# Fate of electronically excited states

What happens after light absorbed and electronically excited species formed.

thermal degradation — to thermal energy of environment
rotation vibration translation

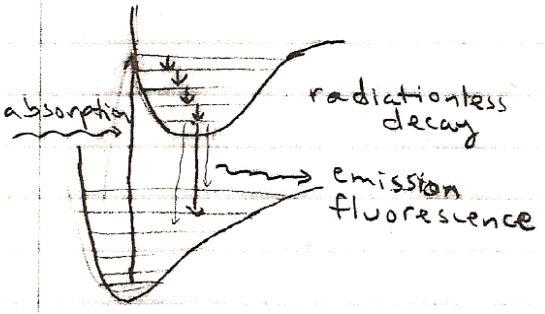
radiative decay — emit a photon

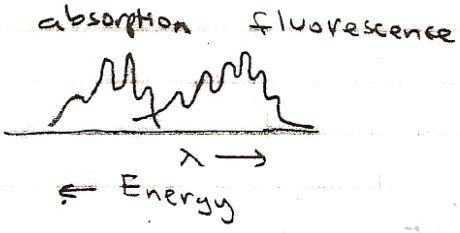
Spontaneous

fluorescence — radiation out stops when source stops

phosphorescence — radiation continues after source has stopped seconds to hour

## Fluorescence (radiative emission between states of same multiplicity)

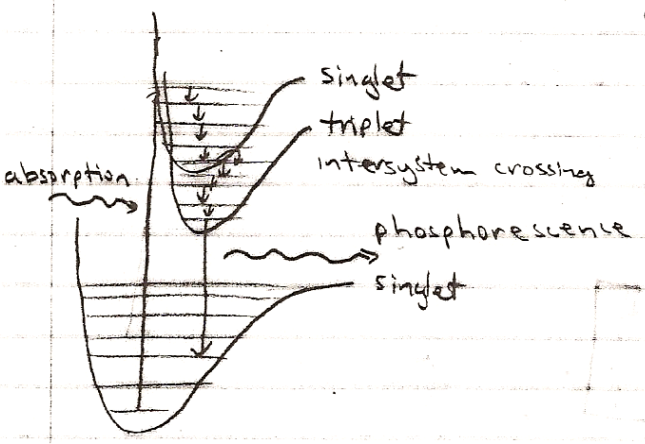



(1) absorption (vibrational structure)
(2) radiationless decay
(3) fluorescence (vibrational structure)

radiationless decay involves transferring energy to surroundings through collisions with solvent. Not possible with the larger electronic change.

## Phosphorescence (radiative emission between state of different multiplicity)




presence of triplet state

singlet (excited electron is parallel to $e^-$ in orbital from which it came)

| | | b | |
|---|---|---|---|
| ↑ | S | 1 | $2(S)+1 = 1$ |
| ↑ | T | 1 | $2(S)+1 = 3$ |
| | | 1 | |

lower energy paired $e^-$ further away

(1) absorption
(2) radiationless decay of excited singlet
(3) intersystem crossing where curves cross
weakly allowed change from singlet (paired spins) to triplet (unpaired spins) thus magnetic)
in molecule with heavy atom (spin-orbit coupling breaks selection rules)
(4) radiationless decay of excited triplet
(5) spin orbit coupling breaks selection rule and get weak triplet* to singlet transition
emit slowly

most intense from solid samples less collisions with environment more time for intersystem crossing to occur as excited state slowly loses energy and falls below intersection point.

example ZnS phosphor on old TV screen

luminescence general term