UCB009-CHEMISTRY

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

Introduction to Spectroscopy
(AES, ICP-AES, AAS, Jablonski)

I. A brief outline of General Spectroscopy:

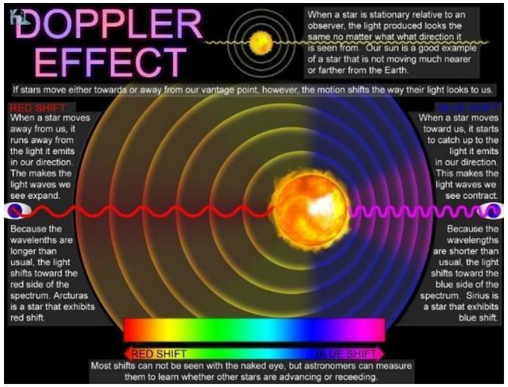
- Introduction to spectroscopy
- Daily life applications
- Spectroscopy: principles and observables
- Electromagnetic radiation
- Types of spectroscopy
- Principles and observables in spectroscopy
- Light-matter interactions
- Absorption and emission spectra
- Transitions in atoms and molecules upon light irradiation

II. A brief outline of AES, ICP-AES, AAS and Jablonski diagram:

- Introduction to Atomic emission spectroscopy (AES) and its principle
- Sequence of events in the flame and effect of temperature
- Fuel-oxidant combinations and limitations of AES
- Introduction to ICP-AES and its working principle.
- Advantages of ICP-AES
- Introduction to Atomic absorption spectroscopy (AAS) and its principle
- A brief introduction to hollow cathode lamp
- Differences between AES and AAS, Advantages and disadvantages of AAS
- Introduction to fluorescence, phosphorescence and other photophysical processes
- Introduction to Jablonski diagram, processes and timescales
- Differences between fluorescence and phosphorescence
- Applications of fluorescence

What is Spectroscopy?





It is the branch of science which deals with the study of interaction of electromagnetic radiation with matter

- To know the molecular structure (qualitative analysis)
- To determine the quantity of species present (quantitative analysis)

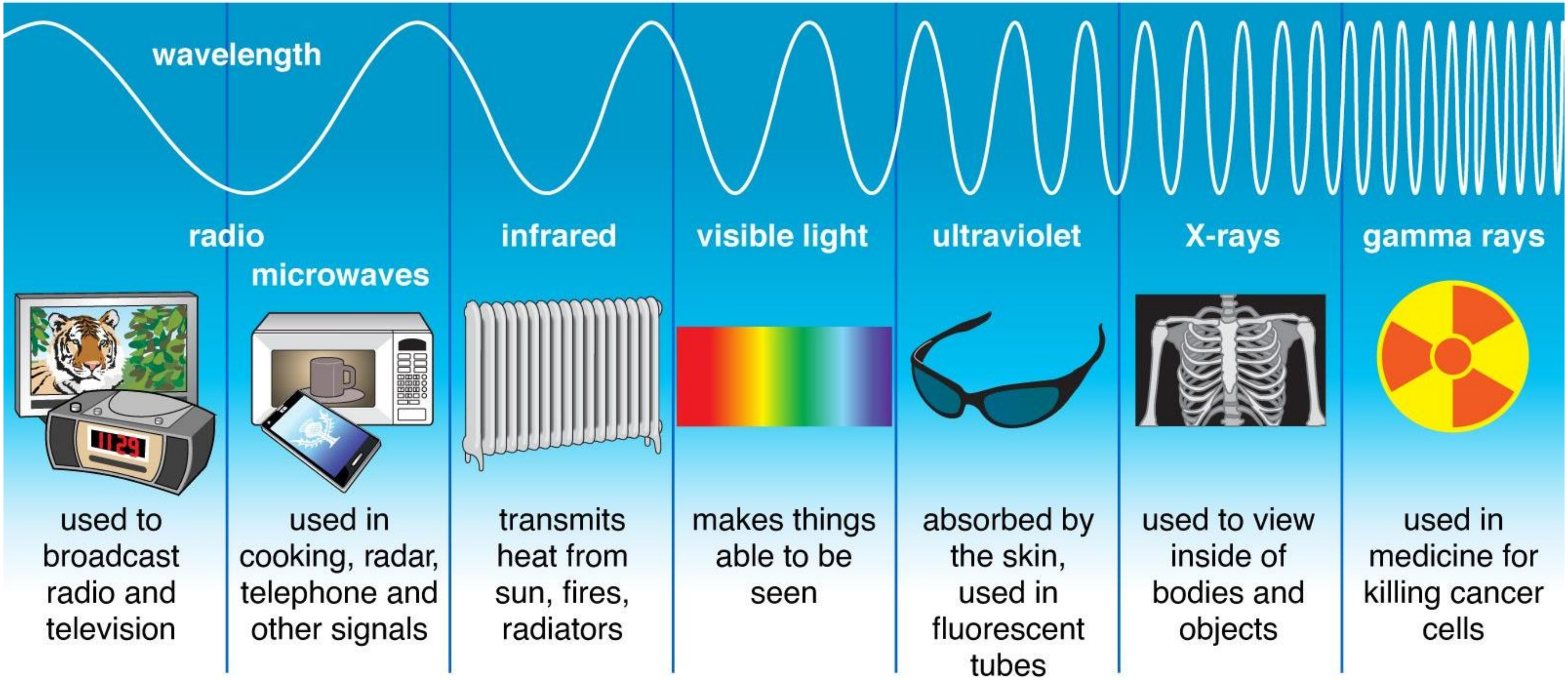
What is Spectroscopy?

To study changes in the properties of light when it interacts with matter.

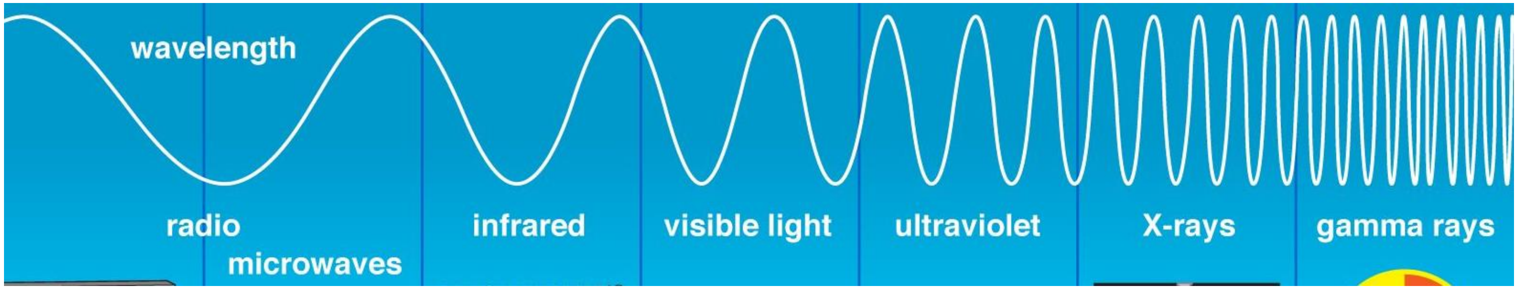
Examples of daily life applications of Spectroscopy:

- Monitoring diffused oxygen content in freshwater and aquatic ecosystems.
- Determining the molecular structure of a sample.
- Determining the metabolic structure of a muscle.
- Studying spectral emission lines of distant galaxies.
- Altering the structure of drugs to improve their effectiveness.
- Space exploration
- Characterization of proteins
- Respiratory gas analysis in hospitals

Electromagnetic Spectrum:



Electromagnetic Radiation: Revision of fundamental concepts



- **Frequency (ν):**
  - It is defined as the number of times electrical field radiation oscillates in one second.
  - The unit for frequency is Hertz (Hz). 1 Hz = 1 cycle per second

- **Wavelength (λ):**
  - It is the distance between two nearest parts of the wave in the same phase i.e. distance between two nearest crests or troughs.

- The relationship between wavelength & frequency can be written as: $c = \nu \lambda$
- As photon is subjected to energy, so $E = h \nu = h c / \lambda$

Types of spectroscopy

Spectroscopy

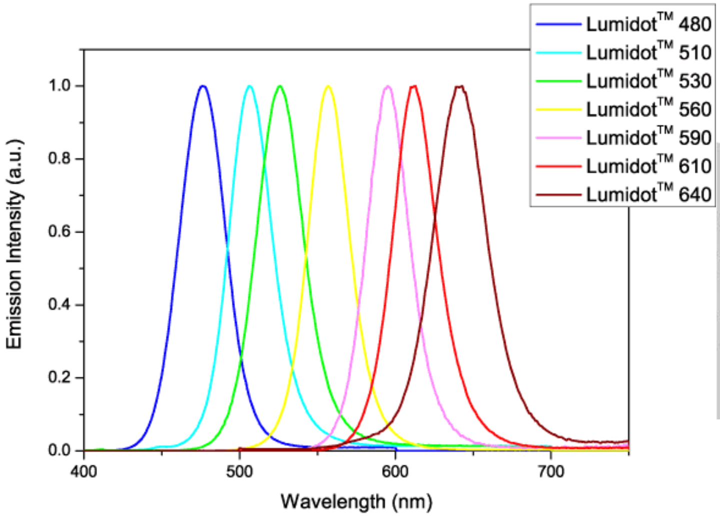
- **Atomic**
  - Absorption
    - Atomic Absorption
  - Emission
    - Flame Emission
  - **Line spectrum**
- **Molecular**
  - Absorption
    - UV-Visible
    - IR
  - Emission
    - Fluorescence
    - Phosphorescence
  - **Band spectrum**

Spectroscopy: Principles and Observables

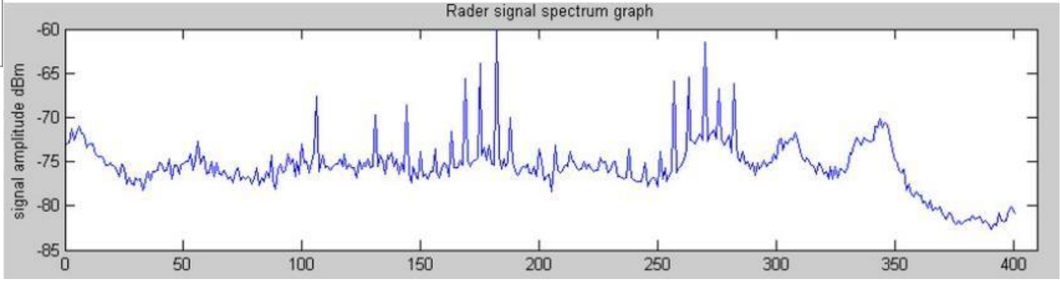
- The principle is based on the measurement of the spectrum of a sample containing atoms/molecules.

- Spectrometer is an instrument used to measure/observe the spectrum of a sample.

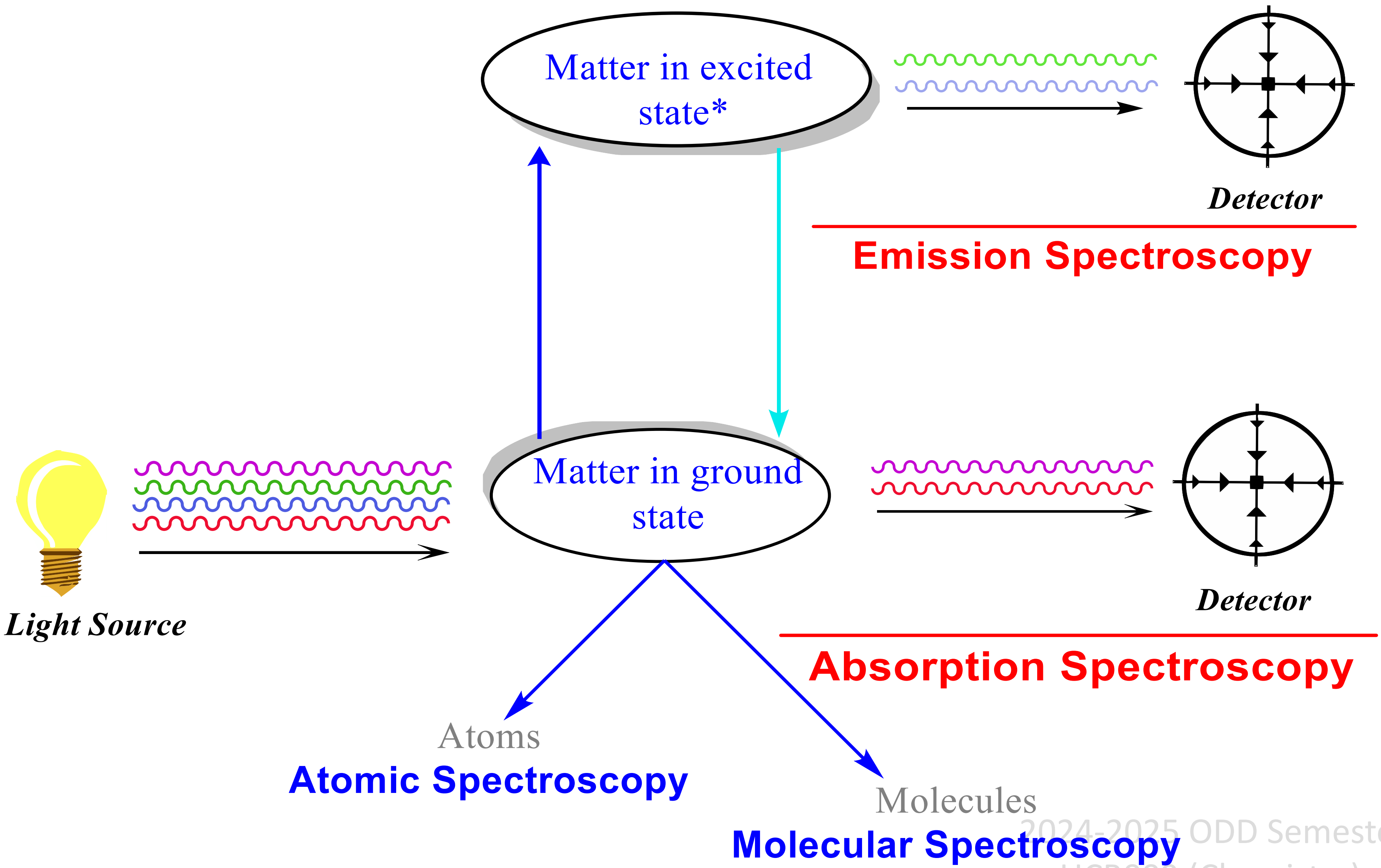
- Spectrum is a graph of the intensity of absorbed or emitted radiation by sample versus frequency (ν) or wavelength (λ).



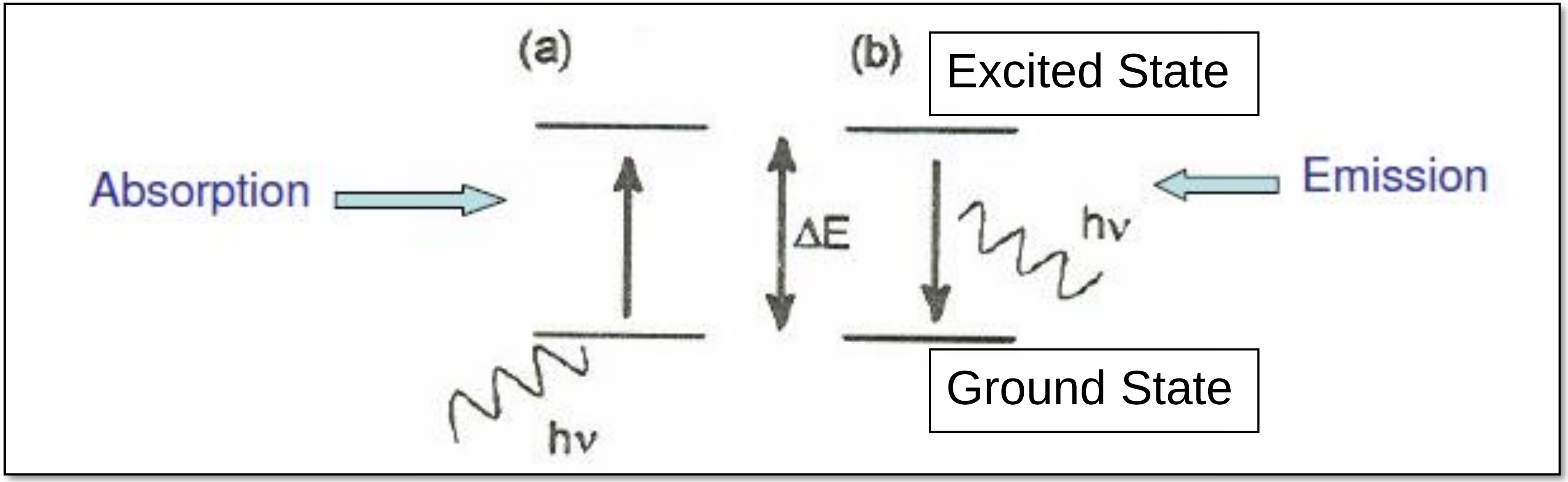
Emission spectra of Lumidot™ CdSe/ZnS nanocrystals

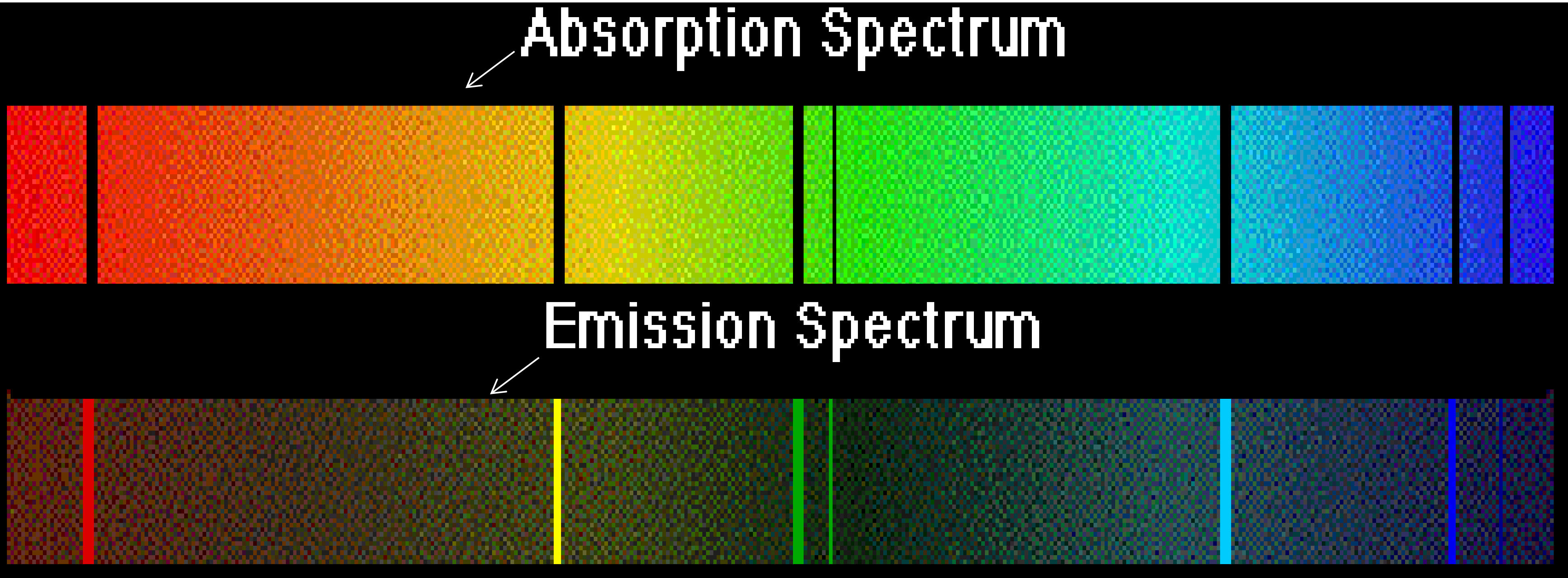


How do we study changes in the properties of light when it interacts with matter?



Atomic absorption and emission spectra

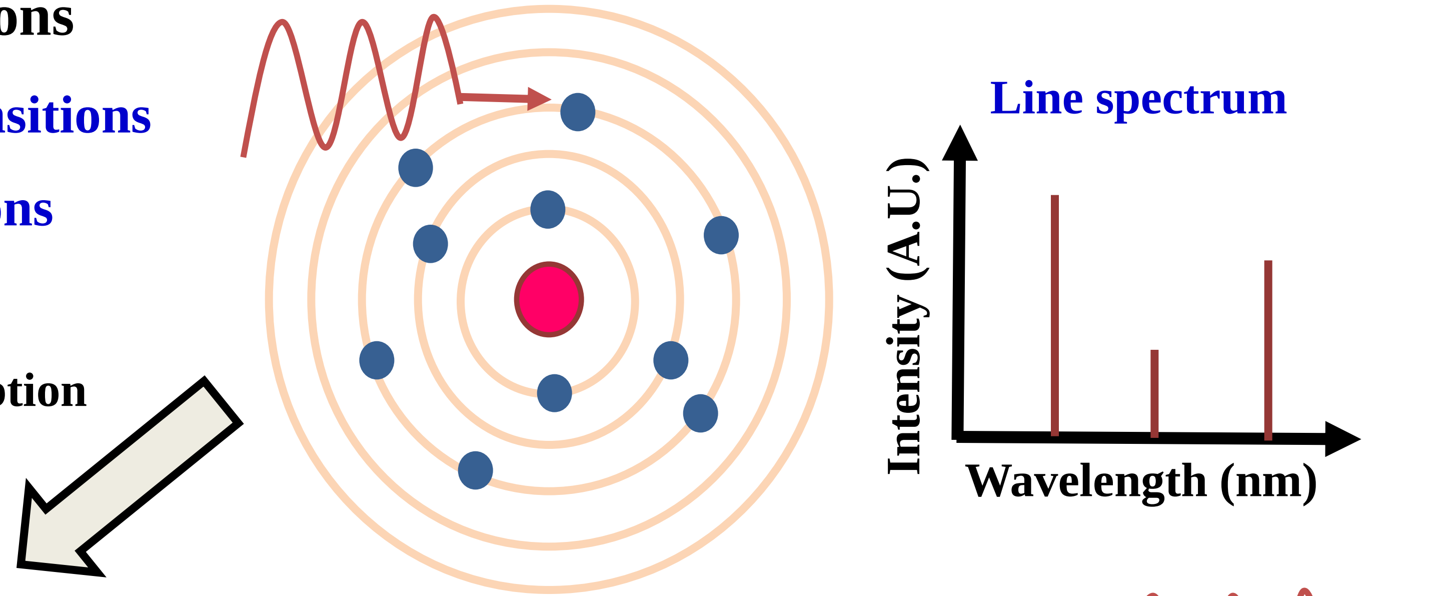


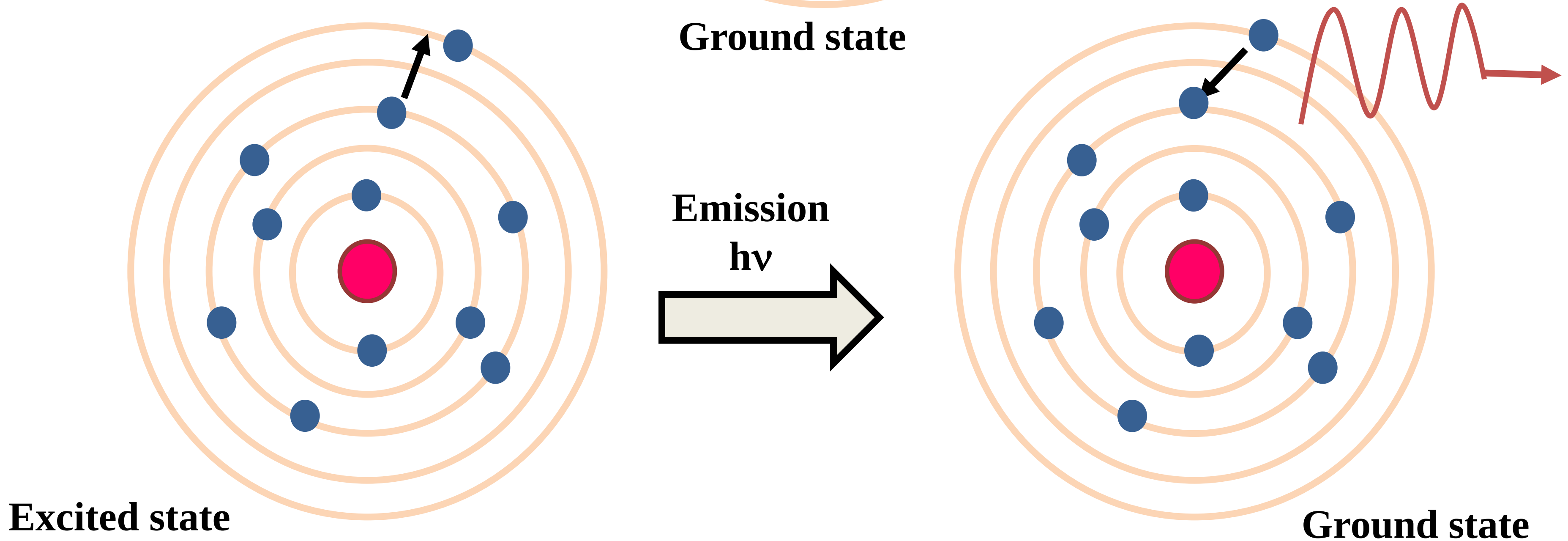


Electromagnetic Radiation and Matter: Interaction

Atomic Transitions

- Electronic Transitions
- Valence Electrons

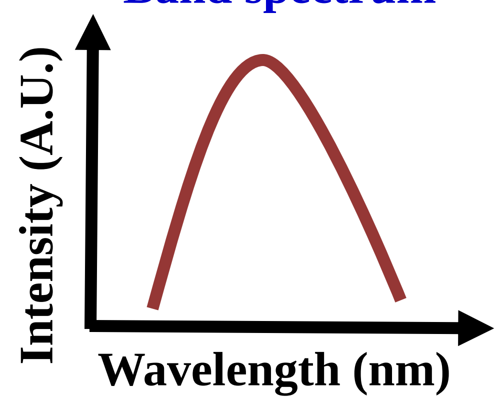


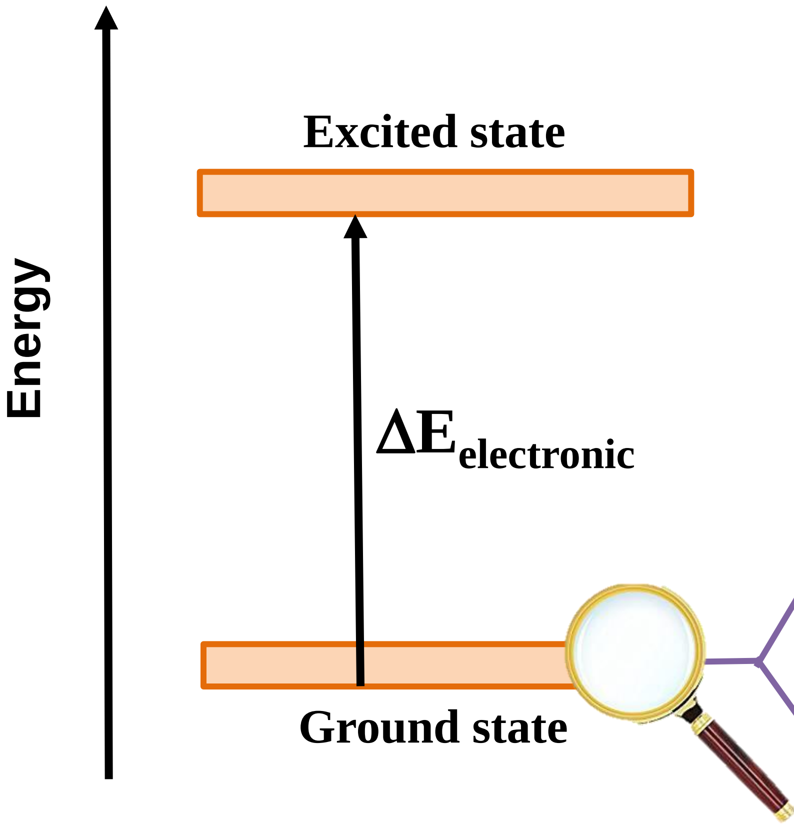


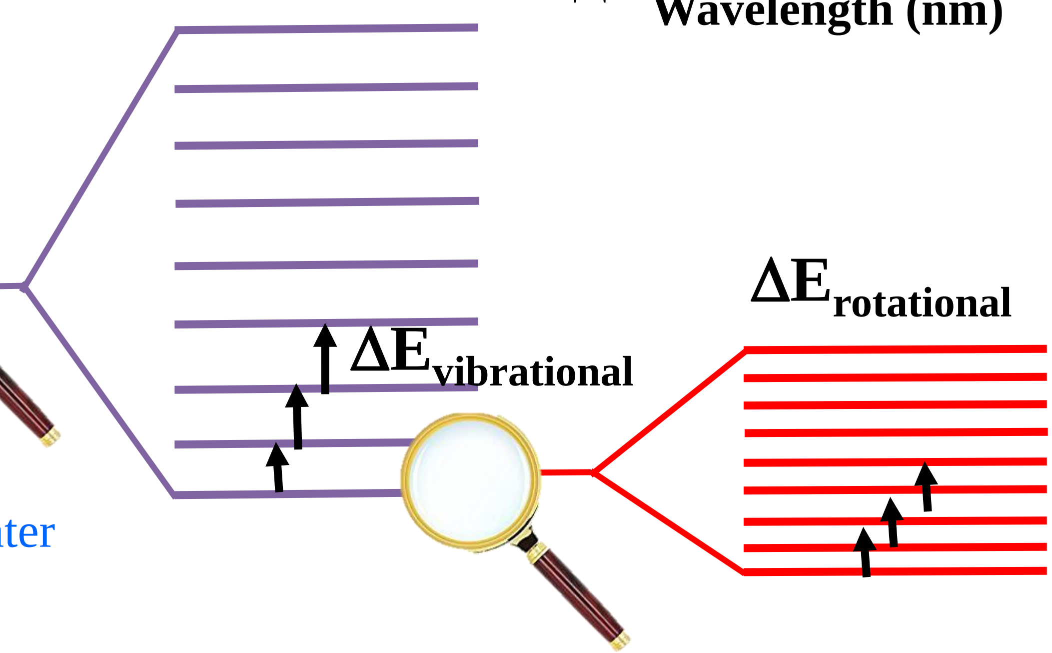
Electromagnetic Radiation and Matter: Interaction

Molecular Transitions ⇨ **Molecular Orbitals**

- ❖ **Atomic Orbitals**
- ❖ **Overlap**

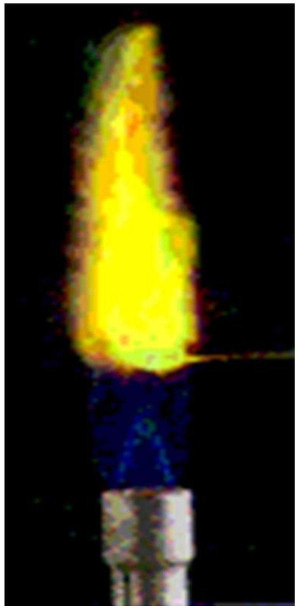






Note: This will be discussed in detail later during molecular spectroscopy

Atomic Emission Spectroscopy (AES)



Atomic emission spectroscopy: Introduction

- Atomic emission spectroscopy is a special area of emission spectroscopy in which a flame/spark/plasma is used to excite the atoms.
  (Note: if flame is used as an excitation source, then it is known as flame emission spectroscopy (FES))

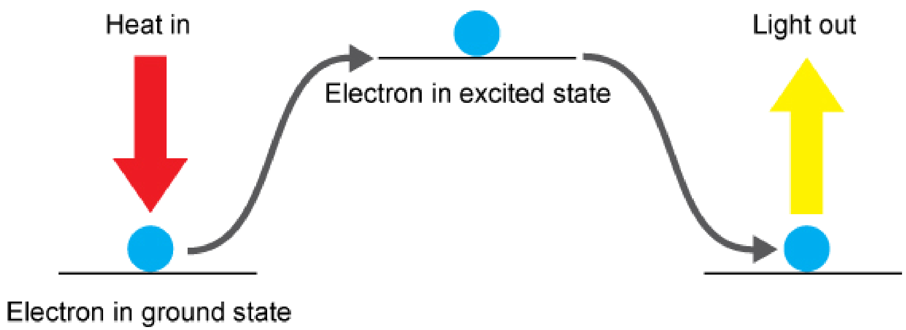
- For a few elements, such as the alkali metals Na and K, the thermal energy is hot enough to not only produce ground-state atoms but also raise some of the atoms to an excited electronic state.

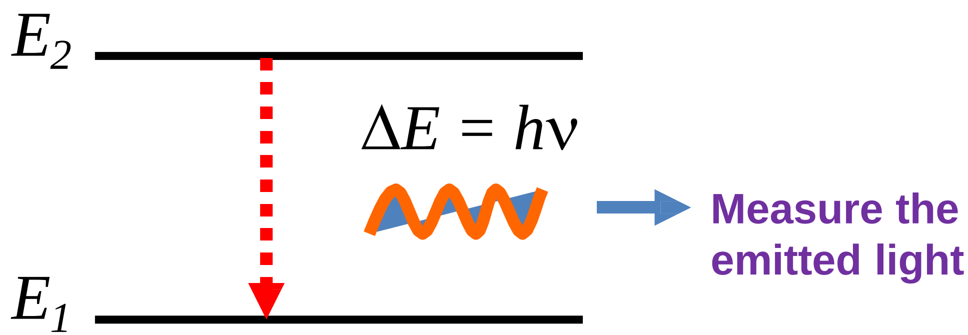
- So flame emission spectroscopy is used for the detection of alkali metals and some of the alkaline earth metals.

- In Flame emission spectroscopy, only one element can be detected at a time in the presence of other elements.

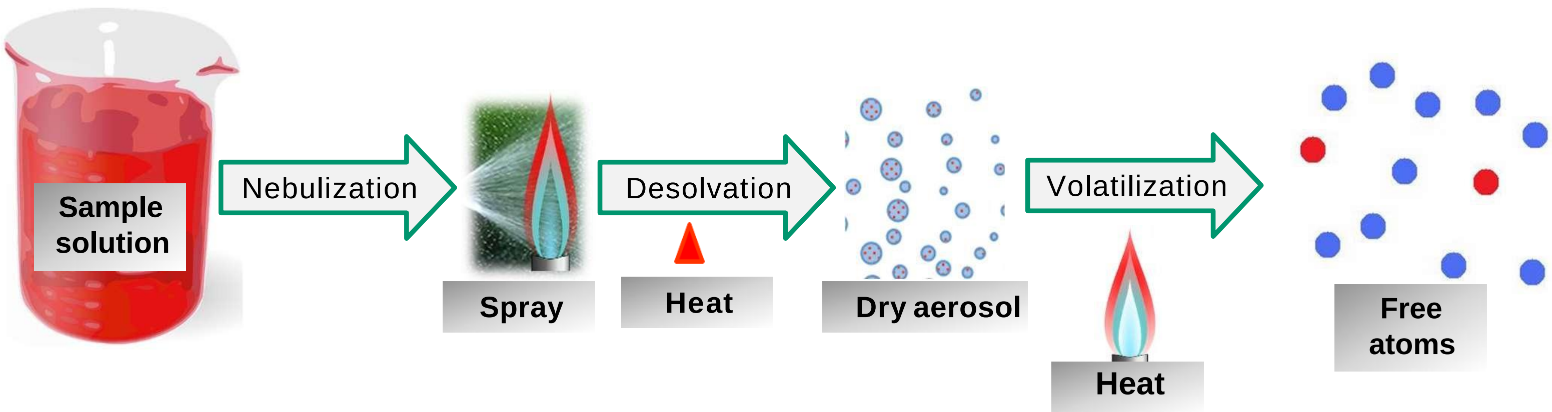
Flame emission spectroscopy: Principle

- Absorption of heat energy by ground state atoms present in the flame results in the excitation of valence electrons of atoms.
- This valence electrons come back to the ground state with the emission of a photons.
- Wavelength and intensity of emitted photons help in qualitative and quantitative analysis of the sample.





Sequence of events in FES:



Nebulization: The solution of the metal salt is sprayed into the flame.

Desolvation: The solvent evaporates, leaving the finely powdered salt.

Sublimation: Vaporization of the salt.

Atomization: Conversion of ions into free gaseous atoms.

Excitation: The valence electron is raised to a higher energy state.

Relaxation & Emission: The excited electrons return to the ground state, and light is emitted.

Occurs in flame

Measurement: The wavelength and intensity of the emitted light are measured.

Effect of temperature on FES:

Boltzmann Distribution : $N^{*} / N_0 = A\, e^{-\Delta E / k T}$

N^* **:** Number of atoms in an excited state (Intensity)
N_0 : Number of atoms in the ground state
ΔE : E_1-E_0 = Difference between two energy states
k : Boltzmann constant
T : Temperature of flame
A : Constant for particular atom

Thus, TEMPERATURE plays an important role in FES.

High temperature = High Excitation = High Intensity (Caution)

"TEMPERATURE OF THE FLAME" depends on a) Fuel & Oxidant
b) Fuel: Oxidant Ratio

Number of atoms in excited state depends on the flame temperature.

Fuel and Oxidant combinations:

Fuel	Oxidant	Flame temperature (°C)
Propane	Air	1900
Propane	Oxygen	2800
Hydrogen	Air	2100
Hydrogen	Oxygen	2800
Acetylene	Air	2200
Acetylene	Oxygen	3000

Limitations of FES

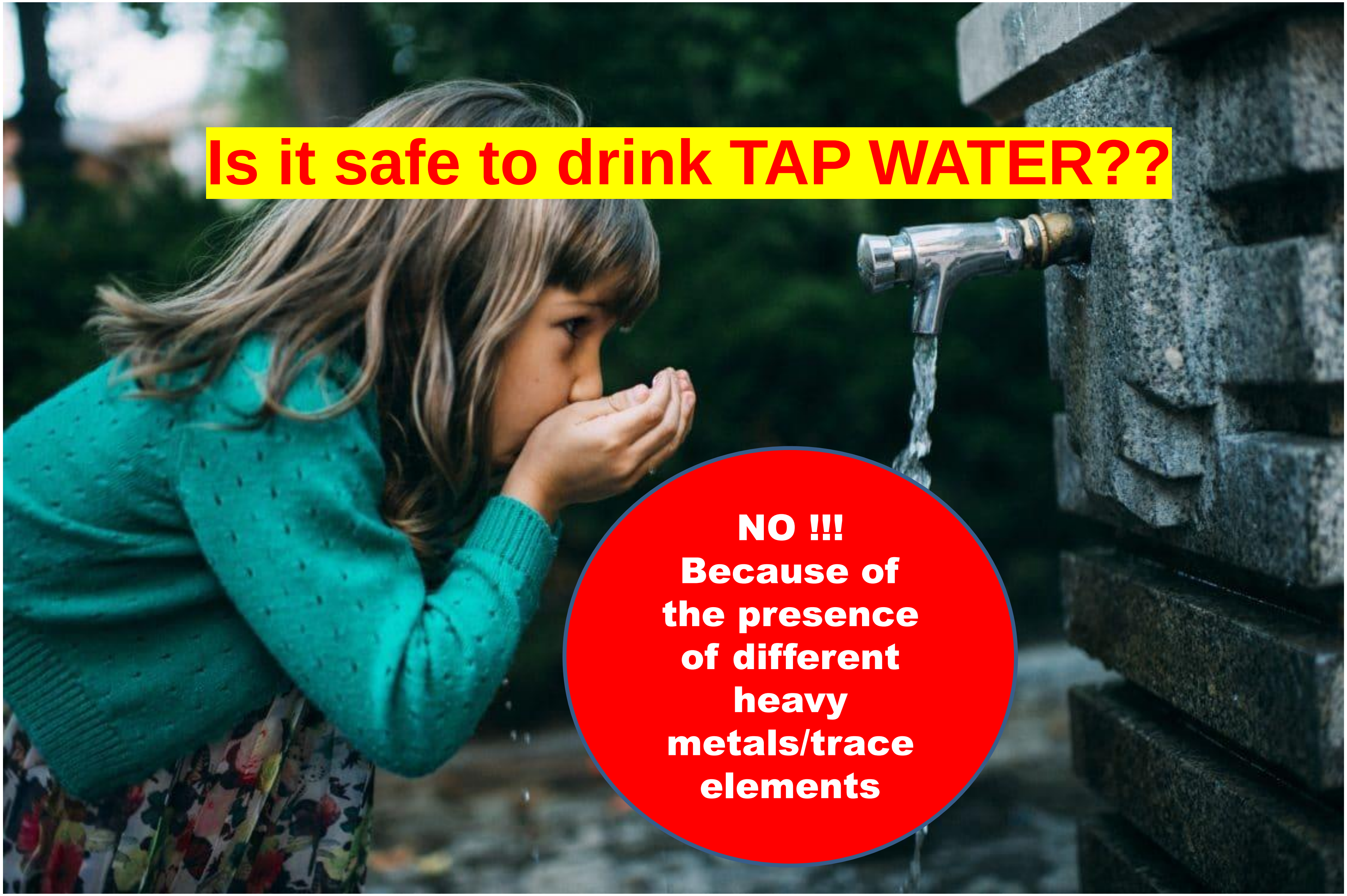
(i) Does not give information about the molecular form of the sample

(ii) FES is mainly applicable to alkali & alkaline earth metals

(iii) Multiple elements can not be detected simultaneously

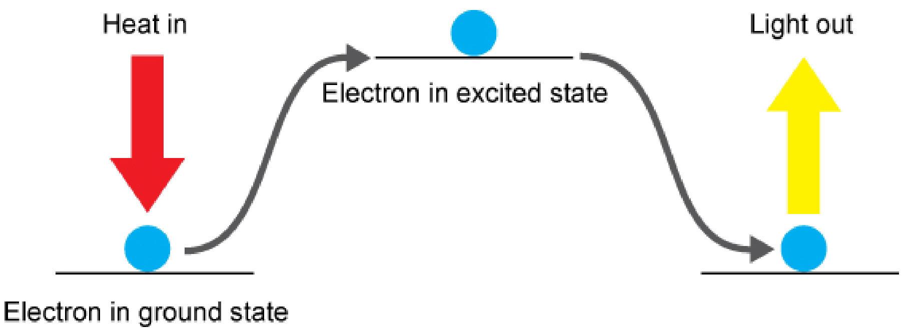
Note: The second and third limitations, mentioned above, can be overcome if we change the excitation source from flame to plasma.

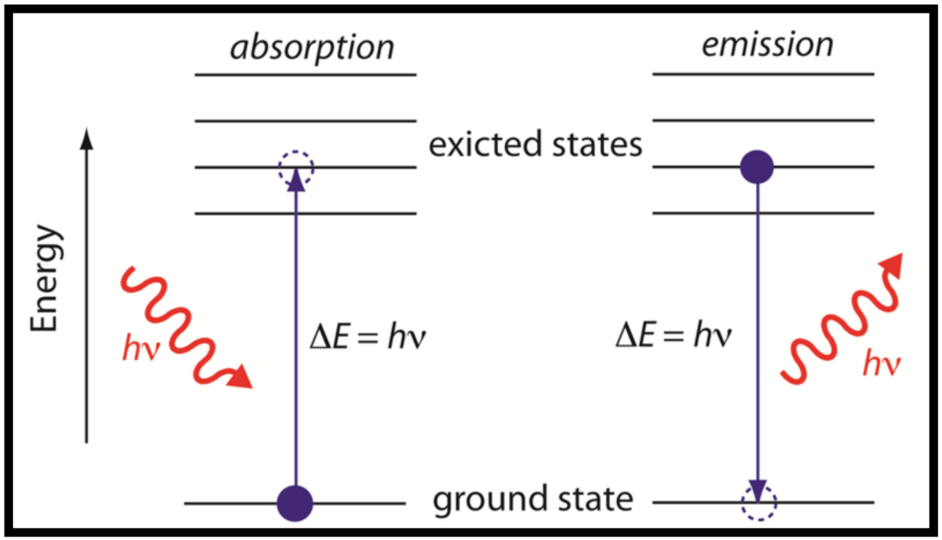
Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)


Is it safe to drink TAP WATER??
NO !!!
Because of the presence of different heavy metals/trace elements

Basics of AES: Revision of fundamental concepts

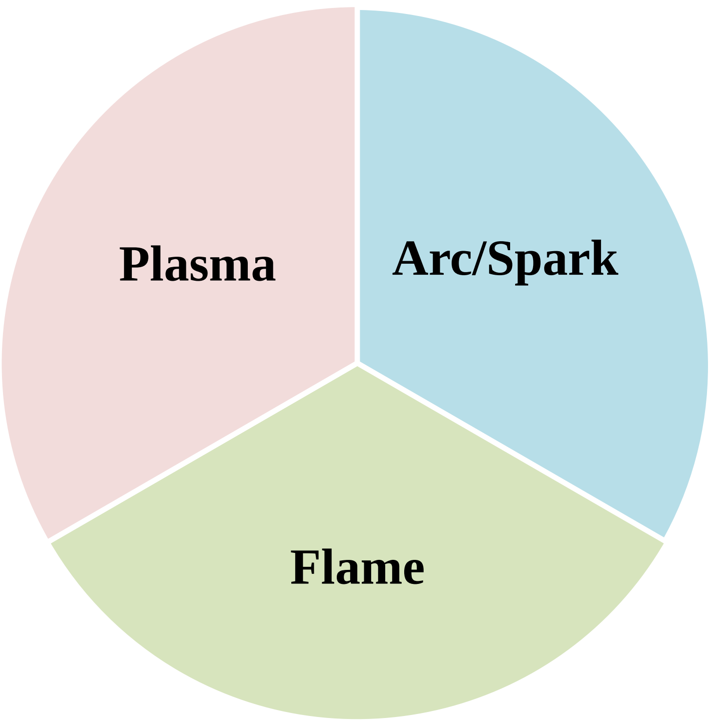
Atomic emission spectroscopy (AES) or optical emission spectroscopy uses quantitative measurement of the optical signals when atoms relax from an excited state to the ground state to determine analyte concentration.





The energy emitted is directly proportional to the concentration of the analyte present in the solution.

Different excitation sources in AES



Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

- ICP-AES utilizes **plasma as an excitation source**. A plasma is an electrically neutral, highly ionized gas that consists of ions, electrons, and atoms.

- Inductively coupled plasma (ICP) is a type of high-temperature plasma **generated by electromagnetic induction, usually coupled with argon gas**.

- **The plasma can reach temperatures up to 10,000 Kelvin.**

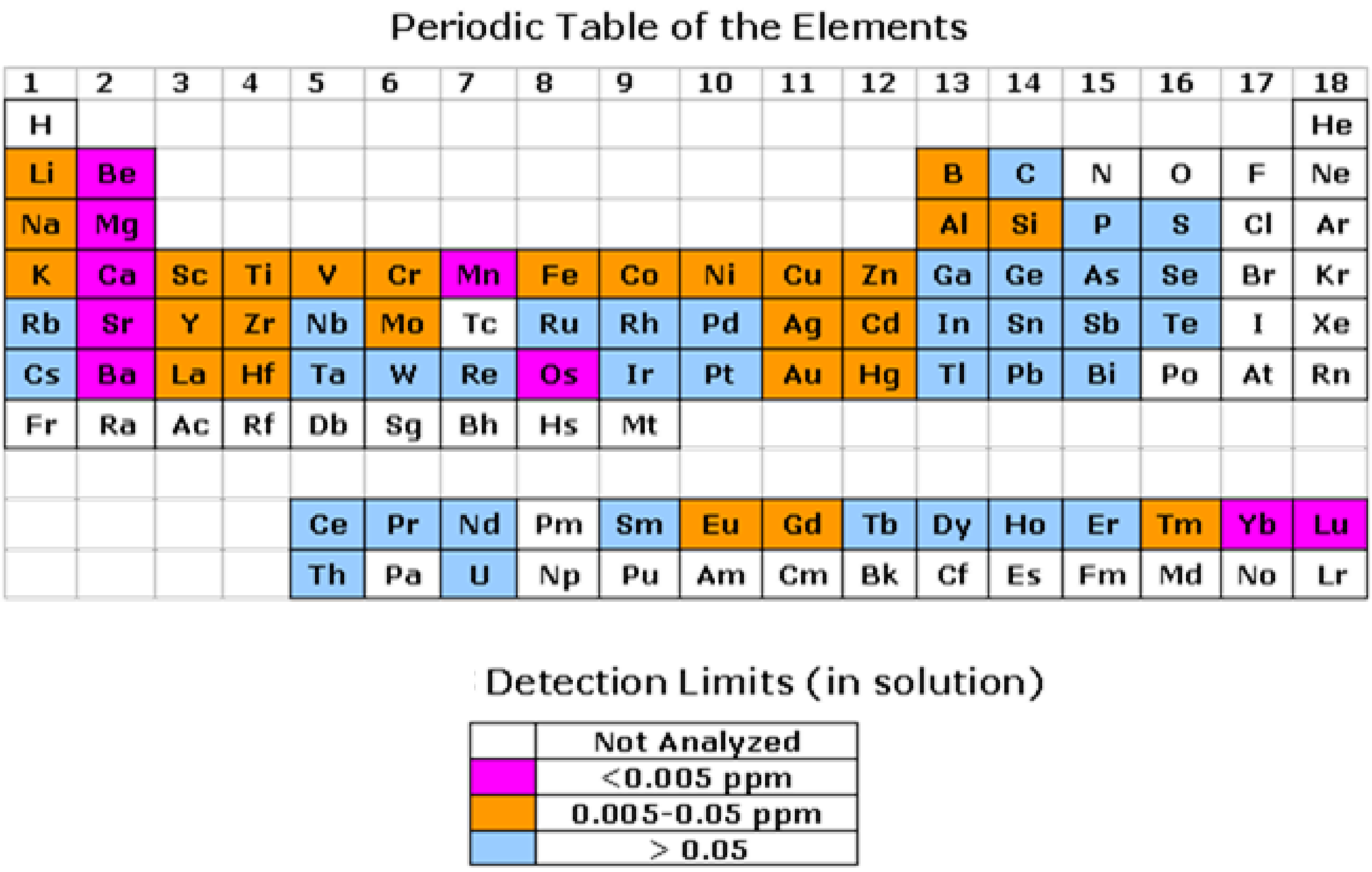
- Hot enough to excite most elements.

- Hot enough to prevent the formation of most interferences, break down oxides, and eliminate most molecular spectral interferences.

- Sensitive approach and most widely applied to determine trace elements.

Advantages of ICP-AES

- It has a wide elemental coverage
- It has extremely low detection limits (ppt/ppm) or (ng/L to mg/L)
- Approximately 10 - 40 elements per sample can be analyzed simultaneously



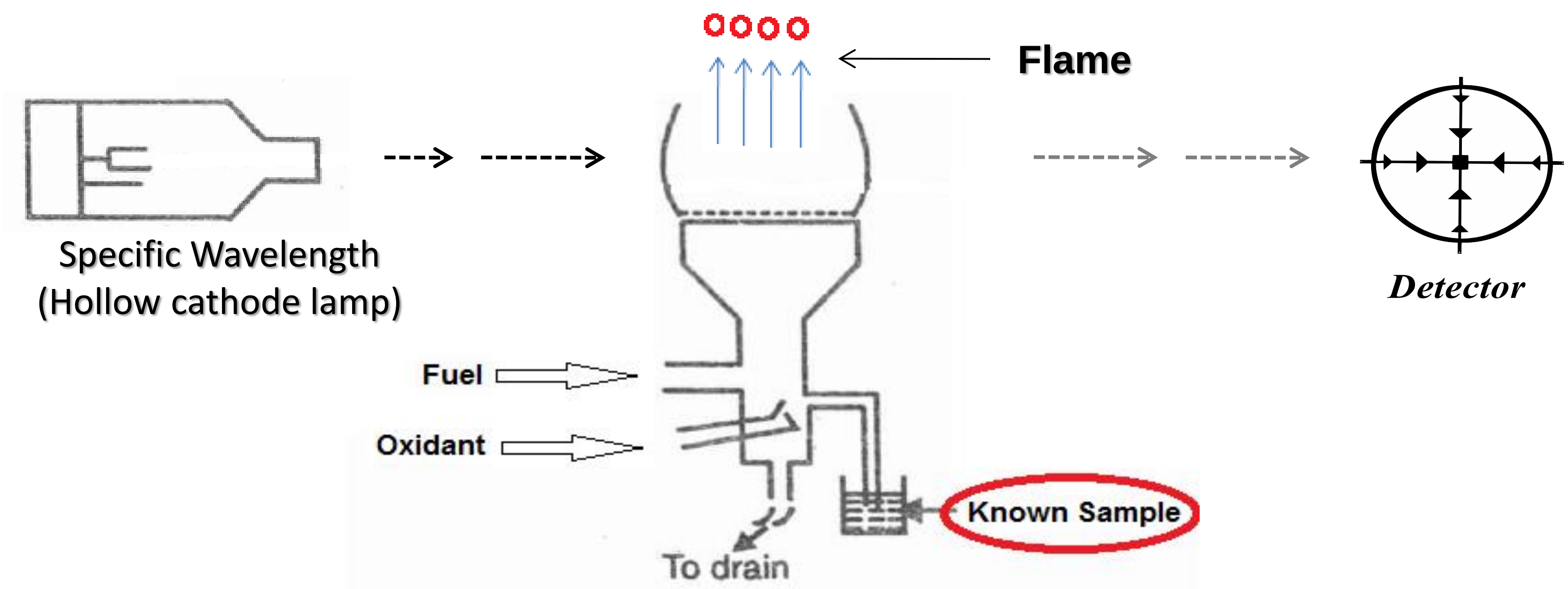
Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectroscopy: Introduction

- Most powerful technique for the determination of trace metals in solution
- 70-80 elements can be detected
- Determination can be made in the presence of many other elements but only one element can be detected at a time
- Wide applications

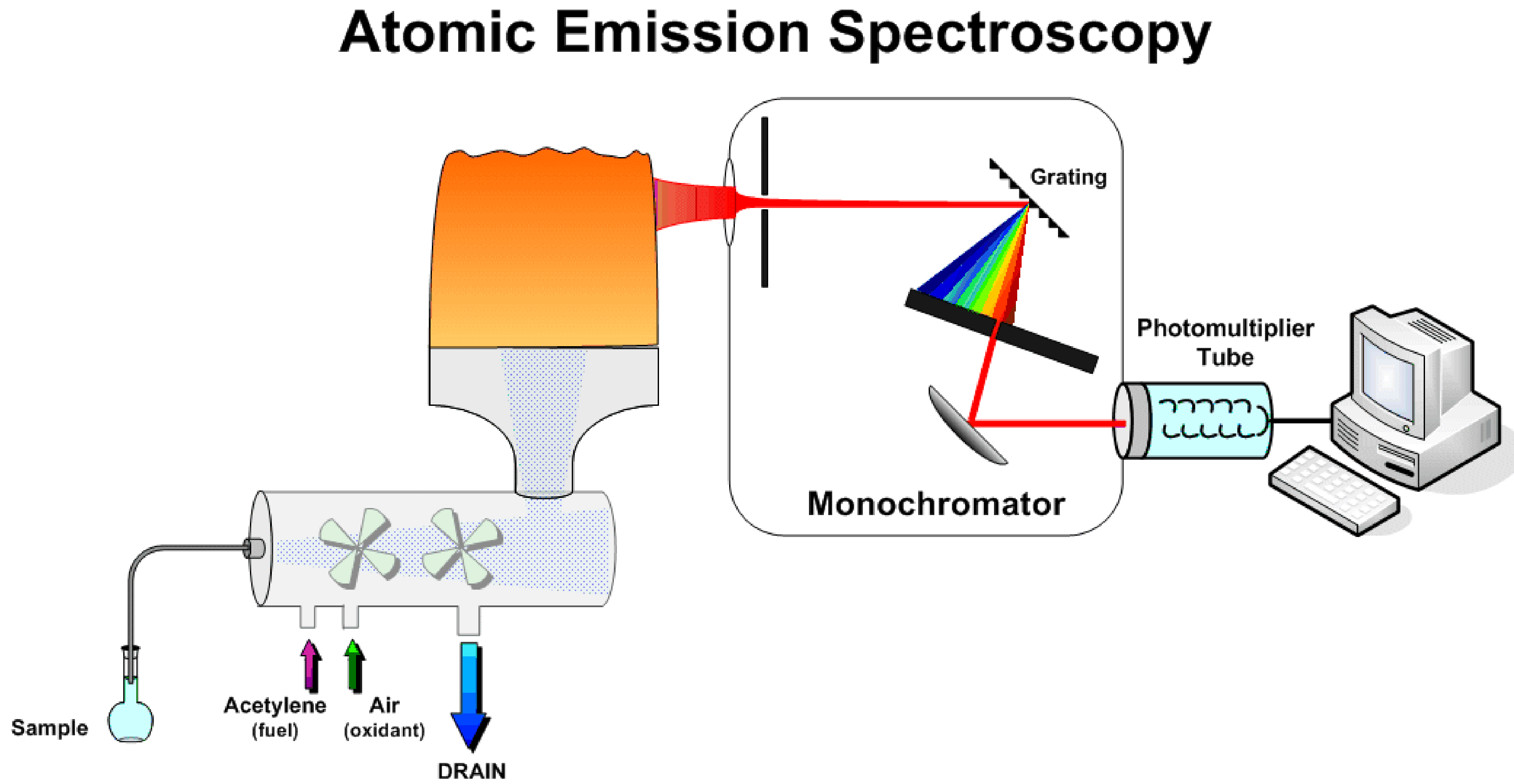
Atomic Absorption Spectroscopy: Principle

A sample solution containing known metal ions, when introduced into the flame and irradiated with light of their own specific wavelength, will absorb light proportional to the density (concentration) of ground state atoms in the flame.



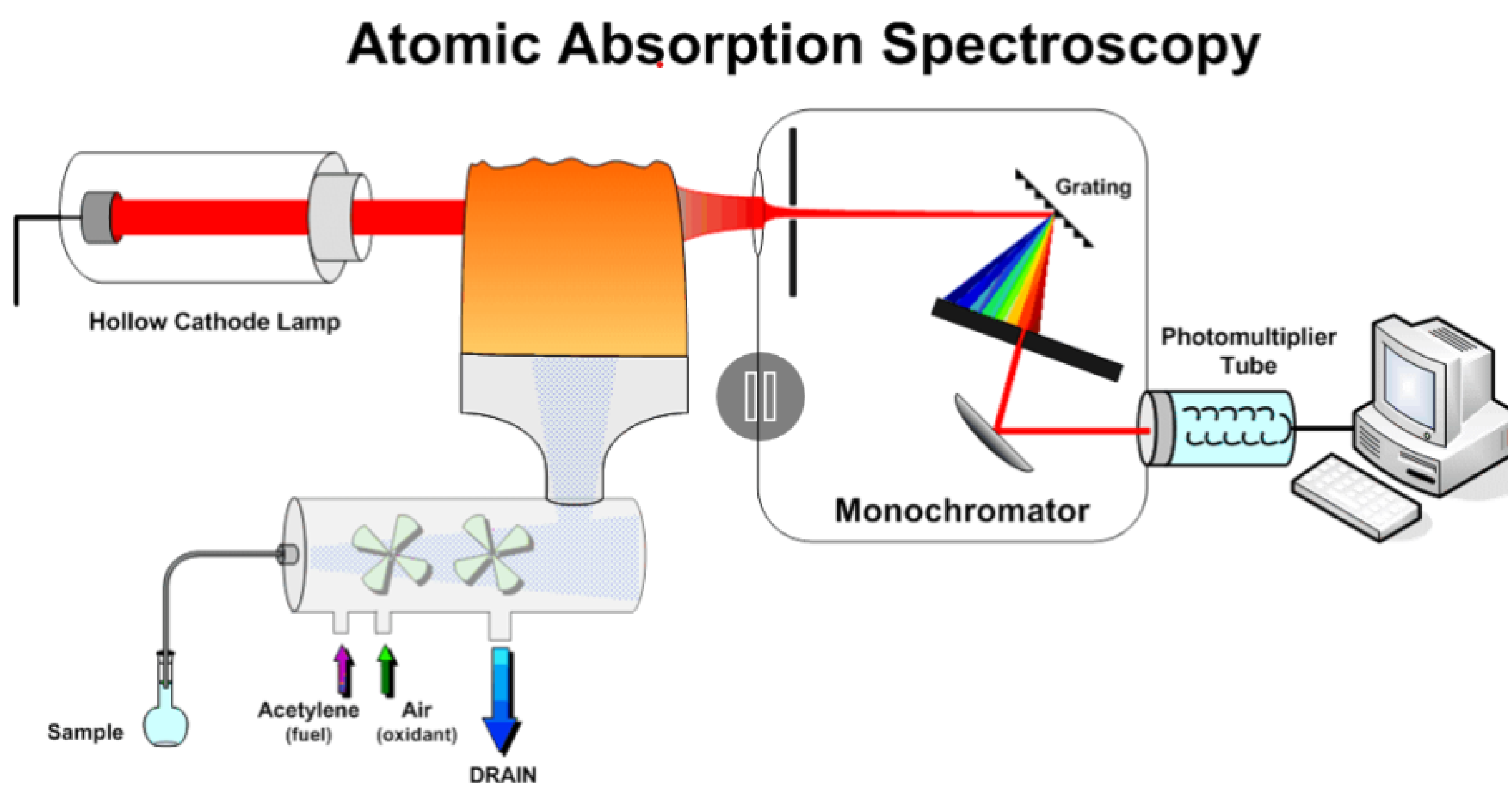
Note: Number of gaseous atoms in the ground state is always greater than 99.9% of the total gaseous atoms at any instant inside flame.

Basic difference between AAS and FES: Set-up perspective



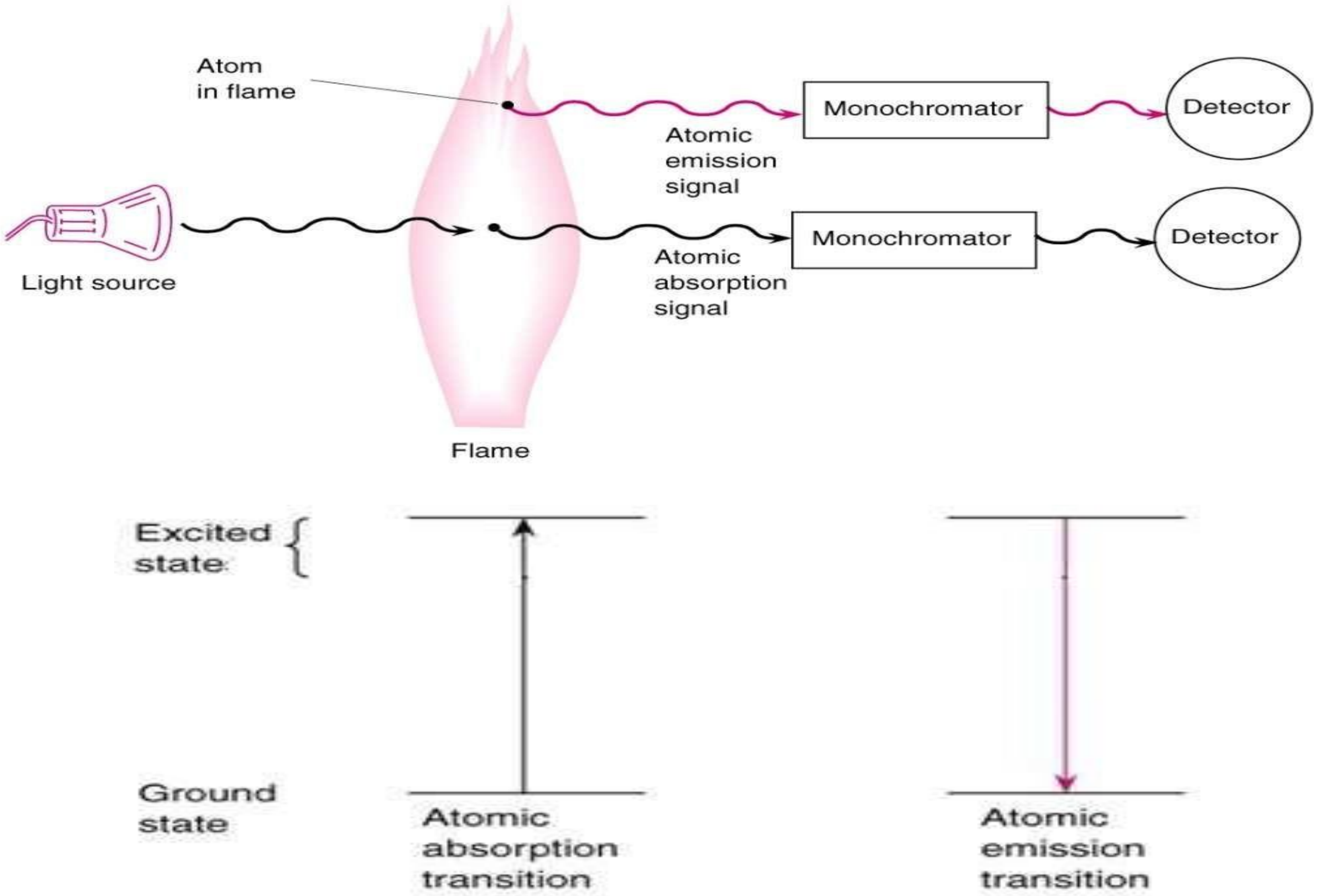
http://faculty.sdmiramar.edu/fgarces/LabMatters/Instruments/AA/AA.htm

Basic difference between AAS and FES: Set-up perspective



http://faculty.sdmiramar.edu/fgarces/LabMatters/Instruments/AA/AA.htm

Recall the difference between AAS and FES:



Difference between AAS and FES

FES	AAS
Emitted radiation is detected	Transmitted radiation is detected
Emission intensity α No. of atoms in excited state	Absorption intensity α No. of atoms in ground state
Emission intensity is very sensitive to change in flame temperature	Absorption intensity is not so sensitive to change in flame temperature
Beer's law is not obeyed	Beer's law is obeyed

Advantages of AAS

- Atoms of a particular element can absorb radiation of their own wavelength – No spectral interference
- Much larger No. of atoms contribute in the AAS signal.
- Variation in flame temperature has less effect on absorption intensity
- 70-80 elements can detected

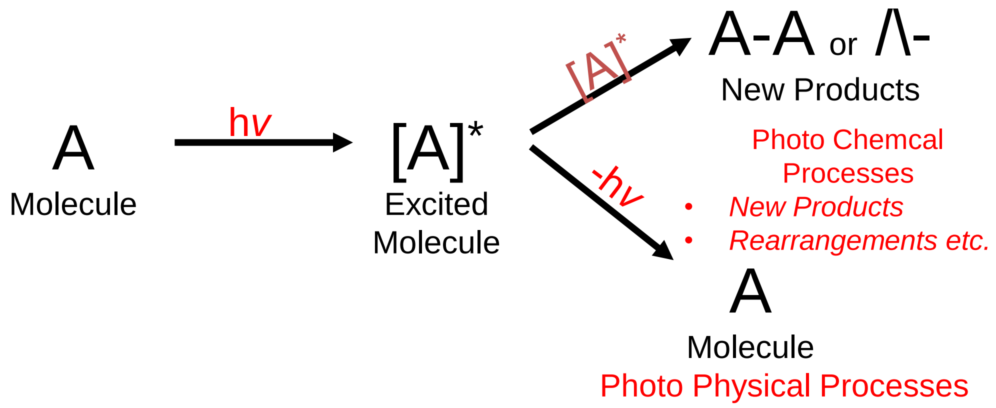
Disadvantages of AAS

- A different Hollow cathode lamp for each element is required
- Elements that form the stable oxides eg. Al, Ti, W, and Mo, do not give very good results

Jablonski energy diagram

Fluorescence
Phosphorescence
&
Other Photophysical Processes

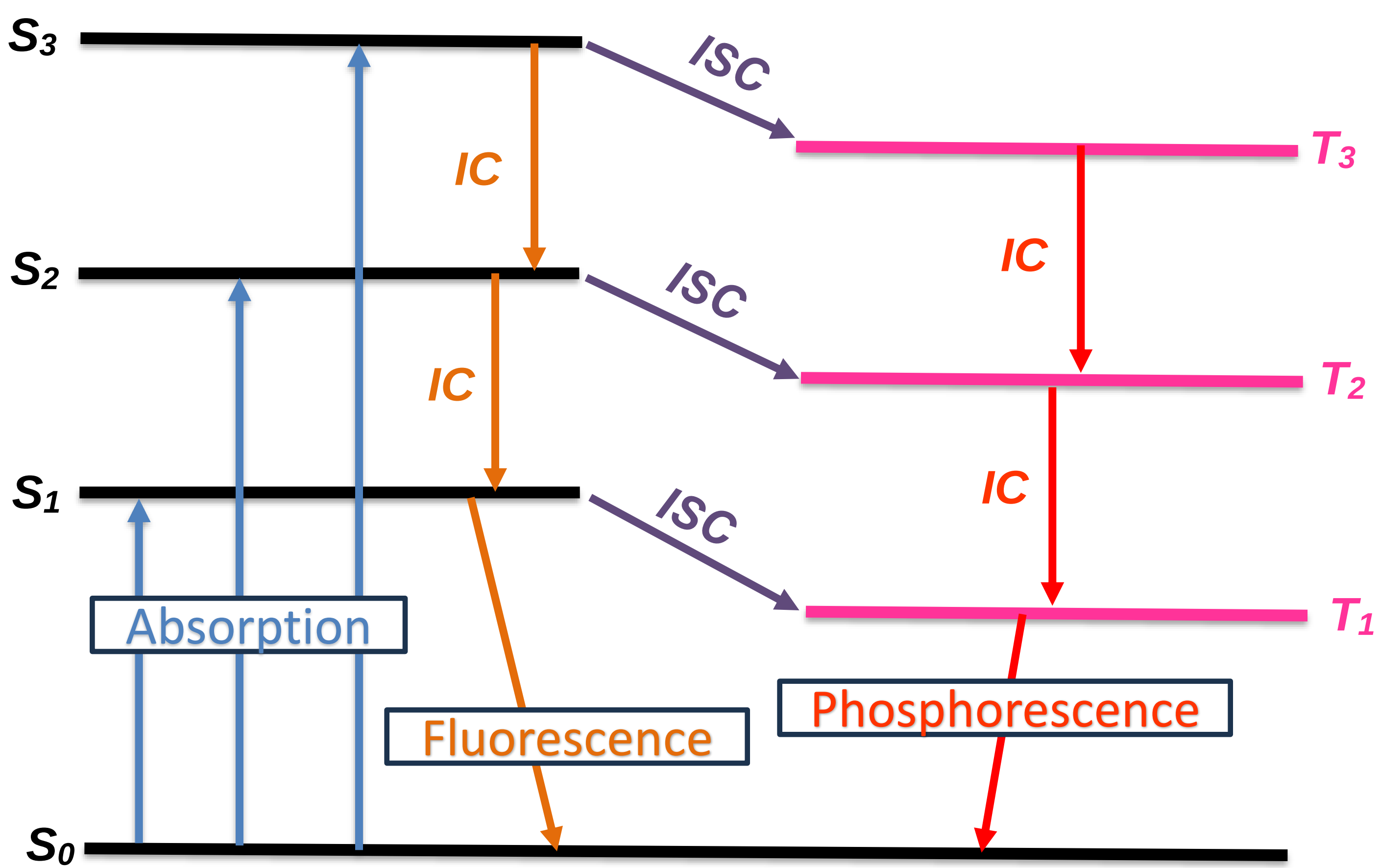
The fate of an excited molecule



A molecule (A) on absorption of desired wavelength of light gets excited to an intermediate excited state [A]*. This short lived excited intermediate state has two possibilities to undergo to achieve the stability.

(a) Photochemical Processes – Organic reaction, Rearrangement etc. <u>(Not Part of Course)</u>
(b) Photophysical Processes Explained by **<u>Jablonski Energy Diagram</u>**

Jablonski energy diagram



Term symbols for photophysical processes

- For any molecule in the ground state, spin quantum number $s = ½ - ½ = 0$
- Substituting this value in ground energy state (E_0) of molecule as shown below

  ($E_0 = 2s+1 = (2 \times 0) + 1 = 1$, represented by S)

For ground state, this energy state is represented by (S_0)

On absorption of suitable energy, one of the electrons from molecular orbital gets exited to higher energy level with two possible orientations – Parallel or Antiparallel as shown below.

Possibility -1 : $s = ½ - ½ = 0$
E_1 $= 2s+1 = (2 \times 0) + 1 = 1$,
(S_1)

Possibility - 2 : $s = ½ + ½ = 1$
E_1 $= 2s+1 = (2 \times 1) + 1 = 3$,
(T_1)

Ground State

Singlet (S_1) Excited State

Anti parallel Spin of electrons

Triplet (T_1)Excited State

Parallel spin of electrons

Photophysical processes in the Jablonski diagram

1. Radiative Processes

Fluorescence: A process in which an excited molecule comes to ground state, from the same spin state (S_1 to S_0), by releasing energy in the form of light is called **Fluorescence**. As per quantum mechanics, this is an allowed transition having a time range of 10^{-10}-10^{-8}s.

Phosphorescence: A process in which an excited molecule comes to ground state, from a different spin state (T_1 to S_0), by releasing energy in the form of light is called **Phosphorescence**. As per quantum mechanics, this is a forbidden transition having a time range of 10^{-6}-10^{-3}s.

Note: Both "Fluorescence & Phosphorescence" fall under a broad classification of a range of well-known radiative processes known as Luminescence. The scope of the present course covers only above mentioned two processes.

Photophysical processes in the Jablonski diagram

2. Non-radiative processes

It involves transition from $S_3 \rightarrow S_2$ or $S_2 \rightarrow S_1$ or $T_3 \rightarrow T_2$ or $T_2 \rightarrow T_1$. It does not involve emission of any radiation and hence, is called Non-radiative transition. It only involves emission of heat.

- **Internal Conversion (IC):**

In this process, energy loss occurs in the form of heat. It involves transition from $S_3 \rightarrow S_2$ or $S_2 \rightarrow S_1$ or $T_3 \rightarrow T_2$ or $T_2 \rightarrow T_1$. It occurs in less than 10^{-11} seconds.

- **Intersystem Crossing (ISC):**

It involves transition from $S_3 \rightarrow T_3$, $S_2 \rightarrow T_2$ or $S_1 \rightarrow T_1$. Both of these transitions are forbidden.

Summary of all photophysical processes

Jablonski energy diagram

Photophysical Process	Lifetime Scale	Types of Transition
Absorption or Excitation	10^{-15} s	$S_0 \rightarrow S_n$ state Radiative, Spin allowed
Internal Conversion (IC)	10^{-12}-10^{-10} s	$S_n \rightarrow S_{n-1}$ state Non-radiative, Spin allowed
Intersystem Crossing (ISC)	10^{-10}-10^{-9} s	$S_n \rightarrow T_n$ state Non-radiative, Spin forbidden
Fluorescence	10^{-10}-10^{-8} s	$S_1 \rightarrow S_0$ state Radiative, Spin allowed
Phosphorescence	10^{-6}-10^{-3} s	$T_1 \rightarrow S_0$ state Radiative, Spin forbidden

Difference between fluorescence & phosphorescence

Fluorescence	Phosphorescence
Fluorescence is the absorption of energy by atoms or molecules followed by immediate emission of light or electromagnetic radiation.	Phosphorescence is the absorption of energy by atoms or molecules followed by delayed emission of electromagnetic radiation
Fluorescence is fast process. Lifetime is short compared to phosphorescence	Phosphorescence is delayed process. Lifetime is much longer compared to fluorescence
Emission wavelength of fluorescence observed at shorter wavelength compared to phosphorescence	Emission wavelength of phosphorescence observed at longer wavelength compared to fluorescence
$S_1 \rightarrow S_0$ state, Spin Allowed Transition	$T_1 \rightarrow S_0$ state, Spin Forbidden Transition
Fluorescence is observed in solids, liquids.	Phosphorescence is observed only in solids.

Applications of fluorescence and phosphorescence

❖ Applied in Fluorescent lamps (LED).

❖ Spectroscopy/chemical sensors: To determine the concentration of the analyte to a very low detection limit, up to ppb/ppt level.

❖ Useful for many biological applications such as fluorescent labeling and pharmaceutical applications.

❖ Forensic applications

❖ As materials for display on electronic devices