

School of Basic and Applied Sciences

Course Code : MSCH6001

Course Name: Photochemistry & Pericyclic reaction

The logo of Galgotias University is a stylized 'G' composed of three curved, overlapping bands in shades of yellow, blue, and red, set against a light grey circular background.

RADIATIVE AND NON RADIATIVE TRANSITION

GALGOTIAS
UNIVERSITY

PREREQUISITE

- Types of excitation and Jablonski diagram
- Ground state and excited state

The logo of Galgotias University is a stylized, multi-colored swirl or 'G' shape, composed of several overlapping curved bands in shades of yellow, orange, blue, and pink.

GALGOTIAS
UNIVERSITY

LEARNING OUTCOMES

- Knowledge of Jablonski diagram
- Electronic energy state
- Absorbance and photochemical phenomenon
- Knowledge of fluorescence and phosphorescence

ABSORBANCE / PRIMARY PROCESS

- When electron present in ground state S_0 , it absorb energy from photon and excited to higher excited state may be S_1 S_2 , etc. This process is known as absorbance or primary process.

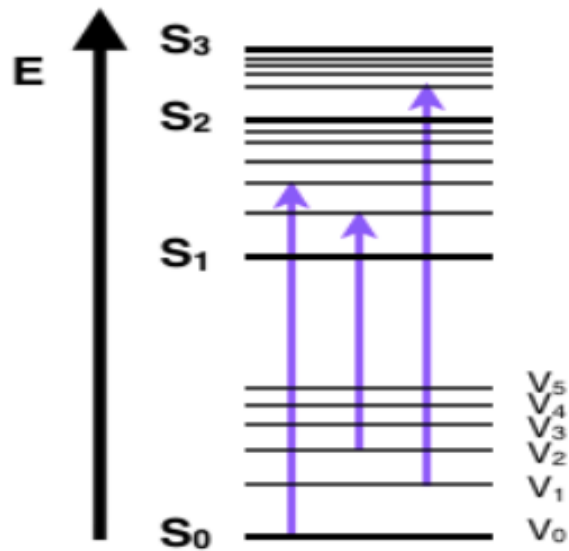


Figure 2: Three possible *absorption* transitions represented.

SECONDARY PROCESS

VIBRATIONAL RELAXATION AND INTERNAL CONVERSION

- Once an electron is excited, there are a multitude of ways that energy may be dissipated. The first is through vibrational relaxation, a non-radiative process
- . This is indicated on the Jablonski diagram as a curved arrow between vibrational levels
- . Vibrational relaxation is where the energy deposited by the photon into the electron is given away to other vibrational modes as kinetic energy.
- This relaxation occurs between vibrational levels, so generally electrons will not change from one electronic level to another through this method.

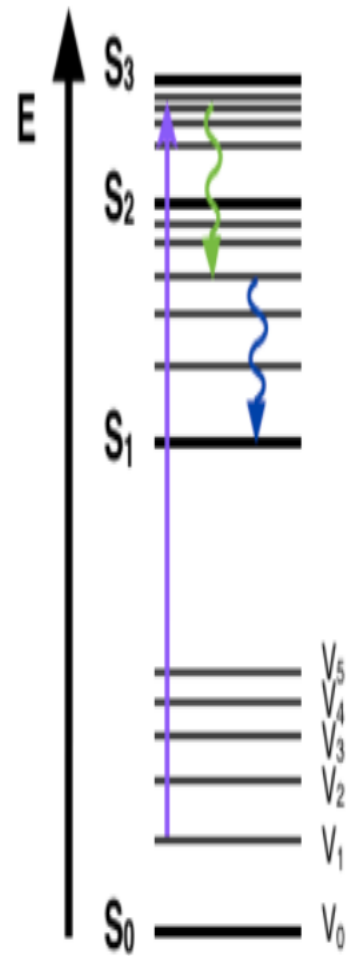


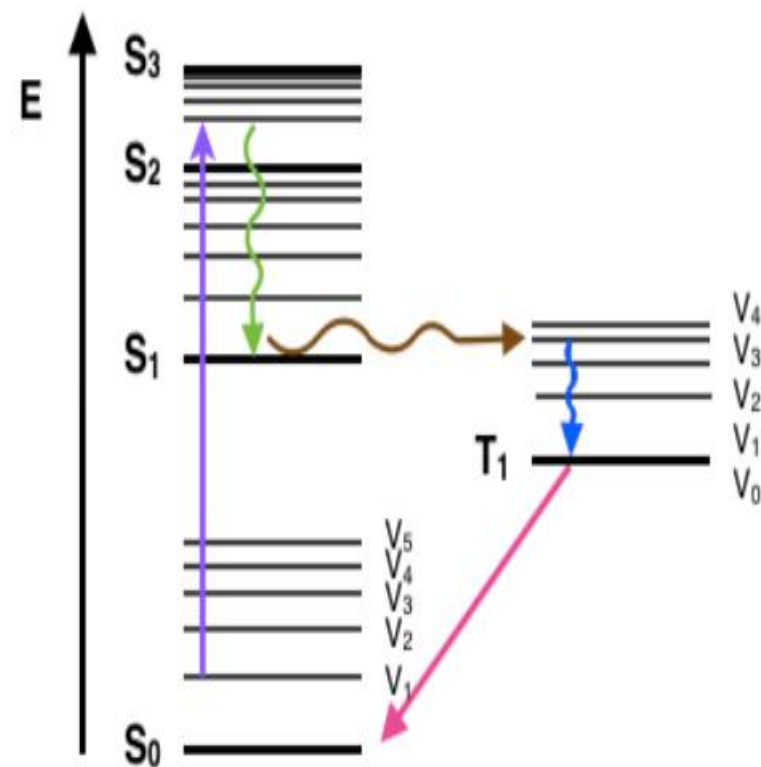
Figure 3: Possible scenario with absorption, internal conversion, and vibrational relaxation processes shown.

Fluorescence

- ❖ Fluorescence is most often observed between the first excited electron state and the ground state
- ❖ While this transition is slow, it is an allowed transition with the electron staying in the same multiplicity manifold.
- ❖ Fluorescence is a slow process on the order of 10^{-9} to 10^{-7} seconds

Intersystem Crossing / PHOSPHORESCENCE

- ❖ the electron changes spin multiplicity from an excited singlet state to an excited triplet state.
- ❖ This is the slowest process in the Jablonski diagram, several orders of magnitude slower than fluorescence.
- ❖ Intersystem crossing leads to several interesting routes back to the ground electronic state
- ❖ One direct transition is phosphorescence, where a radiative transition from an excited triplet state to a singlet ground state occurs



Time Scales

Transition	Time Scale	Radiative Process?
Internal Conversion	$10^{-14} - 10^{-11}$ s	no
Vibrational Relaxation	$10^{-14} - 10^{-11}$ s	no
Absorption	10^{-15} s	yes
Phosphorescence	$10^{-4} - 10^{-1}$ s	yes
Intersystem Crossing	$10^{-8} - 10^{-3}$ s	no
Fluorescence	$10^{-9} - 10^{-7}$ s	yes

REFERENCES

- Lewis, G. N., & Kasha, M. (1944). Phosphorescence and the triplet state. *Journal of the American Chemical Society*, 66(12), 2100-2116.
- Lakowicz, J. R. (1999). Introduction to fluorescence. In *Principles of fluorescence spectroscopy* (pp. 1-23). Springer, Boston, MA.
- Valeur, B., & Berberan-Santos, M. N. (2011). A brief history of fluorescence and phosphorescence before the emergence of quantum theory. *Journal of Chemical Education*, 88(6), 731-738.
- McGOWN, L. B., & Nithipatikom, K. (2000). Molecular fluorescence and phosphorescence.