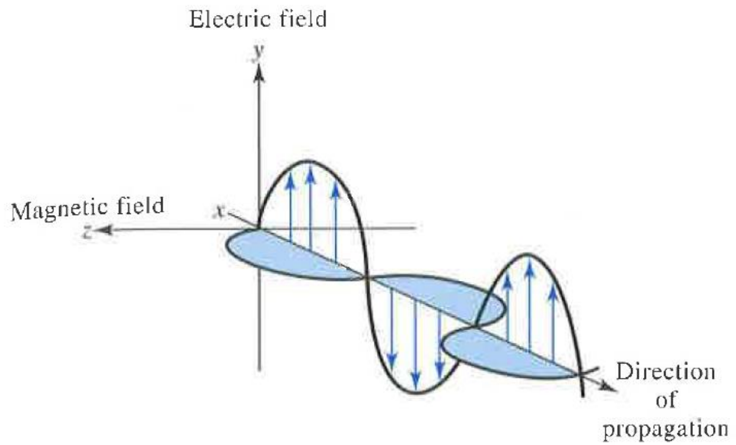
Wave Properties of Electromagnetic Radiation

Two options are available for analytical utility when an analyte interacts with a beam of electromagnetic radiation in an instrument

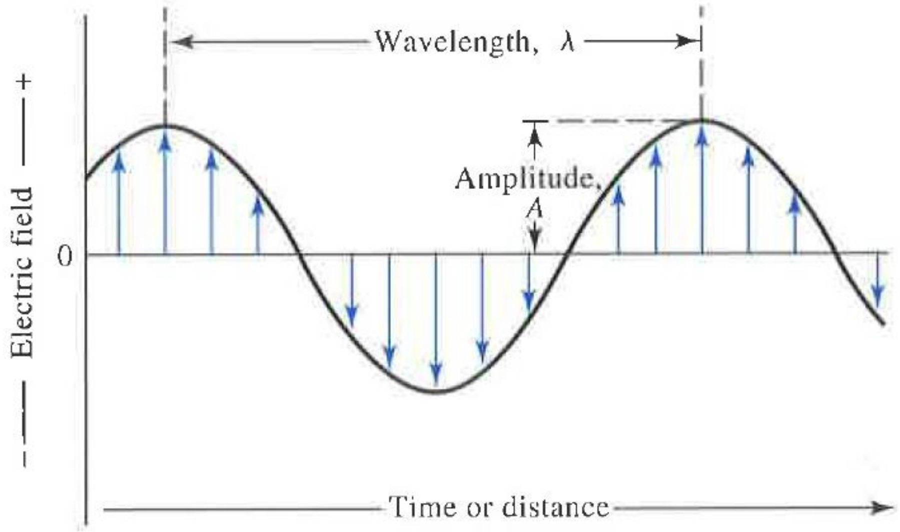
1. We can monitor the changes that occur in the radiation after the interaction, or
   - In this case, wave properties of the electromagnetic radiation is useful in understanding analytical interpretations
   - Upon interaction with matter, electromagnetic radiation can undergo:
     diffraction, transmission, refraction, reflection, scattering, etc.

2. We can study the changes that occur in the analyte itself
   Such changes are quantized, and are utilized in most Spectrochemical methods

Wave Properties of Electromagnetic Radiation



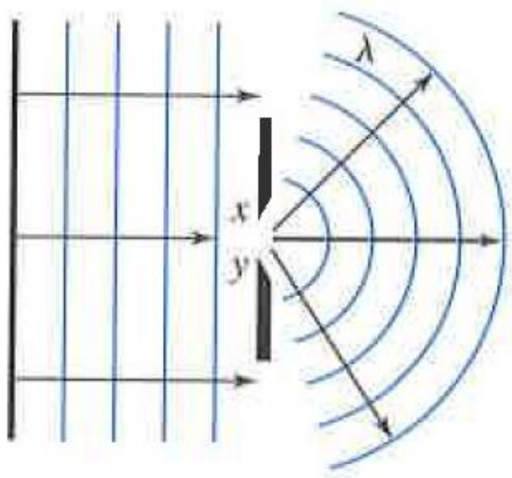
plane-polarized wave

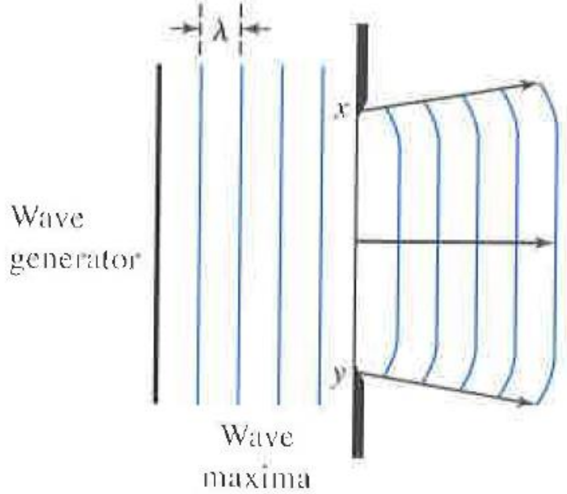


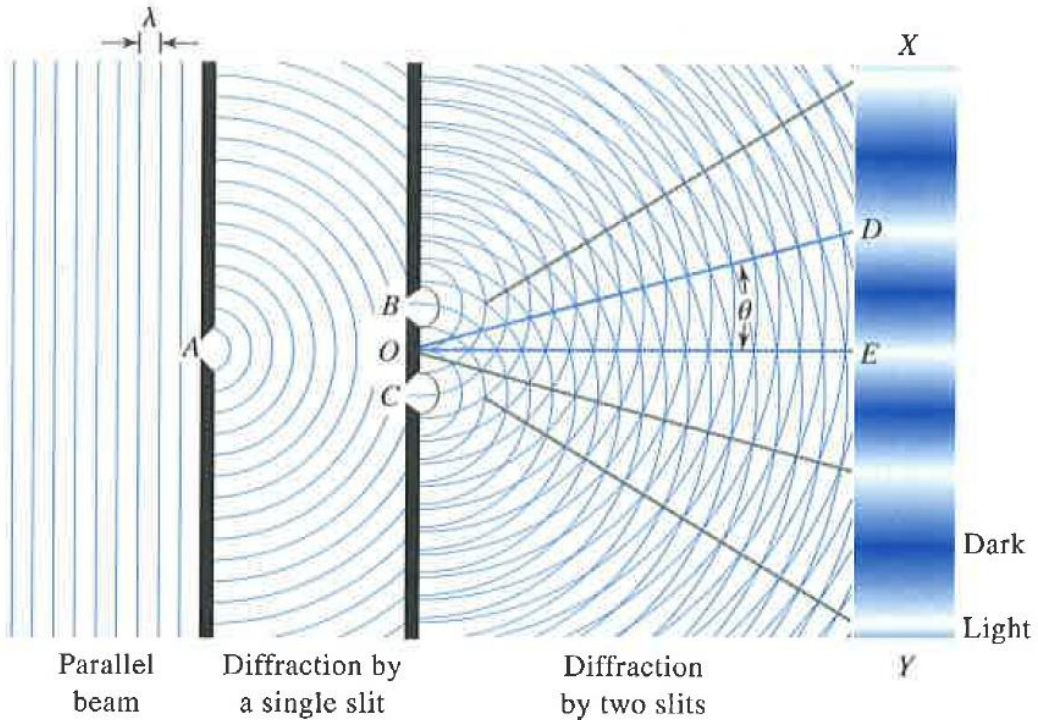
Oscillation of only the electric field

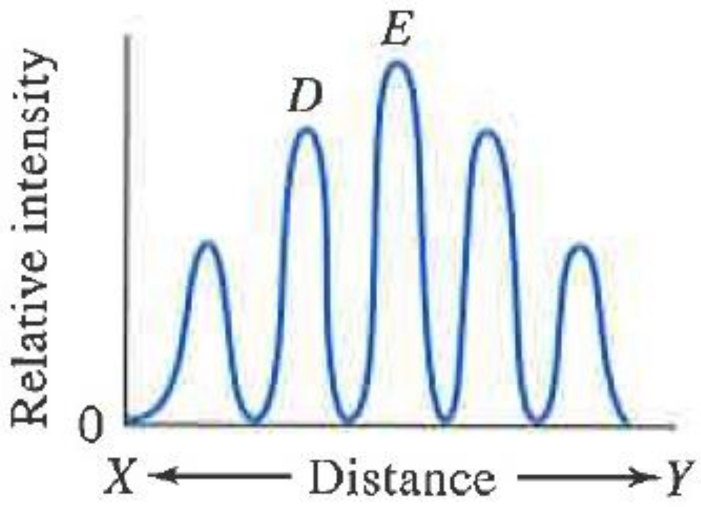
- The electric field is responsible for most phenomena that are of interest in chemical instrumentation
- The magnetic field is responsible for radio frequency absorption in NMR spectroscopy

Diffraction of Radiation









Transmission of Radiation

Interactions involved in transmission is attributed to periodic of atoms or molecular species that make up the medium polarization

polarization refers to temporal deformation of electron clouds associated with atoms and molecules that is brought about the alternation electromagnetic field

The energy required for the polarization is momentarily retained (10^{-15} seconds) by the species involved, and is re-emitted as the substance returns to it’s original state

No energy is absorbed, but the rate of propagation of the radiation is slowed by the time needed for retention and re-emission to occur.

Transmission of Radiation

Refractive Index (n_i):

$$n_i = \frac{c}{v_i}$$

n_i = refractive index at specific frequency, i
v_i =velocity of the radiation in the medium
c = velocity in vacuum

Dispersion→ variation of refractive index with frequency or wavelength

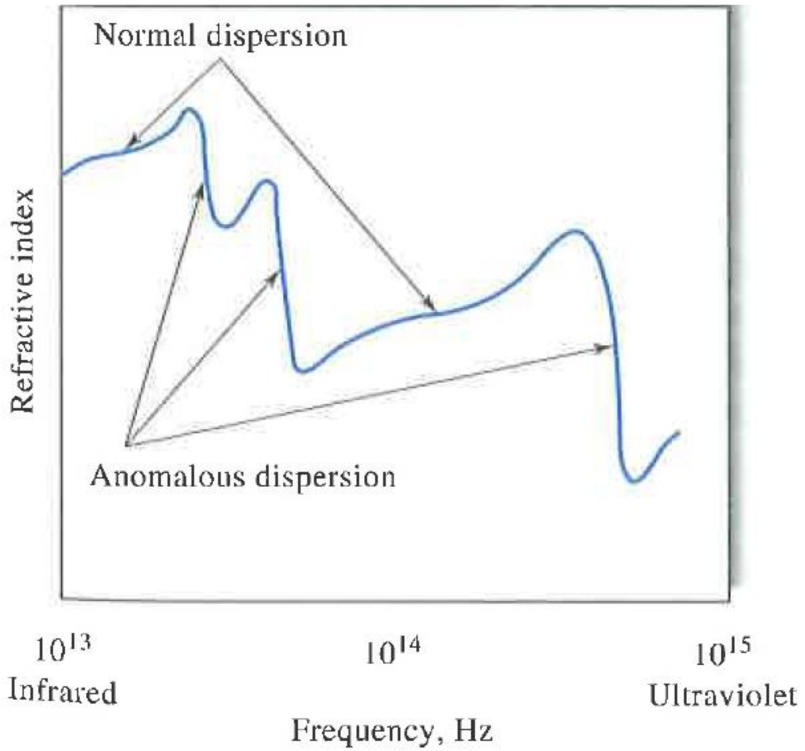
Normal Dispersion: gradual increase in n_i with frequency

Anomalous Dispersion: sharp changes in n_i with frequency

- At such frequencies, permanent energy transfer occur, and absorption of the beam is observed

Instrumental Significance

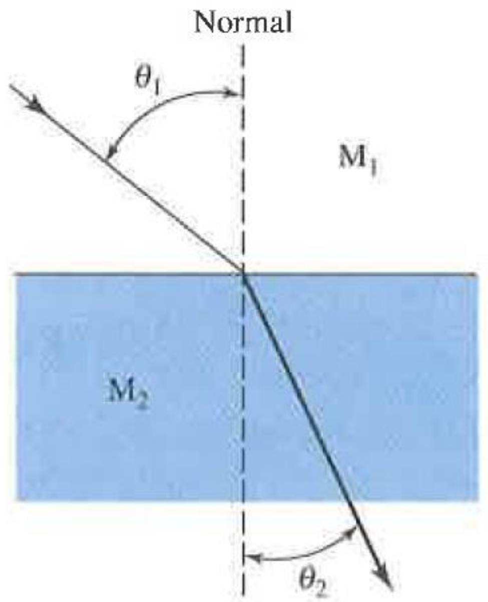
- A material that exhibit normal dispersion is good for the manufacturing of lenses
- A material that exhibit anormalous dispersion is highly frequency dependent, and is selected for fabrication of prisms



Refraction of Radiation

Refraction:

The change in direction as a beam passes one medium to the other is a consequence of differences in velocity (*v*) of the radiation n the two media that have different densities (*n*)



Snell's law:

$$\frac{sin\theta_1}{sin\theta_2} = \frac{n_1}{n_2} = \frac{v_1}{v_2}$$

$$n_{vac} = 1.0027n_{air}$$

Reflection of Radiation

$$\frac{I_r}{I_o} = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2}$$

Reflection always occurs when a beam crosses an interface between media that differ in refractive index

The fraction of reflected radiation increases with increasing differences in refractive index

Scattering of Radiation

Transmission of radiation → momentary retention of the radiant energy by matter, followed by re-emission of the radiation in all directions

For small molecules → path of beam appears to be unchanged as a consequence of destructive interference

For large molecules → destructive interference is incomplete, and small fraction of the emitted radiation is transmitted at all angles. Intensity of the scattered beam increases with particle size.

Rayleigh Scattering:

- Scattering of light by molecules significantly smaller than the wavelength of the radiation

Mie Scattering:

- With large molecules, scattering can be different in different directions.
- Measurement of type of scattered radiation is used to determine the size and shape of large molecules, including colloidal particles

Raman Scattering:

- The Raman scattering effect differs from ordinary scattering in that part of the scattered radiation suffers quantized frequency changes
- These changes are the result of vibrational energy level transitions that occur in the molecule as a consequence of the polarization

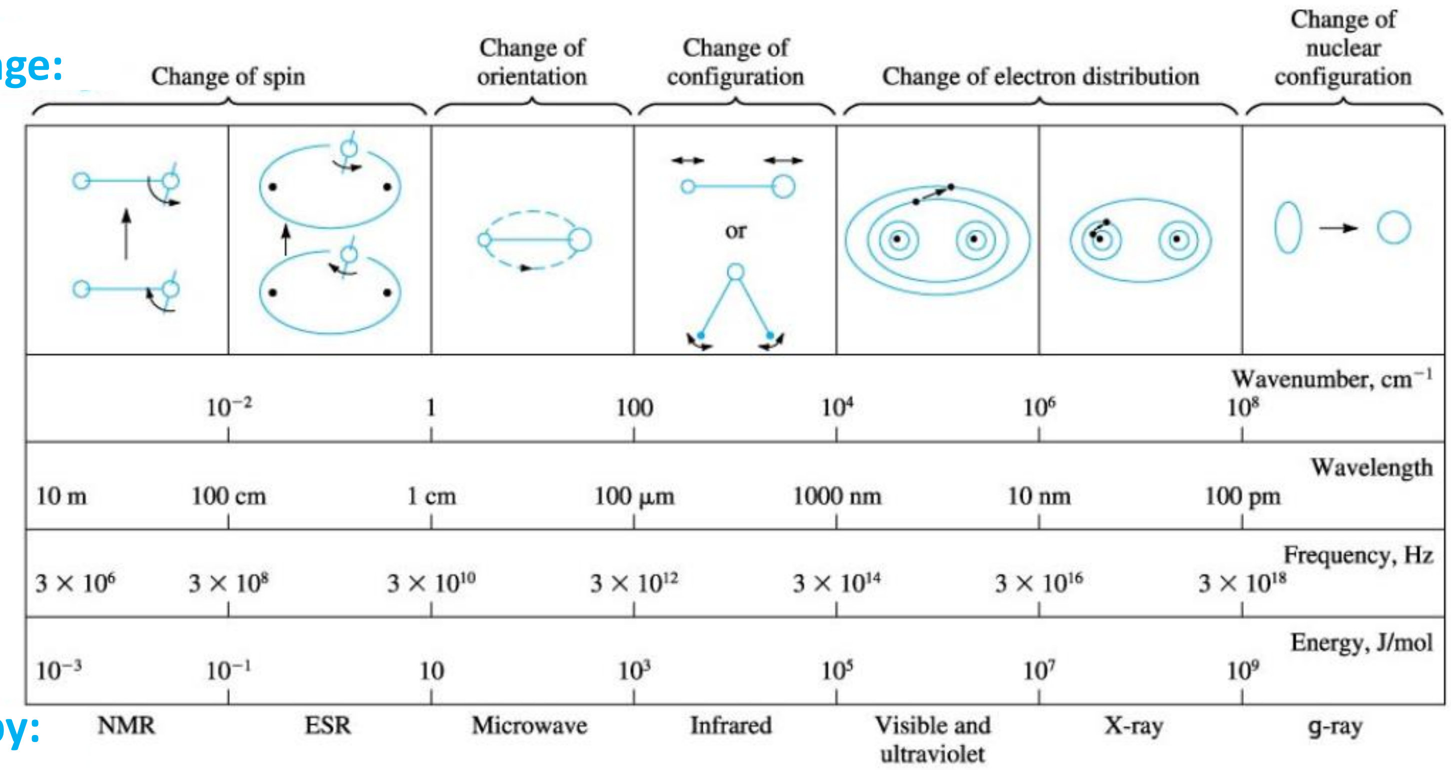
Spectrochemical method

Focuses on the measurement of the amount of radiation produced or absorbed by molecular or atomic species of interest

Classified according to the region of the electromagnetic spectrum involved: X-ray, ultraviolet (UV), visible, infrared (IR), microwave, and radio frequency (RF)

The absorbed or emitted radiation is quantized!

Type of quantum change:



Type spectroscopy:

UV-Visible Spectroscopy

Principle

- Required radiation wavelength: 200 – 700
- Electrons in bonds within the molecule under electronic transitions to occupy higher energy states through absorption of the UV-Vis radiation
- Loosely bound electrons (lone pairs and π-electrons) are most susceptible to this radiation

  → these types of compounds are usually colored

Strengths

- Sensitive
- Easy to use, cheap and robust, good for quantitation
- Routine method for many industrial applications

Limitation

- Moderately selective
- Not specific
- Not applicable for mixture analysis

Infrared (IR) Spectroscopy

Principle

- Required radiation wavelength: 500 – 4000 cm^{-1}
- Bonds within the molecule under vibrational transitions through stretching and bending modes

Strengths

- Provides complete fingerprint unique to compound under investigation
- Applicable to solids, liquids and gases

Limitation

- Not quantitative
- Requires extensive sample preparation
- Not sensitive
- Technique is lacking mainly because sample handling has huge effect on the resulting spectrum

Main Applications

- Authentication of raw materials
- Used as preliminary check for the presence or absence of a particular functional group

Atomic Absorption Spectroscopy (AAS)

Principle

- Ground state gaseous atoms are produced by vaporization
- The atoms are exposed to specific line radiations generated by a lamp made from the particular metal under investigation
- Change is intensity of the light from the lamp is measured

Strengths

- Highly specific
- Quantitative

Limitation

- Applicable to only metals
- Each element requires a different lamp for its determination

Fluorescence Spectroscopy

Principle

- Certain molecules containing chromophore and rigid structure can be excited by UV/vis radiation, and will then emit the radiation absorbed at a longer wavelength
- The emitted radiation can be measured

Strengths

- Selective detection
- Very sensitive due to high signal-to-noise ratio
- Quantitative
- Widely used in bioanalysis

Limitation

- Applicable to only limited number of molecules
- Subject to interference including the presence of heavy metal ions, UV absorbing species, and temperature changes

General Instrumentation for Spectrochemical Methods

- Source of Radiation
- Wavelength Selector
- Sample Containers
- Transducers
- Measurement Systems