Molecular Luminescence

- Quick review of luminescent processes

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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 = $
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)
  \[ P = P_0 10^{-\varepsilon bc} \]
  \[ F = K P_0 (1 - 10^{-\varepsilon bc}) \]

• At low concentrations (small $A$), $F$ becomes:
  \[ F = 2.303 K \varepsilon bc P_0 = \]

• 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 accounts for source variation

- Cell considerations