Photoluminescence spectroscopy
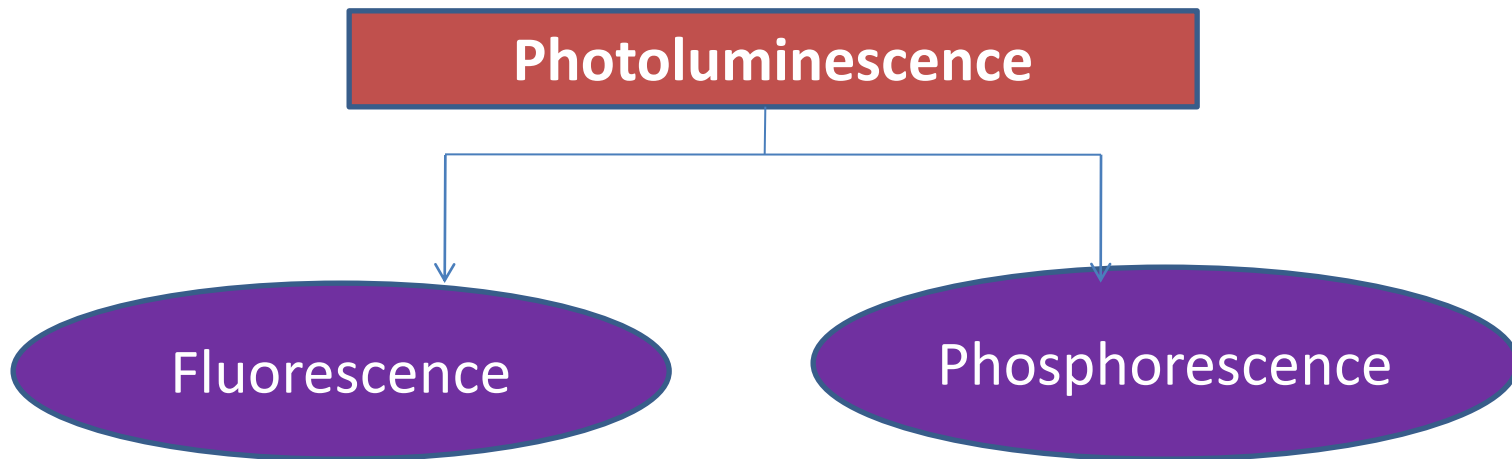
By

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"The sample is excited with a laser or lamp with photon energy greater than the band gap. The spectrum is obtained by recording the emission as a function of wavelength."

Photoluminescence

Fluorescence

Phosphorescence

1. Electronic energy transitions responsible for fluorescence
2. Do not involve a change in electron spin.
3. Because of this, the excited states involved in fluorescence are short-lived («10-' s).

1. Change in electron spin is responsible for phosphorescence,
2. Lifetimes of the excited states are much longer. (of the order seconds or even minutes)

Electron Spin

- The Pauli exclusion principle states that no two electrons in an atom can have the same set of four quantum numbers.

Singlet/Triplet Excited States
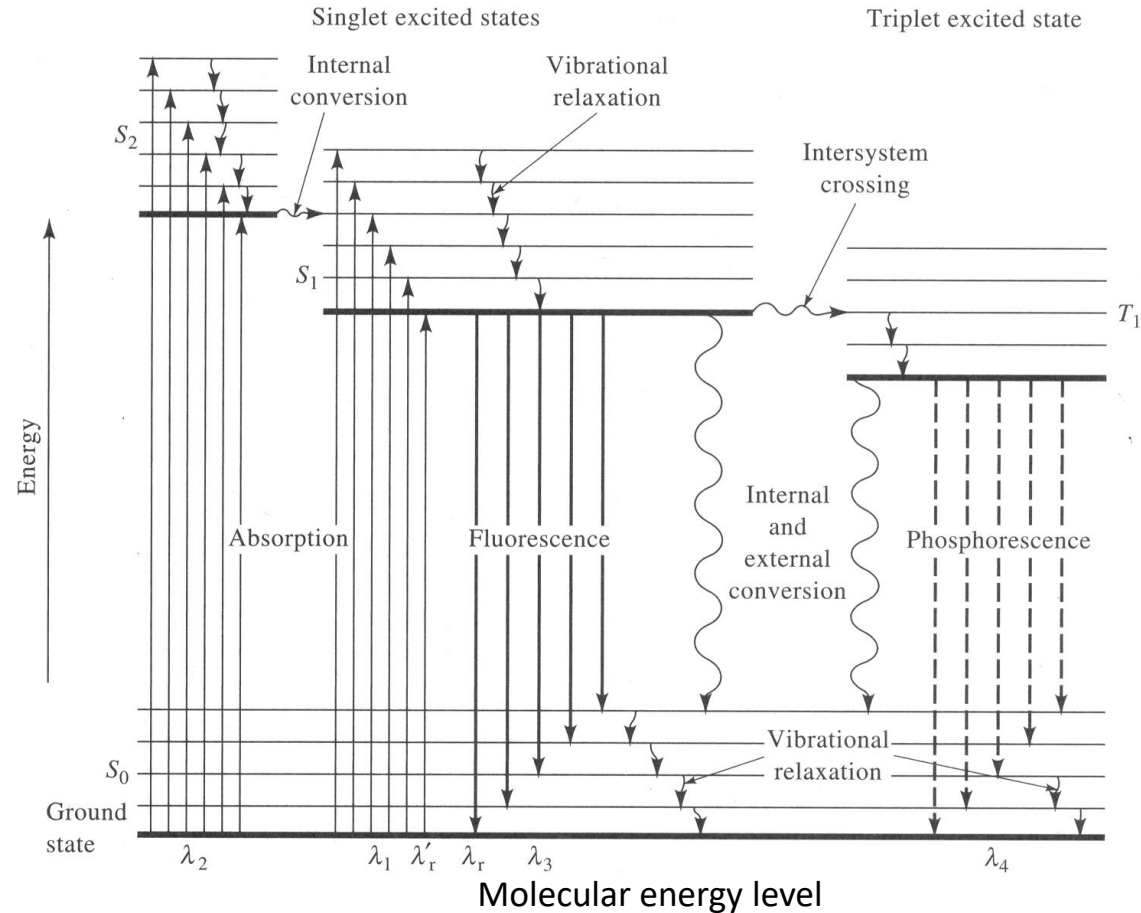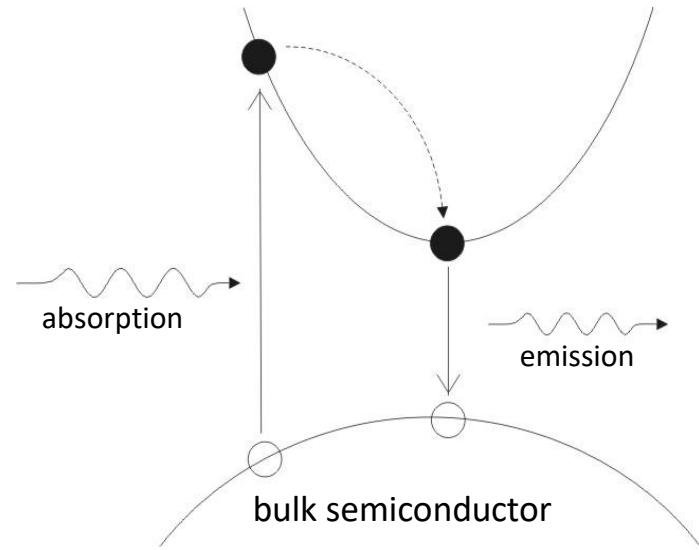
Ground state

Excited singlet state
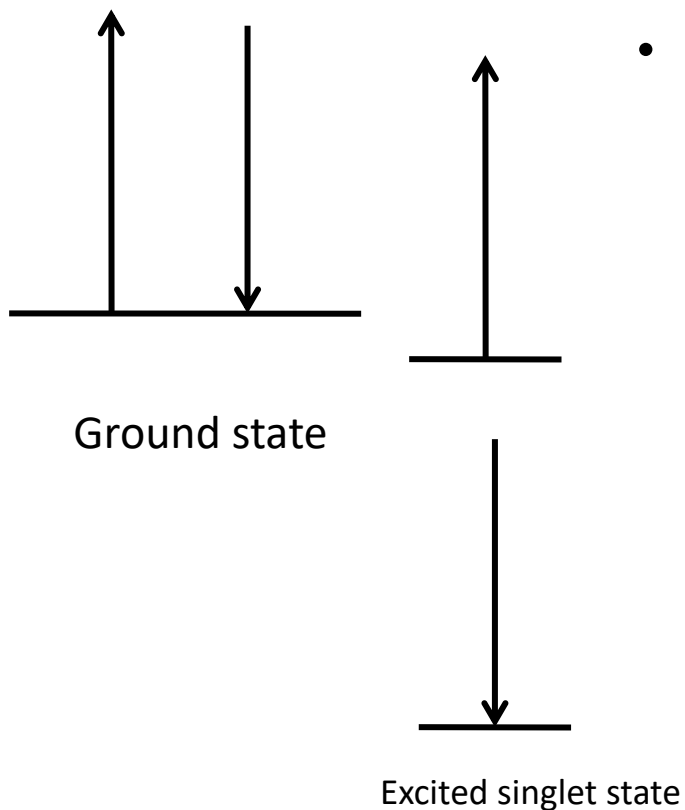
- A molecular electrons state in which all electron spins are paired is called a singlet state and no splitting of electronic energy levels occurs when the molecule is exposed to a magnetic field.

Excited triplet state
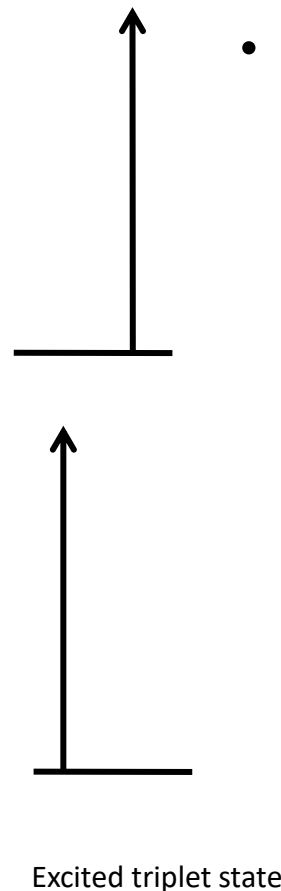
- The ground state for a free radical, on the other hand, is a doublet state because the odd electron can assume two orientations in a magnetic field, which imparts slightly different energies to the system

Energy levels in molecules and semiconductors

absorption

emission

bulk semiconductor

Singlet excited states

Triplet excited state

Internal conversion

Vibrational relaxation

Intersystem crossing

S_2

S_1

T_1

Energy

Absorption

Fluorescence

Internal and external conversion

Phosphorescence

Vibrational relaxation

S_0

Ground state

λ_2 λ_1 λ_r' λ_r λ_3 λ_4

Molecular energy level

- In molecules absorption and PLE peaks are couple of S_1 and S_2 with vibrational energy, while PL peaks are couple of S_0 and vibrational energy.

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Absorption and Emission

Selection Rules:

$$\Delta J = \pm 1$$

$$\Delta v = \pm 1, \pm 2, \pm 3, \ldots$$

$$\Delta S = 0 \text{ (i.e. } S \rightarrow S, T \rightarrow T)$$

Very Fast $\rightarrow 10^{-14} - 10^{-15}$ sec.

Emission
fluorescence
slower rate: 10^{-5} to 10^{-10} s
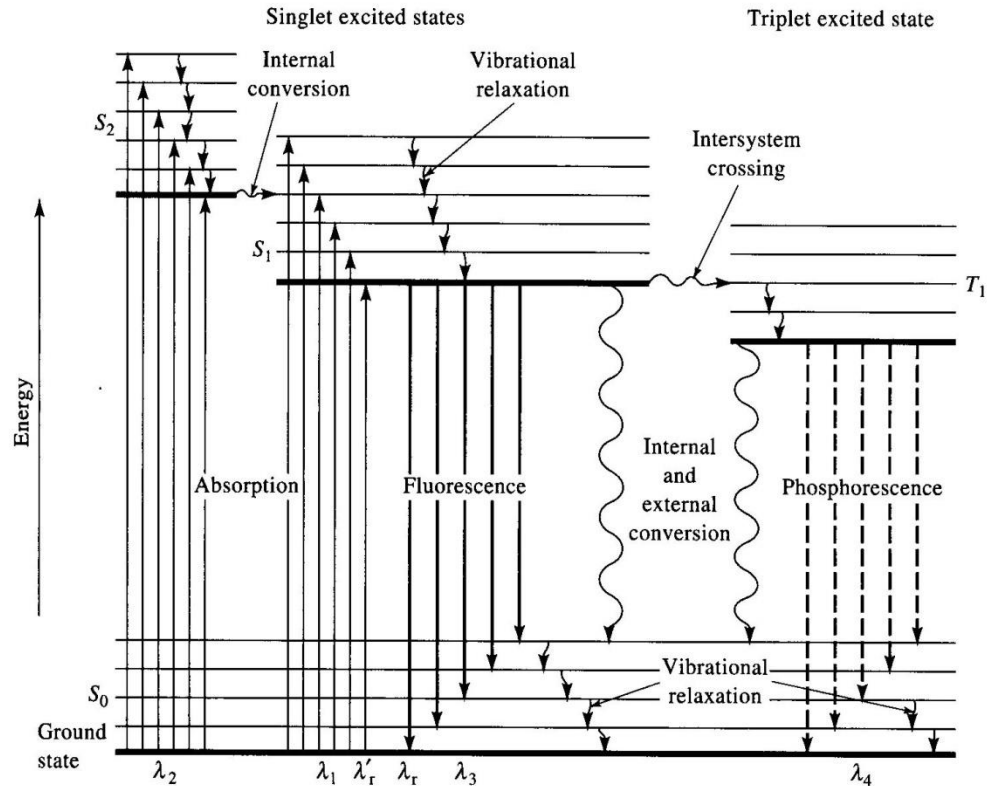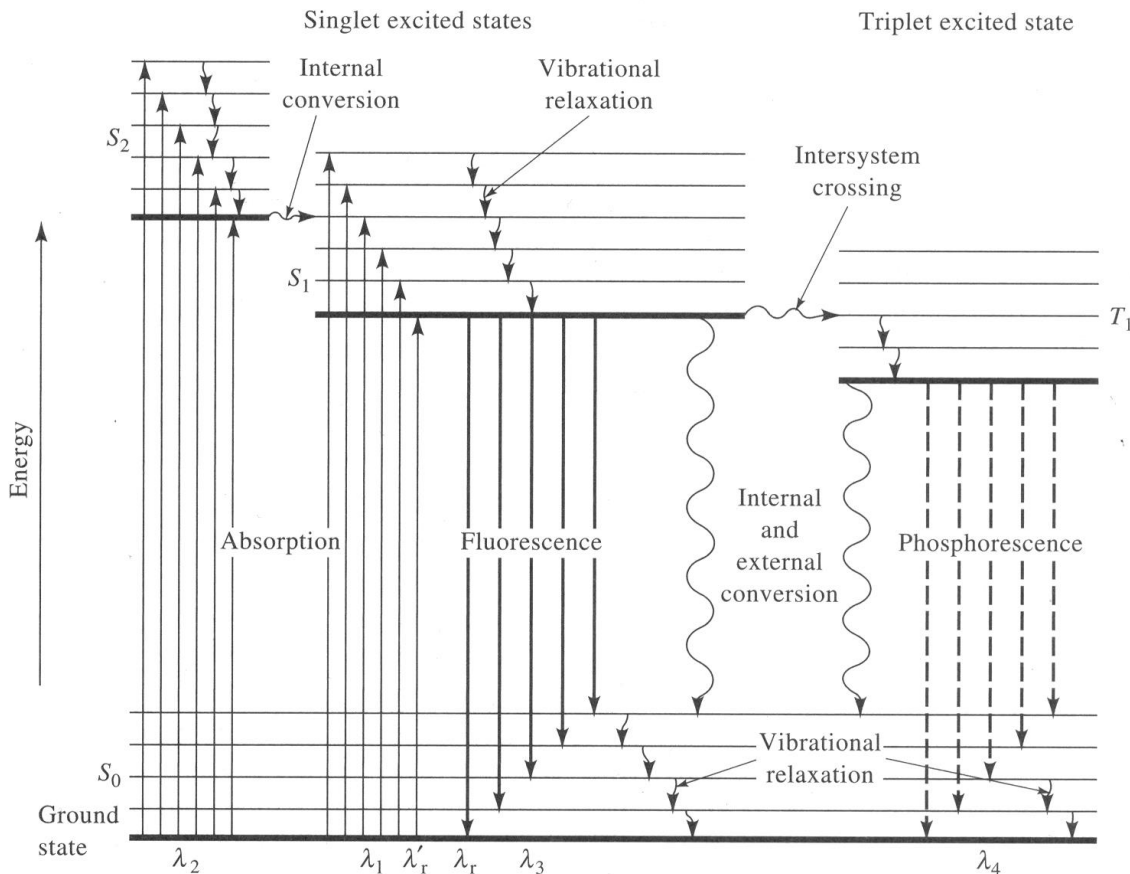phosphorescence
10^{-4} to 10 s or more to occur

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

Deactivation Processes

- An excited molecule can return to its ground state by a combination of several mechanistic steps. The deactivation steps, indicated by wavy arrows, are radiationless processes. The favored route to the ground state is the one that minimizes the lifetime of the excited state.

- Vibration Relaxation
- Internal Conversion
- External Conversion
- Intersystem Crossing
- Fluorescence
- Phosphorescence

Vibrational Relaxation

- Excited molecule rapidly transfers excess vibrational energy to the solvent / medium through collisions.

- Molecule quickly relaxes into the ground vibrational level in the excited electronic level.

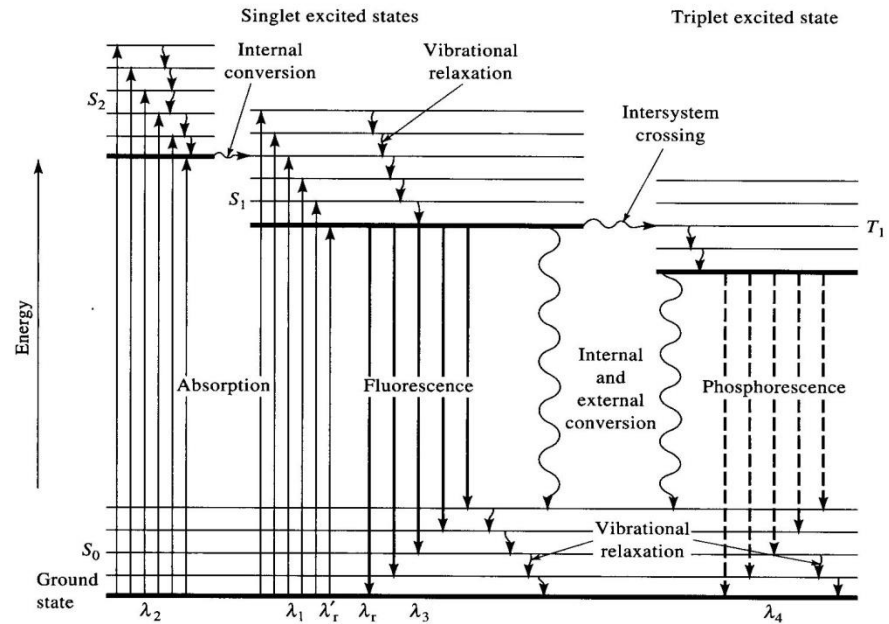- Non-radiative process

- $10^{-11} – 10^{-10}$ sec.

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

Internal Conversion

- Transfers into a lower energy electronic state of the same multiplicity without emission of a photon.

- Favored when there is an overlap of the electronic states' potential energy curves.

- Non-radiative process (minimal energy change)
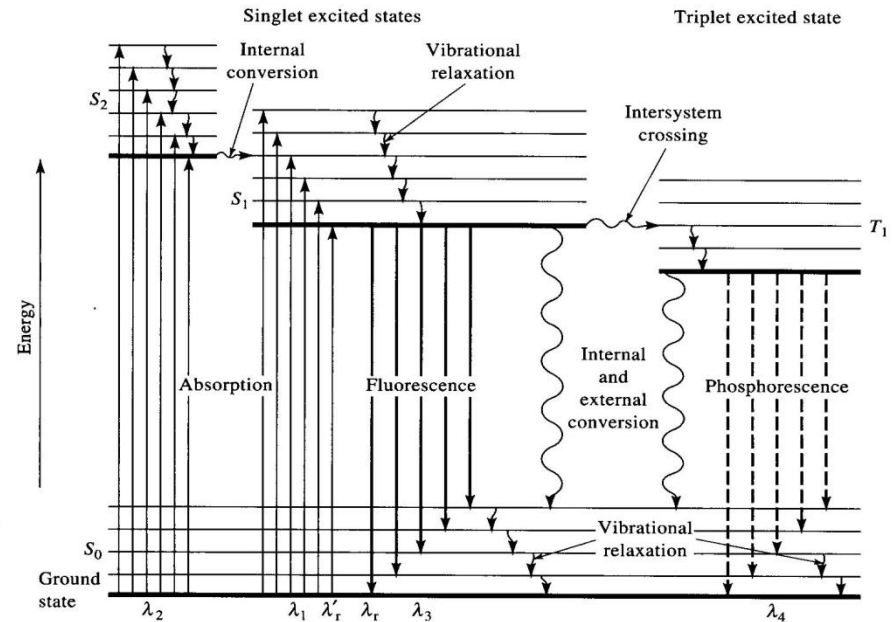
- ~10^{-12} s between excited electronic states.

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

External Conversion

- Non-radiative transition between electronic states involving transfer of energy to other species (solvent, solutes).

- Also referred to as quenching.

- Modifying conditions to reduce collisions reduces the rate of external conversion.
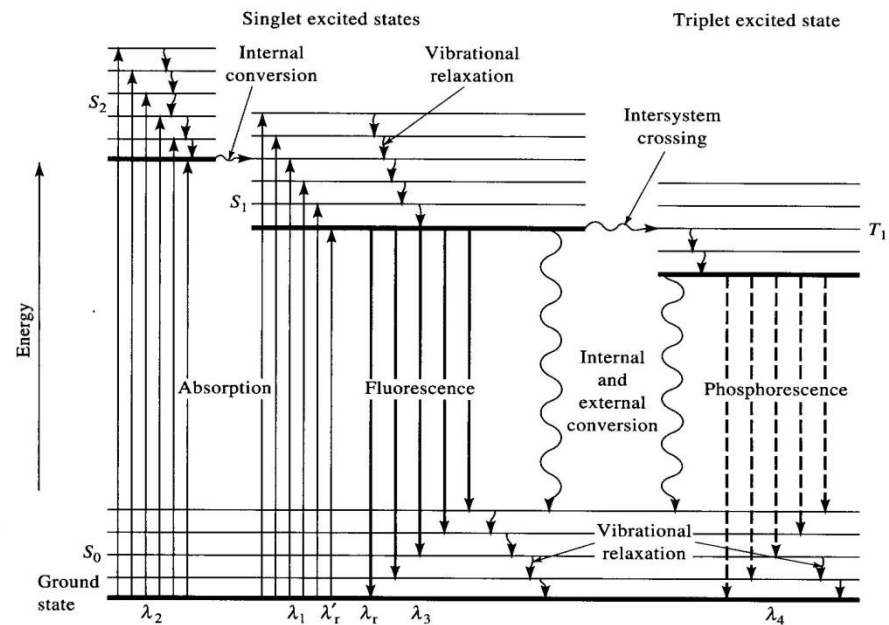

Figure 15-1 Partial energy diagram for a photoluminescent system.

Intersystem Crossing

- Similar to internal conversion except that it occurs between electronic states with different multiplicities.

- Slower than internal conversion.

- More likely in molecules containing heavy nuclei.

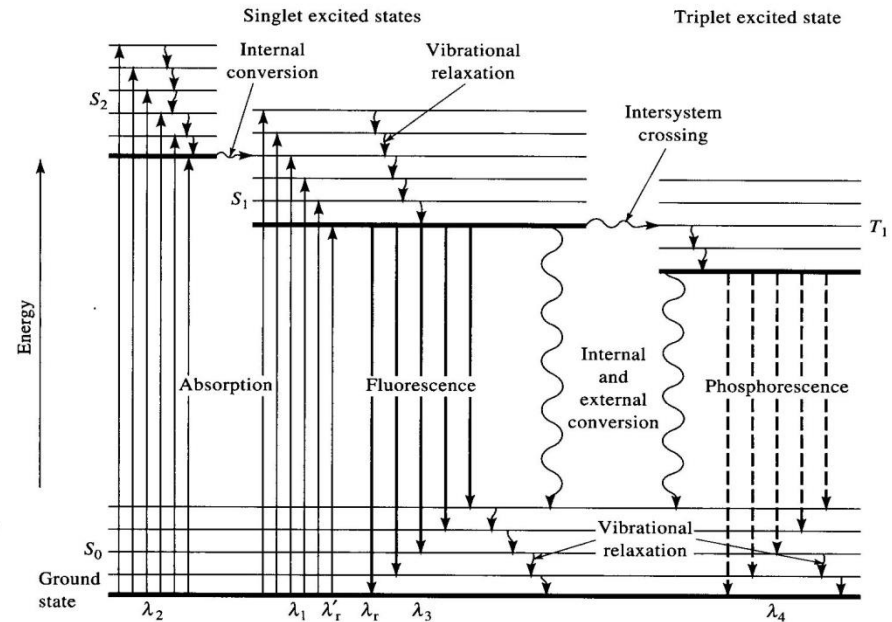- More likely in the presence of paramagnetic compounds.

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

Fluorescence

- Radiative transition between electronic states with the same multiplicity.

- Almost always a progression from the ground vibrational level of the 1st excited electronic state.

- $10^{-10} - 10^{-6}$ sec.

- Occurs at a lower energy than excitation.

Phosphorescence

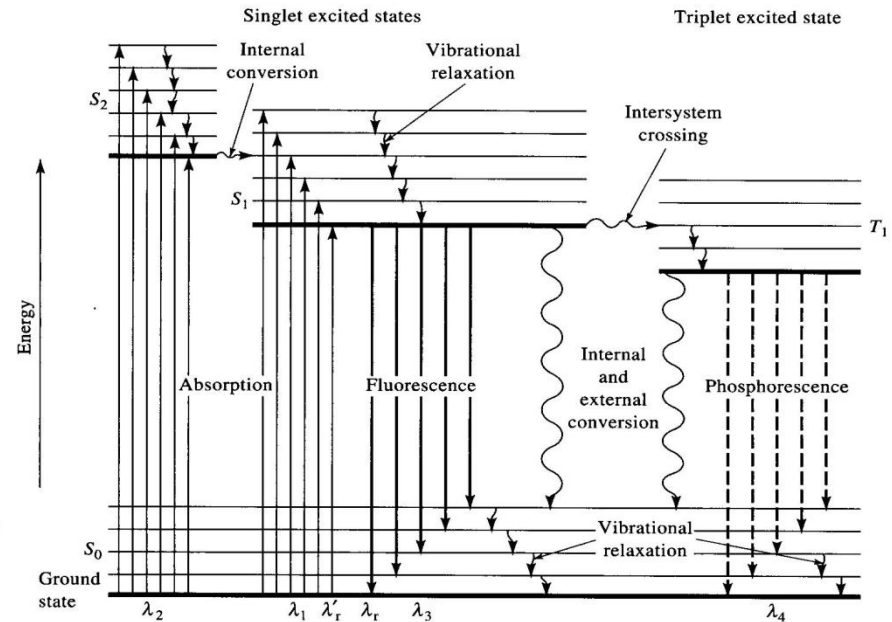Radiative transition between electronic states with the different multiplicity.

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

Variables That Affect Fluorescence and Phosphorescence

- Both molecular structure and chemical environment influence whether a substance will or will not luminesce; these factors also determine the intensity of emission when luminescence does occur.

- Quantum Yield
- Transition Types in Fluorescence
- Quantum Efficiency and Transition Type
- Fluorescence and Structure

Quantum Yield

Fraction of absorbed photons that are converted to luminescence, fluorescence or phosphorescence photons.

$$\phi_L = \frac{\Phi_{L,p}}{\Phi_{A,p}}$$

May approach unity in favorable cases.

Fluorescence Quantum Yield

Fluorescence Quantum Efficiency of a Molecule:

$$\phi_F = \frac{\Phi_{F,p}}{\Phi_{A,p}} = \frac{k_F}{k_F + k_{nr}}$$

$$\phi_F = \frac{k_F}{k_F + k_{ec} + k_{ic} + k_{isc} + k_{pd} + k_d}$$

k_{ec} = external conversion ($S_1 \rightarrow S_0$)
k_{ic} = internal conversion ($S_1 \rightarrow S_0$)
k_{isc} = intersystem crossing ($S_1 \rightarrow T_1$)
k_{pd} = predissociation
k_d = dissociation
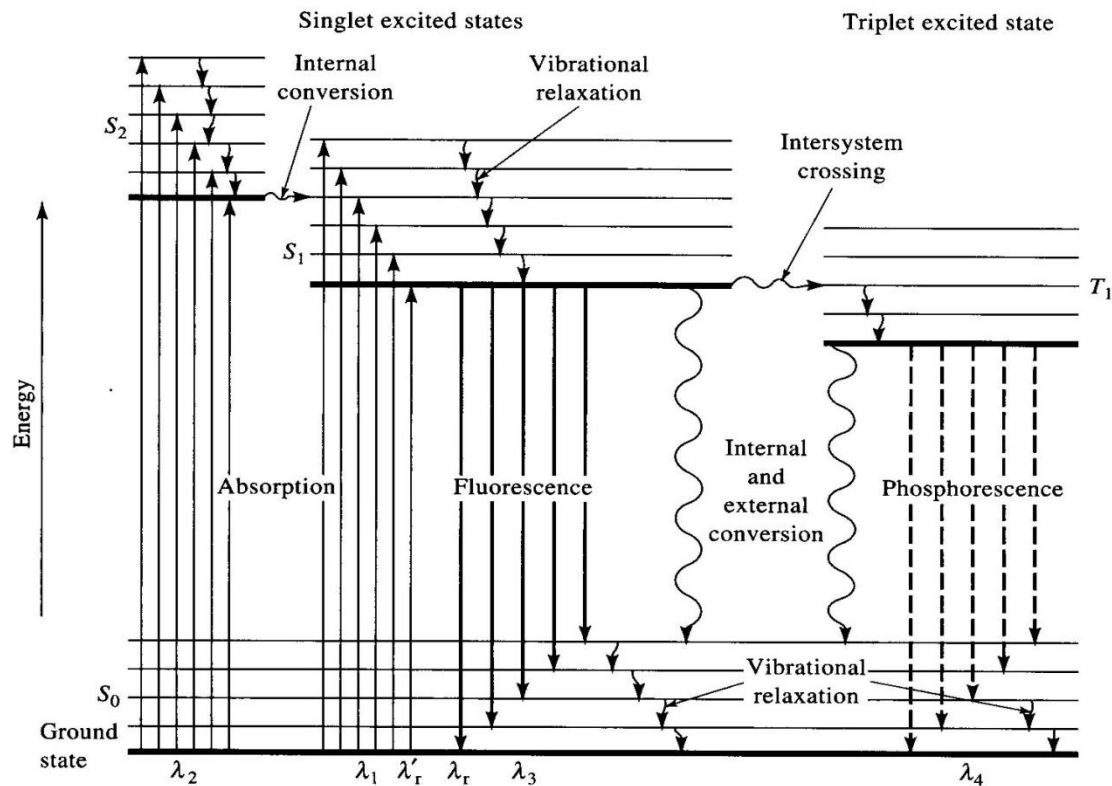
Phosphorescence Quantum Yield

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

Phosphorescence Quantum Yield

Product of two factors:

- fraction of absorbed photons that undergo intersystem crossing.

- fraction of molecules in T_1 that phosphoresce.

$$\phi_P = \left(\frac{k_{isc}}{k_F + k_{nr}} \right)\left(\frac{k_P}{k_P + k'_{nr}} \right)$$

k_{nr} = non-radiative deactivation of S_1.

k'_{nr} = non-radiative deactivation of T_1.
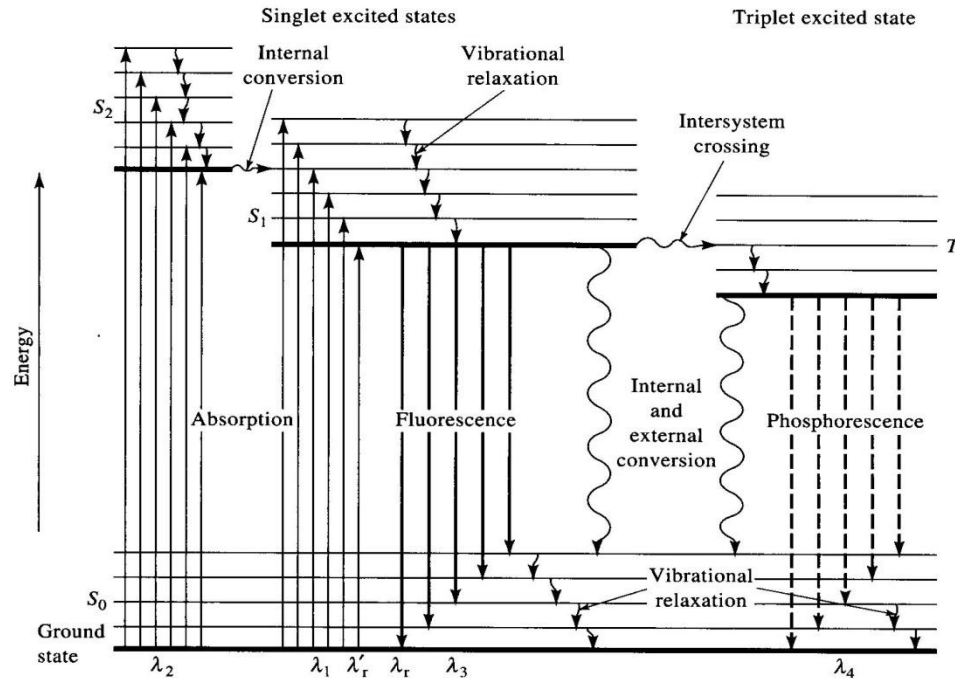
Conditions for Phosphorescence

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

$$k_{isc} > k_F + k_{ec} + k_{ic} + k_{pd} + k_d$$

$$k_P > k'_{nr}$$

Effect of

1. Temperature and Solvent Effects
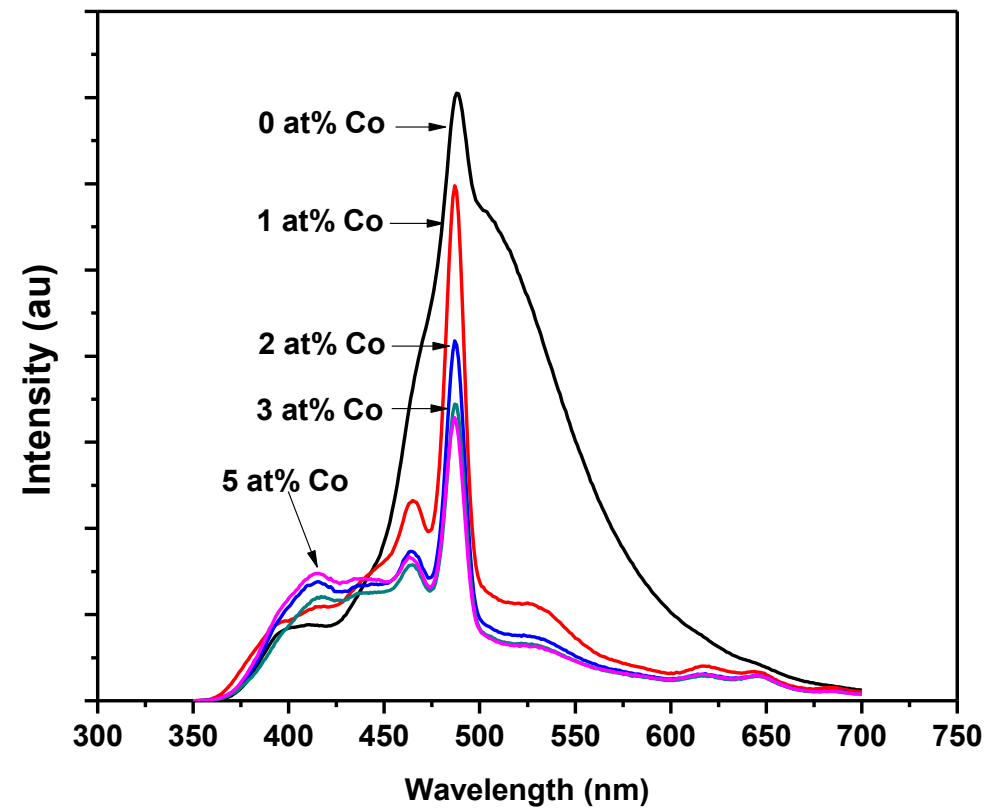2. Concentration on Fluorescence Intensity

Figure: PL spectra for various Co doping concentrations of CZO thin films

Peak no	0 at% Co	1 at% Co	2 at% Co	3 at% Co	5 at% Co
1	397.47	397.13	397.44	397.01	397.34
2	-	414.23	416.58	417.44	417.51
3	434.76	435.68	440.37	441.06	443.30
4	467.46	466.10	465.51	465.20	465.39
5	488.26	486.95	487.31	487.43	487.12
6	508.05	508.10	505.13	504.78	505.64
7	-	616.14	-	-	-
8	-	633.03	632.26	632.60	631.72

Thank You