Molecular Photochemistry

What is molecular photochemistry?

Is a science that is concerned with the description of physical and chemical processes
Induced by the absorption of photons / light.

The **notion of structure, energetics, and dynamics** are crucial for understanding of
molecular photochemistry.

Photochemical Reactions

Differences to thermal reaction

• The **initiating activation of a photoreaction** is mainly provided by the **absorption of light**; activation of a **thermal reaction** is mainly provided by **heat**.

• The **electronic distribution** and **nuclear configuration** of a photochemically activated molecule generally **differ substantially** from those of a thermally activated one.
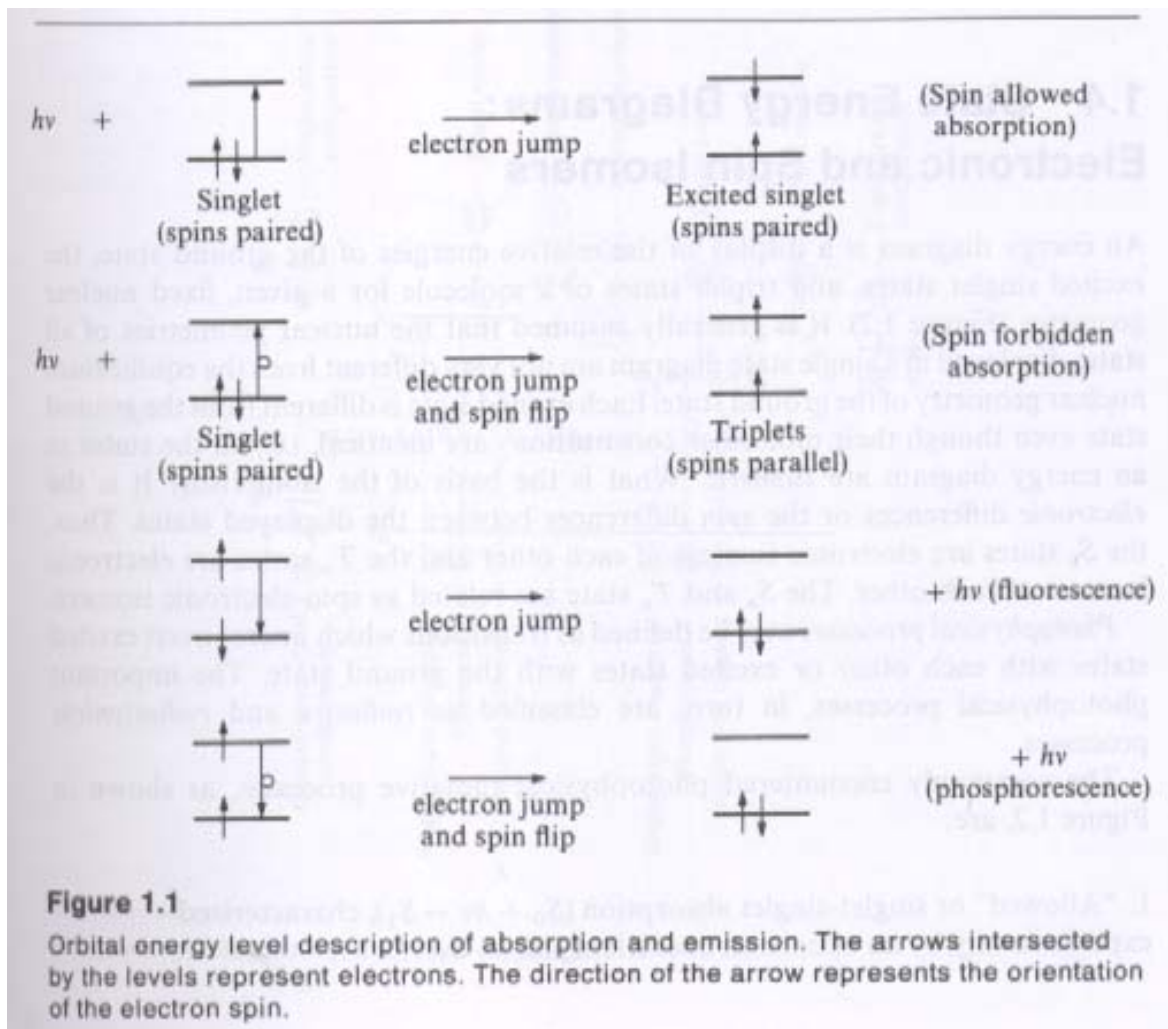
electronic isomer of the ground state molecule

• The **thermodynamically favorable products** accessible to a photoexcited molecule **are far greater** than those accessible to a ground state molecule.

possesses an excess energy content

Chronologically of Photoreactions

• **<u>absorptive act</u>** – **interaction of photon and molecule**, resulting in absorption of photon and formation of an **electronically excited molecule**

• **<u>primary photochemical processes</u>** – involving electronically excited molecules

• **<u>secondary or "dark" processes</u>** – occur from the intermediates formed by the primary photochemical process

Electronic Excitation and De-excitation of Organic Molecules

Figure 1.1
Orbital energy level description of absorption and emission. The arrows intersected by the levels represent electrons. The direction of the arrow represents the orientation of the electron spin.

S_0 - singlet ground state; S_1 - lowest singlet excited state, T_1 - lowest triplet excited state

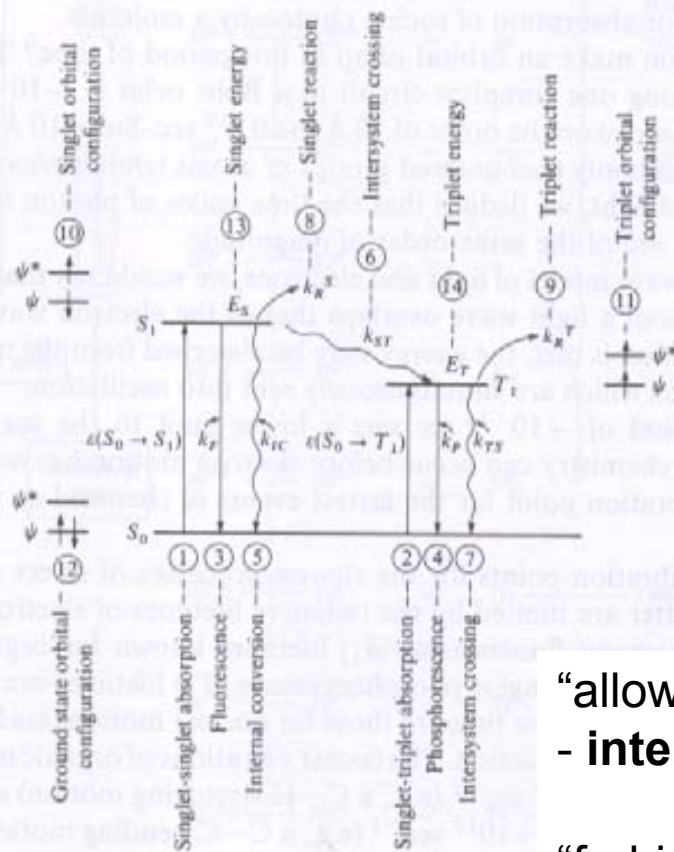# State Energy Diagrams: Electronic and Spin Isomers

Figure 1.2
State energy diagram. A standard paradigm.

allowed: singlet-singlet absorption
forbidden: singlet-triplet absorption
allowed: singlet-singlet emission
forbidden: triplet-singlet emission

"allowed" transitions between states of same spin
- **internal conversion**

"forbidden" transitions between excited states of
Different spin – **intersystem crossing**

"forbidden" transitions between triplet states and
The ground state – **intersystem crossing**

Calibration Points for Molecular Dimensions and Motions

atoms or groups that are involved in absorption or photoreactions are **2 – 10 Å**

a **particle / photon**, traveling at the speed of light, **moves 3 x 10^{18} Å / sec**

if we associate the wavelength of light with the size of a photon, than **blue light** have **"the size" of 4000 Å**

"size" of photon is their **ability to collide with a molecule**

time it takes a **blue photon to pass a point in space** $t = d/v$ is ~ **10^{-15} sec**

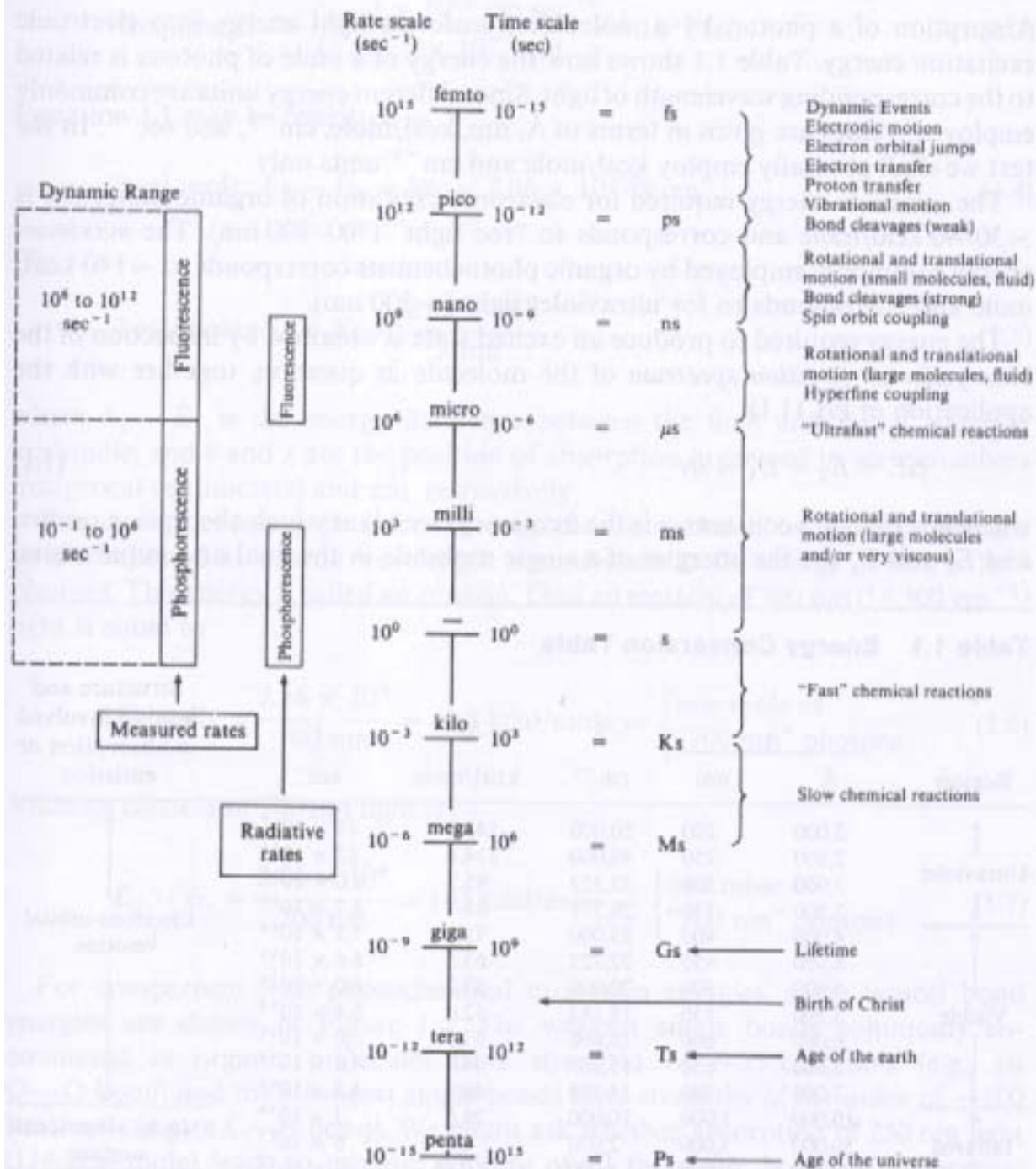~ **10^{-15} sec** is maximum **interaction time**

velocity of an electron is **10^{-16} sec**

electron may move on the order of **10 Å** in **10^{-15} sec**

10 Å is the size of commonly used chromophores

wave model of light and electrons:
    frequency of the oscillation of a **light wave overlaps** that of **the electron wave**

Rate scale (sec^{-1})		Time scale (sec)			Dynamic Events
10^{15}	femto	10^{-15}	=	fs	Electronic motion
					Electron orbital jumps
					Electron transfer
					Proton transfer
10^{12}	pico	10^{-12}	=	ps	Vibrational motion
					Bond cleavages (weak)
					Rotational and translational motion (small molecules, fluid)
10^9	nano	10^{-9}	=	ns	Bond cleavages (strong)
					Spin orbit coupling
					Rotational and translational motion (large molecules, fluid)
10^6	micro	10^{-6}	=	μs	Hyperfine coupling
					"Ultrafast" chemical reactions
10^3	milli	10^{-3}	=	ms	Rotational and translational motion (large molecules and/or very viscous)
10^0		10^0	=	s	
					"Fast" chemical reactions
10^{-3}	kilo	10^3	=	Ks	
					Slow chemical reactions
10^{-6}	mega	10^6	=	Ms	
10^{-9}	giga	10^9	=	Gs	Lifetime
					Birth of Christ
10^{-12}	tera	10^{12}	=	Ts	Age of the earth
10^{-15}	penta	10^{15}	=	Ps	Age of the universe

Dynamic Range

10^6 to 10^{12} sec^{-1} — Fluorescence

10^{-1} to 10^6 sec^{-1} — Phosphorescence

Fluorescence

Phosphorescence

Measured rates

Radiative rates

longest fluorescence (S_1) lifetimes for organic molecules are **~10^{-6} sec**

longest phosphorescence (T_1) lifetimes for organic molecules are **30 sec**

fastest vibration of organic molecules occur with a frequency of **10^{13} sec^{-1}**

slowest vibration of organic molecules occur with a frequency of **10^{12} sec^{-1}**

in **~10^{-6} sec** an organic molecule will have executed **10^6 – 10^7 vibrations**

in **30 sec** an organic molecule will have executed **10^{13} – 10^{14} vibrations**

plenty of time

Calibration Points for Molecular Energetics and Reaction Dynamics

absorption of a photon by a molecule transforms light energy into electronic excitation energy

Table 1.1 Energy Conversion Table

	λ		$\bar{\nu}$	ΔE	ν	Structure and motion involved in absorption or emission
Region	Å	nm	cm^{-1}	kcal/mole	sec^{-1}	
Ultraviolet ↑↓	2,000	200	50,000	143.0	15×10^{15}	
	2,500	250	40,000	114.4	12×10^{15}	
	3,000	300	33,333	95.3	1.0×10^{15}	
	3,500	350	28,571	81.7	8.7×10^{14}	Electrons-orbital motion
	4,000	400	25,000	71.5	7.5×10^{14}	
	4,500	450	22,222	63.5	6.6×10^{14}	
	5,000	500	20,000	57.2	6.0×10^{14}	
Visible	5,500	550	18,182	52.0	5.4×10^{14}	
	6,000	600	16,666	47.7	5.0×10^{14}	
	6,500	650	15,385	44.0	4.6×10^{14}	
	7,000	700	14,286	40.8	4.2×10^{14}	
Infrared ↑↓	10,000	1,000	10,000	28.6	3×10^{14}	Nuclei-vibrational motion
	50,000	5,000	2,000	5.8	6×10^{13}	
	100,000	10,000	1,000	2.86	3×10^{13}	
Microwave	10^8	10^7	10	3×10^{-2}	3×10^{11}	Electron spin-precessional motion
	10^{10}	10^9	0.1	3×10^{-4}	3×10^9	
Radiowave	10^{12}	10^{11}	0.001	3×10^{-6}	3×10^7	Nuclear spin-precessional motion

minimum energy required is ~30-40 kcal/mol – "red light" (**700 – 800 nm**)

maximum energy commonly used is ~149 kcal/mol – "UV light" (**200 nm**)

energy required to produce an excited state is obtained by inspection of the **absorption** and **emission spectra**

$$\Delta E = E_2 - E_1 = h\nu$$

h = Planck's constant
v = Frequency at which absorption occurs
E_2 / E_1 = Energies of the molecule in the final (2) and initial (1) states

the **position** of an absorption band is often expressed by its
wavelength in nanometer
wave number in reciprocal centimeters
frequency in sec^{-1}

300 nm: **frequency (ν) = c / λ = 3 x 10^{10} cm sec^{-1} / 3 x 10^{-5} cm**
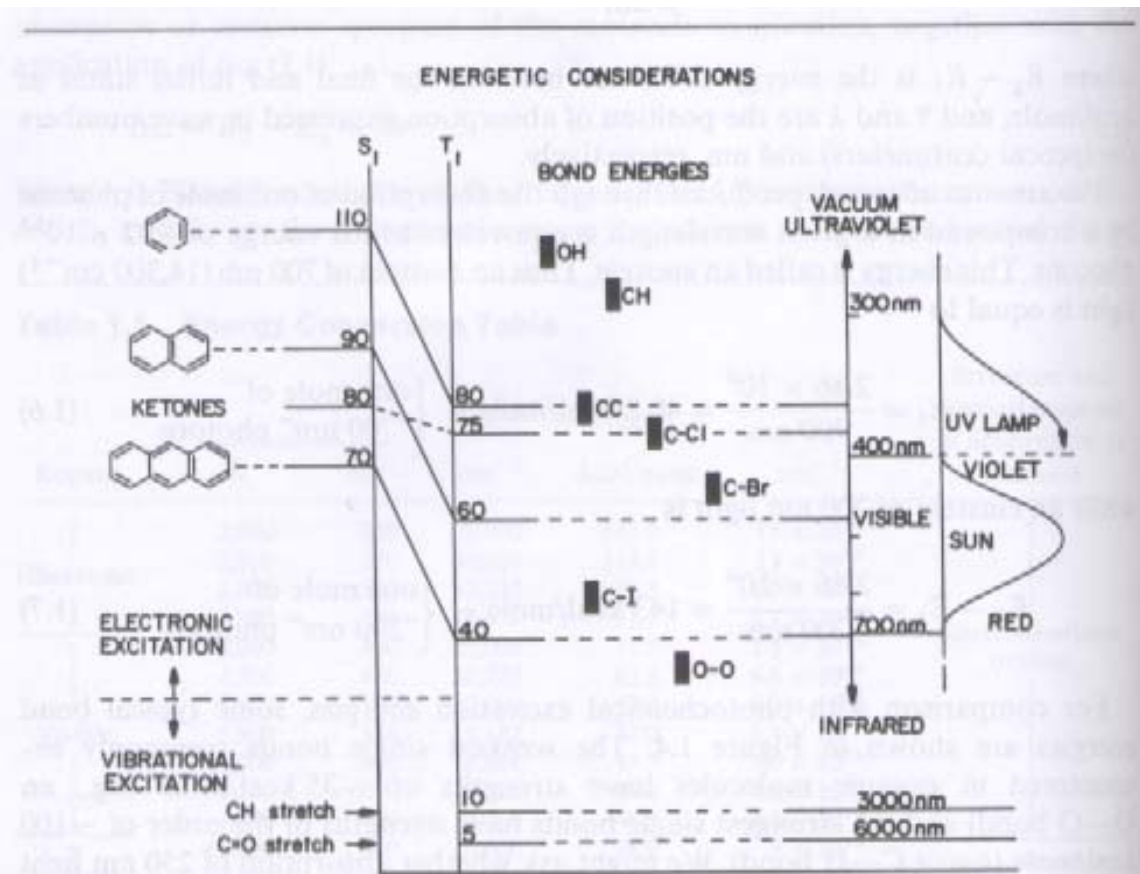
Figure 1.4

Some energetic considerations. The "energy spread" of conventional photochemistry is compared to the emission spectrum of the sun. Vibrational energies are shown for comparison.

Reaction Dynamics

the **energy of activation (E$_a$)** is the quantity of interest

Often rates are represented in term of two factors:

    A (sec^{-1}): the probability of a reaction from a state with the minimum energy

    E$_a$ (kcal / mol): the minimum energy required for a reaction

$$\textbf{Rate = A exp} - \textbf{E}_a \textbf{ / RT = A x 10}^{-Ea/(0.0046T)}$$

Maximal values of A are 10^{12} to 10^{15} sec^{-1} (unimolecular reactions)
Minimal values of A are 10^6 to 10^8 sec^{-1} (bimolecular reactions)

A reflects entropy of a reaction: if the entropy of **reaction is highly positive**
- increase in freedom of the particles of the system -
then A is very large

Nuclear Geometry of Electronically Excited States

nuclear shape or geometry of an electronically excited state such as

energy
electronic configuration
electronic spin

might be different from that of the ground state

sp^2 sp^3

H—C=O ground state Planar	H—C—O n, π* state Pyramidal
Formaldehyde	
H—C=C—H Ground state Planar	H—C—C—H n, π* excited state Pyramidal
Ethylene	also twisted
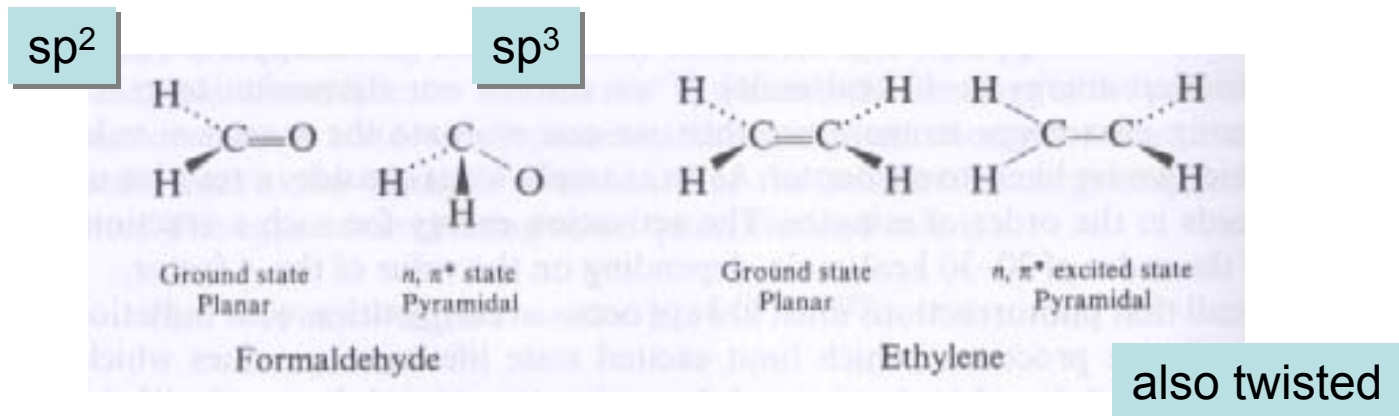
A number of interesting questions concerning **photochemical properties and reactions** arise:

1) Are the photochemical properties of S_1 and T_1 the same if they possess the same **two electron configurations**?

2) Do the photochemical properties of states of the **same spin but different electron configuration** differ?

3) What are the photochemical reactions for **different electronic spin isomers**?

An Energy Surface Description of Molecular Photochemistry

potential energy curves control **nuclear motion**

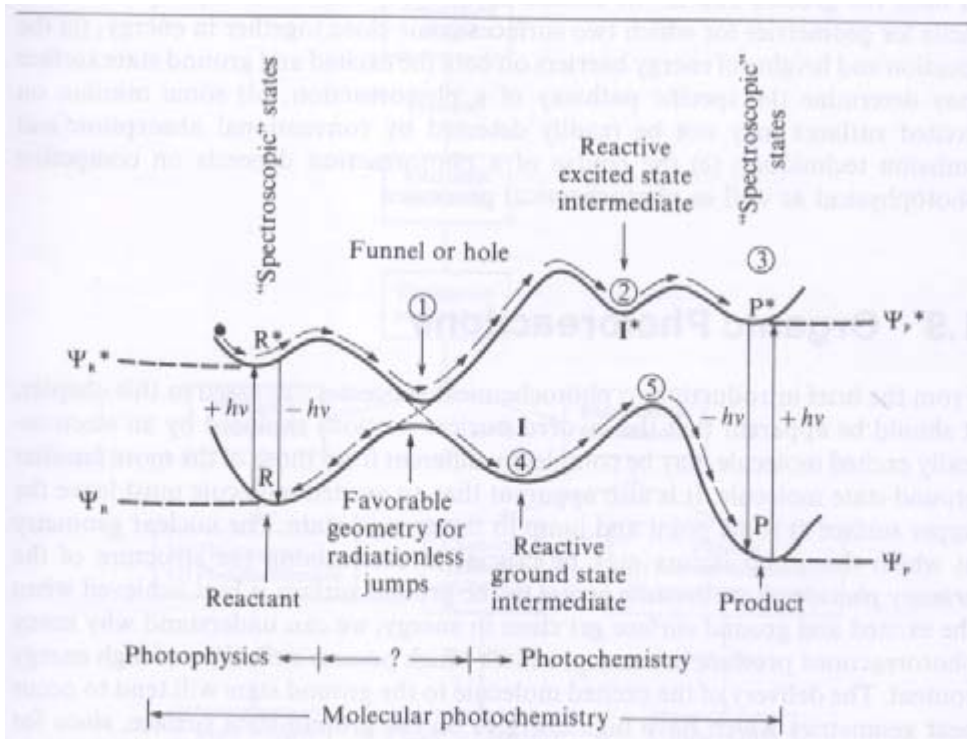**except** when two **surfaces come close together**

Figure 1.5

Schematic representation of a ground-state and excited-state surface. The arrows on the surface indicate the motion of a point which represents a molecule whose nuclear geometry is moving along the reaction coordinate.

each point represents a specific **nuclear geometry**

– horizontal axis

and a **specific energy**

– vertical axis

Summary
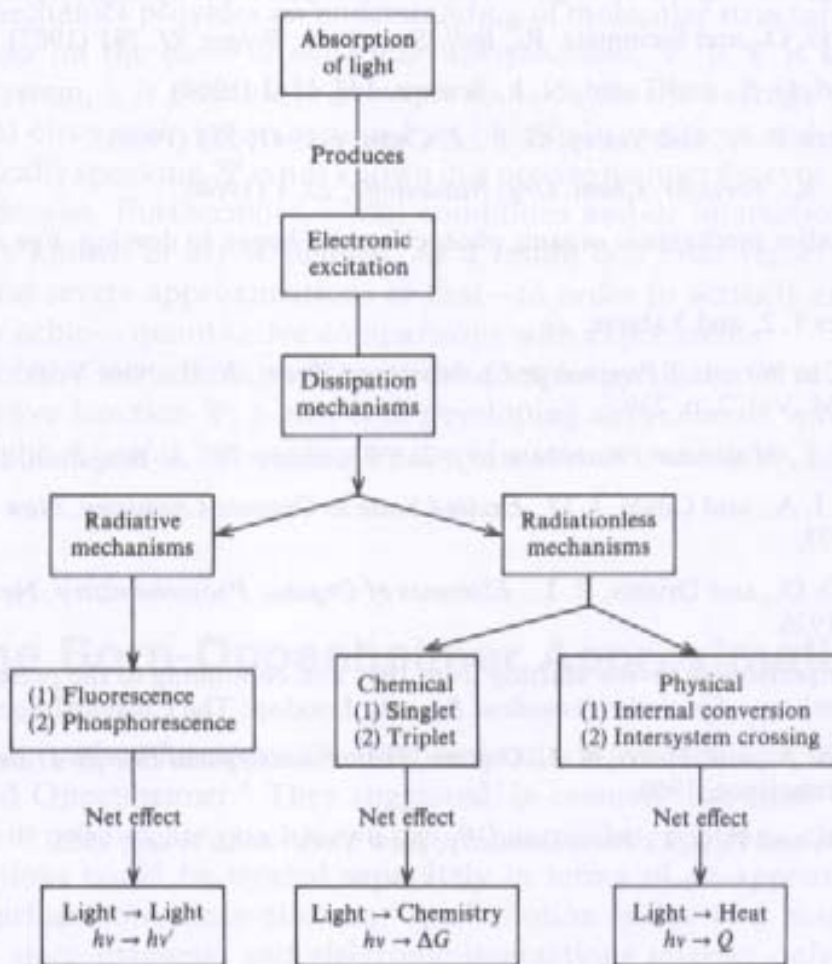
Scheme 1.1
Schematic of the network of processes of interest to a molecular photochemist.