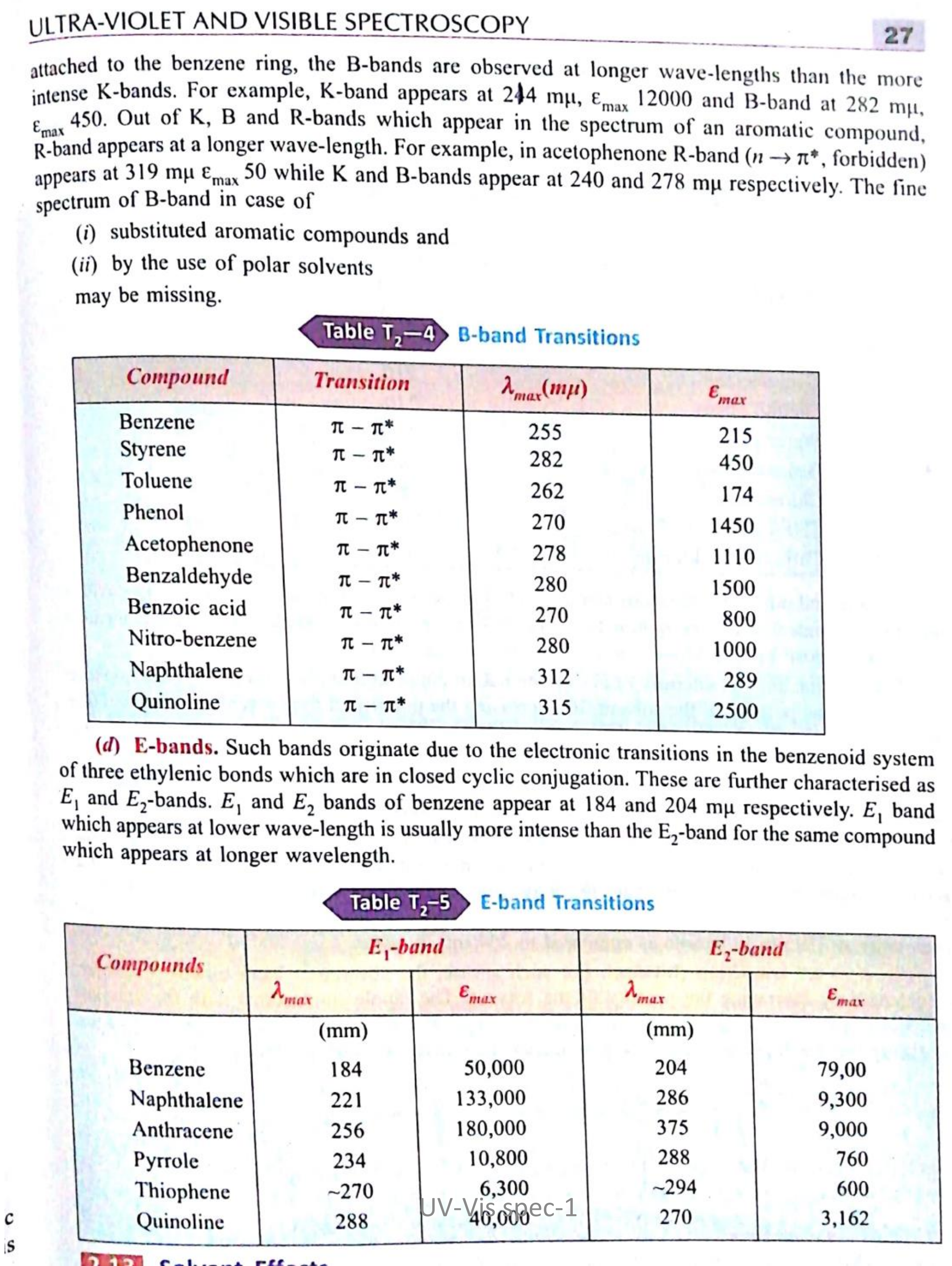
* Konjugierte-German.

* R-band or *n* → π* transition is most characteristic for a carbonyl group of aldehyde or ketone. For aldehydes, it usually appears at higher wavelengths compared to a ketone but at lower value of ε_{max}.



attached to the benzene ring, the B-bands are observed at longer wave-lengths than the more intense K-bands. For example, K-band appears at 244 mμ, ε_{max} 12000 and B-band at 282 mμ, ε_{max} 450. Out of K, B and R-bands which appear in the spectrum of an aromatic compound, R-band appears at a longer wave-length. For example, in acetophenone R-band ($n \to \pi^*$, forbidden) appears at 319 mμ ε_{max} 50 while K and B-bands appear at 240 and 278 mμ respectively. The fine spectrum of B-band in case of

(*i*) substituted aromatic compounds and
(*ii*) by the use of polar solvents

may be missing.

Table T_2—4 B-band Transitions

Compound	*Transition*	λ_{max}(mμ)	ε_{max}
Benzene	$\pi - \pi^*$	255	215
Styrene	$\pi - \pi^*$	282	450
Toluene	$\pi - \pi^*$	262	174
Phenol	$\pi - \pi^*$	270	1450
Acetophenone	$\pi - \pi^*$	278	1110
Benzaldehyde	$\pi - \pi^*$	280	1500
Benzoic acid	$\pi - \pi^*$	270	800
Nitro-benzene	$\pi - \pi^*$	280	1000
Naphthalene	$\pi - \pi^*$	312	289
Quinoline	$\pi - \pi^*$	315	2500

(*d*) E-bands. Such bands originate due to the electronic transitions in the benzenoid system of three ethylenic bonds which are in closed cyclic conjugation. These are further characterised as E_1 and E_2-bands. E_1 and E_2 bands of benzene appear at 184 and 204 mμ respectively. E_1 band which appears at lower wave-length is usually more intense than the E_2-band for the same compound which appears at longer wavelength.

Table T_2–5 E-band Transitions

Compounds	E_1-*band*		E_2-*band*	
	λ_{max} (mm)	ε_{max}	λ_{max} (mm)	ε_{max}
Benzene	184	50,000	204	79,00
Naphthalene	221	133,000	286	9,300
Anthracene	256	180,000	375	9,000
Pyrrole	234	10,800	288	760
Thiophene	~270	6,300	~294	600
Quinoline	288	40,000	270	3,162

Selection Rules

1. Not all transitions that are possible are observed

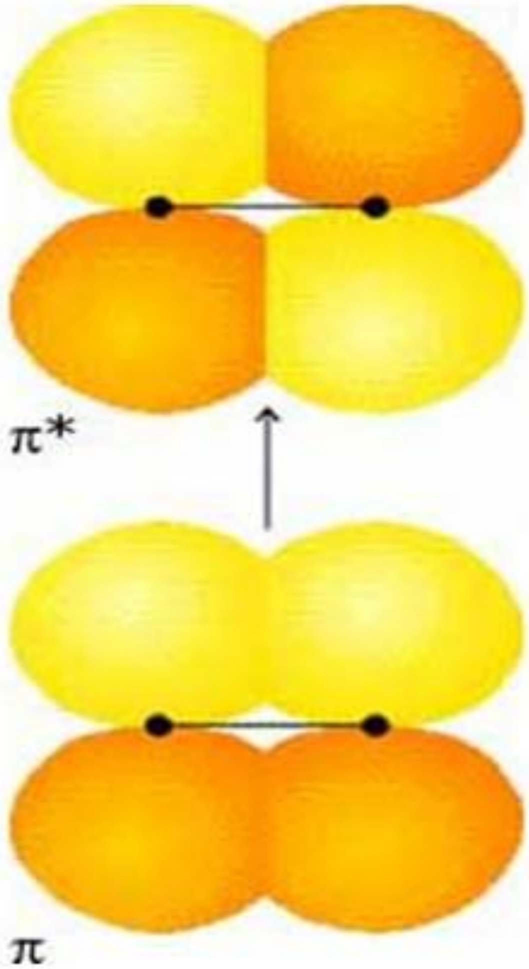
2. For an electronic transition, certain quantum mechanical constraints apply – these are called “selection rules”

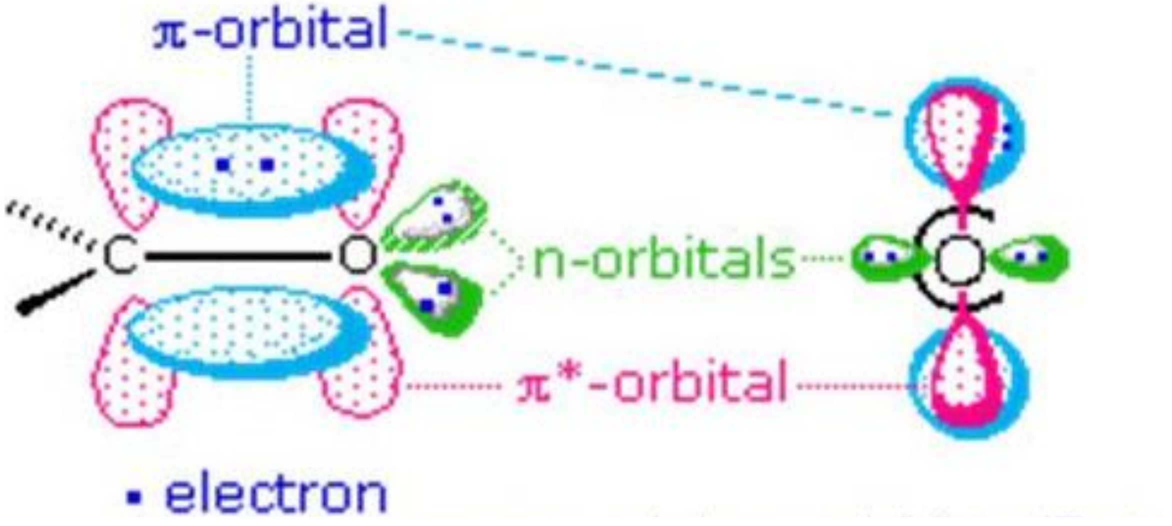
3. For example, an electron cannot change its spin quantum number during a transition – these are “forbidden”

   Other examples include:
   - the number of electrons that can be excited at one time
   - symmetry properties of the molecule
   - symmetry of the electronic states

4. To further complicate matters, “forbidden” transitions are sometimes observed (although at low intensity) due to other factors

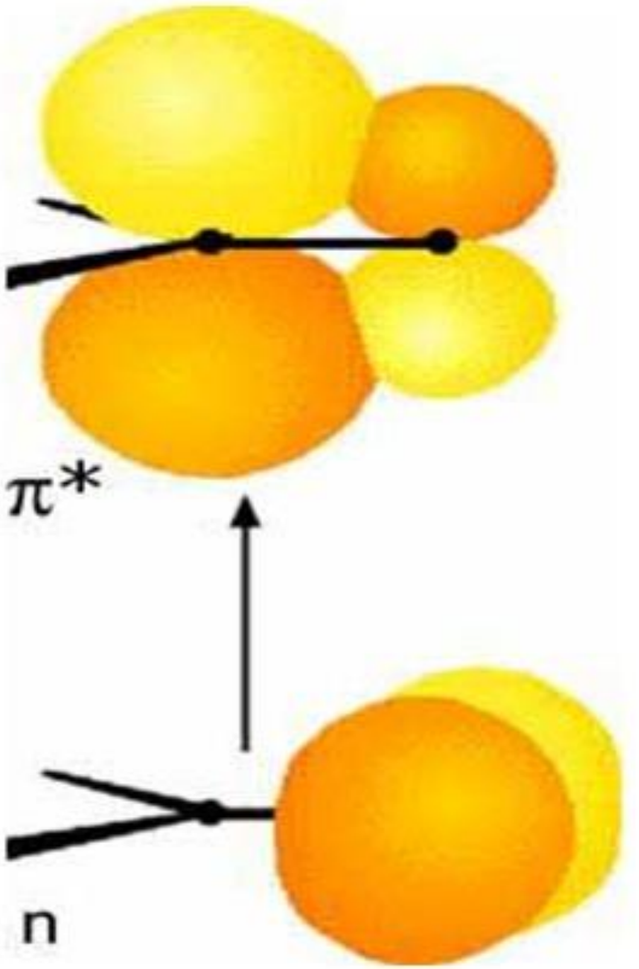
Electronic Transitions: $\pi \rightarrow \pi^*$

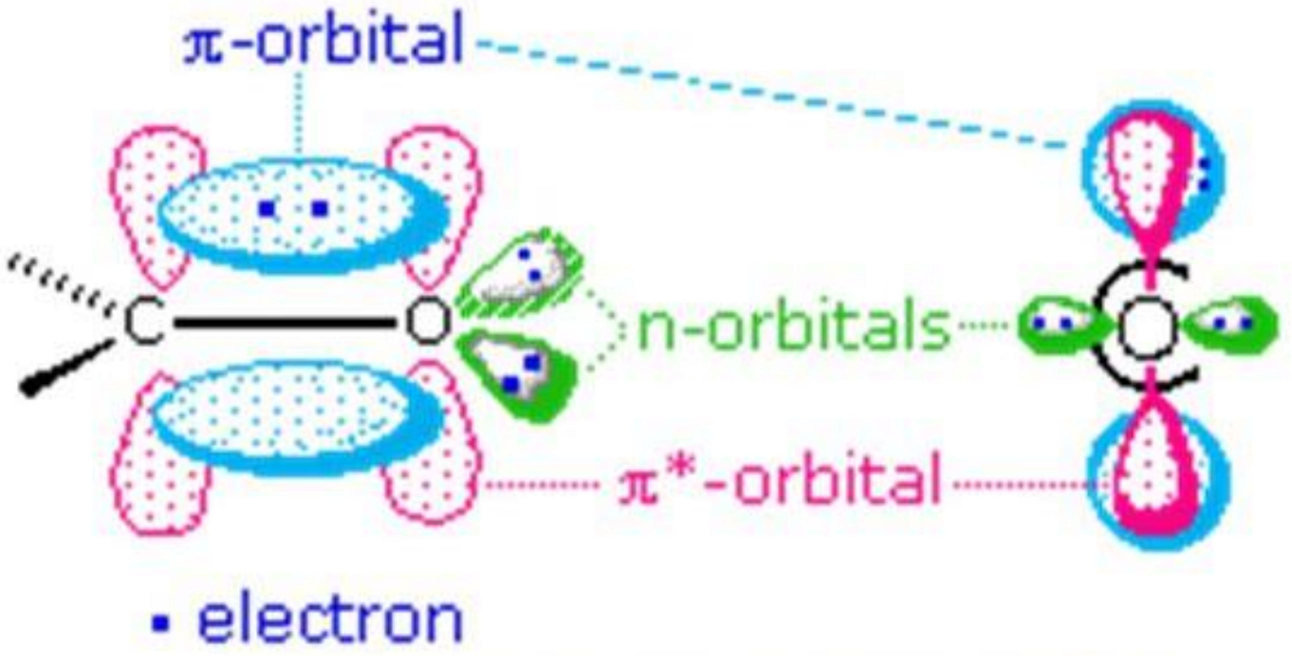




The $\pi \rightarrow \pi^*$ transition involves orbitals that have significant overlap, and the probability is near 1.0 as they are “symmetry allowed”.

Electronic Transitions: $n \rightarrow \pi^*$





The n-orbitals do not overlap at all well with the π^* orbital, so the probability of this excitation is small. The ε of the $n \rightarrow \pi^*$ transition is about 10^3 times smaller than ε for the $\pi \rightarrow \pi^*$ transition as it is "symmetry forbidden".

E. Band Structure

1. Unlike IR (or later NMR), where there may be upwards of 5 or more resolvable peaks from which to elucidate structural information, UV tends to give wide, overlapping bands.

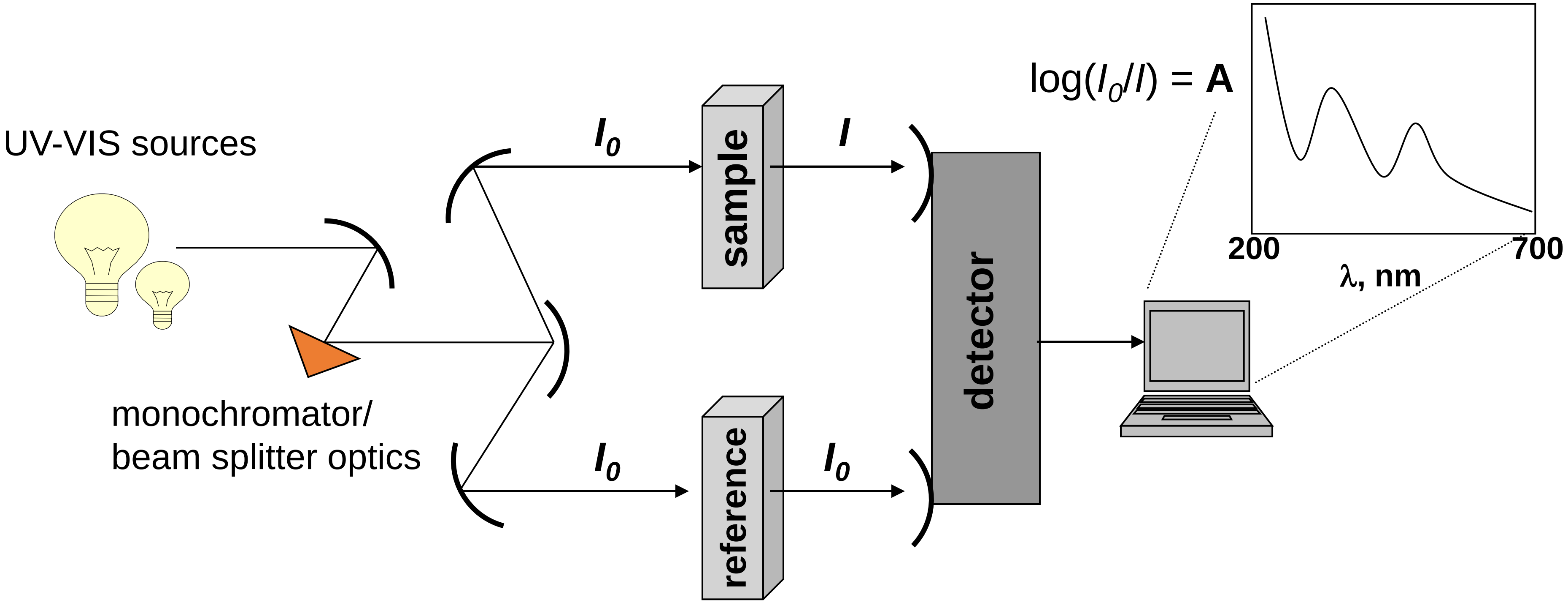
2. It would seem that since the electronic energy levels of a pure sample of molecules would be quantized, fine, discrete bands would be observed – for atomic spectra, this is the case.

3. In molecules, when a bulk sample of molecules is observed, not all bonds (read – pairs of electrons) are in the same vibrational or rotational energy states.

4. This effect will impact the wavelength at which a transition is observed – very similar to the effect of H-bonding on the O-H vibrational energy levels in neat samples.

Instrumentation and Spectra

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



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 inciden light (I_0) and sends this information to the recorder

Instrumentation and Spectra

1. Virtually all UV spectra are recorded in solution-phase

2. Cells can be made of plastic, glass or quartz

3. Only quartz is transparent in the full 200-700 nm range; plastic and glass are only suitable for visible spectra

A typical sample cell (commonly called a *cuvet*)

Chromophores

Remember the electrons present in organic molecules are involved in covalent bonds or lone pairs of electrons on atoms such as O or N

Since similar functional groups will have electrons capable of discrete classes of transitions, the characteristic energy of these energies is more representative of the functional group than the electrons themselves

A functional group capable of having characteristic electronic transitions is called a chromophore (*color loving*)

Structural or electronic changes in the chromophore can be quantified and used to predict shifts in the observed electronic transitions

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 p systems or carbonyls

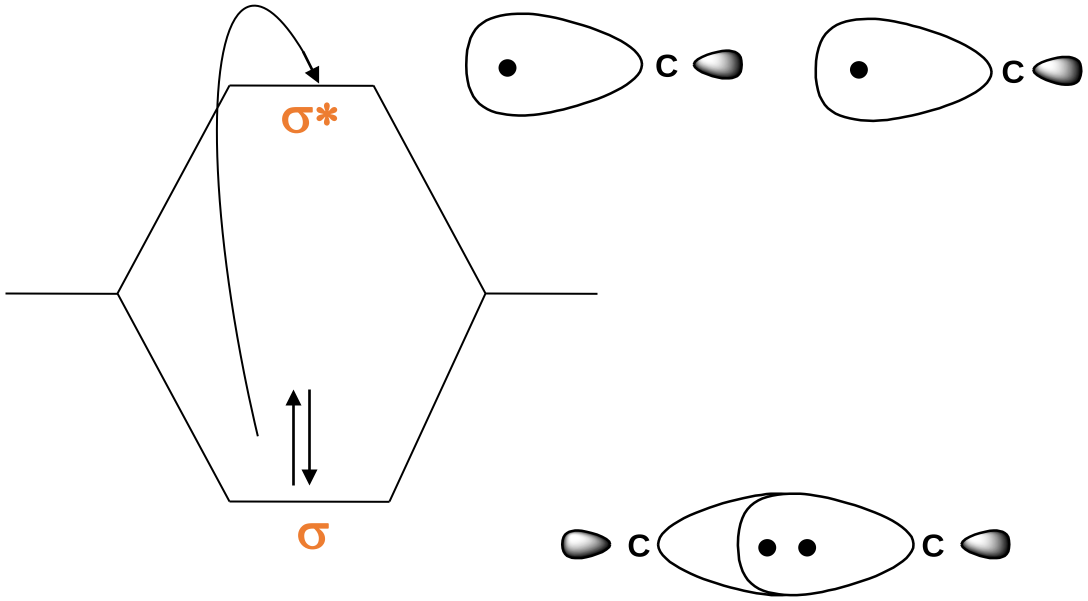
Common solvents and cutoffs:

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

Organic Chromophores

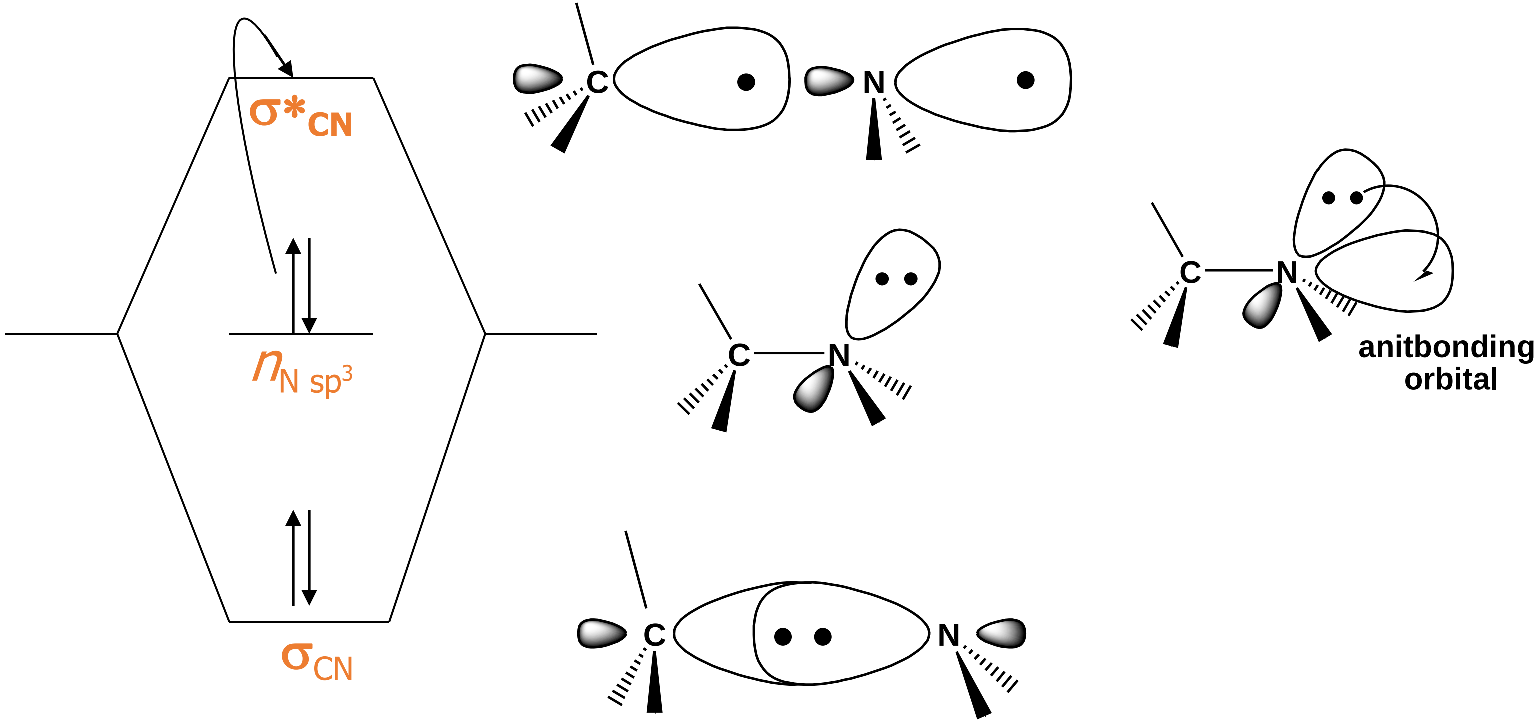
Alkanes – only posses sigma-bonds and no lone pairs of electrons, so only the high energy σ → σ* transition is observed in the far UV

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



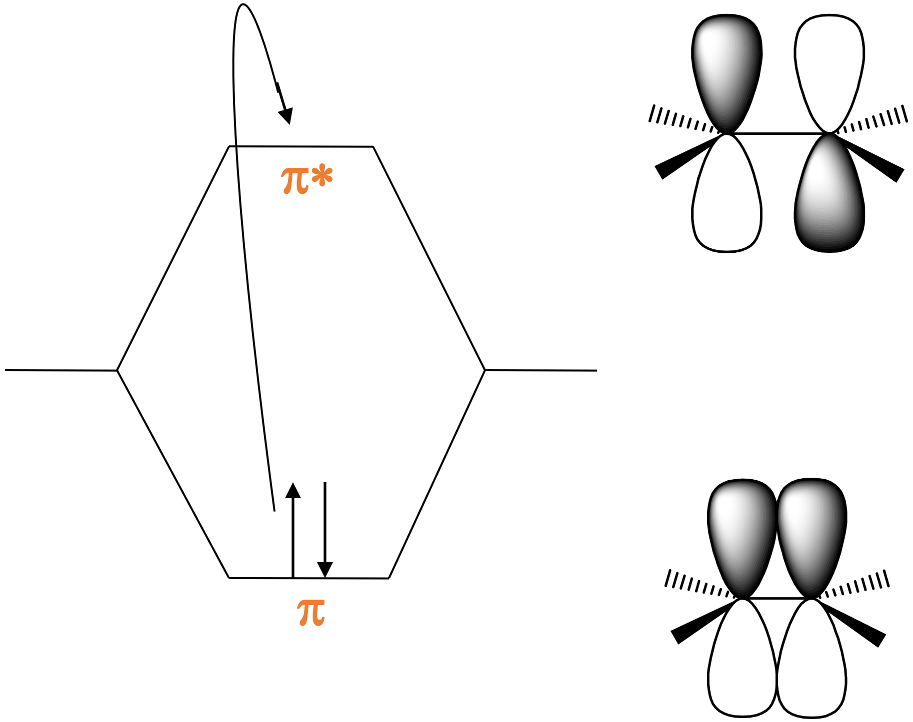
Alcohols, ethers, amines and sulfur compounds – in the cases of simple, aliphatic examples of these compounds the $n \rightarrow \sigma*$ is the most often observed transition; like the alkane $\sigma \rightarrow \sigma*$ it is most often at shorter λ than 200 nm

Note how this transition occurs from the HOMO to the LUMO



Alkenes and Alkynes – in the case of isolated examples of these compounds the $\pi \rightarrow \pi^*$ is observed at 175 and 170 nm, respectively

Even though this transition is of lower energy than $\sigma \rightarrow \sigma^*$, it is still in the far UV – however, the transition energy is sensitive to substitution

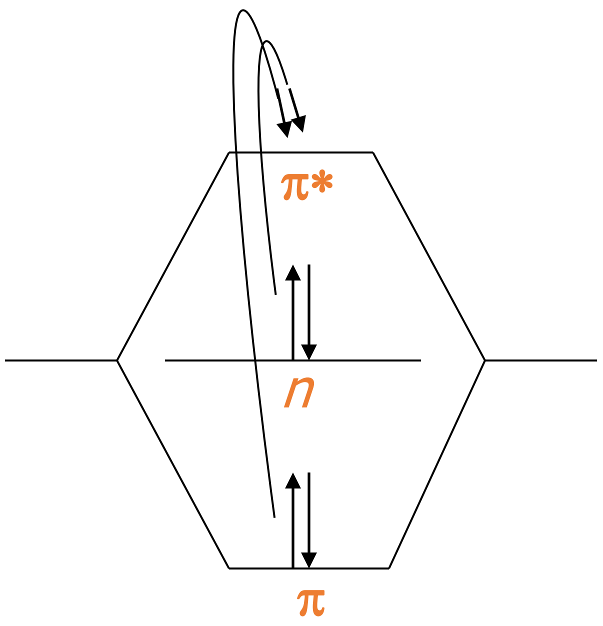


Carbonyls – unsaturated systems incorporating N or O can undergo *n* → π* transitions (~285 nm) in addition to π → π* (188 nm)

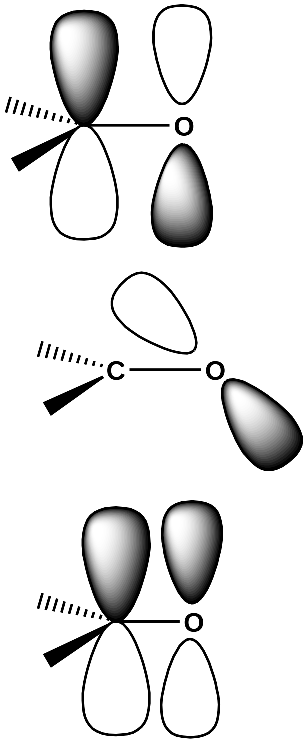
Despite the fact this transition is forbidden by the selection rules (ε = 15), it is the most often observed and studied transition for carbonyls. This transition is also sensitive to substituents on the carbonyl

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

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



σ$_{CO}$ transitions omitted for clarity



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