

CHM 535/635
Molecular and Supramolecular Photochemistry

Radiationless Transitions

↑ Spin allowed
 ↓ Spin forbidden

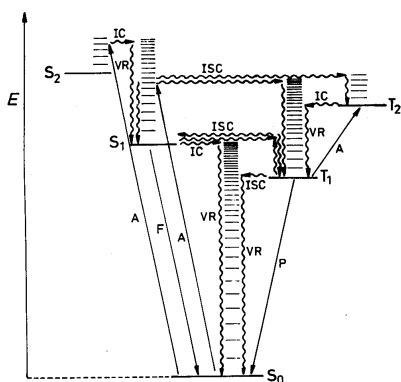
Chapters 3 & 5
 Principles of Molecular Photochemistry: An Introduction
 NJT, VR and JCS

Fundamental Research:
 The presentations/reports are **not "subject"** to the EAR – Fundamental Research as per EAR Part 734.8 (a) and (c).

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1

Transition Between States



$S_0 + h\nu \longrightarrow S_1$ spin allowed absorption

$S_1 \longrightarrow S_0 + h\nu$ spin allowed emission (fluorescence)

$S_1 \longrightarrow S_0 + \Delta$ spin allowed radiationless transition (internal conversion; IC)

$S_1 \longrightarrow T_1 + \Delta$ spin forbidden radiationless transition (intersystem crossing; ISC)

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Why radiationless transition matters?
Competes with fluorescence and phosphorescence

$$S_0 + h\nu \xrightarrow{I_{abs}} S_1$$

$$S_1 \xrightarrow{k_f} S_0 + h\nu$$

$$S_1 \xrightarrow{k_{isc}} T_1$$

$$S_1 \xrightarrow{k_{ic}} S_0$$

The diagram shows energy levels for S₁, T₁, and S₀. Transitions are numbered 1 through 7. 1: Absorption to S₁. 2: Non-radiative decay from S₁ to S₀. 3: Fluorescence from S₁ to S₀. 4: Phosphorescence from T₁ to S₀. 5: Intersystem crossing from S₁ to T₁. 6: Non-radiative decay from T₁ to S₀. 7: Internal conversion from S₁ to S₀. Energy gaps are labeled ε(S₀→S₁) and ε(S₀→T₁). Rate constants k_f, k_{ic}, k_{isc}, k_{rs}, k_{qs}, k_{rt}, k_{qt}, k_R^S, and k_R^T are indicated.

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

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

3

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Radiationless Transitions

$(\Phi_1 \cdot \chi_1 \cdot S_1) * 1$

$\Phi_0 \cdot \chi_0 \cdot S_0$

The diagram shows energy levels for S₁, T₁, and S₀. A blue arrow labeled k_{rs} and -hν points from S₁ to S₀. A green arrow labeled -hν' points from T₁ to S₀. Red wavy arrows represent radiationless transitions: k_{qs} from S₁ to S₀, k_{rt} from S₁ to T₁, and k_{qt} from T₁ to S₀. A red arrow labeled k_{isc} points from S₁ to T₁.

$(\Phi_2 \cdot \chi_1 \cdot S_1) * 3$

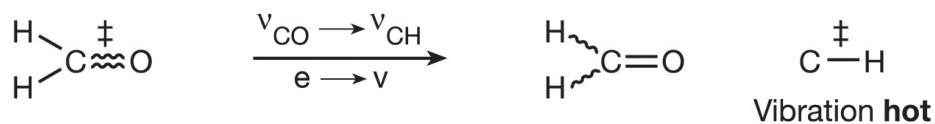
- Changes in electronic, vibrational and spin configurations (without the help of photon)
- Energy redistribution (electronic to vibrational)

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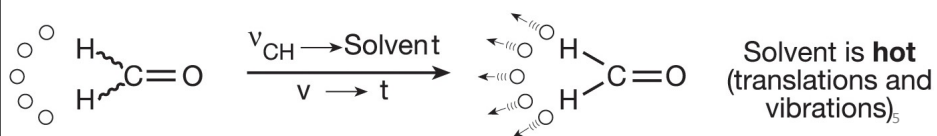
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Visualization of Electronic Energy to Vibrational Energy Transfer

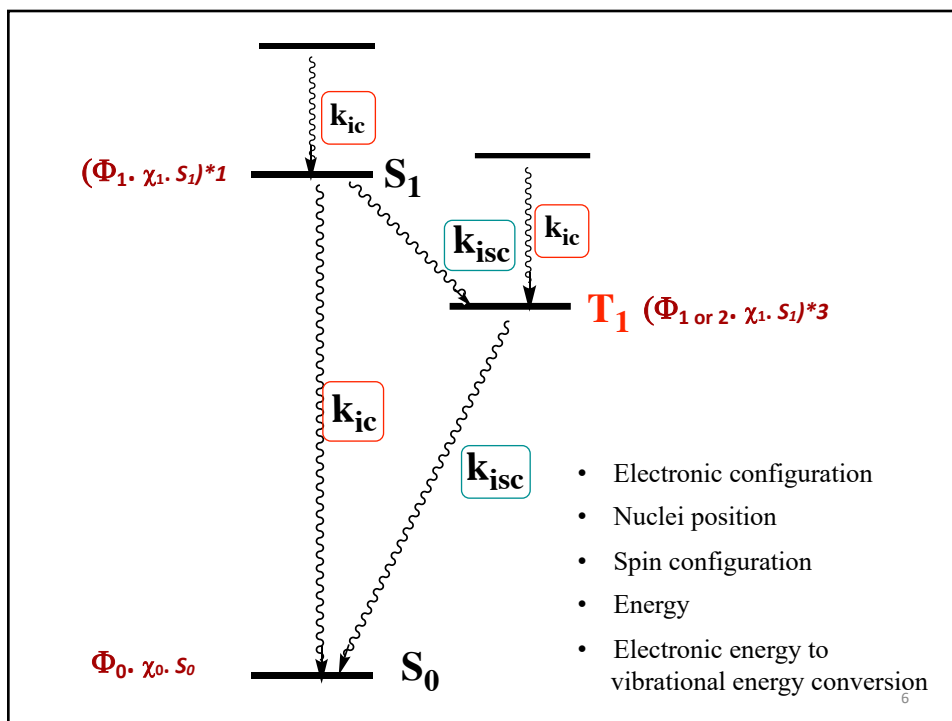
Intramolecular vibrational relaxation (IVR) occurs within
10 to 0.1 ps



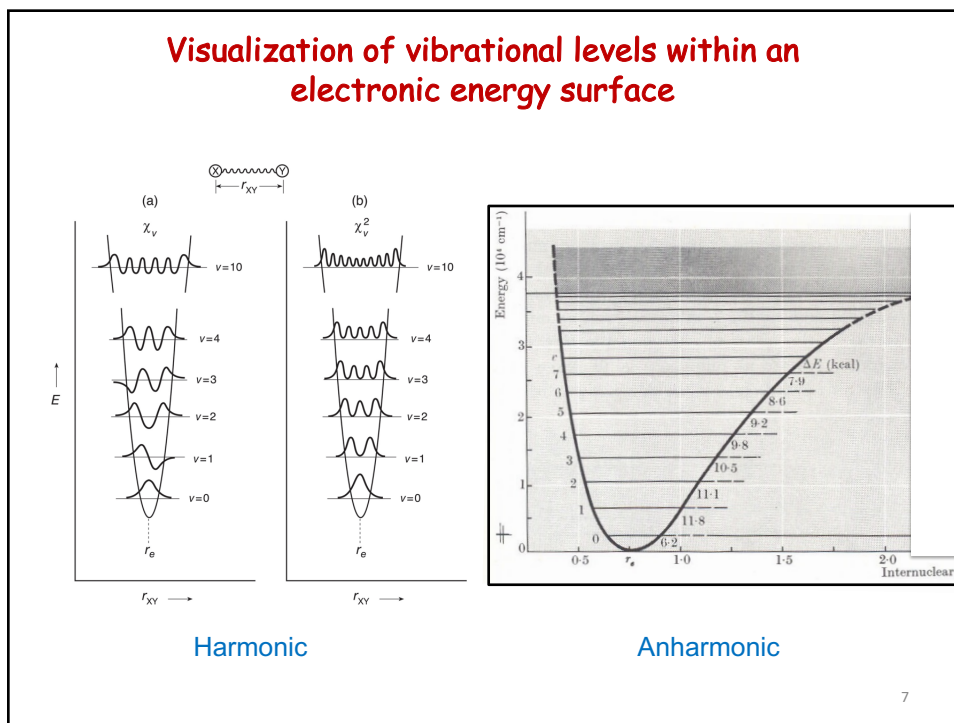
Intermolecular vibrational energy transfer (VET) from
the molecule to the solvent occurs in the time range
100 to 10 ps



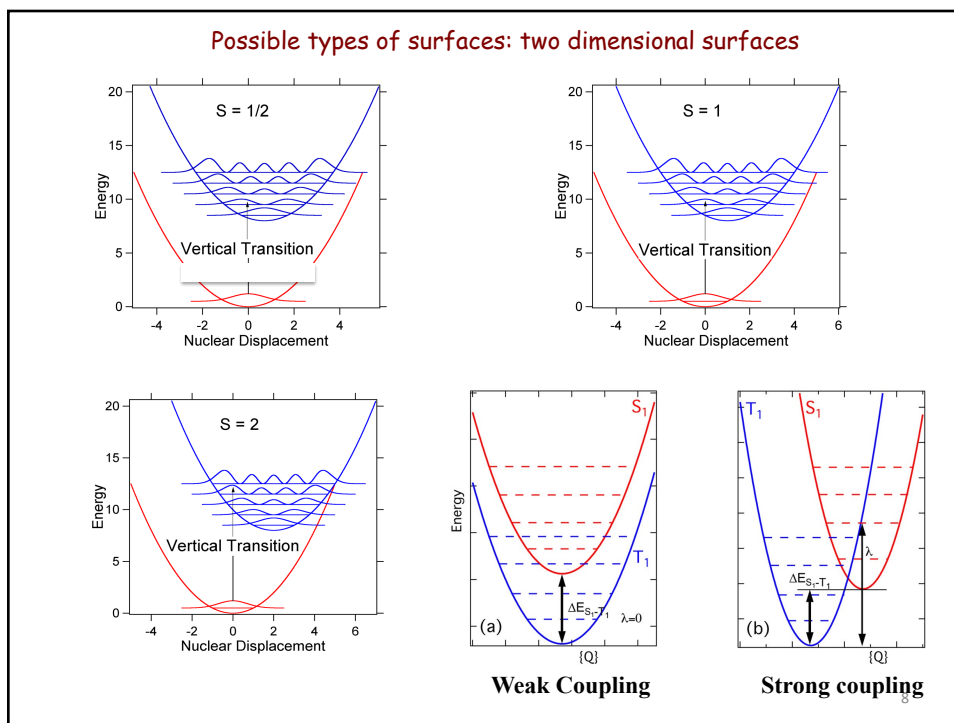
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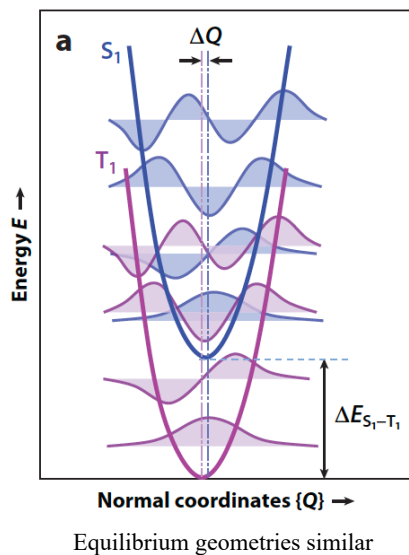


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Matching surfaces (e.g., polyaromatics)

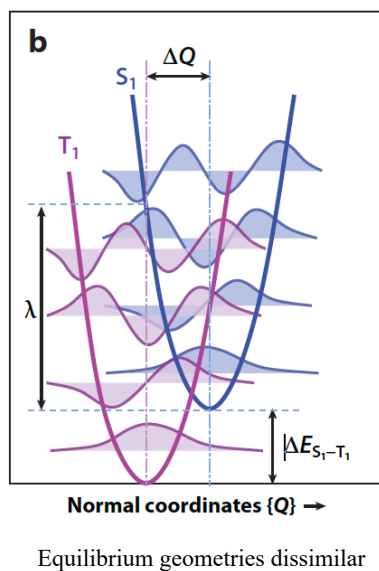


The S_1 and T_1 potentials exhibit small relative displacements in all normal coordinates $\{Q\}$. Significant overlaps between their vibrational wave functions are obtained only for small singlet–triplet energy separations, ES_1-T_1 . The ISC probability decreases exponentially with increasing energy gap. This exponential dependence of the transition probability on E is usually dubbed the Energy Gap Law.

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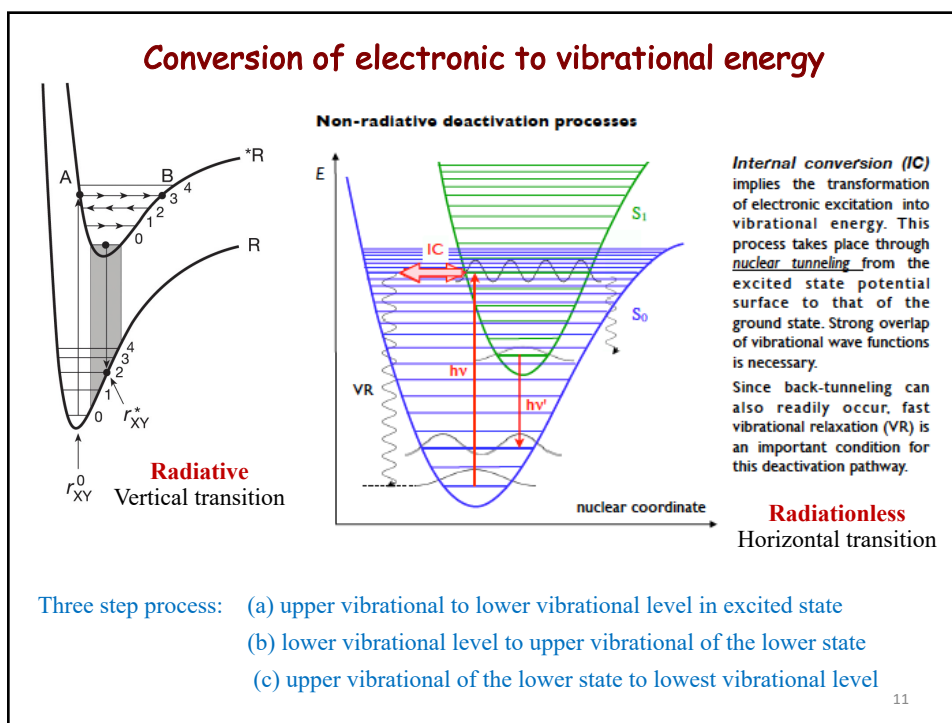
Crossing surfaces (e.g., olefins; singlet/triplet surfaces)



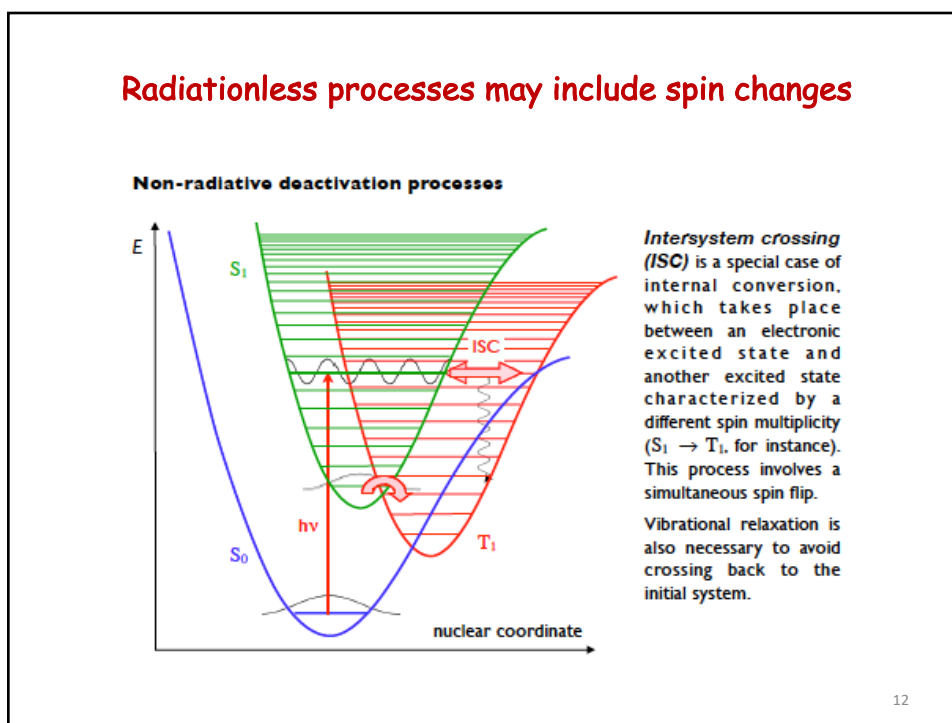
The S_1 and T_1 potentials exhibit large relative displacements in some coordinates. The ISC probability typically exhibits a Gaussian dependence on $ES_1-T_1-\lambda$, where λ is the reorganization energy in the S_1 state. In the inverted region, the probability increases with increasing ES_1-T_1 until a maximum is reached at $ES_1-T_1-\lambda$, where the S_1 and T_1 potentials cross at the S_1 minimum. At even-higher-energy separations, the probability decreases in a regular fashion with increasing ES_1-T_1 .

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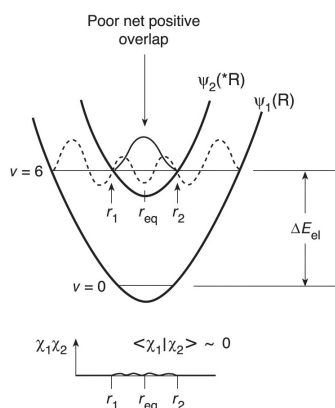


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Horizontal transitions not involving photon

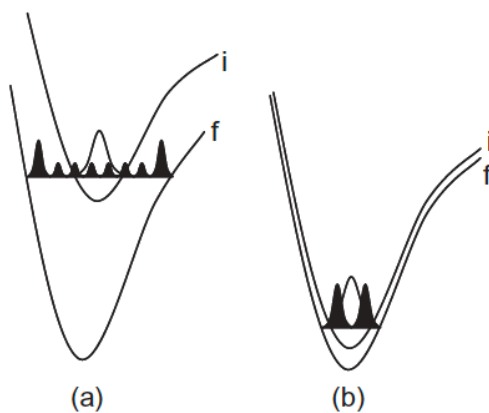


- Energy (potential and kinetic)
- Momentum of nuclei
- Spin of electron
- Orbital spatial relationship

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Basis of energy gap law during radiationless transition in nested surfaces: Vibrational overlap



Nested or matching surfaces:
Extent of vibrational overlap depends on the energy gap

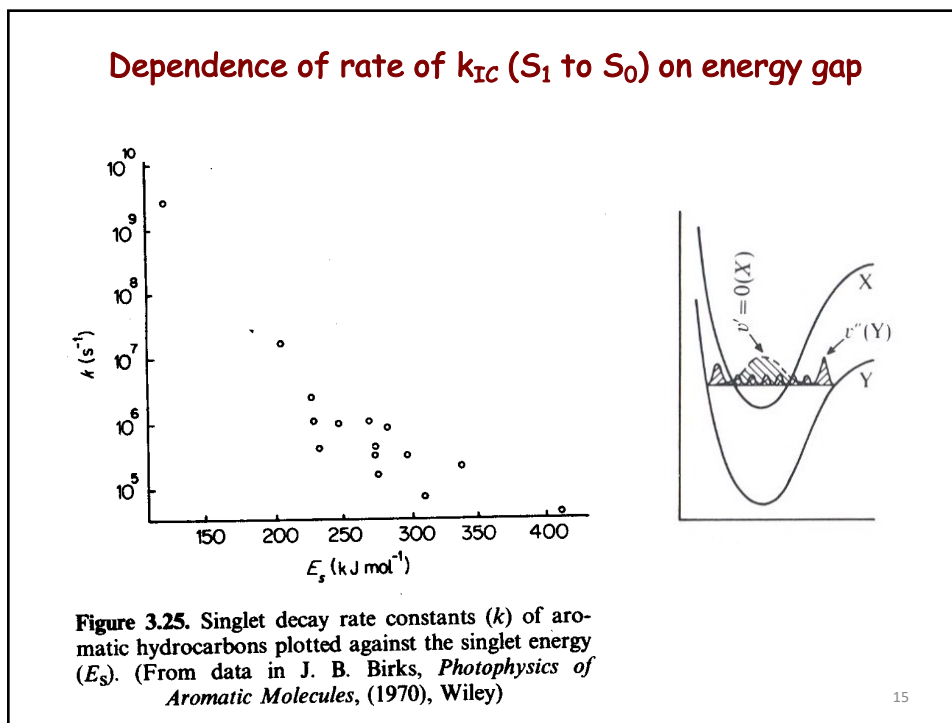
$$f \sim \exp^{-\Delta E}$$

$$k_{IC} \sim 10^{13} f_v$$

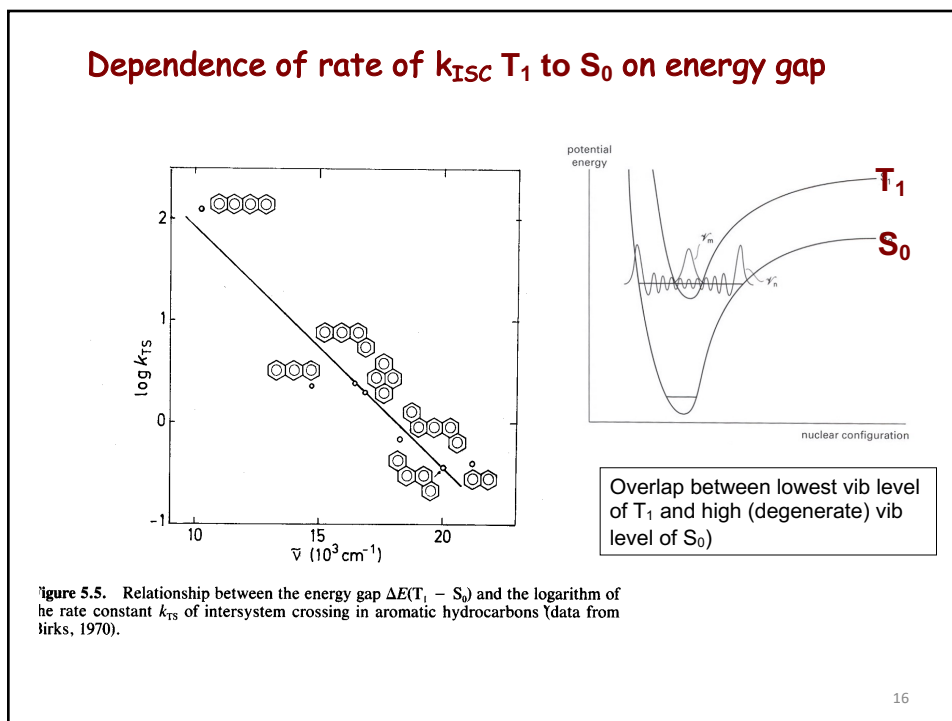
$$k_{IC} \sim 10^{13} \exp^{-\alpha \Delta}$$

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Effect of deuteration on radiationless process (T_1 to S_0)

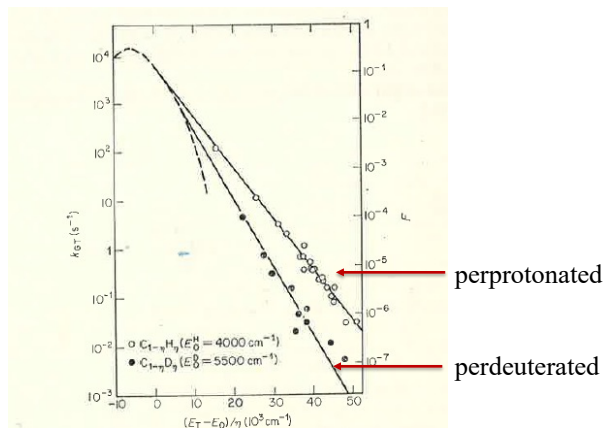


Figure 5.2 $T_1 - S_0$ intersystem crossing rate k_{CIT} (s^{-1}) and Franck-Condon factor F against normalized triplet state energy $(E_T - E_0)/\eta$ for unsubstituted perprotonated and perdeuterated aromatic hydrocarbons. The broken line represents F as derived from phosphorescence spectra. The F -scale is normalized by drawing the two solid lines as tangents to this function (after Siebrand⁸)

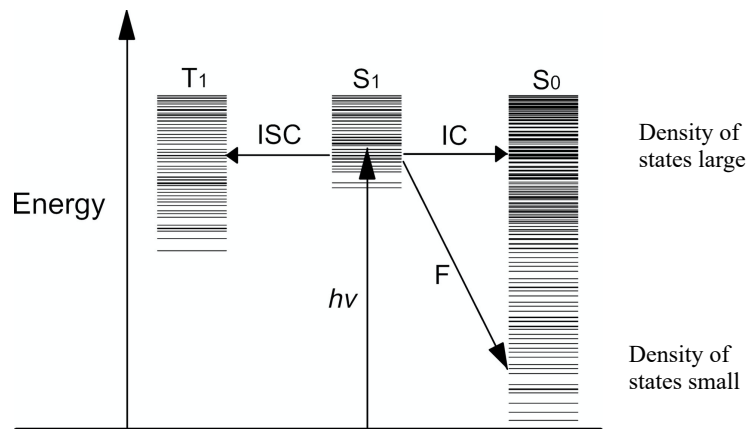
Birks book

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Matching (nested) surfaces

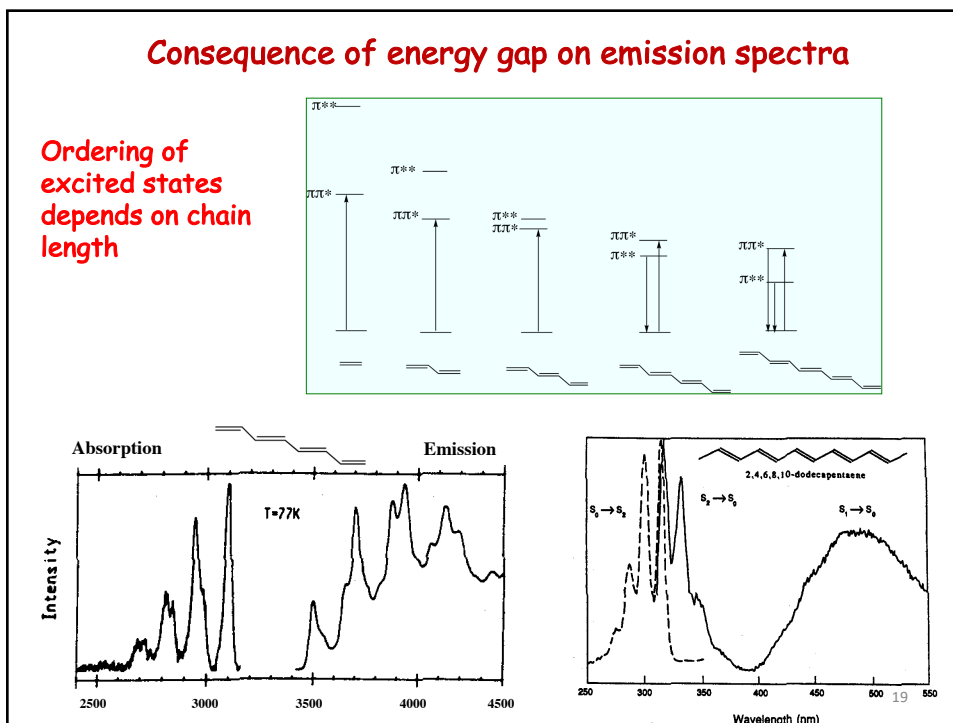
Vibrational overlap can be off-set by density of states



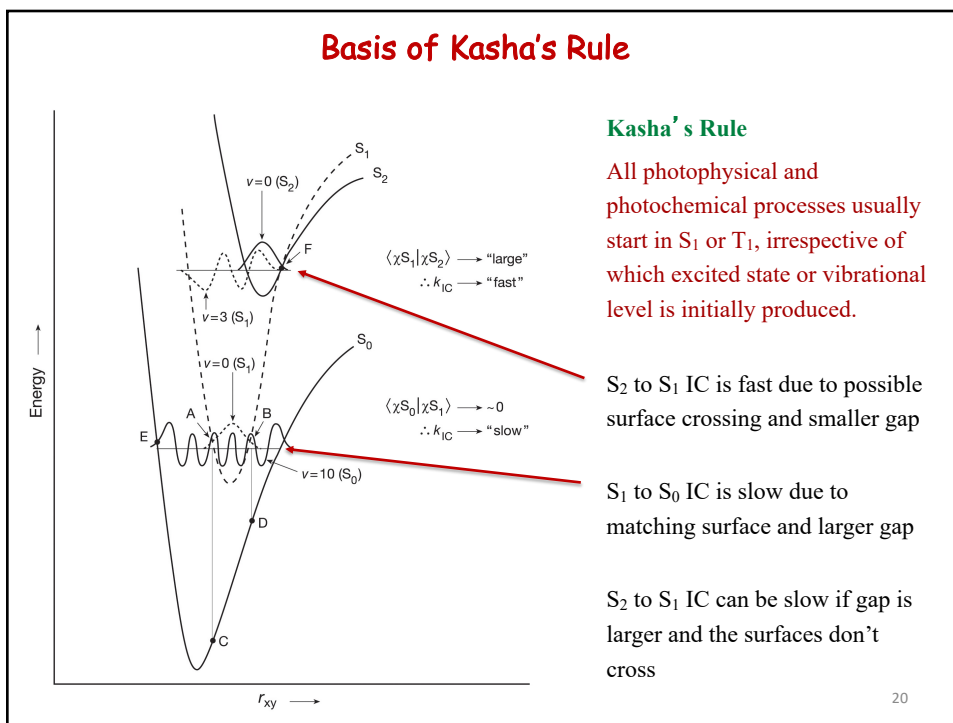
Large energy gap favors higher density of states as the vibrational levels that overlap would be in the region with have higher density. Thus energy gap and density of states work in opposite direction.

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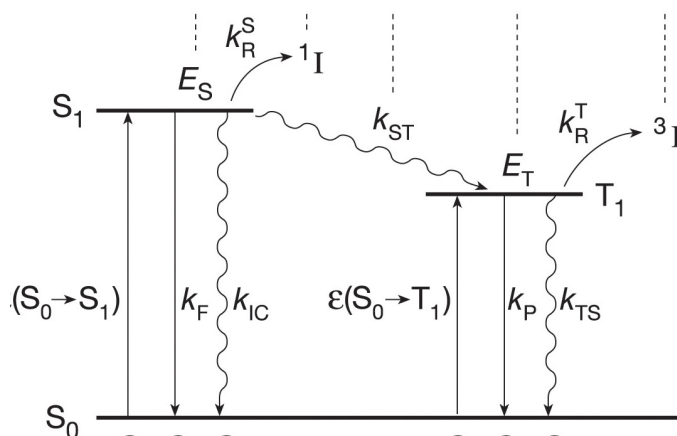


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S_1 to S_0 and T_1 to S_0 have large energy gaps
Most actions are from S_1 and T_1

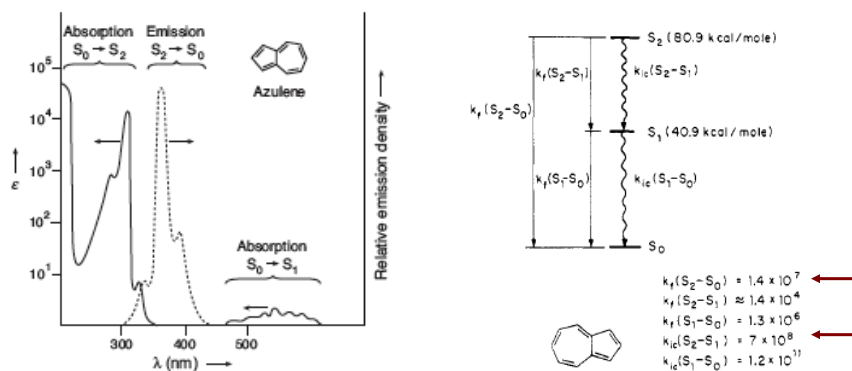


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Energy Gap Law and Azulene Anomaly

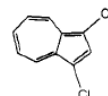
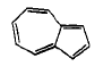
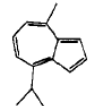
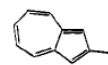
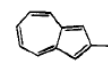
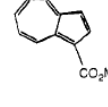
Fluorescence occurs only from S_1 to S_0 ; phosphorescence occurs only from T_1 to S_0 ; S_n and T_n emissions are extremely rare (Kasha's rule).



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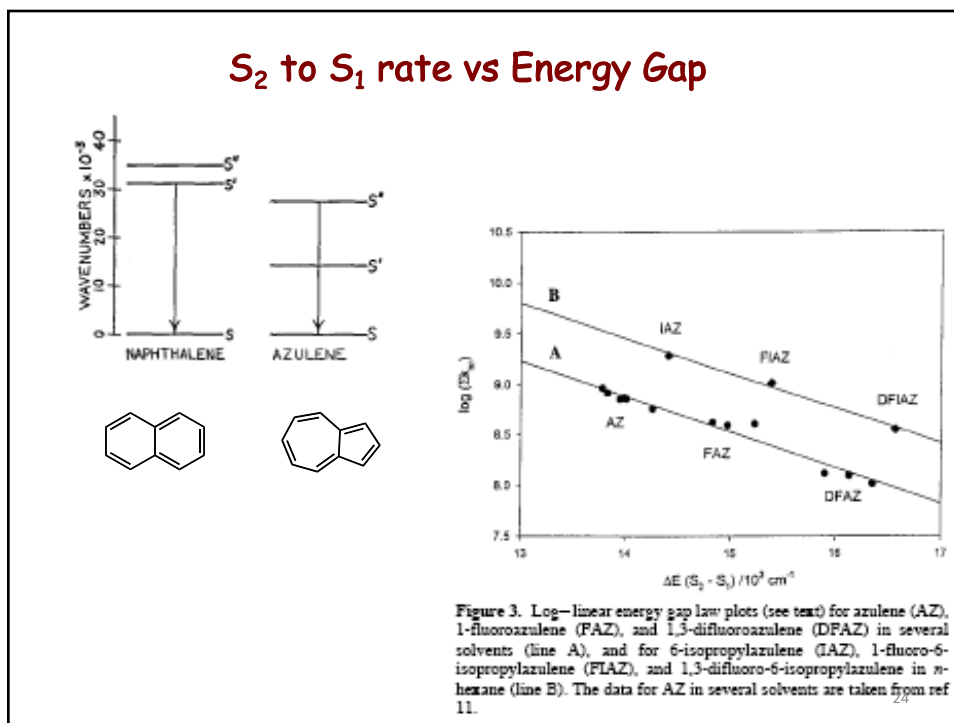
TABLE I. Fluorescence Quantum Yields and the Energies of the First Two Excited Singlet States of Substituted Azulenes^a

	Φ_{fl}	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

↑ ↑

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Effect of deuteration on radiationless process (T_1 to S_0)

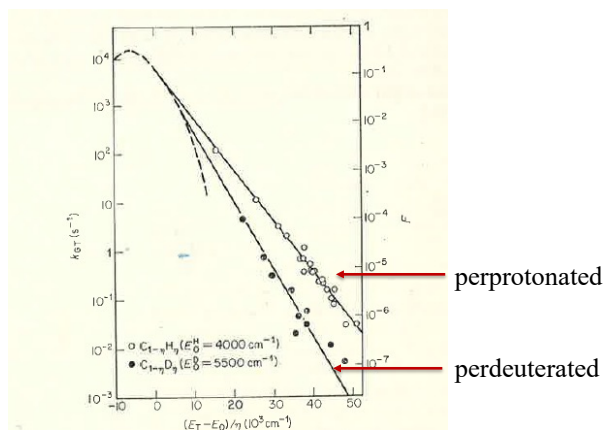


Figure 5.2 $T_1 - S_0$ intersystem crossing rate $k_{T_1-S_0}$ (s^{-1}) and Franck-Condon factor F against normalized triplet state energy $(E_T - E_0)/h$ for unsubstituted perprotonated and perdeuterated aromatic hydrocarbons. The broken line represents F as derived from phosphorescence spectra. The F -scale is normalized by drawing the two solid lines as tangents to this function (after Siebrand⁸)

Birks book

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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.

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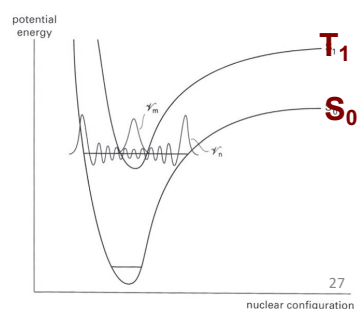
Table 5.4 Some Representative Values of Triplet Energies, Phosphorescence Radiative Rates, Intersystem Crossing Rates, and Phosphorescence Yields^a

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

Isotope Effect on Rate of T_1 to S_0

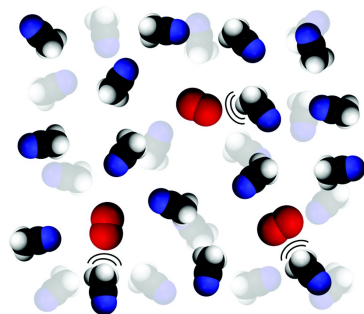
a. In organic solvents at 77 K. E_T in kcal mol⁻¹, k , in s⁻¹.

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



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Decay of singlet oxygen depends on solvent and deuteration



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

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

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Vibrational effects on singlet oxygen lifetime

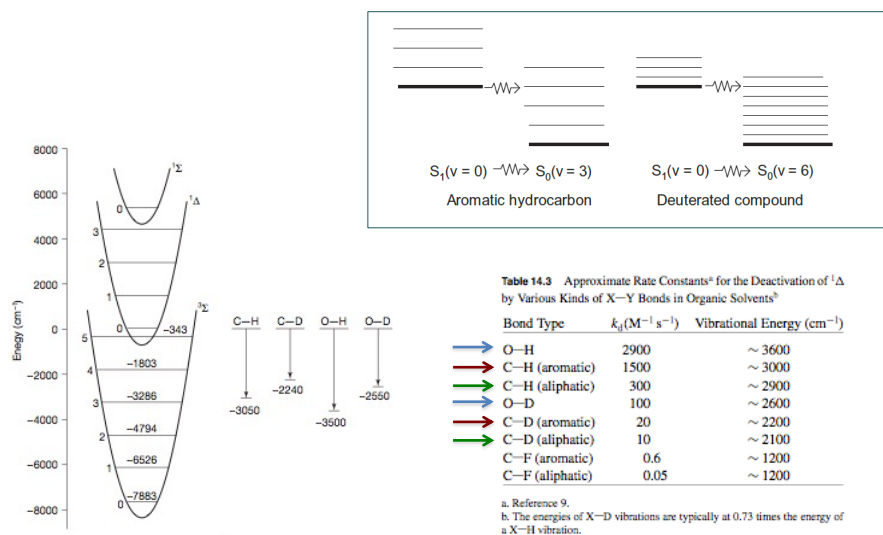


Figure 14.3 Comparison of the energy levels of $^1\Delta$ to common high frequency X-H and X-D vibrations of solvents. Energies in cm^{-1} .

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In aromatics because of the large S_1 to S_0 energy gap internal conversion does not compete with k_{ISC} and k_f

Table 4.2 Quantum yields for fluorescence ($S_1 \rightarrow S_0 + h\nu$) and intersystem crossing ($S_1 \rightsquigarrow T_1$) for some aromatic hydrocarbons in ethanol solution (Data from Birks, J. B. (ed.) (1975). Organic molecular photophysics, Vol. 2, Tables 2.6 and 3.4. Wiley, London)

Compound	ϕ_f	ϕ_{ISC}	$\phi_f + \phi_{\text{ISC}}$
Benzene	0.04	0.15	0.19 (exception)
Naphthalene	0.80	0.21	1.01
Fluorene	0.32	0.68	1.00
Anthracene	0.72	0.32	1.02
Tetracene	0.66	0.16	0.82
Phenanthrene	0.85	0.13	0.98
Pyrene	0.38	0.65	1.03
Chrysene	0.85	0.17	1.03

For large aromatic molecules the sum of the quantum yields of fluorescence and ISC is one i.e., rate of internal conversion is very slow with respect to the other two (Ermolaev's rule).

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

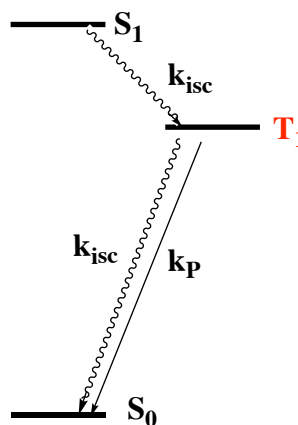
**Intersystem crossing in
carbonyl compounds ($n\pi^*$)**

**Intersystem Crossing in
Diradicals and Radical Pairs**

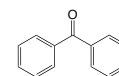
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Spin forbidden transitions

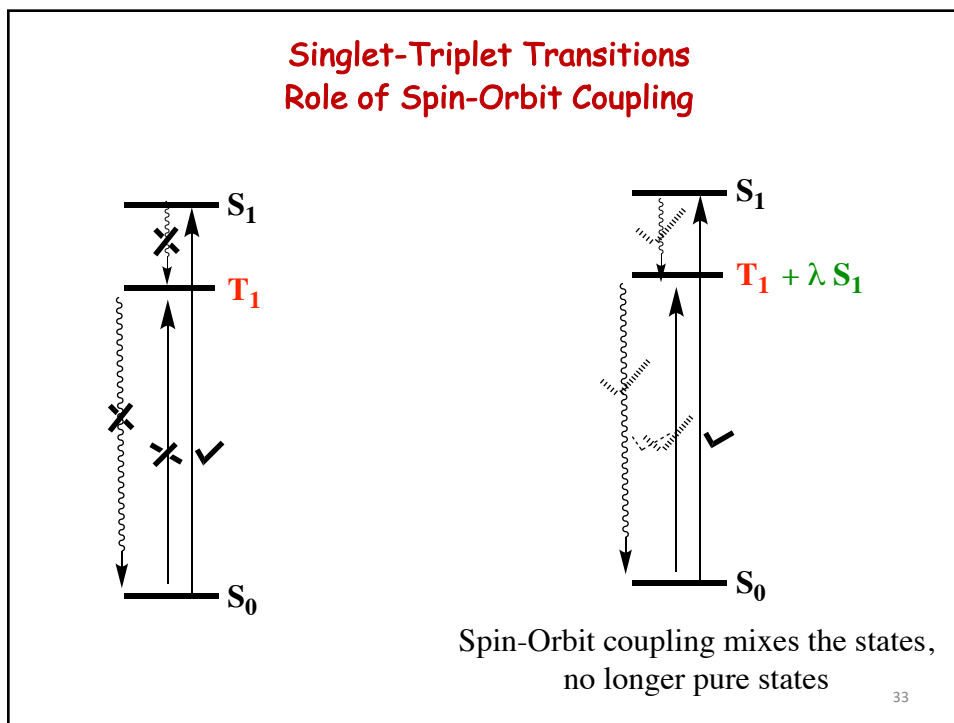


**Intersystem crossing in
molecules with $n\pi^*$ and $\pi\pi^*$ states**

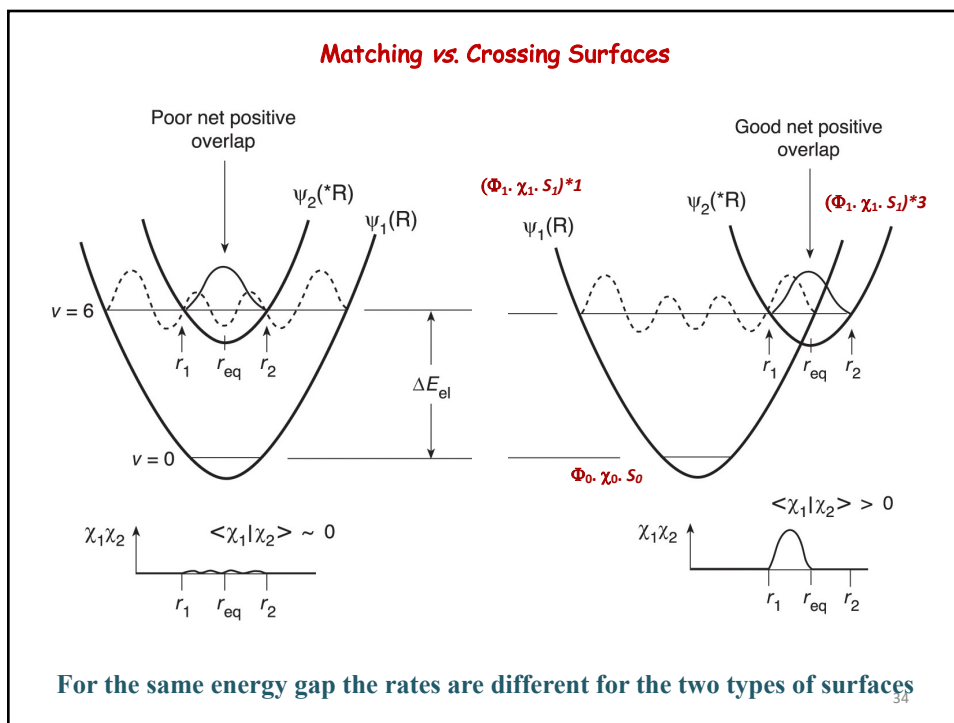


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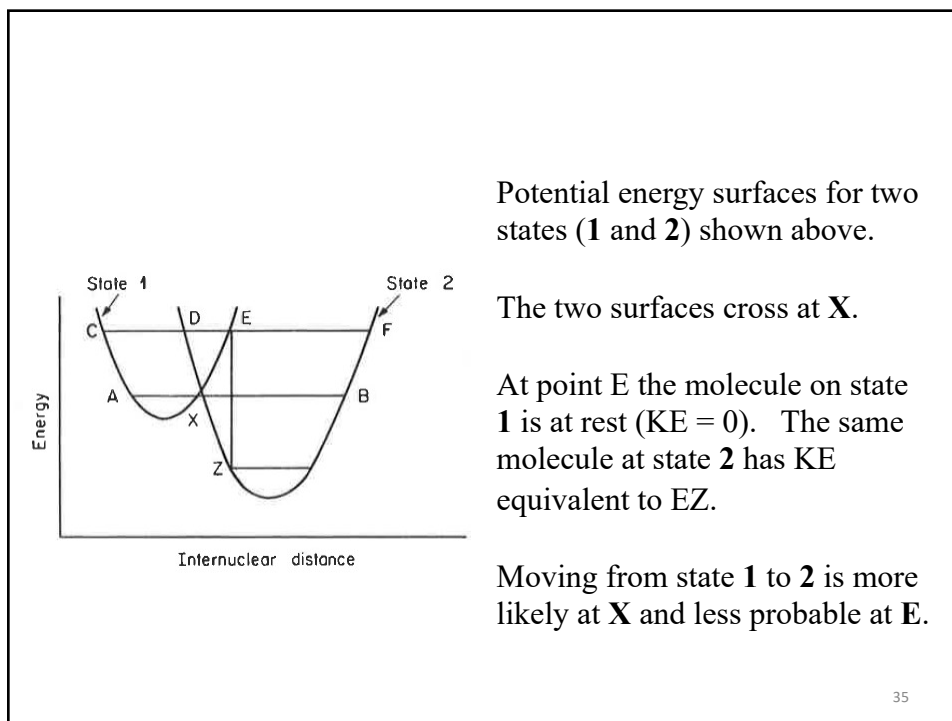
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Breakdown of Born-Oppenheimer Approximation

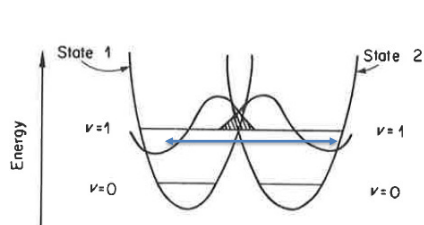


Figure 3.22. Large vibrational overlap at the crossing point of approximately degenerate electronic states

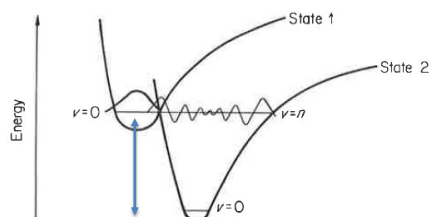


Figure 3.23. Vibrational overlap with a large energy difference between states

The energy difference between crossing surfaces may vary from 0 to ∞ .

When the gap is zero the transition between surfaces is more likely due to large vibrational overlap.

Energy gap law works even for crossing surfaces

When the gap is large the transition between surfaces is less likely due to poor vibrational overlap.

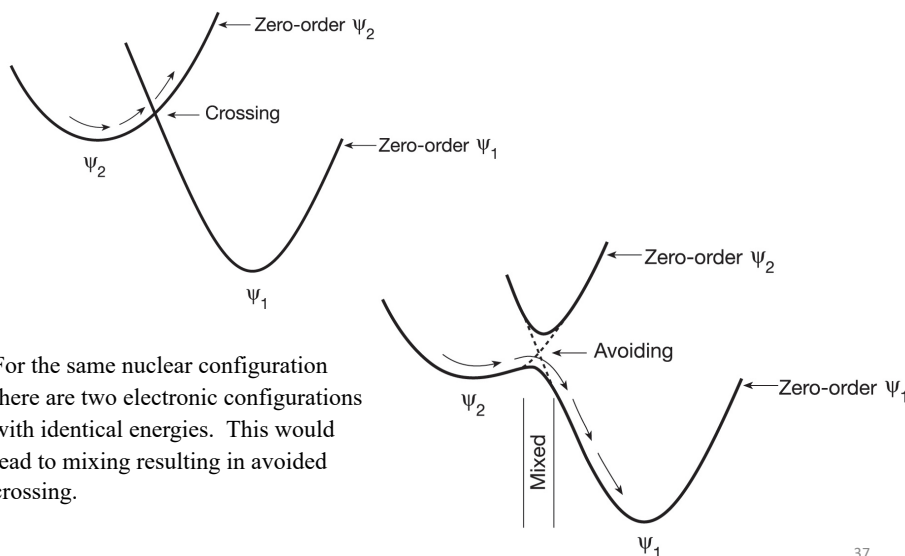
Larger the gap smaller the overlap and lower the rate of IC.

However, density of states is larger when the gap is larger. Higher vibrational levels would be closer. This would favor IC.

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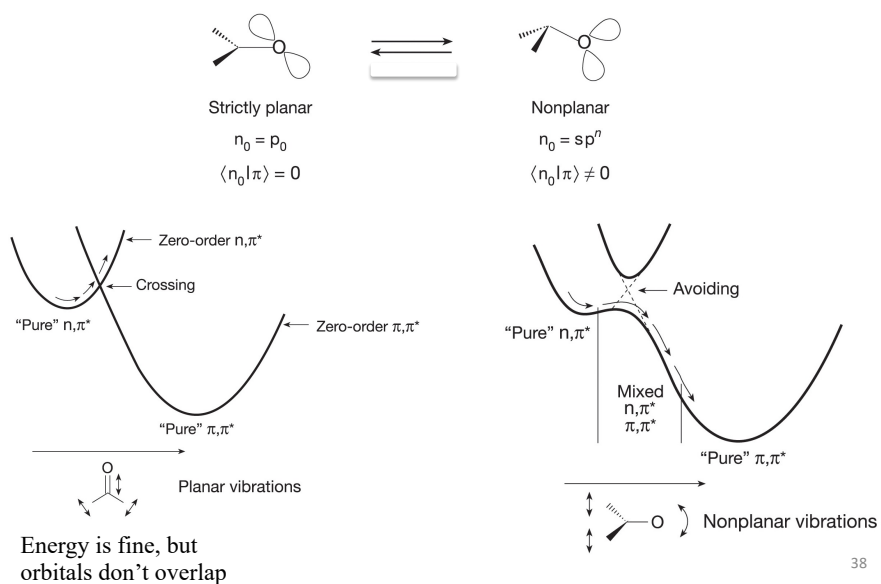
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Breakdown of Born-Oppenheimer Approximation Mixing of surfaces



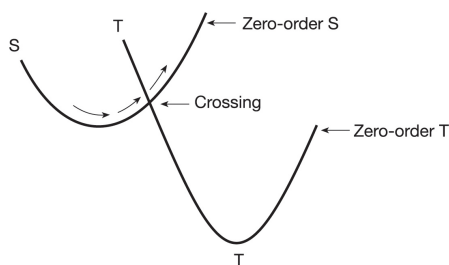
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Breakdown of Born-Oppenheimer Approximation Vibronic mixing enables surface mixing

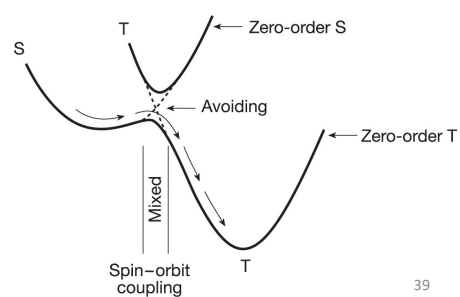


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Breakdown of Born-Oppenheimer Approximation Spin-Orbit coupling enables surface mixing

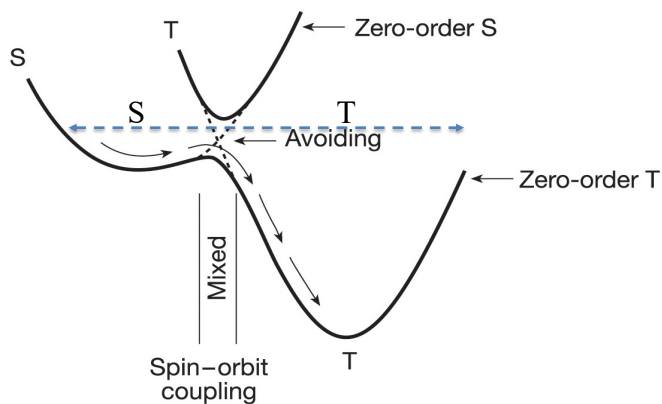


For the same nuclear configuration there are two electronic and spin configurations. If they don't mix the two will have identical energies. SO coupling could lead to mixing and result in avoided crossing.



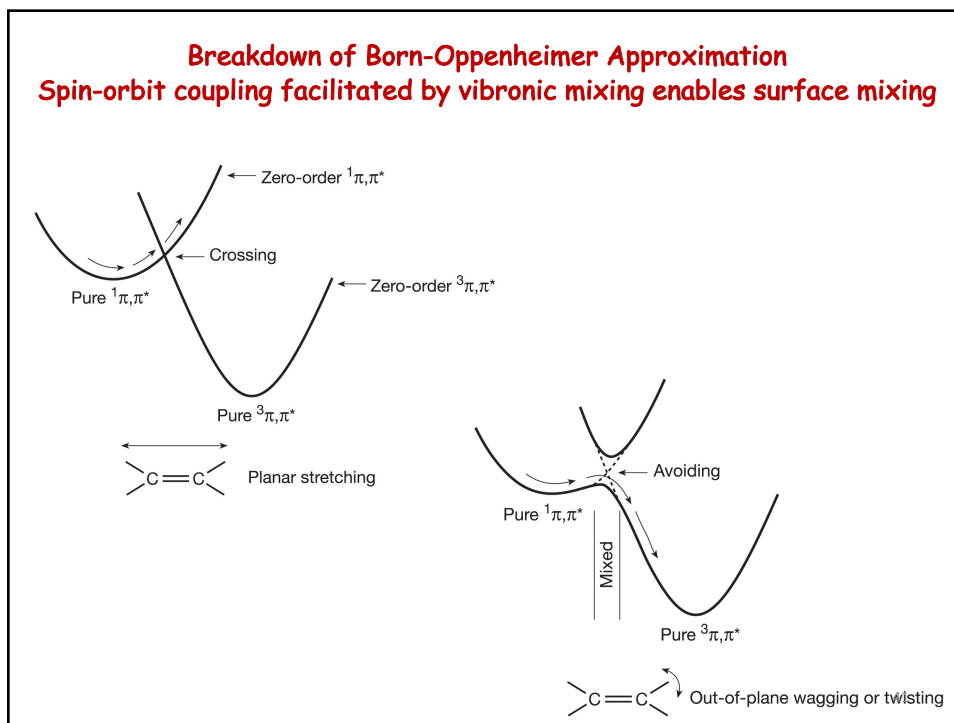
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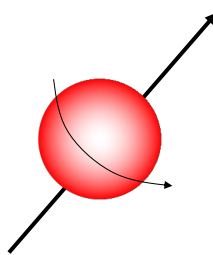
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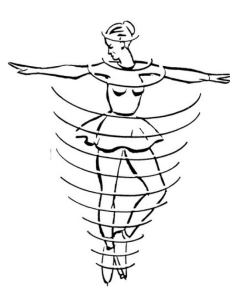


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Spin



- Classically **angular momentum** is a property of a macroscopic object which is in rotation about an axis
- 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



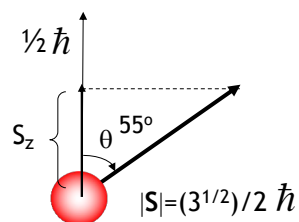
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Spin

- 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.

For quantum particles only certain directions of the spin are allowed. This is termed **spin multiplicity**.

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Quantum rules of electron spin angular momentum

- **S**, the **spin quantum number**, related to the length of the spin vector for an electron can assume only value $\frac{1}{2}$

examples

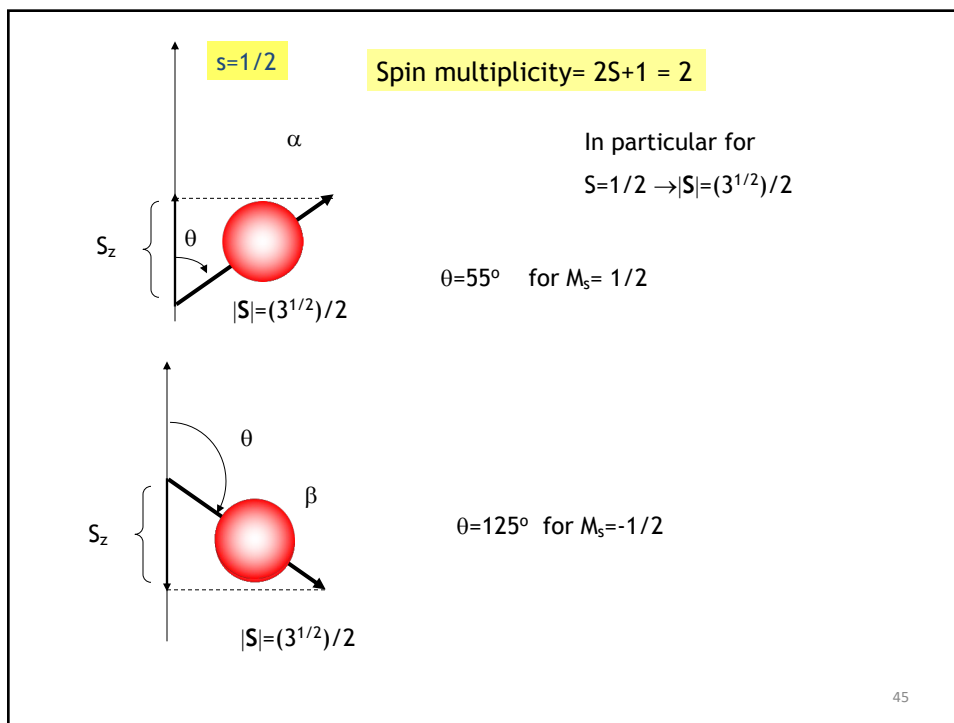
S=0	1	singlet
S=1/2	2	doublet
S=1	3	triplet

- **M_s** (**spin multiplicity**) related to the orientation of the spin vector

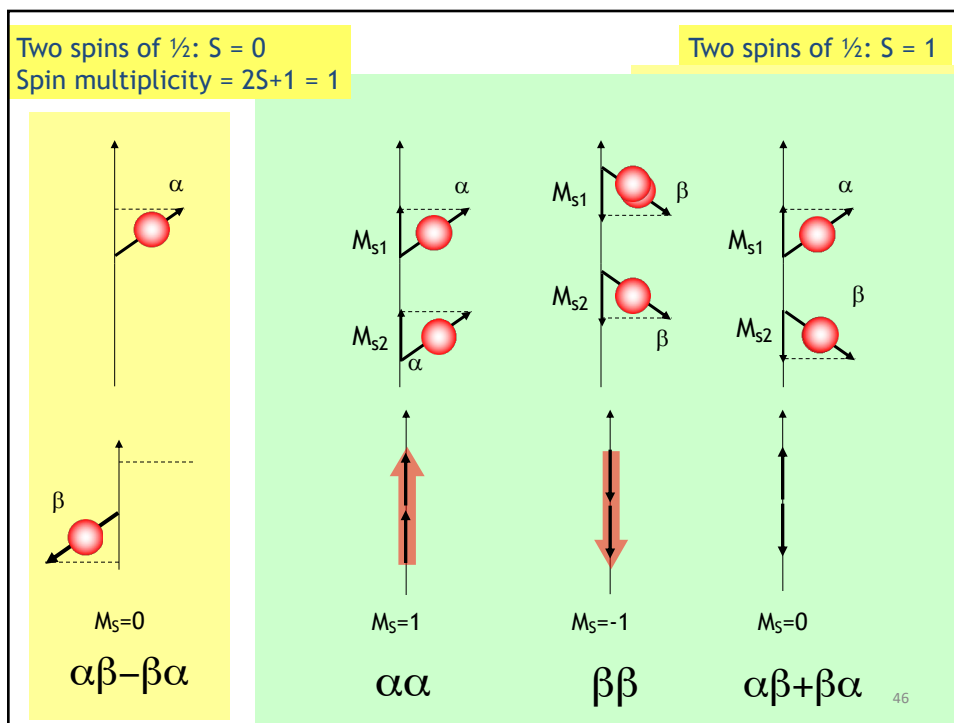
$$\text{Spin multiplicity} = 2S + 1$$

44

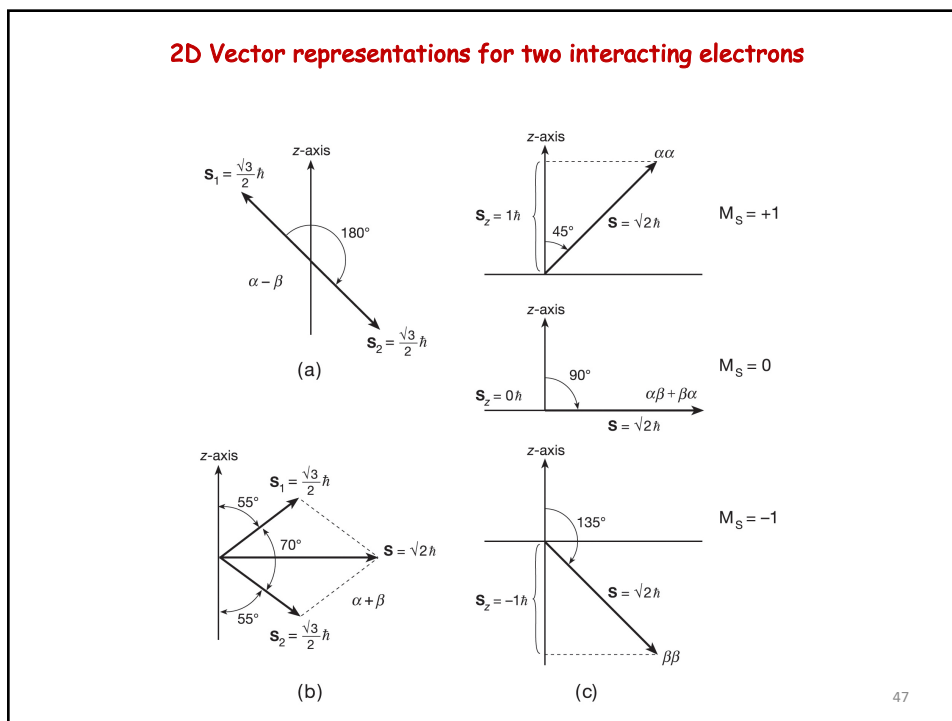
44



45



46



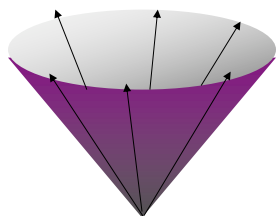
47

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 $|\mathbf{S}|$ 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

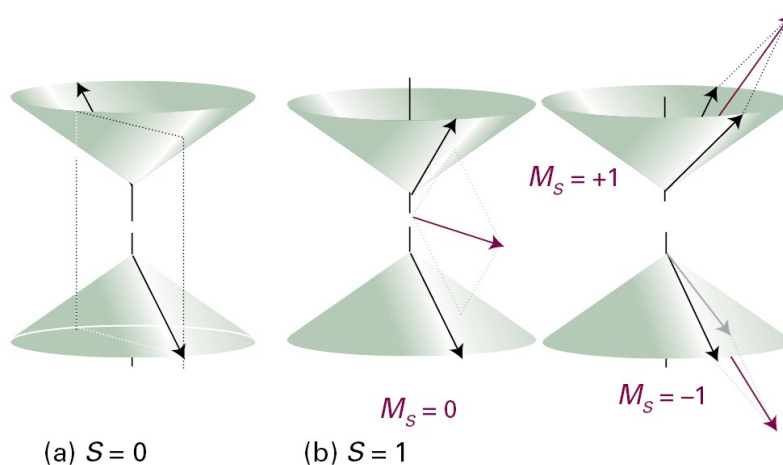


There is an infinite set of positions that the spin vector can assume in space making an angle of 55° with the z -axis, any one of which could correspond to the actual position of the spin vector. This is represented as a cone in a 3-D.

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Angular momentum vector representations of two electron system: Singlet and Triplet



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Angular momentum

Magnetic moment

Electron possesses a fixed and characteristic spin angular momentum (S) of $\frac{1}{2}\hbar$ independent of where it is.

Electron's orbital angular momentum (L) depends on the orbital where it is.

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spin angular momentum

z axis
Spin angular momentum vector along z axis, S_z
Magnetic moment vector along z axis, μ_z

z axis
Angular momentum vector S
Magnetic moment vector μ_S

orbital angular momentum

Orbital angular momentum vector L

Orbital angular momentum vector L
Magnetic moment vector μ_L

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Electron has magnetic moment due to its spin

\vec{B}
 \vec{S}
 μ_s

S
 μ_s

S
 μ_s

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

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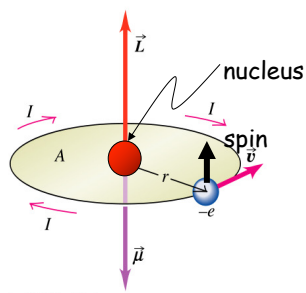
52

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 an **orbital** magnetic moment:

$$\mu_L = -\frac{e}{2m} \mathbf{L}$$

$\swarrow \gamma_e$
 $\searrow \hbar$



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

$$\hbar \left(\frac{e}{2m} \right)$$

Bohr magneton

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

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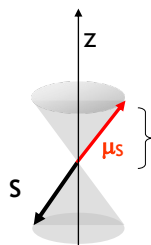
53

Magnetic moment of a spinning electron

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

~~$$\mu_s = -\left(\frac{e}{2m}\right) \mathbf{S}$$~~

Analogues to L
 $\mu_L(r) = \left(\frac{e}{2m_e}\right) \mathbf{L}$

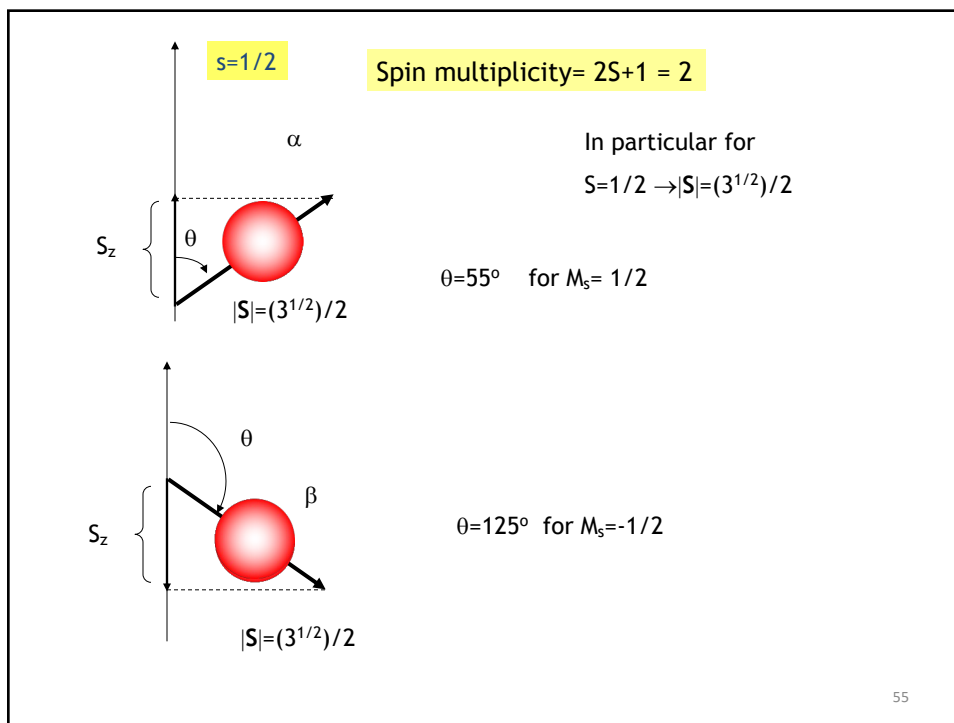


$$\mu_s = -\left(\frac{e}{2m}\right) g_e \mathbf{S} = -\gamma_e g_e \mathbf{S}$$

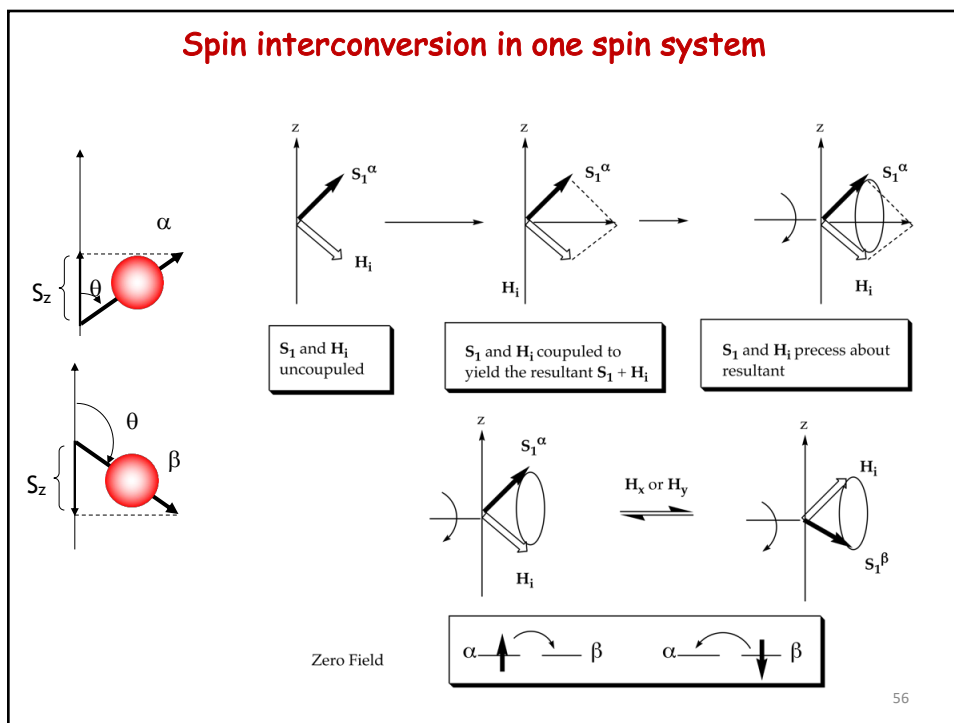
g factor for free electrons and most organic molecules ≈ 2

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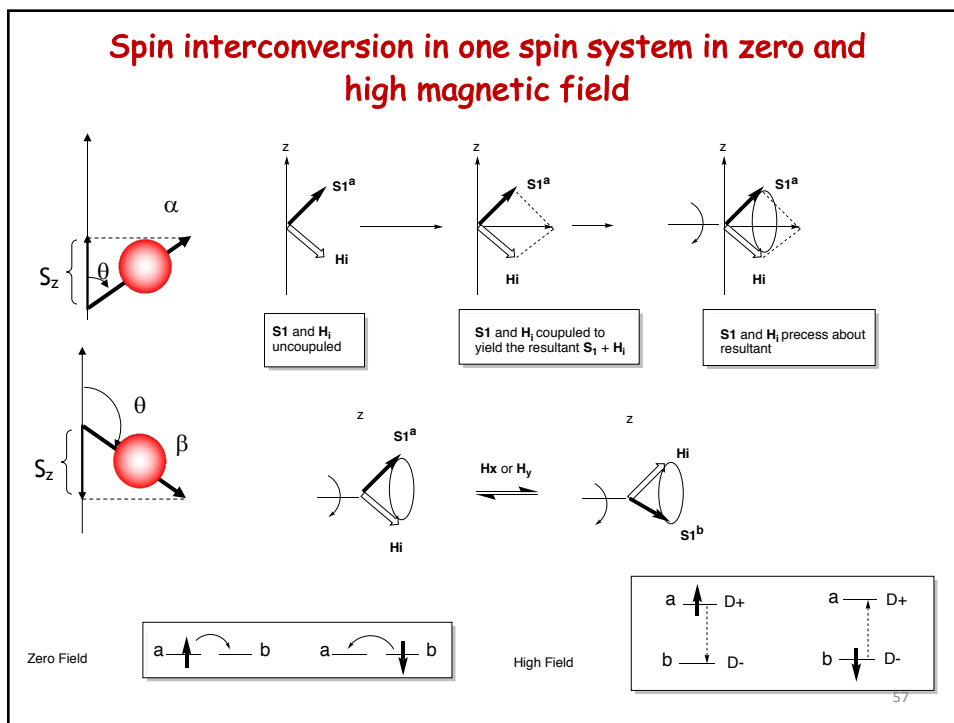
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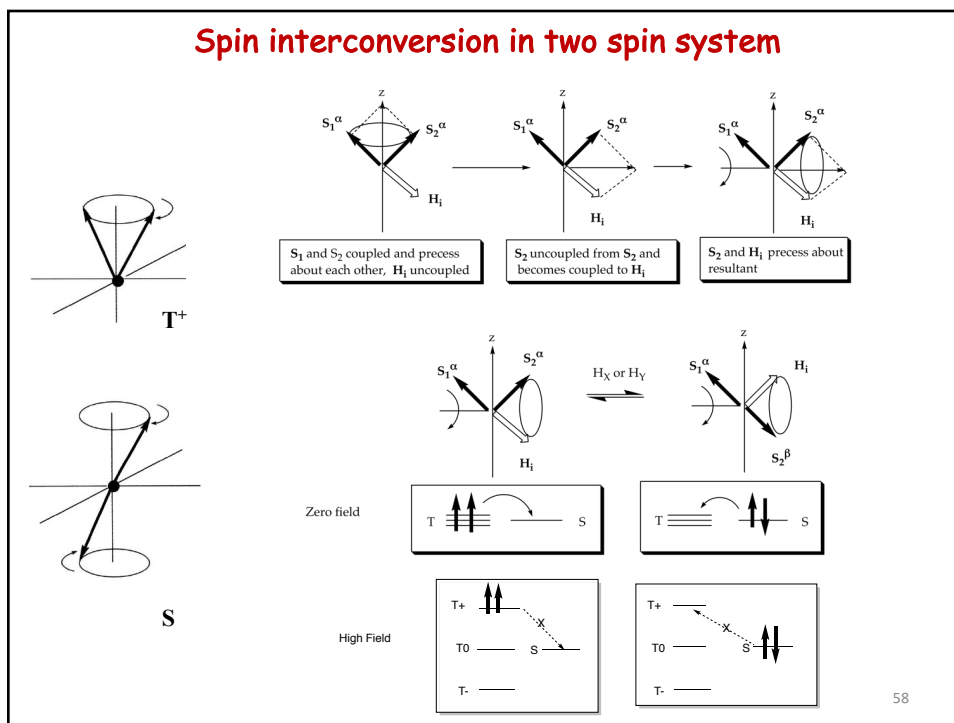
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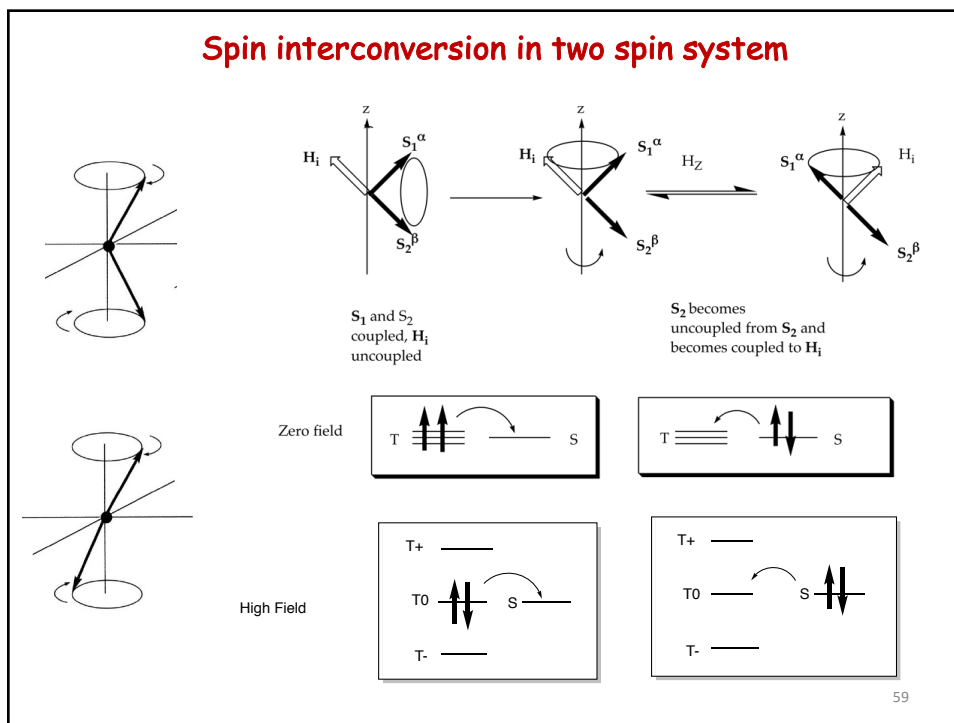
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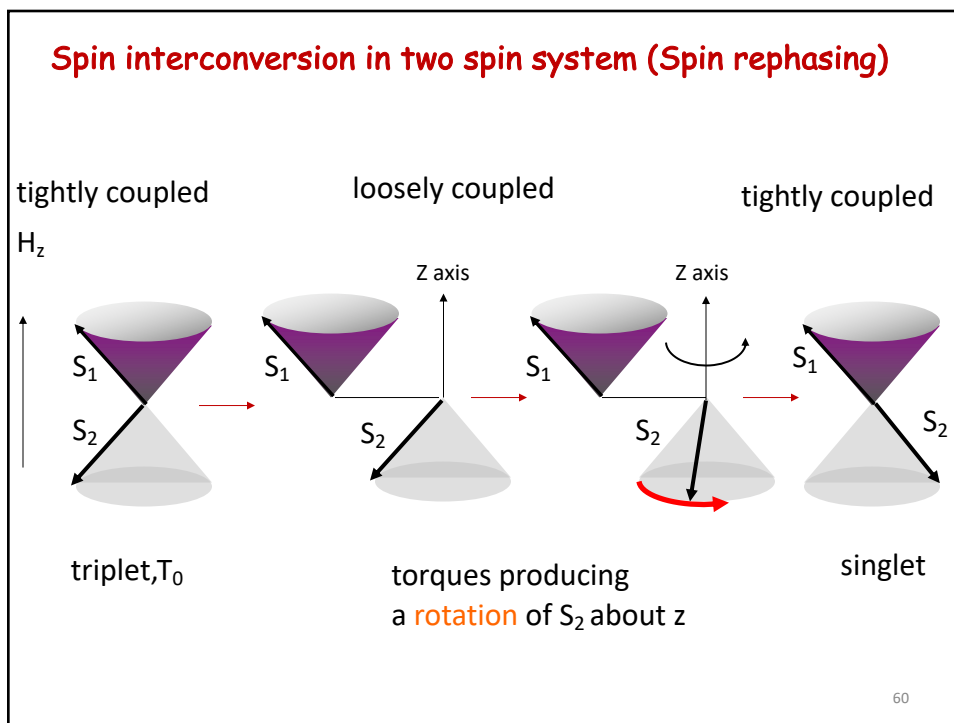
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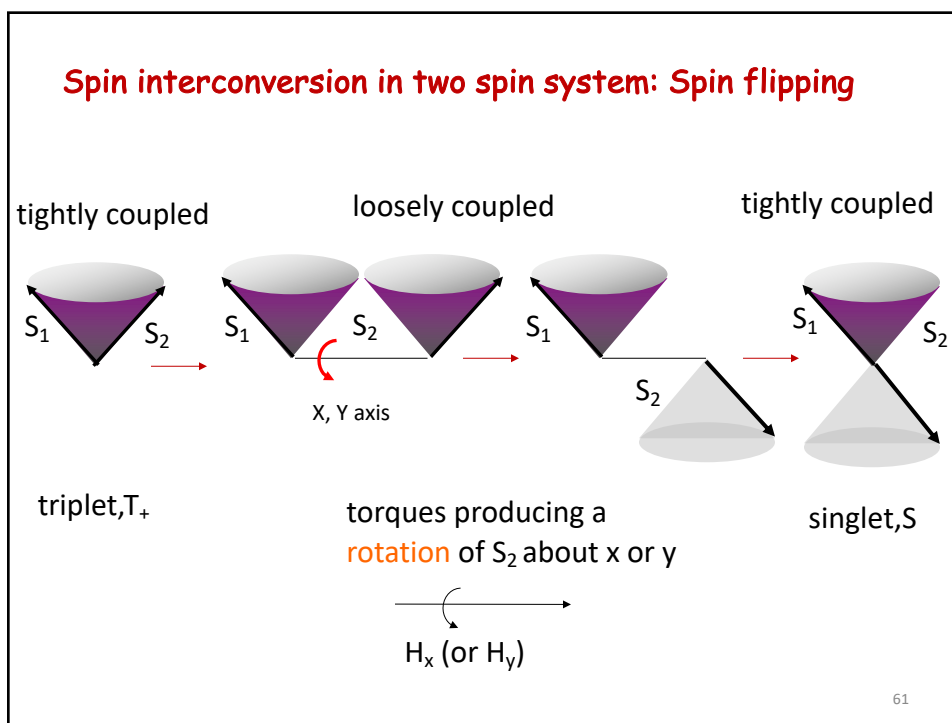
58



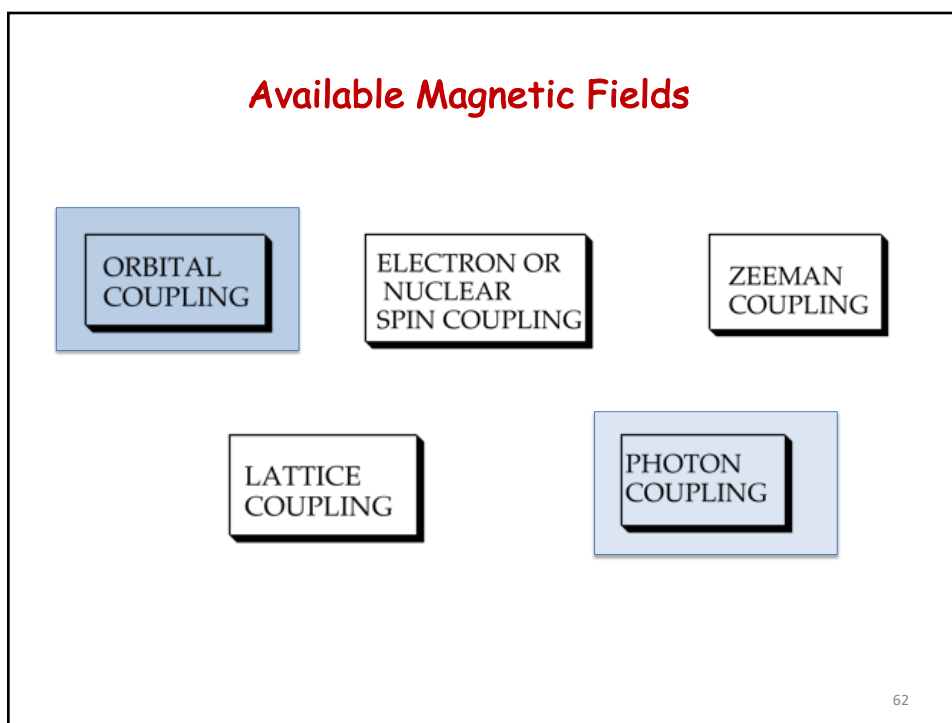
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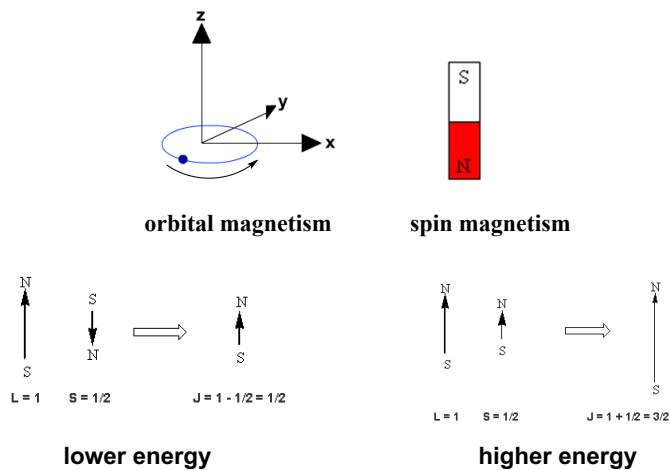
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Spin Orbit Coupling

- There is a magnetic interaction between the magnetism generated by the spin and orbital motions
 - results in different values for the **total angular momentum, J**



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

When L and S are strongly coupled it is difficult for other forces to break the coupling

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

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Summary

- 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).
- 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, $\zeta_{SO} \sim Z^4$.
- 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!

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Spin-Orbit Coupling and Heavy Atom Effect

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.

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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

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Spin-orbit coupling parameter is related to atomic number

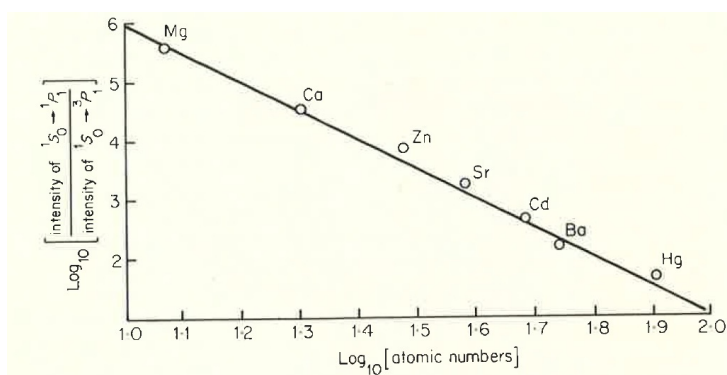


Figure 2.3 A log-log plot illustrating the effect of atomic number on the intensity of a spin-forbidden transition. (From R. M. Hochstrasser, *Behaviour of Electrons in Atoms*, W. A. Benjamin, N.Y., 1964, p. 103.)

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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).

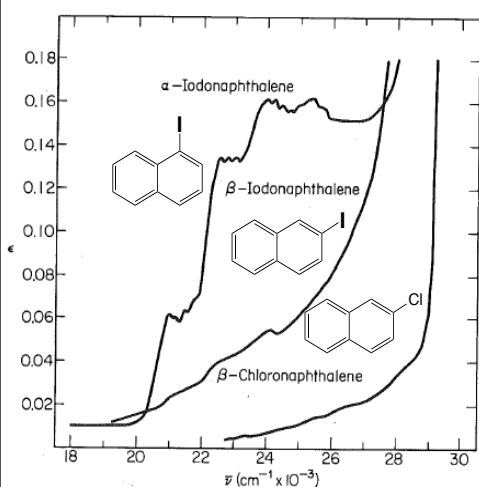
Most commonly, the HAE refers to the rate enhancement of a spin forbidden photophysical radiative or radiationless transition that is due to the presence of an atom of high atomic number, Z .

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

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Internal Heavy Atom Effect: Spin forbidden absorption



THE JOURNAL OF CHEMICAL PHYSICS VOLUME 17, NUMBER 10 OCTOBER, 1949

Triplet-Singlet Transitions in Organic Molecules. Lifetime Measurements of the Triplet State*
DONALD S. MCCURTAIN
Department of Chemistry, University of California, Berkeley, California
(Received December 30, 1948)

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 11, NUMBER 12 DECEMBER, 1949

Effects of Perturbations on Phosphorescence: Luminescence of Metal Organic Complexes
PHILIP VOYNA* AND S. L. WEISSBERG
Department of Chemistry, Washington University, Saint Louis, Missouri
(Received February 16, 1949)

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 29, NUMBER 1 JANUARY, 1952

Collisional Perturbation of Spin-Orbital Coupling and the Mechanism of Fluorescence Quenching. A Visual Demonstration of the Perturbation*
MORRIS KAMAT
Department of Chemistry, University of Manchester, England
(Received August 13, 1951)

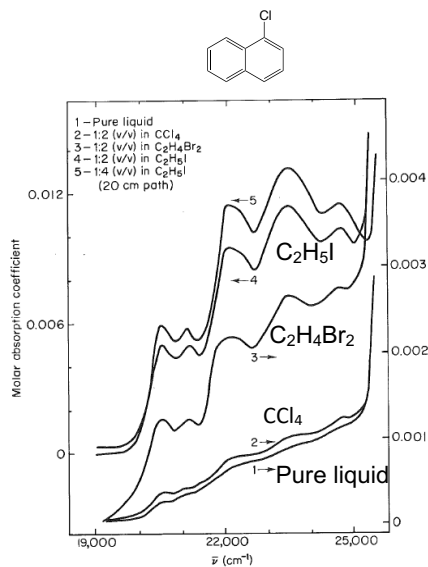
THE JOURNAL OF CHEMICAL PHYSICS VOLUME 22, NUMBER 2 FEBRUARY, 1954

Singlet-Triplet Absorption Bands in Some Halogen Substituted Aromatic Compounds†
DONALD S. MCCURTAIN, NORMAN W. BEAZLE AND PHILIP L. HAYES
Department of Chemistry and Chemical Engineering, University of California, Berkeley, California
(Received August 13, 1953)

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External Heavy Atom Effect: Spin forbidden absorption



THE JOURNAL OF CHEMICAL PHYSICS VOLUME 31, NUMBER 8 OCTOBER 15, 1952

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

S. P. MCGILVER, R. SUNDEN, AND N. CHRISTODOULAKIS
Coker Chemical Laboratories, Louisiana State University, Baton Rouge 7, Louisiana

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 40, NUMBER 2 15 JANUARY 1964

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

S. P. MCGILVER AND T. ARMSTRONG
Coker Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803

AND
M. KASRA
Department of Chemistry and Institute of Molecular Biophysics, The Florida State University, Tallahassee, Florida 32301
(Received 10 September 1963)

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

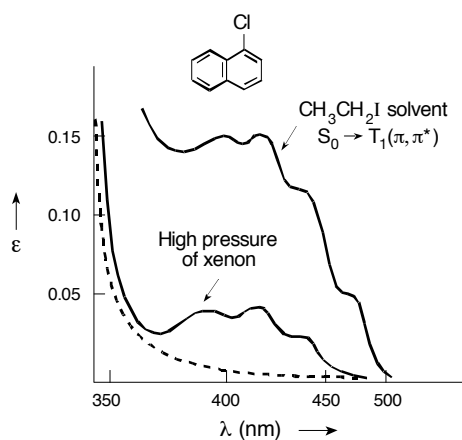
V. RAMAMURTHY* J. V. CASPAR, D. F. EATON, ERICA W. KOO, AND D. R. CORBIN
Contribution No. 6068 from Central Research and Development, Experimental Station, The Du Pont Company, Wilmington, Delaware 19880-0328. Received December 2, 1991

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

71

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External Heavy Atom Effect: Spin forbidden absorption



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 KASRA†
Department of Chemistry, University of Manchester, England
(Received August 13, 1951)

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

M. R. WAGNER, R. P. FROSCHE, AND G. W. ROBINSON
Gates and Crellin 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 α -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

Spectrochimica Acta, **1963**, 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

72

72

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

Fundamental Research:

The presentations/reports are **not “subject”** to the EAR – Fundamental Research as per EAR Part 734.8 (a) and (c).

73

73

Spin-Orbit Coupling and Heavy Atom Effect

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

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

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

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

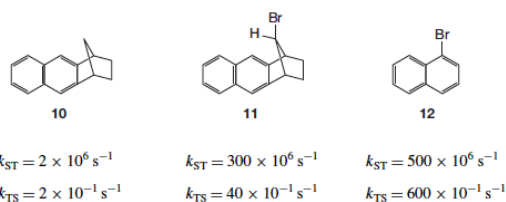
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Influence of Heavy Atom Effect on ISC and phosphorescence

Molecule	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	0.002	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



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

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TABLE 7.2
Spectroscopic Data on Group IV Tetraphenyls^a

Molecule	Fluorescence band maximum (Å)	Phosphorescence band maxima (Å)	Φ_P/Φ_F	τ_P (sec) ^b	τ_P (sec) ^c	$\sum_{\text{K}} \xi_{\text{np}}^2$ (cm ⁻¹) ² ^d	$\sum_{\text{K}} \xi_{\text{K}}^2$ (cm ⁻¹) ² ^e	τ_{IP} (sec) ^f	k_{ISC} (sec ⁻¹) ^g
C(C ₆ H ₅) ₄	3200	4500, 4700, 5100	≤ 0.1	2.9	—	7.84×10^3	5.49×10^8	≅ 2.9	10^8 - 10^7
Si(C ₆ H ₅) ₄	3100	4300, 4600	0.1	1.1	—	2.02×10^4	2.49×10^4	0.66	10^8
Ge(C ₆ H ₅) ₄	3200	4500, 4700, 5100	1	0.055	0.003	7.74×10^2	7.79×10^2	0.021	10^8
Sn(C ₆ H ₅) ₄	3200	4500, 4700	10	0.003	0.0006	4.39×10^2	4.39×10^2	0.0038	10^{11}
Pb(C ₆ H ₅) ₄	—	4250, 4550	≫ 10	(0.0008)	0.00008	5.32×10^7	5.32×10^7	0.0003	—

^a All data refer to glassy solutions at 77°K; the experimental data are taken from LaPaglia (11).

^b Phosphorescence emission data.

^c Calculated from $T_1 \leftarrow S_0$ absorption data.

^d Spinorbit coupling factors squared for the np^2 configurations of C(I), Si(I), Ge(I), Sn(I), and Pb(I), respectively.

^e Sum of squares of spinorbit coupling factors, ξ_{np}^2 , over all atoms in the molecule.

^f Calculated from the equation $\tau_{IP} = \tau_P^0 [C(C_6H_5)_4]^{-1} \sum_{\text{K}} \xi_{\text{K}}^2$, with $\tau_P^0 [C(C_6H_5)_4] \equiv 2.9$ sec (K here refers to C, Si, Ge, Sn, and Pb).

^g Obtained using Eq. 7.15 and the approximation $k_{QP} \sim 0$ (which is known to be wrong).

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TABLE 7.3
Spectroscopic Data on Naphthalene Derivatives^a

Molecule	$\bar{\nu}_{0,0}$ (cm^{-1})	$\bar{\nu}'_{0,0}$ (cm^{-1})	Φ_F	Φ_P	Φ_P/Φ_F (approx.)	τ_P (sec)	k_{ISC} (sec^{-1})	k_P (sec^{-1})
Naphthalene	31750	21250	0.55	0.051 ± 0.003	0.093	2.3 ± 0.1	$\sim 10^6$	$\sim 10^6$
1-Methylnaphthalene	31450	21000	0.85 ± 0.19	0.044 ± 0.013	0.053	2.1 ± 0.1	$\sim 2 \times 10^6$	$\sim 3 \times 10^6$
1-Hydroxynaphthalene	30775	20600	0.76 ± 0.04	0.036 ± 0.004	0.047	1.9	$\sim 2 \times 10^6$	$\sim 3 \times 10^6$
1-Fluoronaphthalene	31600	21150	0.84 ± 0.08	0.056 ± 0.009	0.068	1.5	$\sim 2 \times 10^6$	$\sim 3 \times 10^6$
1-Chloronaphthalene	31360	20700	0.058 ± 0.005	0.30 ± 0.06	5.2	0.29 ± 0.01	$\sim 1.5 \times 10^7$	$\sim 3 \times 10^6$
1-Bromonaphthalene	31280	20650	0.0016 ± 0.0005	0.27 ± 0.04	164	2.0×10^{-3}	$\sim 5 \times 10^6$	$\sim 3 \times 10^6$
1-Iodonaphthalene	—	20500	< 0.0005	0.38 ± 0.06	> 1000	2.0×10^{-3}	$> 3 \times 10^6$	$\sim 3 \times 10^6$

^a All data refer to glassy solutions at 77°K; these data are taken from Ermolaev and Svitashv (22, 23) and Ermolaev, Kotlyar, and Svitashv (24).

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Radiative decay from T_1
Non-Radiative decay from T_1

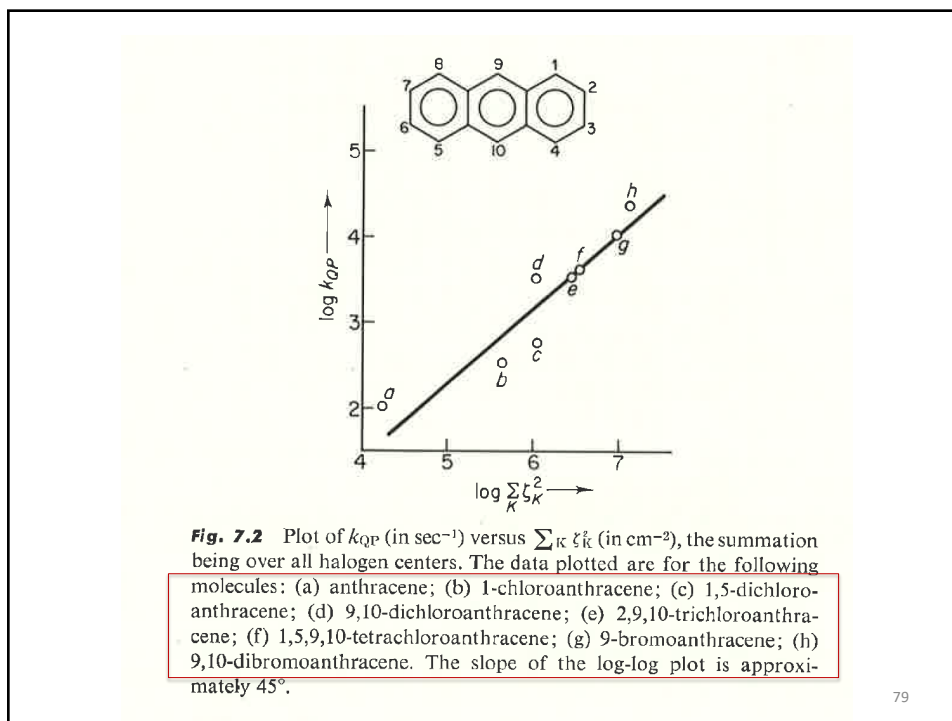
Table 1. Fluorescence 0-0 band ($\bar{\nu}_f$), phosphorescence 0-0 band ($\bar{\nu}'_p$), fluorescence quantum yield (Φ_f), phosphorescence quantum yield (Φ_p), phosphorescence lifetime (τ_p), quantum yield (Φ_T) of triplet formation, rate constant of the radiative (k_{PT}) and non-radiative (k_{GT}) $T_1 \rightarrow S_0$ transition (ethanol, 77 K).

Compound	$\bar{\nu}_f$ [cm^{-1}]	$\bar{\nu}'_p$ ^a [cm^{-1}]	Φ_f	Φ_p	τ_p [sec]	Φ_T	k_{PT} [sec^{-1}]	k_{GT} [sec^{-1}]
Benzo[b]furan (1)	33 110	25 130 (25 157)	0.63	0.24	2.35	0.37	0.28	0.15
Benzo[b]thiophene (2)	32 895	24 040 (24 010)	0.02	0.42	0.32	0.98	1.34	1.79
Benzo[b]selenophene (3)	32 360	23 585 (23 585)	$5 \cdot 10^{-4}$	0.27	$7 \cdot 10^{-3}$	≈ 1	38.6	104
Benzo[b]tellurophene (4)	—	22 730 (22 573)	$< 5 \cdot 10^{-4}$	0.18	$6 \cdot 10^{-4}$	≈ 1	300	1370
Dibenzo[b, d]furan (5)	33 110	24 450 (24 510)	0.40	0.29	5.6	0.60	0.086	0.092
Dibenzo[b, d]thiophene (6)	30 395	24 330 (24 272)	0.025	0.47	1.5	0.97	0.32	0.35
Dibenzo[b, d]selenophene (7)	29 670	23 980 (23 866)	$1 \cdot 10^{-3}$	0.74	0.04	≈ 1	18.5	6.5
Dibenzo[b, d]tellurophene (8)	—	23 530 (23 585)	$< 5 \cdot 10^{-4}$	0.79	$2.5 \cdot 10^{-3}$	≈ 1	316	84

^a Figures in brackets: phosphorescence 0-0 band in n-pentane, 77 K.

M Zander, G Kirsch - Zeitschrift für Naturforschung A, 1989,205

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**Intersystem crossing
in carbonyl compounds and others with $n\pi^*$)**

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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.

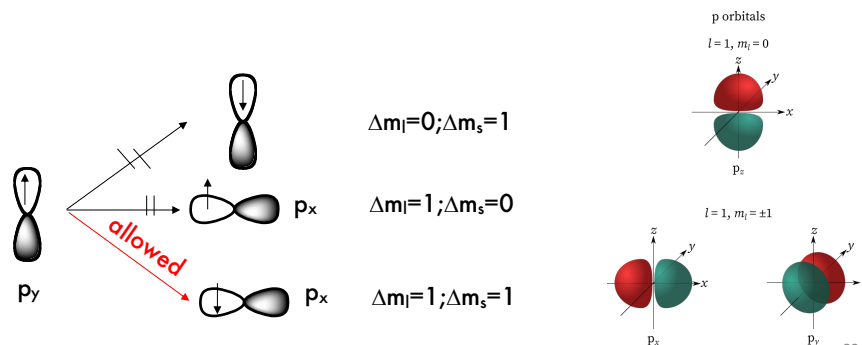
Spin-orbit coupling in organic molecules will be effective in inducing transitions between states of different spin if a “ $p_x \rightarrow p_y$ ” orbital transition *on a single atom* is involved in the electronic transition. This orbital transition provides both a means of conserving total angular 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.

81

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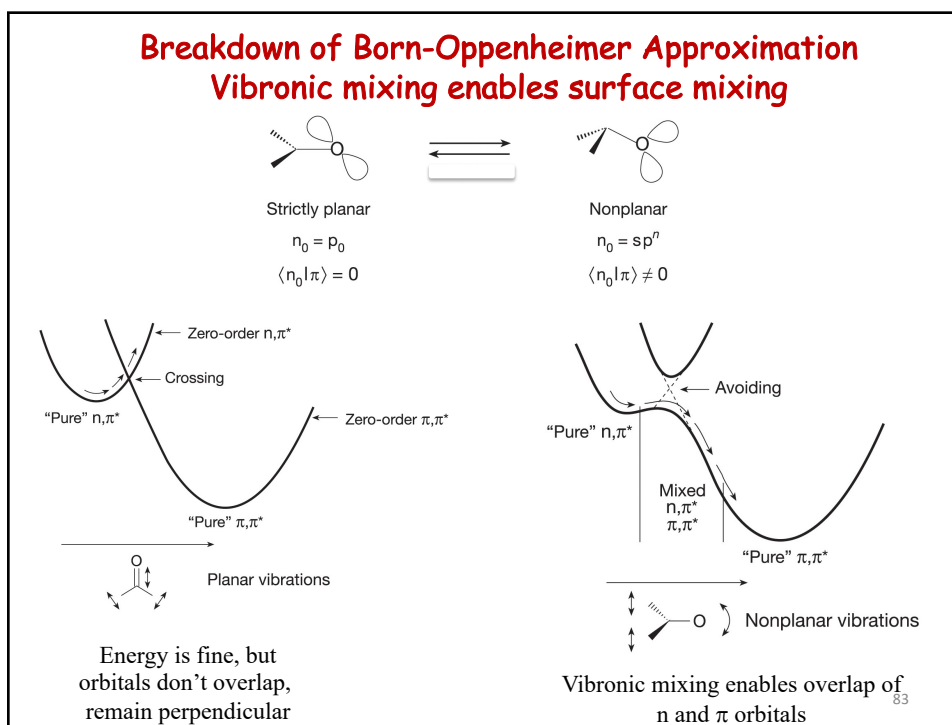
Energy and angular momentum conservation

- The electron spin must either remain unchanged or *change by one unit of angular momentum*, \hbar (say, $+1/2 \hbar \rightarrow -1/2 \hbar$).
- 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 .

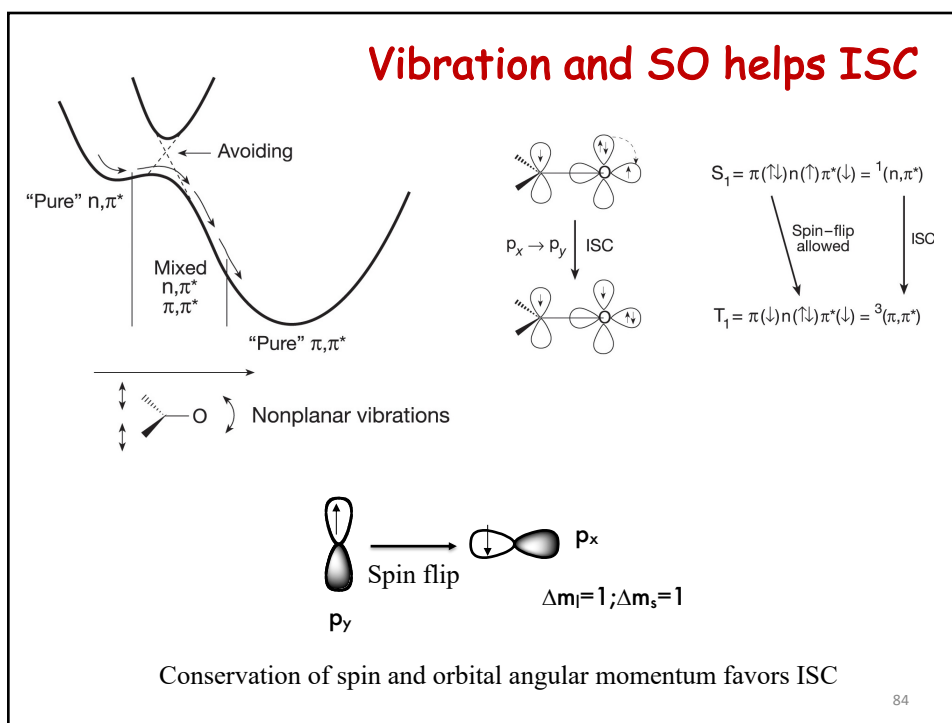


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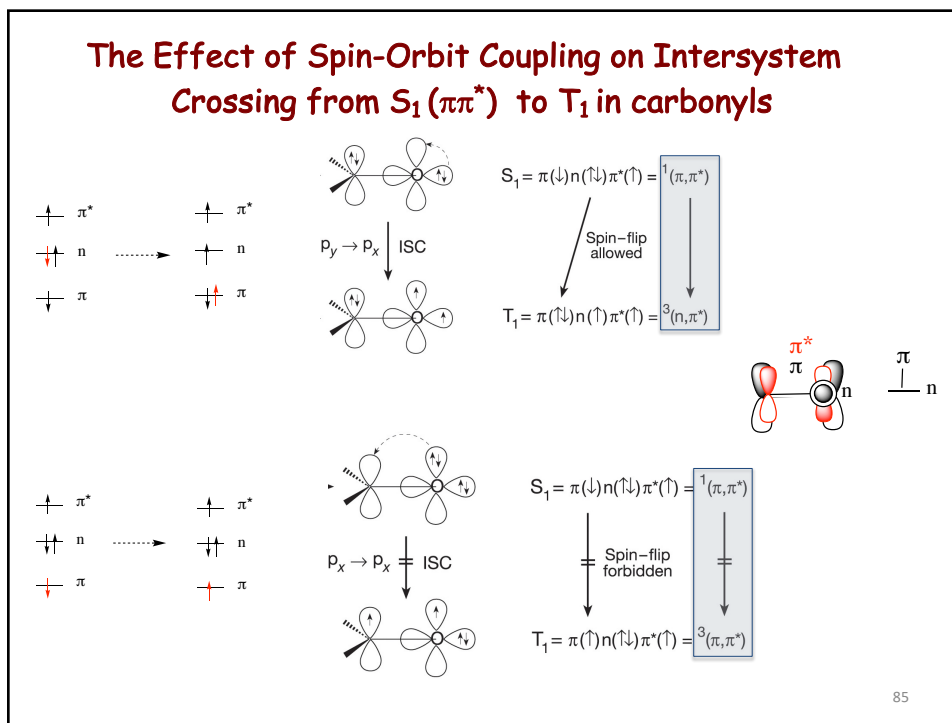


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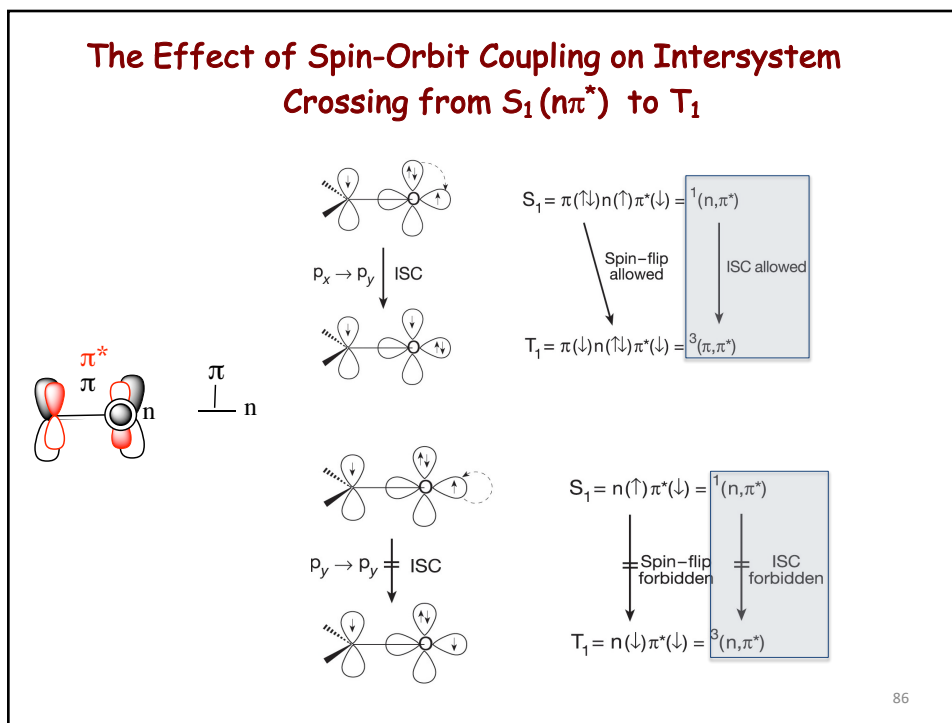


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84



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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

THE TRIPLET STATE AND MOLECULAR ELECTRONIC PROCESSES
IN ORGANIC MOLECULES

S. K. LOWER¹ AND M. A. EL-SAYED²

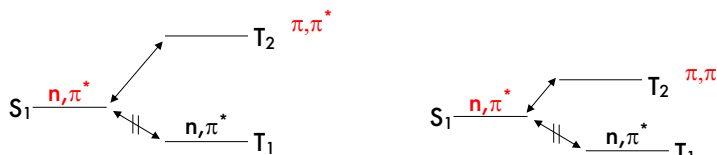
¹Department of Chemistry, ²University of California, Los Angeles, California 90084
Received June 25, 1965

Chem. Rev., **1966**, *66*, 199-241

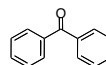
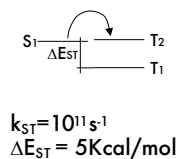
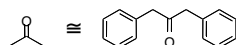
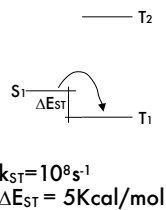
87

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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 $T_1(n, \pi^*)$

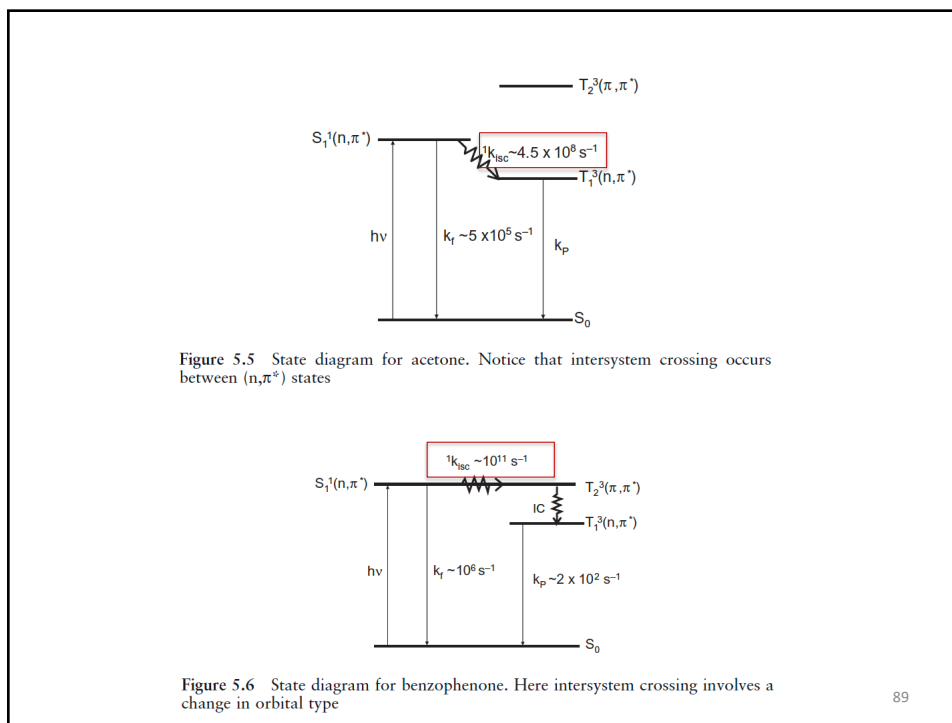


Thus, the ISC crossing rate depends whether or not it is allowed and on the energy gaps involved.

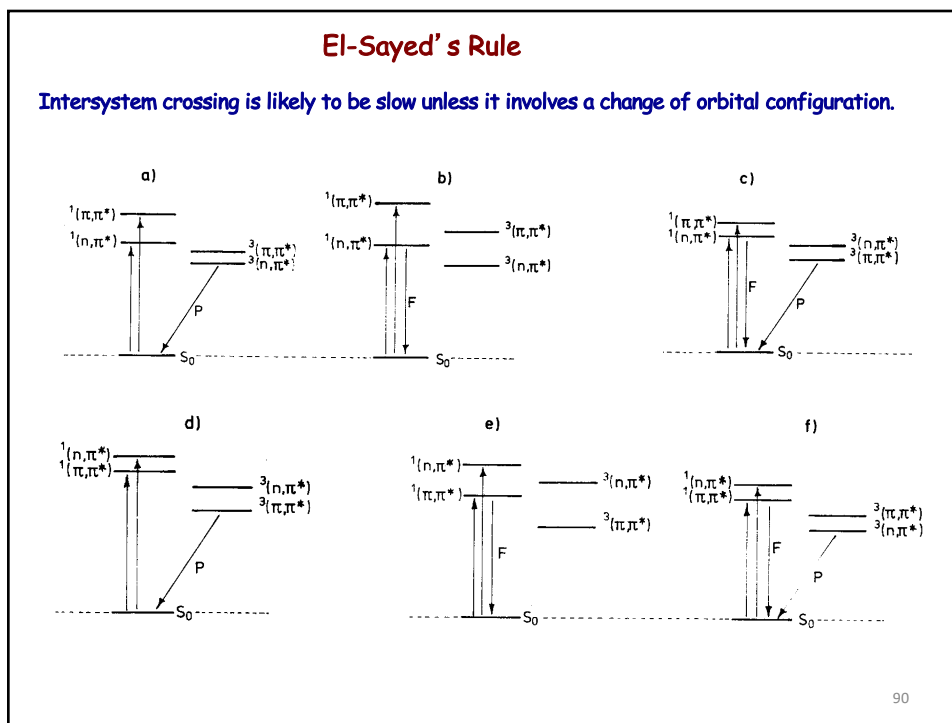


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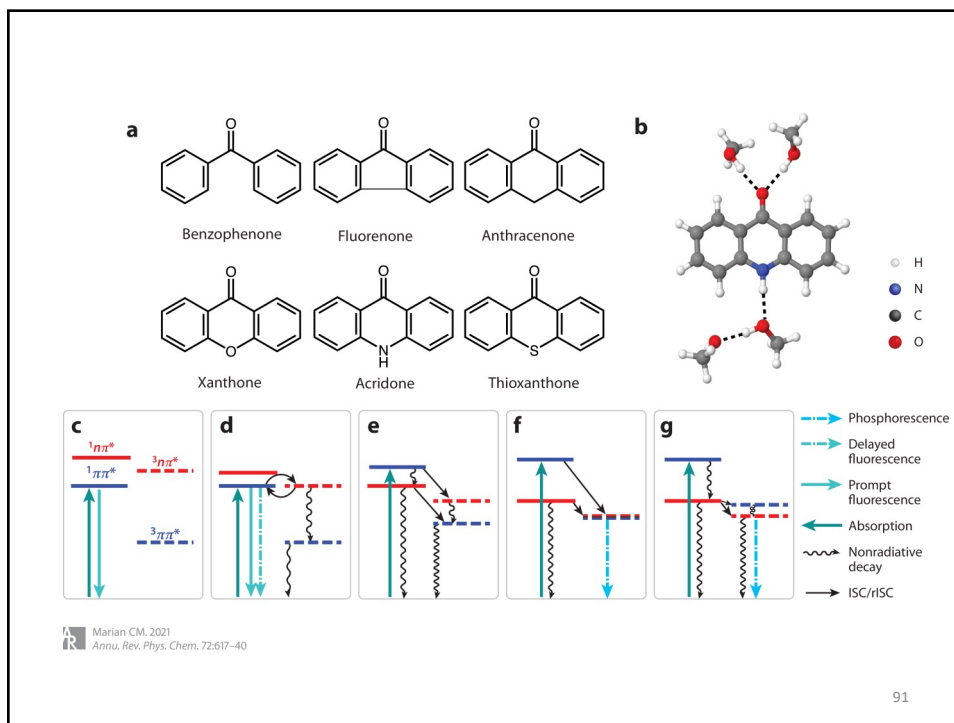
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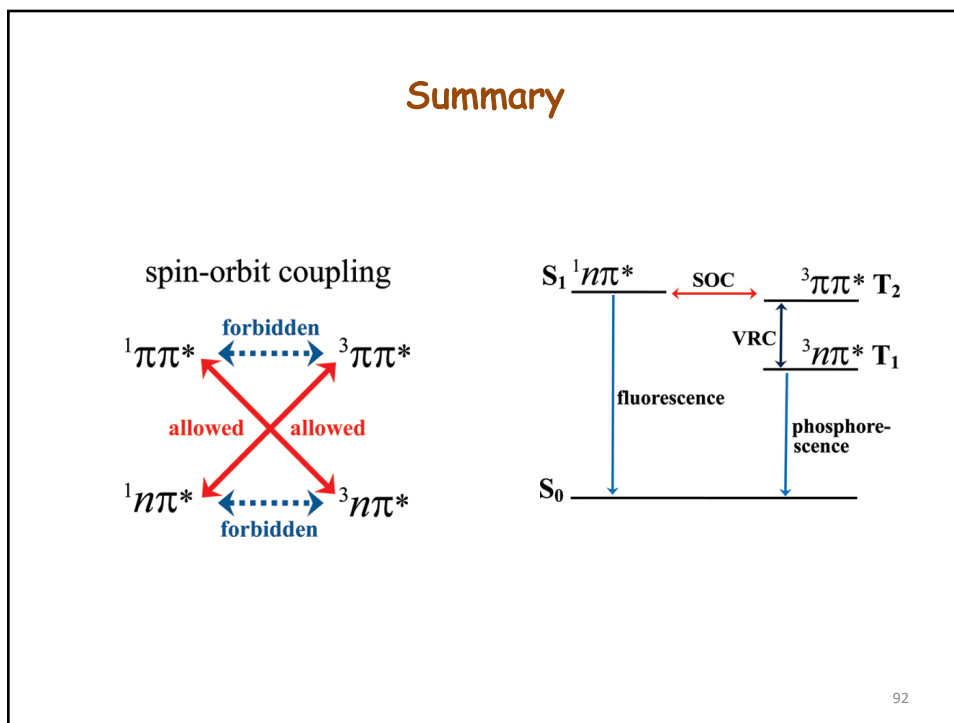
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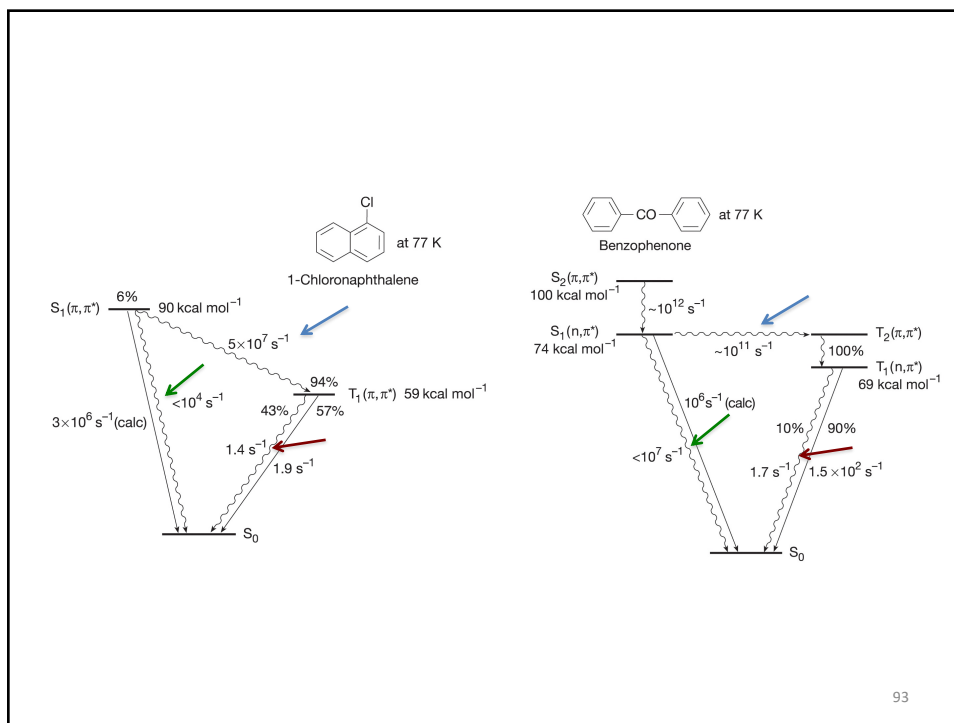
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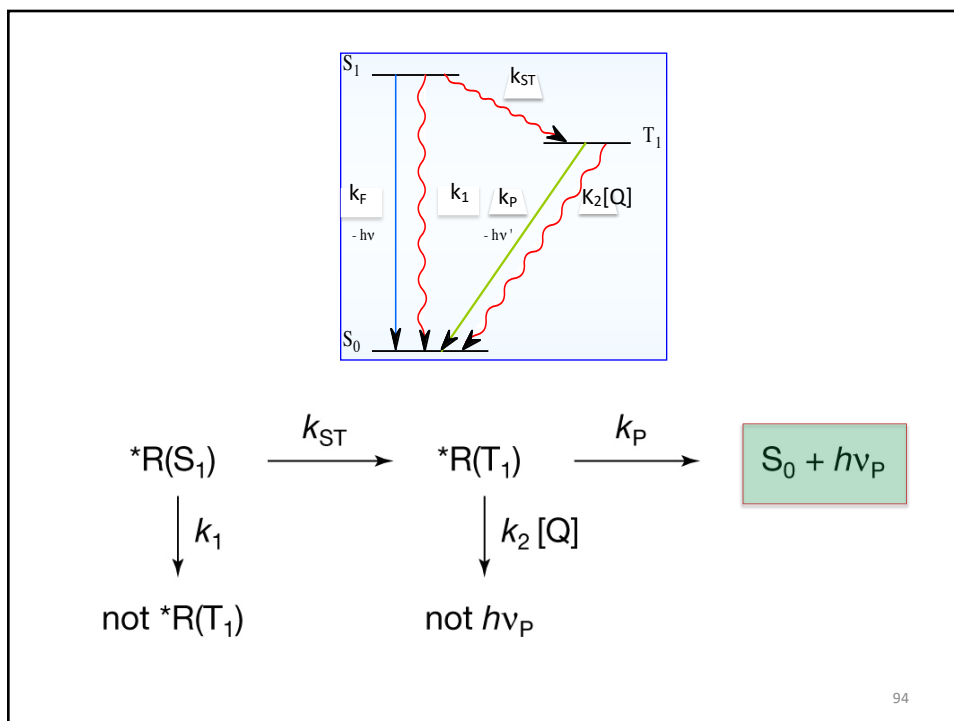
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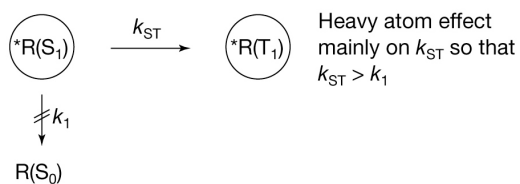
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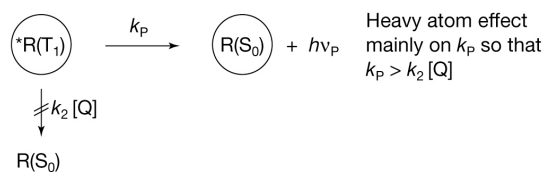
Strategy to record phosphorescence at room temperature through supramolecular approach

Stage 1



Make more triplets through the heavy atom effect

Stage 2

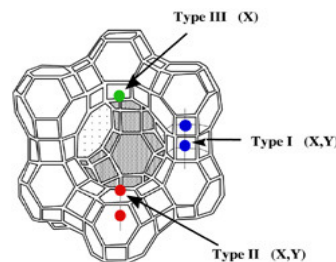
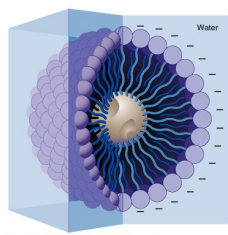
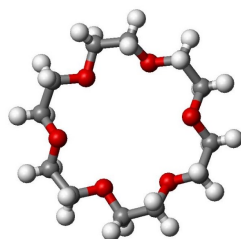


Make triplets emit faster in competition with quenching processes

95

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Crown ethers, micelles and zeolites contain cations

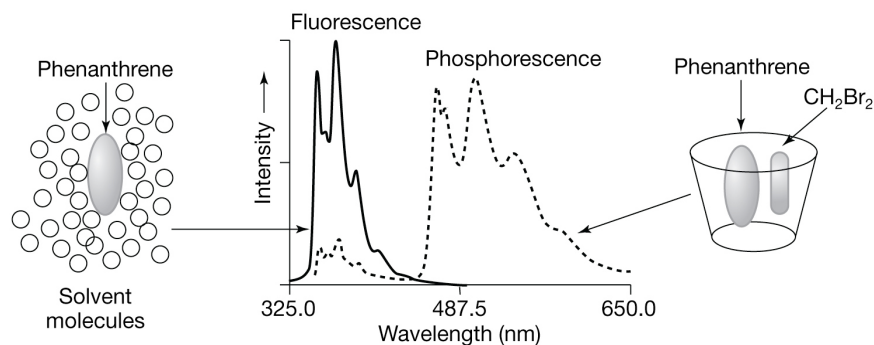


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Cyclodextrins as hosts

Phenanthrene@Cyclodextrin: effect of CH_2Br_2 as co-guest



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

Atom	Ionic Radius of the Cation (Å)	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

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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



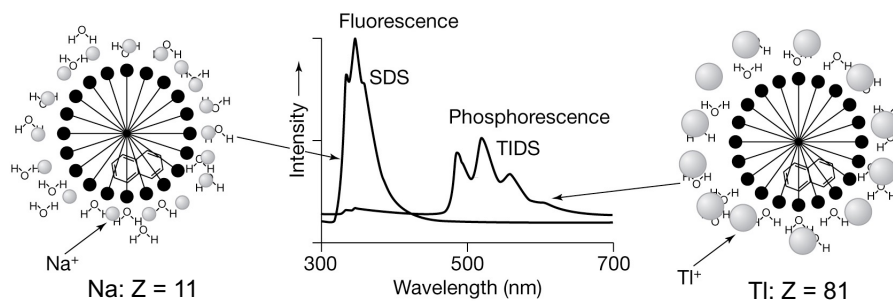
^a All rate constants in s^{-1} . ^b $k_f = \phi_f \tau_f^{-1}$; $k_{nr} = (1 - \phi_f) \tau_f^{-1}$; $k_p = \phi_p (1 - \phi_f)^{-1} \tau_p^{-1}$; $k_{dt} = \tau_p^{-1} - k_p$. ^c See note 4. ^d With $\phi_f + \phi_{isc} = 1.0$ assumed. ^e Estimated from 77 K UV absorption spectra.

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Micelles as hosts

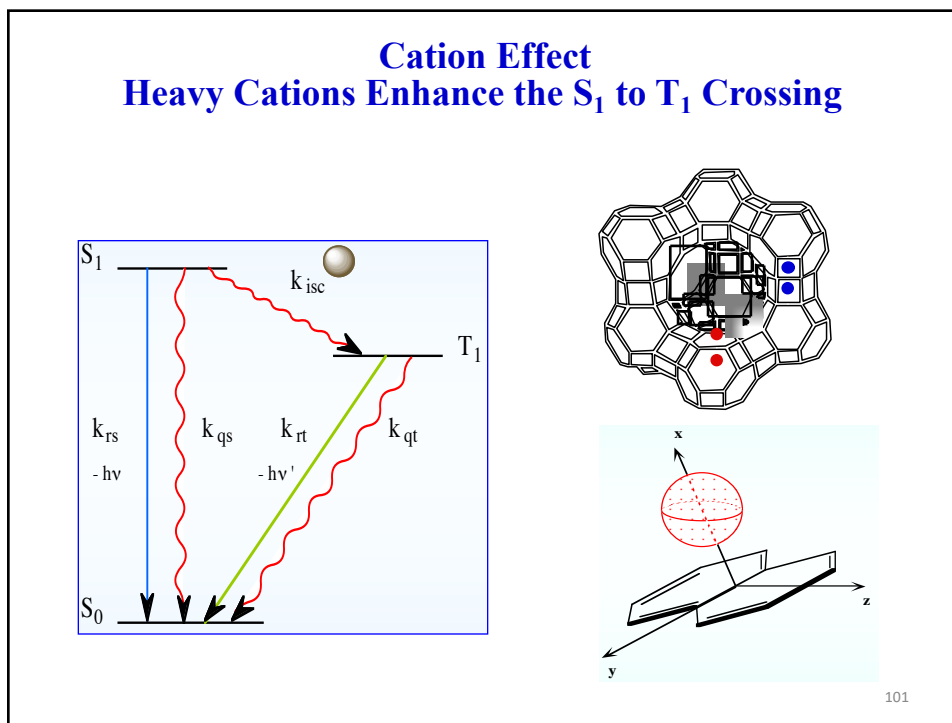
Naphthalene@SDS micelle: effect of heavy atom counterions



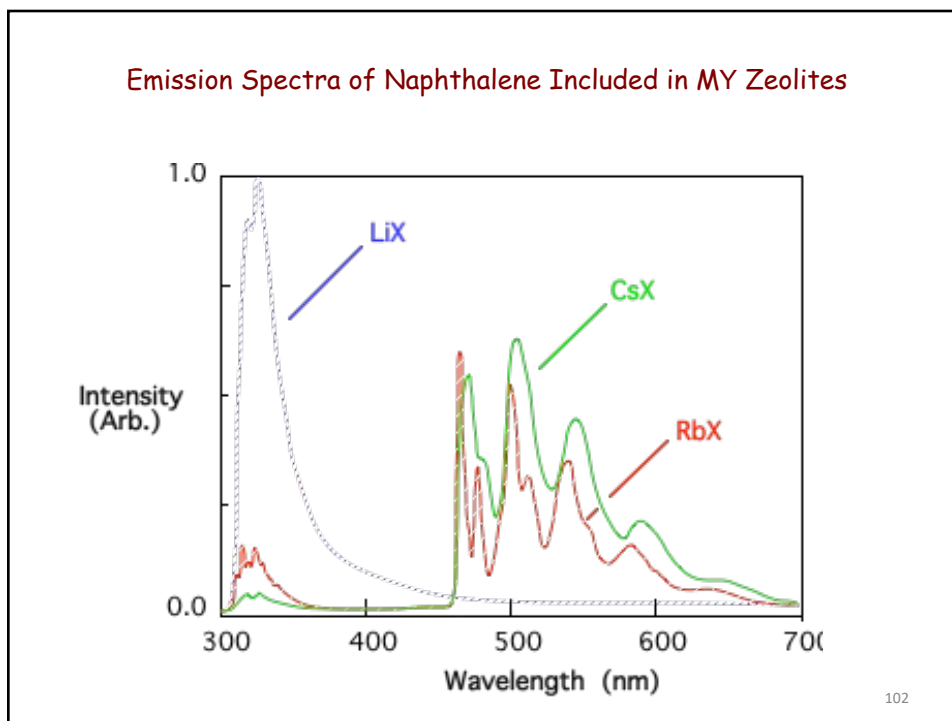
Heavy atom produces more triplets and the triplets produced phosphoresce at a faster rate

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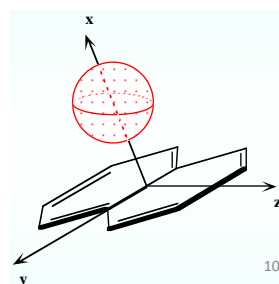
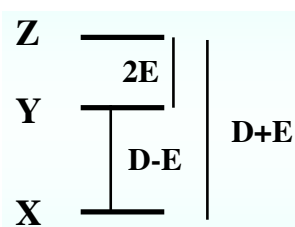
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Heavy Atom Effect is Specific: ODMR Studies

Optical Detection of Magnetic Resonance (ODMR) -

Triplet Sub-Level Specific Kinetics at 1.2 ° K

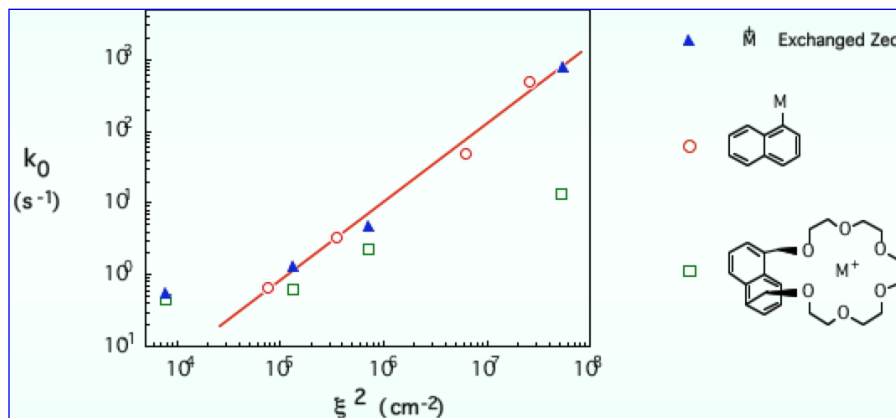
- Total decay constants from each sub-level
- Relative radiative rates from each sub-level
- Relative intersystem crossing rates to each sub-level
- Slow Passage ODMR Transitions



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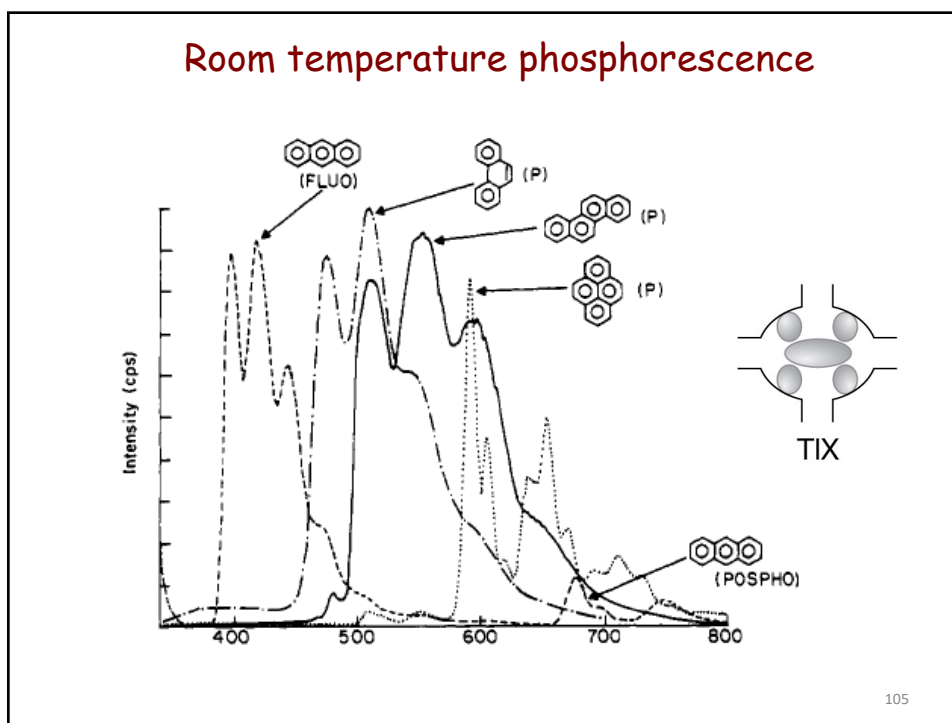
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External Heavy Atom Effect on Triplet Decay Rates of Naphthalene

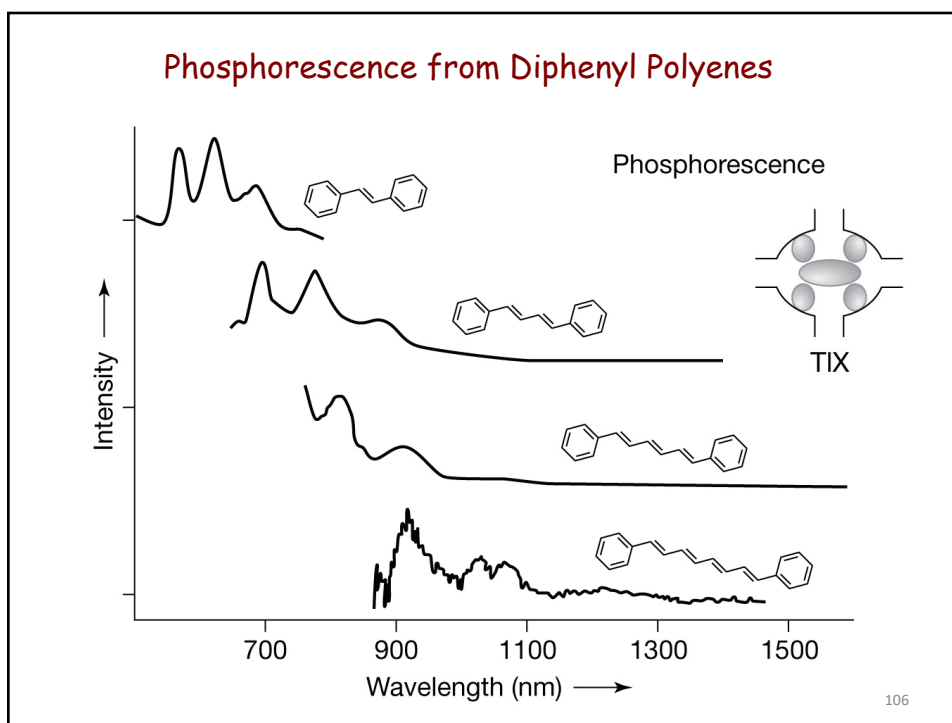


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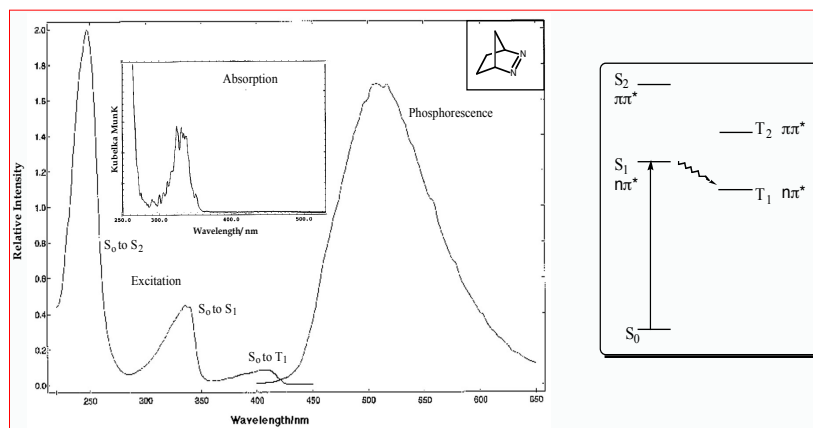


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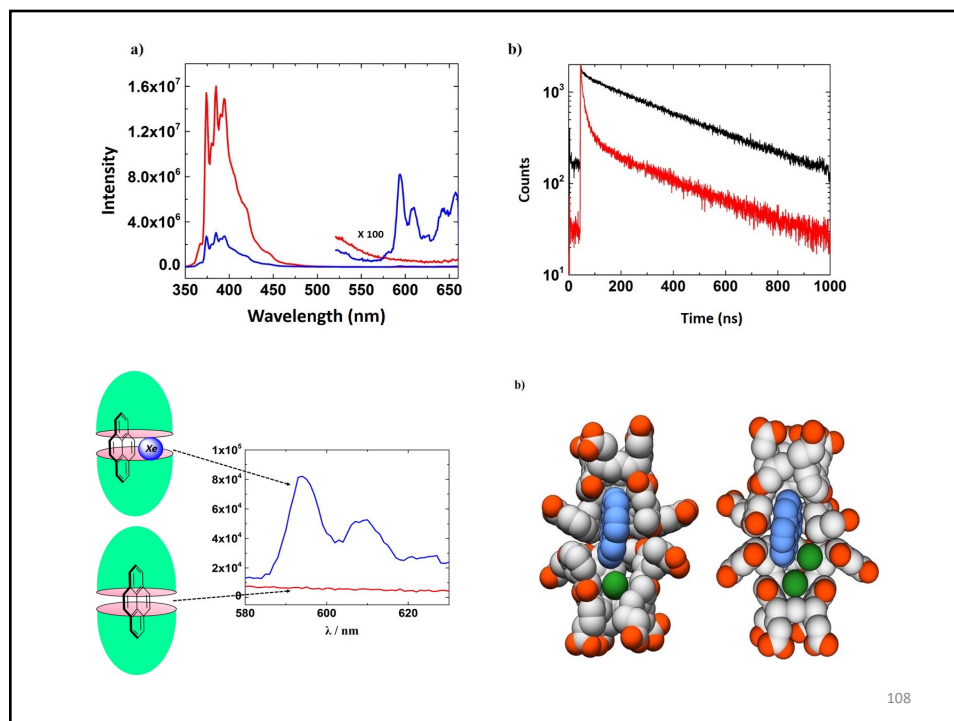
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Phosphorescence from Azo Compounds in TIY at 77 K $n\pi^*$ - $n\pi^*$ crossing



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