

**M.Sc. Semester-IV
Core Course-9 (CC-9)
Synthetic Organic Chemistry**



III. Photochemistry

1. Jablonski Diagram, Allowed and Forbidden Transitions



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III Photochemistry 10 Hrs

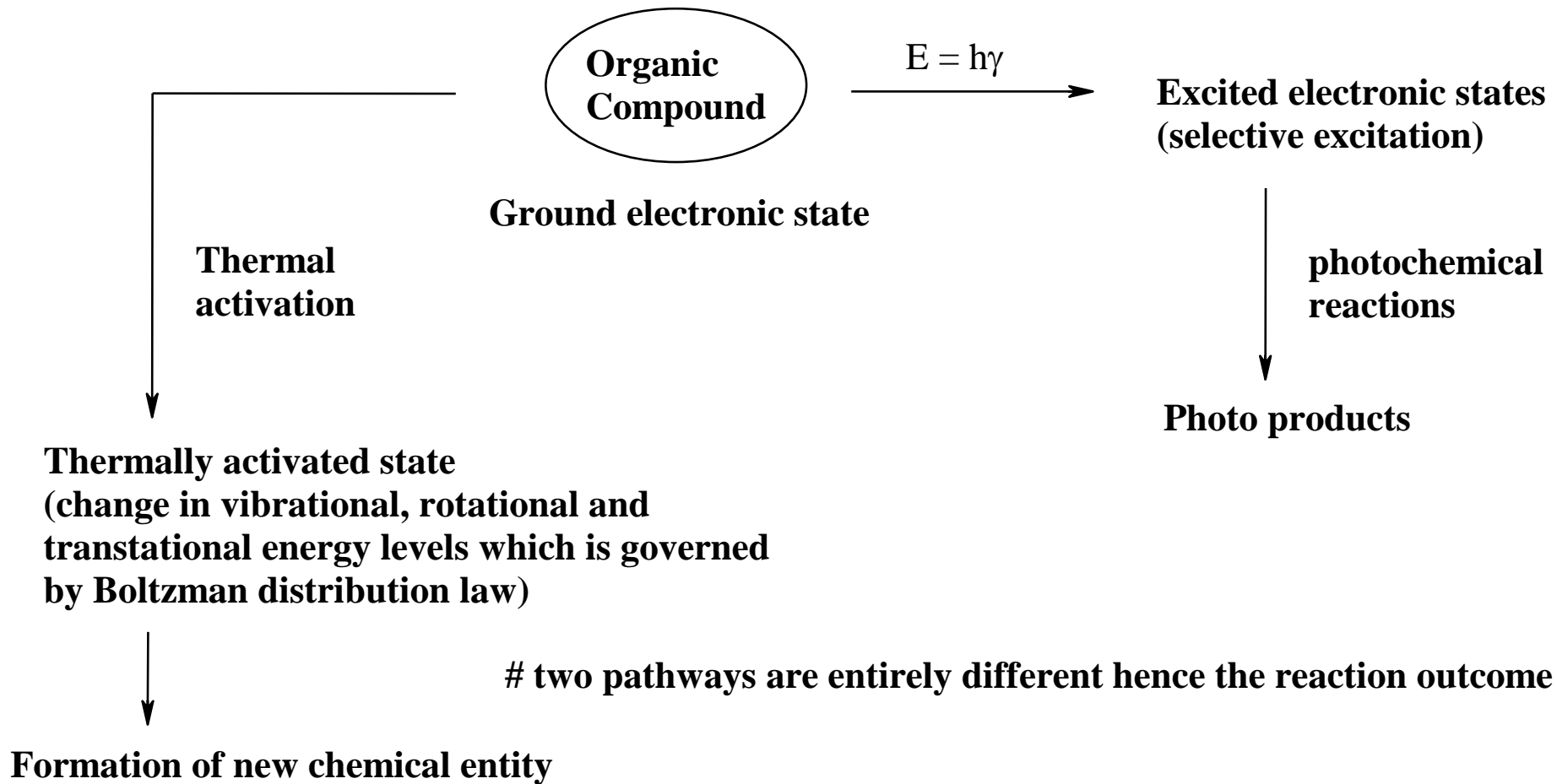
Thermal versus photochemical reactions, Electronic excitations: $n-\pi^*$ and $\pi-\pi^*$ transitions. Singlet and Triplet energy states: Comparison of energies, Lifetimes and Reactivity. Jablonski diagram, Allowed and forbidden transitions: Fluorescence, Phosphorescence and Internal conversion and Intersystem crossing.

Photochemical reactions of saturated ketones : Norrish Type I and Norrish Type II reaction, Photoreduction of ketone, Photoaddition reactions, Paterno Buchi reaction. Photochemistry of simple olefins : Cis-trans isomerization, Di-pi methane rearrangement. Photooxidation : Formation of peroxy compounds, oxidative couplings : Barton reaction. Photo rearrangements : Photo-Fries rearrangement and Photo rearrangement of 2,5-Cyclohexadienones.

Coverage:

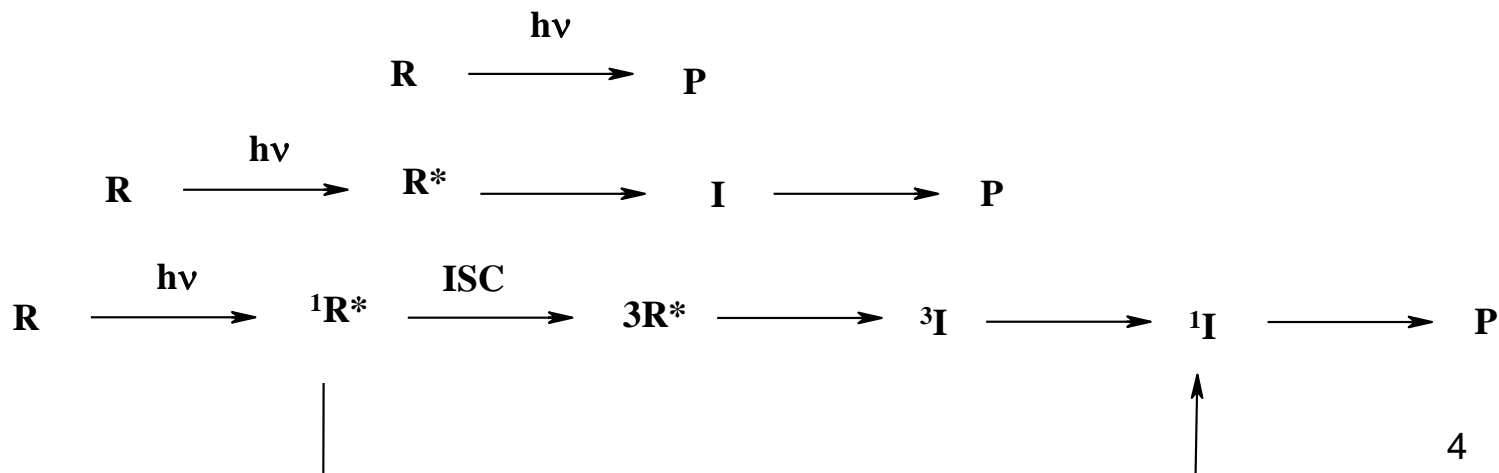
1. Thermal Versus Photochemical Reactions.
2. Electronic Excitations: $n-\pi^*$ and $\pi-\pi^*$ Transitions.
3. Singlet and Triplet Energy States: Comparison of Energies, Lifetimes and Reactivity.
4. Jablonski Diagram.
5. Allowed and Forbidden Transitions: Fluorescence, Phosphorescence and Internal conversion and Intersystem crossing.

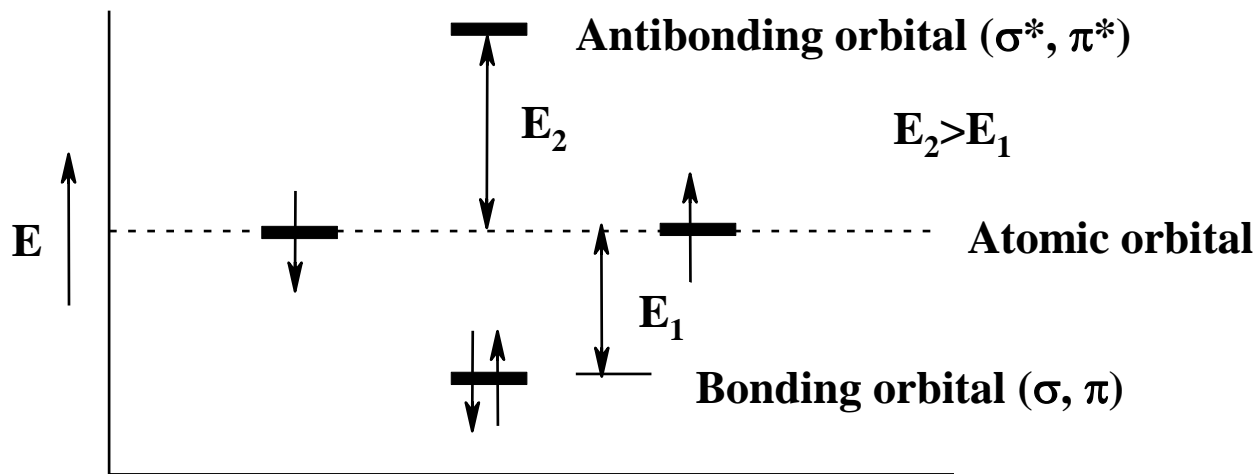
Jablonski Diagram, Allowed and Forbidden Transitions



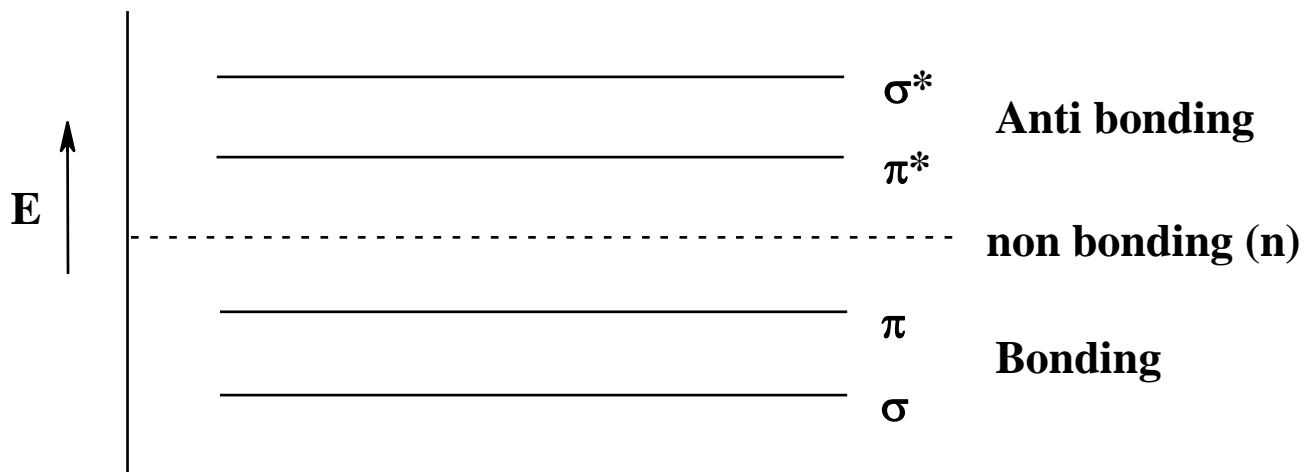
Questions need to be asked during the analysis of photochemical reaction

1. What are the products of the photo reaction
2. what are the electronic characters of the reactive state
3. what are the spin characters of the reactive state
4. what intermediates are involved in the reaction
5. what orbitals are involved and how do they react
6. what are the various chemical and physical processes and what are their rates with which a reaction of interest competes

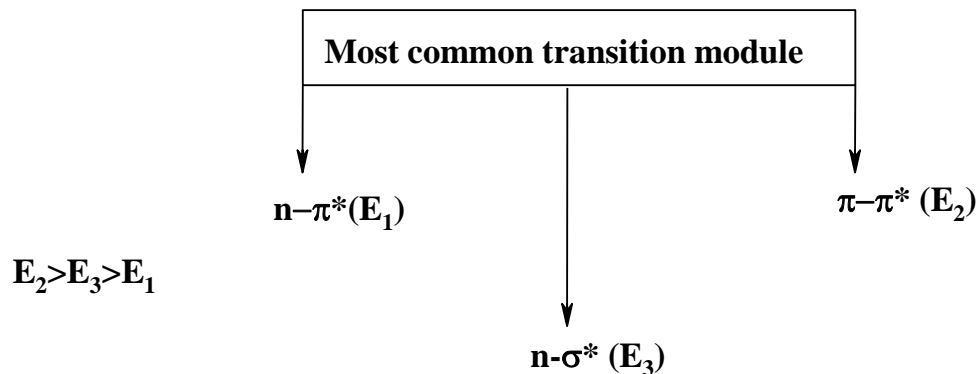




Relative energies of atomic and molecular orbitals

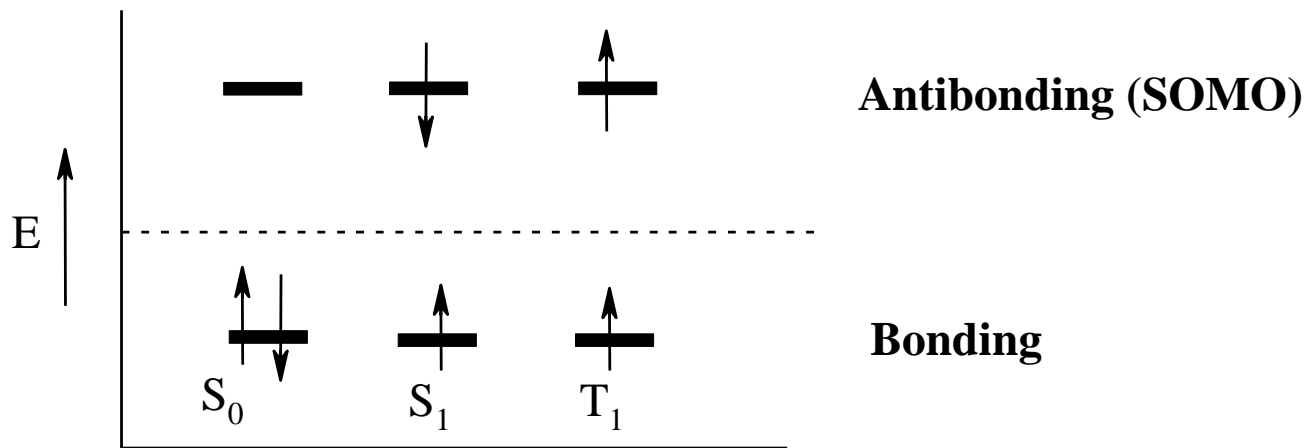


Relative energies of σ , π and n MOs

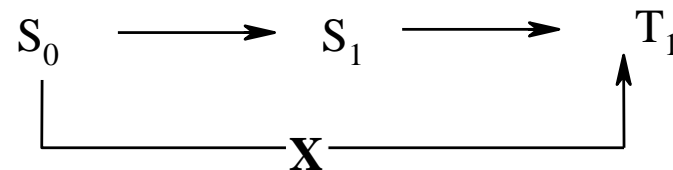


Absorption maxima for few molecules and functional groups

Molecule	Transition	λ_{\max} (nm)	E (Kcal/mol)
Iodobutane	n- σ^*	224	127.7
Ethylene	π - π^*	165	173.3
Ethyne	π - π^*	173	165.3
Acetone	π - π^*	150	190.7
	n- σ^*	188	152.1
	n- π^*	279	102.5
Butadiene	π - π^*	217	131.8
Acrolein	π - π^*	210	136.2
	n- π^*	315	90.8
Functional group			
RCH = CHR		165	173.3
		193	148.2
Alkyne		173	165.3
Ketones		188	152.1
		279	102.5
Aldehydes		290	98.6
Carboxylic acids		<205	<137.5



Excited states



S_0 : Ground state (spin paired, Pauli exclusion principle)

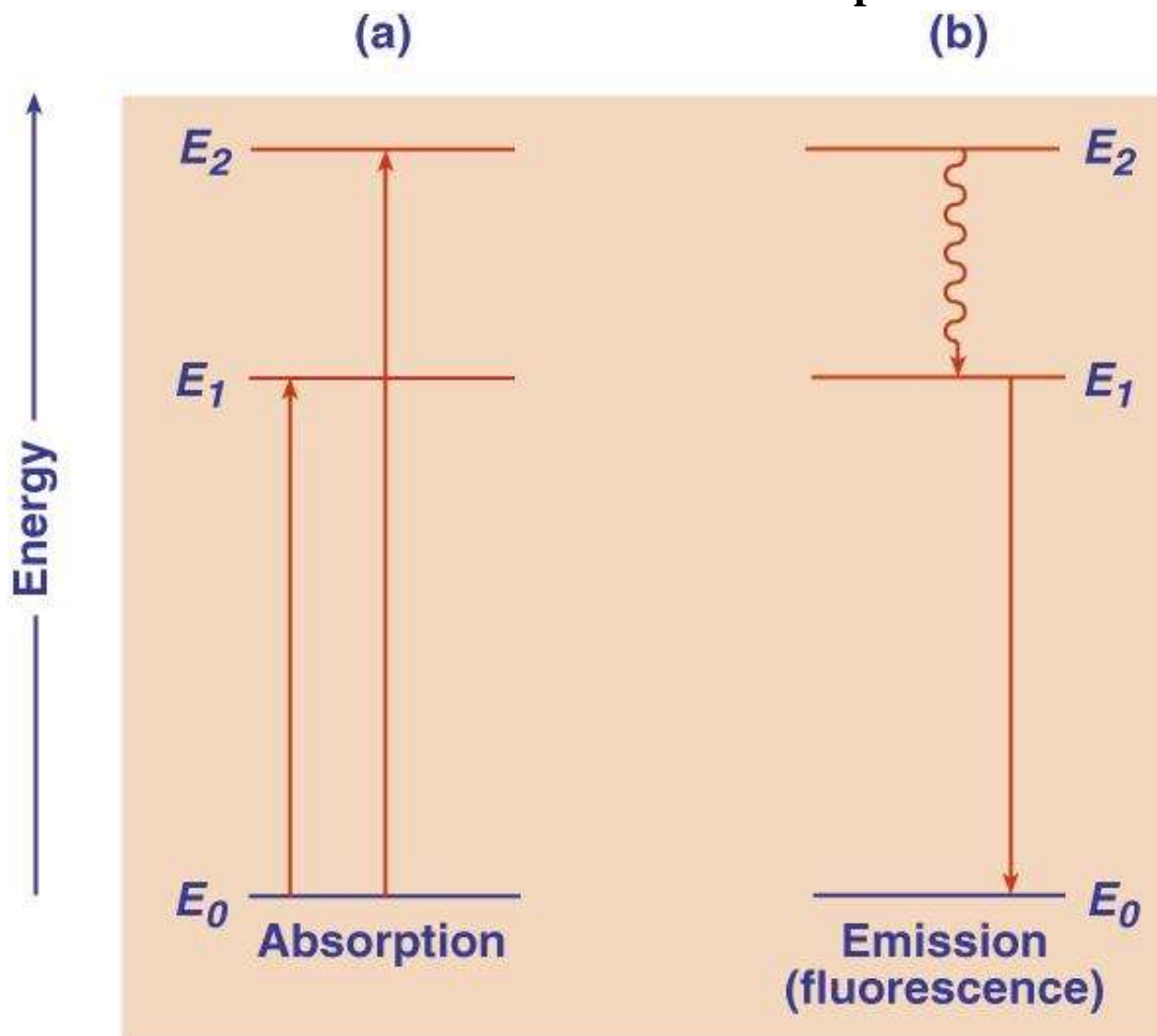
S_1 : Excited singlet state

T_1 : Excited triplet state (spin inversion)

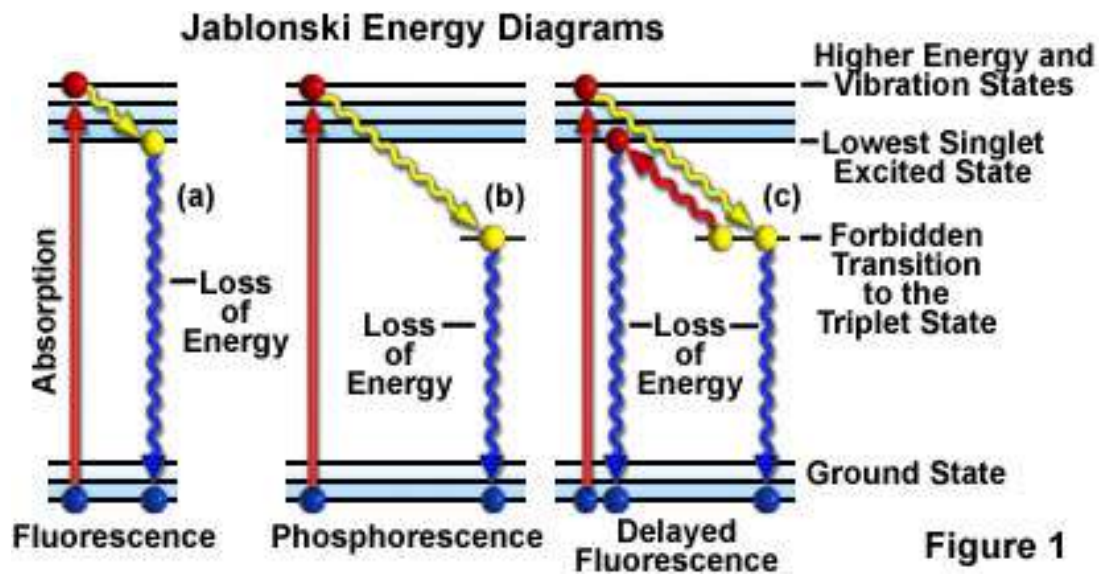
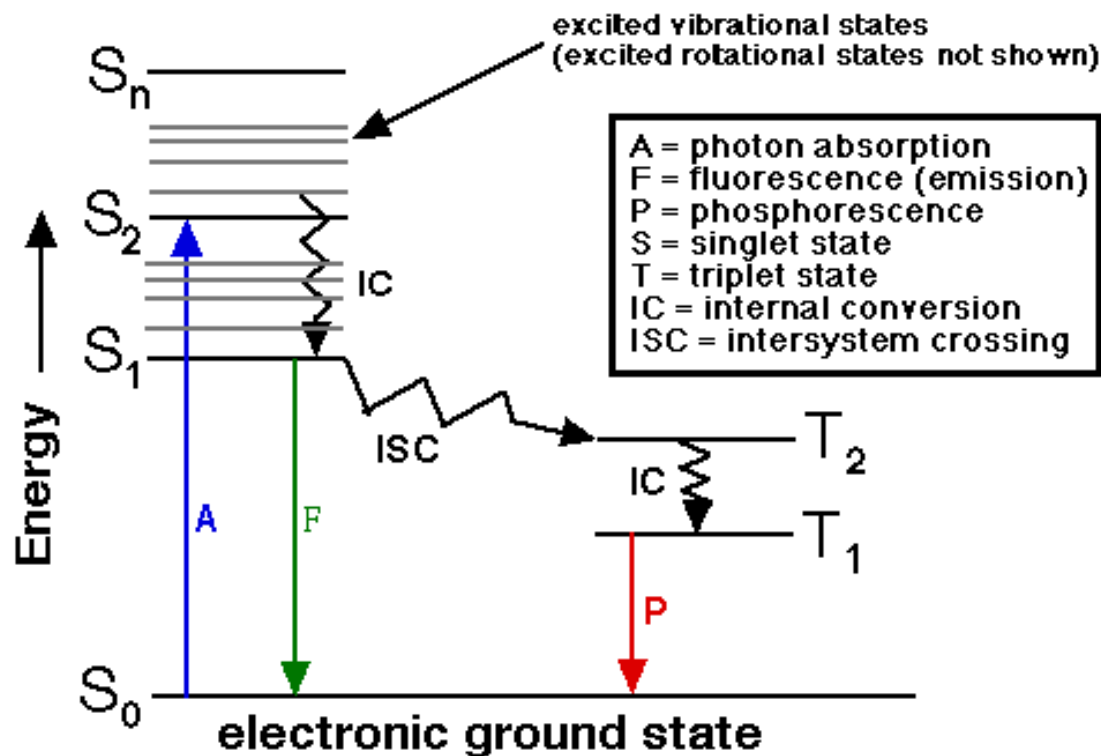
T_1 is more stable than S_1 (parallel spin, lesser inter-electronic repulsion)

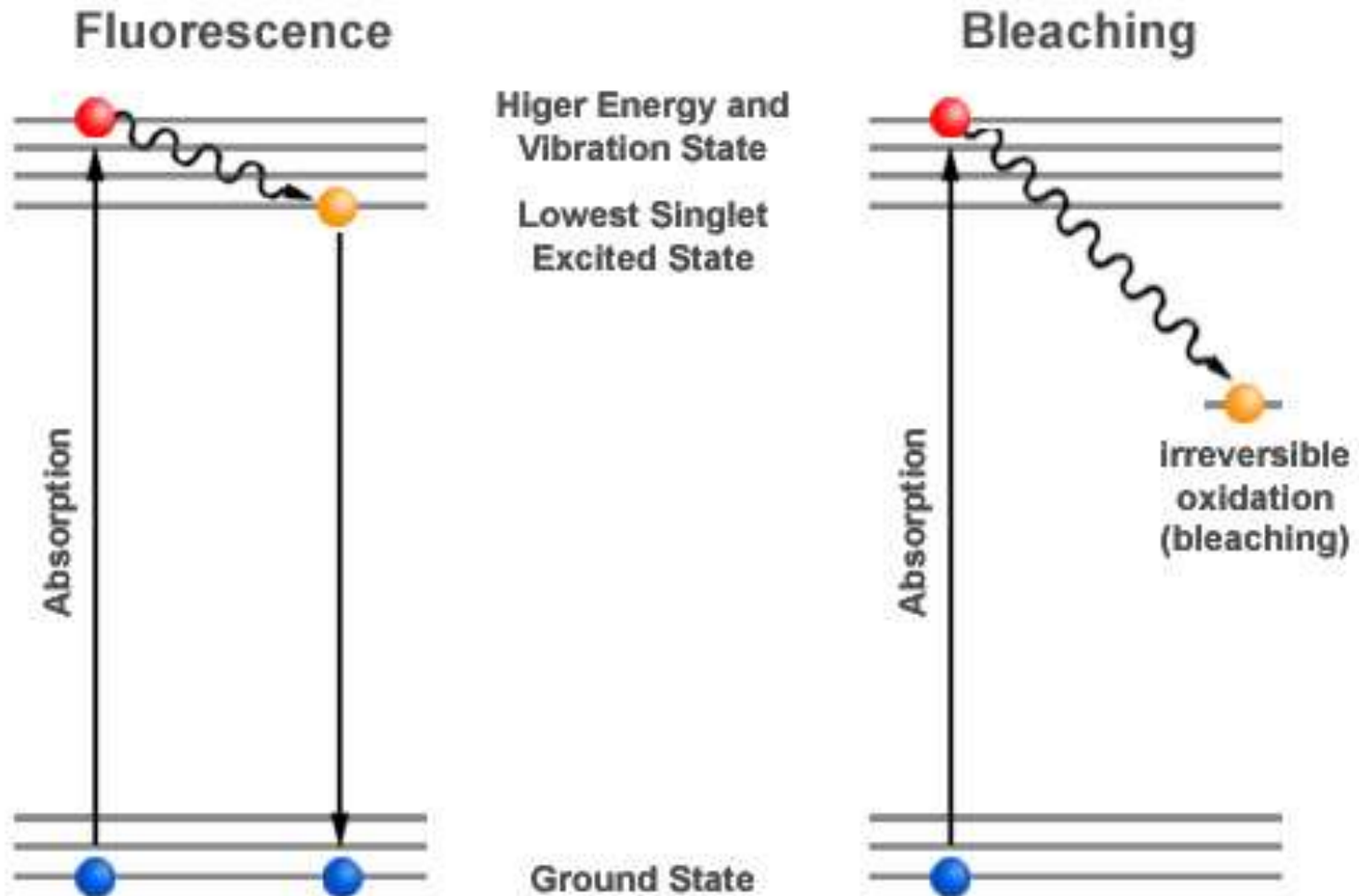
LIGHT ABSORPTION AND FATE OF EXCITATION ENERGY:

Franck-Condon Principle



Ground state (E_0) and two excited states (E_1 , E_2) of a molecule (vibrational and rotational levels are not shown).

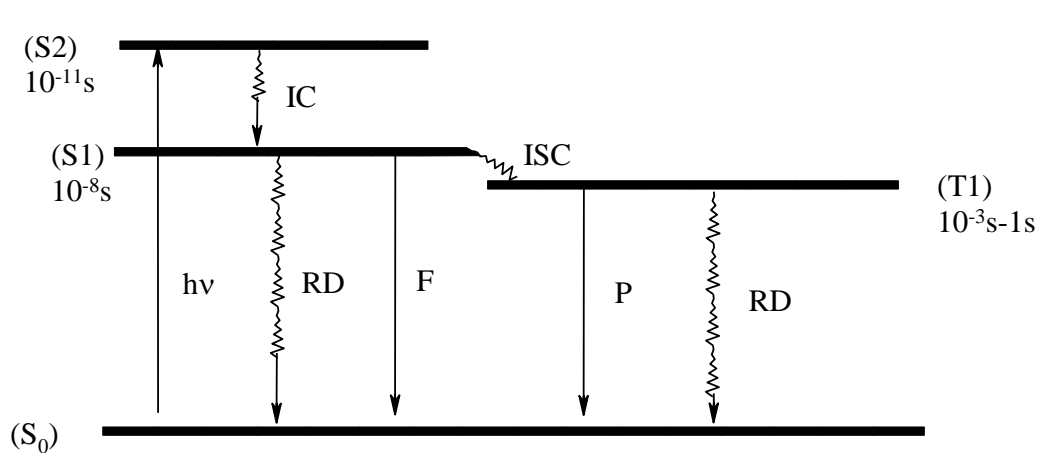




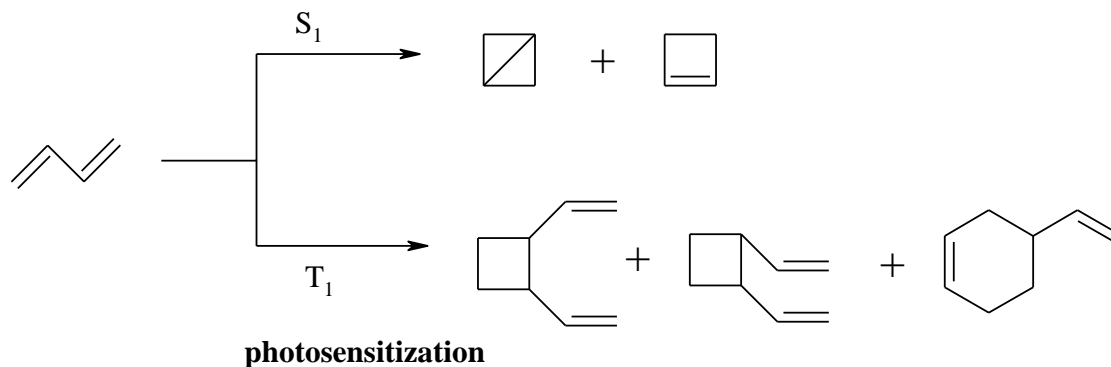
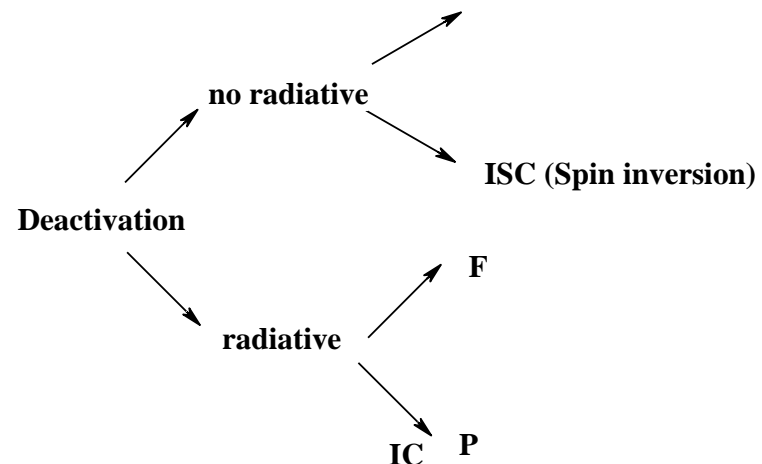
Jablonski diagram

Instead of relaxation to the ground state with the emission of a photon, in photobleaching the fluorophore may interact with another molecule (i.e. oxygen) to produce irreversible covalent modifications.

Modes of Dissipation of Energy (Jablonski diagram)

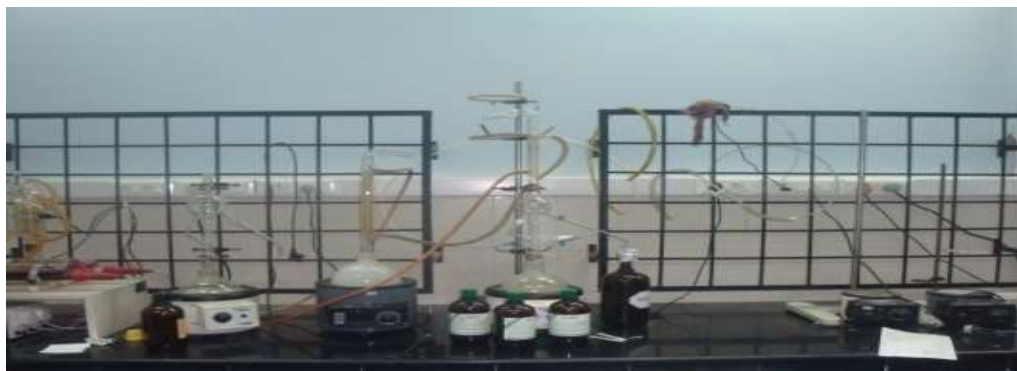


S_2 : The higher vibrational level of the excited singlet state S_1
IC: Internal conversion; **RD**: Radiative deactivation
F: Fluorescence (spin conservation); **ISC**: Inter system crossing
P: Phosphorescence (Spin inversion).



photosensitization

Thank You



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