# Interactions of Light and Matter: Spectroscopy

- **Spectroscopy:**
  - Interaction of nuclei, atoms, ions, or molecules with electromagnetic radiation
  - Based on quantum theory: quantized energy states

- **Several possible processes**:
  - Absorption: "excitation" of species by interaction with EM radiation
    - UV-VIS:
    - Infrared:
    - Atomic:
  - Emission: release of EM radiation from excited atoms (hot)
  - Luminescence: release of EM radiation from excited atoms, ions and molecules (cool)
    - Fluorescence, Phosphorescence, etc.
  - Scattering**:**

EM Radiation: "Light"
Key concepts and terms

- Light has *electric* and *magnetic* components
  - Oriented at 90º
  - Can be *polarized*
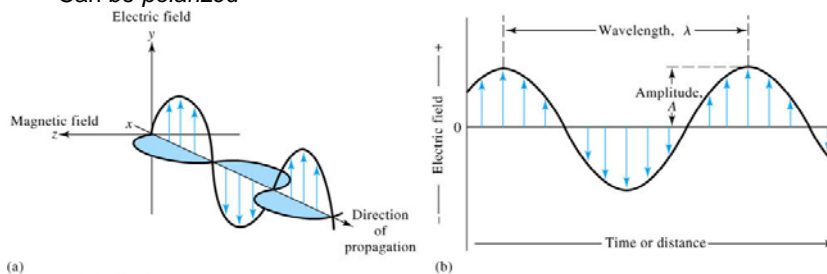
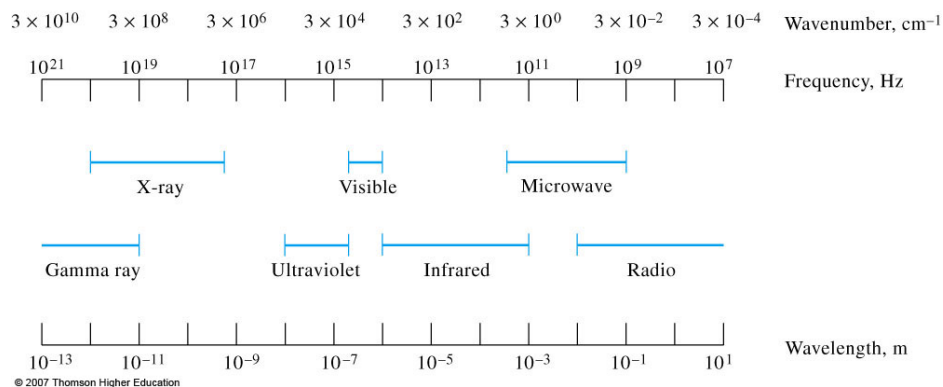

- <u>Wavelength</u> (λ):

- <u>Frequency</u> (ν):

- <u>Velocity</u> (c or v):

Relationships You Should Know

- <u>Einstein-Planck Relationship:</u>

- <u>Wavelength/Frequency Conversion:</u>

- <u>Combined Relationship:</u>

- <u>Refractive Index:</u>

EM Radiation: "Light"
Key concepts and terms

- Electromagnetic Spectrum

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EM Radiation: "Light"
Key concepts and terms

- Quantum Transitions

TABLE 6-1 Common Spectroscopic Methods Based on Electromagnetic Radiation

Type of Spectroscopy	Usual Wavelength Range*	Usual Wavenumber Range, cm^{-1}	Type of Quantum Transition
Gamma-ray emission	0.005–1.4 Å	—	Nuclear
X-ray absorption, emission, fluorescence, and diffraction	0.1–100 Å	—	Inner electron
Vacuum ultraviolet absorption	10–180 nm	1×10^6 to 5×10^4	Bonding electrons
Ultraviolet-visible absorption, emission, and fluorescence	180–780 nm	5×10^4 to 1.3×10^4	Bonding electrons
Infrared absorption and Raman scattering	0.78–300 μm	1.3×10^4 to 3.3×10^1	Rotation/vibration of molecules
Microwave absorption	0.75–375 mm	13–0.03	Rotation of molecules
Electron spin resonance	3 cm	0.33	Spin of electrons in a magnetic field
Nuclear magnetic resonance	0.6–10 m	1.7×10^{-2} to 1×10^3	Spin of nuclei in a magnetic field

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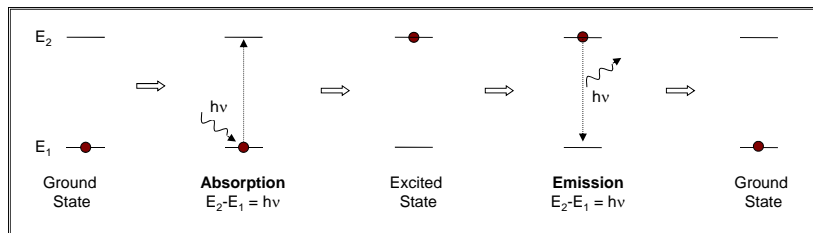

More Enlightening Stuff

- Radiant Power: Measurement of energy of a beam per unit area.
    - Detectors respond to Power

$$P = E\phi$$

- Intensity vs. Power

- Interference: Superposition of waves

- Dispersion:

The Quantum Leap

- Much of the utility of spectroscopy is a result of the dual nature of light and quantized energy levels in atoms/molecules

- Absorption/emission correspond to discrete changes in atom/molecule

E_2 ———   ———   ●   ●   ———

$\Rightarrow$ $h\nu$ $\Rightarrow$ $\Rightarrow$ $h\nu$ $\Rightarrow$

E_1 ●   ●   ———   ———   ●

Ground State | **Absorption** $E_2-E_1 = h\nu$ | Excited State | **Emission** $E_2-E_1 = h\nu$ | Ground State

- Atoms vs. Molecules

Atomic Processes

- Discrete electronic energy levels, governed by e⁻ configuration

- Energy Levels can be described by <u>Term Symbols</u> derived from quantum numbers
  - Derived from solutions to Schrödinger eqn for multi-electron atoms

  - Reflect the energy of an electron in each state
    - Each possible combination of quantum numbers (l, s, m_l, and m_s) for valence electrons gives rise to a term symbol
    - Each term symbol describes an electron in a "unique" energy state
    - Gives rise to fine structure in the spectrum

  - Term symbols take the form: $^{2S+1}L_J$
    - S = Total spin quantum number or "spin multiplicity"
    - L = Orbital quantum number (S,P,D,F)
    - J = Total angular momentum quantum number
      - J = S + L
    - Example: Ground state for Na

Atomic Energy Level Diagrams and Spectra

- Graphically depicted in Atomic Energy (Grotrian) diagrams.
  - Graphical representation of available energy levels for valence electrons
- Selection "Rules"
  - QM predictions of probably and improbable transitions
    - "allowed" = probable; "forbidden" = improbable
    - Ex. Most transitions are between levels where *l* increases or decreases by one (s → p, etc)
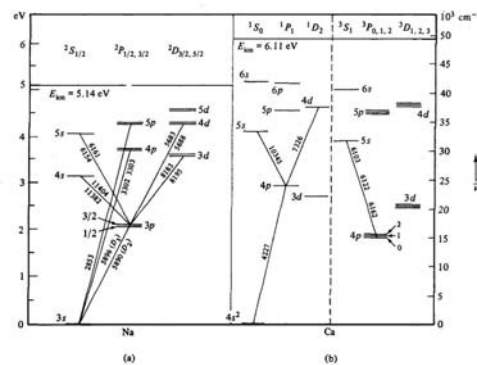
FIGURE 7-11 Energy-level diagram for sodium (a) and calcium (b). The height of each line corresponds to the energy in eV (left scale) relative to the ground level. The ionization limit is the top dashed line (5.14 eV for Na and 6.11 eV for Ca). The right scale expresses the energy in wavenumbers relative to the ground level. Allowed transitions and their wavelengths (Å) are shown by the lines connecting levels. The term symbols are shown at the top of each diagram.

Molecular Processes

- Similar to atomic: Excitation/relaxation between quantized energy levels.
  - Perturbed by rotational and vibrational motion.

Inter-nuclear Distance
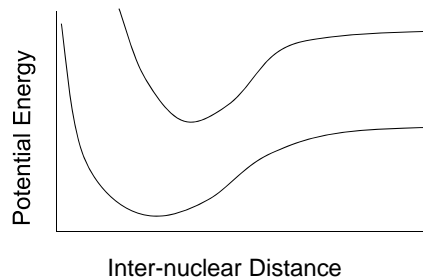
- Possible to define molecular terms symbols also. Gets complex in a hurry!

- Vibrations cause changes in inter-nuclear distance, so change in PE!

Molecular Electronic Processes (UV-VIS)

- Several pathways for loss of absorbed radiation. Favored route is the fastest route back to GS

- Collisional Deactivation (Radiationless):

- Fluorescence:
  - Vibrational Relaxation (10^{-12} s)
  - Internal Conversion
  - Radiative Decay (10^{-7} - 10^{-9} s)

- Phosphorescence (10^{-4} s or longer)
  - Intersystem Crossing

S_2

S_1

T_2

T_1

S_0
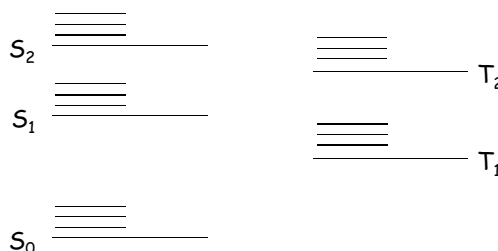
Molecular Vibrational Processes
(IR/Raman)

- Lower energy modes

- For a diatomic molecule, a mass-on-a-spring model works well (Hooke's Law). Quantum mechanical solution gives:

$$E_{vib} = \left(v + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

- Only Δv of 1 is permitted

- This results in a pattern of vibrational levels with equal spacing so that

$$\Delta E_{vib} = E_{vib} - E_{GS} = h\nu$$

- In IR, only vibrations which result in changes in dipole moment are observed
  - O_2 doesn't absorb IR light, but O_3 does.

Molecular Vibrational Processes
(IR/Raman)

Gas Phase Carbon Monoxide
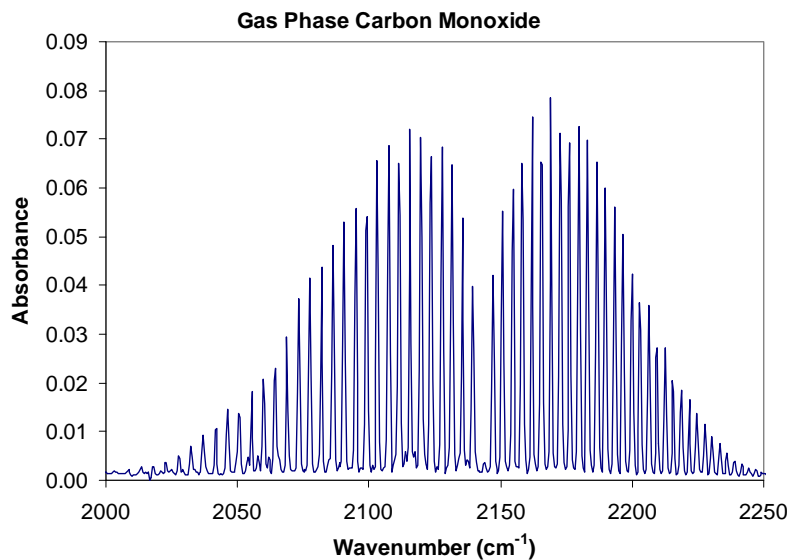
Molecular Vibrational Processes
(IR/Raman)

- Raman Spectroscopy (Raman Scattering)
- What happens when a molecule interacts with a photon?

Figure 18-2 Origin of Rayleigh and Raman scattering.
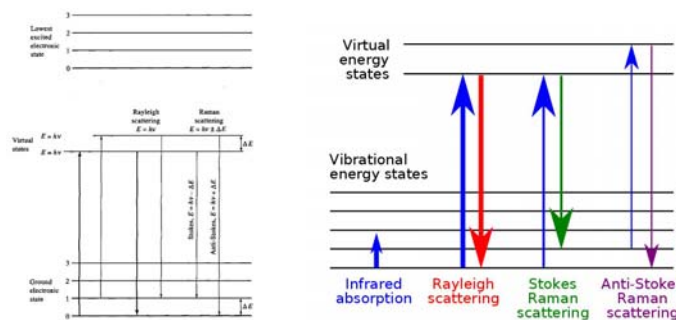
- If there is a change in polarizability of the molecule that results from a vibration, this is transferred to the scattered radiation
  - additive or subtractive effect(rare)
  - corresponds to a specific vibrational transition
  - does NOT involve change in dipole moment

Generic Spectroscopy Experiment

- Arrangement and identity of components vary
  - Depends on sample

| Source | → | λ-Disperser | $\xrightarrow{P_0}$ | Sample (Blank) | $\xrightarrow{P}$ | Detector | → | Readout |
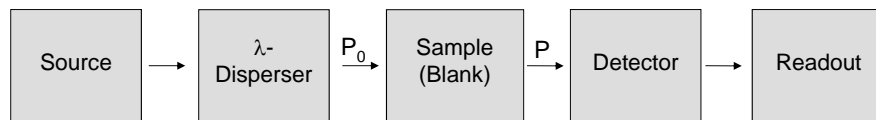
- Questions we'll explore:
  - How do we probe a particular interaction?
  - What requirements will the hardware have?
    - What components fit the requirements?
  - How do we extract useful information from the data?