B.Sc. Semester-VI
GroupA / DSE-4
Organic Synthesis

III. Photochemistry

1. Jablonski Diagram, Allowed and Forbidden Transitions

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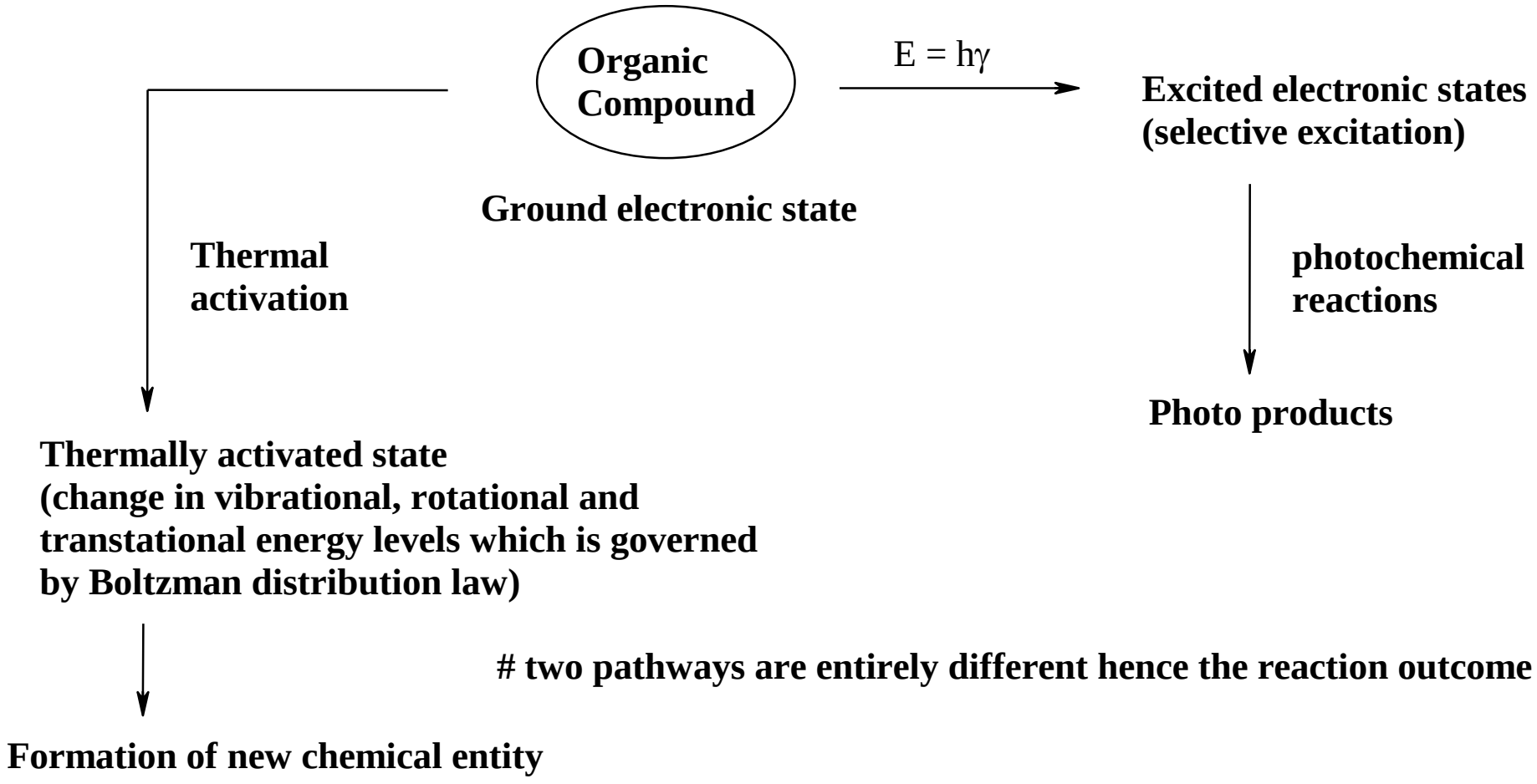
Jablonski Diagram, Allowed and Forbidden Transitions



Questions need to be asked during the analysis of photochemical reaction

1. What are the products of the photo reaction

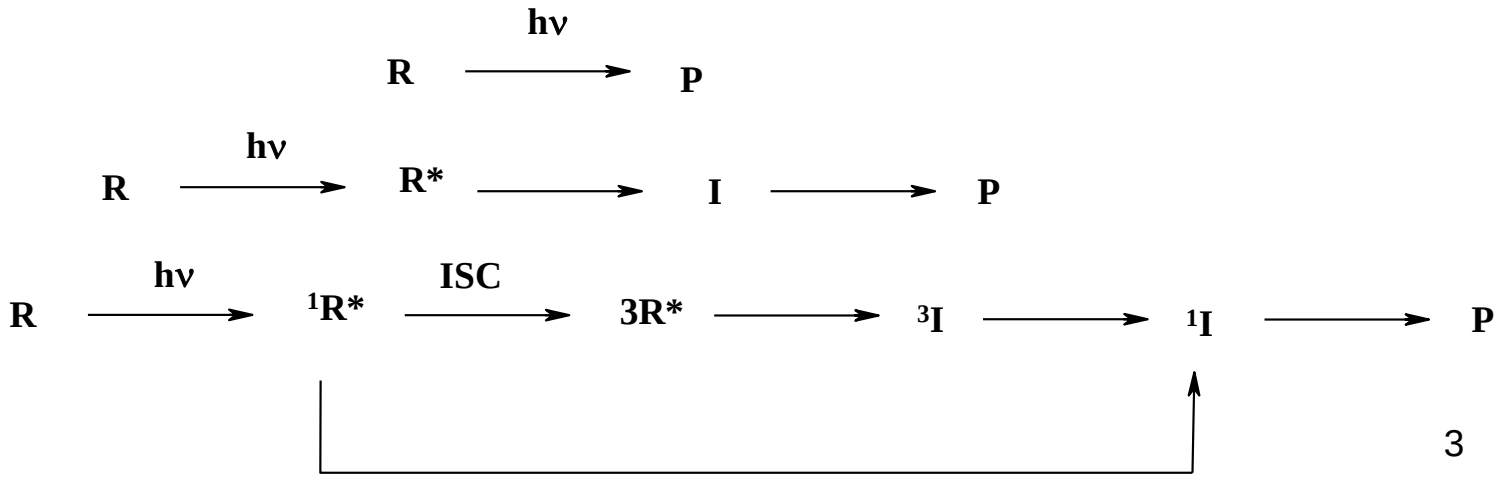
2. what are the electronic characters of the reactive state

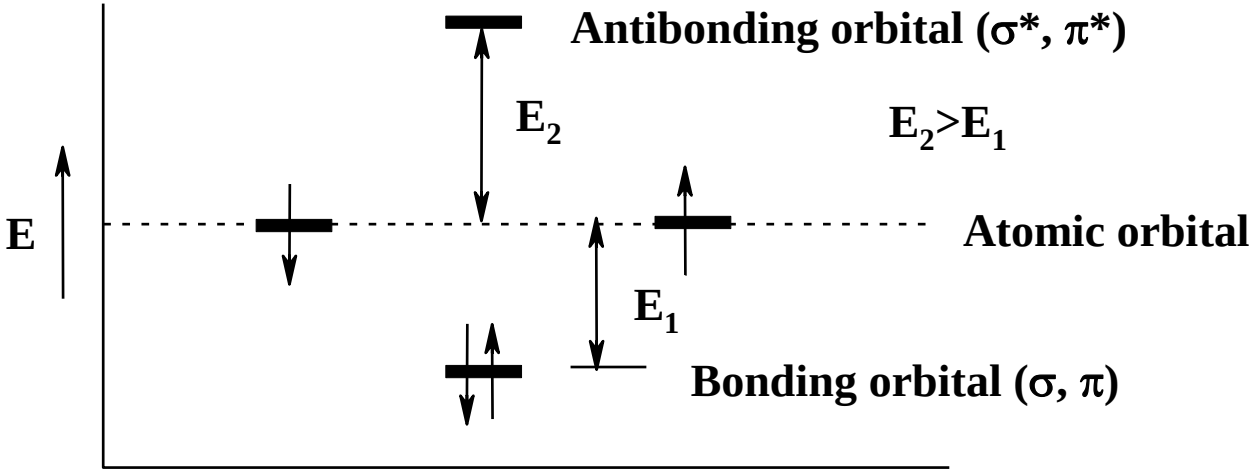
3. what are the spin characters of the reactive state

4. what intermediates are involved in the reaction

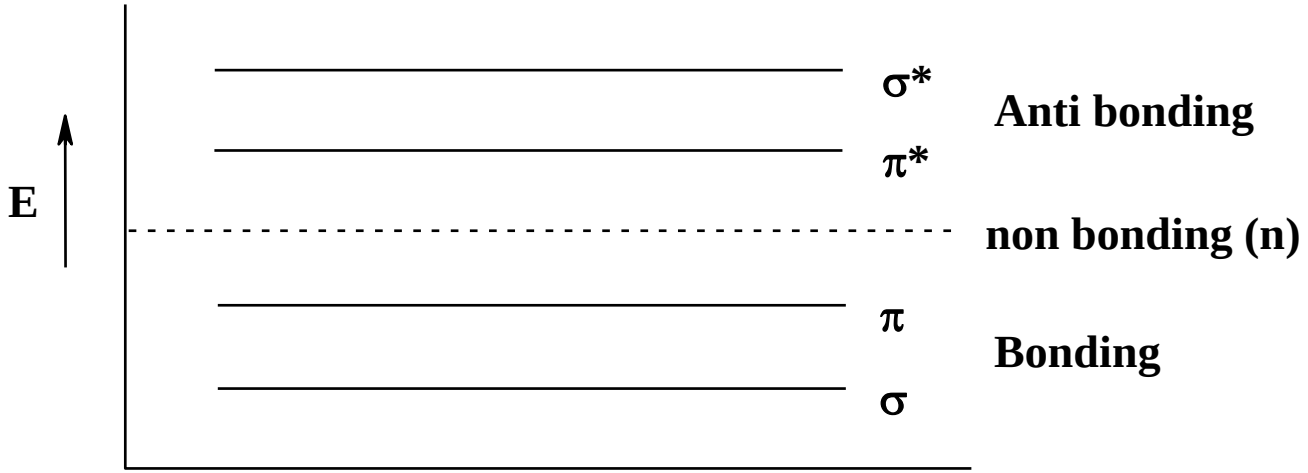
5. what orbitals are involved and how do they react

6. what are the various chemical and physical processes and what are their rates with which a reaction of interest competes

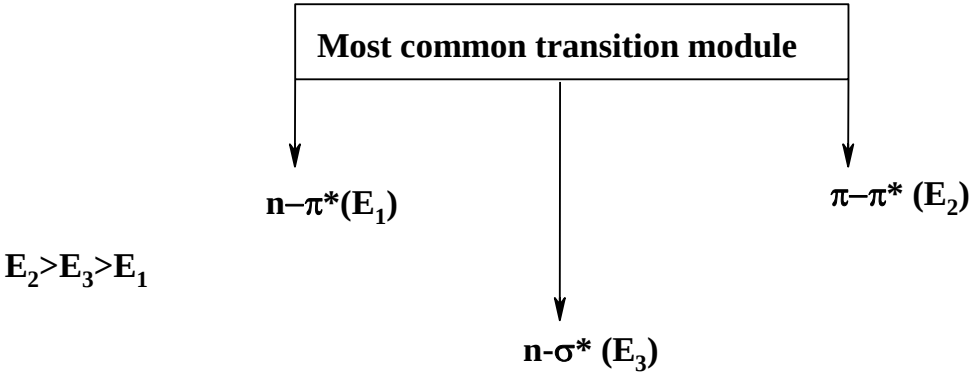




Relative energies of atomic and molecular orbitals

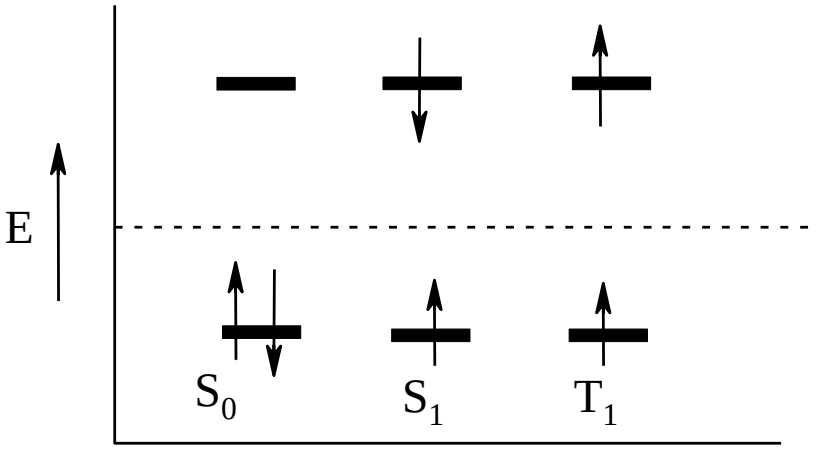


Relative energies of σ, π and n MOs



Absorption maxima for few molecules and functional groups

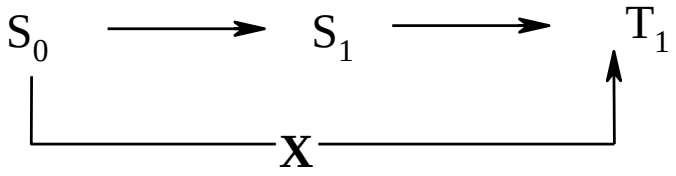
Molecule	Transition	λ_{max} (nm)	E (Kcal/mol)
Iodobutane	n-σ*	224	127.7
Ethylene	π–π*	165	173.3
Ethyne	π–π*	173	165.3
Acetone	π–π*	150	190.7
	n-σ*	188	152.1
	n-π*	279	102.5
Butadiene	π–π*	217	131.8
Acrolein	π–π*	210	136.2
	n-π*	315	90.8
Functional group			
RCH = CHR		165	173.3
		193	148.2
Alkyne		173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



Antibonding (SOMO)

Bonding

Excited states



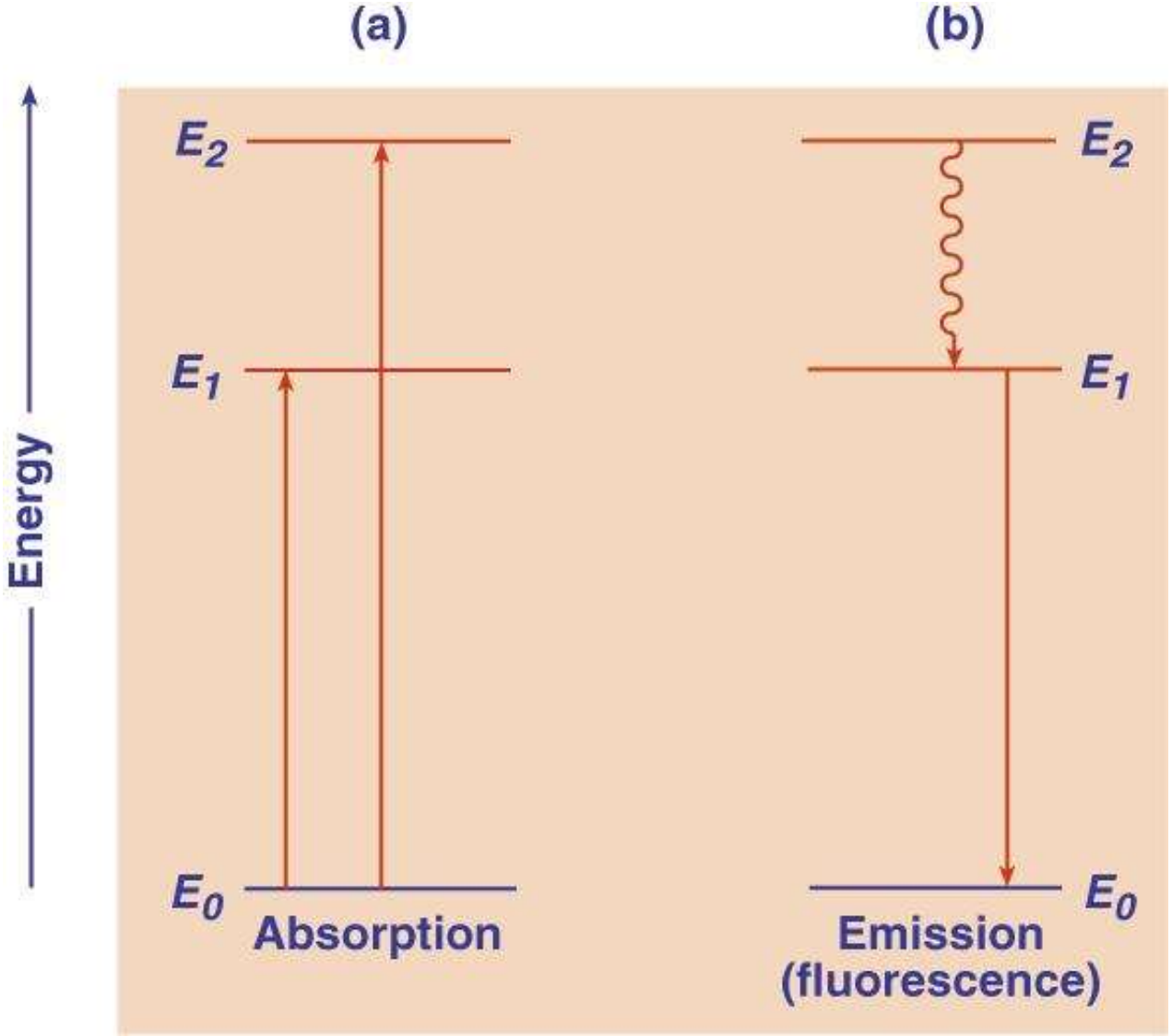
S_0 : Ground state (spin paired, Pauli exclusion principle)

S_1: Excited singlet state

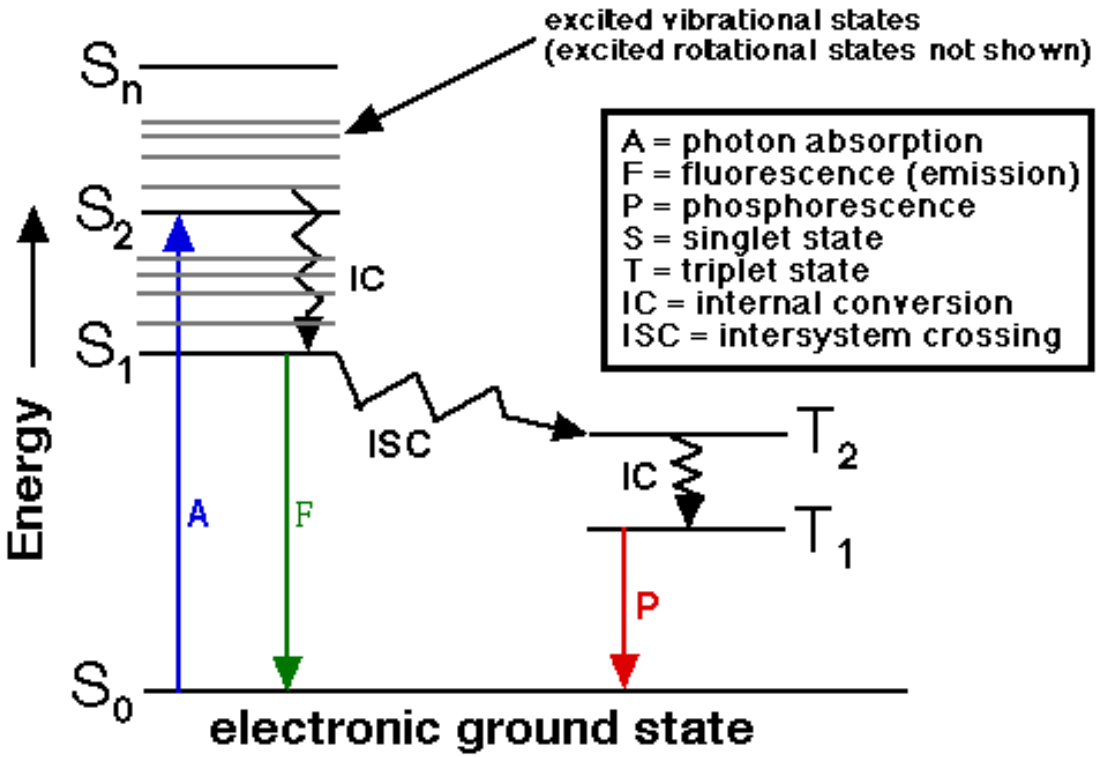
T_1: Excited triplet state (spin inversion)

 # 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 (E0) and two excited states (E1, E2) of a molecule (vibrational and rotational levels are not shown).


excited vibrational states
(excited rotational states not shown)
S_n
S_2
S_1
S_0
IC
ISC
IC
T_2
T_1
A
F
P
Energy
electronic ground state
A = photon absorption
F = fluorescence (emission)
P = phosphorescence
S = singlet state
T = triplet state
IC = internal conversion
ISC = intersystem crossing

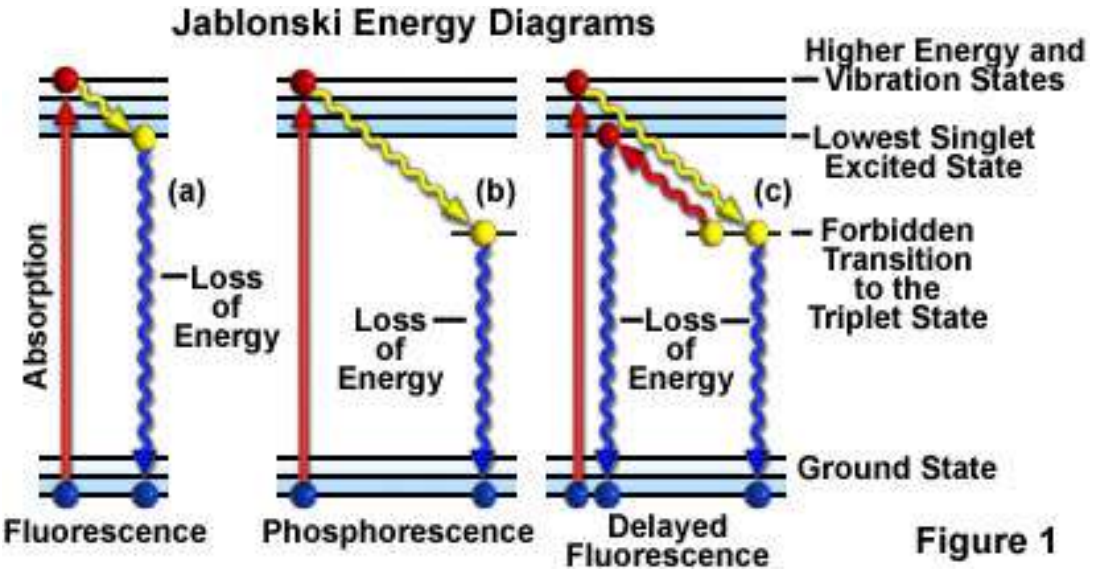
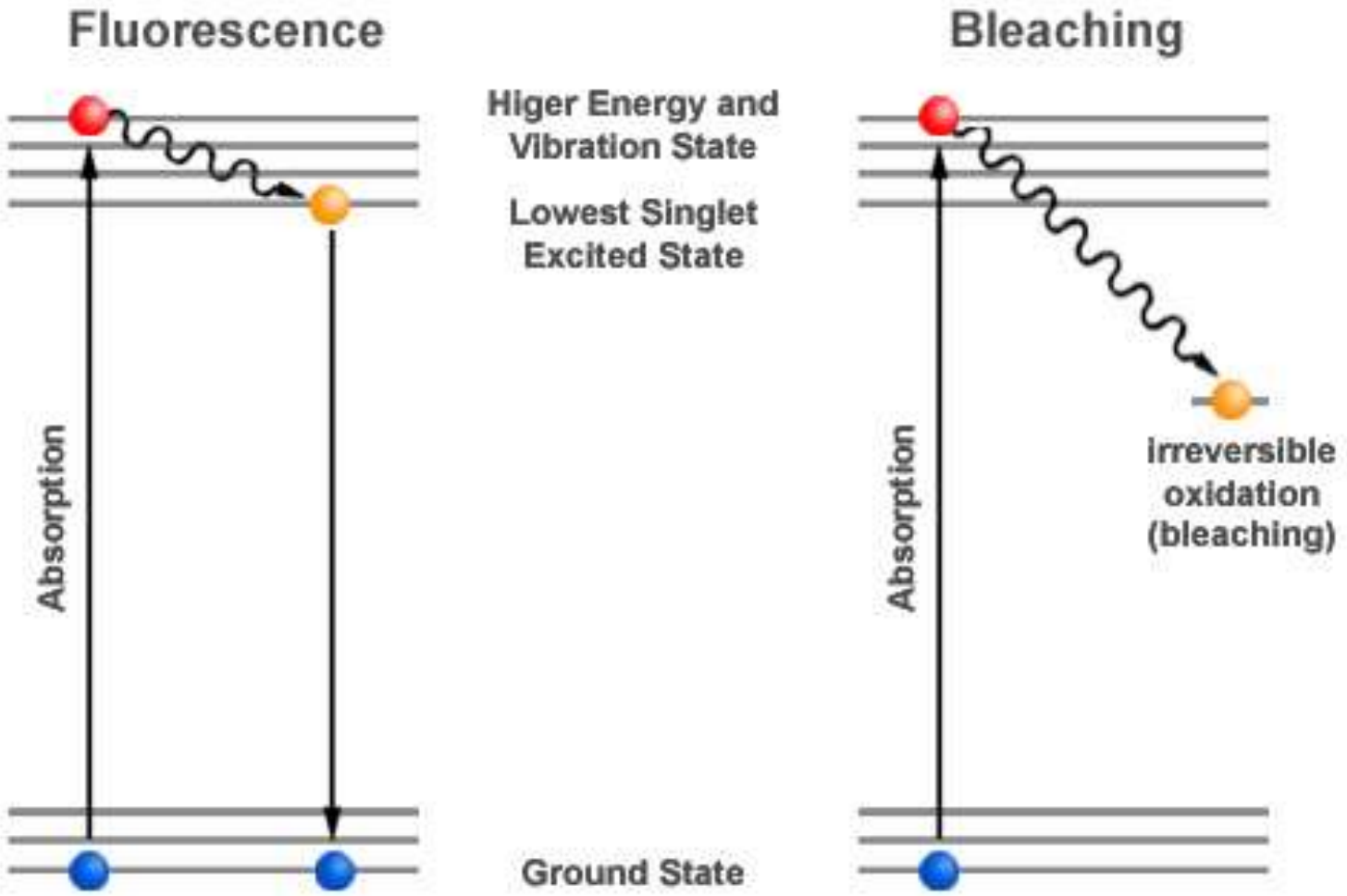

Jablonski Energy Diagrams
Higher Energy and Vibration States
Lowest Singlet Excited State
Forbidden Transition to the Triplet State
Ground State
(a)
(b)
(c)
Absorption
Loss of Energy
Loss of Energy
Loss of Energy
Fluorescence
Phosphorescence
Delayed Fluorescence

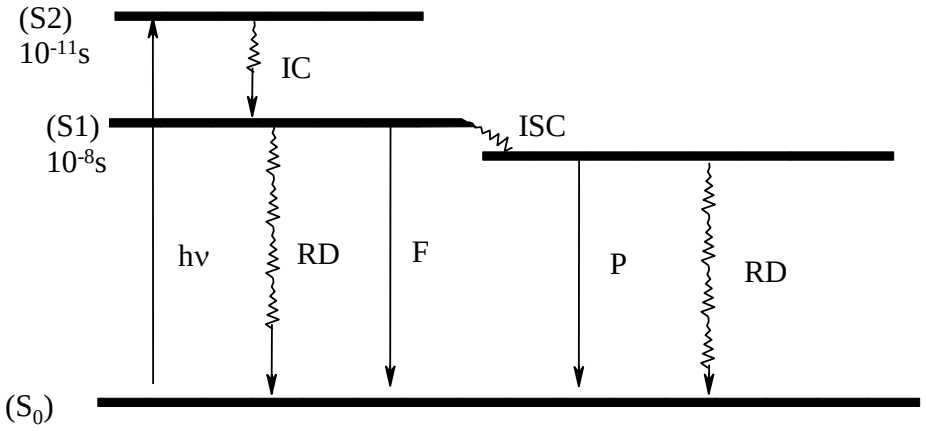
Figure 1

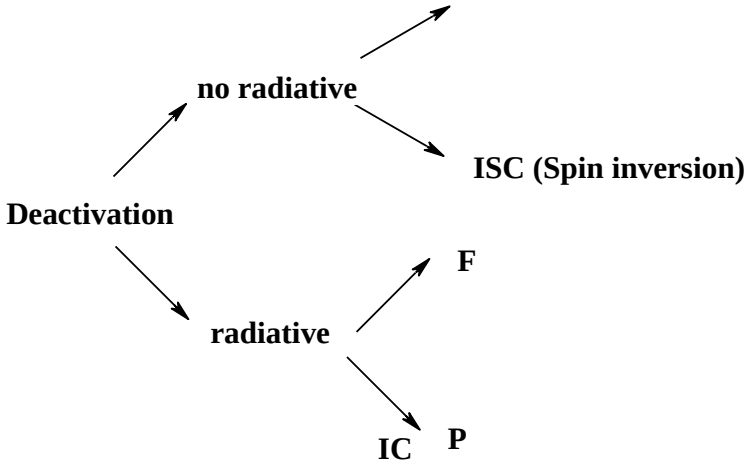


Jablonski diagram

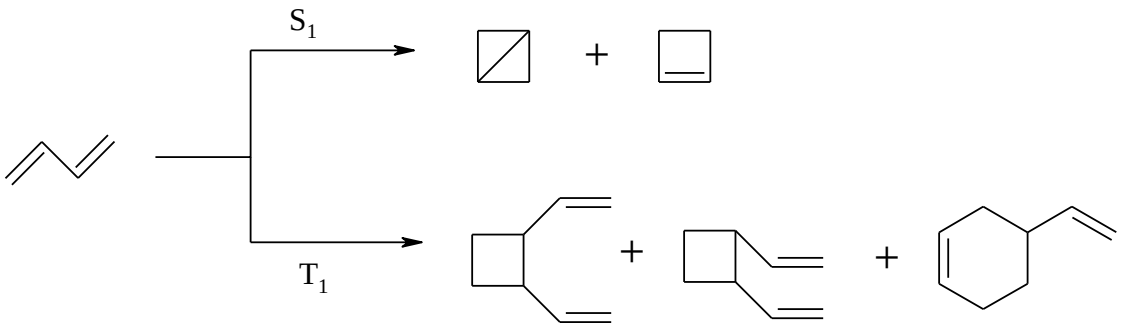
Instead of relaxation to the ground state with the emission of a photon, in photobleaching the fluorophore may interact with another molecule (i.e. oxygen) to produce irreversible covalent modifications.

Modes of Dissipation of Energy (Jablonski diagram)



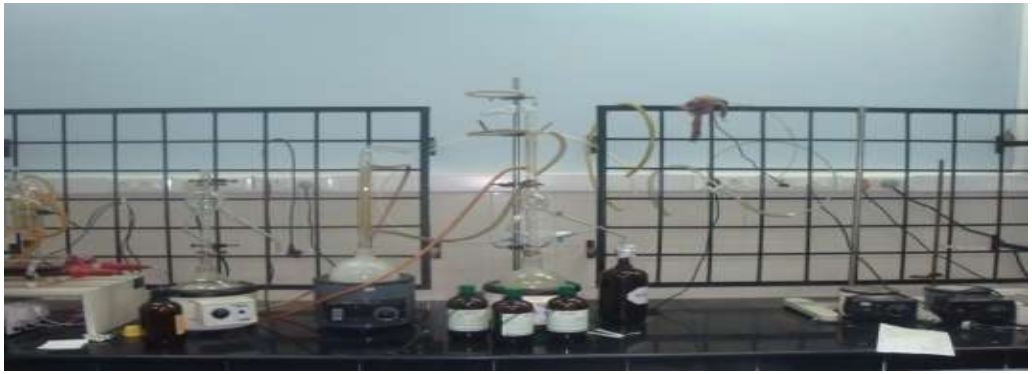


S_2 : The higher vibrational level of the excited singlet state S_1
IC: Internal conversion; RD: Radiative deactivation
F: Fluorescence (spin consevation); ISC: Inter system crossing
P: Phosphorescence (Spin inversion).



photosensitization

Thank You



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