

Interaction of Light with Matter

The interaction of light with matter can take many forms.

(1) Absorption and Emission of Photons

Photons are annihilated or created.

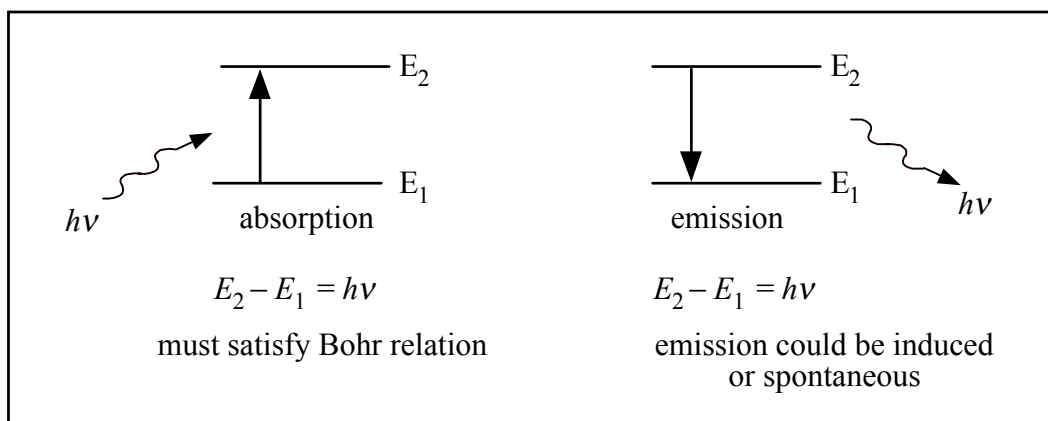


Figure 9-1

Most absorbing materials satisfy the Beer-Lambert Law.

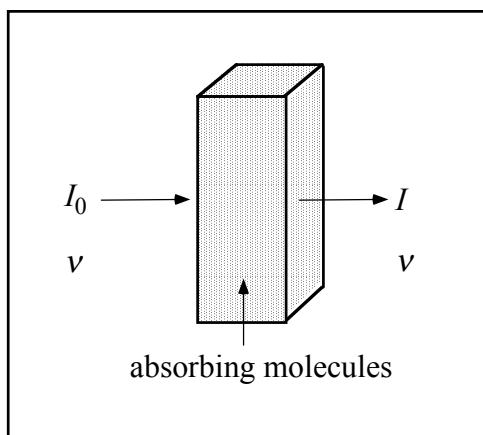


Figure 9-2

If $I_0 \equiv$ incident light intensity at frequency ν
 $I \equiv$ intensity of transmitted light at same frequency
 $C \equiv$ concentration of absorbers
 $\epsilon \equiv$ molar extinction coefficient
 $l \equiv$ length of light path through the absorbers

then $\log_{10} \frac{I_0}{I} = \epsilon l C$

Quantity $\log_{10} \frac{I_0}{I} = A$ is called the absorbance or sometimes optical density (OD).

(2) Light Scattering

An isolated atom scatters light because the electric field of the incident light wave forces the electrons in the atom to oscillate back and forth about their equilibrium position. By the laws of electromagnetism, when a charge changes its velocity, it emits radiation. Light is emitted uniformly in all directions in the plane \perp to oscillation, but decreases in amplitude as the viewing angle shifts away from that plane.

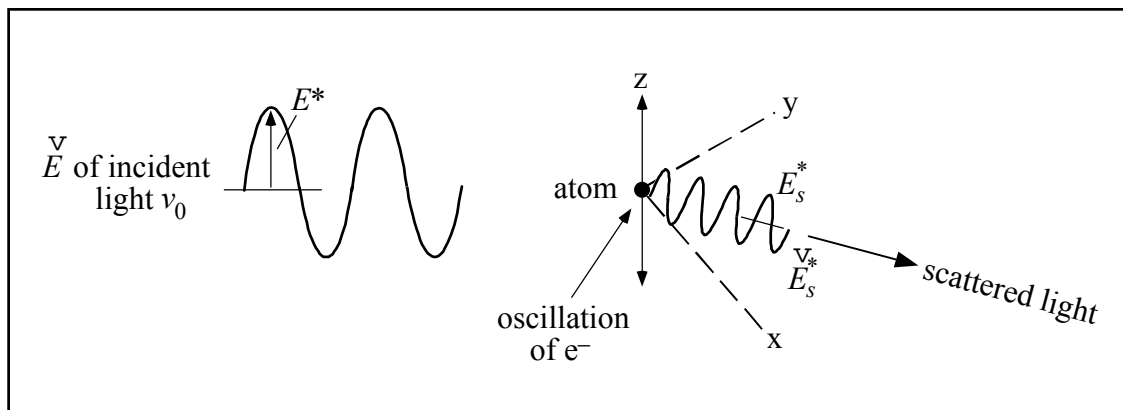


Figure 9-3

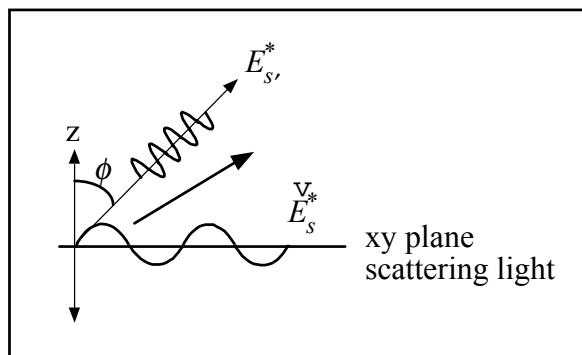


Figure 9-4

$$E_s^* = \frac{|e|a \sin \phi}{c^2 r}$$

where $-|e|$ = electron charge

a = acceleration of electron

c = velocity of light

r = distance from oscillator

ϕ = angle between axis of oscillation and plane

containing direction of propagation of scattered light

$$\text{Intensity of scattered light} \propto |E_s^*|^2$$

⇒ Scattered light is not necessarily at the same frequency as incident light.

(a) Rayleigh Scattering

Scattered light is essentially at the same frequency as incident light.

Frequency shift due to

- (i) Molecular motion → Doppler Shift
- (ii) Change in internal energy states of scattering molecule

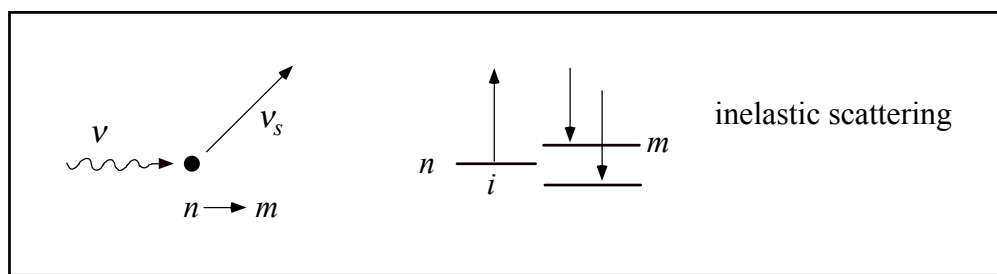


Figure 9-5

Inelastic scattering is important for gases, e.g., rotational Raman. In liquids, random molecular motions broaden Rayleigh scattering.

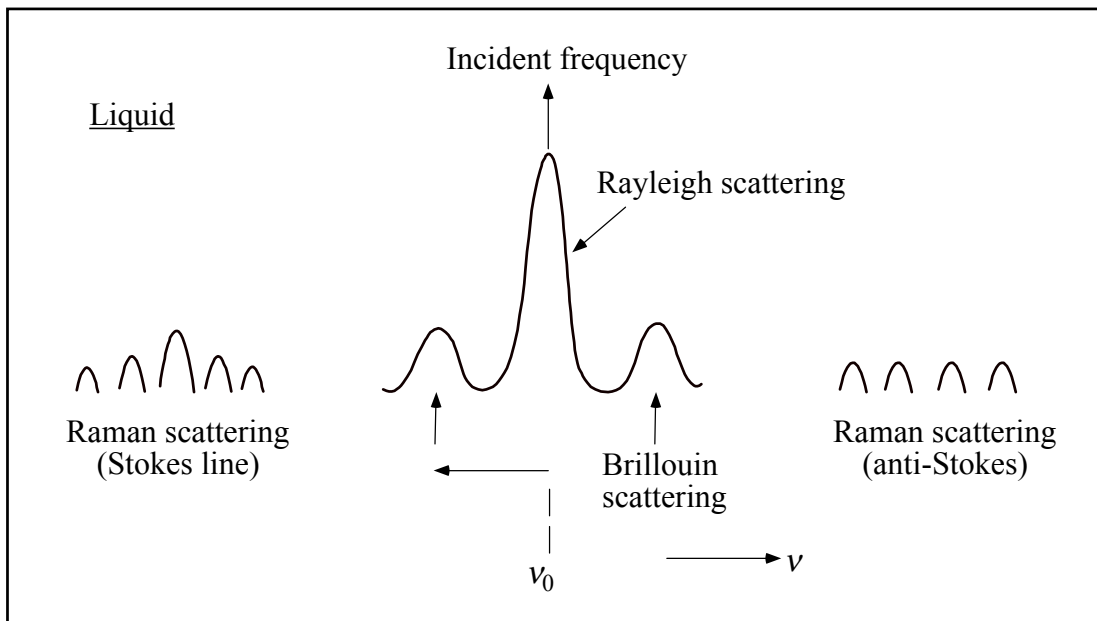


Figure 9-6

(b) **Brillouin Scattering**

In addition, in liquids, two special scattered lines, the Brillouin lines, appear because of coherent molecular motion in sound waves that propagate through the fluid.

(c) **Raman Scattering**

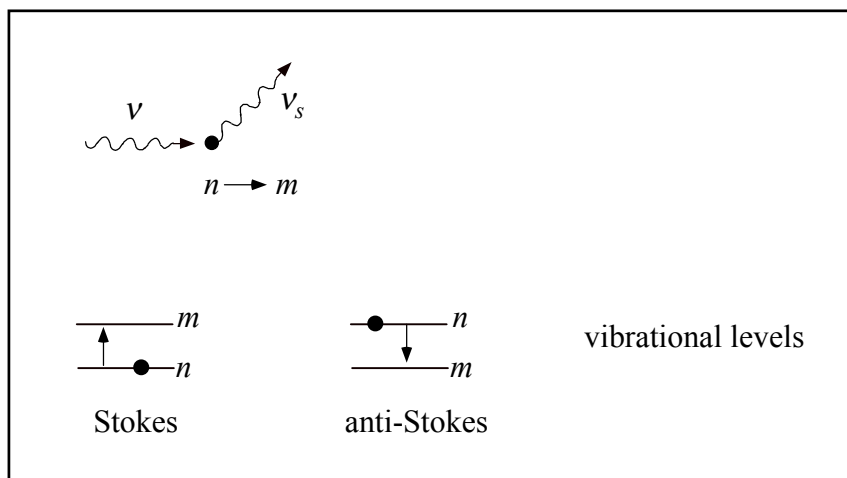


Figure 9-7

Phenomena Related to Light Scattering

- (a) **Reflection** — Light scattered in the opposite direction of incident light.
- (b) **Refraction** — Light scattered in the forward direction combines with the incident beam to give rise to the phenomenon of refraction. The physical effect of this combination is to make the transmitted light appear as though it has travelled more slowly through the sample than through a vacuum.

$$\text{index of refraction} = n = \frac{\text{velocity of light in vacuum}}{\text{velocity of light in substance}}$$

- (c) **Diffraction** — Superposition of scattered waves from individual atoms or molecules in the sample. If the sample is highly ordered, diffraction pattern periodicity in the distribution of atoms and molecules in the sample can be used to deduce or infer the relative positions of atoms in a sample.

Fluorescence and Phosphorescence

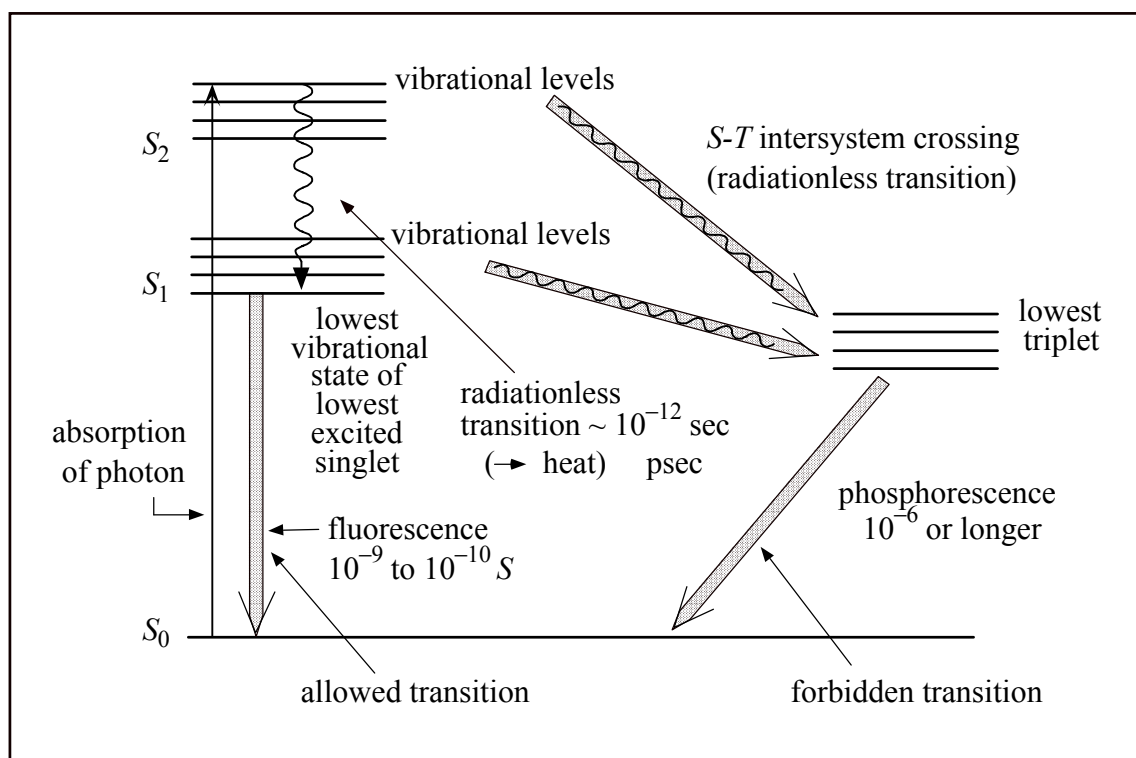


Figure 9-8

Optical Rotation and Circular Dichroism

- (a) **Optical Rotation** — Chiral molecules can rotate the plane of polarization of plane-polarized light as light passes through the sample.
- (b) **Circular Dichroism** — Chiral molecules will absorb right and left circularly polarized light differentially.

The Electromagnetic Spectrum and Molecular Spectroscopy

Study Table 12-2, p. 530-531.