Photophysical mechanistic aspects of AOPs

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Photochemical proceses

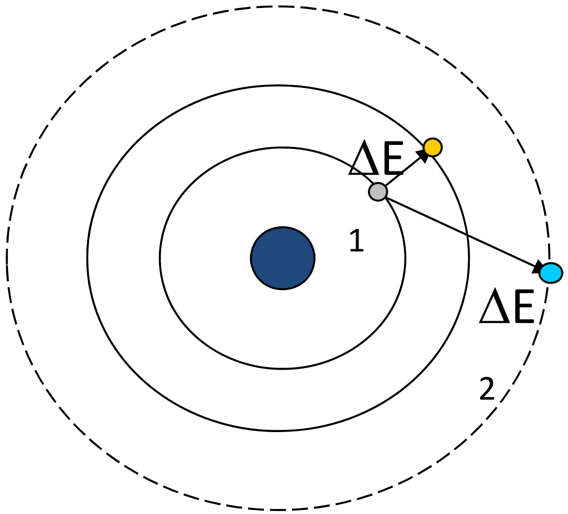
Interaction radiation-matter

- Electromagnetic radiation is able to induce important changes in matter.
- In the energy range employed in photochestry, excited electronic states are generated, which in turn, can undergo chemical reactions.

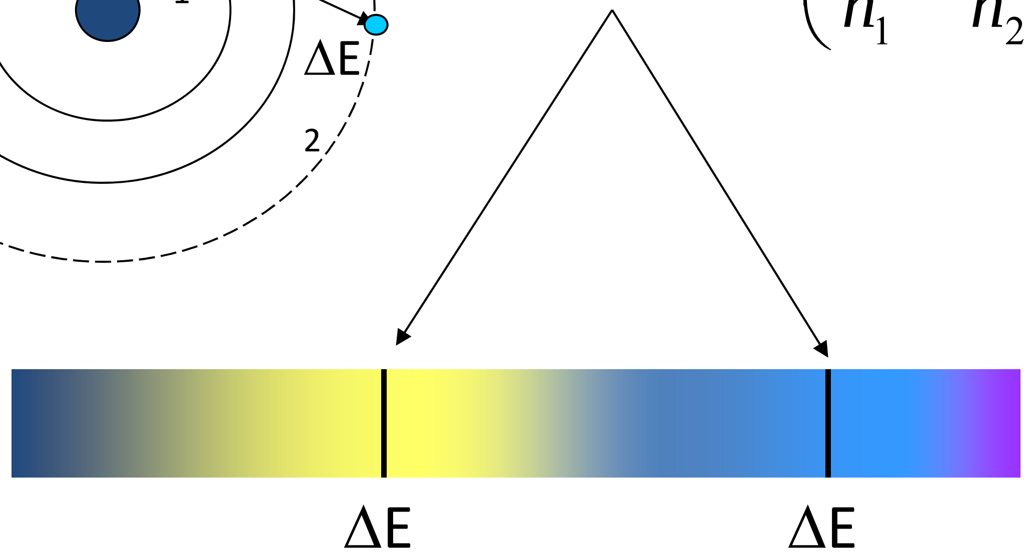
Interaction radiation-matter

- Energetic law: Electromagnetic radiation can only dirve a chemical transformation if its energy is, at least, that required for the process.
- Grotthus-Draper law: light must be absorbed by a compound for a photochemical reaction to take place
- Stark-Einstein law: for each photon of light absorbed by a chemical system, only one molecule is activated for subsequent reaction.

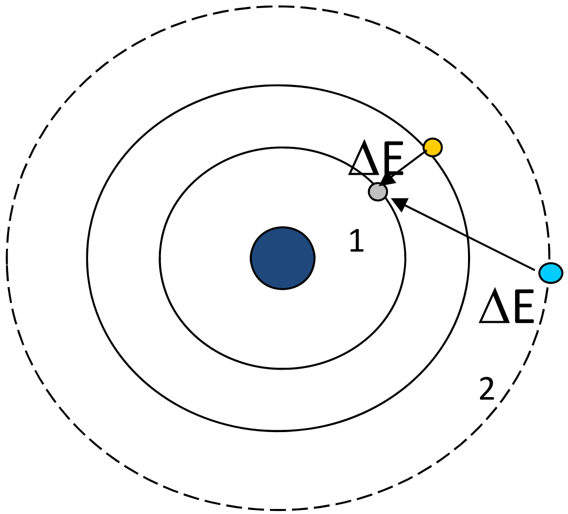
Atomic absorption: Böhr's model



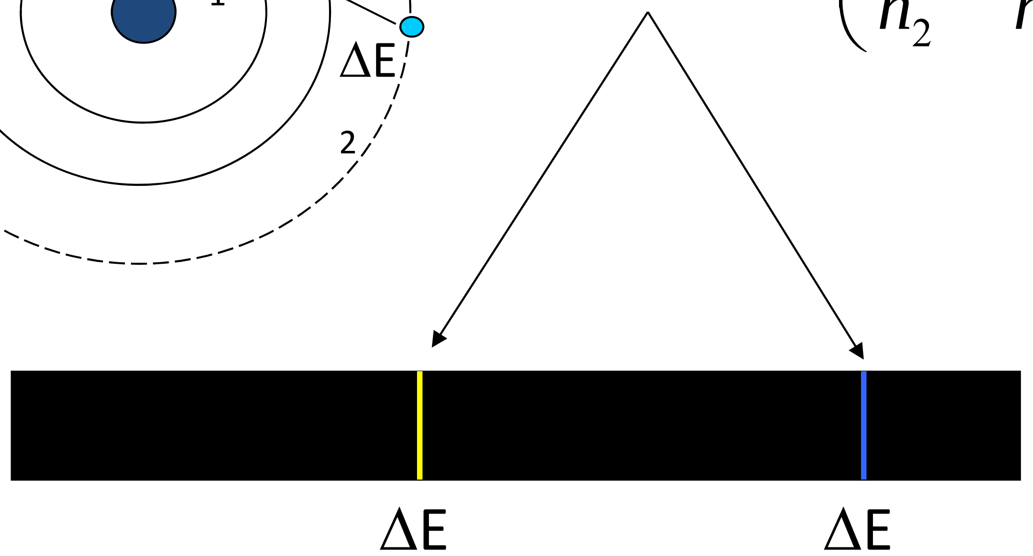
$$\Delta E = h\nu = R\left(\frac{1}{n_1} - \frac{1}{n_2}\right)$$



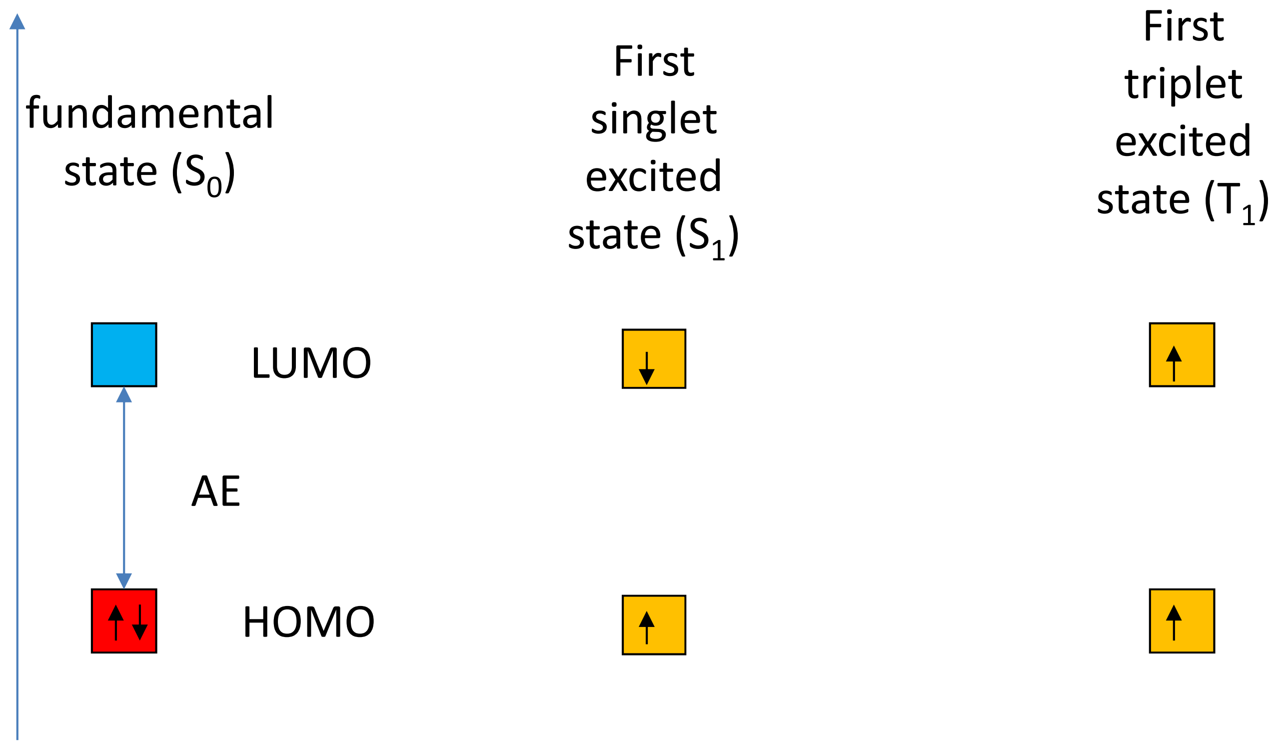
Atomic emission: Böhr's model



$$\Delta E = h\nu = R\left(\frac{1}{n_2} - \frac{1}{n_1}\right)$$

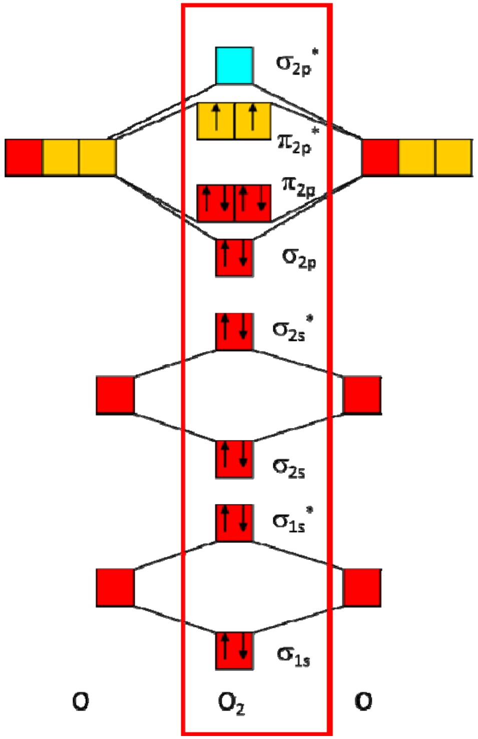


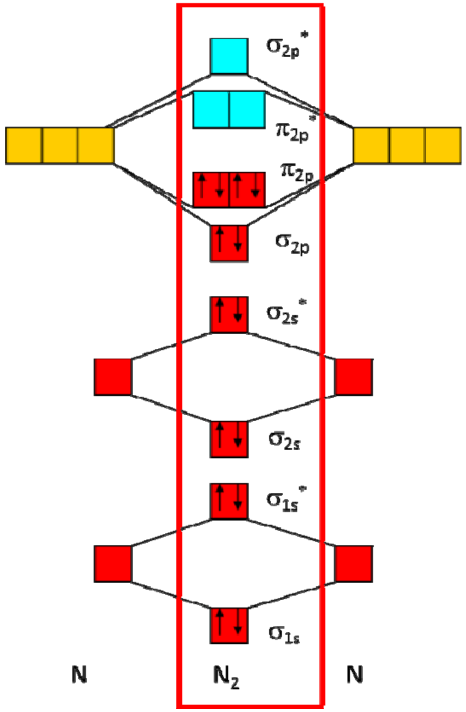
Aborption: quantum theory



Aborption: quantum theory

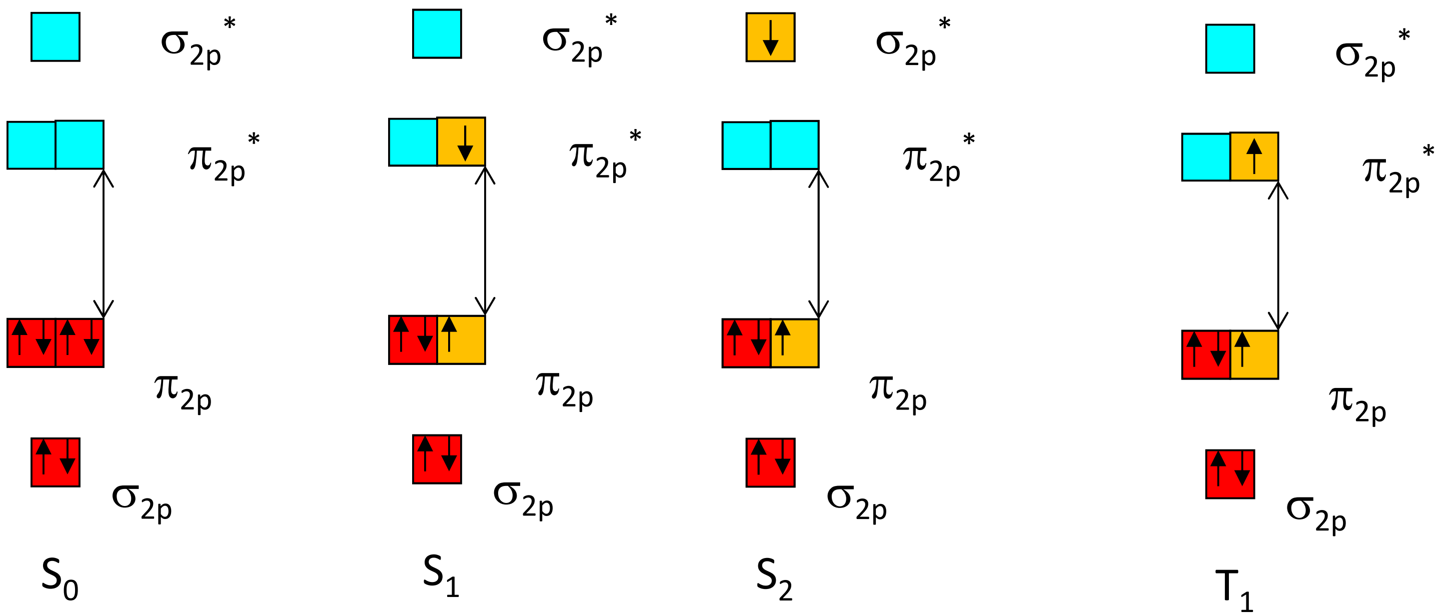
O_2





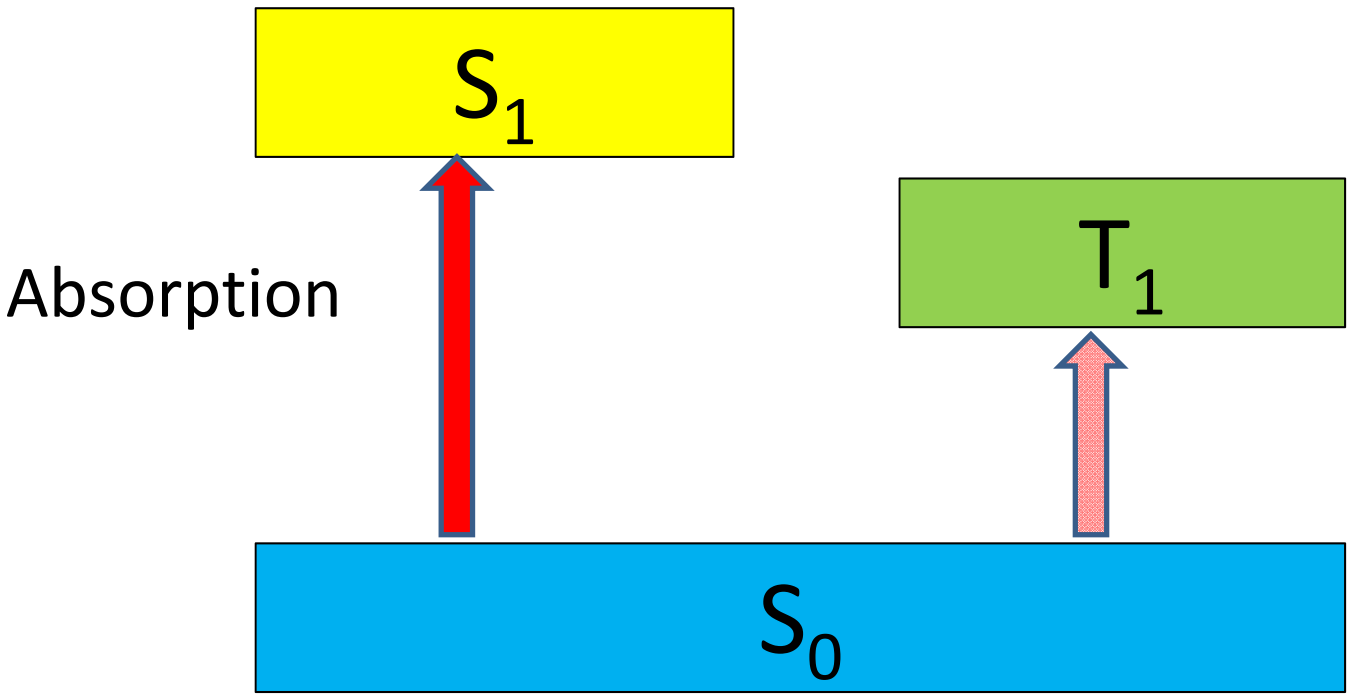
N_2

N_2

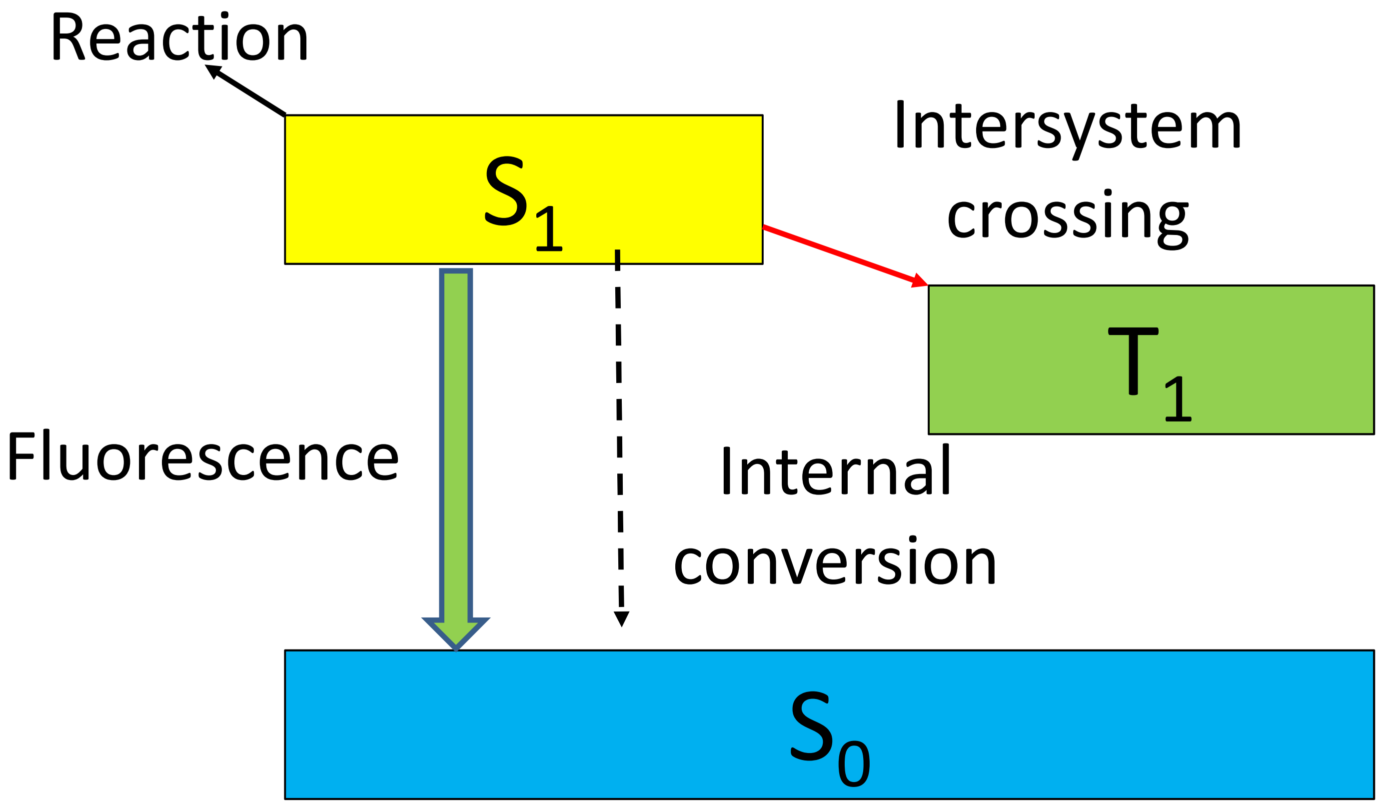


σ_{2p}^*
π_{2p}^*
π_{2p}
σ_{2p}
S_0
σ_{2p}^*
π_{2p}^*
π_{2p}
σ_{2p}
S_1
σ_{2p}^*
π_{2p}^*
π_{2p}
σ_{2p}
S_2
σ_{2p}^*
π_{2p}^*
π_{2p}
σ_{2p}
T_1

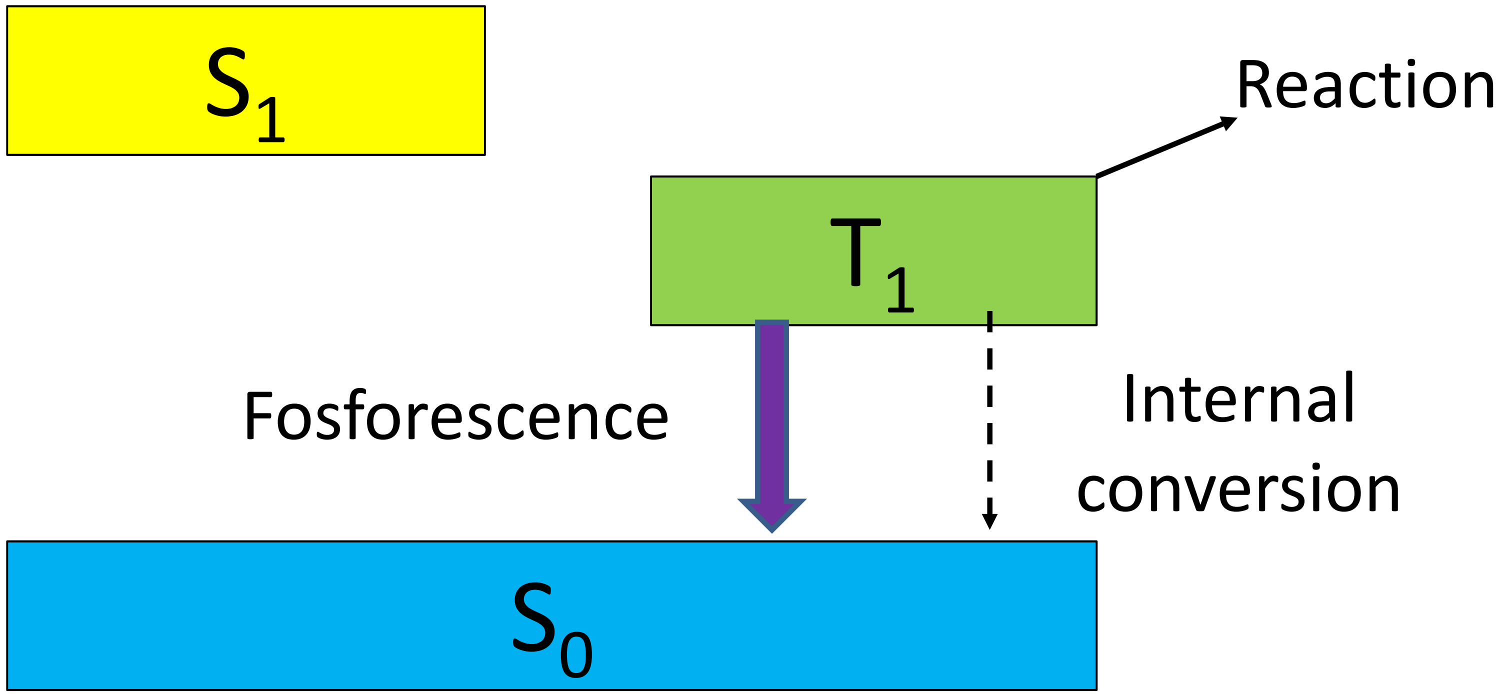
Photochemical processes



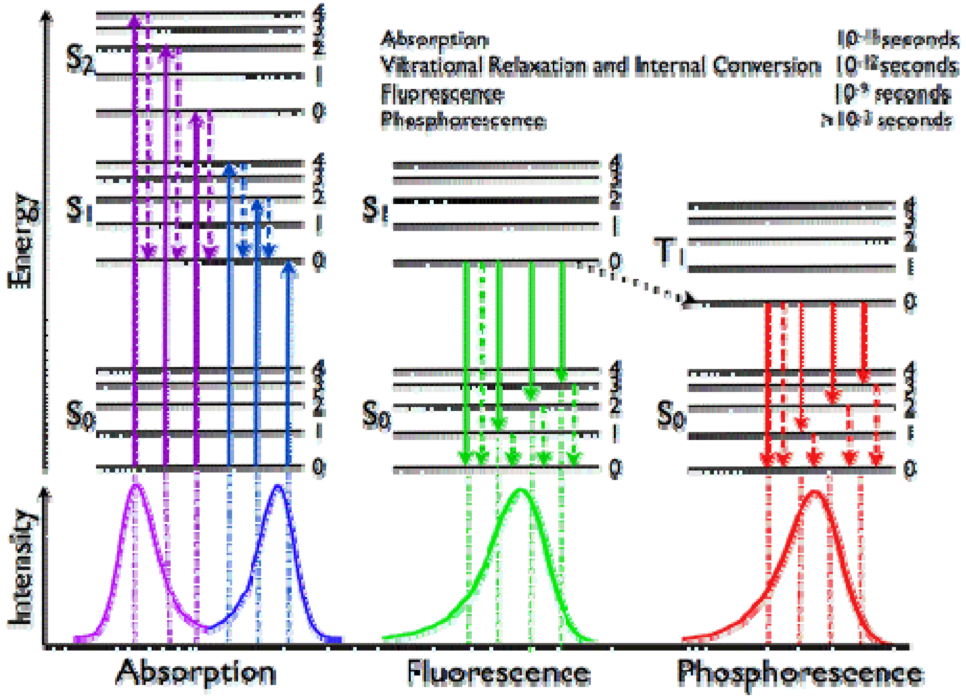
Photochemical processes



Photochemical processes

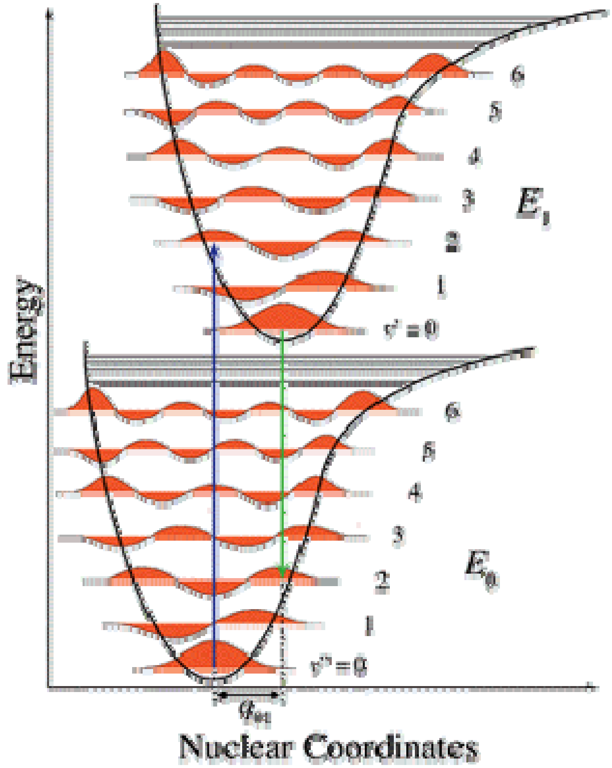


Jablonski diagram

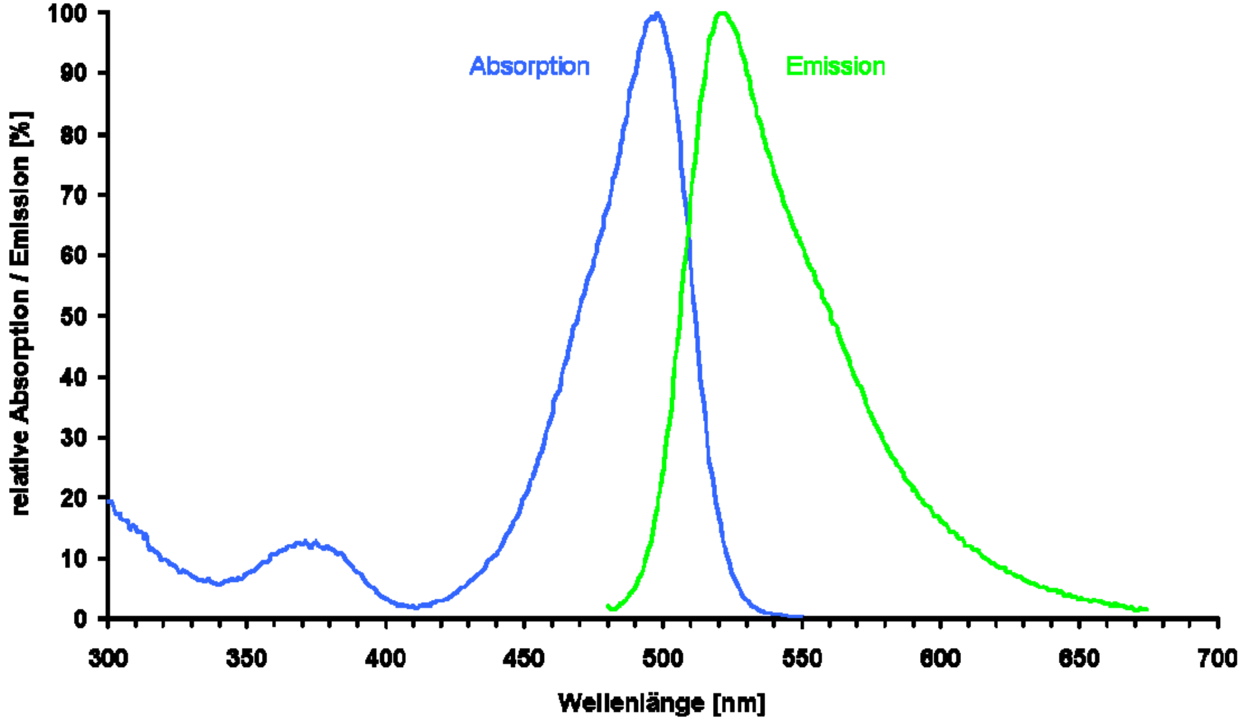


Jablonski diagram

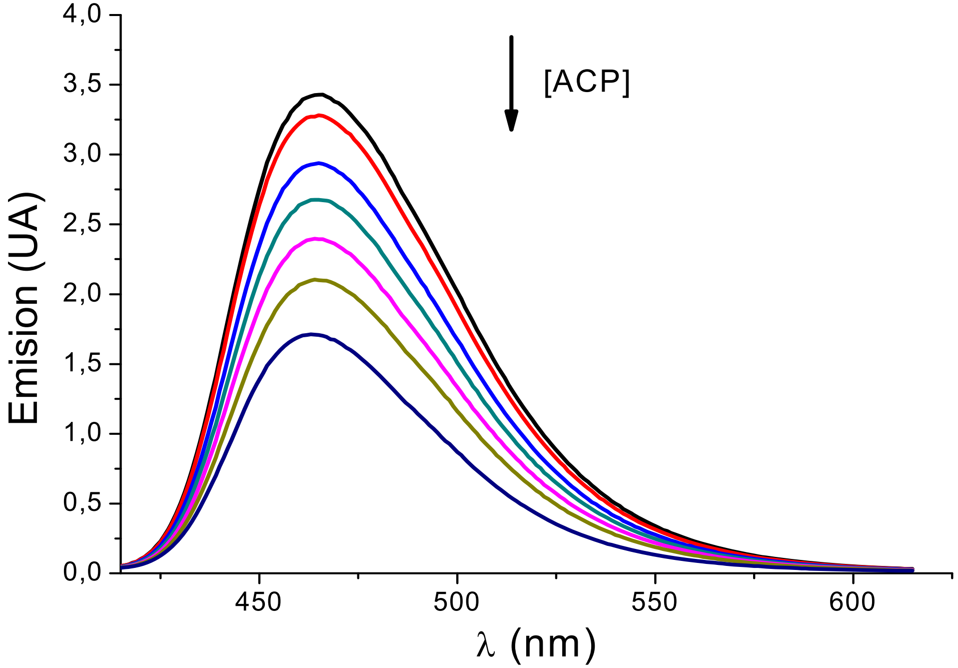
- During electronic transitions the distance between nuclei is preserved. Hence, an excited vibrational orbital is reached
- The maximum of fluorescence emission is shifted towards longer wavelenth than that of the excitation spectrum



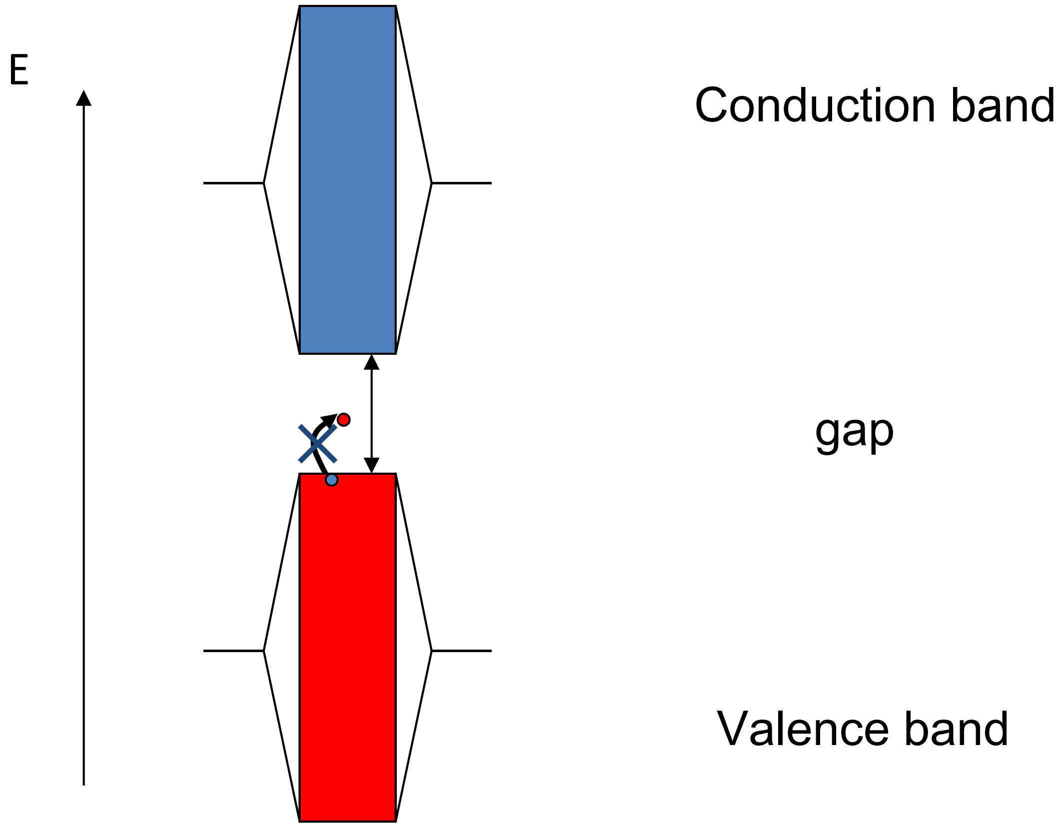
Absorption and fluorescence spectra



Why fluorescence deactivates?

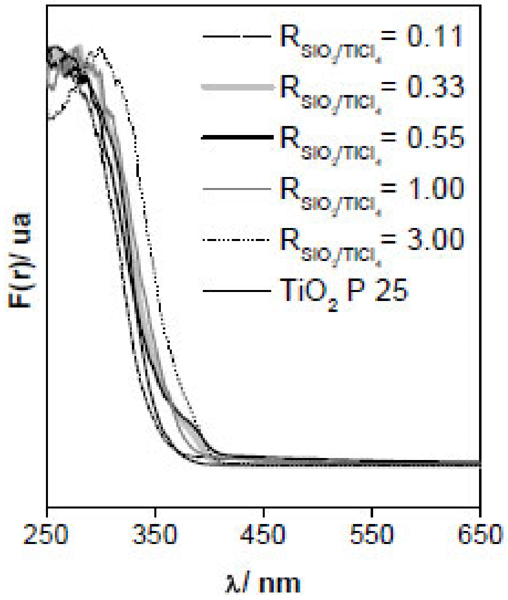


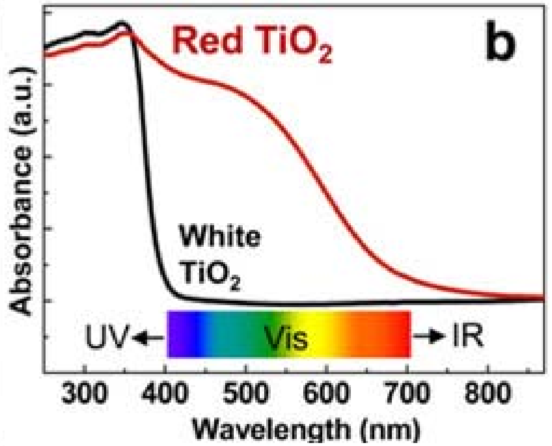
Interaction light-matter in solids

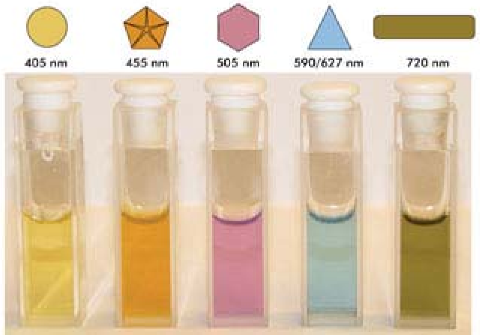


$$E_{gap} = h\frac{c}{\lambda}$$

Interaction light-matter in solids







Photochemical reactions

The photochemical reaction

- The activation energy is mainly supplied as radiation
- Reaction occurs from an excited state, which has very different charasteristics than the ground state
- Excited molecules exhibit an excess of energy, and they can undergo more reactions than from their ground state.

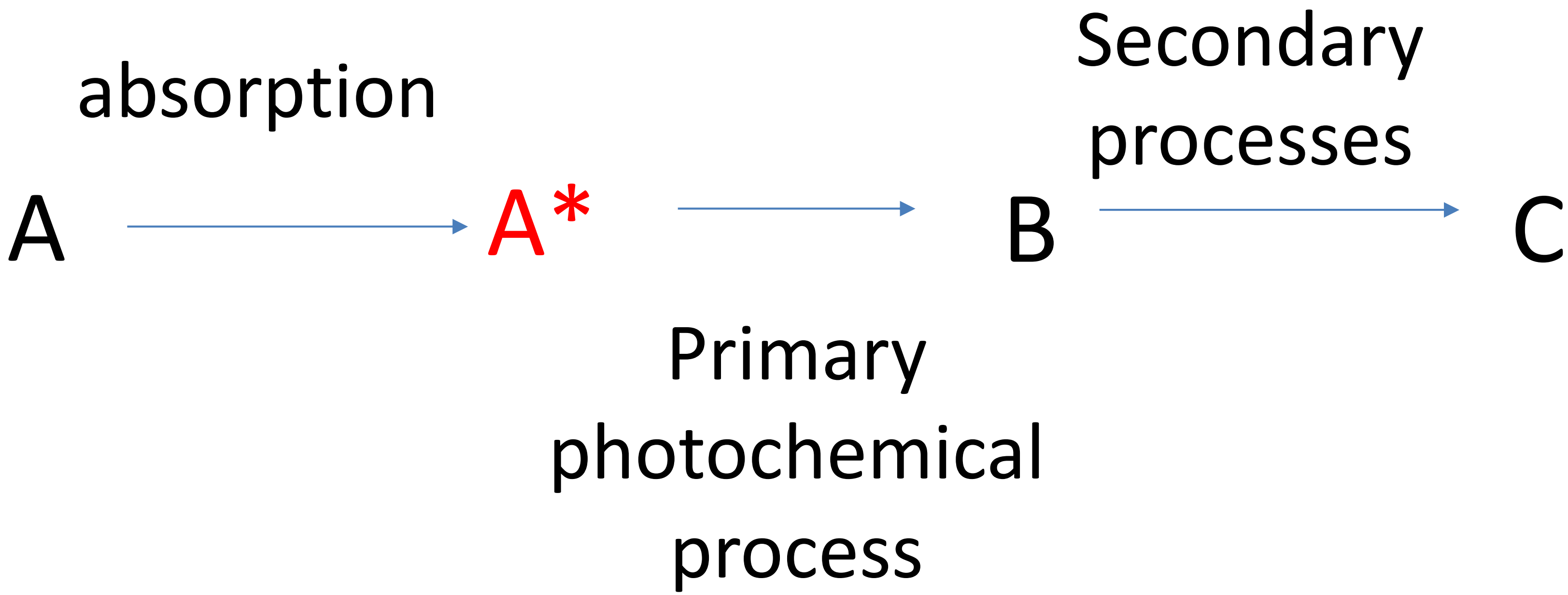
Photochemical reaction

$$A \xrightarrow{\text{photon}} A^*$$

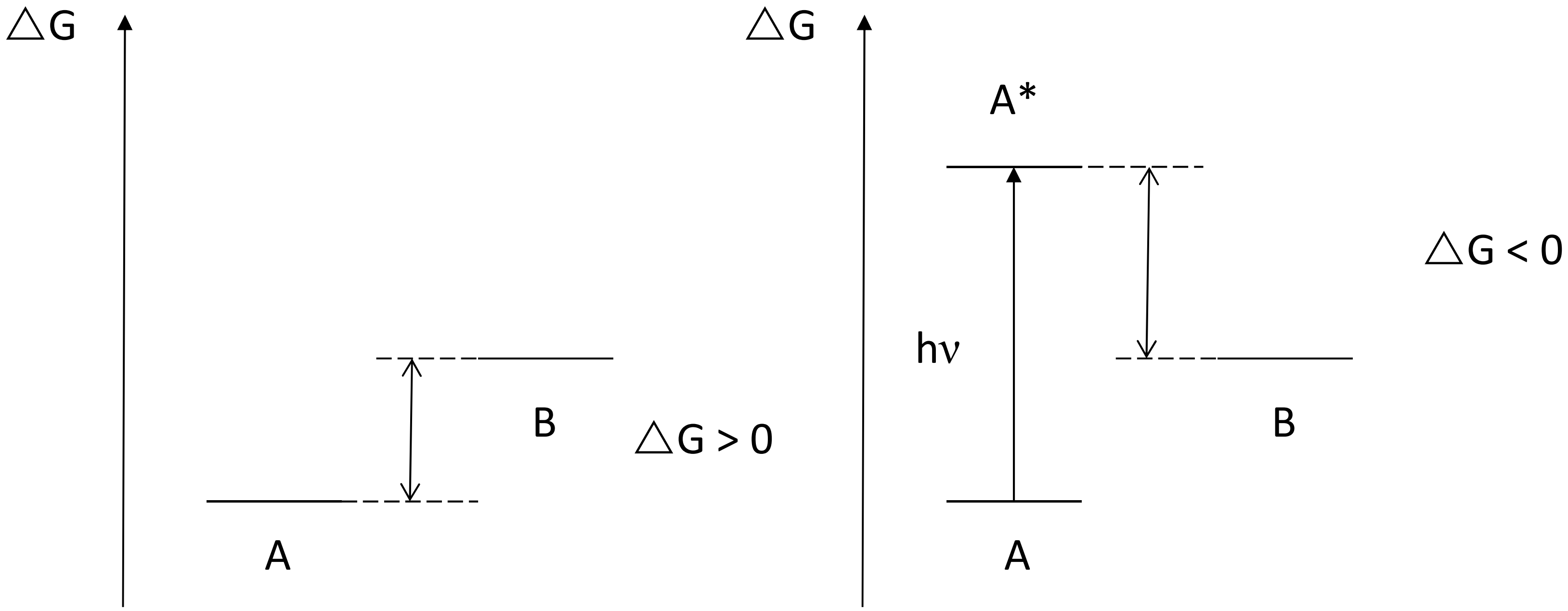
A^* →

- Photophysical process
- Photochemical process

Photochemical processes



The photochemical reaction: thermodinamics



Quantum yield

- Number of transformed molecules per absorbed photon

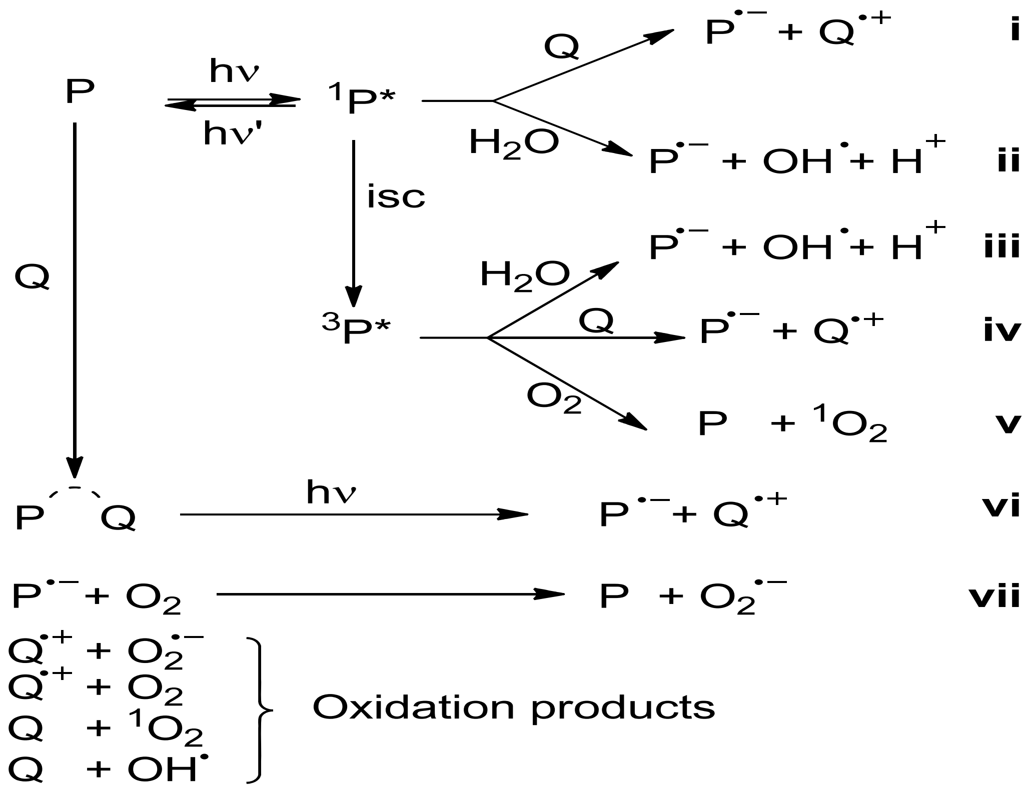
$$\phi = \frac{transformed\ molecules}{absorbed\ photons}$$

- It can take a wide number of values, even higher than 1
- If defined as the primery quantum yiel (affecting only to the photochemical transformation) the value is always lower than 1.

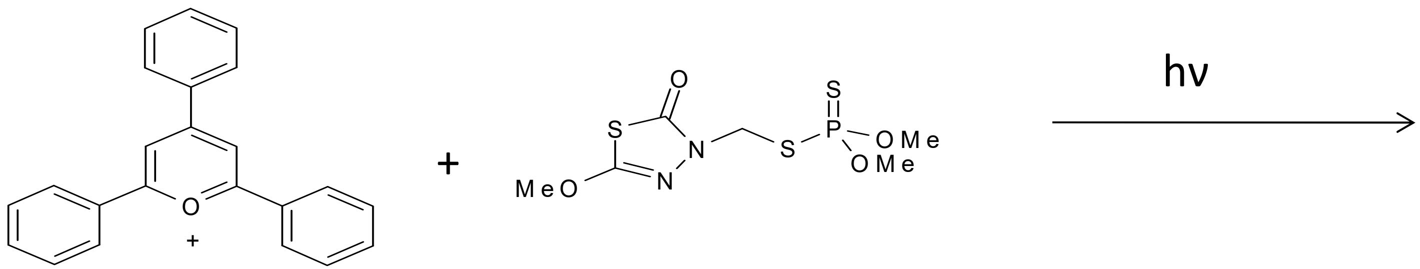
Reaction mechanisms

Alternative mechanistic pathways

P= Photocatalyst, Q= Pollutant or model compound

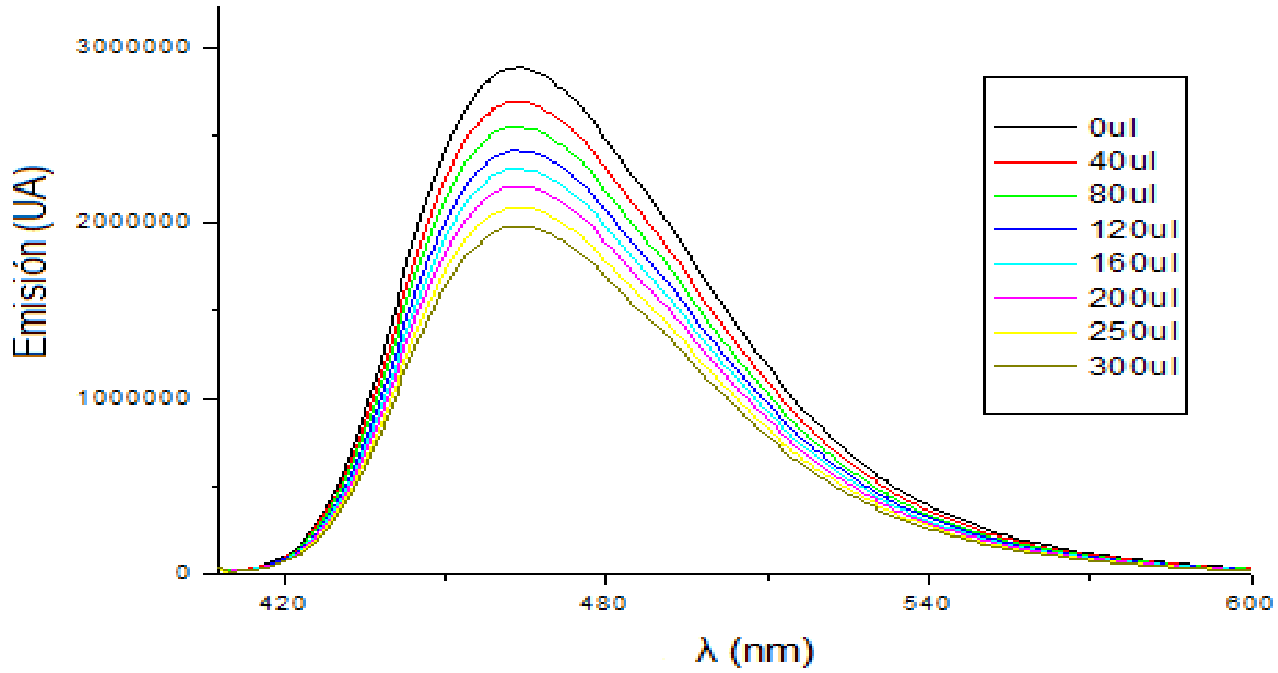


Determination of a mechanistic pathway: TPP vs MTDT

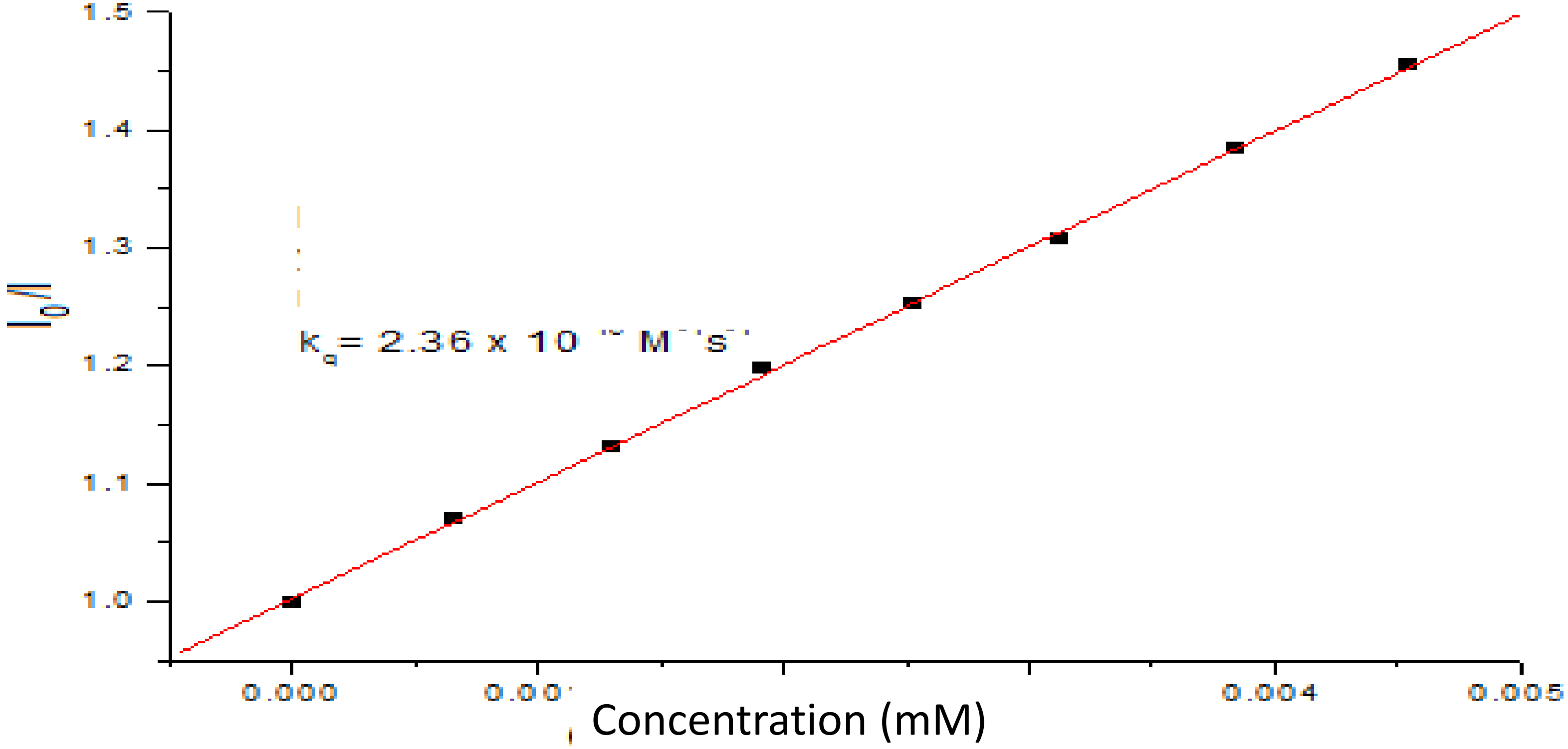


Arques, A.; Amat, A.M.; Santos-Juanes, L.; Vercher, R.F.; Marín, M.L.; Miranda, M.A. *Catal. Today* **2009**, *144*, 106-111

Possible involvement of $^1P^*$ (pathway i)



Possible involvement of $^1P^*$ (pathway i): fluorescence measurements

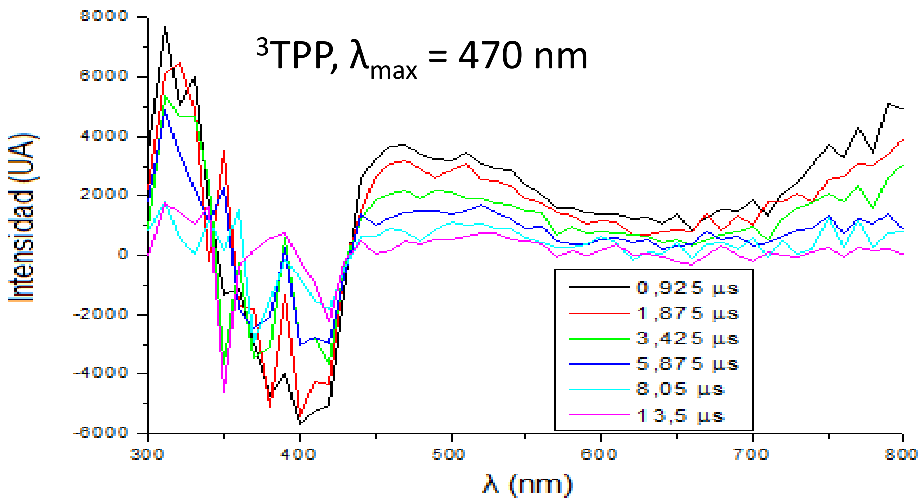


Possible involvement of $^1P^*$ (pathway i): fluorescence measurements

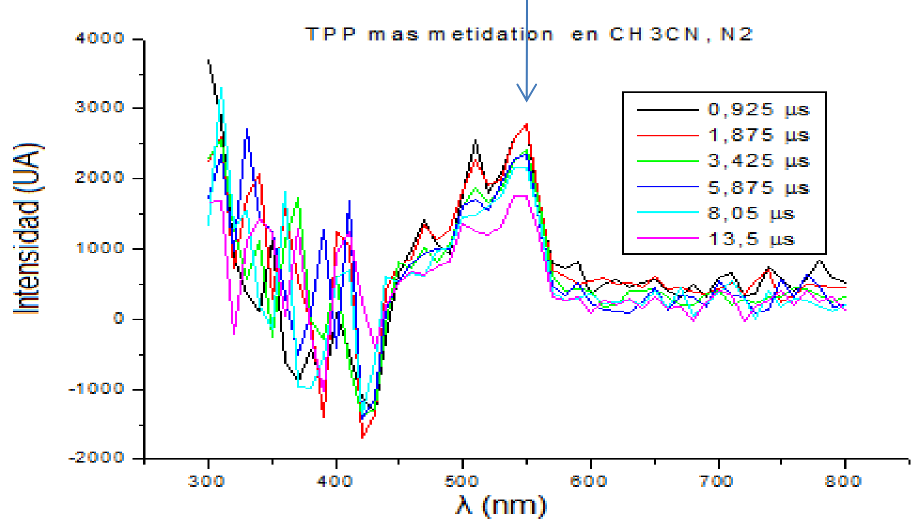
- Obtained rate constants are above diffusion limits
- There is no dinamic quenching of the fluorescence (lifetime does not depend on the concentration of pollutant)

Possible involvement of $^3P^*$: laser flash photolysis

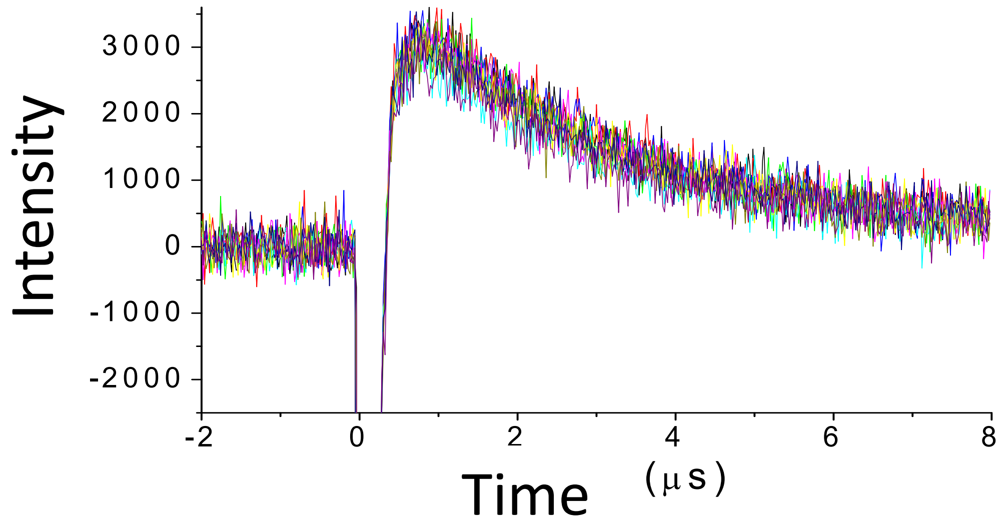
Transient absorption spectrum



Pyranil radical

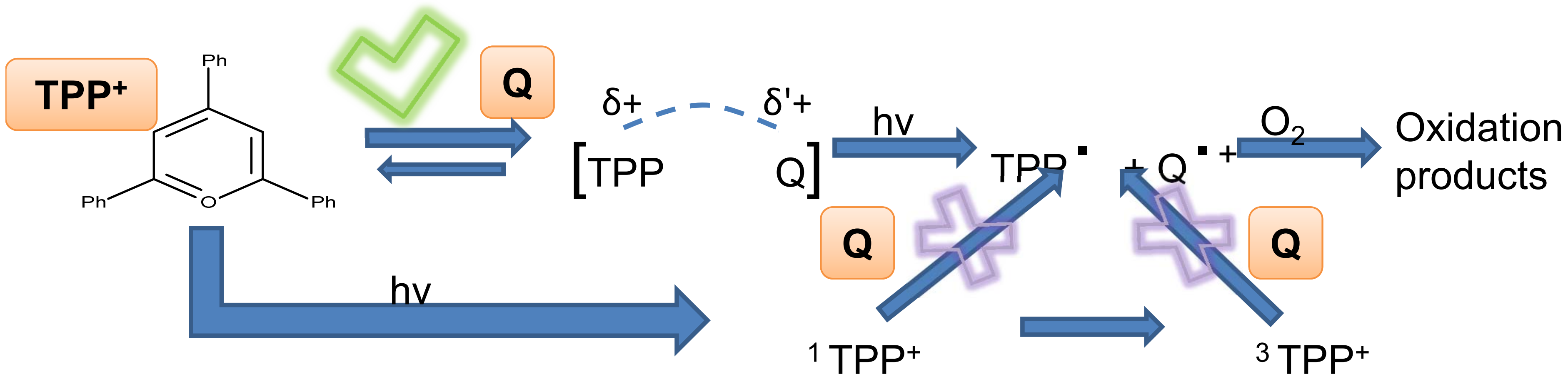


Possible involvement of $^3P^*$: laser flash photolysis



Lifetimes did not change in the presence of the pollutant

Photoinduced electron transfer from a ground state complex (pathway vi)



Photoinduced electron transfer from a ground state complex (pathway vi)