Spectroscopy:
Intro/Background

Chem 221
Instrumental Analysis
Spring 2005

Definition and Overview

- The study of the interaction of *electromagnetic radiation (EMR)* with matter
- **Scope and Purview:**
  - ***Properties of EMR***
  - ***Atomic and Molecular Interactions with EMR***
  - ***Instrumentation***
  - ***Molecular Spectroscopy***
    - Infrared Absorption Spectrophotometry
    - Luminescence Spectrometry
    - Raman Spectroscopy
  - ***Atomic Spectroscopy***
    - ✓ Absorption
    - ✓ Emission

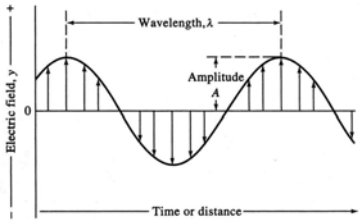
Electromagnetic Radiation (EMR)

- So, just what is **EMR?**
  - an *oscillating* electric and magnetic field which travels through space
  - a discrete series of "particles" that possess a specific energy but have no mass

BOTH!

It's a Wave!

- Consider an oscillating electric field:



Characterized by:

- **λ** - wavelength
- ***A*** - amplitude
- **ν** - frequency

Wave Properties of EMR

- The product of λ and ν is constant:

$$\lambda \times \nu = c$$

Since ν has units of sec^{-1} and λ has units of length, their product, c, is the *velocity* of the wave:

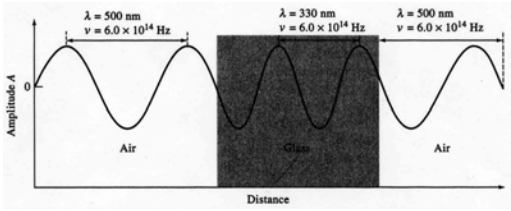
-***in a vacuum***, *all EMR* travels at a velocity of:

2.99792458 x 10^8 m/s (= c)

("The Speed of Light")

Propagation Velocity

- What happens as an EMR wave propagates from a *vacuum* into another medium?



Wavelength ***decreases***; Frequency is ***unchanged***; Velocity ***decreases***

Refractive Index (n_i)

- Quantifies the magnitude of the EMR velocity decrease in a particular medium:

$$n_i = c/v_i$$

Refractive Index
- varies with:
  - -medium
  - -frequency of EMR
  ($n\uparrow$ as $\nu\uparrow$, generally)

EMR propagation velocity

Propagation Direction

- Propagation *direction* can also change:

Reflection

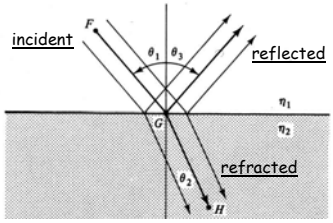
For $\theta_1 = 0°$: Fresnel Eqn

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

Refraction

Snell's Law:

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

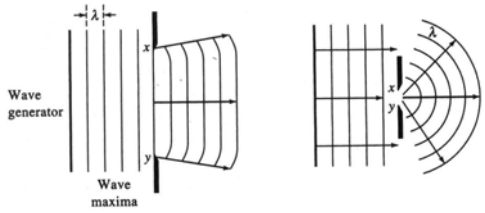


Scattering

- Most EMR is *transmitted* through a medium (no direction change)
- BUT: a *small* amount is **scattered** isotropically:
  - **Rayleigh Scattering**
    - *Elastic (no energy loss)*
    - Due to interactions with "particles" << λ
      - ✓ e.g., molecules, aggregates, etc.
    - Scatter intensity (I_S) $\propto \lambda^{-4}$ (blue sky!)
    - I_S increases with increasing particle size

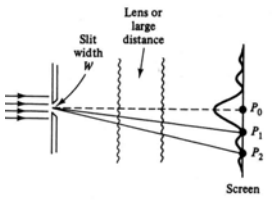
Diffraction

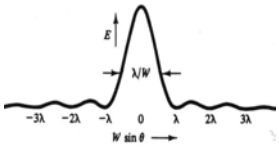
- EMR can also be "bent" as it passes through a *narrow* (width ≈ λ) opening or barrier:



Fun with Diffraction!

- Consider the following experiment (Fraunhofer Diffraction):



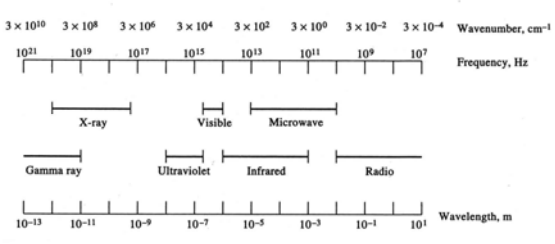


NOTE: There is a *wavelength dependence to the diffraction pattern*

See: http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/sinslit.html#c1

The Electromagnetic Spectrum

- EMR covers a very *wide range* of wavelengths and frequencies:



EMR: Particle Properties

- Energy of a *photon* can be related to its frequency:

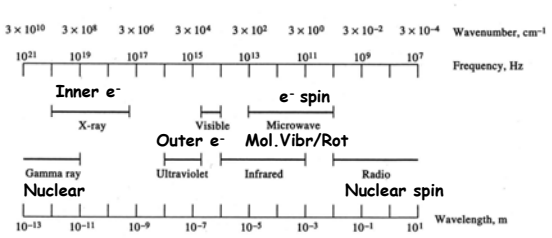
$$E = h\nu$$

- Where ***h*** = Planck's Constant = 6.626×10^{-34} Joule-sec
- The photon energy is *inversely proportional* to the wavelength of the EMR:

$$E = hc/\lambda$$

Photon Energy: Absorption/Emission of EMR

- The EMR ***ENERGY*** determines which atomic/molecular properties can be probed via spectroscopy:



Units

- Varies with the spectral region:
  - **UV/Visible**

    Wavelength: Å = 10^{-8} cm = 10^{-10} m
    nm = 10^{-7} cm = 10 Å
    μm = 10^{-4} cm = 10^{4} Å
  - **Infrared (IR)**

    Wavelength: **μm**

    Wavenumber($\bar{\nu}$): $\bar{\nu} = \lambda^{-1}$ (λ in cm gives cm^{-1})

    NOTE: $\bar{\nu} \propto$ Energy

Jablonski Diagram