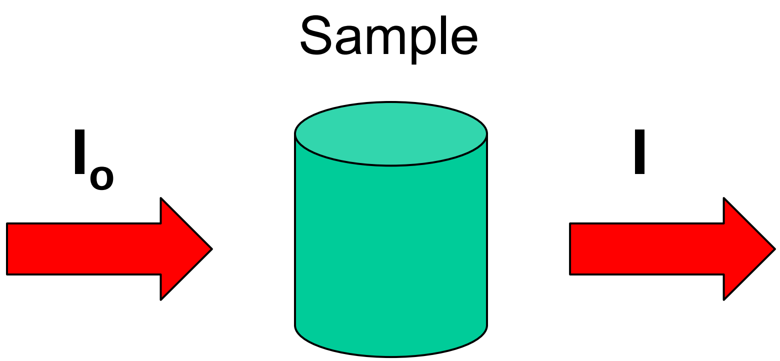
Chapter 6 – Introduction to Spectrometric Methods

Read pp. 132-159   Problems: 1,2,3,4,7,8,9,14,15

Spectrometric methods = general term for the science that deals with the interactions of various types of electromagnetic radiation (e.g., visible light) with matter.



What can happen to the light intensity as it passes through the sample?

For many measurements, the amount of light **absorbed** (only) is related to the analyte concentration!

$$I_{abs} \sim [\text{analyte}]$$

Ultraviolet = < 180 nm
Ultraviolet/visible = 180 – 780 nm
Infrared = 0.78 – 300 μm

$$E = h\upsilon = hc/\lambda$$

photon

Electromagnetic radiation (EMR) has properties of a wave

energy ⟶ $E = h\upsilon = hc/\lambda$

velocity ⟶ $v_i = \upsilon\lambda_i$

Oscillating electric field

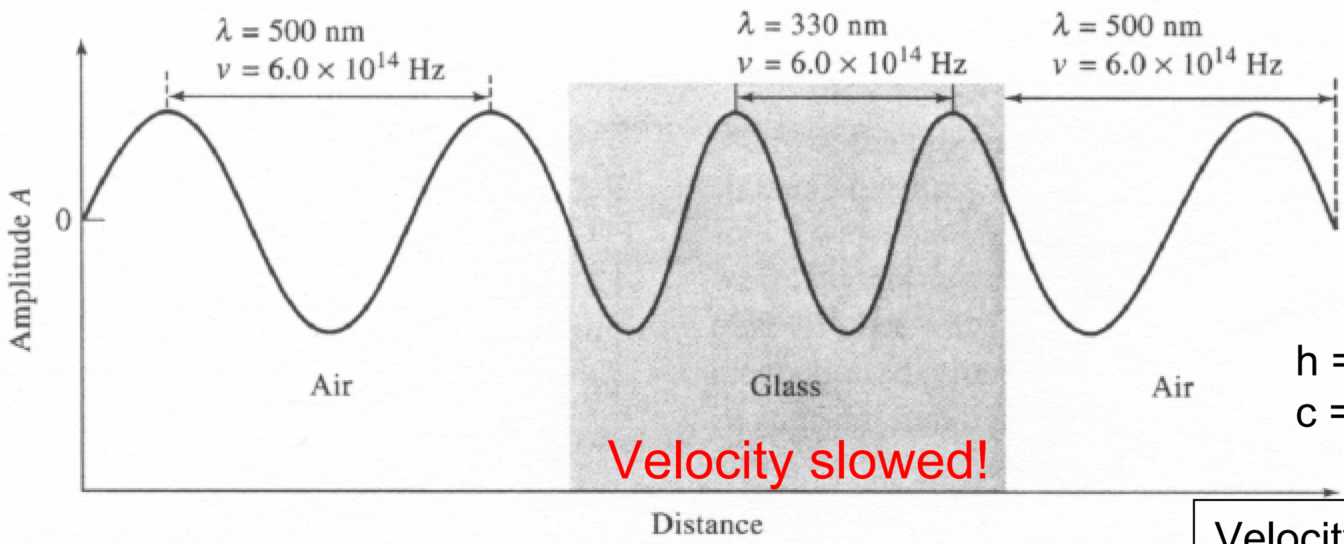


Figure 6-2 Effect of change of medium on a monochromatic beam of radiation.

$h = 6.62 \times 10^{-34}$ Js
$c = 3.00 \times 10^{8}$ m/s

Velocity in vacuum
$v_{vac,air} = c = 3.00 \times 10^{8}$ m/s

Amplitude, frequency (s^{-1}, Hz), period (time in s for passage of successive maxima or minima), wave length (linear distance between two equiv. Pts., nm), velocity of propagation (m/s).

Monochromatic means **one** wavelength of light (EMR).

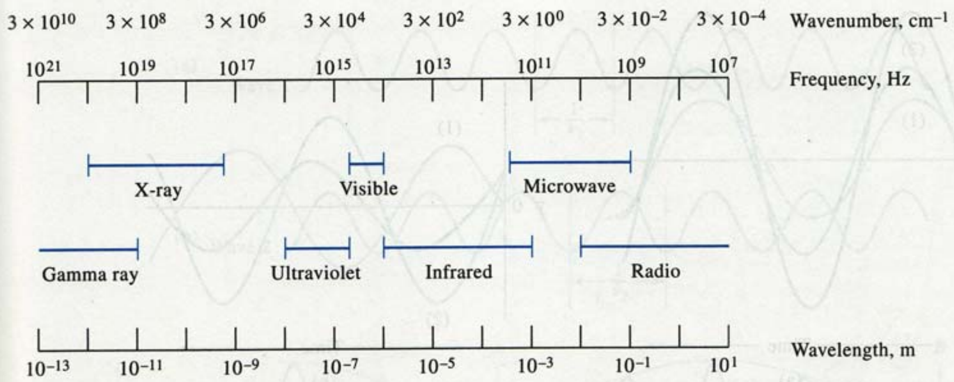


FIGURE 6-3 Regions of the electromagnetic spectrum.

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

*1 Å = 10^{-10} m = 10^{-8} cm

1 nm = 10^{-9} m = 10^{-7} cm

1 μm = 10^{-6} m = 10^{-4} cm

y = magnitude of the electric field

A = amplitude or max value of y

$\omega = 2\pi\nu$

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

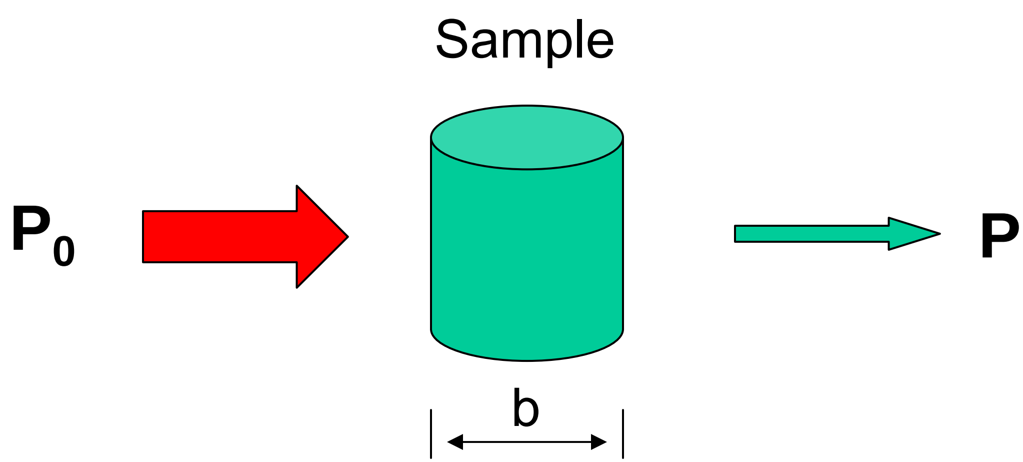
What can happen to EMR when interacting with matter (e.g., an analyte sample)?

- Diffraction
- Transmission
- Refraction
- Reflection
- Scattering
- *Absorption* (quantized event!)

Power = Energy/cm^2-s

Intensity = Power/angle

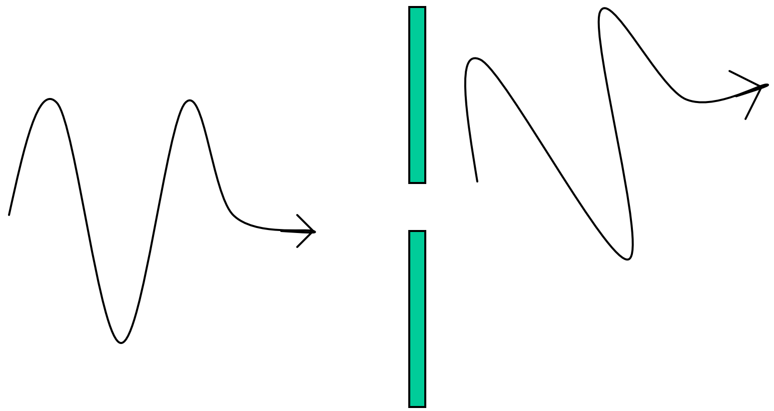
$$T = \frac{P}{P_o}$$



$$A = \log \frac{P_o}{P}$$

$$= -\log T$$

Diffraction = process whereby a parallel beam of radiation is bent as it passes a sharp barrier or through a narrow opening.

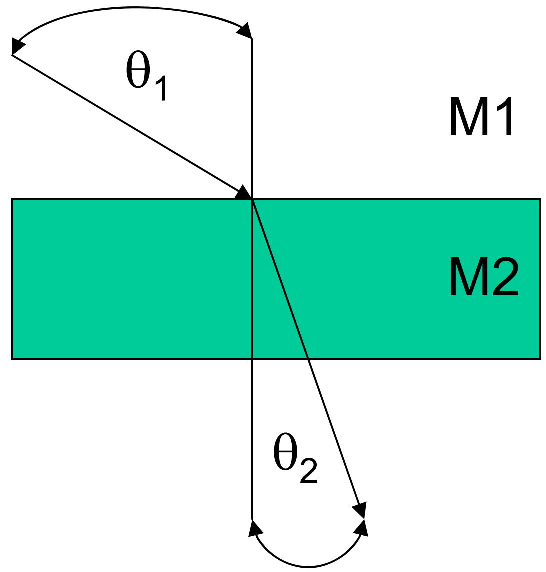


Transmission = rate at which radiation propagates through a transparent medium is less than in vacuum and depends on kinds and concentrations of atoms, ions and molecules making up the medium.

Refractive **index** = $\eta_i = c/\nu_i$

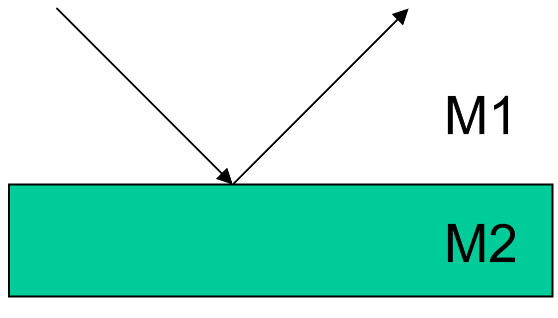
Stepwise process that involves polarized atoms, ions or molecules.

Refraction = when radiation passes at an angle through the interface between two transparent media that have different optical densities, an abrupt change in the direction of propagation occurs.



$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{\eta_2}{\eta_1} = \frac{\nu_2}{\nu_1}$$

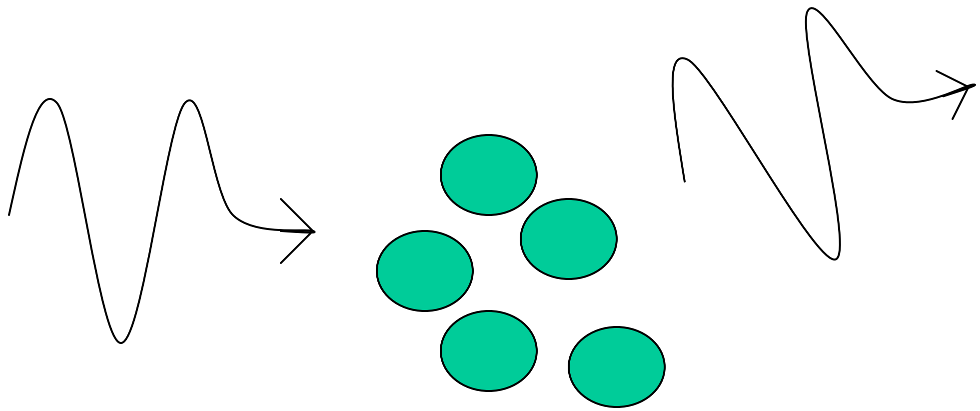
Reflection = when radiation crosses an interface between media that differ in refractive index, reflection occurs.



$$\frac{I_r}{I_o} = \frac{(\eta_2 - \eta_1)^2}{(\eta_2 + \eta_1)^2}$$

$> 60\%$ ~ $100\ \%\ I_r$

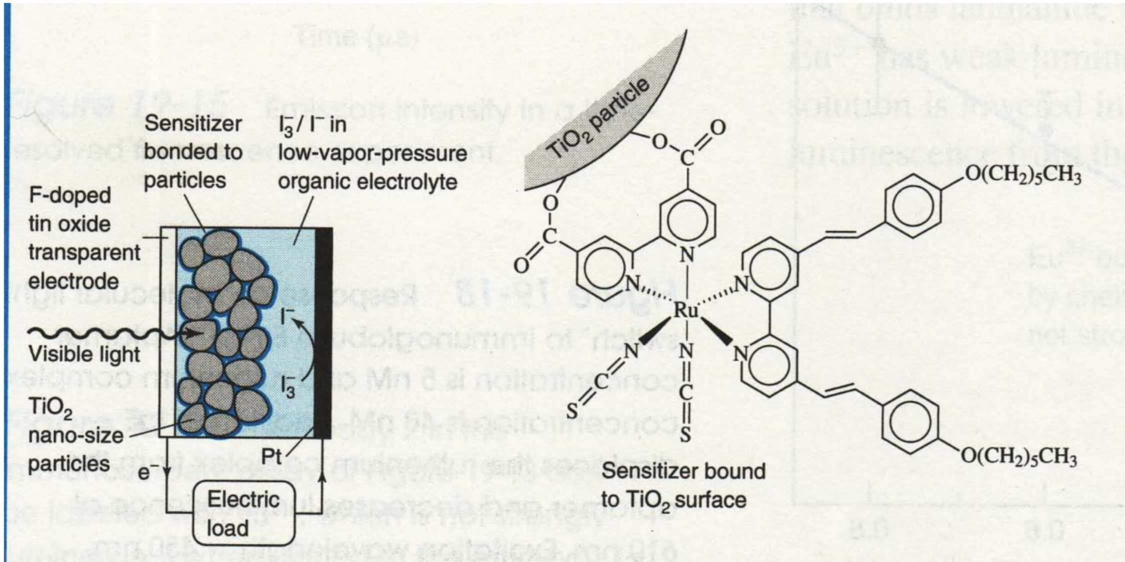
Scattering = small fraction of radiation is transmitted in all angles from the original path.



$$I_s \ \alpha \ \frac{1}{\lambda^4}$$

Transmission of radiation in matter can be pictured as a momentary retention of the radiant energy. When atomic or molecular particles are large with respect to the wavelength of light, radiation can be transmitted in all directions. Scattered radiation increases with particle size.

Converting Light (Energy) Into Electricity



Essential features of a photocell based on sensitizer-coated nanometer-size TiO_2 particles.

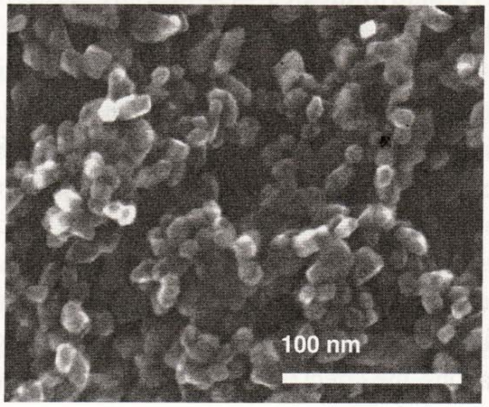
Ru(II) + $h\upsilon$ $\rightarrow$ Ru(II)* (*denotes and excited species)

Ru(II)* $\rightarrow$ Ru(III) + e- (injected into the TiO_2)

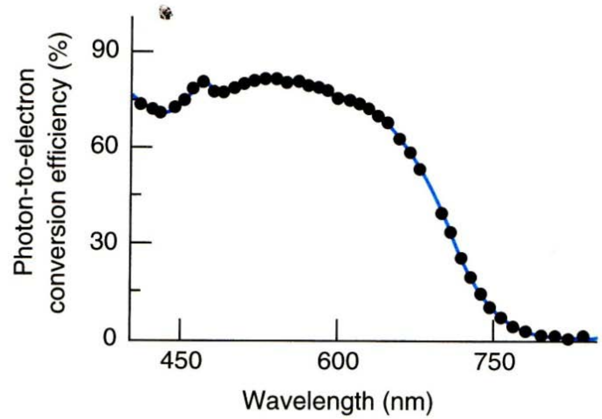
$I_3^- + 2e^- \rightarrow 3I^-$

$3I^- + 2Ru(III) \rightarrow I_3^- + 2Ru(II)$

} At Pt electrode



Scanning electron micrograph of sintered, nanocrystalline TiO_2. *Sintering* is a heat treatment at 450°C that causes small particles to grow together by forming bridges ("necks") between particles. *[From A. Hagfeldt and M. Grätzel, "Molecular Photovoltaics," Acc. Chem. Res.* ***2000,*** *33, 269.]*



Photoaction spectrum showing the efficiency with which photons incident on the solar cell are converted into electrons in the circuit. *[From P. Wang, C. Klein, R. Humphry-Baker, S. M. Zakeeruddin, and M. Grätzel, "A High Molecular Extinction Coefficient Sensitizer for Stable Dye-Sensitized Solar Cells," J. Am. Chem. Soc.* ***2005,*** *127, 808.]*

High surface area ~100-300 m^2/g) TiO_2 "support"

Major Classes of Spectrometric Methods

Class	Radiant Power Measured	Conc. Relationship	Method Types
Emission	Emitted, P_e	$P_e = kC$	Atomic emission
Luminescence	Luminescent, P_l	$P_l = kC$	Atomic and molecular fluorescence and chemi-luminescence
Scattering	Scattered, P_{sc}	$P_{sc} = kC$	Raman spectroscopy and turbidimetry
Absorption	Incident, P_o & transmitted, P	$A = -\log P/P_o = \varepsilon bC$	Atomic and molecular absorption

Quantized Nature of EMR and its Interaction with Matter

$$h\upsilon = eV_o + \omega$$

(KE) (WF)

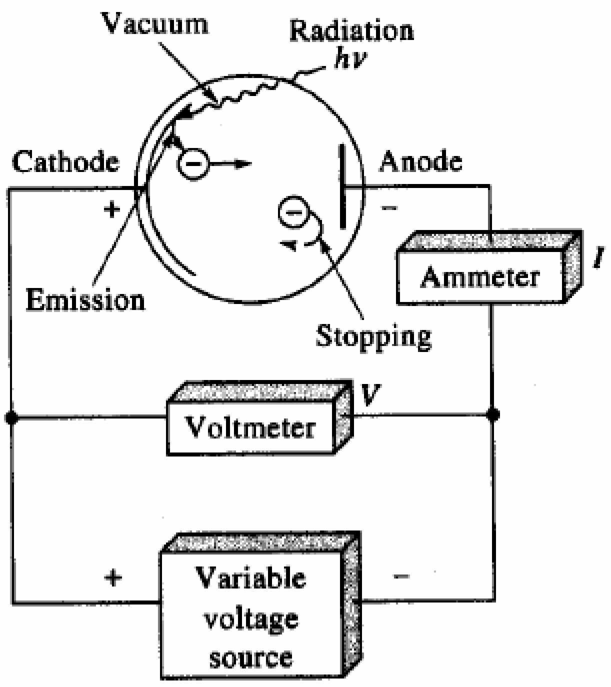


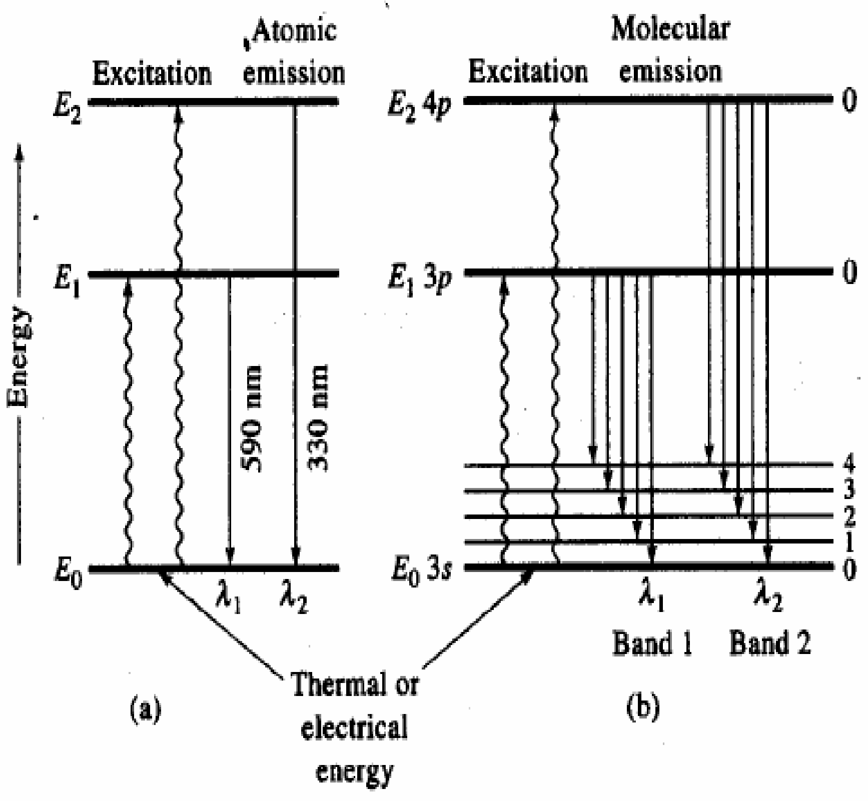
Figure 6-13 Apparatus for studying the photoelectric effect.

EMR is form of energy that releases electrons from metallic surfaces and imparts to these electrons some kinetic energy.

When EMR is emitted or absorbed, a permanent transfer of energy from the emitting object or to the absorbing medium occurs.

1. Photocurrent proportional to intensity of incident radiation.
2. Magnitude of stopping voltage depends on frequency (energy) of incident radiation.
3. Stopping voltage depends on photocathode material.
4. Stopping voltage is independent of intensity of incident radiation.

Quantized Nature of EMR and its Interaction with Matter



Energy Level Diagram

- $E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational}$
- Excitation photon, hυ, must equal the energy difference between the ground energy state (lower) and the excited energy state (higher).
- Energy differences are unique for each chemical species (atom or molecule).
- Relaxation from the excited state – (i) radiative and (ii) nonradiative.

Quantitative Aspects of Spectrochemical Measurements

$$A = \varepsilon bC = -\log T = \log P_o/P$$

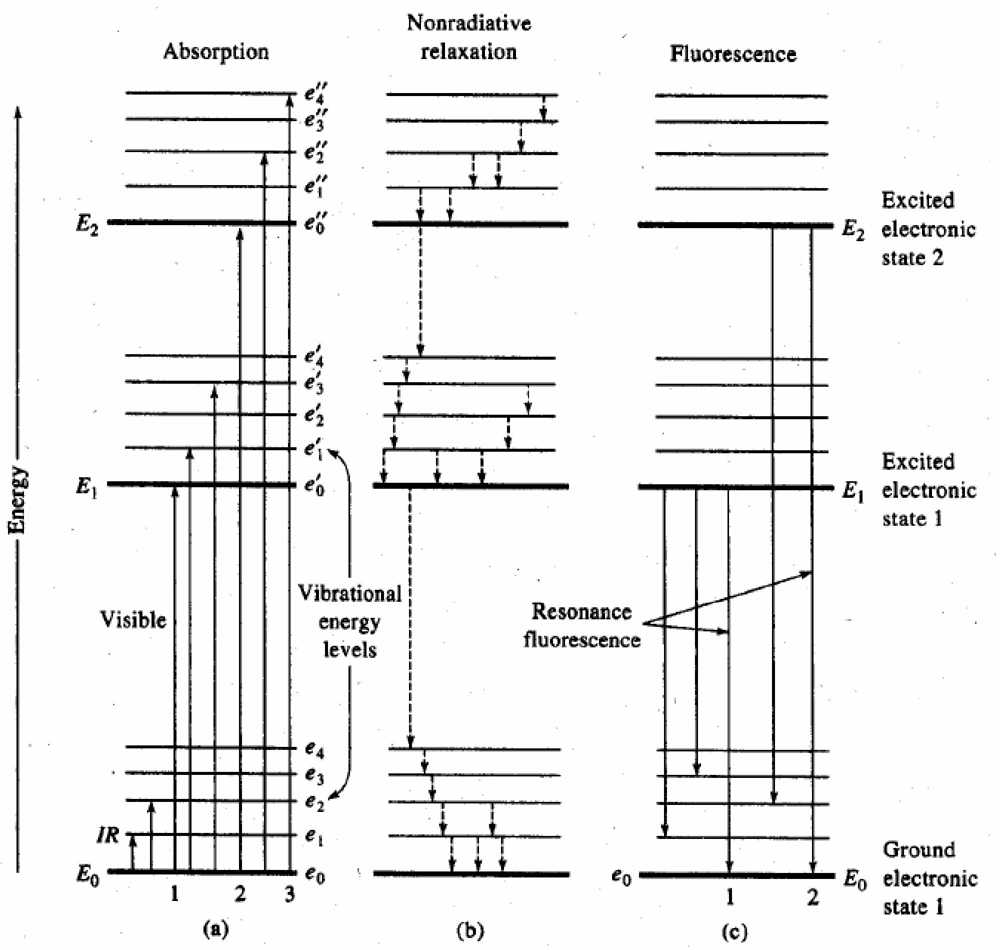


Figure 6-20 Partial energy-level diagrams for a fluorescent organic molecule.