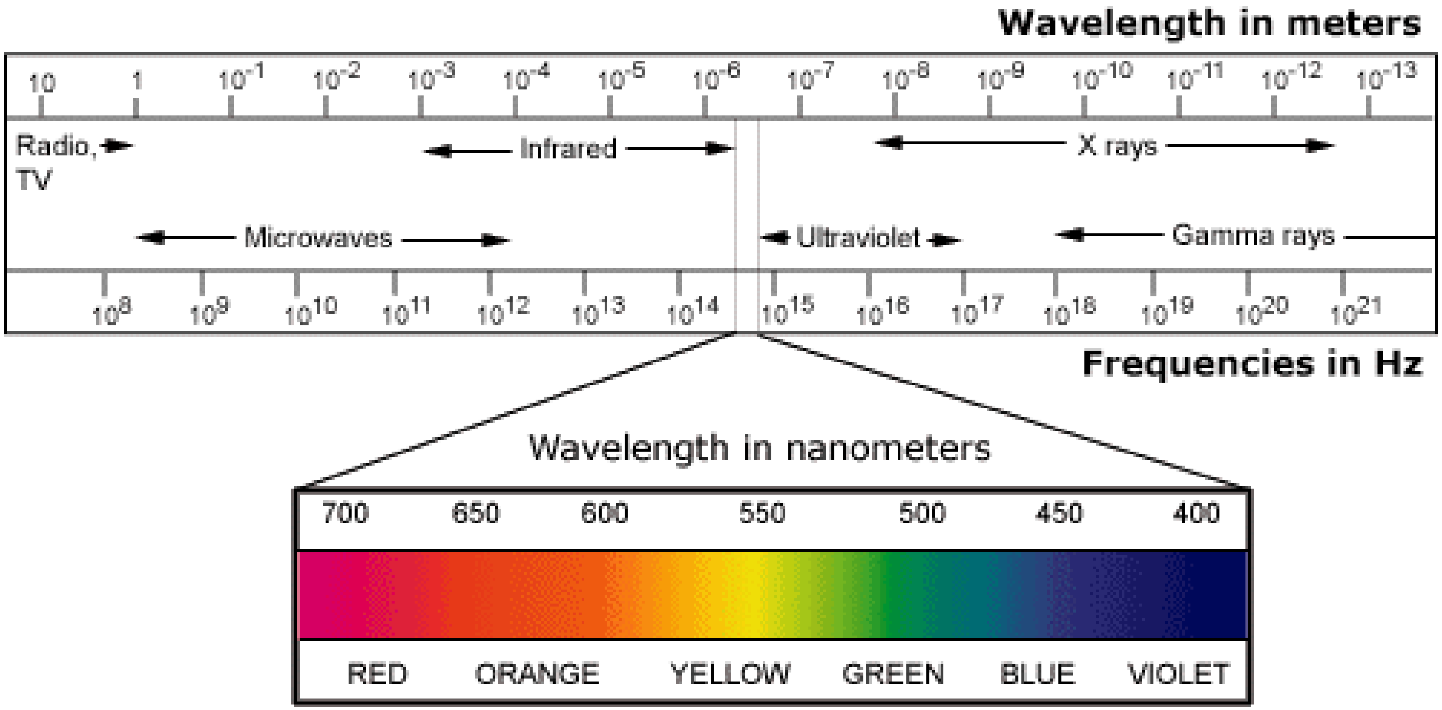
Introduction to Spectroscopy

- Spectroscopy = interaction of matter w/ electromagnetic radiation
- Entire rest of course:
  - General ideas
  - Uv-vis absorption
  - IR
  - NMR
  - X-ray

EM spectrum



Photons – wave-particle duality

EM waves: $\vec{E}(x,t) = \vec{E}_o \cos\left(\frac{2\pi x}{\lambda} - \frac{2\pi t}{T}\right)$ where T=1/f; v=fλ

In 1 dimension

EM radiation

- Wave phenomena:
  - Interference
  - Diffraction
  - polarization
- Particle-like properties: photons
  - Energy = hf = hc/λ
  - Intensity = (# photons/sec/area) $\propto |E|^2$
  - Photoelectric effect, Compton scattering
  - Localized wave packet

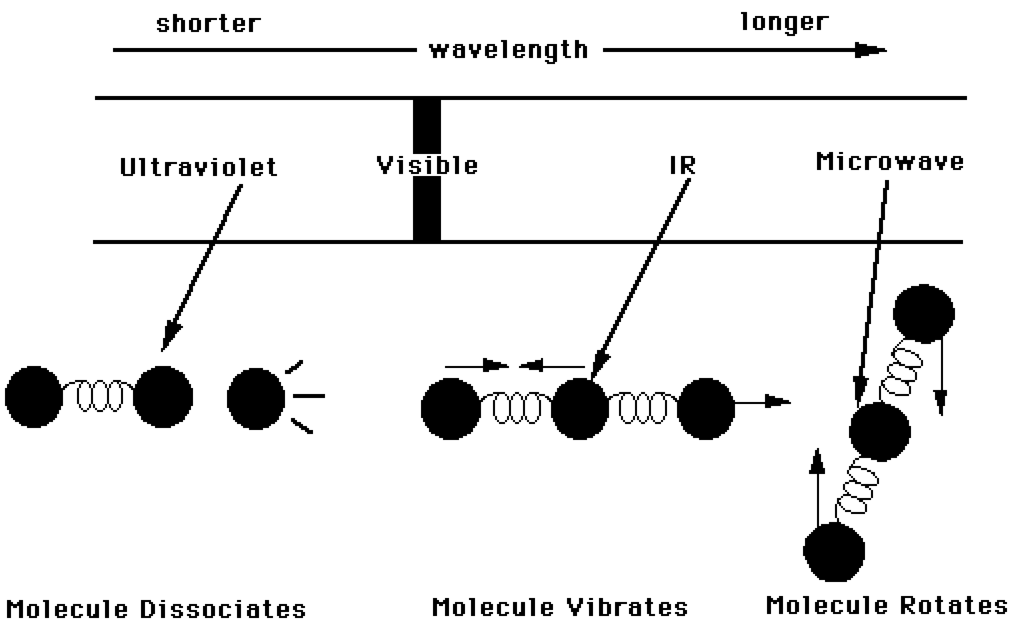
Interactions with matter

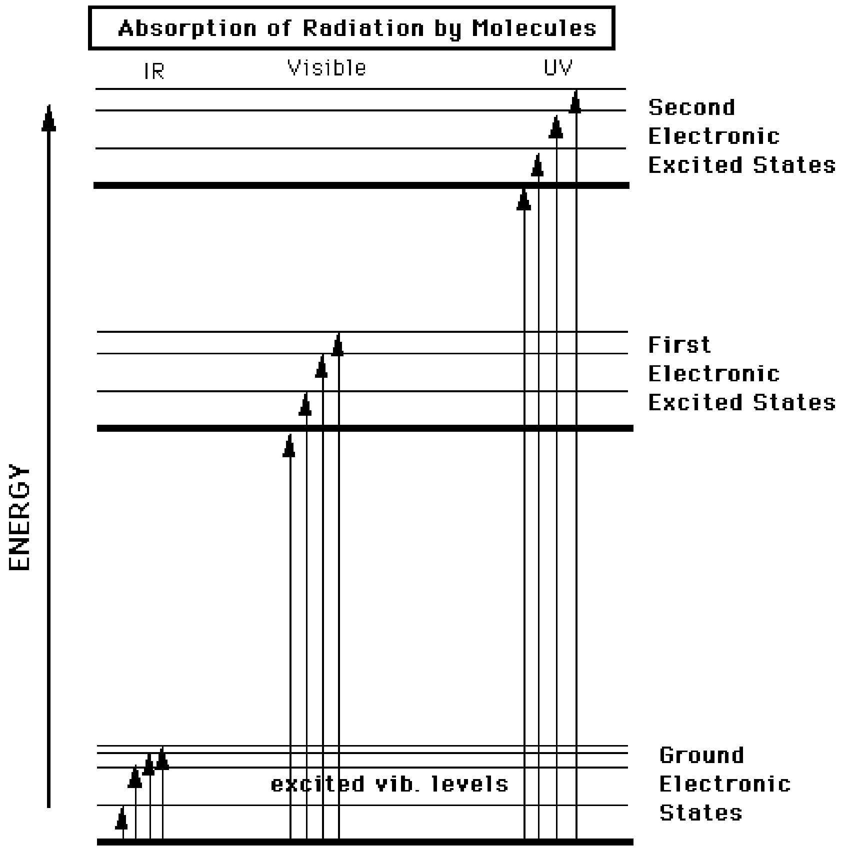
- Ionizing – enough energy to liberate e^-
- Non-ionizing – in general: reflection, transmission or absorption
  - Absorbed radiation may be re-radiated (scattered) at the original frequency (Rayleigh scattering) or at a different frequency (Raman, Brillouin, fluorescence, etc.) or be degraded to heat or initiate a photochemical event or …
- Energy levels – quantized allowed energies – predicted by quantum mechanics for atomic/molecular systems

Energy Levels

- H atom – simplest: $E_n = -13.6/n^2$ eV; transitions between levels; absorption/emission lines
- Classify E levels into 4 types:
  - Electronic – due to orbital motion of e^-; lowest = ground state – quantum number n, with typical $\Delta E \sim$ eV (remember $k_B T \sim 1/40$ eV at Room T); transitions produces uv-vis spectra
  - Vibrational – spring-like oscillations of atoms; if the molecule has N atoms, then 3N coordinates are needed to specify positions; of these 3 give c of m & 3 give overall rotation about c of m – the rest (3N-6) describe relative positions of atoms and give rise to vibrational modes (large number for macromolecule); $\Delta E \sim 0.1$ eV typically and these give rise to IR spectra
  - Rotational – specifies overall rotation of molecule; $\Delta E \sim 0.01$ eV gives a far IR (or microwave) spectra contribution
  - Nuclear energy levels – these have $\Delta E \sim 10^{-4} – 10^{-6}$ eV and are important for NMR

Energy Levels





Rotational and nuclear level
not shown here

Electron on a spring model

- Damped, driven harmonic oscillator:

  ma = F_{net} = - kx - fv +$F_{applied}$ or

$$m\ddot{x} + f\dot{x} + kx = F_{applied} = F_o \cos \omega t$$

- Solution is of the form:

In-phase → ; 90° out of phase →

$$x = x_1 \cos \omega t + x_2 \sin \omega t \quad where$$

$$x_1 = F_o \left[\frac{m(\omega_o^2 - \omega^2)}{m^2(\omega_o^2 - \omega^2)^2 + f^2\omega^2} \right] \quad and$$

$$x_2 = F_o \left[\frac{f\omega}{m^2(\omega_o^2 - \omega^2)^2 + f^2\omega^2} \right] \quad with \quad \omega_o = \sqrt{\frac{k}{m}}$$

Electron on a spring II

- Limiting case of negligible damping (f ~ 0) – then

$$x_1 \rightarrow \frac{F_o}{m(\omega_o^2 - \omega^2)} \quad and \quad x_2 \rightarrow 0$$

  - Only in-phase motion (purely elastic) and can have resonance when $\omega \rightarrow \omega_o$ so that amplitude grows
  - Since x_2 goes to 0, we can connect it with damping or energy loss
- What is the connection of this with spectroscopy?
  - $F_{applied}$ is due to EM radiation (monochromatic at ω)
  - When ω is far from ω_o then e^- is forced to oscillate at ω and not the natural frequency of the bond – energy is absorbed and there is a transition to an excited state – explains absorption in a simple classical picture – what happens next?
  - Accelerating charges radiate according to classical physics

Electron on a spring III

- EM Radiation:

$$E_{scattered} \propto acceleration\ of\ e^- = \frac{d^2(x_1 \cos \omega t)}{dt^2} = \frac{-F_o \omega^2 \cos \omega t}{m(\omega_o^2 - \omega^2)}$$

Or

$$E_{scattered} \propto \frac{-F_o \cos \omega t}{m\left(\frac{\omega_o^2}{\omega^2} - 1\right)^2}$$

- We can find 3 limiting cases of this radiation:

1. Rayleigh limit ($\omega << \omega_o$) –

$$I_{scattered} \sim \frac{\omega^4}{\omega_o^4} \sim \frac{\lambda_o^4}{\lambda^4} \sim \frac{1}{\lambda^4}$$

   very strong wavelength dependence – blue sky/sunsets

2. Thompson limit ($\omega >> \omega_o$) –

$$I_{scattered} \sim \text{constant} \quad \textit{independent of frequency}$$

   x-rays are color blind – no wavelength dependence

Electron on a spring IV

3. When $\omega \sim \omega_o$ then we need to include damping – this results in new phenomenon = dispersion and absorption – dispersion is the variation in the index of refraction with frequency, leading to phase changes in the light that are frequency dependent