



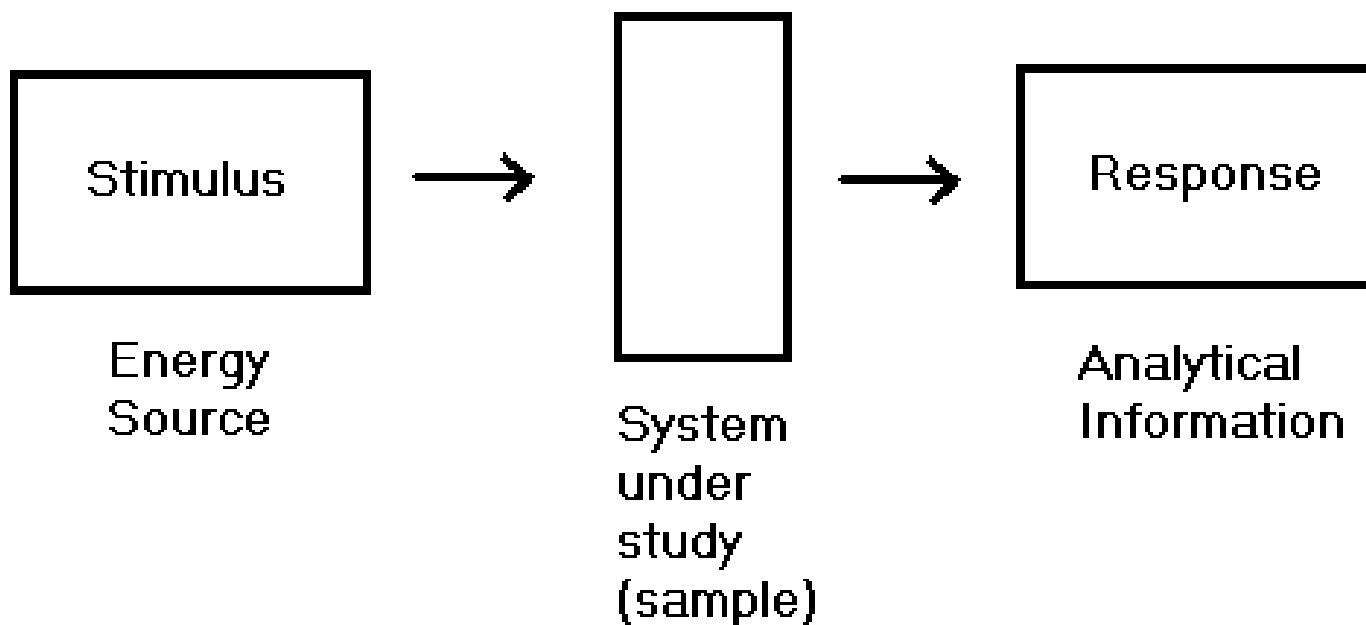
Chemistry 4631

Instrumental Analysis

Lecture 2

Instruments

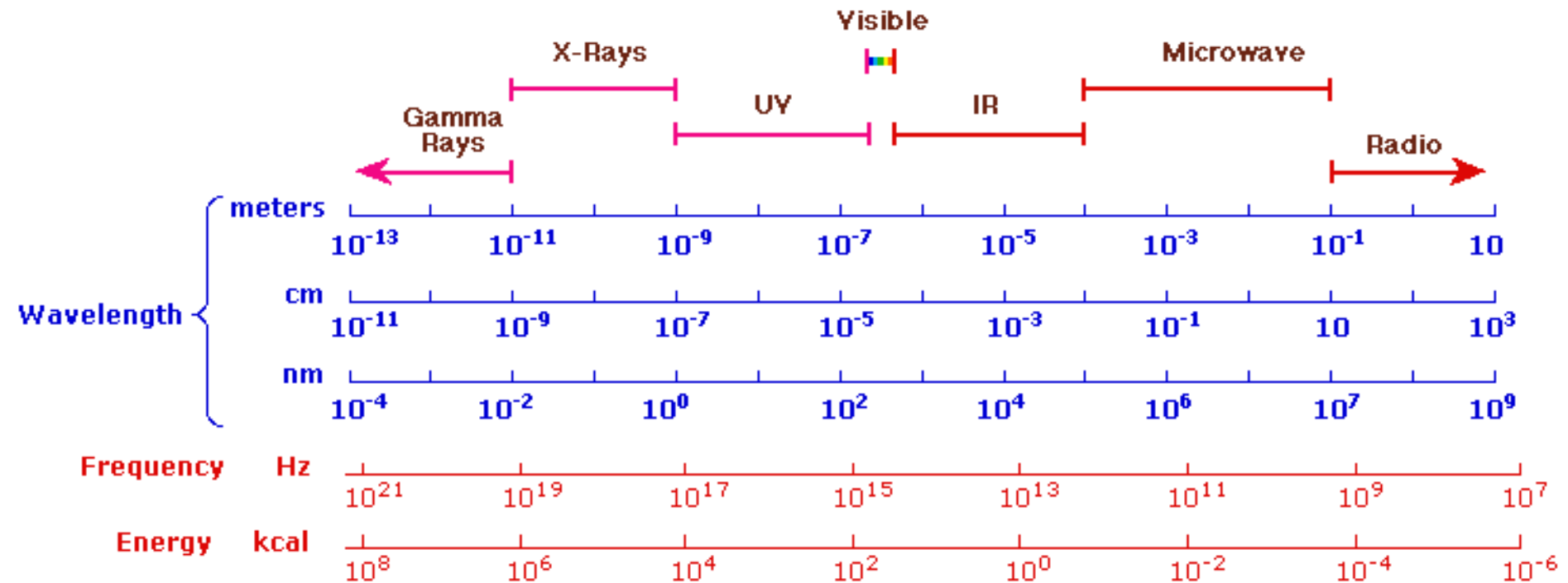
All instruments have the same basic components:



Applications of UV/vis Spectrometry

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

The Electromagnetic Spectrum



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 (Einstein 1905)

$$eV_0 = h\nu - \omega$$

eV_0 – maximum kinetic energy

h – Planks constant = 6.6254×10^{-34} J s

ν – frequency

ω – work function (depends on the surface material of photocathode)

Atomic Spectroscopy

Quantum Transitions

Photoelectric Effect

$$eV_0 = h\nu - \omega$$

if $E = h\nu$, then

$$E = h\nu = eV_0 + \omega$$

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.



Atomic Spectroscopy

Quantum Transitions

Molecules also absorb incoming radiation and undergo some type of quantized 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

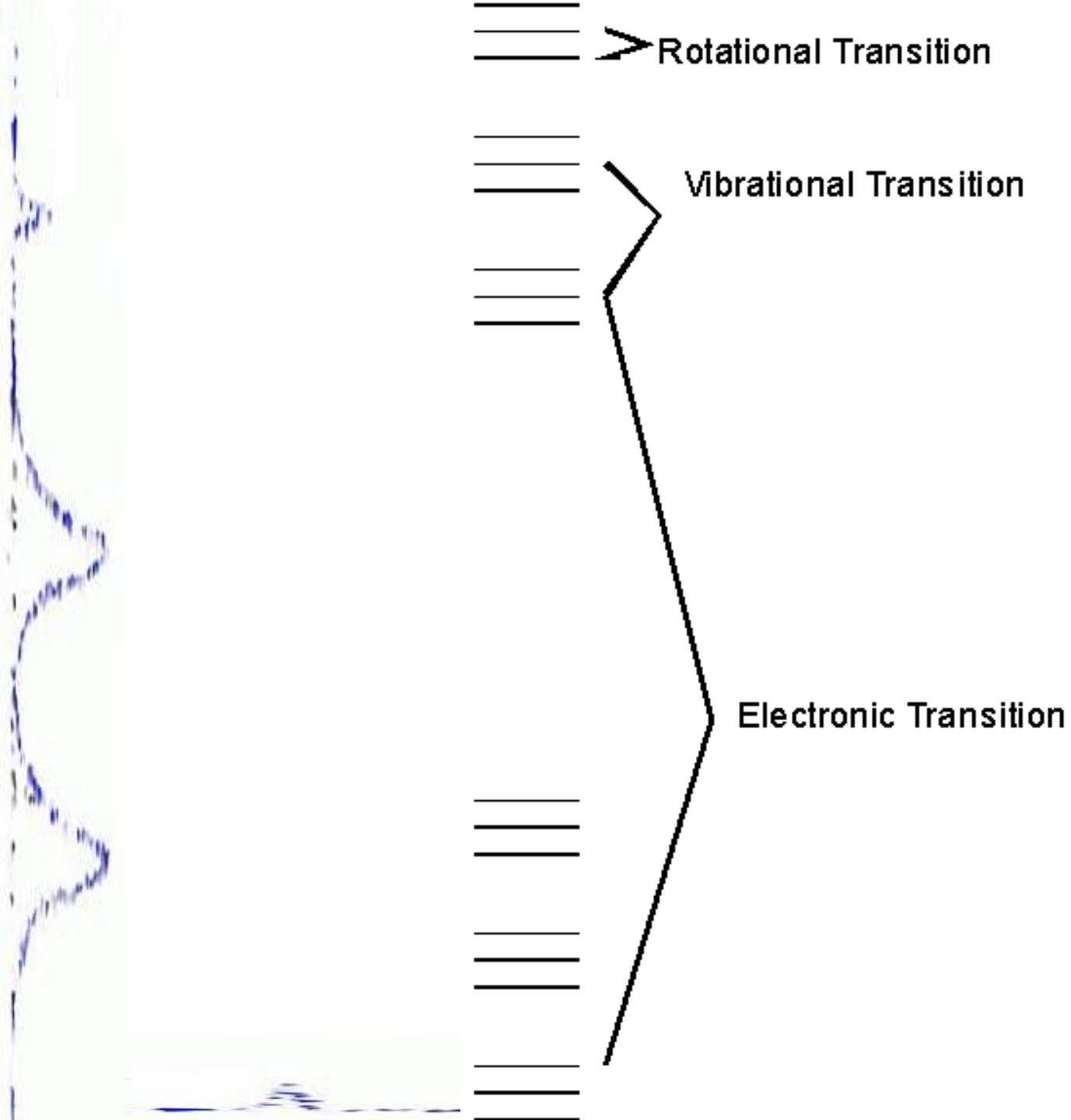
Atomic Spectroscopy

Quantum Transitions

Overall energy of a molecule:

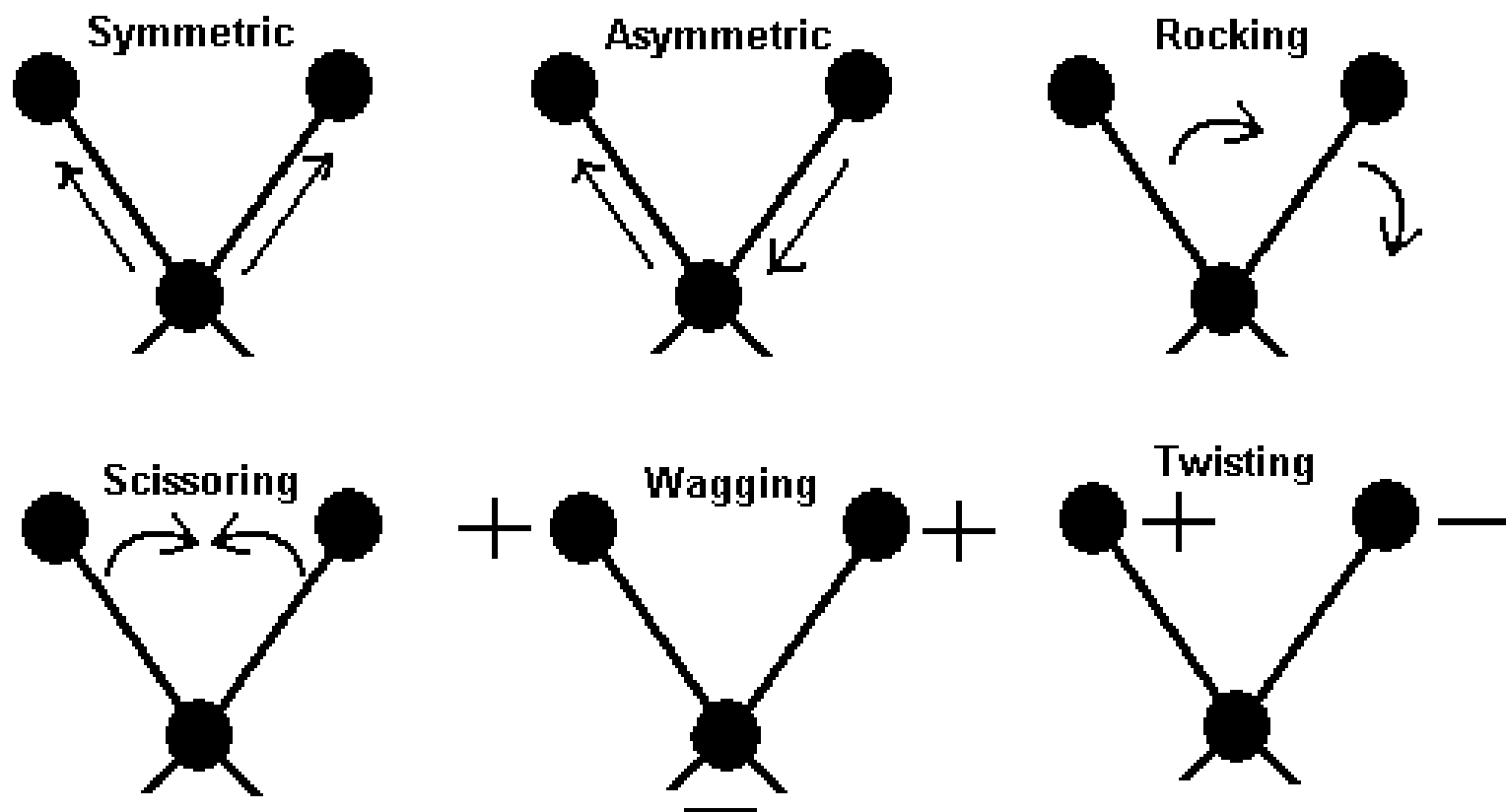
$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$


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



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.

□ Ultraviolet Radiation

- UV radiation is energetic enough to cause electronic 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.

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

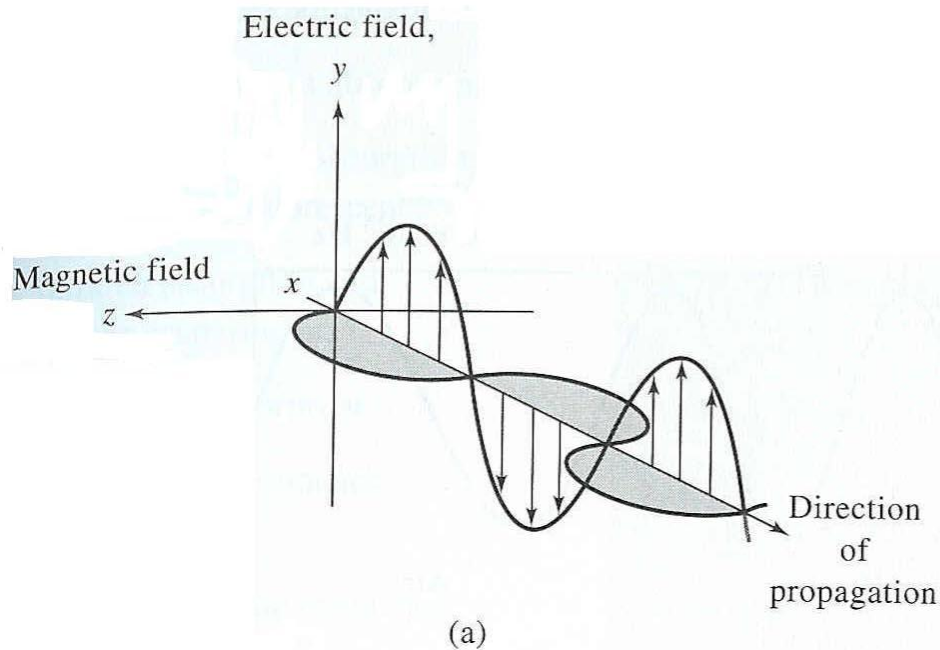


Figure 6-1 Representation of a beam of monochromatic, plane-polarized radiation:
(a) electrical and magnetic fields at right angles to one another and direction of propagation, (b) two-dimensional representation of the electric vector.

Atomic Spectroscopy

Electromagnetic Radiation

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

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

Atomic Spectroscopy

Electromagnetic Radiation

1. Wave Parameters

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

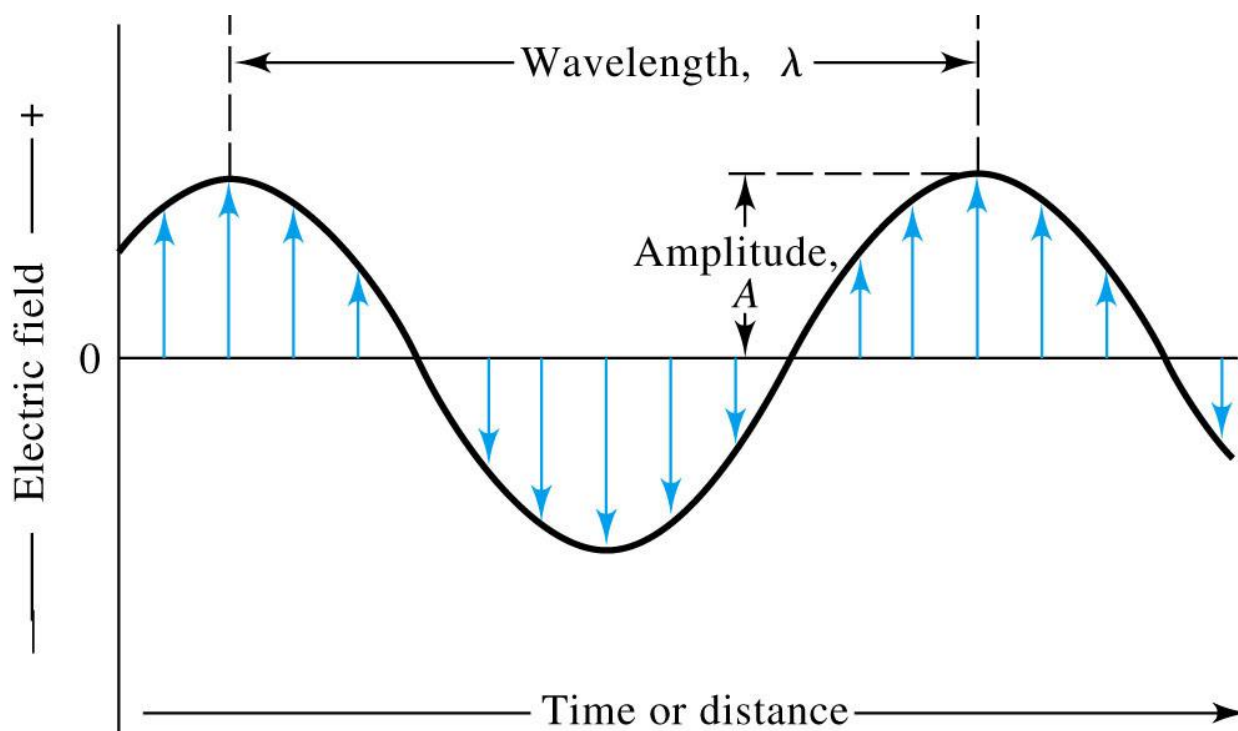
Also $E = h\nu = hc/\lambda$

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

Atomic Spectroscopy

Electromagnetic Radiation

1. Wave Parameters



(b)

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Atomic Spectroscopy

Electromagnetic Radiation

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

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

λ changes with the medium.

Atomic Spectroscopy

Electromagnetic Radiation

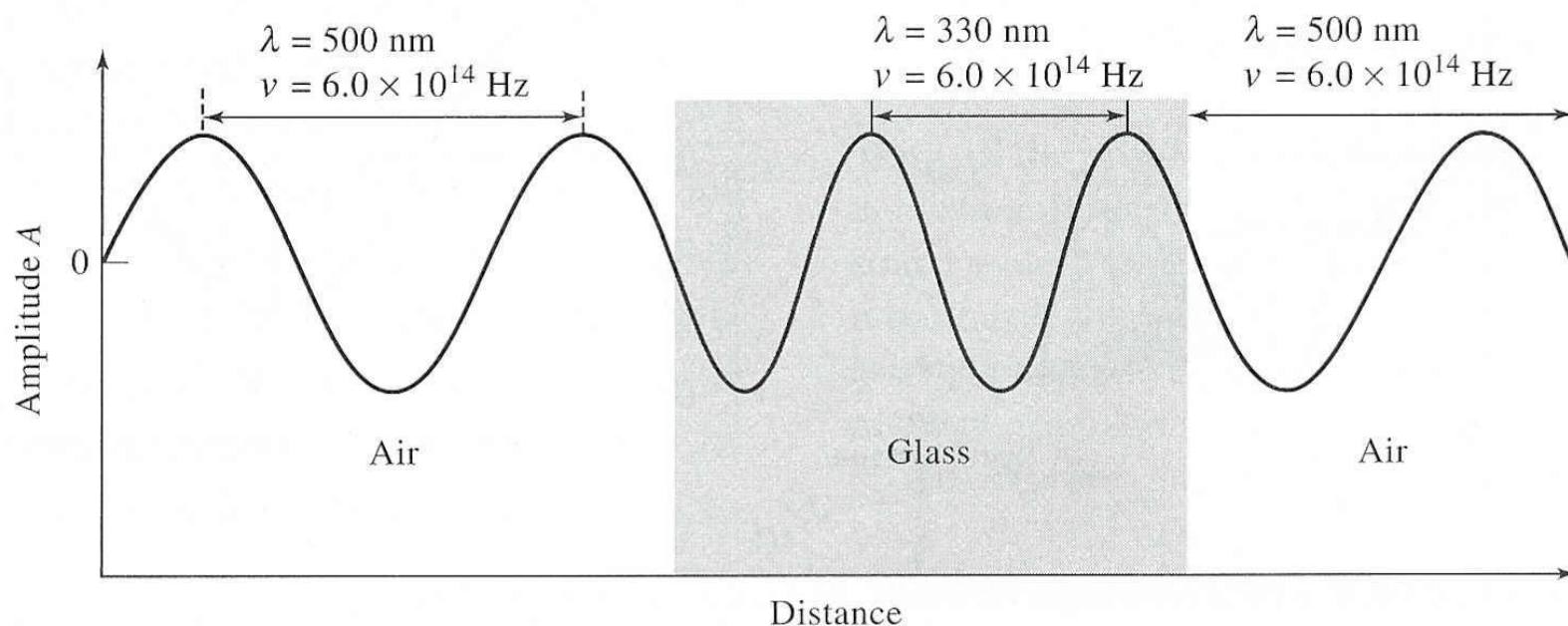


Figure 6-2 Effect of change of medium on a monochromatic beam of radiation.

Atomic Spectroscopy

Electromagnetic Radiation

Wavenumber, $\bar{\nu}$

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.

$$\bar{\nu} = k\nu$$

k – proportionality constant – depends on the medium.

Atomic Spectroscopy

Propagation of Radiation

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

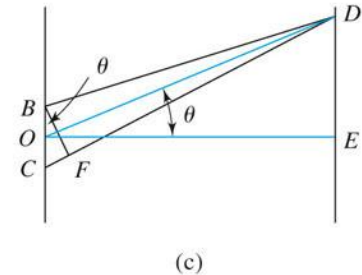
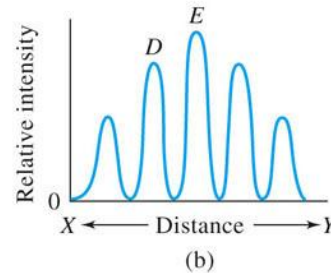
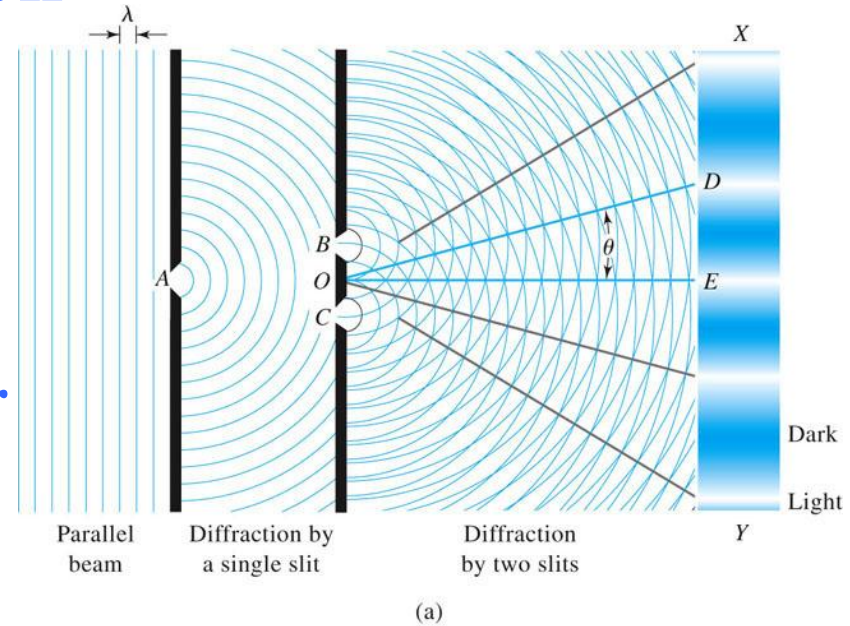
Atomic Spectroscopy

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.

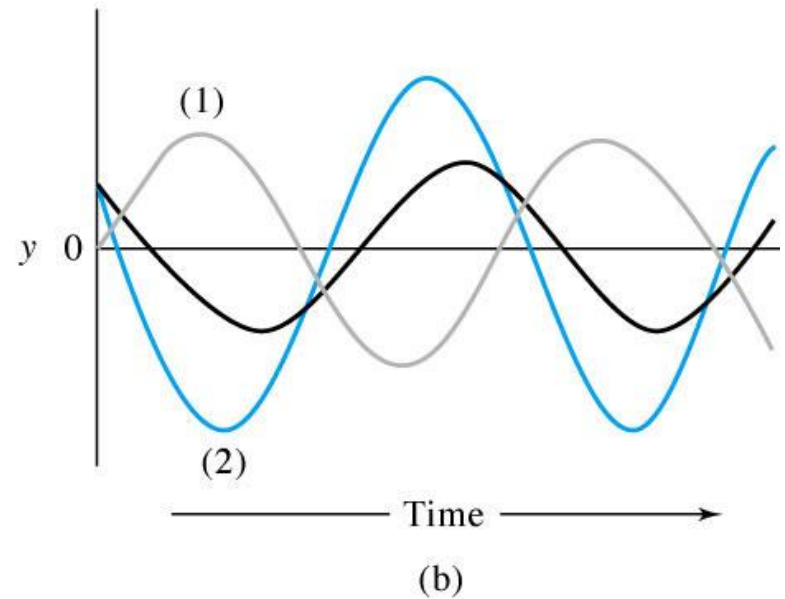
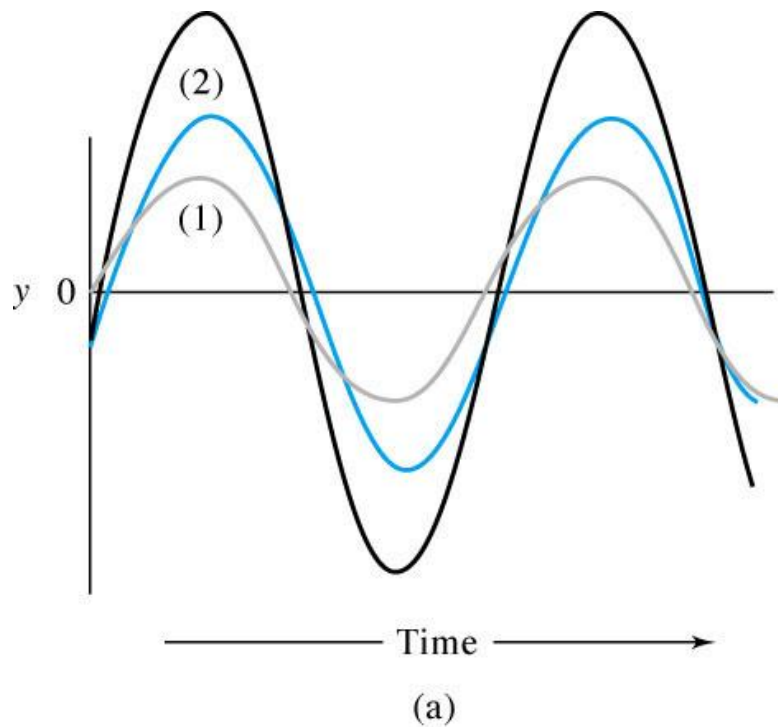
Consequence of interference.



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Atomic Spectroscopy

Electromagnetic Radiation



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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.

$$T = P/P_0$$

$$\%T = P/P_0 \times 100\%$$

P_0 - initial power of the beam

P - attenuated power of the beam

- **Absorbance, A**

$$A = -\log T = \log P_0/P$$

Atomic Spectroscopy

Propagation of Radiation

- Diffraction
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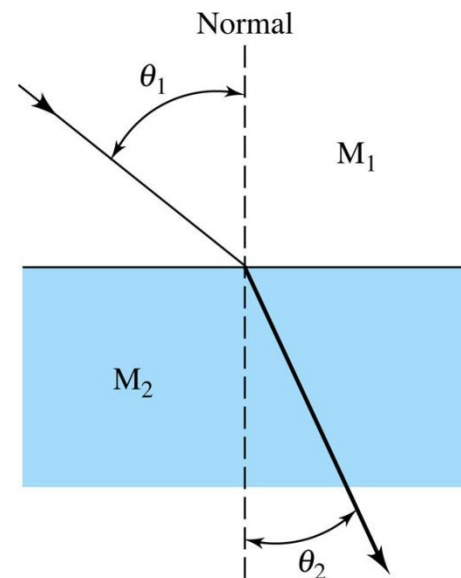
Atomic Spectroscopy

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



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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

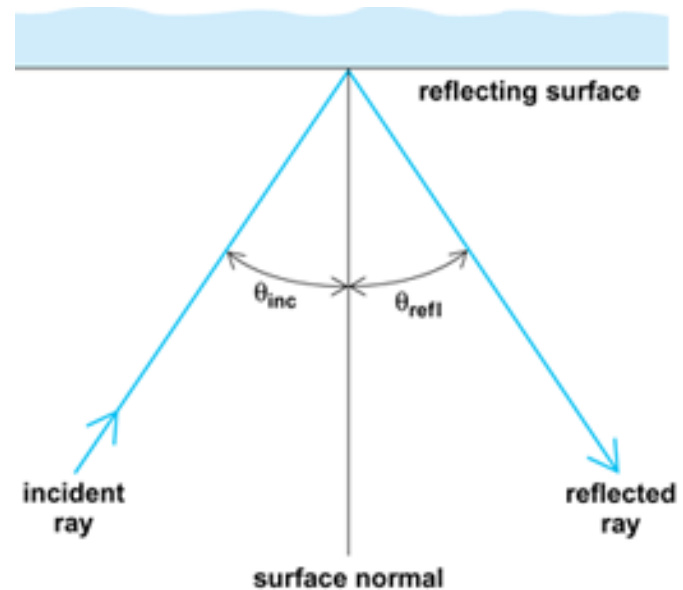
Propagation of Radiation

- 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

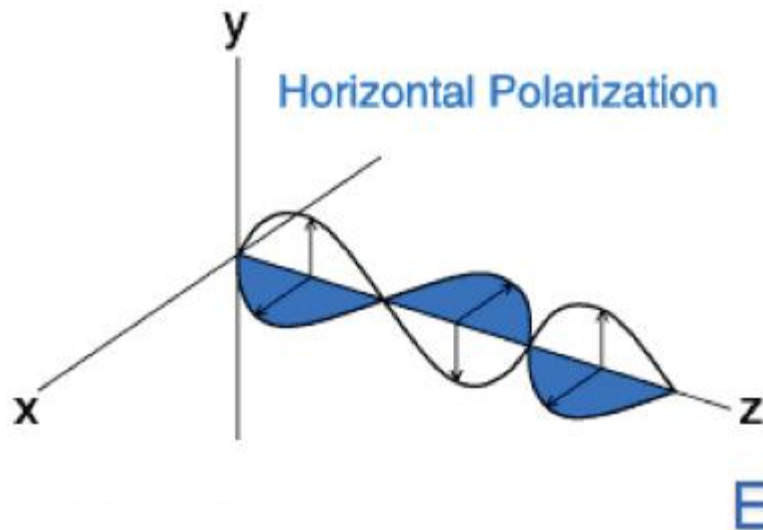
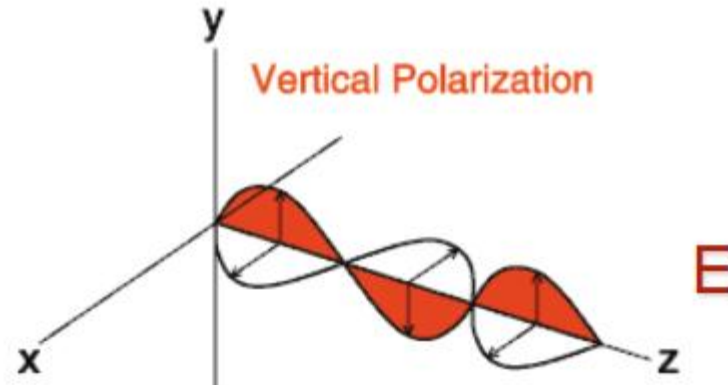
Propagation of Radiation

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

Atomic Spectroscopy

Propagation of Radiation

- Polarization



Assignment

- Read Chapter 1 from textbook
- Read Appendix 1 from textbook
- Go over Lab Lecture 1 before UV-vis Lab
- Homework 1: Ch. 1: 11 and
Appendix 1: 1, 2, 10, and 12
(extra credit) – Due Jan 16th
- Read Chapter 6 from textbook
- If interested in topic then Read chapter on the dual nature of light: pages 964-1010
- https://archive.org/details/lm_20220102/mode/2up

Atomic Spectroscopy

Electromagnetic Radiation

A wave can be described by an equation, with time as a variable,

$$y = A \sin (\omega t + \phi)$$

y – electric field

A – amplitude or maximum number of y

t – time

ϕ – phase angle

ω – angular velocity

Atomic Spectroscopy

Electromagnetic Radiation

A wave can be described by an equation, with time as a variable,

$$y = A \sin (\omega t + \phi)$$

y – electric field

A – amplitude or maximum number of y

t – time

ϕ – phase angle

ω – angular velocity

$$\omega = 2 \pi \nu$$

ν – frequency

$$y = A \sin (2\pi\nu t + \phi)$$

using this equation, equations can be written to describe the superposition (overlapping) of waves.

Atomic Spectroscopy

Electromagnetic Radiation

A complex waveform can be broken down into simple components by a mathematical operation called a Fourier transformation. (FTIR)

While decomposing a complex waveform into its sine and cosine components is tedious and time consuming, computer software can be used to easily analyze any results.