



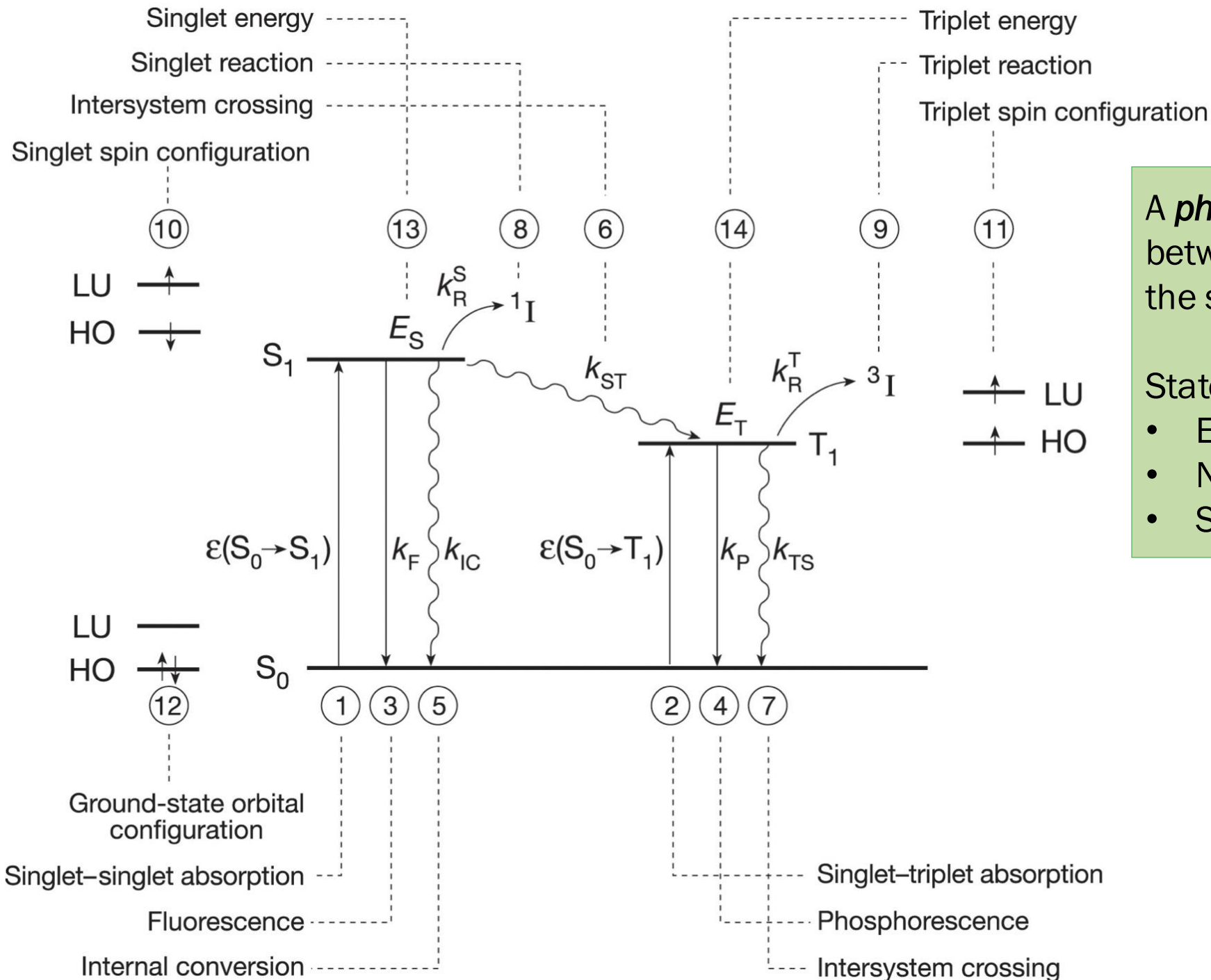
Photophysical Transitions: Definitions, Allowedness, and Rates

Molecular Photochemistry

CHEM 4801

Overview of Photophysical Transitions; The Spirit of “Allowedness”

Photophysical Properties and Transitions



A **photophysical transition** occurs between initial and final states with the same chemical structure.

States may differ in:

- Electron configuration
- Nuclear (vibrational) configuration
- Spin configuration

Classical Dynamics

Interactions change the motion of the particles of a system

Actions are accompanied by equal and opposite reactions

Law of Conservation of Energy

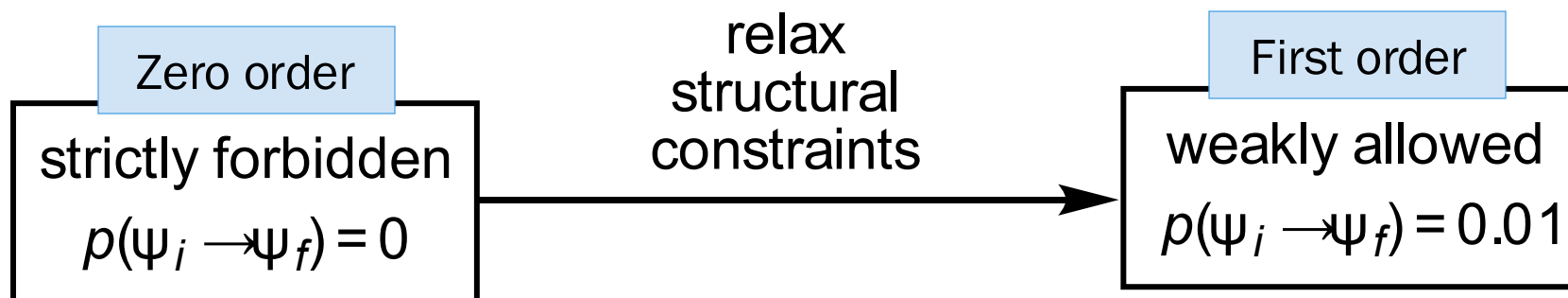
Law of Conservation of Momentum

A *mechanism* for a transition includes:

- Structural, energetic, and momentum differences between the initial and final states
- Interactions or forces that can convert the initial state into the final state

Selection Rules

A **selection rule** is a criterion governing allowed transitions in an idealized situation involving precisely defined initial and final states. “Rules are made to be broken.”



Recall our earlier connection of the **overlap integral** $\langle \psi_f | \hat{P} | \psi_i \rangle$ to the probability of a transition taking place.

$$p \propto \left| \langle \psi_f | \hat{P} | \psi_i \rangle \right|^2 \rightarrow k_P$$

Electron spin cannot change (S and T states are orthogonal)

Initial and final orbitals must overlap

Vibrational wavefunctions must overlap

Quantum Origins of the Rates of Photophysical Transitions

Photophysical Properties and Transitions

Quantum States of a Molecule

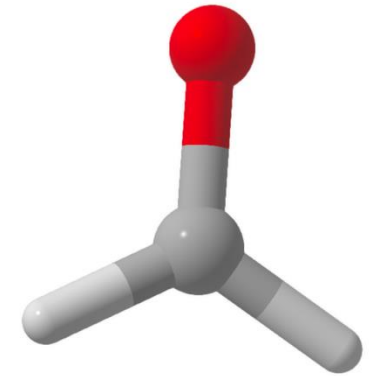
The **quantum state** of a molecular system is described as a product of three separable wave functions: electronic, nuclear, and spin.

$$\Psi = \psi_e \times \psi_v \times \psi_s$$

ψ_e : orbital configuration (NBO + Hückel)

ψ_v : spatial dependence and occupancy of vibrational modes

ψ_s : electron spins (particularly *unpaired* spins)



The assumption that ψ_e and ψ_v are independent is the **Born-Oppenheimer approximation**.

Transition Rates and Prohibition Factors

The observed rate constant of a transition is equal to the theoretically maximal rate constant ($\sim 10^{14} \text{ s}^{-1}$) times ***prohibition factors*** due to orbital, vibrational, and spin effects.

$$k_{obs} = k_{max}^0 \times f_e \times f_v \times f_s$$

$$f \sim \left| \frac{\langle H \rangle}{\Delta E} \right|^2$$

The ***matrix element*** $\langle H \rangle$ captures the overlap of the initial and final wave functions.

$$\langle H \rangle = \langle \psi_f | H | \psi_i \rangle$$

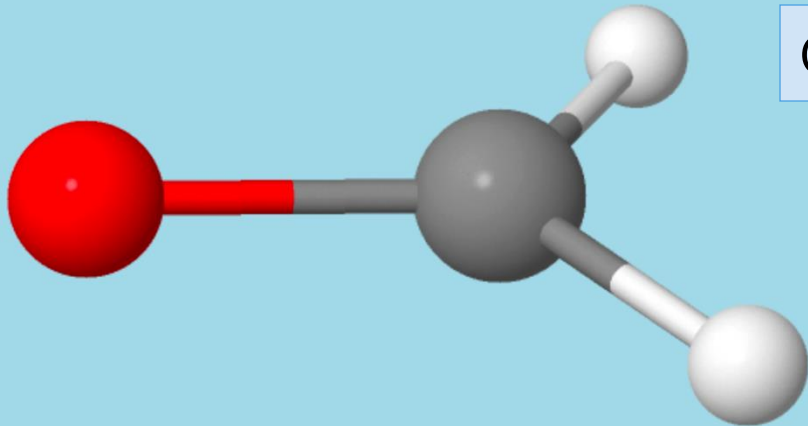


Vibronic Coupling

Photophysical Properties and Transitions

Coupled Nuclear and Electronic Motion

Nuclear motion (vibrations) can serve as a mechanism for the interconversion of excited electronic states. The transfer of vibrational energy to electronic energy is called ***vibronic coupling***.



In-plane vibrations have no effect

Out-of-plane vibration enables an otherwise forbidden IC process

$$\text{rate}(\text{s}^{-1}) = \frac{2\pi\rho}{h} \langle \Psi_1^0 | H_v | \Psi_2^0 \rangle^2$$

<http://openmopac.net/Manual/Individual%20JSmol%20paths/Formaldehyde%20vibrations/Formaldehyde%20vibrations.html>

The Franck-Condon Principle and Fermi's Golden Rule

Photophysical Properties and Transitions

Relative Speeds of Nuclei and Electrons

Nuclei move at *much* slower speeds than electrons.
This has two important implications for photophysical transitions.

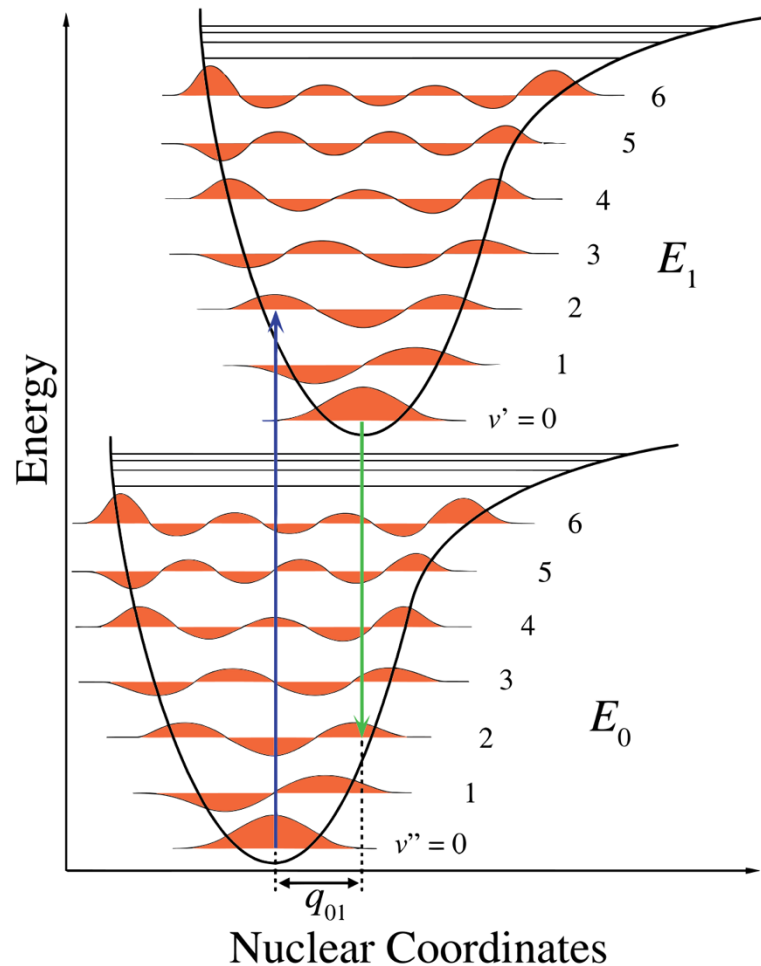
Nuclear *positions* do not change during *radiative* transitions.

Nuclear *motions* do not change during *non-radiative* transitions.

Particle	Mass (kg)
proton	1.67×10^{-27}
electron	9.11×10^{-31}

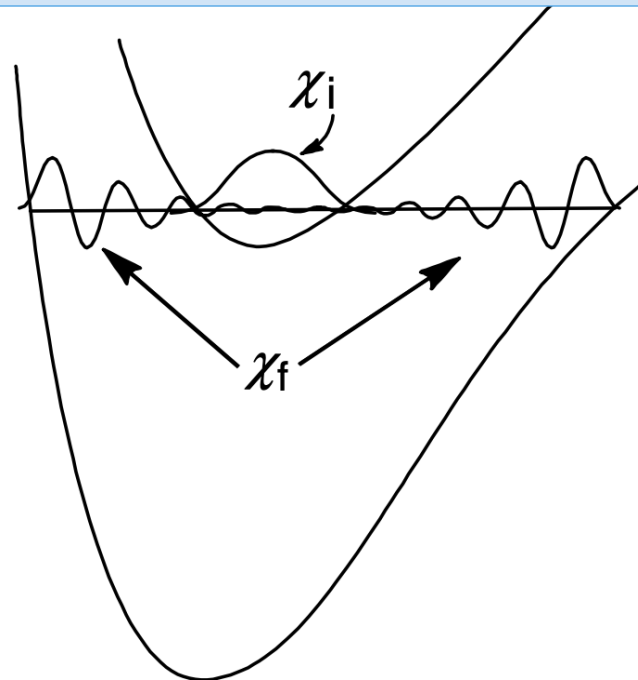
The Franck-Condon Principle

According to the ***Franck-Condon principle***, electronic transitions occur most favorably when the nuclear structures of the initial and final states are most similar.



Video describing the Frank-Condon principle [link](#)

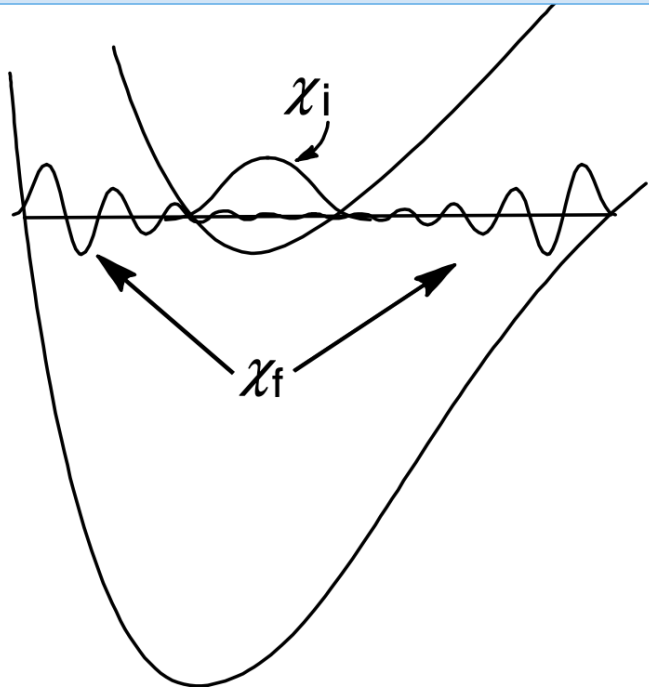
Franck-Condon (FC) factor for a transition is defined as $\langle \chi_f | \chi_i \rangle$, the overlap integral of the vibrational wave functions.



Fermi's Golden Rule

Non-radiative transitions require a perturbation that mixes initial and final states. Transition rate is directly related to the perturbation matrix element and the final density of states (**Fermi's golden rule**).

Rapidly decreasing FC factors with increasing ΔE result in slower rates at greater ΔE , the **energy gap law**.



$$k_{i \rightarrow f} = \frac{dp(t)}{dt} = \frac{2\pi}{\hbar} V_{fi}^2 \rho(E_f)$$

Perturbation matrix element

$$V_{fi} = \langle \psi_f | \hat{P} | \psi_i \rangle$$

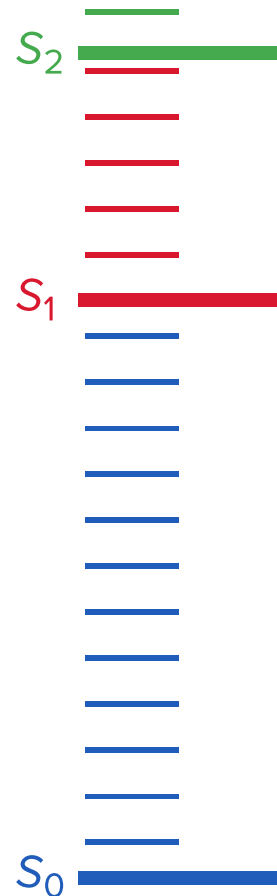
Density of states, final



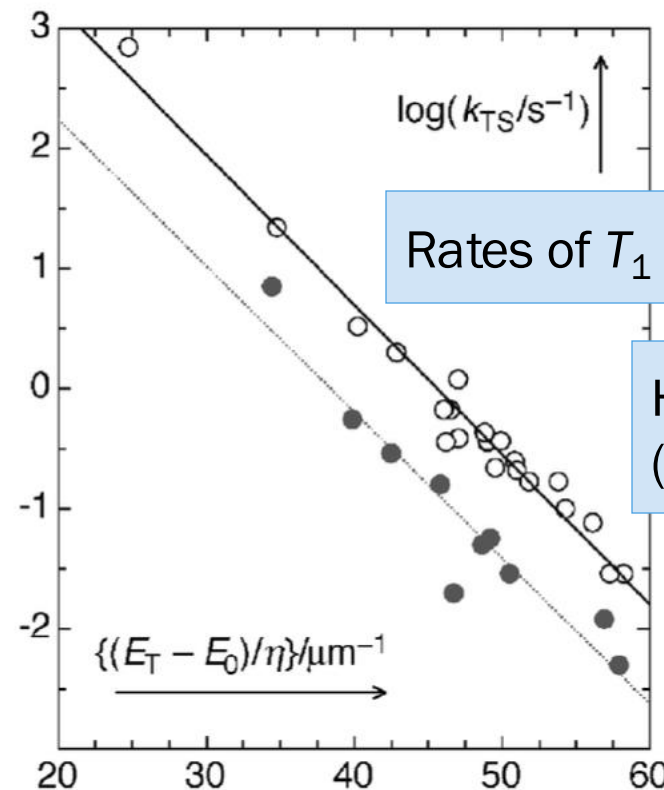
Energy Gap Law

As a result of Fermi's golden rule, rates of non-radiative transitions (IC, ISC) generally follow an **energy gap law**: the greater ΔE between initial and final states, the slower the rate.

Kasha's rule: Internal conversion from $S_n \rightarrow S_1$ is generally much more rapid than $S_1 \rightarrow S_0$.



$$f \sim e^{-\Delta E}$$



Rates of $T_1 \rightarrow S_0$ ISC as a function of ΔE

Higher-energy vibrations (D vs. H) result in greater k

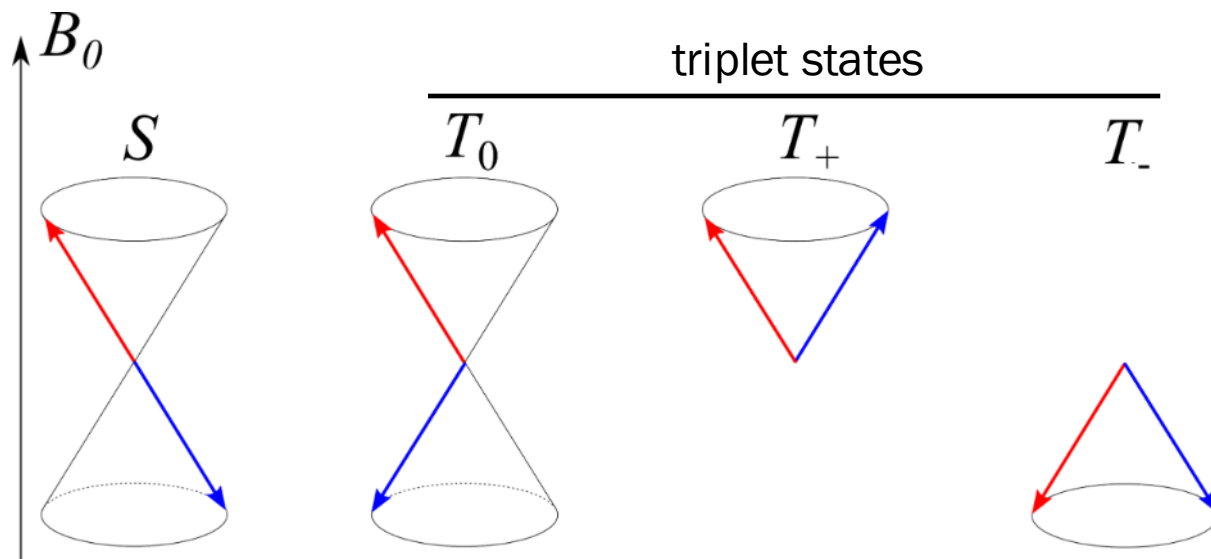
Singlet-Triplet Interconversions: Sources of “Magnetic Torque” and El-Sayed’s Rules

Photophysical Properties and Transitions

Magnetic Torques in Intersystem Crossing



Intersystem crossing is governed by **conservation of angular momentum**; orbital or spin angular momentum (or an external magnetic field) can serve as a source or sink when $S \rightarrow T$ or $T \rightarrow S$ takes place.



Spin “flipping” or “rephasing” converts S to T or vice versa.

External magnetic field (B_1)

Change in nuclear spin

Change in orbital configuration

Heavy Atom Effect

Excited states in which there is significant unpaired electron density on a heavy atom exhibit enhanced rates of intersystem crossing. This is called the **heavy atom effect (HAE)**.

$$H_{so} = -\frac{Z^4 e^2}{8\pi\epsilon_0 m_e^2 c^2} \vec{l} \cdot \vec{s}$$

The magnitude of spin-orbit coupling depends strongly on Z.

Greater H_{so} facilitates ISC as a change in spin can be more easily “powered” by changes in orbital motion.

Solvents and other additives containing heavy atoms also facilitate ISC via the **external HAE**. Excited S states of the “perturber” mix with the T state of the “perturbed.”

Compound	k_f^0	k_{ST}	k_p^0	k_{TS}	Φ_f	Φ_p
Naphthalene	10^6	10^6	10^{-1}	10^{-1}	0.55	0.05
1-Fluoronaphthalene	10^6	10^6	10^{-1}	10^{-1}	0.84	0.06
1-Chloronaphthalene	10^6	10^8	10	10	0.06	0.54
1-Bromonaphthalene	10^6	10^9	50	50	0.00	0.55
1-Iodonaphthalene	10^6	10^{10}	500	500	0.00	0.70
Perylene	2.0×10^8	10^7	—	0.98	0.98	—
3-Bromoperylene	2.0×10^8	10^7	—	0.98	0.98	—

External Heavy Atom Effect

Solvents and other additives containing heavy atoms also facilitate ISC via the **external heavy atom effect**. Excited S states of the “perturber” mix with a low-lying T state of the “perturbed.”

TABLE III. Phosphorescence data for naphthalene in heavy-atom-containing hosts.

Host	Purity	0-0 band (naph- h_8)	Lifetimes ^a		
			Naph- h_8 (msec)	Naph- d_8	$(1/\tau)h_8 - (1/\tau)d_8$
<i>p</i> -Br ₂ φ	Zone refined	4830 Å	33	33.5	0.4±3
<i>s</i> -Br ₃ φ	Rextal	4750	70	81	2.0±1.3
124-Br ₃ φ	Vac. sub.	4820	b
<i>s</i> -Br ₄ φ	Zone refined	4820	33	36.5	2.8±2.9
C ₆ Br ₆	Rextal	4800	96	105	0.9±0.6
<i>p</i> -ClBr φ	Zone refined	4830	c	c	...
<i>p</i> -Cl ₂ φ	Zone refined	4830	776	1 370	0.56±0.1
<i>s</i> -Cl ₃ φ	Rextal	4810	950±50	2 200±200	0.6±0.1
<i>s</i> -Cl ₄ φ	Zone refined	4800	790±70	1 840 ^d ±50	0.7±0.1
C ₆ Cl ₆	Zone refined	4770	1380	4 100±300	0.48±0.05
<i>p</i> -I ₂ φ	Vac. sub.	4820	14.9±1.2	15.1±0.9	0.8
φ - φ	Zone refined	4750	2100	13 500±700	0.40±0.03

^a Average deviation of several runs (over several time scales) was better than ±5% unless noted.

^b Nonexponential—host crystal (impurity) phosphoresces.

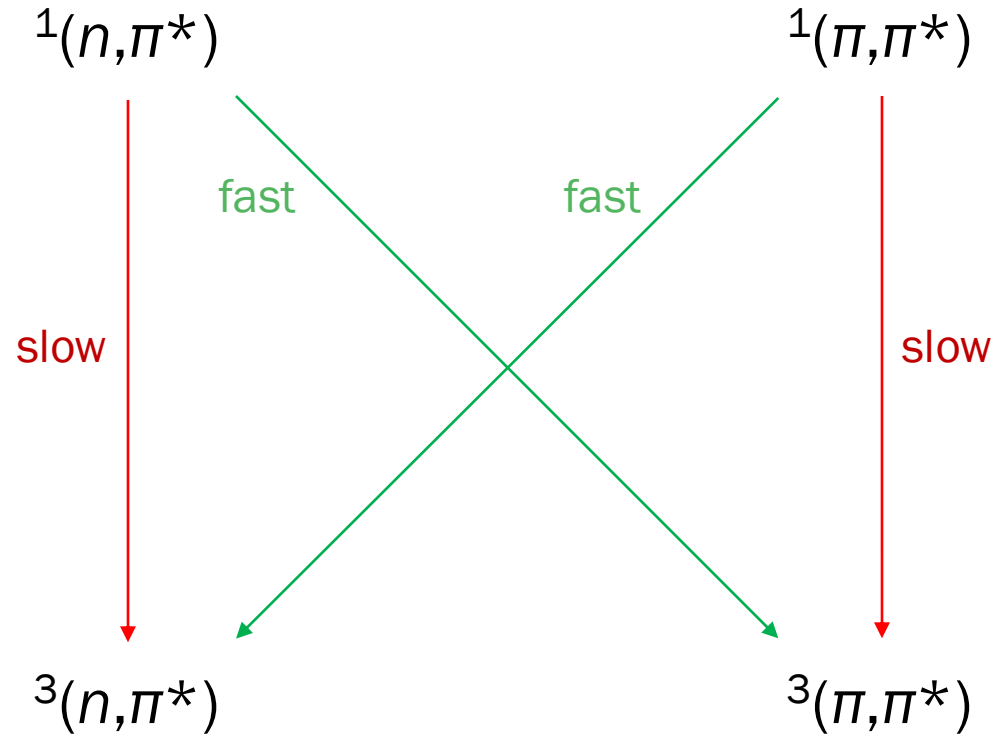
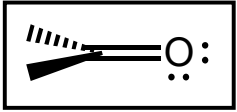
^c Nonexponential, lifetime seems to be on the order of 50 msec for naph- h_8

and 60 msec for naph- d_8 .

^d No 6-sec phosphorescence observed as reported by E. T. Harrigan and N. Hirota, J. Chem. Phys. **49**, 2301 (1968).

El-Sayed's Rules

El-Sayed's rules suggest that in photo-excited organic molecules, intersystem crossing is allowed only when a change in orbital occupancy occurs. A spin flip is coupled to a $p_x \rightarrow p_y$ transition.



Radiative Transitions: Transition Dipole and Oscillator Strength

Photophysical Properties and Transitions

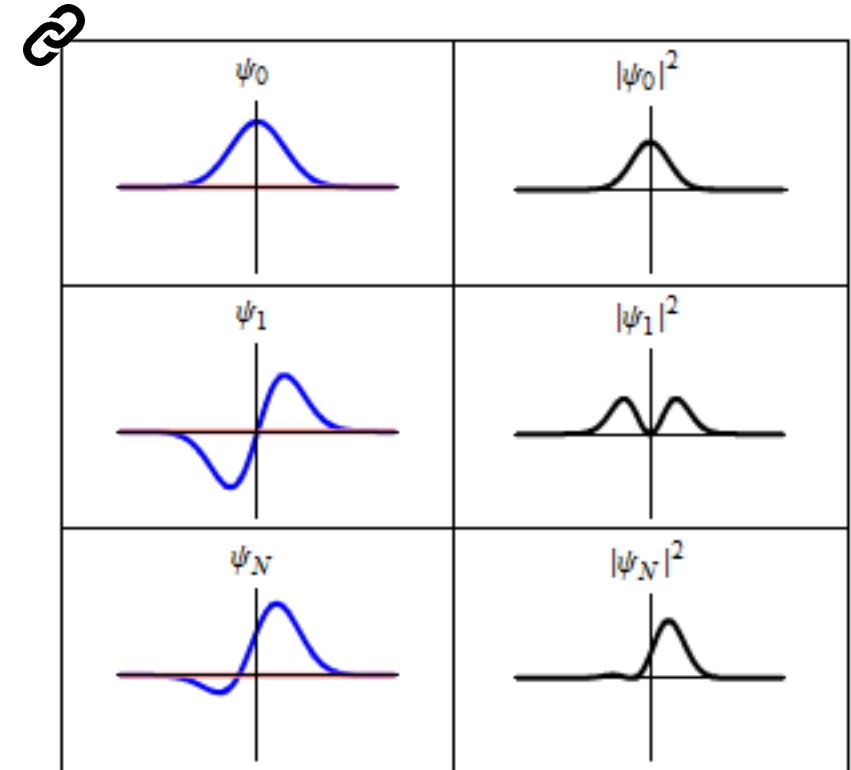
Transition Dipole Moment

Interaction of electromagnetic radiation with molecular electrons results in a **transition dipole moment** μ_{mn} . Forbidden radiative transitions have $\mu_{mn} = 0$.

$$\hat{\mu} = e \sum^N \vec{r}_i$$

$$\mu_{mn} = \langle \psi_m | \hat{\mu} | \psi_n \rangle$$

The probability of the $n \rightarrow m$ transition is proportional to $|\mu_{mn}|^2$.



Transition Dipole Moment

Electronically forbidden transitions involve either no net overlap of ψ_m and ψ_n or no net displacement of electrons by the incident radiation.

$n \rightarrow \pi^*$ in H_2CO : zero net orbital overlap

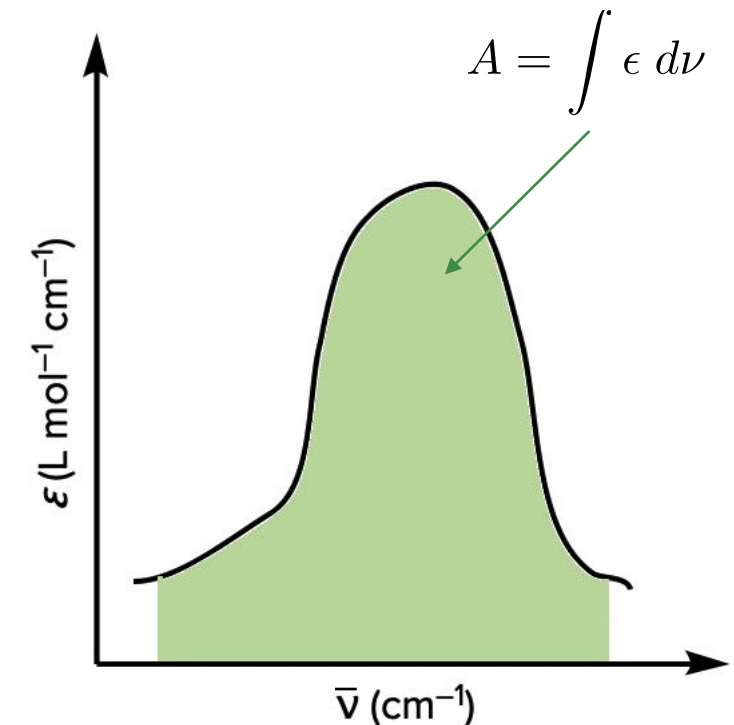
\perp -polarized light and C_6H_6 : zero electron displacement

Oscillator Strength

Oscillator strength f for an electronic transition relates the strength of an electronic transition to that of a classical harmonic oscillator. It is related to the size of a peak in an absorption spectrum.

$$f_{mn} = (4.702 \times 10^{-7} \text{ D}^{-2} \text{ cm}) \bar{\nu} |\mu_{mn}|^2$$

For a transition with $f = 1$ and $\bar{\nu} = 40,000 \text{ cm}^{-1}$,



$$f_{mn} = (4.319 \times 10^{-9} \text{ mol L}^{-1} \text{ cm}^2) A$$

$$f_{mn} \approx (6.784 \times 10^{-9} \text{ mol L}^{-1} \text{ cm}^2) \epsilon_{max} \bar{\nu} f_{whm}$$