Introduction to Spectroscopy

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.
   - $E_2 - E_1 = h\nu$
   - Absorption
   - Emission could be induced or spontaneous

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 perpendicular to oscillation, but decreases in amplitude as the viewing angle shifts away from that plane.

Most absorbing materials satisfy the Beer-Lambert Law.

If

\[ I_0 = \text{incident light intensity at frequency } \nu \]
\[ I = \text{intensity of transmitted light at same frequency} \]
\[ C = \text{concentration of absorbers} \]
\[ \varepsilon = \text{molar extinction coefficient} \]
\[ l = \text{length of light path through the absorbers} \]

then

\[ \log_{10} \frac{I_0}{I} = \varepsilon l C \]

Quantity $\log_{10} \frac{I_0}{I} = A$ is called the absorbance or sometimes optical density (OD).
Figure 9-4

\[ E_z = \frac{|e| \alpha \sin \phi}{c^2 r} \]

where 
- \(|e|\) = electron charge
- \(\alpha\) = acceleration of electron
- \(c\) = velocity of light
- \(r\) = distance from oscillator
- \(\phi\) = angle between axis of oscillation and plane containing direction of propagation of scattered light

(a) **Rayleigh Scattering**

Scattered light is not necessarily 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

(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**

Inelastic scattering is important for gases, e.g., rotational Raman. In liquids, random molecular motions broaden Rayleigh scattering.
Light is a traveling plane wave.

\[ E(\mathbf{r}, t) = E_0 e^{i(k \cdot r - \omega t)} \]

If wave is propagating in the \(+z\) direction,
\[ E(z, t) = E_0 e^{i(kz - \omega t)} \]

- \( E_0 \) is the amplitude of the wave,
- \(|k| = \frac{2\pi}{\lambda} \), \((\lambda \text{ is the wavelength})\)
- \( \omega = 2\pi \nu \), \((\nu \text{ is the frequency of the light})\)
- and \( \nu \lambda = c \). \((c \text{ is the speed of light})\)
- \( c = 299,792,458 \text{ meters/sec} \) or \( 2.998 \times 10^8 \text{ m/s} \) or \( 3 \times 10^{10} \text{ cm/s} \)

Polarization of light

Polarized light: If all the waves have the same \( E \) linearly polarized as above, the light is plane polarized (plane defined by the electric field direction and the direction of propagation of the light wave).

Unpolarized light:
\( E \) of different waves as viewed along direction of propagation.
Electric fields oscillating in all directions.
Linearly versus Circularly Polarized Light

Various Forms of Spectroscopy

Where does it occur?

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, pp. 530-531 in Chapter 12 of text by Eisenberg and Crothers.
**Suggested reading**

Eisenberg and Crothers (EC), Chapter 12, pp. 516-535.