Molecular Spectroscopy

Introduction

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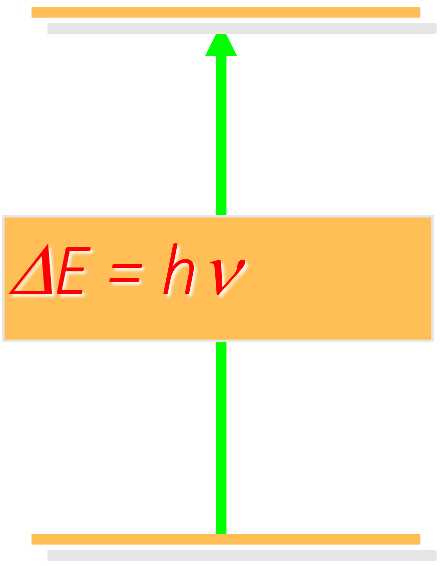
SPECTROSCOPY

- Interaction of Electromagnetic Radiation with matter (sample)
- The study of molecular or atomic structure of a substance by observation of its interaction with electromagnetic radiation
- QUANTITATIVELY - For determining the amount of material in a sample
- QUALITATIVELY – For identifying the chemical structure of a sample

Molecular interaction with electromagnetic radiation



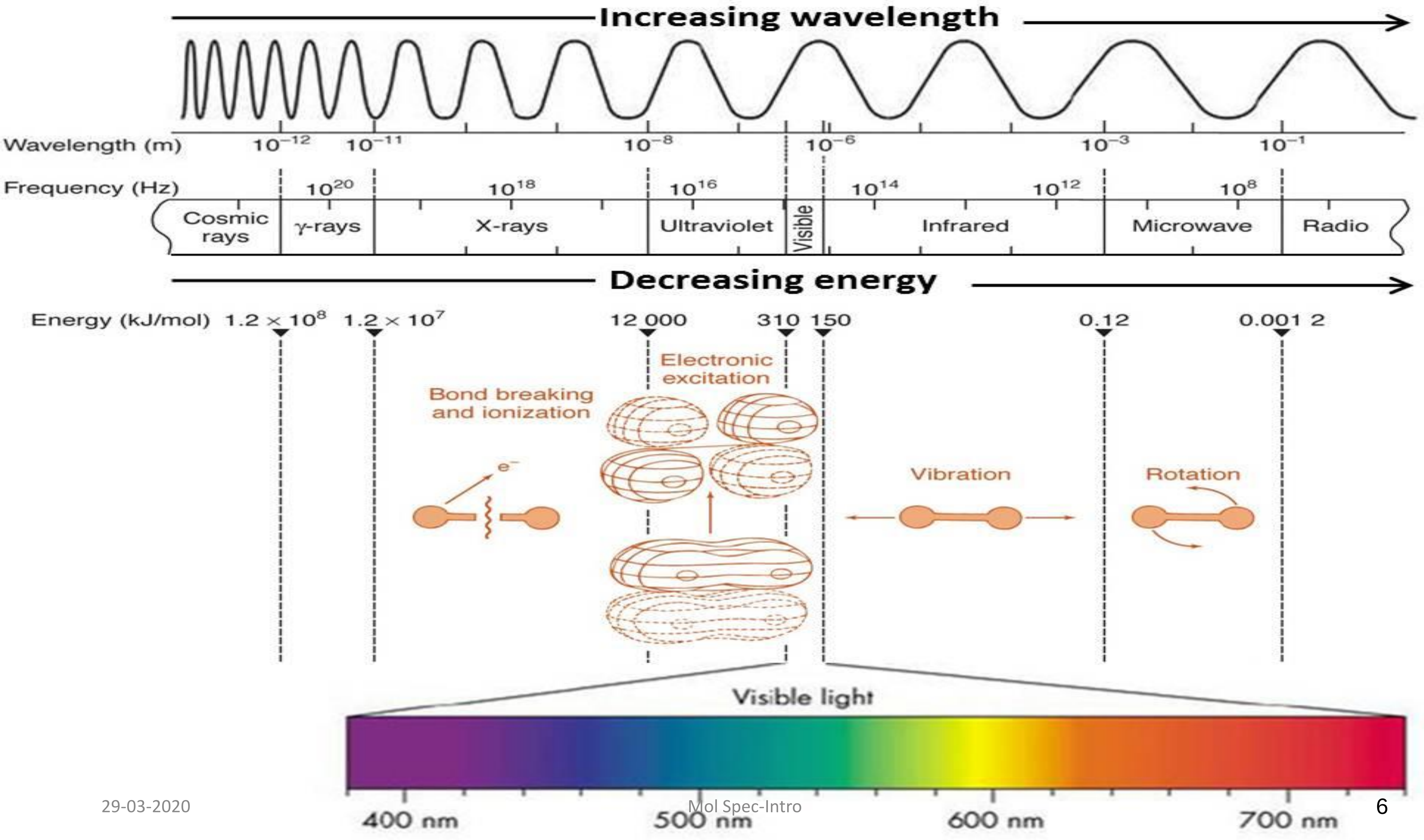
Electromagnetic radiation is absorbed when the energy of photon corresponds to difference in energy between two states.

THE ELECTROMAGNETIC SPECTRUM

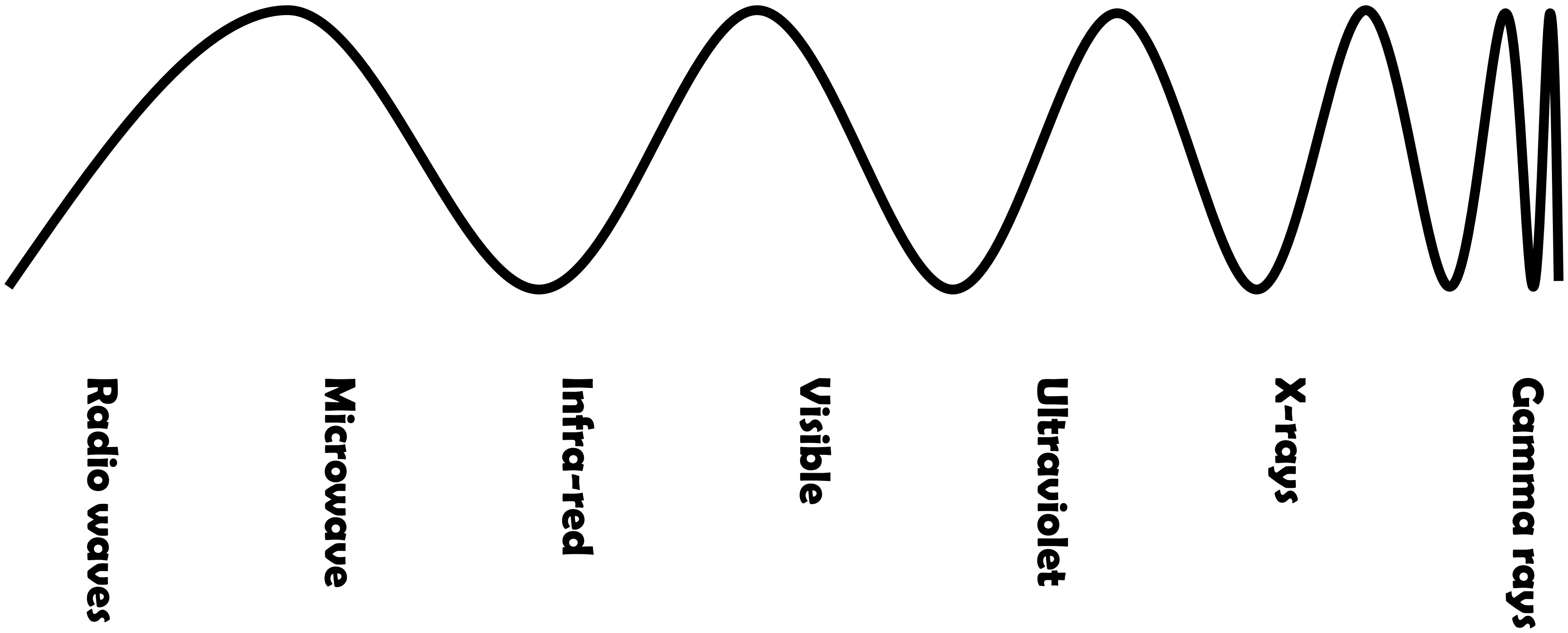
- **Most of us are aware of many different ways of transmitting energy and these phenomena come together in one physical entity called the ELECTROMAGNETIC SPECTRUM**
- **The difference between these *sources of radiation* is the amount of *energy* they radiate.**
- **The radiation from these and other sources covers a range of energies**

Strength of radiation energy will interact with molecules in different ways

- High energy sources produce breaking of bonds
  - X-Ray, γ-Rays
- Medium energy sources excite electrons
  - UV / VISIBLE Spectroscopy
- Low energy sources produce vibrations in chemical bonds
  - Infrared Energy
- Very low energy sources produce rotation of the chemical bonds
  Microwaves
- Further lower energy source produce inversion of nuclear spin state
  - Radio waves


Increasing wavelength
Wavelength (m)
10−12
10−11
10−8
10−6
10−3
10−1
Frequency (Hz)
1020
1018
1016
1014
1012
108
Cosmic rays
γ-rays
X-rays
Ultraviolet
Visible
Infrared
Microwave
Radio
Decreasing energy
Energy (kJ/mol)
1.2 × 108
1.2 × 107
12 000
310
150
0.12
0.001 2
Electronic excitation
Bond breaking and ionization
e−
Vibration
Rotation
Visible light
400 nm
500 nm
600 nm
700 nm

The Electromagnetic Spectrum



Long ← **Wavelength** ← **Short**

Low → **Energy** → **High**

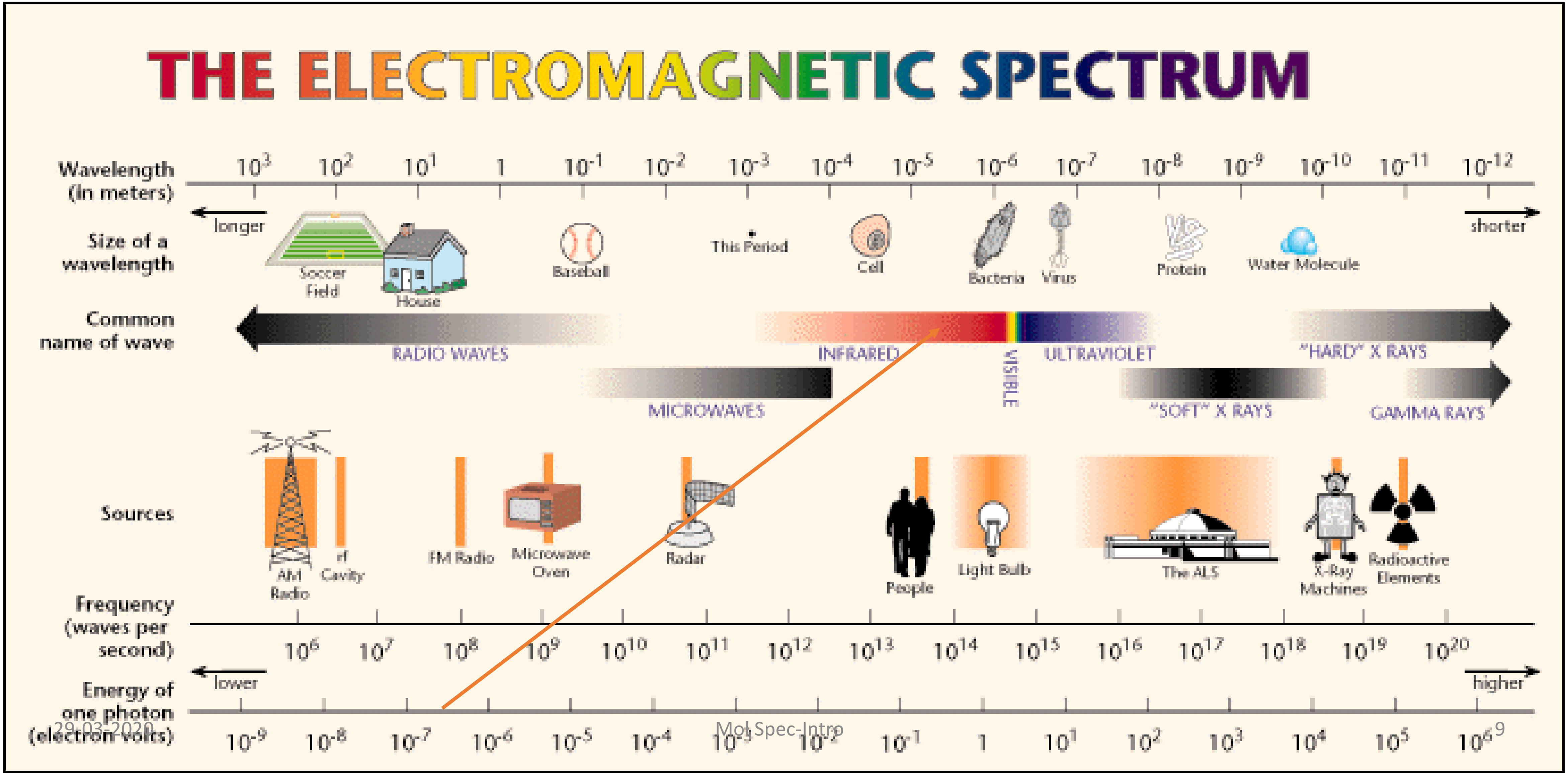
Low → **Frequency** → **High**

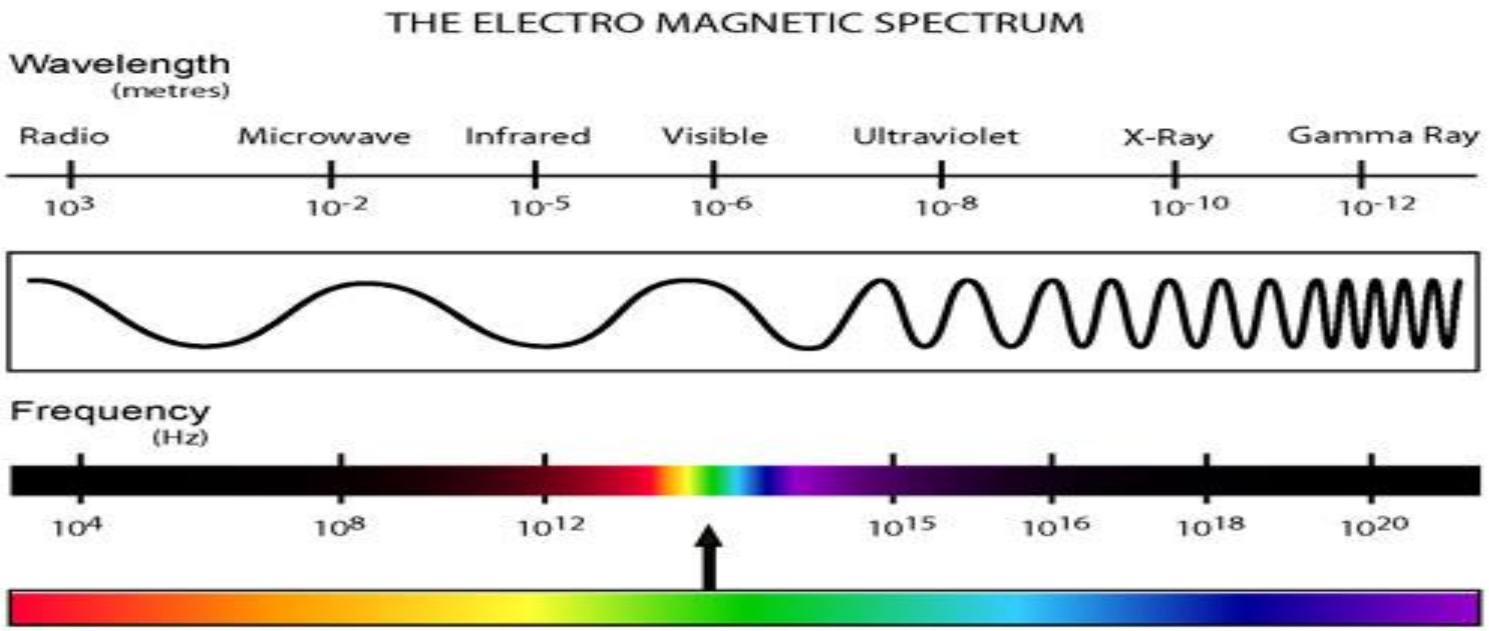
Molecules have electromagnetic fields derived from their electrons and nuclei

We saw earlier that plane-polarized light interacts by being rotated by an enantiomer

Energy varies across the spectrum and matches that required for various interactions.

Where in the spectrum are these transitions?





Radiowave: **NMR**

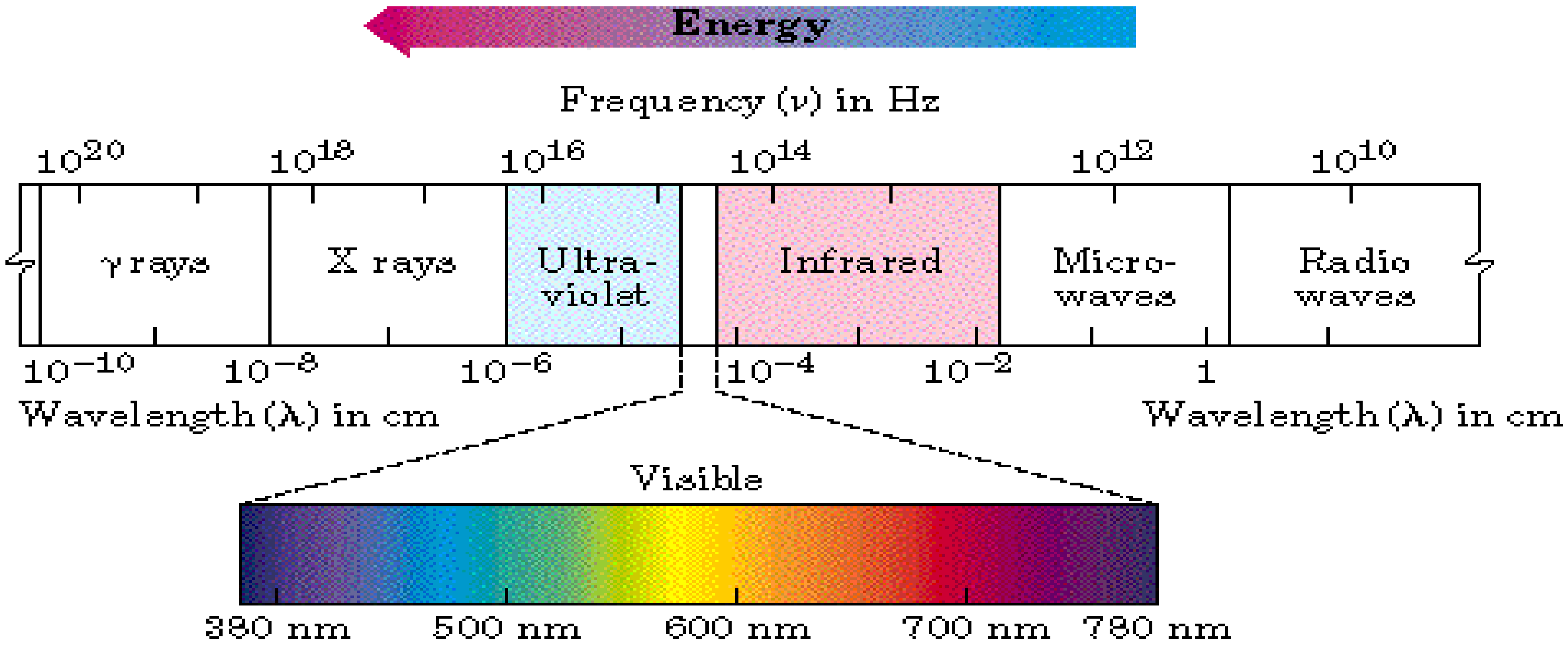
Microwave: **ESR, EPR, Rotational Spectroscopy**

Infrared: **Vibrational spectroscopy**

UV-Visible: **Electronic Spectroscopy**

UV-X-Ray: **Photo Electron Spectroscopy**

Gamma Ray: **Mössbauer Spectroscopy**



Energy increases going to the left

Ultraviolet and visible have sufficient energy to effect electronic transitions.

Infrared has sufficient energy only to effect transitions between vibrational energy states.

Microwave has only enough energy to effect transitions between rotational energy states.

Radio waves have insufficient energy to effect molecules but affect nuclear spin energy states found in magnetic fields. This latter interaction is most important because it is used in Nuclear Magnetic Resonance spectroscopy.

Emission Spectroscopy

Thermal or electrical excitation of atoms leading electrons to metastable state. The electrons jump to ground state releasing some energy as radiation. This radiation is analyzed with spectroscope. Ex: Fluoroscence, Phosphorescence

Absorption Spectroscopy

Substances are excited by electromagnetic radiation and energy of certain wavelength are absorbed by the substance which are characteristics of some functionalities. These missing wavelengths can be detected by allowing the light coming from the sample to fall on a photographic plate or other device. These pattern of spectral lines (corresponding to the wavelengths absorbed) are called absorption spectra. After absorption, the transmitted light is analyzed by a spectrometer relative to the incident light of given frequency.

Ex: UV-Vis, IR,NMR etc.

Spectroscopy	Energy levels	Selection rule
NMR/ ESR	Zeeman level	$\Delta m = \pm 1$ Ext B perp to B of light
Microwave	Rotational level	$\Delta J = \pm 1$ Molecule must be polar
Infrared	Vibrational level	$\Delta V = \pm 1$ Dipole mom must change
UV-Vis	Electronic level	Spin selection rule Franck-Condon Principle

Spectroscopy (Molecular Absorption Spectroscopy)
Interaction of light with molecules

Radiation absorbed	Effect on the molecule of a substance and information obtained
(*i*) **Ultra-violet** (190–400 nm) and **visible** (400–800 nm)	Changes in electronic energy levels within the molecule, conjugated unsaturation, conjugation with non-bonding electrons, extent of π-electron system.
(*ii*) **Infra-red** 667 – 4000 cm^{-1}	Changes in the vibrational and rotational movements of the molecule. Detection of almost all functional groups which have specific vibrational frequencies such as C = O, O—H, NH_2, C ≡ C etc.
(*iii*) **Radio-frequency** Frequency 60-300 MHz	Nuclear magnetic resonance, induces changes in the magnetic properties of certain atomic nuclei, notably that of hydrogen (hydrogen atoms in different environments can be detected, counted and analysed for structure determination.
(*iv*) **Electron beam impact** 70 eV, 6000 kJ mol^{-1}	Ionisation and fragmentation of the molecule into a spectrum of fragment ions (determination of molecular weight and deduction of molecular structure from the fragments obtained)