BASICS OF SPECTROSCOPY

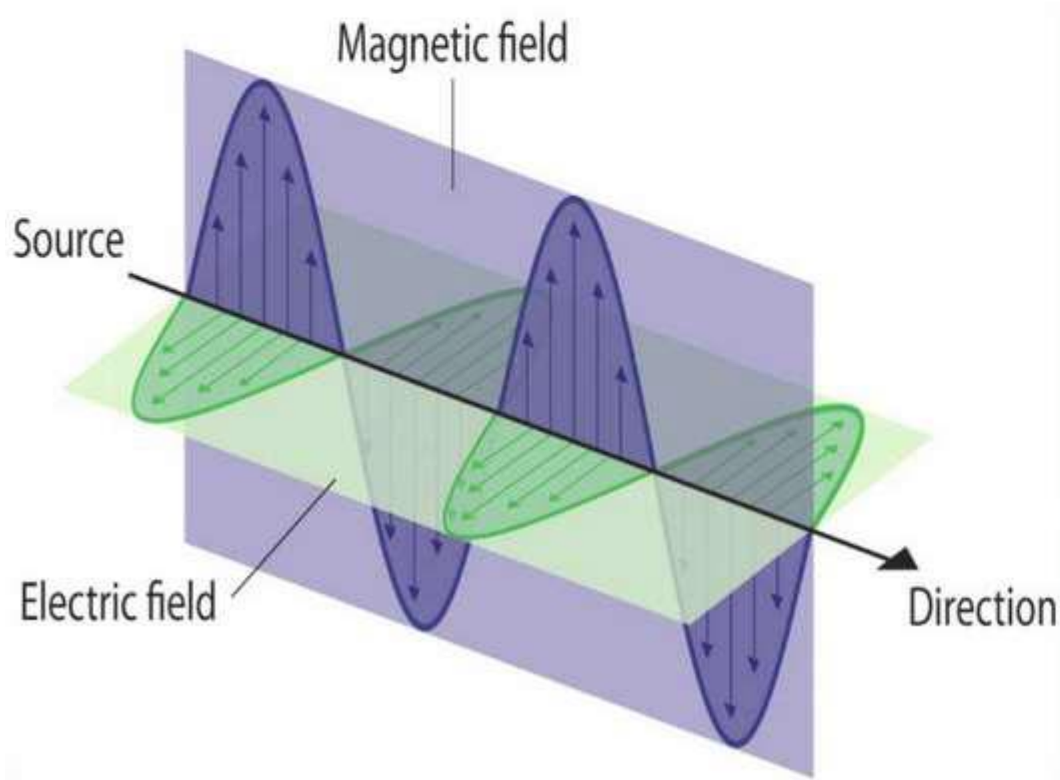
Definition of Spectroscopy

It is a branch of science that deals with interaction of matter with light or electromagnetic radiation.

Electromagnetic Radiation

- Wave produced by motion of electrically charged particles (Photon)

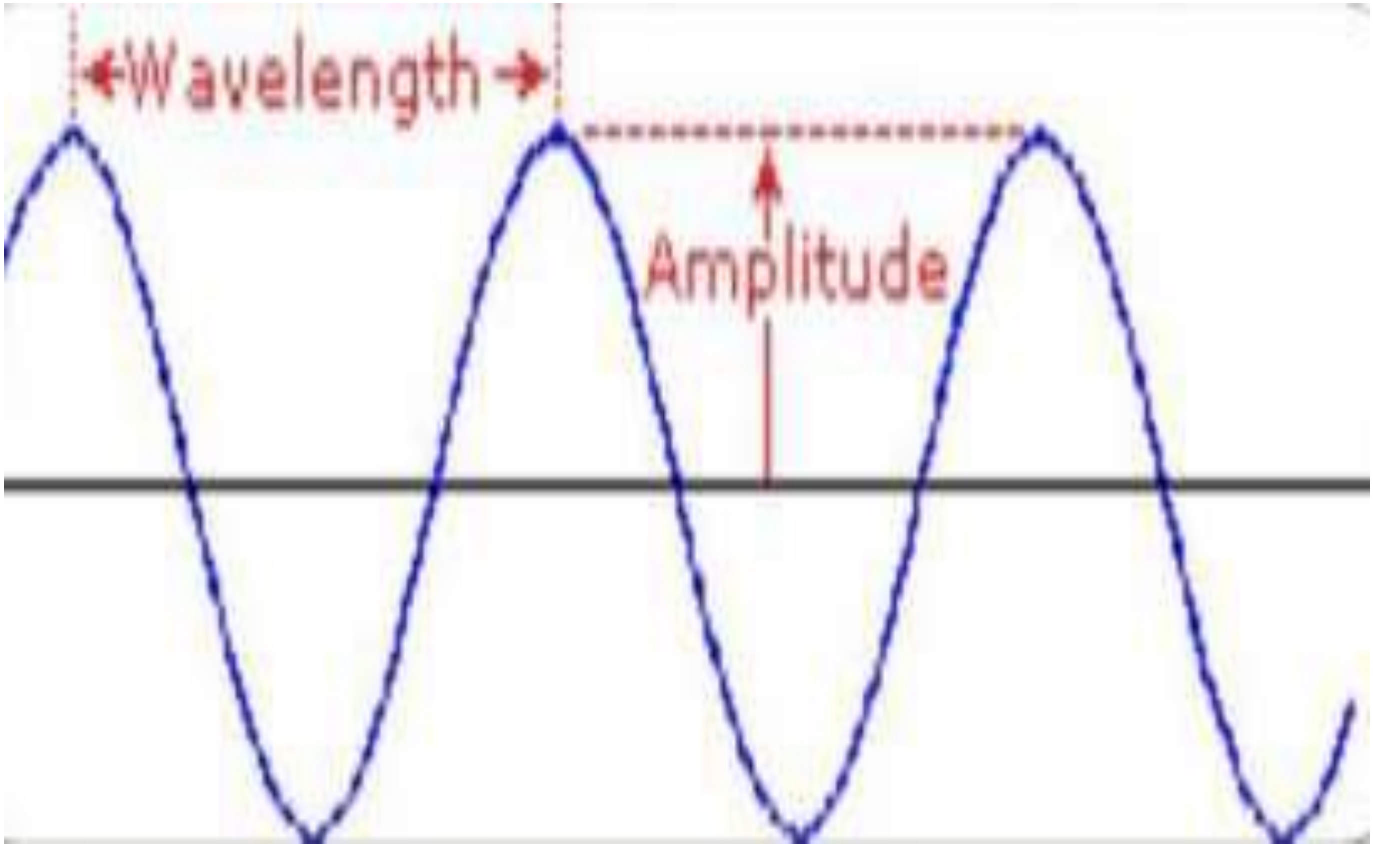
- Consists of two components – Electric and Magnetic



Magnetic field
Source
Electric field
Direction

Properties of Waves

- Wavelength (λ) – Distance between two nearest crest or troughs
- Frequency – Number of wave cycle in a given time, measured in Hertz (Hz)
- Amplitude – Wave's height or length


Wavelength
Amplitude

- Spectrum – graph or plot of intensity of absorbed/ emitted radiation by sample verses frequency or Wavelength
- Spectrometer – Instrument design to measure the spectrum of a sample
- **Types of Spectra**

  Absorption Spectra

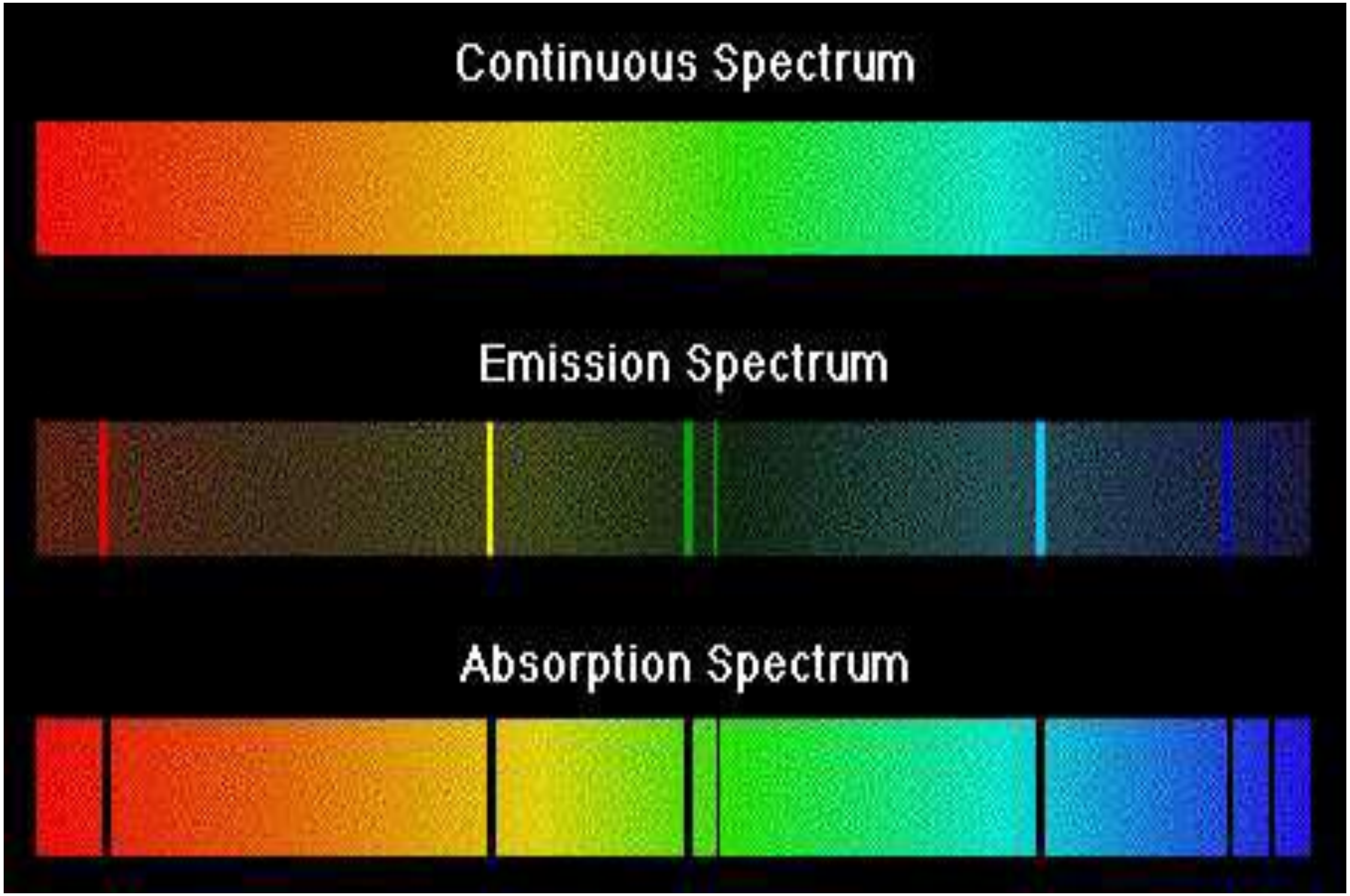
  Emission Spectra

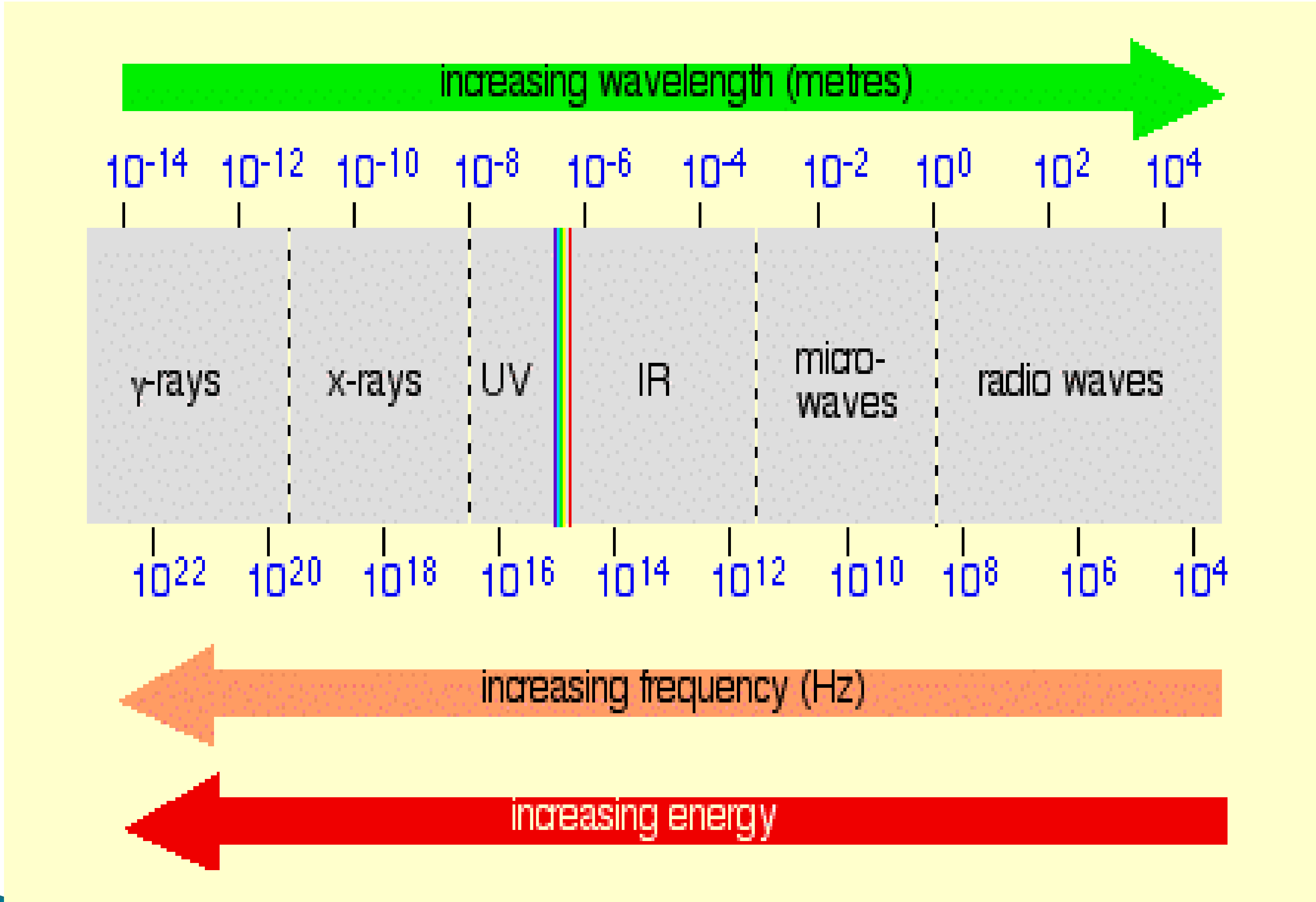
  Continuous spectra

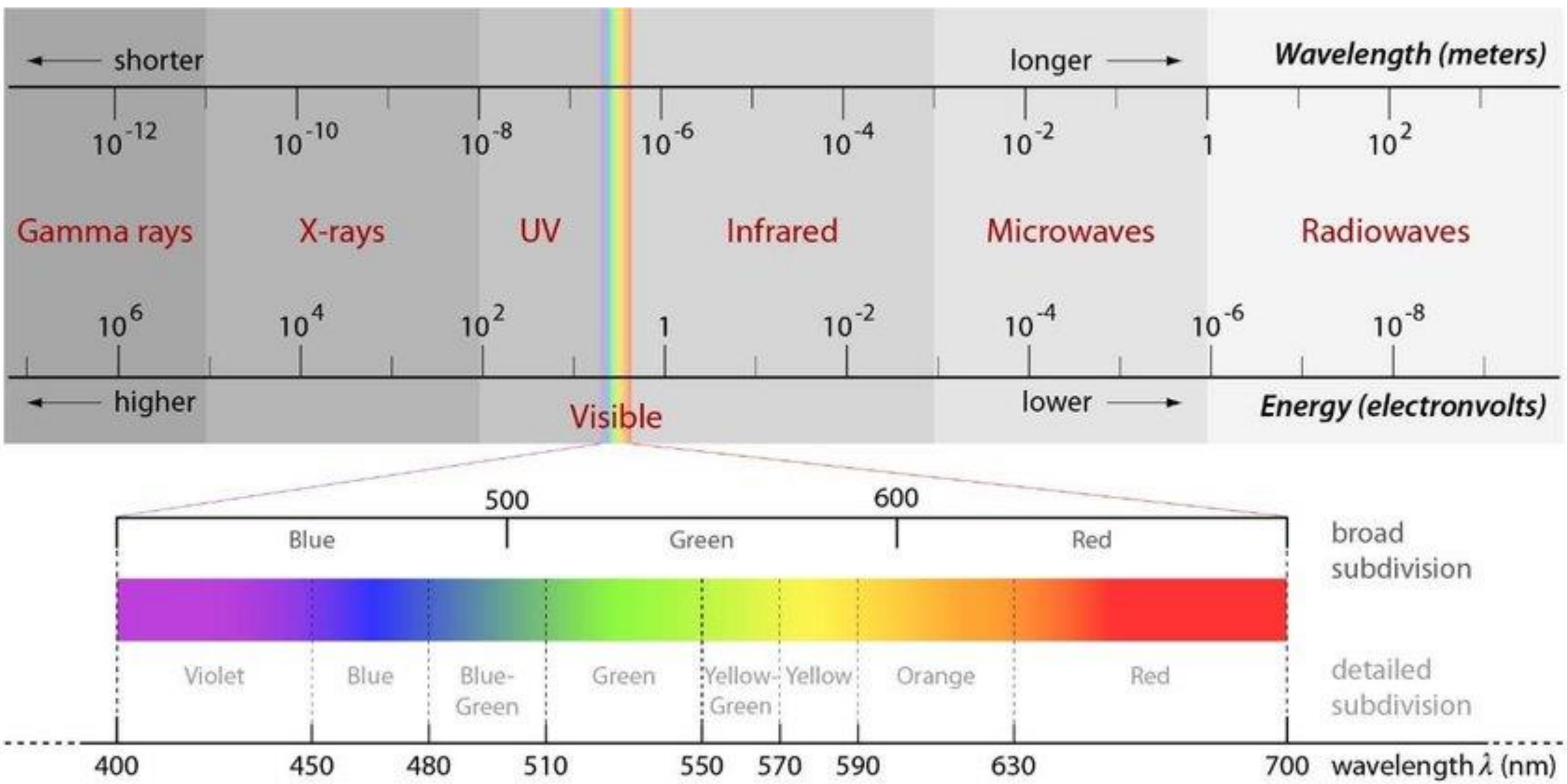
- **Continuous Spectra** – Spectra obtained when white light passed through a prism

- **Absorption Spectra** – Spectra obtained by absorption of electromagnetic radiation to the atoms, ions or molecules of sample (UV/Visible, etc.,)

- **Emission Spectra** – Spectra obtained by emission of electromagnetic radiation to the atoms, ions or molecules of sample


Continuous Spectrum
Emission Spectrum
Absorption Spectrum


increasing wavelength (metres)
10-14
10-12
10-10
10-8
10-6
10-4
10-2
100
102
104
γ-rays
x-rays
UV
IR
micro-
waves
radio waves
1022
1020
1018
1016
1014
1012
1010
108
106
104
increasing frequency (Hz)
increasing energy



shorter
longer
Wavelength (meters)
10^-12
10^-10
10^-8
10^-6
10^-4
10^-2
1
10^2
Gamma rays
X-rays
UV
Infrared
Microwaves
Radiowaves
10^6
10^4
10^2
1
10^-2
10^-4
10^-6
10^-8
higher
lower
Energy (electronvolts)
Visible
500
600
Blue
Green
Red
broad subdivision
Violet
Blue
Blue-Green
Green
Yellow-Green
Yellow
Orange
Red
detailed subdivision
400
450
480
510
550
570
590
630
700
wavelength λ (nm)

Interaction of EMR with matter

Absorption of Radiation

1. Electronic energy level

- Molecules at – lowest energy level E_0
- Molecules absorbs energy (UV/ Visible) – promoted to higher energy level E_1 E_2 …….. E_4
- Difference in Energy $\Delta E = E_n - E_0$

Common Spectroscopic Methods Based on Electromagnetic Radiation

Type of Spectroscopy	Usual Wavelength Range	Usual Wave number Range, cm^{-1}	Type of Quantum Transition
Gamma-ray emission	0.005-1.4 Å	_	Nuclear
X-ray absorption, emission, fluorescence, and diffraction	0.1-100 Å	_	Inner electron
Vacuum ultraviolet absorption	10-180 nm	$1x10^6$ to $5x10^4$	Bonding electrons
Ultraviolet visible absorption, emission, fluorescence	180 -780 nm	$5x10^4$ to $1.3x10^4$	Bonding electrons
Infrared absorption and Raman scattering	0.78-300 mm	$1.3x10^4$ to $3.3x10^1$	Rotation/vibration of molecules
Microwave absorption	0.75-3.75 mm	13-27	Rotation of molecules
Electron spin resonance	3 cm	0.33	Spin of electrons in a magnetic field
Nuclear magnetic resonance	0.6-10 m	$1.7x10^{-2}$ to $1x10^3$	Spin of nuclei in a magnetic field

- Spectroscopy is used as a tool for studying the structures of atoms and molecules. The large number of wavelengths emitted by these systems makes it possible to investigate their structures in detail, including the electron configurations of ground and various excited states.

- Spectroscopy also provides a precise analytical method for finding the constituents in material having unknown chemical composition. In a typical spectroscopic analysis, a concentration of a few parts per million of a trace element in a material can be detected through its emission spectrum.

Practical considerations

Production and analysis of a spectrum usually require the following

(1) A source of light (or other electromagnetic radiation)

(2) A disperser to separate the light into its component wavelengths

(3) A detector to sense the presence of light after dispersion. The apparatus used to accept light, separate it into its component wavelengths, and detect the spectrum is called a spectrometer.

- Spectra can be obtained either in the form of emission spectra, which show one or more bright lines or bands on a dark background, or absorption spectra, which have a continuously bright background except for one or more dark lines.

Absorption spectroscopy

- Absorption Spectroscopy measures the loss of electromagnetic energy after it illuminates the sample under study.
- For example, if a light source with a broad band of wavelengths is directed at a vapour of atoms, ions or molecules the particles will absorb those wavelengths that can excite them from one quantum state to another.
- As a result, the absorbed wavelengths will be missing from the original light spectrum after it has passed through the sample.

Absorption spectroscopy

- Since most atoms and many molecules have unique and identifiable energy levels, a measurement of the missing absorption lines allows identification of the absorbing species.

- Absorption within a continuous band of wavelengths is also possible.

Absorption spectroscopy

- This is particularly common when there is a high density of absorption lines that have been broadened by strong perturbations by surrounding atoms (e.g., collisions in a high-pressure gas or the effects of near neighbours in a solid or liquid).

Emission spectroscopy

- The second main type of spectroscopy, emission spectroscopy, uses some means to excite the sample of interest.
- After the atoms or molecules are excited, they will relax to lower energy levels, emitting radiation corresponding to the energy differences, $\Delta E = h\nu = hc/\lambda$, between the various energy levels of the quantum system.

- In its use as an analytical tool, this fluorescence radiation is the complement of the missing wavelengths in absorption spectroscopy. Thus, the emission lines will have a characteristic “fingerprint” that can be associated with a unique atom, ion, or molecule.

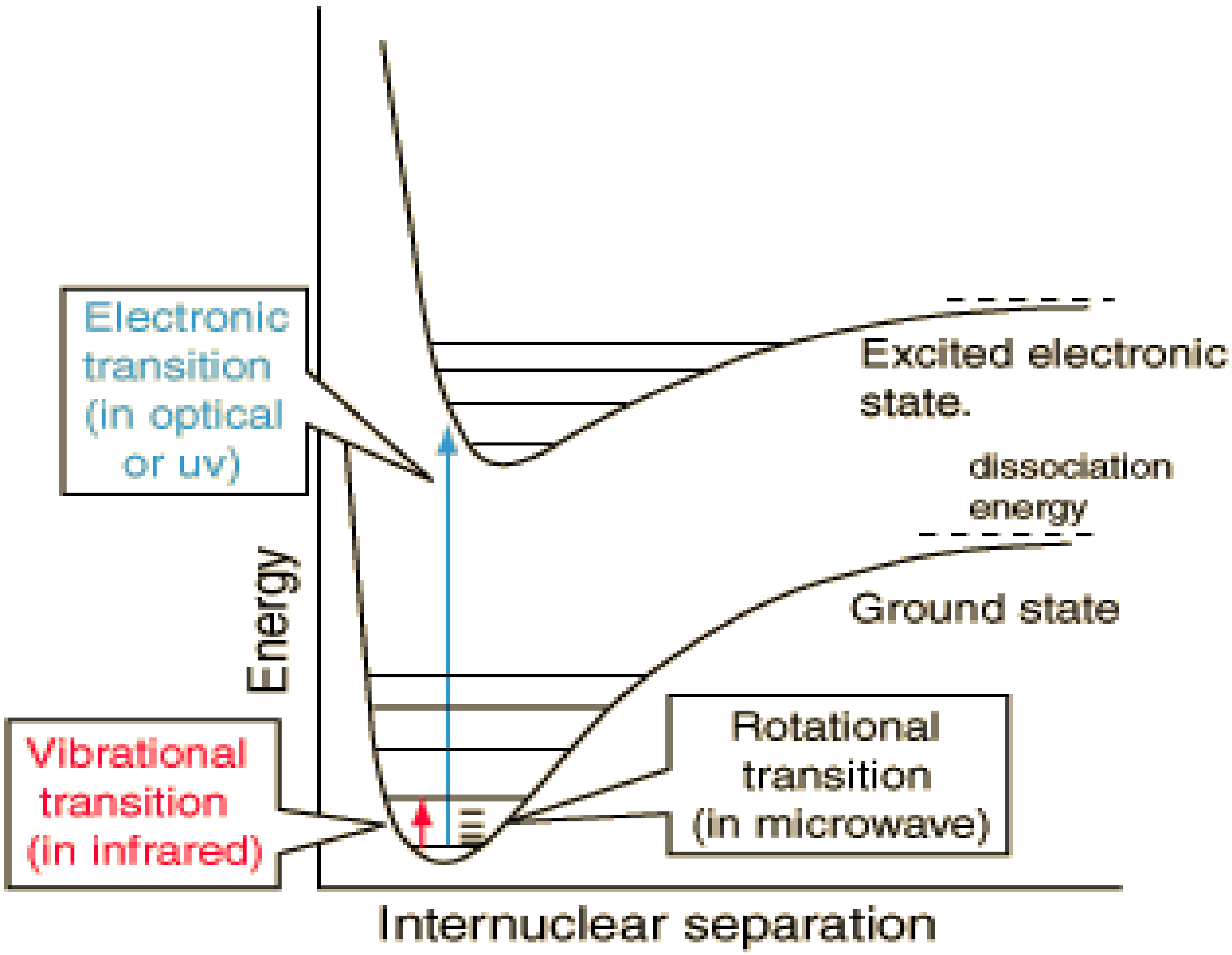
Emission spectroscopy

- Early excitation methods included placing the sample in a flame or an electric-arc discharge.
- The atoms or molecules were excited by collisions with electrons, the broadband light in the excitation source, or collisions with energetic atoms. The analysis of the emission lines is done with the same types of spectrometer as used in absorption spectroscopy.

- Atomic particles – gaseous states – emits radiation containing only few wavelengths – discontinuous spectrum or line spectrum
- Atomic particles – closely packed particles or molecules produce continuous radiation –Continuous spectrum
- Solid particles – heated to incandescence – Thermal radiation – produce continuous spectra

Atomic Absorption:

- Mono atomic particles –absorption spectra consisting of few well-defined frequencies called absorption lines.
- Polyatomic particles - Absorption spectra is more complex as the number of energy states is enormous.
- The energy associated with the bands of a molecule is made up of three components – electronic, vibrational and rotational
- Molecular spectrum – band spectrum – consists of a closely spaced absorption lines



Electronic transition (in optical or uv)
Excited electronic state.
dissociation energy
Ground state
Energy
Vibrational transition (in infrared)
Rotational transition (in microwave)
Internuclear separation

Interaction of EMR with matter

- **Absorption** – Light is absorbed
- **Emission**–Light is emitted or released
- **Transmission**– light is allowed to pass through
- **Reflection**– light is reflected or bounced away
- **Diffraction**– shows wave nature
- **Refraction**– shows particle nature
- **Interference**– light is disturbed
- **Scattering**– light is dispersed
- **Polarization**– light vibration is restricted to one direction

Spectroscopy in Astronomy

- In astronomy the study of the spectral emission lines of distant galaxies led to the discovery that the universe is expanding rapidly and isotropically (independent of direction).

Mars Exploration Mission

The Mars Exploration Rovers were launched with the goal of searching for and analyzing rock and soils on Mars. They utilized several spectrometers to analyze samples.

Mini-TES: **mini**ature **t**hermal **e**mission **s**pectrometer (examine rock, soil & atmosphere)

MB: **M**ossbauer **S**pectrometer (examine mineralogy of rocks & soils)

APXS: **A**lpha **P**article **X**-ray **S**pectrometer (analyze elements in rocks & soils)

The SIR-2 instrument is an infrared spectrometer build for remote sensing of the lunar surface. SIR-2 (Spectrometer Infra Red) represents the German scientific contribution to the Indian Chandrayaan-1 lunar mission

- Map lunar surface composition by infrared fingerprints of minerals
- Learn more about lunar history and formation from the composition of different surface features (Mare, Crater Peaks) and the changes in the continuum slope over the Moon

- Search for the presence of water in the form of hydrated minerals or ices at the lunar poles in the permanently shaded areas
- Extend the scientific knowledge about resources for a later human exploration of the Moon

- In Chandrayaan-2, CLASS (Chandrayaan-2 Large Area Soft X-ray spectrometer) measures the Moon's X-ray Fluorescence (XRF) spectra to examine the presence of major elements such as Magnesium, Aluminium, Silicon, Calcium, Titanium, Iron, and Sodium. The XRF technique will detect these elements by measuring the characteristic X-rays they emit when excited by the Sun's rays

Thank you