Instrumental Methods of Analysis

An Introduction to Spectrometric Methods

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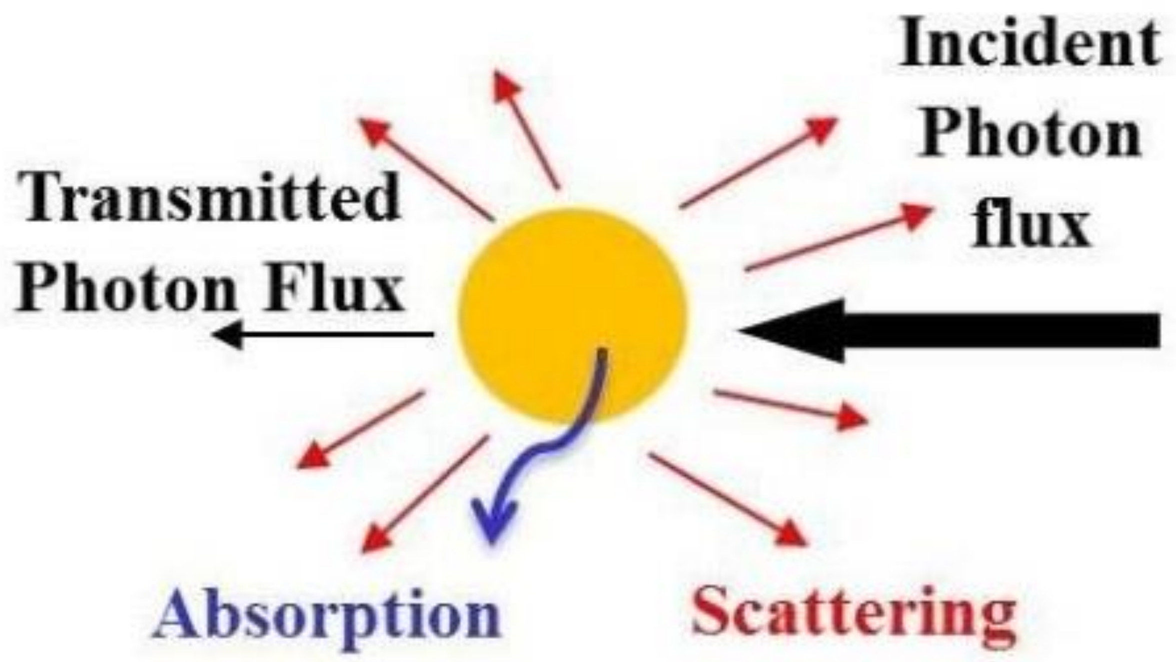
Overview of Spectroscopy

Spectroscopy is the **interactions** of **radiation** with **matter**.



Spectroscopy provide perhaps the most widely used tools for the elucidation of molecular structure as well as the quantitative and qualitative determination of both inorganic and organic compounds.

What is Electromagnetic Radiation

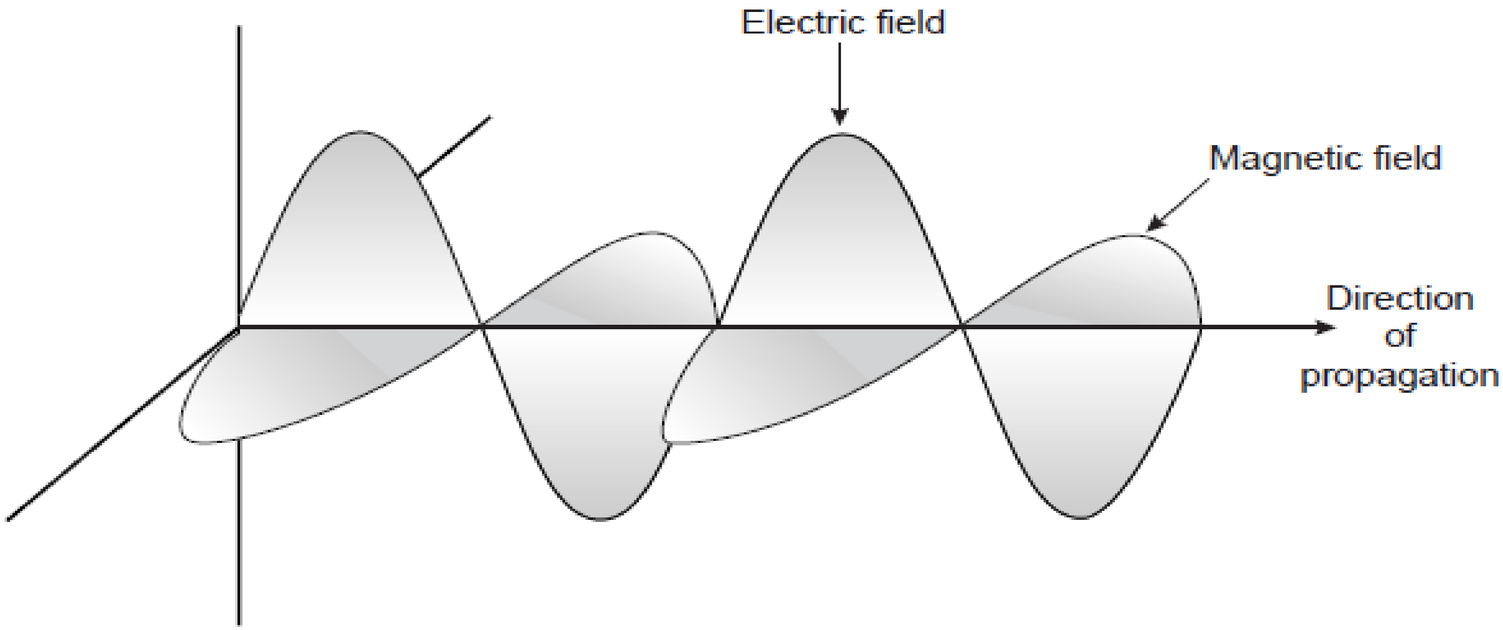
Electromagnetic radiation, or light, is a form of energy whose behavior is described by the properties of both **waves** and **particles** (dual model).

The exact nature of electromagnetic radiation remains unclear.

The dual models of wave and particle behavior provide a useful description for electromagnetic radiation.

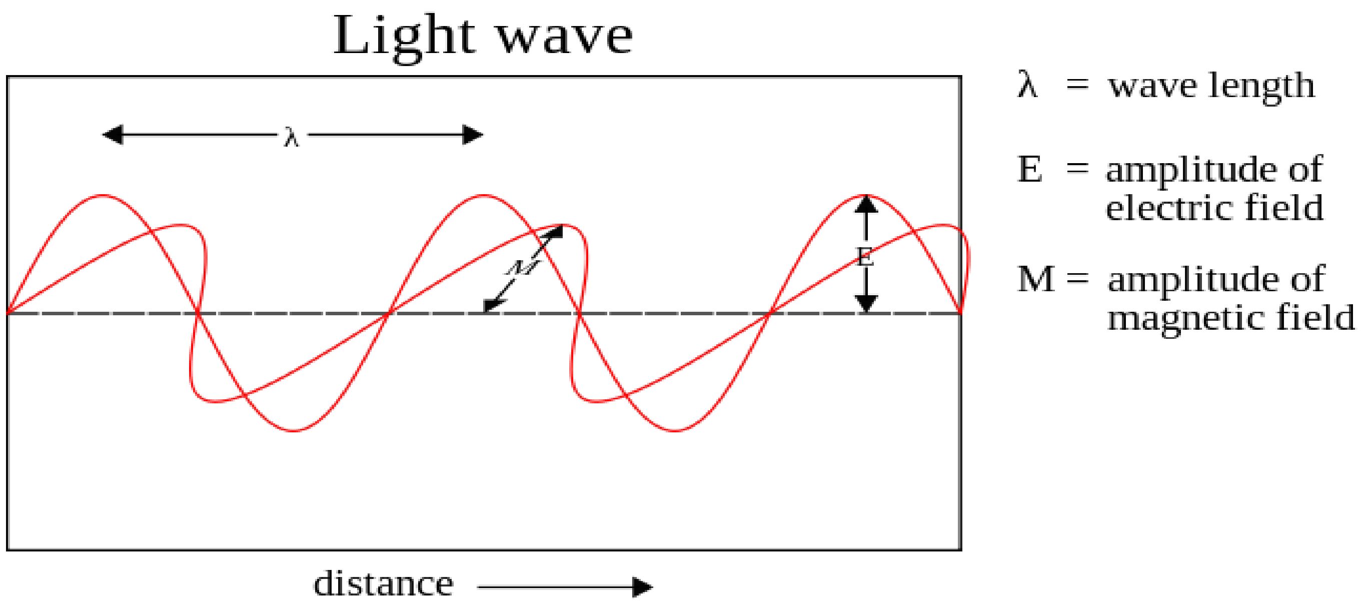
Wave Properties of Electromagnetic Radiation

Electromagnetic radiation consists of oscillating electric and magnetic fields that propagate through space along a linear path and with a constant velocity. Oscillations in the electric and magnetic fields are perpendicular to each other, and to the direction of the wave's propagation.



The interaction of electromagnetic radiation with matter can be explained using either the electric field or the magnetic field.

An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, direction of propagation, wavelength, wavenumber, power and intensity.

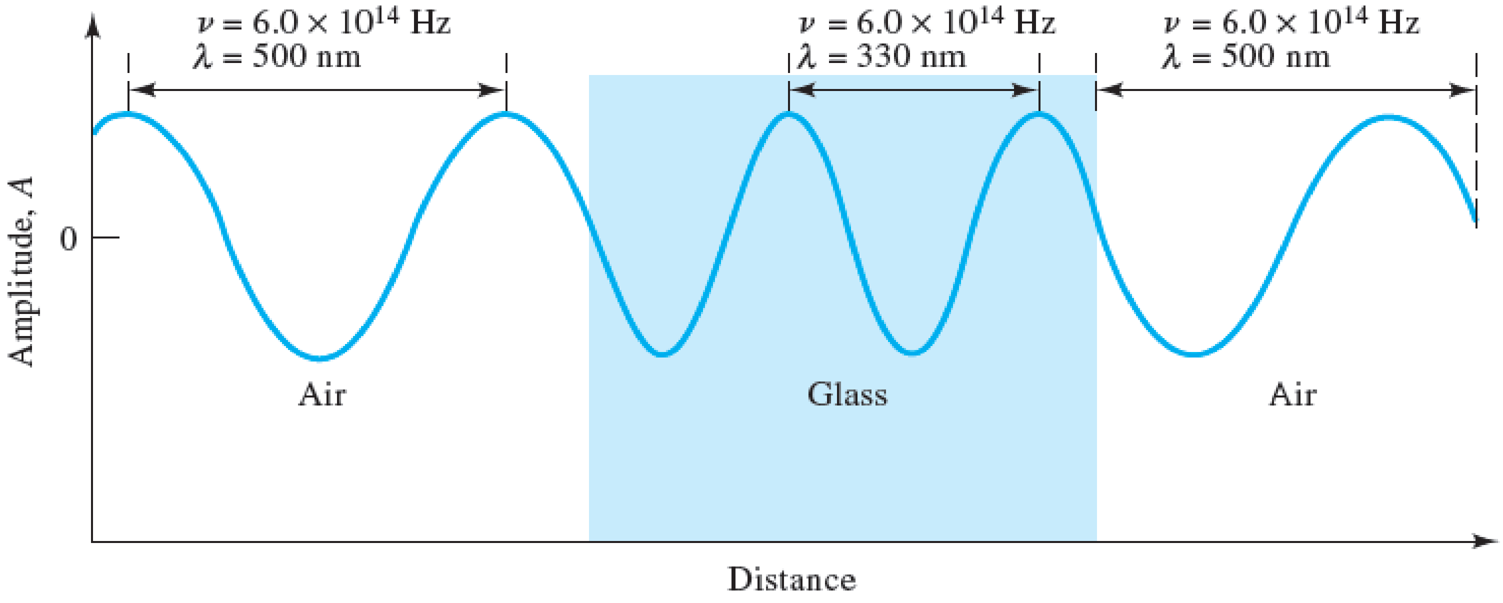


Frequency: the number of oscillations of an electromagnetic wave per second (υ).
Wavelength: the distance between any two consecutive maxima or minima of an electromagnetic wave (λ).
Wavenumber: the reciprocal of wavelength ($\bar{\upsilon}$).

$$\lambda = \frac{v}{\upsilon} = \frac{c}{\upsilon} \qquad \bar{\upsilon} = \frac{1}{\lambda}$$

-The speed of light (in vacuum), *c,* which is 2.99792x10^8 m/s (3x10^8m/s).
-Electromagnetic radiation moves through a medium other than a vacuum with a velocity, *v,* less than that of the speed of light in a vacuum.

Effect of change of medium on a monochromatic beam of radiation.



Radiation velocity and wavelength both decrease as the radiation passes from a vacuum or from air to a denser medium. Frequency remains constant.

The **refractive index**, η,

Refractive index of a medium measures the extent of interaction between electromagnetic radiation and the medium through which it passes.

The refractive index of a material is defined as the ratio of the speed of light in a vacuum to the speed of light in that material. ratio of the speed of light in a vacuum to the speed of light in that material.

$$\eta = \frac{c}{v}$$

For example, the refractive index of water at room temperature is 1.33, which means that radiation passes through water at a rate of (c / 1.33) or 2.26×10^{10} cms^{-1}.
In other words, light travels 1.33 times slower in water than it does in vacuum.

Material	η
Vacuum	1
Gases at 0 ºC and 1 atm	
Air	1.000293
Helium	1.000036
Hydrogen	1.000132
Carbon dioxide	1.00045
Liquids at 20 °C	
Water	1.33
Ethanol	1.36
Olive oil	1.47
Solutions at room temperature	
NaCl	1.49
KCl	1.46
AgCl	2.0

Example:

In 1859, Gustav Kirchhoff studied the solar radiation, he showed that the dark "D" line in the solar spectrum was due to the absorption of solar radiation by sodium atoms. The wavelength of the sodium D line is 589 nm. What are the frequency and the wavenumber for this line?

Solution:

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{589 \times 10^{-9}\ \text{m}} = 5.09 \times 10^{14}\ \text{s}^{-1}$$

$1\ \text{s}^{-1} = 1\ \text{Hz}$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{589 \times 10^{-9}\ \text{m}} \times \frac{1\ \text{m}}{100\ \text{cm}} = 1.70 \times 10^{4}\ \text{cm}^{-1}$$

Particle Properties of Electromagnetic Radiation

When a sample absorbs electromagnetic radiation it undergoes a change in energy.

The interaction between the sample and the electromagnetic radiation is easiest to understand if we assume that electromagnetic radiation consists of a beam of energetic particles called **photons.**

Photon: a particle of light carrying an amount of energy equal to $h\,\upsilon$.

When a photon is absorbed by a sample, it is "destroyed," and its energy acquired by the sample.

The energy of a photon, in joules, is related to its frequency, wavelength, or wavenumber.

$$\mathbf{E = h\upsilon = \frac{hc}{\lambda} = hc\bar{\upsilon}}$$

where *h* is Planck's constant, which has a value of $6.626\text{x}10^{-34}$ J.s

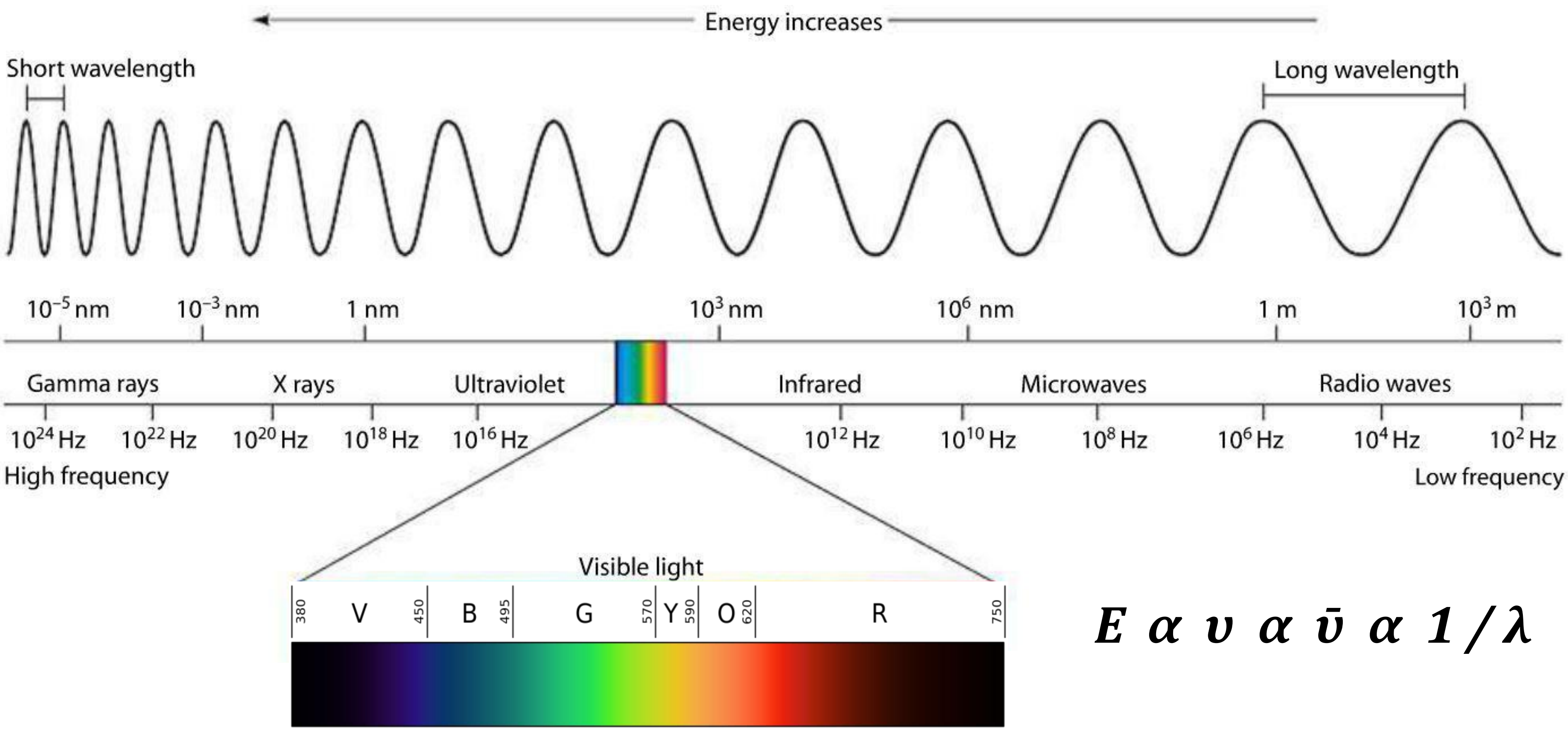
Example:

What is the energy per photon of the sodium D line (λ = 589 nm)?

Solution:

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J} \bullet \text{s})\,(3.00 \times 10^{8}\ \text{m/s})}{589 \times 10^{-9}\ \text{m}} = 3.37 \times 10^{-19}\ \text{J}$$

The Electromagnetic Spectrum



$$E \propto \nu \propto \bar{\nu} \propto 1/\lambda$$

The division of electromagnetic radiation on the basis of a photon’s energy.

The boundaries describing the **electromagnetic spectrum** are not rigid, and an overlap between spectral regions is possible.

Classification of Spectroscopic Methods

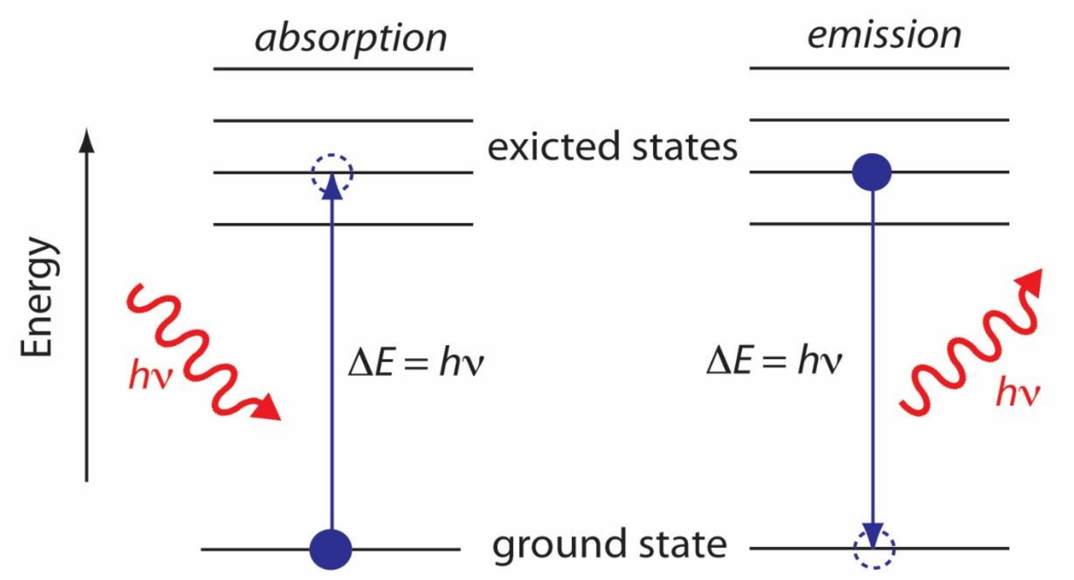
Spectroscopy is divided into two broad classes:

(1) Spectroscopies involving an exchange of energy

In this class, energy is transferred between a photon of electromagnetic radiation and the analyte. Such as absorption spectroscopy and emission spectroscopy.

Absorbance: the attenuation of photons as they pass through a sample.

Emission: the release of a photon when an analyte returns to a lower-energy state from a higher-energy state.



(2) Spectroscopies that do not involve an exchange of energy

In this class, the electromagnetic radiation undergoes a change in amplitude, phase angle, polarization or direction of propagation as a result of its refraction, reflection, scattering or diffraction by the sample.

Classification based on;
the type of radiative energy

Types of spectroscopy are distinguished by the type of radiative energy involved in the interaction.

Techniques that employ electromagnetic radiation are typically classified by the wavelength region of the spectrum and include:

- Microwave spectroscopy
- Infrared spectroscopy
- Near infrared, visible and ultraviolet spectroscopy
- X-ray spectroscopy
- Gamma spectroscopy

Classification based on;
the nature of the interaction

Types of spectroscopy can also be distinguished by the nature of the interaction between the energy and the material. These interactions include:

- **Absorption** occurs when energy from the radiative source is absorbed by the material.
- **Emission** indicates that radiative energy is released by the material.
- **Elastic scattering and reflection** spectroscopy determine how incident radiation is reflected or scattered by a material.
- **Impedance spectroscopy** studies the ability of a medium to impede or slow the transmittance of energy.
- **Inelastic scattering** phenomena involve an exchange of energy between the radiation and the matter that shifts the wavelength of the scattered radiation.
- **Coherent or resonance** spectroscopy are techniques where the radiative energy couples two quantum states of the material in a coherent interaction that is sustained by the radiating field.

Classification based on;
the type of material

(1) Atoms

Atomic spectroscopy is a technique which deals with the determination of atomic or elemental analysis (usually shorter wavelengths are used). Since unique elements have characteristic (signature) spectra, atomic spectroscopy, specifically the electromagnetic spectrum or mass spectrum, is applied for determination of elemental compositions.

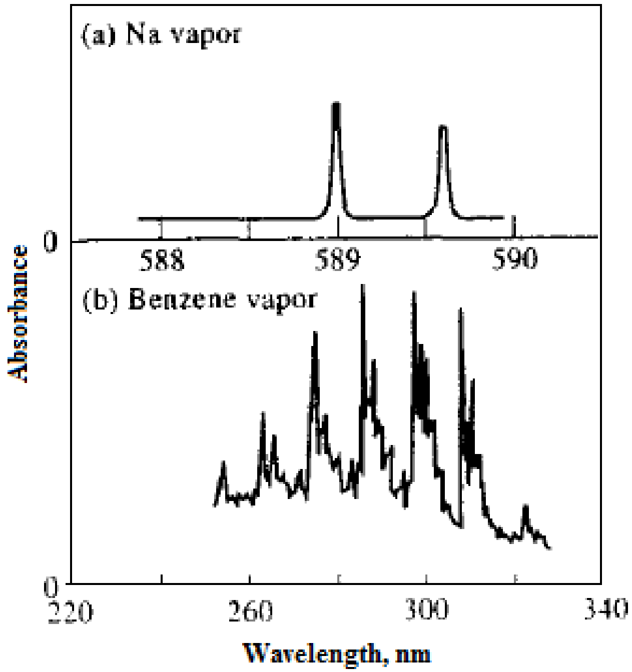
(2) Molecules

Molecular spectroscopy technique of determination of the structure of the molecule by shining the beam of light on the analyte and studying its vibrations and rotations using various instruments (usually longer wavelengths are used).

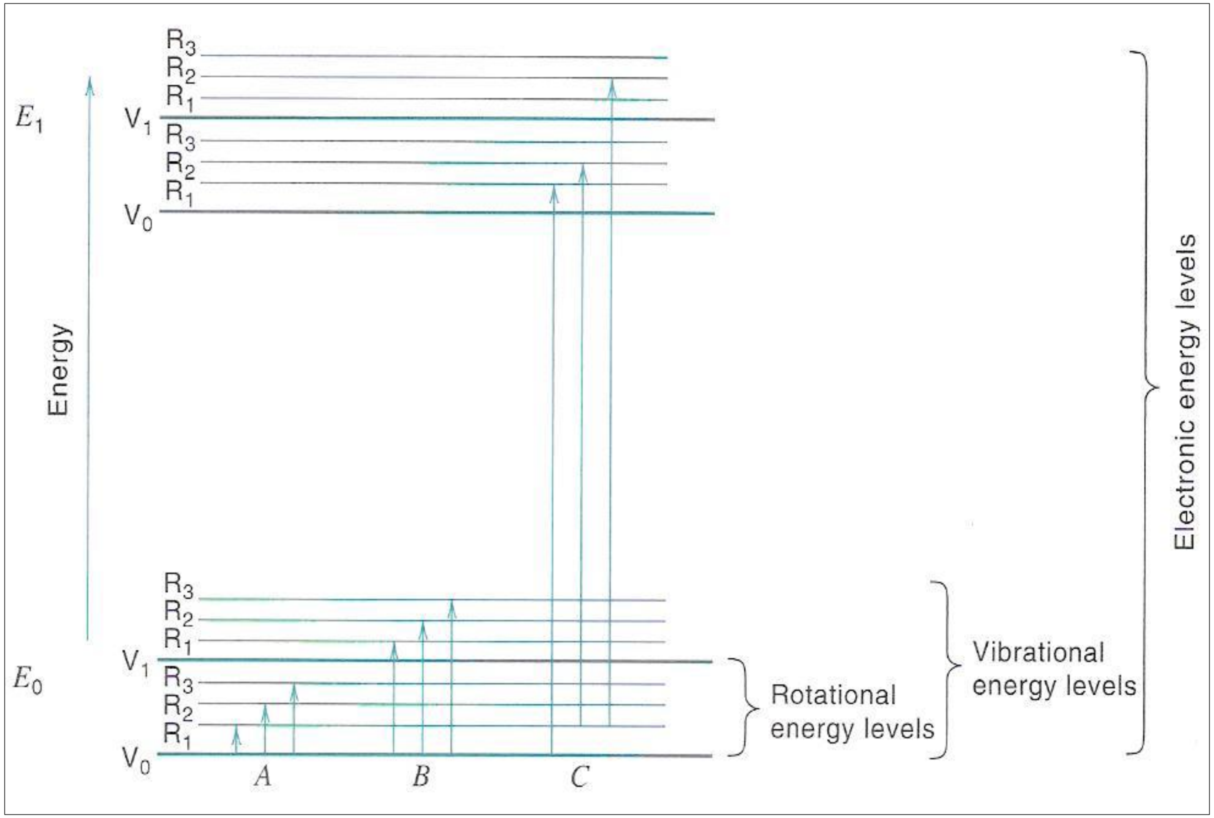
(3) Nuclei

Nuclei also have distinct energy states that are widely separated and lead to gamma ray spectra. Distinct nuclear spin states can have their energy separated by a magnetic field, and this allows for NMR spectroscopy.

Atomic vs. Molecular spectra

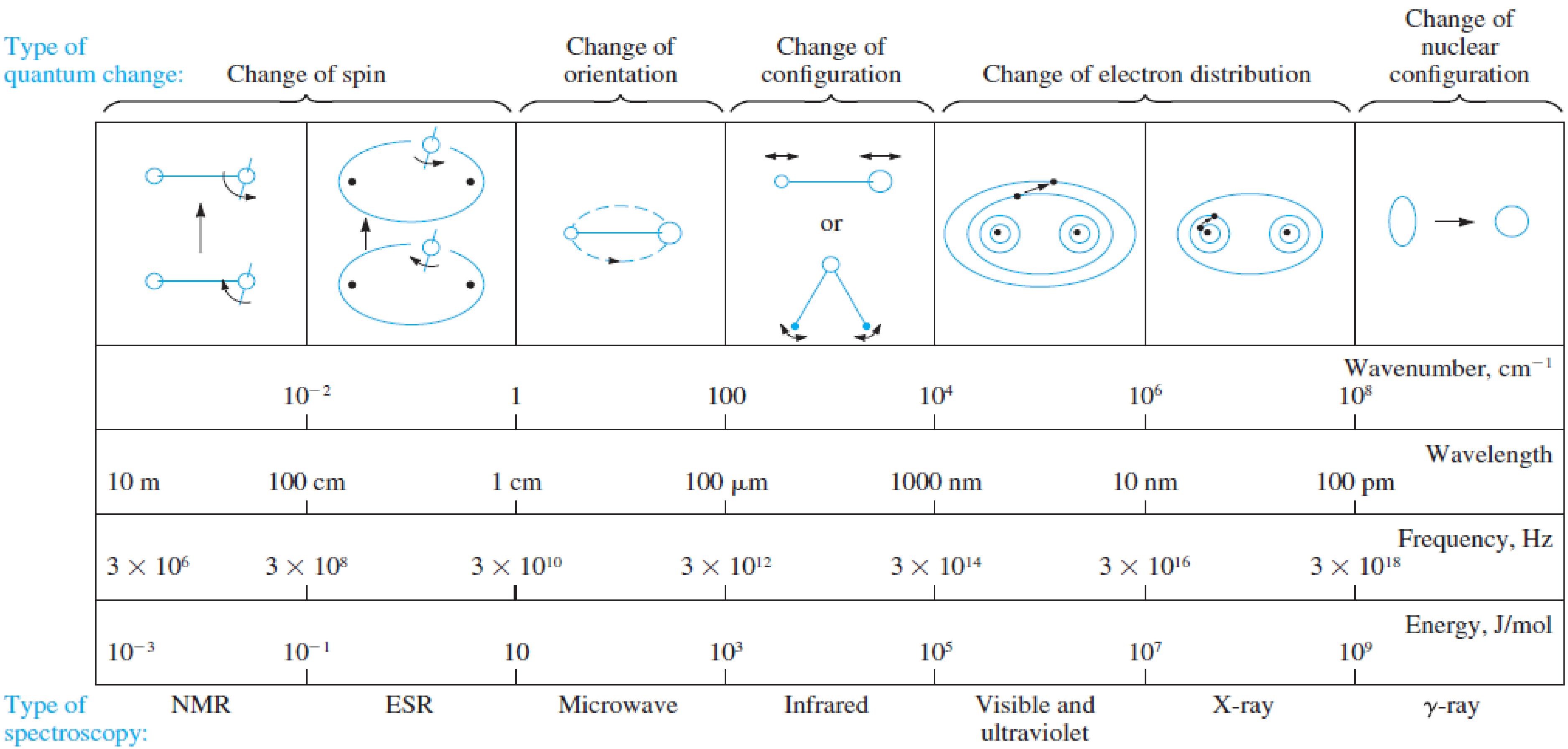


Molecular spectra are considerably more complex than atomic spectra because the number of energy states of molecules is generally enormous when compared with the number of energy states for isolated atoms. No vibrational and rotational transitions for atoms.



rotational-vibrational-electronic transitions

Spectroscopy is possible only if the photon's interaction with the sample leads to a change in one or more of the electromagnetic radiation characteristic properties (energy, velocity, amplitude, frequency, phase angle, polarization and direction of propagation).



The regions of the electromagnetic spectrum. Interaction of an analyte with electromagnetic radiation can result in the types of changes shown.

Type of spectroscopy	Wavelength range	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
Ultraviolet absorption	10-180 nm	Bonding electrons
Ultraviolet-visible absorption, emission and fluorescence	180-780 nm	Bonding electrons
Infrared absorption and Raman scattering	0.78-300 μm	Rotation/vibration of molecules
Microwave absorption	0.75-3.75 mm	Rotation of molecules
Electron spin resonance	3 cm	Spin of electrons in a magnetic field
Nuclear magnetic resonance	0.6-10 m	Spin of nuclei in a magnetic field


Thank You!