Luminescence – light emission accompanying a transition from higher to lower energy levels

1) Phosphorescence – example of photoluminescence (excited state generated by photons) often exhibited by solids like glow in the dark key chains, television screens (CRTs) & “fluorescent” lights
2) Fluorescence – also photoluminescence which is usually observed in solution like quinine that is added to tonic water many analytical applications

3) Bioluminescence – excited state induced biologically (enzymatic process) exhibited by fireflies, some algae & fish
4) Chemiluminescence – excited state induced chemically by bond breakage, often oxidation & used for light sticks & some analytical applications
5) Triboluminescence – excited state induced mechanically → bite down on hard candy, also Curad bandaids
6) Electroluminescence – electrical excitation found in some polymers & electric pickle

Photoluminescence is the most useful kind of luminescence for analysis because:

1) Many compounds exhibit this phenomenon
2) The effect can be readily produced
3) Several variables can be used to control the process (e.g. excitation λ, emission λ, pulsing or modulating excitation source, gating or synchronizing detector response)

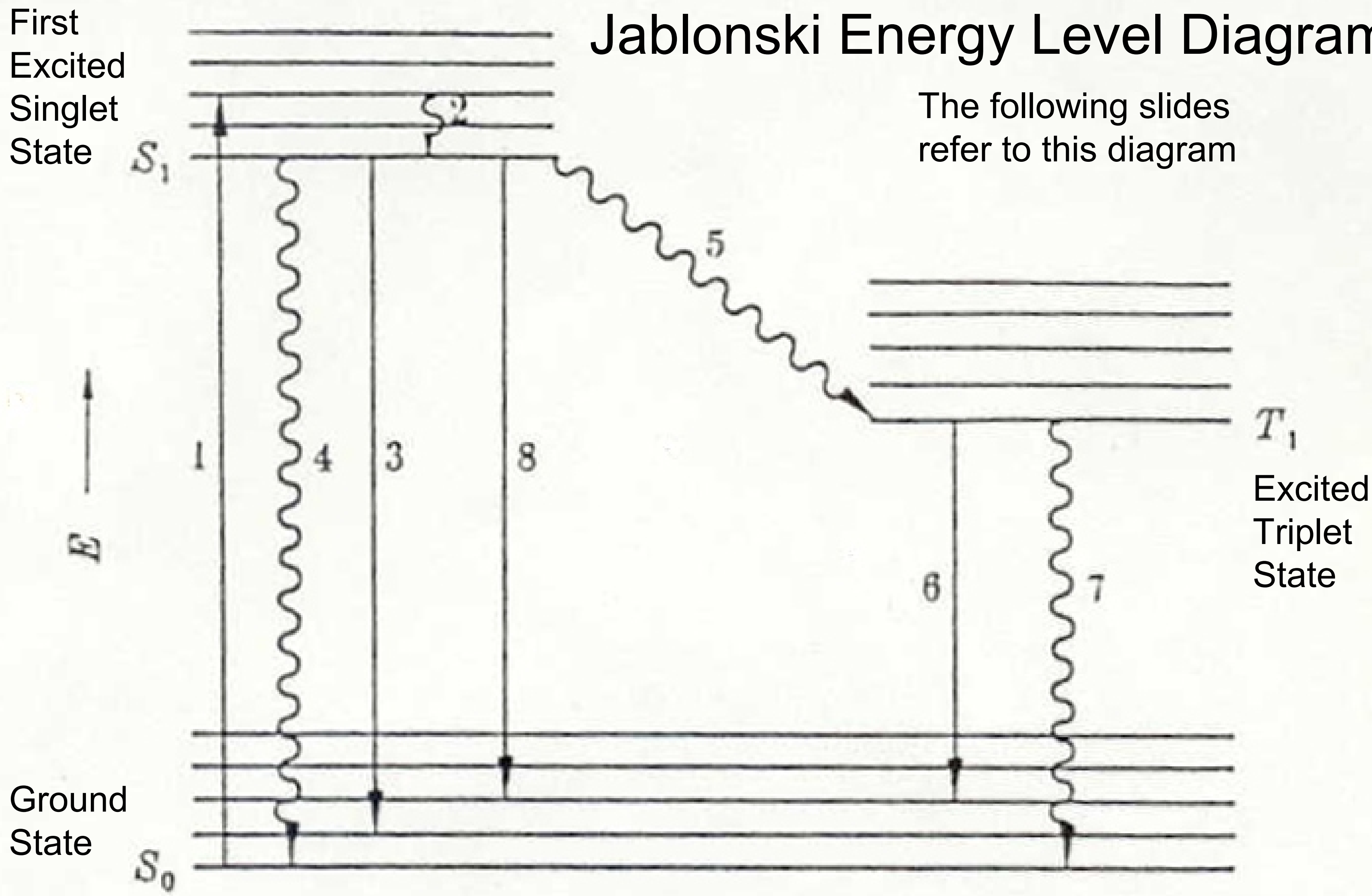
Chemiluminescence can be used for analysis also, but it is harder to control

Bioluminescence is chemiluminescence

Others are basically useless analytically

Jablonski Energy Level Diagram

The following slides refer to this diagram



1 = absorption, 2 = vibrational relaxation, 3 = fluorescence, 4 & 7 = radiationless deactivation, 5 = intersystem crossing, 6 = phosphorescnce

When absorption of a photon occurs (process #1), several things can happen:

Vibrational Relaxation (VR) - is a non-radiative process (#2) by which the upper vibrational levels lose energy & go to the lowest vibrational level in a given electronic energy state (very fast ~ 10^{-12} s)

Internal Conversion (IC) - non-radiative process (#4) where excited state couples to upper vibrational level of lower electronic energy level followed by VR

Because of Vibrational Relaxation (VR) all absorbed photons result in the promoted electron ending up in the lowest vibrational level of the **first excited singlet state**

This level can then do one of three things:

1) **<u>Fluoresce</u>** → make transition to one of the vibrational levels of the ground state giving up energy as a photon (process #3)

2) **Radiationless Deactivation** (#4) – return to ground state giving up energy as heat, by internal conversion or some sort of collisional deactivation

3) **Intersystem Crossing** (#5) – lowest vibrational level of first excited singlet couples to upper vibrational level of triplet state followed by vibrational relaxation

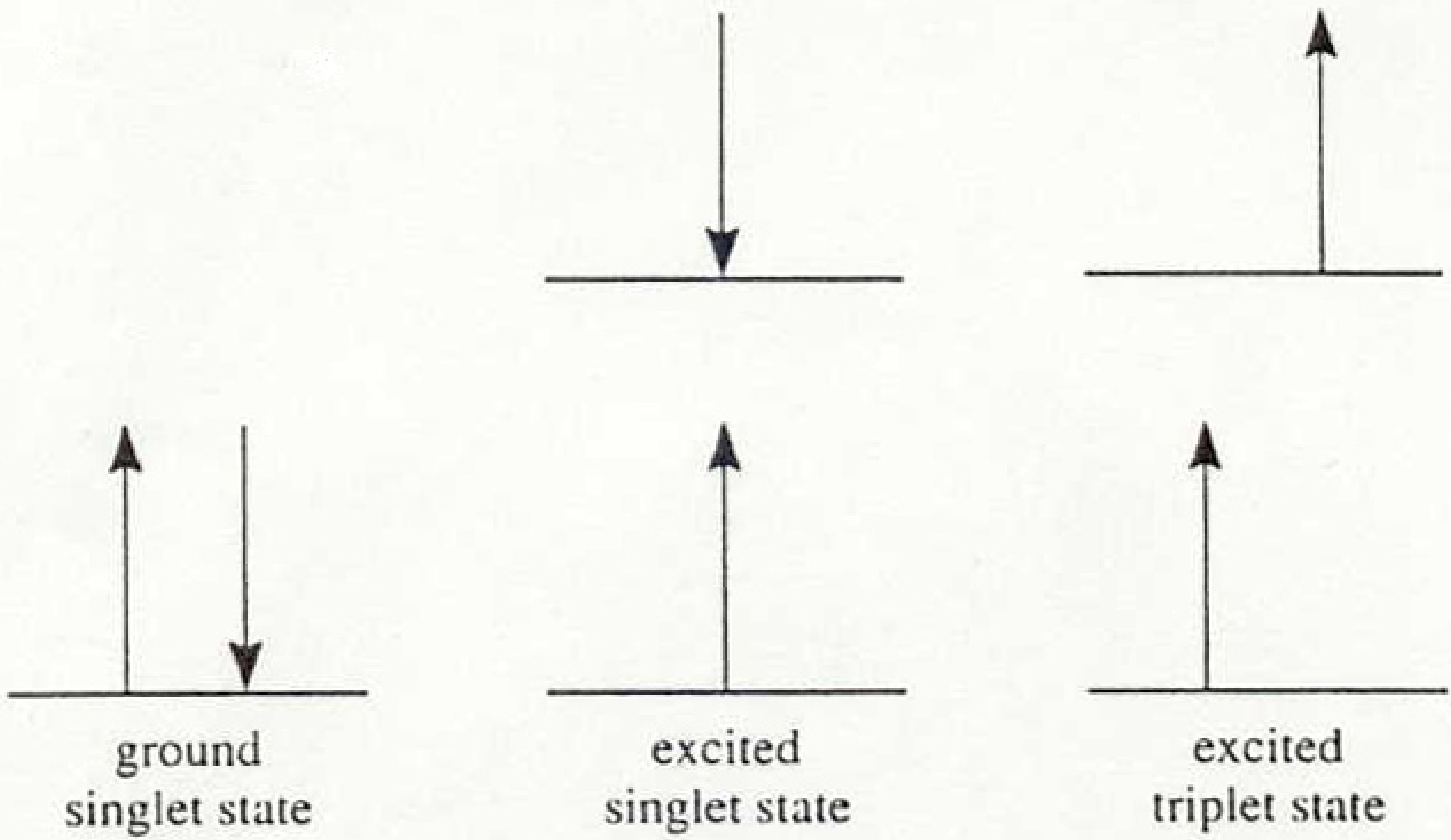
   Once formed the triplet state can go to ground state radiationlessly or by emitting a photon = **phosphorescence** (#6)

The transition $T_1 \rightarrow S_o$ (G) with emission of a photon is spin forbidden, has a low probability and a slow rate

Fluorescence involves a spin allowed transition → very probable → fast rate & short lifetime (typically 1-20 nsec)

Phosphorescence involves spin forbidden transition → not so probable → slower rate & longer lifetime (from 10^4 – 10 sec)

Spin States


ground
singlet state
excited
singlet state
excited
triplet state

Moderately interesting website showing an animated Jablonski Diagram for absorption, VR, fluorescence, phosphorescence, etc.

http://micro.magnet.fsu.edu/primer/java/jablonski/lightandcolor/

Spectra

1) Excitation Spectrum – fluorescence or phosphorescence intensity (at fixed λ) as a function of excitation λ or absorption λ
2) Fluorescence Emission Spectrum - fluorescence emission intensity vs. λ for a fixed excitation λ (= absorption λ, max.)
3) Phosphorescence Emission Spectrum – phosphorescence emission intensity vs. λ for a fixed excitation λ (= absorption λ, max.)

Phenanthrene Spectra