

CHM 535/635
Molecular and Supramolecular Photochemistry

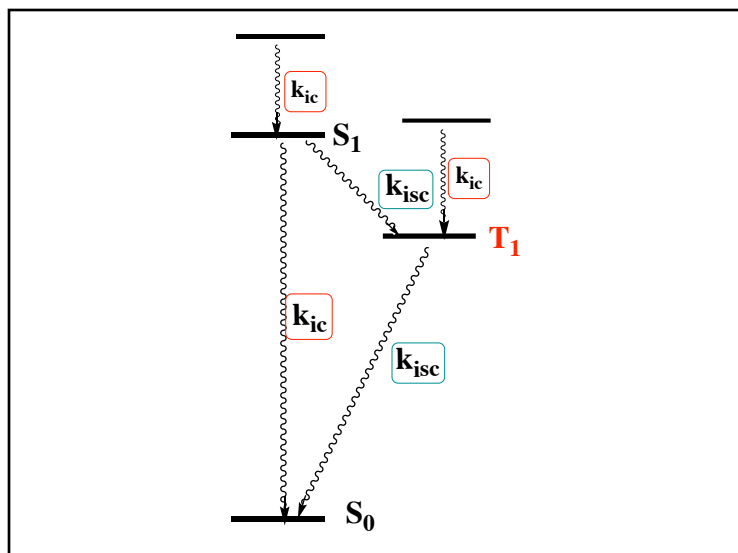
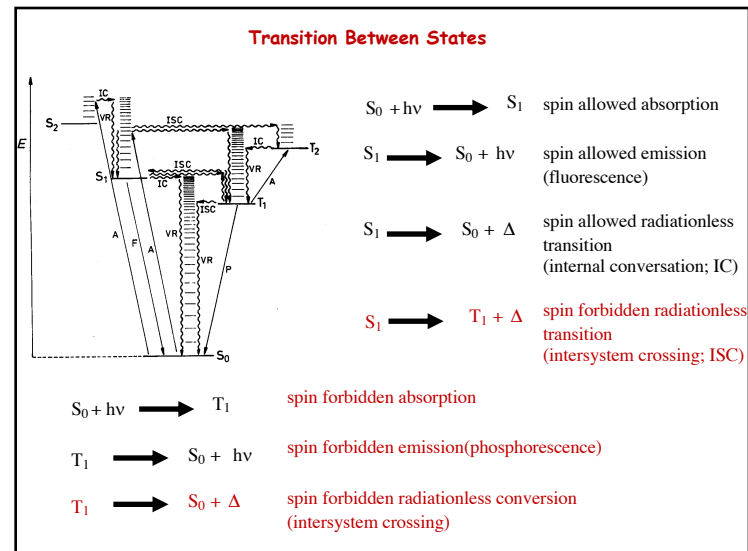
Radiationless Transitions

↑ Spin allowed
↑ Spin forbidden

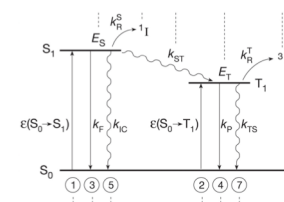
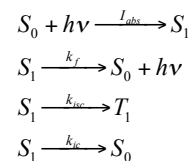
Chapters 3 & 5

Principles of Molecular Photochemistry: An Introduction

NJT, VR and JCS



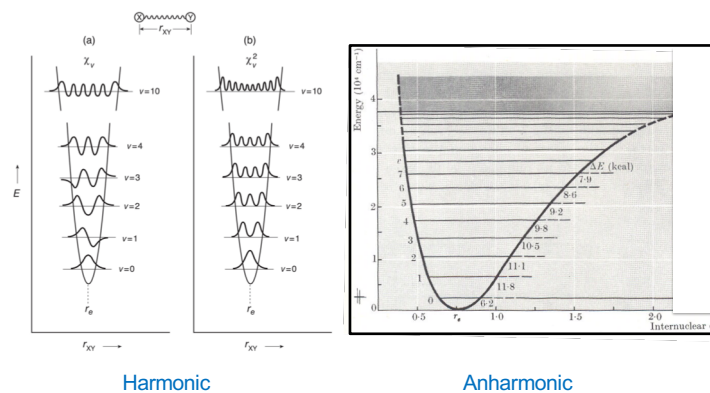
Competition with fluorescence and phosphorescence Why radiationless transition matters?



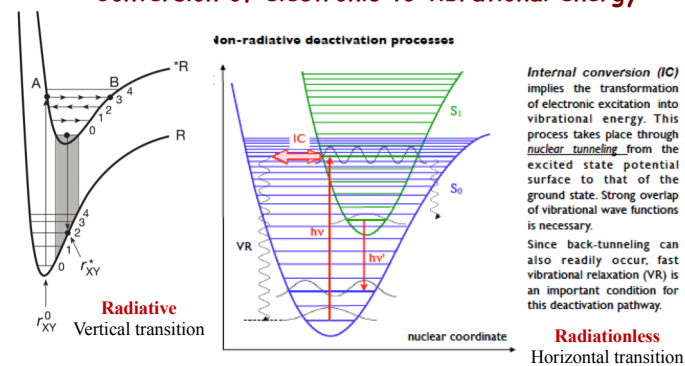
$$\phi_f = \frac{k_f[S_1]}{(k_f + k_{isc} + k_{ic} + \dots)[S_1]}$$

$$\tau_f = \frac{1}{k_f + k_{isc} + k_{ic} + \dots}$$

Visualization of vibrational levels within an electronic energy surface

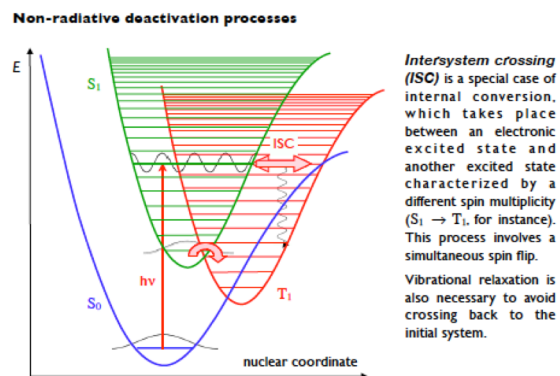


Conversion of electronic to vibrational energy



- Three step process:
- upper vibrational to lower vibrational level in excited state
 - lower vibrational level to upper vibrational of the lower state
 - upper vibrational of the lower state to lowest vibrational level

Radiationless processes may include spin changes

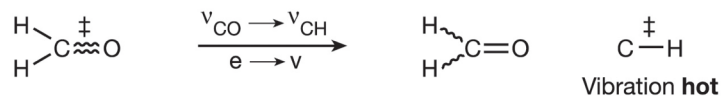


Horizontal transitions not involving photon

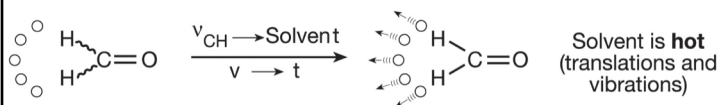
- Conservation of energy
- Conservation of momentum of nuclei
- Conservation of spin
- Conservation of symmetry of orbitals

Electronic to Vibrational Energy Transfer

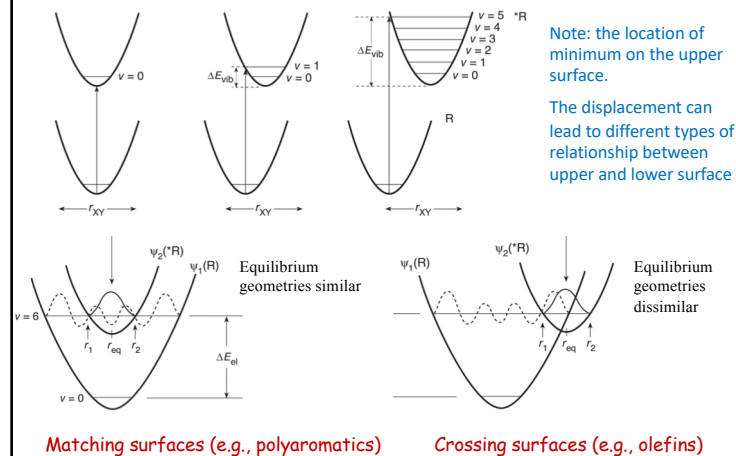
Intramolecular vibrational relaxation (IVR) occurs within 10 to 0.1 ps



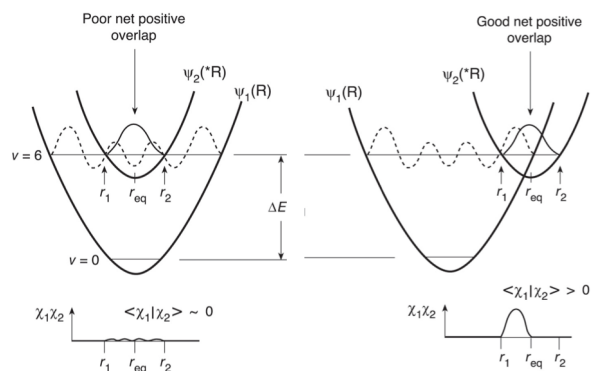
Intermolecular vibrational energy transfer (VET) from the molecule to the solvent occurs in the time range 100 to 10 ps



Visualization of vibrational levels within a ground state and excited state electronic energy surfaces



Radiationless Process: Surface Crossing and Matching



Initial & final spins are the same. The only prohibition is vibronic.
The rate of IC will depend on vibrational overlap of the initial and the final states.

The Energy Gap Law for Internal Conversion

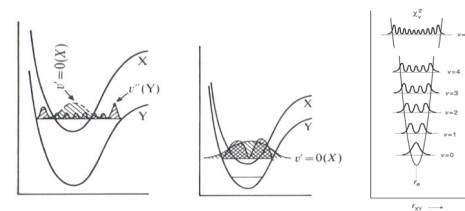
Matching surfaces

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

$$k_{\text{IC}} \sim 10^{13} f_{\text{v}}$$

$$k_{\text{IC}} \sim 10^{13} \exp^{-\alpha \Delta E}$$

ΔE is the energy separation between the surfaces involved in the transition at the nuclear geometry r_c .



Dependence of rate of $k_{IC} S_1$ to S_0 on energy gap

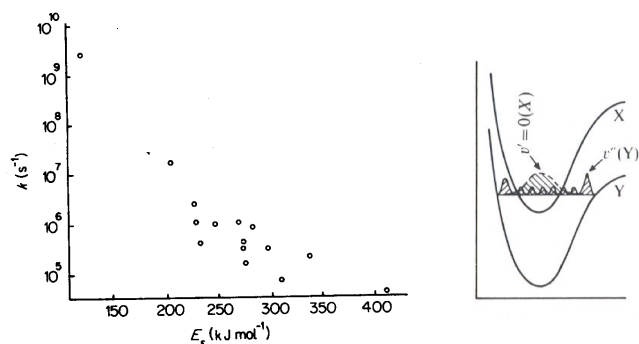


Figure 3.25. Singlet decay rate constants (k) of aromatic hydrocarbons plotted against the singlet energy (E_s). (From data in J. B. Birks, *Photophysics of Aromatic Molecules*, (1970), Wiley)

Dependence of rate of $k_{ISC} T_1$ to S_0 on energy gap

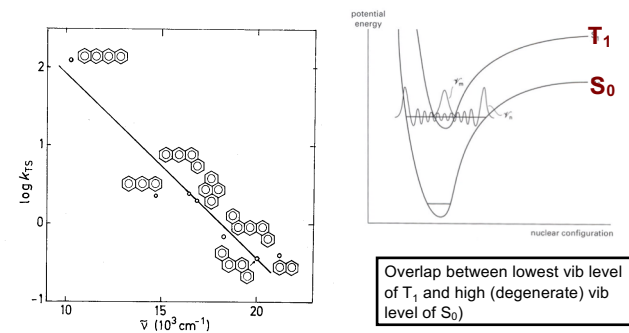
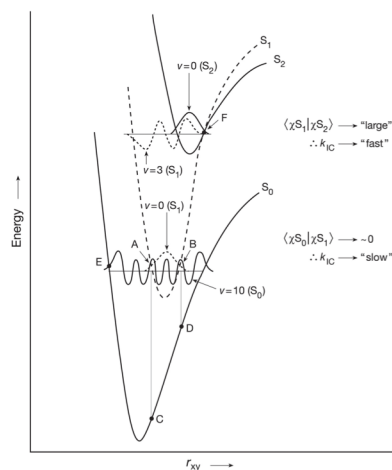


Figure 5.5. Relationship between the energy gap $\Delta E(T_1 - S_0)$ and the logarithm of the rate constant k_{ISC} of intersystem crossing in aromatic hydrocarbons (data from Birks, 1970).

Basis of Kasha's Rule



Kasha's Rule

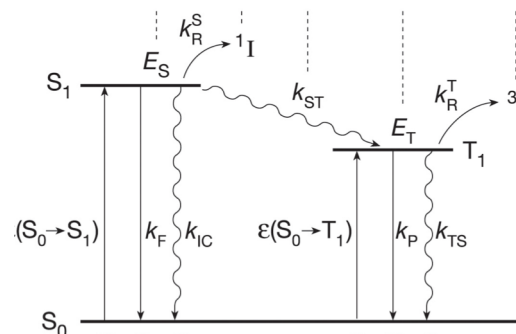
All photophysical and photochemical processes usually start in S_1 or T_1 , irrespective of which excited state or vibrational level is initially produced.

S_2 to S_1 IC is fast due to possible surface crossing and smaller gap

S_1 to S_0 IC is slow due to matching surface and larger gap

S_2 to S_1 IC can be slow if gap is larger and the surfaces don't cross

S_1 to S_0 and T_1 to S_0 have large energy gaps Most actions are from S_1 and T_1



Azulene Anomaly and Energy Gap Law

Fluorescence occurs only from S_1 to S_0 ; phosphorescence occurs only from T_1 to S_0 ; S_n and T_n emissions are extremely rare (Kasha's rule).

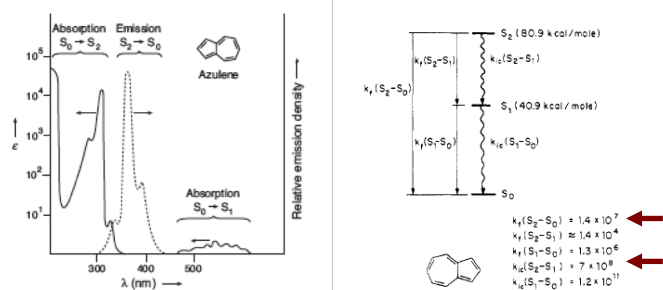


TABLE I. Fluorescence Quantum Yields and the Energies of the First Two Excited Singlet States of Substituted Azulenes*

	Φ_F	E_{S_1} , kcal/mol	E_{S_2} , kcal/mol	ΔE , kcal/mol
	0.058	36.3	77.0	40.9
	0.031	40.9	80.9	40.0
	0.014	39.5	77.8	38.3
	0.0081	42.6	79.5	36.9
	0.0034	42.9	77.5	34.6
	$\sim 10^{-4}$	44.3	77.2	32.9

S_2 to S_1 rate vs Energy Gap

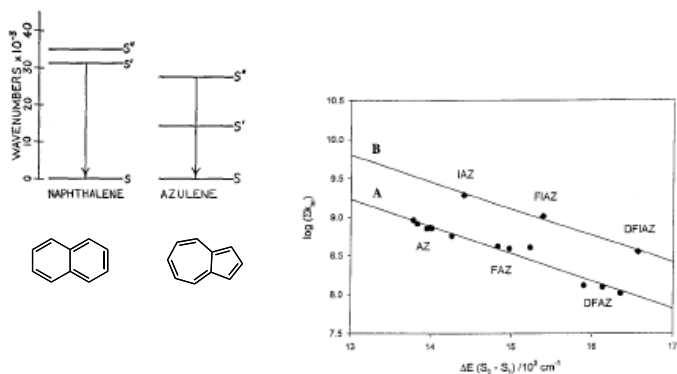
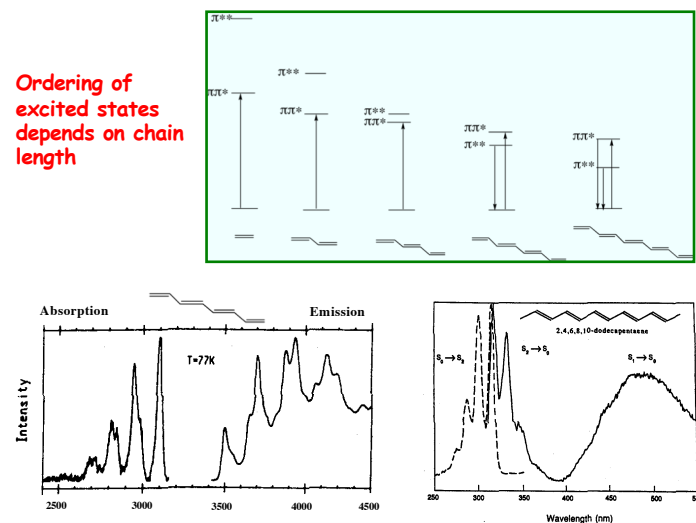


Figure 3. Log-linear energy gap law plots (see text) for azulene (AZ), 1-fluoroazulene (FAZ), and 1,3-difluoroazulene (DFAZ) in several solvents (line A), and for 6-isopropylazulene (IAZ), 1-fluoro-6-isopropylazulene (FIAZ), and 1,3-difluoro-6-isopropylazulene in *n*-hexane (line B). The data for AZ in several solvents are taken from ref 11.

Ordering of excited states depends on chain length



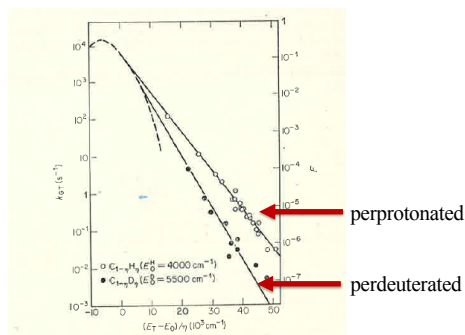
Effect of deuteration on radiationless process (T_1 to S_0)

Figure 5.2 $T_1 - S_0$ intersystem crossing rate k_{IS} (s^{-1}) and Frank-Condon factor F against normalized triplet state energy $(E_T - E_0)/h$ for unsubstituted perprotonated and perdeuterated aromatic hydrocarbons. The broken line represents F as derived from phosphorescence spectra. The F -scale is normalized by drawing the two solid lines as tangents to this function (after Siebrand⁴)

Birks book

Electronic to Vibrational Energy Transfer

Bond Type	Vibrational Type	Frequency
C=C	stretch	2200 cm^{-1}
C=O	stretch	1700 cm^{-1}
C=C	stretch	1600 cm^{-1}
N=N	stretch	1500 cm^{-1}
C-H	bend	1000 cm^{-1}
C-C	stretch	1000 cm^{-1}
C-C	bend	500 cm^{-1}
C-H	stretch	3000 cm^{-1}
C-D	stretch	2100 cm^{-1}

High frequency vibrations are important in radiationless transitions.

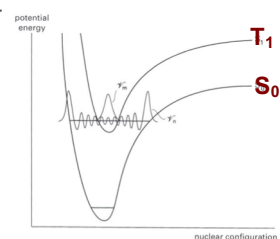
Vibrational level to match the gap is of lower # with high frequency vibrations.

Table 5.4 Some Representative Values of Triplet Energies, Phosphorescence Radiative Rates, Intersystem Crossing Rates, and Phosphorescence Yields^a

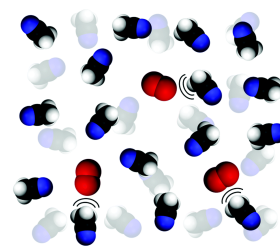
Molecule	E_T	k_p	k_{TS}	Φ_p
Benzene- h_6	85	~ 0.03	0.03	0.20
Benzene- d_6	85	~ 0.03	< 0.001	~ 0.80
Naphthalene- h_8	60	~ 0.03	0.4	0.05
Naphthalene- d_8	60	~ 0.03	< 0.01	~ 0.80
$(CH_3)_2C=O$	78	~ 50	1.8×10^3	0.043
$(CD_3)_2C=O$	78	~ 50	0.6×10^3	0.10

a. In organic solvents at 77 K. E_T in kcal mol⁻¹, k , in s⁻¹.

C-H stretch 3000 cm^{-1}
C-D stretch 2100 cm^{-1} Higher vibrational level needed to match; poor overlap, slow decay, large Φ_p

Isotope Effect on Rate of T_1 to S_0

Decay of singlet oxygen depends on solvent and deuteration



Mikkel Bregnhj, Michael Westberg, Frank Jensen and Peter R. Ogilby, *Phys. Chem. Chem. Phys.*, 2016, 18, 22946

Solvent	$\tau_1/\mu s$	
	Averaged published data ^a	Current data ^b
Benzene- h_6	30.6 \pm 0.9	30.4
Benzene- d_6	640 \pm 150	747
Toluene- h_8	28.6 \pm 0.7	30.5
Toluene- d_8	303 \pm 17	314
α, α, α -Trifluorotoluene	62.5	61.7
<i>o</i> -Xylene	21.0 \pm 2.0	23.4
Mesitylene	15.5 \pm 0.5	16.9
Chlorobenzene	45 \pm 3	43.6
Iodobenzene	37 \pm 2	38.9
1,2-Dichlorobenzene	—	57.0
1,2,4-Trichlorobenzene	—	93.8
Cyclohexane- h_{12}	23.3 \pm 0.5	24.0
Cyclohexane- d_{12}	450	483
<i>n</i> -Pentane	34.8 \pm 0.2	34.8
<i>n</i> -Hexane- h_{14}	30.8 \pm 0.6	32.2
<i>n</i> -Hexane- d_{14}	—	586
<i>n</i> -Heptane	28.9 \pm 0.5	30.1
<i>n</i> -Octane	—	28.6
<i>n</i> -Decane	27.6	26.5
Methanol- h_4	9.8 \pm 0.6	9.4
Methanol-OD	31 \pm 5	31.4
Methanol- d_4	246 \pm 16	276
1-Propanol	17.2 \pm 0.9	15.9
1-Octanol	18.5	17.8
Benzyl alcohol	—	14.4
Acetone- h_6	48 \pm 4	45.6
Acetone- d_6	770 \pm 140	1039
Acetonitrile- h_3	77 \pm 4	81.0
Acetonitrile- d_3	890 \pm 330	1610
Benzonitrile	36 \pm 4	40.0
H ₂ O	3.7 \pm 0.4	3.5 ^c
D ₂ O	68 \pm 1 ^f	68.9 ^c

Vibrational effects on singlet oxygen lifetime

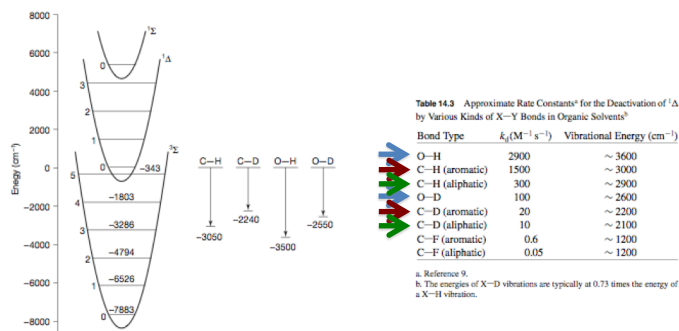
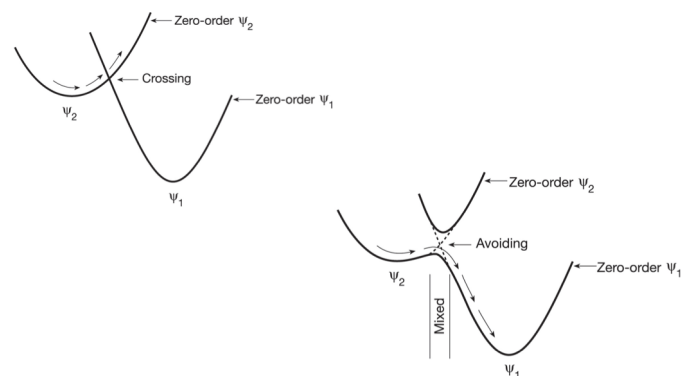


Figure 14.3 Comparison of the energy levels of $^1\Delta$ to common high-frequency X-H and X-D vibrations of solvents. Energies in cm^{-1} .

Crossing from one to another surface depends on the allowedness of the transition: (a) electronic and (b) spin



Strictly planar

$$n_0 = p_0$$

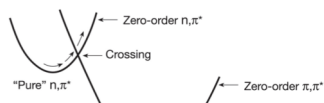
$$\langle n_0 | \pi \rangle = 0$$



Nonplanar

$$n_0 = sp^n$$

$$\langle n_0 | \pi \rangle \neq 0$$



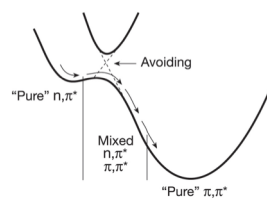
"Pure" n, π^*

"Pure" π, π^*

Planar vibrations



Energy is fine, but
Orbitals don't overlap



"Pure" n, π^*

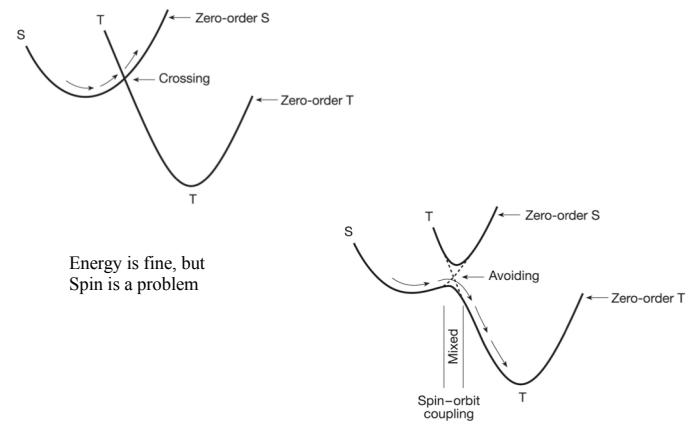
Mixed n, π^*, π, π^*

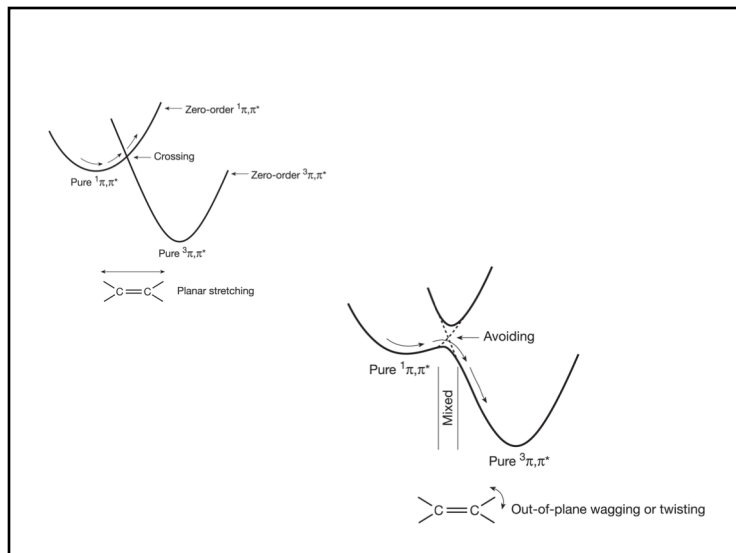
"Pure" π, π^*

Nonplanar vibrations



Role of Spin-Orbit Coupling on ISC





Spin

Principles of Molecular Photochemistry: An Introduction NJT, VR and JCS

Chapter 2: pages 82 - 108

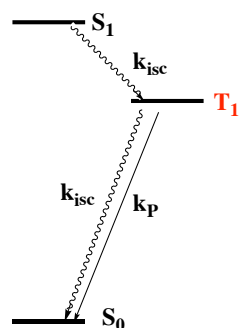
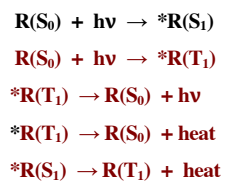
Chapter 3: pages 134 - 167

Chapter 4: pages 235 - 244

Chapter 5: pages 281 - 287

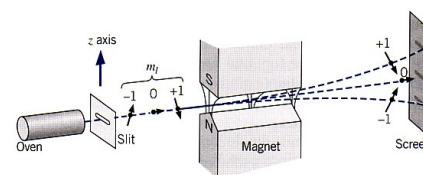
Chapter 13: pages 955 - 959

Spin forbidden transitions



Otto Stern
Nobel Prize, 1943

Expectation and Observation Stern & Gerlach ~1922



¹It is because an atom's behavior in a magnetic field depends on m_l , that it is known as the "magnetic quantum number."

²In the original Stern-Gerlach experiment of 1922, two lines were seen, but neutral *silver* atoms were used. Although the silver atoms, having one $5s$ electron beyond a closed $n = 4$ shell, should behave as atoms of $\ell = 0$, the Stern-Gerlach apparatus was later used with hydrogen (1925, Phipps and Taylor), to rule out any complication multiple electrons might introduce.

The Stern-Gerlach experiment

- Experiment was confirmed using:

Element Electronic Configuration

H $1s^1$

Na $\{1s^22s^22p^6\}3s^1$

K $\{1s^22s^22p^63s^23p^6\}4s^1$

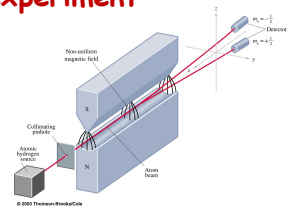
Cu $\{1s^22s^22p^63s^23p^63d^{10}\}4s^1$

Ag $\{1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}\}5s^1$

Cs $\{[Ag]5s^25p^6\}6s^1$

Au $\{[Cs]5d^{10}4f^{14}\}6s^1$

- In all cases, $l = 0$ and $s = 1/2$.



Visualization of Spin Chemistry

- Quantum mechanics requires **mathematics** for a **quantitative** treatment.
- Much of the mathematics of quantum mechanics can be visualized in terms of **pictures** that capture the **qualitative** aspects of the phenomena under consideration.
- Visualizations are **incomplete**, but it is important to note “**correct**” mathematical representations fail for complex systems as molecules.

Spin

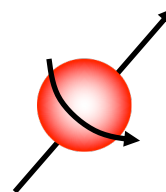
Visualize spin by resorting to a classical analogy of a spherical object executing a spinning motion about an axis, *i.e.*, a top or a gyroscope.



Develop a model which associates specific magnetic properties, *i.e.*, a magnetic moment, with the electron's spin angular momentum

Angular momentum is a property of a macroscopic object which is in a state of rotation about an axis.

Spin



- Quantum particles possess an intrinsic angular momentum called **spin** which is not associated to a rotation about an axis, although we can visualize it as if it was generated by a rotation of the particle about its own axis
- Classically **angular momentum** is a property of a macroscopic object which is in rotation about an axis

Understanding through models

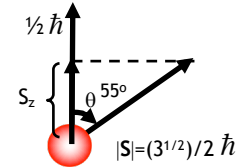
As a scientist, it is best to take the perspective that no scientific theory, model, or idea is really “true.” A theory is just a collection of ideas that can stick in the human mind as a useful way of imagining the natural world. Given enough time, every scientific theory will ultimately be replaced by a more correct one. And often, the more correct theory feels entirely different philosophically from the one it replaces. But the ultimate arbiter of what makes good science is not whether the idea is true, but only whether it is useful for predicting the outcome of some future event. (It is, of course, that predictive power that allows us to build things, fix things, discover things, and generally improve the quality of human life.)

<https://gravityandlevity.wordpress.com/>

Spin

- Electron possesses a fixed and characteristic spin angular momentum of $\frac{1}{2} \hbar$

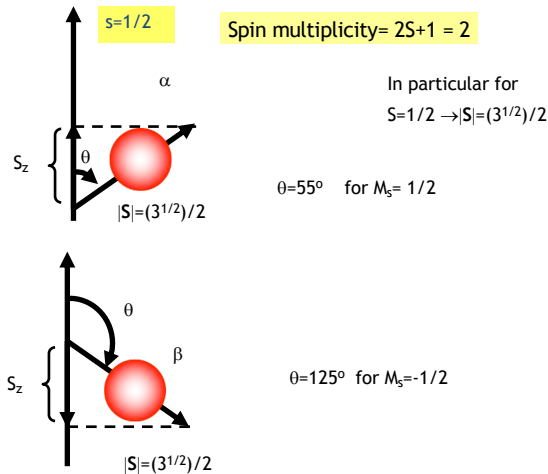
$$\hbar = \text{Planck's constant } (h) / 2\pi$$



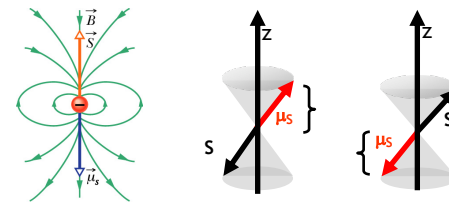
This is fixed independent of whether it is free or associated with a nucleus, regardless the orbital that it occupies, e.g., **s, p, d, nπ*, ππ***; always the same.

If the electron spin were a **classical** quantity, the magnitude and direction of the vector representing the spin could assume any length and any orientation.

Only certain directions of the spin are allowed. This is termed **spin multiplicity**.



Electron has magnetic moment due to its spin



The electron possesses a **spin magnetic** moment due to its charge and spin. The magnetic moment μ_s is quantized in magnitude and orientation as the angular momentum **S** from which it arises

$$\mu_s = -(e/2m_e) g_e S = -\gamma_e g_e S \quad \text{where } g = -2.0023$$

γ_e gyromagnetic ratio = $e/2m$

For electron $\mu_s = -9.284764620(57) \times 10^{-24}$ Joules/Tesla
It is a fixed number.

Cones of possible orientations

The uncertainty principle (Heisenberg) states that the **length** and the **direction** of the spin angular momentum are conjugate quantities: if one is measured precisely the other cannot be measured with any precision



The length of the spin $|S|$ and S_z are known because of the quantistic principles

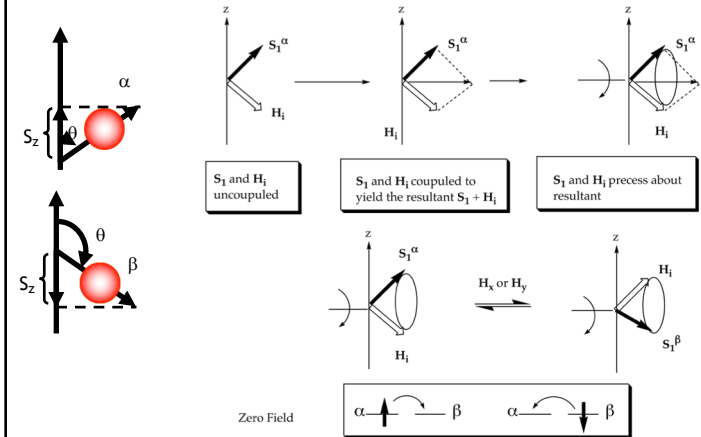


The angle the spin forms with z is known but not its x and y components: it lies on a definite cone



There is an infinite set of positions that the spin vector can assume in space making an angle of 55° with the z-axis, any one of which could correspond to the actual position of the spin vector. This is represented as a cone in a 3-D.

Spin interconversion in one spin system

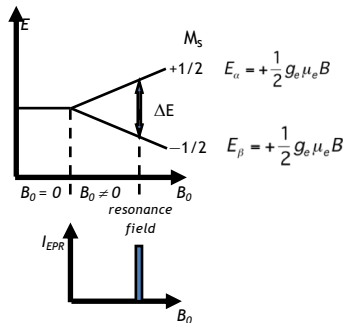


Basic requirements for spin change-Energy

1. Conservation of energy

Transitions between the two electronic Zeeman levels may be induced by an electromagnetic field \mathbf{B}_1 of the appropriate frequency ν such that the photon energy matches the energy-level separation ΔE

Simplest energy level scheme for a $S=1/2$ system (free electron) in an external applied B_0 (we assumed $B_0 \parallel z$ axis):



Varying B_0 one may change the energy level separation.

Resonant absorption may occur if the frequency ν is adjusted so that:

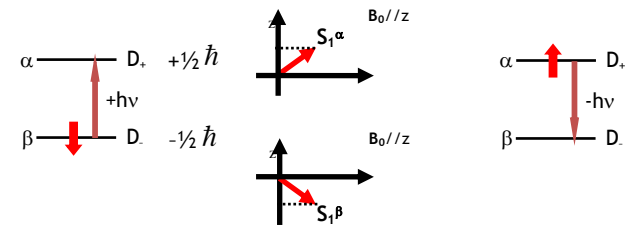
$$\Delta E = E_\alpha - E_\beta = g_\beta \mu_e B = h\nu$$

Basic requirements for spin change-Angular Momentum

2. Conservation of angular momentum

When a photon is absorbed or emitted by an electron (or atom, or molecule) the angular momentum of the combined (total) system must be conserved.

The transitions between the Zeeman levels require a change in the orientation of the electron magnetic moment (+1):



If photon can serve as the source of angular momentum the total angular momentum could be conserved.

Spin interconversion in one spin system

Zero Field

High Field

Photon has angular momentum (\hbar)

Photon has one unit (\hbar) of angular momentum and has its spin component ($\pm\hbar$) along or opposed to its direction of motion.

direction of propagation $+1$ σ_{hv}

-1 σ_{hv}

So along z the allowed values of σ_{hv} are $+1$ and -1 (in units of \hbar)

The two possible spin states along the selected z axis correspond to the magnetic vector moving clockwise around z and counterclockwise around z

$\sigma_{hv+} = +1\hbar$

$\sigma_{hv-} = -1\hbar$

These two cases correspond to left (σ_{hv+}) and right (σ_{hv-}) polarized light

Photon induced electron spin change

Representation of the radiative transition for a *free electron* involving the absorption or the emission of a photon:

Stimulated absorption

α D_+

β D_-

$+h\nu$

Photon's magnetic component H_1 $S_{1\beta}$

α D_+

β D_-

$+h\nu$

$S_{1\beta}$ couples to H_1 and precesses about the resultant $S_{1\beta} + H_1$

This precession causes β state to α state transition (stimulated absorption)

$\beta(-1/2)\hbar + h\nu (+1)\hbar \xrightarrow{h\nu (+1)\hbar} \alpha(+1/2)\hbar$

EPR signal detected

From an experimental point of view the approach to the detection of resonant energy absorption or emission by a paramagnetic sample is keeping the microwave frequency ν fixed and varying the B_0 until the resonance condition is met.

For the **free electron**: $\Delta E = g_e \mu_e B = h\nu$

E

M_s

$+1/2$ $E_\alpha = +\frac{1}{2}g_e\mu_e B$

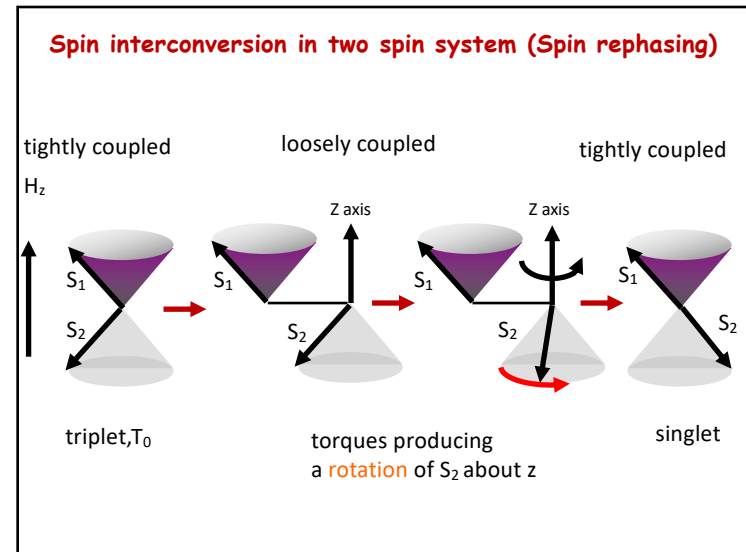
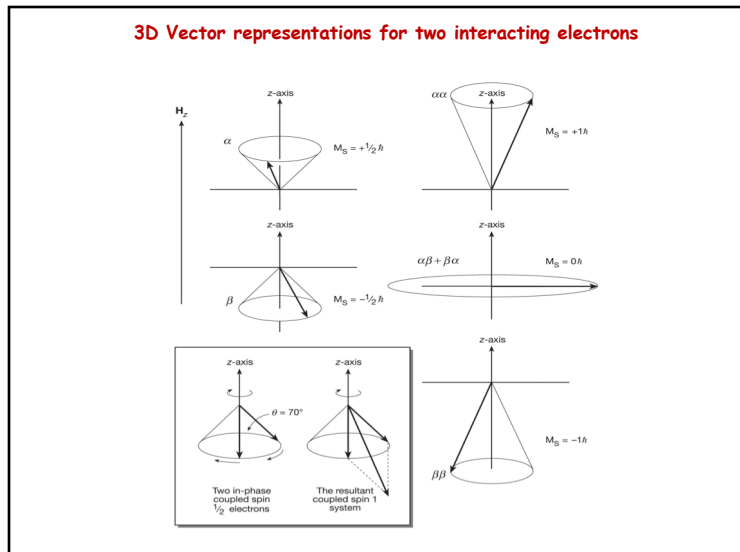
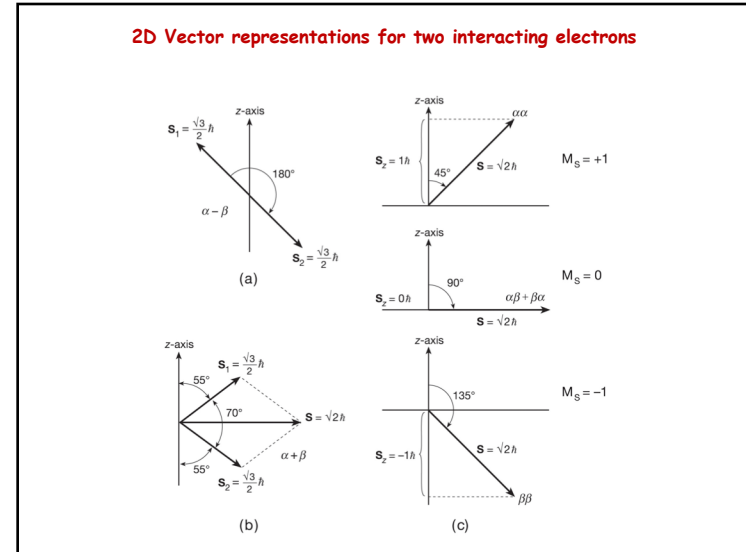
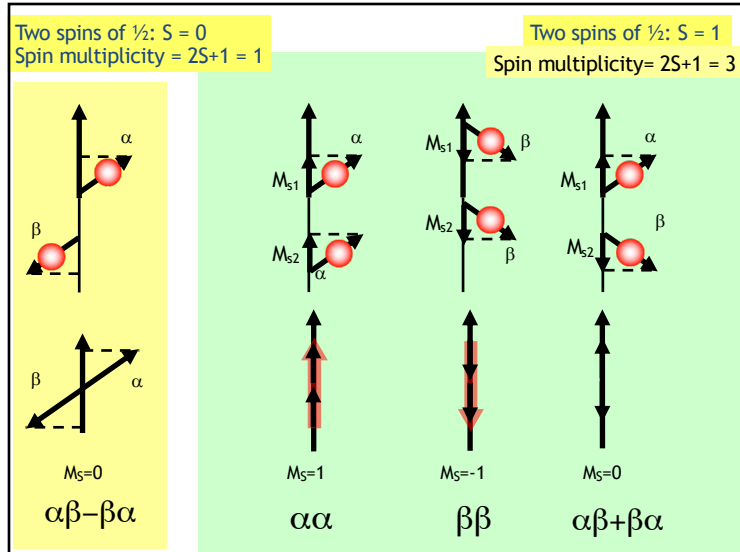
$-1/2$ $E_\beta = -\frac{1}{2}g_e\mu_e B$

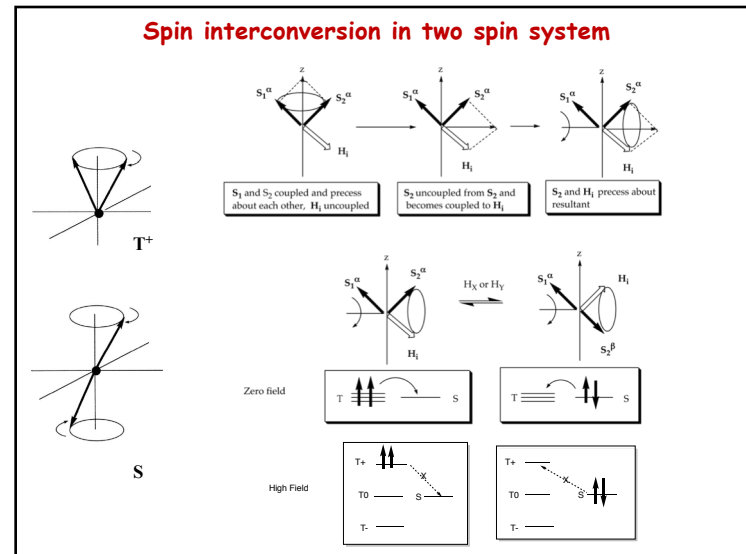
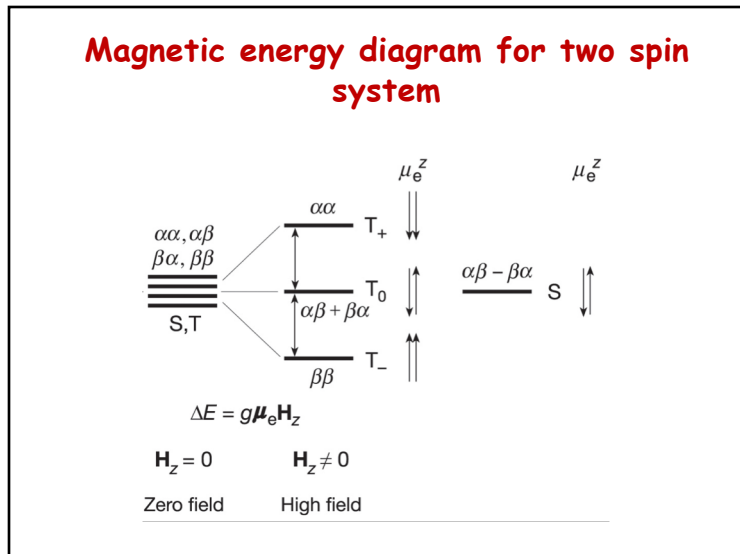
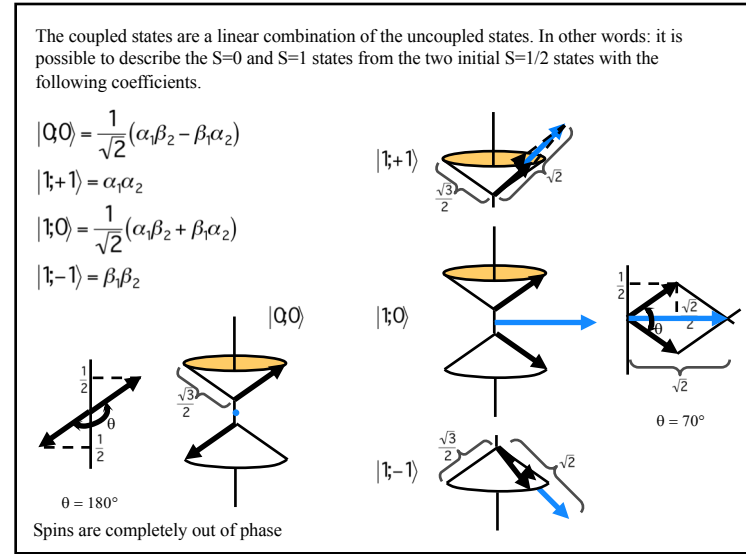
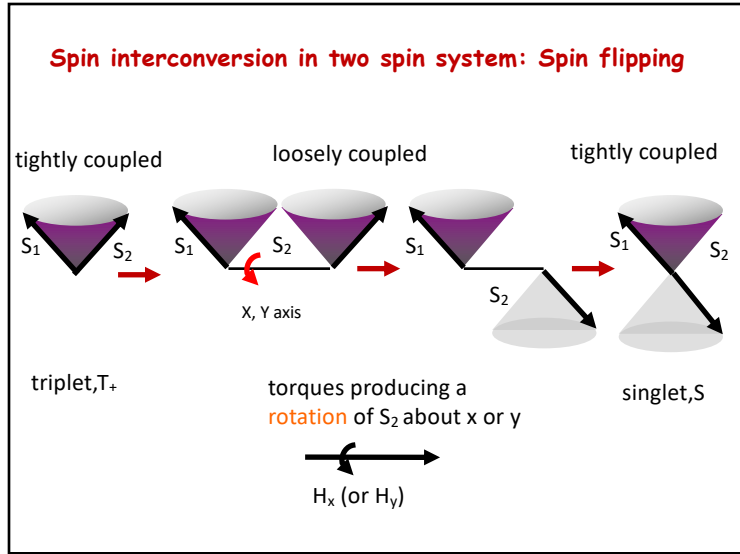
$B_0 = 0$ $B_0 \neq 0$ B_0

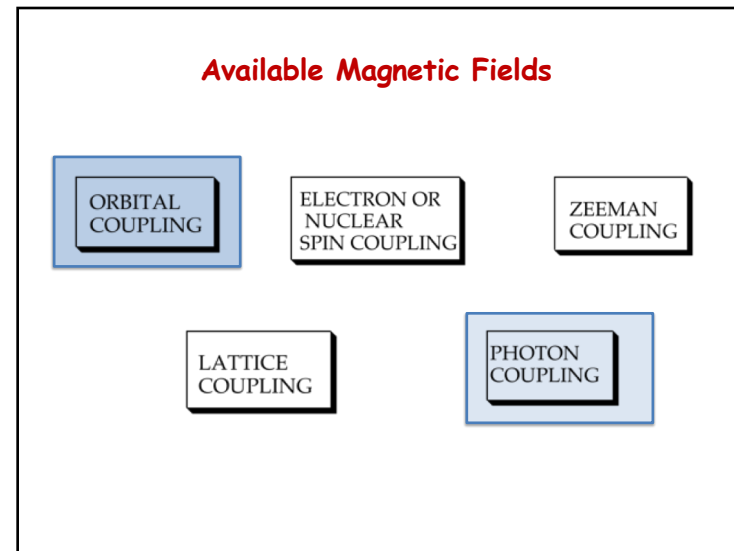
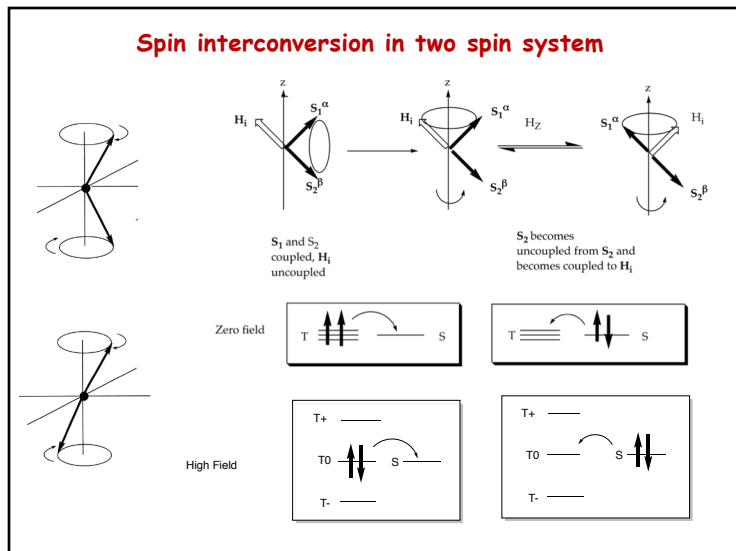
resonance field

B_0 (G)

The frequency used in the majority of EPR spectrometers is approximately 9.5 GHz (X-band microwave region). With this frequency the resonance of free unpaired electron system ($g_e=2.0023$) occurs at about 3300 gauss.







Precession and Spin-Orbit coupling

An **external magnetic fields** cannot be responsible for the Singlet-Triplet transition, because it would act equally on both spins.

Besides an external magnetic field another source of coupling is the **spin-orbit coupling**: if L is coupled to S , they both precess around their resultant. If they are strongly coupled they precess rapidly, if they are weakly coupled they precess slowly.

The rate of precession about an axis is proportional to the strength of the coupling of the spin to the new magnetic field.

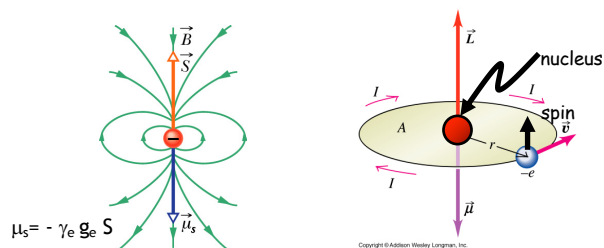
The power of the magnetic field generated is proportional to the rate of precession.

Selection rules for spin change in organic molecules Singlet \leftrightarrow Triplet

- Conservation of energy and angular momentum.
 - At the time of change, the **energy** of the two states should be degenerate or very close in energy.
 - At the time of change, the total **angular momentum** should be conserved.
 - A spin change is exactly compensated by an equal and opposite change of angular momentum which occurs from some other (coupled) interaction with another source of angular momentum.
- The electron spin must either remain unchanged or *change by one unit of angular momentum*. Singlet-triplet transition involves a total change of one unit. \hbar ($0 \hbar \rightarrow \pm 1 \hbar$).

Orbital angular momentum and magnetic moment

The electron "sees" a magnetic field from the apparent orbit of the positively charged nucleus.

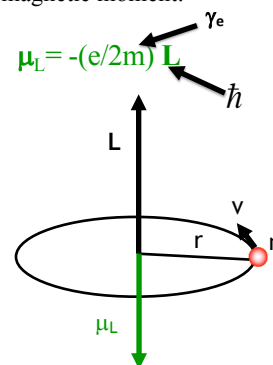


The electron possesses an **orbital** magnetic moment:

$$\mu_L(r) = (e/2m_e) L = -\gamma_e L$$

Magnetic moment of an orbiting electron

An electron in a Bohr atom is modeled as a point charge rotating about a fixed axis centered in the nucleus. Then it possesses a **orbital** magnetic moment:



If the electron possesses one unit of angular momentum (\hbar) its magnetic moment is equal to

$$\hbar(e/2m)$$

Bohr magneton

$$\mu_L = \beta_e = \mu_B = \hbar \gamma_e$$

Magnetic moment of a spinning electron

The electron possesses a **spin** magnetic moment:

~~$$\mu_s = -(e/2m) S$$~~

Analogues to L
 $\mu_L(r) = (e/2m_e) L$

$$\mu_s = -(e/2m) g_e S = -\gamma_e g_e S$$

g factor for free electrons and most organic molecules ≈ 2

Precession and Spin-Orbit coupling

The rate of precession about an axis is proportional to the strength of the coupling of the angular momentum to that axis.

If L is coupled to S, they both precess around their resultant. If they are strongly coupled they precess rapidly, if they are weakly coupled they precess slowly.

When L and S are strongly coupled it is difficult for other forces to break the coupling, in the second case it is easy.

Larmor precession of electron

In the absence of the magnetic field there is no precession. Precession starts only on application of magnetic field

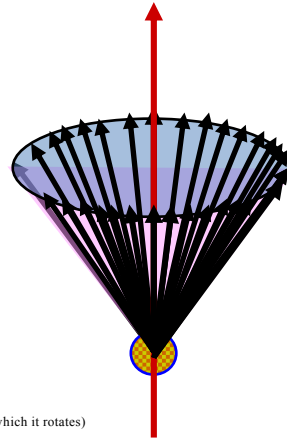
The electron would precess only as long as the magnetic field is on

The angular momentum vector precesses about the external field axis with an angular frequency known as the **Larmor frequency**.

The frequency (ω_s) of the Larmor precession, (the number of rotations per second of the vector μ , about the vector H) is independent of the orientation angle (θ).

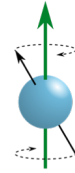
$$\omega_s = \frac{g_e \gamma_e H_z M_s}{\hbar}$$

g_e : fixed number for electron
 γ_e : gyromagnetic ratio
 H_z : applied mag. field (mag vector about which it rotates)
 M_s : spin state (1/2; 0; 1)
 \hbar : Planck's constant



Larmor precession

- (1) For a given orientation and magnetic moment, the value of ω_s decreases with decreasing field, and in the limit of $H_z = 0$, the precession would cease and the vector would lie motionless at some indeterminate value on the cone of possible orientations. (Note the notation H and B are the same)
- (2) For a given field strength and for a state with several values of M_s (multiplicity = or >1), the spin vector precesses fastest for the largest absolute values of M_s and is zero for states with $M_s = 0$ (e.g., T_0 and S).
- (3) For the same absolute value of M_s different signs of M_s correspond to different directions of precession, which have identical rates of precession, but different energies (e.g., T_+ and T_-).
- (4) A high precessional rate ω_s corresponds to a strong coupling to the field H_z and the magnetic energy corresponds to the strength of the coupling field.
- (5) High precessional rate \rightarrow high energy



Precession

- decreasing the field the rate of precession slows down
- different precession frequencies according to M_s
- different directions of precession according to the sign of M_s
- high precessional rate \rightarrow high energy
- g_e and β_e are fixed numbers for electron

$$\omega_s = \frac{g_e \beta_e B M_s}{\hbar}$$

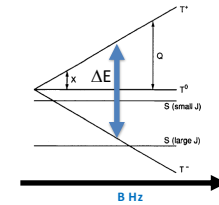
Notations B and H are the same

$$\hbar \omega_s = g_e \beta_e B M_s \quad \hbar \omega = h\nu = \Delta E$$

Relationship Between the Rate of Precession of an Electron Spin as a Function of Magnetic Field Strength.

Relationship Between the Rate of Precession of an Electron Spin as a Function of Magnetic Field Strength

B (Gauss)	ω (rad s ⁻¹)	ν (s ⁻¹)	$E = h\nu$ kcal/mole
1	1.7×10^7	2.8×10^6	2.7×10^{-7}
10	1.7×10^8	2.8×10^7	2.7×10^{-6}
100	1.7×10^9	2.8×10^8	2.7×10^{-5}
1000	1.7×10^{10}	2.8×10^9	2.7×10^{-4}
10000	1.7×10^{11}	2.8×10^{10}	2.7×10^{-3}
100000	1.7×10^{12}	2.8×10^{11}	2.7×10^{-2}
1000000	1.7×10^{13}	2.8×10^{12}	2.7×10^{-1}



$$\Delta E = h\nu = \hbar \omega$$

Some quantitative relationships

$$\gamma_e = e/2m = 1.760\,859\,74(15) \times 10^{11} \text{ s}^{-1} \text{ T}^{-1}$$

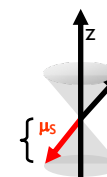
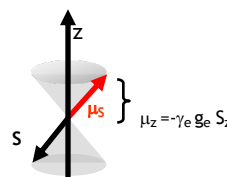
$$\omega_e = 1.8 \times 10^7 \text{ s}^{-1} \text{ B (if B is expressed in G)}$$

$$\nu_e = 2.8 \times 10^6 \text{ s}^{-1} \text{ B (if B is expressed in G)}$$

$$\Delta E = h\nu = \hbar\omega$$

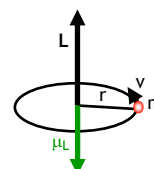
Momentum and magnetic moments: Summary

Spin and orbital motions generate magnetic moments



Spin magnetic moment

$$\mu_s = -(e/2m_e) g_e S = -\gamma_e g_e S$$



Orbital magnetic moment:

$$\mu_L(r) = (e/2m_e) L = -\gamma_e L$$

An electron in the first Bohr orbit with $L = \hbar$ has a magnetic moment defined as $= 9.27 \times 10^{-24} \text{ Am}^2$

$$\mu_B = \frac{e}{2m} \hbar \quad \text{Bohr Magnetron}$$

Magnitude of Spin-Orbit Coupling

$$H_{so} = \frac{ze^2}{8\pi\epsilon_0 m^2 c^3} \frac{1}{r^3} \vec{L} \cdot \vec{S}$$

operates on radial part of wavefunction

operates on orbital ang. mom. part of wavefunction

operates on spin ang. mom. part of wavefunction

Strength of L-S coupling is defined by

$$\hat{H}_{SO} = \xi \mathbf{l} \cdot \mathbf{s}$$

$$\xi_{n,l} \propto \frac{Z^4}{n^3(l+1/2)(l+1)}$$

- the magnitude of the spin orbital coupling operator (H_{SO}) depends on ξ which in turn depends on Z
- ξ depends only on the quantum numbers n (principal qn) and l (angular qn), not on m_l (magnetic qn). The effect of the spin-orbit interaction is to cause an admixture of orbitals with identical radial dependence but different angular dependences.

The heavy atom effect on spin transitions

The “heavy atom” effect is an “atomic number” effect that is related to the coupling of the electron spin and electron orbital motions (spin-orbit coupling, *SOC*).

Most commonly, the HAE refers to the rate enhancement of a spin forbidden photophysical radiative or radiationless transition that is due to the presence of an atom of high atomic number, Z .

The heavy atom may be either internal to a molecule (molecular) or external (supramolecular).

Spin-orbit coupling energies for selected atoms

Table 4.7 Spin-Orbit Coupling in Atoms^{a,b}

Atom	Atomic number	ζ (kcal mol ⁻¹)	Atom	Atomic number	ζ (kcal mol ⁻¹)
C ^c	6	0.1	I	53	14.0
N ^c	7	0.2	Kr	36	15
O ^c	8	0.4	Xe	54	28
F ^c	9	0.7	Pb	82	21
Si ^c	14	0.4	Hg	80	18
P ^c	15	0.7	Na	11	0.1
S ^c	16	1.0	K	19	0.2
Cl ^c	17	1.7	Rb	37	1.0
Br	35	7.0	Cs	55	2.4

Summary-1

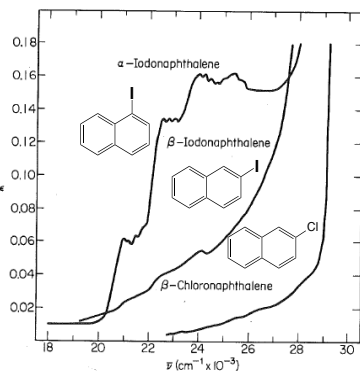
- The strength or energy (E_{SO}) of spin-orbit coupling is directly proportional to the magnitude of the magnetic moment due to electron orbital motion, μ_L (a variable quantity depending on the orbit), and the electron spin, μ_S (a fixed quantity).
- The magnitude of E_{SO} will increase, for a given orbit, as the atomic number, Z , the charge on the nucleus, increases, since both the accelerating force attracting the electron and the spin-orbit coupling constant ζ_{SO} are proportional to Z .
- For maximum effect of the nuclear charge, the electron must be in an orbital that approaches the nucleus closely, i.e., an orbital with some s-character, since s-orbitals have a finite probability of being located near or even in the nucleus!
- Irrespective of the magnitude of E_{SO} for spin-orbit coupling to induce a transition between states of different spin, the total angular momentum of the system, orbit plus spin, must be conserved. For example, a transition from an α spin orientation to a β spin orientation (angular momentum change of one unit) may be completely compensated by a transition from a p orbital of orbital angular momentum 1 to a p orbital of angular momentum 0 (e.g., a $p_x \rightarrow p_y$ type of transition).

Summary-2

- The orbitals involved in the $p_x \rightarrow p_y$ transition must be similar in energy. For a large energy difference between these orbitals, orbital angular momentum and therefore spin-orbit coupling through orbital angular momentum is “quenched”.
- Spin-orbit coupling in organic molecules will be effective in inducing transitions between different spin states if a “ $p_x \rightarrow p_y$ ” orbital transition *on a single atom* is involved because such an orbital transition provides both a means of conserving total angular momentum and also a means of generating orbital angular momentum that can be employed in spin-orbit coupling.
- Spin-orbit coupling in organic molecules will be effective in inducing transitions between different spin states if one (or both) of the electrons involved approaches a “heavy” atom nucleus that is capable of causing the electron to accelerate and thereby create a strong magnetic moment as the result of its orbital motion for a one electron atom, ($\zeta_{SO} \sim Z^4$).

Intersystem crossing in aromatic molecules and olefins ($\pi\pi^*$)

Internal Heavy Atom Effect: Spin forbidden absorption



THE JOURNAL OF CHEMICAL PHYSICS VOLUME 11, NUMBER 10 OCTOBER, 1943

Triplet-Singlet Transitions in Organic Molecules. Lifetime Measurements of the Triplet State*

*FRANK S. MCLELLAN

Department of Chemistry, University of California, Berkeley, California (Received December 16, 1942)

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 10, NUMBER 12 DECEMBER, 1942

Effects of Perturbations on Phosphorescence: Luminescence of Metal Organic Complexes

*RUPAK YADAV AND E. L. WATSON

Department of Chemistry, Purdue University, West Lafayette, Indiana (Received February 16, 1943)

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 20, NUMBER 1 JANUARY, 1952

Collisional Perturbation of Spin-Orbital Coupling and the Mechanism of Fluorescence Quenching. A Visual Demonstration of the Perturbation*

*MICHAEL KASAT

Department of Chemistry, University of London, England (Received August 13, 1951)

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 21, NUMBER 3 FEBRUARY, 1954

Singlet-Triplet Absorption Bands in Some Halogen Substituted Aromatic Compounds*

*DONALD S. MCELRENE, STANLEY W. BEAL, and FRANK L. HAYES

Department of Chemistry and Chemical Engineering, University of California, Berkeley, California (Received August 13, 1953)

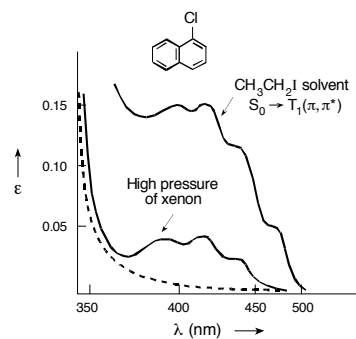
THE JOURNAL OF CHEMICAL PHYSICS VOLUME 21, NUMBER 2 FEBRUARY, 1954

Singlet-Triplet Absorption Bands in Some Halogen Substituted Aromatic Compounds*

*DONALD S. MCELRENE, STANLEY W. BEAL, and FRANK L. HAYES

Department of Chemistry and Chemical Engineering, University of California, Berkeley, California (Received August 13, 1953)

External Heavy Atom Effect: Spin forbidden absorption



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*MICHAEL KASAT

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Phosphorescence Lifetime of Benzene. An Inter-molecular Heavy-Atom Effect, a Deuterium Effect, and a Temperature Effect*

*M. R. WAGNER, R. P. FROCHA, and G. W. ROBINSON

*Case and Crain Laboratories of Chemistry, California Institute of Technology, Pasadena, California (Received June 20, 1960)

J. Chem. Phys. 33, 934 (1960).

Enhancement of the singlet-triplet absorption band of alpha-chloronaphthalene in the presence of xenon under high pressure

*ANNA GRABOWSKA

Institute of Physical Chemistry, Polish Academy of Sciences, ul. Pasteura 1, Warszawa 22, Poland (Received August 13, 1953)

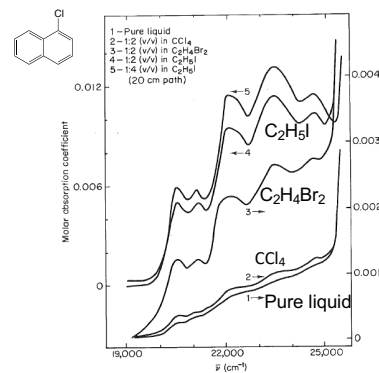
Spectrochimica Acta, 1962, Vol. 19, pp. 307 to 313.

J. Am. Chem. Soc. 1994, 116, 1345-1351

Organic Guests within Zeolites: Xenon as a Photophysical Probe*

*V. RAMAMURTHY

External Heavy Atom Effect: Spin forbidden absorption



THE JOURNAL OF CHEMICAL PHYSICS VOLUME 17, NUMBER 4 OCTOBER 15, 1949

External Heavy-Atom Spin-Orbital Coupling Effect. I. The Nature of the Interaction*

*R. P. McLELLAN, M. SUTHERLAND, and R. C. CHAMBERLAIN

Case Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana (Received 10 September 1948)

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 16, NUMBER 1 11 JANUARY 1948

External Heavy-Atom Spin-Orbital Coupling Effect. V. Absorption Studies of Triplet States*

*R. P. McLELLAN and T. ANGE

Case Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803 (Received 10 September 1947)

Heavy-Atom-Induced Phosphorescence of Aromatics and Olefins Included within Zeolites

*V. RAMAMURTHY, J. V. CASPER, D. F. EATON, ERIC W. KOV, and D. R. CULPIN

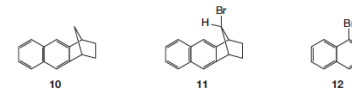
Contribution No. 6068 from Central Research and Development, Experimental Station, The Du Pont Company, Wilmington, Delaware 19880-1028. Received December 2, 1991

J. Am. Chem. Soc. 1992, 114, 3882-3892

Influence of Heavy Atom Effect on ISC and phosphorescence

Molecule	k_F^0	k_{ST}^0	k_P^0	k_{TS}^0	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^{10}	50	50	0.002	0.55
1-Iodonaphthalene	10^6	10^{10}	500	100	0.000	0.70

F. Wilkinson in Organic molecular physics, J. B. Birks (ed), Wiley, 1975, p. 126



$$k_{ST} = 2 \times 10^6 \text{ s}^{-1}$$

$$k_{TS} = 2 \times 10^{-1} \text{ s}^{-1}$$

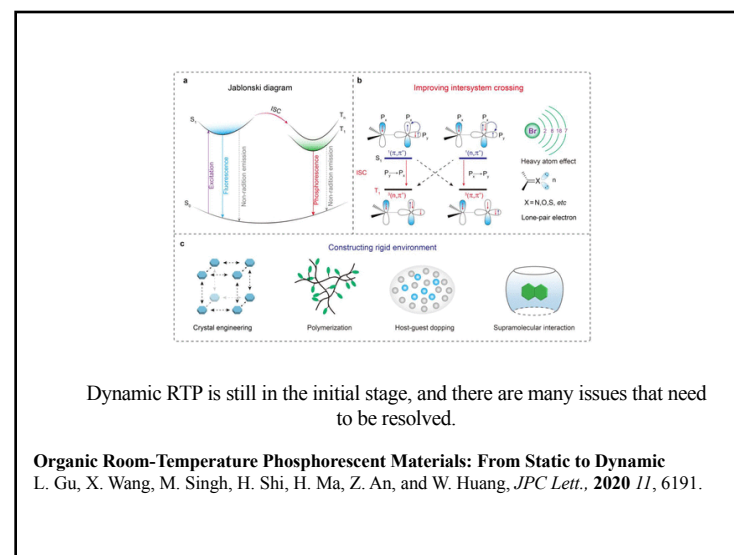
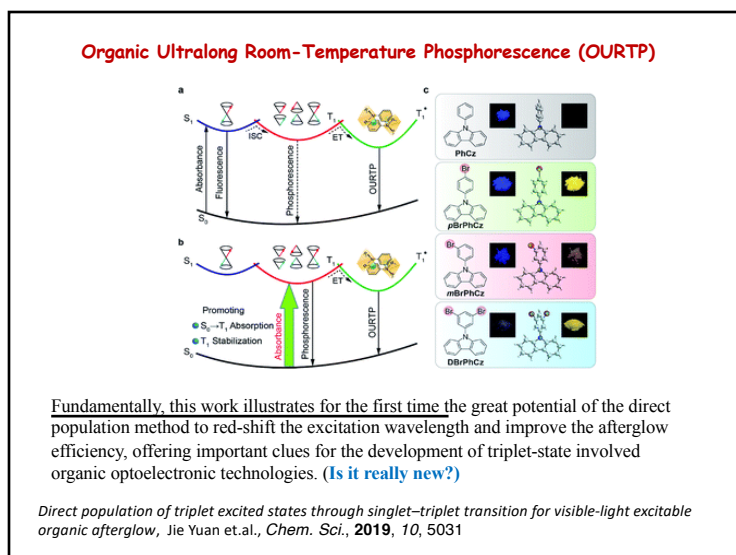
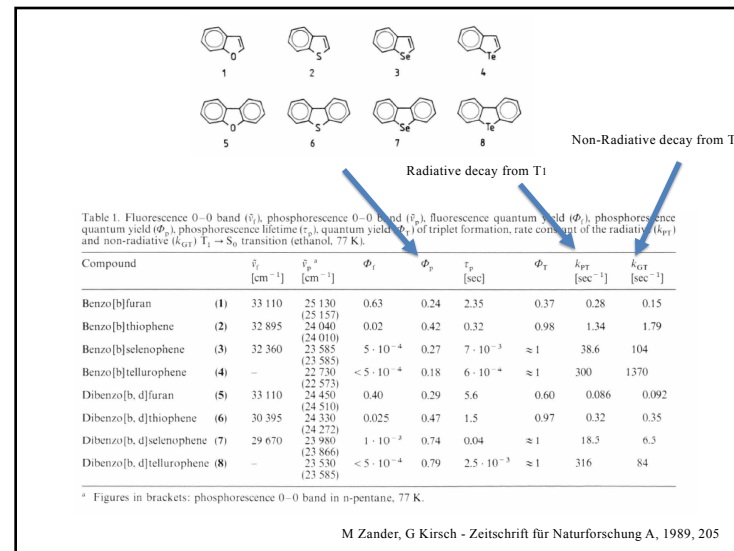
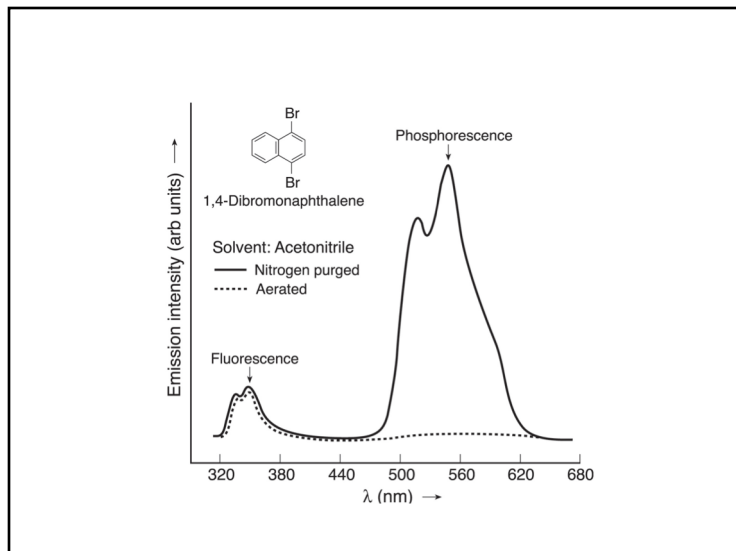
$$k_{ST} = 300 \times 10^6 \text{ s}^{-1}$$

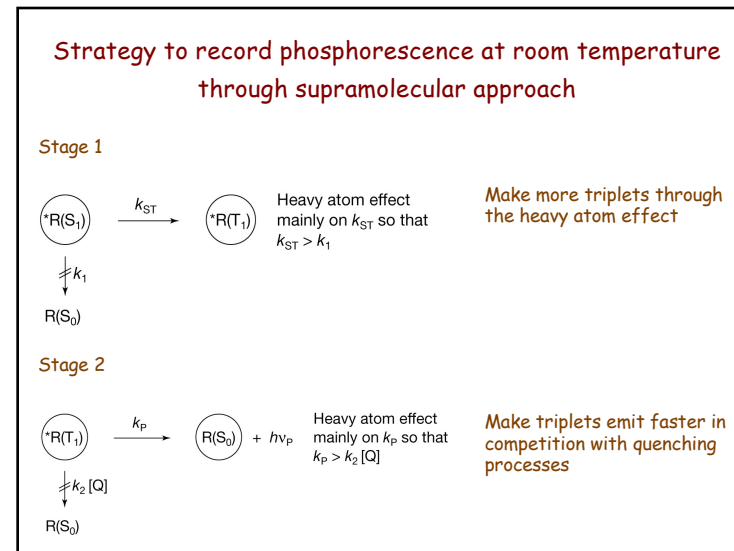
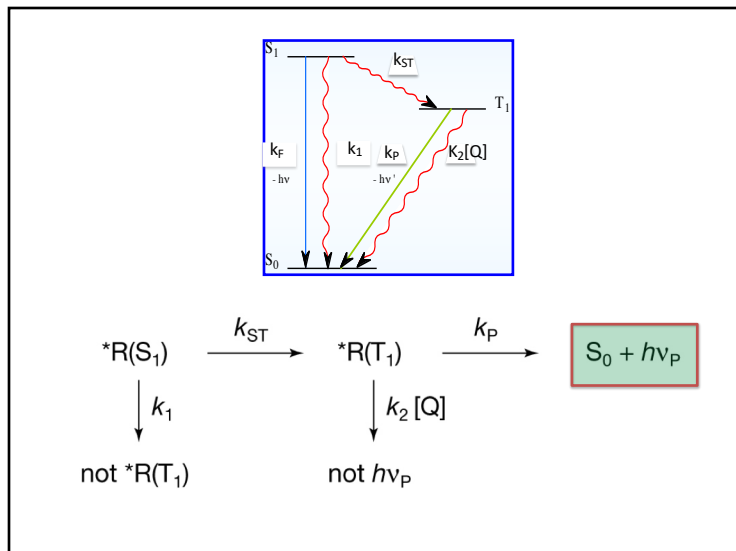
$$k_{TS} = 40 \times 10^{-1} \text{ s}^{-1}$$

$$k_{ST} = 500 \times 10^6 \text{ s}^{-1}$$

$$k_{TS} = 600 \times 10^{-1} \text{ s}^{-1}$$

Turro et al., JACS, 93, 1032, 1971





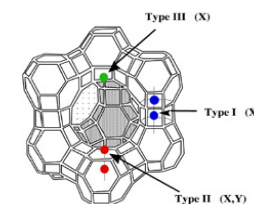
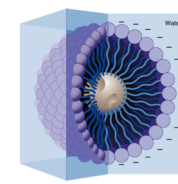
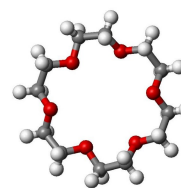
The heavy atom effect on spin transitions

The "heavy atom" effect is an "atomic number" effect that is related to the coupling of the electron spin and electron orbit motions (spin-orbit coupling, SOC).

Most commonly, the HAE refers to the rate enhancement of a spin forbidden photophysical radiative or radiationless transition that is due to the presence of an atom of high atomic number, Z .

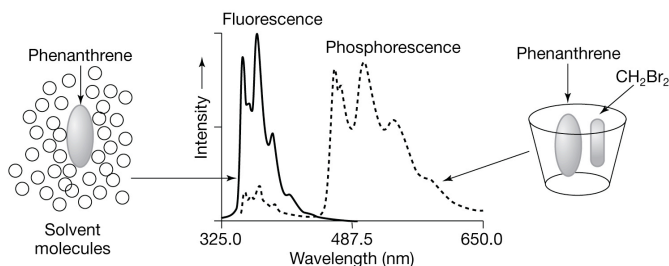
The heavy atom may be either internal to a molecule (molecular) or external (supramolecular).

Crown ethers, micelles and zeolites contain cations

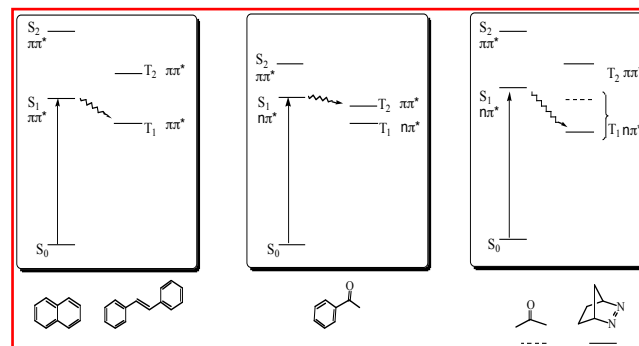


Cyclodextrins as hosts

Phenanthrene@Cyclodextrin: effect of CH_2Br_2 as co-guest



Whether the Heavy Alkali Ion Could Influence the Intersystem Crossing Depends on the Electronic Configurations of the States Involved (El Sayed's Rule)



Induced Intersystem Crossing Depends on the SOC: Cations as the heavy atom perturber

Atom	Ionic Radius of the Cation (\AA)	Spin-Orbit Coupling ζ cm^{-1}
Li	0.86 (+)	0.23
Na	1.12	11.5
K	1.44	38
Rb	1.58	160
Cs	1.84	370
Tl	1.40	3410
Pb	1.33 (2+)	5089

External heavy atom effect: Crown ether approach

Table II. Estimates^{a,b} of Rate Constants for Excited-State Processes of 1,5-Naphtho-22-crown-6 (**1**) in Alcohol Glass^c at 77 K with Alkali Metal Chloride Salts Added in 5:1 Molar Excess (Crown at $1.00 \times 10^{-4} F$)

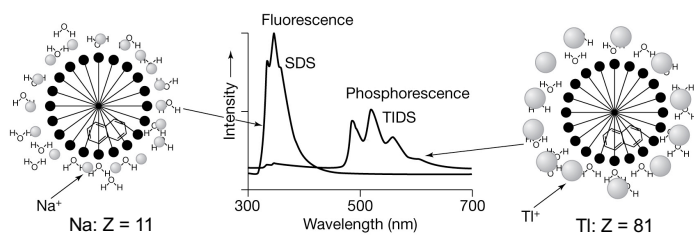
Salt added	$10^{-6}k_f$	$10^{-6}k_{nr}$	$10^2k_p^d$	k_{dt}^d
None	3.1	25	8.7	0.37
NaCl	2.6	32	6.7	0.41
KCl	2.3	35	5.8	0.39
RbCl	1 ^e	52	12.	0.50
CsCl	1 ^e	670	81.	1.57



^a All rate constants in s^{-1} . ^b $k_f = \phi_f \tau_f^{-1}$; $k_{nr} = (1 - \phi_f) \tau_f^{-1}$; $k_p = \phi_p (1 - \phi_f)^{-1} \tau_p^{-1}$; $k_{dt} = \tau_p^{-1} - k_p$. ^c See note 4. ^d With $\phi_f + \phi_{isc} = 1.0$ assumed. ^e Estimated from 77 K UV absorption spectra.

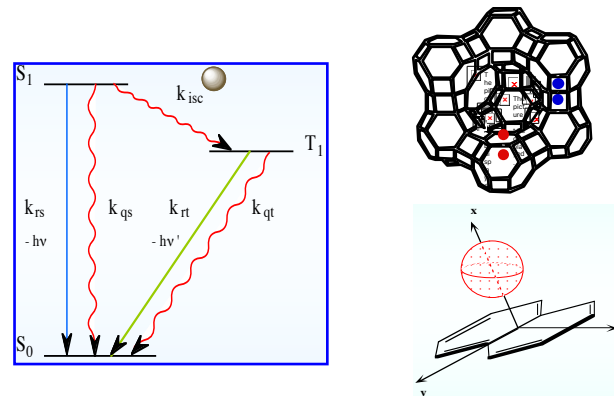
Micelles as hosts

Naphthalene@SDS micelle: effect of heavy atom counterions

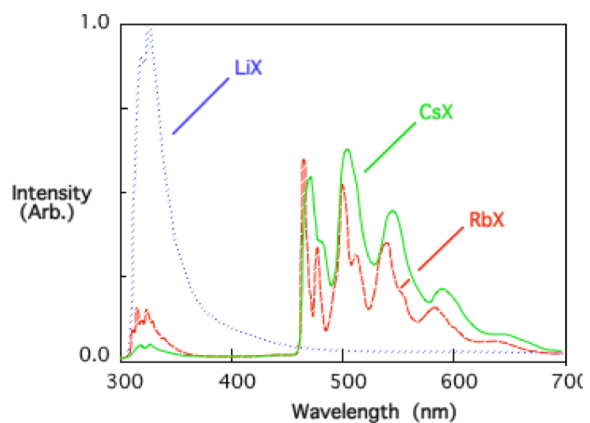


Heavy atom produces more triplets and the triplets produced phosphoresce at a faster rate

Cation Effect Heavy Cations Enhance the S_1 to T_1 Crossing



Emission Spectra of Naphthalene Included in MY Zeolites

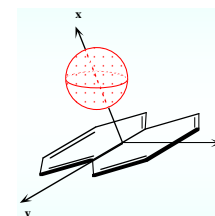
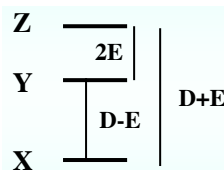


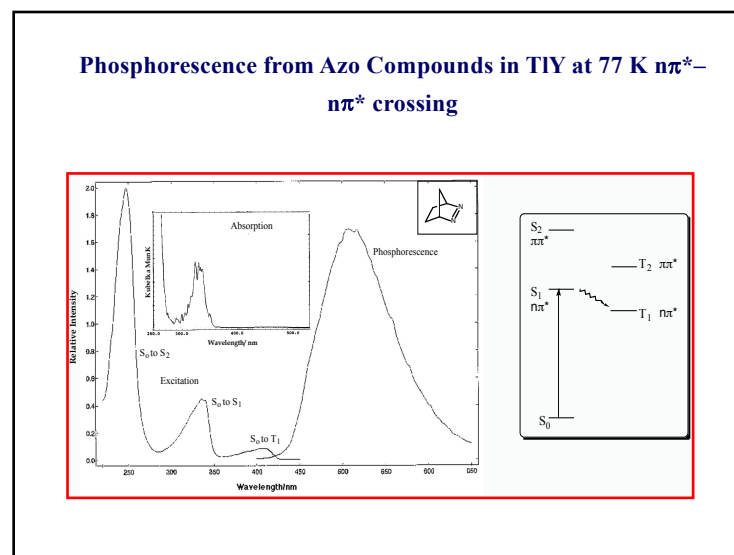
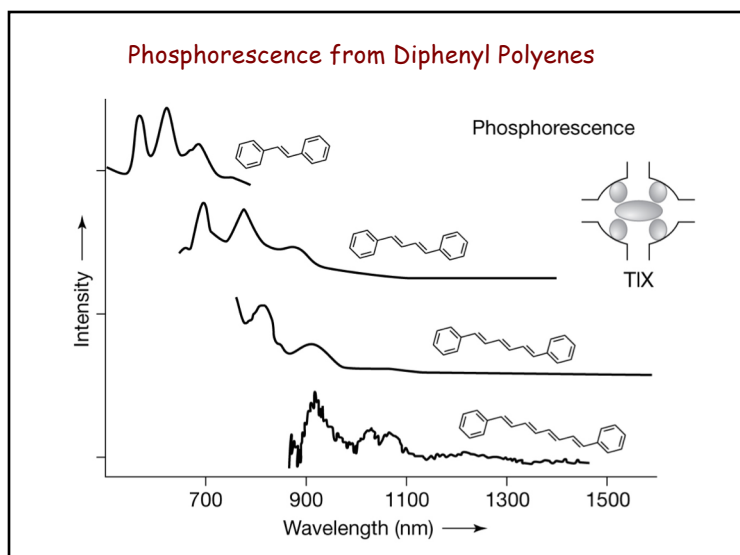
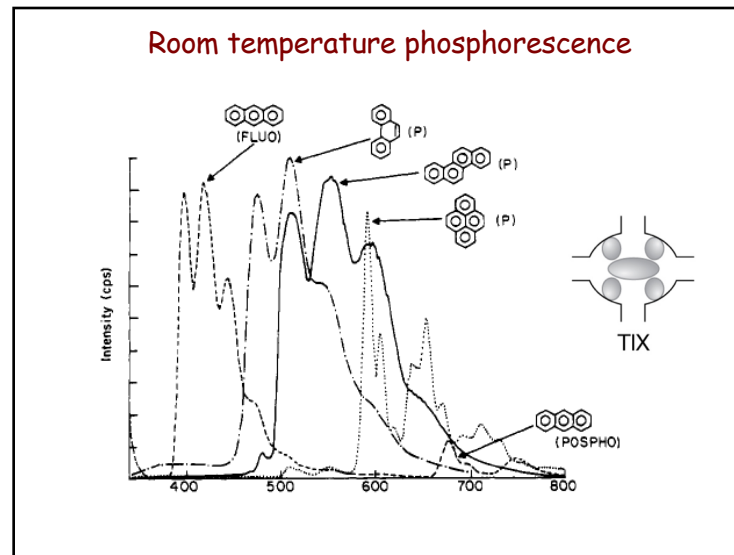
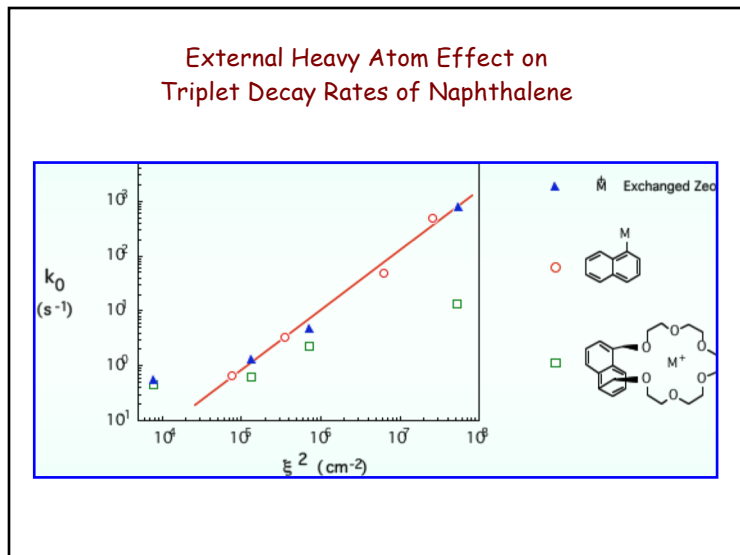
Heavy Atom Effect is Specific: ODMR Studies

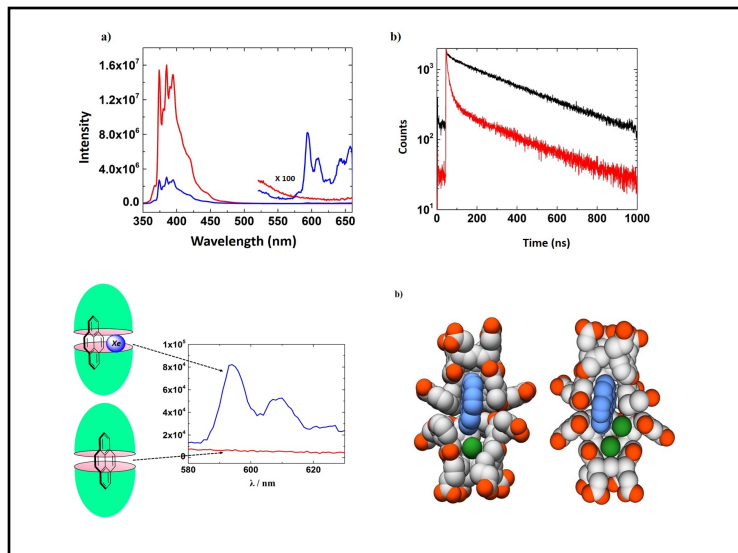
Optical Detection of Magnetic Resonance (ODMR) -

Triplet Sub-Level Specific Kinetics at 1.2 ° K

- Total decay constants from each sub-level
- Relative radiative rates from each sub-level
- Relative intersystem crossing rates to each sub-level
- Slow Passage ODMR Transitions







Role of spin-orbit coupling on spin forbidden transitions

An external magnetic field cannot be responsible for the Singlet-Triplet transition, because it would act equally on both spins.

Field at a molecular level is generated from the *orbital motion* of the electron around the nucleus.

$$\hat{H}_{SO} = \zeta l \cdot s$$

$$\zeta_{n,l} \propto \frac{Z^4}{n^3 l(l+1/2)(l+1)}$$

The Spin-Orbit coupling constant depends on the fourth power of the atomic number and its effect is very large for heavy atoms.

Intersystem crossing in molecules with $n\pi^*$ and $\pi\pi^*$ states

Triplet State: Singlet \leftrightarrow Triplet Interconversion

ϵ_{\max} (S_0 to T_1) and k_p^0 (T_1 to S_0) values – depend on the orbital configuration of T_1 ($\pi\pi^*$, $n\pi^*$)

Molecules possessing pure π , π^* configurations

the value of ϵ_{\max} is $\sim 10^{-5}$ to 10^{-6}
 k_p^0 is $\sim 10^1$ to 10^{-1} s^{-1}

Molecules possessing pure n , π^* configurations

the value of ϵ_{\max} is $\sim 10^{-1}$ to 10^{-2}
 k_p^0 is $\sim 10^3$ to 10^2 s^{-1}

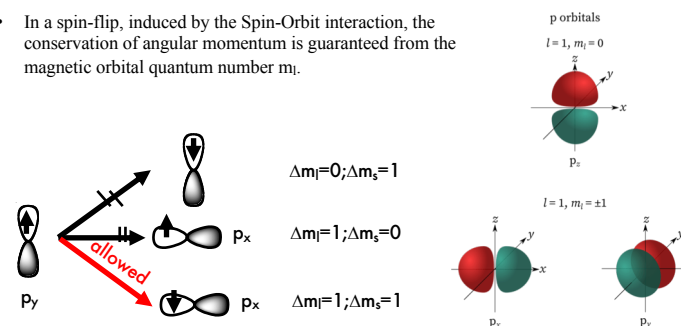
Conservation of energy and angular momentum (spin & orbit coupling)

Spin change will occur at a place where the energies of singlet and triplet are identical. Occurs at curve crossing.

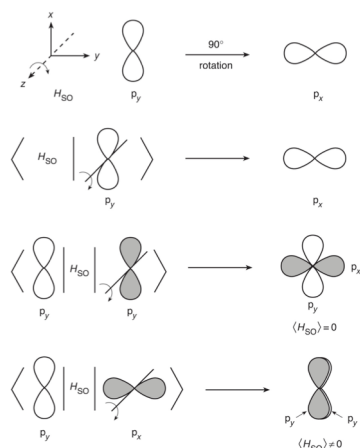
Spin-orbit coupling in organic molecules will be effective in inducing transitions between states of different spin if a " $p_x \rightarrow p_y$ " orbital transition *on a single atom* is involved in the electronic transition. This orbital transition provides both a means of conserving total angular momentum during the transition and also a means of generating orbital angular momentum that can be employed in spin-orbit coupling. This works in the case of $n\pi^*$ state.

Energy and angular momentum conservation

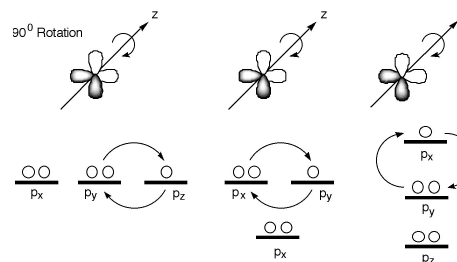
- The electron spin must either remain unchanged or *change by one unit of angular momentum*, h (say, $+1/2 h \rightarrow -1/2 h$).
- A spin change is exactly compensated by an equal and opposite change of angular momentum which occurs from some other (coupled) interaction with another source of angular momentum.
- In a spin-flip, induced by the Spin-Orbit interaction, the conservation of angular momentum is guaranteed from the magnetic orbital quantum number m_l .



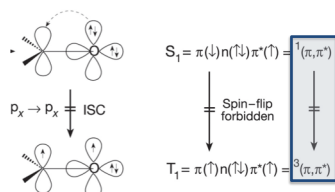
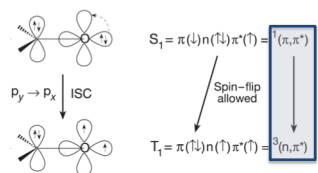
One center p-p transition favors spin forbidden transitions



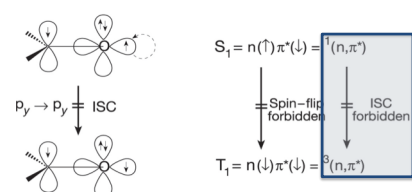
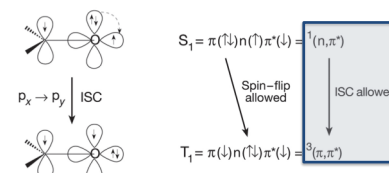
For angular momentum to be conserved during a change in spin orientation, the p orbital that is coupled to the electron spin must change its orientation by exactly one unit of angular momentum. The orbital involved in the " $p_x \rightarrow p_y$ " transition must be similar in energy.



The Effect of Spin-Orbit Coupling on Intersystem Crossing from $S_1(\pi\pi^*)$ to T_1



The Effect of Spin-Orbit Coupling on Intersystem Crossing from $S_1(n\pi^*)$ to T_1



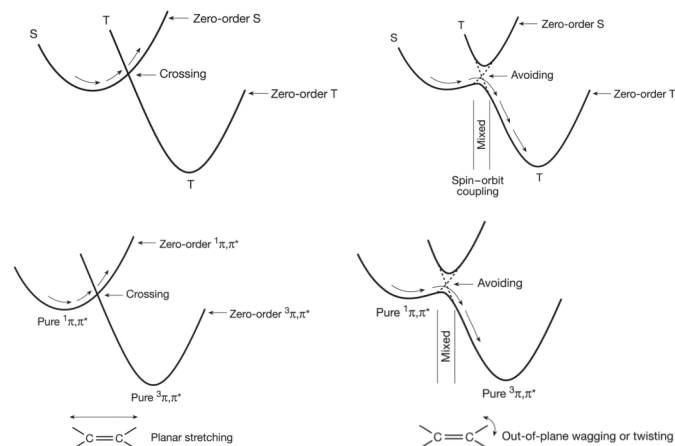
El-Sayed's Rule

Intersystem crossing is likely to be very slow unless it involves a change of orbital configuration.



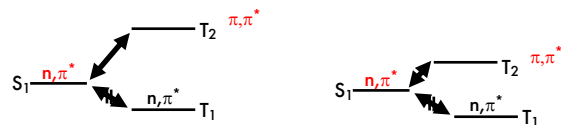
$S_1(n,\pi^*) \rightarrow T_1(n,\pi^*)$	Forbidden
$S_1(n,\pi^*) \rightarrow T_1(\pi,\pi^*)$	Allowed
$S_1(\pi,\pi^*) \rightarrow T_1(n,\pi^*)$	Allowed
$S_1(\pi,\pi^*) \rightarrow T_1(\pi,\pi^*)$	Forbidden

$T_1 \rightarrow S_0$	$T_1(n,\pi^*) \rightarrow S_0(n^2)$	Allowed
Transitions	$T_1(\pi,\pi^*) \rightarrow S_0(\pi^2)$	Forbidden

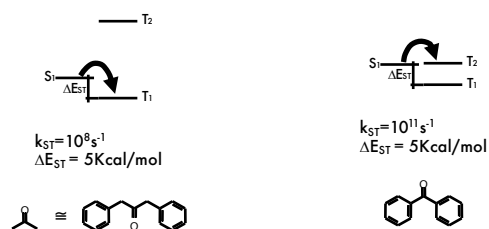


When direct SOC is very small, it is often meaningful to include vibronic spin-orbit effects.

Thus, for ketones with $T_1 (n, \pi^*)$, the only mechanism to undergo a Singlet-Triplet ISC is going through a $T_2 (\pi, \pi^*)$ followed by internal conversion to $T_1 (n, \pi^*)$



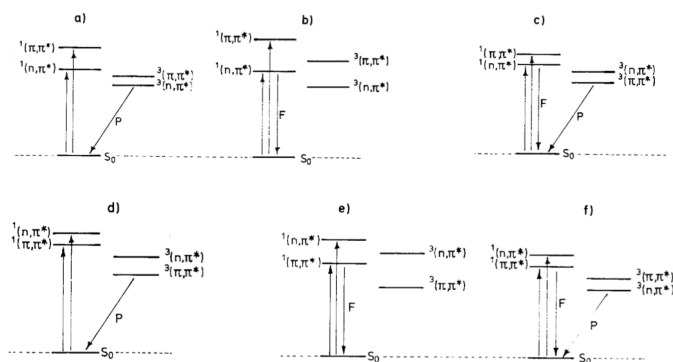
Thus, the ISC crossing rate depends whether or not it is allowed and on the energy gaps involved.



Compound	Φ_p		Φ_{ST}	k_p^0	Configuration of T_1
	77 K	25 °C			
Benzene	~0.2	(<math><10^{-4}</math>)	~0.7	~ 10^{-1}	π, π^*
Naphthalene	~0.05	(<math><10^{-4}</math>)	~0.7	~ 10^{-1}	π, π^*
1-Fluoronaphthalene	~0.05	(<math><10^{-4}</math>)	~0.3	~0.3	π, π^*
1-Chloronaphthalene	~0.3	(<math><10^{-4}</math>)	~1.0	~2	π, π^*
1-Bromonaphthalene	~0.3	(<math><10^{-4}</math>)	~1.0	~30	π, π^*
1-Iodonaphthalene	~0.4		~1.0	~300	π, π^*
Triphenylene	~0.5	(<math><10^{-4}</math>)	~0.9	~ 10^{-1}	π, π^*
Benzophenone	~0.9	(~0.1) ^b	~1.0	~ 10^2	n, π^*
Biacetyl	~0.3	(~0.1) ^c	~1.0	~ 10^2	n, π^*
Acetone	~0.3	(~0.01) ^c	~1.0	~ 10^2	n, π^*
4-Phenylbenzophenone			~1.0	1.0	π, π^*
Acetophenone	~0.7	(~0.03) ^b	~1.0	~ 10^2	n, π^*
Cyclobutanone	0.0	0.0	0.0		n, π^*

El-Sayed's Rule

Intersystem crossing is likely to be slow unless it involves a change of orbital configuration.



Summary

El-Sayed Rule:

The rate of ISC is relatively large if the radiationless transition involves a change of orbital type.

Application to locally excited (LE) states of organic chromophores with singlet ground state (GS)

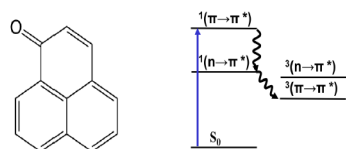
ISC is expected to be fast for

- $1,3(\pi\pi^*) \rightsquigarrow 3,1(n\pi^*)$
- $1,3(n\pi^*) \rightsquigarrow 3,1(\pi\pi^*)$
- $3(n\pi^*) \rightsquigarrow \text{GS}$
- $1,3(\pi\sigma^*) \rightsquigarrow 3,1(\pi\pi^*)$

ISC is expected to be slow for

- $1,3(\pi\pi^*) \rightsquigarrow 3,1(\pi\pi^*)$
- $3(\pi\pi^*) \rightsquigarrow \text{GS}$
- $1,3(n\pi^*) \rightsquigarrow 3,1(n\pi^*)$
- $1,3(\pi\sigma^*) \rightsquigarrow 3,1(\pi\sigma^*)$

Consider an organic molecule (here phenalenone) lying in the yz plane.

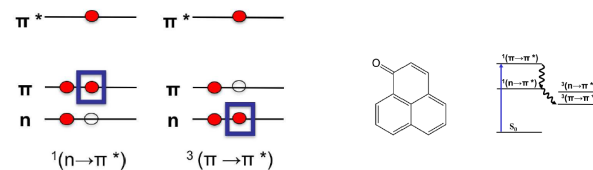


Absorption of light takes the molecule to the $1(\pi\pi^*)$ state from which it rapidly decays via internal conversion (IC) to the $1(n\pi^*)$ state. Energetically close-by is the $3(n\pi^*)$ state. The lowest excited triplet state is the $3(\pi\pi^*)$ state. There is no change of orbital type upon the $1(n\pi^*) \rightsquigarrow 3(n\pi^*)$ transition. El-Sayed rules predict this ISC to be slow.

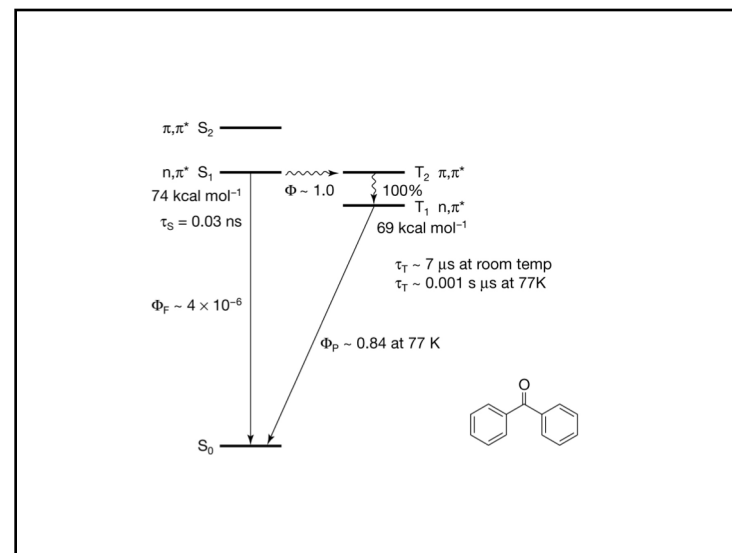
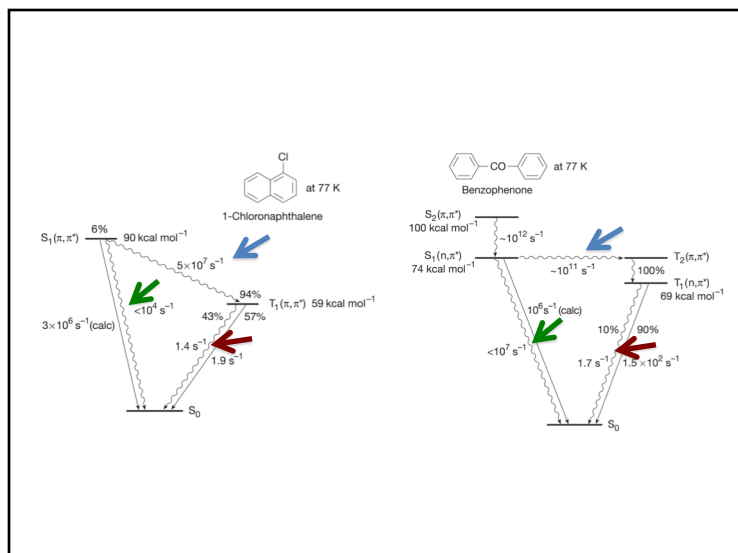
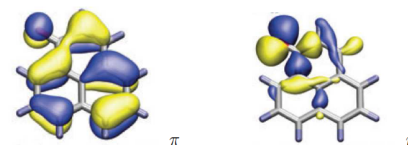
Now look at $1(n\pi^*) \rightsquigarrow 3(\pi\pi^*)$.

There is a change of orbital type upon this transition. El-Sayed rules predict ISC to proceed fast in this case.

The $1(n\pi^*)$ and $3(\pi\pi^*)$ states are singly excited with respect to each other.



The π and n orbitals both exhibit electron density at the oxygen center.



Sensitizers

- Should be able to excite the sensitizer alone even in presence of acceptor.
- Sensitizer should have high intersystem crossing efficiency (S_1 to T_1).
- Sensitizer should have triplet energy higher than the acceptor.
- Sensitizer should be photostable.

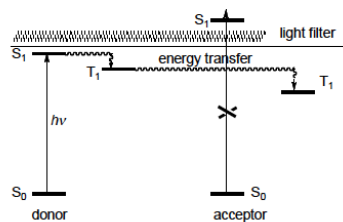
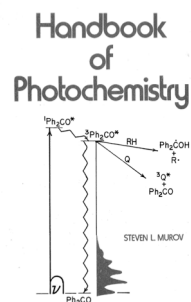
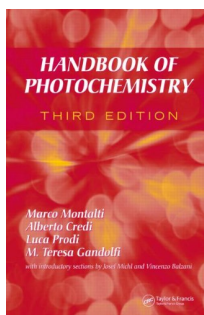


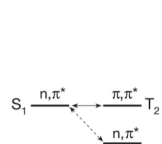
Table 10.3 Important Parameters for Triplet Photosensitizers

Compound	E_S	E_T	τ_S	τ_T	Conf. T_1	Φ_{ST}
	(kcal mol ⁻¹)		(s)			
Benzene	110	84	$\sim 10^{-7}$	10^{-6}	π, π^*	0.2
Acetone	~ 85	~ 78	10^{-9}	10^{-5}	n, π^*	1.0
Xanthone		74			π, π^*	1.0
Acetophenone	~ 79	74	10^{-10}	10^{-4}	n, π^*	1.0
4-CF ₃ Acetophenone		71			n, π^*	1.0
Benzophenone	~ 75	69	10^{-11}	10^{-4}	n, π^*	1.0
Triphenylene	83	67	$\sim 5 \times 10^{-8}$	10^{-4}	π, π^*	0.9
Thioxanthone	78	~ 65				
Anthraquinone		62			n, π^*	1.0
4-Ph-benzophenone	77	61		10^{-4}	π, π^*	1.0
Michler's ketone		61				1.0
Naphthalene	92	61	10^{-7}	10^{-4}	π, π^*	0.7
2-Acetonaphthalene	78	59		10^{-4}	π, π^*	1.0
1-Acetonaphthalene	76	57		10^{-4}	π, π^*	1.0
Chrysene	79	57	5×10^{-8}		π, π^*	0.8
Biacetyl	~ 60	55	10^{-8}	10^{-3}	n, π^*	1.0
Benzil	~ 59	54	$\sim 10^{-8}$	10^{-4}	n, π^*	1.0
Camphorquinone	~ 55	50	$\sim 10^{-8}$		n, π^*	1.0
Pyrene	77	49	$\sim 10^{-6}$		π, π^*	0.3
Anthracene	76	47	$\sim 5 \times 10^{-9}$	10^{-4}	π, π^*	0.7
9,10-Dichloroanthracene	~ 74	40	$\sim 5 \times 10^{-9}$	10^{-4}	π, π^*	0.5
Perylene	66	~ 35	5×10^{-9}		π, π^*	0.005



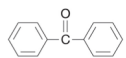
El-Sayed's Rule

Intersystem crossing is likely to be very slow unless it involves a change of orbital configuration.

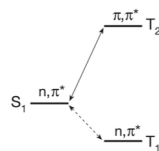


$$k_{ST} \sim 10^{11} - 10^{10} \text{ s}^{-1}$$

"Fast"

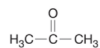


Benzophenone

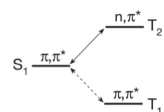


$$k_{ST} \sim 10^9 - 10^8 \text{ s}^{-1}$$

"Intermediate"

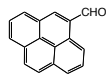


Acetone



$$k_{ST} \sim 10^7 - 10^6 \text{ s}^{-1}$$

"Slow"



Pyrenealdehyde