Luminescence Spectroscopy (Chapter 15)

fluorescence, phosphorescence, chemiluminescence

all follow electronic excitation

**Excited Electronic States**:

Each electron has unique set of *quantum numbers* (Pauli Exclusion Principle)

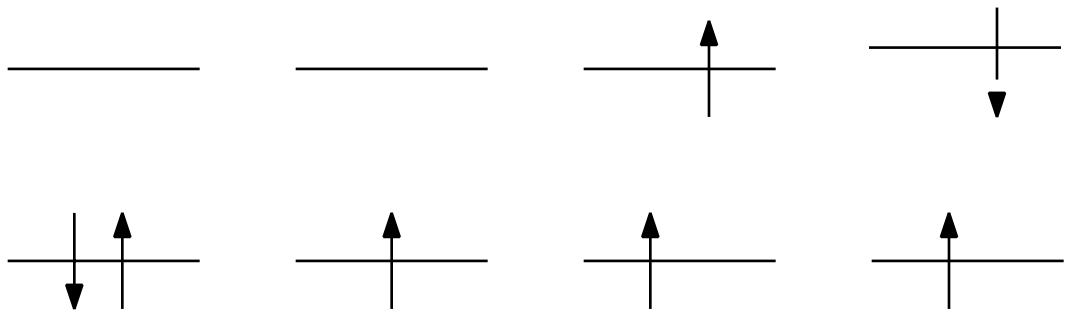
- n principal (1s, 3p… )
- l angular momentum (l=0=s, l=1=p... )
- s spin
- m magnetic

Any two electrons in same orbital (n, l, m) must have different spins

$$s = +\frac{1}{2} \quad \text{or} \quad -\frac{1}{2}$$

$$S = \sum |s_i|$$

**Multiplicity**: $2S+1$ (either 1, 2, 3... )



| Ground State Singlet $S_0$ | Ground State Doublet $D_0$ | Excited State Triplet $T_1$ | Excited State Singlet $S_1$ |
|---|---|---|---|

Multiplicities:

$S_0$ - common, diamagnetic (not affected by B fields)

$D_0$ - unpaired electron, many radicals, two equal energy states

$T_1$ - rare, paramagnetic (affected by B fields)

($T_0$ - doesn't exist, not ground state)

$$\text{Energy}(S_1) > \text{Energy}(T_1)$$

(difference is energy required to flip electron spin)

Example: Na ground state $1s^2\ 2s^2\ 2p^6\ 3s^1$

s=1/2, 2S+1=2, ground state doublet s electron

written $3(^2S)$

Two spin states of equal energy (up/down)

Na 1st excited state $1s^2\ 2s^2\ 2p^6\ 3p^1$

$D_1$ written $3(^2P)$

BUT two spins states?

J (total ang. mom)=L+S or L-S

now $1s^2\ 2s^2\ 2p^6\ 3s^1$ = $3(^2P_{1/2})$ and $3(^2P_{3/2})$

Term Symbol $^{2S+1}L_J$

Na $3p \longrightarrow 3s$ fluorescence two lines at 589.6 nm ($^2P_{3/2}$) and 589.0 nm ($^2P_{1/2}$)

$$\left(S_1 \xrightarrow{\text{Emission}} S_0 \qquad S_1 \xleftarrow{\text{Absorption}} S_0\right)$$

## What about Lifetimes?

- Absorption:

  $S_1 \leftarrow S_0$ very fast $10^{-15}$-$10^{-13}$ s

- Relaxation:

  *Resonant* emission $S_1 \rightarrow S_0$ fast $10^{-9}$-$10^{-5}$ s (fluorescence)

  common in atoms

  strong absorber $\Rightarrow$ shorter lifetime

  *Non-resonant* emission $S_1 \rightarrow S_0$ fast $10^{-9}$-$10^{-5}$ s (fluorescence)

  common in molecules

  v. fast vibrational relaxation

  red shifted emission (Stokes shift)

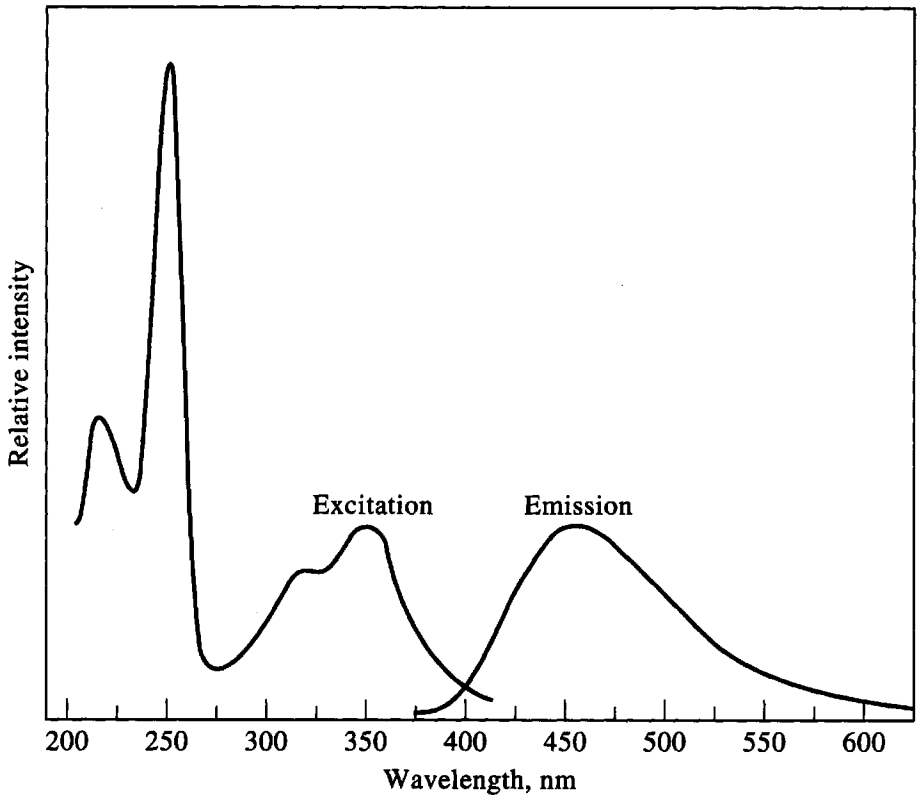



Fig. 15-2

*Non-resonant* emission $T_1 \rightarrow S_0$ slow $10^{-5}$-10 s (phosphorescence)

Transitions between states of different multiplicities are improbable "forbidden" (e.g. T←S or T→S)

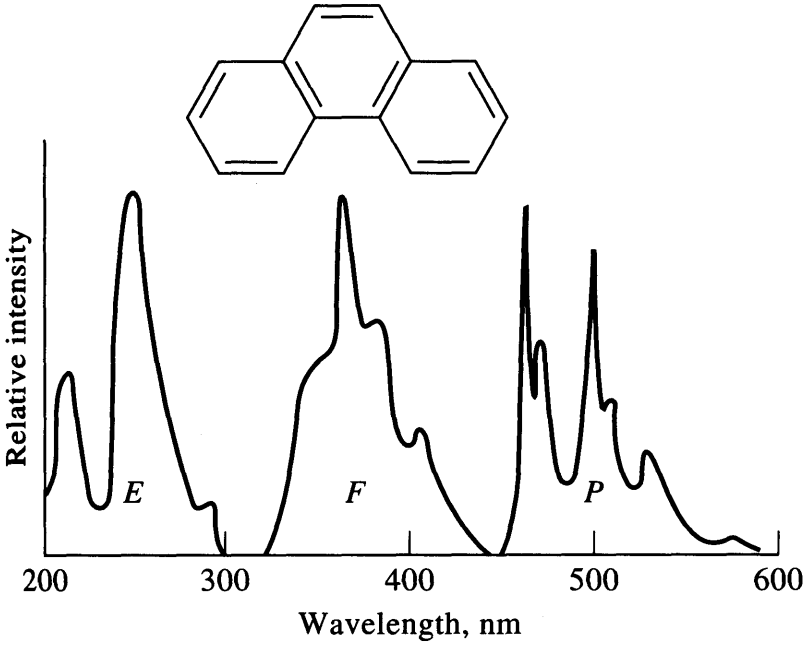



Fig. 15-3

phosphorescence

fluorescence

excitation

**Internal Conversion**: radiationless transition to lower state when vibrational energy levels "match"

**External Conversion**: radiationless transition to lower state by collisional deactivation

**Intersystem Crossing**: transition with spin change (e.g. S to T)

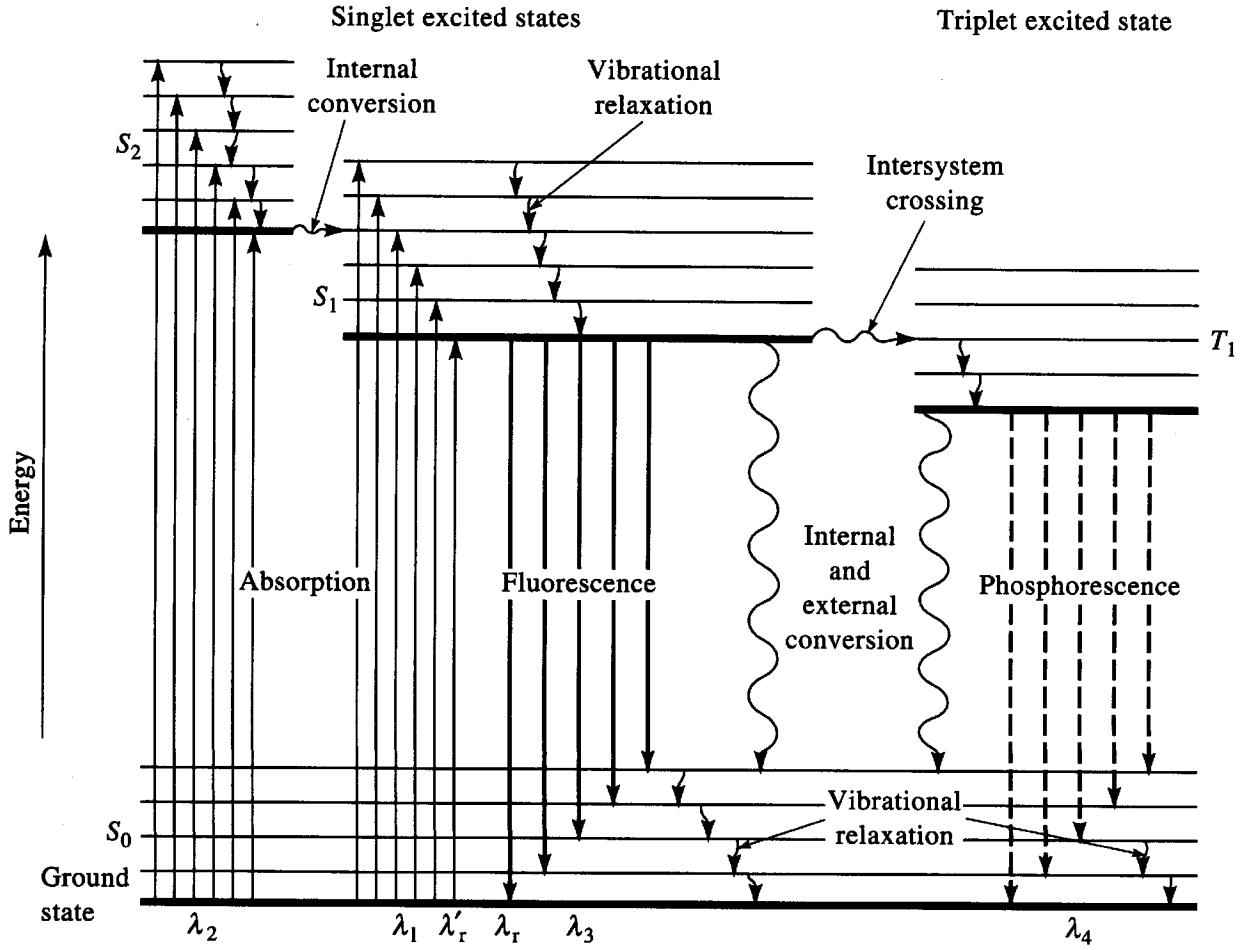
**Fluorescence**: emission not involving spin change (e.g. S→S, T→T), efficient, short-lived $<10^{-5}$ s

**Phosphorescence**: emission involving spin change (T→S), improbable, long-lived $>10^{-5}$ s

**Dissociation**: excitation to vibrational state with enough energy to break bond

**Predissociation**: relaxation to state with enough energy to break bond

## **Energy Level Diagram**: (Fig. 15-1)



## How likely is fluorescence?

Fluorescence Quantum Yield - ratio of number of molecules fluorescing to number excited

$$\Phi_{fluor} = \frac{\text{\# photons fluor}}{\text{\# species excited}} \qquad (\Phi_{fluor} = 0.0 \text{ to } 1.0)$$

$$= \frac{k_{fluor}}{k_{fluor} + k_{int\ con} + k_{ext\ con} + k_{ISC} + k_{pre\ dis} + k_{dis}}$$

## What Factors Affect $\Phi_{fluor}$?

(1) Excitation λ

Short λ's break bonds increase $k_{pre\text{-}dis}$ and $k_{dis}$

rarely observed most common

$\sigma^* \rightarrow \sigma$ $\pi^* \rightarrow n$ $\pi^* \rightarrow \pi$

emission usually from *lowest lying* excited state

(2) Lifetime of state

Transition probability measured by ε

Large ε implies short lifetime

Largest fluorescence from short lifetime/high ε state

$\pi^* \rightarrow \pi$ > $\pi^* \rightarrow n$ ($10^{-9}$-$10^{-7}$ s > $10^{-7}$-$10^{-5}$ s)

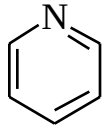
(3) Structure

Few conjugated aliphatics fluoresce

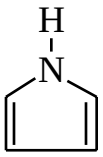
Many aromatics fluoresce

Desire short lifetime $S_1$, no/slowly accessible $T_1$

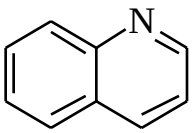
Fluorescence increased by # fused rings and substitution on/in ring



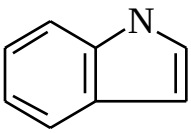

Pyridine




Pyrrole




Quinoline

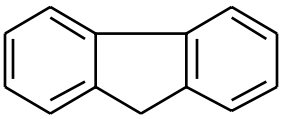



Indole

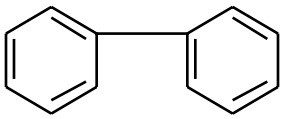
(4) Rigidity

Rigid structures fluoresce

Increase in fluorescence with chelation



Fluorene



Biphenyl

(5) Temperature, pH, solvent (p 363-364)

## Quantitative Luminescence Spectrophotometry:

$$\overbrace{F}^{\text{Fluorescence}} = K'\overbrace{(I_0 - I)}^{\text{Absorbed}}$$
$$= K' \cdot 2.303 \varepsilon b c \cdot I_0$$
$$= K \cdot c$$

Only works at low A (<0.05)

(i) self quenching (collisions between excited states

(ii) self absorption (when absorption and fluorescence band overlap)

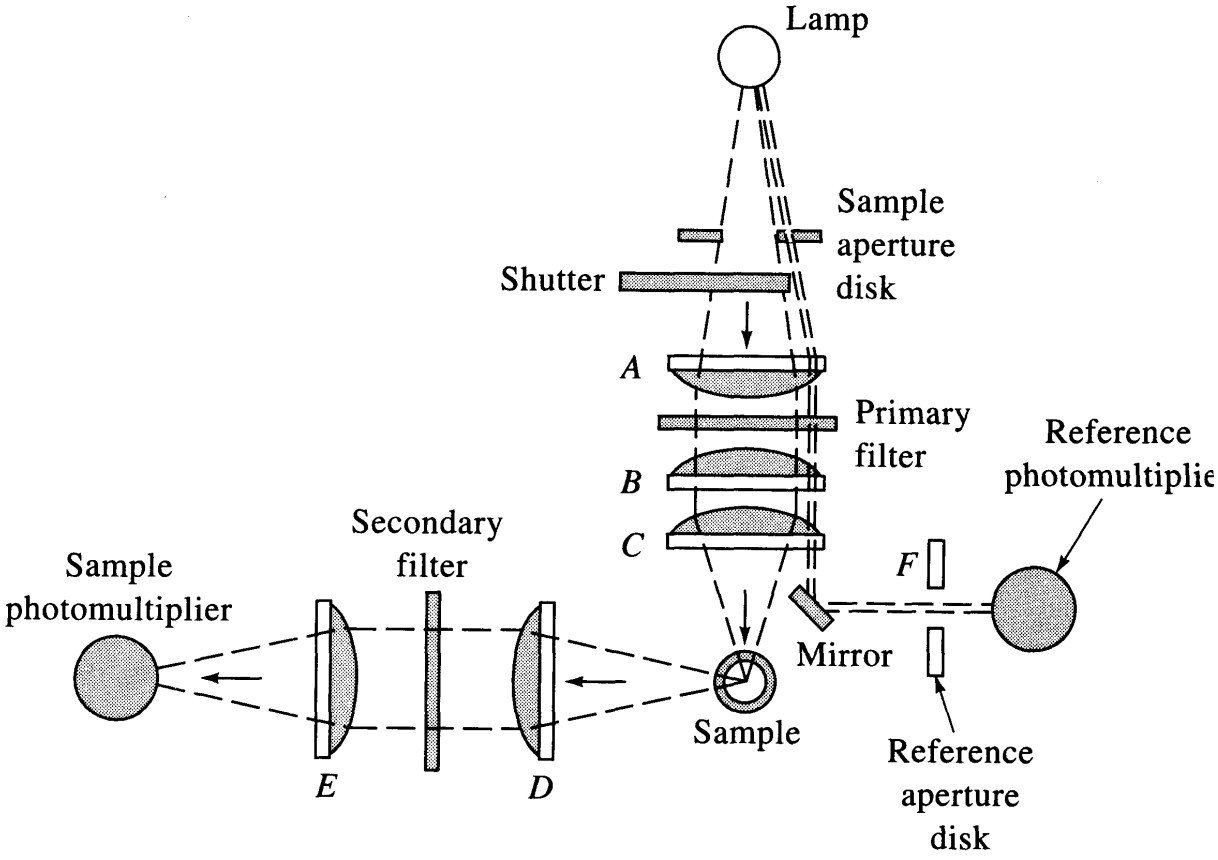



Fig. 15-6

*Fluorometer* - filters to isolate excitation and fluorescence wavelengths (but no scanning)

*Spectrofluorometer* - two monochromators for excitation scanning or fluorescence scanning

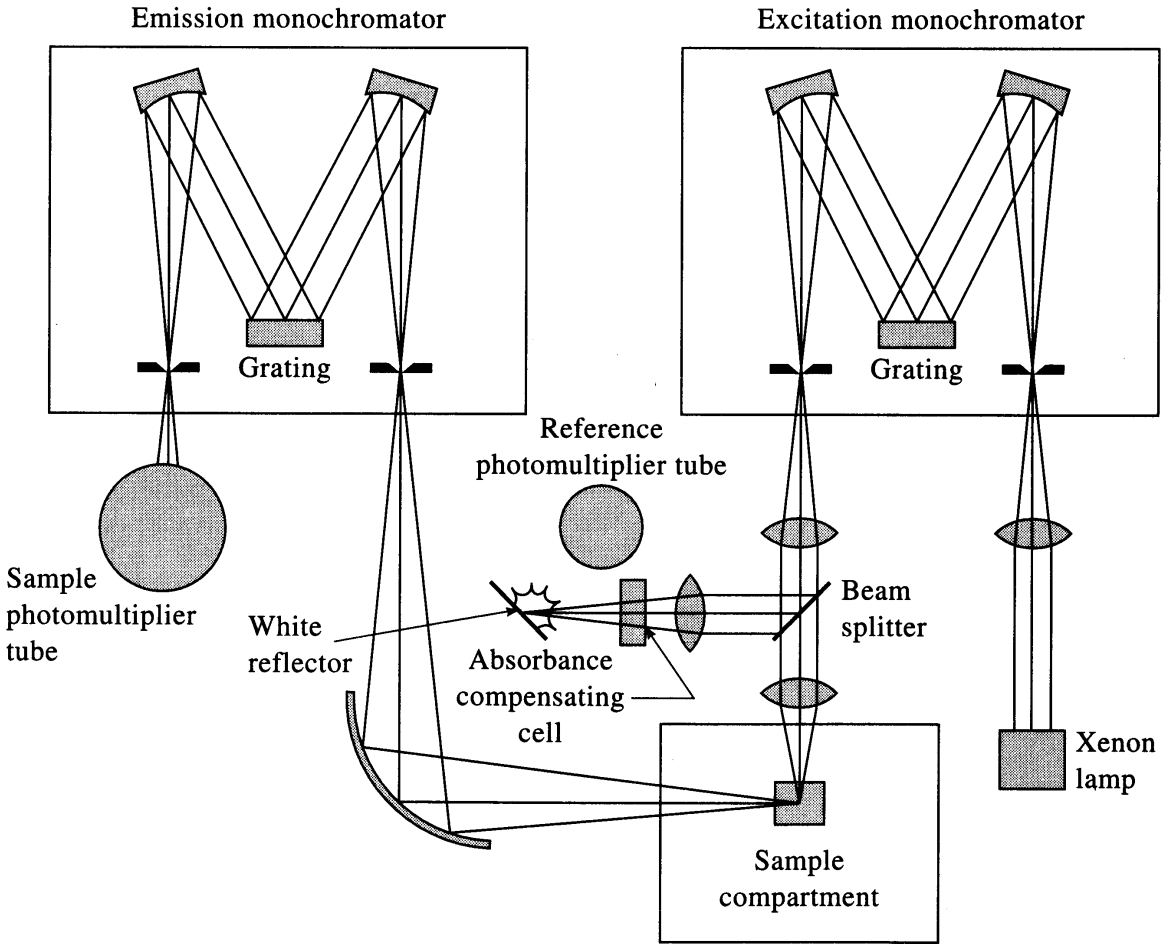



Fig 15-7

# Total Luminescence Measurements:

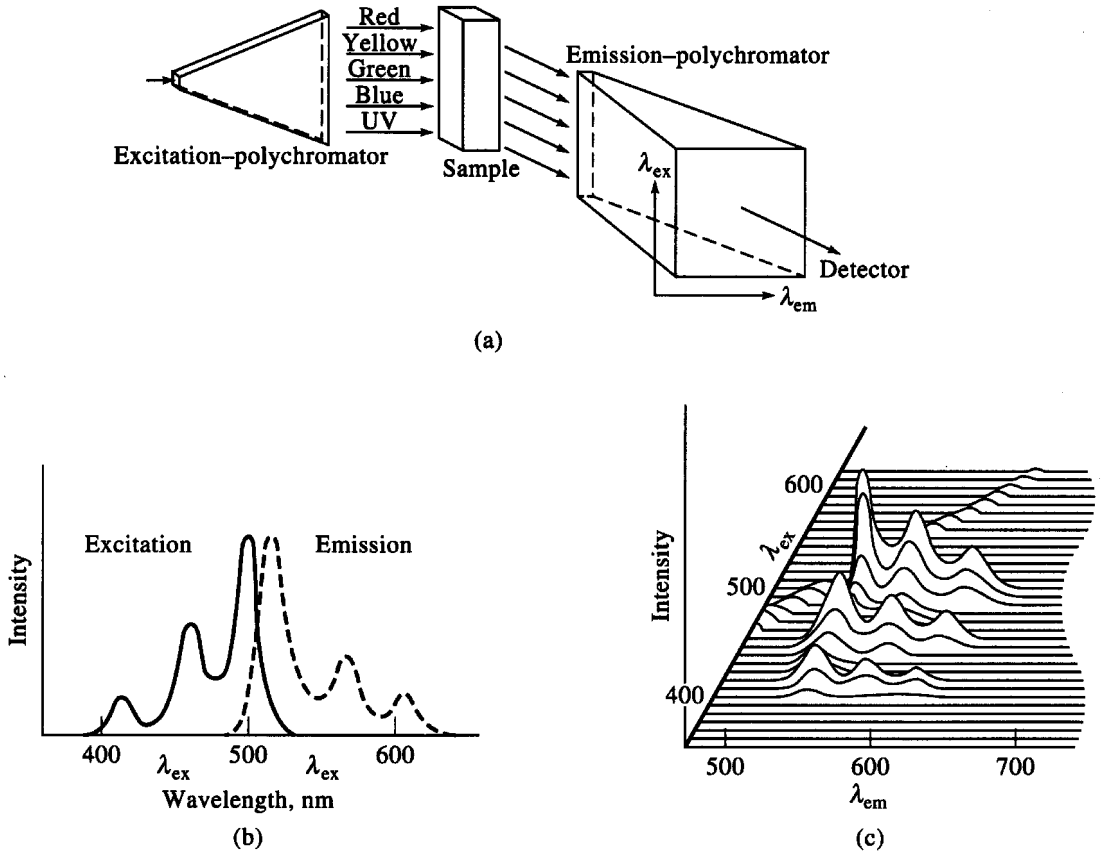



Fig 15-8

**Chemiluminescence**: (see www article)

Reaction produces molecule in electronically excited state

$$A + B \rightarrow C^* + D$$

$$C^* \rightarrow C + h\nu$$

Example:

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + h\nu\,(600 - 2800\ nm)$$

Used to detect NO from 1 ppb to 10 ppt

Intensity depends on **rate** of reaction of production of C*

$$I_{CL} = \phi_{CL} \frac{d[C^*]}{dt}$$

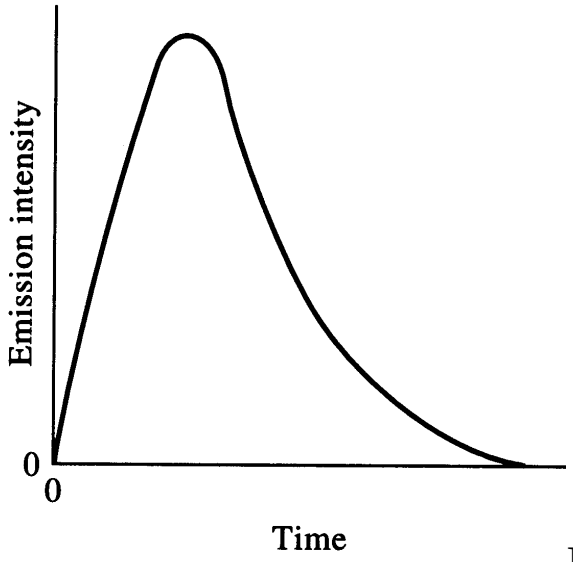



Fig. 15-11

Advantages: (i) simple instrumentation (no excitation hν) (ii) high sensitivity (ppm to <ppb)

Disadvantages: (i) few reactions