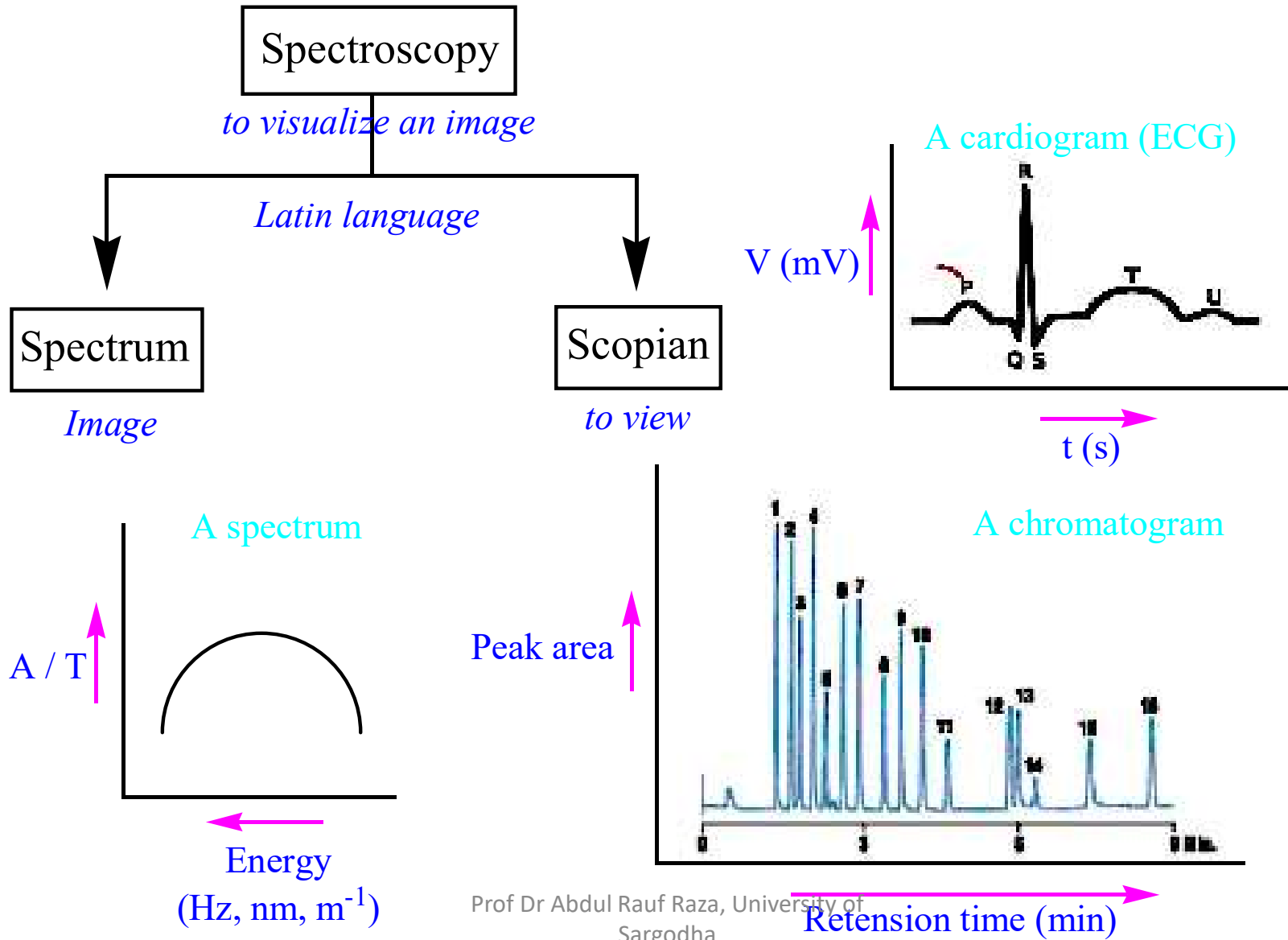


Spectroscopic Methods in Organic Chemistry  
CHEM-6124, Organic Chemistry (Minor)

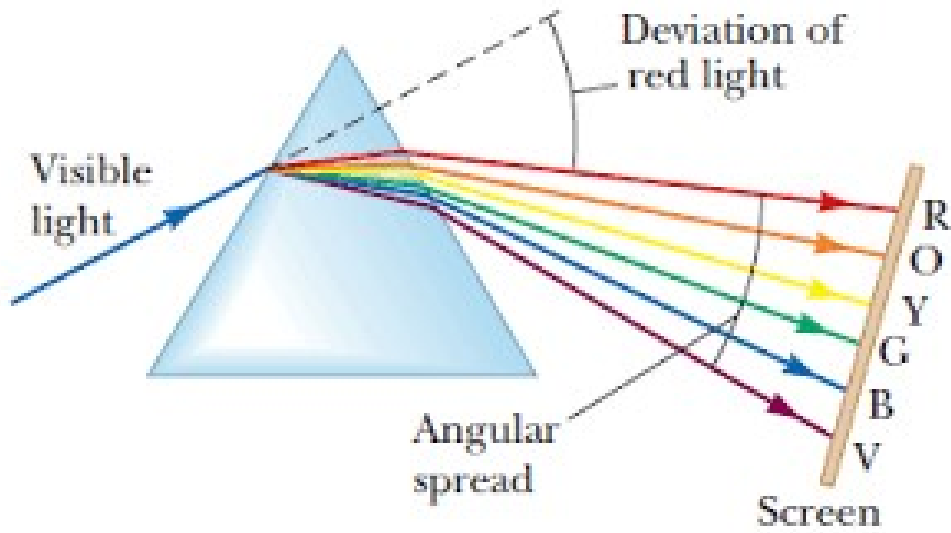
Introduction to Spectroscopy

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Institute of Chemistry  
University of Sargodha, Sargodha

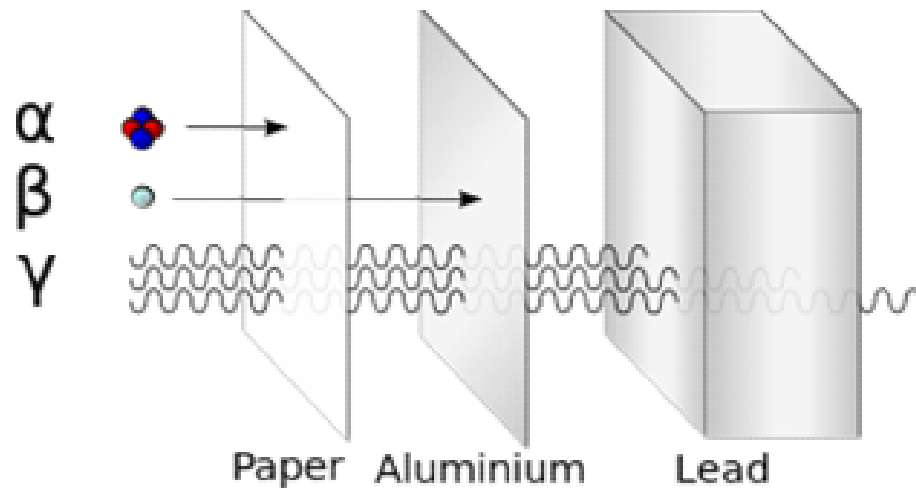
# Spectroscopy



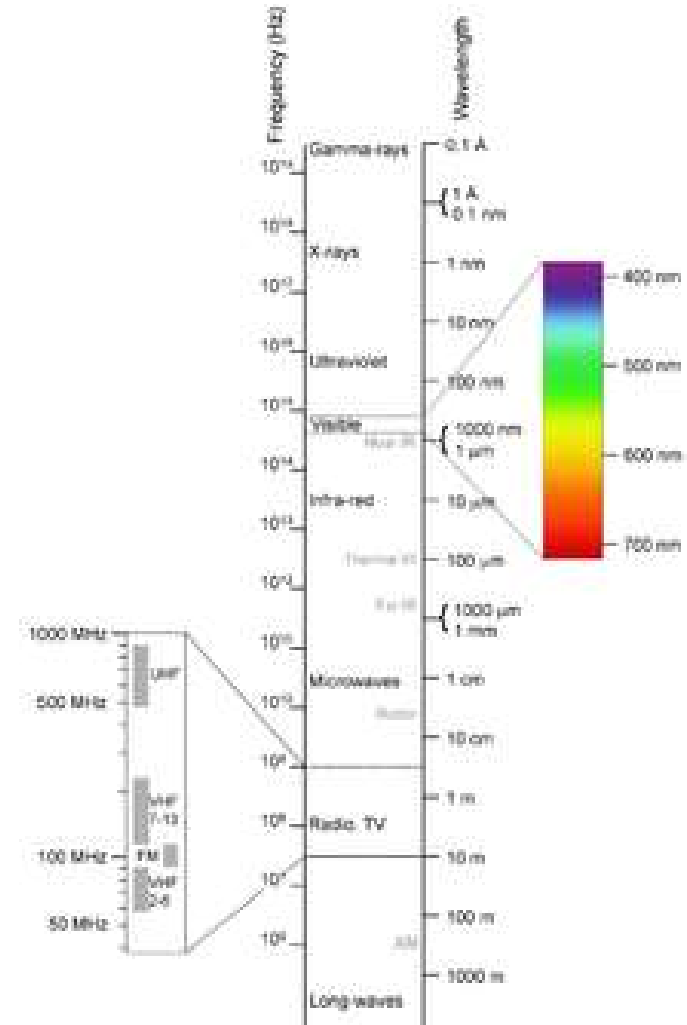
# Spectroscopy



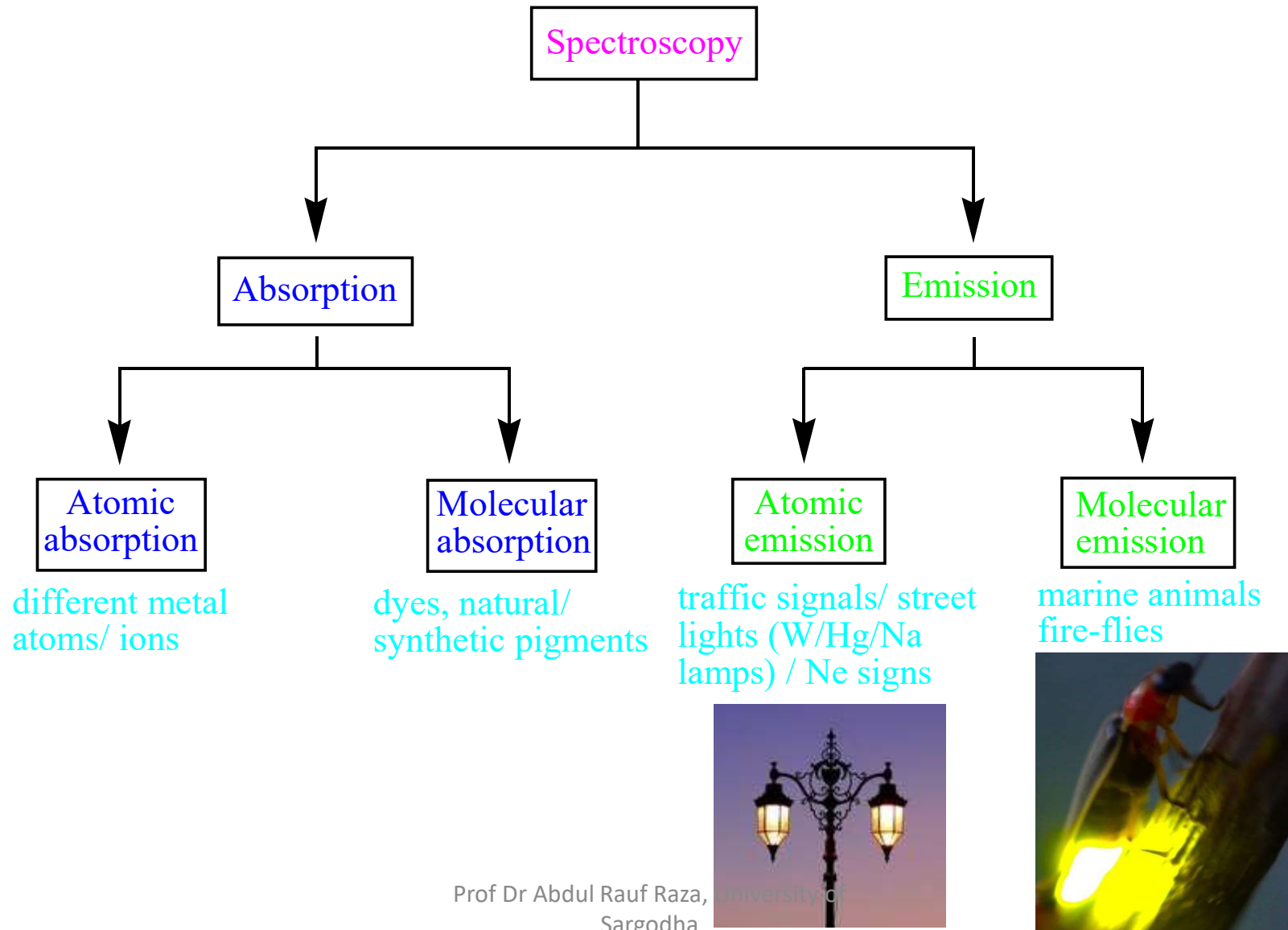
# Spectroscopy



The international symbol for types and levels of radiation that are unsafe for unshielded humans. Radiation, in general, exists throughout nature, such as in light and sound.



# Classification of Spectroscopy

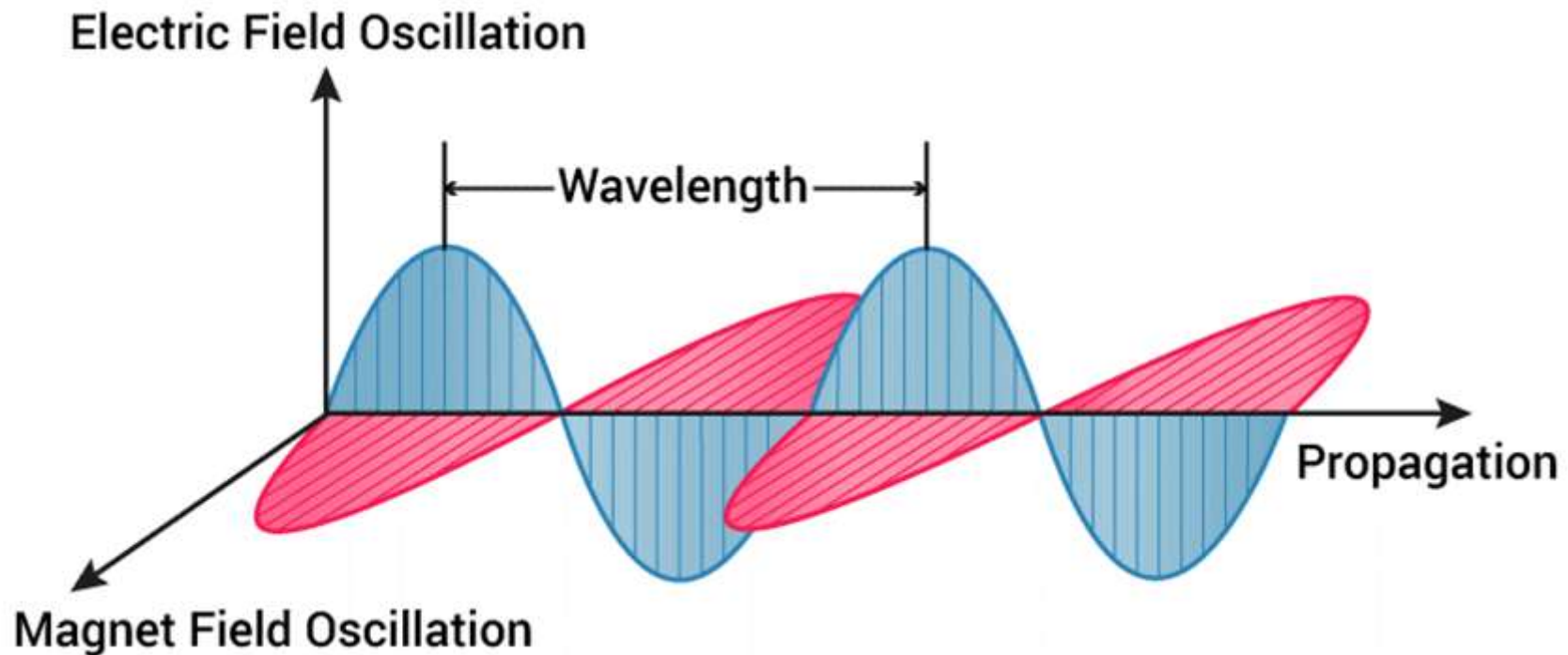


# Electromagnetic Radiations (EMR)

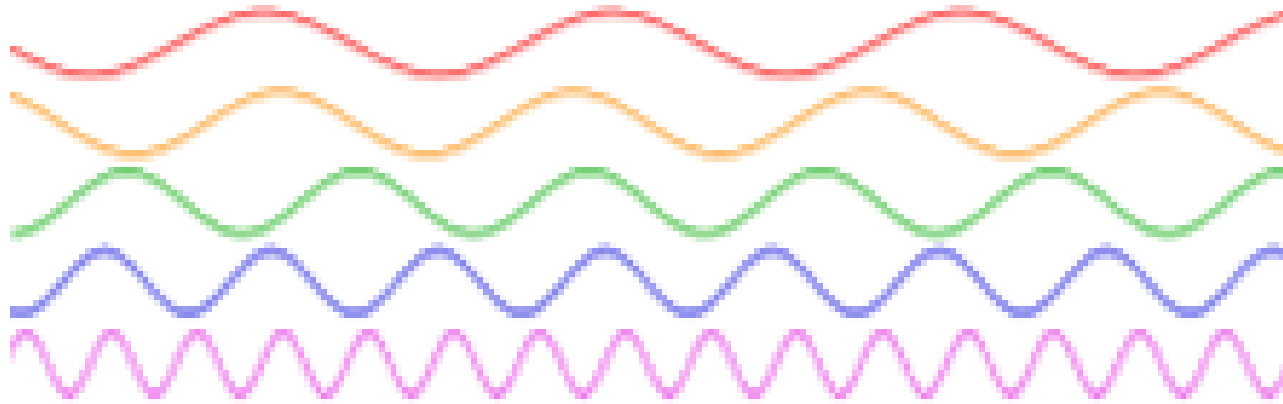
**Waves:** (sound, ocean etc.) propagates with frequency **less** than 100 Hz and needs a medium

**Rays:** (sun) propagates with frequency **higher** than 100 Hz and needs not a medium

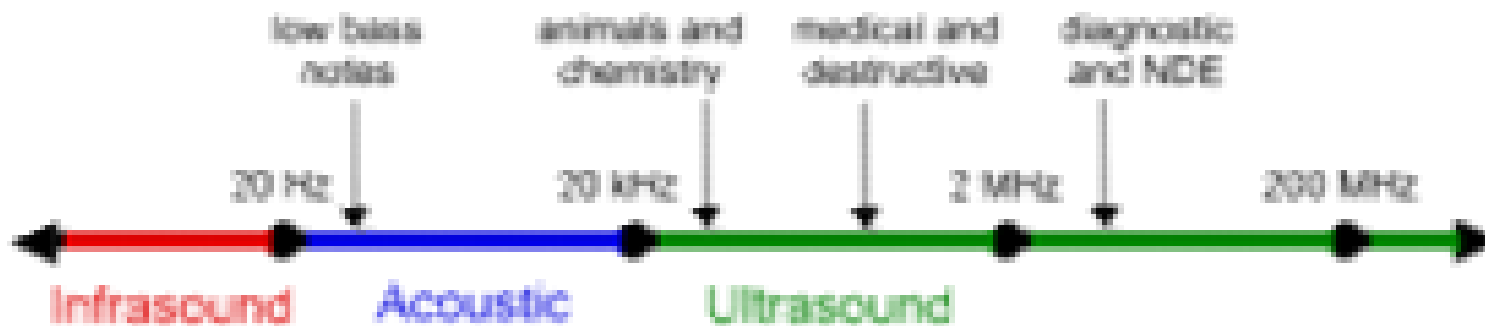
**EMR:** composed of electrical and magnetic components (perpendicular to each other), propagates with velocity of light ( $3.0 \times 10^8$  m/s) in space and frequency in MHz or higher.



# Sound waves



The direction of propagation is same to oscillation (non-polarized).  
What is  $v$ ,  $\lambda$  and  $u$ ?



# $\nu$ , $\lambda$ and $\bar{\nu}$

The direction of propagation of EMR is perpendicular to oscillation (polarization) and moves with  $c$ . James Clerk Maxwell postulated it and Heinrich Hertz confirmed it. No effect on speed of EMR is observed in vacuum but is affected in crystals (Faraday effect) or solids (Kerr effect).

$$E (\text{EMR}) = h\nu \longrightarrow \text{eq. 1}$$

$$h = 6.6 \times 10^{-34} \text{ J.s}$$

$$E = mc^2 \quad (\text{Einstein's theory}) \longrightarrow \text{eq. 2}$$

$$c = 3.0 \times 10^8 \text{ m.s}^{-1}$$

$$h\nu = mc^2 \quad (\text{since LHS of eq 1 \& 2 are equal})$$

$$\text{if } c > \nu; h\nu = m\nu^2 \longrightarrow \nu = m\nu^2/h$$

$$\text{because } \nu = c/\lambda, \text{ therefore } 1/\lambda = m\nu^2/ch$$

$$\lambda = h / m\nu \longrightarrow \lambda \propto (1/\nu)$$

UNITS:  $\nu = \text{s}^{-1}$ , Hz, cycles/s, revolutions/s

$\lambda = \text{m}, \mu\text{m}, \text{nm}, \text{pm}$

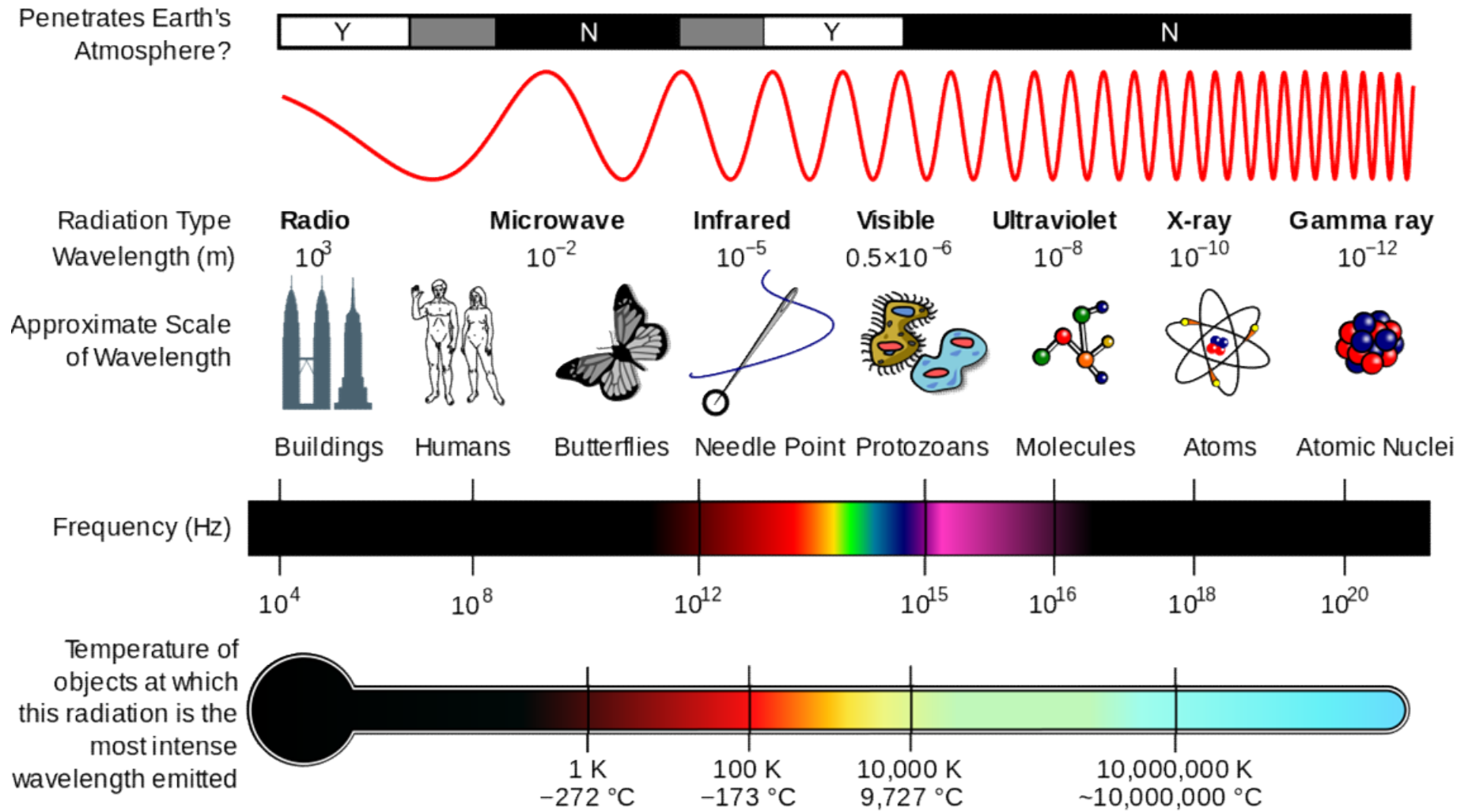
wave number =  $\text{m}^{-1}$ ,  $\text{cm}^{-1}$

$$\begin{aligned} E &= h\nu \quad (\text{per photon}) \\ E &= hc/\lambda \\ E &= hc\bar{\nu} \end{aligned}$$

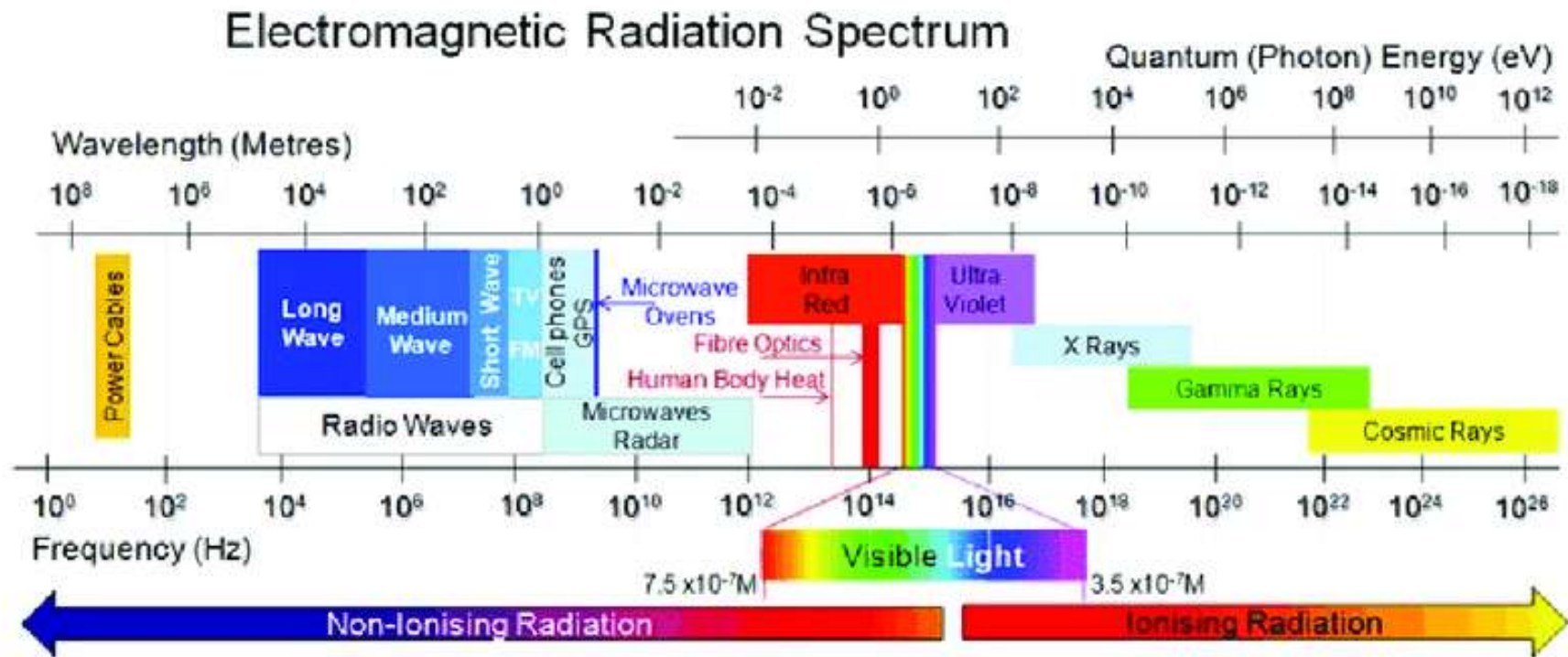
$$\begin{aligned} E &= N_A h\nu \\ &(\text{per mole of photon}) \\ E &= N_A hc/\lambda \\ E &= N_A hc\bar{\nu} \\ N_A &= 6.02 \times 10^{23} \\ &(\text{Avogadro's number}) \\ N_A h &= 3.99 \times 10^{-10} \text{ J.s} \end{aligned}$$



# EMR Spectrum



# EMR Spectrum



$\nu$ (Hz)	$\lambda$	$\bar{\nu}$ ( $\text{m}^{-1}$ )	E (eV)	Sub-Band	Abrev.	Spectral Band
3	100 Mm	0.01 m	12.4 f	Extremely Low $\nu$	ELF	Radio Frequency
30	10 Mm	0.1 m	124 f	Super Low $\nu$	SLF	
300	1 Mm	1 m	1.24 p	Ultra Low $\nu$	ULF	
3 k	100 km	10 m	12.4 p	Very Low $\nu$	VLF	
30 k	10 km	0.1 m	124 p	Low $\nu$	LF	
300 k	1 km	1 m	1.24 n	Medium $\nu$	MF	
3 M	100 m	10 m	12.4 n	High $\nu$	HF	
30 M	10 m	0.1	124 n	Very High $\nu$	VHF	
300 M	1 m	1	1.24 $\mu$	Ultra High $\nu$	UHF	
3 G	1 dm	10	12.4 $\mu$	Super High $\nu$	SHF	
30 G	1 cm	100	124 $\mu$	Extremely High $\nu$	EHF	
300 G	1 mm	1,000	1.24 m			

$\nu$ (Hz)	$\lambda$	$\sigma$ ( $\text{m}^{-1}$ )	E (eV)	Sub-Band	Abrev.	Spectral Band
3 T	100 $\mu\text{m}$	10,000	12.4 m	Far-InfraRed	FIR	InfraRed
30 T	10 $\mu\text{m}$	100,000	124 m	Mid-InfraRed	MIR	
300 T	1 $\mu\text{m}$	1,000,000	1.24	Near-InfraRed	NIR	
480 T	700 nm	1.43 M	1.99	Visible	Vis	UV-Vis
750 T	400 nm	2.5 M	3.11	Near Ultraviolet	NUV	
3 P	121 nm	8.3 M	10.2	Extreme UV	EUV	
30 P	10 nm	0.1 G	124	Vacuum UV	VUV	VUV
3 E	100 pm	10 G	12.4 k	X-Rays	X-Ray	X-Ray
30 E	10 pm	100 G	124 k	$\gamma$ -Rays	$\gamma$ -Ray	$\gamma$ -Ray

# Merits of Spectroscopy

Bond lengths between bonds

Microwave (MW), XRD spectroscopy

Force constants between two atoms

Infrared (IR) spectroscopy

Bond energies of different bonds/  
Energy levels

UV/Visible (UV/Vis) spectroscopy

Nature of atomic states

Electron spin resonance (ESR) spectroscopy

Configuration of an asymmetric centre/  
Conformational analysis

Optical rotary dispersion (ORD)  
Circulatory dichroism (CD) spectroscopy

Molecular mass of a molecule/  
Exact molecular formula of a molecule

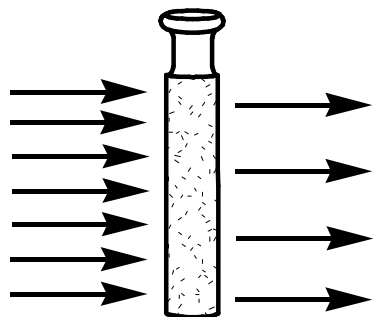
Mass spectrometry

Total structure of a molecule

IR, UV/Vis, NMR, MS

# Spectroscopy vs Spectrometry

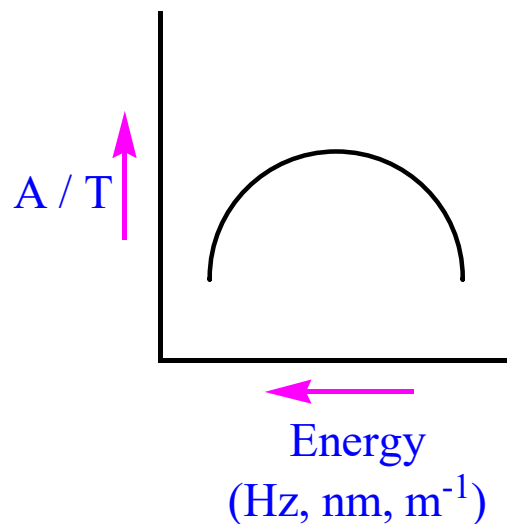
1) Involves a physical change



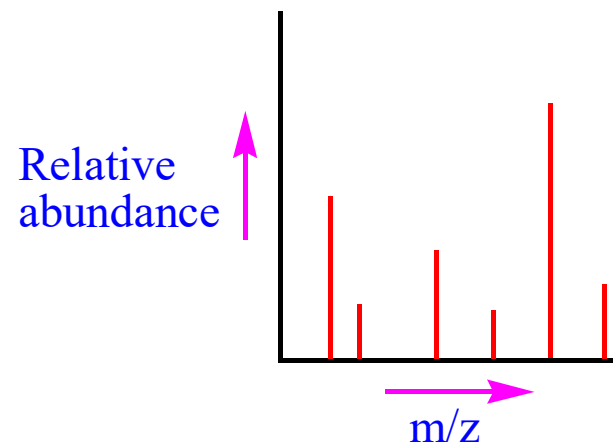
1) Involves a chemical change



2) a spectrum



2) a spectrum



# Transition

Quick change of state (lower energy level to higher or vice versa) is called transition.

Transition from lower energy level to higher is called **absorption**.

Transition from higher energy level to lower is called **emission**.

- i) Rotational transition (J)
- ii) Vibrational transition (V)
- iii) Translational transition (T)
- iv) Electronic transition (E)

## Selection Rule

$(J \pm 1), (V \pm 1), (E \pm 1)$  **Allowed Tr**

$(J \pm 2), (V \pm 3), (E \pm 2)$  **Overtones**

