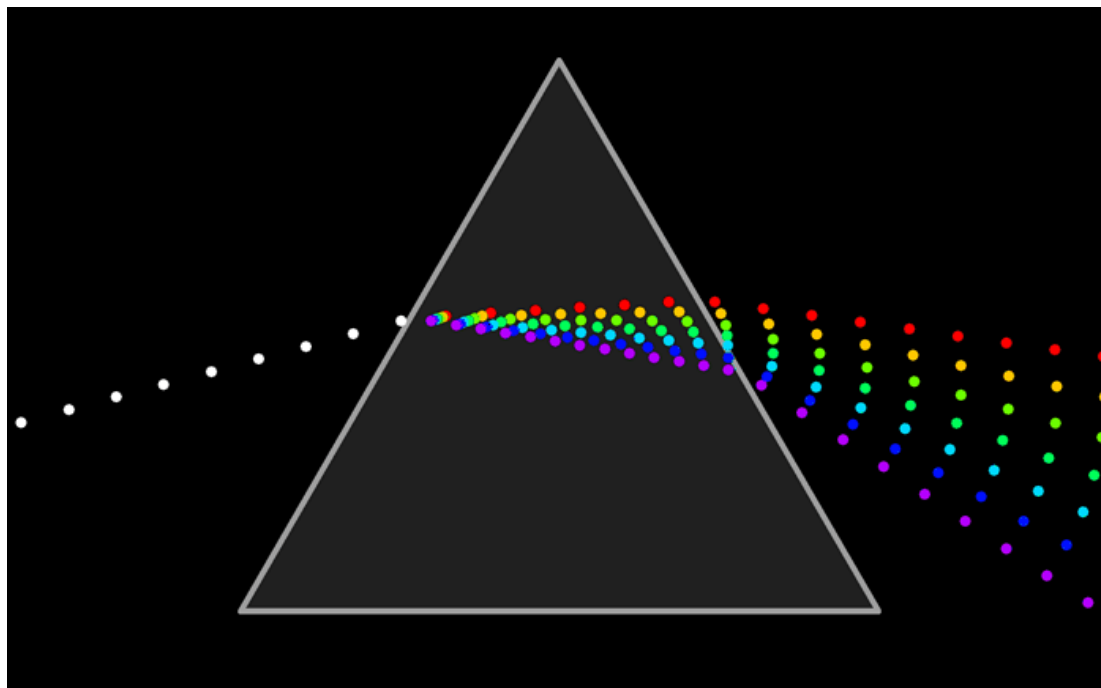


Introduction : Spectroscopy



DR.S. ANAND GIRI

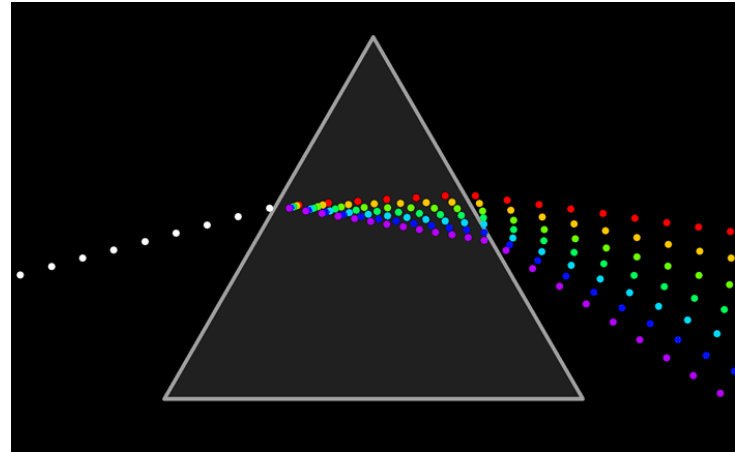
ANANLYTICAL CHEMISTRY

Ph.D. Jadavpur University

Kolkata, India

Introduction

Spectroscopy

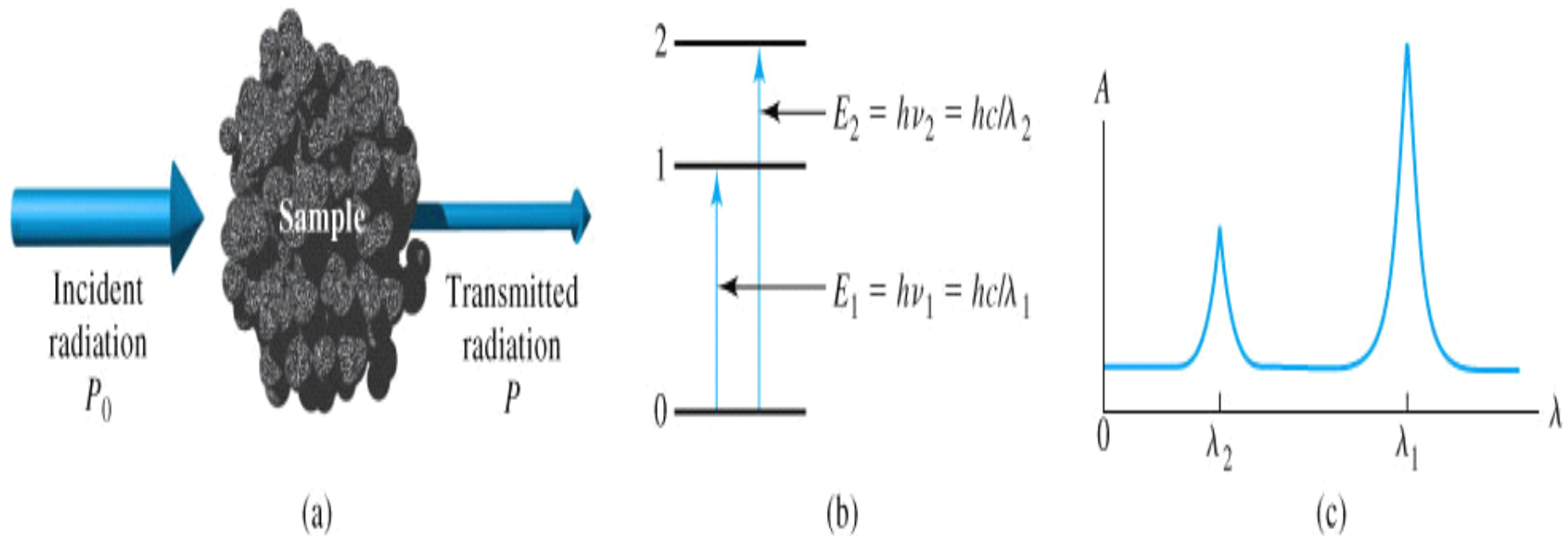


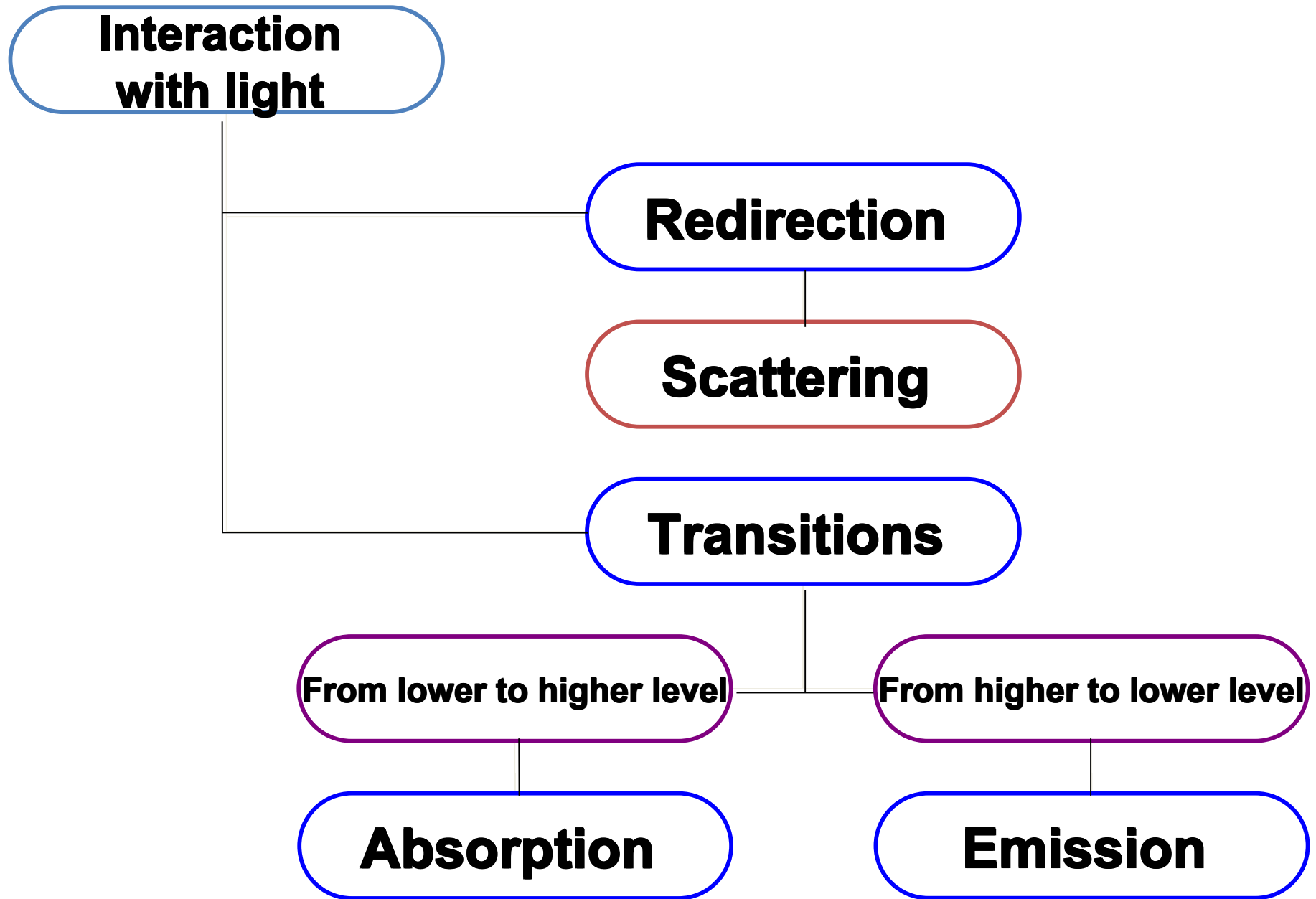
Any procedures that uses light to measure chemical concentrations

The use of *absorption, emission, or scattering of electromagnetic radiation* by atoms, molecules or ions to study the *quantity, quality or physical processes of them.*

Spectroscopy

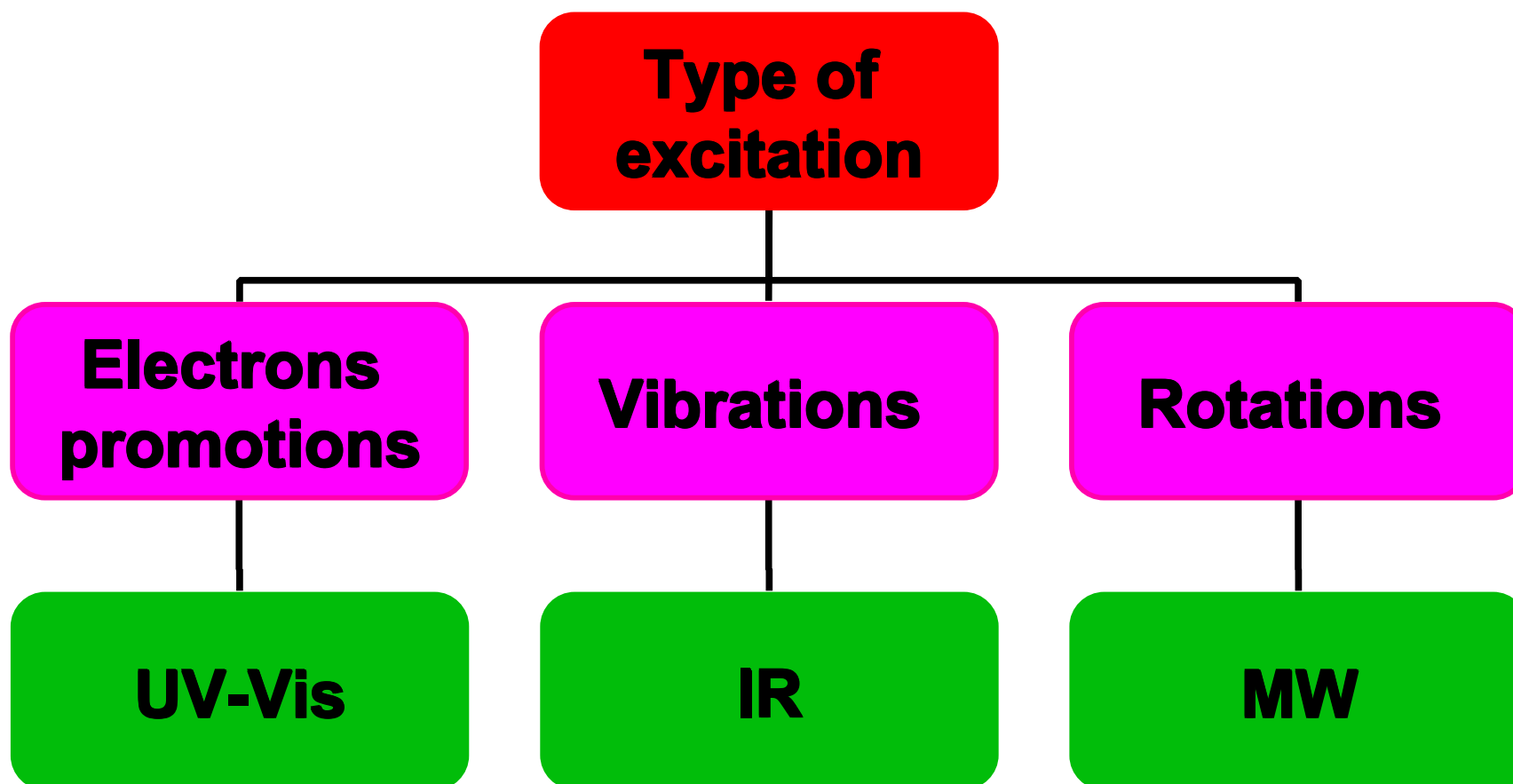
Interaction with radiation causes **redirection** of radiation or **transitions** between energy levels of atoms or molecules.





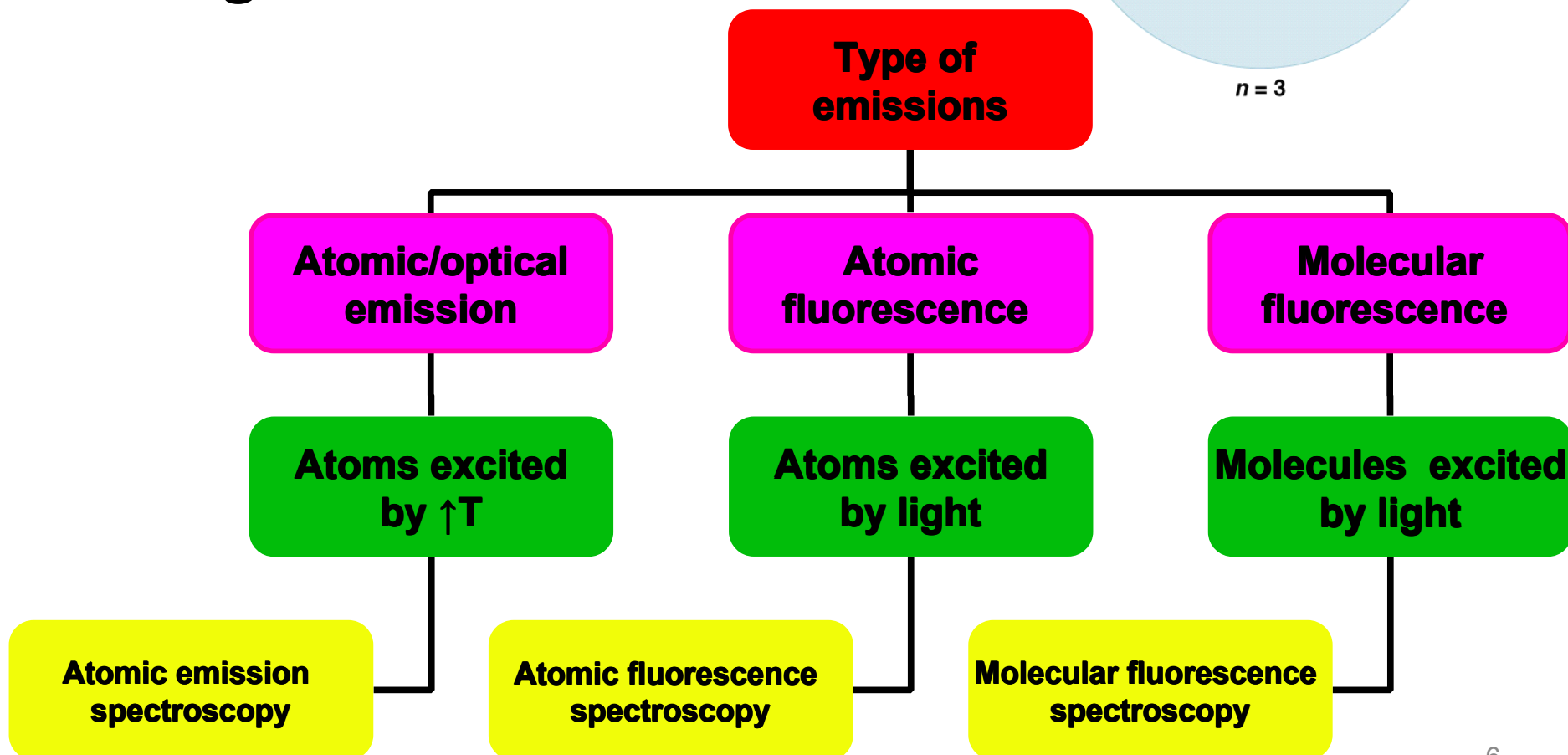
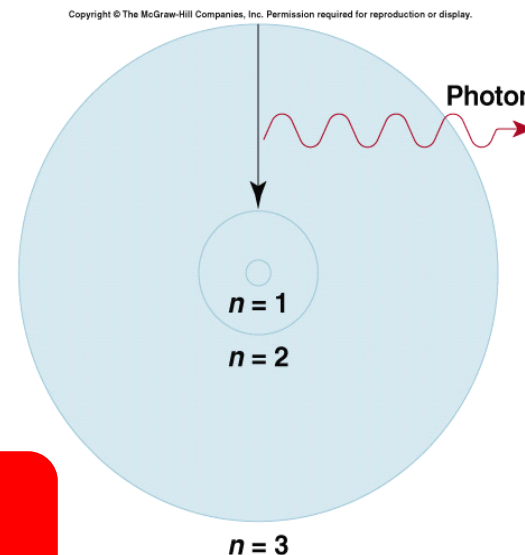
Absorption

When light absorbed, **the structure** of a molecule or atom is excited to a **higher energy level**.



Emission

Excited molecule or atom decay to a lower energy level by emitting radiation.

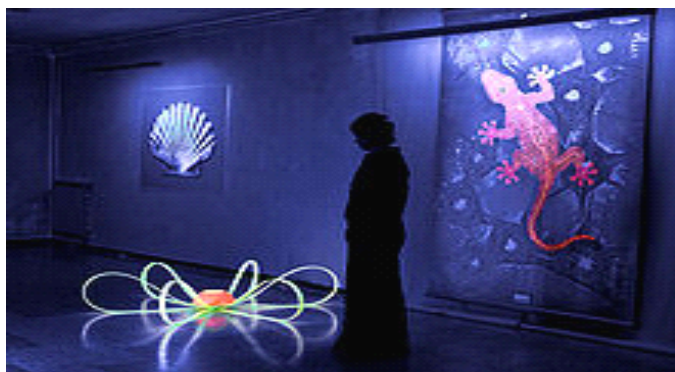


Emissions

Molecular emissions

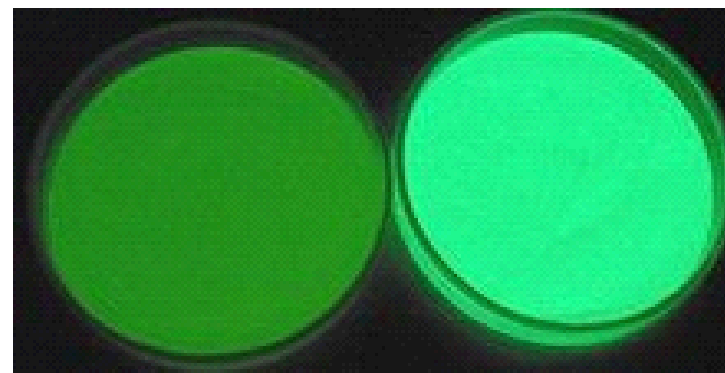
Molecular fluorescence

Transition of Same spin

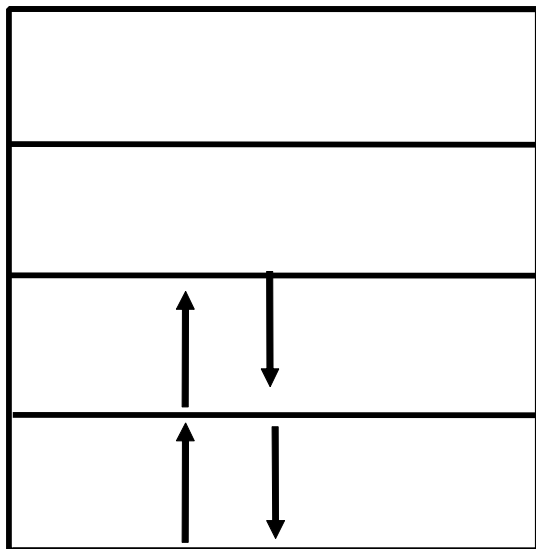


Molecular phosphorescence

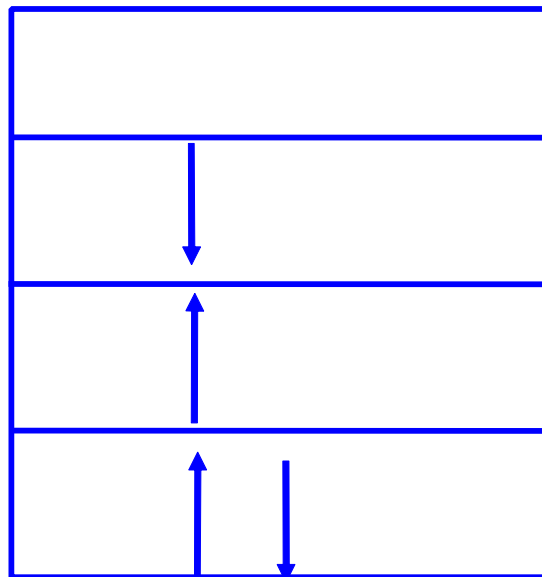
Transition of different spin



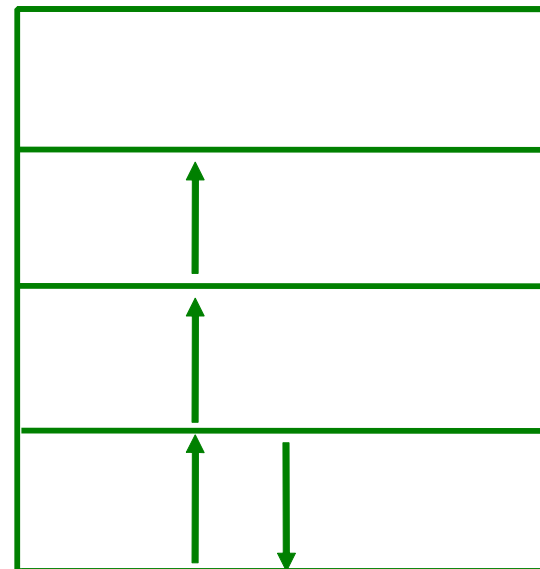
Excitation



Ground state



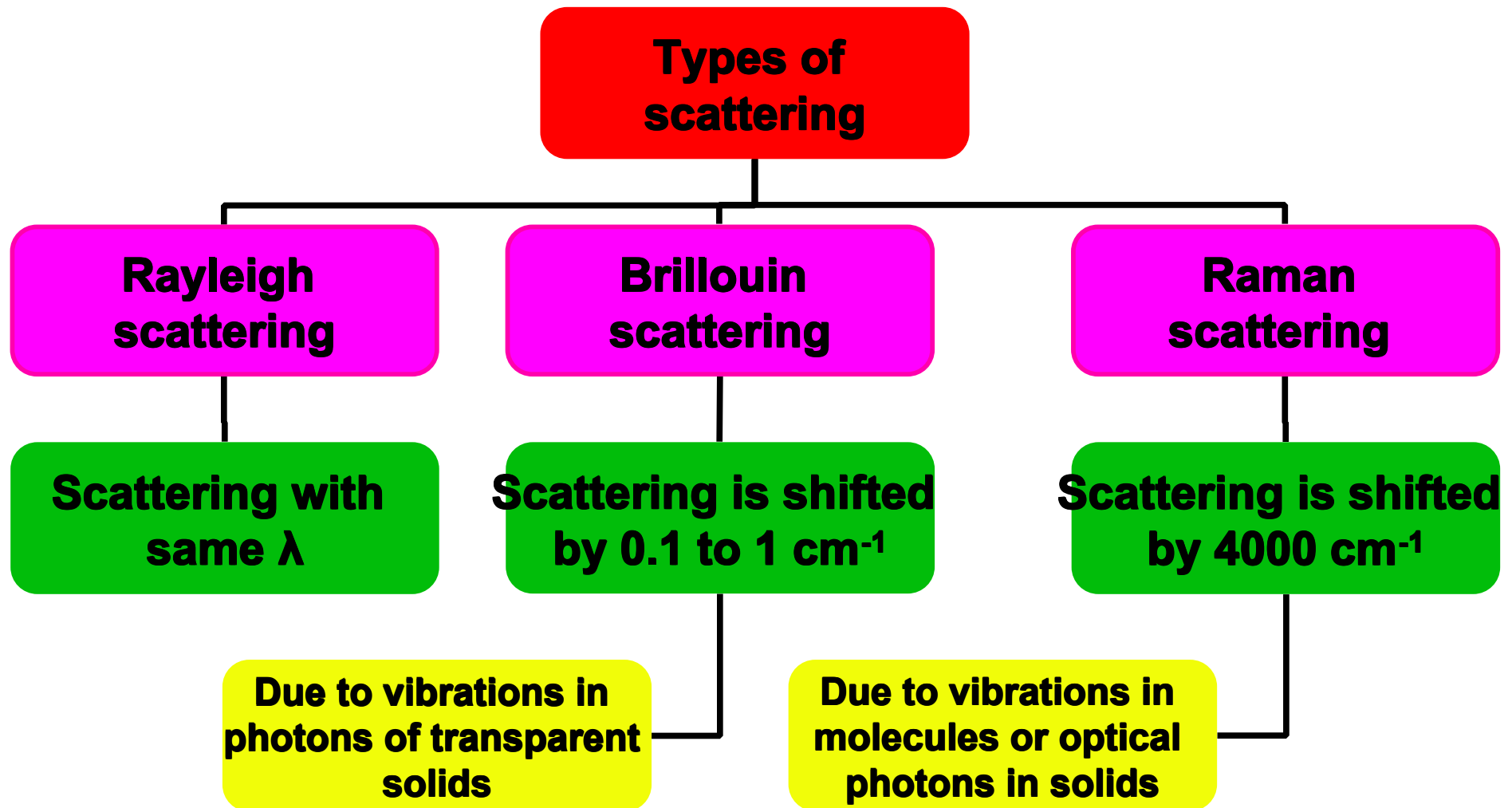
**Singlet state
Opposed spin**



**Triplet state
Parallels spin**

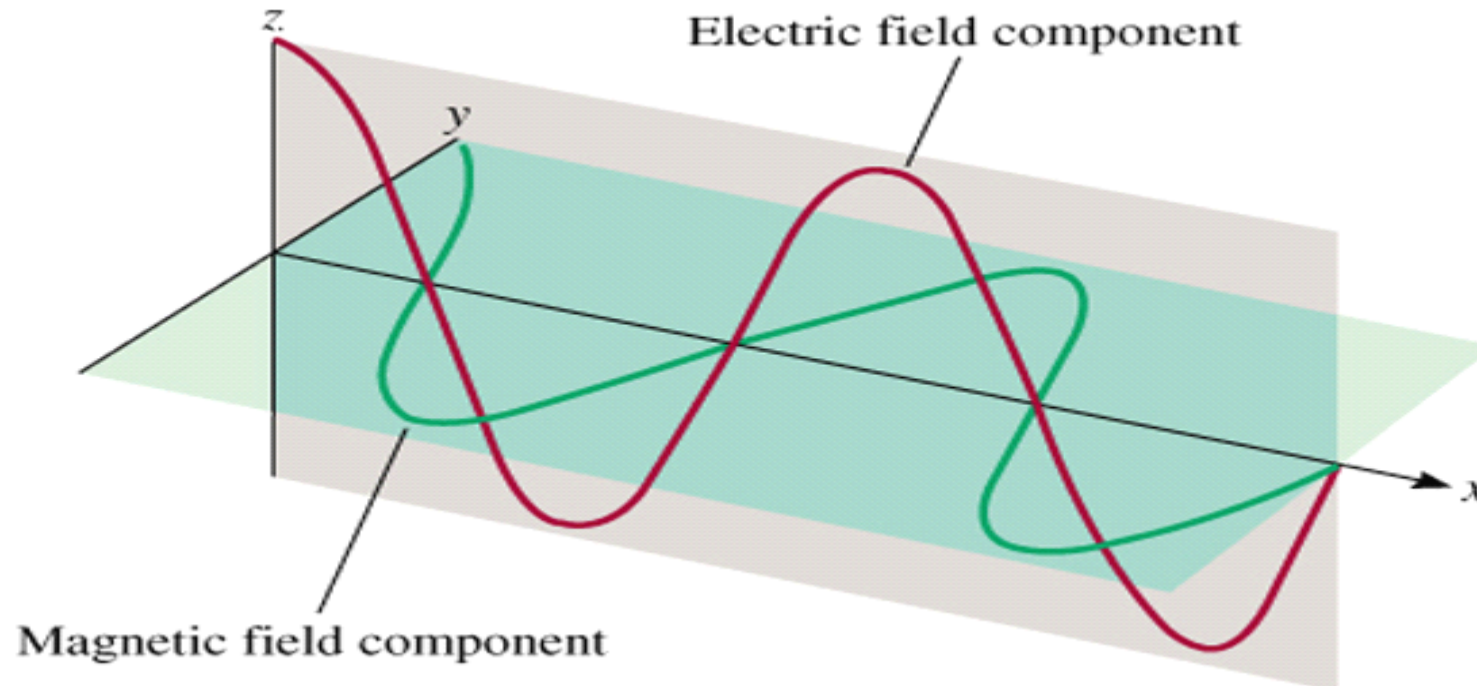
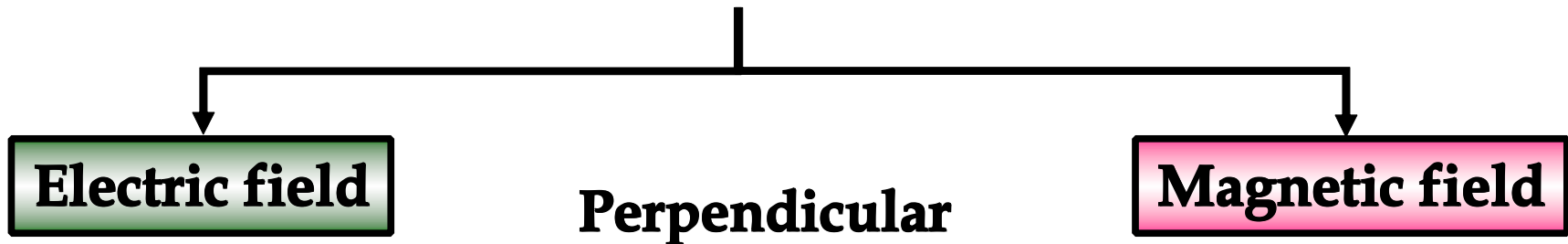
Scattering

Redirection of light due to its interaction with matter



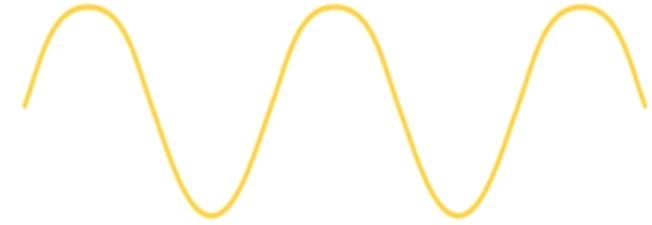
Electromagnetic Radiation

Light is electromagnetic radiation (EMR)



Light

EMR



Light as a wave phenomenon



Light as a stream of photons

Wave theory

EMR

- Undergoes **sinusoidal oscillations**
- Travel through a vacuum
- Has a wavelength

Particle theory

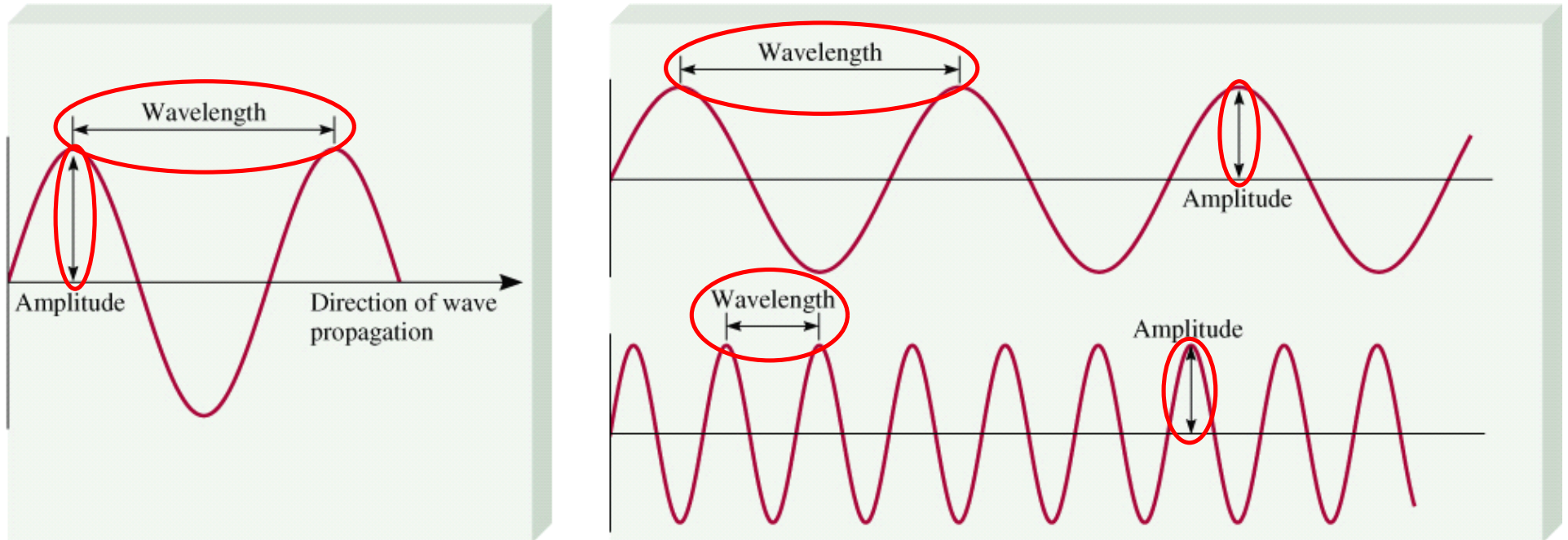
EMR

- is made up of **packets of energy called photons or quanta**
- a photon depends upon the frequency of radiation

QUANTUM MECHANICS

- Electromagnetic radiation
 - Properties of waves:
 - Wavelength (λ)
 - Frequency (ν)
 - Speed (equal to speed of light)

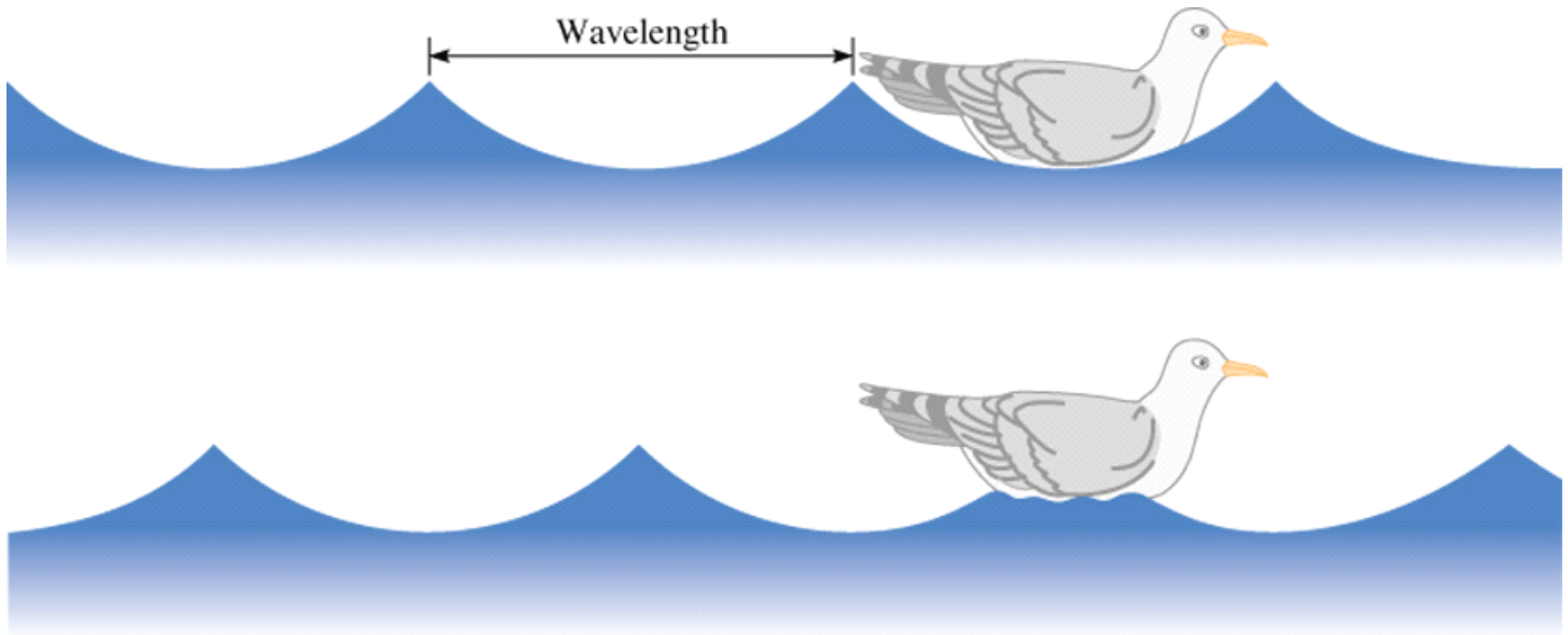
Properties of Waves



Wavelength (λ) is the distance between identical points on successive waves.

Amplitude is the vertical distance from the midline of a wave to the peak or trough.

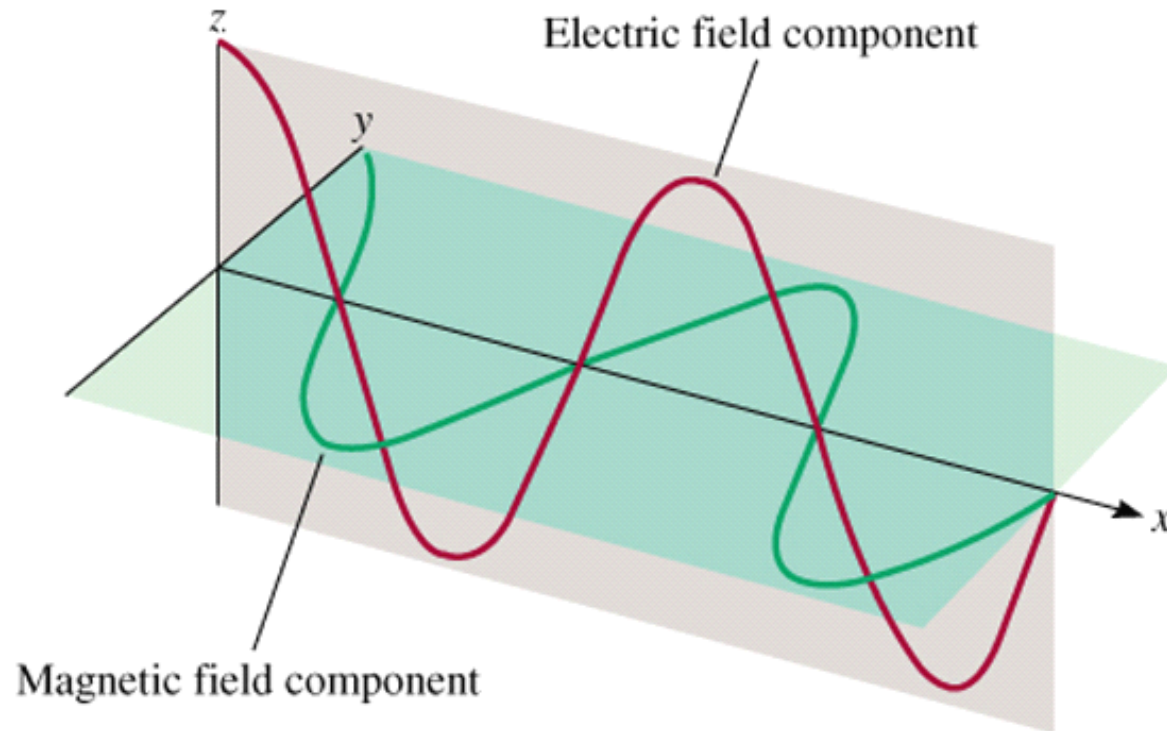
Properties of Waves



Frequency (ν) is the number of waves that pass through a particular point in 1 second (Hz = 1 cycle/s).

The speed (c) of the wave = $\lambda \times \nu$

Maxwell (1873), proposed that **visible light consists of electromagnetic waves.**



Electromagnetic radiation is the emission and transmission of energy in the form of electromagnetic waves.

**Speed of light (c) in vacuum = 3.00×10^8 m/s
= 3.00×10^{10} cm/s**

All electromagnetic radiation

$$C = \lambda \times \nu$$

A photon has a frequency of 6.0×10^4 Hz.
Convert this frequency into wavelength (nm).
Does this frequency fall in the visible region?

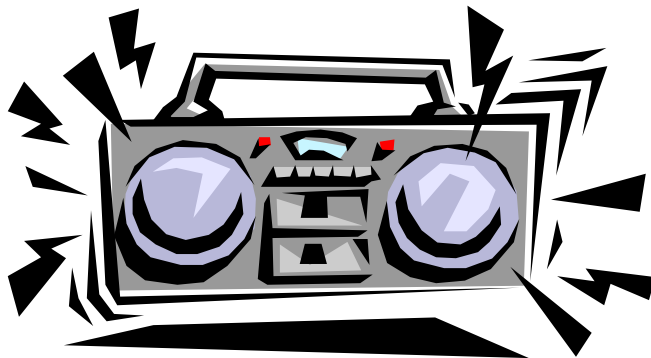
$$\lambda \times \nu = c$$

$$\lambda = c/\nu$$

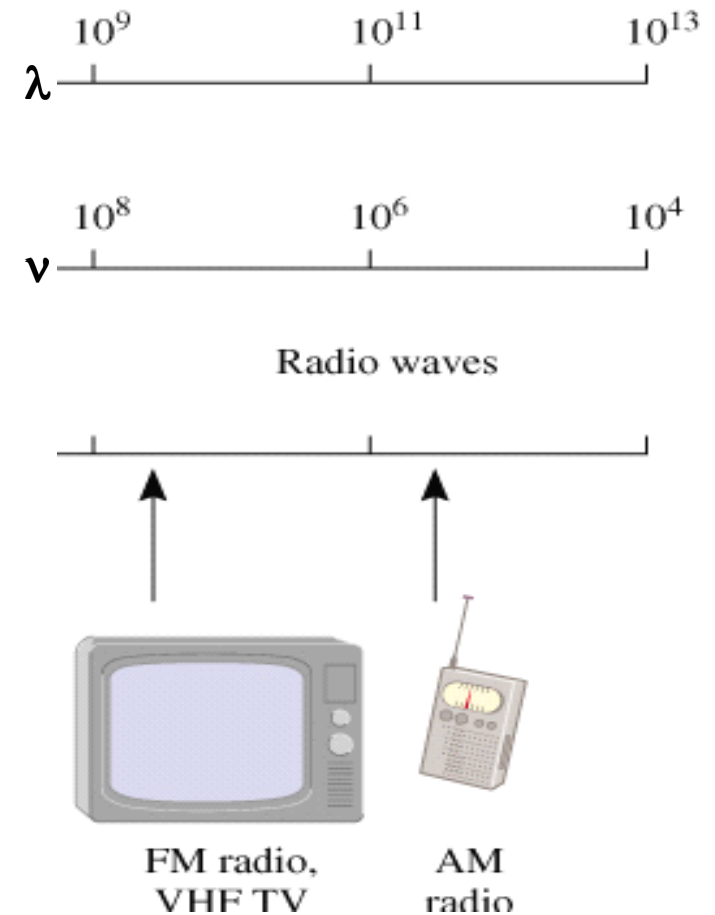
$$\lambda = 3.00 \times 10^8 \text{ m/s} / 6.0 \times 10^4 \text{ Hz}$$

$$\lambda = 5.0 \times 10^3 \text{ m}$$

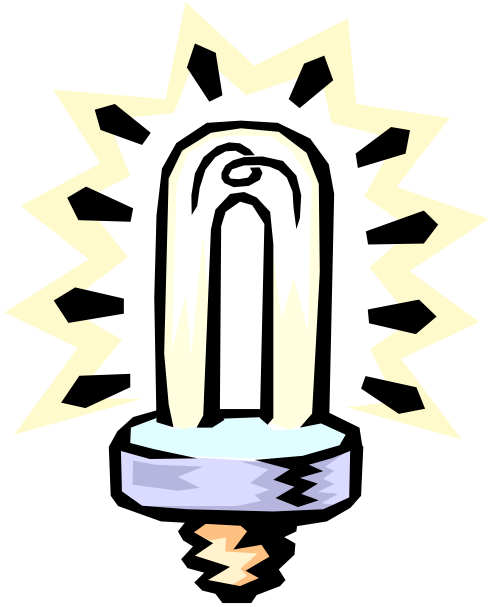
$$\lambda = 5.0 \times 10^{12} \text{ nm}$$



Radio
wave



Energy (light) is emitted or absorbed in discrete units (quantum).



$$E = h \times \nu = h c / \lambda$$

Planck's constant (h)

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$c = \text{speed of light} = 2.998 \times 10^8 \text{ m s}^{-1}$$

When copper is bombarded with high-energy electrons, X rays are emitted. **Calculate the energy (in joules)** associated with the photons if the **wavelength of the X rays is 0.154 nm.**

$$E = h \times \nu$$

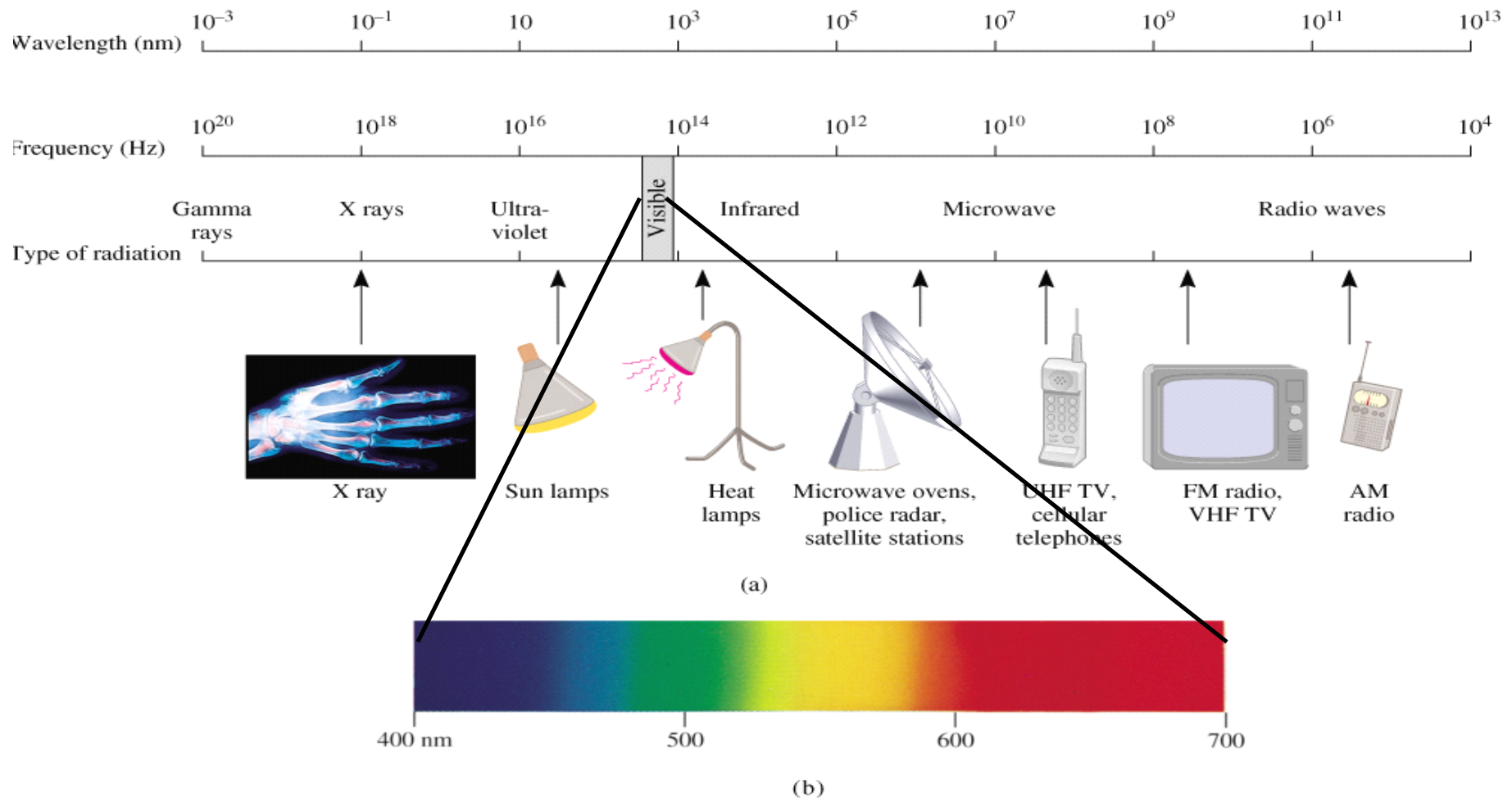
$$E = h \times c / \lambda$$

$$E = \frac{6.63 \times 10^{-34} \text{ (J}\cdot\text{s)} \times 3.00 \times 10^8 \text{ (m/s)}}{0.154 \times 10^{-9} \text{ (m)}}$$

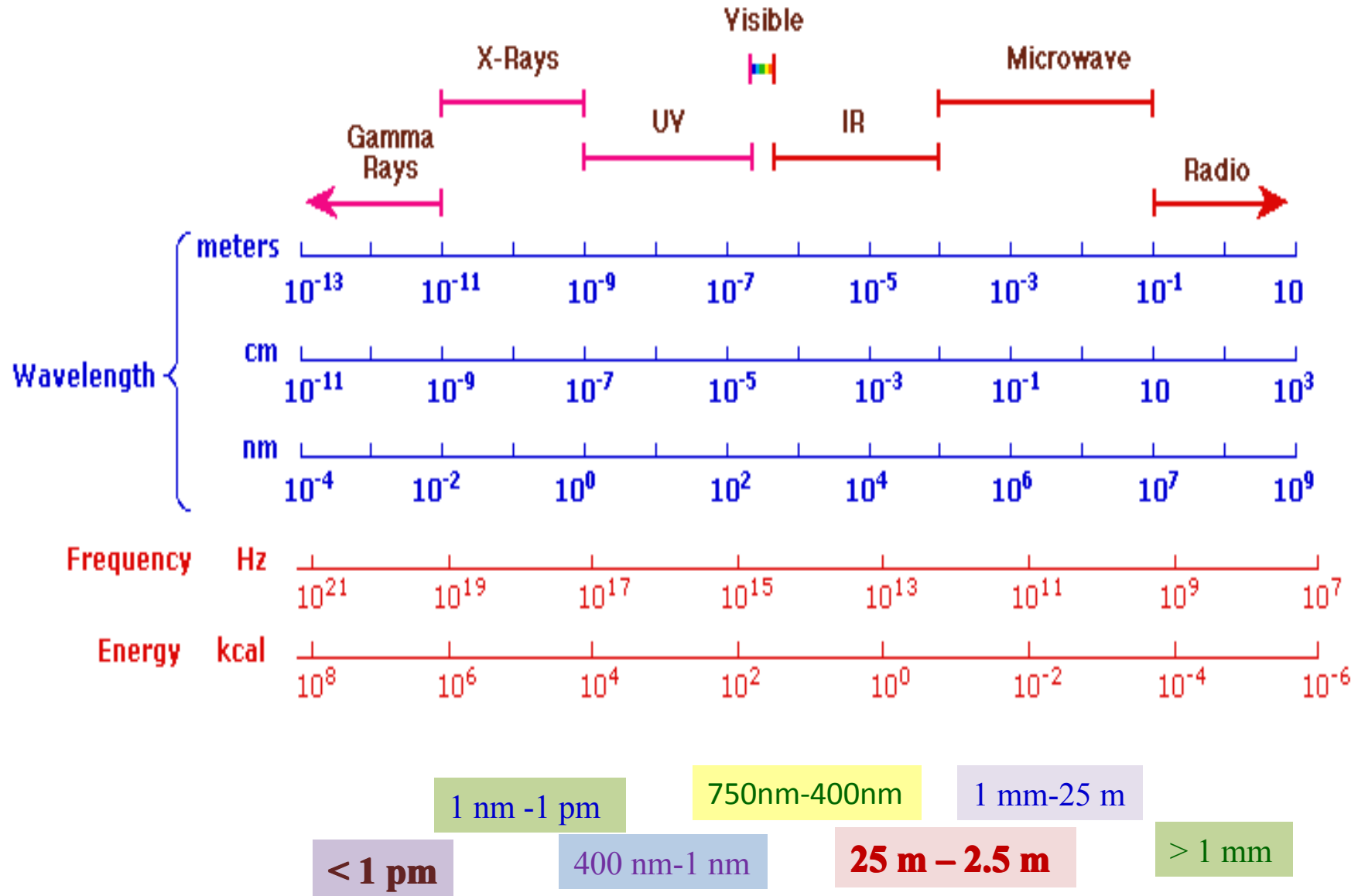
$$E = 1.29 \times 10^{-15} \text{ J}$$

Electromagnetic Spectrum

A continuum of all electromagnetic waves arranged according to frequency and wavelength.



The Electromagnetic Spectrum



Spectral bands of incoming solar energy and atmospheric effects

Band	Hz	Wavelength (nm)	Type of transition
Gamma ray	10^{20}-10^{24}	< 1 pm	Nuclear
X-Ray	10^{17}-10^{20}	1 nm -1 pm	Inner electron
Ultraviolet, UV	10^{15}-10^{17}	400 nm-1 nm	Outer electron
Visible	4-7.5×10^{14}	750 nm – 400 nm	Outer electron
near-infrared	1×10^{14}-4×10^{14}	2.5 m – 750 nm	Outer electron molecular vibrations
Infrared, IR	10^{13}-10^{14}	25 m – 2.5 m	Molecular vibrations
microwaves	3×10^{11}-10^{13}	1 mm-25 m	Molecular rotations, electron spin flips
radio waves	< 3×10^{11}	> 1 mm	Nuclear spin flips

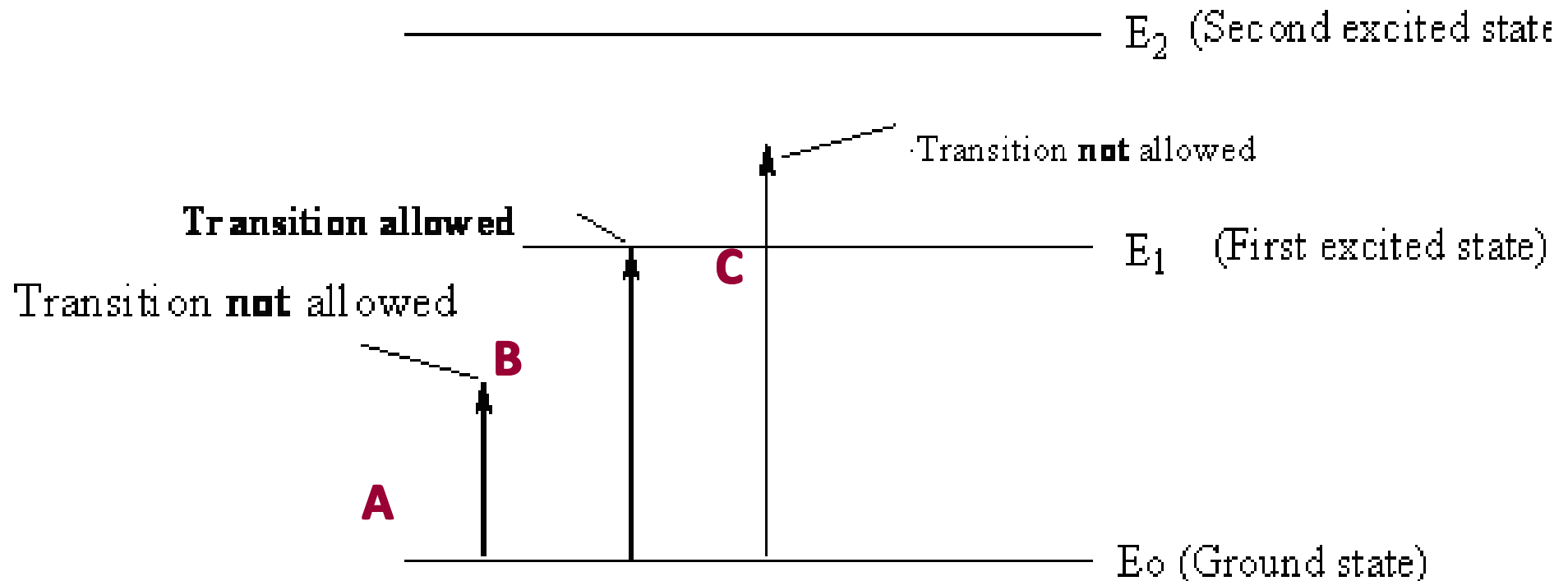
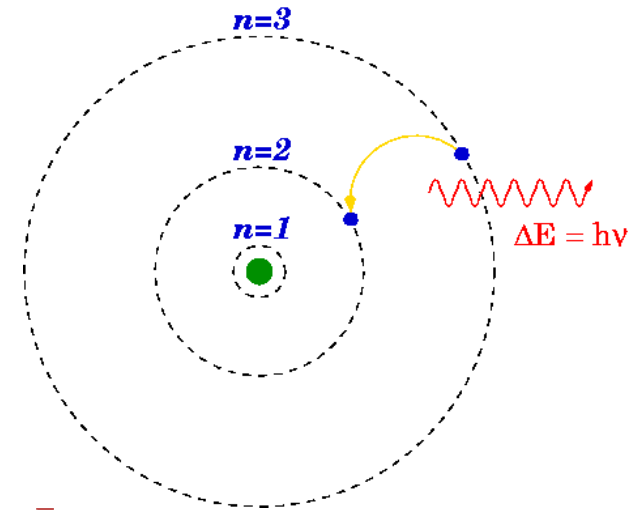
Absorption and Emission of Electromagnetic radiations

The structure of the atoms and molecules cause some wavelength to be absorbed and some to be reflected

Atoms at room temperature are usually in their lowest electronic energy state known as the ground state

Electrons atoms can move from one energy level to a higher one if;

1. They absorb the right amount of energy
2. There are vacant higher energy levels



Energy Transition

$$E_0 = E_{\text{electronic}} + E_{\text{rotational}} + E_{\text{vibrational}}$$



Only the absorption of radiation in the **visible and ultra-violet** region of the electromagnetic spectrum can cause $E_{\text{electronic}}$.

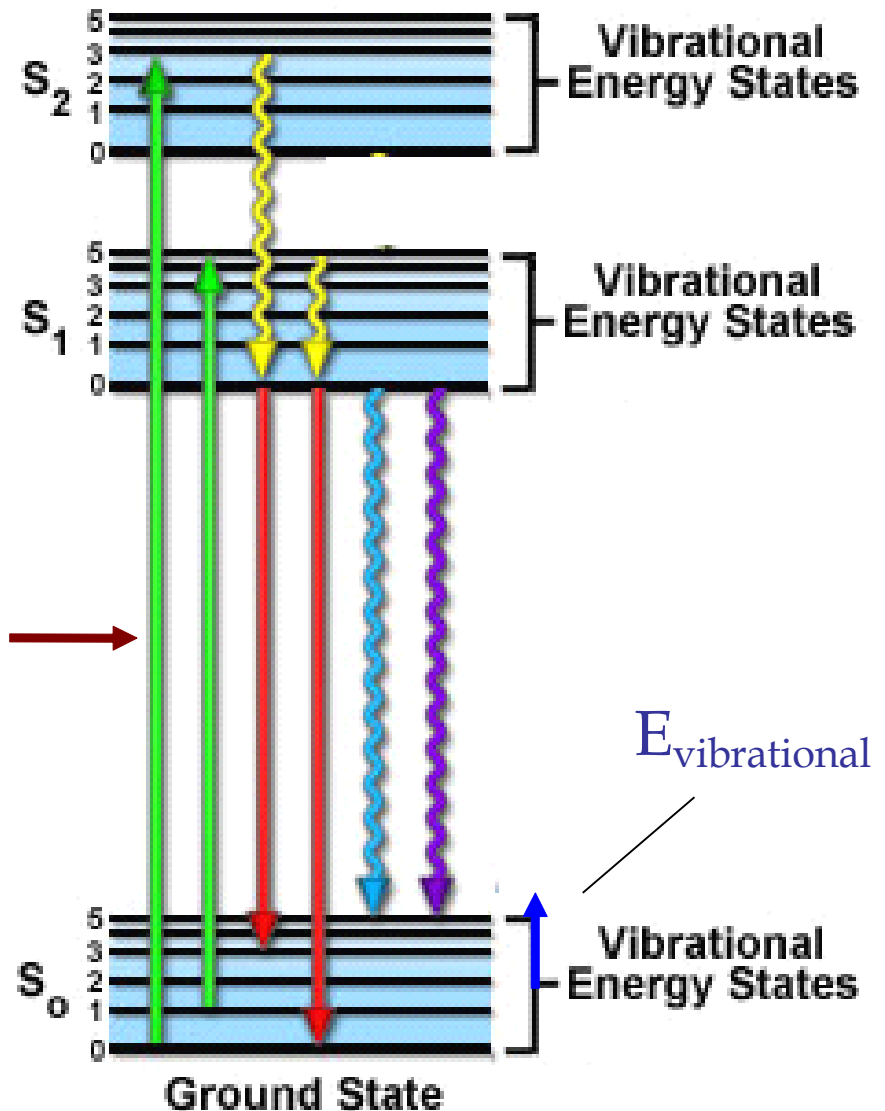
A^*

Unstable

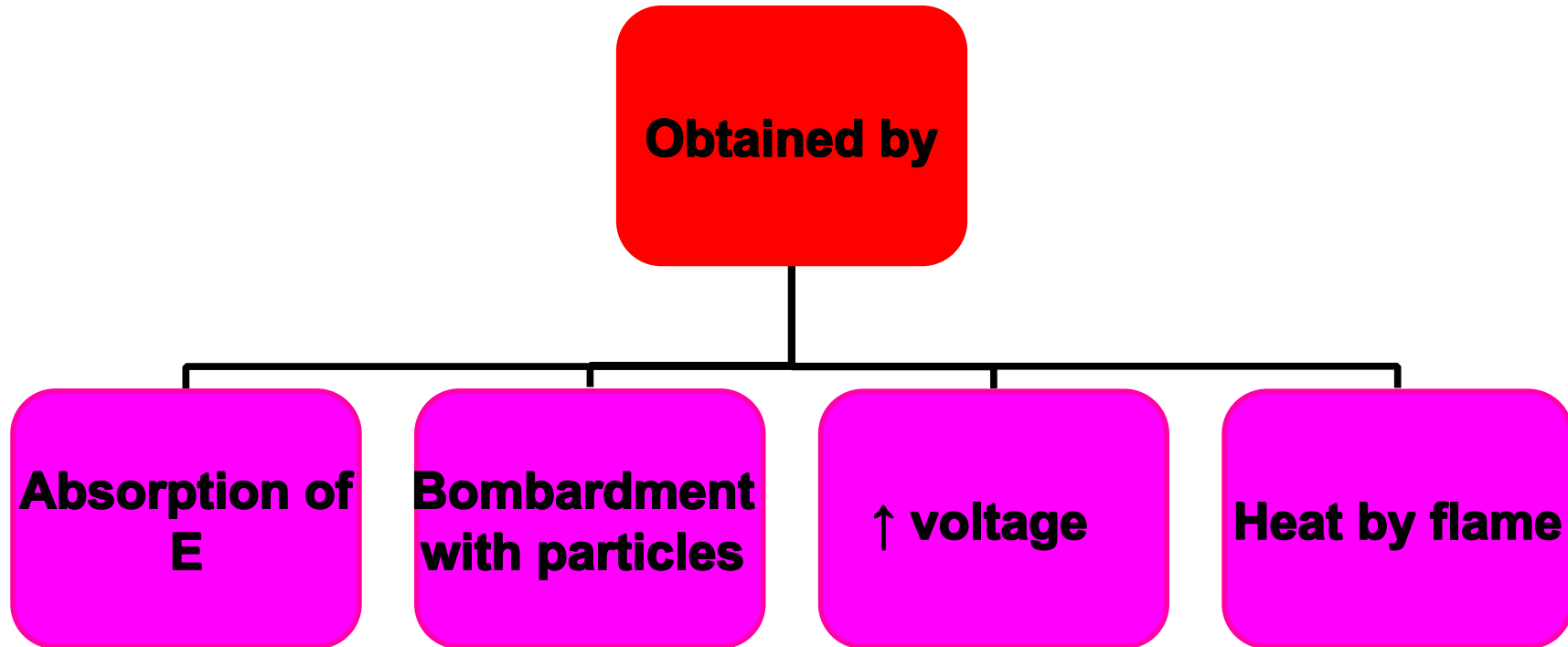
Relaxes within 10^{-6} - 10^{-9} s



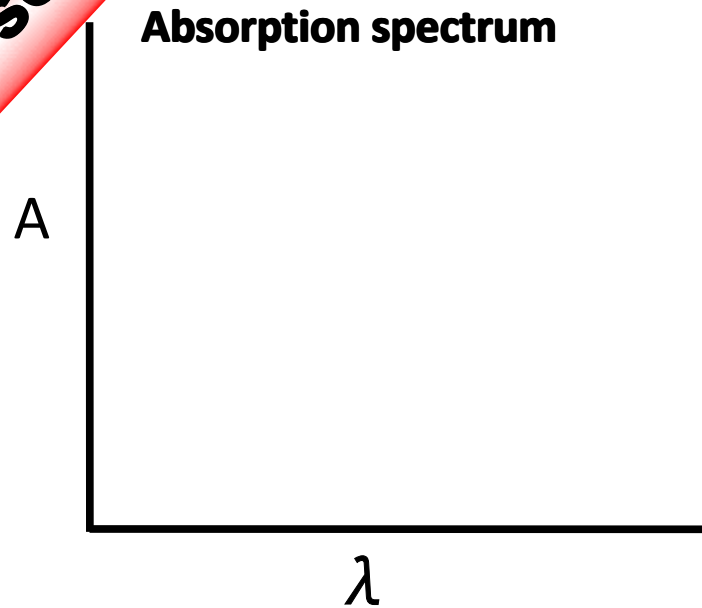
$E_{\text{electronic}}$ →



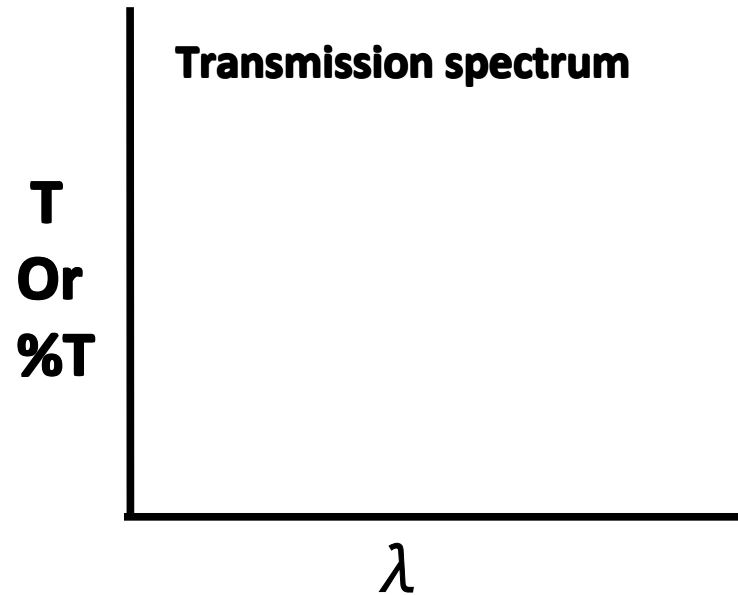
Excited state atoms obtained by



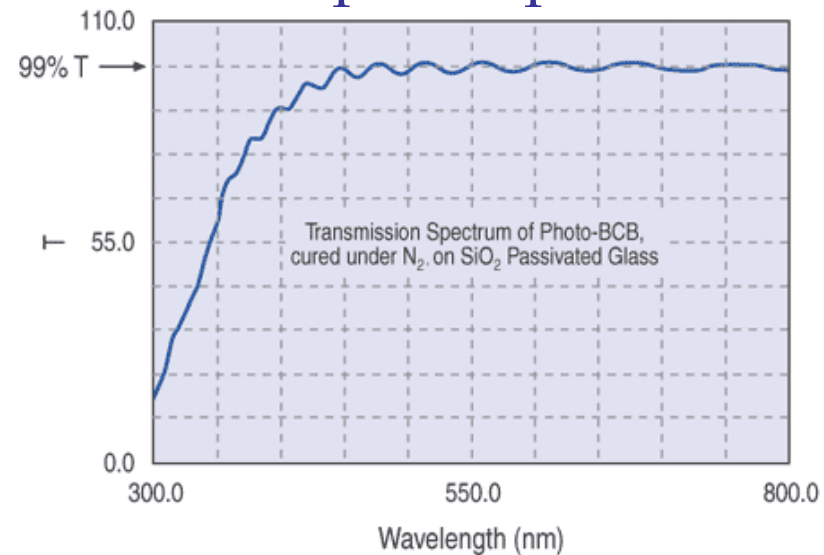
Absorption



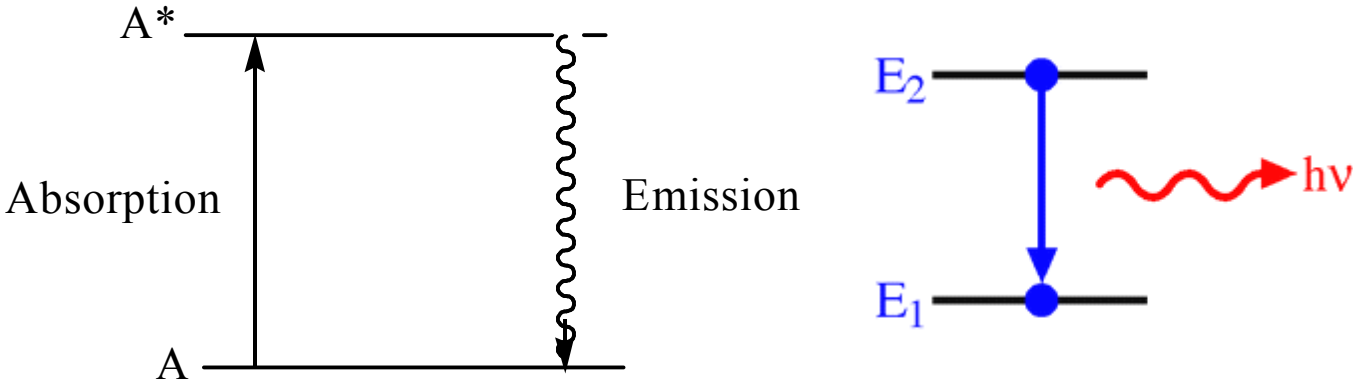
A plot of the amount of radiation absorbed by a sample versus the wavelength of the radiation



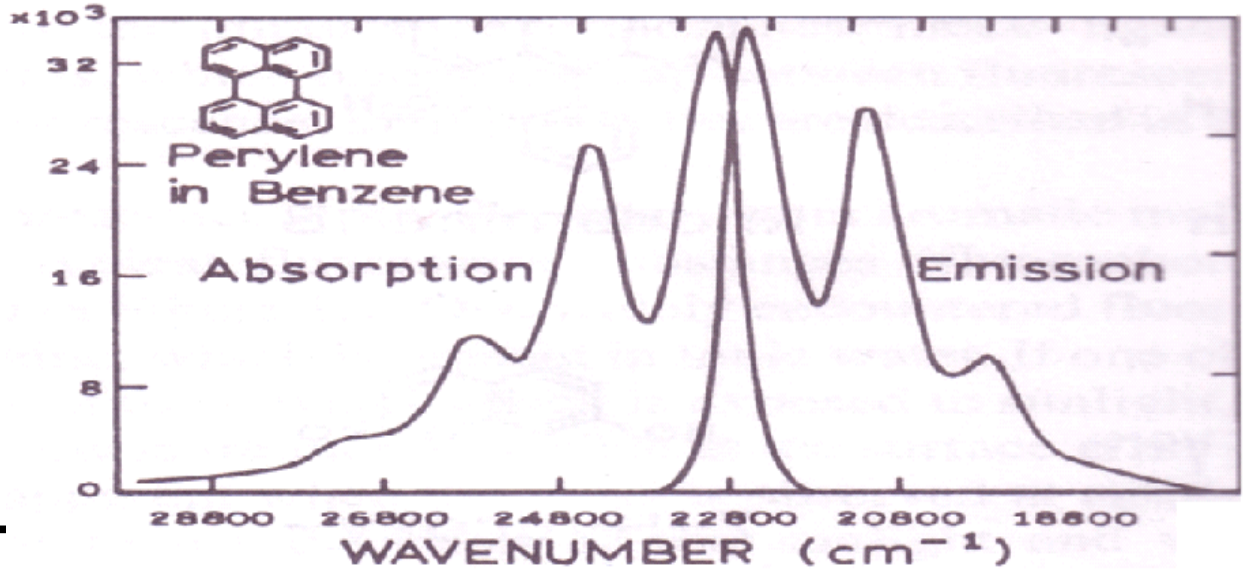
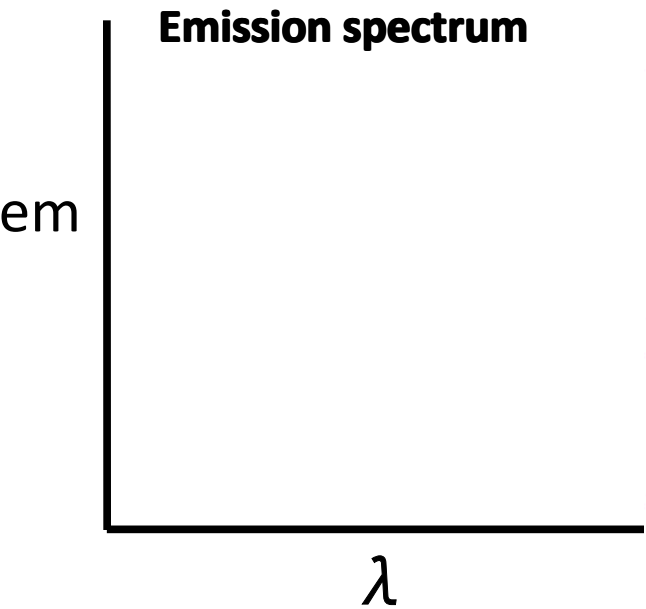
a continuous spectrum except that it is upside down relative to the absorption spectrum.



Emission



Excited atoms generated by the use of **thermal or electrical energy** return to the ground state because the ground state is the lowest energy state



Emission

advantage of emission spectra

- give quantitative results
- can be used for the **identification of elements** based on the peak wavelength which is **unique for each element**.

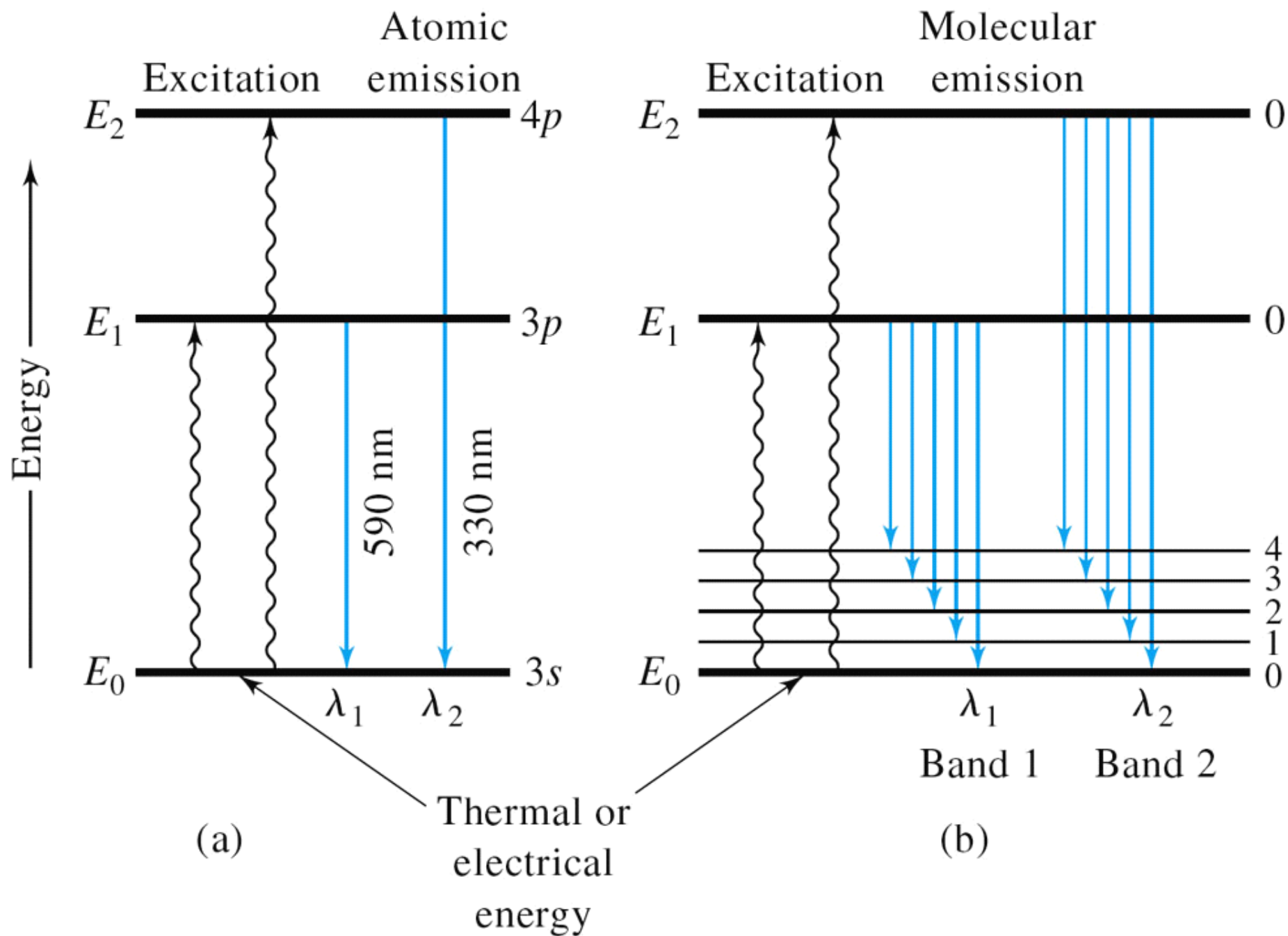
Atomic and Molecular Spectroscopy

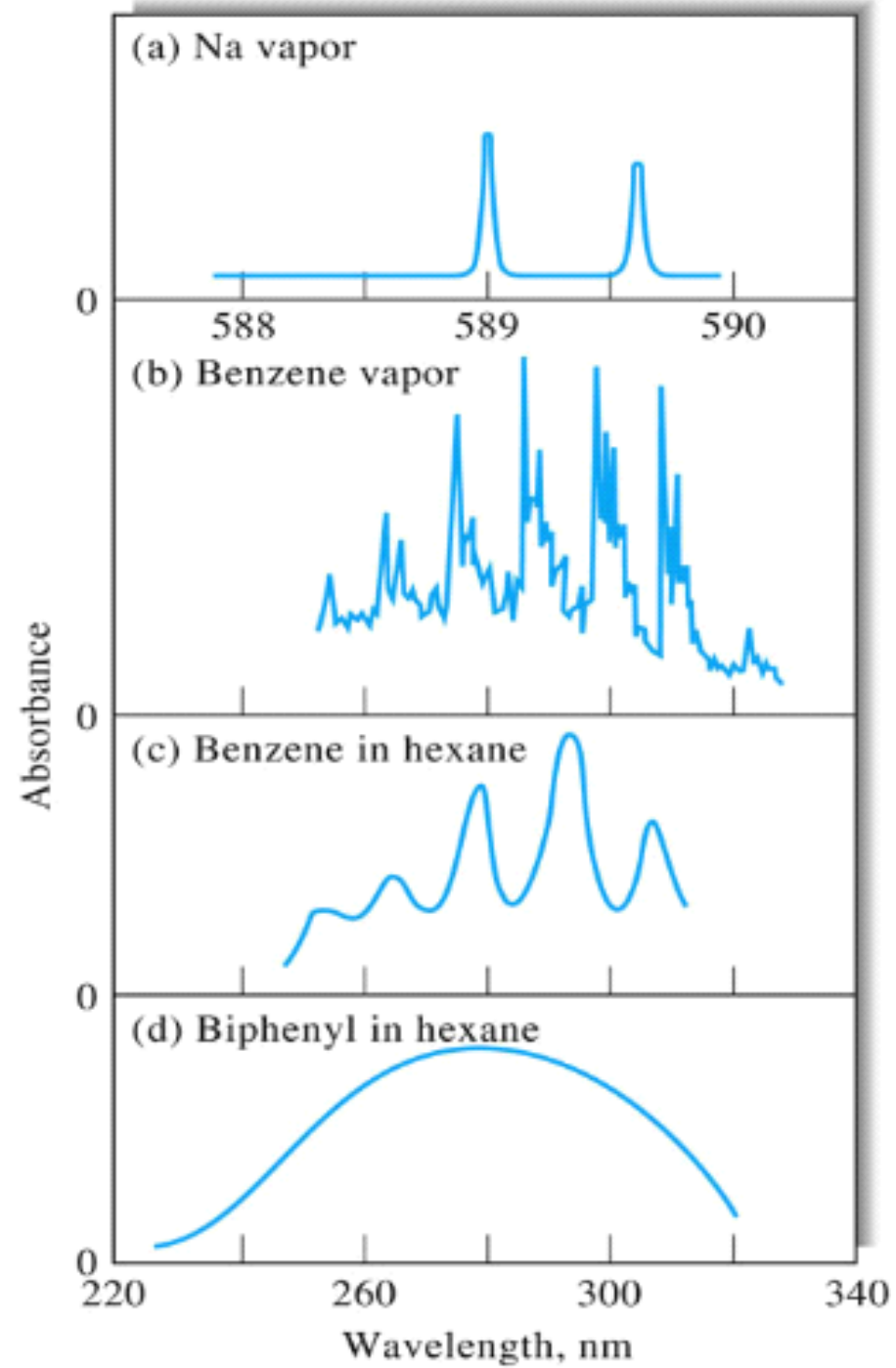
atomic spectroscopy

- Measurement of **atoms** in the UV-visible region

UV-visible spectrophotometry

- Measurement of **molecules** in the UV-visible region





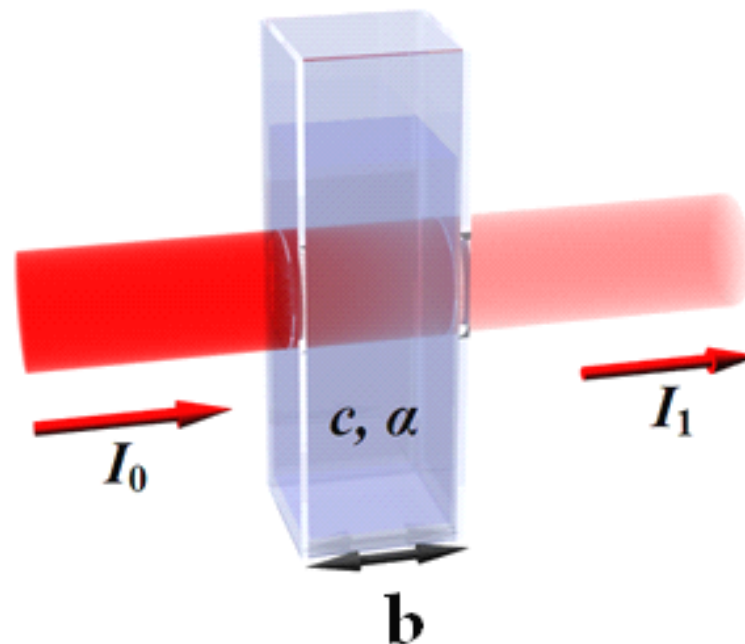
	Atomic spectroscopy	UV-VIS spectrophotometry
1	Atoms must be in free gas phase in the ground state.	Samples are usually in solution
2	Absorption spectrum formed is a line spectrum .	Absorption spectrum formed is a continuous spectrum .
3	Sources of radiation are spectral line sources .	Sources of radiation emit all the wavelengths in the given region
4	Highly limited , only elements (metals) can be analysed.	Large numbers of molecules and complex ions can be analysed.
5	Wavelengths of measurements are known and can be simply looked up in books.	Need to sometimes scan the absorption spectral in order to obtain wavelength for maximum absorption.

How compounds absorb ultraviolet (UV) or visible light?

We can describe how the light is absorbed by either the transmittance or the absorbance:

$$T = I / I_0 \quad \%T = T \times 100$$

$$A = -\log T = -\log I / I_0$$



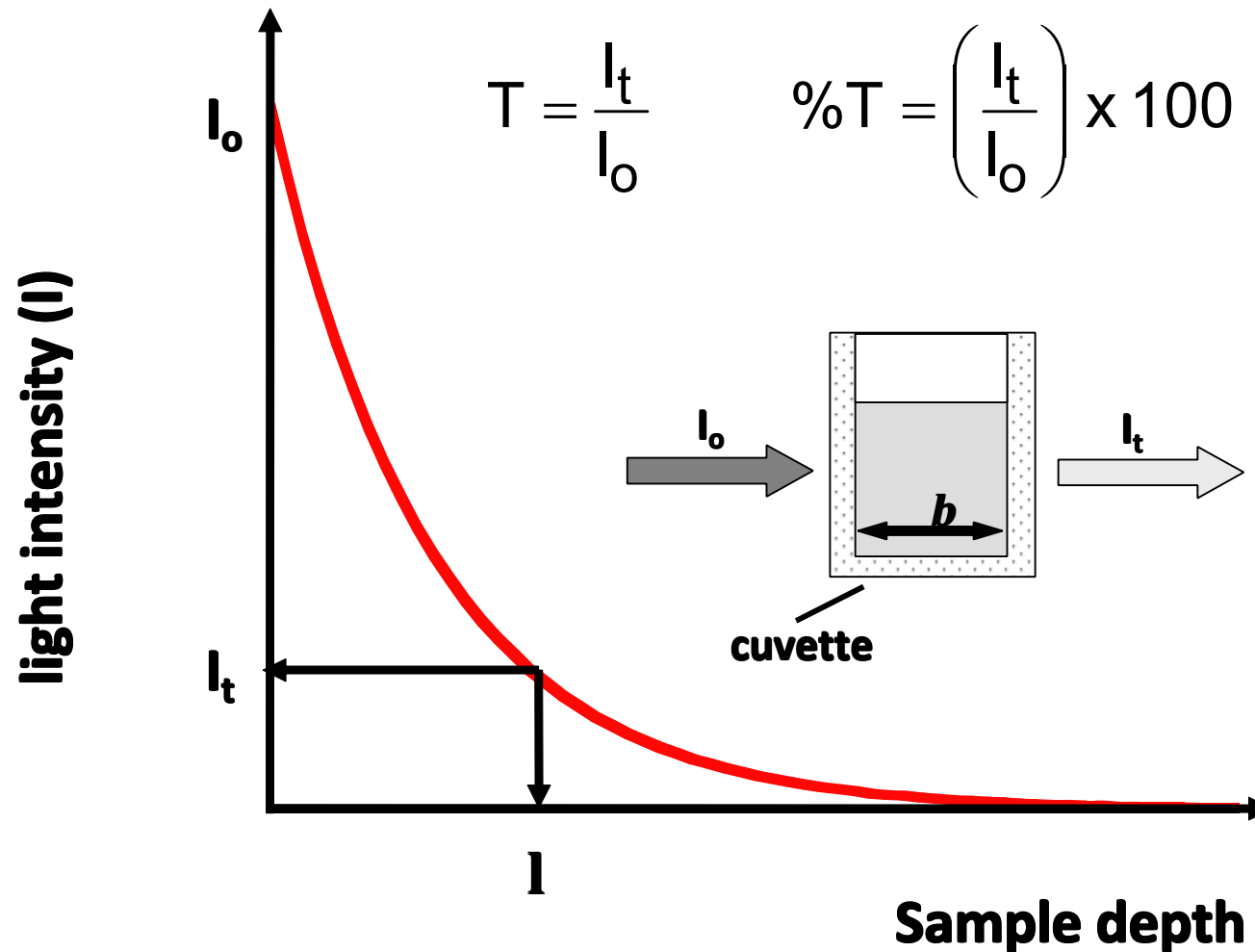
I_0 is the incident radiant power or intensity

I is the radiant **intensity that remains**

b is the path length

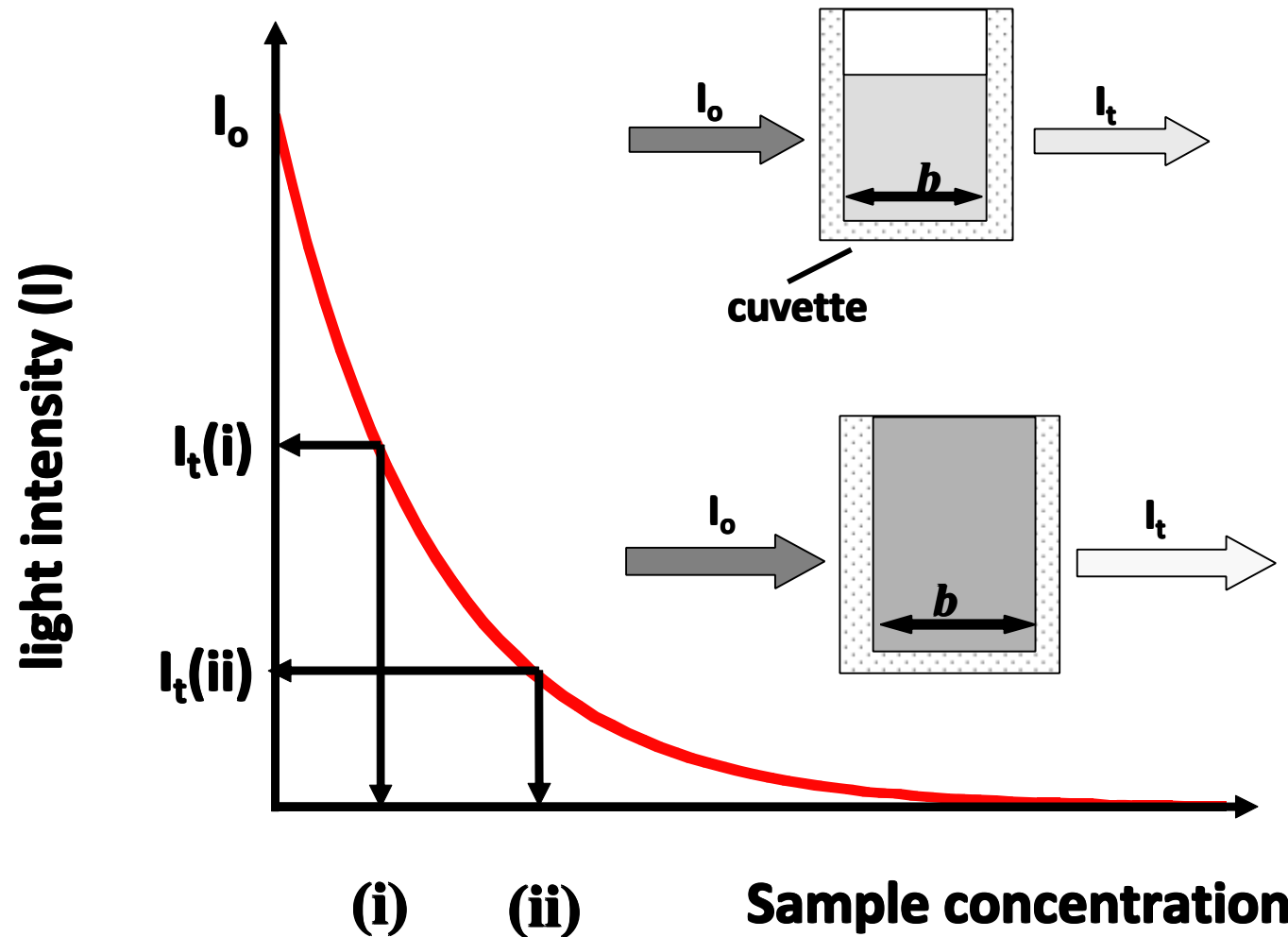
THE BEER-LAMBERT LAW

- For a light absorbing medium, the **light intensity falls exponentially** with **sample depth**.
- T = transmittance.



THE BEER-LAMBERT LAW

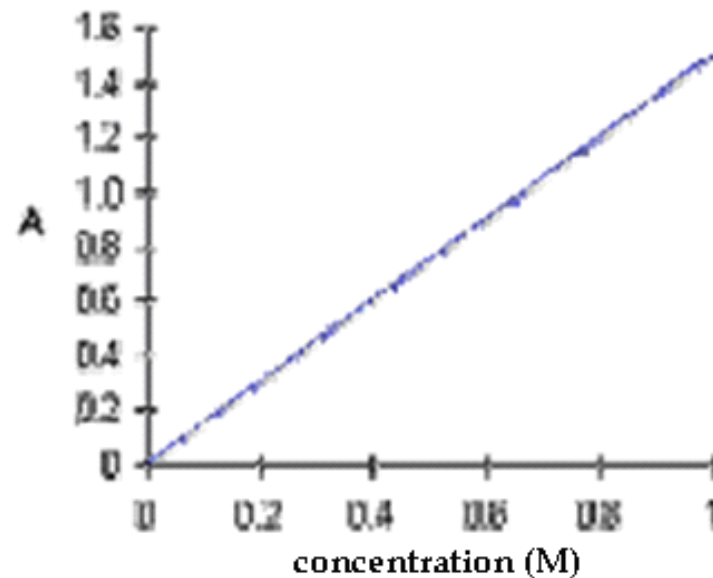
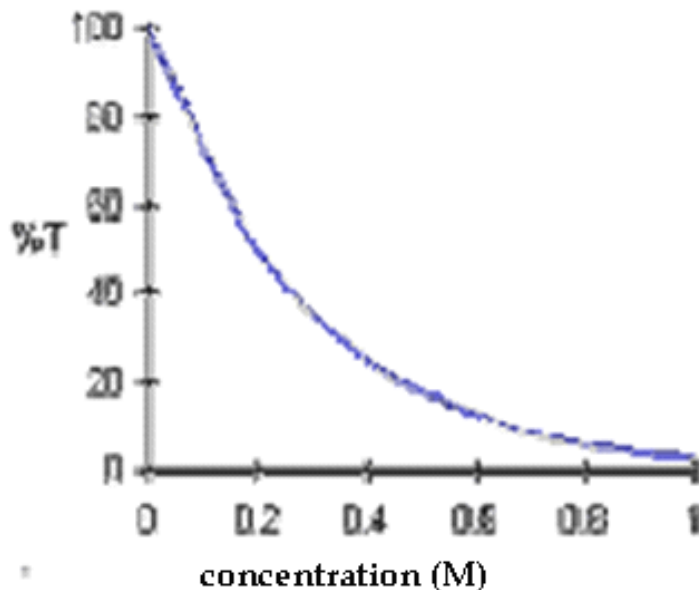
- For a light absorbing medium, the light intensity falls exponentially with increasing sample concentration.



THE BEER-LAMBERT LAW

$$A = \varepsilon_{\lambda} cb \quad A = -\log_{10} T$$

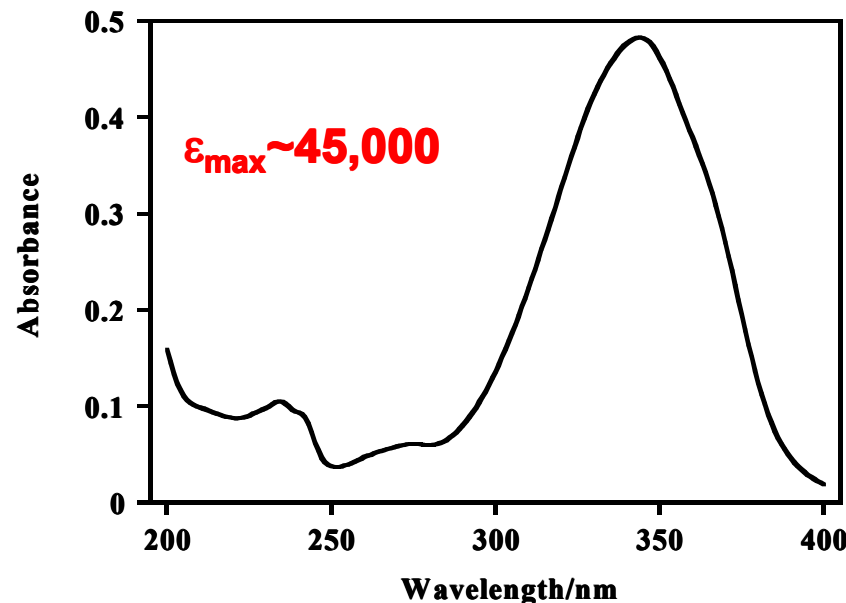
- The negative logarithm of T is called the absorbance (A) and this is directly proportional to sample depth (called pathlength, b) and sample concentration (c).
- The equation is called the **Beer-Lambert law**.



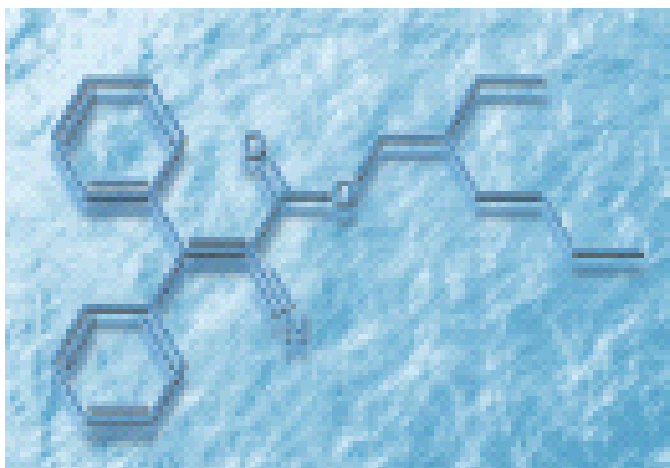
The Beer-Lambert law is **more useful** because the relationship between absorbance and concentration is **linear**.

THE BEER-LAMBERT LAW

- A plot of A versus c is called a Beer-Lambert plot.
- ϵ_λ is called the molar absorptivity $A = \epsilon_\lambda cb$ and has units of $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$
- b is the path length of the cuvette in which the sample is contained (in cm)
- In the UV-VIS region, the maximum value of ϵ_λ observed is $\sim 10^5 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$, which is found in many natural pigments (e.g. chlorophyll) and in sunscreens.

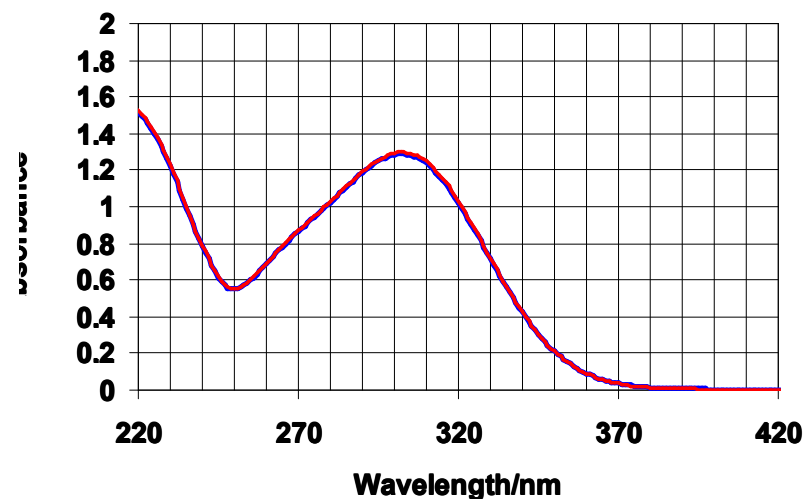


THE BEER-LAMBERT LAW



Parsol[®] 340

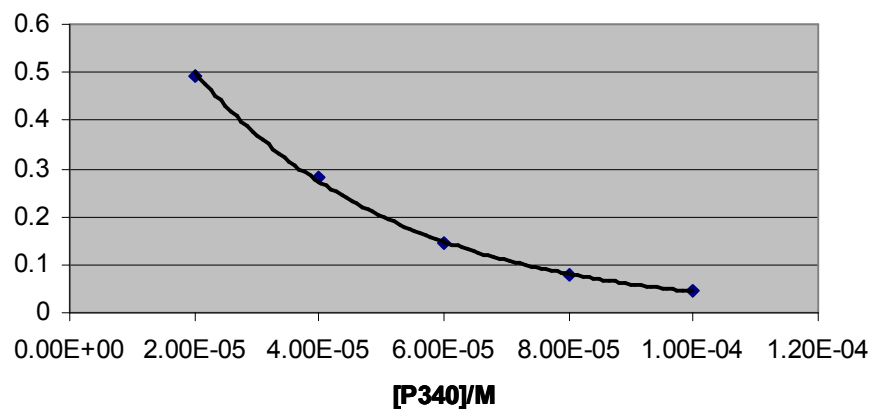
Parsol 340 (10^{-4} M in MEOH)



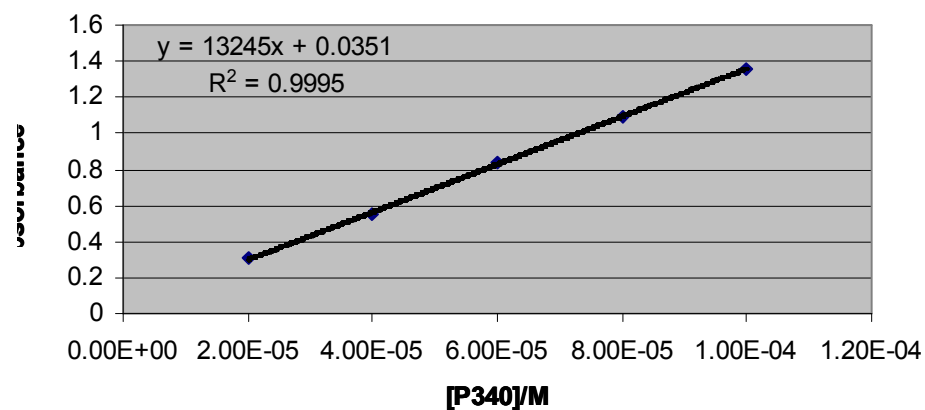
T vs [P340]

$$y = 0.9224e^{-30498x}$$

$$R^2 = 0.9995$$



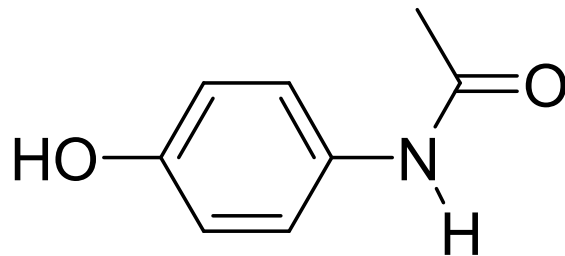
Beer-Lambert plot for Parsol 340 in ethanol



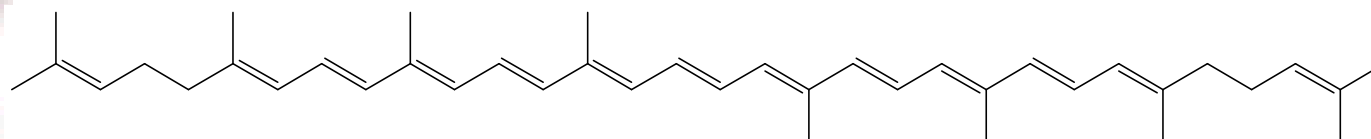
$$A = \varepsilon_{\lambda} cl$$

$$A = -\log_{10} T$$

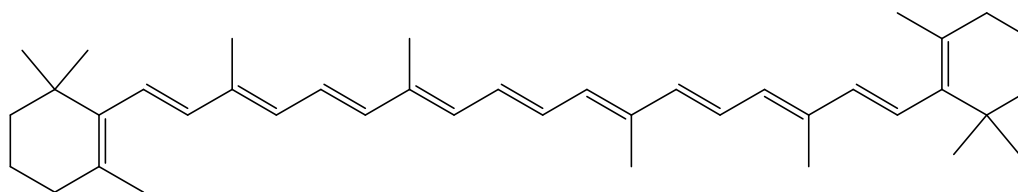
HIGHLY 'CONJUGATED' MOLECULES ARE COLOURED



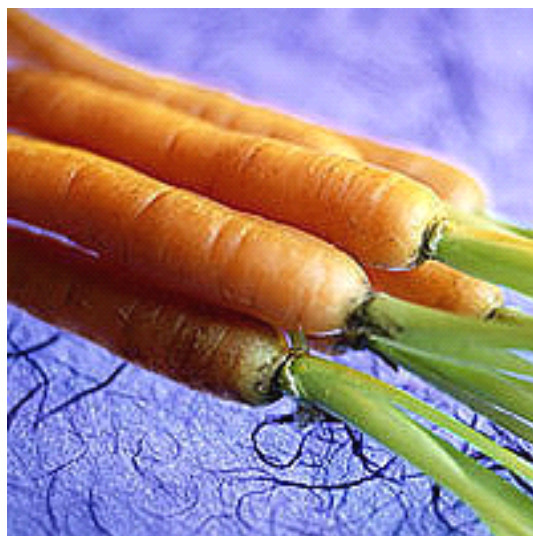
PARACETAMOL



LYCOPENE



β-CAROTENE



Limitations of the Beer Lambert Law

- 1. At $\uparrow c$, the linear relationship between A and c does not hold good.**
- 2. Absorbitivity depends on the refractive index of the medium which is a function of concentration.**

Non-linearity of Beer-Lambert's law

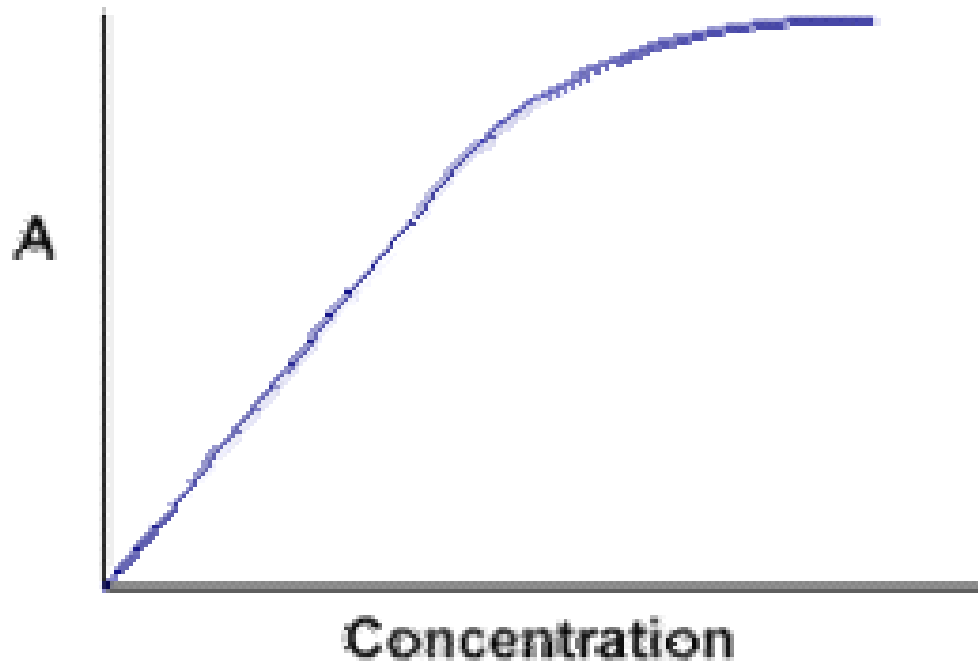
Beer's law is linear in most cases, except:

- at high concentrations
- if there is scattering of light due to particulates in the sample
- if the sample fluoresces or phosphoresces
- if the radiation is not monochromatic
- if there is stray light

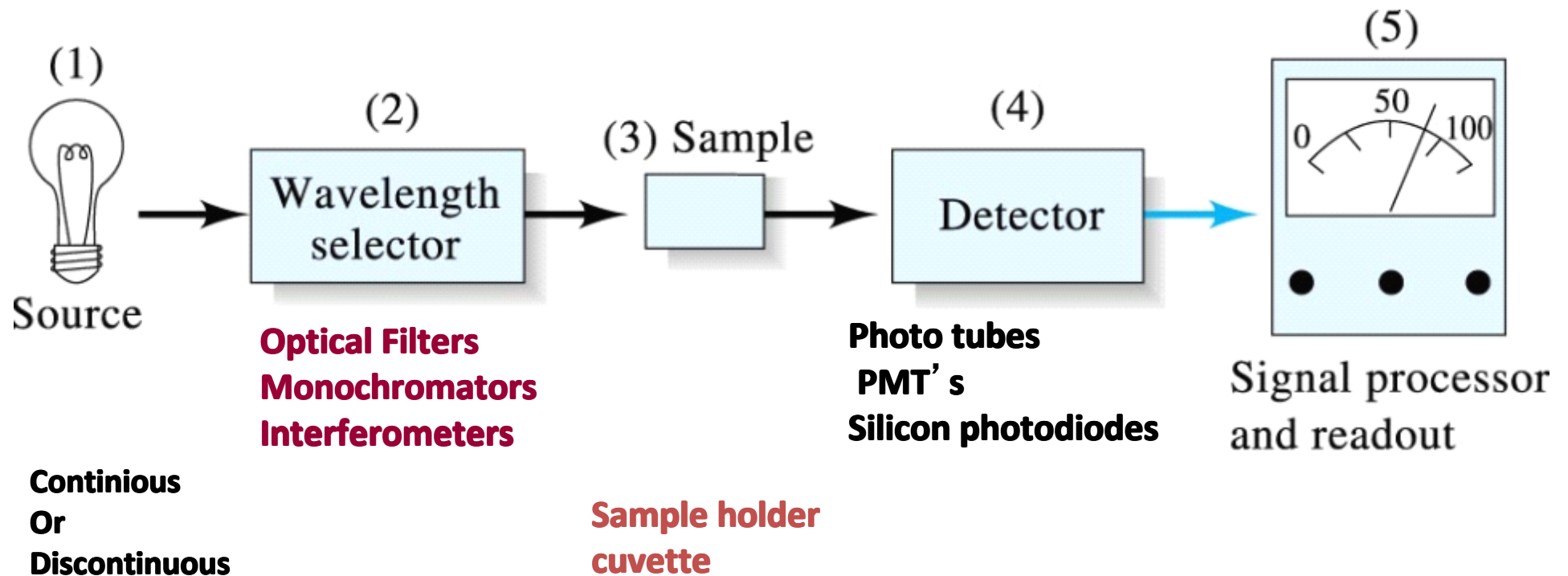
Concentration Effects

High concentration results in non-linearity because:

- Strong electrostatic interactions between molecules
- Might cause changes in refractive index
- In a system in chemical equilibrium, equilibrium may shift at high concentrations



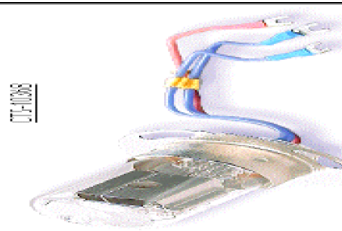
Instrumentation



Source

Continuous sources

Produce spectra over broad band



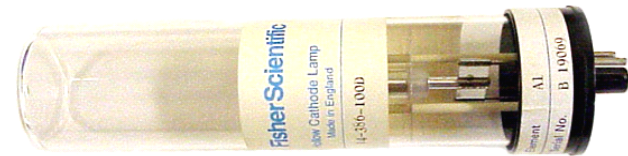
Deuterium Arc Lamp



Tungsten Lamp

Discontinuous (discrete) sources

Produce only specific wavelengths



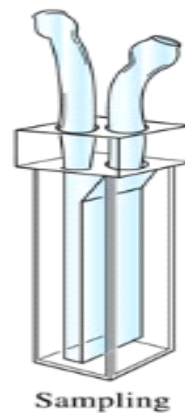
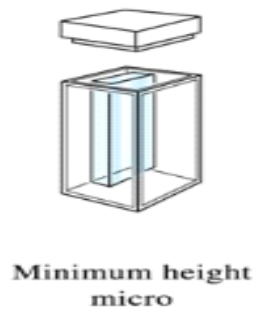
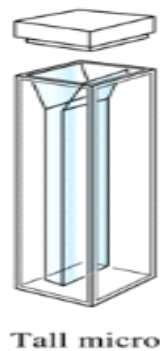
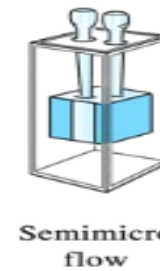
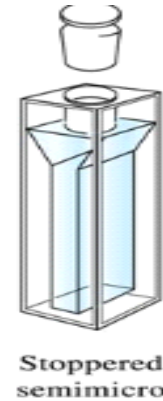
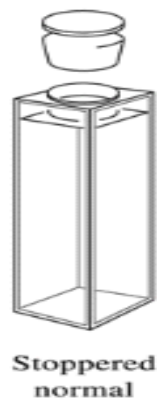
A Hollow cathode lamp

Sample Holder

Receptacle for Sample.

Material

- Quartz, Fused Silica (Using over 190nm)
- Glass (Using Over Visible Region)



CLASS PROBLEMS

1. In a UV-VIS study of commercial alcoholic drinks, it was found that an alcopop sample had an absorbance of 0.21 at its λ_{max} (630 nm) in a 1 cm cuvette. Given that the molar absorption coefficient of the dye is $50,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, what is the dye concentration and what colour is the dye likely to be?

$$A = \epsilon_{\lambda} cb$$

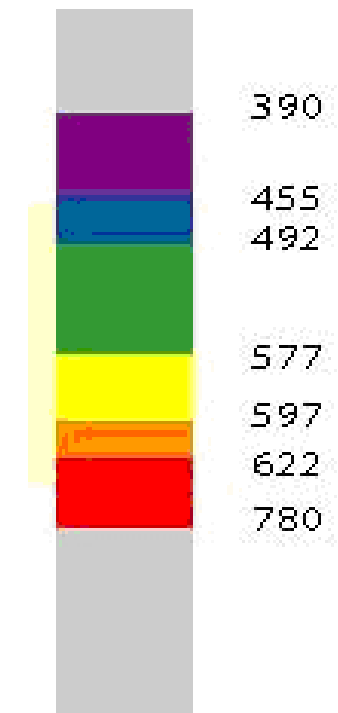
$$A = 0.21 \quad b = 1 \text{ cm} \quad \epsilon_{\lambda} = 50,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

$$c = \frac{A}{\epsilon b}$$

$$c = \frac{0.21}{50,000 \text{ dm}^3 \text{ mol}^{-1} \cancel{\text{cm}^{-1}} \times 1 \cancel{\text{cm}}}$$

$$c = 4.2 \times 10^{-6} \text{ mol dm}^{-3}$$

Wavelength, nm



●_{max} (630 nm) is **Red**

Color	Wavelength (nm)	Frequency (THz)
Red	780 - 622	384 - 482
Orange	622 - 597	482 - 503
Yellow	597 - 577	503 - 520
Green	577 - 492	520 - 610
Blue	492 - 455	610 - 659
Violet	455 - 390	659 - 769

Quantitative Analysis

- **A < 1**
 - If $A > 1$:
 - Dilute the sample
 - Use a narrower cuvette
 - (cuvettes are usually 1 mm, 1 cm or 10 cm)
- Plot the data (A v C) to produce a calibration ‘curve’
- Obtain equation of straight line ($y=mx$) from line of ‘best fit’
- Use equation to calculate the concentration of the unknown(s)

Quantitative Analysis

Calibration curve showing absorbance as a function of metal concentration

