Excited State Processes

Photophysics

- Fluorescence
- Phosphorescence
- Internal conversion
- Intersystem crossing

Photochemistry

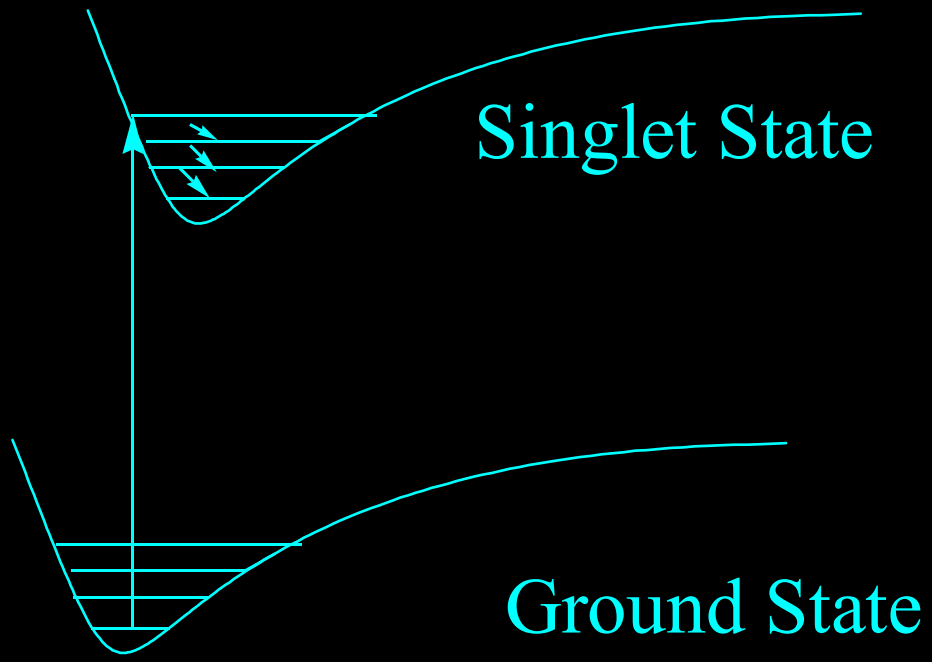
- Electron transfer
- Isomerization
- Photolysis

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

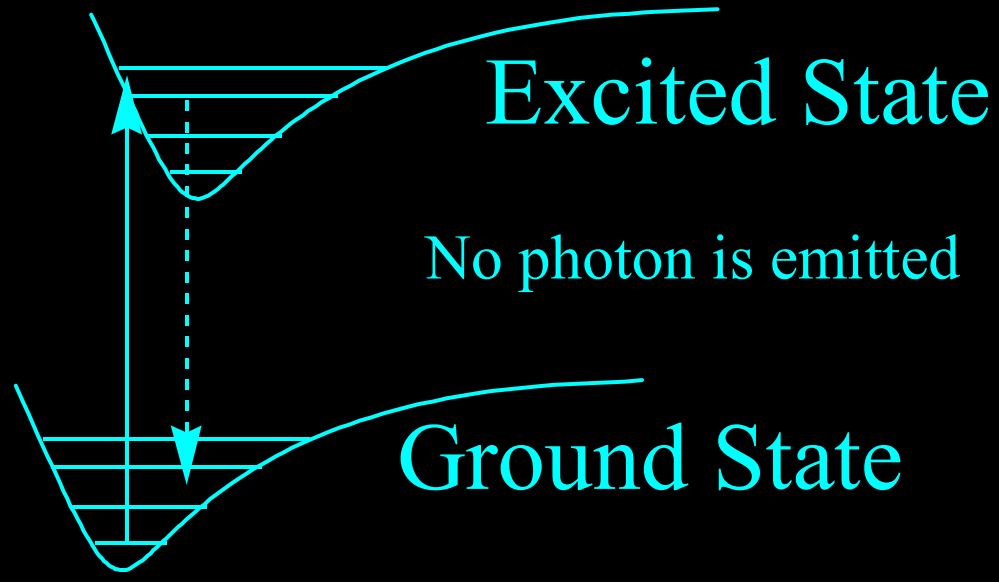
Vibrational relaxation

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.



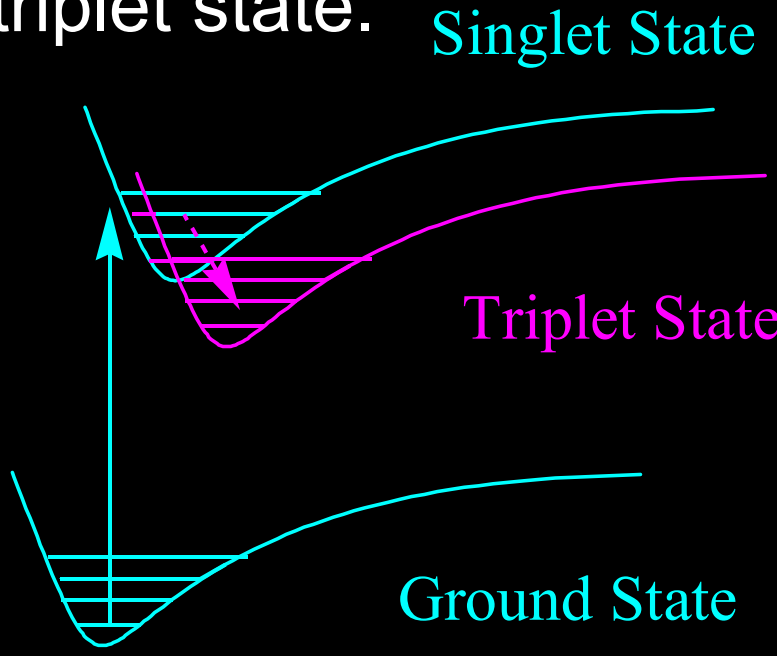
Fluorescence

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 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.



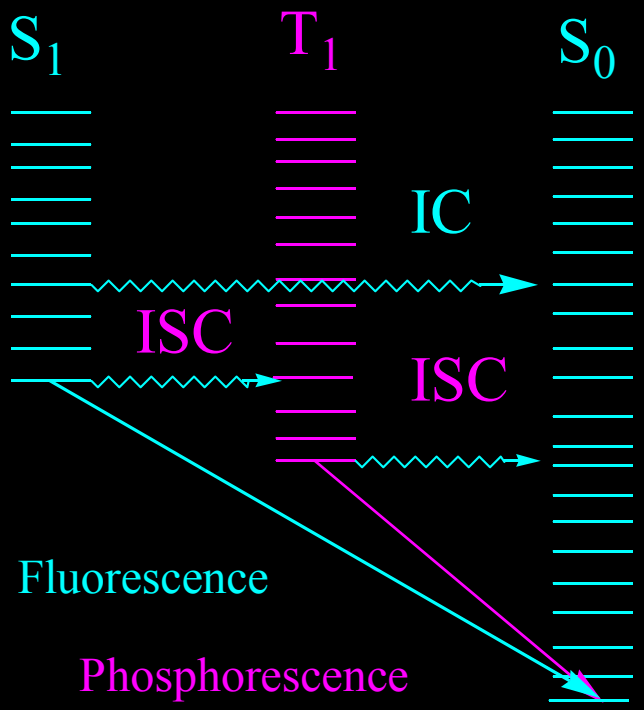
Phosphorescence

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

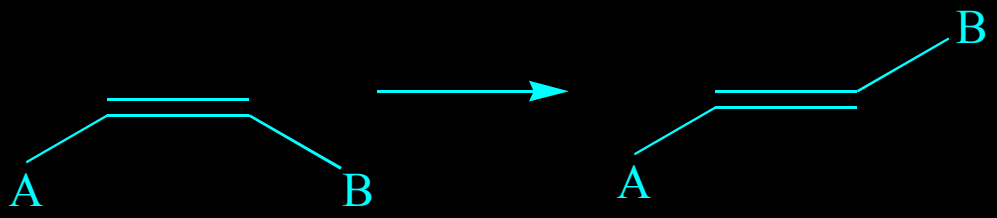
The radiative and non-radiative decay processes can be represented using a diagram. Vertical shifts represent changes in nuclear position.



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.



Photolysis

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