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)

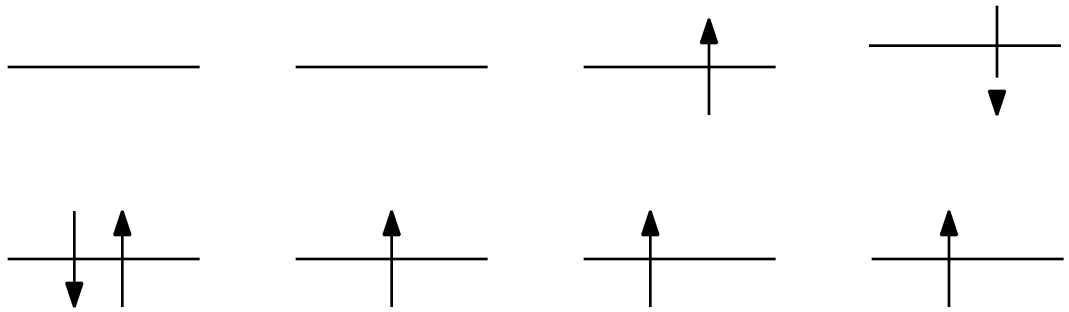
- n principal (1s, 3p…)
- l angular momentum (l=0=s, l=1=p...)
- s spin
- m magnetic

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

S_1 ¾¾¾¾¾ $\xrightarrow{\text{Emission}}$ S_0 $\qquad$ S_1 $\xleftarrow{\text{Absorption}}$ ¾¾¾¾¾ S_0

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 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)

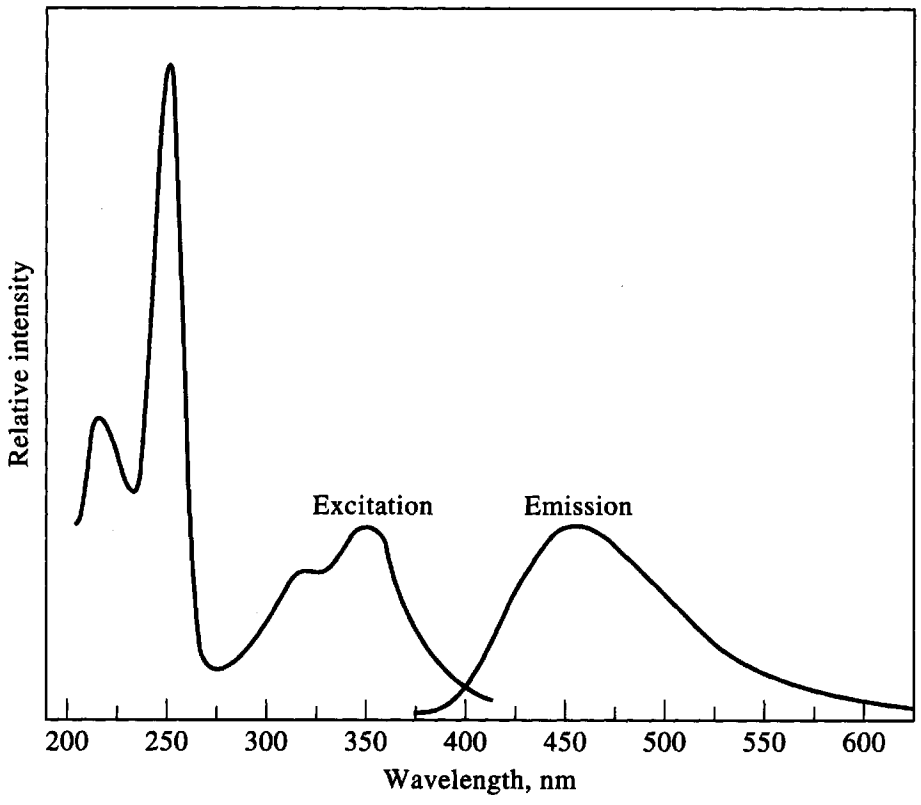


Fig. 15-2

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. $T \leftarrow S$ or $T \rightarrow S$)

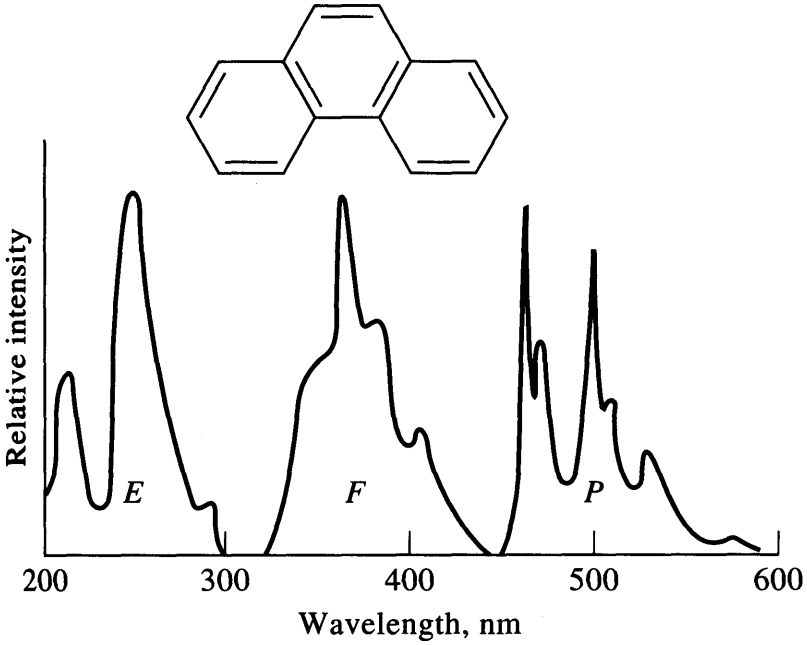


Fig. 15-3

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)

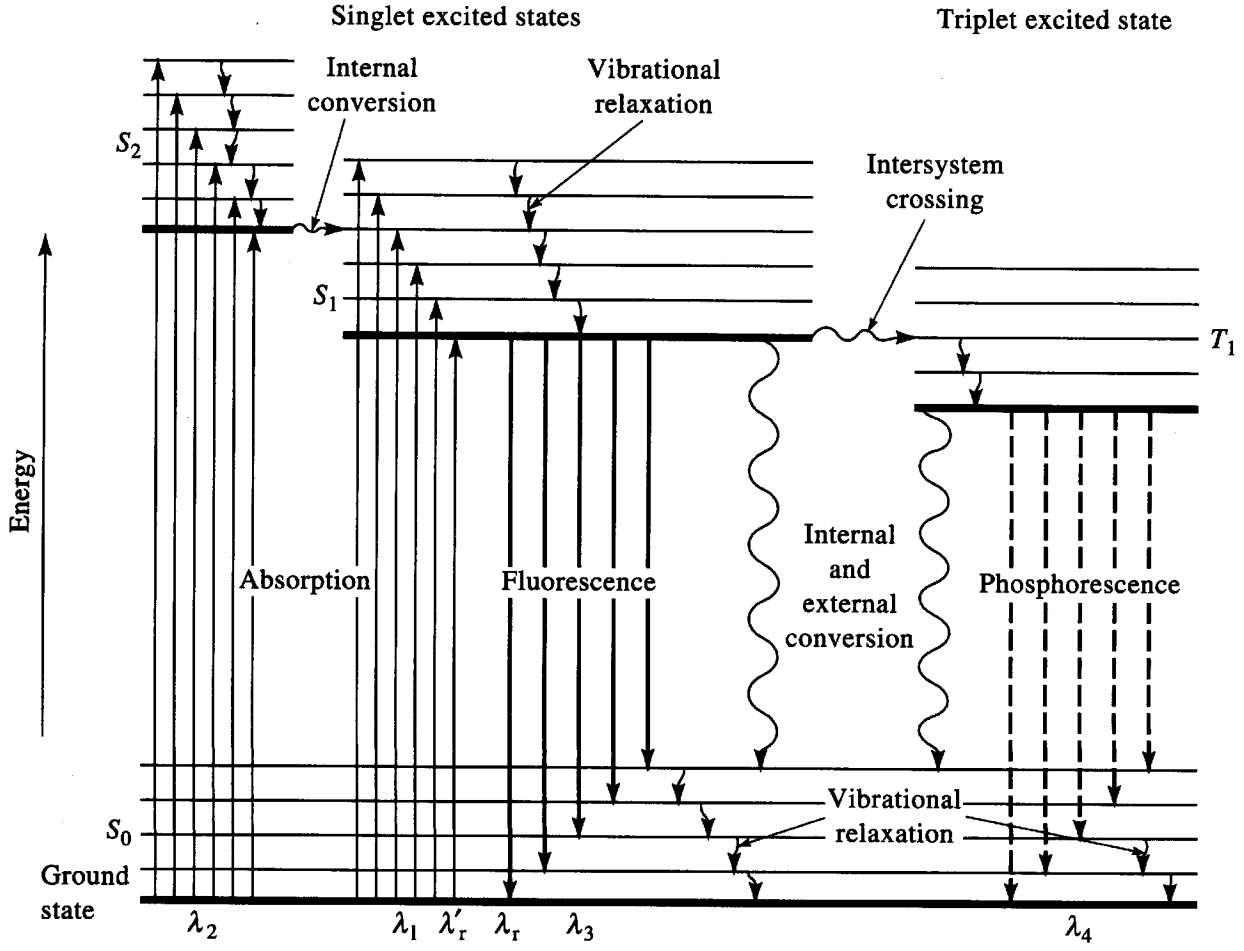
Fluorescence: emission not involving spin change (e.g. $S \rightarrow S$, $T \rightarrow T$), efficient, short-lived $<10^{-5}$ s

Phosphorescence: emission involving spin change ($T \rightarrow S$), 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 Φ_{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)

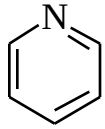
(3) Structure

Few conjugated aliphatics fluoresce

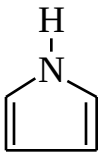
Many aromatics fluoresce

Desire short lifetime S_1, no/slowly accessible T_1

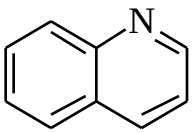
Fluorescence increased by # fused rings and substitution on/in ring



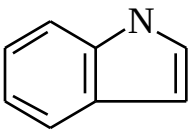
Pyridine



Pyrrole



Quinoline

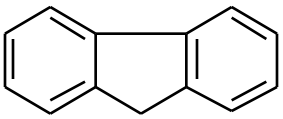


Indole

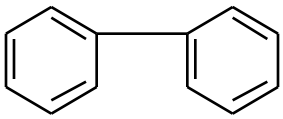
(4) Rigidity

Rigid structures fluoresce

Increase in fluorescence with chelation



Fluorene



Biphenyl

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

Quantitative Luminescence Spectrophotometry:

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

Only works at low A (<0.05)

(i) self quenching (collisions between excited states

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

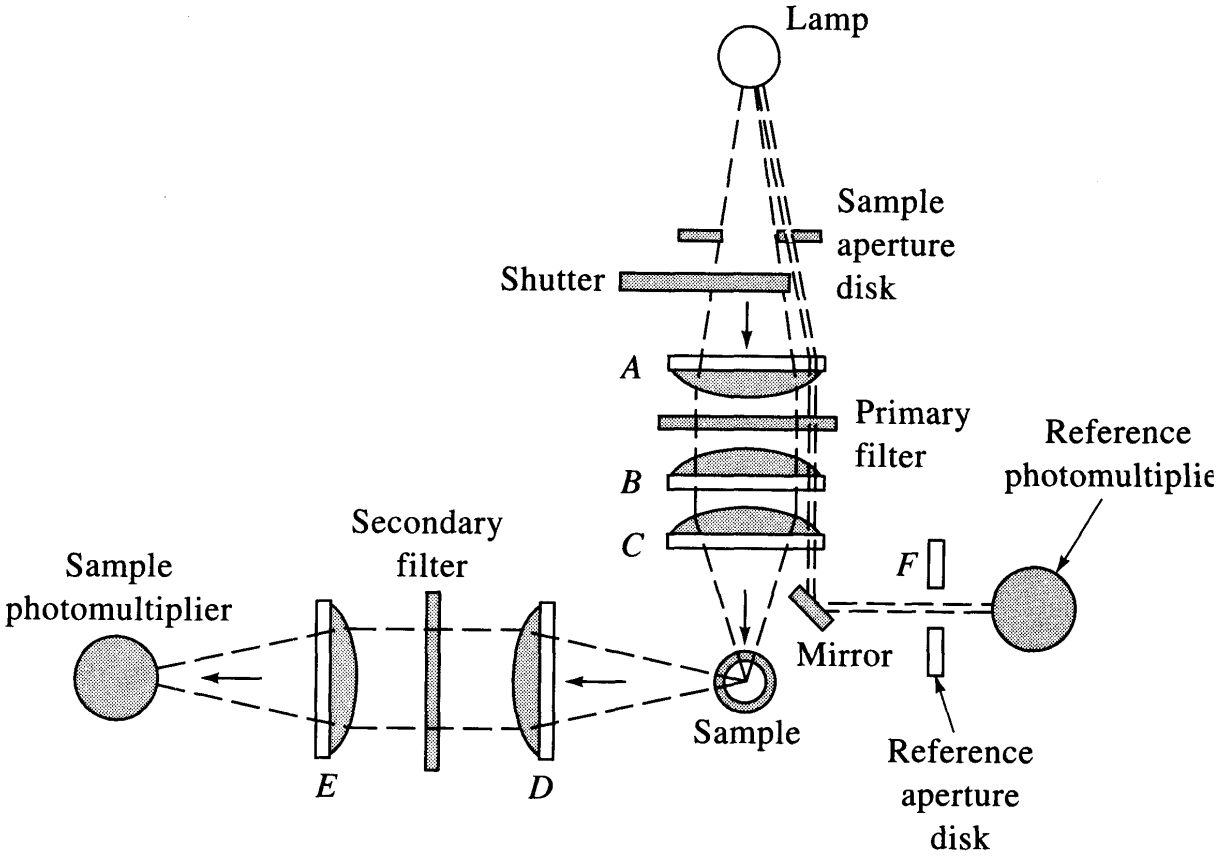


Fig. 15-6

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

Spectrofluorometer - two monochromators for excitation scanning or fluorescence scanning

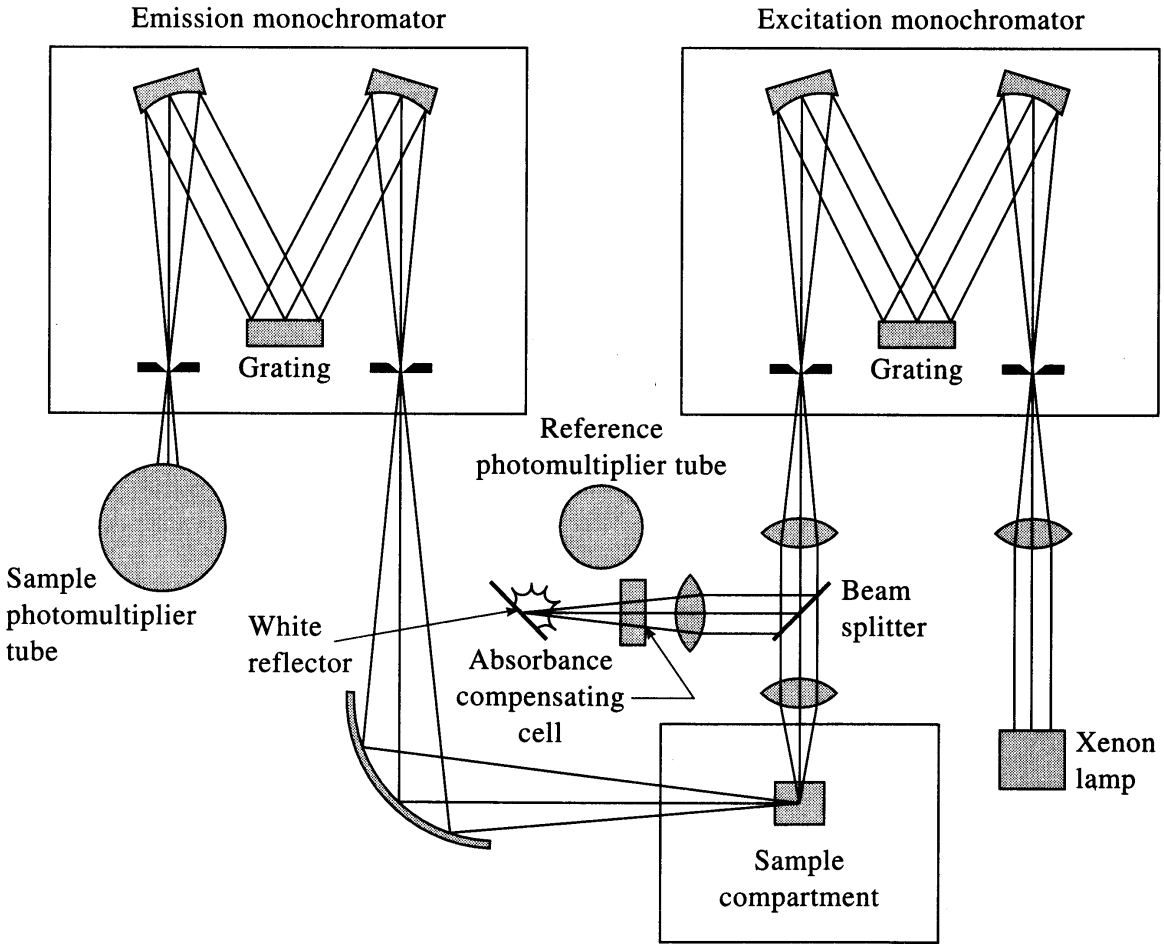


Fig 15-7

Total Luminescence Measurements:

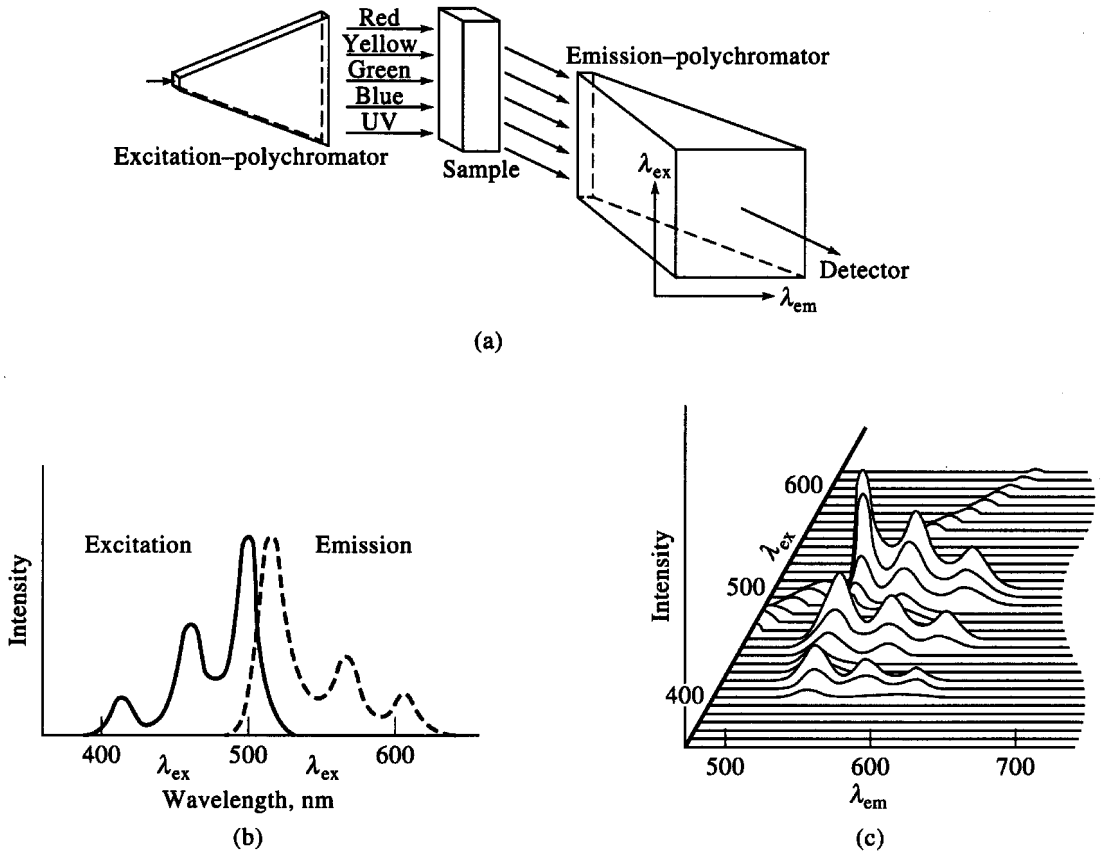


Fig 15-8

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*

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

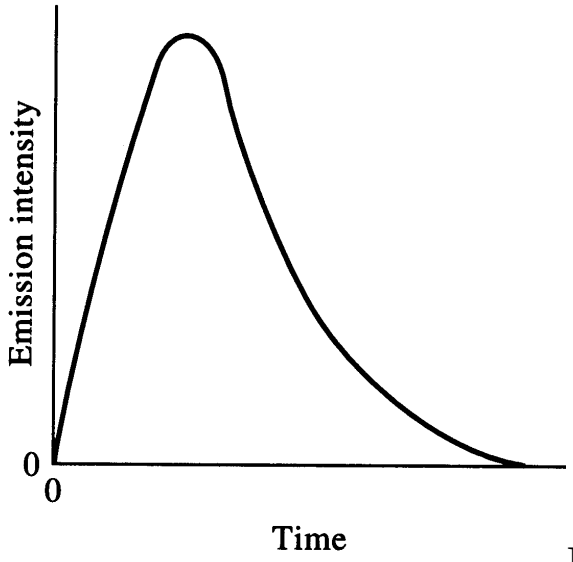


Fig. 15-11

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

Disadvantages: (i) few reactions