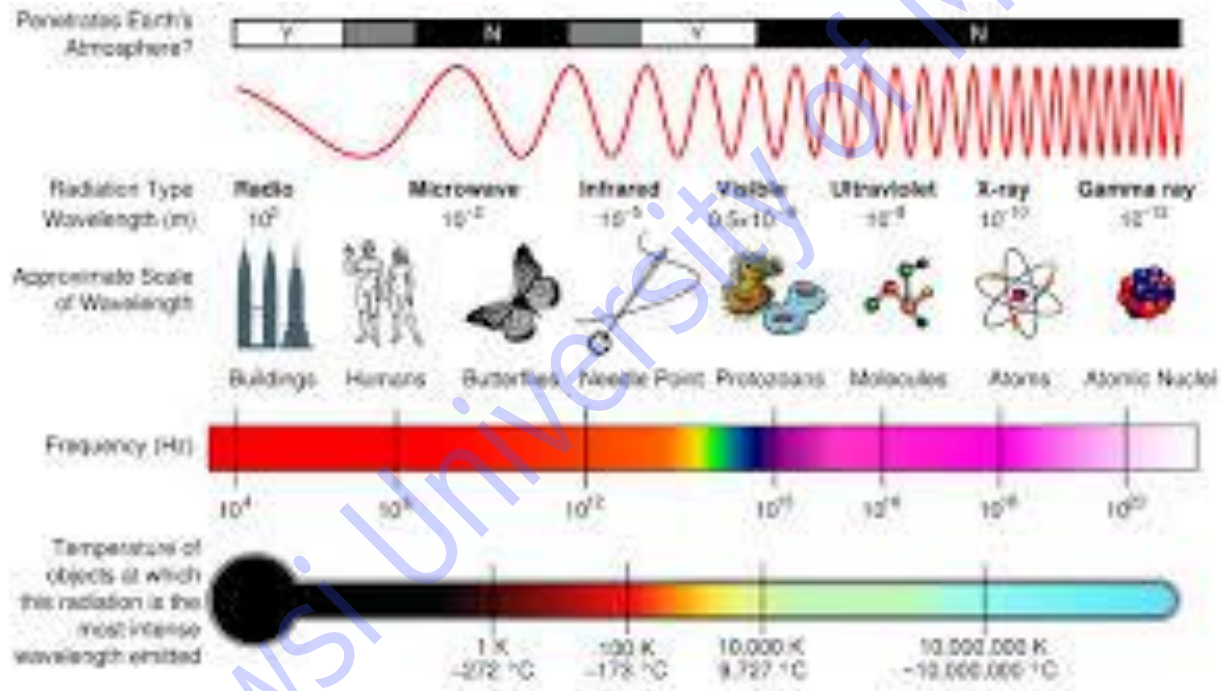


# Spectroscopy in Inorganic Chemistry

Ferdowsi University of Mashhad

# General Introduction of spectroscopy

- **Electromagnetic radiation**

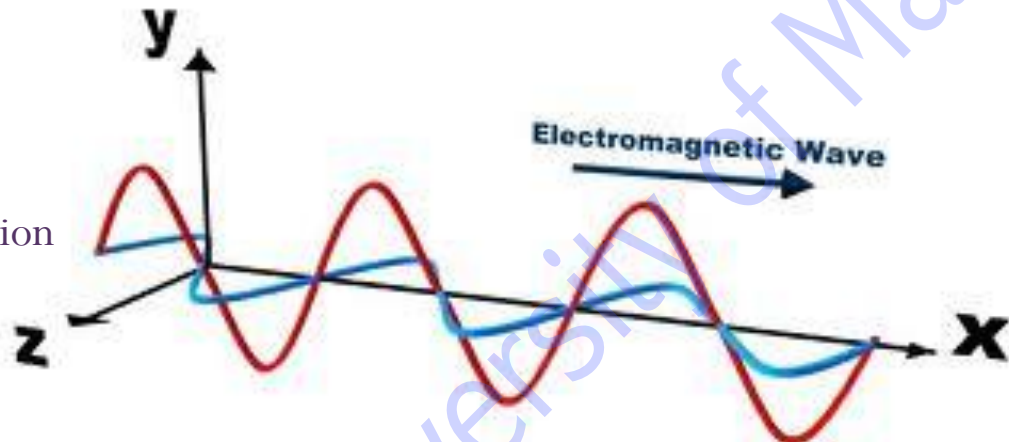


wavelength consists of: radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays.

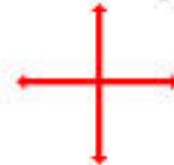
# General Introduction of spectroscopy

- **Electromagnetic radiation**

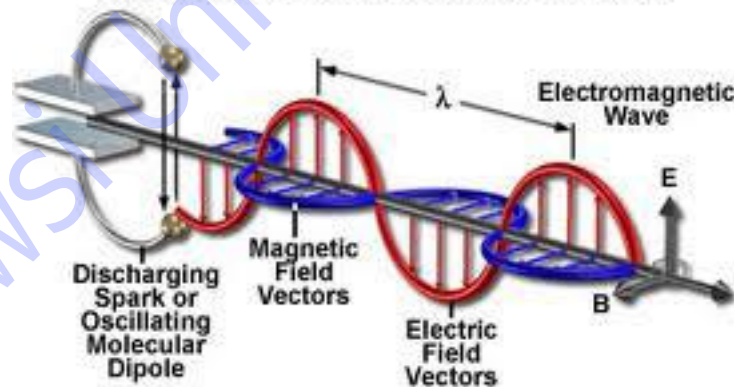
Plane-polarized radiation



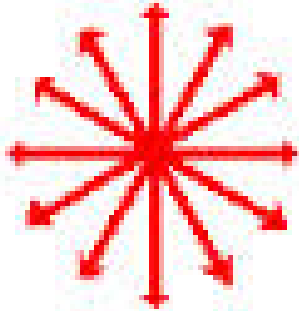
... In general, a light wave can be thought of as vibrating in a vertical and in a horizontal plane.



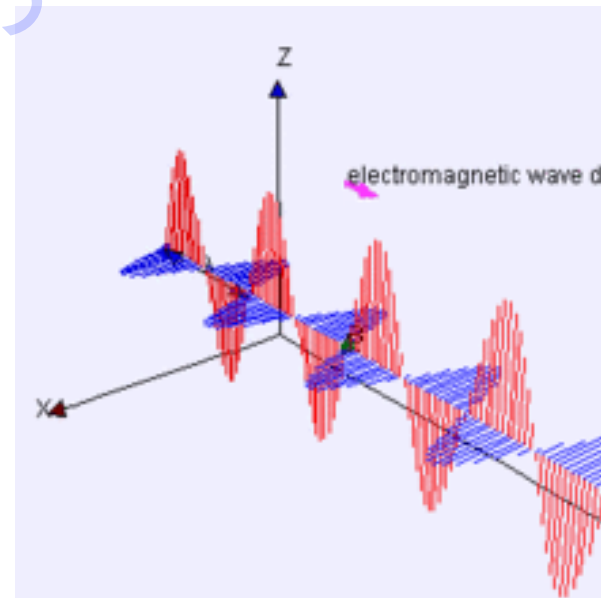
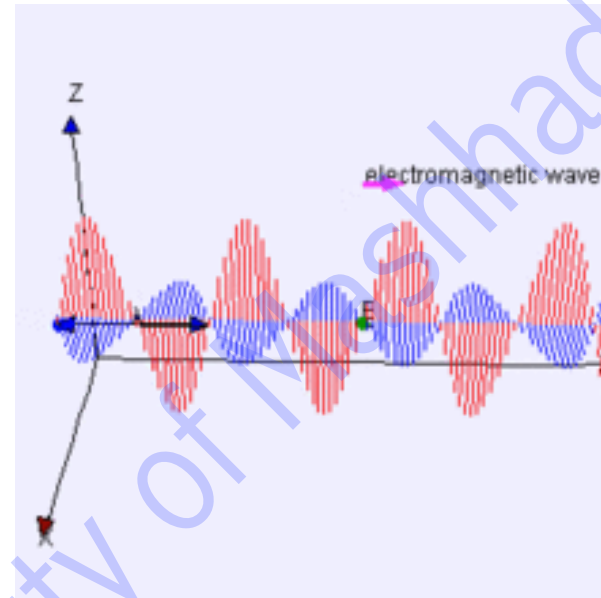
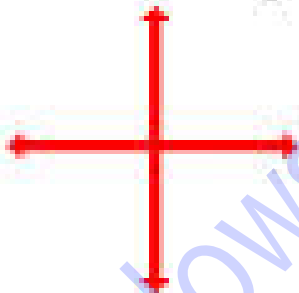
Propagation of an Electromagnetic Wave



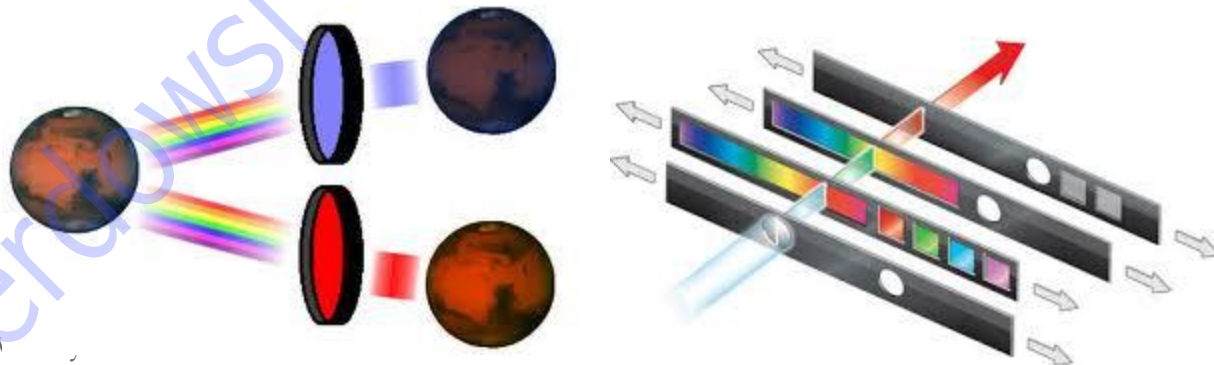
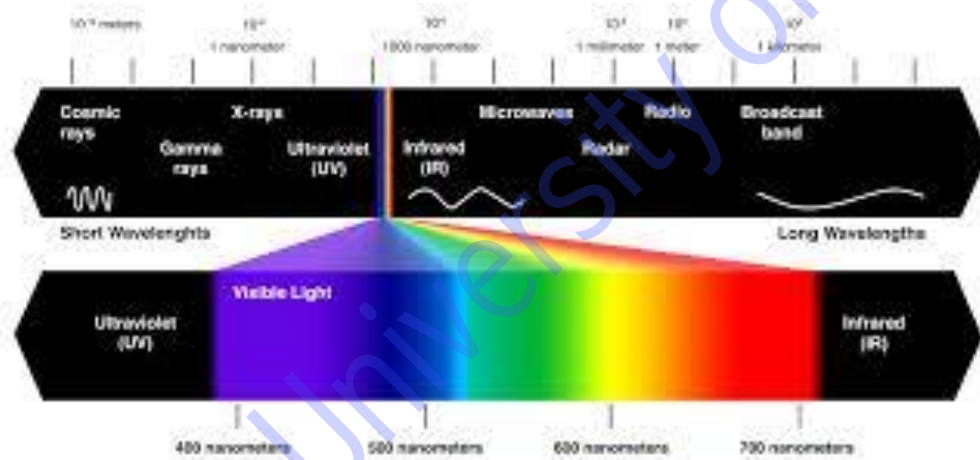
A light wave is known to vibrate in a multitude of directions ...



... In general, a light wave can be thought of as vibrating in a vertical and in a horizontal plane.



- Polychromatic radiation
- Monochromatic beam



# photon

$$\lambda = \frac{h}{mv}$$

## *The Wave Behavior of Matter*

- DeBroglie proposed that there is a wave/particle duality.
- Knowing that light has a particle nature, it seems reasonable to assume that matter has a wave nature.
- DeBroglie proposed the following equation to describe the relationship:

The momentum,  $mv$ , is a particle property, where as  $\lambda$  is a wave property.



**L. de Broglie**  
**(1892-1987)**

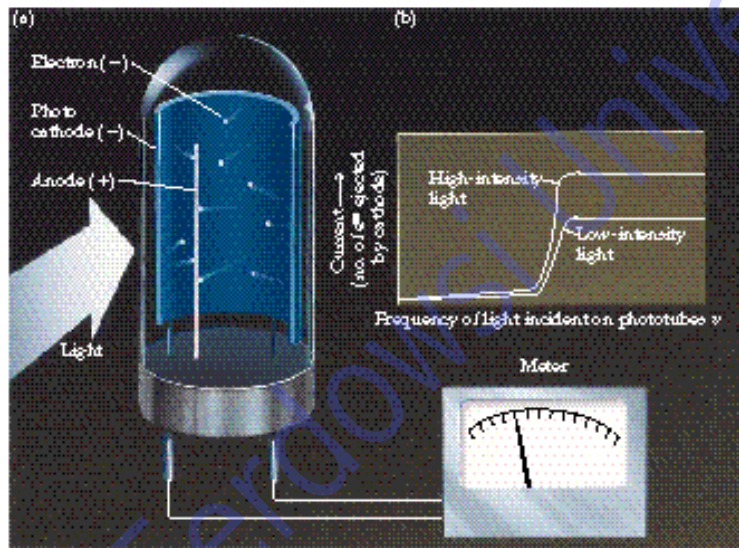
# Quantum

## Photoelectric Effect

Hertz UV 1887

Albert Einstein (1879-1955)

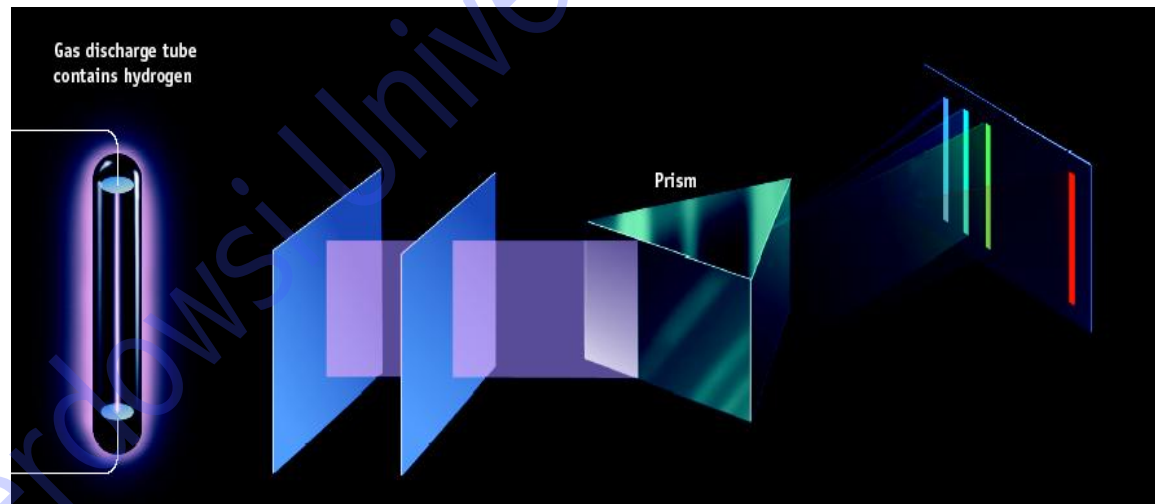
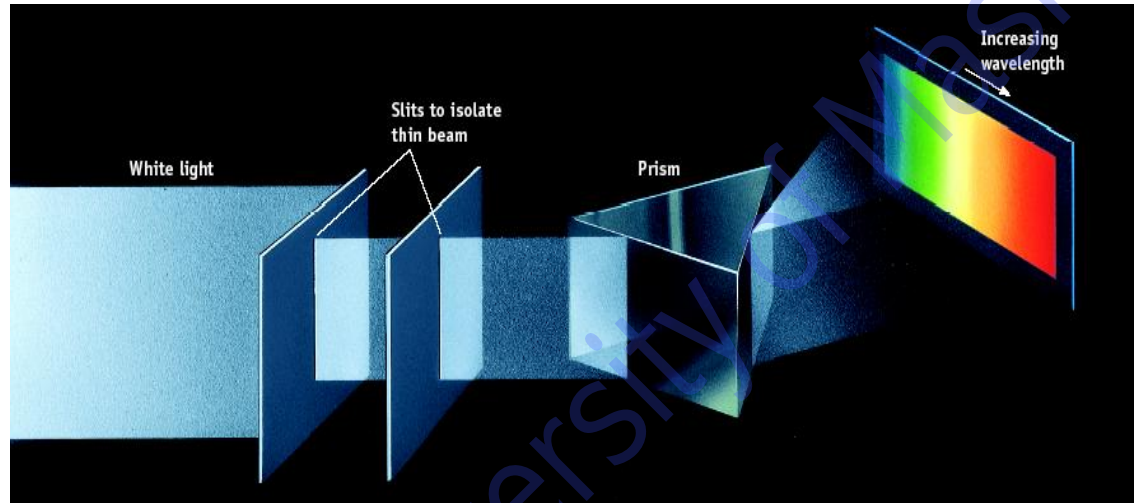
Photoelectric effect demonstrates the particle nature of light.



No  $e^-$  observed until light of a certain minimum  $E$  is used.

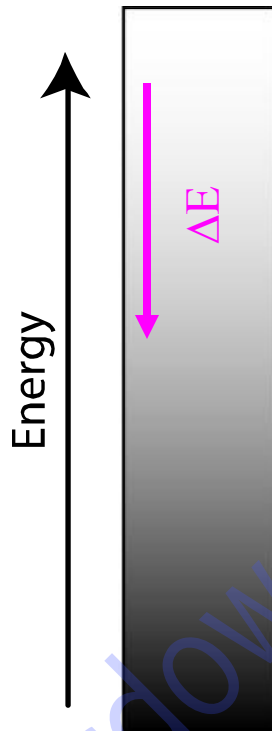
Number of  $e^-$  ejected does NOT depend on frequency, rather it depends on light intensity.

# atomic emission spectrum

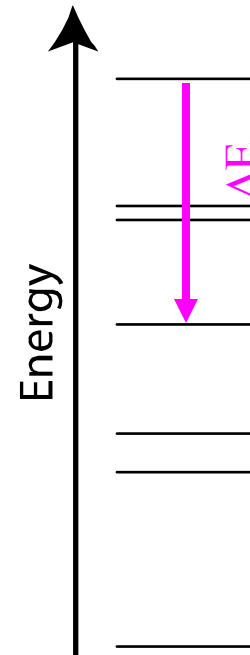




## “Continuous” spectrum



Any  $\Delta E$  is possible



$$\Delta E = \frac{hc}{\lambda}$$

h  $6.623 \times 10^{-27}$  erg s/ molecule

# Energy corresponding to various kinds of radiation

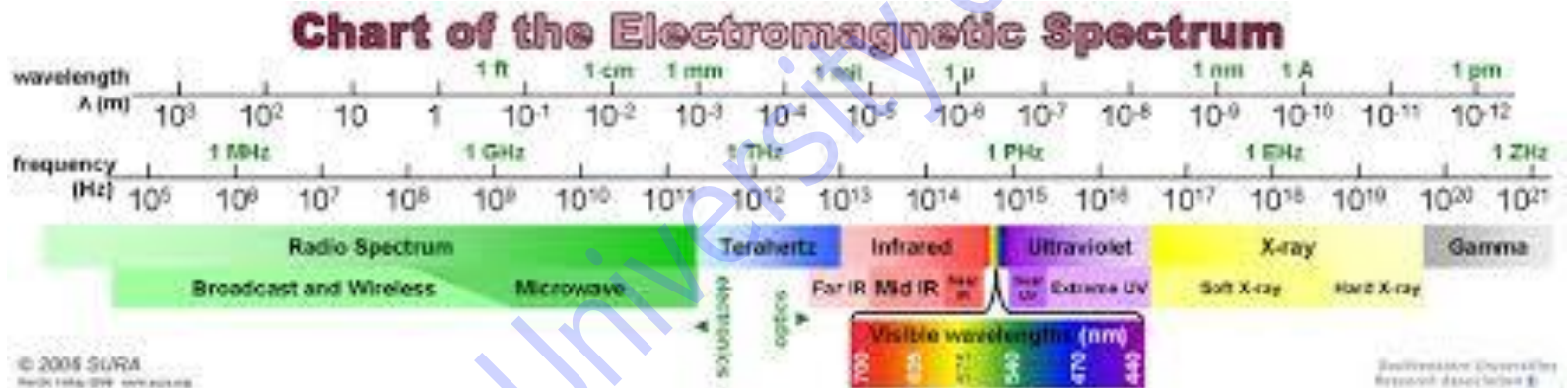
$$s^{-1} \quad \nu = \frac{C \text{ Cm/s}}{\lambda \text{ cm}}$$

$$cm^{-1} \quad \bar{\nu} = \frac{1}{\lambda \text{ cm}}$$

$$\Delta E = \frac{hC}{\lambda} = h\nu = hC\bar{\nu}$$

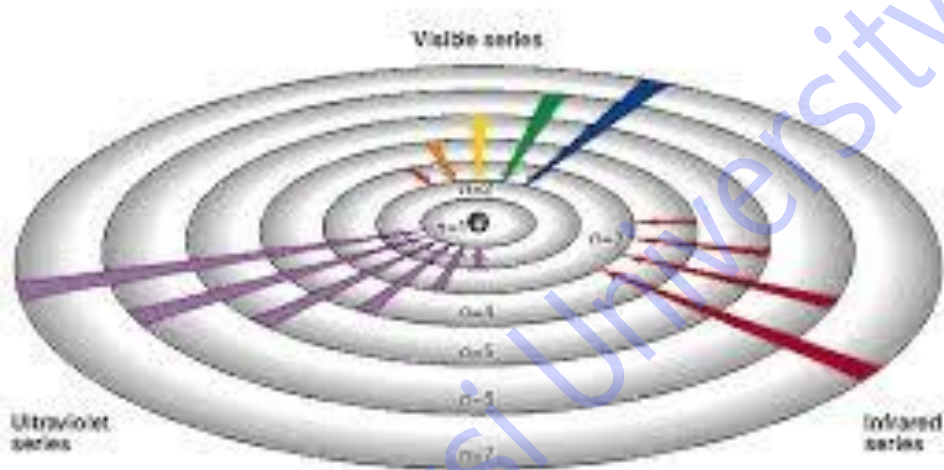
unit

Self study



# Atomic & Molecular Transition

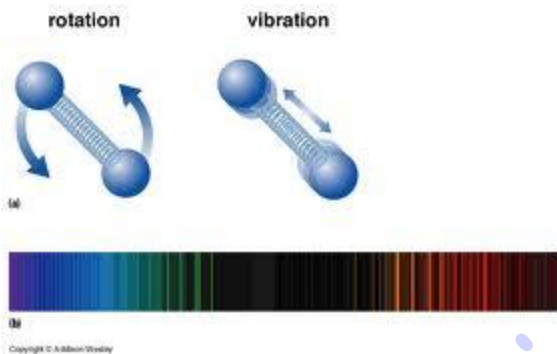
- **atomic transition**, quantum jump, or quantum leap.



# Atomic & Molecular Transition

- Molecular transition

electronic > vibration > rotation



## Molecular Energy Levels

Different electronic states (electronic arrangements)

*i.e., typically  $\Delta E_{el} \gg \Delta E_{vib} \gg \Delta E_{rot}$*

$\Delta E \approx 2 \times 10^4 - 10^5 \text{ cm}^{-1}$

Transitions at  $\lambda \approx$

Electronic

500 – 100 nm  
Vis – UV

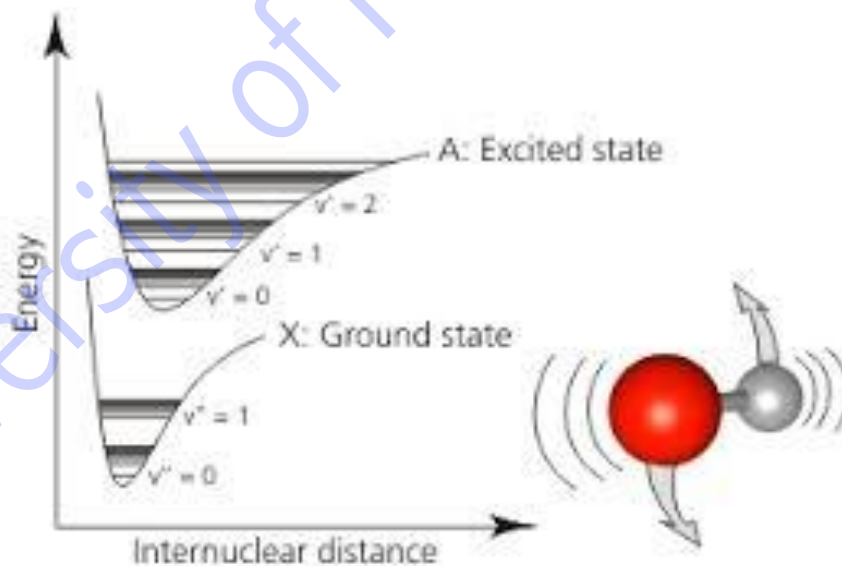
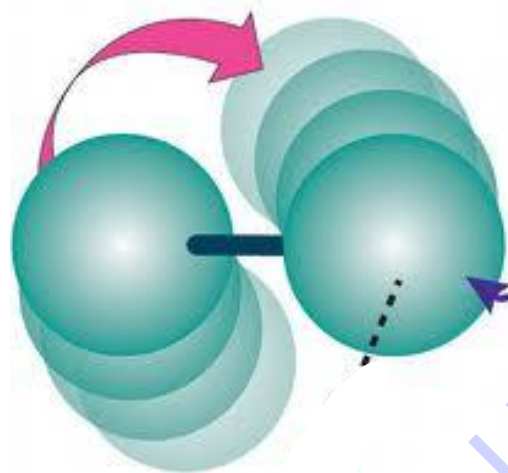
Vibrational

$10^2 - 5 \times 10^3 \text{ cm}^{-1}$   
100  $\mu\text{m}$  – 2  $\mu\text{m}$   
infrared

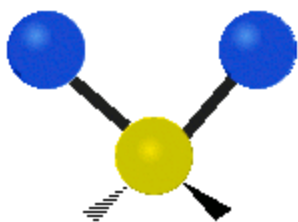
Rotational

3 – 300 GHz  
(0.1 – 10  $\text{cm}^{-1}$ )  
10 cm – 1 mm  
microwave

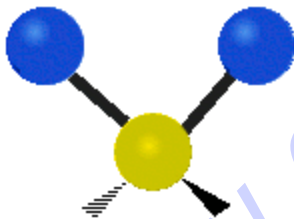
# Rotational Transition



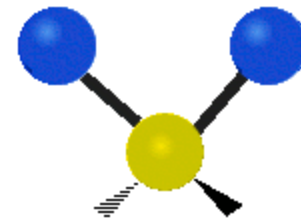
# Vibrational Transition



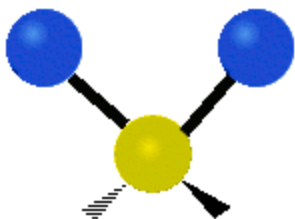
Asymmetrical\_stretching



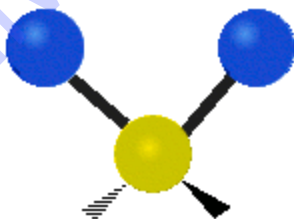
Rocking



Scissoring



Symmetrical\_stretching



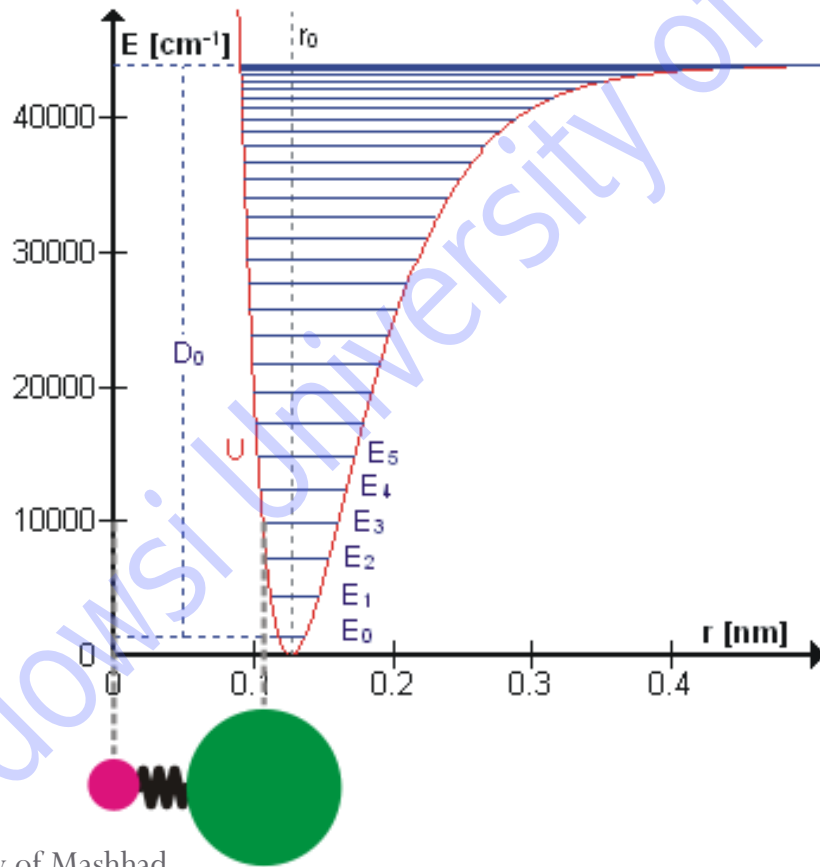
Twisting



Wagging



- $3N-6$  mode for non linear molecule

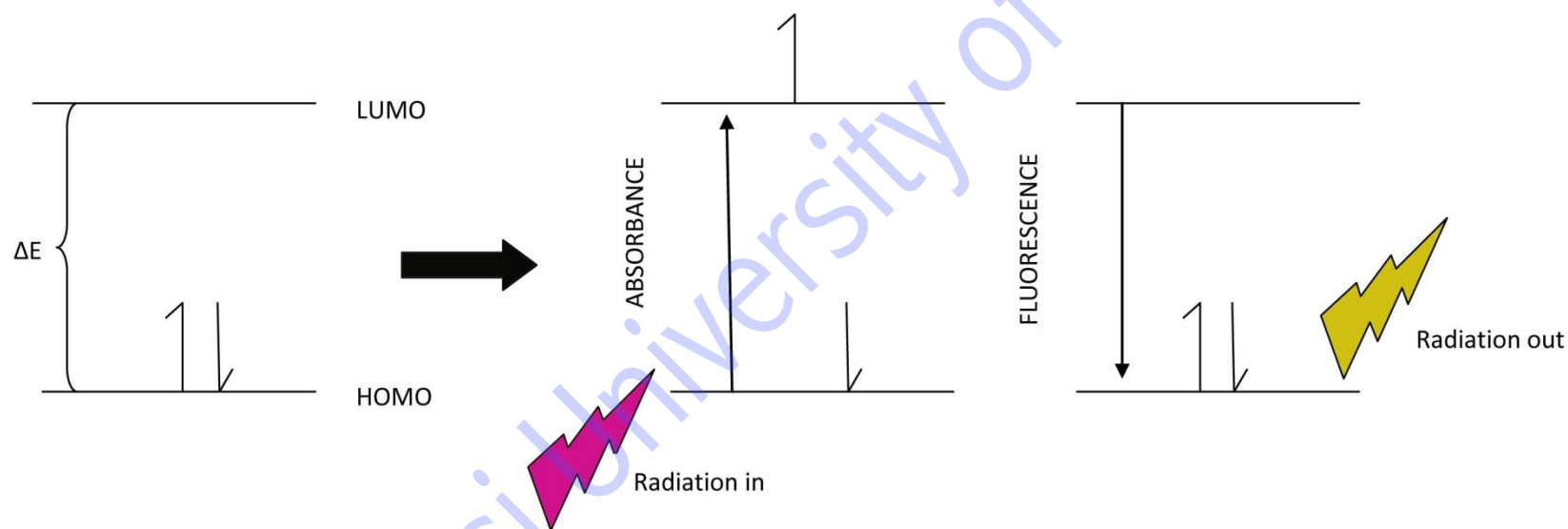


Direction  
Frequency  
Amplitude

# Electronic Transition

- Electronic Spectroscopy relies on the quantized nature of energy states. Given enough energy, an electron can be excited from its initial ground state or initial excited state (hot band) and briefly exist in a higher energy excited state. Electronic transitions involve exciting an electron from one principle quantum state to another. Without incentive, an electron will not transition to a higher level. Only by absorbing energy, can an electron be excited. Once it is in the excited state, it will relax back to it's original more energetically stable state, and in the process, release energy as photons.

# Electronic Transition



# Non-linear normal modes vibration

Total vibration state  $\psi_v = \prod_{n=1}^{3N-6} \psi_n$  Normal vibrational modes of  $\psi_n$

$n$  vibrational modes production

$$\psi_0 = \left(\frac{a_0}{\pi}\right)^{1/4} \exp\left[\left(-\frac{1}{2}\right)a_0 q^2\right]$$

$$\psi_1 = 2\left(\frac{a_1}{\pi}\right)^{1/4} q \exp\left[\left(-\frac{1}{2}\right)a_1 q^2\right]$$

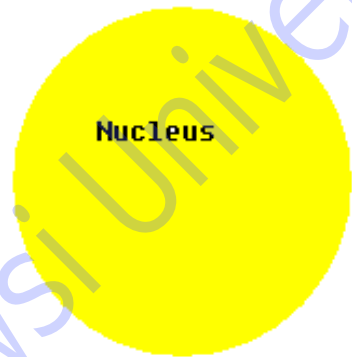
$$\psi_2 = 2\left(\frac{a_2}{\pi}\right)^{1/4} (2a_2 q^2 - 1) \exp\left[\left(-\frac{1}{2}\right)a_2 q^2\right]$$

# Born–Oppenheimer approximation

$$\Psi_{\text{molecule}} = \Psi_{\text{electron}} \times \Psi_{\text{nuclei}}$$

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{nuclear}}$$

Born-Oppenheimer Approximation



**Nucleus**

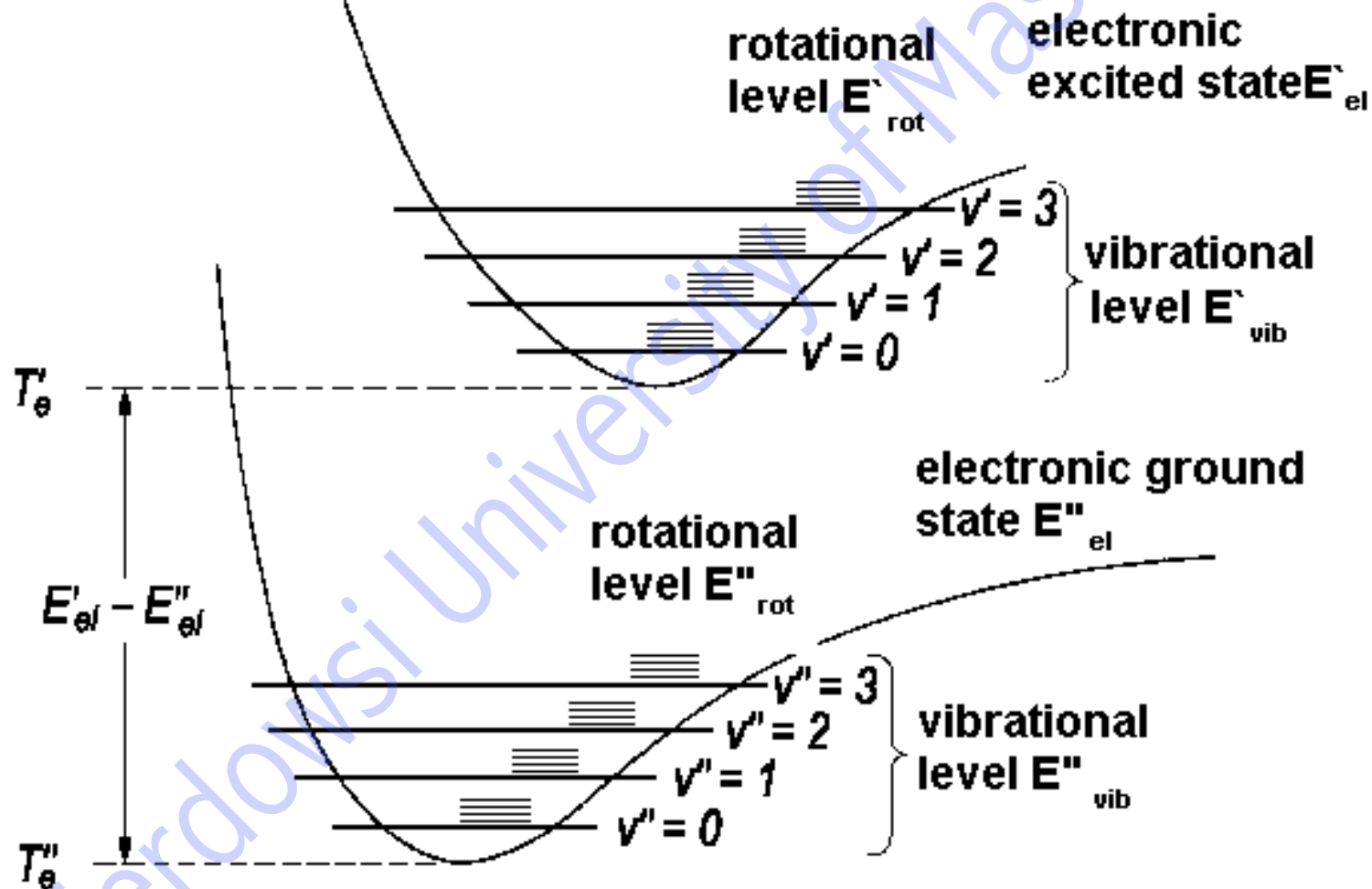
too heavy to move



**electron**

moves around

# Energy level for diatomic molecule



# Selection rules

- After resonance condition is met, the electromagnetic radiation must be able to do electrical work on the molecule
- For this to happen, transition in the molecule must be accompanied by a change in the electrical center of the molecule
- Selection rules address the requirements for transitions between states in molecules
- Selection rules are derived from the evaluation of the properties of the transition moment integral (beyond scope of this course)

# Selection Rule Terminology

- Transitions that are possible according to the rules are termed “allowed”
- Such transitions are correspondingly intense
- Transitions that are not possible are termed “forbidden” and are weak
- Transitions may be “allowed” by some rules and “forbidden” by others



## Intensities

$$\varepsilon = 0.87 \times 10^{20} P \bullet a$$

$P$  is the transition probability; ranges from 0 to 1

$a$  is the target area of the absorbing system (the chromophore)

chromophores are typically 10 Å long, so a transition of  $P = 1$  will have an  $\varepsilon$  of  $10^5$