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Date:
Naqib's
15 Nov, 2017

15 nov, 2017

The interaction between the matter and electromagnetic radiation.

Spectroscopy

Definition:

* Spectroscopy is the study of interaction

* of electromagnetic radiation with matter.

*

What is atomic spectroscopy?

* Atomic spectroscopy is concerned with interaction of electro-magnetic radiations with atoms which are most commonly in there low energy state or ground state.

*

What is molecular spectroscopy?

* Molecular spectroscopy is concerned with interaction of electromagnetic radiations with molecule. In this case transitions occur between rotational and vibrational energy levels, in addition to electronic transition.

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What is electro-magnetic radiation?

Definition:

* "It is the form in which energy can be transfer from one point to another point through space."

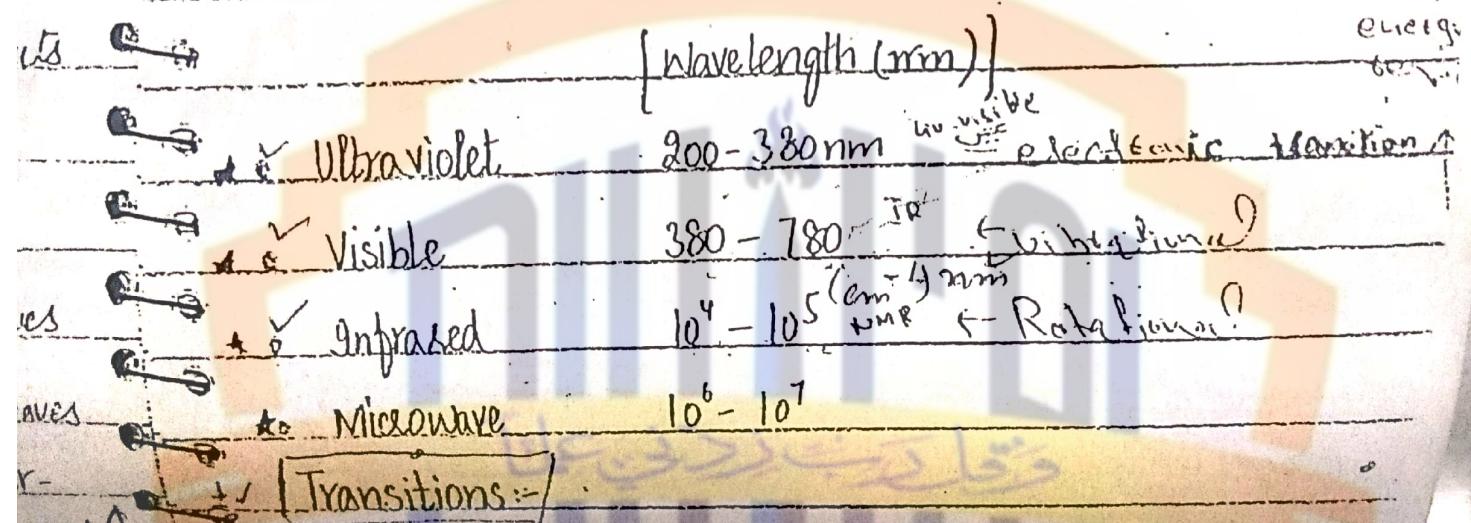
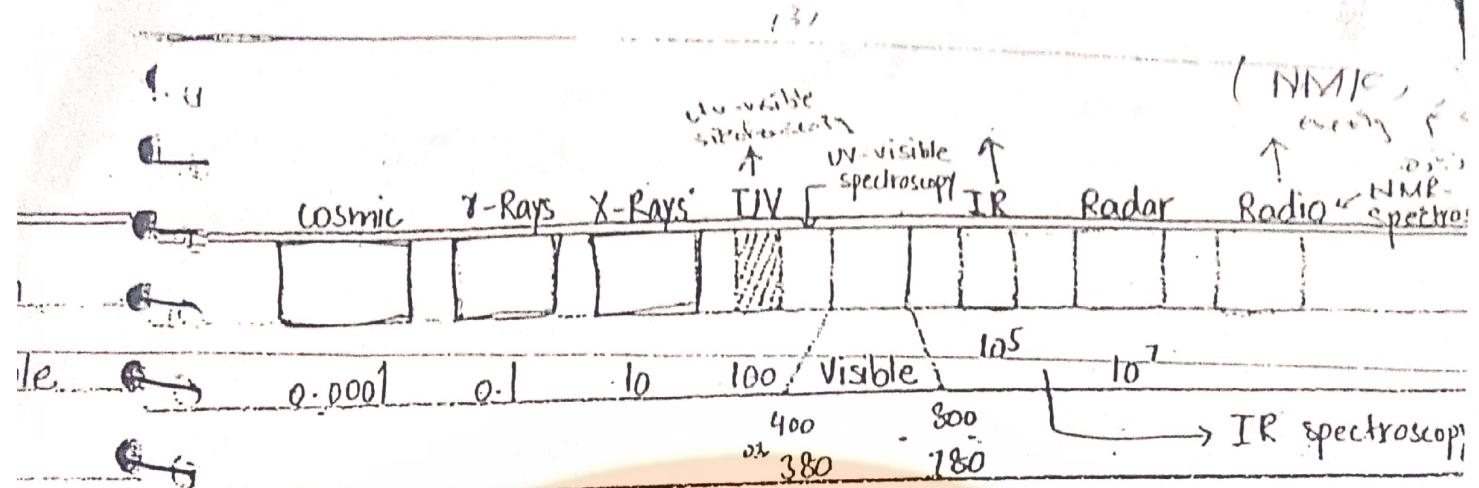
* When an electrical current passes from one point to another through a conductor a magnetic field is placed in its vicinity.

* Similarly, a change in magnetic field can produce an electrical current in a suitable conductor. It means that both effects are inter-related. Like radiation both these effects can be transmitted through space no material/medium is required.

* According to Maxwell electrical disturbances are accompanied by emission of electrical waves. Since electrical and magnetic field are inter-related it is now considered that an electrical field will be accompanied by a magnetic field/wave. Therefore, electromagnetic radiations can be considered as wave of energy propagating from a source in space and consisting of oscillating electrical and magnetic fields at right angles to each other as well as to the direction of propagation.

Characteristics of

- Electromagnetic radiations possess dual nature.
- They can travel through space.



Transitions:- There are three basic processes by

which a molecule can absorb radiations All these processes involve raising the molecule to

a high energy level. The increase in energy is

equal to the energy of absorbed radiation

The three types of internal energy are quantised.

$$\text{Incident Energy} = \text{Energy required for Transition} = \Delta E$$

First the molecule rotates about various axes

The energy of rotation for a definite ratio level is definite As, the molecule absorbs the

radiation it can go to higher rotational energy level This type of transition is

$\Delta E = \text{vibrational energy}$ called rotational transition

$\Delta E = \text{NMR energy}$ Secondly an atom or group of atoms

Within a molecule vibrates relative to each other and energy of vibration occurs at a definite quantised level. The molecule can absorb a discrete amount of energy and be raised to higher vibrational energy levels. This type of transition is called vibrational transition.

⇒ In the third transition, electrons of the molecule may be raised to higher electronic energy level. This is called electronic transition.

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Since each of internal energy transition is quantised they will occur at a definite wavelength. The relative energy levels of these transition processes are in the

order of: Energy order | V.I.P
Electronic \rightarrow Vibrational \rightarrow Rotational

(Rotational) transition takes place at a very low energy and longer wavelength. Therefore, such type of transitions takes place in microwave or far infrared region.

Vibrational transition requires higher energy and takes place in near infrared region.

in visible spectrum

UV/VIS 5

+ While electronic transition require still more energy therefore it will take place in UV and visible region.

Rotational Transitions

Purely rotational transitions can take place in the far infrared and microwave region where the energy is insufficient to cause vibrational or electronic transition. The molecule at room temperature is in lowest energy state called ground state. Therefore, the pure rotational transitions will occur at ground state. discrete absorption lines will formed in the spectrum. The wavelength of each line correspond to a particular transition. Fundamental information can be obtained about rotational energy levels of a molecule.

Vibrational Transitions:-

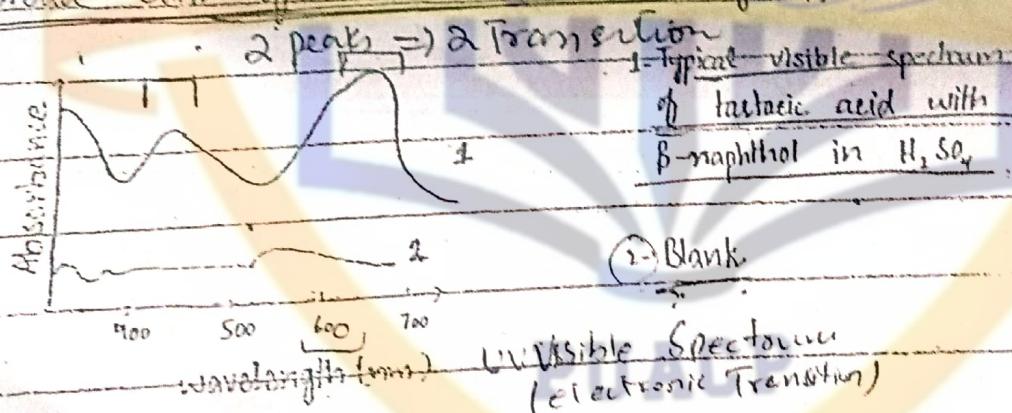
As the energy is increase rotational transition takes place in addition to vibrational transitions. In rotational level to the lowest vibrational level can be excited to

Super-imposed

recent rotational levels of the excited bivalent level.

Electronic Transitions \rightarrow Electrons

At higher energy electronic transition takes place. And rotational and vibrational transitions are super-imposed on these. This results in even larger number of possible transitions. Though all the transitions occurs in quantised manner absorbed though all the transitions occurs in quantised manner absorbed but these individual wavelengths are too close to be resolved into individual lines and rotational peaks. The net result is a spectrum broad band of absorbed wavelengths.



UV-Visible Spectroscopy- (Electronic Spectroscopy)

50nm 200nm 400nm 800nm
(Vacuum UV region) (UV region) (Visible Region)

Principle:

When a molecule is irradiated with

UV visible

molecule

higher

generally

orbitals

orbitals

The wave

upon it

the wave

is scattered

in all

directions

at different

intensities

and the

intensity

is proportional

to the

intensity

of the

radiation

and the

intensity

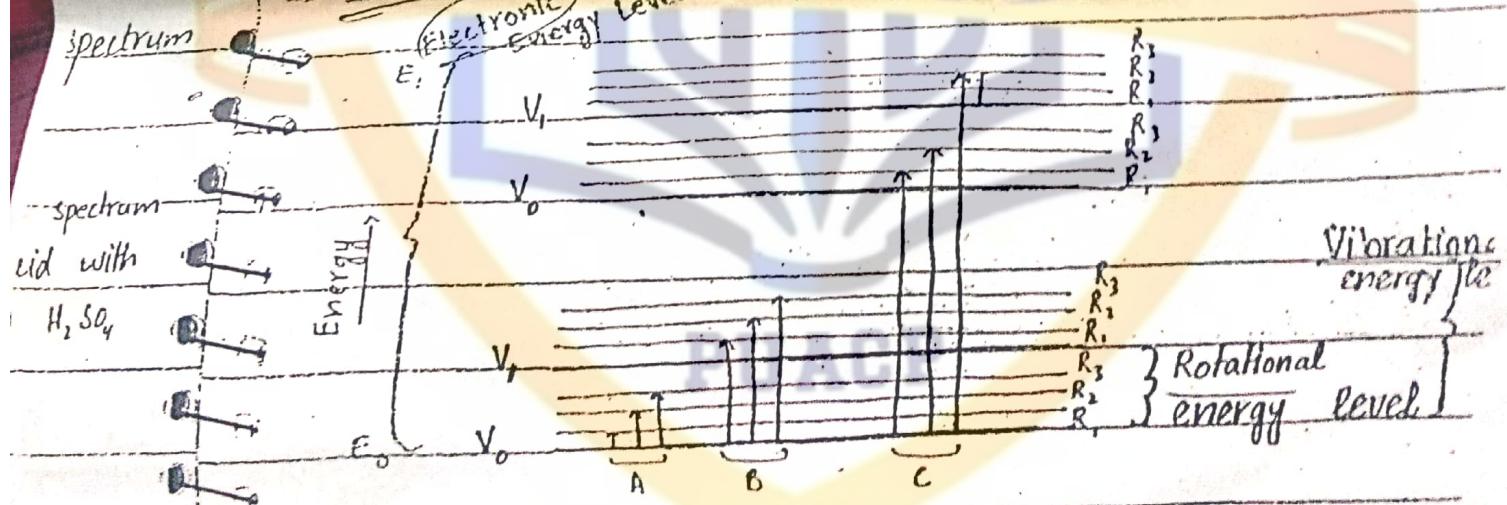
is proportional

to the

intensity

UV visible light valence shell electrons of the molecule are excited from a ground state to higher energy state. These electronic transitions generally occur in higher unoccupied molecular orbitals to the lowest unoccupied molecular orbital results.

The wavelength of the absorbed radiation depends upon the difference between the two energy levels. and the two energy levels.



A = pure rotational change (Far IR).

B = Rotational - Vibrational change (Near IR).

C = Rotational - Vibrational - Electronic change (UV-Visible Region).

E = Electronic ground state.

F = First electronic excited state.

Maxima and minima

maximum

minimum light absorption will take place at a

point when the energy of light of

certain wavelength becomes equal to the energy

which is required for excitation. Since the

absorption

orption of UV-Visible radiation results in the

insitions among electronic energy level of the

molecule. It is therefore called as electronic

spectroscopy electronic Spectroscopy)

Electronic transitions-

* On the absorption of light

energy by molecule, the σ , π and non-bonding

electrons are promoted from the ground state

to higher energy state. These higher energy states

are nothing but anti-bonding orbitals. The electronic

transitions involved in UV-Visible region are of

following types; $S \rightarrow S^*$, $A \rightarrow A^*$, $n \rightarrow S^*$, $n \rightarrow A^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $\pi \rightarrow \delta^*$ (rare)

Out of these 5 possible transitions only two

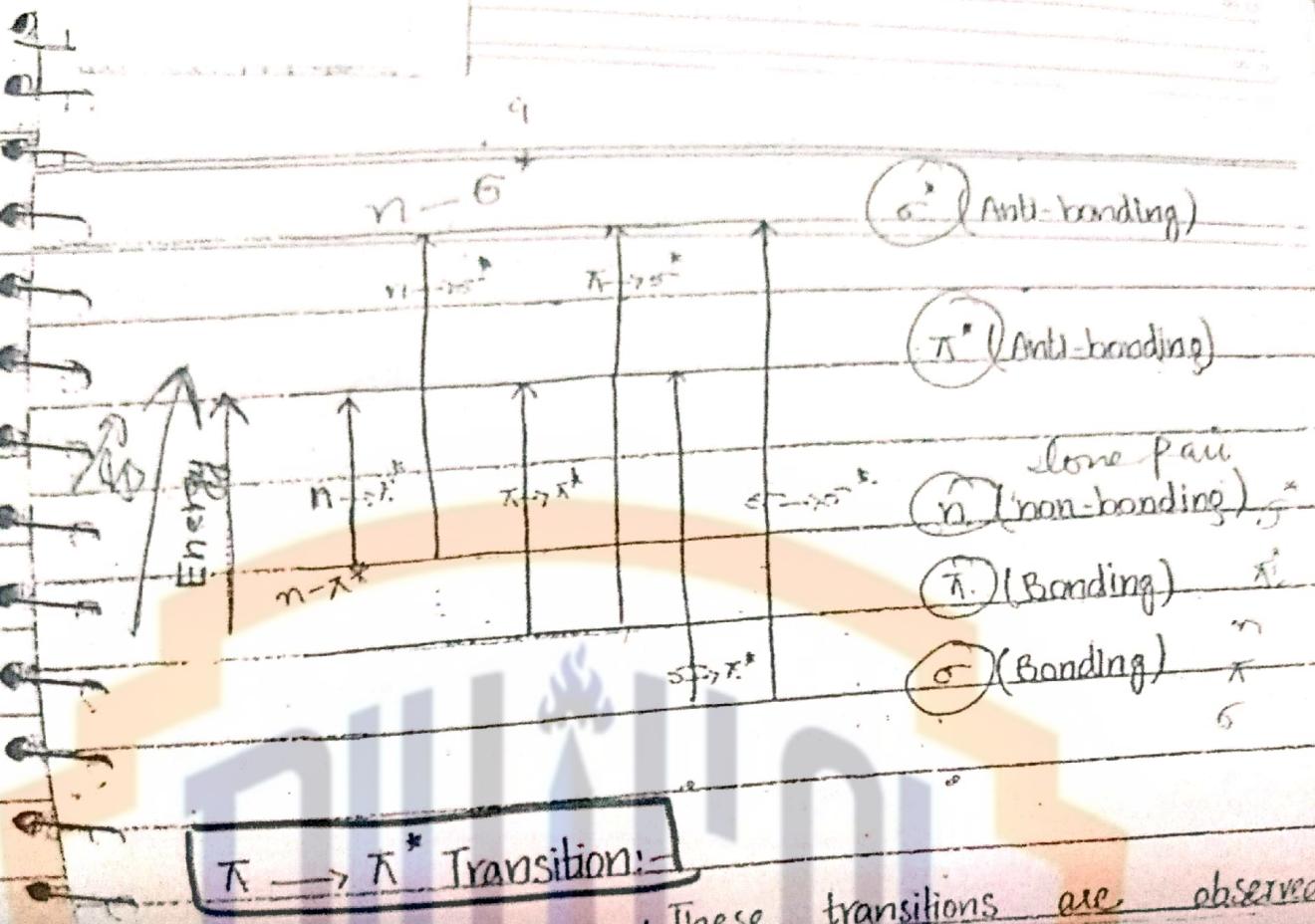
i) the lowest energy transitions i.e. $n \rightarrow \pi^*$

and $\pi \rightarrow \pi^*$ can be achieved or possibly

achieved by the energy provided between

200-800nm.

200-800nm



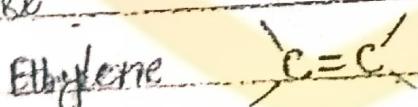
$\pi \rightarrow \pi^*$ Transition:

* These transitions are observed

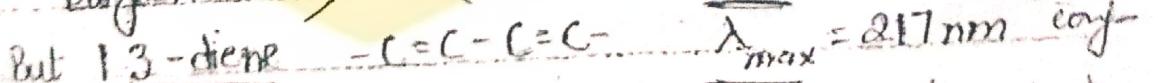
in molecules containing π -electrons. These transitions

takes place at wavelengths approaching near ultra-violet region. The hydrocarbons containing double and triple bonds are typical examples.

* For example, ethylene absorb at 110nm. The conjugation of unsaturation further increases it.



$$\lambda_{\max} = 110\text{nm}$$



$$\lambda_{\max} = 217\text{nm}$$

The effect of conjugation is quite important in organic molecule (for example) determining absorb in the vicinity of 217nm which naphthalene (II) at 300nm and anthracene (III)

$n \rightarrow \pi^*$ Transitions

UV/Vis

$\pi \rightarrow \pi^*$ Transitions

* These transitions are

observed in molecules having lone-pairs, or

non-bonding electrons. In these transitions one of

the non-bonding electrons may be excited to an empty π^* orbital. The energies required

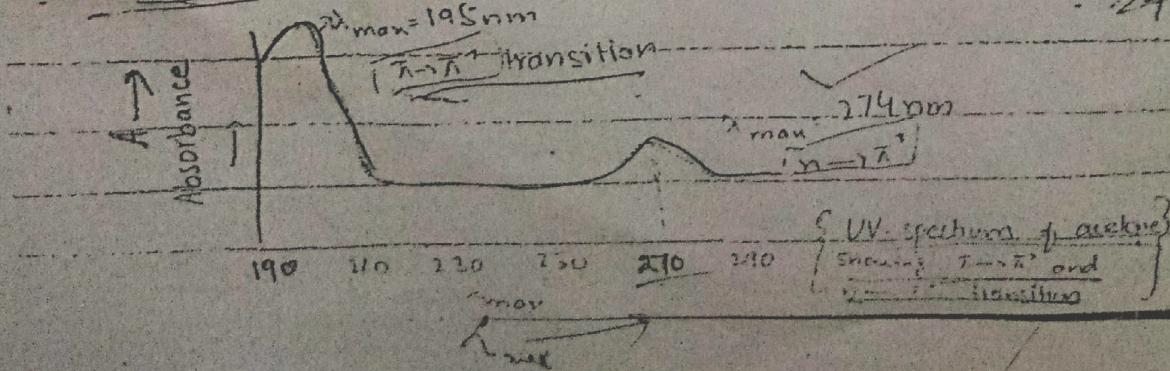
for these transitions are lower than that of

$\pi \rightarrow \pi^*$ transitions. As a result absorption will take place in the UV and Visible region.

The presence of atoms or groups containing n electrons can cause a remarkable change in the spectrum. Therefore, (nitrogen, sulphur) and halogens tend to move absorptions to higher wavelengths.

The $(n \rightarrow \pi^*)$ transitions are generally intense, while $n \rightarrow n^*$ transitions are weak.

For example (acetone) shows a high intensity $n \rightarrow \pi^*$ transition at 195 nm and low intensity $n \rightarrow n^*$ transition at 274 nm.



UV spectrum of acetone showing $n \rightarrow \pi^*$ and $n \rightarrow n^*$ transitions

(13-12-17) :-

Imp terminologies in UV spectrum

λ_{max} :- (Max. Absorption)

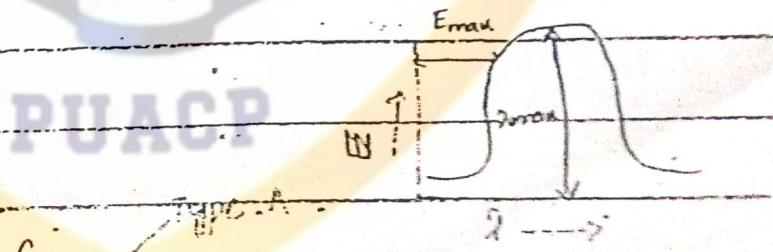
* It is the point of maximum absorption, when the energy of incidence radiation becomes equal to that required for excitation.

E_{max} (Max. Intensity) :-

* It reflects the intensity of maximum absorption and its magnitude is proportional to the probability of that particular electronic transition.

UV Spectrum :-

A UV spectrum is a plot of wavelength of absorption and intensity of absorption.



* Chromophore Group

It may be defined as an isolated covalently bonded unsaturated group responsible for electronic absorption.





Chromophore

Type A:-

These are those chromophores in which the group contains π electrons.

i.e. they undergo $\pi \rightarrow \pi^*$ transition.

e.g. Acetylene, ethylene



Type B:-

These are those chromophores which contain both π and n electrons. They can undergo two types of transitions.

i.e. $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. e.g. $-\text{C}=\ddot{\text{O}}$, $-\text{N}=\text{N}$: azo group

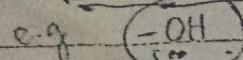


1. Chromophores can change both E_{\max} and λ_{\max}

Auxochromic Group (Colour Enhancer)

It may be defined as;

* A saturated group with non-bonded electrons, which when attach to a chromophore alters both wavelength and intensity of adsorption.

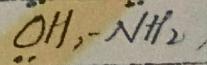


etc.

ABSORPTION

AND INTENSITY

SHIFTS



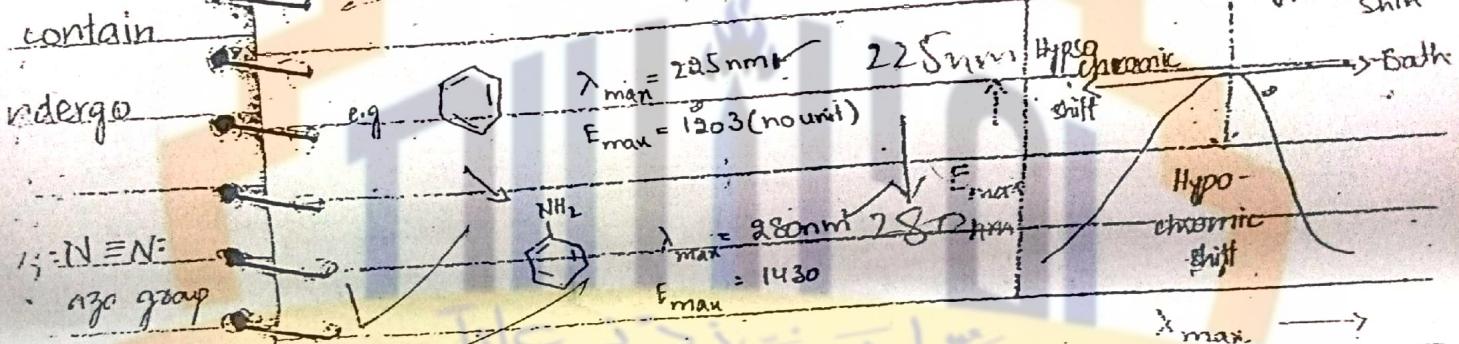
Bathochromic shift (Red shift) ~~V. dnf~~

* It is an effect

due to which the absorption maximum is

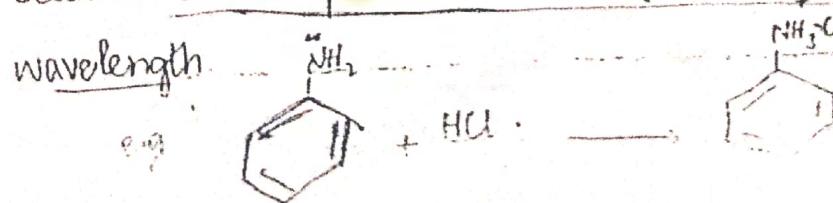
shifted towards longer wavelength due to in the presence of an auxochrome or by changing the nature of solvent.

e.g. The transition for carbonyl compounds experiences bathochromic shift when the polarity of solvent is decreased.



* Hypsochromic Shift : (Blue Shift)

It is an effect due to which absorption maximum is shifted towards shorter wavelength. This happens due to the removal of conjugation or by changing the polarity of solvent. It is also called blue shift because absorption shifts towards shorter wavelength.



$$\lambda_{\text{max}} = 280 \text{ nm}$$

$$\lambda_{\text{max}} = 203 \text{ nm}$$