Chapter 1
Introduction: Spectroscopy Fundamentals

Course Code: SSCP 4473

Course Name: Spectroscopy & Materials Analysis

Sib Krishna Ghoshal (PhD)
Advanced Optical Materials Research Group
Physics Department, Faculty of Science, UTM

Aims & Scopes of Spectroscopy

Spectroscopy & Quantum Mechanics Go hand in hand!!

Discrete…. Perturbation…Transitions…

Used for Qualitative & Quantitative Analyses of Microscopic & Macroscopic Samples

Look at Energy, Length and Time Scales of Motions

Usefulness: Those beyond the resolution and detection limit of our eye

In spectroscopy we ask for..

- ✓ What type of materials or samples for analysis?
- ✓ Experimental expectations?

Results, Analysis & Interpretation depends of types of techniques exploited

Layman Questions….

What is spectroscopy? Why do we need them?

What is the meaning of spectra/spectrum?

How do we get a spectrum?

What exactly the spectrum measure?

How important spectroscopy is?

What information we get from spectroscopy?

What kind of fingerprints?

Why? How? When? Where? What? Which?

Why Spectroscopy so Useful?

Information (quantitative and qualitative)

Material Identification: The unknown spectra is compared with standard spectra in computer databases or a spectrum obtained from a known material to determine the identity of the material being analyzed.

Quantification: Quantitative (concentration) information of a compound can be determined from the area under spectra.

Applicability

Metals, inorganic, organics, complexes, molecules etc.

Sensitivity

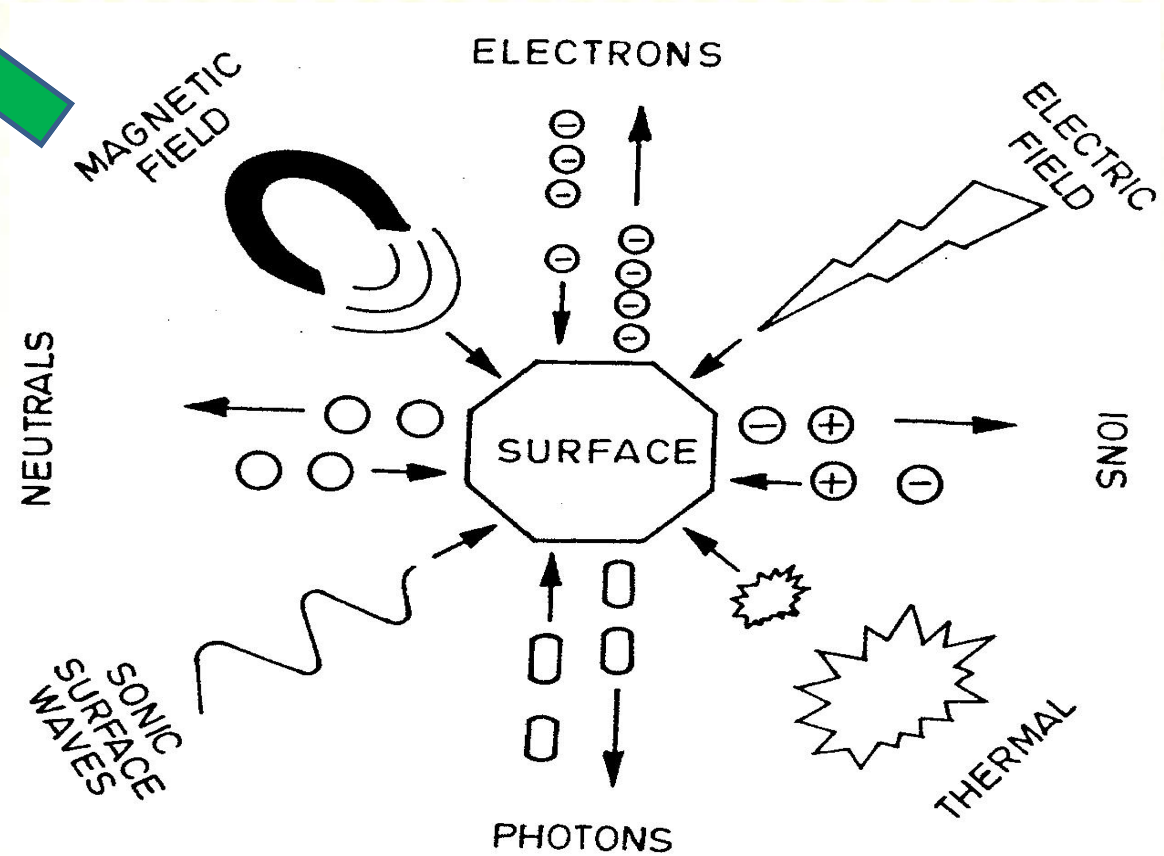
Speed

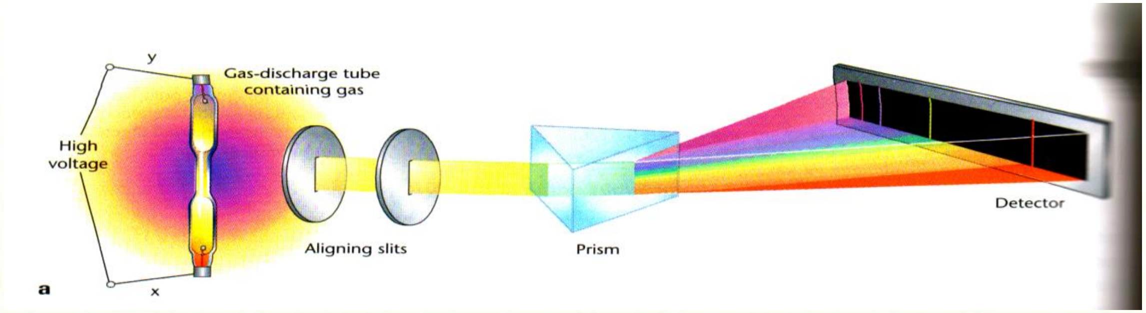
Specificity

Recurring Themes….

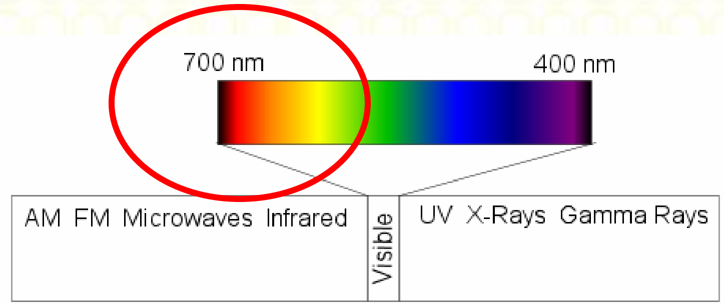
Out

In





Interaction Processes

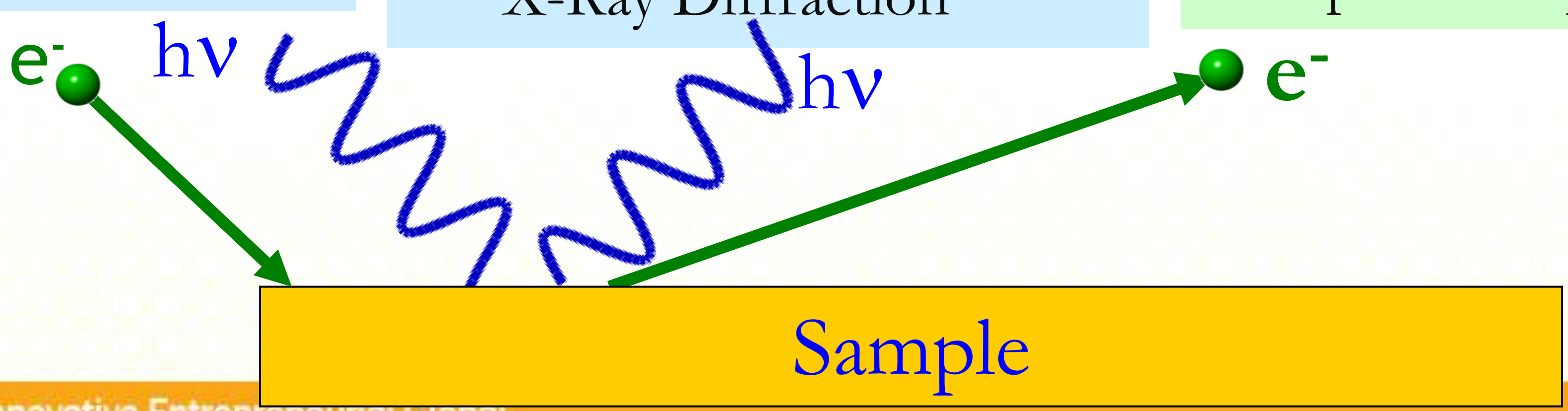


Probe: Photons

Photons In
- Infrared
- Visible
- Ultraviolet
- X-Rays

Photons Out
- Fourier Transform
- Infrared Spectroscopy
- Raman
- Visible
- Ultraviolet
- X-Ray Fluorescence
- X-Ray Diffraction

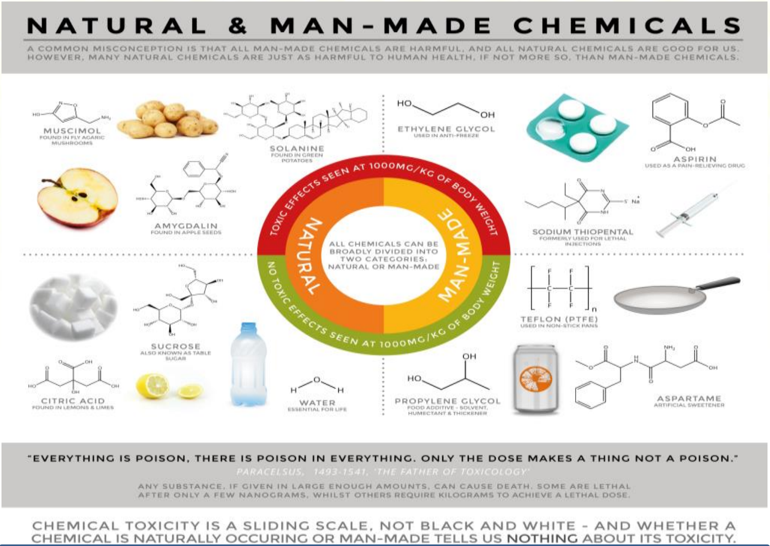
Electrons Out
- XPS, X-ray
- Photoelectron
- Spectroscopy



The Wonderful Materials World

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr



- ✓ **118** Different Elements
- ✓ **80** Stable Elements

- ✓ About 10 million or so chemical compounds
- ✓ About 9 million of those contain carbon

- ✓ About 300,000 different known materials used by human
- ✓ Few thousands are in the advanced materials listing
- ✓ About 10^{90} electrons in the visible universe

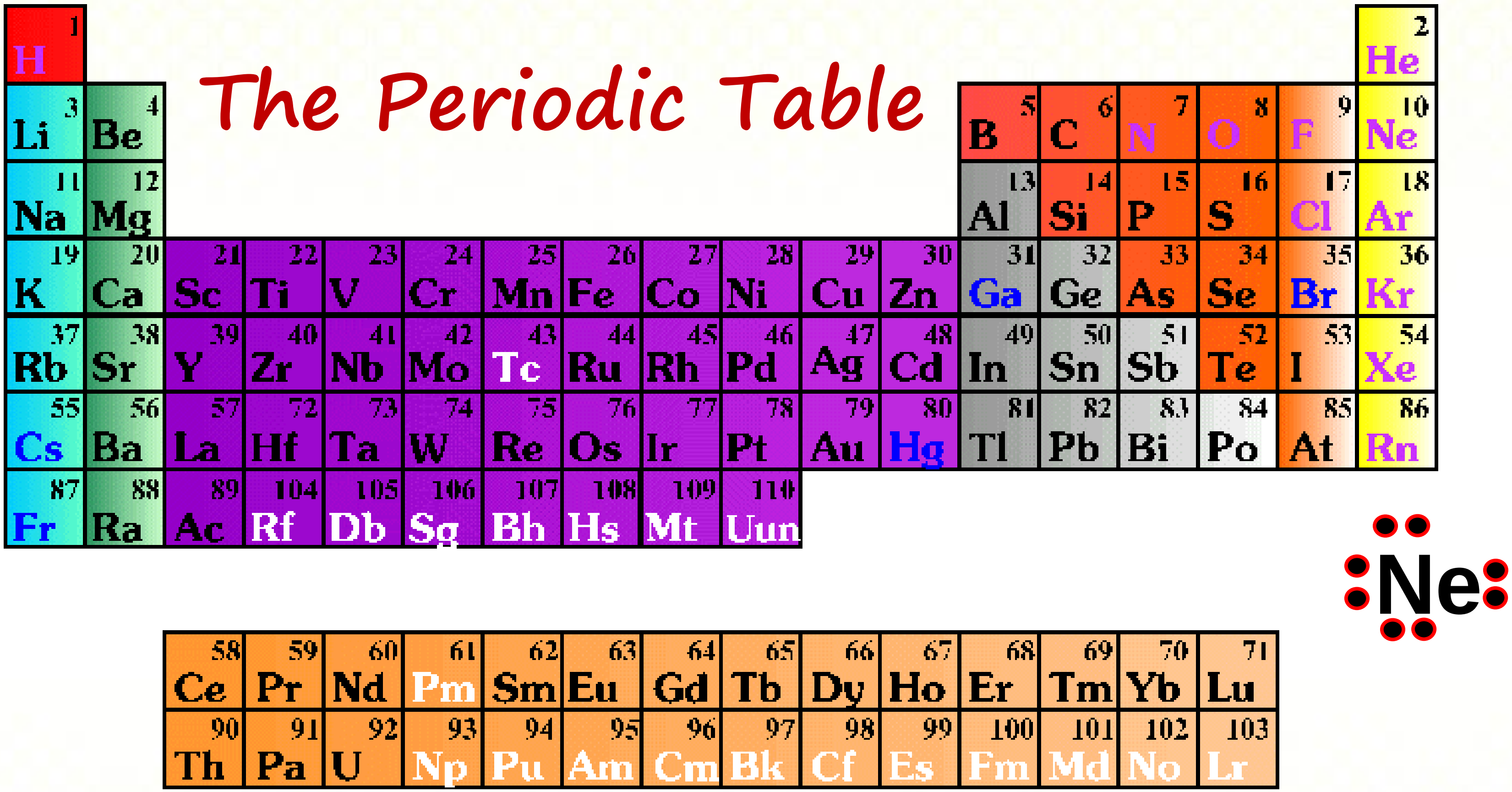
Matter Made of ?

Elements want to achieve the stable electron configuration of the nearest noble gas

n = 2

n = 3

The Periodic Table



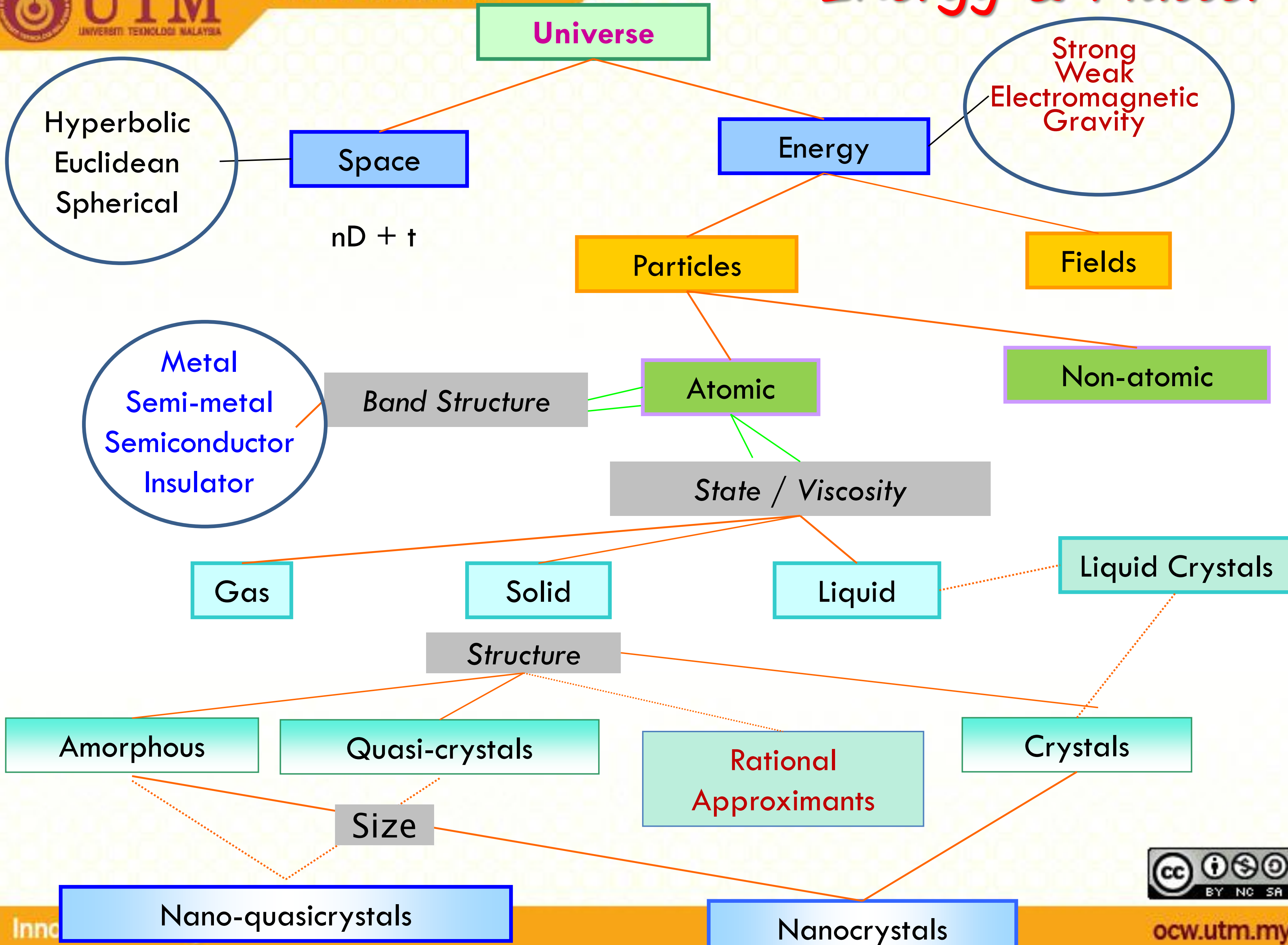
Atoms tend to gain, lose or share electrons until they are surrounded by 8 electrons

Octet Rule

Material Classification

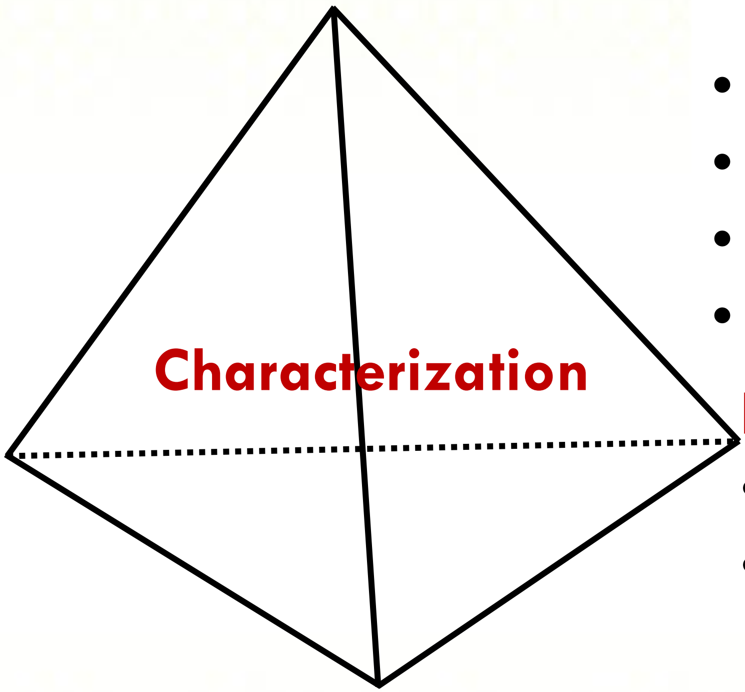
- ✓**Matter Based on Phase:** Solid, Liquid, Gas, Plasma, Quark-Gluon, Bose Condensate
- ✓**Matter Based on Structure:** Amorphous, Crystal, Quasi-crystal, Liquid-crystals, Modulated Structures
- ✓**Material Classes:** Ceramics, Glass, Metals, Polymers, Elastomers, Composites, Meta-materials, Functional Materials, Alloys, Biomaterials, Smart-materials, Semiconductors, Superconductors, Nanomaterials
- ✓**Matter Based on Conductivity:** Metal, Insulator, Semiconductor, Superconductor
- ✓**Matter Based on Magnetism:** Diamagnetic, Paramagnetic, Ferromagnetic, Ferri-magnetic, Anti-ferromagnetic
- ✓**Matter Based on Optical Properties:** Transparent, Opaque, Translucent
- ✓**Matter Based on Electrostatics:** Dielectric, Para-electric, Ferroelectric, Piezo-electric, Pyro-electric
- ✓**Matter Based on Chemical Properties:** Acid, Alkali, Neutral
- ✓**Matter Based on Mechanical Properties:** Elastic, Plastic, An-elastic, Ferro-elastic, Para-elastic

Energy & Matter



Materials Science and Engineering Needs Spectroscopy for Characterization

Structure



- arrangement of internal components
- subatomic
- atomic
- microscopic
- macroscopic (bulk)

Properties

- material characteristic
- response to external stimulus
- mechanical, electrical, thermal, magnetic, optical, deteriorative

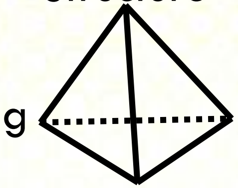
Processing

- method of preparing material

Performance

- behavior in a particular application

Levels of Structure



Structure (length scale)

Sub-atomic	Atomic	Microscopic	Bulk
< 0.2 nm 1 nm = ?	0.2-10 nm	1-1000 μm	> 1 mm

Important Engineering Characteristics of Materials

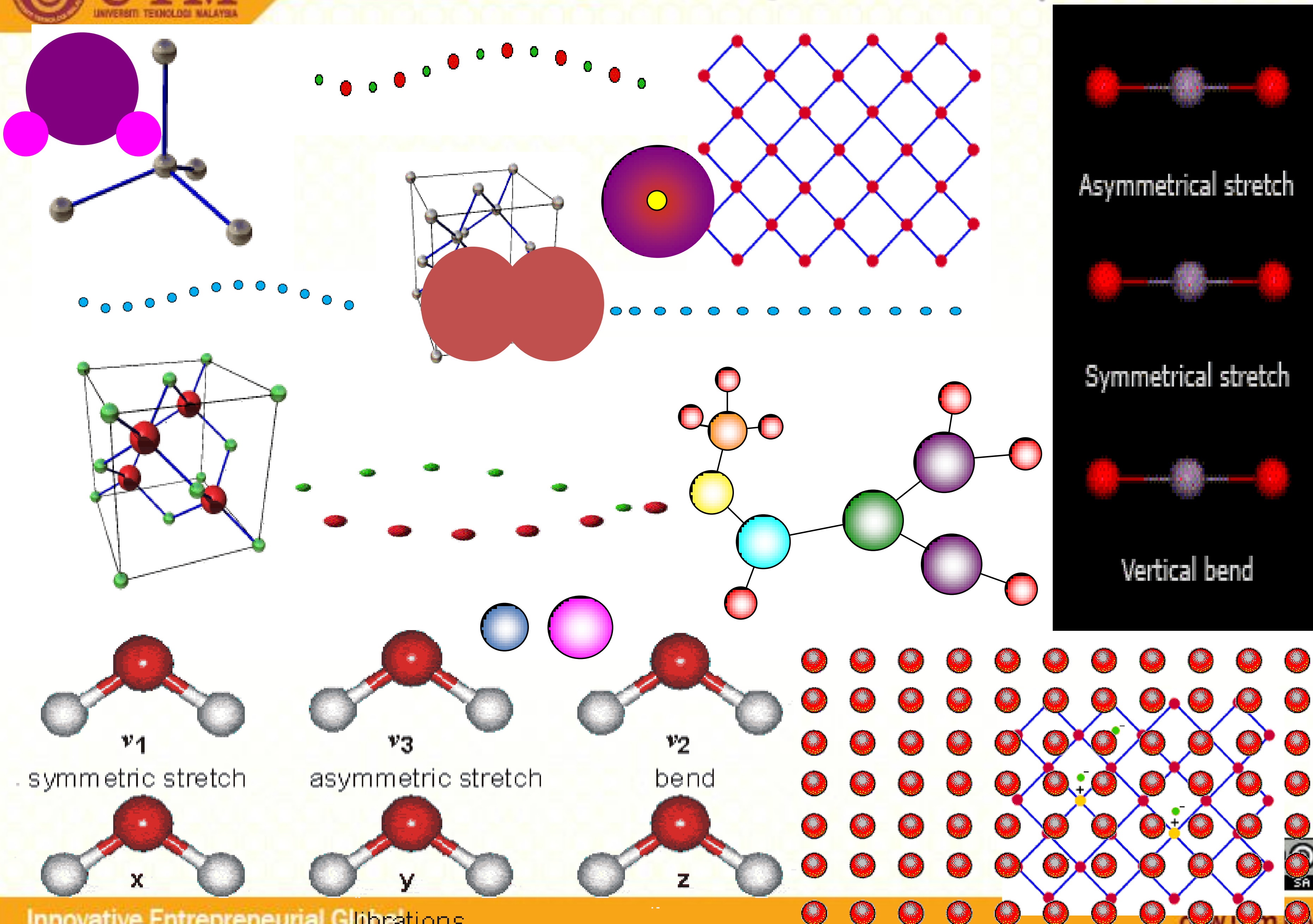
- Mechanical properties
  - Density
  - Strength
  - Hardness
  - Ductility
  - Toughness
  - Fatigue resistance
  - Creep
- Chemical properties
  - Reactivity
  - Combustibility
  - Corrosion resistance
- Dielectric properties
  - Polarizability
  - Capacitance
  - Ferroelectric properties
  - Piezoelectric properties
  - Pyroelectric properties
- Thermal properties
  - Thermal conductivity
  - Coefficient of expansion
  - Melting point
- Electrical properties
  - Conductivity
- Optical properties
  - Transmissivity
  - Colour
- Magnetic properties
  - Paramagnetic properties
  - Diamagnetic properties
  - Ferromagnetic properties
- Biological properties
  - Toxicity
  - Bio-compatibility
- Deteriorative properties

Other Concerns about Materials

- ✓ Sustainability – plentiful sustainable resources
- ✓ Availability - sizes, minimum quantities.
- ✓ Ease of manufacture - machinability, weldability.
- ✓ Compatibility - electrochemical compatibility with other parts of the system.
- ✓ Reliability - how consistent are the material properties.
- ✓ Cost - although 5th in this list, this factor may well be used first to eliminate a large number of possible options.
- ✓ Recyclability - increasing environmental concern (and resulting legislation) worldwide is driving manufacturers to use materials that can be recycled with minimum difficulty.

What to Probe in Materials?

Probing Microscopic Modes



What is Spectroscopy?

- Interaction of EMW with matter
- Purely QM of perturbation theory ! COMPLEXITY!!

"Branch of analysis devoted to identifying elements and compounds and elucidating atomic and molecular structure by measuring the radiant energy absorbed or emitted by a substance at characteristic wavelengths of the electromagnetic spectrum (including gamma ray, X ray, ultraviolet, visible light, infrared, microwave, and radiofrequency radiation) on excitation by an external energy source."

- Encyclopedia Britannica

Everyday "spectroscopy" :
Expose objects to white light, monitor absorption by eye
We need "Source", "Spectrometer", and "Detector"
color!

What is Spectroscopy?

✓ Determining the materials properties via the interaction with different frequency components of the EM spectrum

✓ Using light one observes the interaction with different degrees of freedom of the materials constituents (molecules)

✓ Each type of spectroscopy with different light frequency provides a unique *spectrum*

✓ Spectroscopy is the study of the interactions of electromagnetic radiation with matter (atoms or molecules, electrons, ions ….) and explanation of the spectral patterns

✓ Spectra show how this interaction varies with the frequency of EMW. Spectral features tell us the spacing of the energy levels, not the energy level themselves

Electromagnetic Radiation?

Relationship Between Wavelength and Frequency

Speed of light: 299,792,458 meters/second (exact by definition)
186,282 mile/s

(Speed of light) = (Wavelength) x (Frequency)

$$c = \lambda \nu$$

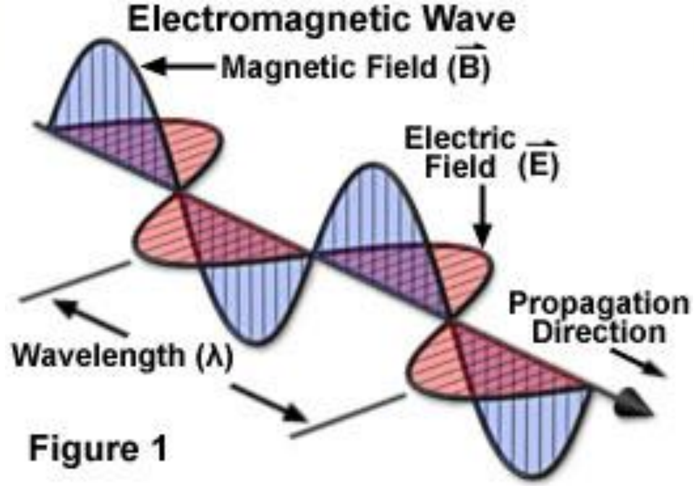
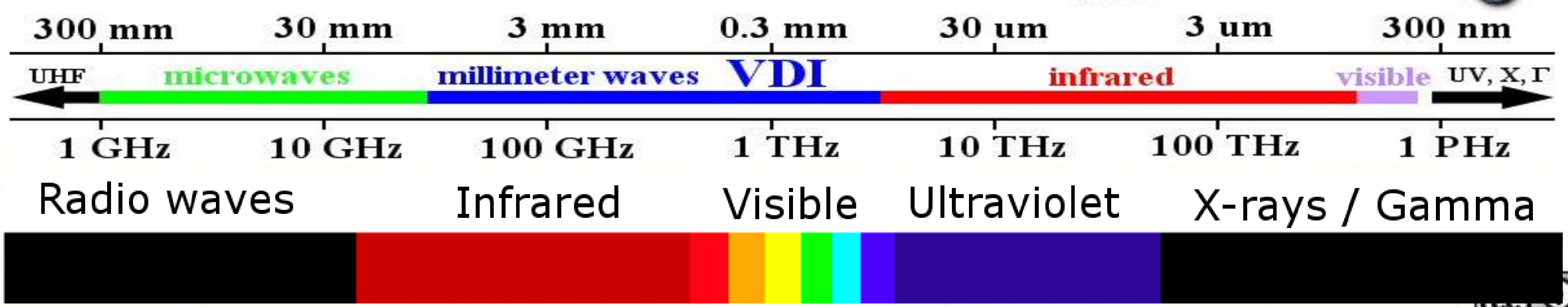


Figure 1

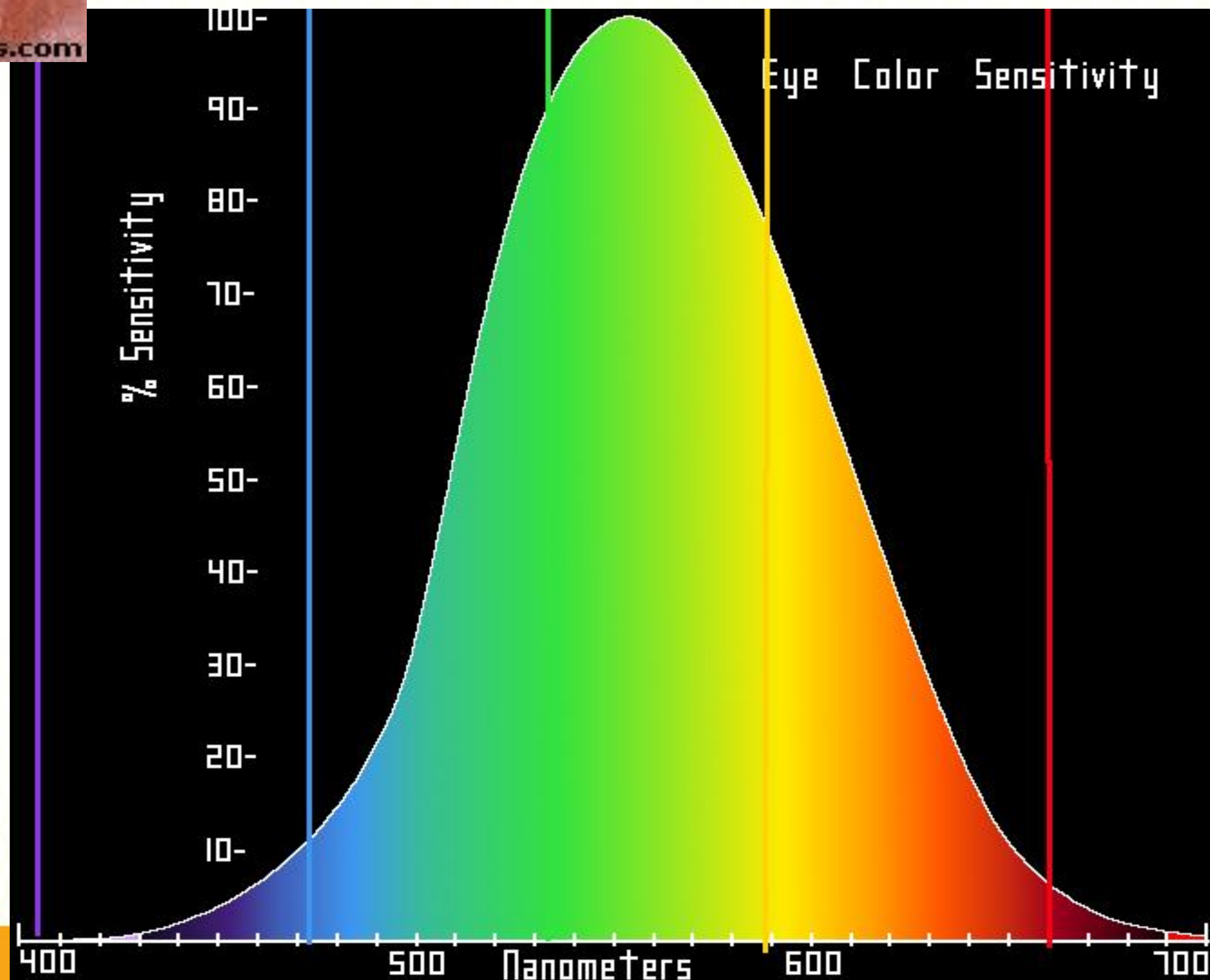


Sources of EM Radiation

Type	Source
Radio	*Vibrating electrons e.g. AC current*
Microwaves	*Excited semiconductors or vibrating electrons*
Infra-red	*Electrons transitions between energy levels*
Visible	*Electrons transitions between energy levels*
Ultraviolet	*Electrons transitions between energy levels*
X Ray	*Emitted when decelerate rapidly electrons e.g. when they hit a metal target*
Gamma	*Emitted by nuclei after a nuclear reaction*

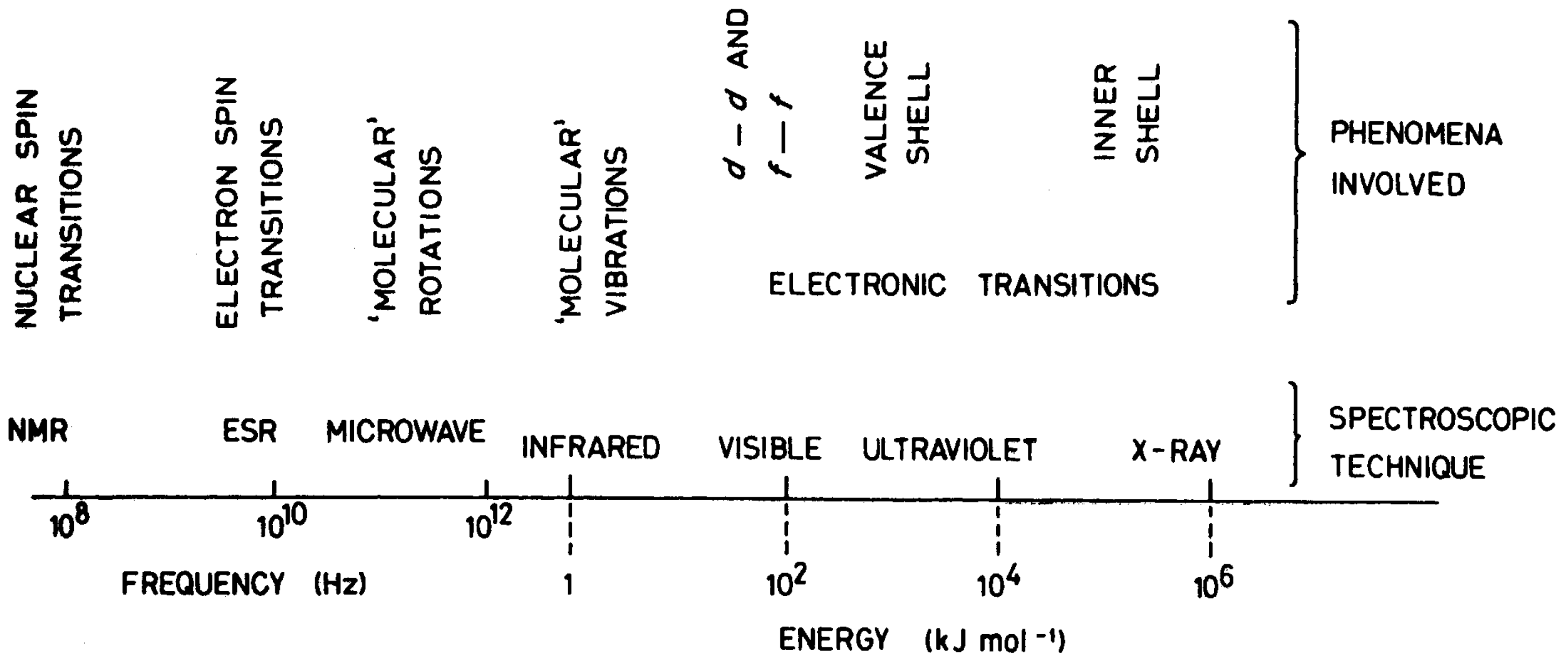
Single Color Sensitivity Diagram of the Human Eye

Most sophisticated nature built detector with all spectroscopic software built in ….



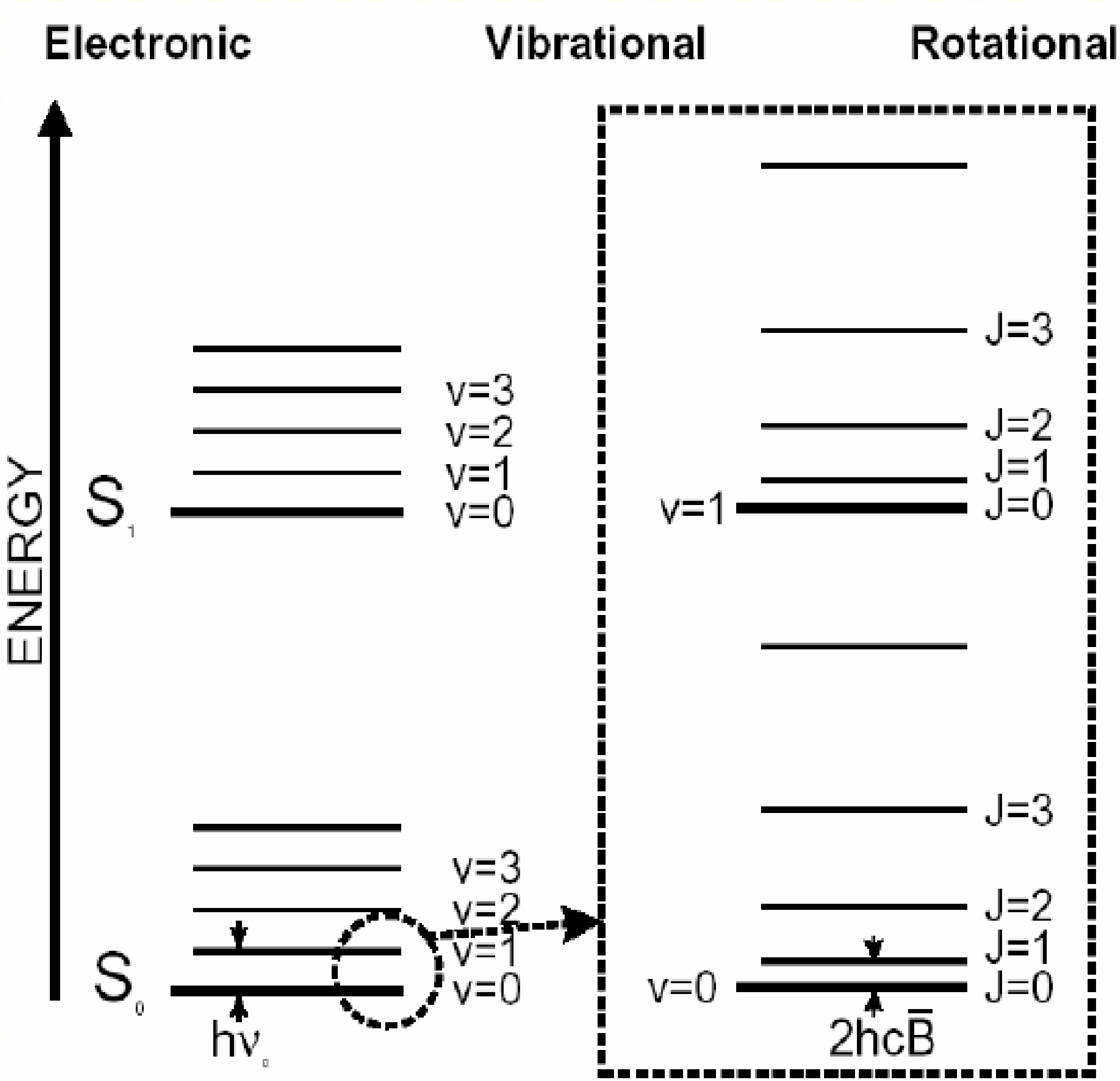
Need of Spectroscopy!!

Orders of magnitude in energy → Spectroscopic techniques



Principle regions of electromagnetic spectrum and the associated spectroscopic techniques

Energy Level Diagrams



MATTER
(Discrete Levels)
+
EMR
(Perturbing Energy)

Atom/ Molecule/ Cluster/ Bulk/ Solid/ Liquid/ Gas/ Plasma/ Bose Condensate/ Quark-Gluon

Wavenumber & Wavelength

Important Relations

$$\nu[cm^{-1}] = \frac{10^7}{\lambda[nm]}$$

$$\nu[cm^{-1}] = 8065.54 * E[eV]$$

Wavenumber

$$\bar{\upsilon}(cm^{-1}) = \frac{1}{\lambda}$$

1 eV = 2.418×10^{14} Hz (frequency)

8065.54 cm^{-1} (wavenumber)

1239.85 nm (wavelength)

11604.5 K (temperature)

1.602×10^{-19} J (energy)

$\nu = c/\lambda$, $\sigma = \nu/c = 1/\lambda$, $E = h\nu = hc/\lambda = hc\sigma$

(ν: frequency, $c = 3 \times 10^8$ m/s, λ: wavelength,

σ: wavenumber, E: energy, $h = 6.626 \times 10^{-34}$ J s)

Various Energy Scales & Spectral Regions

$E_{electronic}$ → 10^5-10^6 kJ/mole → UV-Vis

UV-Vis range: 200 - 700 nm

$E_{vibrational}$ → 10 - 40 kJ/mole → IR

Near IR: 800 - 2500 nm (5000 nm)

Mid-IR : 5000 nm - 25,000 nm (5 μm - 25 μm)

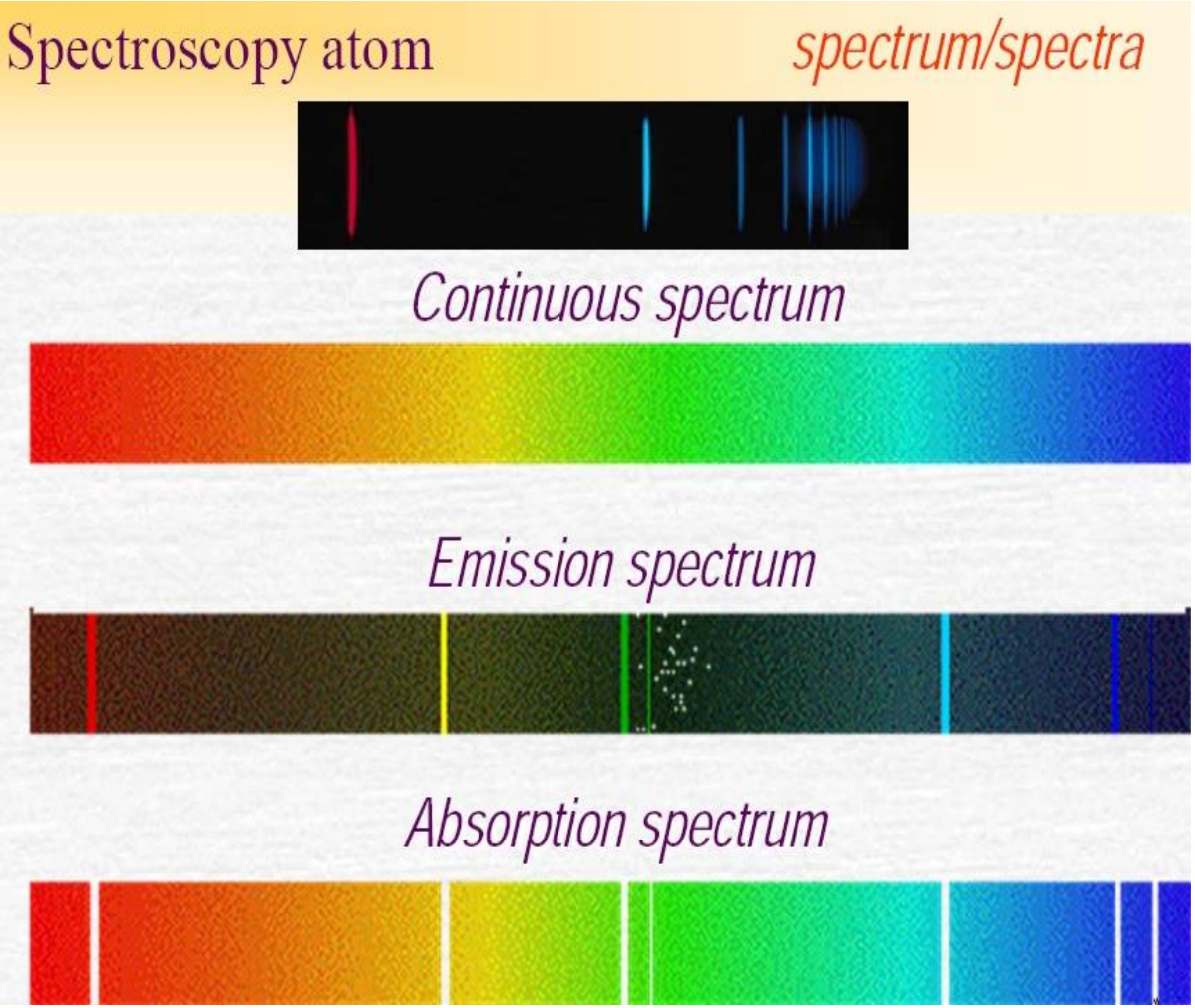
$E_{rotational}$ → 10 kJ/mole → Microwaves

E_{spin} → 10^{-3} J/mole → Radiofrequency

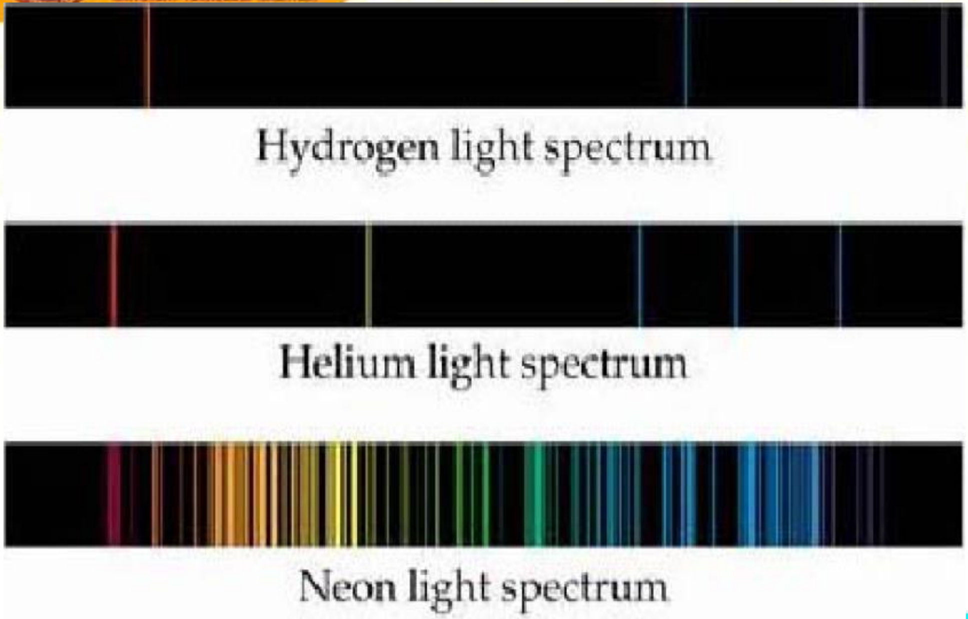
$E_{translational}$ → Continuous

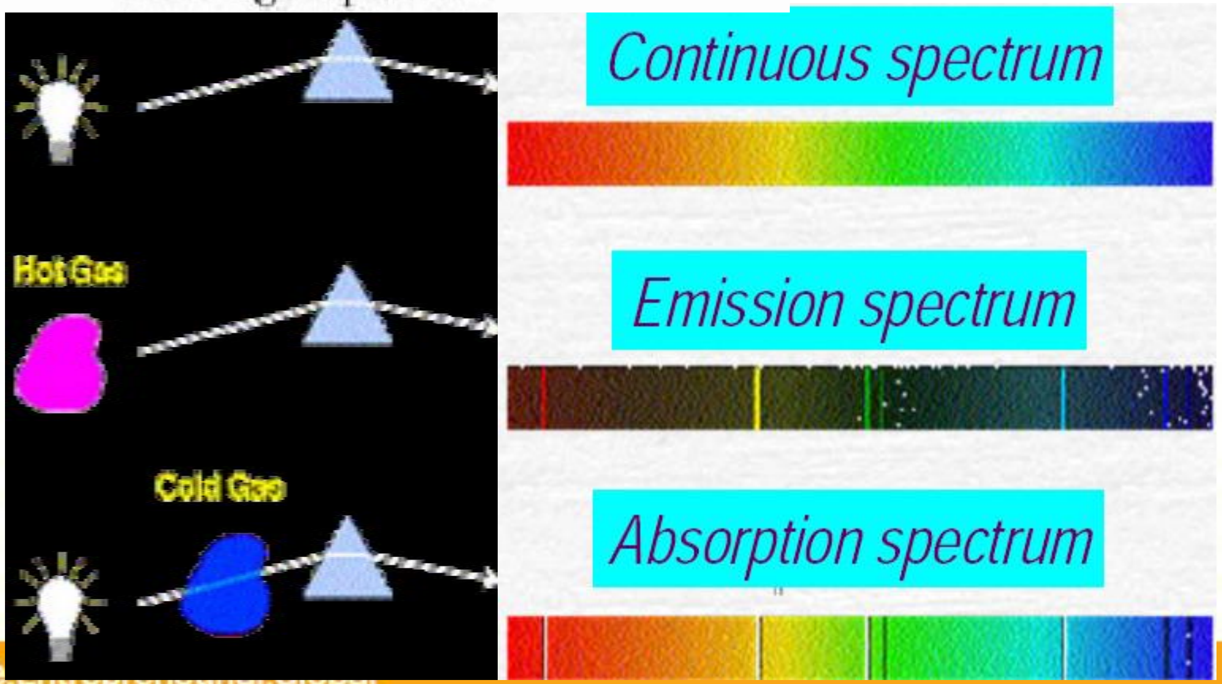
(Important to know Energy/Structure Relationship)

Examples of Spectrum/Spectra



Examples of Spectrum/Spectra





Analyses of Samples Fingerprints Captured by Spectra

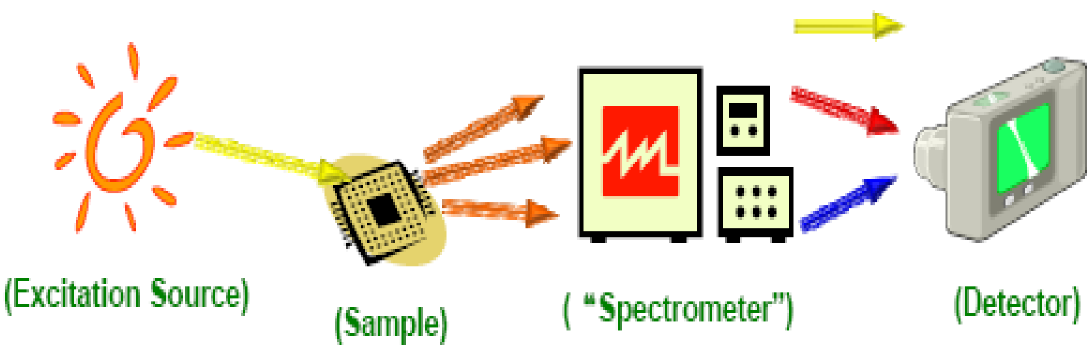
Characteristics frequencies (position)	→	Composition
Changes in Frequency of peaks	→	Stress/Strain State
Polarization of peak	→	Symmetry/ Orientation
Width of peak	→	Quality
Intensity of peak	→	Amount

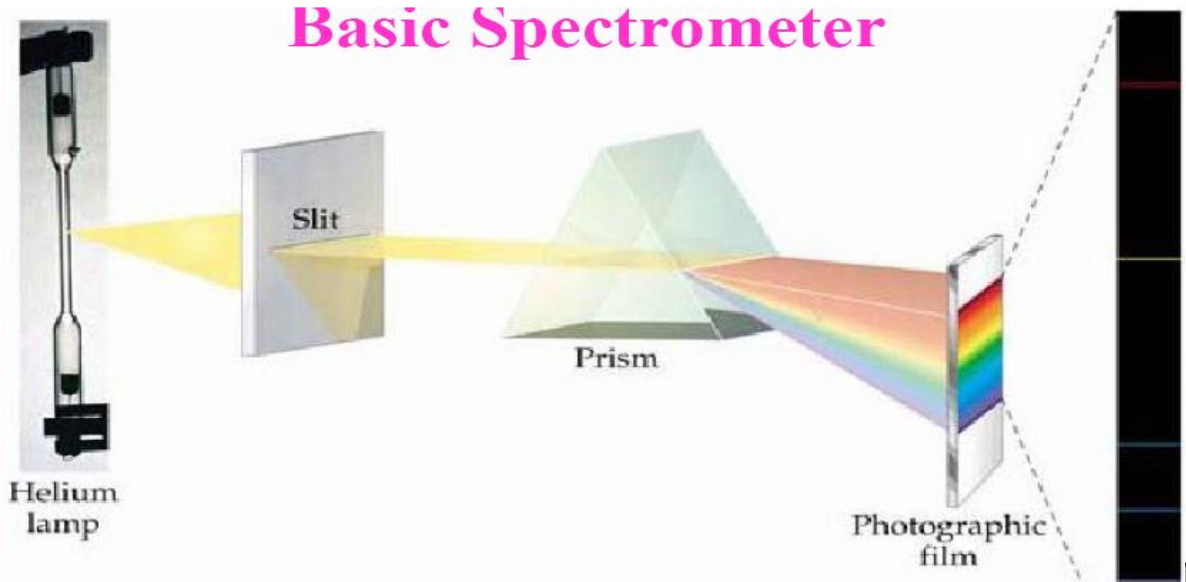
- ✓ Number of peaks
- ✓ Peak intensities
- ✓ Peak position
- ✓ FWHM
- ✓ Peak shape
- ✓ Peak shift

One broad peak may be superposition of two or several peaks: De-convolution is needed

What is Optical Spectroscopy?

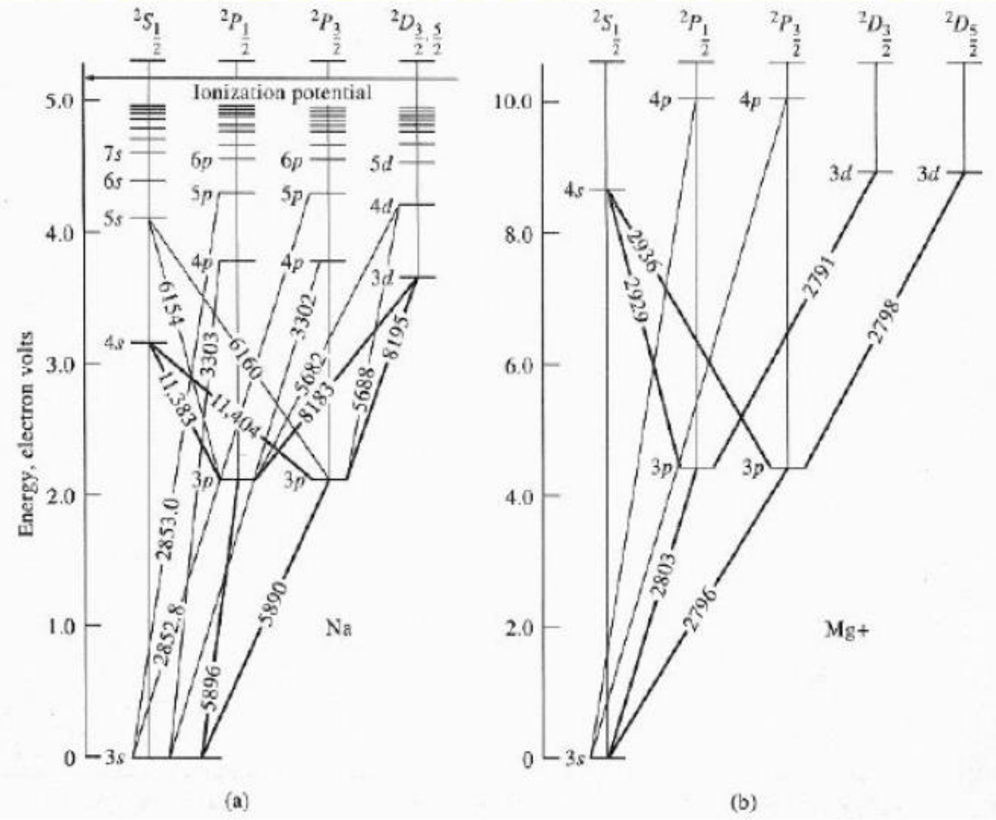
We need...





To have spectroscopy we need source, sample, wavelength (energy) analyser and detector

Atomic Energy Levels: Some Concepts



Transitions

Selection Rules

Term Symbols

Broadening

Intensity

Fermi's Golden Rule

The Energy Levels

The origins of absorption/emission lie in exchanges of energy between molecules and EMF.

In general, total energy of a molecule can be given as:

$E = E_{rot} + E_{vib} + E_{el} + E_{tr}$

The Born-Oppenheimer Approximation

$E_{rot} < E_{tr} < E_{vib} < E_{el}$

$$\psi_{molecule}(\hat{r}_i, \hat{R}_j) = \psi_{electrons}(\hat{r}_i, \hat{R}_j)\psi_{nuclei}(\hat{R}_j)$$

E_{rot} ~1 - 500 cm^{-1} (far-infrared to microwave region)

E_{vib} ~500 - 10^4 cm^{-1} (near- to far-IR)

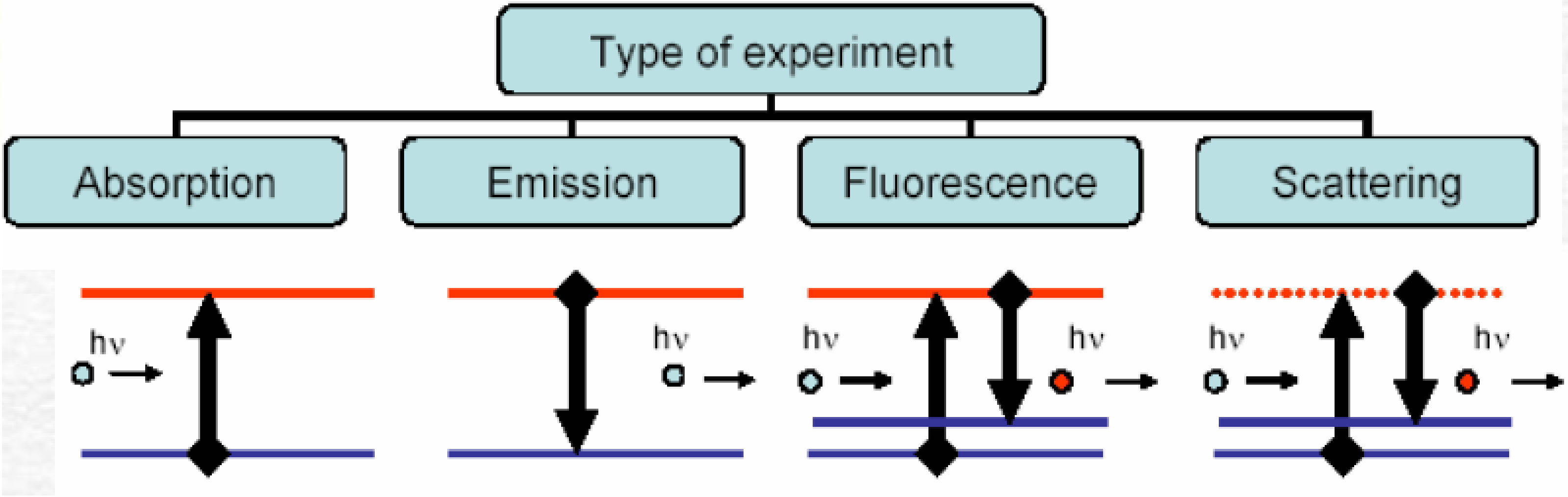
E_{el} ~10^4 - 10^5 cm^{-1}(UV and visible)

E_{tr} ~ 400 cm^{-1} for T =300 K

Types of Spectroscopic Processes

- ✓ Atomic Absorption
  - flame, electro-thermal, volatile formation
- ✓ Atomic Emission
  - flame, inductively coupled plasma, arcs, sparks
- ✓ Molecular absorption
  - ultra violet visible, infrared
- ✓ Molecular emission
  - fluorescence, phosphorescence, luminescence
- ✓ Molecular scattering
  - Raman, nephelometry, turbidimetry
- ✓ Nuclear Magnetic Resonance
- ✓ Electron Spin Resonance
- ✓ Gamma-ray
- ✓ X-ray
- ✓ Microwave absorption

What we Achieve?



✓ Molecular structure and properties are derived principally by spectroscopic methods.

✓ Spectroscopy is the study of photon emitted or absorbed by photons upon changes in the energy states of molecules or atoms or matter.

Conclusion

Electromagnetic Radiation

Matter & Materials

What matter?
Theory of rotation?
Theory of vibration?

Analysis? Specktrometer?

Quantum Mechanics & Selection Rules

Length, Energy and Time Scales

Type of Spectroscopy

- ✓ Absorption
- ✓ FTIR
- ✓ Raman
- ✓ MW
- ✓ NMR

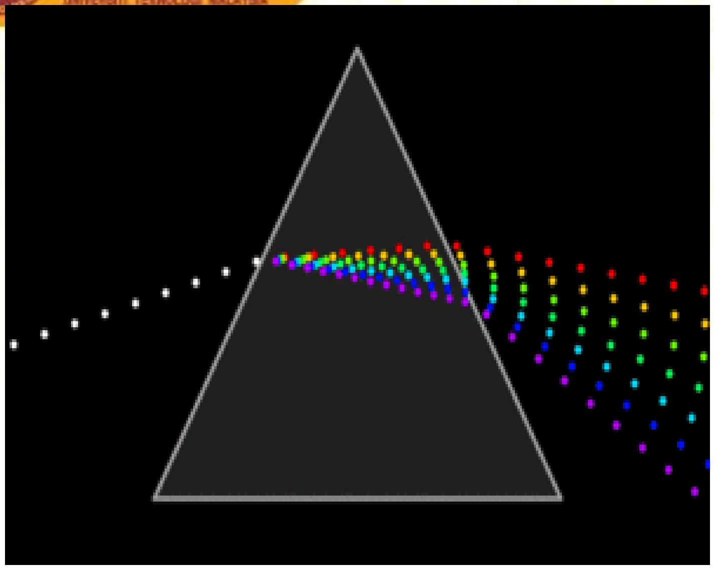
Electron population is dictated by the Boltzmann distribution

$$n_0 = Np_0 \sim N \exp(-E_0/k_BT)$$

$$n_1 = Np_1 \sim N \exp(-E_1/k_BT)$$

$$n_1/n_0 = \exp[-(E_1-E_0)/k_BT] = \exp(-\Delta E/\ k_BT)$$

Questions ?



Thank You