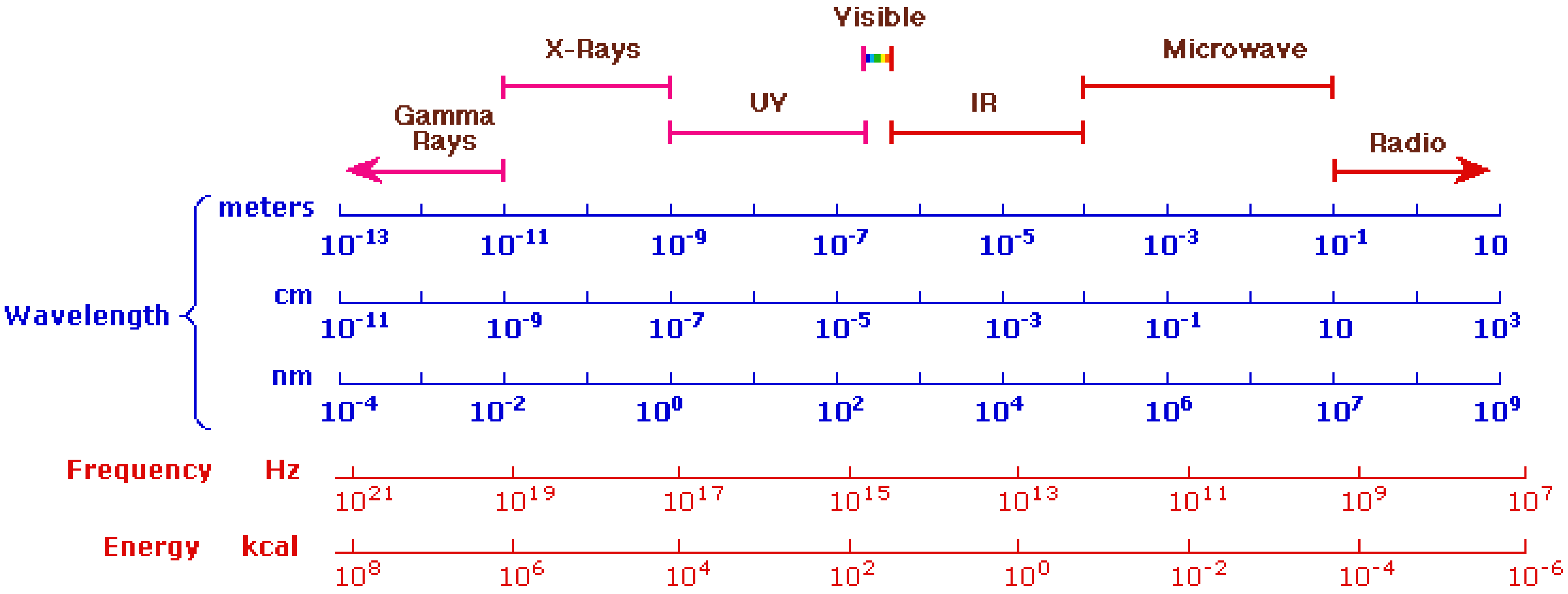
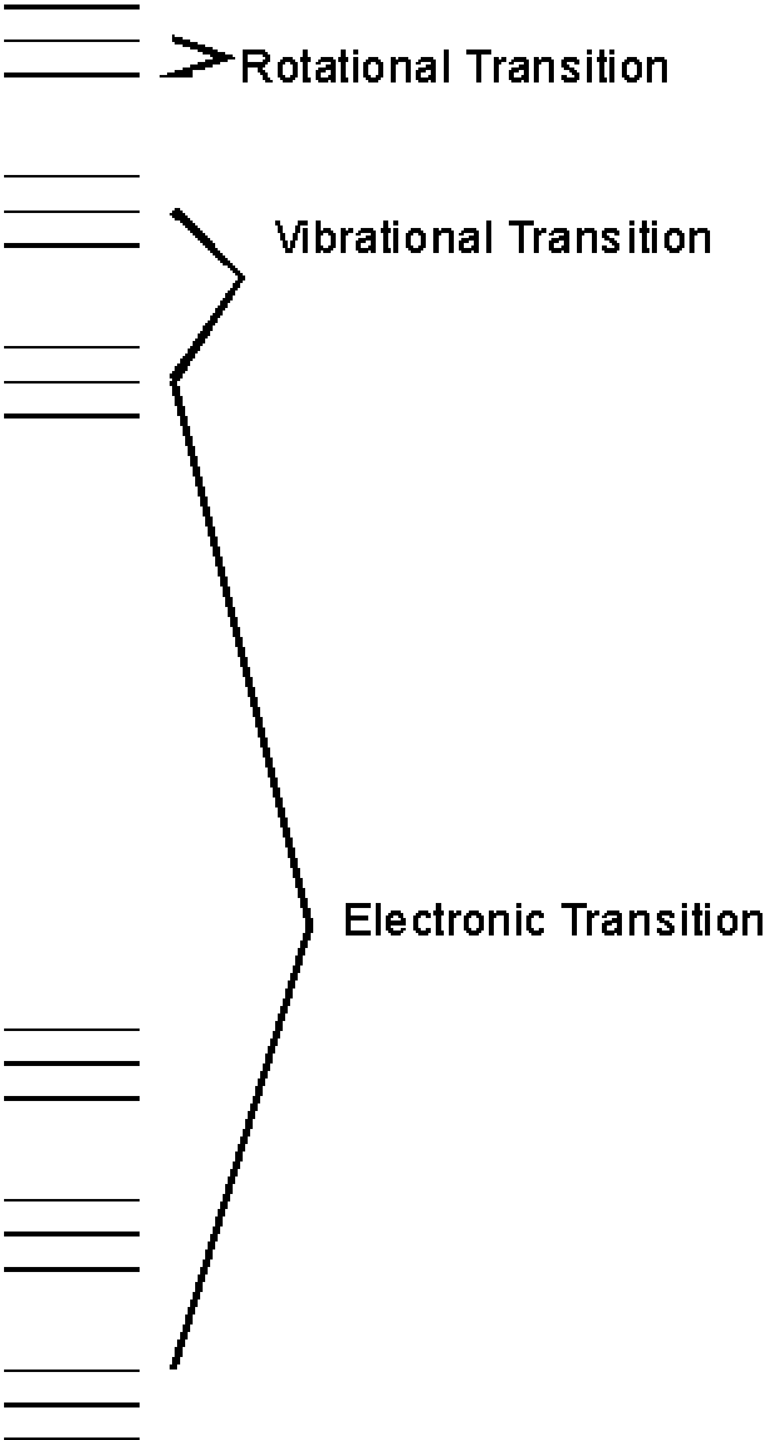
Chemistry 4631

Instrumental Analysis

Lecture 4

The Electromagnetic Spectrum





Rotational Transition

Vibrational Transition

Electronic Transition

IR Spectroscopy

Infrared Spectroscopy

FTIR is Fourier-Transform Infrared Spectroscopy

It is a chemically specific technique – used to identify chemical compounds and functional groups.

IR Spectroscopy

Infrared Spectroscopy

IR radiation occurs between 0.7 and 1000 μm.

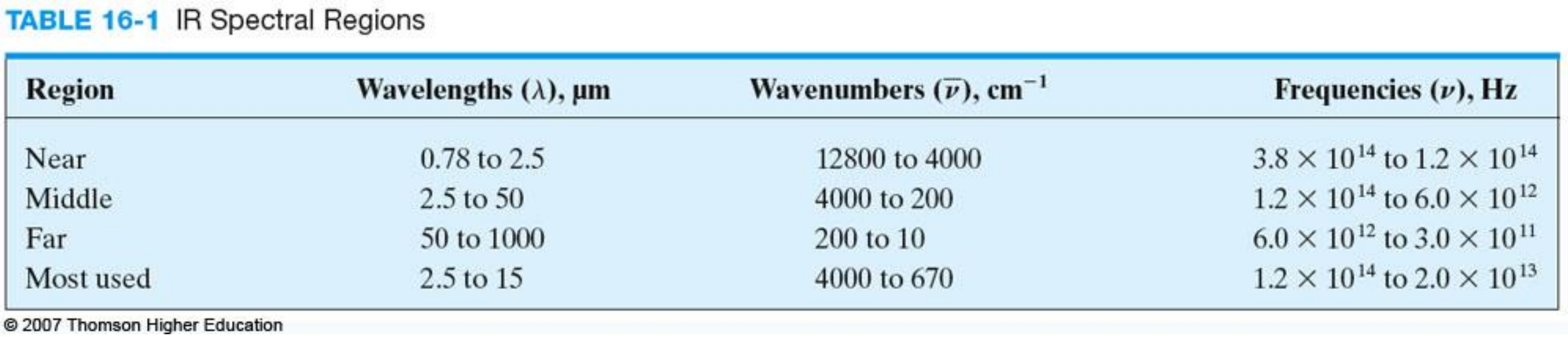


TABLE 16-1 IR Spectral Regions

Region	Wavelengths (λ), μm	Wavenumbers ($\bar{\nu}$), cm^{-1}	Frequencies (ν), Hz
Near	0.78 to 2.5	12800 to 4000	3.8×10^{14} to 1.2×10^{14}
Middle	2.5 to 50	4000 to 200	1.2×10^{14} to 6.0×10^{12}
Far	50 to 1000	200 to 10	6.0×10^{12} to 3.0×10^{11}
Most used	2.5 to 15	4000 to 670	1.2×10^{14} to 2.0×10^{13}

Wavelength is measured in "wavenumbers", which have the units cm^{-1}.

wavenumber = 1 / wavelength in centimeters

IR Spectroscopy

Infrared Spectroscopy

IR radiation does not have enough energy to induce electronic transitions as seen with UV.

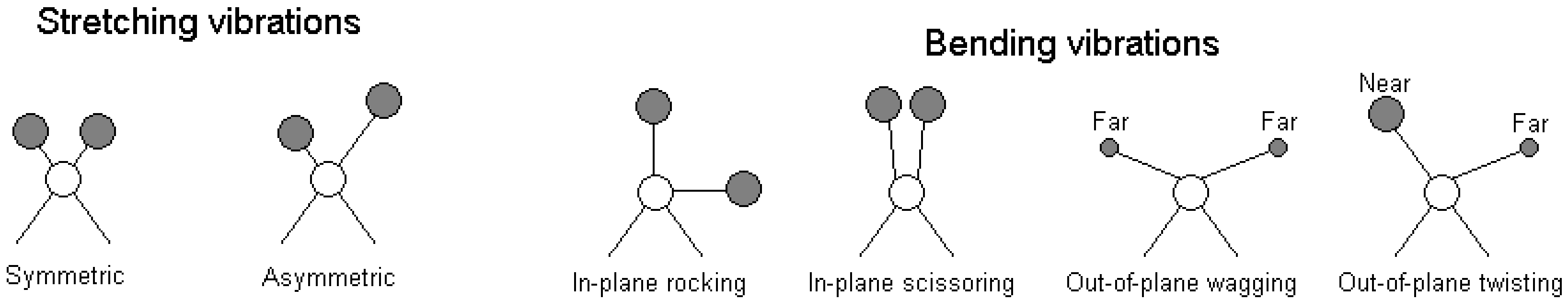
IR is an absorption technique which measures vibrations of molecules.

Absorption only occurs when the photon interacts with a molecule undergoing a change in dipole.

IR Spectroscopy

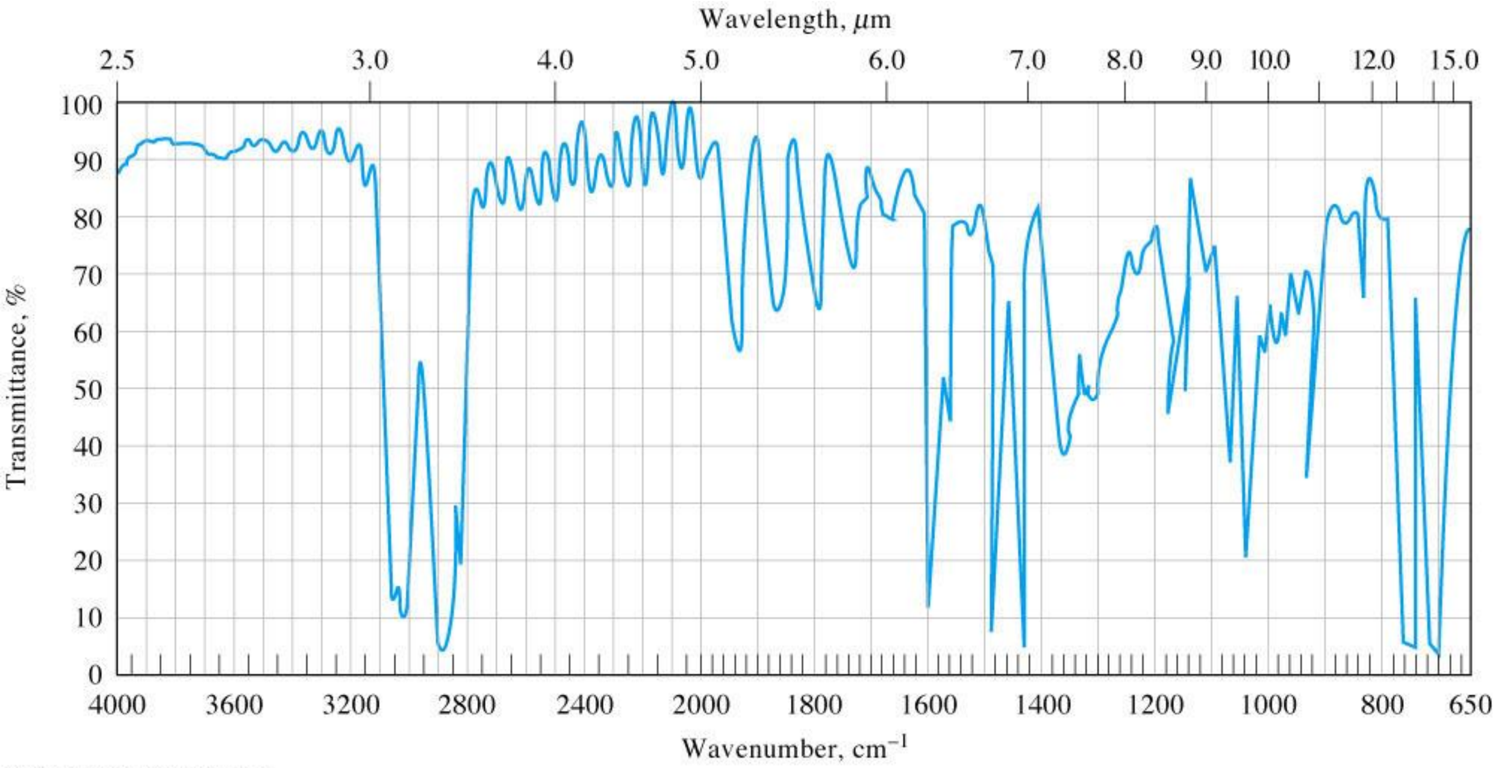
Molecular vibrations fall into 2 main categories

- **Stretching**
- **Bending**



IR Spectroscopy

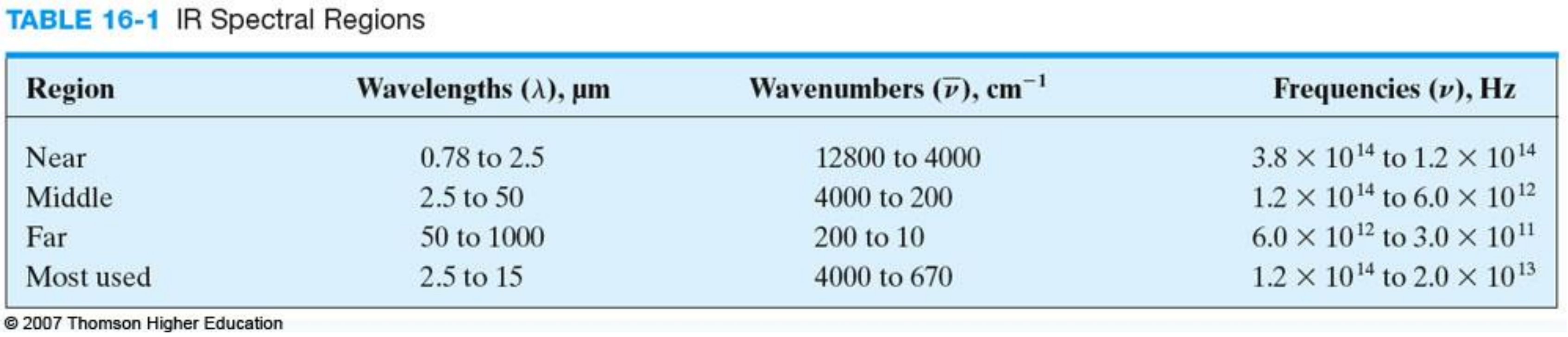
Typical IR spectrum



IR Spectroscopy

Mid-IR Reflection – most widely used IR region

Can obtain absorption, reflection, and emission spectra.



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IR Spectroscopy

Quantitative Analysis

- **Usually not as good as UV/vis.**
- **Deviation from Beer’s Law is more common.**
- **Using matched cells is difficult, so use a cell in/cell out procedure.**

So use FTIR for Qualitative analysis.

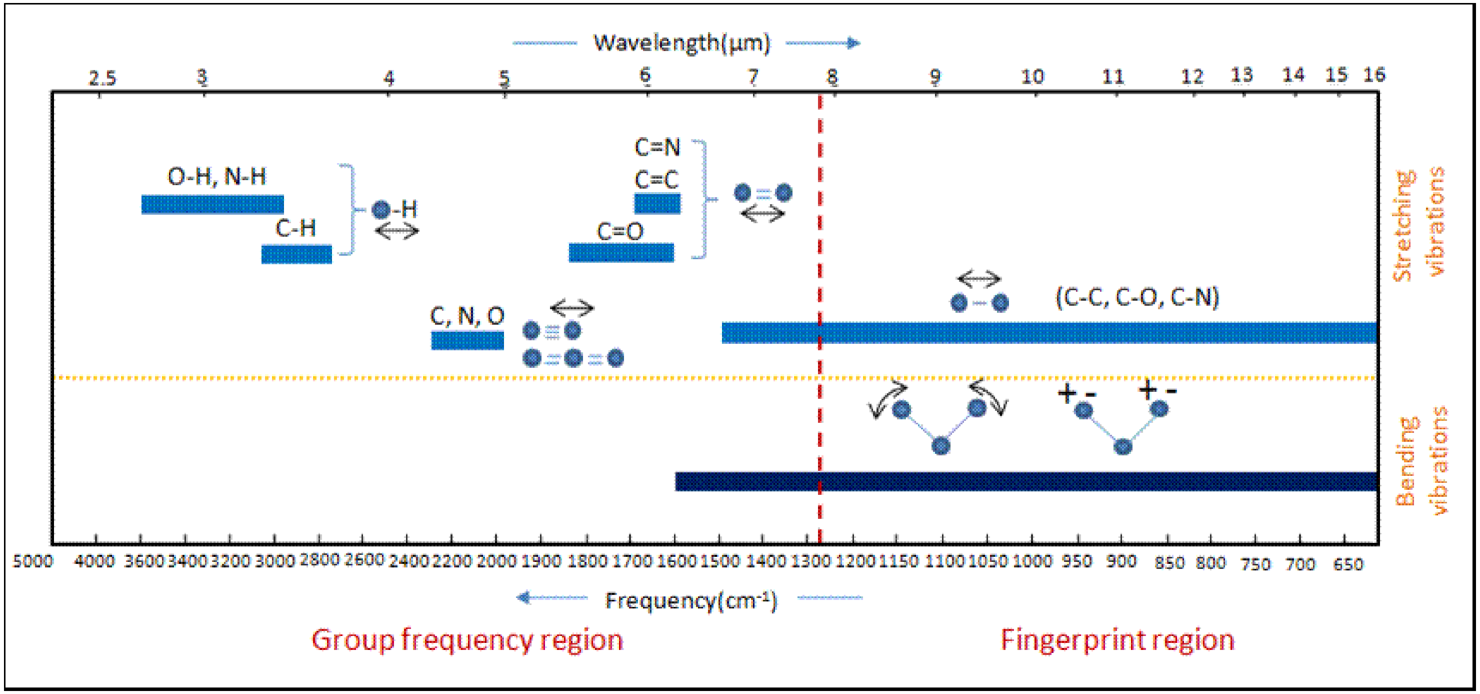
IR Spectroscopy

Mid-IR Reflection

When measuring compounds in the mid-IR region – first examine the *group frequency region* (3600 – 1250 cm^{-1}), then compare the *fingerprint region* (1200 – 600 cm^{-1}) to pure standards.

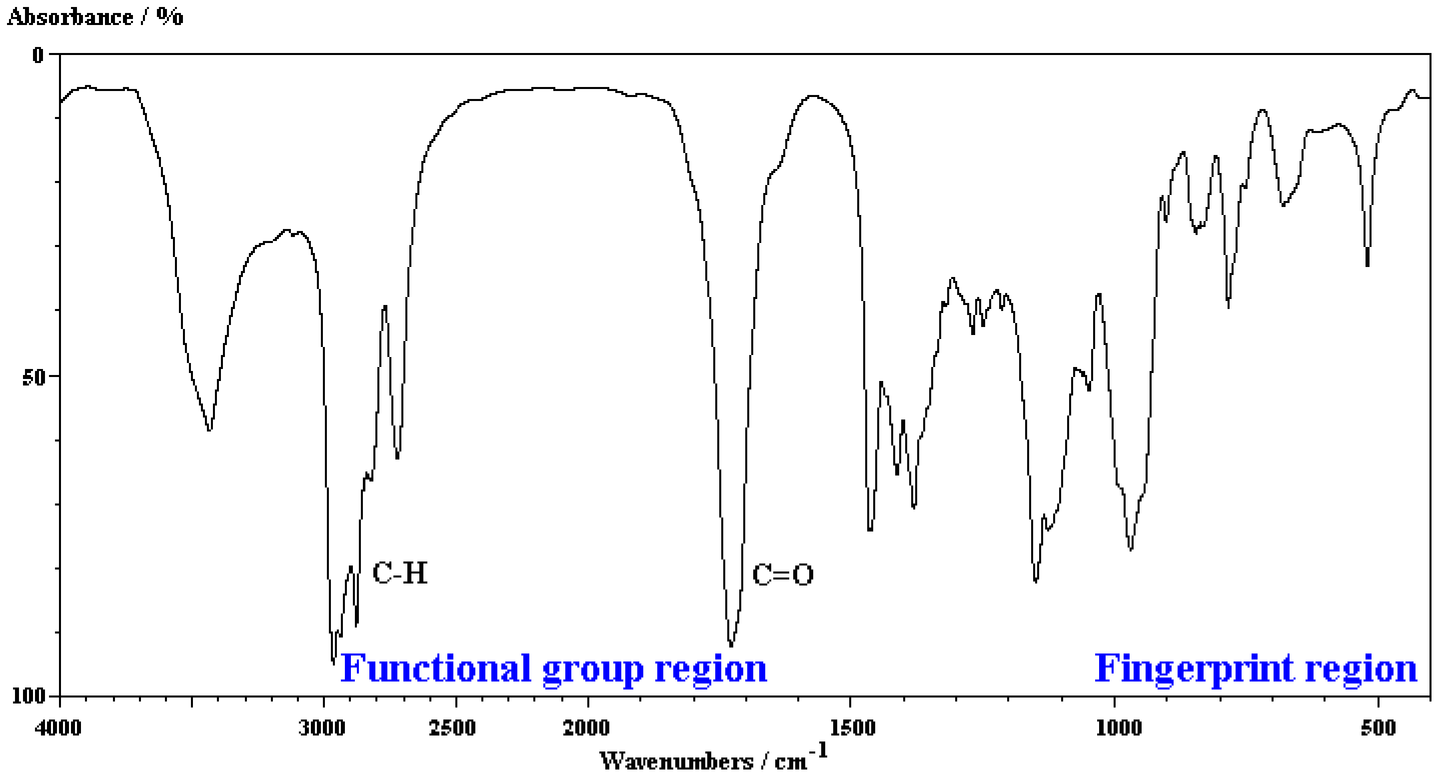
IR Spectroscopy

Mid-IR Reflection – most widely used IR region



IR Spectroscopy

Mid-IR Reflection



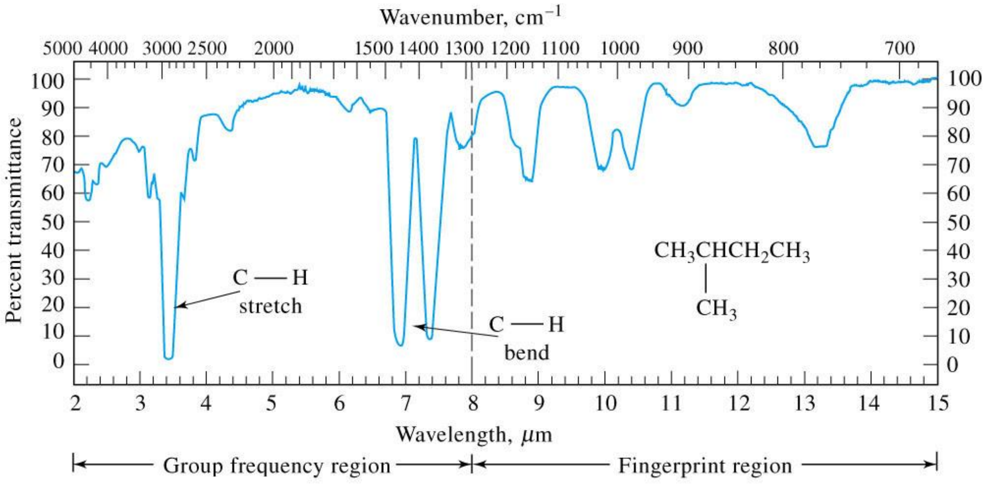
IR Spectroscopy

Mid-IR Reflection

Group frequency region identifies the organic functional groups, i.e. C=O, C=C, C-H, O-H…

IR Spectroscopy

Mid-IR Reflection



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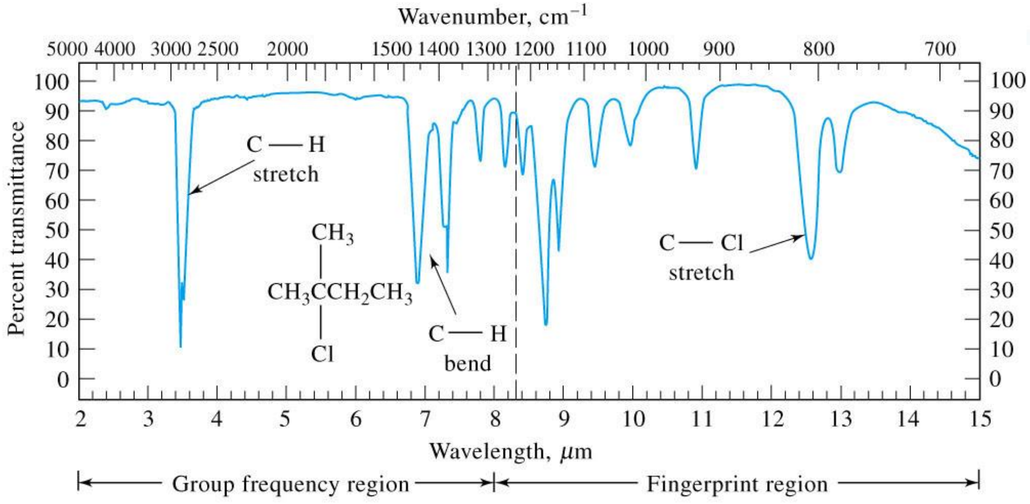

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IR Spectroscopy

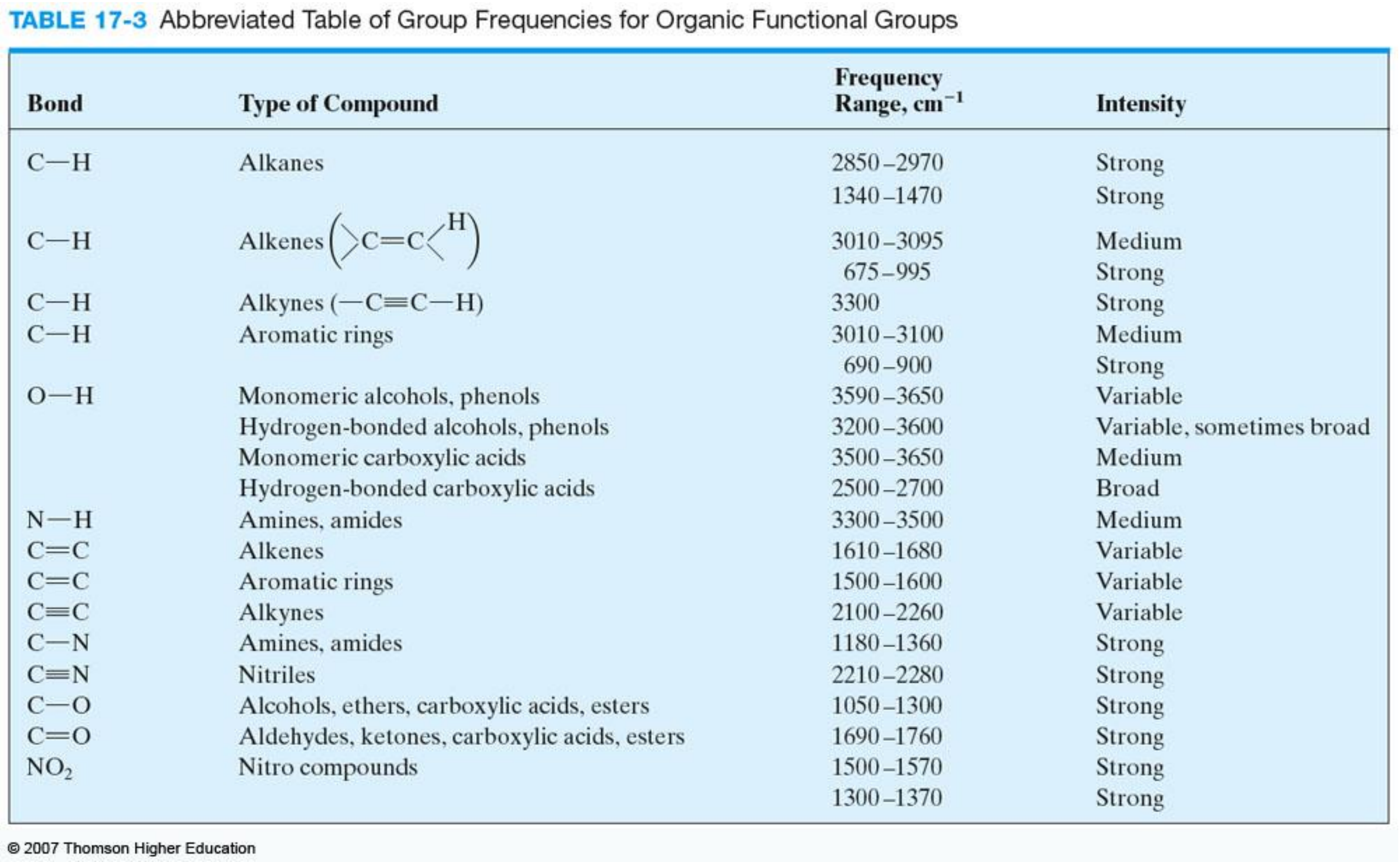


TABLE 17-3 Abbreviated Table of Group Frequencies for Organic Functional Groups

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes $\left(\rangle C{=}C\langle^{H}\right)$	3010–3095	Medium
		675–995	Strong
C—H	Alkynes (—C≡C—H)	3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C═C	Alkenes	1610–1680	Variable
C═C	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C≡N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C═O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO_2	Nitro compounds	1500–1570	Strong
		1300–1370	Strong

IR Spectroscopy

Mid-IR Reflection

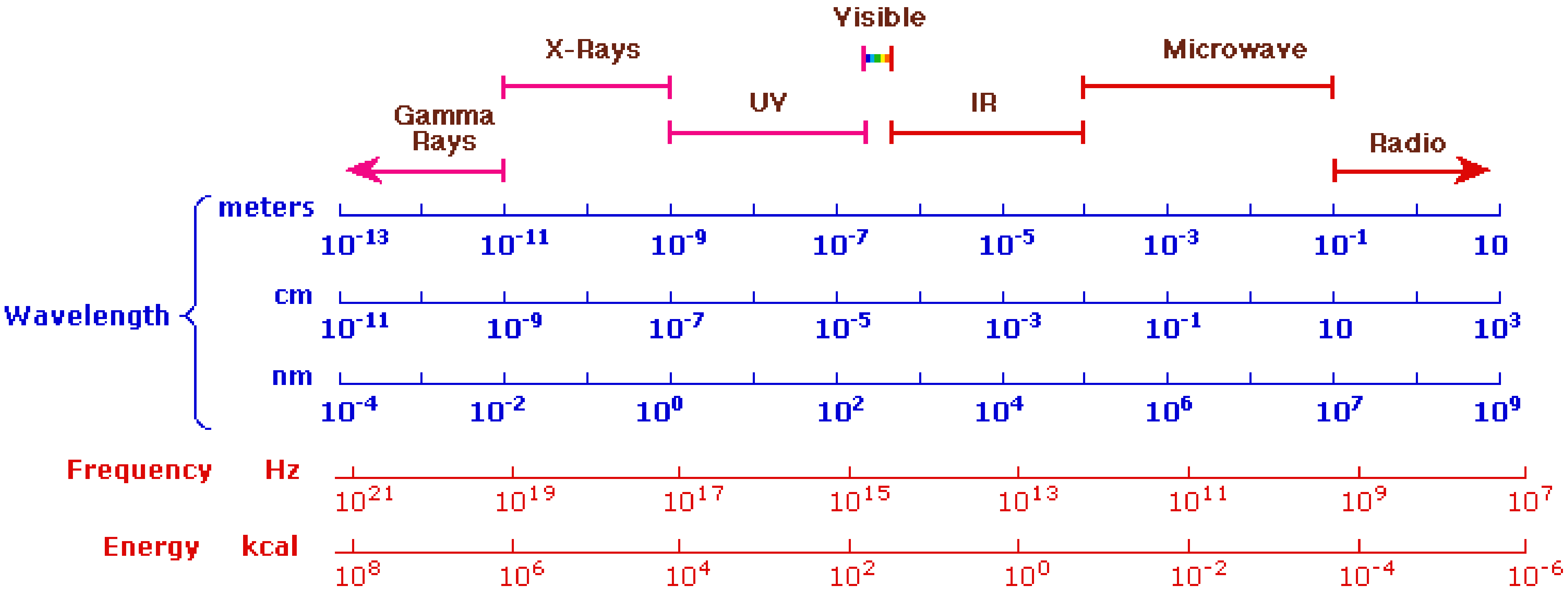
- Specular reflection
- Diffuse reflection
- Internal reflection
- Attenuated total reflection (ATR)

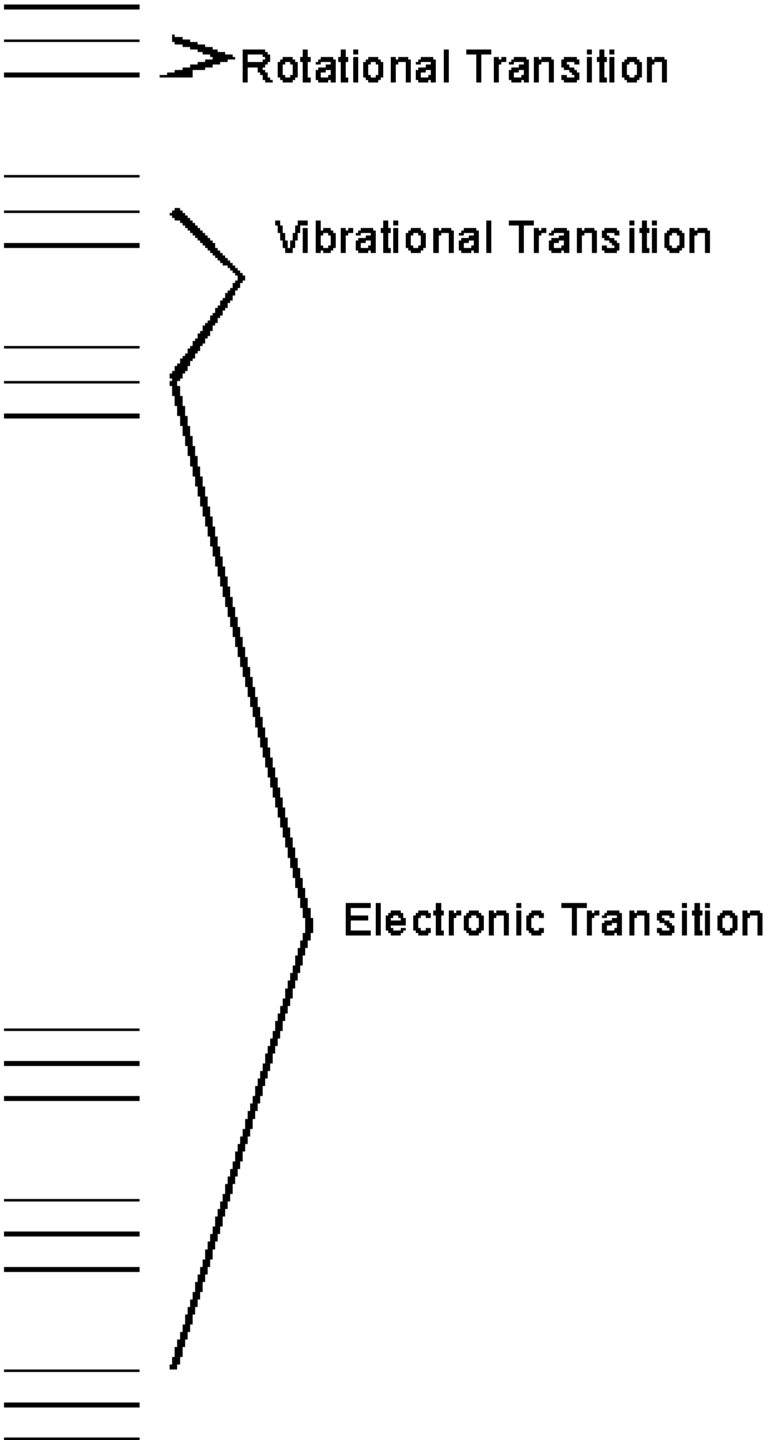
Fluorescence Spectroscopy

When photons are absorbed, the following processes can occur:

- **Molecular dissociation**
- **Photochemical reaction**
- **Fluorescence**
- **Phosphorescence**
- **Nonradiative return to ground state**

The Electromagnetic Spectrum





Rotational Transition

Vibrational Transition

Electronic Transition

Molecular Luminescence Spectrometry

Photoluminescence

Excitation brought about by absorption of photons. Sensitive method with detection limits in parts per billion range, also has a large linear range.

- Fluorescence
- Phosphorescence

Molecular Luminescence Spectrometry

Theory

Typically molecular fluorescence bands are found at wavelengths longer than the resonance line. This shift to longer wavelengths (lower energies) is the Stokes shift.

Molecular Luminescence Spectrometry

Theory

Electron spin

- Paired electrons have opposite spin states and thus exhibit no net magnetic field (diamagnetic) (not attracted or repelled by static magnetic fields).
- Free radicals contain unpaired electrons and have a magnetic moment and attracted to a magnetic field (paramagnetic).

Molecular Luminescence Spectrometry

Theory

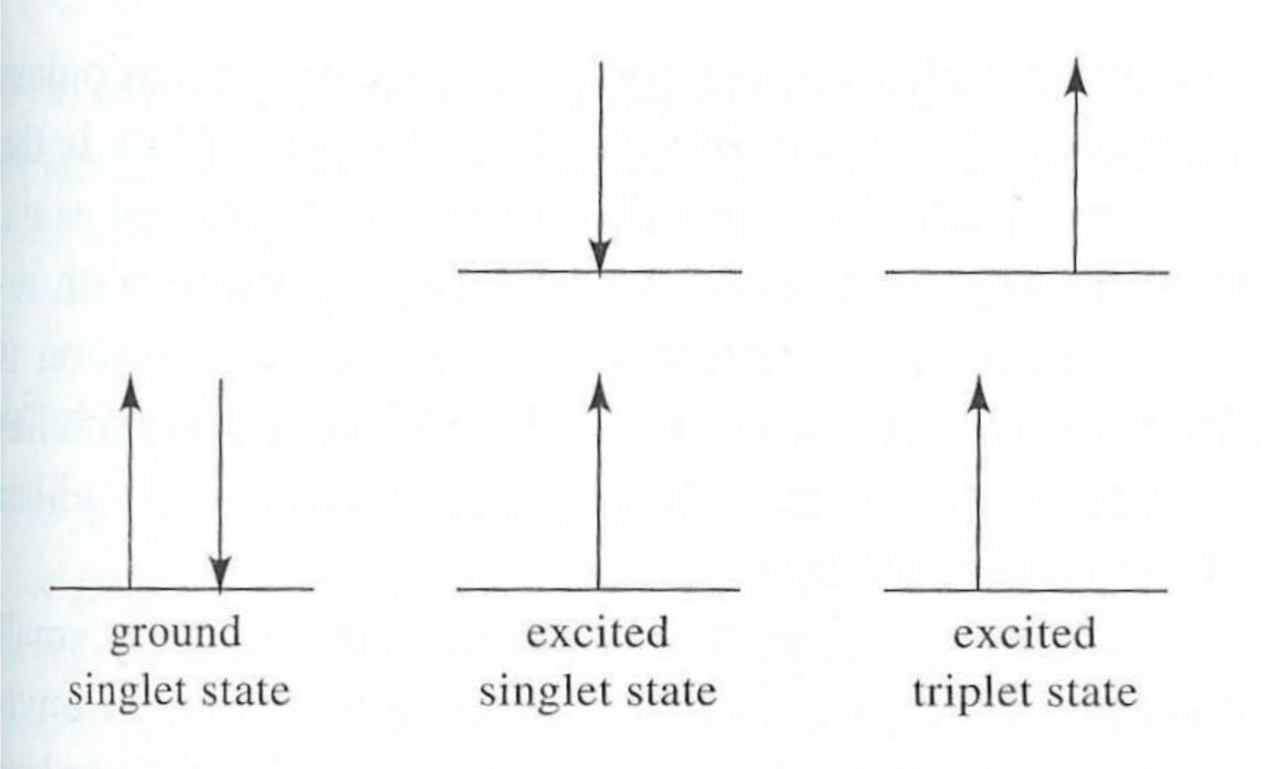
Singlet/Triplet Excited States

- When a pair of electrons in a molecule are excited to a higher energy level, a singlet or triplet is formed.
- For the excited singlet state, the electrons are still paired, for the triplet state the spin of the electrons are unpaired.

Molecular Luminescence Spectrometry

Theory

Singlet/Triplet Excited States



Molecular Luminescence Spectrometry

Theory

Singlet/Triplet Excited States

- A singlet-triplet transition is significantly less probable than the singlet-singlet transition. The lifetime of a triplet state may range from 10^{-4} to several seconds.

Energy-level Diagrams

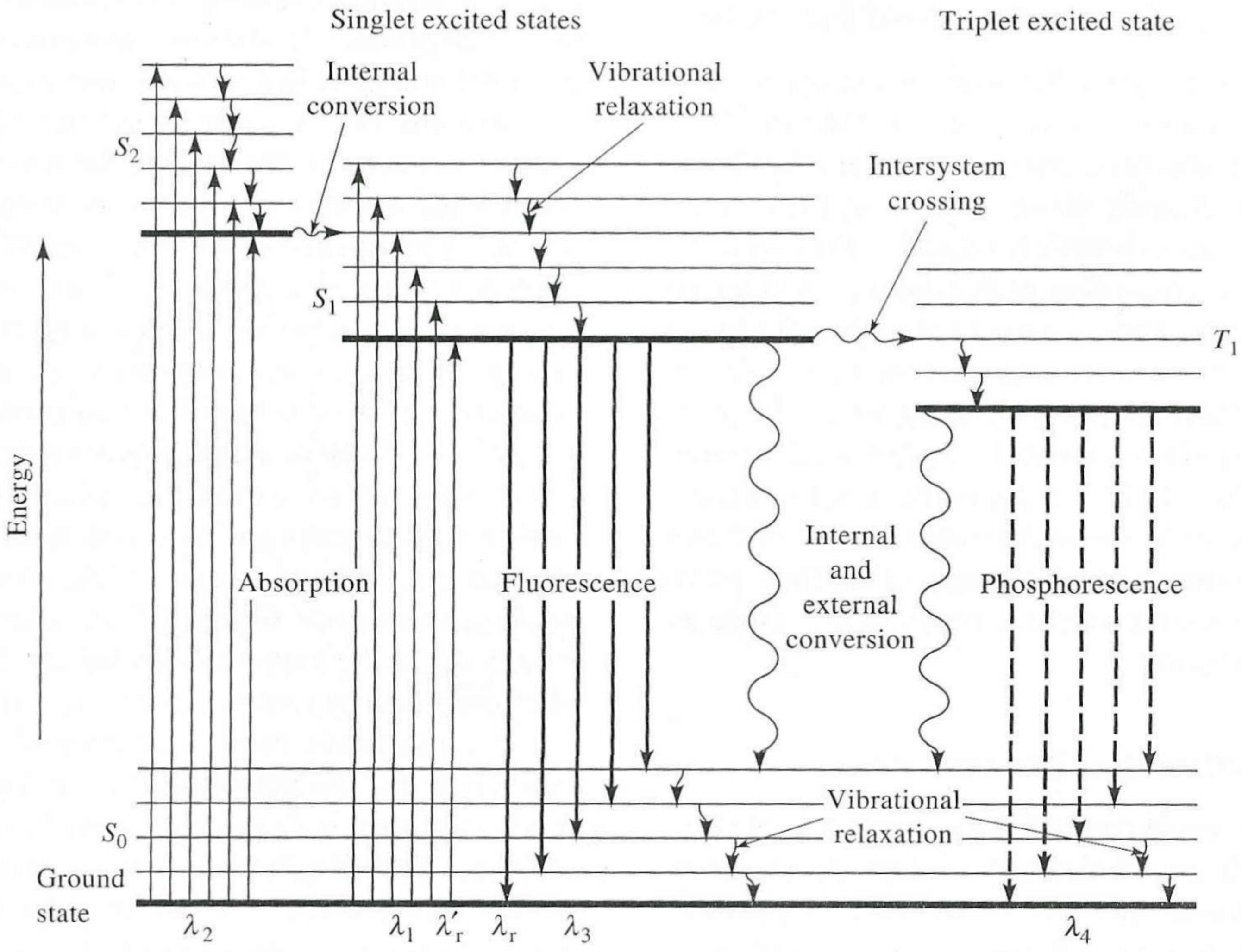


Figure 15-1 Partial energy diagram for a photoluminescent system.

Molecular Luminescence Spectrometry

Internal conversion

Intermolecular process by which a molecule passes to a lower energy electronic state without emission of radiation.

The process is poorly understood but seems to occur when two electronic energy levels have overlap in vibrational energy levels. May or may not result in fluorescence.

Molecular Luminescence Spectrometry

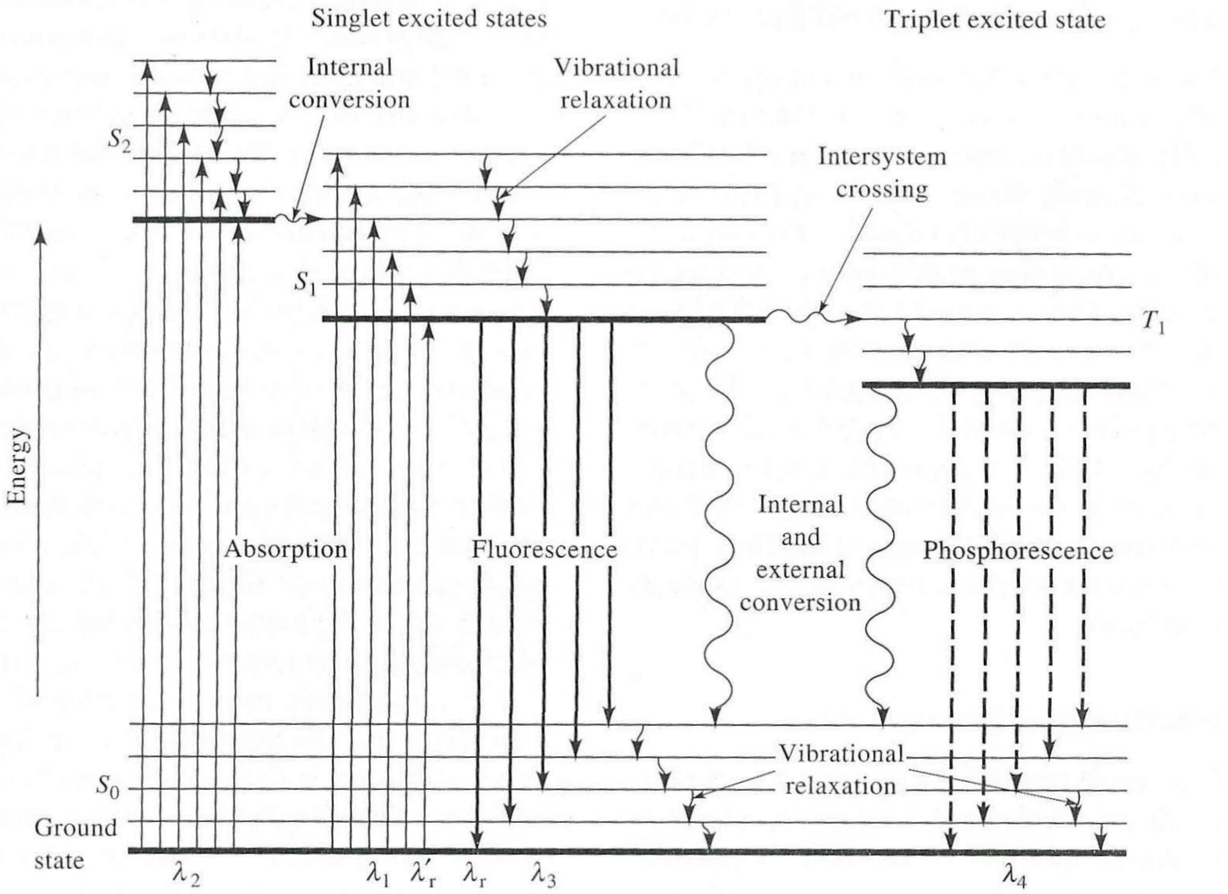


Figure 15-1 Partial energy diagram for a photoluminescent system.

Molecular Luminescence Spectrometry

Vibrational Relaxation

Molecule may be promoted to several vibrational levels during the electronic excitation process, excess vibrational energy can easily be lost due to collisions of excited molecules with solvent molecules.

This process is so efficient that fluorescence must occur from lowest vibrational level of an excited electronic state.

Molecular Luminescence Spectrometry

Vibrational Relaxation

The result of this vibrational relaxation is to displace the fluorescence band to lower frequencies (longer λ's) (Stokes shift)

Molecular Luminescence Spectrometry

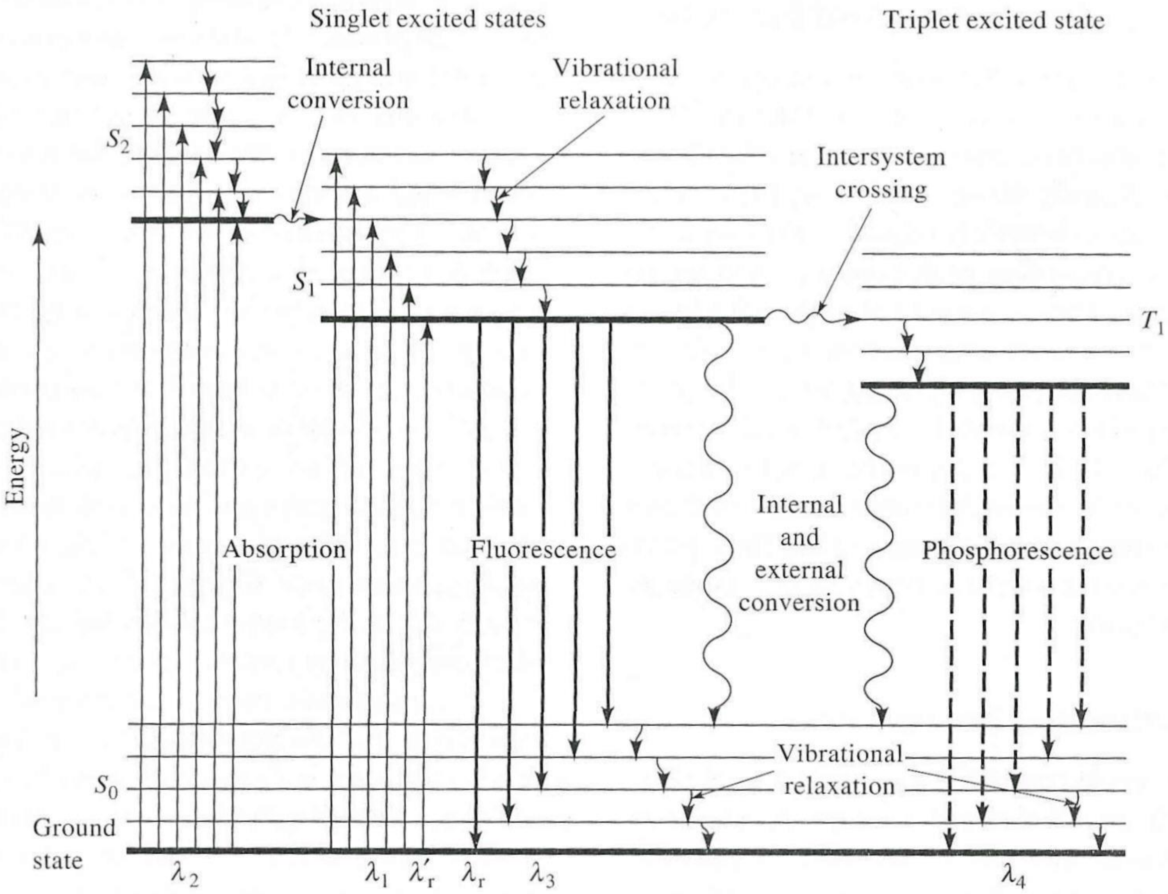


Figure 15-1 Partial energy diagram for a photoluminescent system.

Molecular Luminescence Spectrometry

External conversion (collisional quenching)

Energy transfer between the excited molecule and the solvent or other solutes. Mostly heat transfer.

Molecular Luminescence Spectrometry

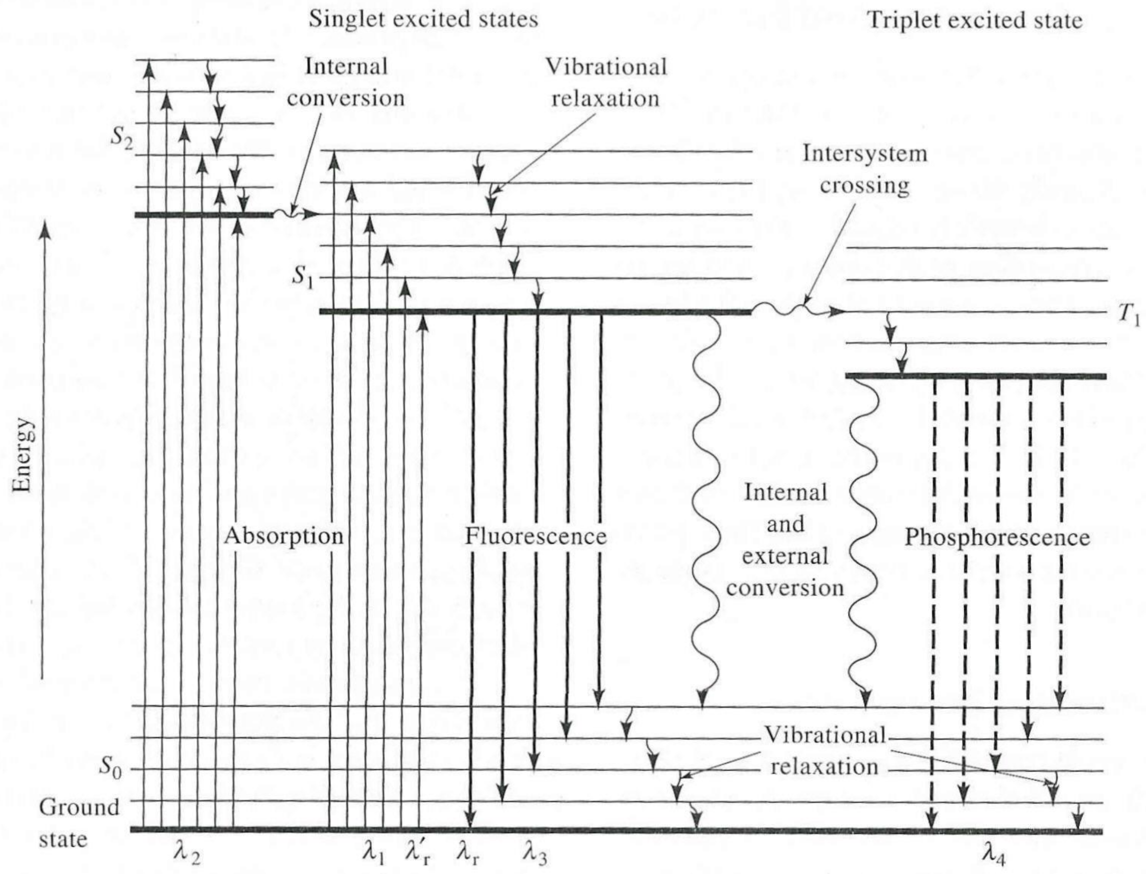


Figure 15-1 Partial energy diagram for a photoluminescent system.

Molecular Luminescence Spectrometry

Intersystem crossing

Spin of an excited electron is reversed giving a change in multiplicity of the molecule. This occurs more when the vibrational levels overlap. More common in molecules having heavy atoms (i.e. I or Br)

Molecular Luminescence Spectrometry

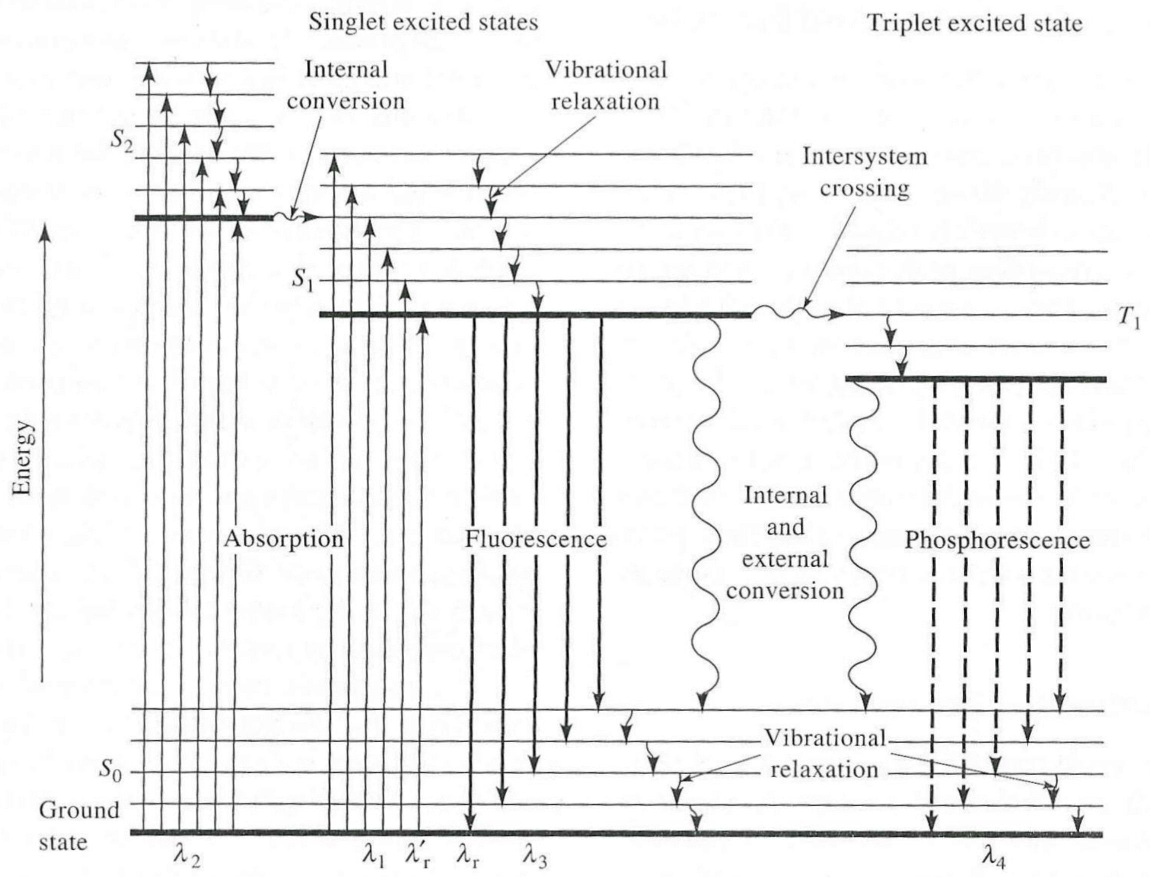


Figure 15-1 Partial energy diagram for a photoluminescent system.

Molecular Luminescence Spectrometry

Emission and Excitation Spectra

- Excitation spectrum
  - absorbance spectrum
- Fluorescence and Phosphorescence
  - excitation at fixed λ while recording emission intensity as a function of λ

Molecular Luminescence Spectrometry

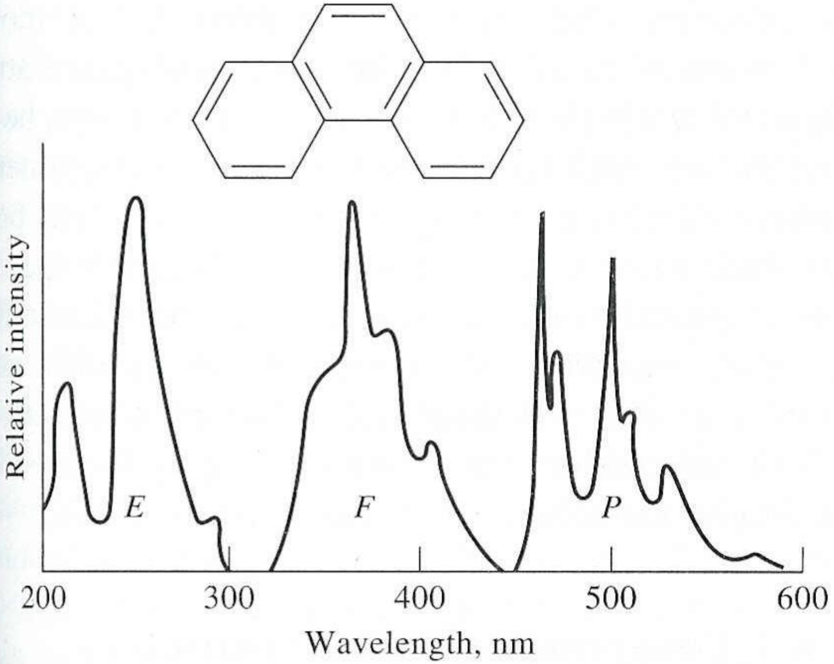


Figure 15-3 Spectra for phenanthrene: *E*, excitation; *F*, fluorescence; *P*, phosphorescence. *(From W. R. Seitz, in* Treatise on Analytical Chemistry, *2nd ed., P. J. Elving, E. J. Meehan, and I. M. Kolthoff, Eds., Part I, Vol. 7, p. 169. New York: Wiley, 1981. Reprinted by permission of John Wiley & Sons, Inc.)*

Assignment

- Homework 1: Ch. 1: 11 and
- Appendix 1: 1, 2, 10, and 12
- (extra credit) – Due Jan 24th
- Read Chapter 6
- HW2: Ch. 6: 2-12, 14, 15, 18, 19 (extra credit) (Due 1-29)

- Read Chapter 15
- Read Chapter 16
- Read Chapter 17

- HW 3: Ch. 16: 7, 8, 11 and Ch. 17: 2, 4, 5 (Due 1-31)