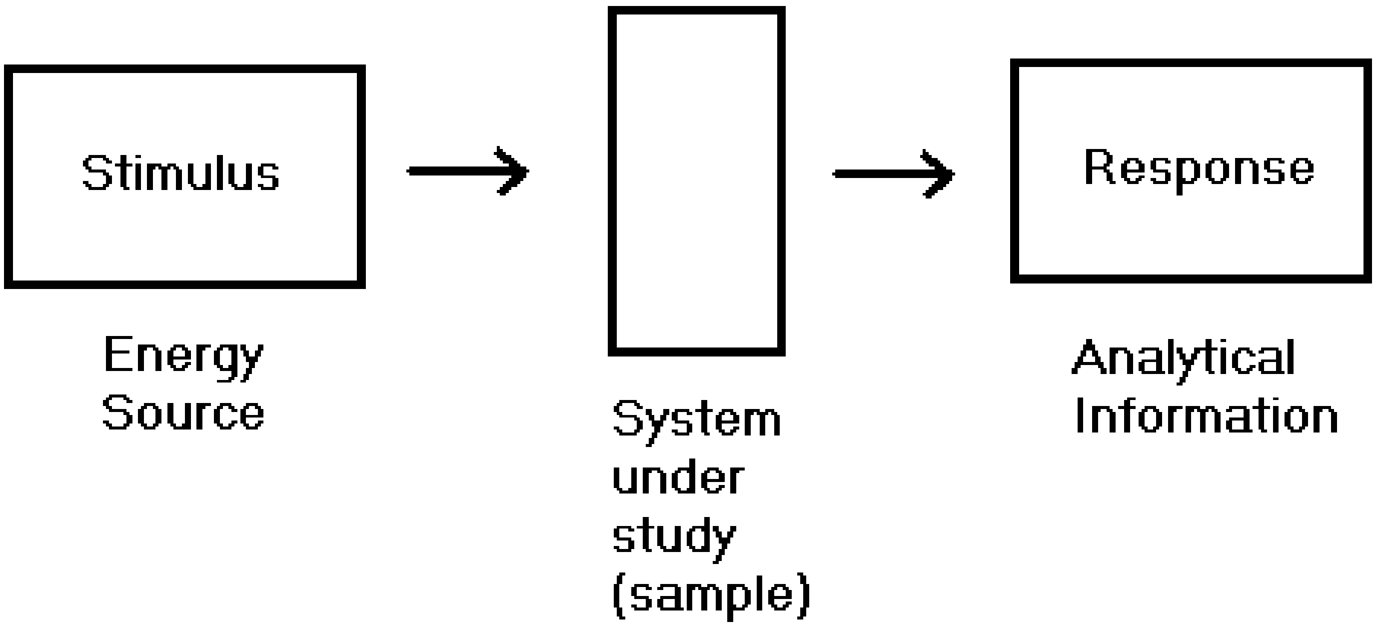
Chemistry 4631

Instrumental Analysis

Lecture 2

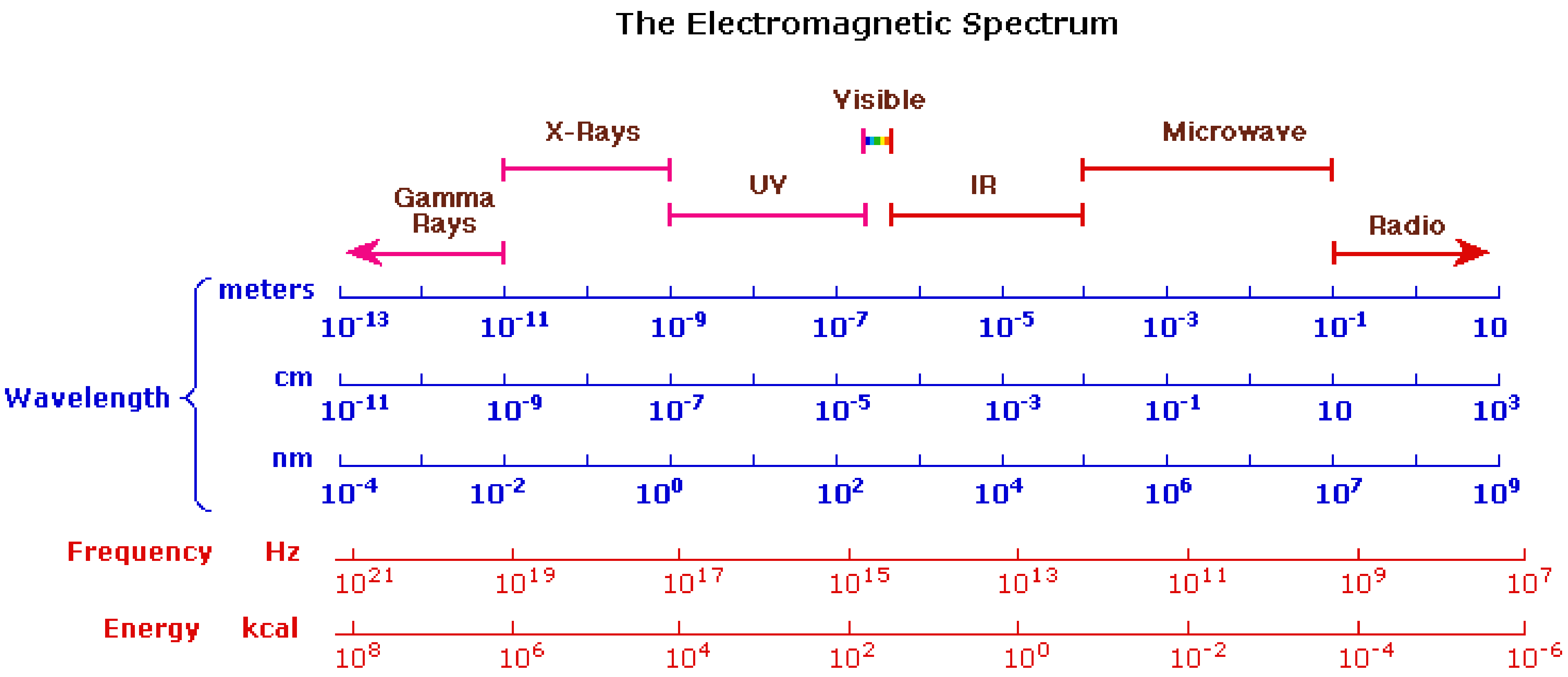
Instruments

All instruments have the same basic components:



Applications of UV/vis Spectrometry

Let's begin with some theory to help us understand instrumentation.


The Electromagnetic Spectrum
Visible
X-Rays
Microwave
UV
IR
Gamma Rays
Radio
Wavelength
meters
10-13 10-11 10-9 10-7 10-5 10-3 10-1 10
cm
10-11 10-9 10-7 10-5 10-3 10-1 10 103
nm
10-4 10-2 100 102 104 106 107 109
Frequency Hz
1021 1019 1017 1015 1013 1011 109 107
Energy kcal
108 106 104 102 100 10-2 10-4 10-6

Atomic Spectroscopy

Quantum Transitions

When electromagnetic radiation is emitted or absorbed, a permanent transfer of energy occurs.

The emitted electromagnetic radiation is represented by discrete particles known as photons or quanta.

Atomic Spectroscopy

Quantum Transitions

Photoelectric Effect

One use of electromagnetic radiation is to release electrons from metallic surfaces and imparts to these electrons sufficient kinetic energy to cause them to travel to a negatively charged electrode.

Atomic Spectroscopy

Quantum Transitions

Photoelectric Effect

- Heinrich Hertz in 1887
- Found that light whose frequency was lower than a certain critical value did not eject any electrons at all.
- This dependence on frequency didn't make any sense in terms of the classical wave theory of light.

Atomic Spectroscopy

Quantum Transitions

Photoelectric Effect

- **Heinrich Hertz in 1887**
- **This dependence on frequency didn't make any sense in terms of the classical wave theory of light.**
- **It should have been amplitude (brightness) that was relevant, not frequency.**

Atomic Spectroscopy

Quantum Transitions

Photoelectric Effect (Einstein 1905)

$$eV_o = h\upsilon - \omega$$

- eV_o – maximum kinetic energy
- h – Planks constant = 6.6254×10^{-34} J s
- υ – frequency
- ω – work function (depends on the surface material of photocathode)

Atomic Spectroscopy

Quantum Transitions

Photoelectric Effect

$$eV_o = h\upsilon - \omega$$

if $E = h\upsilon$, then

$$E = h\upsilon = eV_o + \omega$$

so the energy of an incoming photon is equal to the kinetic energy of the ejected photoelectron plus energy required to eject the photoelectron from the surface being irradiated.

Atomic Spectroscopy

Quantum Transitions

The energy of a photon can also be transferred to an elementary particle by adsorption if the energy of the photon exactly matches the energy difference between the ground state and a higher energy state. This produces an excited state (*) in the elementary particle.

$$M + h\nu \text{ -----> } M^*$$

Atomic Spectroscopy

Quantum Transitions

Molecules also absorb incoming radiation and undergo some type of quantitized transition.

The transition can be:

- Electronic transition - transfer of an electron from one electronic orbital to another.
- Vibrational transition - associated with the bonds that hold molecules together.
- Rotational transitions

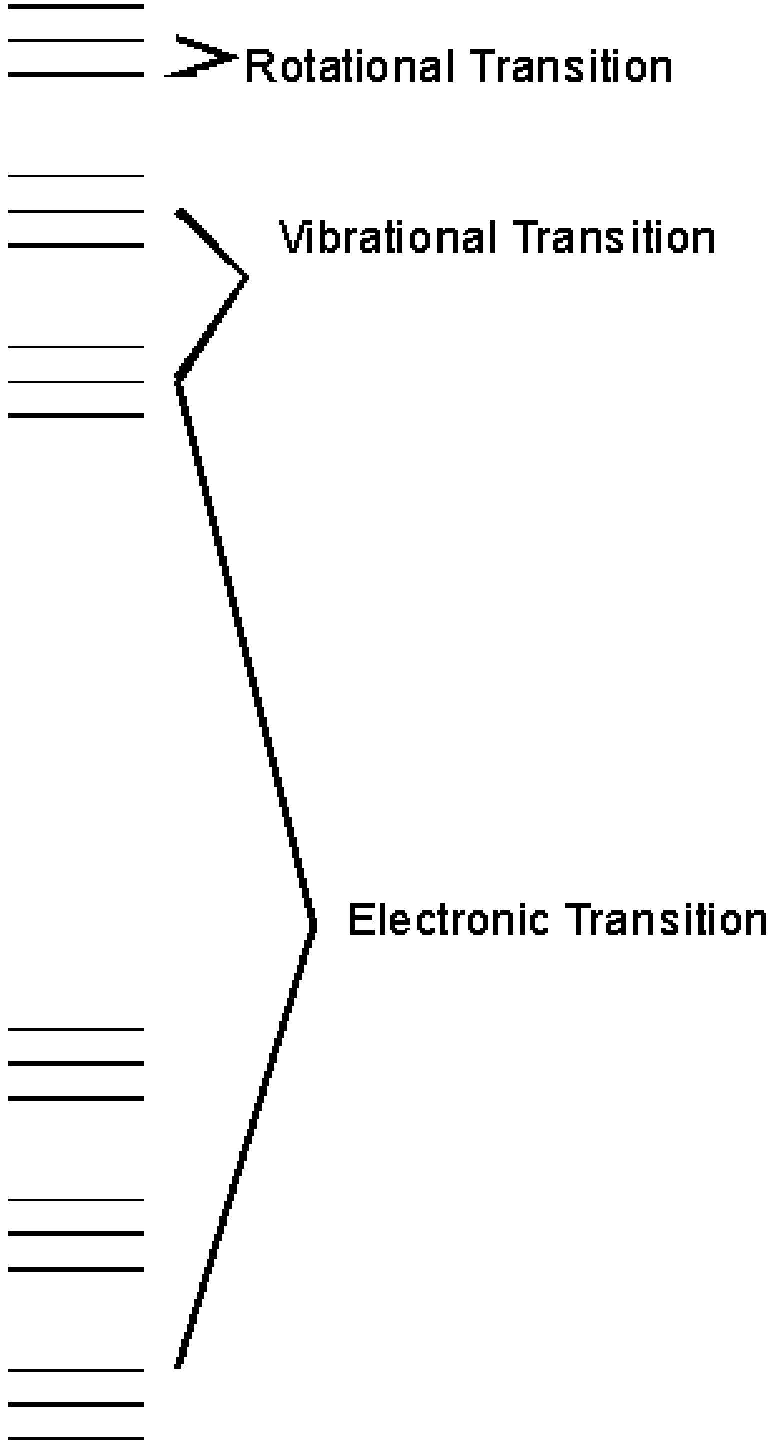
Atomic Spectroscopy

Quantum Transitions

Overall energy of a molecule:

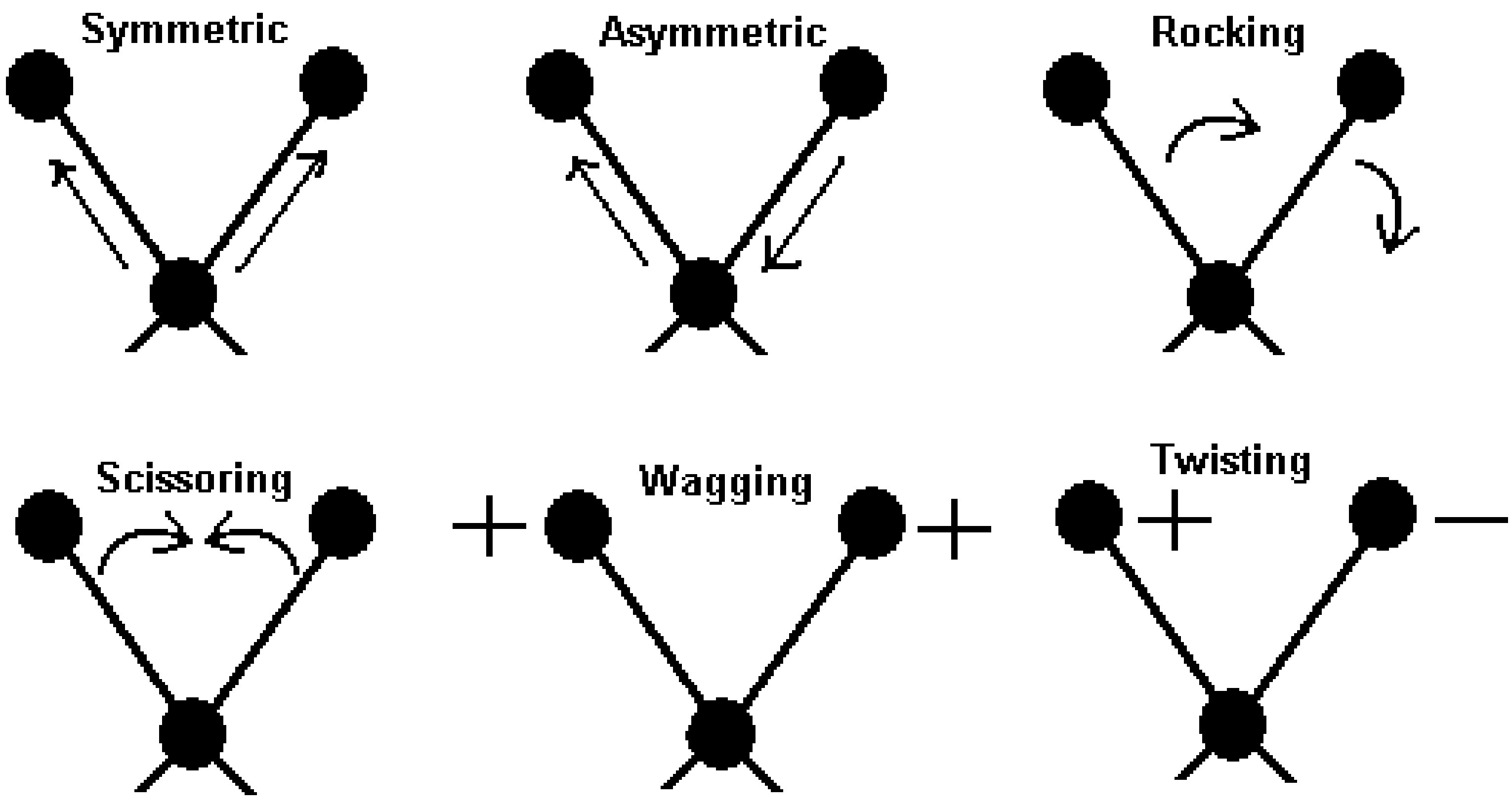
$$E = E_{electronic} + E_{vibrational} + E_{rotational}$$

$$\Delta E_{electronic} \sim 10 \Delta E_{vibrational} \sim 10 \Delta E_{rotational}$$


Rotational Transition
Vibrational Transition
Electronic Transition

Molecular vibrations include:

- Symmetric stretching, asymmetric stretching, in-plane rocking, in-plane scissoring, out of plane wagging (bending), out of plane twisting.



We will Start with the UV-vis, (Fluorescence), and IR transitions and how to build an Instrument to measure these transitions.

- Infrared Absorption
  - IR radiation is not energetic enough to cause electronic transitions - so used to probe the vibrational and rotational states of the molecule.
- Ultraviolet Radiation
  - UV radiation is energetic enough to cause electronic transitions.

Atomic Spectroscopy

Electromagnetic Radiation

Can be described by means of a classical sinusoidal wave model. Oscillating electric and magnetic field. (Wave model)

wavelength, frequency, velocity, amplitude, energy

Also can be described as a stream of discrete particles.

photons

Atomic Spectroscopy

Electromagnetic Radiation

Wave Properties

Represented as electric and magnetic fields that undergo in-phase, sinusoidal oscillations at right angles to each other and to the direction of propagation.

Atomic Spectroscopy

Electromagnetic Radiation

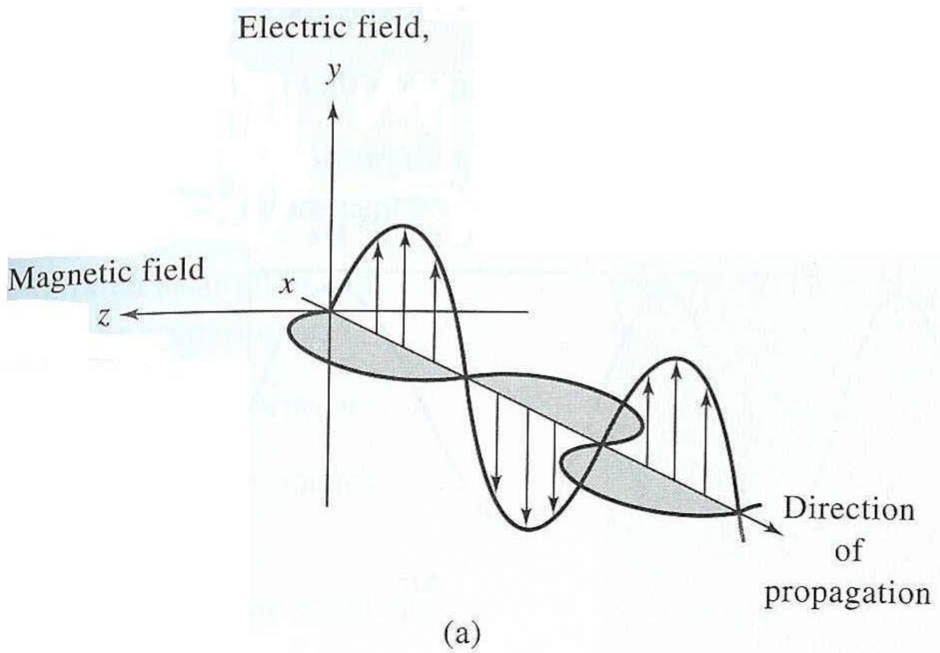


Figure 6-1 Representation of a beam of monochromatic, plane-polarized radiation: (a) electrical and magnetic fields at right angles to one another and direction of propagation, (b) two-dimensional representation of the electric vector.

Atomic Spectroscopy

Electromagnetic Radiation

The <u>electric component</u> of radiation is responsible for most phenomena of interest, i.e. transmission, reflection, refraction, and absorption. (Only consider electrical component for most instrumentation)

The <u>magnetic component</u> of radiation is responsible for absorption of radio-frequency waves in nuclear magnetic resonance.

Atomic Spectroscopy

Electromagnetic Radiation

1. Wave Parameters

- Amplitude – A
- Frequency, υ, units (s^{-1}) or hertz (Hz)
- Wavelength, λ, units (angstroms, nanometers, micrometers, etc..)

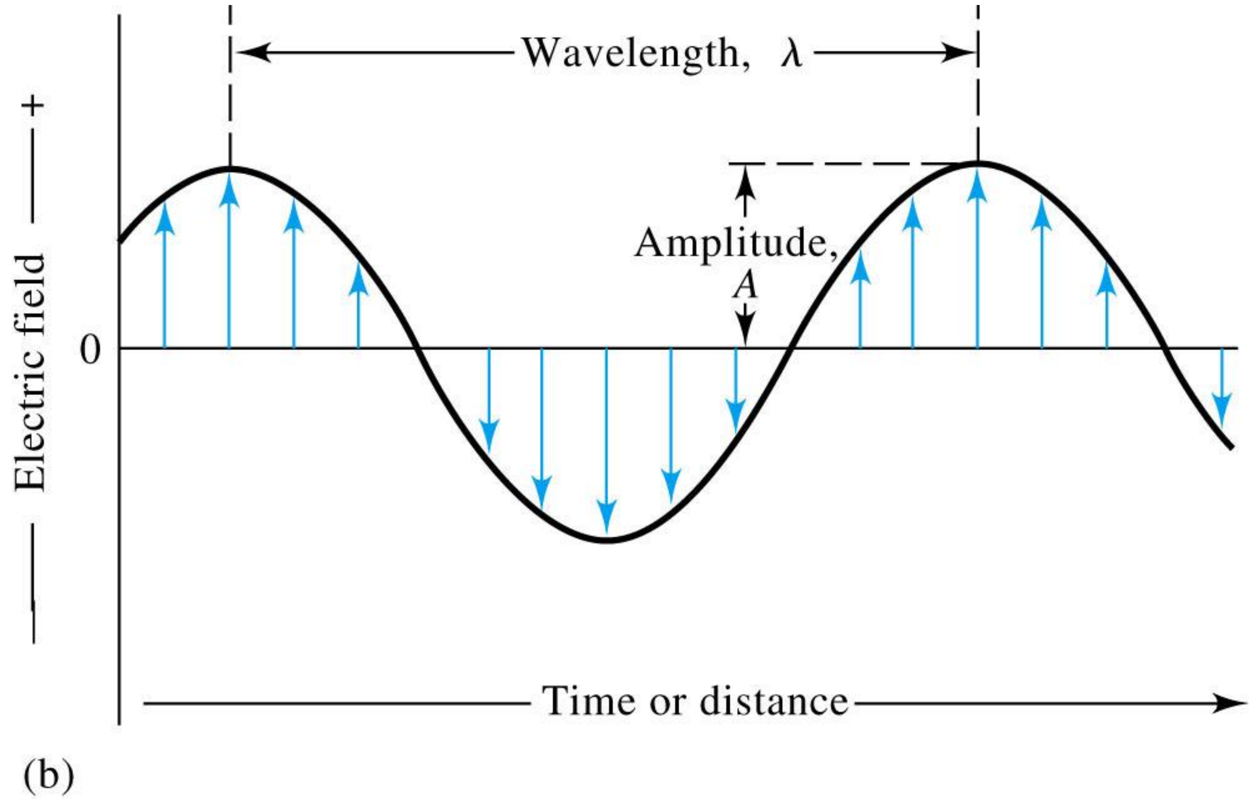
Also E = hυ = hc/λ

- where E – Joules, h – Planck's cnst (6.62×10^{-34} J s)
- 1 eV = 1.6022×10^{-19} J

Atomic Spectroscopy

Electromagnetic Radiation

1. Wave Parameters



Atomic Spectroscopy

Electromagnetic Radiation

In a vacuum, velocity is equal to 2.99792×10^8 m/s and is defined as c.

$c = \upsilon\lambda = 3.00 \times 10^8$ m/s = 3.00×10^{10} cm/s

λ changes with the medium.

Atomic Spectroscopy

Electromagnetic Radiation

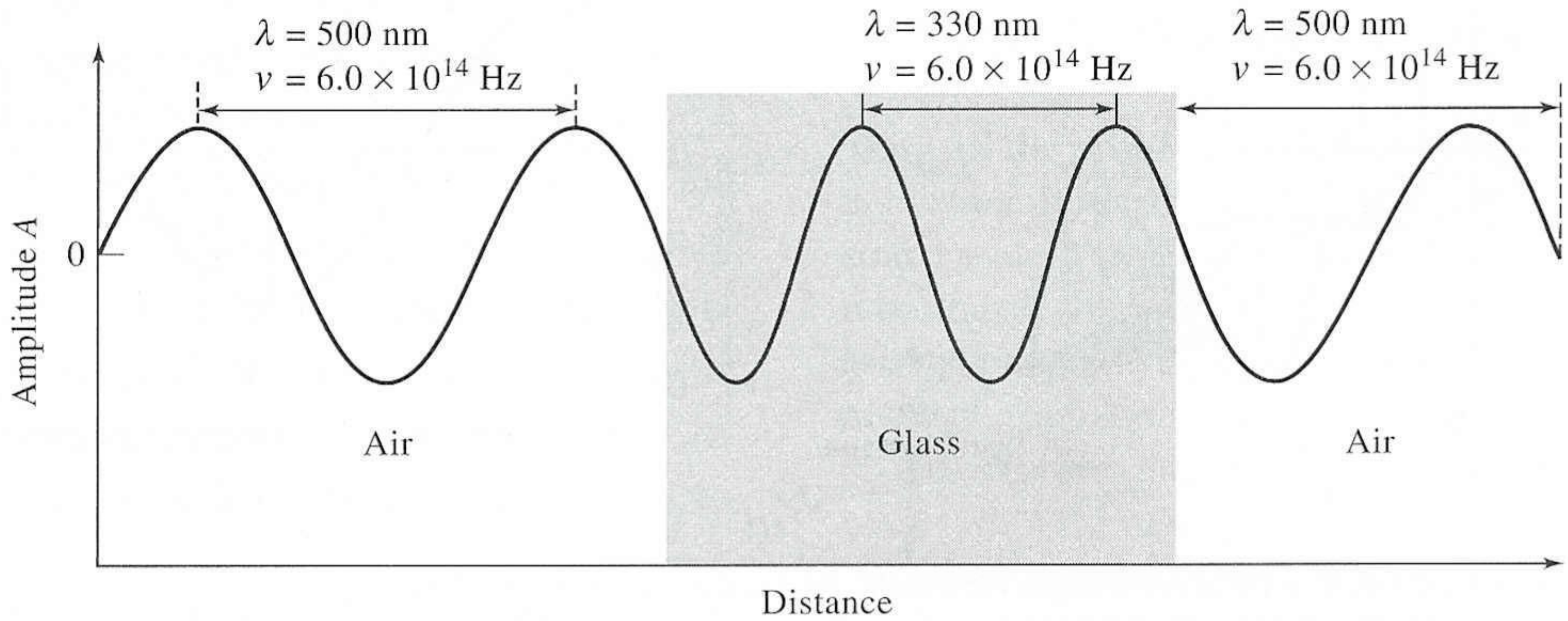


Figure 6-2 Effect of change of medium on a monochromatic beam of radiation.

Atomic Spectroscopy

Electromagnetic Radiation

Wavenumber, $\bar{\upsilon}$

reciprocal of the wavelength in centimeters (cm^{-1}) (mostly used in IR)

Wavenumber is directly proportional to the frequency, and thus the energy, of radiation.

$$\bar{\upsilon} = k\upsilon$$

k – proportionality constant – depends on the medium.

Atomic Spectroscopy

Propagation of Radiation

- **Diffraction**
- Transmission
- Refraction
- Reflection
- Scattering
- Polarization

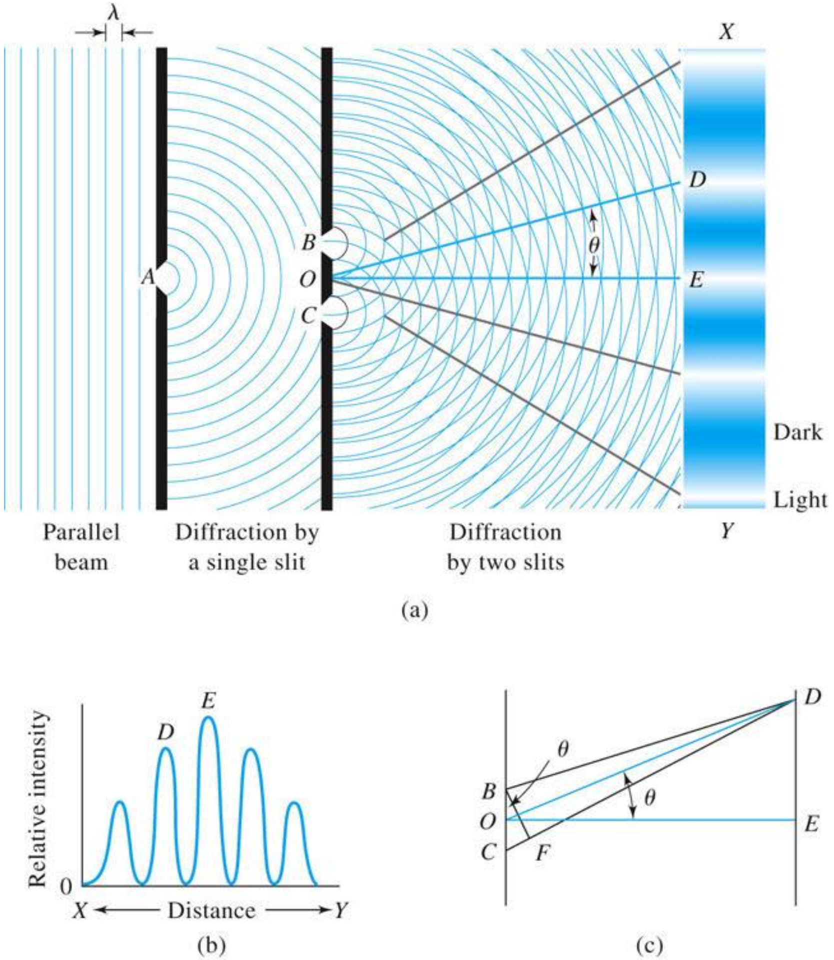
Atomic Spectroscopy

Propagation of Radiation

- **Diffraction**

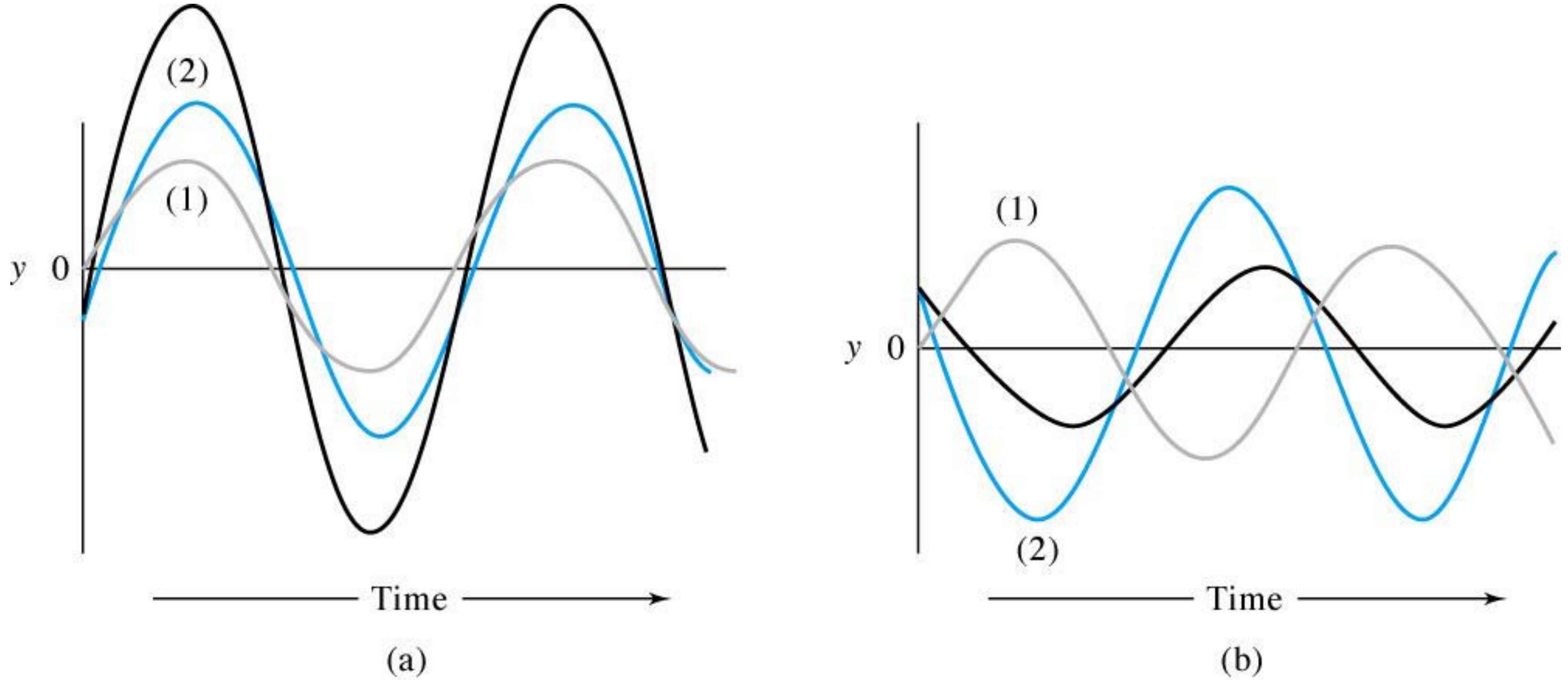
Process where a parallel beam of radiation is bent as it passes by a sharp barrier or through a narrow opening.

Consequence of interference.



Atomic Spectroscopy

Electromagnetic Radiation



Atomic Spectroscopy

Propagation of Radiation

- Diffraction
- **Transmission - T**
- Refraction - index of refraction
- Reflection
- Scattering
- Polarization

Atomic Spectroscopy

- **Transmittance, T, - fraction of the incident electromagnetic radiation that is transmitted by a sample.**

$$T = P/P_o \qquad \%T = P/P_o \times 100\%$$

P_o - initial power of the beam

P - attenuated power of the beam

- **Absorbance, A**

$$A = -\log T = \log P_o/P$$

Atomic Spectroscopy

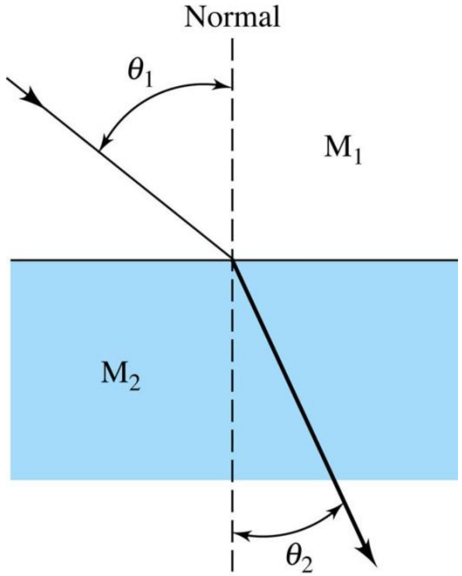
Propagation of Radiation

- Diffraction
- Transmission - T
- **Refraction - index of refraction**
- Reflection
- Scattering
- Polarization

Atomic Spectroscopy

Propagation of Radiation

- Refraction – an abrupt change in direction of a beam as a consequence of a difference in velocity between two media of different densities.



- Snell's Law $$\frac{\sin\theta_1}{\sin\theta_2} = \frac{n_2}{n_1}$$

n – refractive index

Atomic Spectroscopy

Propagation of Radiation

- Diffraction
- Transmission - T
- Refraction - index of refraction
- **Reflection**
- Scattering
- Polarization

Atomic Spectroscopy

Propagation of Radiation

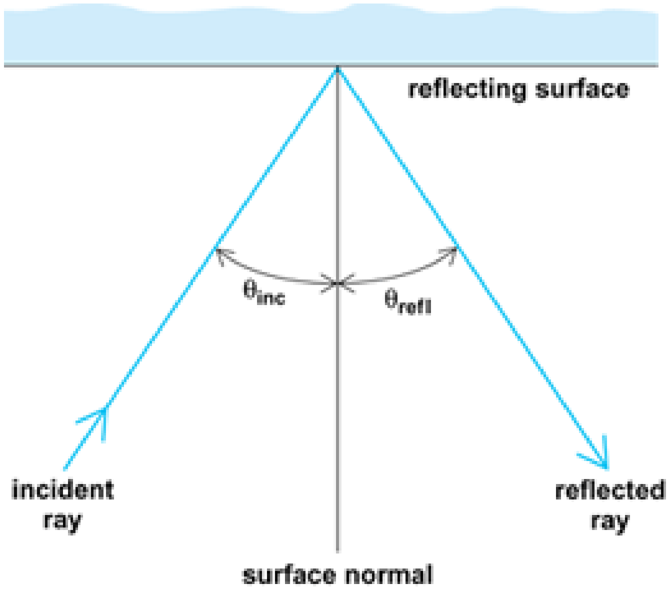
- **Reflection**

The reflection of electromagnetic radiation involves the returning or throwing back of the radiation by a surface upon which the radiation is incident.

Atomic Spectroscopy

Propagation of Radiation

- **Reflection**



Devices designed to reflect radiation are called reflectors or mirrors.

The reflectivity of a surface is a measure of the amount of reflected radiation.

Antireflection coatings are used to reduce the reflection from surfaces of optical equipment and devices.

Atomic Spectroscopy

Propagation of Radiation

- Diffraction
- Transmission - T
- Refraction - index of refraction
- Reflection
- **Scattering**
- Polarization

Atomic Spectroscopy

Propagation of Radiation

- Scattering – small fraction of radiation is transmitted at all angles from the original path and the intensity of this scattered radiation increases with particle size.

Atomic Spectroscopy

Propagation of Radiation

- **Scattering**

Rayleigh Scattering – scattering by molecules smaller than the wavelength of radiation

Mie Scattering – scattering by large particles

Raman Scattering - scattering resulting in quantized frequency shifts

Atomic Spectroscopy

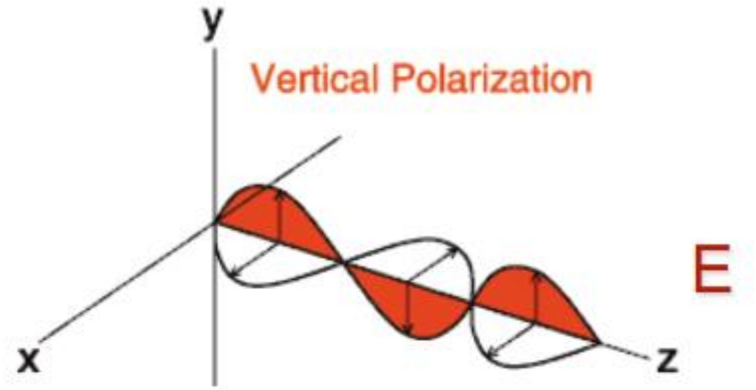
Propagation of Radiation

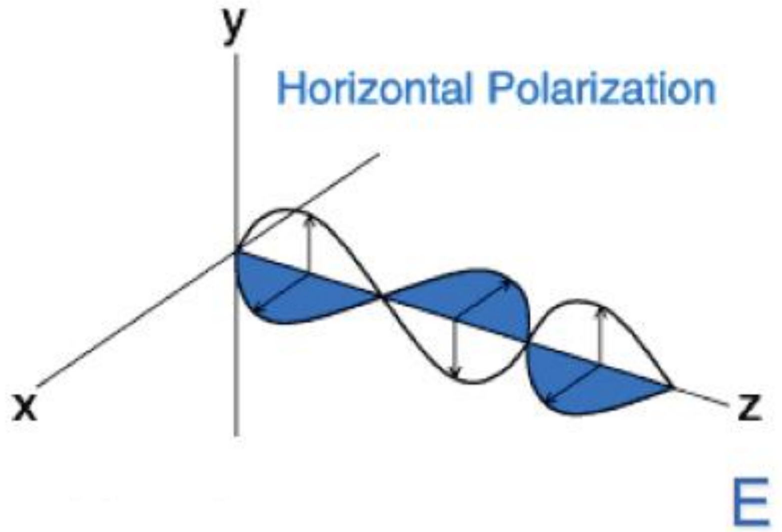
- Diffraction
- Transmission - T
- Refraction - index of refraction
- Reflection
- Scattering
- Polarization

Atomic Spectroscopy

Propagation of Radiation

- Polarization





Assignment

- Read Chapter 1
- Read Appendix 1
- Go over Lab Lecture 1
- Homework 1: Ch. 1: 11 and
  Appendix 1: 1, 2, 10, and 12
  (extra credit) – Due Jan 24th
- Read Chapter 6
- If interested in topic then Read chapter on the dual nature of light: pages 964-1010
- https://archive.org/details/lm_20220102/mode/2up