

Excited State Processes

Photophysics

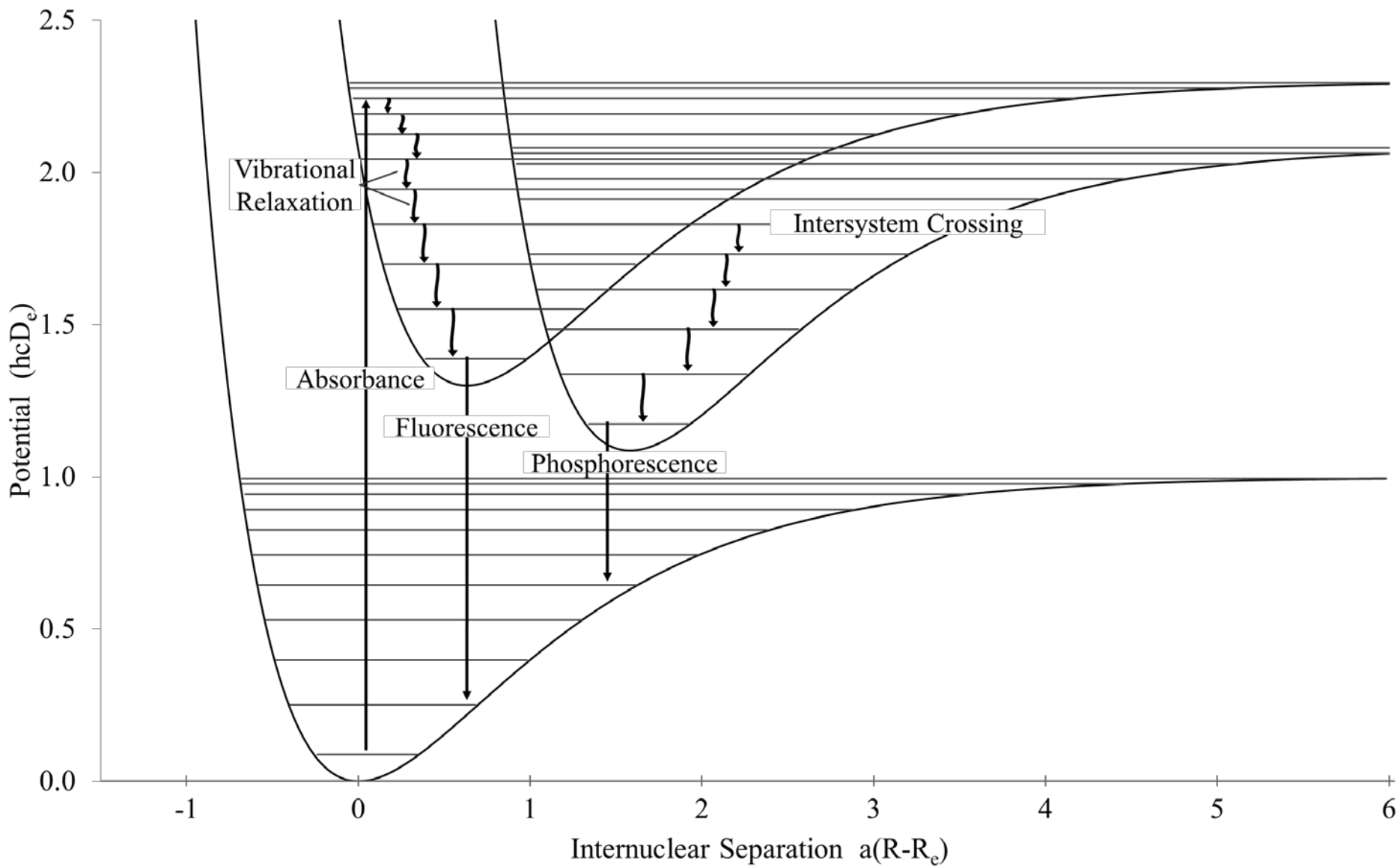
- Fluorescence (singlet state emission)
- Phosphorescence (triplet state emission)
- Internal conversion (transition to singlet gr. state)
- Intersystem crossing (transition to triplet state)

Photochemistry

- Electron transfer
- Isomerization
- Photolysis

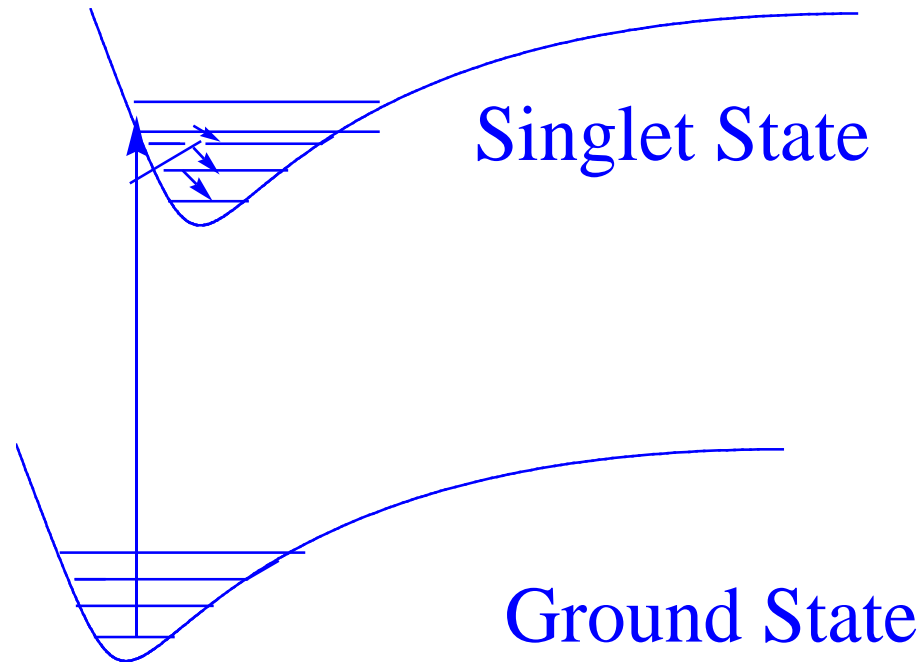
The fate of electronically excited states

- A radiative decay process involves emission of a photon.
- Non-radiative decay involves the transfer of excess energy into vibration, rotation, and translation of surrounding molecules. The result is to heat the surroundings.
 - Vibrational relaxation
 - Internal conversion processes



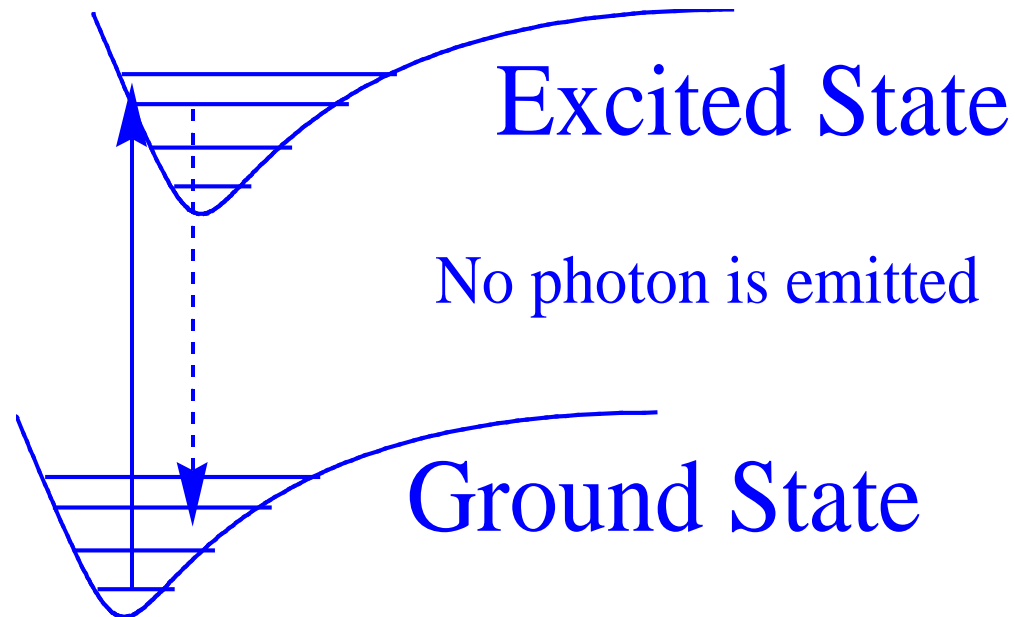
Vibrational relaxation

Absorption populates the Franck-Condon active modes of the excited state. This is NOT the equilibrium population. Therefore, relaxation among the vibrational levels occurs.



Internal conversion

A singlet excited state can decay directly back into the ground state by a process known as internal conversion.



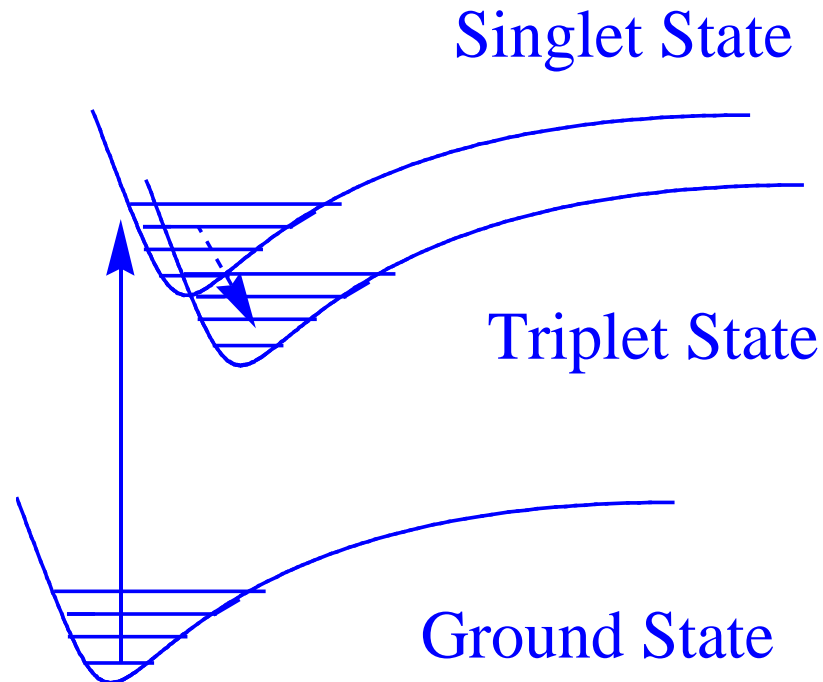
Fluorescence

Fluorescence is the spontaneous emission of radiation from an excited singlet state.

1. Absorption leads to population of Franck-Condon active vibrational modes of the excited state.
2. Vibrational relaxation results in a change of the excited state levels.
3. Emission occurs from an equilibrium population of excited state vibrational levels.

Intersystem crossing

The singlet and triplet state potential surfaces may cross and therefore a change of electron spin due to spin-orbit interactions gives rise to the triplet state.



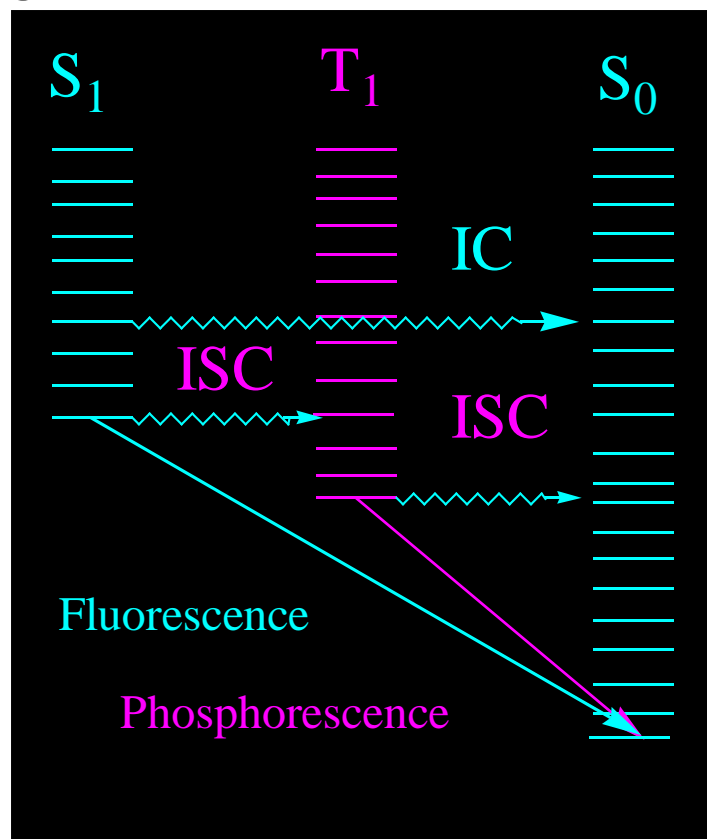
Phosphorescence

Phosphorescence is the emission of radiation from a triplet state.

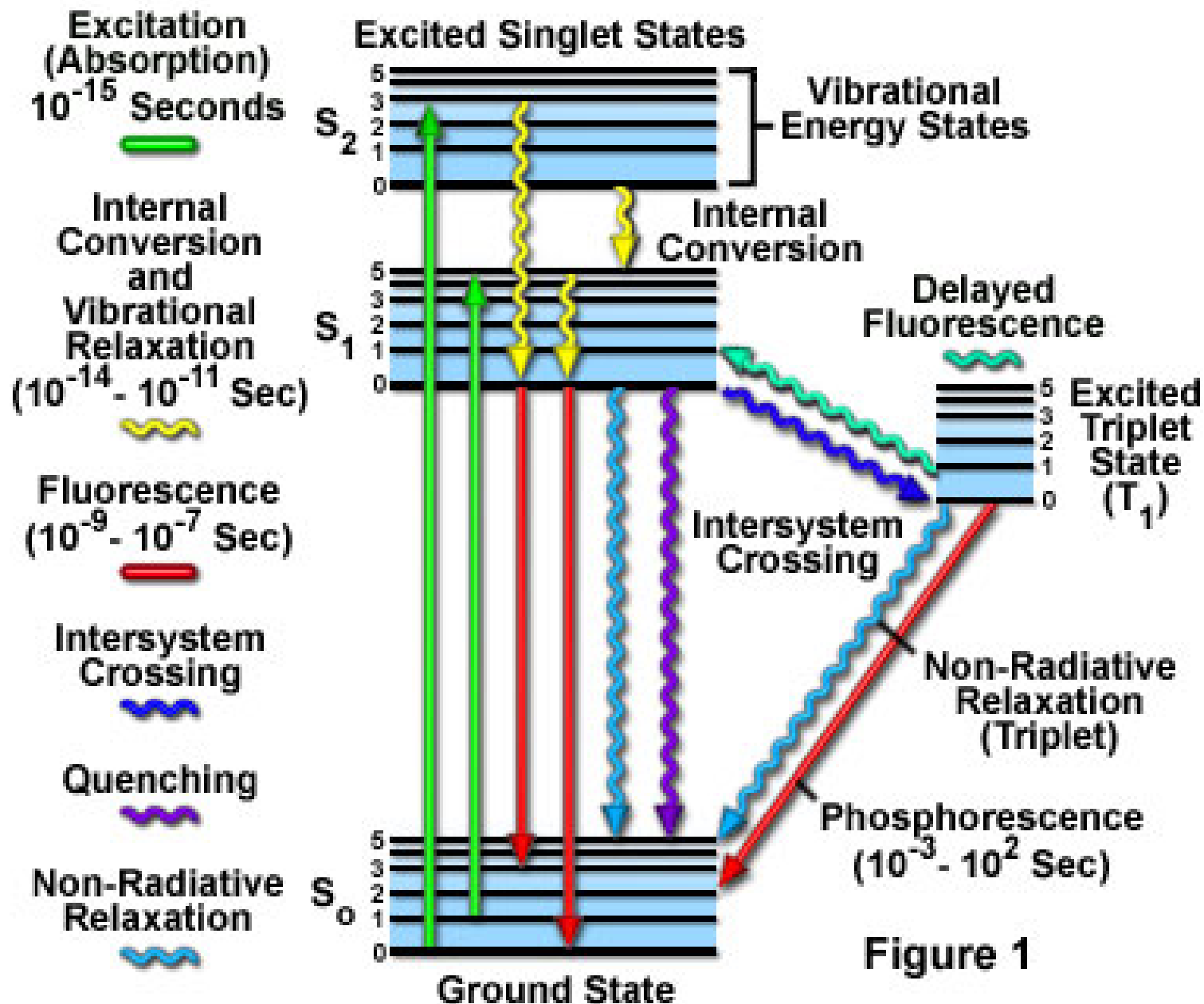
1. Absorption leads to population of the FC active modes of the singlet.
2. After vibrational relaxation in the singlet intersystem crossing produces the triplet state.
3. Vibrational relaxation continues in the triplet state.
4. Emission occurs from the triplet. Because it is spin-forbidden, the emission rate is very low. Consequently, it is long-lived.

Jablonski diagram

The radiative and non-radiative decay processes can be represented using a diagram. Vertical shifts represent changes in nuclear position.



Jablonski Energy Diagram



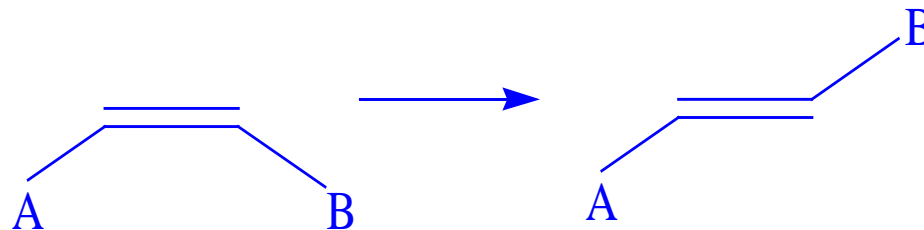
Time scales for excited state processes

Transition	Process	Rate Constant	Timescale (Seconds)
$S(0) \Rightarrow S(1)$ or $S(n)$	Absorption (Excitation)	Instantaneous	10^{-15}
$S(n) \Rightarrow S(1)$	Internal Conversion	$k(ic)$	10^{-14} to 10^{-10}
$S(1) \Rightarrow S(1)$	Vibrational Relaxation	$k(vr)$	10^{-12} to 10^{-10}
$S(1) \Rightarrow S(0)$	Fluorescence	$k(f)$ or Γ	10^{-9} to 10^{-7}
$S(1) \Rightarrow T(1)$	Intersystem Crossing	$k(pT)$	10^{-10} to 10^{-8}
$S(1) \Rightarrow S(0)$	Non-Radiative Relaxation Quenching	$k(nr)$, $k(q)$	10^{-7} to 10^{-5}
$T(1) \Rightarrow S(0)$	Phosphorescence	$k(p)$	10^{-3} to 100
$T(1) \Rightarrow S(0)$	Non-Radiative Relaxation Quenching	$k(nr)$, $k(qT)$	10^{-3} to 100

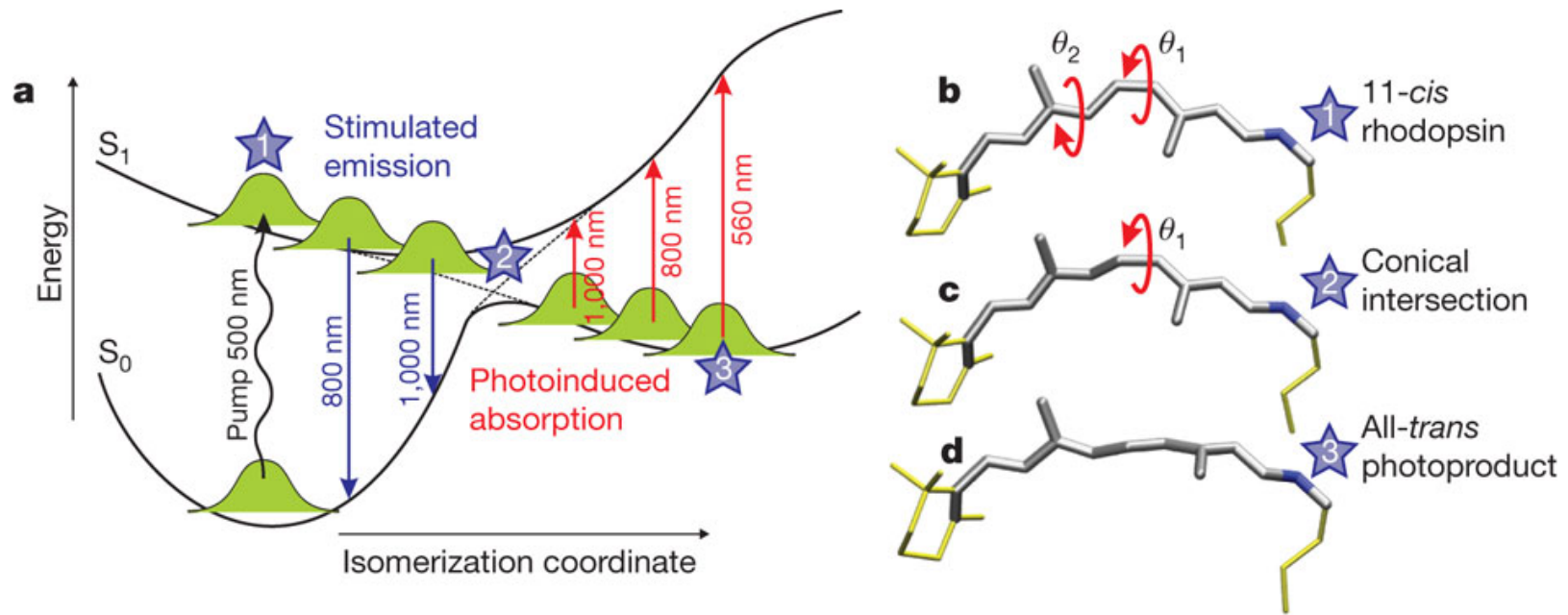
Photochemistry

Excited state processes that result in changes in bonding are photochemical processes.

- Photodissociation or photolysis is the breaking of a chemical bond. $IR \rightarrow I^*R \rightarrow I + R$
- Electron transfer results in a change in bond order due to a process. $DA \rightarrow D^*A \rightarrow D^+A^-$
- Isomerization results in a change in molecular structure.



Potential energy surfaces of rhodopsin.



Sketch of the ground- and excited-state potential energy surfaces of the chromophore in rhodopsin as a function of the isomerization coordinate. Chromophore starts at the 11-*cis* (b) ($t = 0$ fs, $\theta_1 = -12.8^\circ$, $\theta_2 = 173.9^\circ$), conical intersection (c) ($t = 110$ fs, $\theta_1 = -87.8^\circ$, $\theta_2 = -144.6^\circ$) and final all-*trans* (d) ($t = 200$ fs, $\theta_1 = -141.0^\circ$, $\theta_2 = -142.0^\circ$).

Copper dimethyl phenanthroline

Franck-Condon
state

500 fs

e^-

Cu(II)

$h\nu$

Flattened Cu(II)
10-20 ps

Cu(I)

Ground state

Model 1

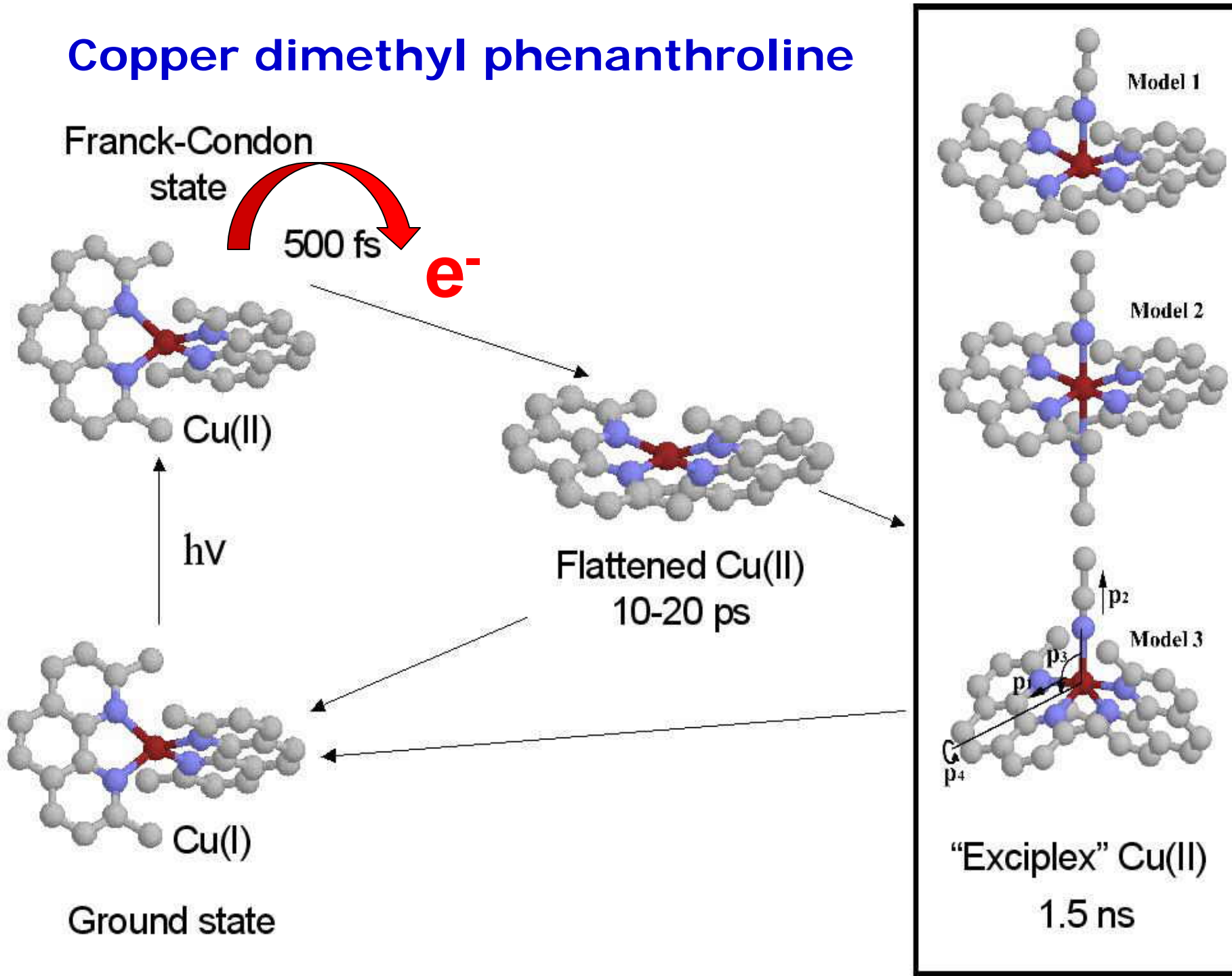
Model 2

Model 3

p_1
 p_2
 p_3
 p_4

“Exciplex” Cu(II)

1.5 ns

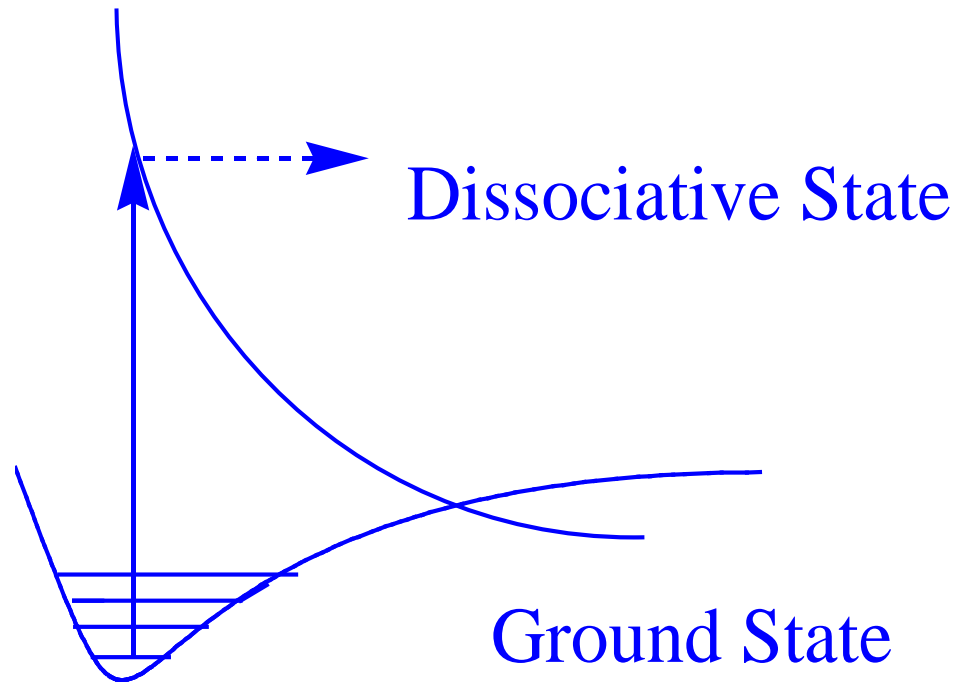


Photochemistry of metal ligand complexes

Photoinduced charge transfer processes have been widely studied in the excited state. Determination of intermediate structure of photoexcited states and their lifetime is crucial for applications such as solar energy conversion, photocatalysts and molecular devices. The previous slides shows photoexcitation of $\text{Cu}(\text{dmp})_2$. The process of photoexcitation by optical or UV radiation involves a few intermediate states with varying lifetimes. The last state has a relatively long lifetime of 1.5 ns. The project aims to select the most realistic model of the "exciplex" state of photoexcited $\text{Cu}(\text{dmp})_2$ and its further refinement in terms of bond lengths and angles.

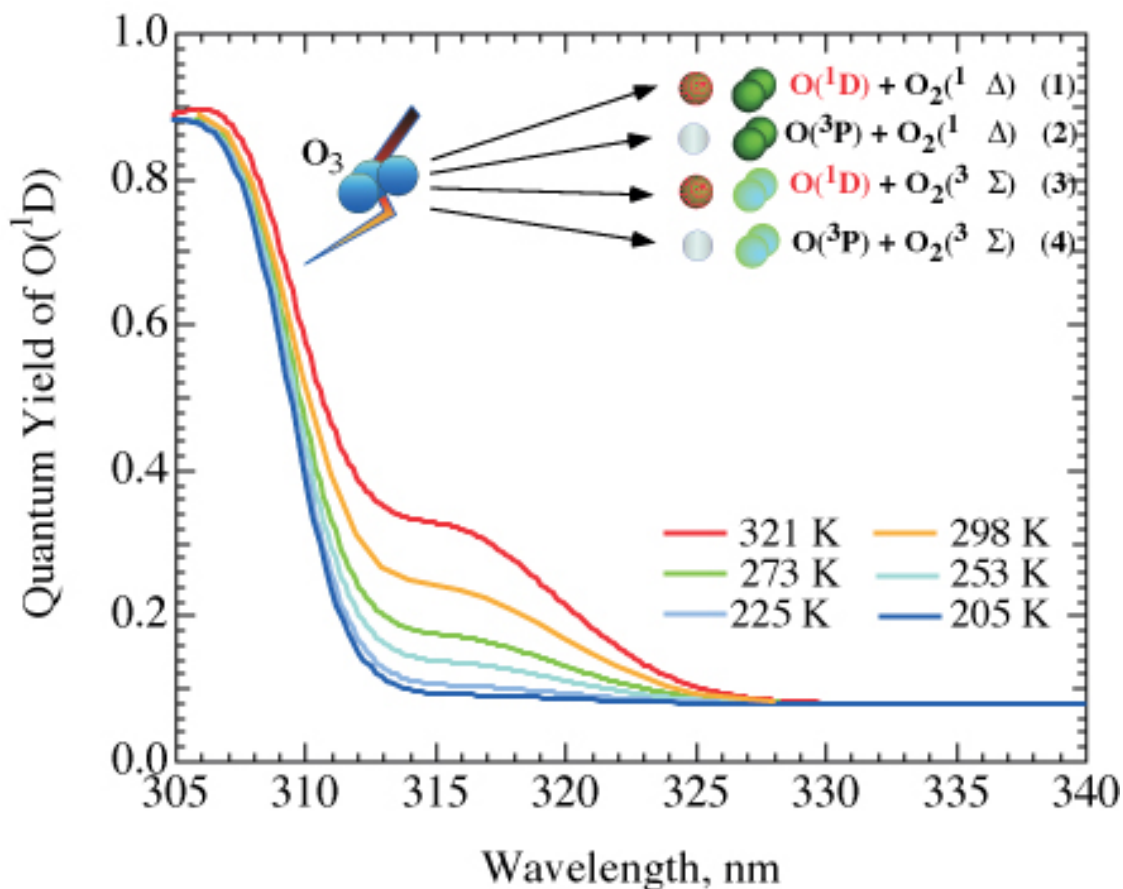
Photolysis

If the excited state is anti-bonding with respect to a particular coordinate the result is dissociation of a chemical bond.

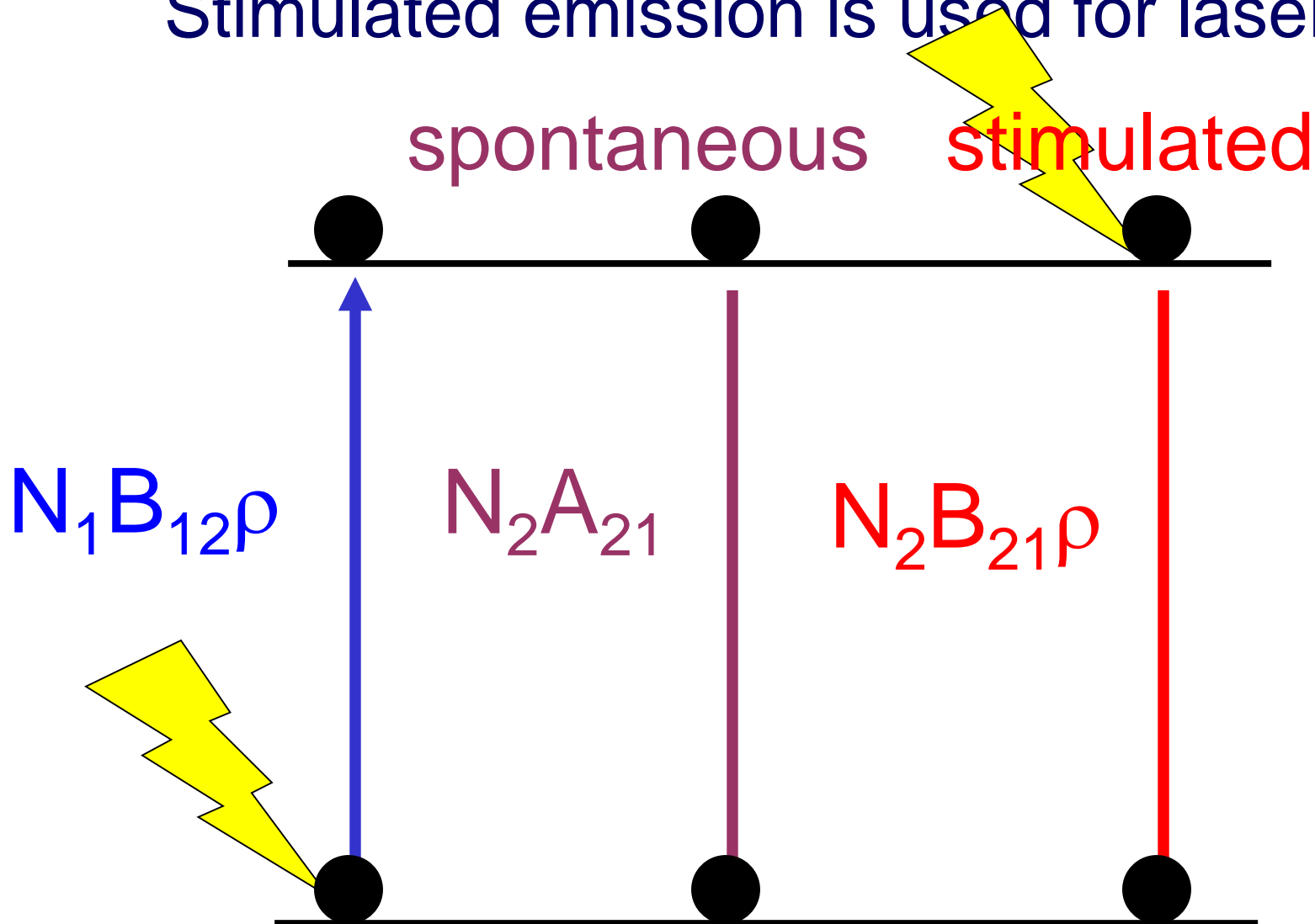


Photolysis of ozone

The photochemical decomposition of ozone to yield $O(^1D)$, the first electronically excited state of the oxygen atom, is a key process in the troposphere and the stratosphere. The reaction of $O(^1D)$ with H_2O is the major source of OH radicals, which are the essential species for the initiation of chemistry in the atmosphere. The reaction of $O(^1D)$ with N_2O is the major source of nitrogen oxides in the stratosphere.



Spontaneous emission is fluorescence
Stimulated emission is used for lasers



It is impossible to obtain a population inversion in a two-level system

The intrinsic coefficients for absorption, B_{12} , and stimulated emission, B_{21} , are equal. Therefore, as the radiation intensity (and therefore energy density, ρ) increase the limiting rate for population of the excited state is equal to the limiting rate for stimulated emission.

$$w_{12} = N_1 B_{12} \rho, \text{ for absorption}$$

$$w_{21} = N_2 B_{21} \rho, \text{ for absorption}$$

Since $w_{12} = w_{21}$, $N_1 = N_2$. The greatest possible Excited state population is 50%.