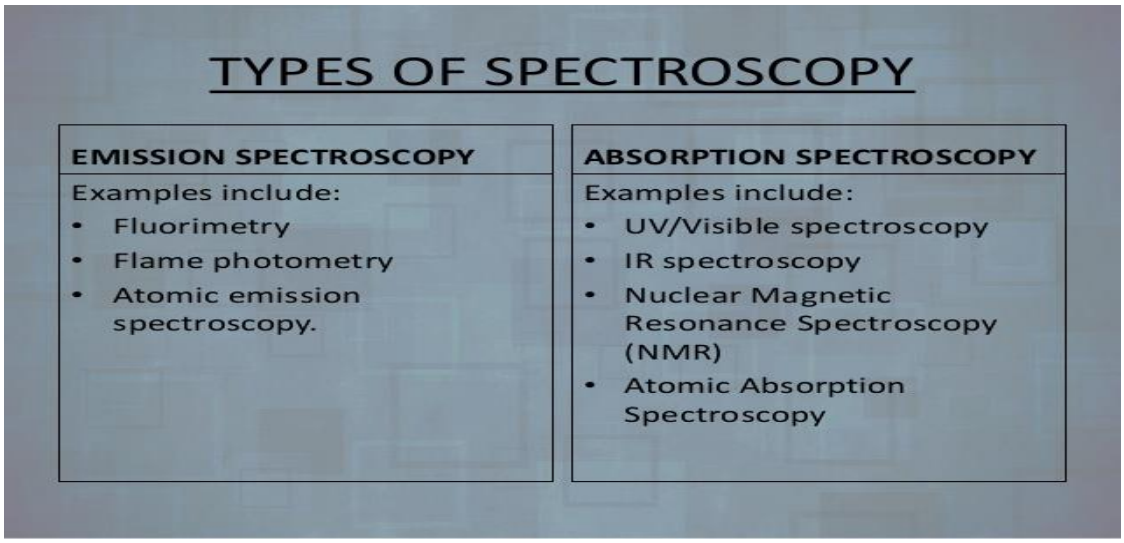
Spectroscopy of Atoms



Common types

- Fluorescence spectroscopy
- X-ray spectroscopy and crystallography
- Flame spectroscopy
  - 1- Atomic emission spectroscopy
  - 2- Atomic absorption spectroscopy
  - 3- Atomic fluorescence spectroscopy
- Plasma emission spectroscopy
- Spark or arc emission spectroscopy
- UV/VIS spectroscopy
- IR spectroscopy
- Raman spectroscopy
- NMR spectroscopy
- Photo thermal spectroscopy
- Thermal infra-red spectroscopy
- Mass Spectroscopy

ATOMIC FLUORESCENCE SPECTROSCOPY

To start with let me ask you that question that **what is fluorescence**; obviously, the fluorescence is a kind of light emission from the molecule to understand this fluorescence better we understand that **what is luminescence**. So, luminescence is a phenomena of light emission from a material which are not solely conditioned by the raise in temperature it is just opposed to the incandescence. In incandescence, what you have seen in the normal filament bulb right in our houses. So, that lights coming from the incandescent bulb is because of the heating, but in fluorescence this is not because of the heating right and this luminescence is termed as a cold light.

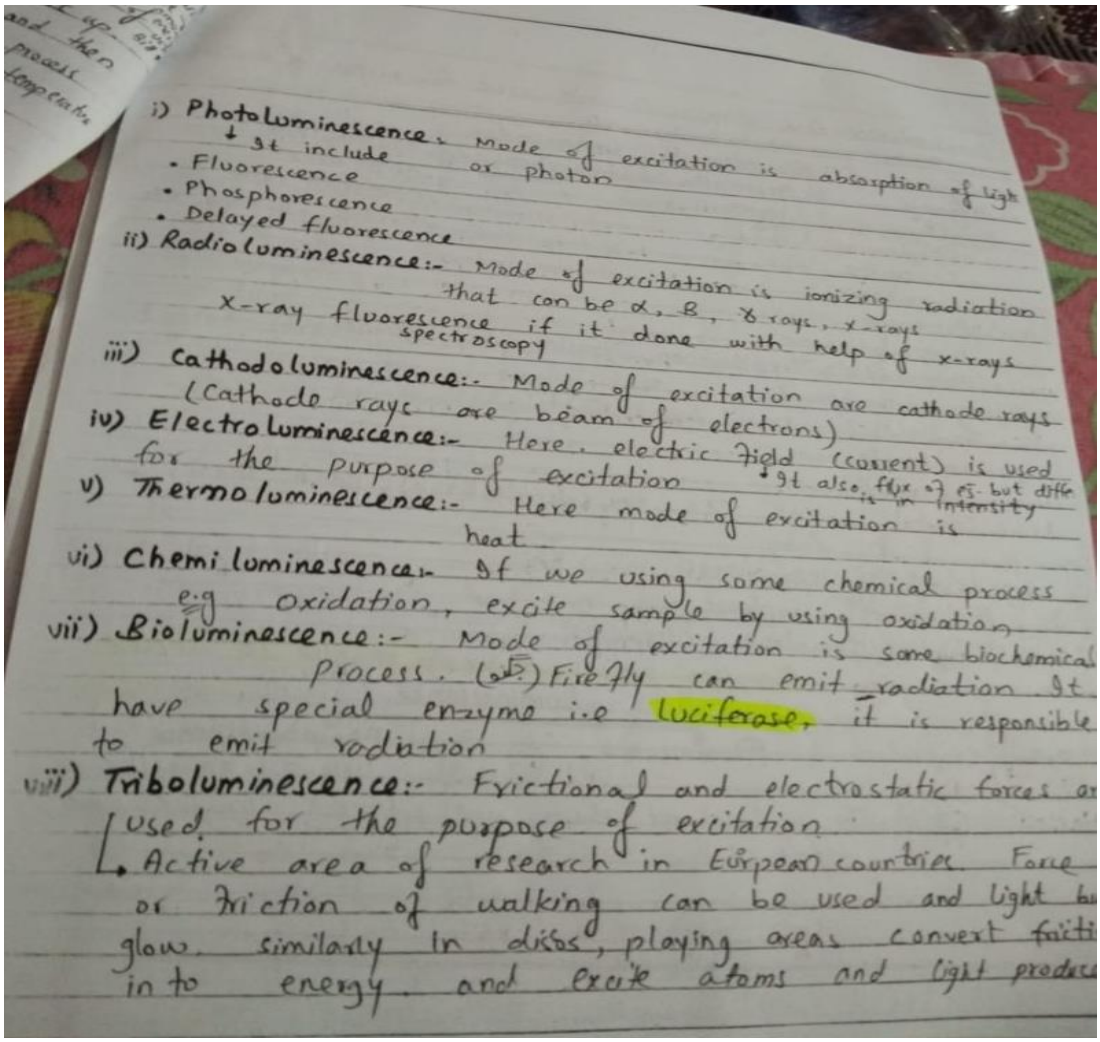
So the term luminescence comes from the word lumen which is a Latin word and; that means, light and was first introduced by a German physicist a Wiedemann. So, in 1888 and if you want to see the modern definition of luminescence one can say that this is a spontaneous emission, spontaneous emission of radiation from an electronically excited species or from a vibrationally excited species which are not in thermal equilibrium with its surrounding.

Types of Luminescence

Some different types of **luminescence** the luminescence the phenomena is categorized in different types based on the mode of excitation for example, let us take this **chemiluminescence**; in the chemiluminescence the mode of excitation is chemical reaction. So, as you have seen in the glow sticks right where the sticks will be broken and the; it will it will start glowing. So, that is basically a chemical reaction which evolves the light. So, the glow stick is now glowing. So, you can see in the dark and like a different kind of chemical reactions like oxidation may be caused for this light emission from this device and these are called the chemiluminescence.

Similarly the **radio luminescence**; so radio luminescence is a kind of luminescence where ionizing radiation like x ray, alpha, beta, gamma rays are the mode of excitation so which can be seen in the ancient clocks that disease and the needles of these clocks are glowing in the dark. So, and the third category of luminescence is the **bioluminescence** where a biochemical reaction is responsible for the mode of excitation and which is now emitting light. So, here you can see for the firefly will get this a luminescence out of it. Similarly, we have

sonoluminescence where the mode of excitation is ultrasound we have **electroluminescence** where the mode of excitation is the electric field and last, but not least we also have these **photoluminescence** right we have this photoluminescence where the mode of excitation is absorption of light. So, where the mode of excitation is absorption of light; that means, photoluminescence is nothing, but the fluorescence. So, here the fluorescence is a special type of luminescence which is known as photoluminescence.



Fluorescence:

1. Fluorescence spectroscopy Fluorescence spectroscopy (fluorometry or spectrofluorometry), is a type of electromagnetic spectroscopy which analyzes fluorescence from a sample. It involves using a beam of light, usually ultraviolet light, that excites the electrons in molecules of certain compounds and causes them to emit light of a lower energy, typically, but not necessarily, visible light. This shift to longer wavelength is called the Stokes shift. Devices that measure fluorescence are called **fluorometers** or **fluorimeters**.

Theory of fluorescence:

Molecular fluorescence is measured by exciting the sample at the absorption wavelength, also called the excitation wavelength, and measuring the emission at a longer wavelength called the emission or fluorescence wavelength.

Relaxation processes: Once the molecule is excited to S1 or S2 several processes can occur that cause the molecule to lose its excess energy. Various mechanism of relaxation: **1. Fluorescence 2. Phosphorescence 3. Vibrational relaxation 4. Internal conversion 5. External conversion 6. Inter system crossing.**

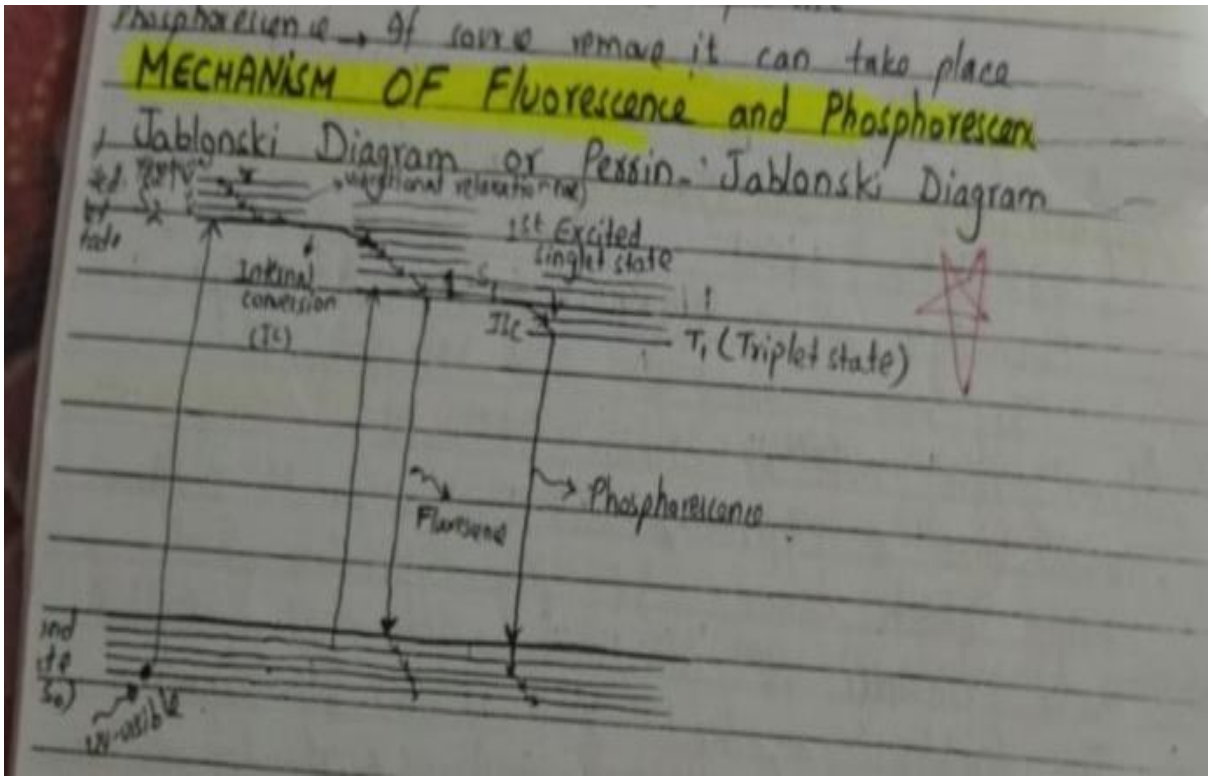


Fig: Jablonski Diagram

History of Fluorescence:

The first observation of fluorescence from a quinine solution in sunlight was reported by Sir John Frederick William Herschel in 1845. Quinine The quinine in tonic water is excited by the ultraviolet light from the sun. Upon return to the ground state the quinine emits blue light with a wavelength near 450 nm.

Types of fluorescence

•There are five basic types of fluorescence:

1) Resonance fluorescence
2) Direct-line fluorescence
3) Step wise-line fluorescence
4) Two step or double fluorescence
5) Thermally assisted fluorescence
6) Sensitized Fluorescence

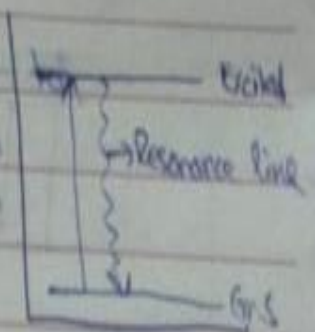
1- Resorance fluorescence

This type acc to mirror image rule in which absorption ~~energy~~ is mirror image of the emission energy spectra

The absorption energy is almost equal to emission energy. hear energy dissipation is minimum.

Energy absobed is always equal

If absorption is 5890.1nm then emission is 5889.8nm very mirror d/f



2- Stoke's direct line fluorescence

Stoke's rule is applicable

3- Stepwise line fluorescence

It shows fluorescence in steps either in two steps or more.

Date:

It gives the example of inter conversions. (1)
Release of extra energy is done.

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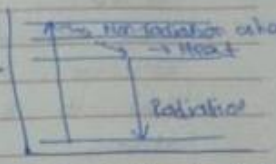
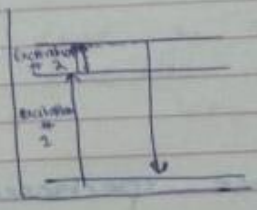
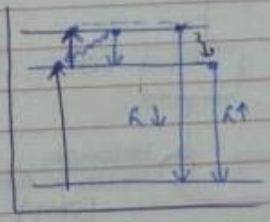


(4) Double Resonance fluorescence



Due to collision in excited state (1), it takes energy & then go to higher excited state (2) It does not lose heat or non-radiation & direct moves to ground state bcoz it has greater energy

5) Thermal Assisted Resonance

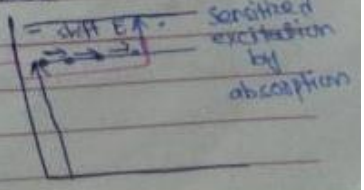


Extra energy in the form of heat is given by the side atom to the atom of 1st excited state then moves to higher excited state. & then moves to the ground state.

It is also known as antistoke line bcoz λ is shorter in this case.
Both λ cases are discussed in this case.

(6) Sensitized fluorescence

Shifting of energy through vibration ↓ is known as sensitized fluorescence
or collision
~~collisional excitation without some source~~



closely spaced energetic atoms transfer their energy to side