

Molecular Photonics

Lecture 1.

Contact Info

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Organizational

- Exercises – once in two/three weeks.
Obligatory, 20% of the final grade.
Dr. Haim Weissman
- Exam – at the end of the course
- The lectures and additional material will be available online (FGS site) next week.

Motivation

- Light-matter interactions are amongst the most fundamental physical phenomena in Nature
- Photosynthesis
- Solar Energy Conversion
- OLEDs

What happens when light hits
organic molecule, metal complex,
nanoparticle?

LUMO

HOMO

Ground state

LUMO

HOMO

Excited state

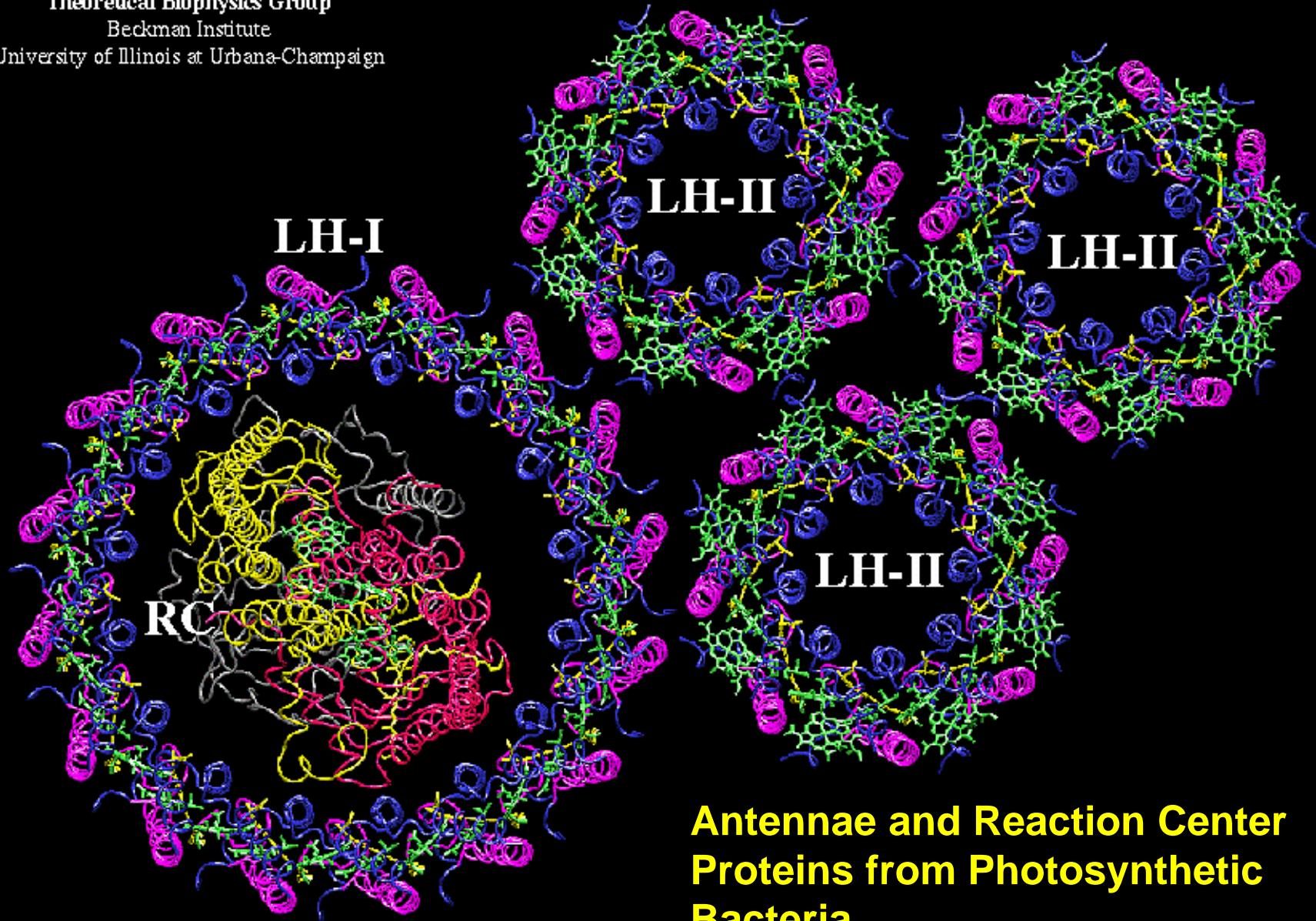


$h\nu$



Natural System

Theoretical Biophysics Group
Beckman Institute
University of Illinois at Urbana-Champaign





Unsustainable energy

Fossil fuels are hydrocarbons formed from the remains of dead plants and animals. These are burnt (CO₂ emission) to make our life comfortable. Will we have soon more dead plants and animals? See *the covers below*.



24 March 2006



3 April 2006



September 2006



INTERGOVERNMENTAL PANEL ON climate change



IPCC PRESS RELEASE

27 September 2013

Human influence on climate clear, IPCC report says

STOCKHOLM, 27 September - Human influence on the climate system is clear. This is evident in most regions of the globe, a new assessment by the Intergovernmental Panel on Climate Change (IPCC) concludes.

It is extremely likely that human influence has been the dominant cause of the observed warming since the mid-20th century. The evidence for this has grown, thanks to more and better observations, an improved understanding of the climate system response and improved climate models.

OLEDs

Sony 13" full color display



Outline of the course

- **Basics – excited states, absorption, emission, etc.**
- **Photoinduced Energy and Electron Transfer**
- OLEDs, Photosynthesis and Solar Energy Conversion

Expectations

- We cover most topics from organic/inorganic chemistry perspective
- We use equations but do not derive them
- This is not a course on quantum chemistry
- We start from basics
- Knowledge of organic chemistry is helpful

Literature

- Modern Molecular Photochemistry by Nicholas J. Turro, 1991
- **Principles of Molecular Photochemistry** by Turro et al., 2009

Vibrations and Simple Excitations

1. *Incandescence*: flames, lamps, carbon arc, limelight
2. *Gas excitations*: vapor lamps, lightning, auroras, some lasers
3. *Vibrations and rotations*: water, ice, iodine, blue gas flame

Transitions Involving Ligand Field Effects

-
4. *Transition metal compounds*: turquoise, many pigments, some fluorescence, lasers, and phosphors
 5. *Transition metal impurities*: ruby, emerald, red iron ore, some fluorescence and lasers

Transitions Between Molecular Orbitals

-
6. *Organic compounds*: most dyes, most biological colorations, some fluorescence and lasers
 7. *Charge transfer*: blue sapphire, magnetite, lapis lazuli, many pigments

Transitions Involving Energy Bands

-
8. *Metals*: copper, silver, gold, iron, brass, “ruby” glass
 9. *Pure semiconductors*: silicon, galena, cinnabar, diamond
 10. *Doped or activated semiconductors*: blue and yellow diamond, light-emitting diodes, some lasers and phosphors
 11. *Color centers*: amethyst, smoky quartz, desert “amethyst” glass, some fluorescence and lasers

Geometrical and Physical Optics

12. *Dispersive refraction, polarization, etc.*: rainbow, halos, sun dogs, green flash of sun, “fire” in gemstones
 13. *Scattering*: blue sky, red sunset, blue moon, moonstone, Raman scattering, blue eyes and some other biological colors
 14. *Interference*: oil slick on water, soap bubbles, coating on camera lenses, some biological colors
 15. *Diffraction*: aureole, glory, diffraction gratings, opal, some biological colors, most liquid crystals
-

Today

We talk about the language (slang) of molecular photonics:

- Basic principles
- Timescales
- Energies
- Nomenclature
- Pictorial representations

Photophysics vs. Photochemistry

Photophysics

No net changes in chemical bonds

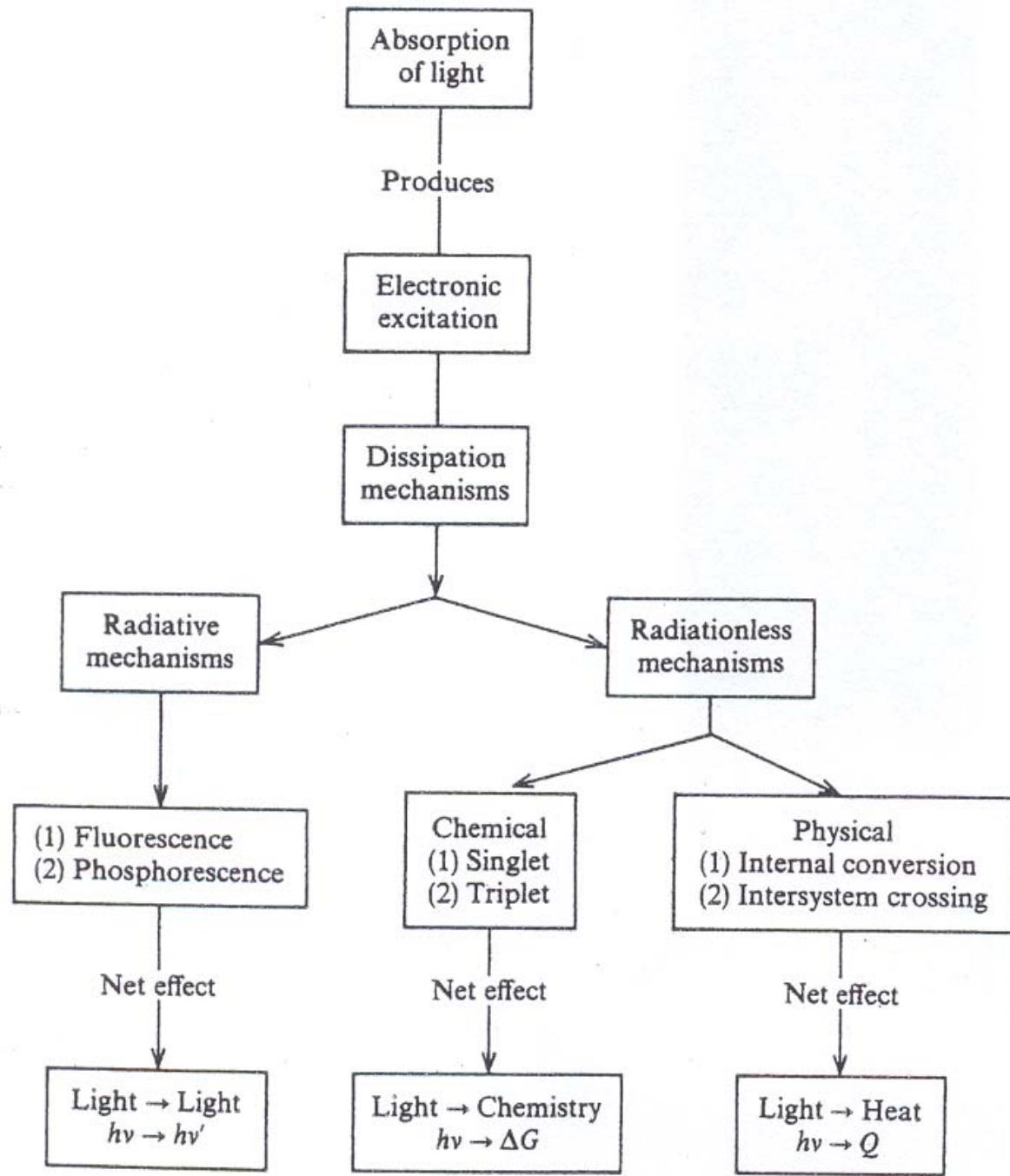
- Absorption
- Emission
- Photoinduced Energy and Electron Transfer

Photochemistry

Changes in chemical bonds

- Photoinduced reactions

Sometimes considered photochemistry



Electronic excitation and deexcitation

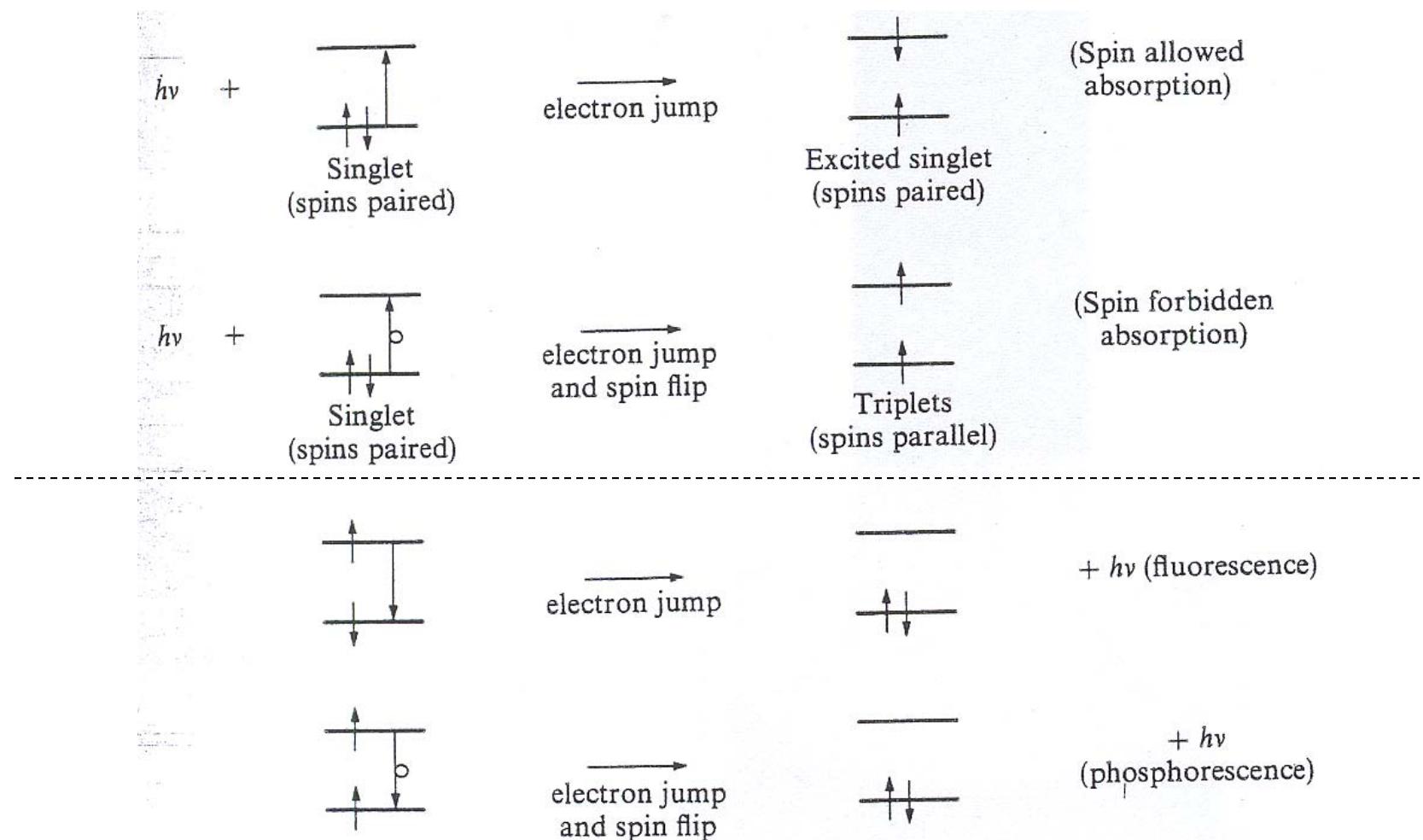
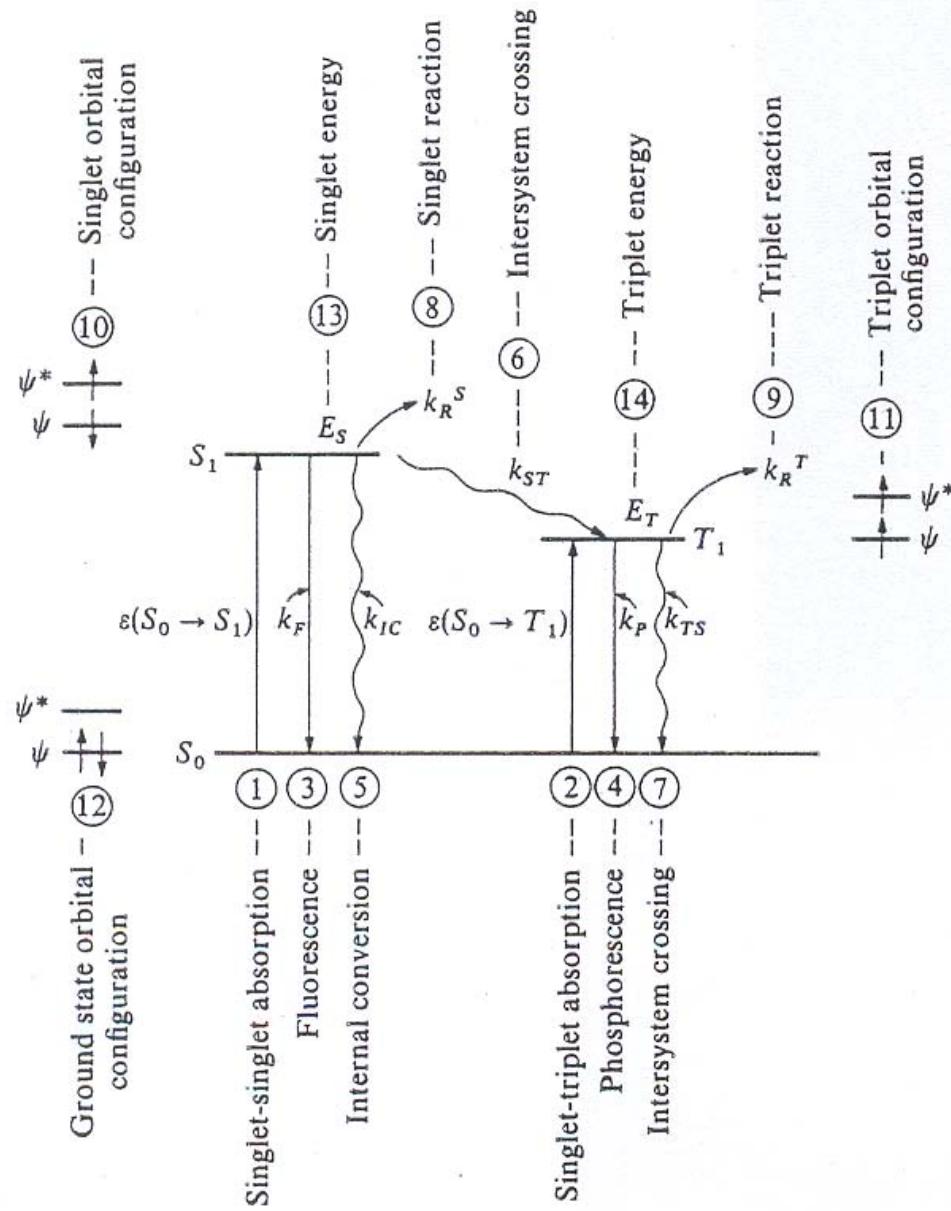


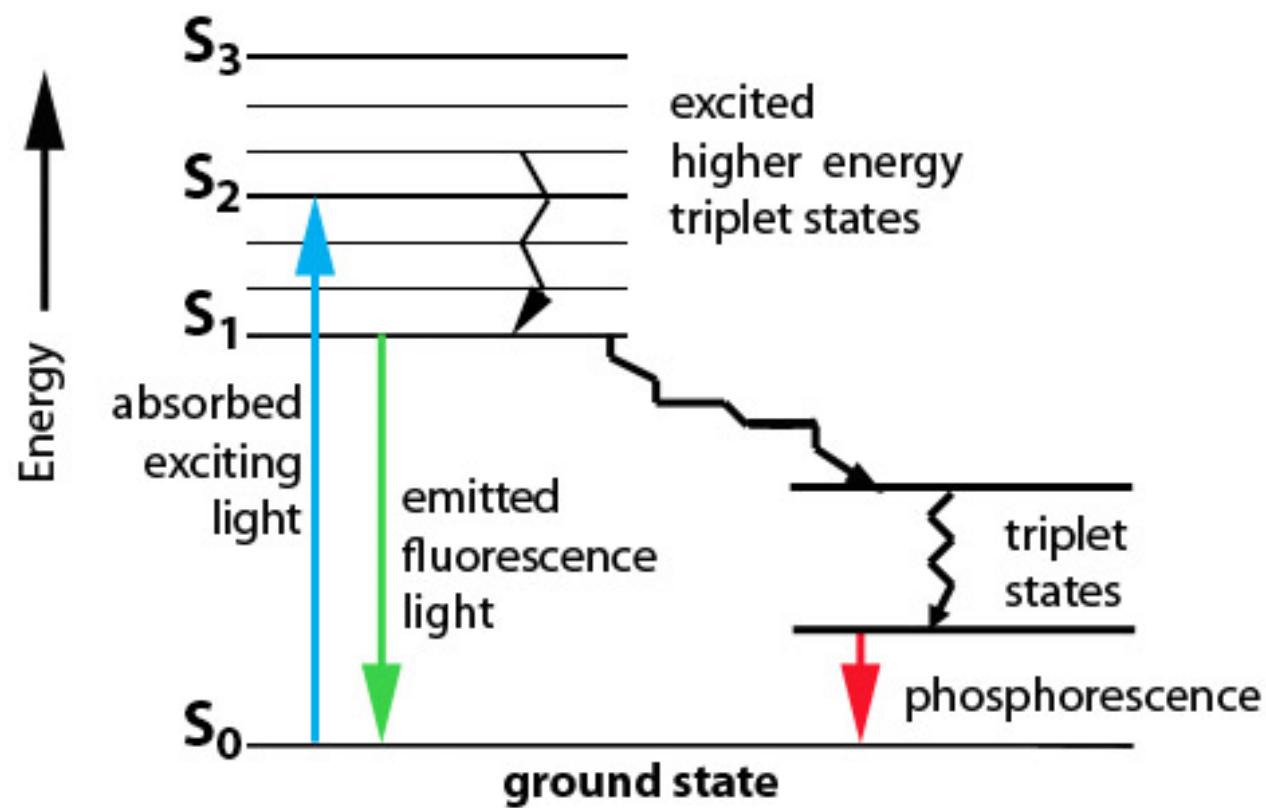
Figure 1.1

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.

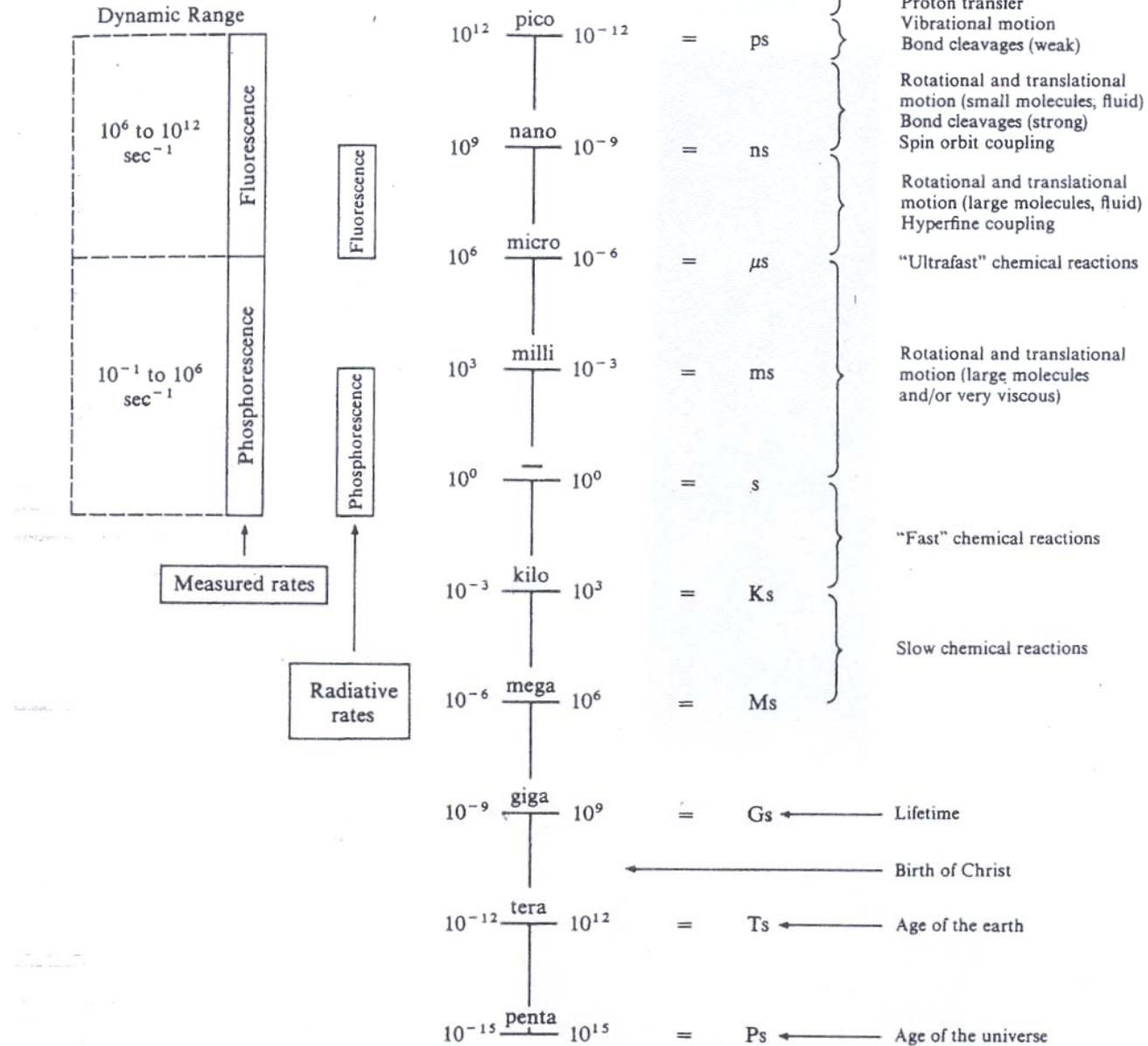
Energy Diagram, Basic Terminology



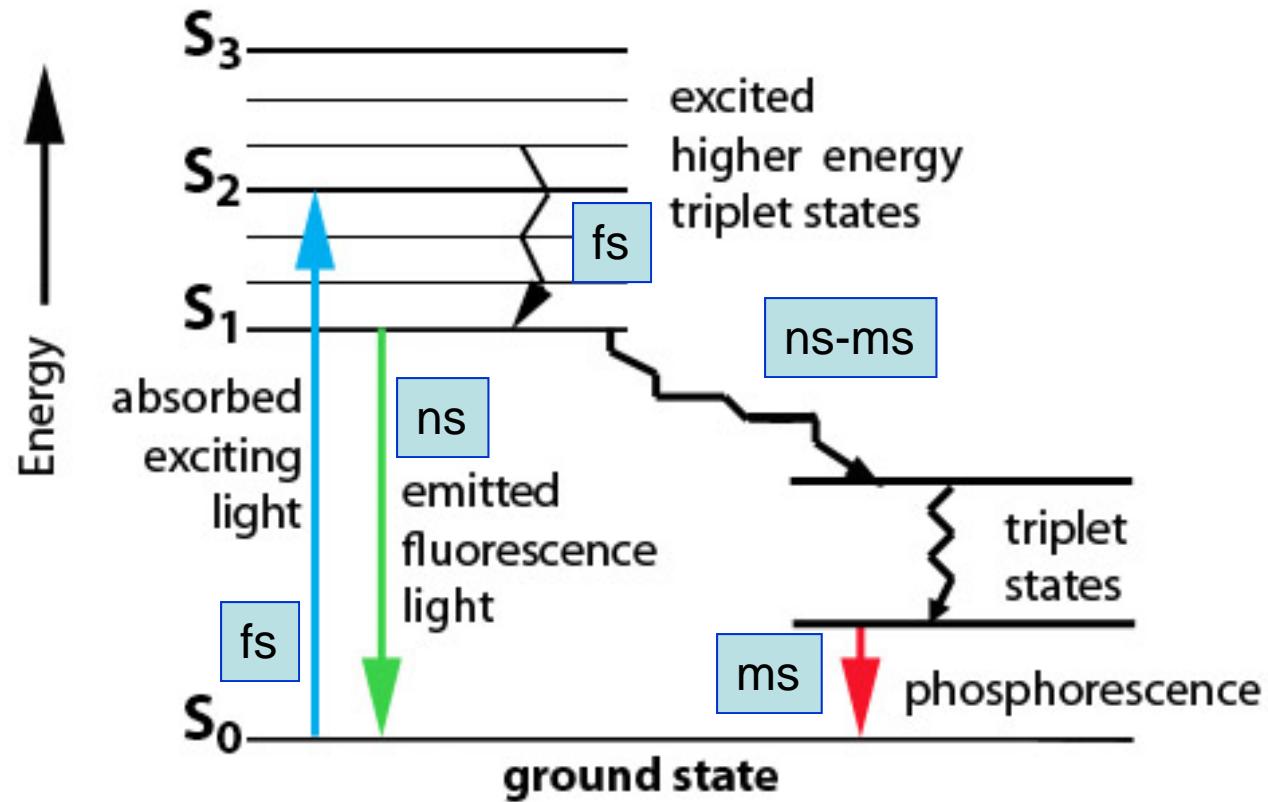
Jablonski Diagram



Timescale



Jablonski Diagram



Energies

Table 1.1 Energy Conversion Table

Region	λ		\bar{v}	ΔE	v	Structure and motion involved in absorption or emission
	\AA	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}	
	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}	
	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}	Electrons-orbital motion
	10^{10}	10^9	0.1	3×10^{-4}	3×10^9	Nuclei-vibrational motion
Radio wave	10^{12}	10^{11}	0.001	3×10^{-6}	3×10^7	Electron spin-precessional motion
						Nuclear spin-precessional motion

Our interest

Energy units

$$\begin{aligned}1 \text{ eV} &= 23.06 \text{ kcal/mole} \\&= 96.4 \text{ kJ/mole} \\&= 8066 \text{ cm}^{-1}\end{aligned}$$

$$\begin{aligned}kT &\sim 0.6 \text{ kcal/mole} \\&\sim 2.5 \text{ kJ/mole} \\&\sim 200 \text{ cm}^{-1} \sim 25 \text{ meV}\end{aligned}$$

$$E(\text{eV}) = \frac{1242}{\lambda(\text{nm})}$$

Quantum mechanics

Very light version!

Classical Mechanics

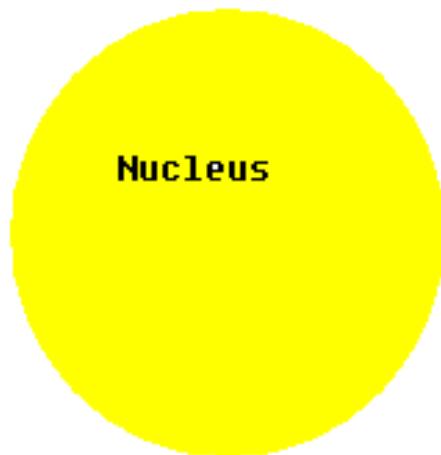
- ***The Law of Conservation of Energy.*** In any isolated system energy may be transformed from one kind to another but cannot be created or destroyed.
- ***The Law of Conservation of Momentum.*** In any isolated system, momentum may be transformed from one kind to another but cannot be created or destroyed.

If these laws are violated the transition is *strictly forbidden*

The Born-Oppenheimer Approximation

- Since the motions of electrons in orbitals are much more rapid than nuclear motions, *electronic and nuclear motions can be treated separately.*
- Since electron spin motion is due to a magnetic interaction, and since magnetic and electronic waves interact weakly in most organic molecules, *the spin motion of electrons may be treated separately from electron orbital motion and nuclei motion in space.*

Born-Oppenheimer Approximation



too heavy to move



electron

moves around

Ψ
“true” molecular wave function

\sim
 $\Psi_0 \chi \mathcal{S}$
orbital nuclear spin
approximate wave functions

$$P = \frac{\text{Average value of observable quantity}}{\int_0^\infty \Psi \Psi d\tau} = \frac{\int_0^\infty \Psi |H| \Psi d\tau}{\int_0^\infty \Psi \Psi d\tau} \equiv \langle \Psi | H | \Psi \rangle \text{ “Matrix element”}$$

$$P \sim \langle \Psi_0 \chi \mathcal{S} | H | \Psi_0 \chi \mathcal{S} \rangle$$

Zeroth-Order Approximation: BO approximation + one-electron wave functions

$$\Psi_0 \sim \psi_1 \psi_2 \cdots \psi_n = \prod_i \psi_i$$

$$P \approx \langle \psi_1 \psi_2 \cdots \psi_n \chi \mathcal{S} | H | \psi_1 \psi_2 \cdots \psi_n \chi \mathcal{S} \rangle$$

First-order approximation would introduce spin-orbit coupling or electron-electron repulsion

Quantum Mechanics and observable rates of processes

Golden Rule:

$$\text{rate (sec}^{-1}\text{)} = \frac{2\pi}{h} \rho \langle H' \rangle^2 \quad (3.1)$$

where ρ corresponds to the “density” or number of final states capable of coupling with the initial state, and $\langle H' \rangle$ represents the matrix element for the (weak) perturbation coupling the initial and final states.

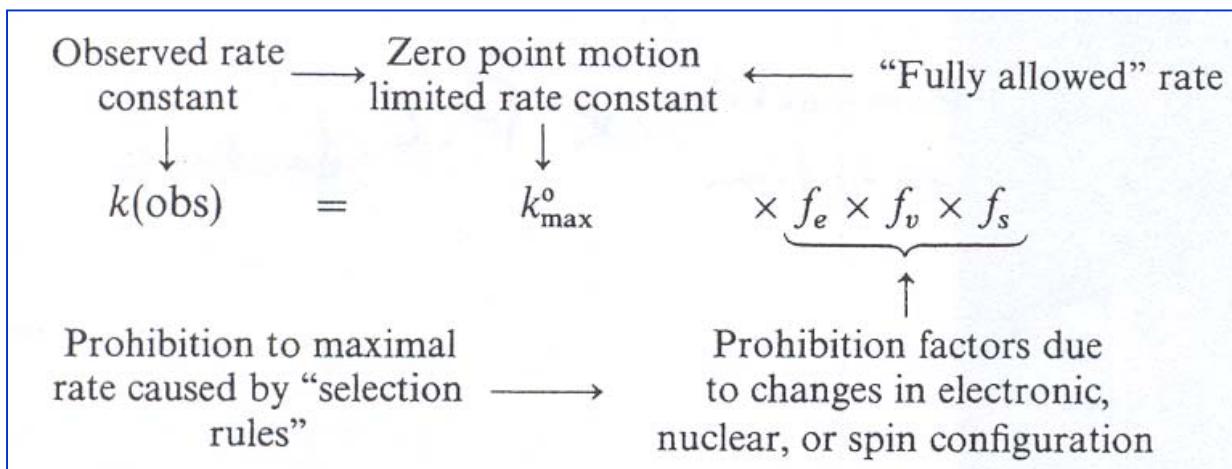
Perturbation

force that reshapes the initial state so that it looks like final

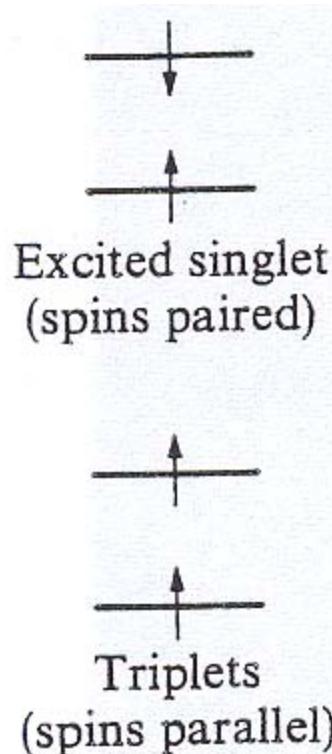
Density of states

number of states capable (close in energy) of coupling

A transition will proceed more rapidly if the coupling between the initial and final states is stronger. This coupling term is traditionally called the "matrix element"



Triplets and Singlets



Singlets are normally higher in energy than triplets. This results from the better correlation of electronic motion in triplet states that minimizes electronic repulsion.

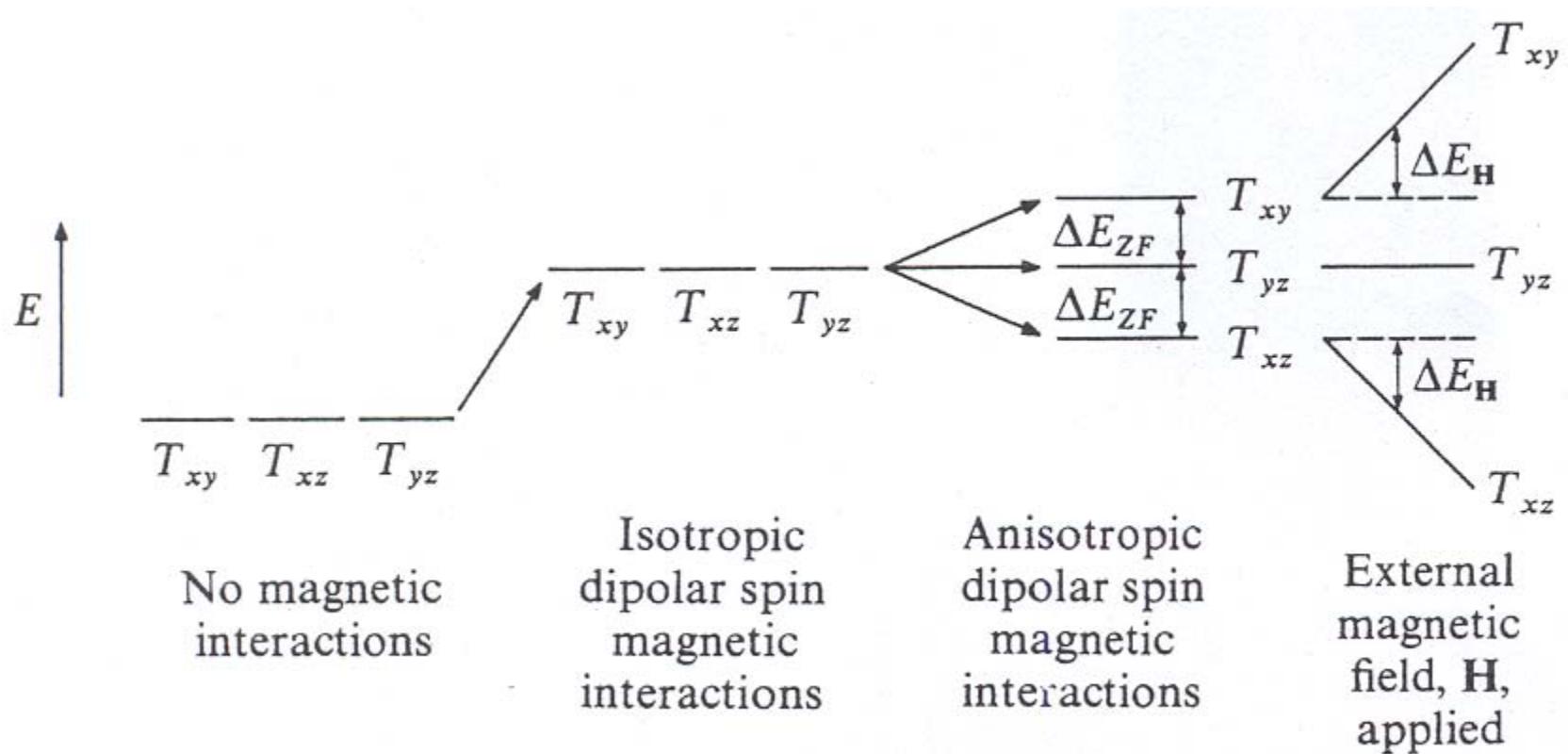
Or in other words:

Pauli Principle: Unpaired electrons avoid one another and thereby correlate their motion to minimize electronic collisions (repulsion). Triplets do it better than singlets— **Purely quantum mechanical phenomenon**

<http://www.users.csbsju.edu/~frioux/stability/HundsRule.pdf>

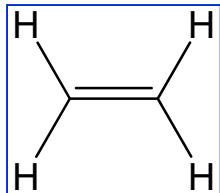
Singlet to triplet transitions (intersystem crossing) – we will talk about it later

Typical triplet behavior

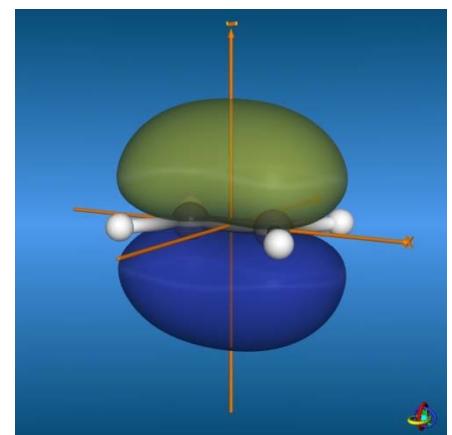
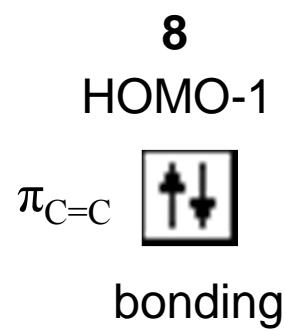
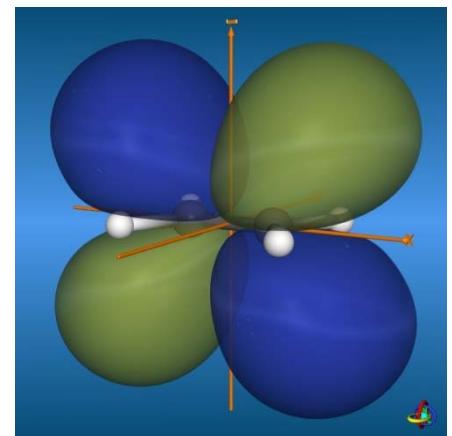
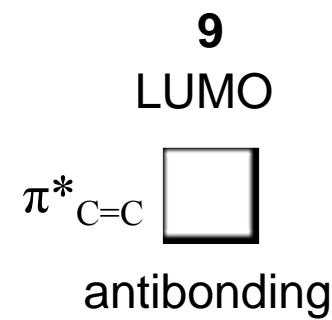
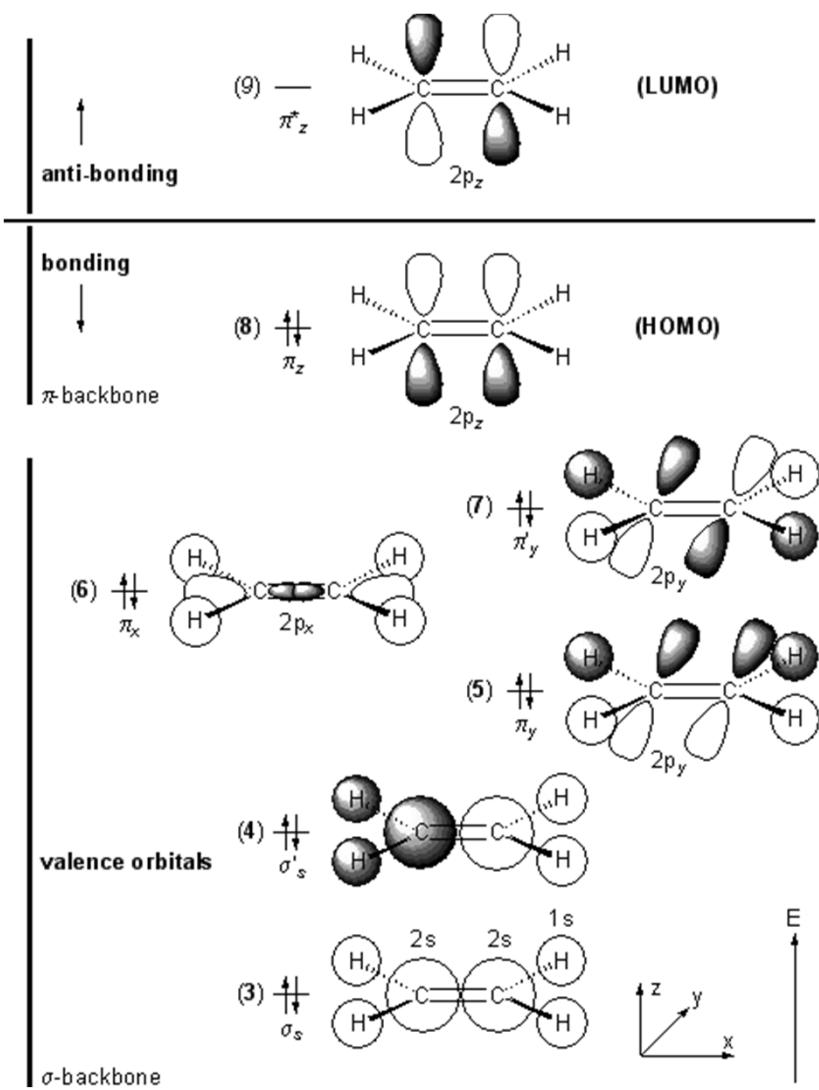


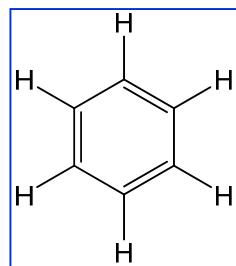
Real Molecules

How do we look at them?

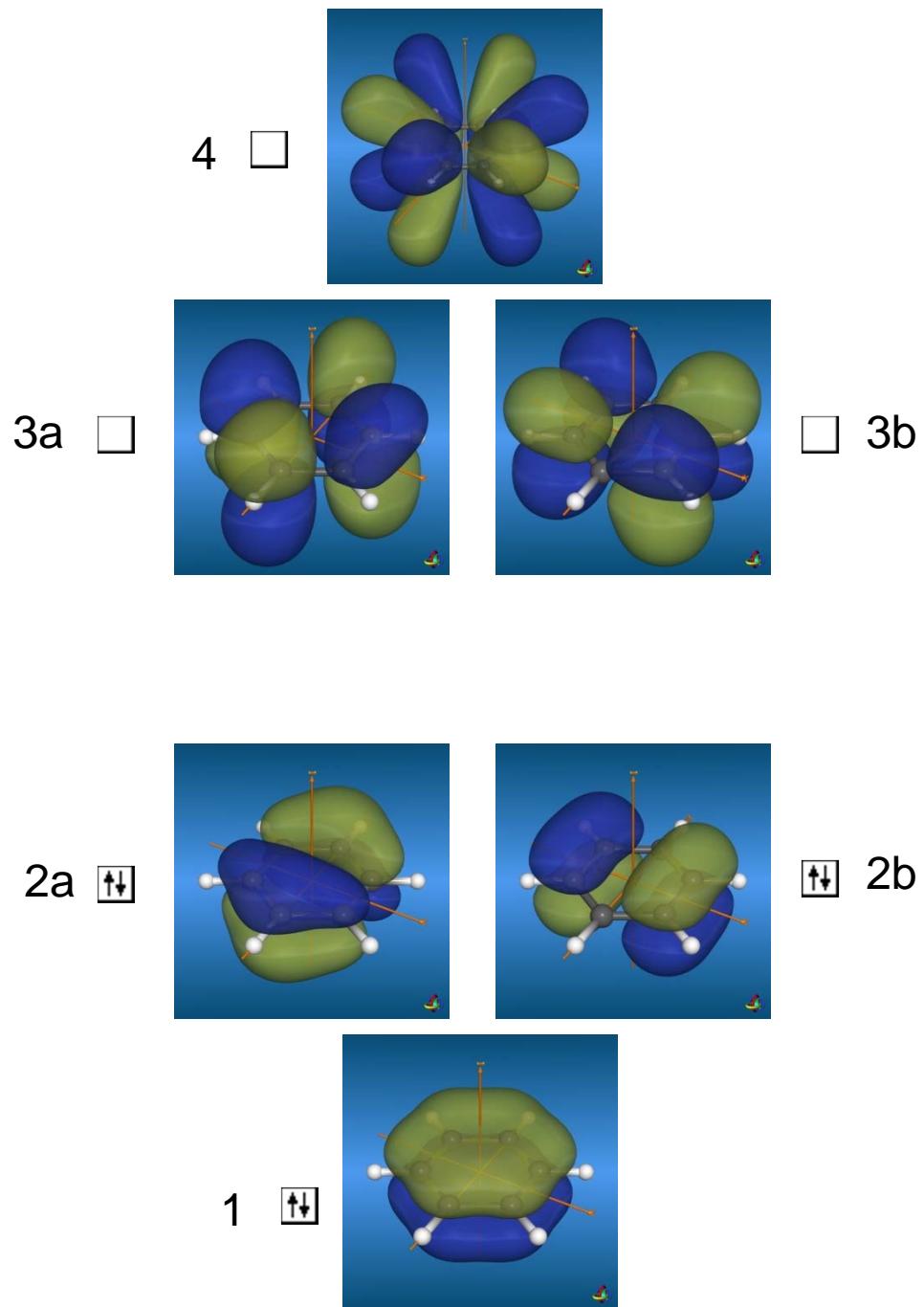
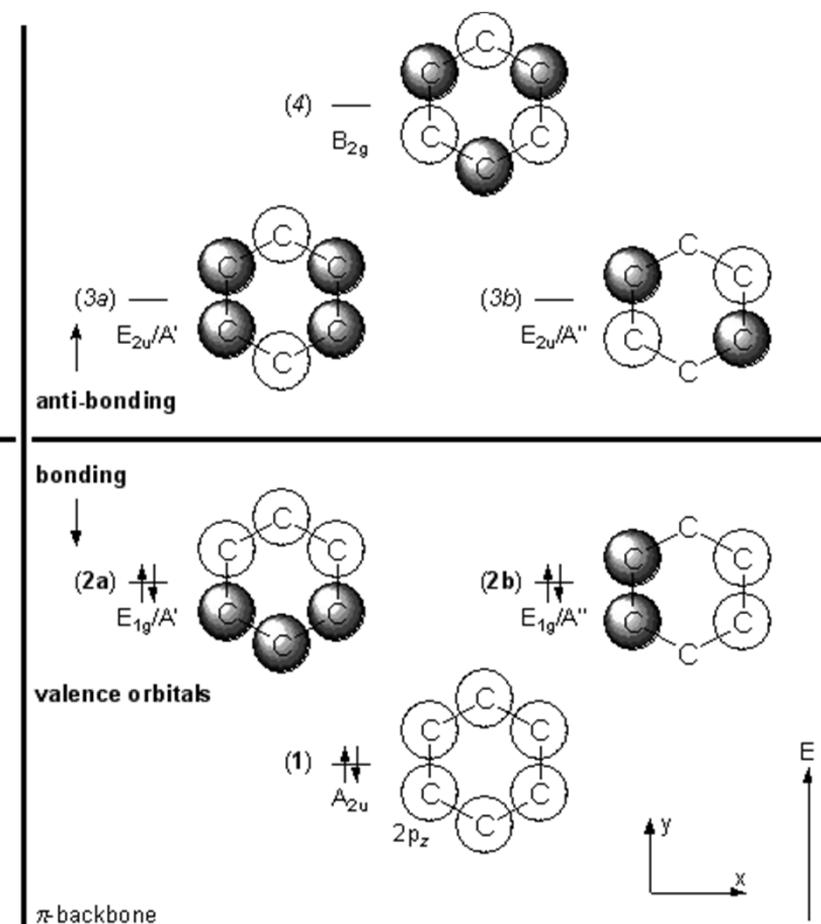


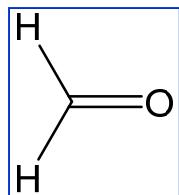
Ethene



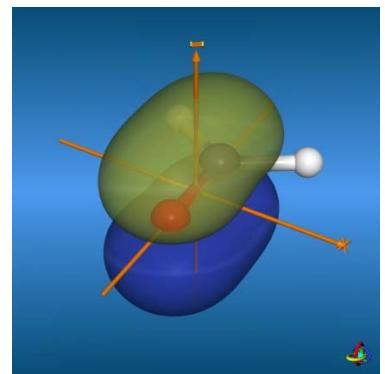
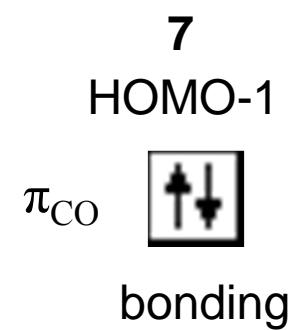
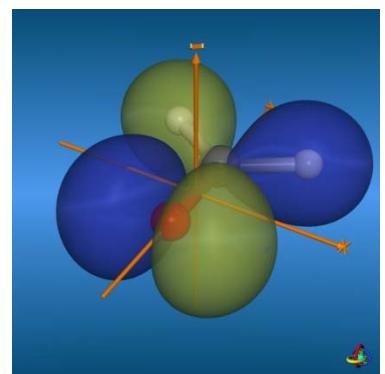
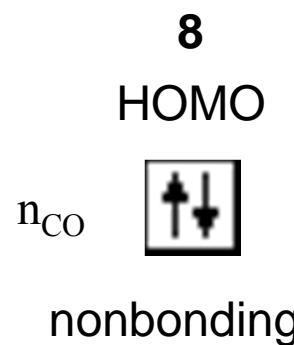
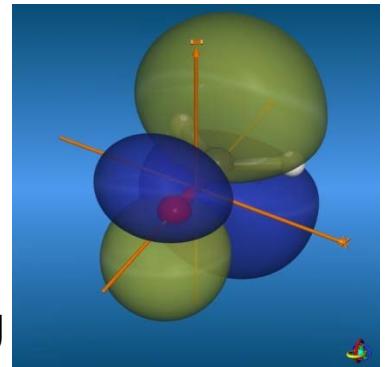
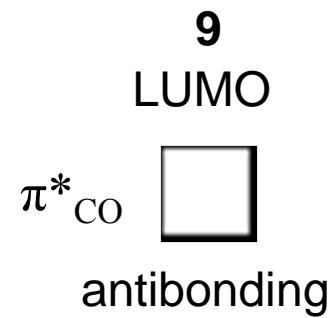
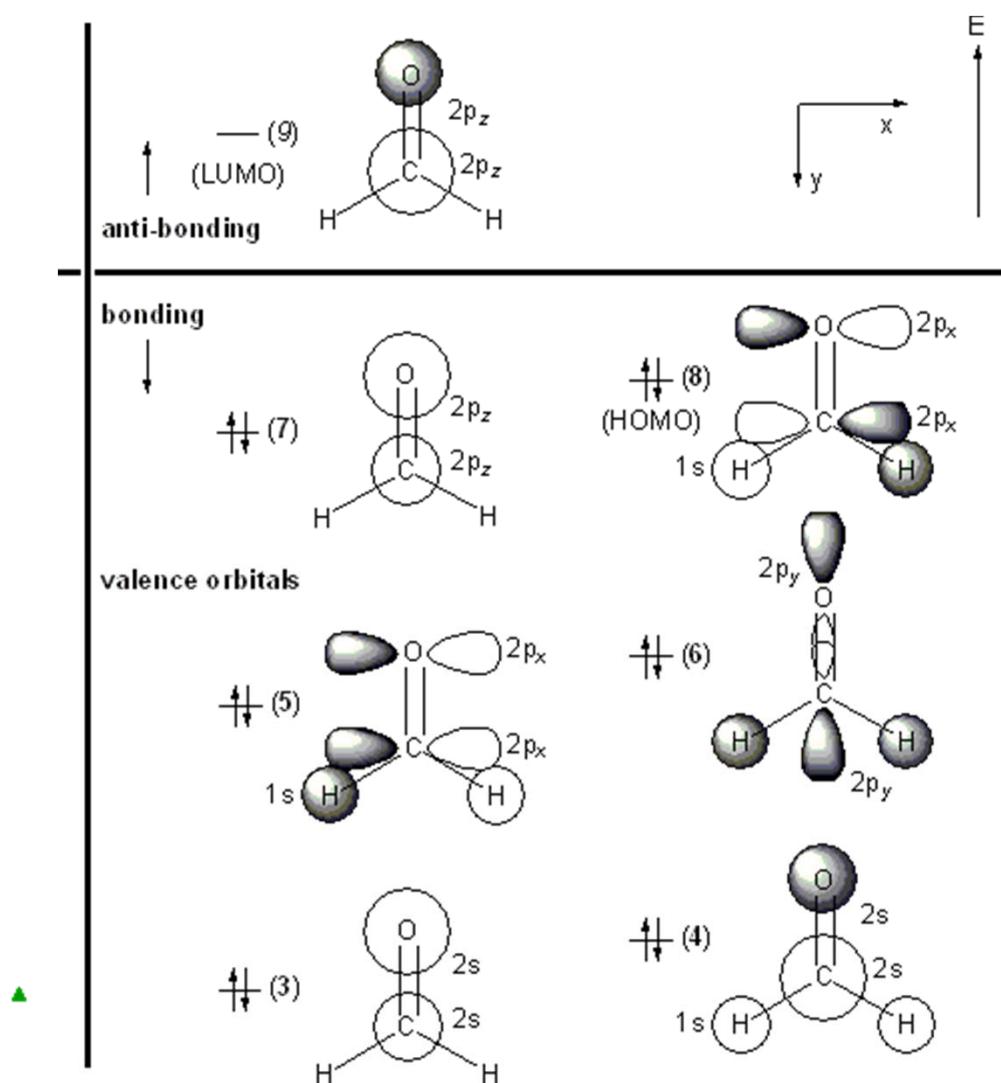


Benzene

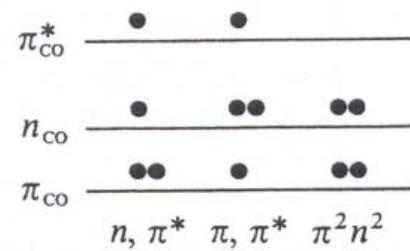
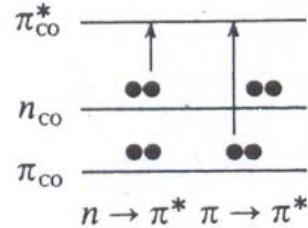




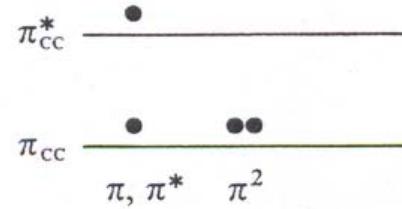
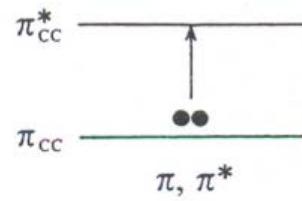
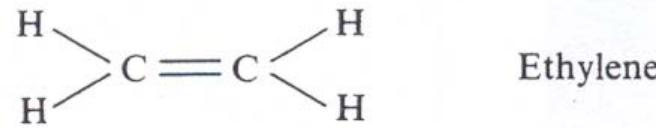
Formaldehyde



Orbital configurations and transitions



$$\begin{array}{c}
 S_2 \xrightarrow{\pi, \pi^*} \xrightarrow{\pi, \pi^*} T_2 \\
 S_1 \xrightarrow{n, \pi^*} \xrightarrow{n, \pi^*} \frac{\pi^2 n^2}{S_0} T_1
 \end{array}$$

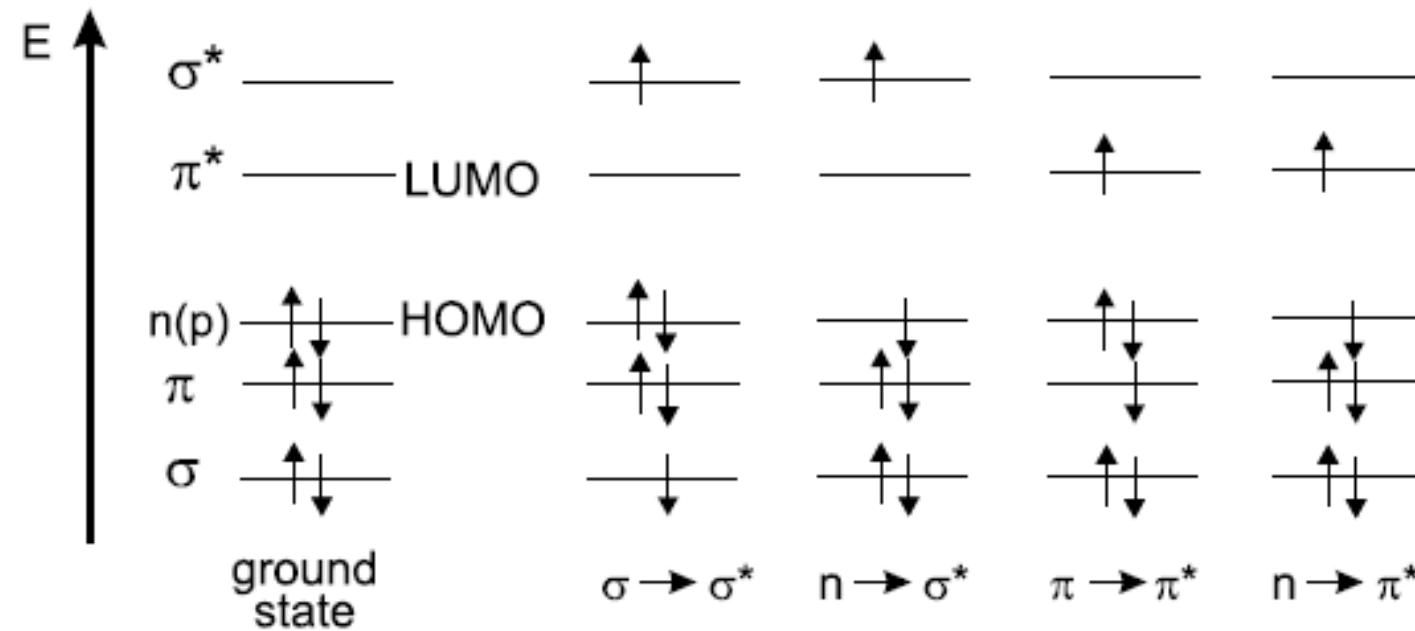
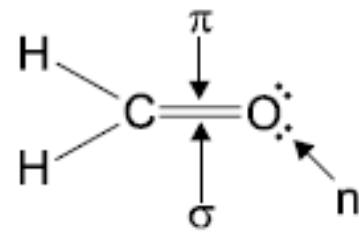


$$\begin{array}{c}
 S_1 \xrightarrow{\pi, \pi^*} \xrightarrow{\pi, \pi^*} T_1 \\
 S_0 \xrightarrow{\pi^2}
 \end{array}$$

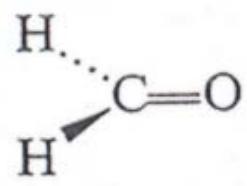
(a) Transitions

(b) Configurations

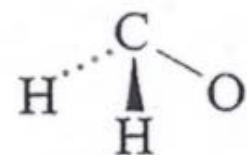
(c) States



Nuclear Geometry of Excited States

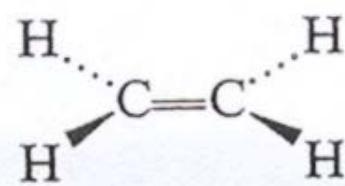


Ground state
Planar

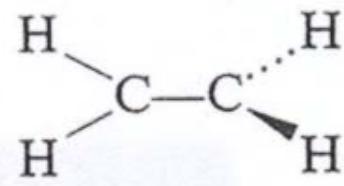


n, π^* state
Pyramidal

Formaldehyde



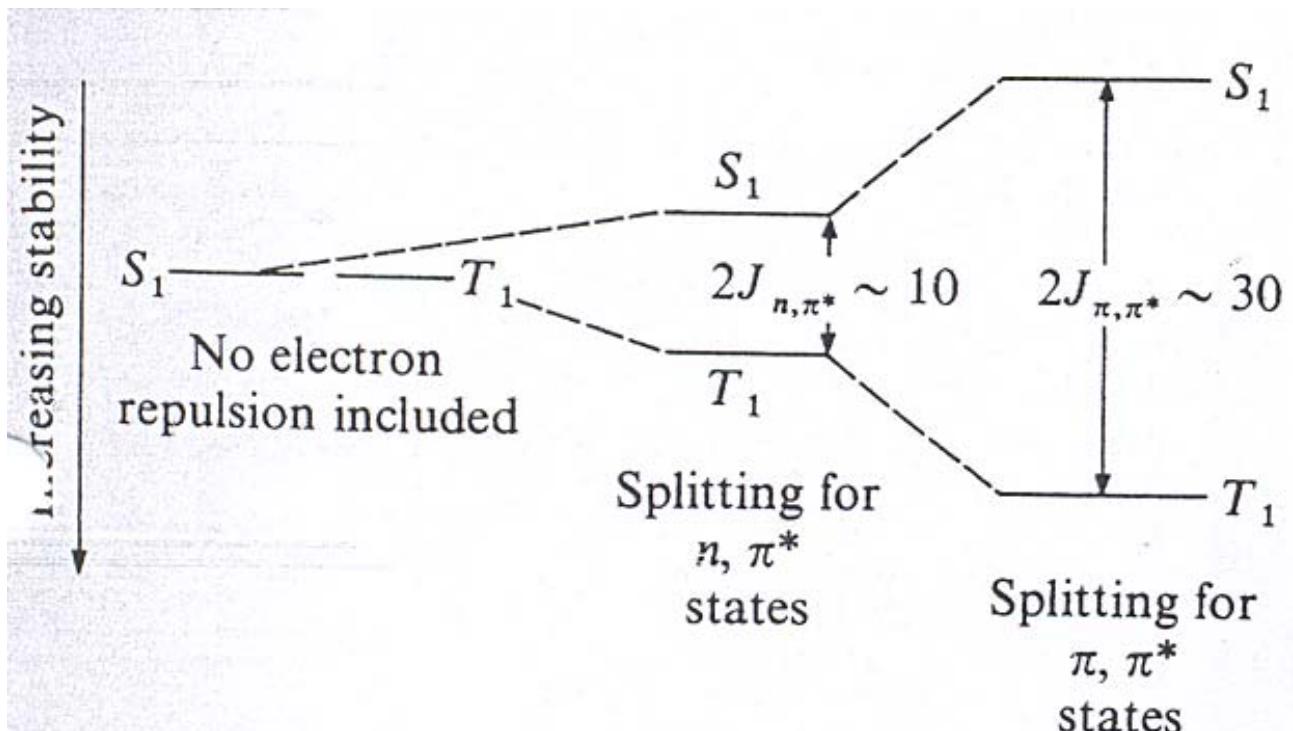
Ground state
Planar



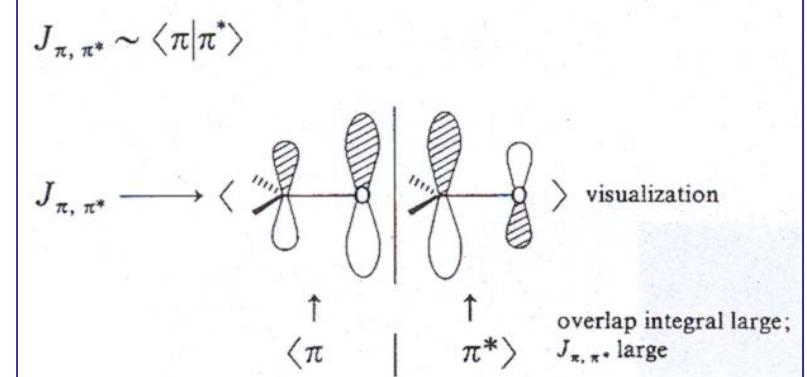
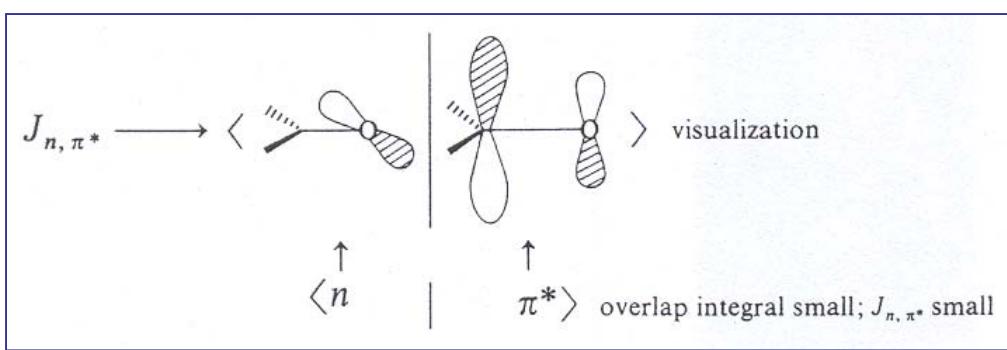
n, π^* excited state
Pyramidal

Ethylene

(1.9)

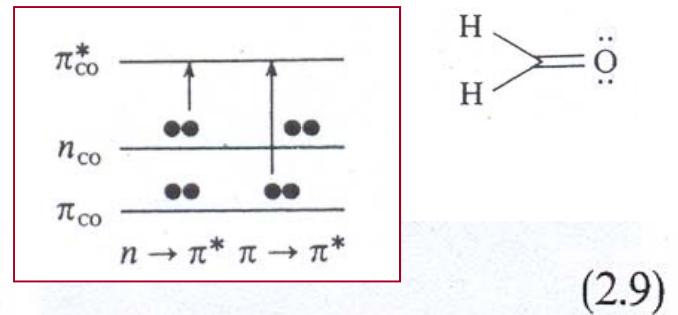


Formaldehyde case



Singlet-Triplet energy difference, formaldehyde case

$$E(S_0) = 0 \quad \text{by definition}$$



(2.9)

$$E(S_1) = E(n, \pi^*) + K(n, \pi^*) + J(n, \pi^*) \quad (2.10)$$

$$E(T_1) = E(n, \pi^*) + K(n, \pi^*) - J(n, \pi^*) \quad (2.11)$$

where J is the matrix element that measures electron repulsion due to electron exchange and K is the matrix element that measures electron repulsion due to Coulombic interactions. Both J and K are positive (energy enhancing) quantities. Note that

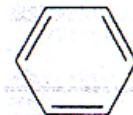
$$\underline{\Delta E_{\text{ST}} = E(S_1) - E(T_1) = 2J(n, \pi^*) > 0} \quad \text{Singlet-Triplet splitting} \quad (2.12)$$

and since J must be positive we conclude that $E(S_1) > E(T_1)$ in general.

Table 2.1 Singlet-Triplet Splittings

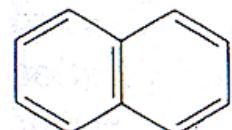
Molecule	Configuration ($S_1 - T_1$)	$\Delta E (S_1 - T_1)$ in kcal/mole
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$\text{CH}_2=\text{CH}_2$	π, π^*	70
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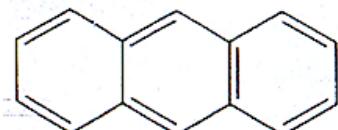
	π, π^*	70
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	π, π^*	40
--	--------------	----



	π, π^*	40
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	π, π^*	35
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	π, π^*	35
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$\text{CH}_2=\text{O}$	n, π^*	10
------------------------	------------	----



	n, π^*	10
--	------------	----

$(\text{CH}_3)_2\text{C}=\text{O}$	n, π^*	7
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	n, π^*	7
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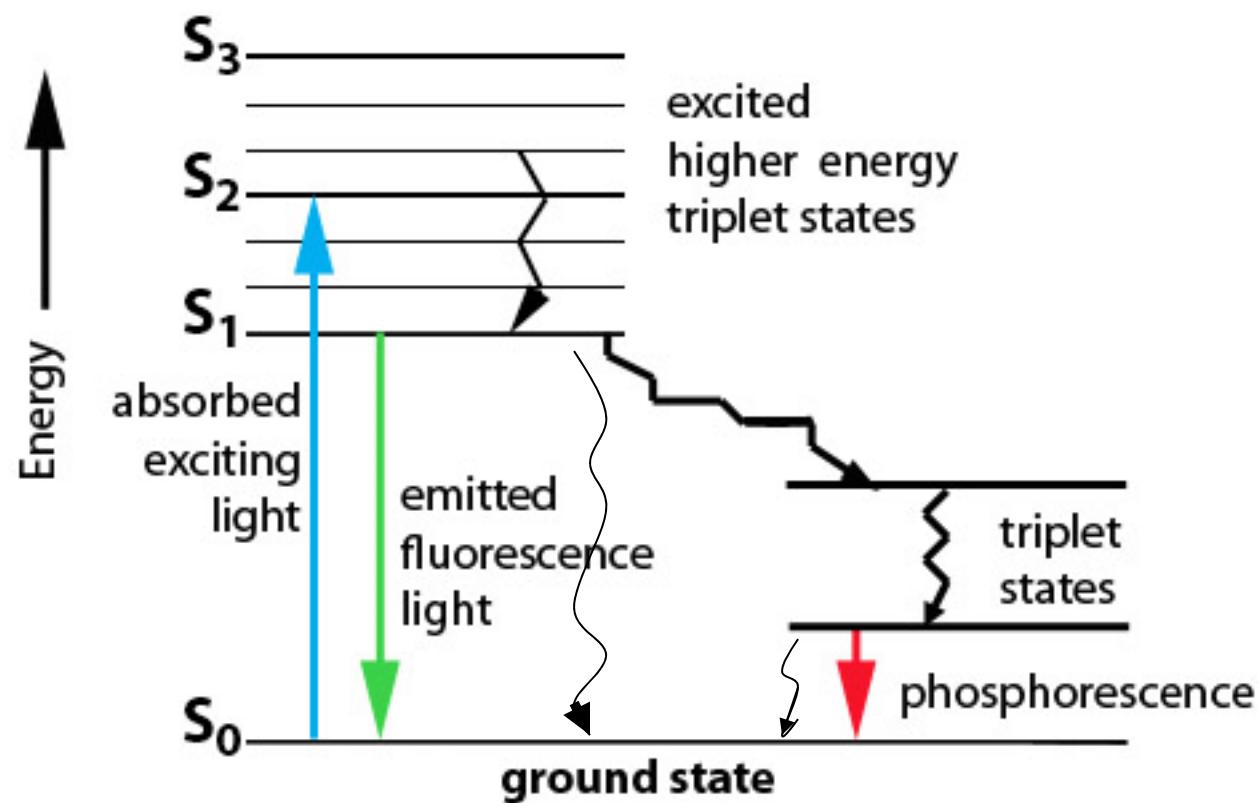
$\text{Ph}_2\text{C}=\text{O}$	n, π^*	7
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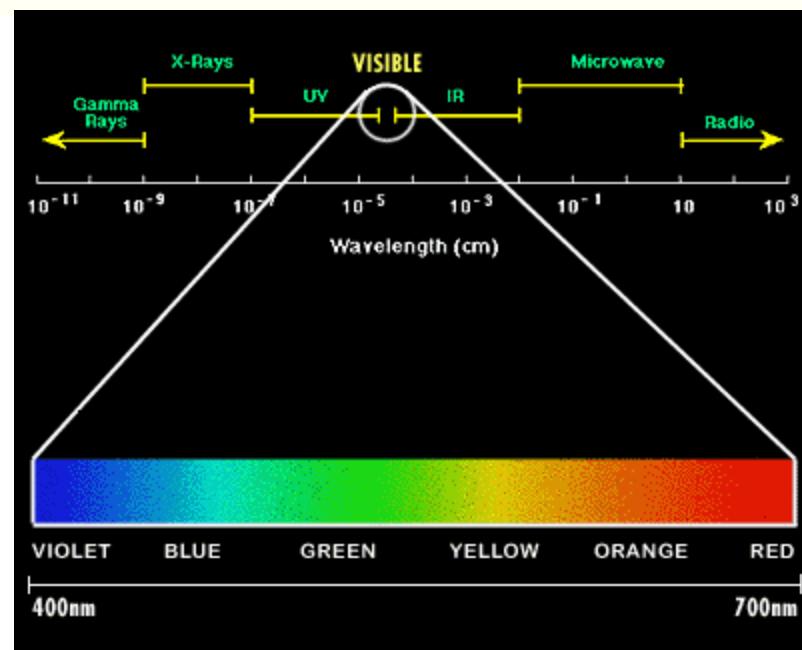
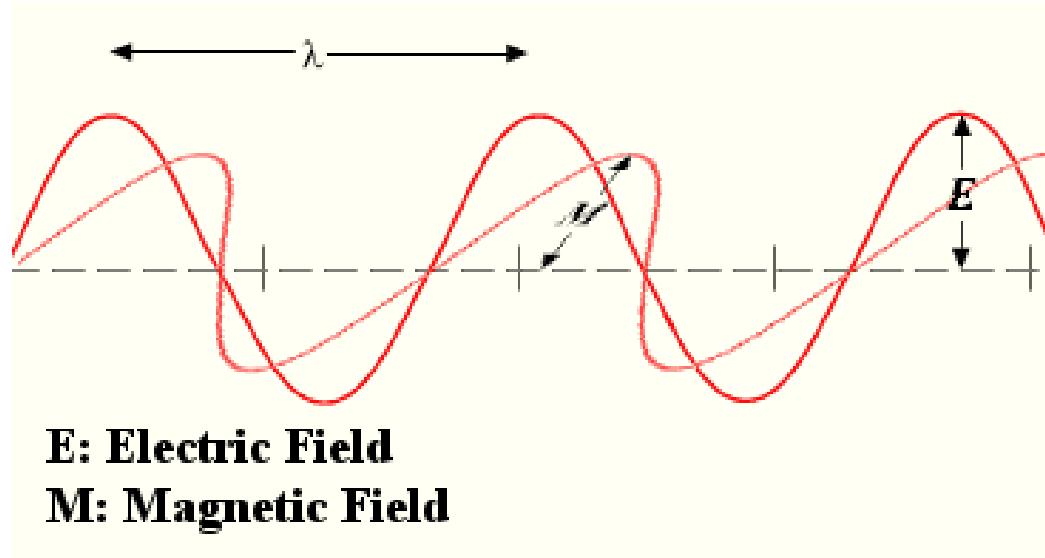
	n, π^*	7
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Radiative Transitions: The Absorption and Emission of Light

Jablonski Diagram



Light

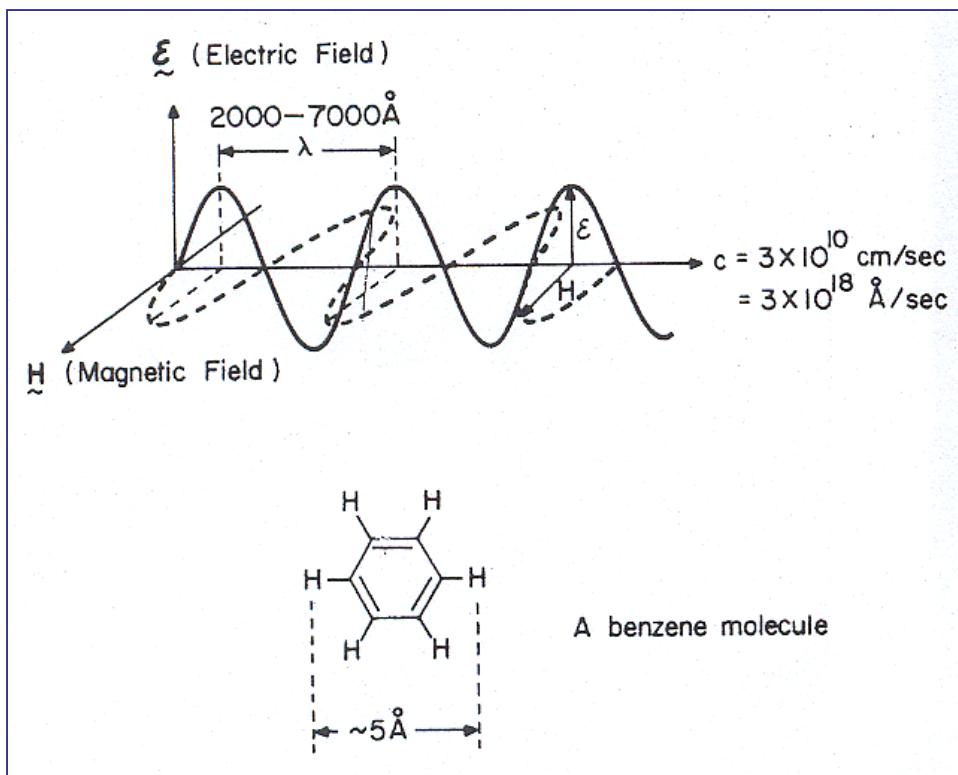


Pictorial (intuitive) view of light absorption

Not rigorous, but useful

General Representation of Light-Molecule Interaction

Electrons may be set in motion by the oscillating electric field of light, i.e. the excited electron behaves as it were an oscillating dipole



The major force operating on the electrons of a molecule under light is electric field.

The oscillation of the dipoles corresponds to the movements of electrons in bonds relative to positively charged nuclei, i.e. electrons oscillate about the nuclear framework of the molecule.

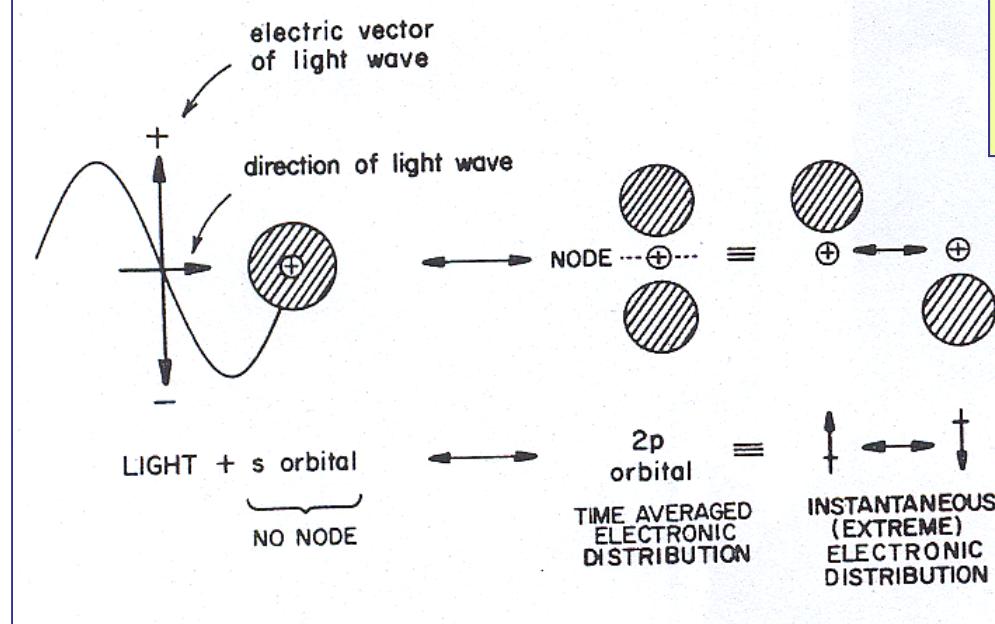
Polarizability and Transition Dipole Moment

Polarizability (α) is defined as the magnitude of the induced dipole moment (μ_i) generated in a molecule by an electric field \mathcal{E} of unit intensity, i.e.,

$$\alpha = \mu_i / \mathcal{E} \quad (5.4)$$

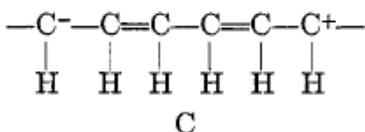
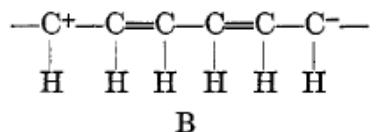
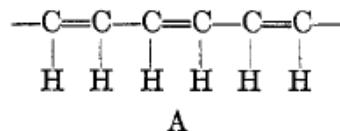
Initially ($\mathcal{E} = 0$), the electron is held, on the average, at some distance r from the center of "electrical gravity" of the molecule. When $\mathcal{E} > 0$, a displacing force $\mathcal{E}e$ will cause the electron to select a new equilibrium distance different from the original distance by the amount δr . The new electronic distribution is related to the induced dipole moment (also called *transition dipole*) by:

$$\mu_i = e\delta r$$



Nodes and dipole moments **have to occur**, otherwise no absorption is observed

Original paper defining transition dipole and oscillator strength



We need not assume that the resonating molecule ever reaches the extreme forms B and C but rather that there may be concerted motions of the electrons from the major structure A, in the direction either of B or of C.

On account of its symmetry the normal state of the molecule has no dipole moment. If, however, it is placed in an electric field, for example, a positive plate at the right and a negative plate at the left, the electrons are shifted in the direction of structure B. The dipole moment produced per unit field strength is the polarizability. We may now consider this electronic displacement in either of two equivalent ways. We may consider the molecule as a whole and the total displacement from one end to the other, or we may consider the individual units ($-\text{C}=\text{C}-$) and, ignoring



end effects, add the dipole moments produced in the several units. Let us choose the latter course. If μ is the moment produced in each unit in a field of strength E , then α , the polarizability, is given by the equation

$$\alpha = \mu/E \quad (1)$$

We do not need to decide how many electrons are involved in our process. If $-e$ is the effective charge which is displaced and x is the displacement from the normal position, then

$$\mu = ex \quad (2)$$

Lewis and Calvin,
Chem. Rev. 1939, 273



Gilbert Lewis

The strength of the interaction between an electron and light (electric field) is related directly to the ability of the electron to follow the light wave.

According to classical theory,^{4,5} f is related to the square of the induced dipole moment μ_i produced by action of a light wave on an electric dipole:

$$\text{Oscillator strength } f \propto \mu_i^2 = \langle e\mathbf{r} \rangle^2 \text{ Transition dipole moment} \quad (5.12)$$

where μ_i is the induced transition dipole moment or *dipole strength* corresponding to the electronic transition. The latter quantity may be set equal to $e\mathbf{r}$, where \mathbf{r} is the dipole length. Quantitatively the expression relating f and μ_i is given by

$$f = \left(\frac{8\pi m_e \bar{v}}{3he^2} \right) \mu_i^2 \cong 10^{-5} \bar{v} |e\mathbf{r}_i|^2 \quad (5.13)$$

where m_e is the mass of the electron, \bar{v} is the energy of the transition (in cm^{-1}), h is Planck's constant, and \mathbf{r} is the length (in cm) of the transition dipole (i.e., $e\mathbf{r}$ is the transition dipole moment).

We can now identify μ_i with an observable quantity related to the quantum mechanical transition moment matrix element or integral, i.e., $\mu \equiv \langle H \rangle$, and produce:

$$\text{Classical} \rightarrow f = \left(\frac{8\pi m_e \bar{v}}{3he^2} \right) \langle H \rangle^2 \leftarrow \text{Quantum mechanical} \quad (5.14)$$