Molecular Luminescence

- **Quick review of luminescent processes**

Process	Radiative?	Time Scale
Absorption		
Vibrational Relaxation		
Internal Conversion		
Fluorescence		
Intersystem Crossing		
Phosphorescence		

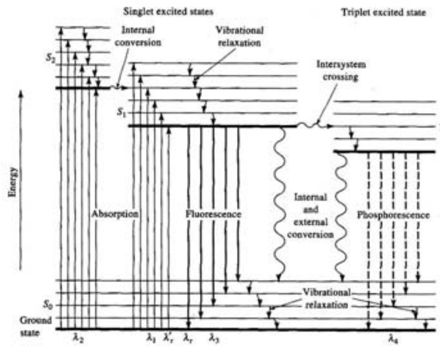

Figure 15-1 Partial energy diagram for a photoluminescent system.

Spectra and Characteristics of Luminescent Species

- Fluorescence quantum yield (ϕ) : efficiency of fluorescence process
  - combination of several factors (possible outcomes)

$$\phi = \frac{k_f}{k_f + k_i + k_{ec} + k_{ic} + k_{pd} + k_d}$$

- k_f =
- k_i =
- k_{ec} =
- k_{ic} =
- k_{pd} =
- k_d =

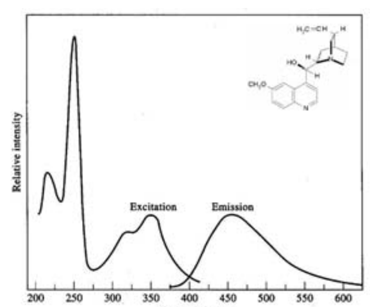

Figure 15-2 Fluorescence excitation and emission spectra for a solution of quinine.

Spectra and Characteristics of Luminescent Species

- Most transitions are $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, other transitions require too energetic incident photons
  - most common are $\pi \rightarrow \pi^*$
- Structure:
  - must have π character, typically aromatic
    - substitution affects both intensity and energy
  - fused aromatic rings increase fluorescence
  - structural rigidity helps

Spectra and Characteristics of Luminescent Species

- **Relating fluorescent intensity (F) and concentration**
- F depends on how much light is absorbed by the analyte

$$F = K(P_o - P)$$

- But P depends on absorbance (Beer's Law)

$$P = P_o 10^{-\varepsilon bc}$$

$$F = Kp_o(1-10^{-\varepsilon bc})$$

- At *low concentrations* (small A), F becomes:

$$F = 2.303K\varepsilon bcP_o =$$

- At higher concentrations, series approximation is no good, deviation from linearity.
- *Quenching* and *self-absorption* also play a role

Luminescence Instruments

- Need two wavelength selectors (monochromators)
- Need intense source: Hg vapor, Xe arc, some lasers
- Need sensitive detector: PMT's, some PDA and CCD

- Our instrument:
  Perkin-Elmer LS-5B

- Reference PMT accounts for source variation
  - What is the purpose of the Rhodamine cell?

- Cell considerations

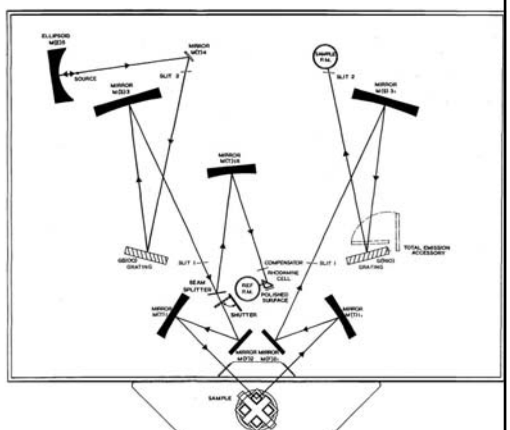

Figure 3.2 Optical System