

Advanced Organic Chemistry
Chm 512/412
Spring 2010

Handout I
“Photochemistry Part 1

Photophysical Processes
Quenching
Alkene *cis-trans* Isomerization

Importance of Photochemistry/Photophysics

Organic Synthesis

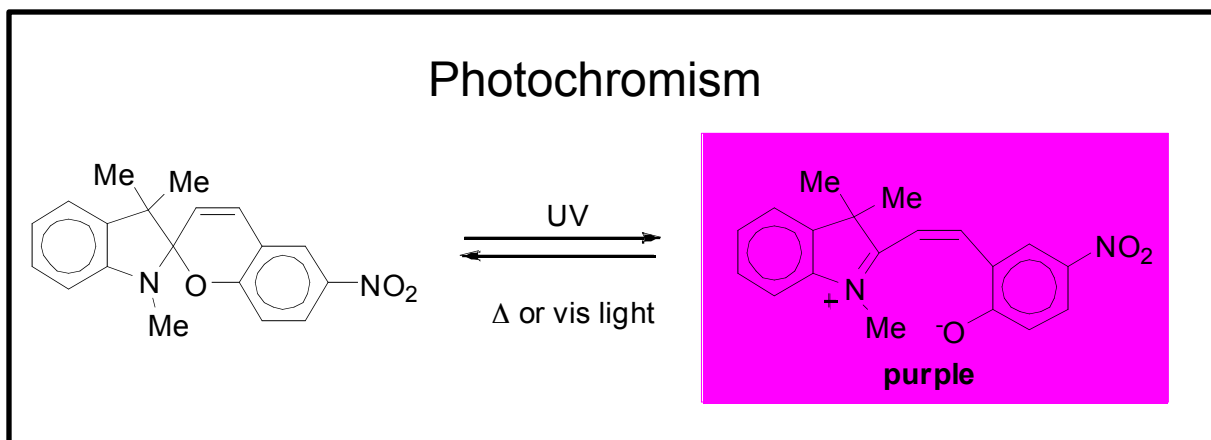
- strained multiple bonds
- cyclobutanes
- oxetanes
- 1,2 diols
- polycyclic compounds
- reactive intermediates: nitrenes; carbenes; radicals

Analytical Chemistry

- Fluorescence Spectroscopy & Luminescence
- Imaging Techniques
- Chemical sensors

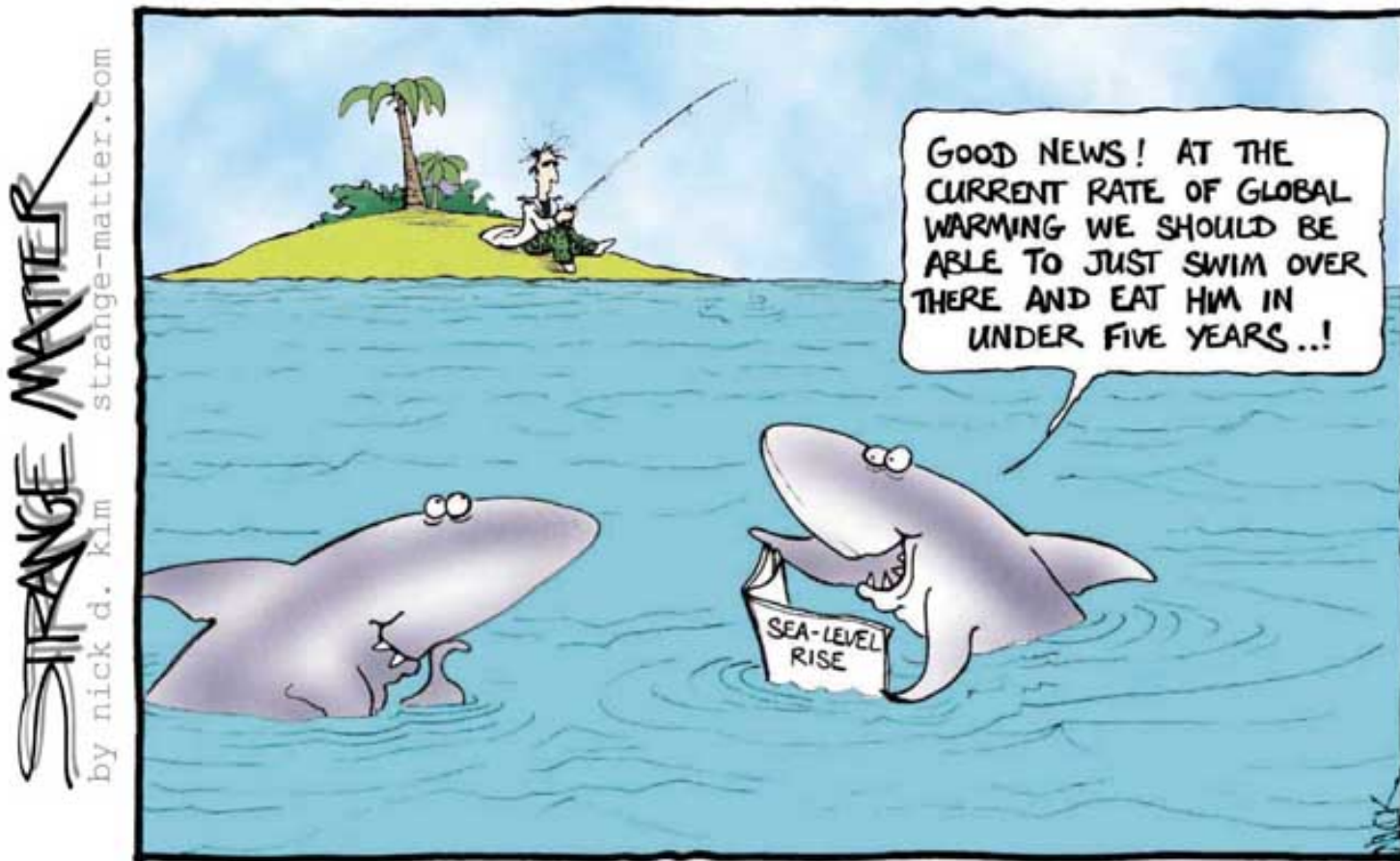
Material Sciences

- Photopolymerization
- Photochromic Materials
- Photography
- Photolithography



Clean Energy through Photochemistry without CO₂ Emission

- Photovoltaic cells
- Photochemical splitting of water



Photobiology

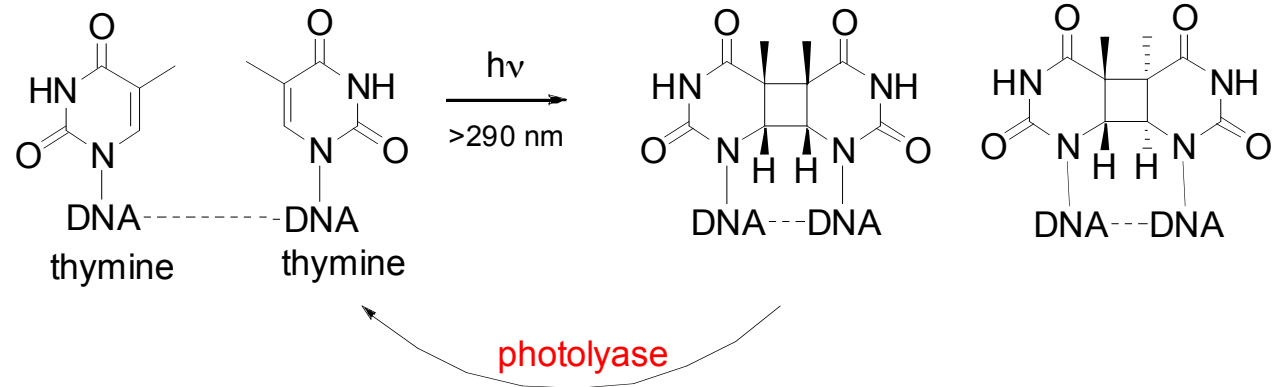
Photochemistry of Biomolecules (Nucleic Acids, Amino acids, Proteins, Lipids)

Photosynthesis

Visual Transduction

Biological Effects of Solar Ultraviolet Radiation

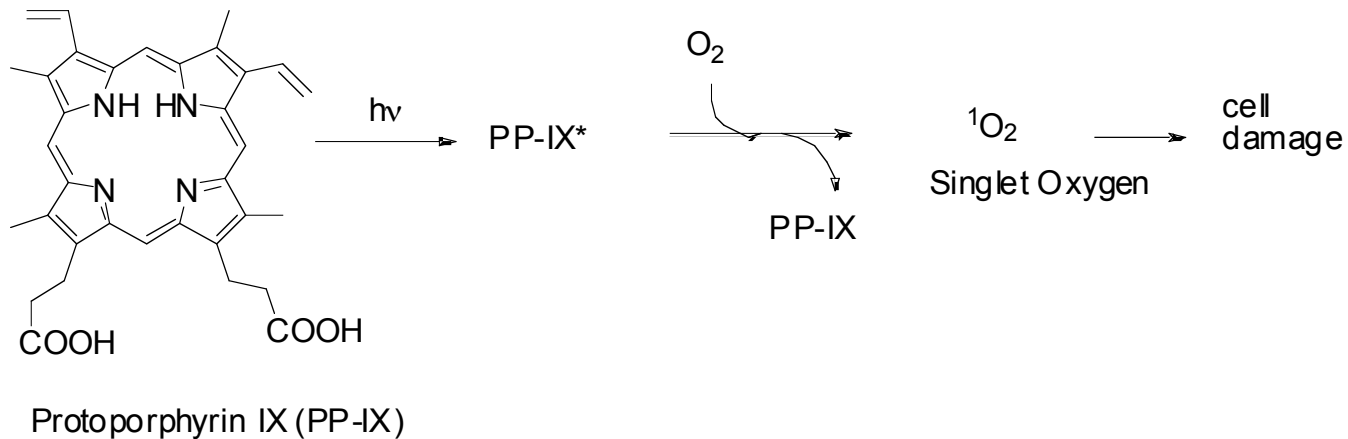
Photocarcinogenesis



Photomedicine

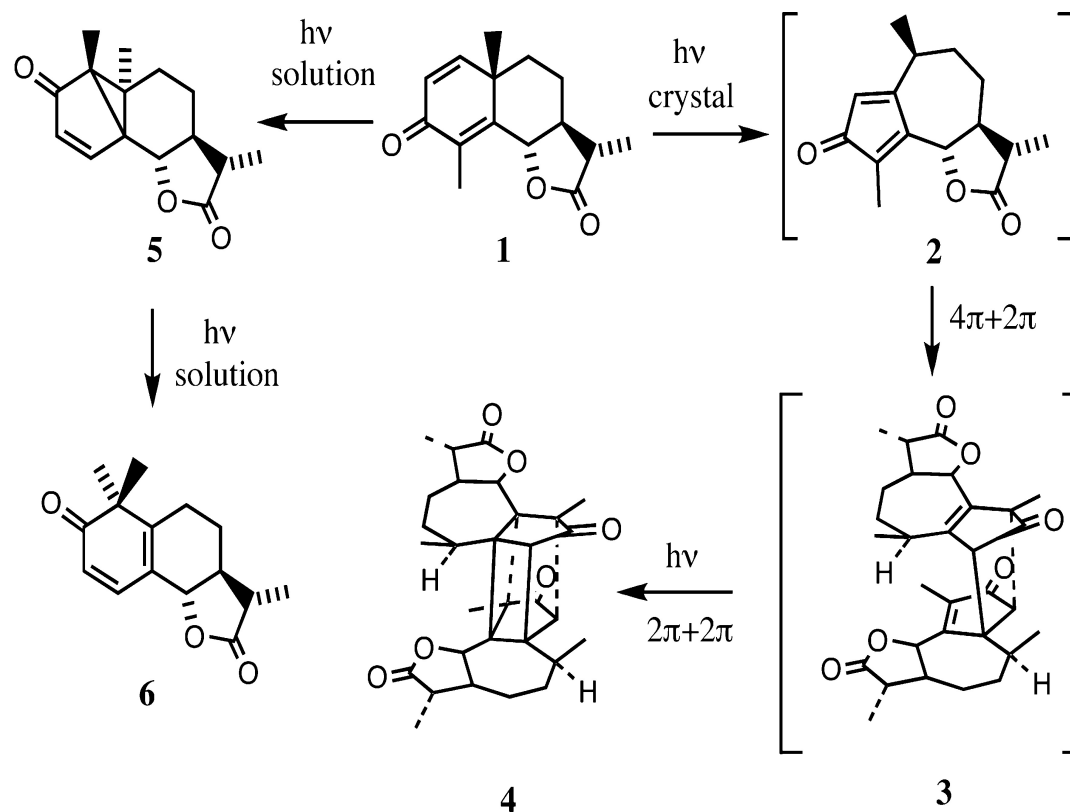
Photochemotherapy

Photodynamic Therapy



The Beginnings of Organic Photochemistry

1834: First photochemical transformation described by Trommsdorff: Exposed α -Santonin (**1**) crystals to sunlight and observed that they turned yellow and bursted. The mechanism was elucidated in 2007 by Arunkumar Natarajan et al.



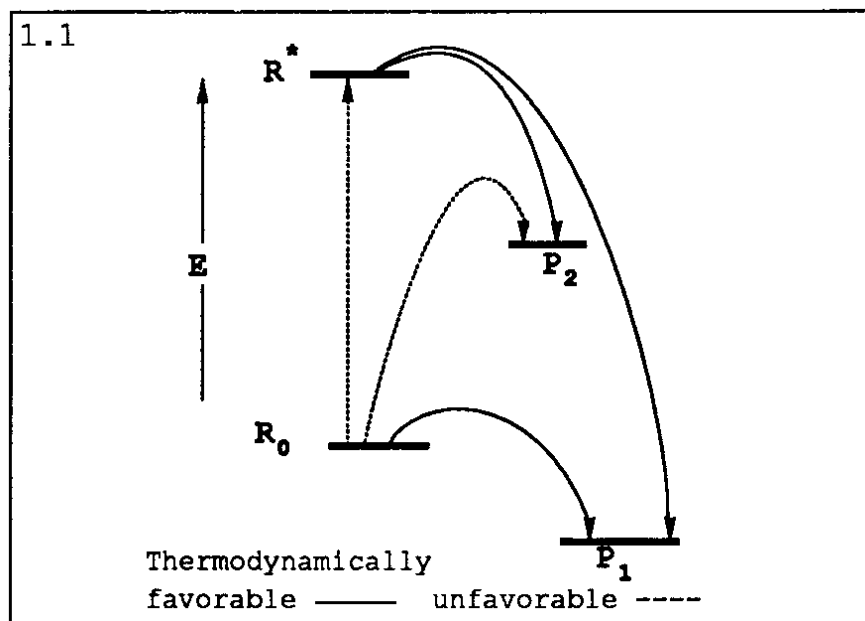
Published in: Arunkumar Natarajan; C. K. Tsai; Saeed I. Khan; Patrick McCarren; K. N. Houk; Miguel A. Garcia-Garibay; *J. Am. Chem. Soc.* **2007**, 129, 9846-9847.

DOI: 10.1021/ja073189o

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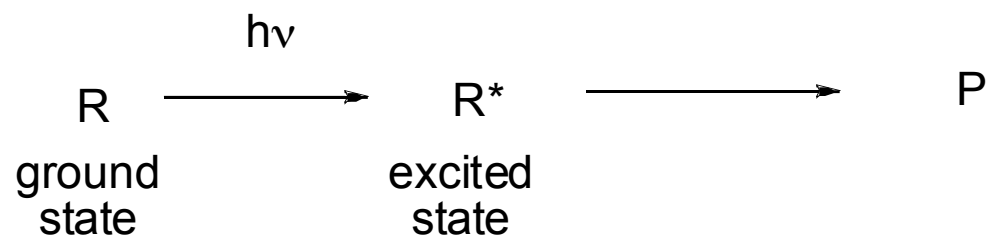
Photochemistry

- Study of reactions that involve excited states of organic molecules
- These reactions are initiated by the absorption of a photon by one reactant leading to its excited state (*Excitation Process*)



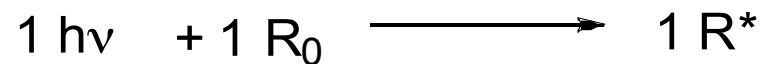
Grotthus-Draper Law (First Law of Photochemistry)

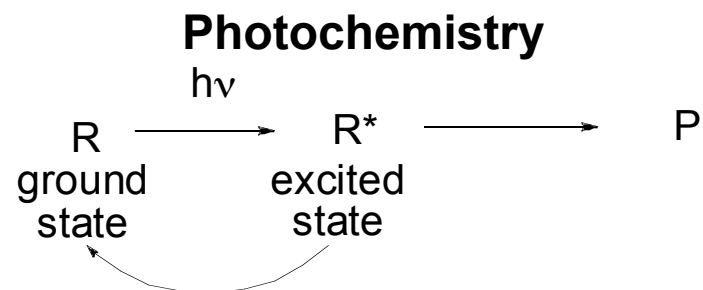
“Only radiation absorbed in a system can produce a chemical change.”



Stark-Einstein Law of Photochemical Equivalence

“Number of activated molecules = number of quanta of radiation absorbed.”





Properties of Excited State: geometry; electronic configuration

Photophysical Processes

1) Relaxation Processes

-Dissipation of energy and change of electronic configuration after excitation

Vibrational Relaxation

Internal Conversion

Intersystem Crossing

2) Decay Processes

-Return to ground state with release of energy

Quenching – energy transfer

Fluorescence

Phosphorescence

Luminescence

Photochemical Processes

- Chemical reactions of the excited state

fragmentations

cis/trans isomerizations

rearrangements

addition/cyclization reactions

photo oxidations

Important Compound Classes

alkenes, dienes & polyenes

aromatic compounds

carbonyl compounds

nitrogen-containing compounds

(R-N₃, RR'C=N₂, R-NO₂, R-N=N-R, R-ONO)

singlet oxygen

halogen-containing compounds

Excited State of the Molecule

- Energy of the molecule has increased by the energy of the absorbed photon
- Photochemistry deals in part with properties of the excited state

$$E_{\text{exc}} = E^* - E_0 = h\nu = hc/\lambda$$

E_{exc} = electronic excitation energy

E^* = energy of excited state

E_0 = energy of ground state

h = Planck's constant

ν = frequency of absorbed radiation

c = speed of light

λ = wavelength of absorbed radiation

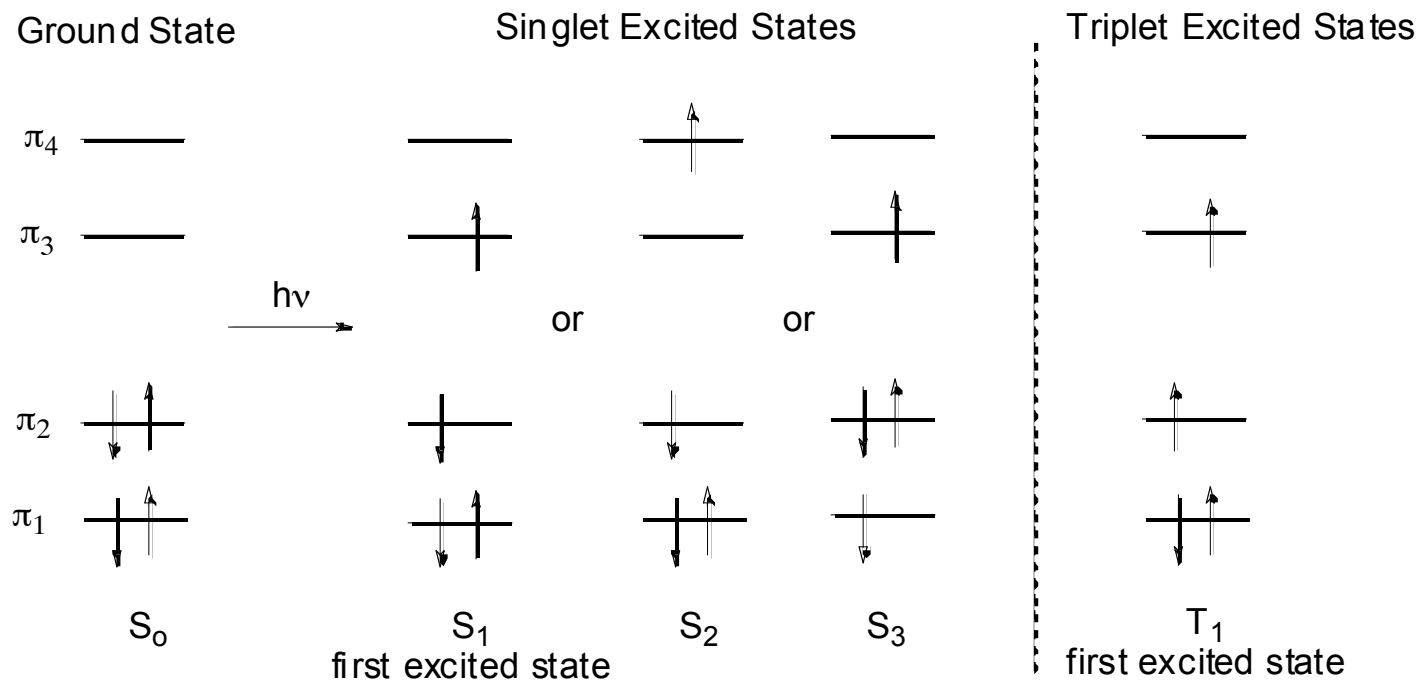
-Wavelength range of most photochemical reactions:

UV/Vis region: $200 \text{ nm} \leq \lambda \leq 700 \text{ nm}$; $143 \text{ kcal/mol} \geq E \geq 40.8 \text{ kcal/mol}$

With modern high intensity light sources (lasers) two photon excitation is possible (IR photolysis)

Photochemical Excitation

Adsorption of a photon is accompanied with an **electronic transition**



Electronic State (enumerative)	Excited State (Kasha)	Electronic Configuration
S_0	-	$(\pi_1 \downarrow \uparrow)^2 (\pi_2 \downarrow \uparrow)^2 (\pi_3)^0 (\pi_4)^0$
S_1	$^1(\pi_2, \pi_3)$	$(\pi_1 \downarrow \uparrow)^2 (\pi_2 \downarrow)^1 (\pi_3 \uparrow)^1 (\pi_4)^0$
S_2	$^1(\pi_2, \pi_4)$	$(\pi_1 \downarrow)^1 (\pi_2 \downarrow \uparrow)^2 (\pi_3 \uparrow)^1 (\pi_4)^0$
S_3	$^1(\pi_1, \pi_3)$	$(\pi_1 \downarrow \uparrow)^2 (\pi_2 \downarrow)^2 (\pi_3)^0 (\pi_4 \uparrow)^0$
T_1	$^3(\pi_2, \pi_3)$	$(\pi_1 \downarrow \uparrow)^2 (\pi_2 \downarrow)^1 (\pi_3 \downarrow)^1 (\pi_4)^0$

Symbolism to denote electronic states, excited states and electronic transitions

1. Electronic states and excited states

(a) Enumerative system

Used if the electronic configuration of the excited state is not known. States are labeled according to multiplicity and increasing energy.

S_0 for ground state and S_1, S_2, \dots and T_1, T_2, \dots for first, second, ... singlet and triplet states.

(b) Kasha's MO representation for excited states

Used, if electronic configuration of excited states are known. Excited states are labeled by type of MOs involved and multiplicity.

$^1(\pi_2, \pi_3), ^1(\pi_2, \pi_4), ^3(\pi_2, \pi_3), ^3(\pi_2, \pi_4)$ for S_1, S_2, T_1 and T_2

Superscript 1 or 3 stands for multiplicity

The two MOs are those involved in the transition.

2. Electronic Transitions

(a) Enumerative system

An arrow denotes the transition from the starting electronic state to the final electronic state.

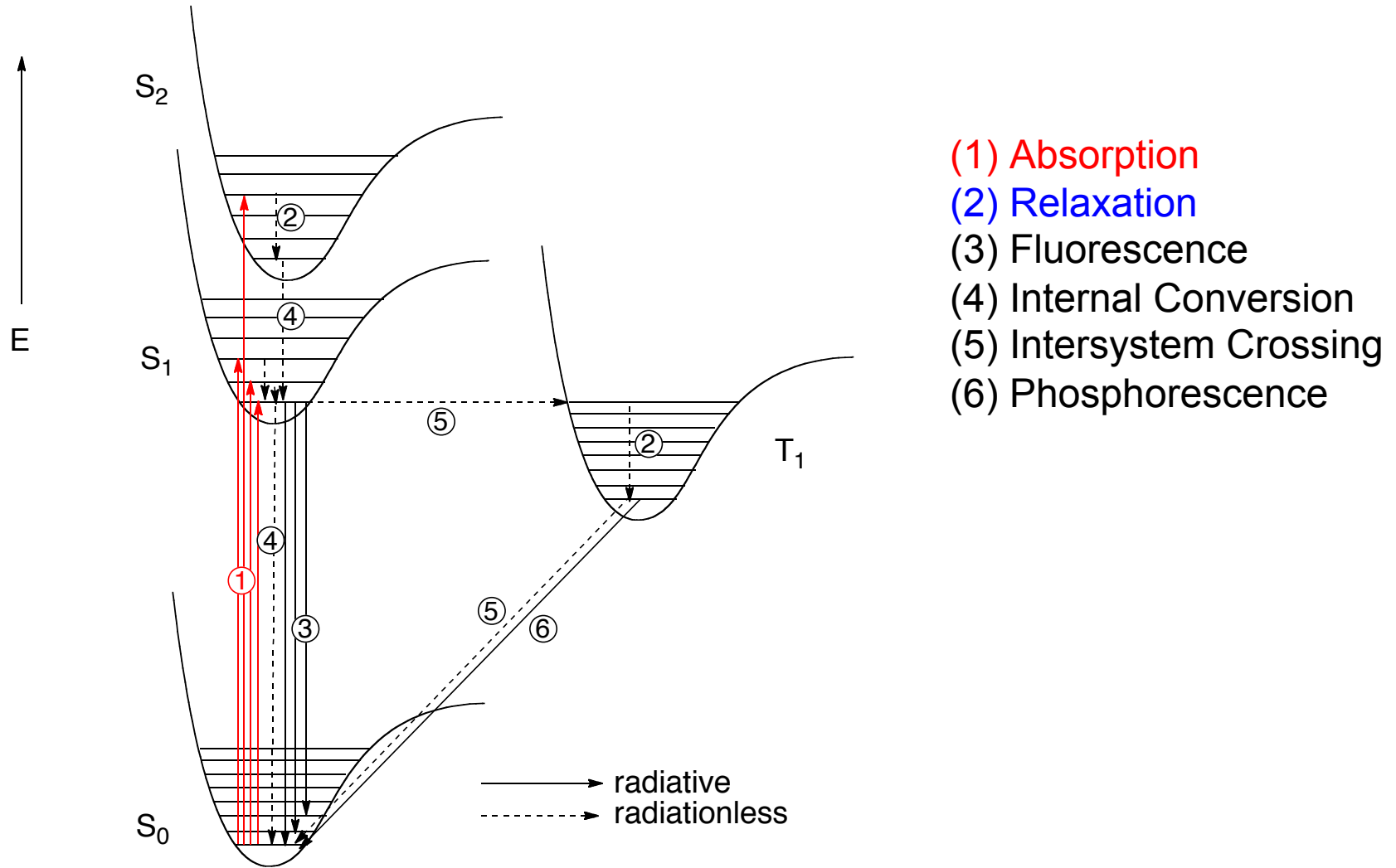
$S_0 \rightarrow S_1, S_0 \rightarrow S_2, T_1 \rightarrow S_1$

(b) Kasha's MO formalism

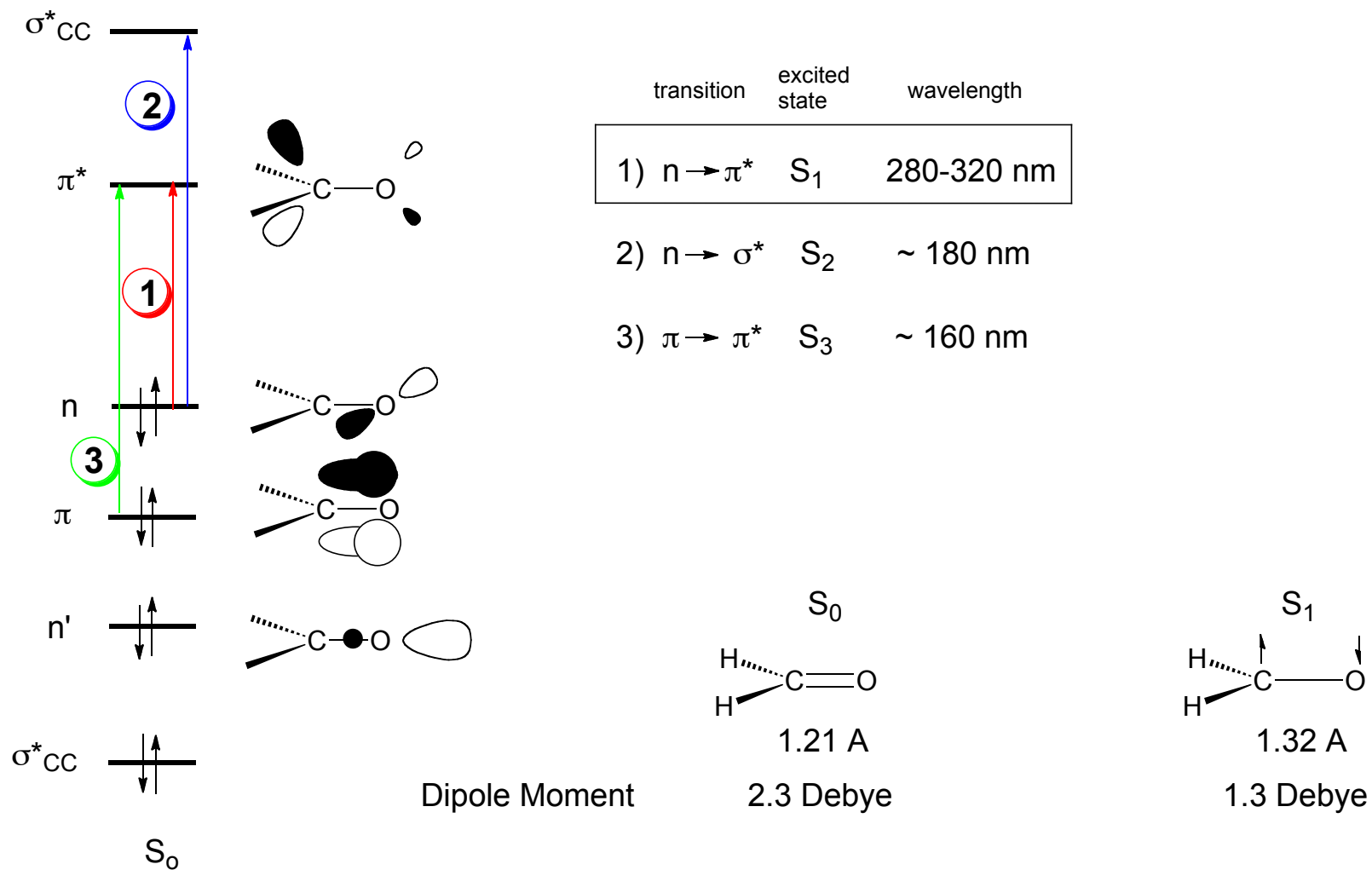
Based on the type of ground state MO involved ($\sigma, \sigma^*, n, \pi, \pi^*$) in process. The transition is denoted by an arrow directed from the symbol of the initially occupied MO to the symbol of the initially unoccupied MO.

$\pi \rightarrow \pi^*, n \rightarrow \pi^*, \sigma \rightarrow \sigma^*$

Jablonski State Diagram



Example: Important electronic transitions of the carbonyl chromophore



(Buckingham et al. Can J. Phys. **1970**, 48, 1242)

Chromophore

Electronic transitions involves a shift of one electrons from a lower to a higher energy molecular orbital. In most cases these molecular orbitals are associated with a specific part (e.g. functional group) of the molecule. *This part, that mainly absorbs the photon is termed the **chromophore**.*

Examples are aryl units, polyenes, and other pi-bonds, carbonyl, -NO₂, -N₃ and C-Hal groups.

Table 16.2
Typical Organic Chromophores

Chromophore	λ_{\max} (nm)	ϵ_{\max} (1/mol•cm)	Type
C–C and C–H	<180	1000	$\sigma \rightarrow \sigma^*$
C–O (alcohol)	~180	200	$n \rightarrow \sigma^*$
C–S (alkyl sulfide)	210	1200	$n \rightarrow \sigma^*$
C–Br (alkyl bromide)	208	300	$n \rightarrow \sigma^*$
C–I (alkyl iodide)	260	400	$n \rightarrow \sigma^*$
C=C	180	10,000	π, π^*
C=C–C=C	220	20,000	π, π^*
C=C–C=C–C=C	260	50,000	π, π^*
C ₆ H ₆	260	200	π, π^*
Styrene	282	450	π, π^*
Acetophenone	278	1100	n, π^*
Naphthalene	310	200	π, π^*
Anthracene	380	10,000	π, π^*
Nitrobenzene	330	125	n, π^*
C=O	280	20	n, π^*
N=N	350	100	n, π^*
–NO ₂	270	20	n, π^*
N=O	660	200	n, π^*
C=C–C=O	350	30	n, π^*
C=C–C=O	220	20,000	π, π^*

Spin Selection Rule

An electronic transitions is allowed by the spin selection rule only if the multiplicity of the initial and final state are identical. E.g.

S → S	T → T	are allowed
S → T	T → S	are forbidden

Symmetry Selection Rule

(restricted to most common electronic transitions)

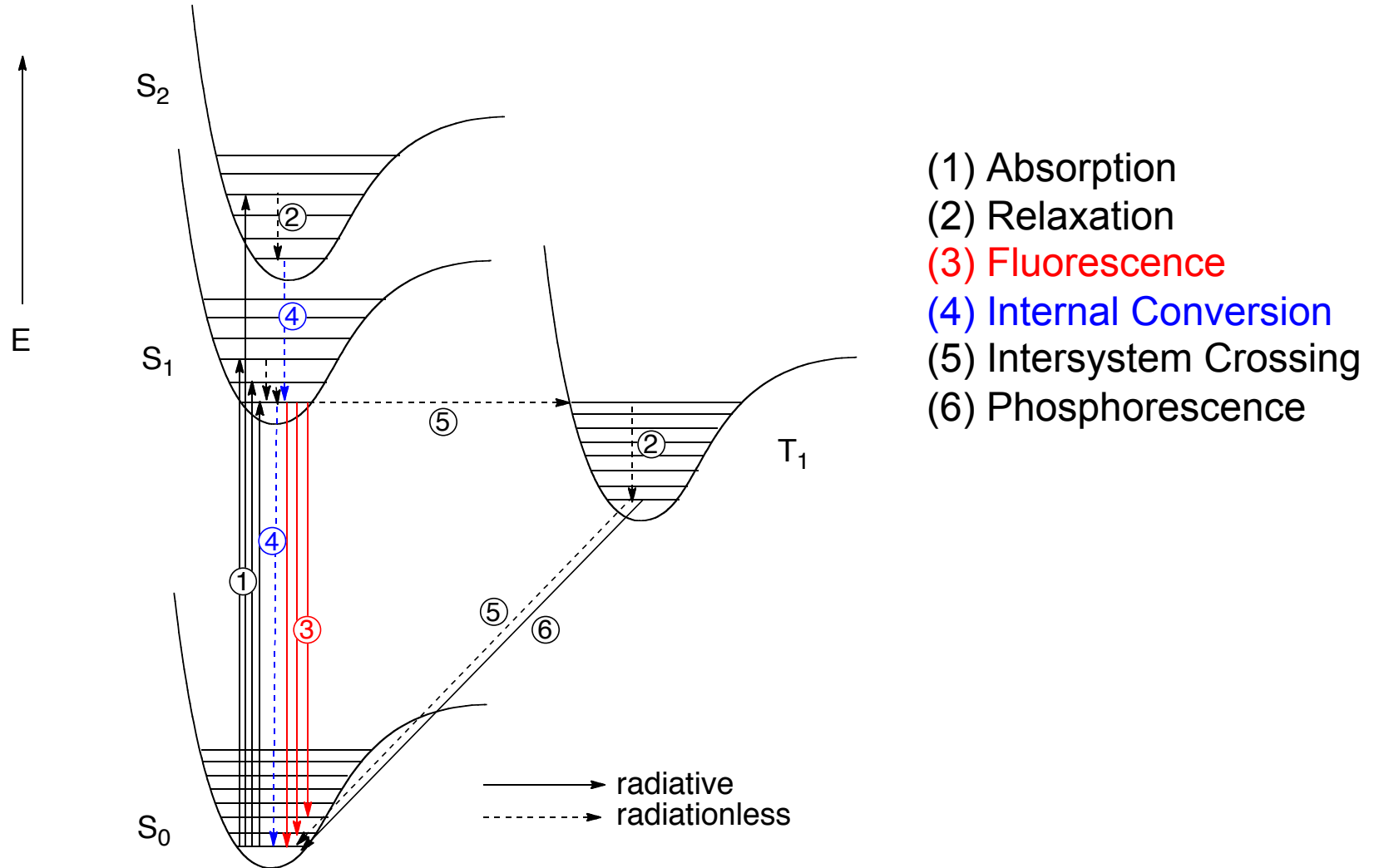
symmetry allowed are:	$\pi \rightarrow \pi^*$; $\sigma \rightarrow \sigma^*$
symmetry forbidden are:	$n \rightarrow \pi^*$; $n \rightarrow \sigma^*$

Allowed transitions are strong (ϵ 1000-10⁵)

Symmetry forbidden transitions are weak (ϵ 1-1000)

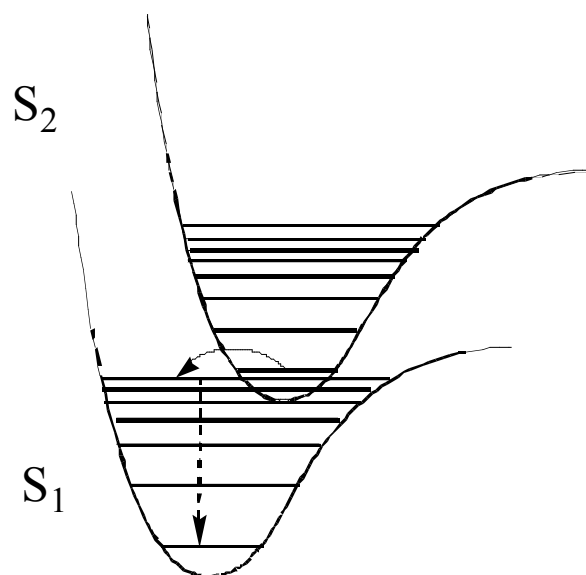
Symmetry and spin forbidden transitions are very weak (ϵ 10⁻⁵ -1)

Jablonski State Diagram



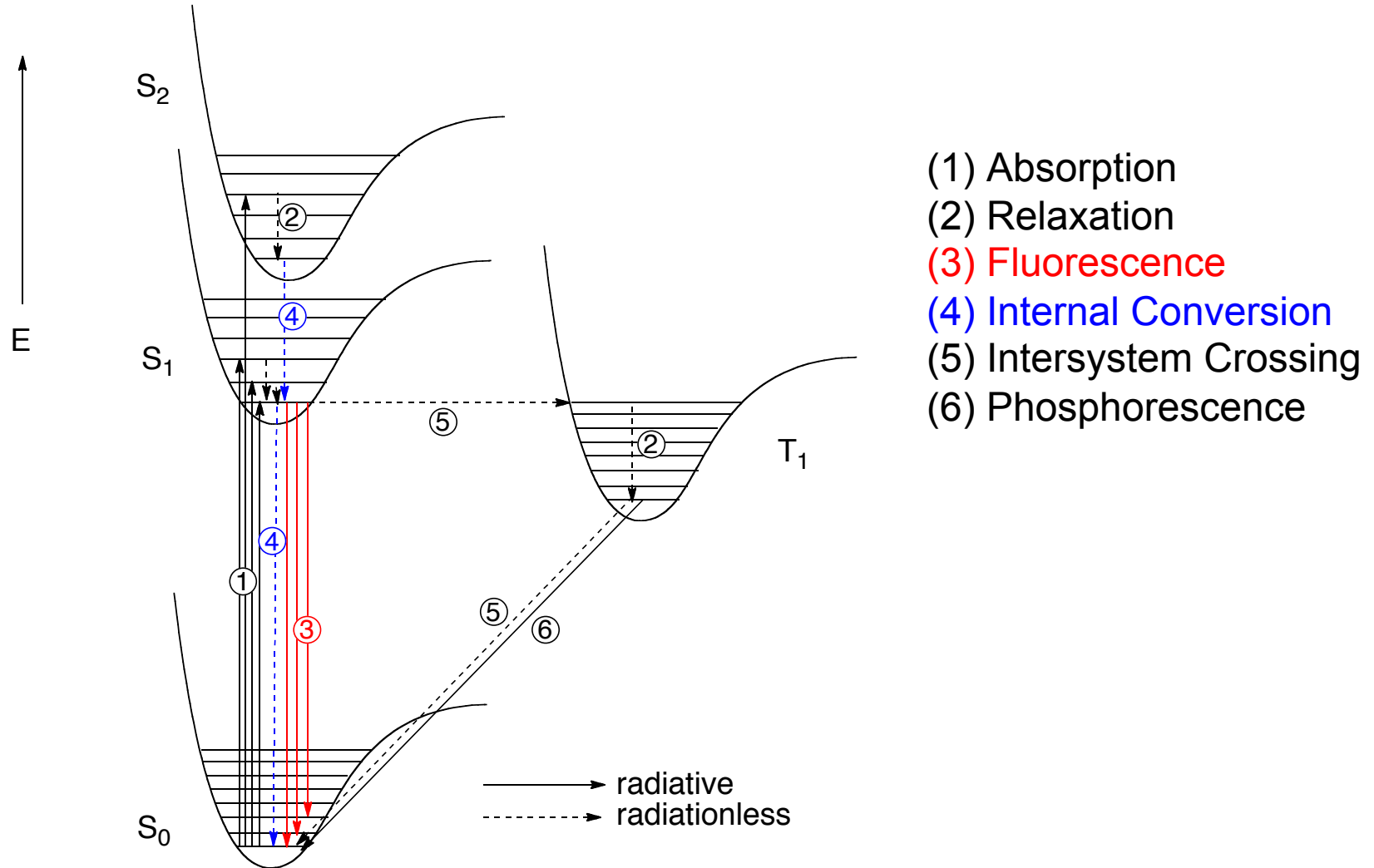
Internal Conversion: Transition between two surfaces having the same multiplicity

Rate k_{IC} depends on energy difference between surfaces



Internal conversion is usually fast if vibrational level 0 of S_{x+1} state overlaps with vibrational level of S_x state. This is typically the case for $x > 1$ ($k'_{IC} > 10^9 \text{ s}^{-1}$). However, it is not the case for $S_1 \rightarrow S_0$ transitions, which is substantially slower ($k_{IC} < 10^6 \text{ s}^{-1}$).

Jablonski State Diagram



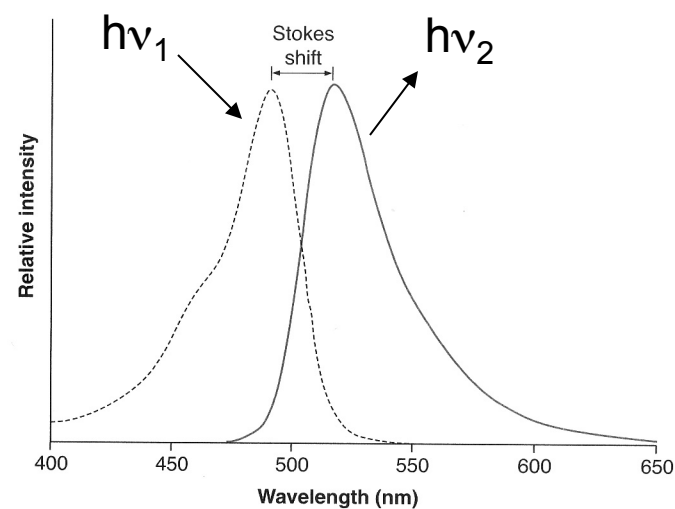
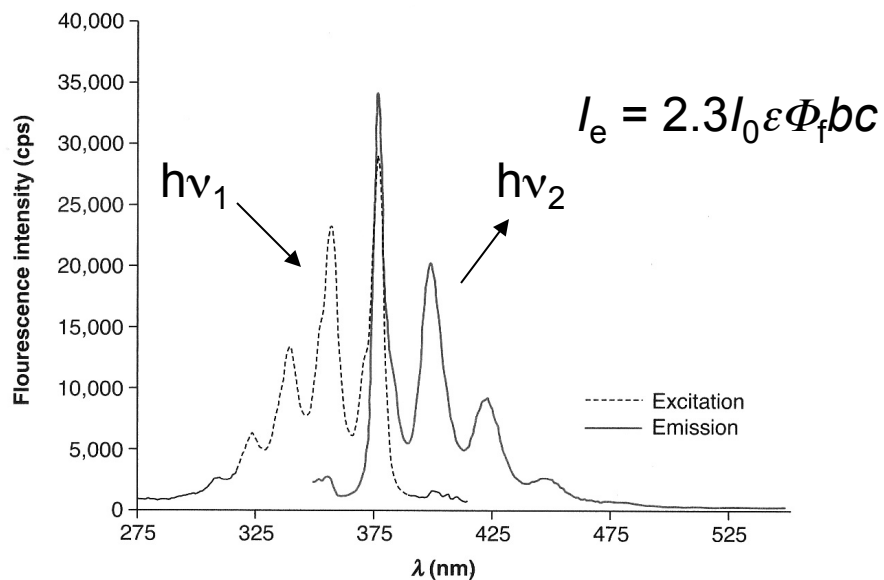
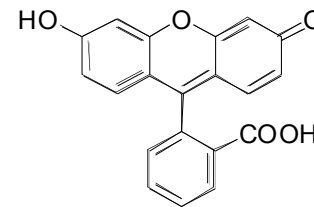
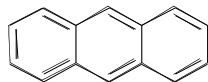
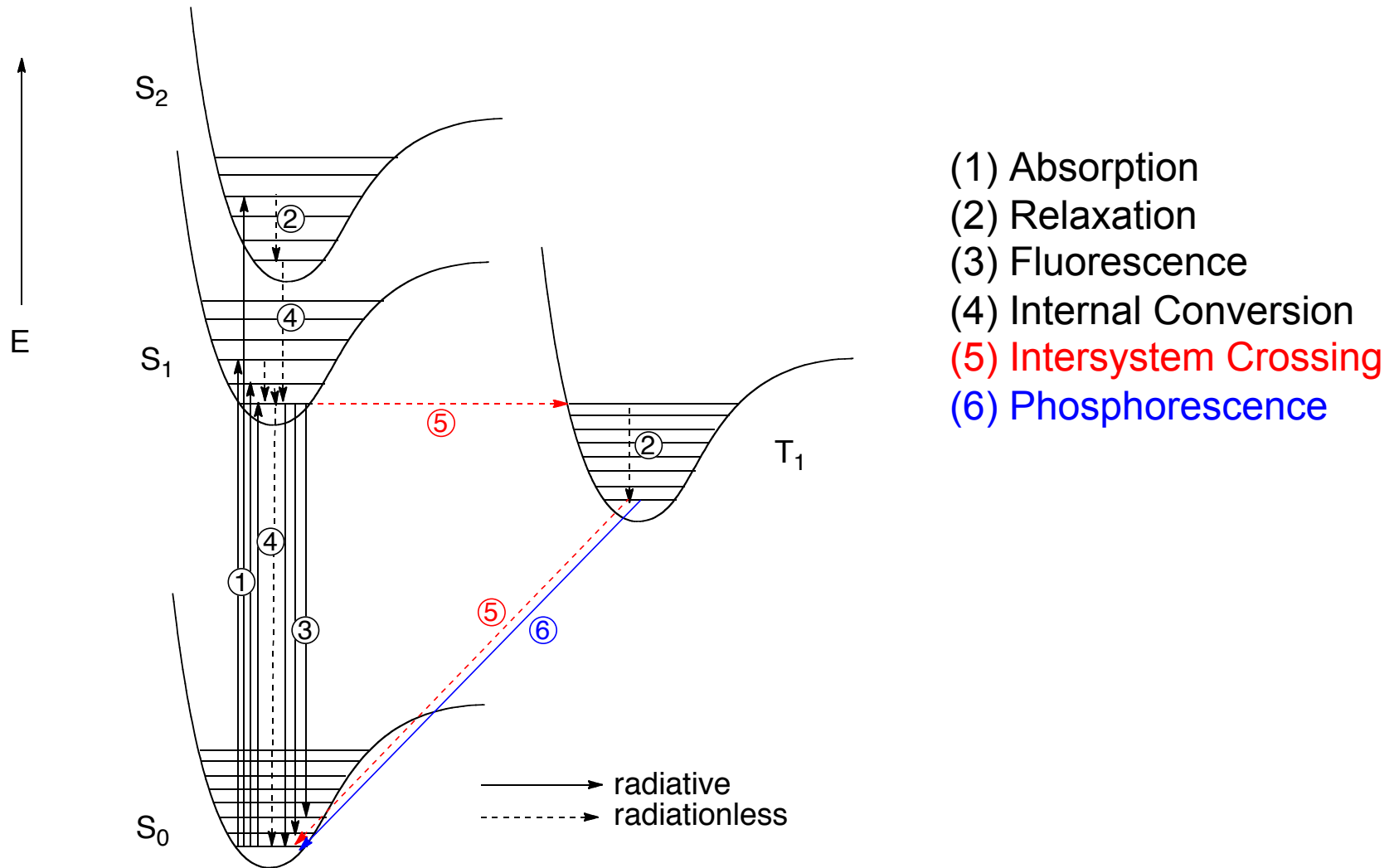


Figure 16.5
 Overlay of the emission and excitation spectra of anthracene. Both are taken in toluene.

Excitation and Emission Spectrum of Fluorescein

- I_e Intensity of emitted light
- I_0 irradiation intensity
- ϵ extinction coefficient
- Φ_f fluorescence quantum yield
- b path length of cell
- c concentration

Jablonski State Diagram



Intersystem Crossing

Crossing of surfaces with different spin multiplicity

singlet \rightarrow triplet	$S_1 \rightarrow T_1, T_2$	non-radiative
triplet \rightarrow singlet	$T_1 \rightarrow S_0$	non-radiative or radiative (phosphorescence)

1) T_1 lower than S_1 (Hund's Rule)

2) Intersystem crossing involves

spin flip \leftrightarrow **change in spin angular momentum**

quantum mechanically forbidden

\Rightarrow slow

3) Intersystem crossing is fast (allowed)

if **change in spin angular momentum** is accompanied by
change in orbital angular momentum

\Rightarrow **total angular momentum conserved**

El Sayed's Rules

Predict, whether intersystem crossing in molecules without heavy atoms (molecules only containing 1st and 2nd row elements H, C, N, O) is allowed (favorable) or forbidden (unfavorable)

Transition between excited states

$^1(n, \pi^*) \leftrightarrow ^3(n, \pi^*)$ forbidden

$^1(\pi, \pi^*) \leftrightarrow ^3(\pi, \pi^*)$ forbidden

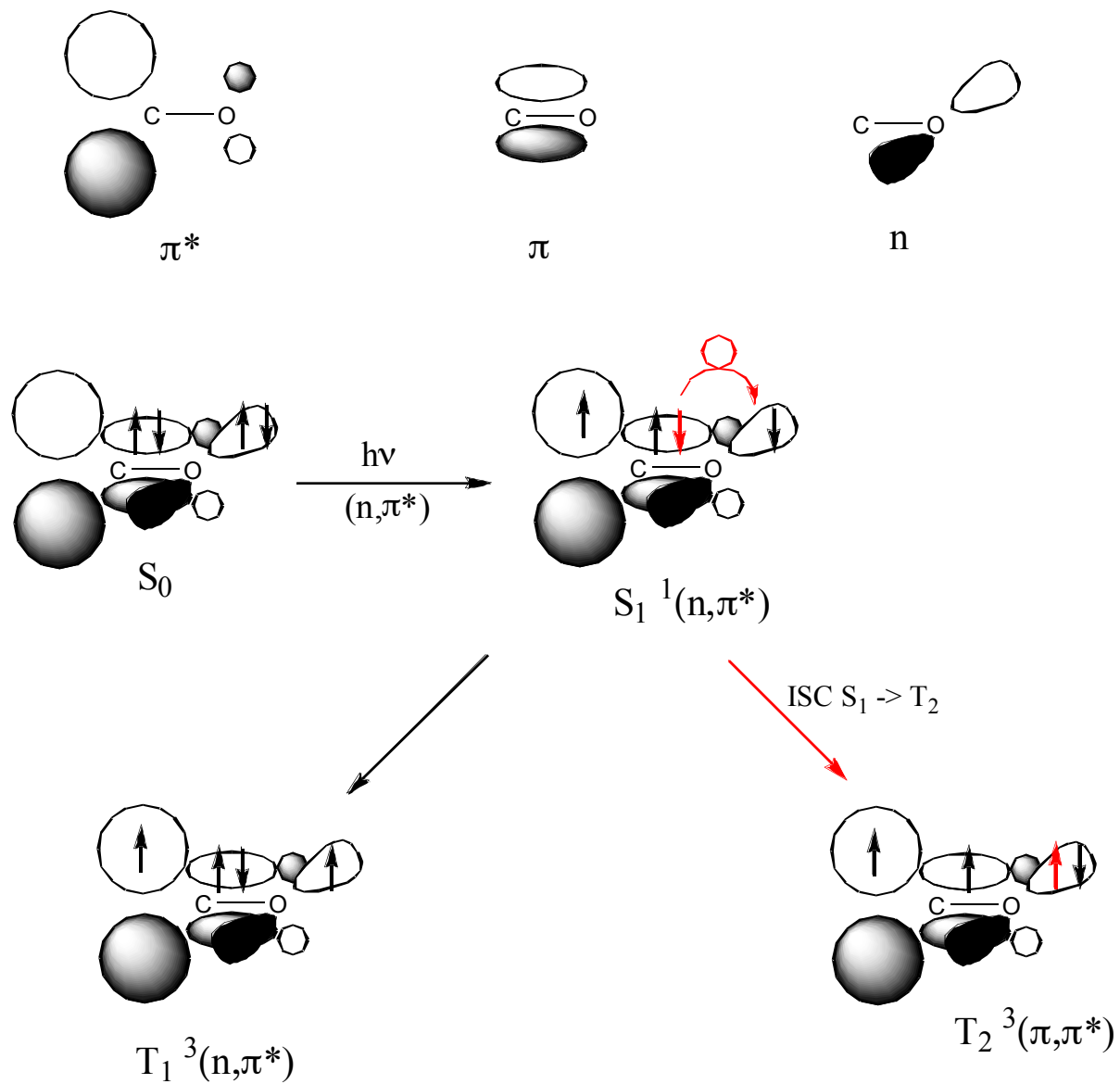
$^1(n, \pi^*) \leftrightarrow ^3(\pi, \pi^*)$ allowed

$^1(\pi, \pi^*) \leftrightarrow ^3(n, \pi^*)$ allowed

$^3(n, \pi^*) \leftrightarrow$ ground state allowed

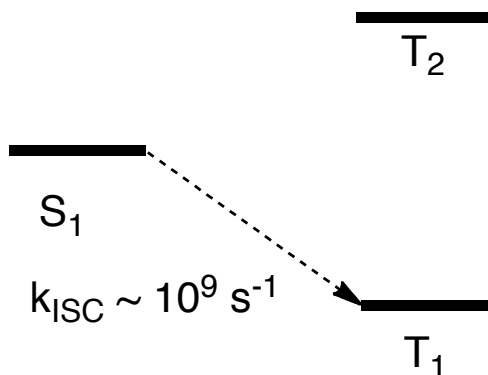
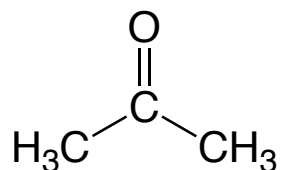
$^3(\pi, \pi^*) \leftrightarrow$ ground state forbidden

Intersystem Crossing of Carbonyl Compounds Spin-Orbit Coupling

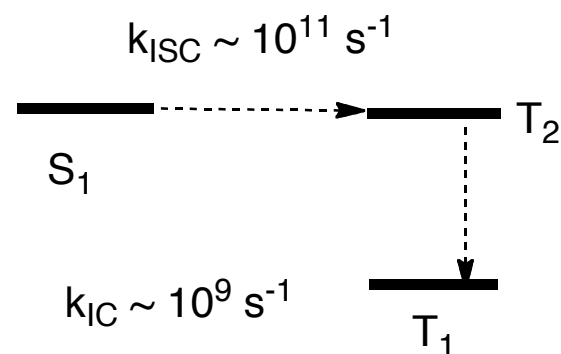
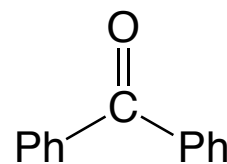


Rate constant of ISC depends on energy difference between S_1 and T_1/T_2

Strongly endotherm \rightarrow no intersystem crossing
Fastest if slightly exotherm or equal in energy



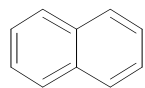
$$k_{ISC} \sim k_{IC} (S_0 \rightarrow S_1)$$



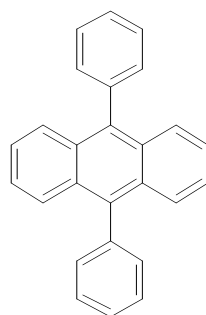
$$k_{ISC} \gg k_f \text{ or } k_{IC} (S_1 \rightarrow S_0)$$

Examples of Intersystem Crossing Rate Constants

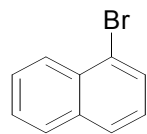
k_{ST} in s^{-1}



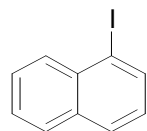
5×10^6



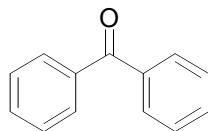
$< 10^7$



10^9



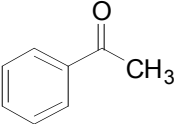
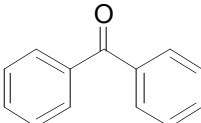
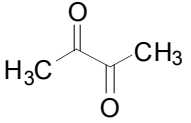
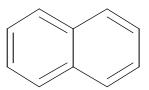
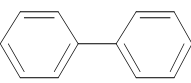
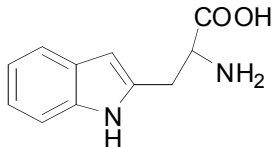
10^{10}



10^{11}

Heavy Atom Effect

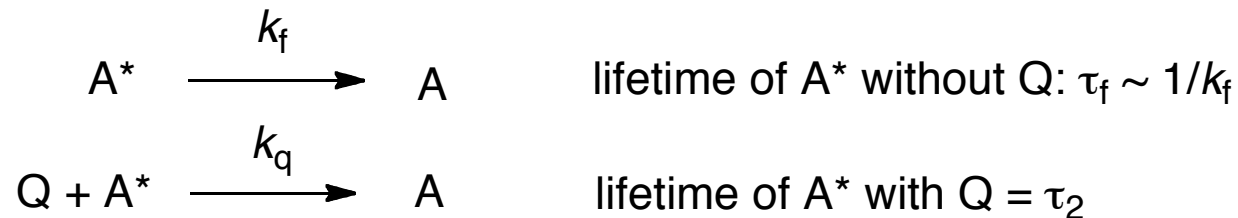
Examples of Phosphorescence Lifetimes of Organic Compounds In Ethanol at 77K

	τ in s	λ_{em} in nm
	0.007	415
	0.007	445
	0.002	507
	2.3	515
	4.2	460
	6.6	440

Analytical Chemistry (1973) 45, 381.

Quenching

- Decay of excited state induced by a collision with another molecule (quencher). **Bimolecular process.**



$$1/\tau_2 = k_f + k_q [Q] = 1/\tau_f + k_q [Q] \quad (\text{Stern-Volmer Equation})$$

- Chemical quenching:** Energy is transferred to quencher and converted into chemical energy. Quencher undergoes a chemical reaction.
- Physical quenching:**
- self-quenching* or *impurity quenching*:
energy transfer, electron transfer or heavy-atom quenching (accelerated decay of excited state upon collision with a molecule (e.g. solvent) containing a heavy atom (3rd row or higher)).

Eximer Spectrum of 9-Methylantracene

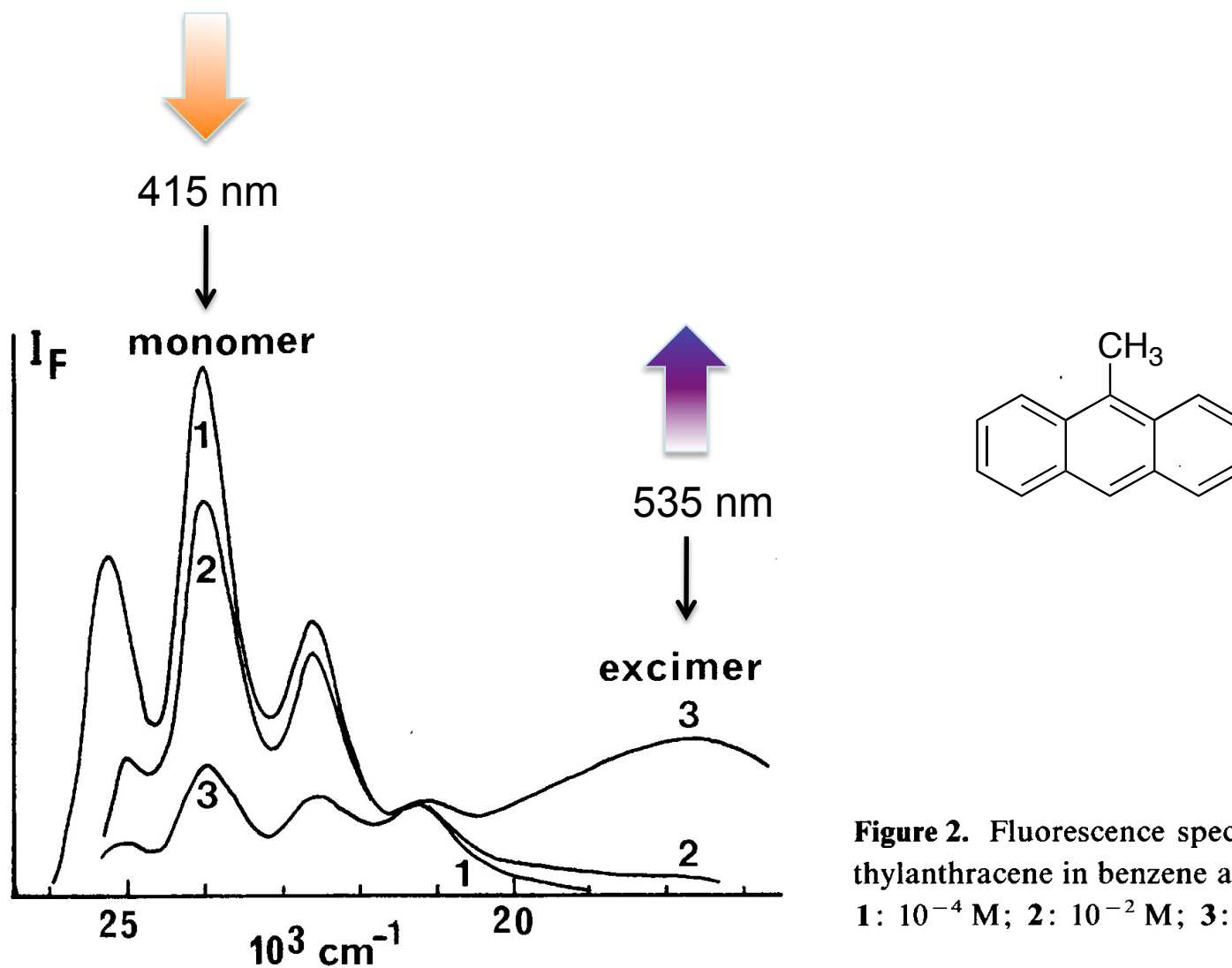


Figure 2. Fluorescence spectra of 9-methylantracene in benzene at R.T.; conc. 1: 10^{-4} M ; 2: 10^{-2} M ; 3: $2 \times 10^{-1} \text{ M}$.

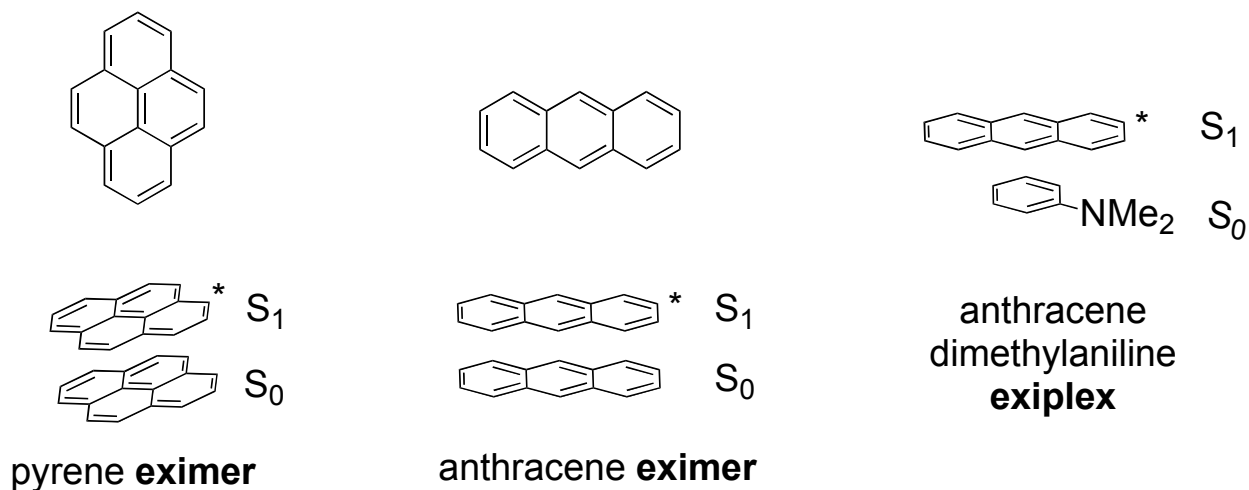
(From: Brinks, J. B. & Aladekomo, J. B., *Photochem. Photobiol.*, **1963**, 2, 415-418)

Exiplex: Excited state complex or absorption complex. Complex between an excited state and a ground state molecule.

Eximer: Complex between two identical molecules of which one is in the excited state and the other in the ground state

Stabilized by *induced dipole-dipole interactions or dispersion interactions*, due to the high polarizability of the excited state, and by *donor-acceptor interactions*

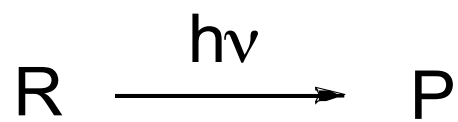
Eximers are often observed for polyaromatic compounds such as anthracene and pyrene and can be identified in the fluorescence spectra of both compounds. The maximum of the emission spectrum of the eximer is shifted to higher wavelength (lower energy) relative to that of the monomeric excited state.



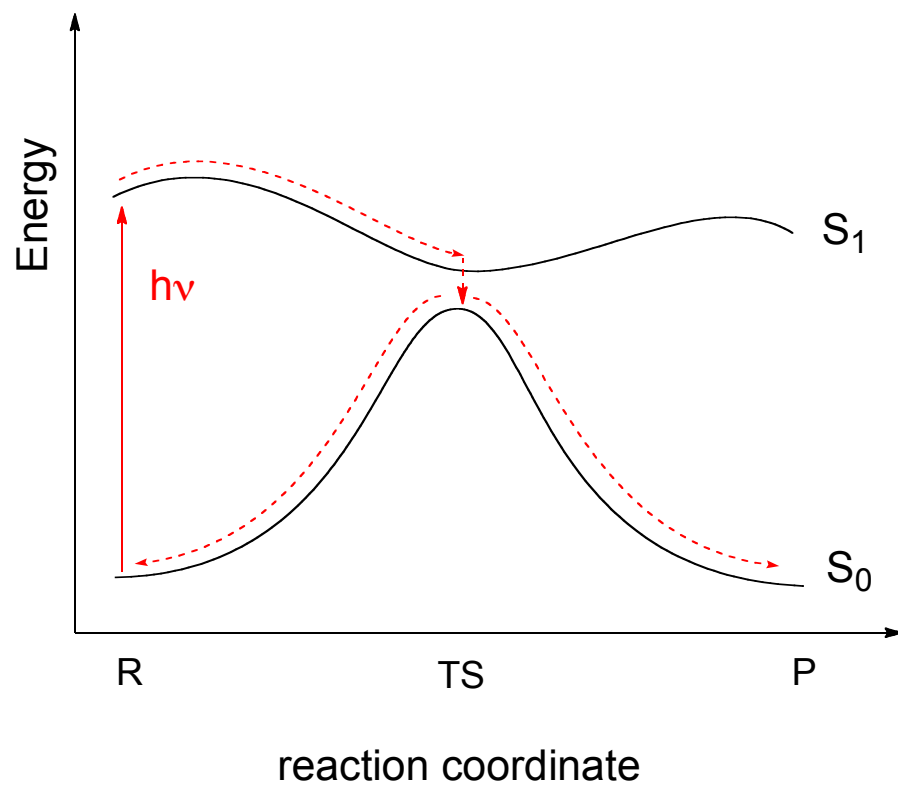
Common Organic and Inorganic Triplet Sensitizer and Triplet Energy E_T

MOLECULE	E_T	
	kJ/mol	kcal/mol
mercury	472	113
pyridine	355	85
benzene	351	84
anisole	339	81
acetone	326	78
benzotrile	322	77
benzaldehyde	301	72
benzophenone	288	69
biphenyl	276	66
<i>trans</i> -stilbene	209	50
anthracene	180	43

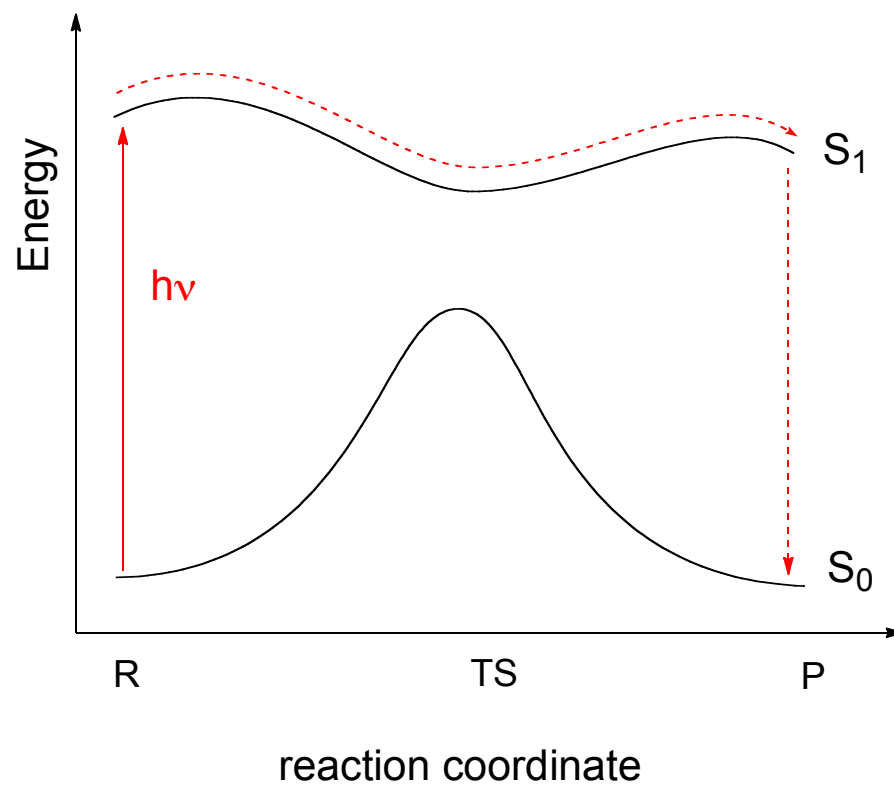
From Kavarnos & Turro, *Chem. Rev.* **1986**, *86*, 401



Diabatic photochemical process



Adiabatic photochemical process



Quantum Yield

$$\Phi_n = \frac{\text{number of molecules that undergo photochemical process } n}{\text{number of photons absorbed}}$$

Fluorescence quantum yield Φ_f

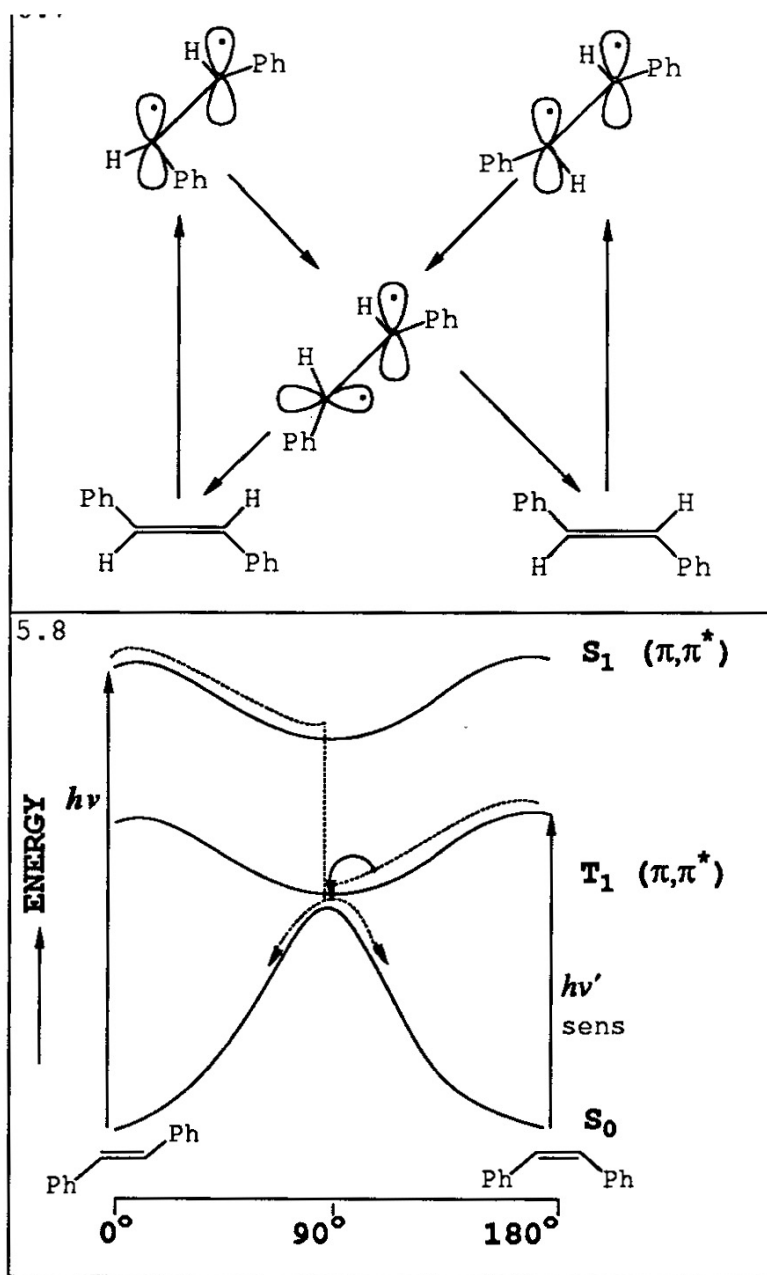
$$\Phi_f = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} < 1$$

Quantum yield of a photochemical reaction Φ_r

$$\Phi_r = \frac{\text{number of product molecules formed}}{\text{number of photons absorbed}}$$

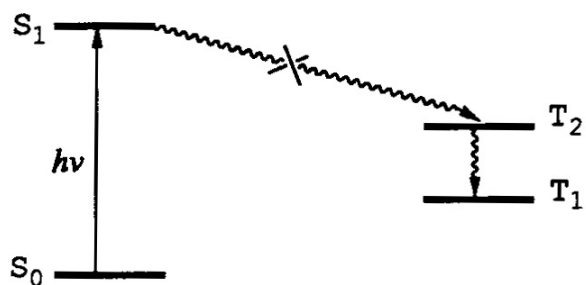
Typically ≤ 1 but can be \gg than 1, e.g. in photo polymerization or light initiated radical chain reactions.

Mechanism of the Photoinduced *cis-trans* Isomerization of Stilbene (PhCH=CHPh)

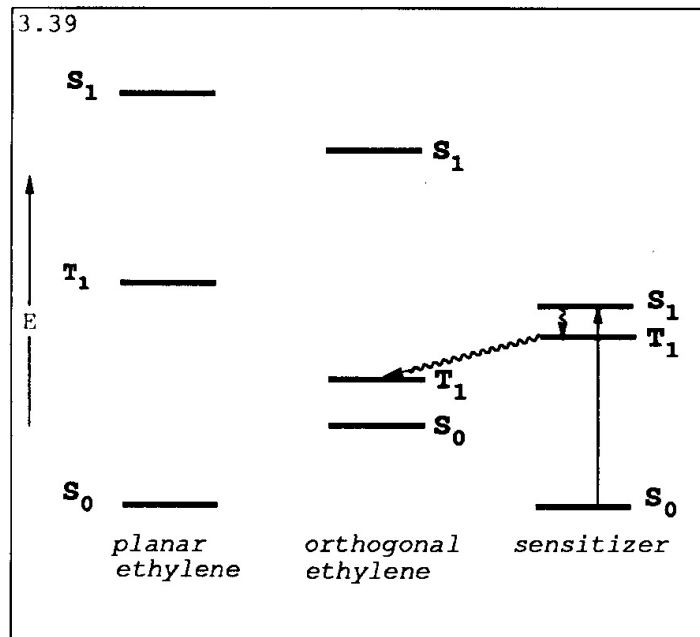
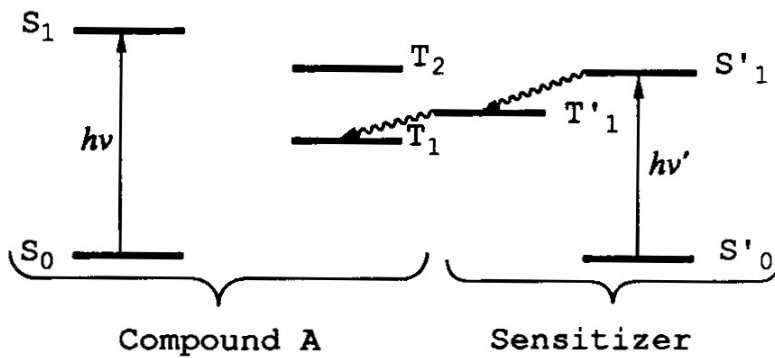


Triplet Sensitization of Organic Molecules

3.37 DIRECT IRRADIATION: EXCITATION $h\nu$



SENSITIZATION: EXCITATION $h\nu' < h\nu$



Dependence of the photostationary state of the triplet sensitized cis-trans stilbene isomerization on the triplet energy E_T of the sensitizer

