Chapter 15 - Molecular Luminescence Spectrometry

Read: pp 399-417

Problems: 15-1, 3, 7

Light emission process!

Radiative or non-radiative decay/relaxation.

Fluorescence and phosphorescence vs. chemiluminescence

Figure 15-1  Partial energy diagram for a photoluminescent system.
**Process of Excitation and Emission**

- **Absorption of light** - $10^{-15}$ s and related to $\varepsilon$
- **Vibrational relaxation** – excess vibrational energy in solution immediately lost in solution due to collisional deactivation, $10^{-12}$ s.
- **Internal conversion** – intermolecular process by which a molecule passes to a lower energy electronic state *without* emission of light. Overlap of vibrational energy levels in two electronic energy levels.
- **External conversion** – deactivation of an excited electronic state by interaction and energy transfer between the excited molecule and solvent or other solutes.
- **Intersystem crossing** – process in which spin of an excited electron is reversed and change in multiplicity results. Most common when vibrational manifold overlap exists and when the molecule has a heavy atom substituent (e.g., Br, I).
- **Fluorescence and Phosphorescence** – relaxation of an excited state via light emission. Time scales range from $10^{-6}$ s to 100’s s.
Quantitative Aspects of Fluorescence Measurements

\[ F = 2.3\Phi \varepsilon bC P_o \]

- \( \Phi \) = quantum efficiency = \# molecules emitting/total \# molecules excited
- \( \varepsilon \) (L/mol-cm) and \( b \) (cm) have their usual meanings
- \( P_o \) in incident radiant power density (watts/cm\(^2\))

- Linear relationship, \( F = KC \)

- **Self-absorption** and **self-quenching** cause negative deviations from linearity (i.e., reduced fluorescence intensity).

- \( \Phi \) increases with lower temperature, increased structural rigidity, \( \pi \rightarrow \pi^* \) transition, and can be affected by solvent type and pH.

- Electron donating groups (NH\(_2\), OH) tend to enhance fluorescence while electron withdrawing groups (Cl, COOH) tend to inhibit it.
Excitation and Emission Spectra

Resonance vs. non-Resonance Fluorescence

Non-Radiant losses result in *red shift* in fluorescence.

Excitation at fixed wavelength and recording the emission spectra.

*Figure 15-2* Fluorescence excitation and emission spectra for a solution of quinine.
Basic Design of a Simple Fluorometer

Figure 15-4 Components of a fluorometer or a spectrofluorometer.
Figure 15-6 A typical fluorometer.  (Courtesy of Farrand Optical Co., Inc.)

Figure 15-7 A spectrofluorometer.  (Courtesy of SLM Instruments, Inc., Urbana, IL.)