

## Molecular Luminescence

- Quick review of luminescent processes

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

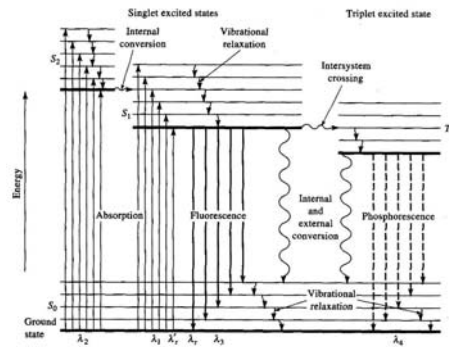


Figure 15-1 Partial energy diagram for a photoluminescent system.

## Spectra and Characteristics of Luminescent Species

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

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

-  $k_f =$

-  $k_i =$

-  $k_{ec} =$

-  $k_{ic} =$

-  $k_{pd} =$

-  $k_d =$

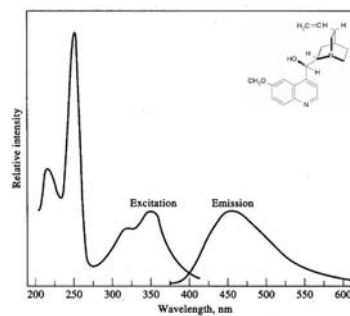


Figure 15-2 Fluorescence excitation and emission spectra for a solution of quinine.

## 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  $\pi$  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

$$F = K(P_0 - P)$$

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

$$P = P_0 10^{-\epsilon bc}$$

$$F = K P_0 (1 - 10^{-\epsilon bc})$$

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

$$F = 2.303 K \epsilon bc P_0 =$$

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

## Luminescence Instruments

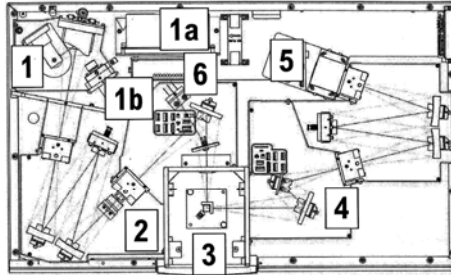
- Need two wavelength selectors (monochromators)
- Need intense source: Hg vapor, Xe arc, some lasers
- Need sensitive detector: PMT's, some PDA and CCD

- Our instrument:  
Horiba FluoroMax-4
- Reference detector account  
for source variation
- Cell considerations

FluoroMax-4 & FluoroMax-4P with USB v. 9 (23 Oct 2009)

System Description

Optical layout



- 1 Xenon arc-lamp and lamp housing
  - 1a Xenon-lamp power supply
  - 1b Xenon flash lamp (FluoroMax-4P only)
  - 2 Excitation monochromator
  - 3 Sample compartment
  - 4 Emission monochromator
  - 5 Signal detector (photomultiplier tube and housing)
  - 6 Reference detector (photodiode and current-acquisition module)
- Host computer (not on diagram)