Radiationless Transitions
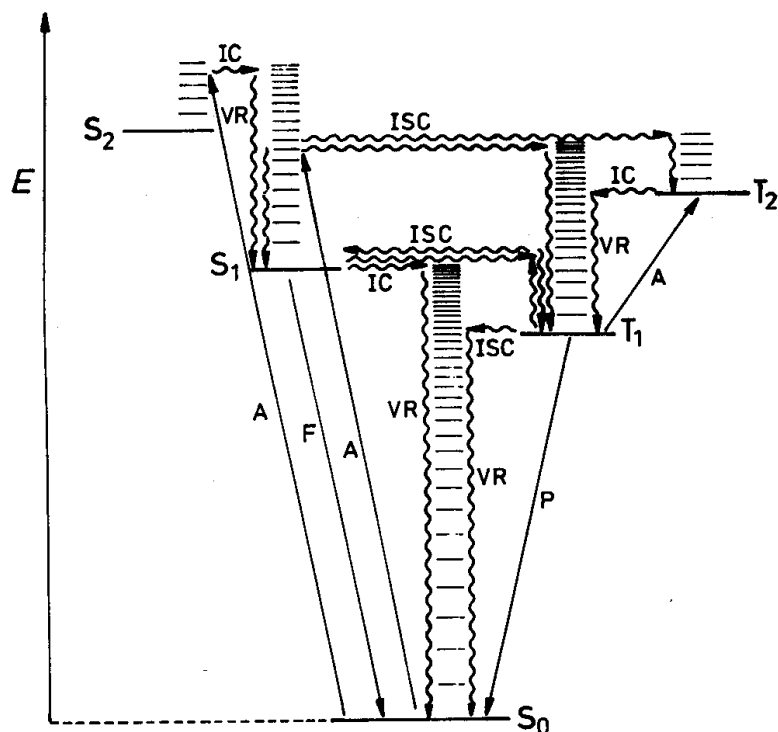
- Spin allowed
- Spin forbidden

Chapters 3 & 5

Principles of Molecular Photochemistry: An Introduction

NJT, VR and JCS

Transition Between States

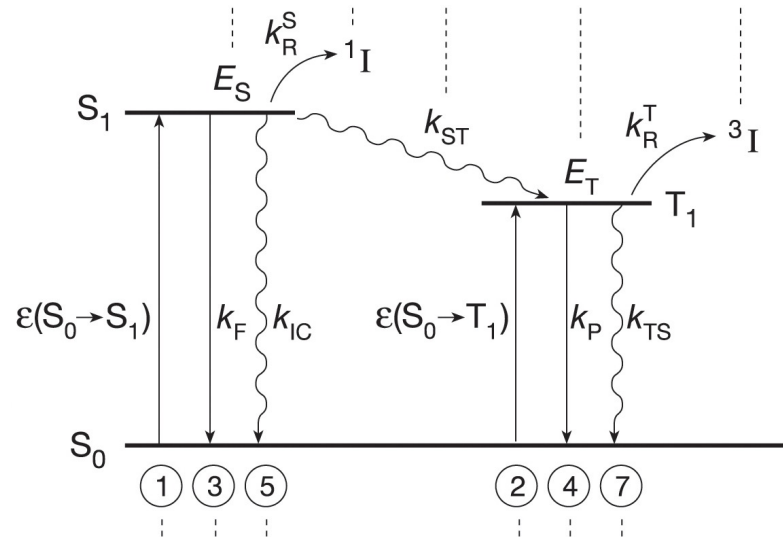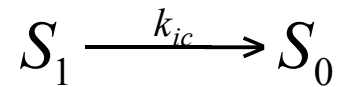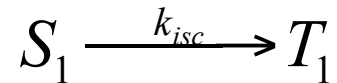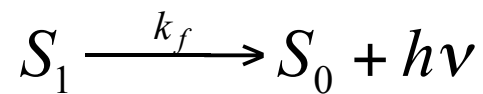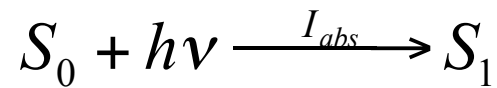$S_0 + h\nu \longrightarrow S_1$ spin allowed absorption

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

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

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

Why radiationless transition matters?
Competes with fluorescence and phosphorescence

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

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

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

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

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

Radiationless Transitions

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

S_1

k_{isc}
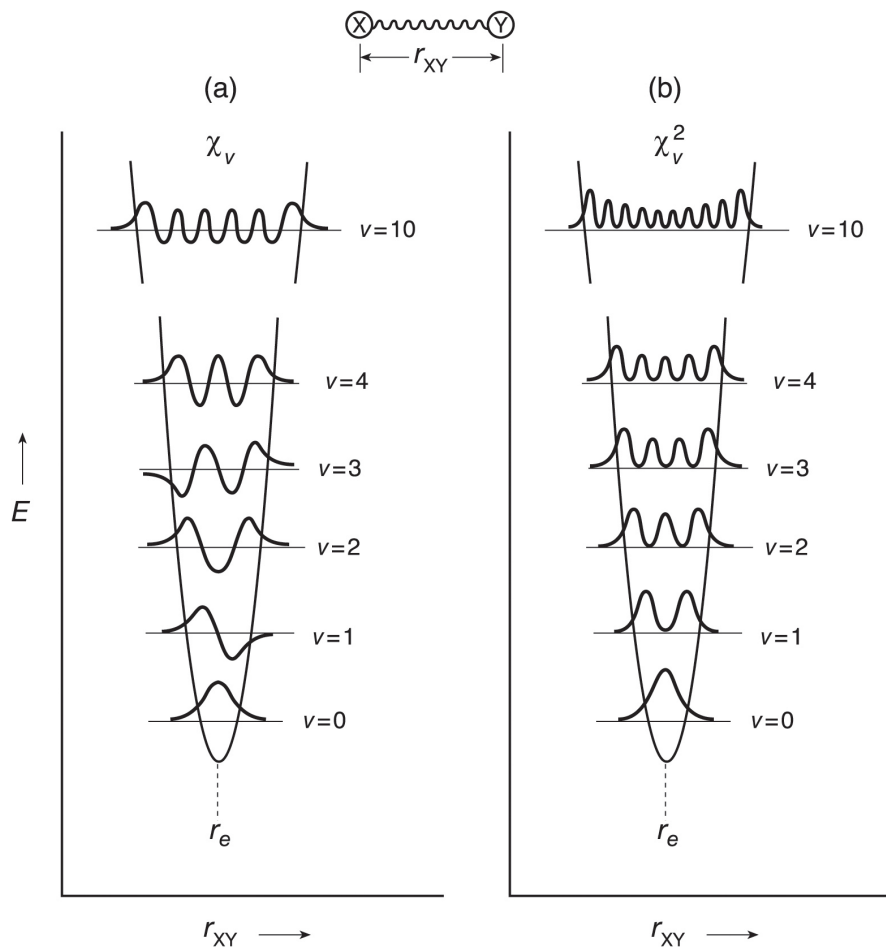
T_1 $(\Phi_2 \cdot \chi_1 \cdot S_1)*3$

k_{rs} k_{qs} k_{rt} k_{qt}

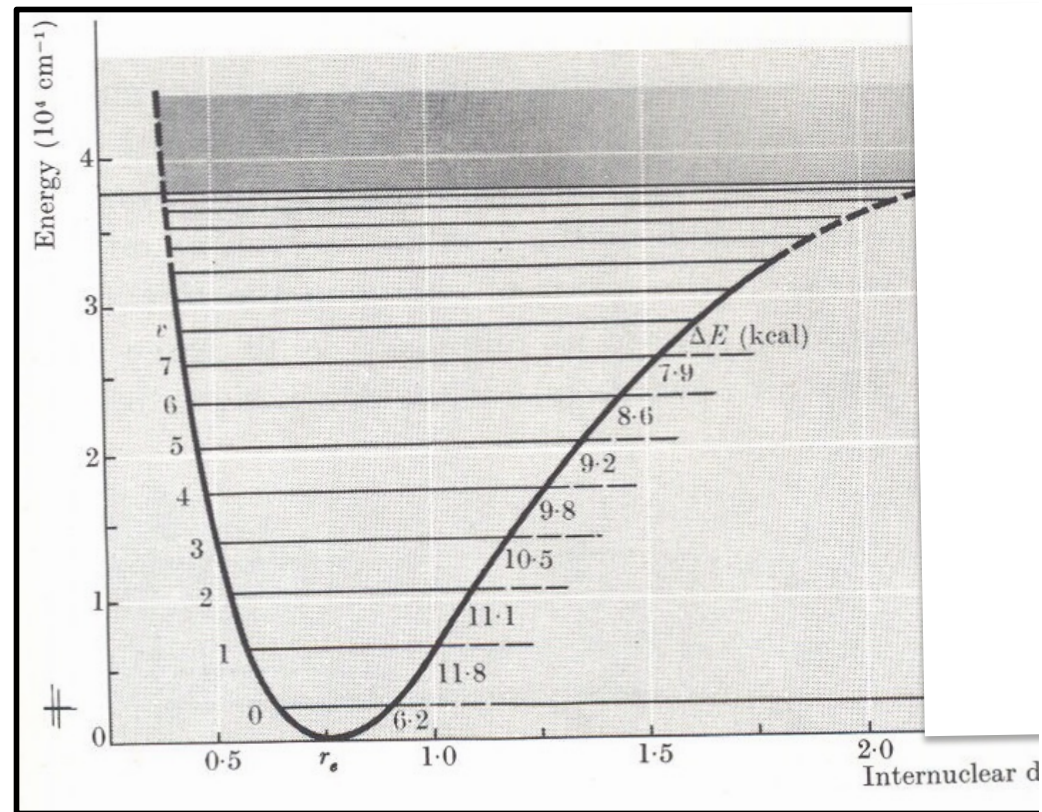$- h\nu$ $- h\nu'$
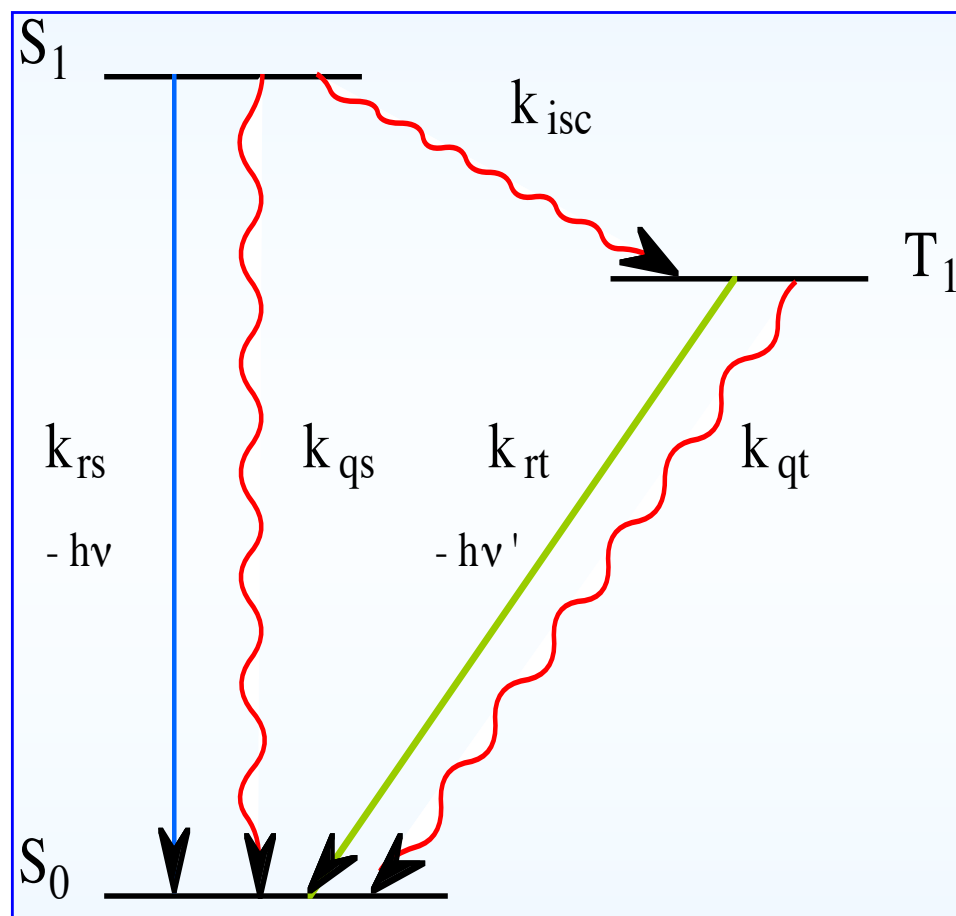
$\Phi_0 \cdot \chi_0 \cdot S_0$

S_0

- **Changes in electronic, vibrational and spin configurations without the help of a photon**

- **Energy redistribution--electronic to vibrational**

Visualization of vibrational levels within an electronic energy surface
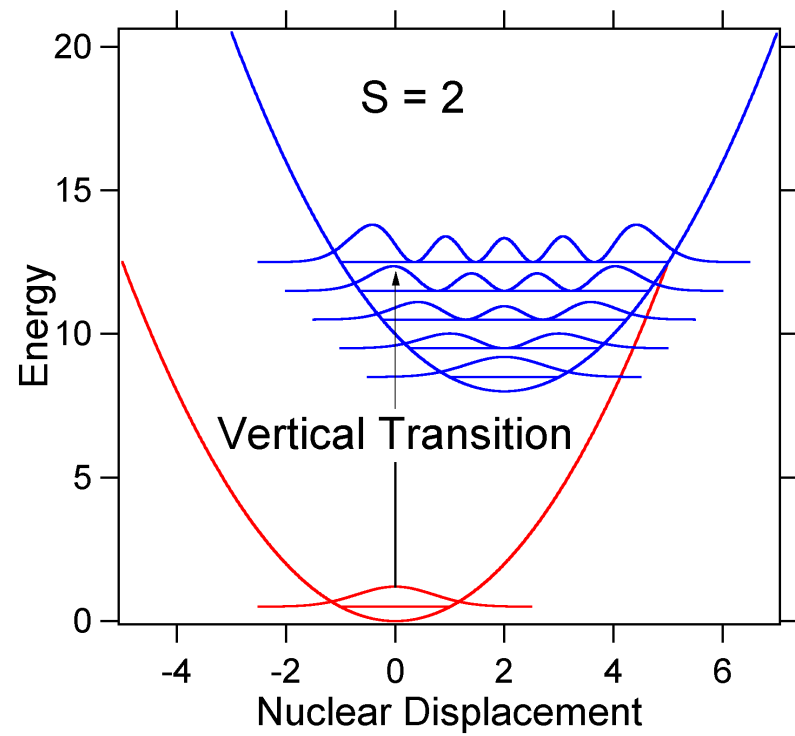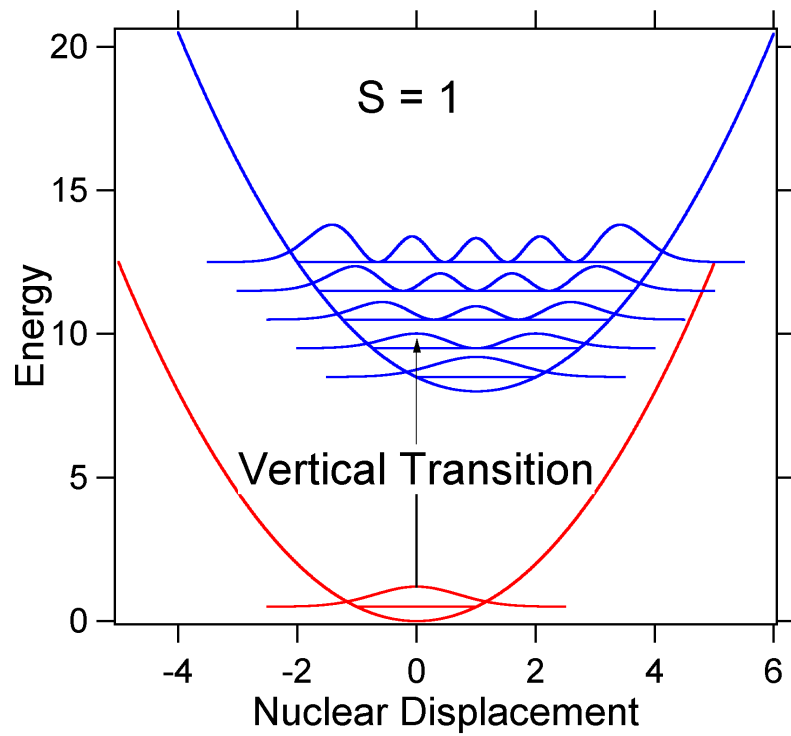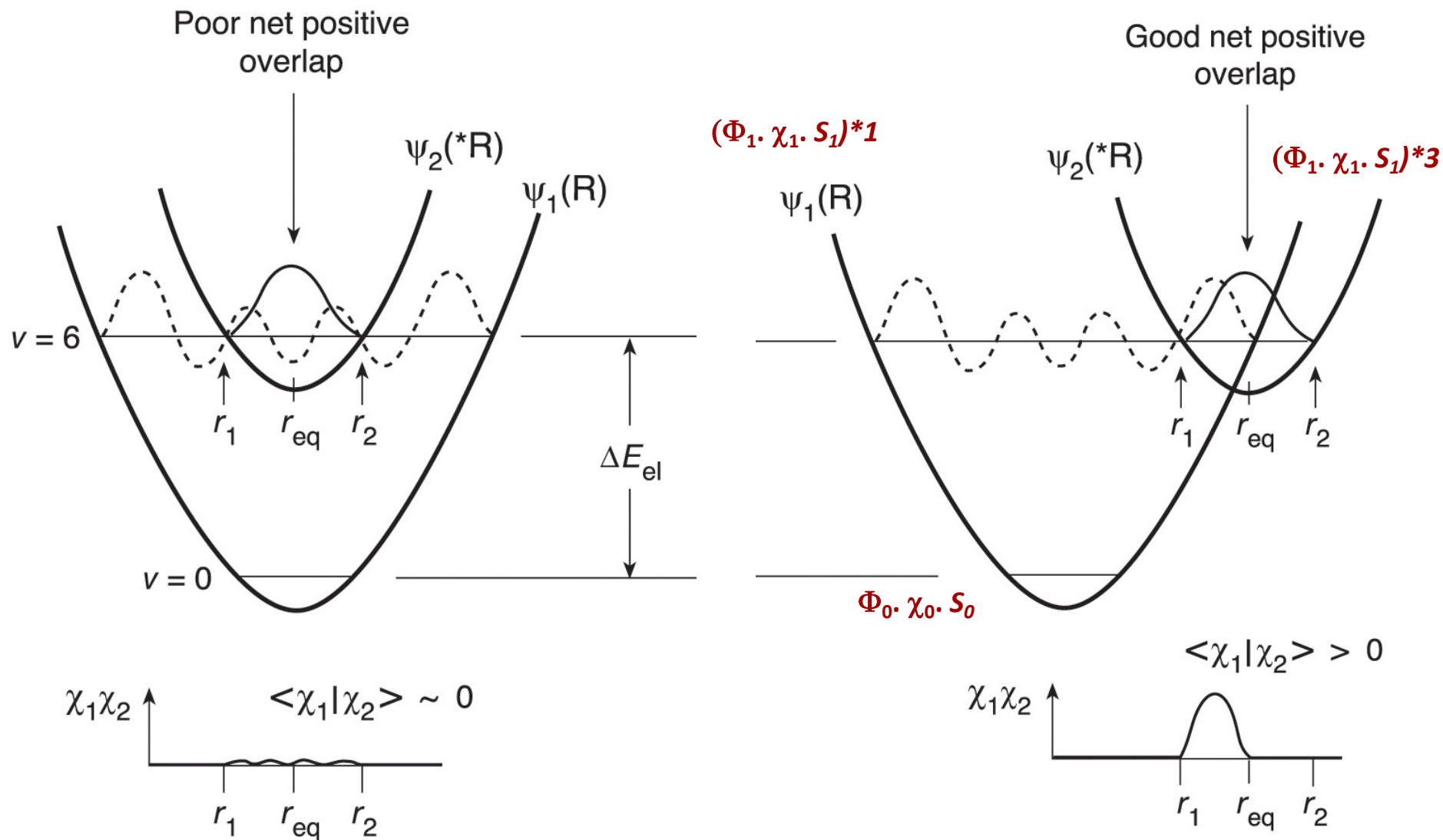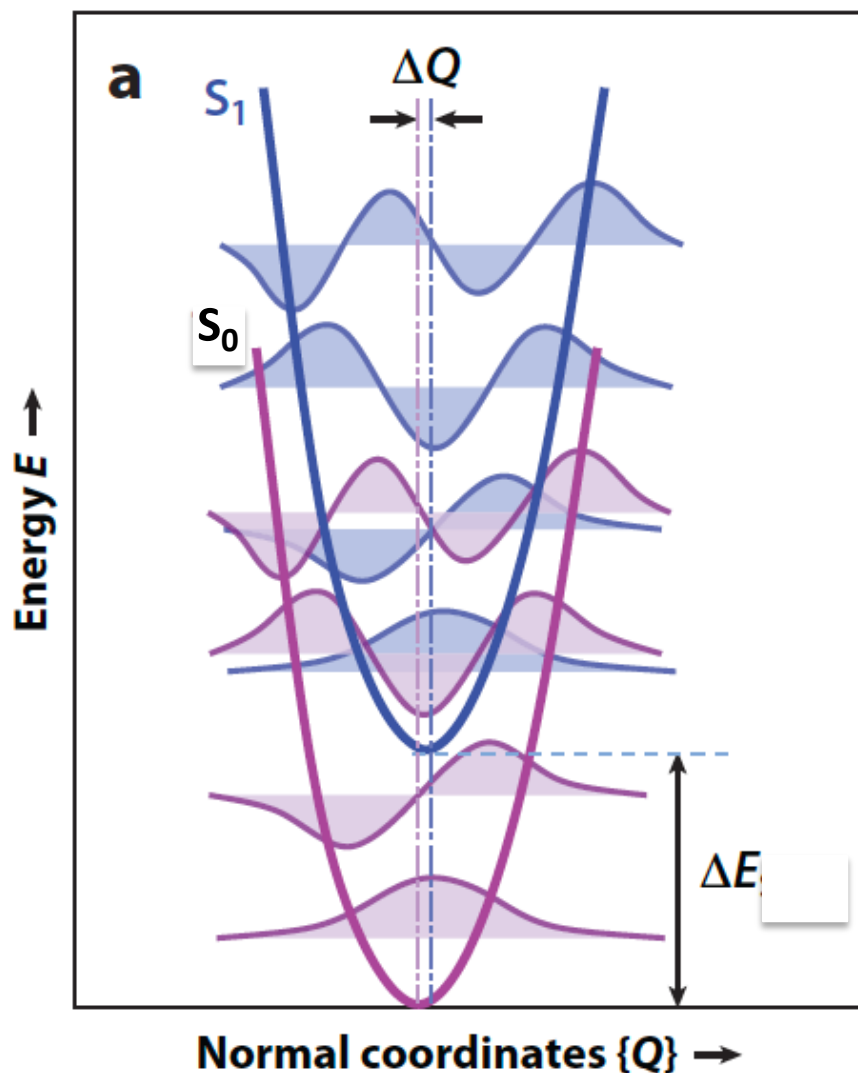

Harmonic

Anharmonic

Relative position of energy surfaces

Matching *vs.* Crossing Surfaces

Poor net positive overlap

$\psi_2(^*R)$

$\psi_1(R)$

$v = 6$

r_1 r_{eq} r_2

ΔE_{el}

$v = 0$

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

$\Phi_0 . \chi_0 . S_0$

$\chi_1\chi_2$

$\langle\chi_1|\chi_2\rangle \sim 0$

r_1 r_{eq} r_2

Good net positive overlap

$\psi_2(^*R)$

$\psi_1(R)$

$(\Phi_1 . \chi_1 . S_1)*3$

r_1 r_{eq} r_2

$\langle\chi_1|\chi_2\rangle > 0$

$\chi_1\chi_2$

r_1 r_{eq} r_2

For the same energy gap the rates are different for the two types of surfaces

Matching surfaces (e.g., polyaromatics)

Equilibrium geometries similar

The S_1 and S_0 potentials exhibit small relative displacements. Significant overlaps between their vibrational wave functions are obtained only for small energy separations, ES_1-S_0. The IC probability decreases exponentially with increasing energy gap. This exponential dependence of the transition probability on E is usually dubbed the **Energy Gap Law**.

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

(a)

(b)

Nested or matching surfaces:
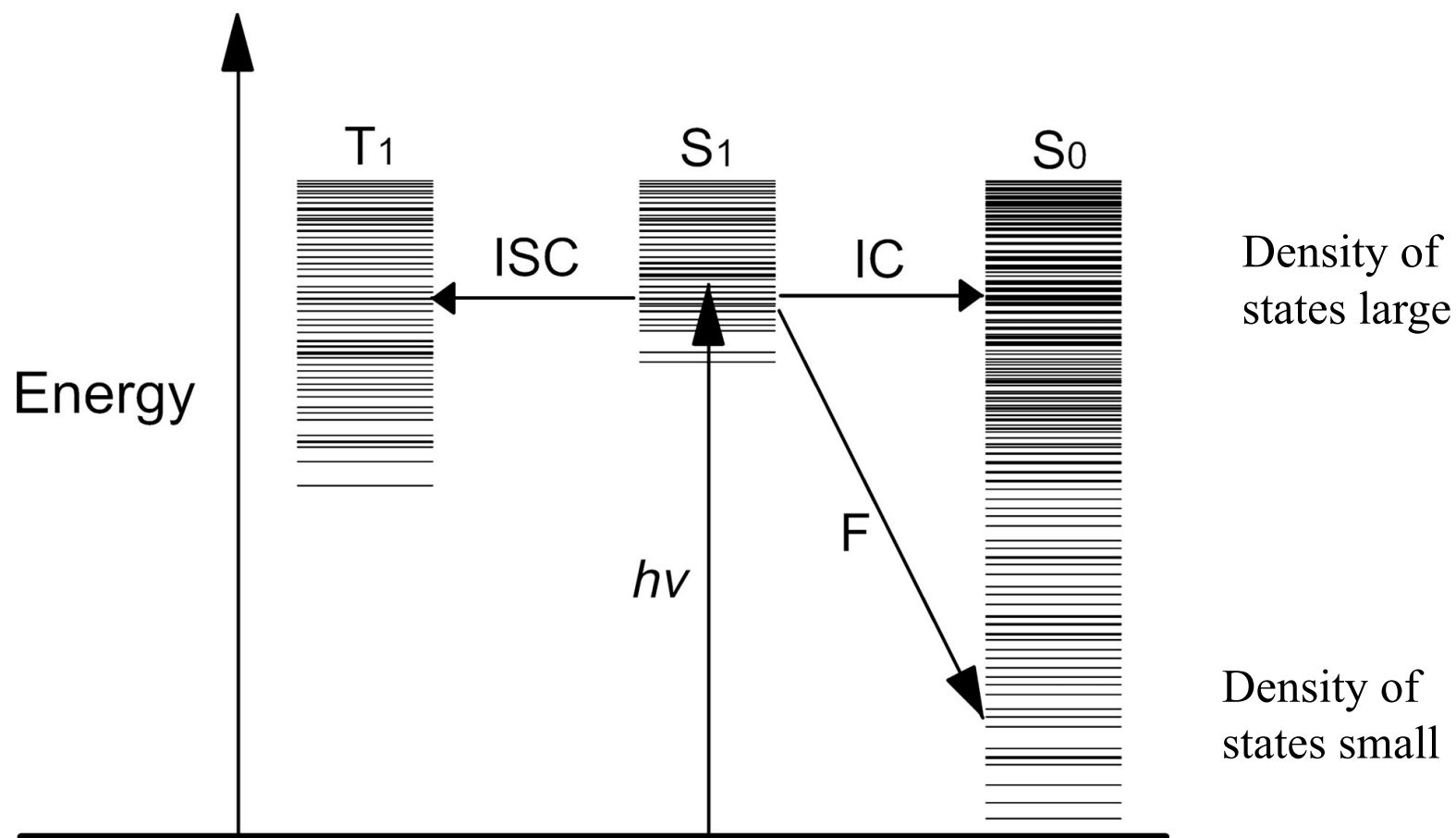Extent of vibrational overlap depends on the energy gap
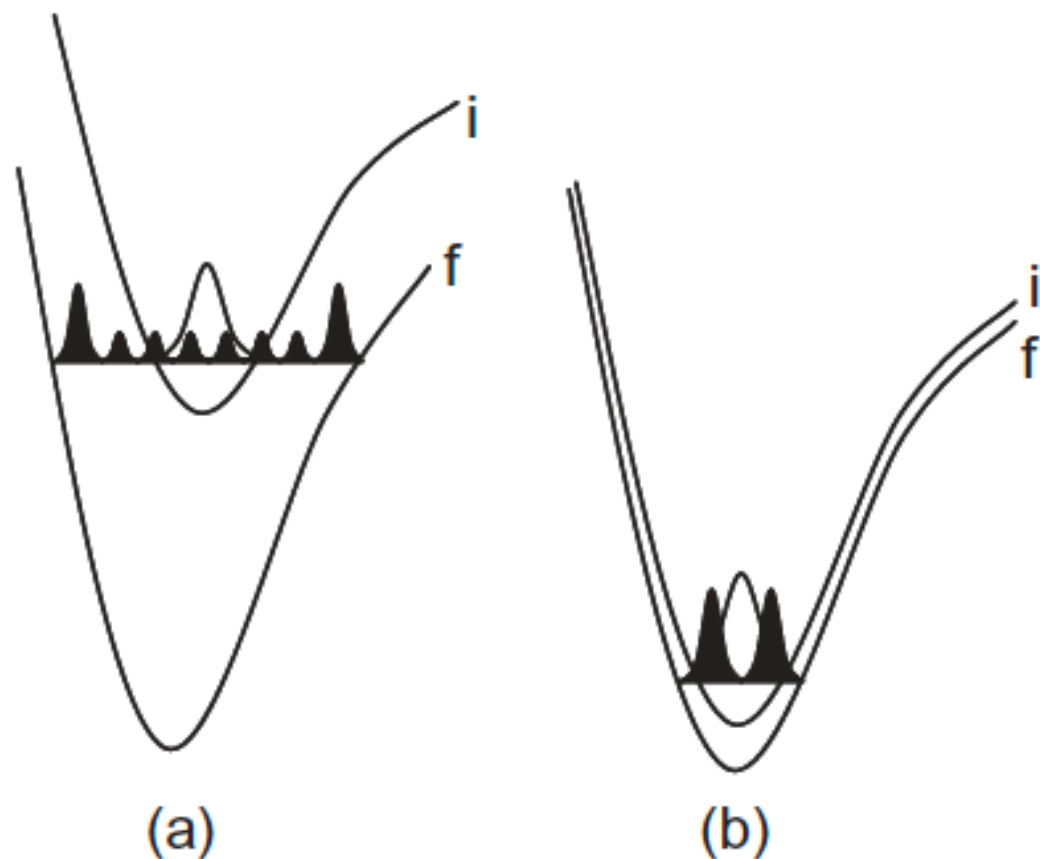
$$f \sim \exp^{-\Delta E}$$
$$k_{IC} \sim 10^{13} f_\nu$$
$$k_{IC} \sim 10^{13} \exp^{-\alpha\Delta}$$

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.

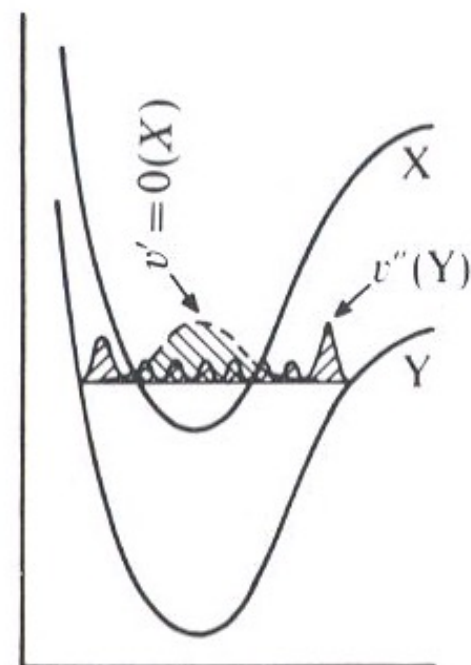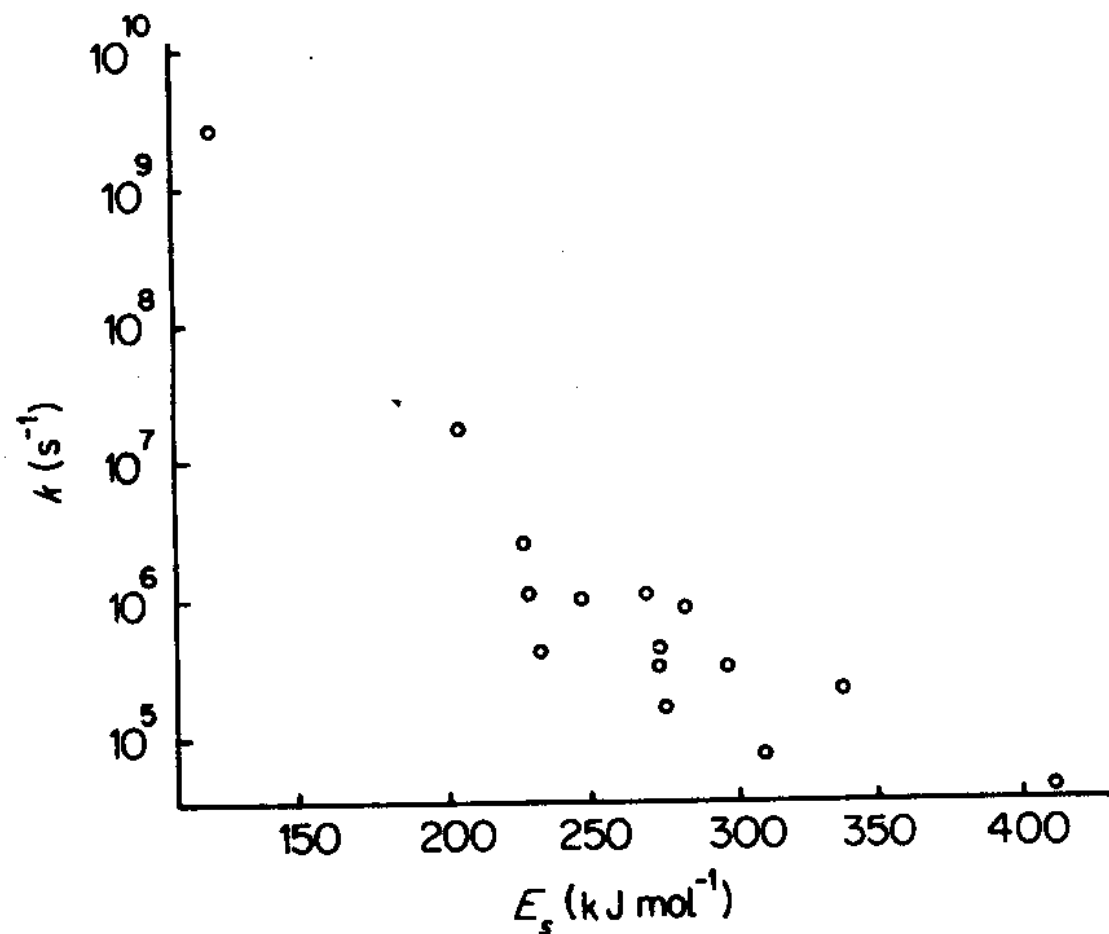# Dependence of rate of k_{IC} (S_1 to S_0) on energy gap

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)

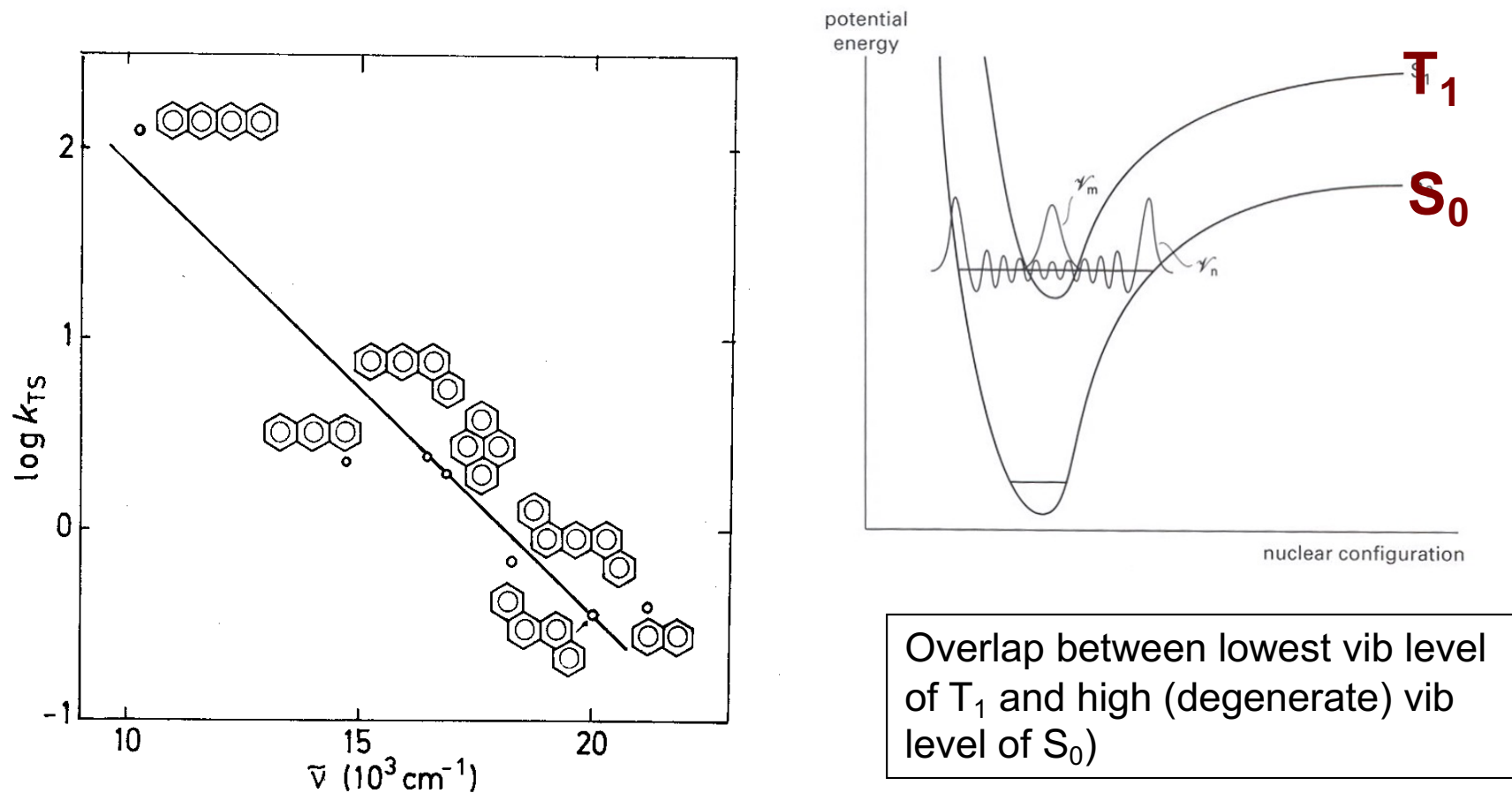# Dependence of rate of k_{ISC} T_1 to S_0 on energy gap

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

Overlap between lowest vib level of T_1 and high (degenerate) vib level of S_0)

Conversion of electronic to vibrational energy


Non-radiative deactivation processes
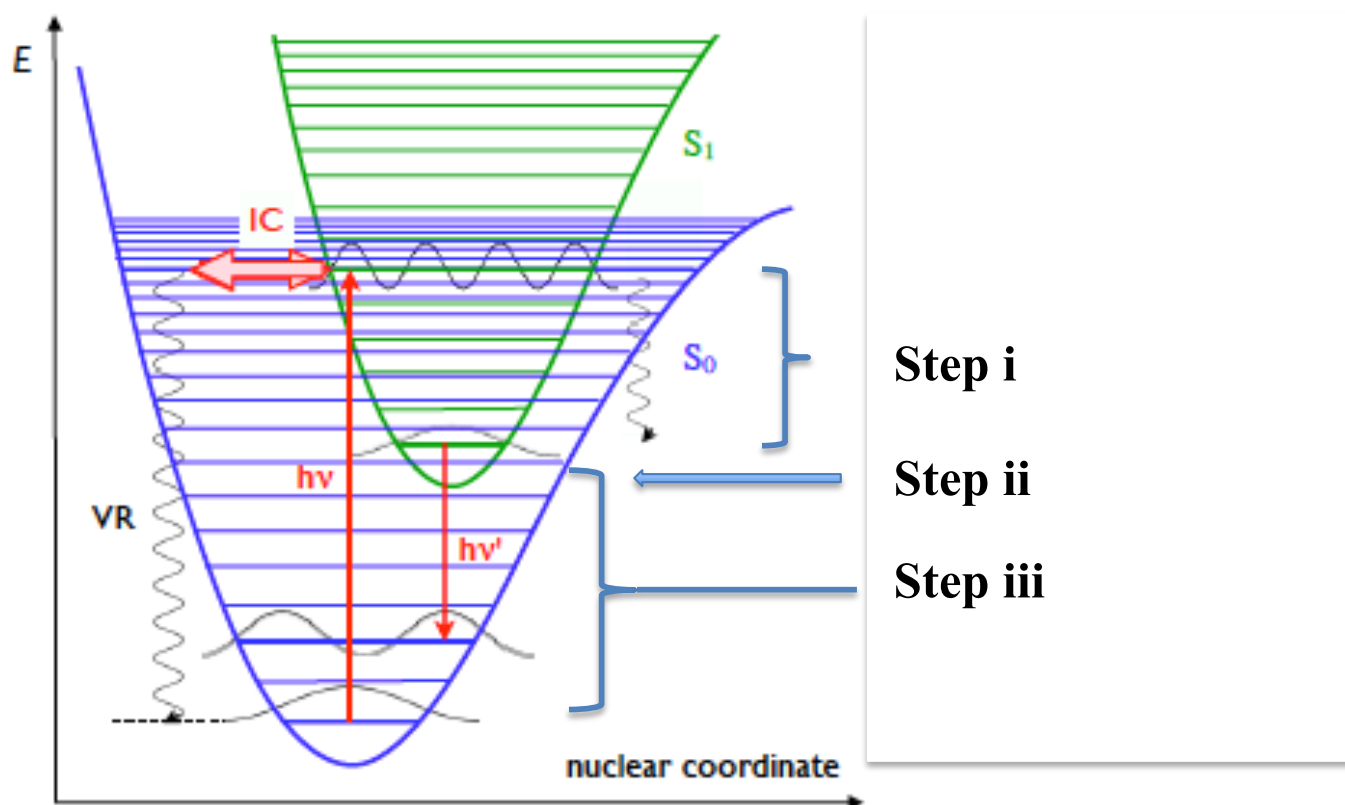
Three step process:
(i) upper vibrational to lower vibrational level in excited state
(ii) lower vibrational level to upper vibrational of the lower state
(iii) upper vibrational of the lower state to lowest vibrational level

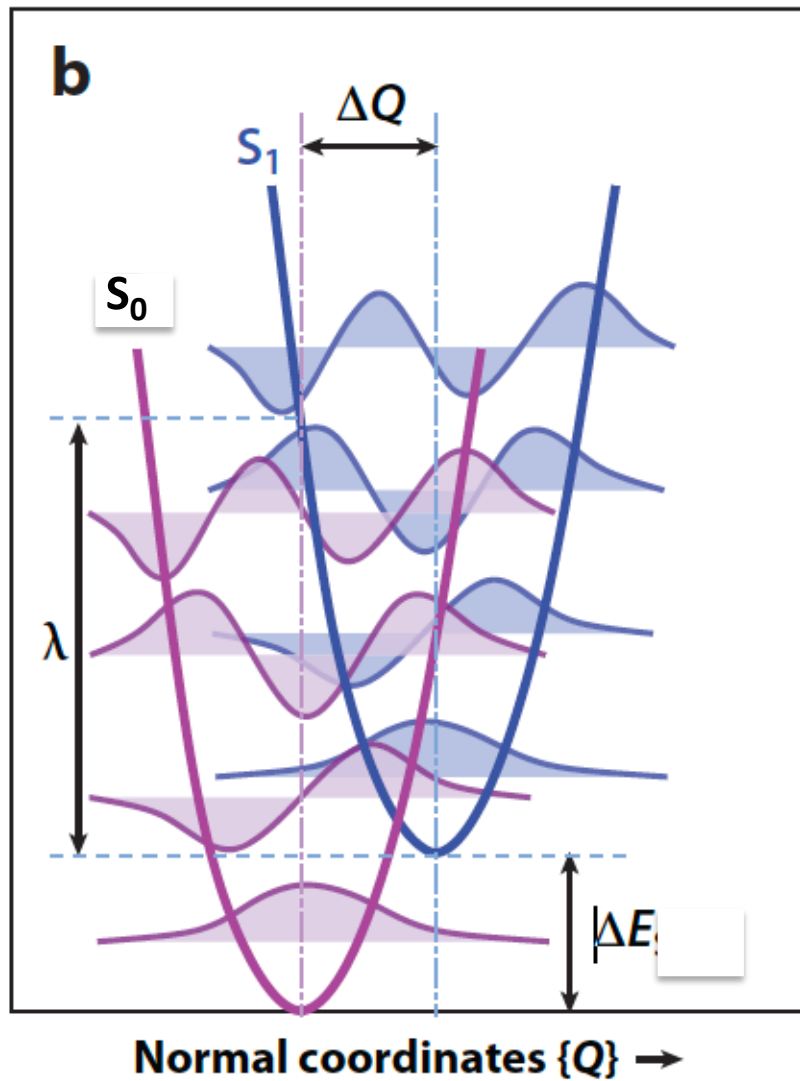# Visualization of Electronic Energy to Vibrational Energy Transfer

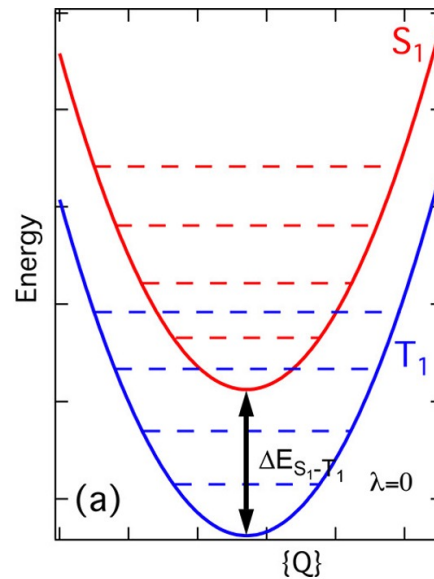**Intra**molecular vibrational relaxation (**IVR**) occurs within 10 to 0.1 ps

$\nu_{CO} \longrightarrow \nu_{CH}$

$e \longrightarrow v$
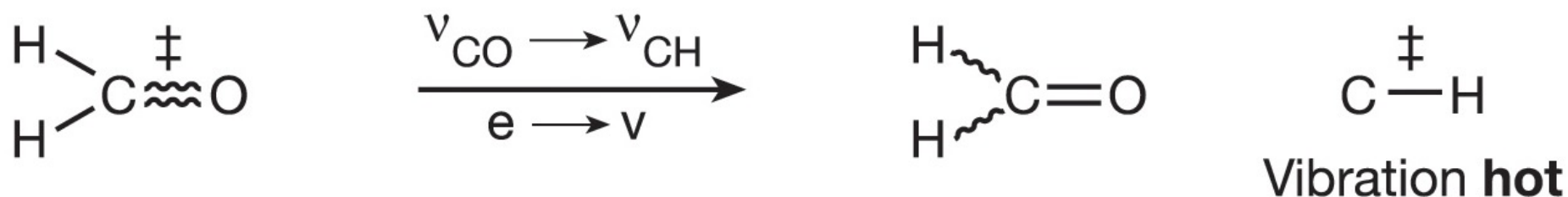
Vibration **hot**

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

$\nu_{CH} \longrightarrow$ Solvent
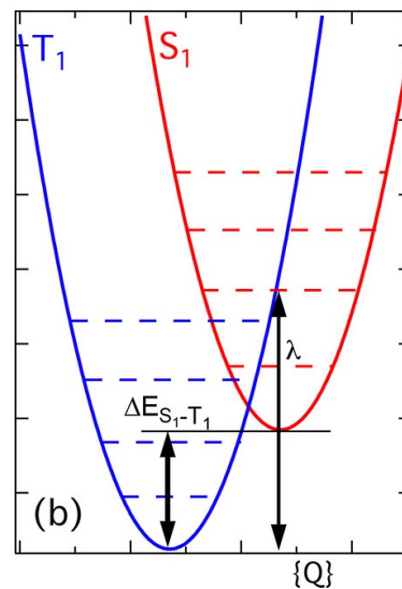
$v \longrightarrow t$

Solvent is **hot** (translations and vibrations)
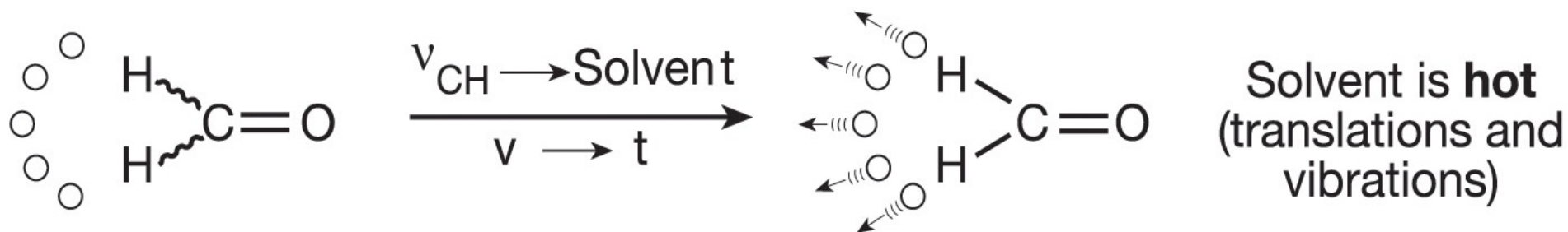
Crossing surfaces

Equilibrium geometries dissimilar

Weak Coupling

Strong coupling

Matching *vs.* Crossing Surfaces

Poor net positive overlap

$\psi_2(^*R)$

$\psi_1(R)$

$v = 6$

$r_1 \quad r_{eq} \quad r_2$

ΔE_{el}

$v = 0$

$(\Phi_1 . \chi_1 . S_1)^*1$

$\Phi_0 . \chi_0 . S_0$

Good net positive overlap

$\psi_2(^*R)$

$(\Phi_1 . \chi_1 . S_1)^*3$

$\psi_1(R)$

$r_1 \quad r_{eq} \quad r_2$

$\chi_1\chi_2$

$\langle\chi_1|\chi_2\rangle \sim 0$

$r_1 \quad r_{eq} \quad r_2$

$\chi_1\chi_2$

$\langle\chi_1|\chi_2\rangle > 0$

$r_1 \quad r_{eq} \quad r_2$
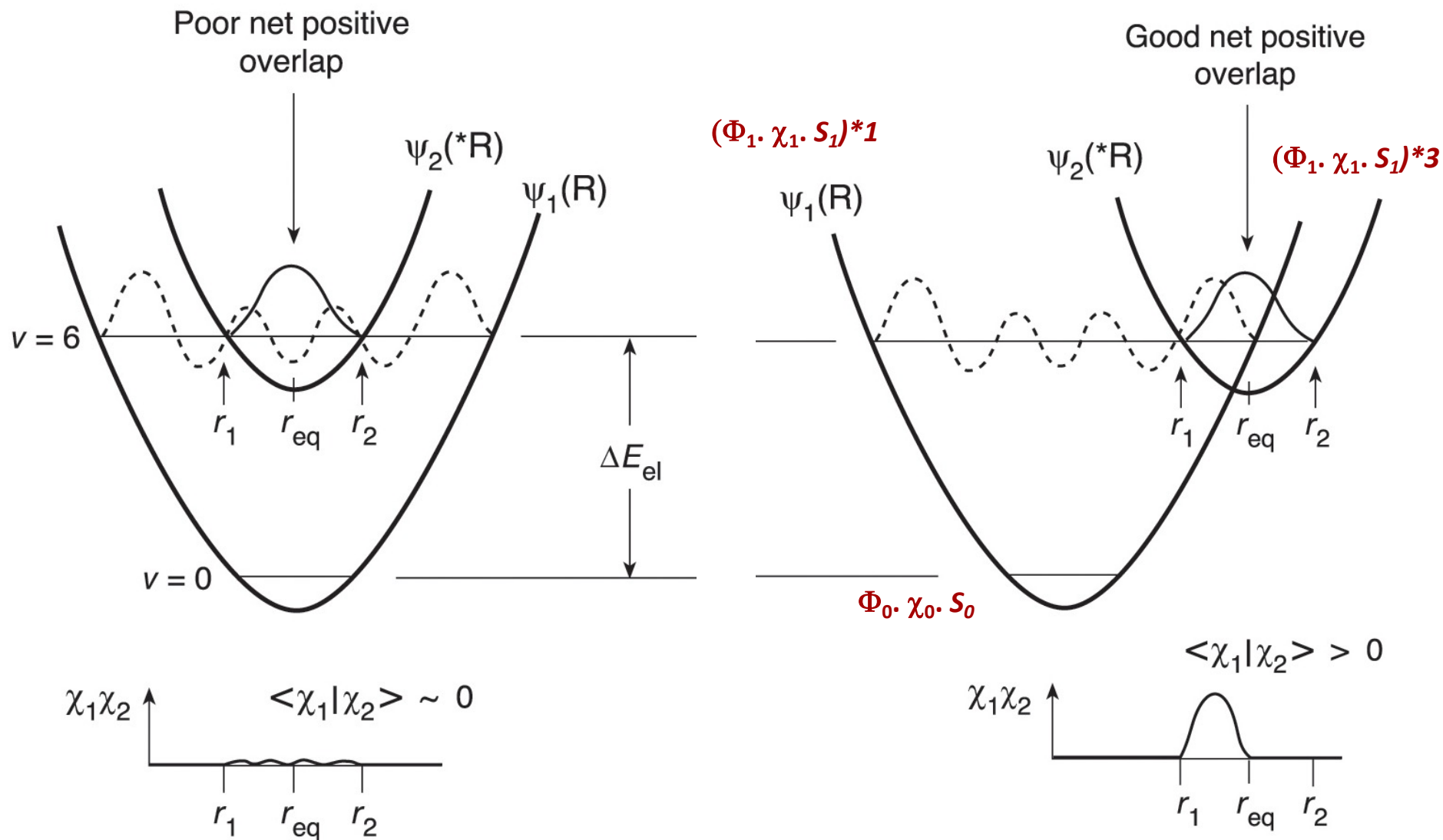
For the same energy gap the rates are different for the two types of surfaces

Basis of Kasha's Rule
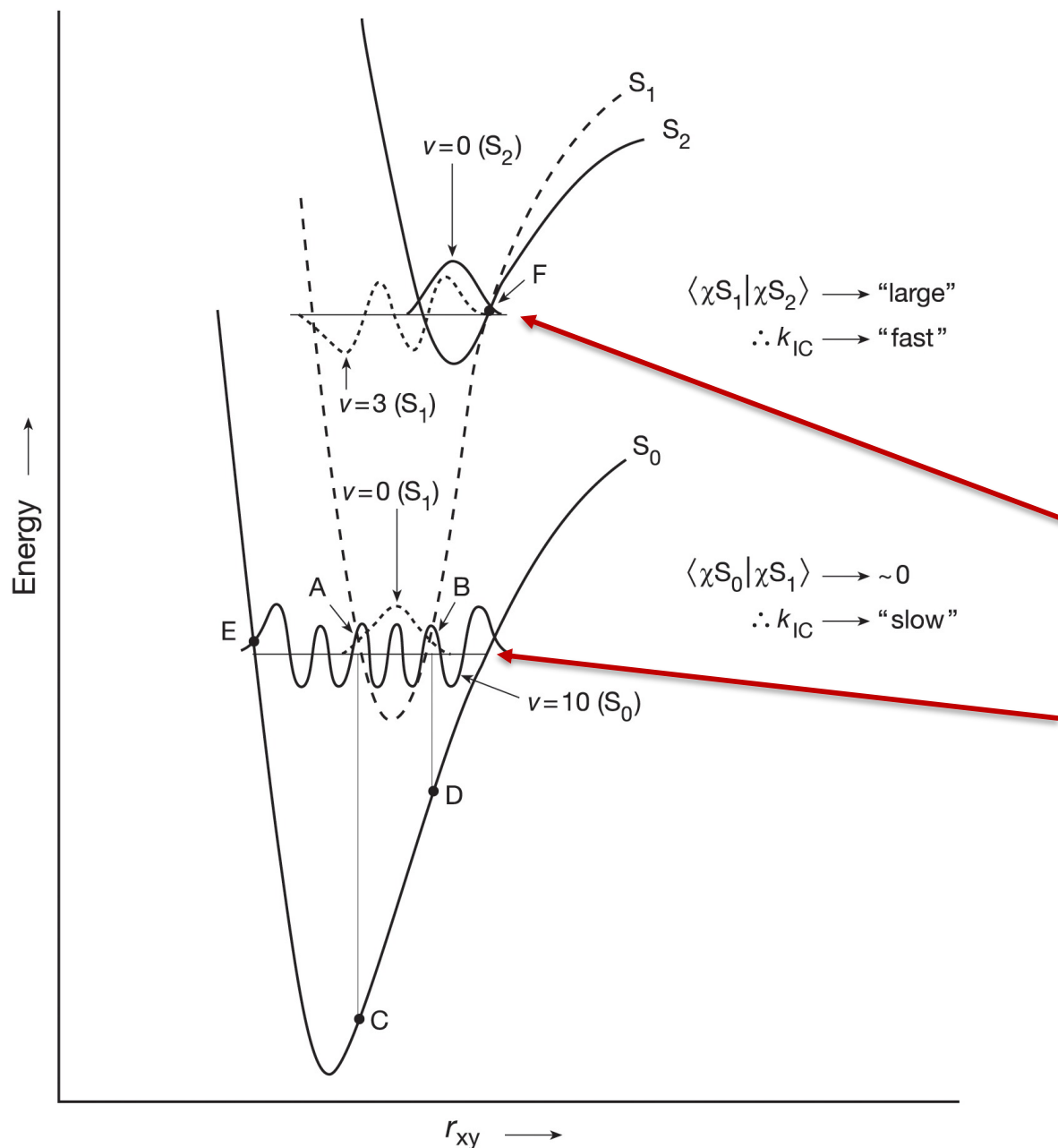
Kasha's Rule

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

In figure:

Energy (y-axis)

r_{xy} (x-axis)

S_1, S_2, S_0

$v=0\ (S_2)$

$v=3\ (S_1)$

$v=0\ (S_1)$

$v=10\ (S_0)$

$\langle \chi S_1 | \chi S_2 \rangle \longrightarrow$ "large"

$\therefore k_{IC} \longrightarrow$ "fast"

$\langle \chi S_0 | \chi S_1 \rangle \longrightarrow \sim 0$

$\therefore k_{IC} \longrightarrow$ "slow"

A, B, C, D, E, F

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).
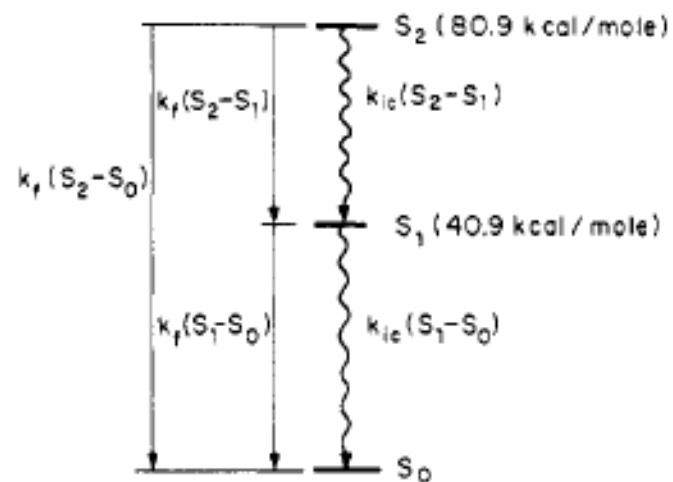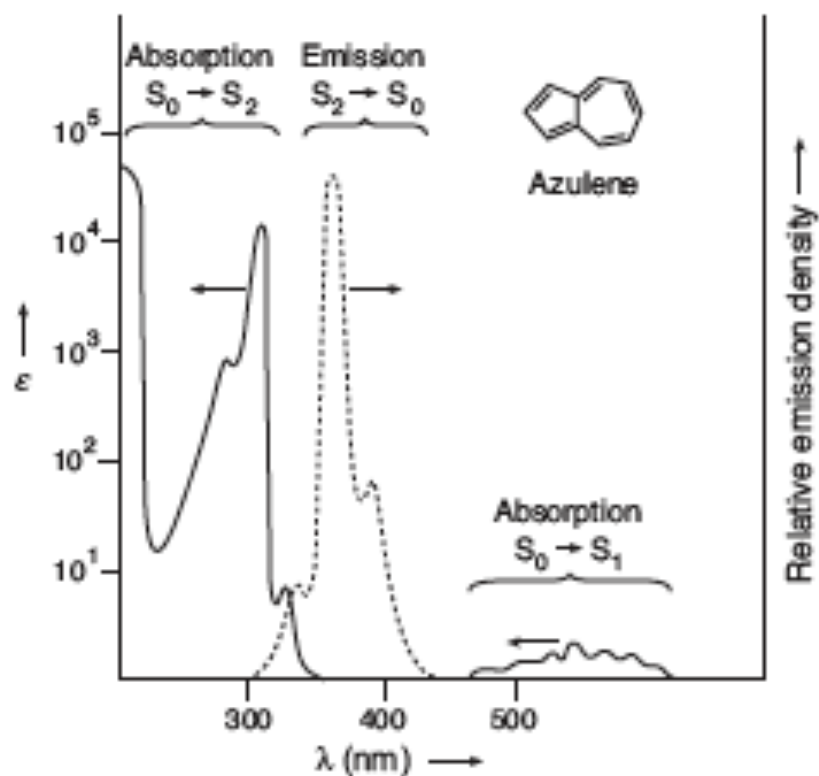
$k_f(S_2-S_0) = 1.4 \times 10^7$
$k_f(S_2-S_1) \approx 1.4 \times 10^4$
$k_f(S_1-S_0) = 1.3 \times 10^6$
$k_{ic}(S_2-S_1) = 7 \times 10^8$
$k_{ic}(S_1-S_0) = 1.2 \times 10^{11}$

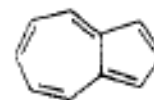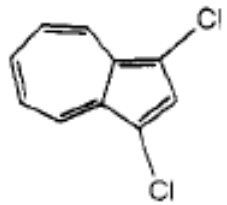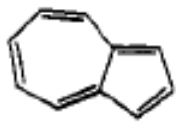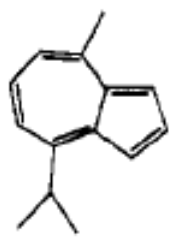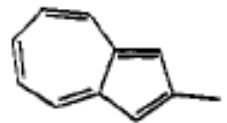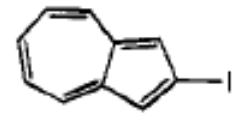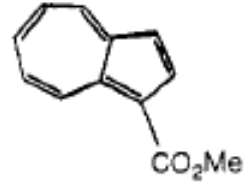**TABLE I. Fluorescence Quantum Yields and the Energies of the First Two Excited Singlet States of Substituted Azulenes**[a]

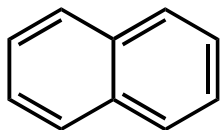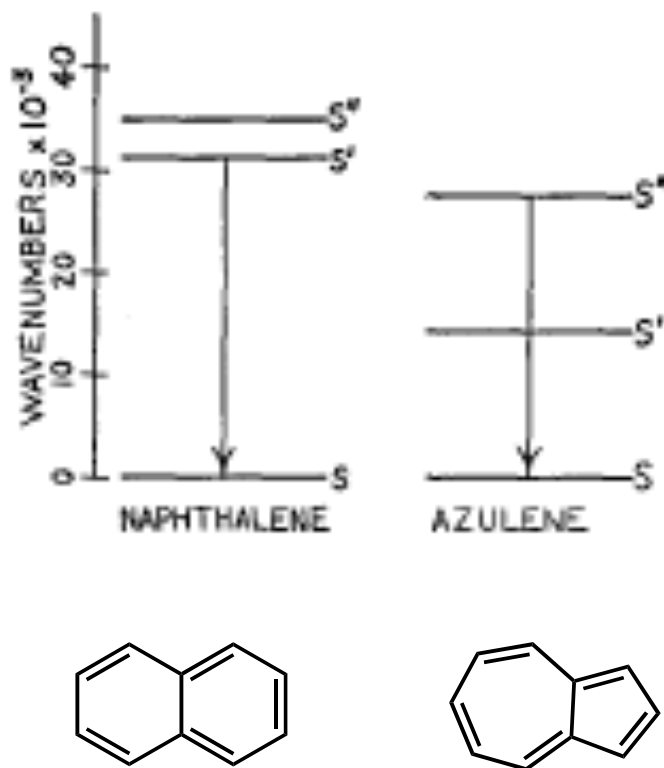|	Φ_{fl}	E_{S_1}, kcal/mol	E_{S_2}, kcal/mol	ΔE, kcal/mol
	0.058	36.3	77.0	40.9
	0.031	40.9	80.9	40.0
	0.014	39.5	77.8	38.3
	0.0081	42.6	79.5	36.9
	0.0034	42.9	77.5	34.6
	$\sim 10^{-4}$	44.3	77.2	32.9

S₂ to S₁ rate vs Energy Gap
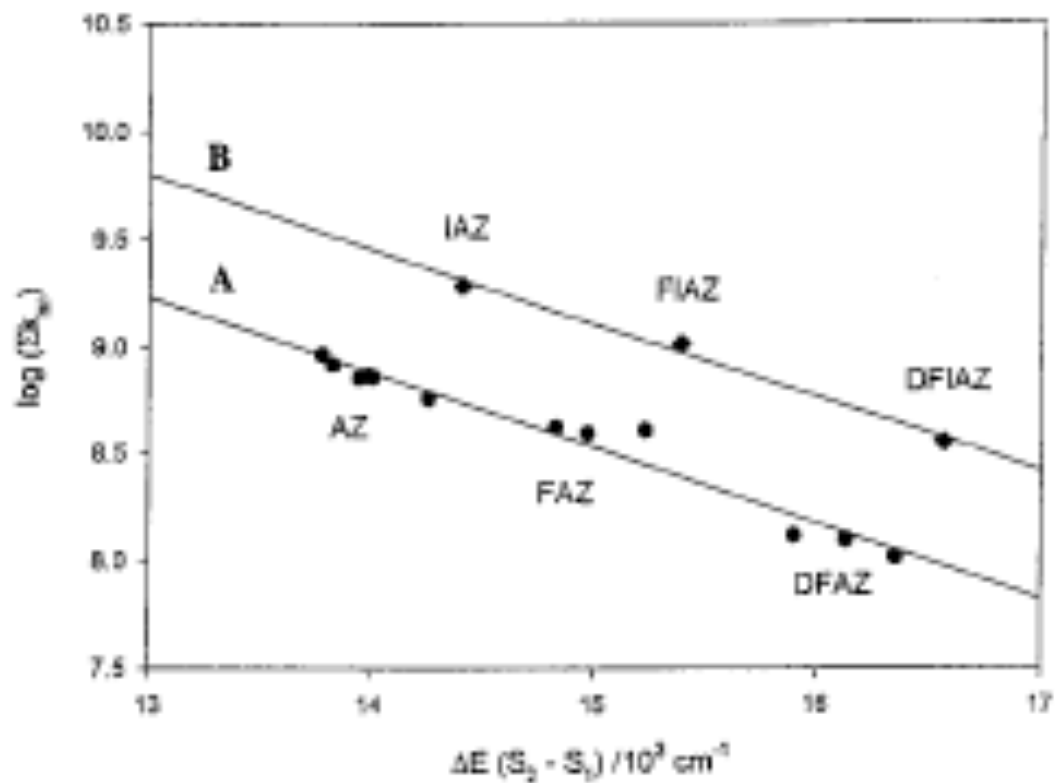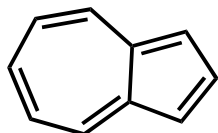
Figure 3. Log–linear energy gap law plots (see text) for azulene (AZ), 1-fluoroazulene (FAZ), and 1,3-difluoroazulene (DFAZ) in several solvents (line A), and for 6-isopropylazulene (IAZ), 1-fluoro-6-isopropylazulene (FIAZ), and 1,3-difluoro-6-isopropylazulene in n-hexane (line B). The data for AZ in several solvents are taken from ref 11.

Role of vibrational level (ν_n) on radiationless process
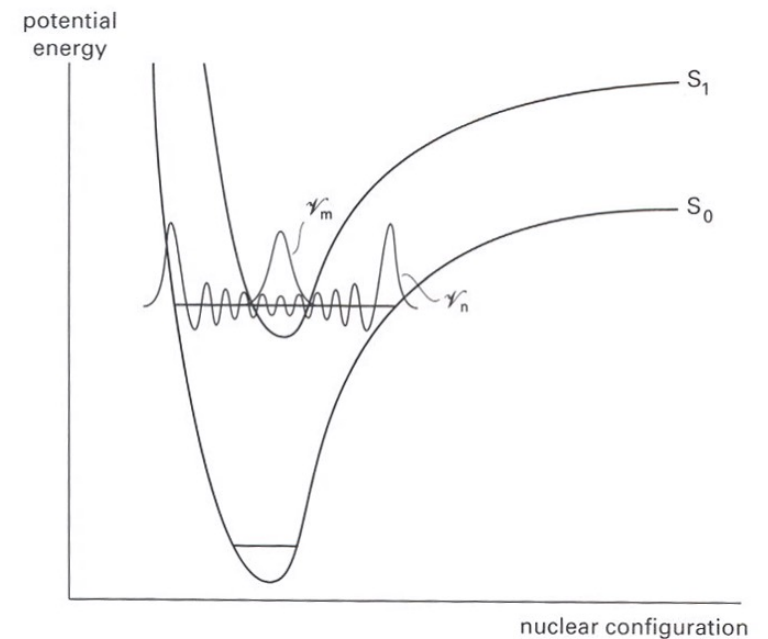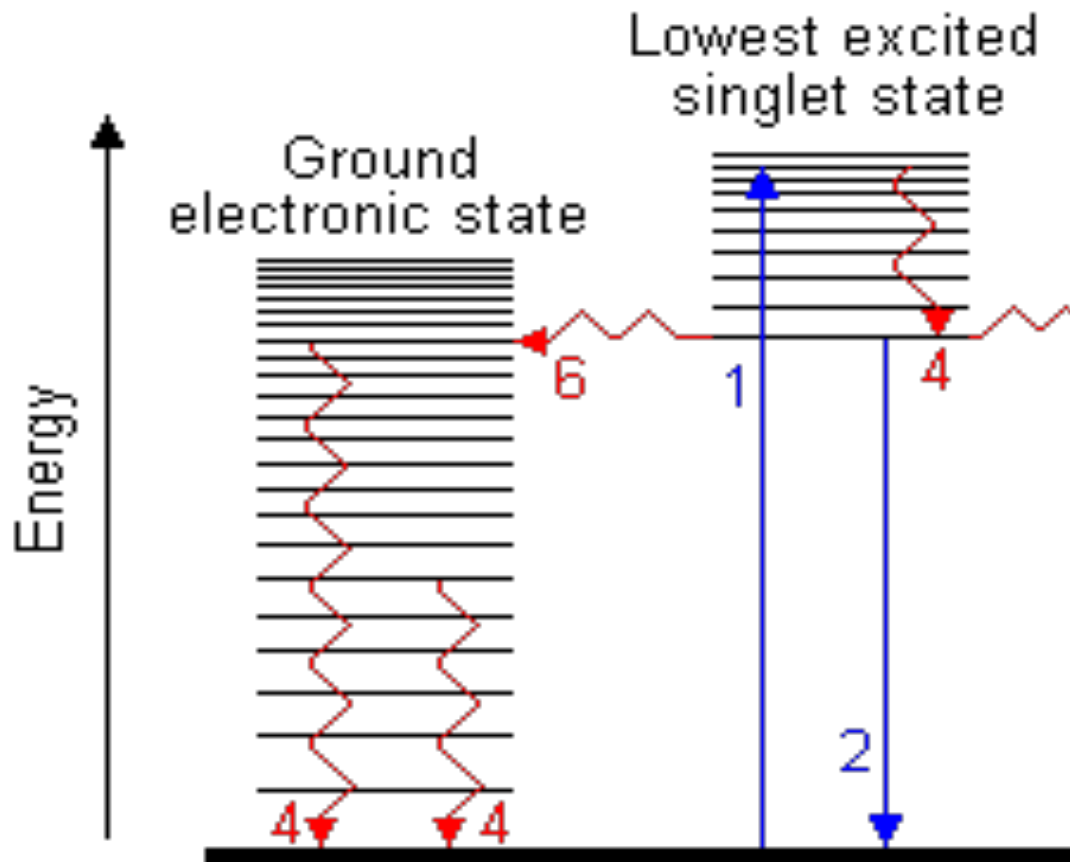
Electronic to Vibrational Energy Transfer

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]

Isotope Effect on Rate of T_1 to S_0

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

potential energy

T_1

S_0

nuclear configuration

Effect of deuteration on radiationless process (T_1 to S_0)

$S_1(v = 0) \; \xrightarrow{\mathsf{\sim\!\!\!\wedge\!\!\!\wedge}} \; S_0(v = 3)$

Aromatic hydrocarbon

$S_1(v = 0) \; \xrightarrow{\mathsf{\sim\!\!\!\wedge\!\!\!\wedge}} \; S_0(v = 6)$

Deuterated compound
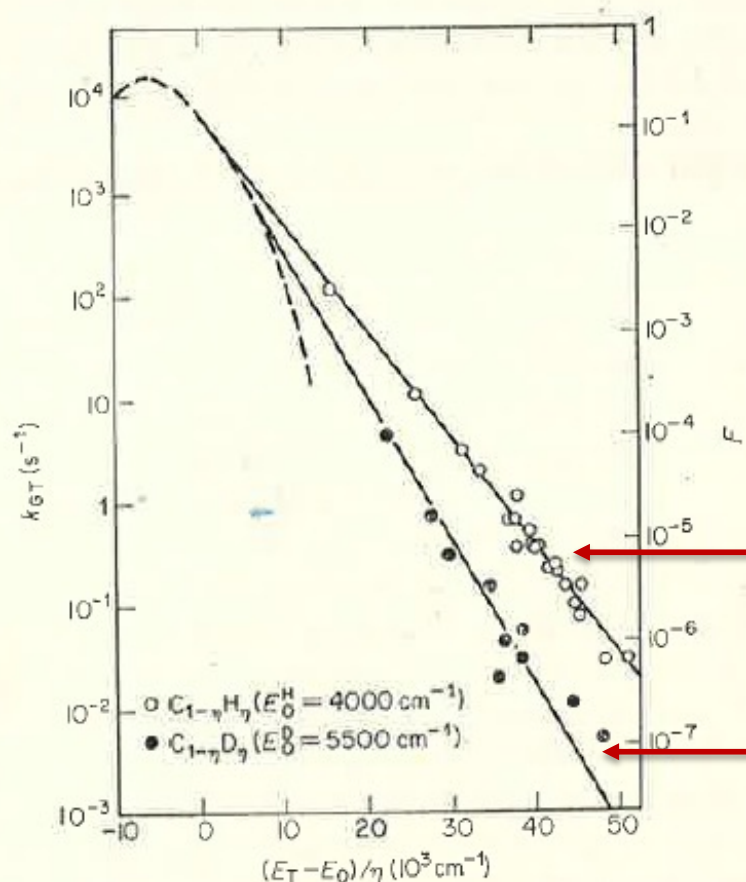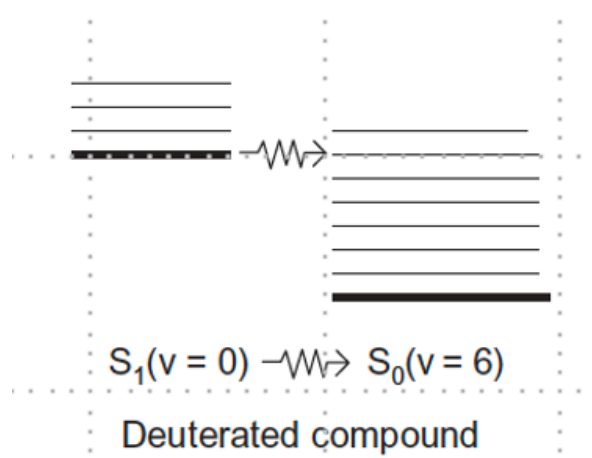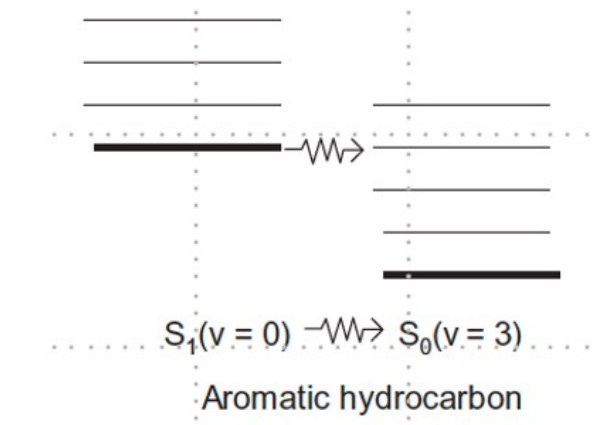
perprotonated

❑ perdeuterated

$\circ \; C_{1-\eta}H_\eta \, (E_0^H = 4000 \, cm^{-1})$

$\bullet \; C_{1-\eta}D_\eta \, (E_0^D = 5500 \, cm^{-1})$

Figure 5.2 $T_1 - S_0$ intersystem crossing rate k_{GT} (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 Siebrand[8])

Birks book

Decay of singlet oxygen depends on solvent and deuteration
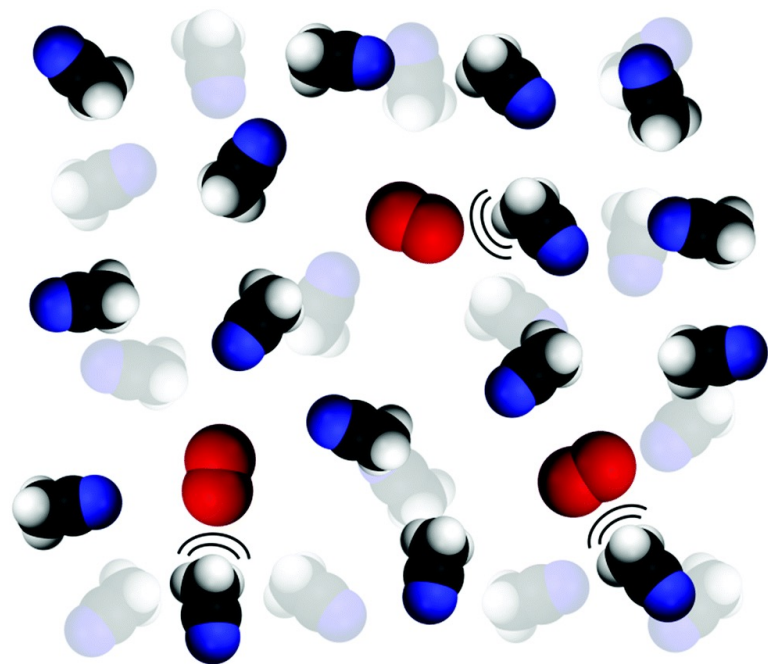
Mikkel Bregnh.j, Michael Westberg, Frank Jensen and Peter R. Ogilby, *Phys. Chem. Chem.Phys*., **2016**, *18*, 22946

Solvent	$\tau_\Delta/\mu s$ 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
o-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
n-Pentane	34.8 ± 0.2	34.8
n-Hexane-h_{14}	30.8 ± 0.6	32.2
n-Hexane-d_{14}	—	586
n-Heptane	28.9 ± 0.5	30.1
n-Octane	—	28.6
n-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_2O	3.7 ± 0.4	3.5^e
D_2O	68 ± 1^f	68.9^e

Vibrational effects on singlet oxygen lifetime

$S_1(v = 0) \rightsquigarrow S_0(v = 3)$

Aromatic hydrocarbon

$S_1(v = 0) \rightsquigarrow S_0(v = 6)$

Deuterated compound

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}.
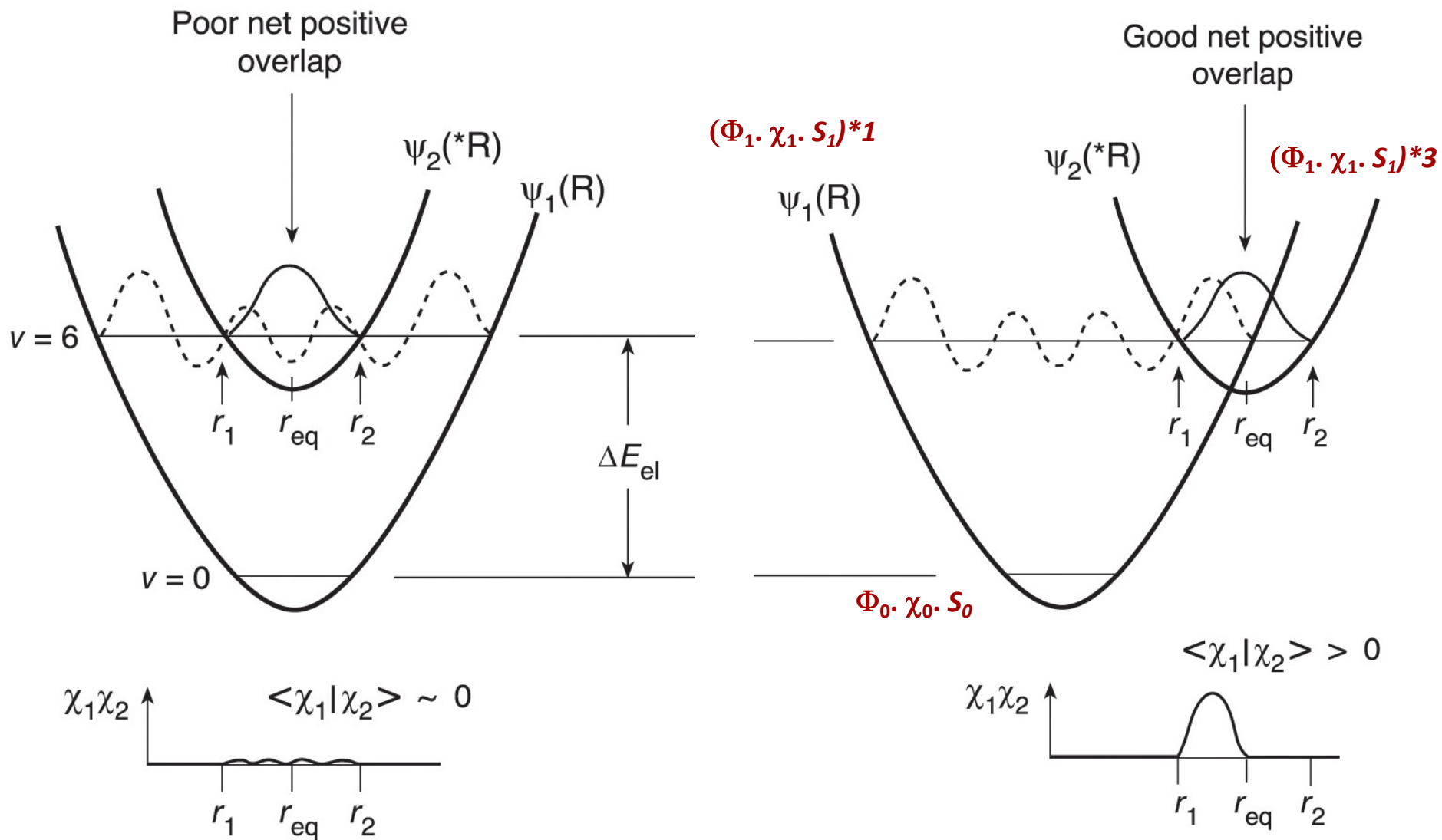
Energy (cm^{-1})

$^1\Sigma$
$^1\Delta$
$^3\Sigma$

−343
−1803
−3286
−4794
−6526
−7883

C—H   C—D   O—H   O—D

−3050   −2240   −3500   −2550
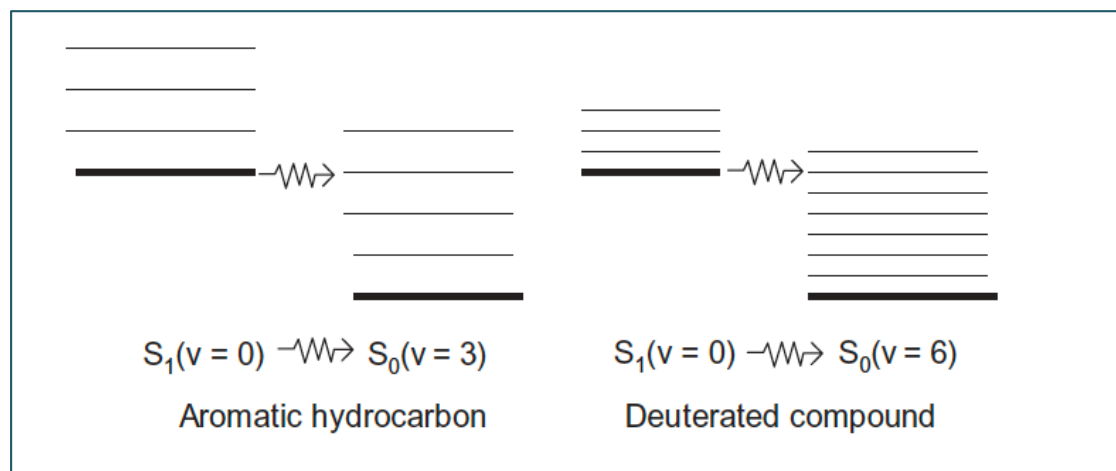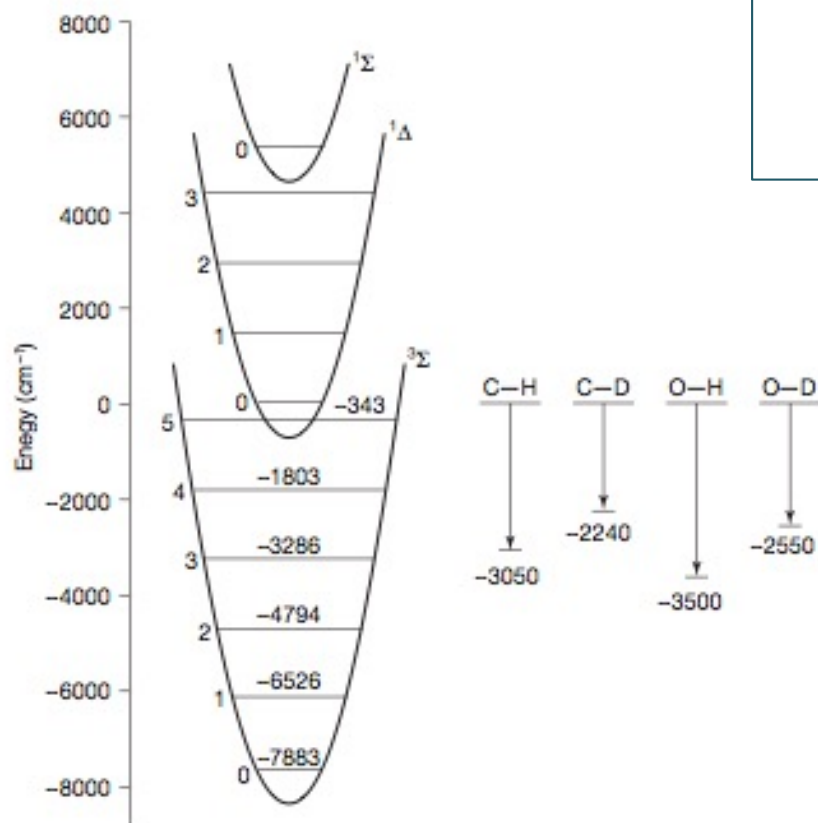
Table 14.3 Approximate Rate Constants[a] for the Deactivation of $^1\Delta$ by Various Kinds of X—Y Bonds in Organic Solvents[b]

Bond Type	k_d(M^{-1} s^{-1})	Vibrational Energy (cm^{-1})
O—H	2900	$\sim$ 3600
C—H (aromatic)	1500	$\sim$ 3000
C—H (aliphatic)	300	$\sim$ 2900
O—D	100	$\sim$ 2600
C—D (aromatic)	20	$\sim$ 2200
C—D (aliphatic)	10	$\sim$ 2100
C—F (aromatic)	0.6	$\sim$ 1200
C—F (aliphatic)	0.05	$\sim$ 1200

a. Reference 9.
b. The energies of X—D vibrations are typically at 0.73 times the energy of a X—H vibration.

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}	$\phi_f + \phi_{ISC}$	
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**).

Internal conversion in matching *vs.* crossing surfaces

Poor net positive overlap

$\psi_2(^*R)$

$\psi_1(R)$

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

$v = 6$

r_1 r_{eq} r_2

ΔE_{el}

$v = 0$

$\chi_1\chi_2$ $\langle\chi_1|\chi_2\rangle \sim 0$

r_1 r_{eq} r_2

Good net positive overlap

$\psi_2(^*R)$

$\psi_1(R)$

$(\Phi_1 \cdot \chi_1 \cdot S_1)^*3$

r_1 r_{eq} r_2

$\Phi_0 \cdot \chi_0 \cdot S_0$

$\langle\chi_1|\chi_2\rangle > 0$

$\chi_1\chi_2$

r_1 r_{eq} r_2

For the same energy gap the rates are different for the two types of surfaces

Breakdown of Born-Oppenheimer Approximation
Mixing of surfaces
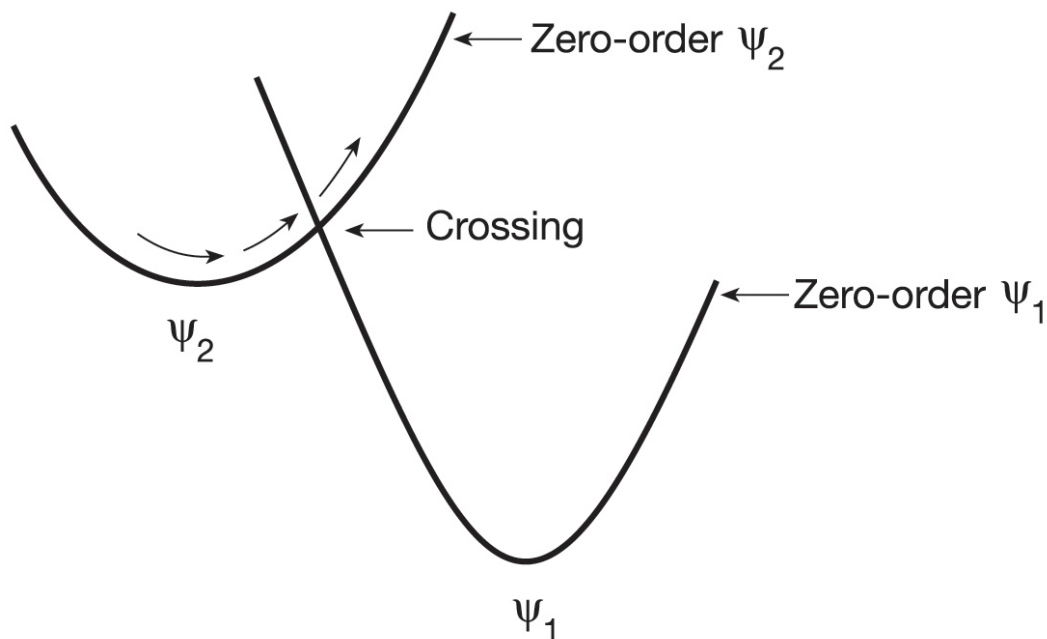
Two surfaces with different electronic or spin configurations

For the same nuclear configuration there are two electronic configurations with identical energies. Under favorable conditions this would lead to mixing resulting in avoided crossing.
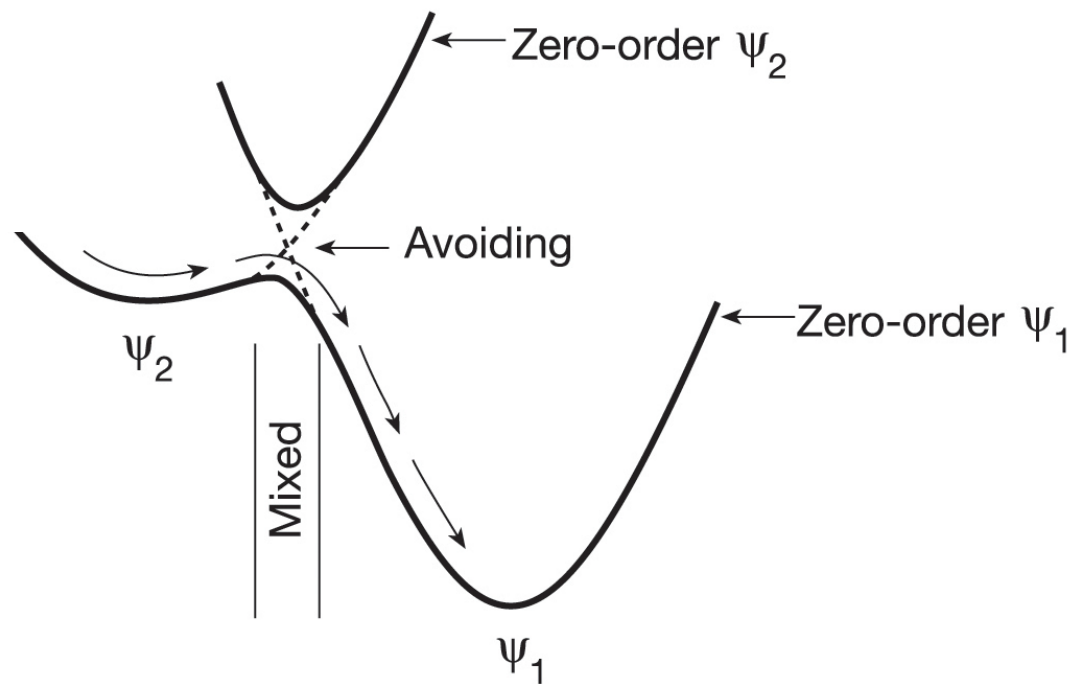
Breakdown of Born-Oppenheimer Approximation
Vibronic mixing enables surface mixing

Strictly planar

$n_0 = p_0$

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

Nonplanar

$n_0 = sp^n$

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

Zero-order n,π^*

Crossing

"Pure" n,π^*

Zero-order π,π^*

"Pure" π,π^*

Planar vibrations

Energy is fine, but
orbitals don't overlap

Avoiding

"Pure" n,π^*

Mixed
n,π^*
π,π^*

"Pure" π,π^*
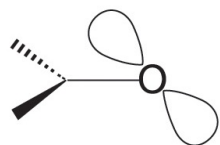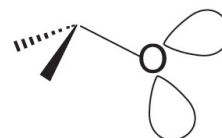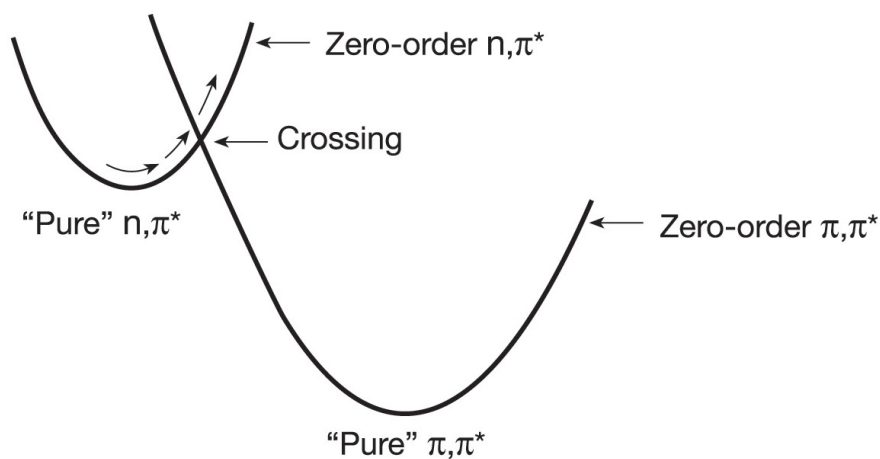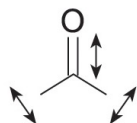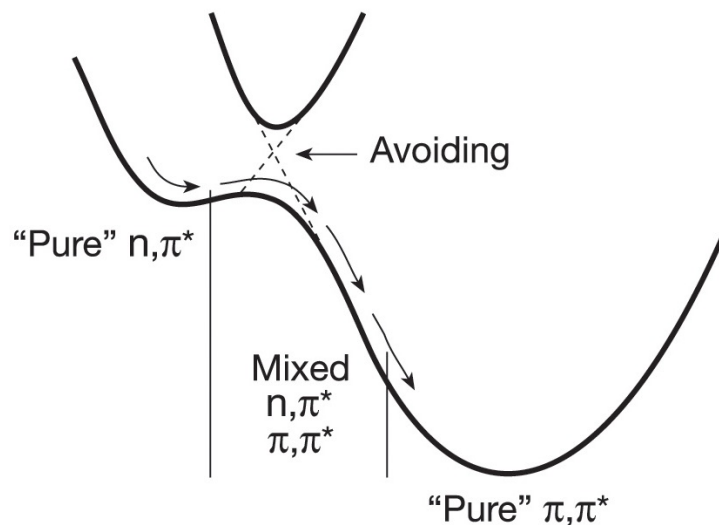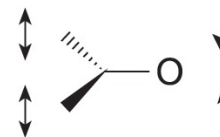
Nonplanar vibrations

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

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

Intersystem Crossing in Diradicals and Radical Pairs

Spin forbidden transitions

$R(S_0) + h\nu \rightarrow {}^*R(S_1)$

$R(S_0) + h\nu \rightarrow {}^*R(T_1)$

${}^*R(T_1) \rightarrow R(S_0) + h\nu$

${}^*R(T_1) \rightarrow R(S_0) + heat$

${}^*R(S_1) \rightarrow R(T_1) + heat$

S_1

k_{isc}

T_1

k_{isc} k_P

S_0
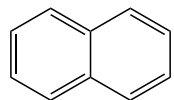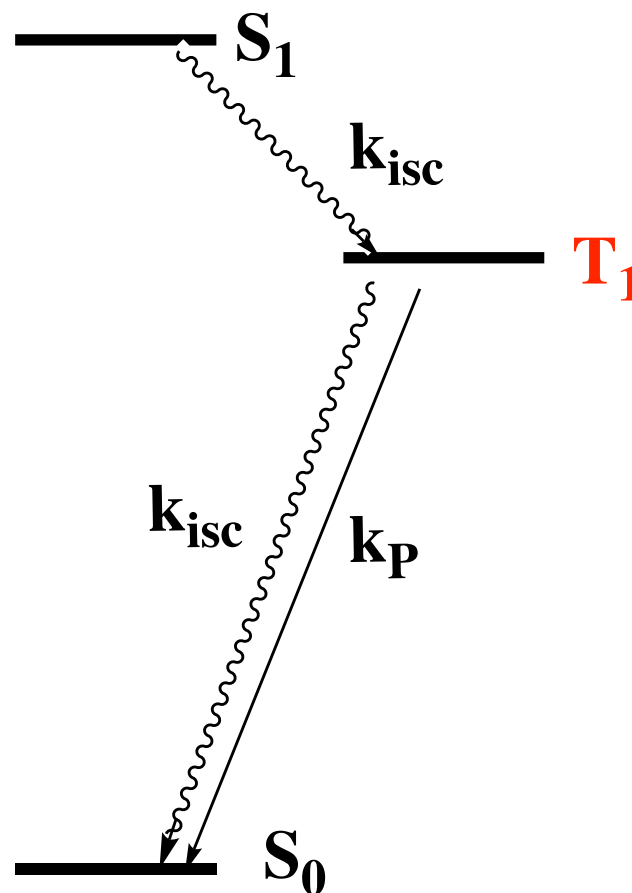
Intersystem crossing in molecules with $n\pi^*$ and $\pi\pi^*$ states
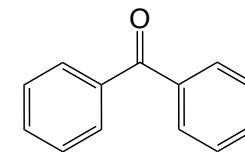
Singlet-Triplet Transitions
Role of Spin-Orbit Coupling
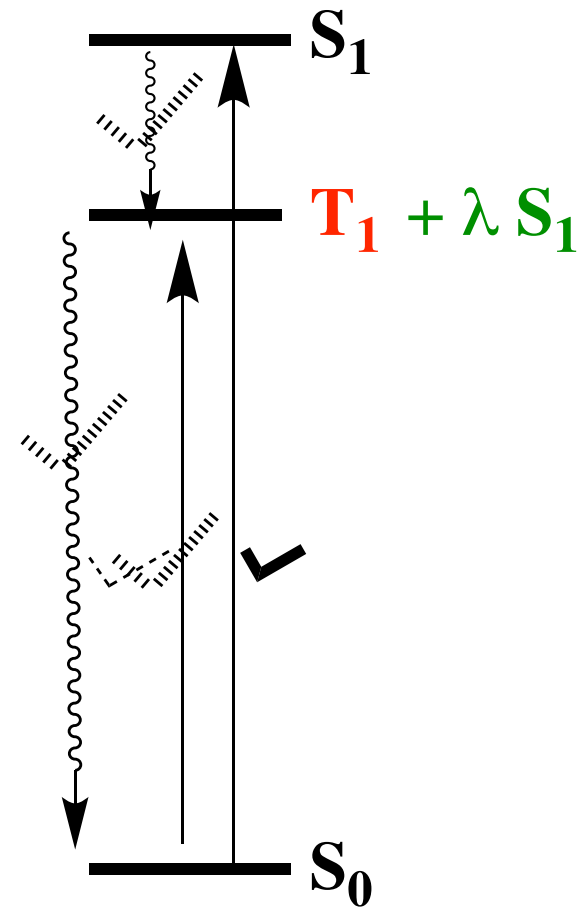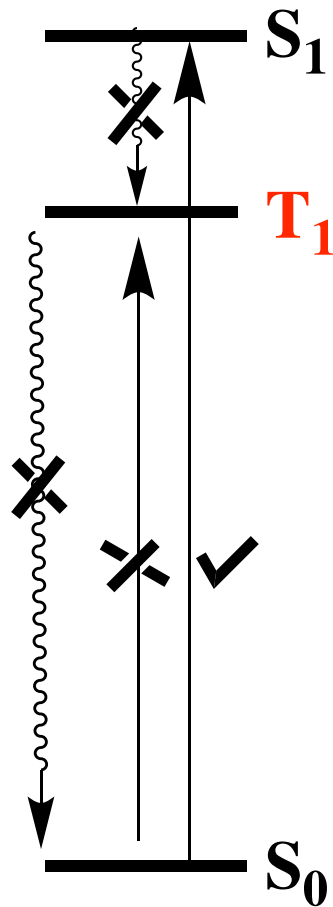
Spin-Orbit coupling mixes the states,
no longer pure states

Breakdown of Born-Oppenheimer Approximation
Spin-Orbit coupling enables surface mixing
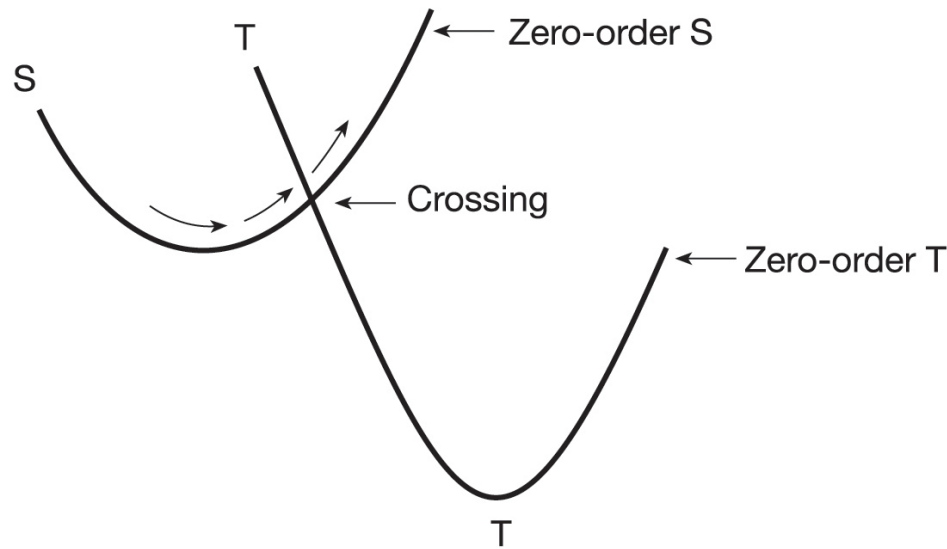
Two surfaces with different spin configurations.

For the same nuclear configuration there are two spin configurations. Coupling between the two surfaces could lead to mixing and result in avoided crossing.
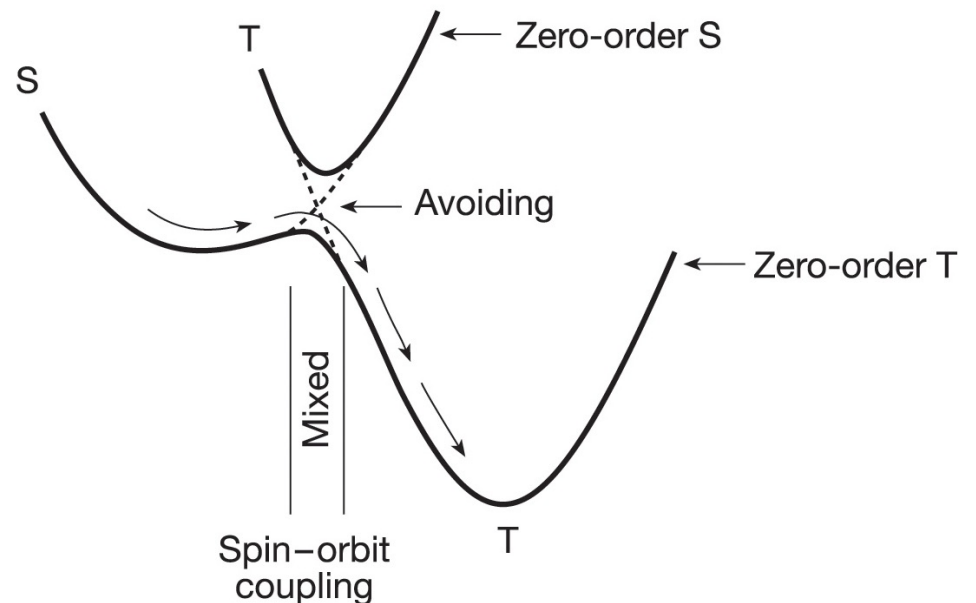
Breakdown of Born-Oppenheimer Approximation
Spin-orbit coupling facilitated by vibronic mixing enables surface mixing

a)

Pure $^1\pi,\pi^*$

Pure $^3\pi,\pi^*$

)

Pure $^1\pi,\pi^*$

Pure $^3\pi,\pi^*$
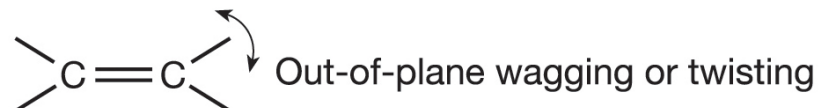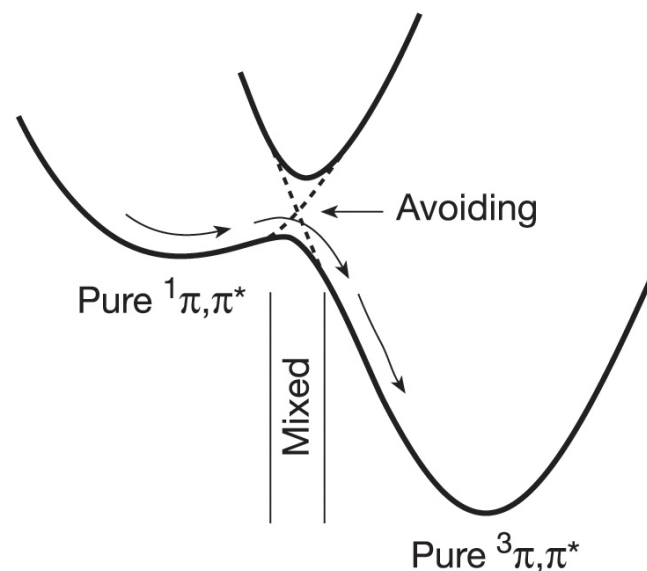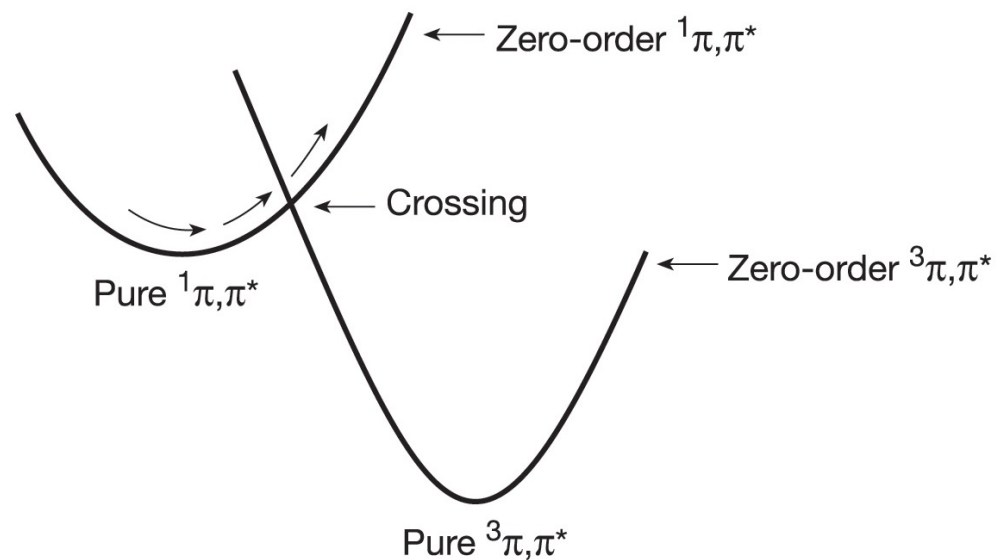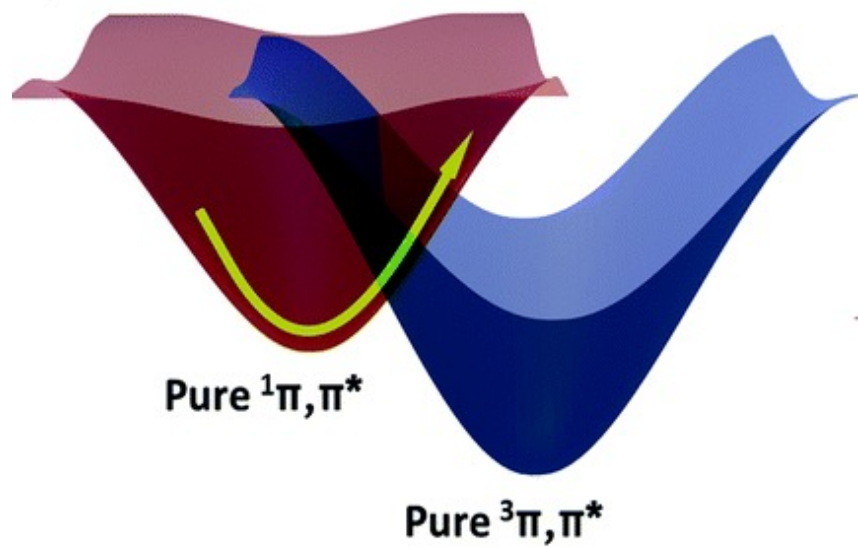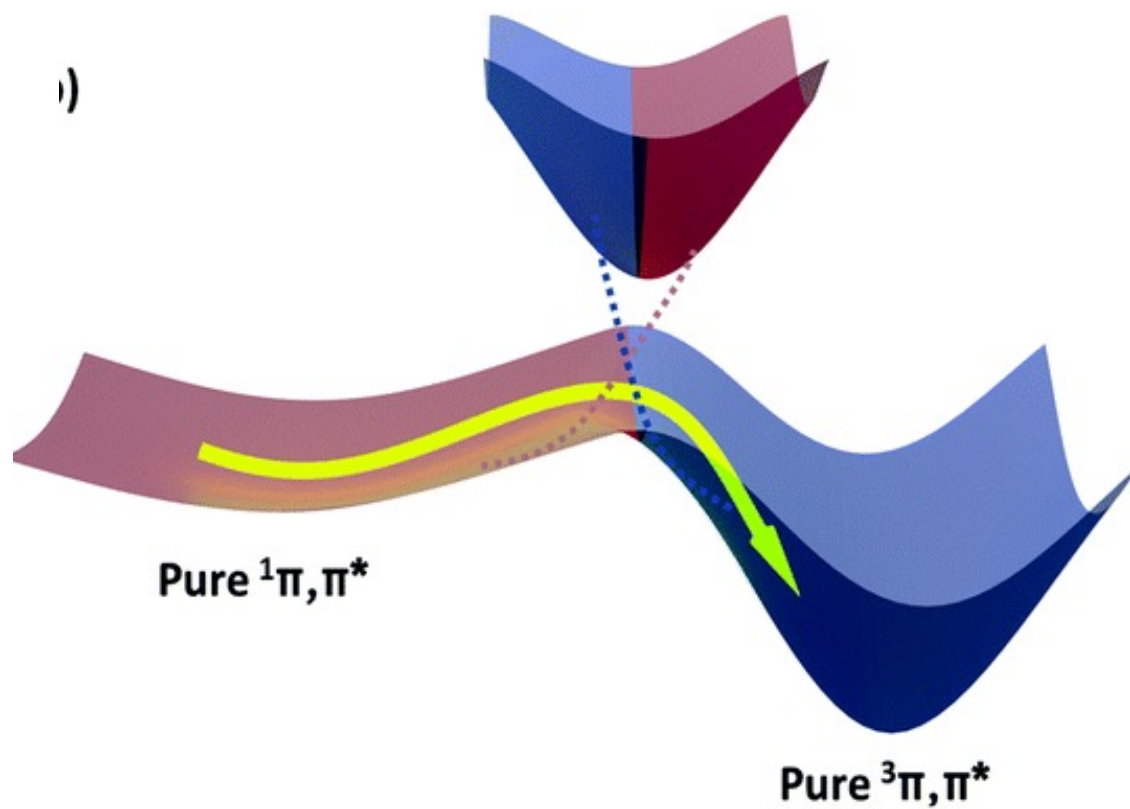
Two spins of ½: S = 0
Spin multiplicity = 2S+1 = 1

Two spins of ½: S = 1

α

β

$M_S=0$

$\alpha\beta - \beta\alpha$

M_{s1} α

M_{s2} α

$M_S=1$

$\alpha\alpha$

M_{s1} β

M_{s2} β

$M_S=-1$

$\beta\beta$

M_{s1} α

M_{s2} β
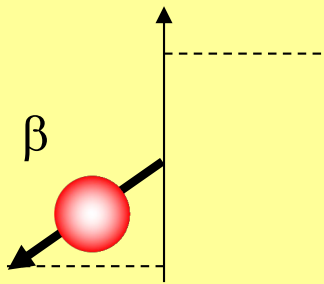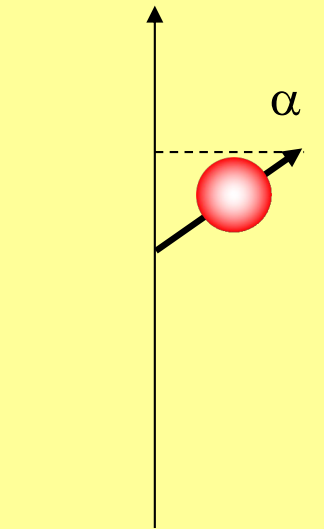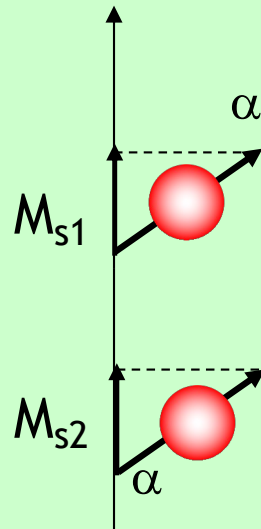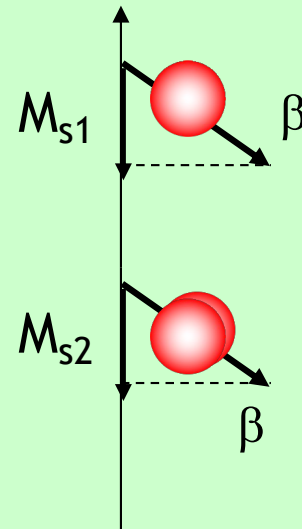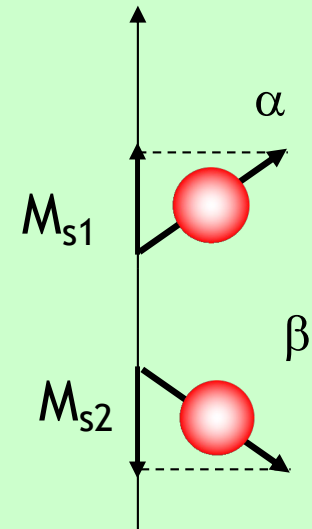
$M_S=0$

$\alpha\beta + \beta\alpha$
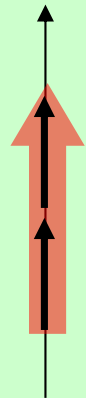
Angular momentum vector representations of two electron system: Singlet and Triplet
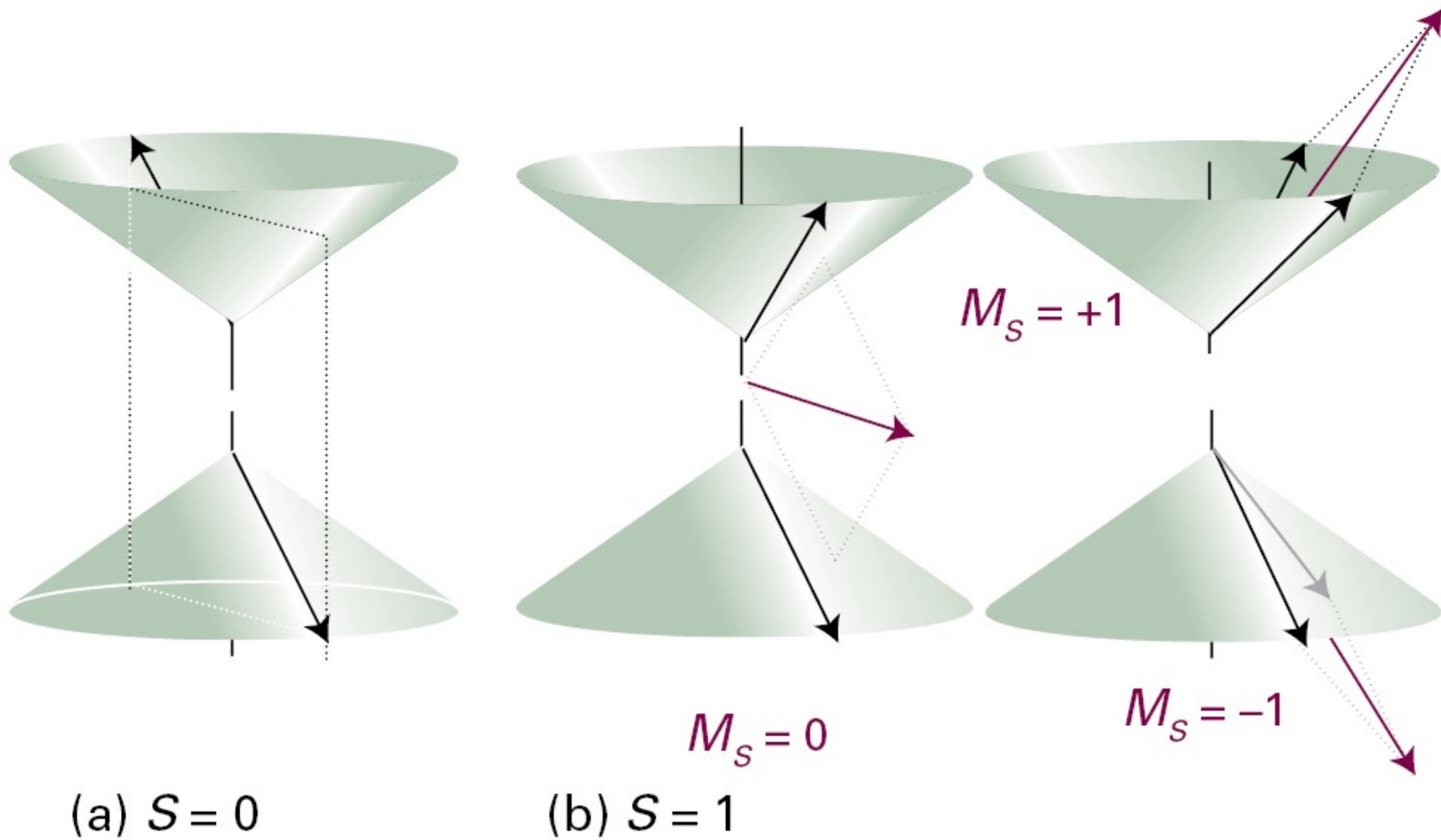
(a) $S = 0$ (b) $S = 1$

$M_S = +1$

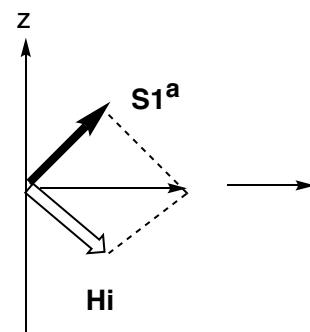$M_S = 0$

$M_S = -1$

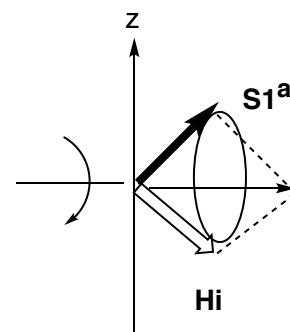# Spin interconversion in one spin system

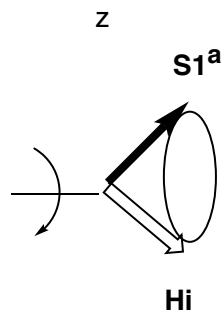# Spin interconversion in one spin system in zero and high magnetic field
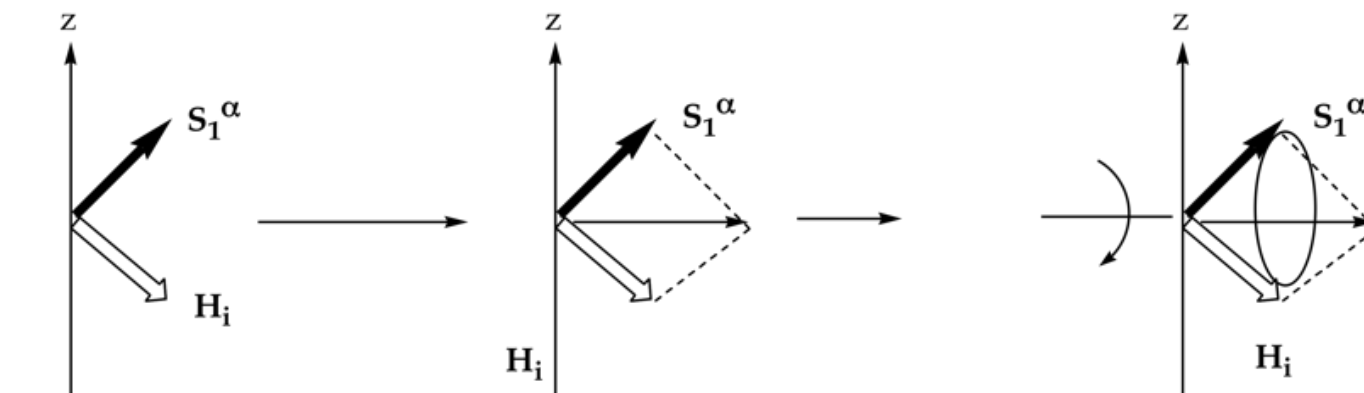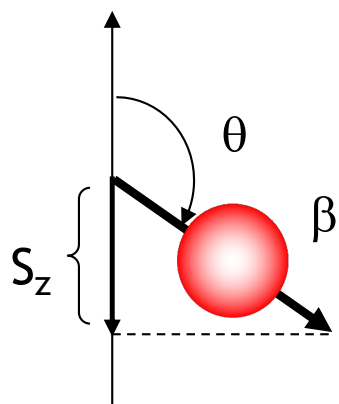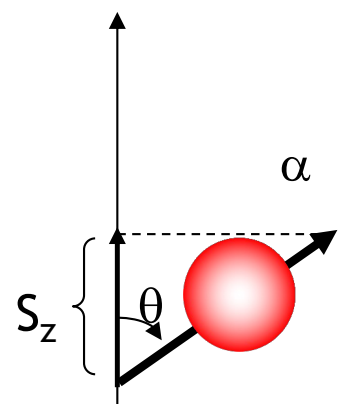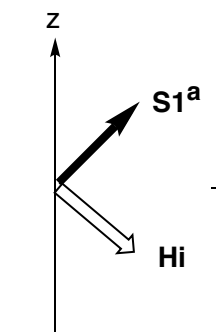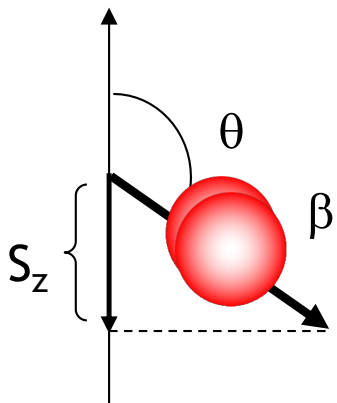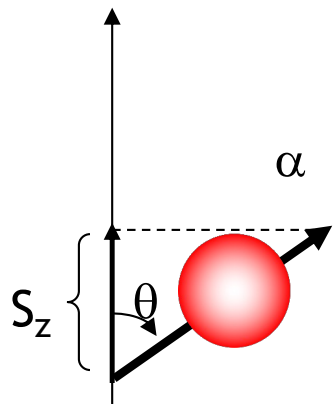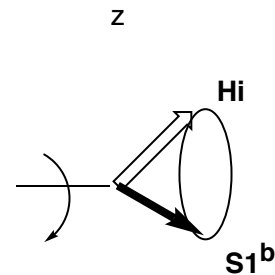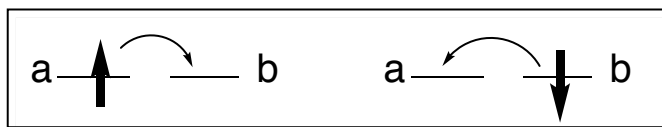

S1 and H_i uncoupuled

S1 and H_i coupuled to yield the resultant S_1 + H_i

S1 and H_i precess about resultant

Hx or Hy

Zero Field

High Field

Spin interconversion in two spin system
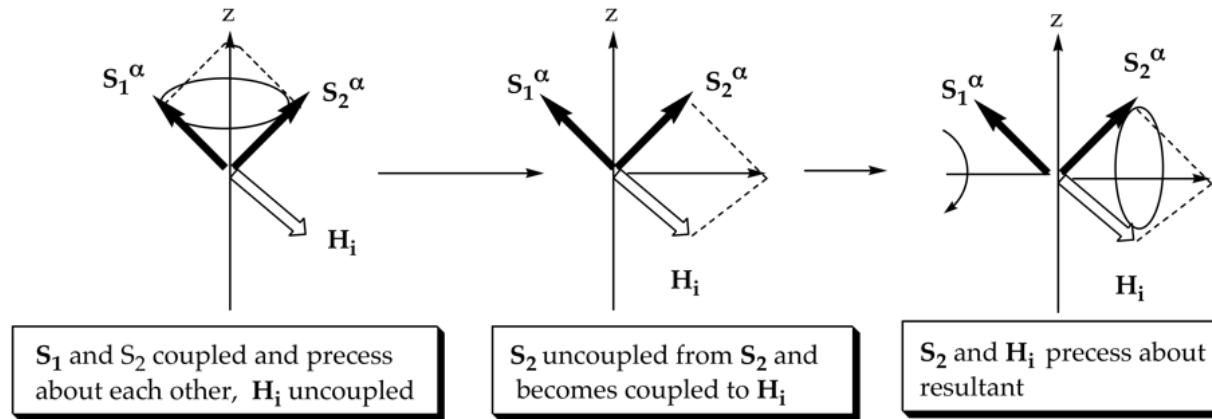

T^+

S

S_1 and S_2 coupled and precess about each other, H_i uncoupled

S_2 uncoupled from S_2 and becomes coupled to H_i

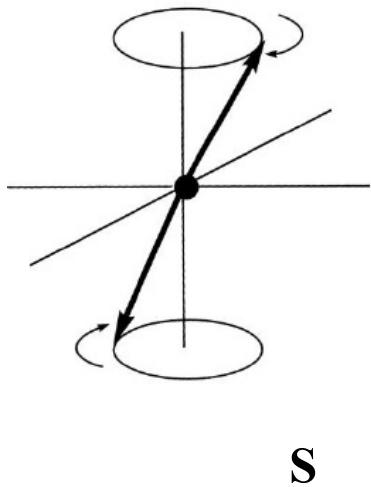S_2 and H_i precess about resultant

H_X or H_Y

Zero field
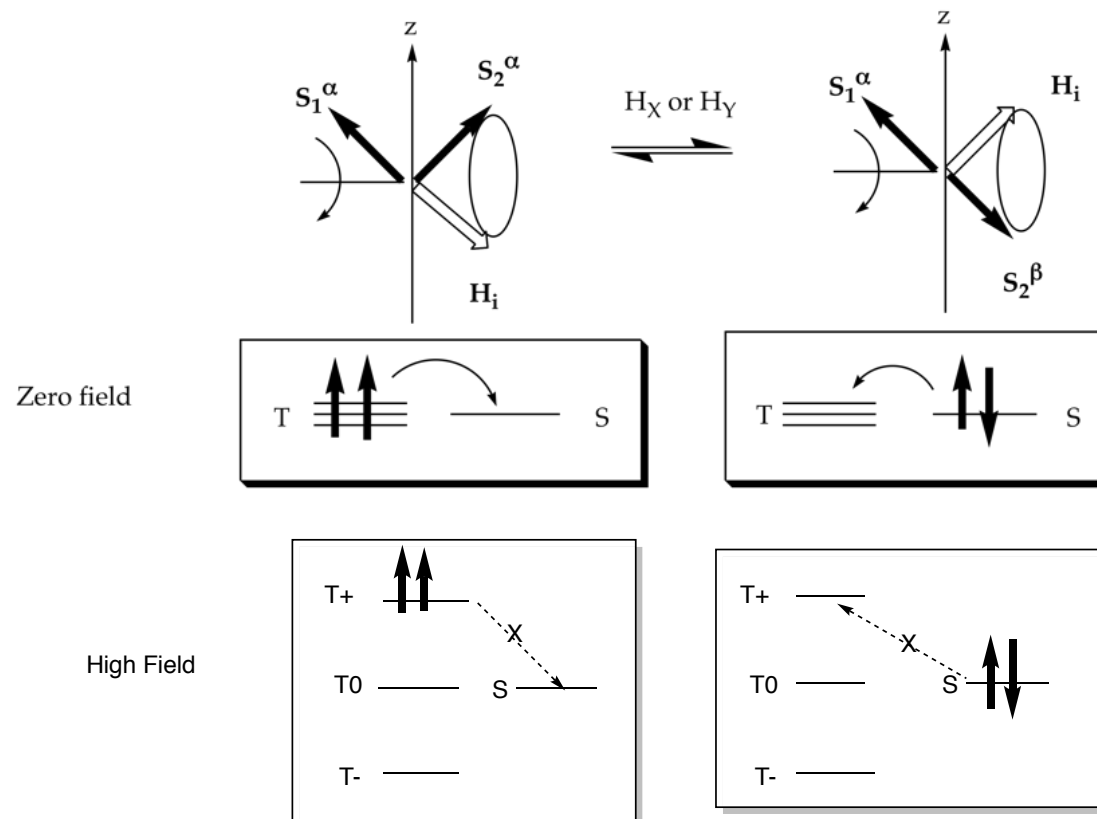
High Field

Spin interconversion in two spin system

S_1 and S_2 coupled, H_i uncoupled
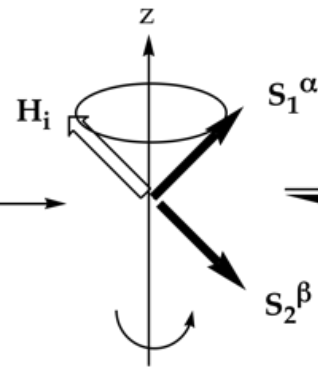
S_2 becomes uncoupled from S_2 and becomes coupled to H_i
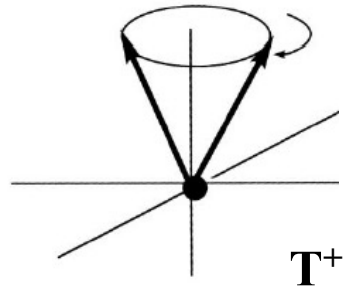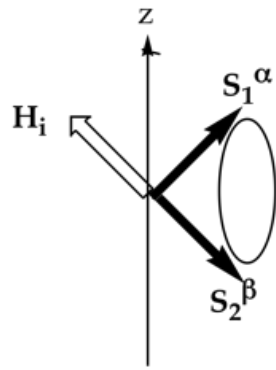
Zero field
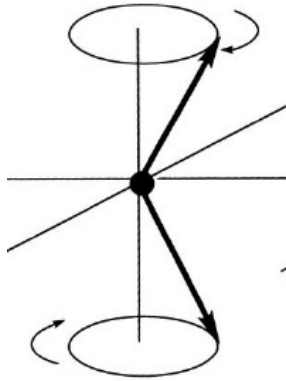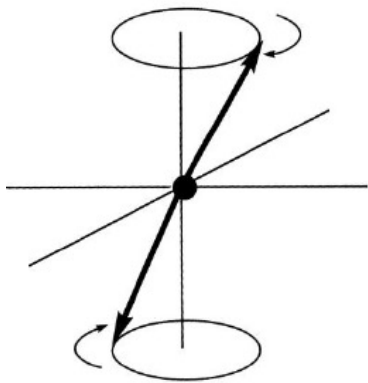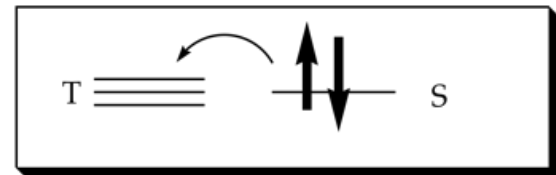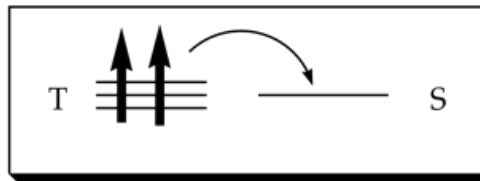
High Field
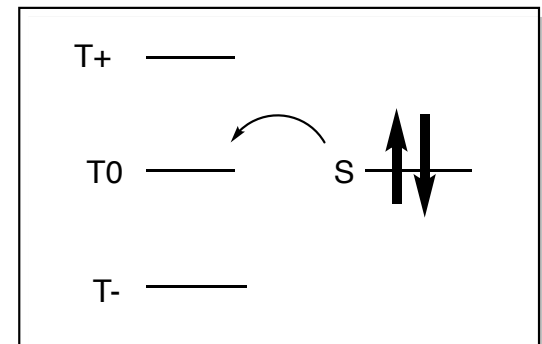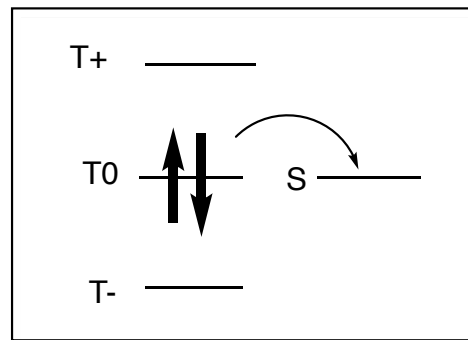
Spin interconversion in two spin system (Spin rephasing)

tightly coupled

H_z

loosely coupled

Z axis

Z axis

tightly coupled

S_1

S_2

S_1

S_2

S_1

S_2

S_1

S_2

triplet, T_0

torques producing
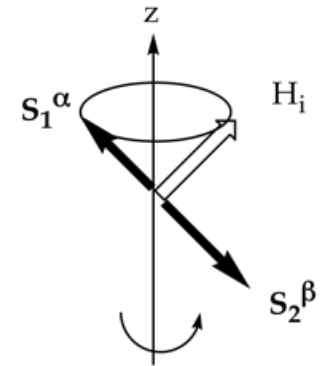a rotation of S_2 about z

singlet

Spin interconversion in two spin system: Spin flipping

tightly coupled   loosely coupled   tightly coupled

S_1 S_2 S_1 S_2 S_1 S_1 S_2

X, Y axis

S_2
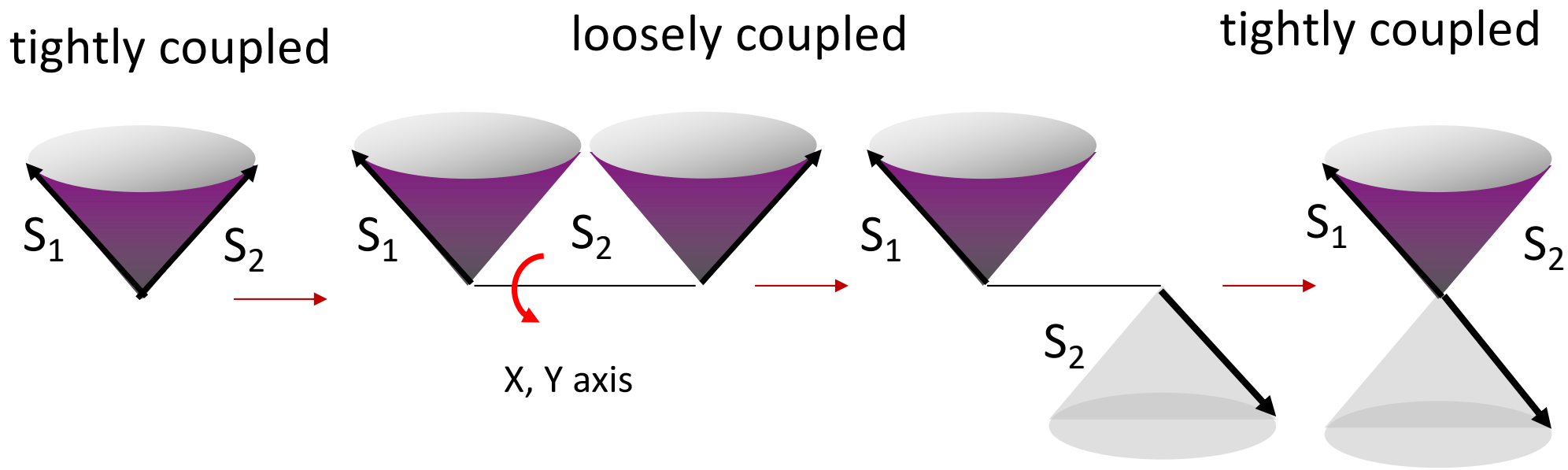
triplet, T_+ torques producing a   singlet, S
rotation of S_2 about x or y

H_x (or H_y)
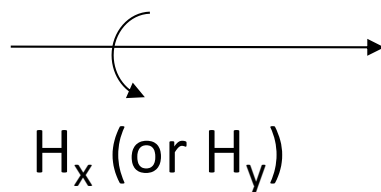
External and Internal Magnetic Fields

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

Available Internal Magnetic Fields

ORBITAL COUPLING

ELECTRON OR NUCLEAR SPIN COUPLING

ZEEMAN COUPLING

LATTICE COUPLING

PHOTON COUPLING

Angular momentum

Magnetic moment

spin

orbital

z axis

Spin angular
momentum vector
along z axis, S_z

v

Magnetic
momentum vector
along z axis, μ_z

z axis

Angular
momentum vector
S

Magnetic
momentum vector
μ_S

Orbital angular
momentum vector
L

v

r

Orbital angular
momentum vector
L

v

r

+

−

μ_L
Magnetic
momentum vector
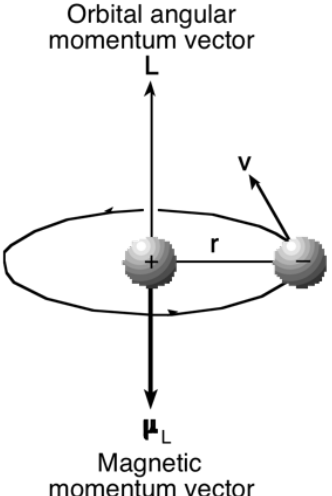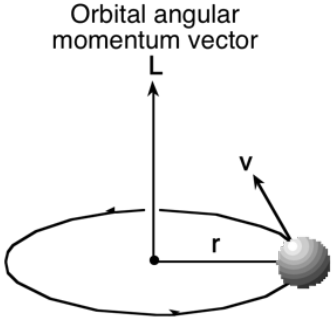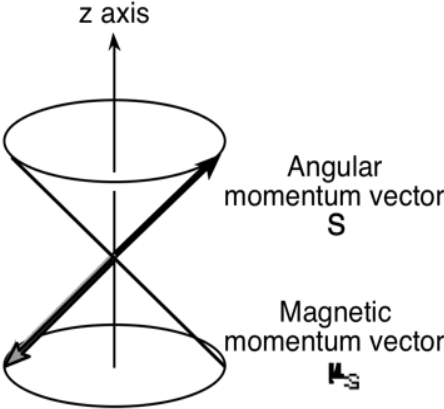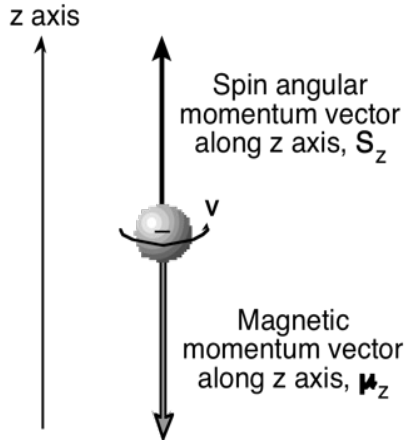
Precession and Spin-Orbit coupling

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.

More on Spin-Orbit Coupling

- 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, $\boldsymbol{\mu}_L$ (a variable quantity depending on the orbit), and the electron spin, $\boldsymbol{\mu}_S$ (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!

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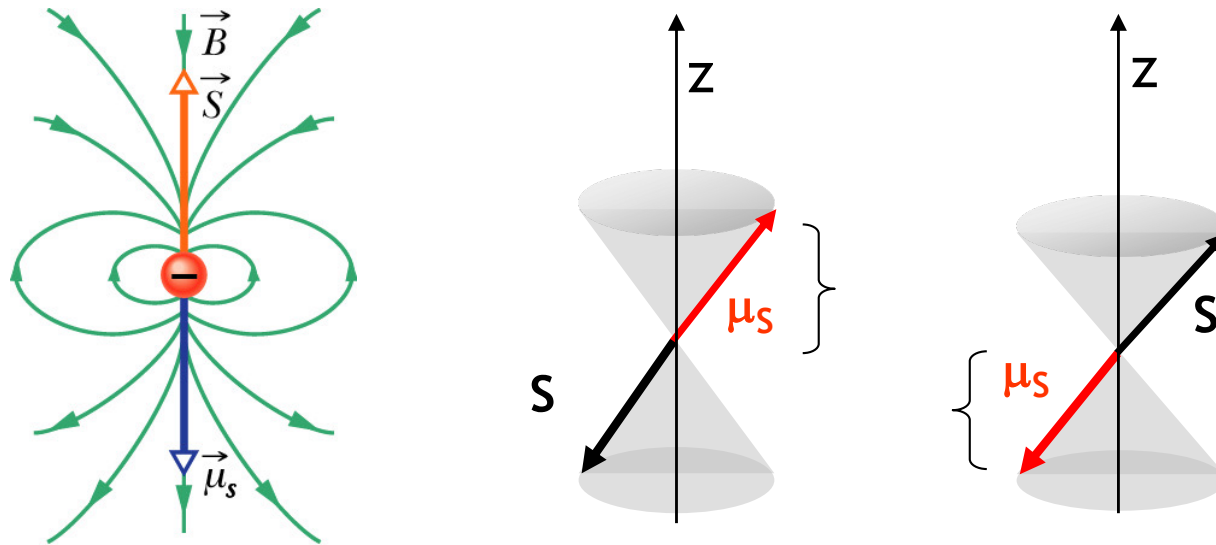
The electron possesses a **spin magnetic** moment due to its charge and spin. The magnetic moment μ_s is quantized in magnitude and orientation as the angular momentum S from which it arises

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:

$$\mu_L = -(e/2m)\ \mathbf{L}$$
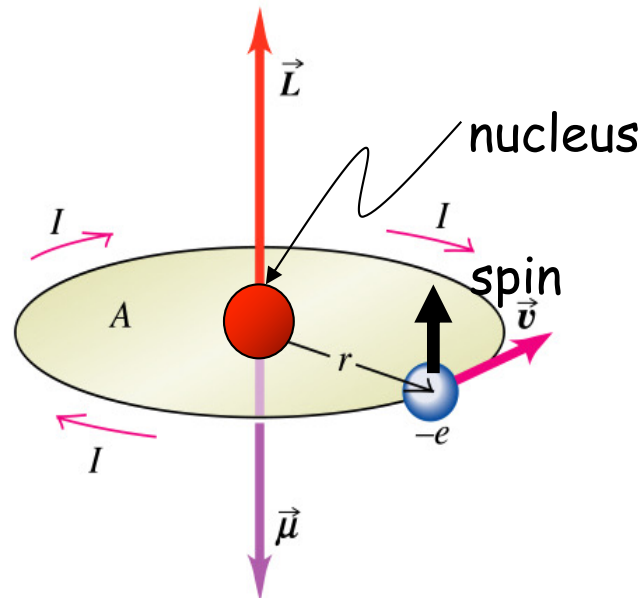
Spin-Orbit Coupling and Heavy Atom Effect

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.

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

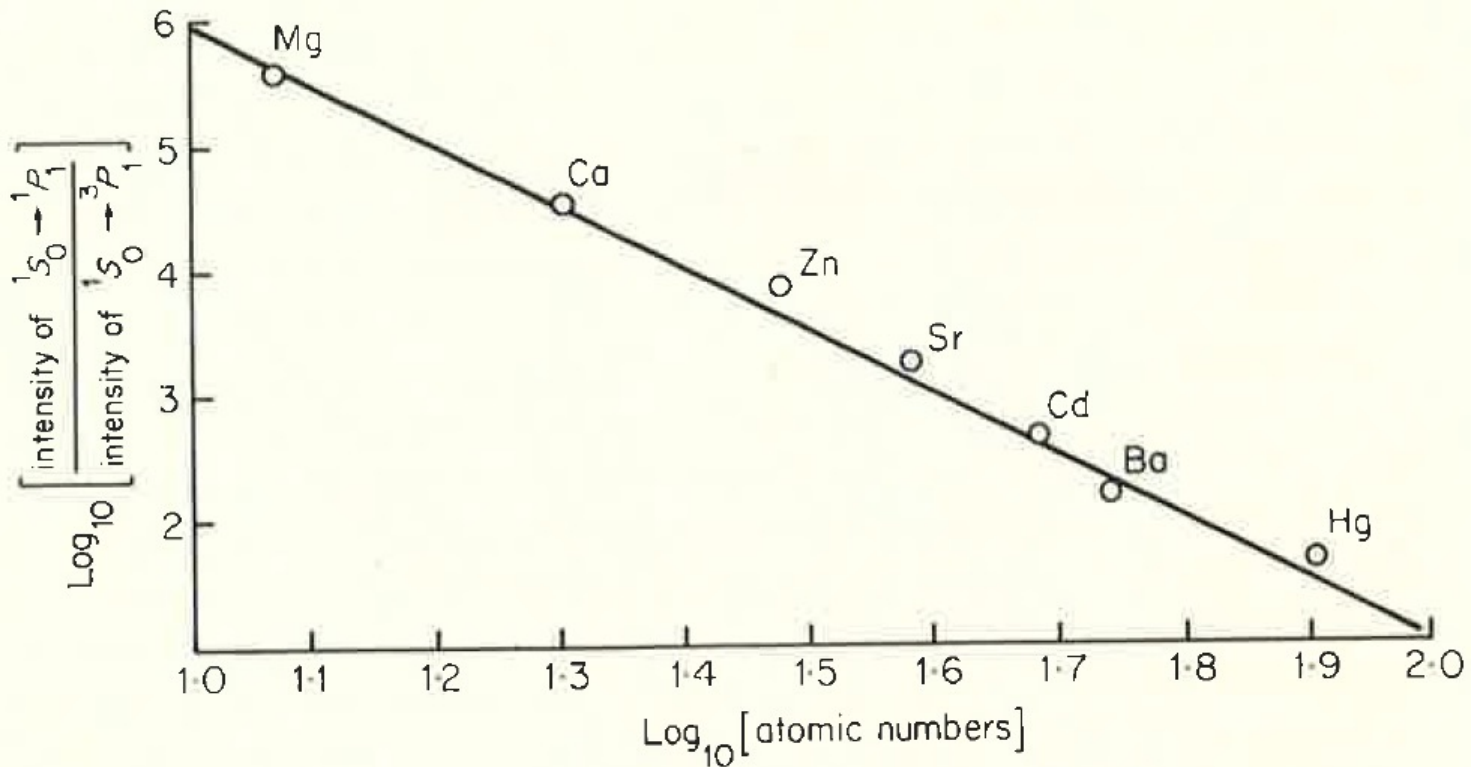# Spin-orbit coupling parameter is related to atomic number

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.)
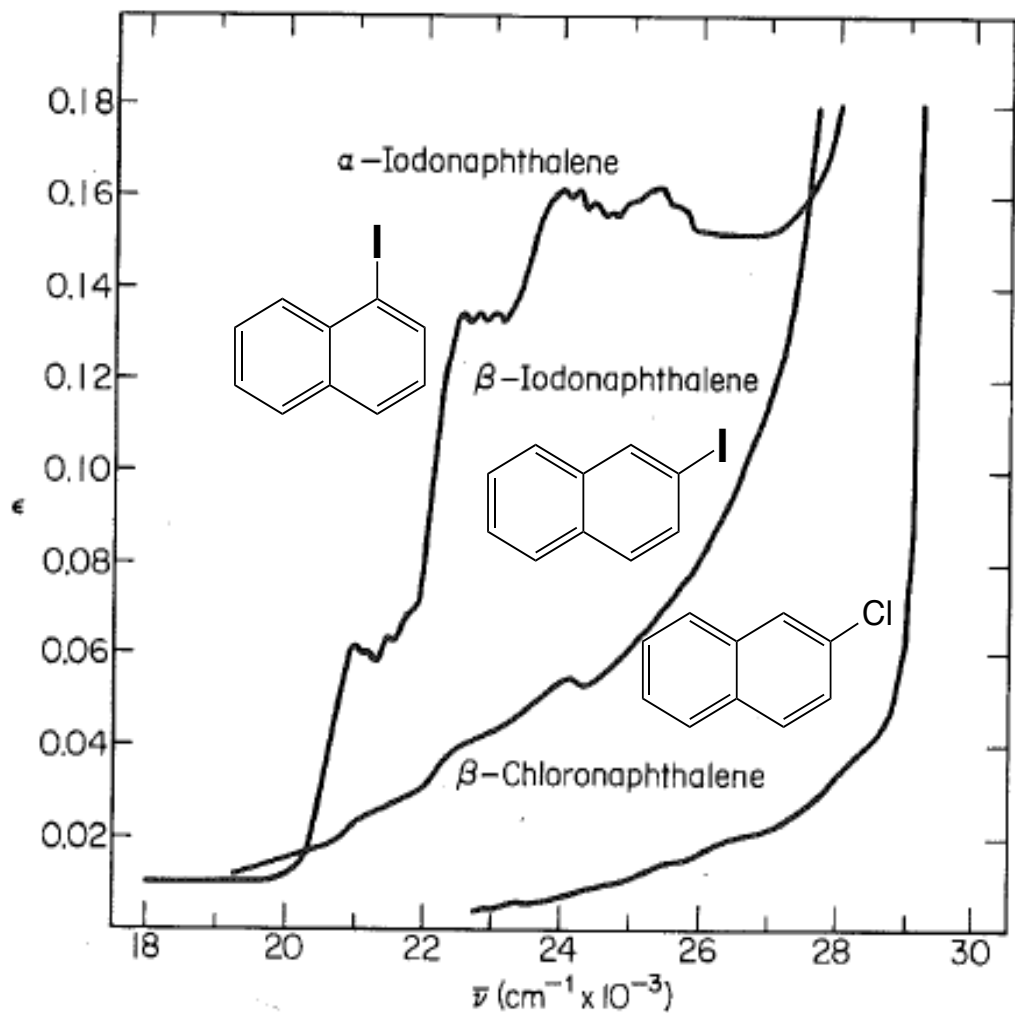
The heavy atom effect on spin transitions

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 <u>internal</u> to a molecule (molecular) or <u>external</u> (supramolecular).

Internal Heavy Atom Effect: Spin forbidden absorption

External Heavy Atom Effect: Spin forbidden absorption

1 – Pure liquid
2 – 1:2 (v/v) in CCl_4
3 – 1:2 (v/v) in $C_2H_4Br_2$
4 – 1:2 (v/v) in C_2H_5I
5 – 1:4 (v/v) in C_2H_5I
(20 cm path)

C_2H_5I

$C_2H_4Br_2$

CCl_4

Pure liquid

Molar absorption coefficient

$\bar{\nu}$ (cm^{-1})

External Heavy Atom Effect: Spin forbidden absorption

CH$_3$CH$_2$I solvent
$S_0 \rightarrow T_1(\pi, \pi^*)$

High pressure of xenon

Cl

ε

0.15
0.10
0.05

350   400   450   500
λ (nm)

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
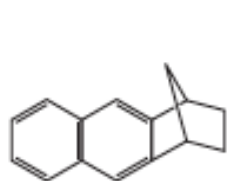
10

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

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

11

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

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

12

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

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

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

TABLE 7.2

Spectroscopic Data on Group IV Tetraphenyls[a]

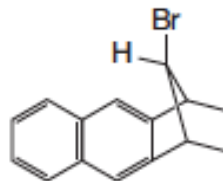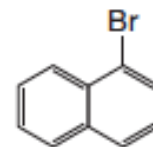| Molecule	Fluorescence band maximum (Å)	Phosphorescence band maxima (Å)	Φ_P/Φ_F	τ_P (sec) [b]	τ_P (sec) [c]	ζ_{np}^2 (cm^{-1})^2 [d]	$\sum_K \zeta_K^2$ (cm^{-1})^2 [e]	τ_P (sec) [f]	k_{ISC} (sec^{-1}) [g]
C(C$_6$H$_5$)$_4$	3200	4500, 4700, 5100	≤ 0.1	2.9	—	7.84×10^2	5.49×10^3	$\equiv 2.9$	10^6–10^7
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	7.74×10^5	7.79×10^5	0.021	10^9
Sn(C$_6$H$_5$)$_4$	3200	4500, 4700	10	0.003	0.0006	4.39×10^3	4.39×10^6	0.0038	10^{11}
Pb(C$_6$H$_5$)$_4$	—	4250, 4550	$\gg 10$	(0.0008)	0.00008	5.32×10^7	5.32×10^7	0.00031	—

[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 $T_1 \longleftarrow S_0$ 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, ζ_{np}^2, over all atoms in the molecule.

[f] Calculated from the equation $\tau_P^0 = \tau_P^0[C(C_6H_5)_4]\zeta_C^2/\zeta_K^2$, 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).

TABLE 7.3

Spectroscopic Data on Naphthalene Derivatives[a]

Molecule	$F_{0,0}$ (cm^{-1})	$P_{0,0}$ (cm^{-1})	Φ_F	Φ_P	Φ_P/Φ_F (approx.)	τ_P (sec)	k_{ISC} (sec^{-1})	k_F (sec^{-1})
Naphthalene	31750	21250	0.55	0.051 ± 0.003	0.093	2.3 ± 0.1	$\sim 10^5$	$\sim 10^6$
1-Methylnaphthalene	31450	21000	0.85 ± 0.19	0.044 ± 0.013	0.053	2.1 ± 0.1	$\sim 2 \times 10^5$	$\sim 3 \times 10^6$
1-Hydroxynaphthalene	30775	20600	0.76 ± 0.04	0.036 ± 0.004	0.047	1.9	$\sim 2 \times 10^5$	$\sim 3 \times 10^6$
1-Fluoronaphthalene	31600	21150	0.84 ± 0.08	0.056 ± 0.009	0.068	1.5	$\sim 2 \times 10^5$	$\sim 3 \times 10^6$
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^{-2}	$\sim 5 \times 10^8$	$\sim 3 \times 10^6$
1-Iodonaphthalene	—	20500	<0.0005	0.38 ± 0.06	>1000	2.0×10^{-3}	$>3 \times 10^9$	$\sim 3 \times 10_6$

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

1   2   3   4

5   6   7   8
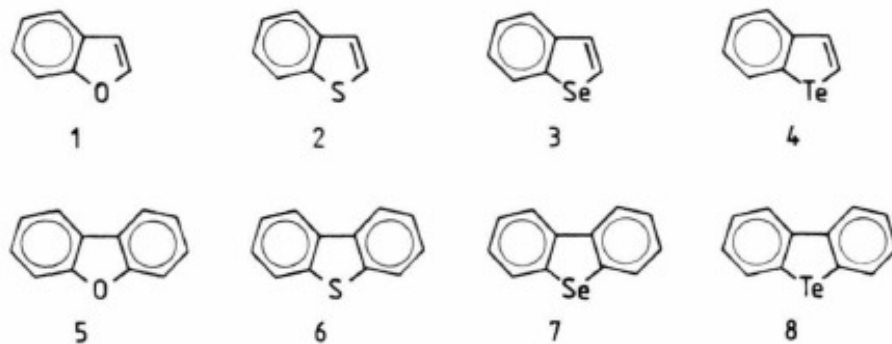
Non-Radiative decay from T_1

Radiative decay from T_1

Table 1. Fluorescence 0–0 band ($\tilde{v}_f$), phosphorescence 0–0 band ($\tilde{v}_p$), 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		$\tilde{v}_f$ [cm^{-1}]	$\tilde{v}_p$ [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)	$1 \cdot 10^{-2}$	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.

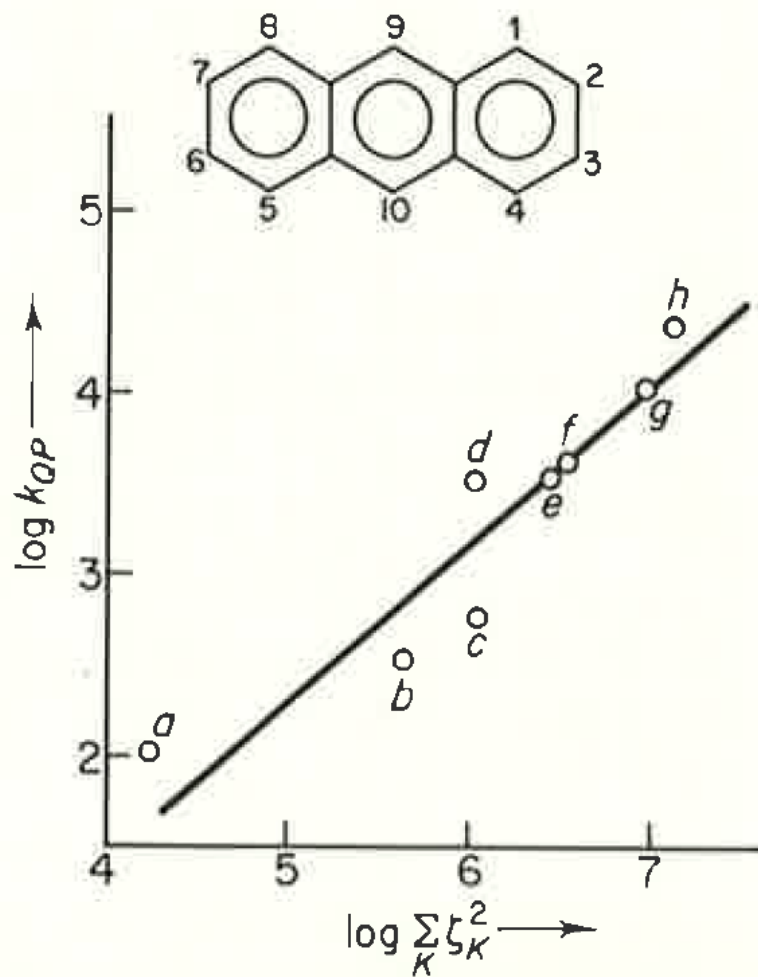M Zander, G Kirsch - Zeitschrift für Naturforschung A, 1989, 205

Fig. 7.2 Plot of k_{QP} (in sec^{-1}) versus $\sum_K \zeta_K^2$ (in cm^{-2}), the summation being over all halogen centers. The data plotted are for the following molecules: (a) anthracene; (b) 1-chloroanthracene; (c) 1,5-dichloroanthracene; (d) 9,10-dichloroanthracene; (e) 2,9,10-trichloroanthracene; (f) 1,5,9,10-tetrachloroanthracene; (g) 9-bromoanthracene; (h) 9,10-dibromoanthracene. The slope of the log-log plot is approximately 45°.

Intersystem crossing
in carbonyl compounds and others with nπ*)

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 (the same) 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, $\hbar$* (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.
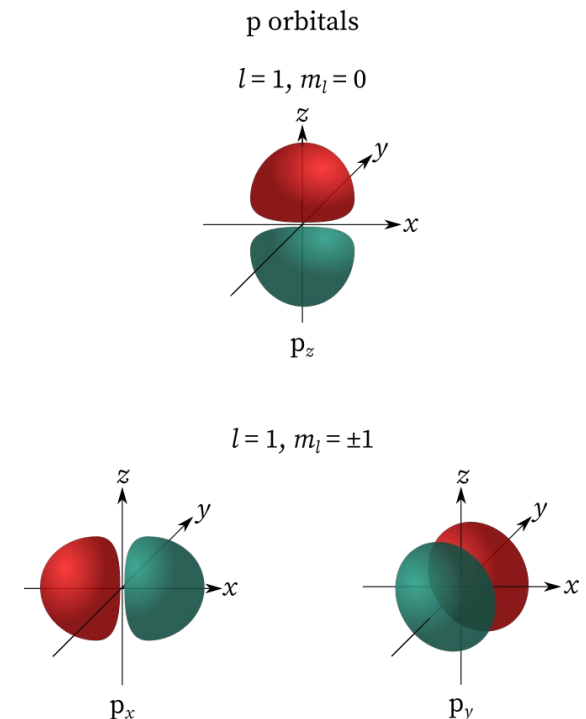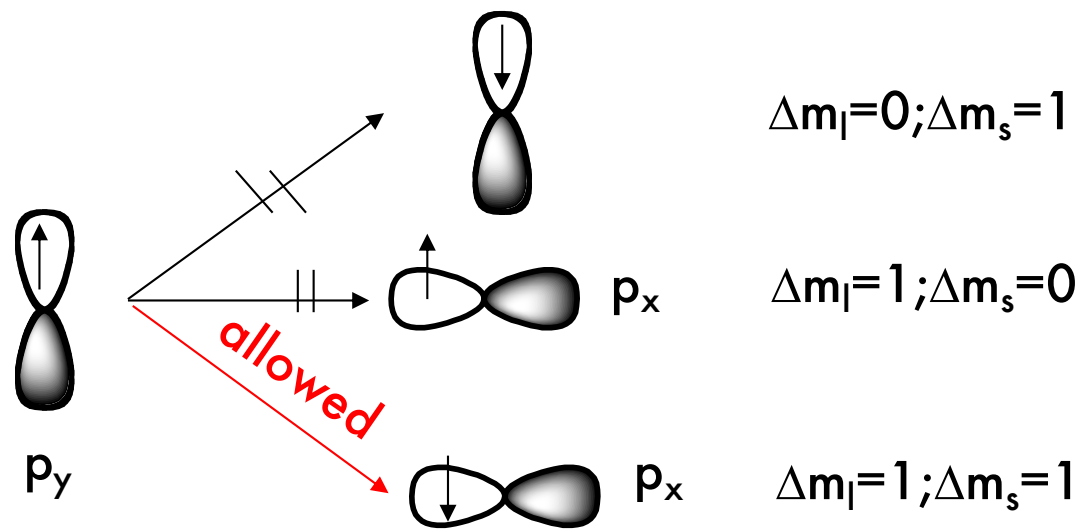
$\Delta m_l = 0; \Delta m_s = 1$

p_x $\Delta m_l = 1; \Delta m_s = 0$

allowed

p_x $\Delta m_l = 1; \Delta m_s = 1$

p_y

p orbitals

$l = 1,\ m_l = 0$

p_z

$l = 1,\ m_l = \pm 1$

p_x p_y

Breakdown of Born-Oppenheimer Approximation
Vibronic mixing enables surface mixing

Strictly planar
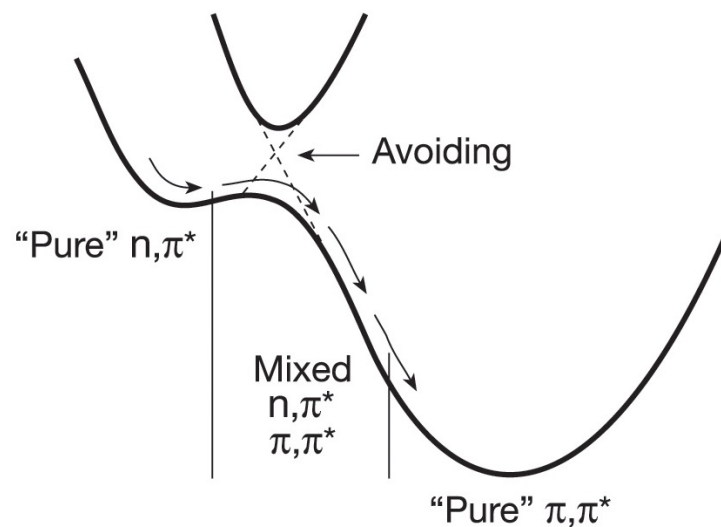
$n_0 = p_0$

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

Nonplanar

$n_0 = sp^n$

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

Zero-order n, π^*

Crossing

"Pure" n, π^*

Zero-order π, π^*

"Pure" π, π^*

Planar vibrations

Avoiding

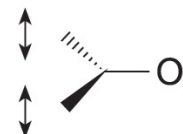"Pure" n, π^*

Mixed n, π^* π, π^*

"Pure" π, π^*
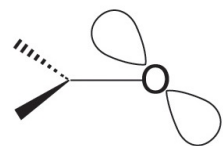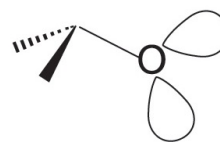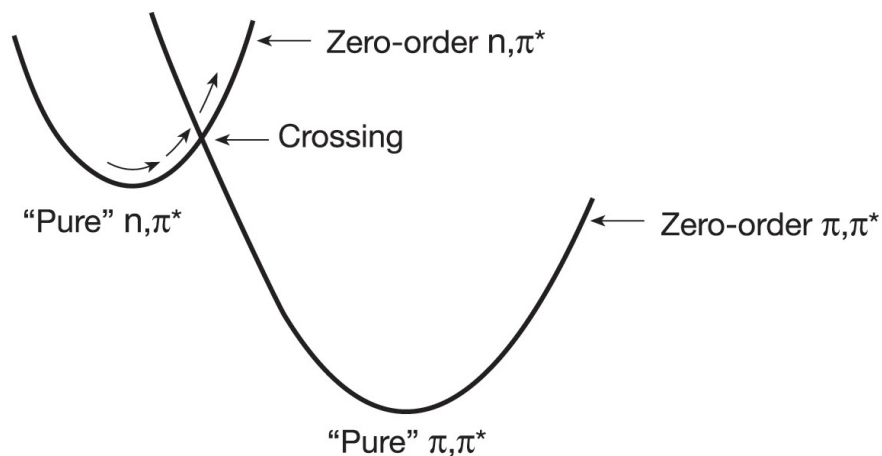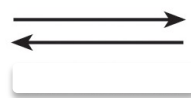
Nonplanar vibrations
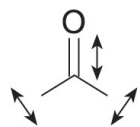
Energy is fine, but
orbitals don't overlap,
remain perpendicular

Vibronic mixing enables overlap of
n and π orbitals

Vibration and SO helps ISC

"Pure" n,π*

Avoiding

Mixed
n,π*
π,π*

"Pure" π,π*

Nonplanar vibrations

$p_x \rightarrow p_y$ ISC

$S_1 = \pi(\uparrow\downarrow)n(\uparrow)\pi^*(\downarrow) = {}^1(n,\pi^*)$

Spin–flip
allowed

ISC

$T_1 = \pi(\downarrow)n(\uparrow\downarrow)\pi^*(\downarrow) = {}^3(\pi,\pi^*)$
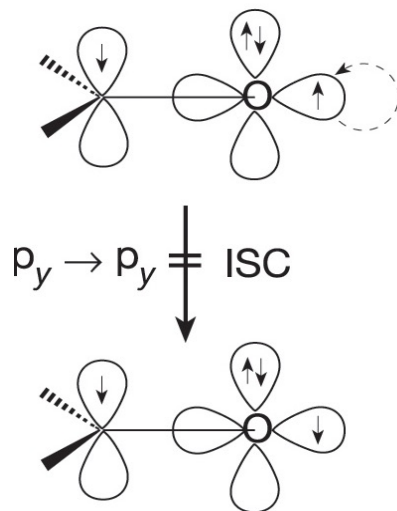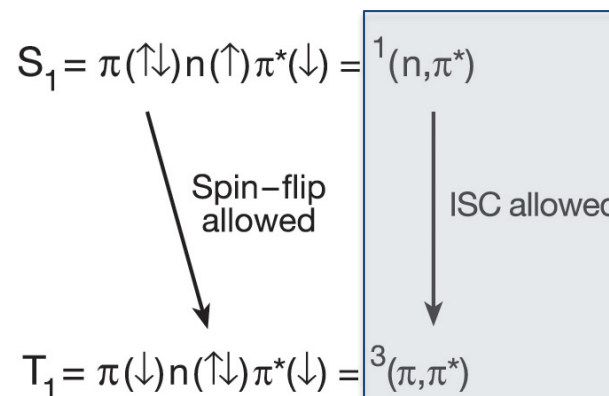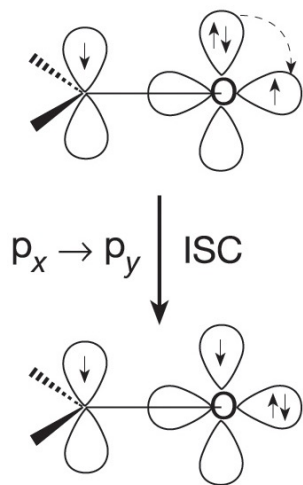
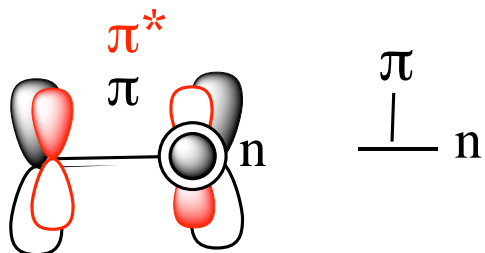Spin flip

p_x

p_y

$\Delta m_l = 1; \Delta m_s = 1$
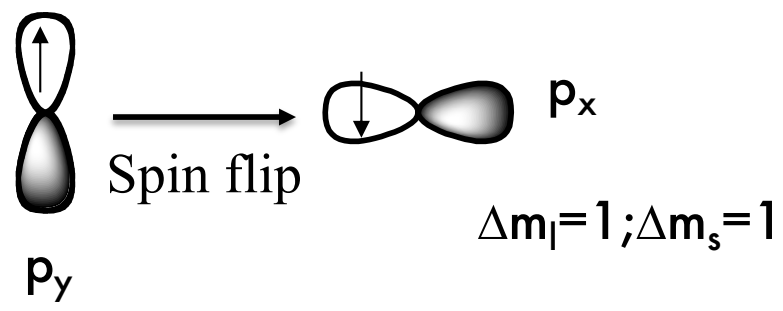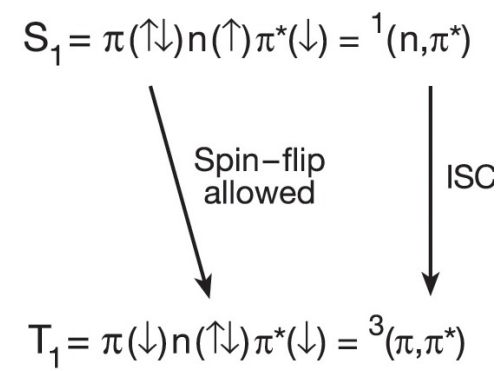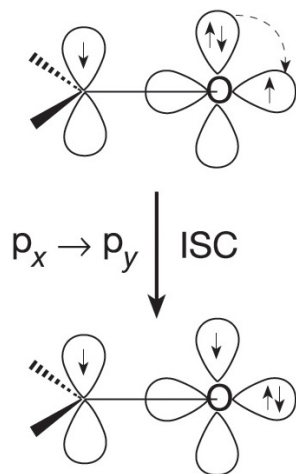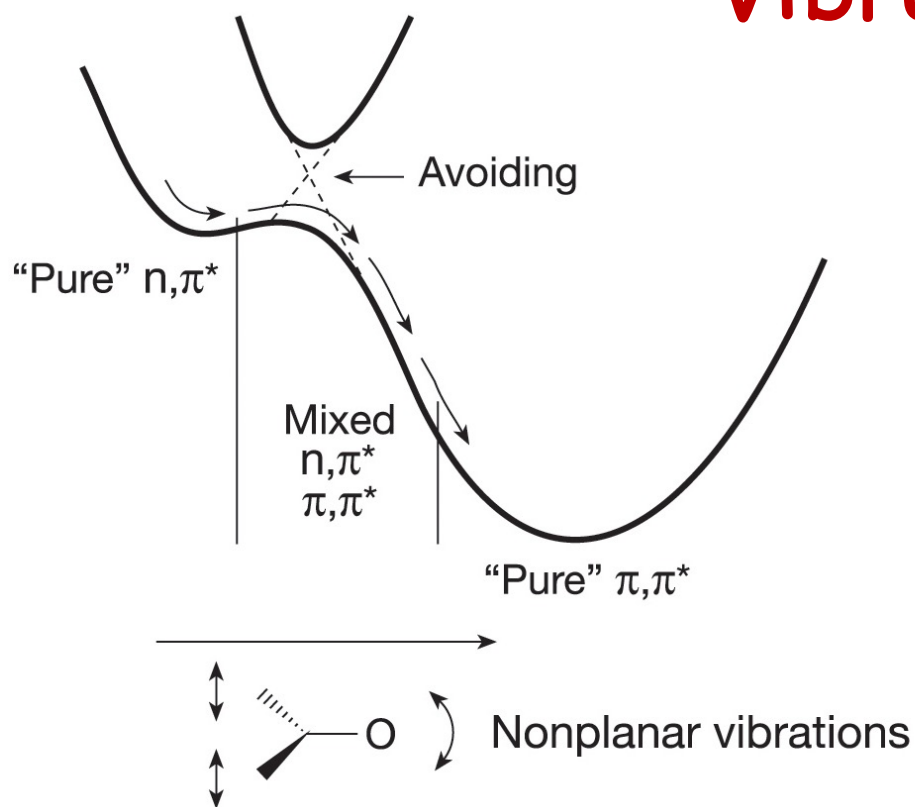
Conservation of spin and orbital angular momentum favors ISC

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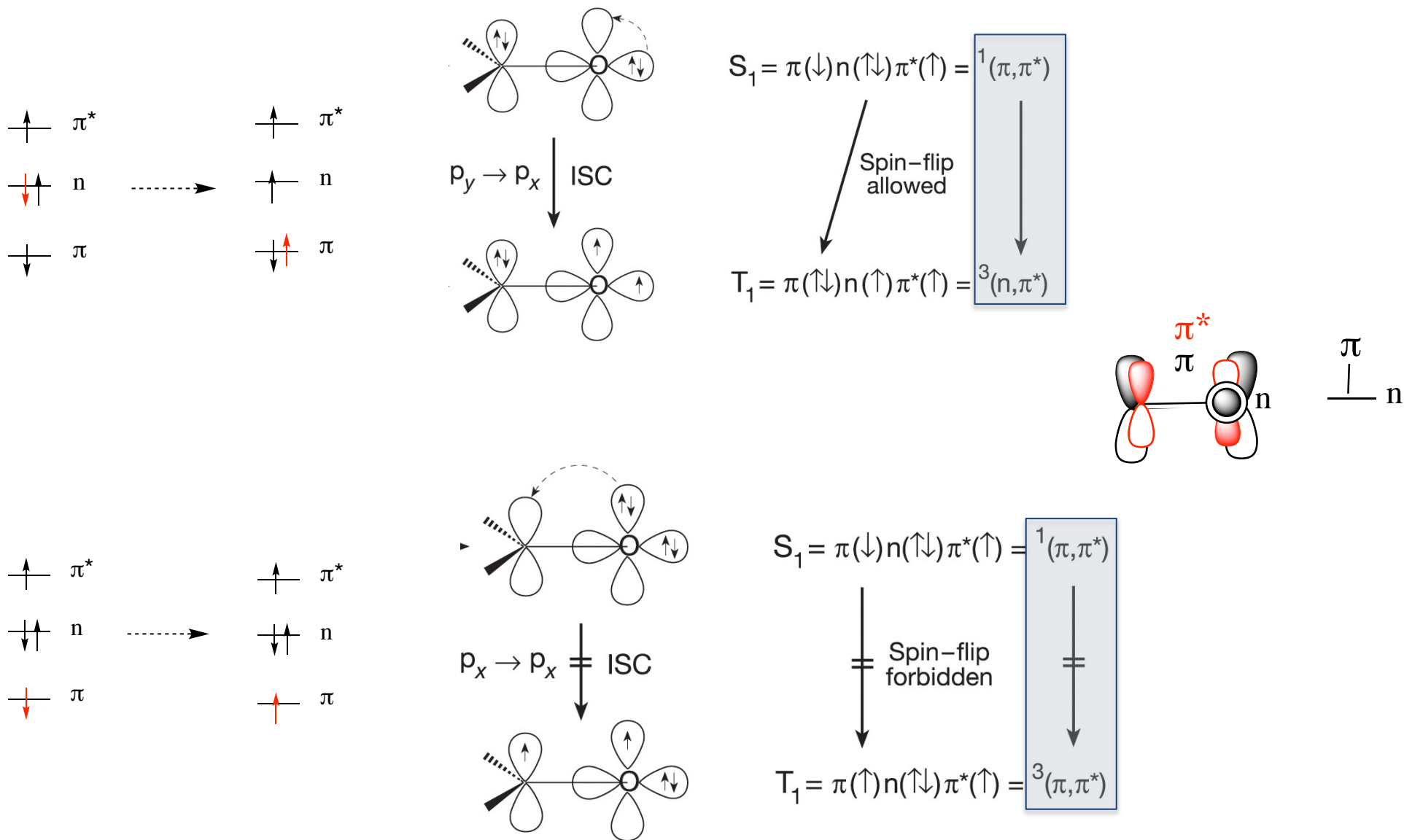
The Effect of Spin-Orbit Coupling on Intersystem Crossing from $S_1 (n\pi^*)$ to T_1

π^*
π

π
___ n

n

$S_1 = \pi(\uparrow\downarrow)\,n(\uparrow)\,\pi^*(\downarrow) = {}^1(n,\pi^*)$

$p_x \rightarrow p_y$ | ISC

Spin–flip allowed

ISC allowed

$T_1 = \pi(\downarrow)\,n(\uparrow\downarrow)\,\pi^*(\downarrow) = {}^3(\pi,\pi^*)$

$S_1 = n(\uparrow)\,\pi^*(\downarrow) = {}^1(n,\pi^*)$

$p_y \rightarrow p_y$ ≠ ISC

Spin–flip forbidden

ISC forbidden

$T_1 = n(\downarrow)\,\pi^*(\downarrow) = {}^3(n,\pi^*)$
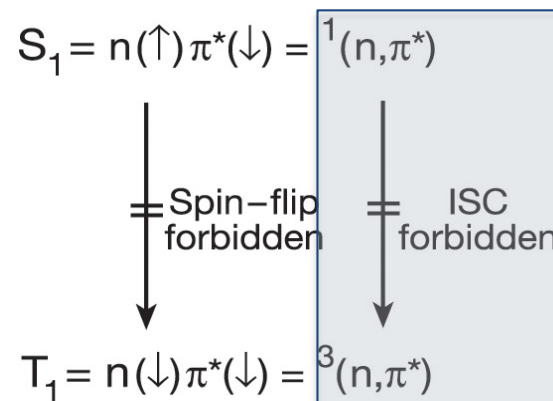
El-Sayed's Rule

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

$T_1 \rightarrow S_0$ Transitions

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

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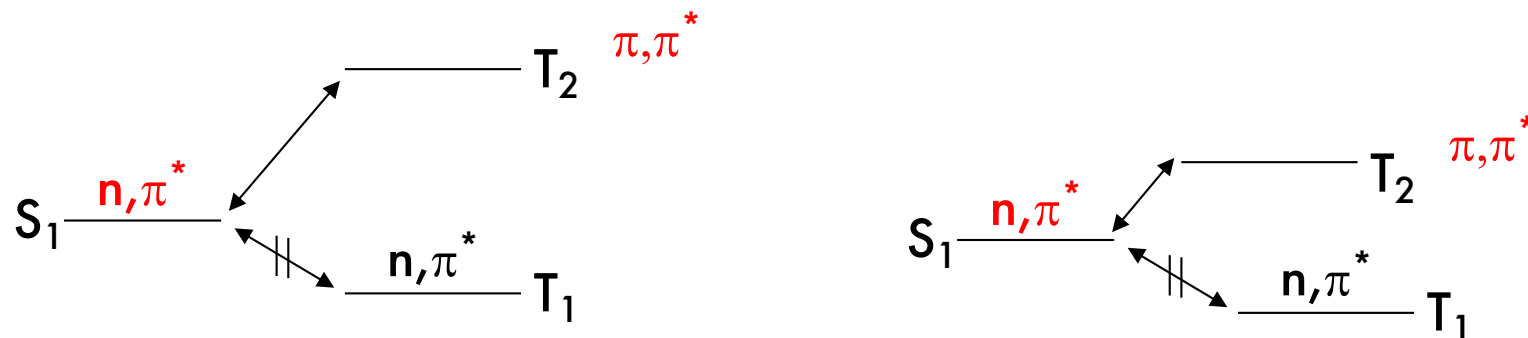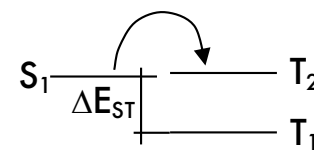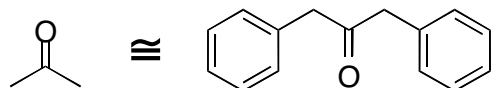

Thus, the ISC crossing rate depends whether or not it is allowed and on the energy gaps involved.
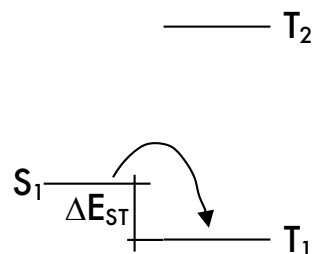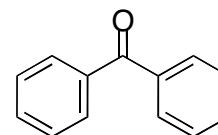

$k_{ST}=10^8 s^{-1}$
$\Delta E_{ST} = 5 Kcal/mol$

$k_{ST}=10^{11} s^{-1}$
$\Delta E_{ST} = 5 Kcal/mol$
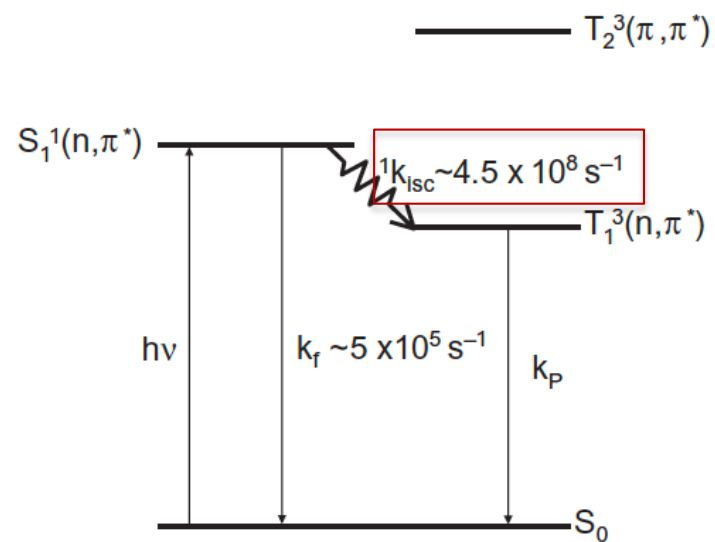
Figure 5.5 State diagram for acetone. Notice that intersystem crossing occurs between (n,π^*) states
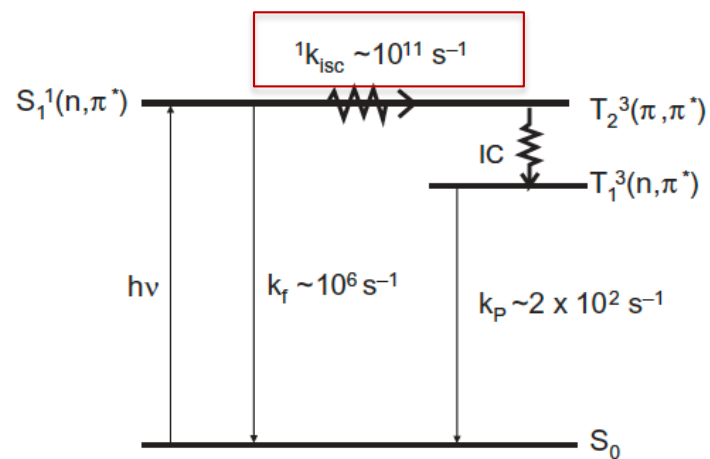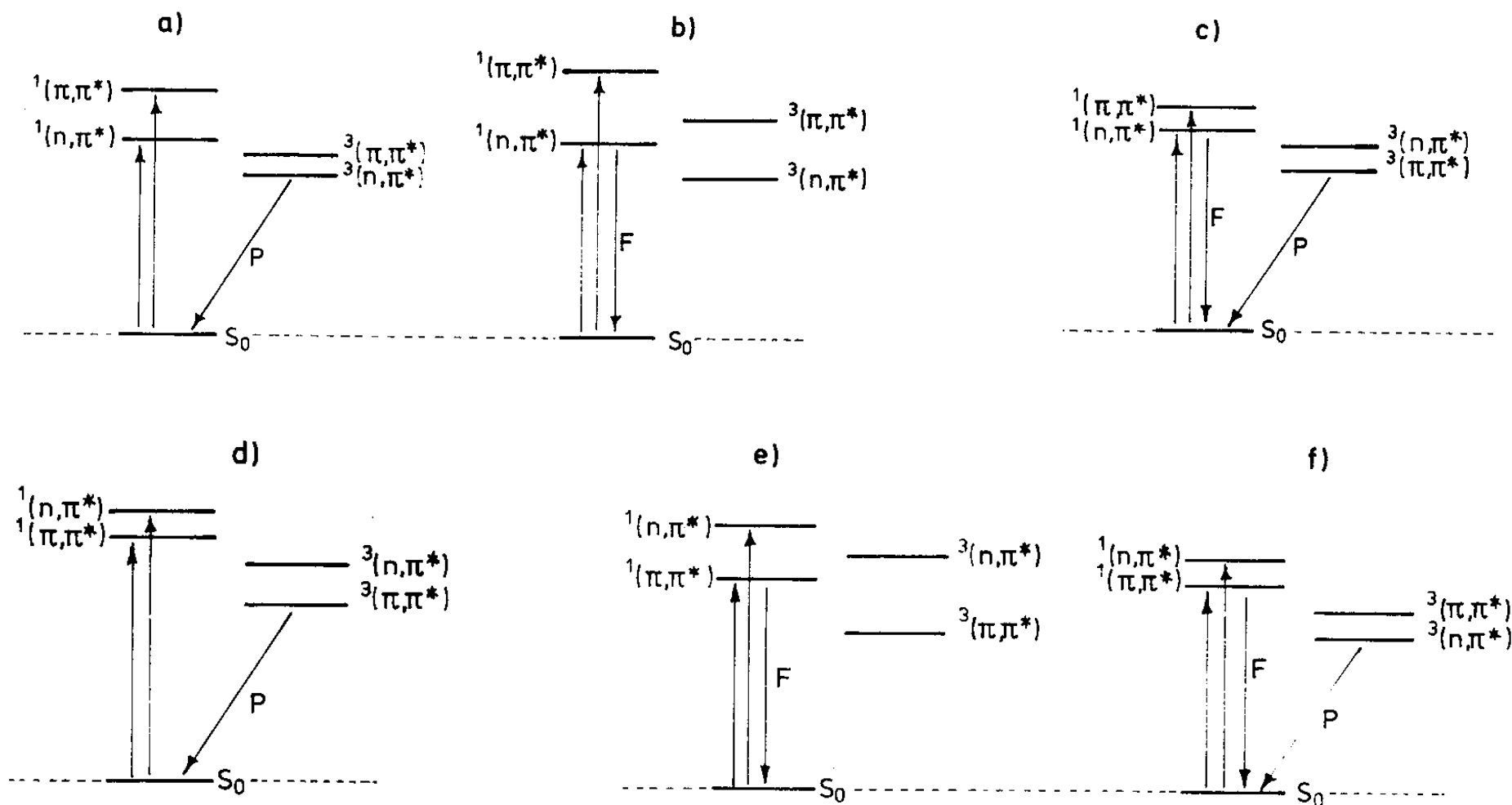

Figure 5.6 State diagram for benzophenone. Here intersystem crossing involves a change in orbital type
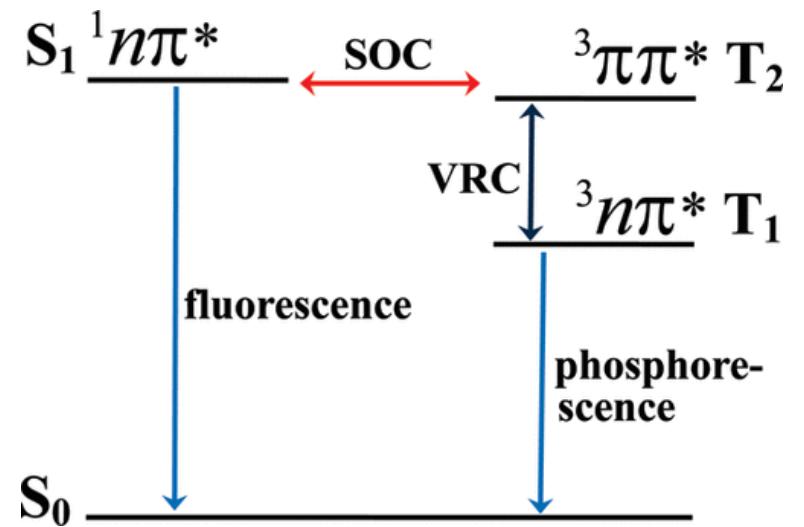
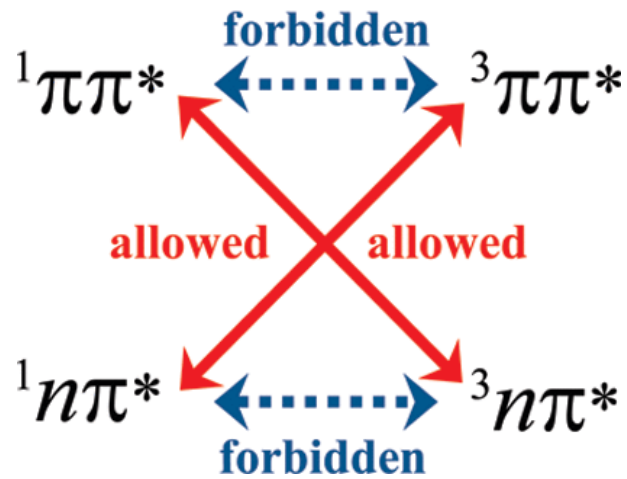# El-Sayed's Rule

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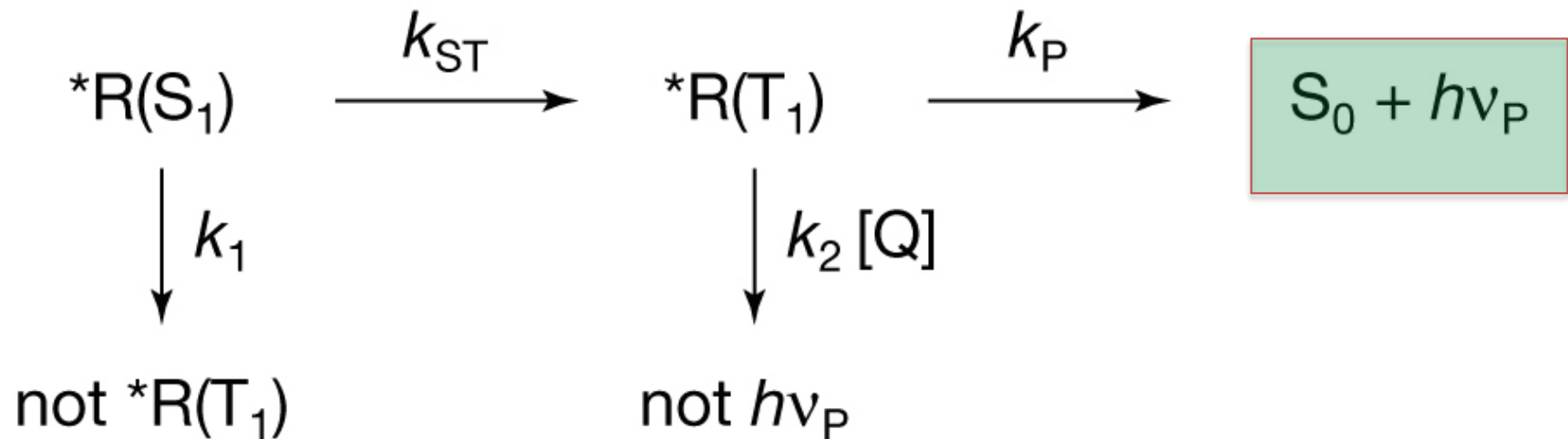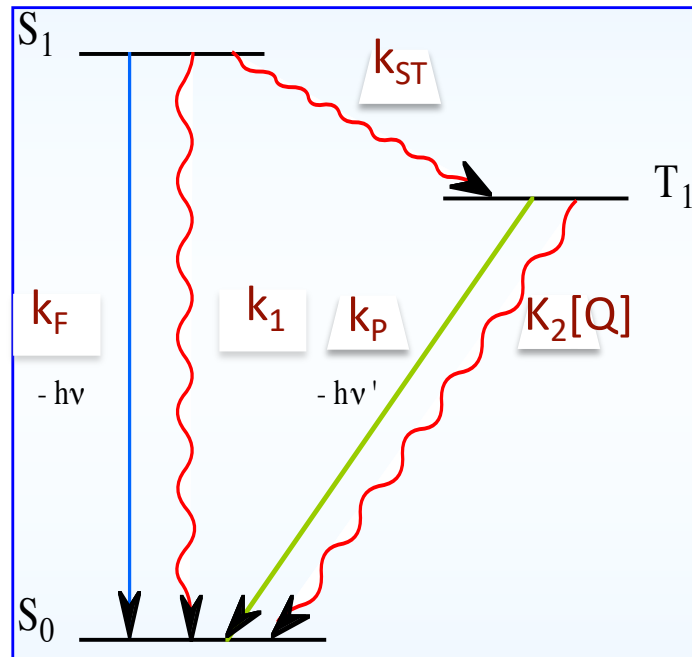
Summary

Room Temperature Phosphorescence

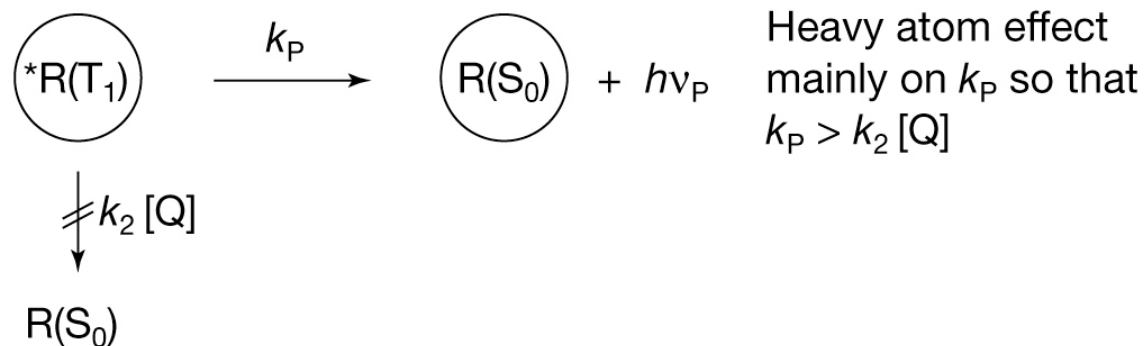$$*R(S_1) \xrightarrow{\quad k_{ST} \quad} *R(T_1) \xrightarrow{\quad k_P \quad} \boxed{S_0 + h\nu_P}$$

$$*R(S_1) \downarrow k_1$$

$$*R(T_1) \downarrow k_2[Q]$$

not $*R(T_1)$

not $h\nu_P$

Strategy to record phosphorescence at room temperature through supramolecular approach

Stage 1

$$*R(S_1) \xrightarrow{\ k_{ST}\ } *R(T_1)$$

$$*R(S_1) \xmapsto{\ k_1\ } R(S_0)$$

Heavy atom effect mainly on k_{ST} so that $k_{ST} > k_1$

Make more triplets through the heavy atom effect

Stage 2

$$*R(T_1) \xrightarrow{\ k_P\ } R(S_0) + h\nu_P$$

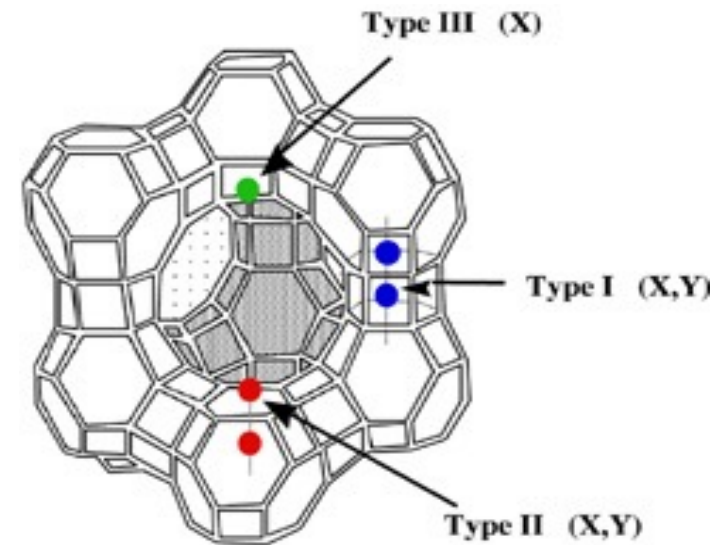$$*R(T_1) \xmapsto{\ k_2\,[Q]\ } R(S_0)$$

Heavy atom effect mainly on k_P so that $k_P > k_2\,[Q]$

Make triplets emit faster in competition with quenching processes

Crown ethers, micelles and zeolites contain cations

Water

Type III (X)

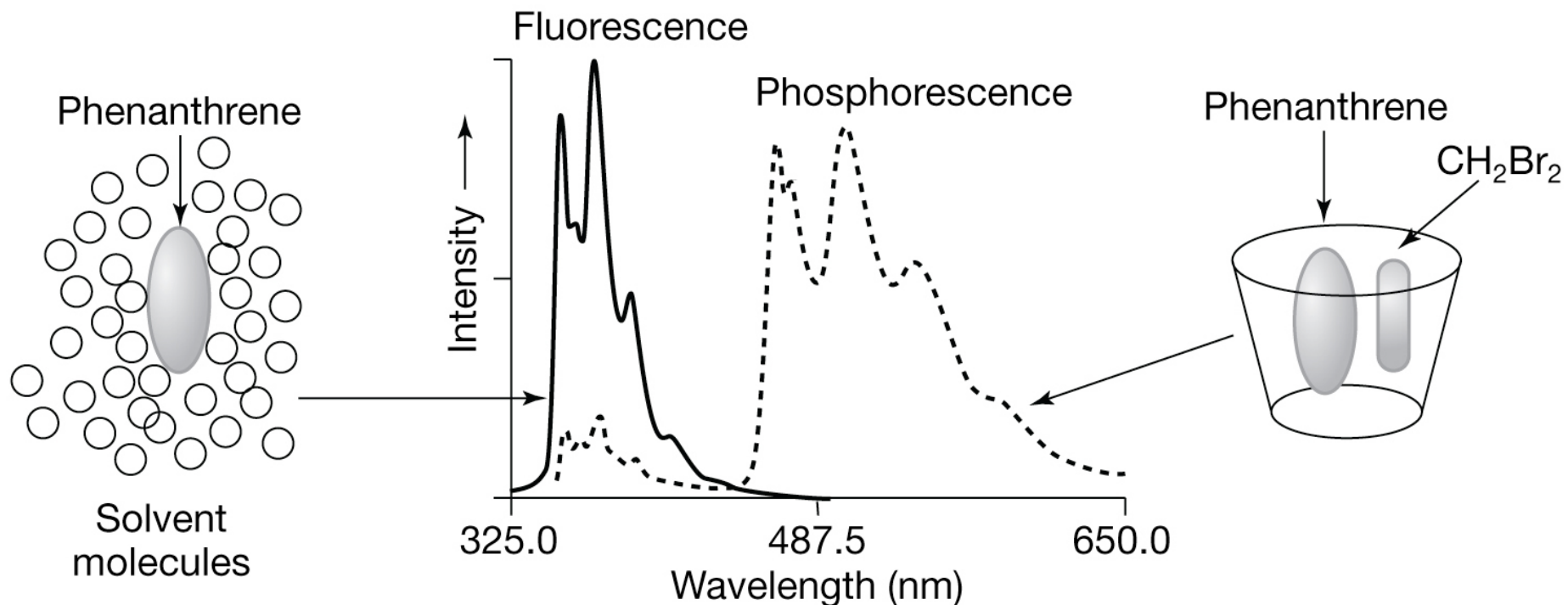Type I (X,Y)

Type II (X,Y)
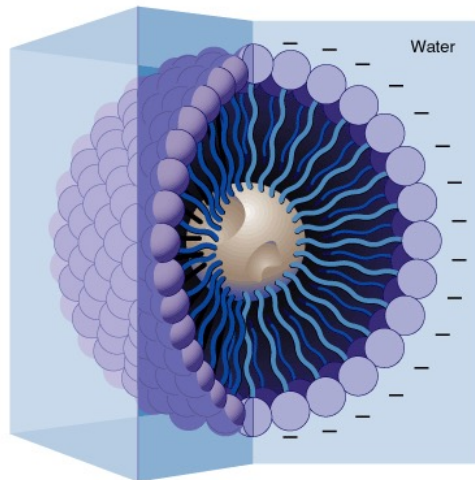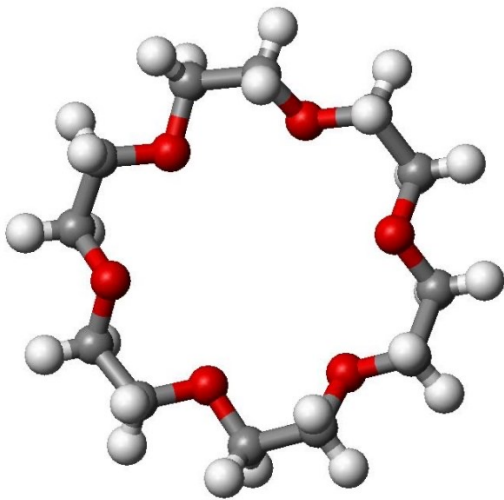
Cyclodextrins as hosts

Phenanthrene@Cyclodextrin: effect of CH_2Br_2 as co-guest

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

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

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 1.00×10^{-4} F)
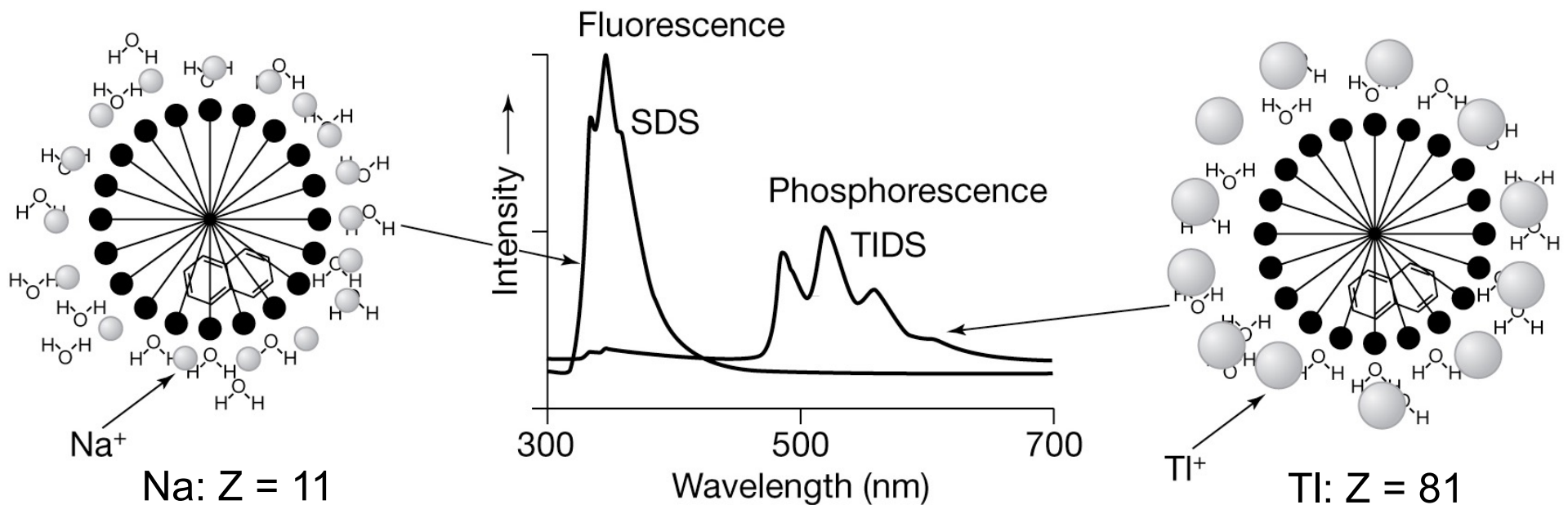
Salt added	$10^{-6}k_f$	$10^{-6}k_{nr}$	$10^2 k_p{}^d$	$k_{dt}{}^d$
None	3.1	25	8.7	0.37
NaCl	2.6	32	6.7	0.41
KCl	2.3	35	5.8	0.39
RbCl	1[e]	52	12.	0.50
CsCl	1[e]	670	81.	1.57
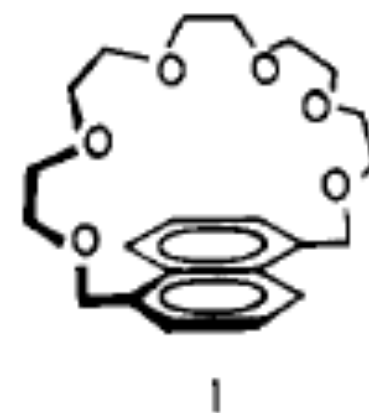
[a] All rate constants in s^{-1}. [b] $k_f = \phi_f \tau_f^{-1}$; $k_{nr} = (1 - \phi_f)\tau_f^{-1}$; $k_p = \phi_p(1 - \phi_f)^{-1}\tau_p^{-1}$; $k_{dt} = \tau_p^{-1} - k_p$. [c] See note 4. [d] With $\phi_f + \phi_{isc} = 1.0$ assumed. [e] Estimated from 77 K UV absorption spectra.
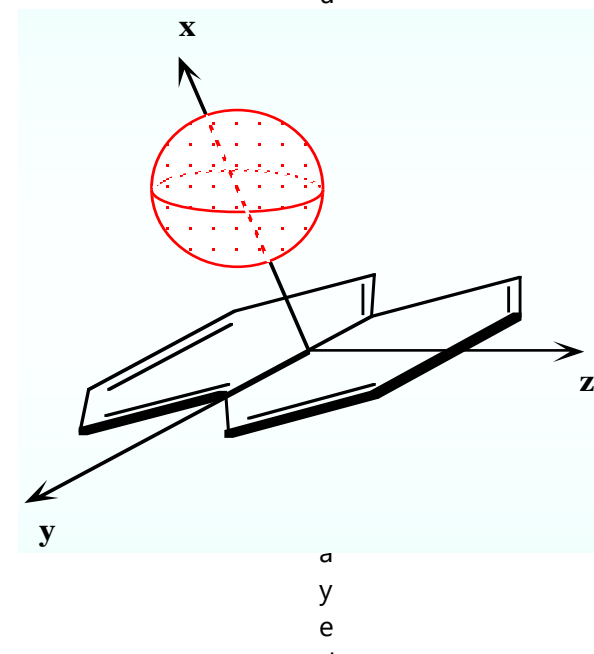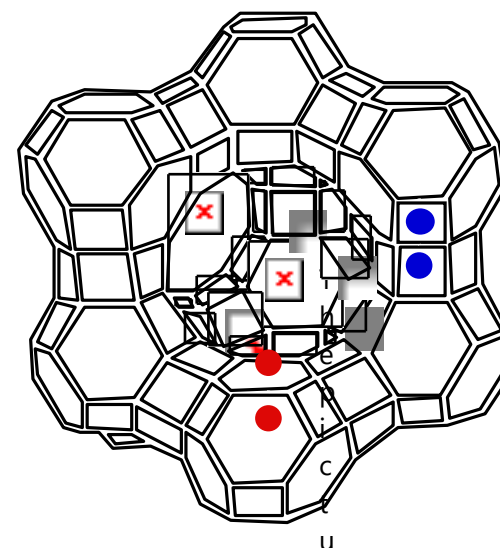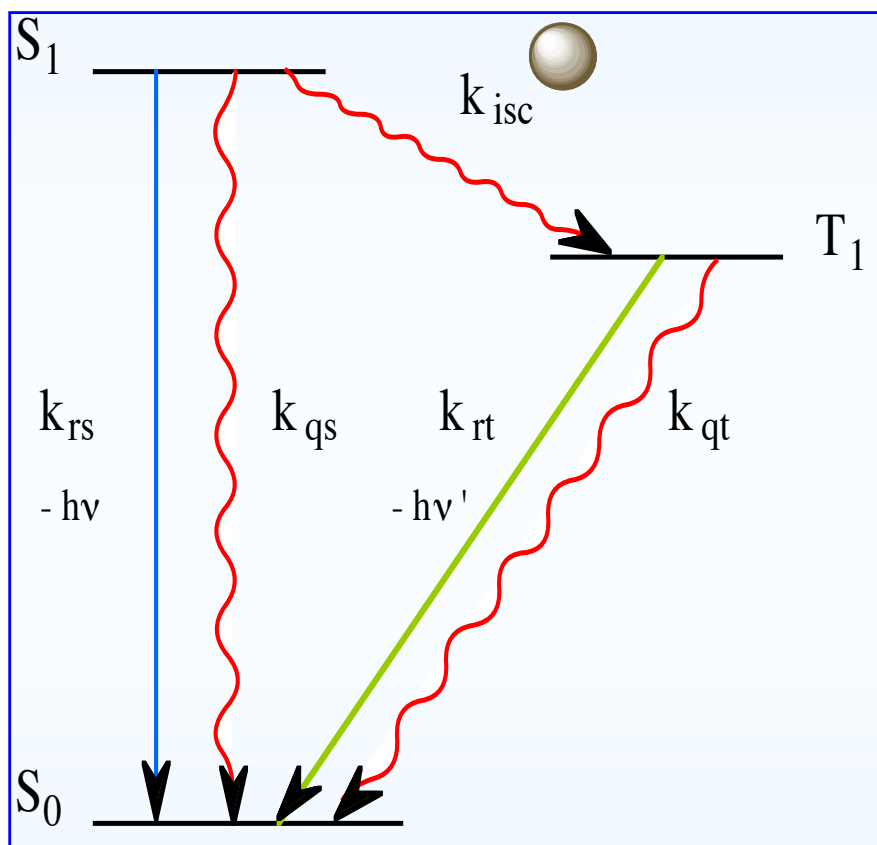

1

Micelles as hosts
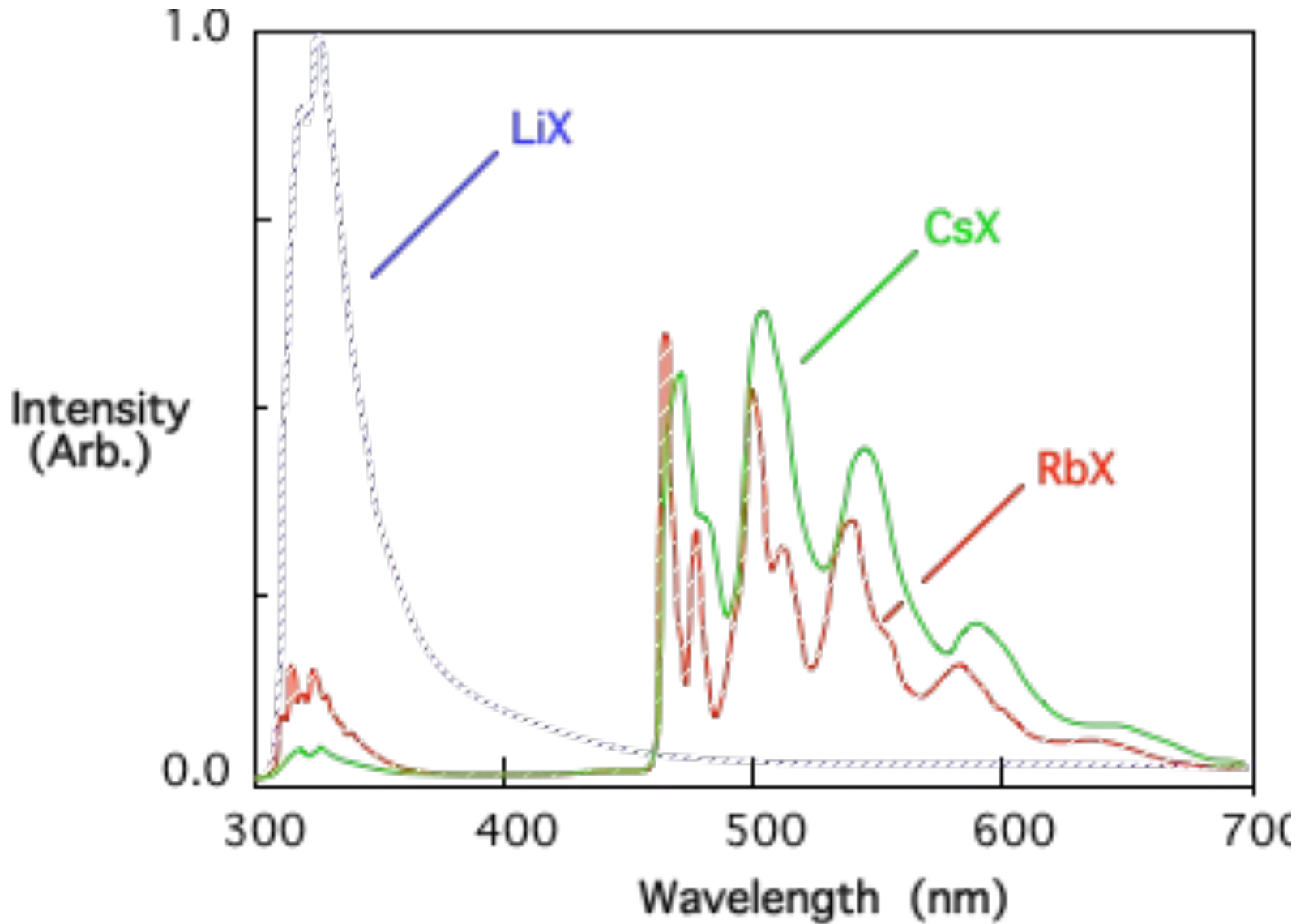
Naphthalene@SDS micelle: effect of heavy atom counterions

Na: Z = 11

Tl: Z = 81

Heavy atom produces more triplets and the triplets produced phosphoresce at a faster rate
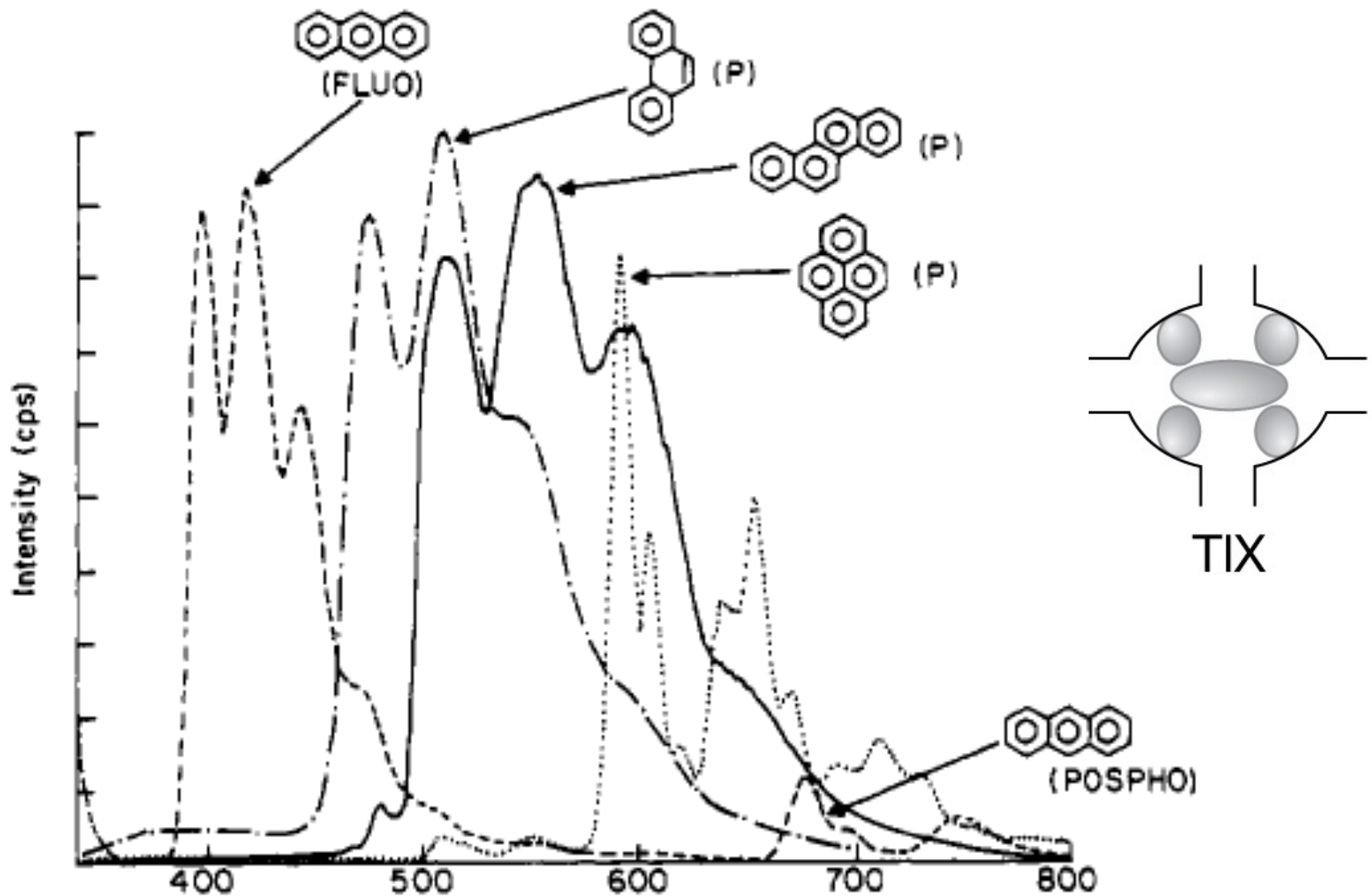
Cation Effect
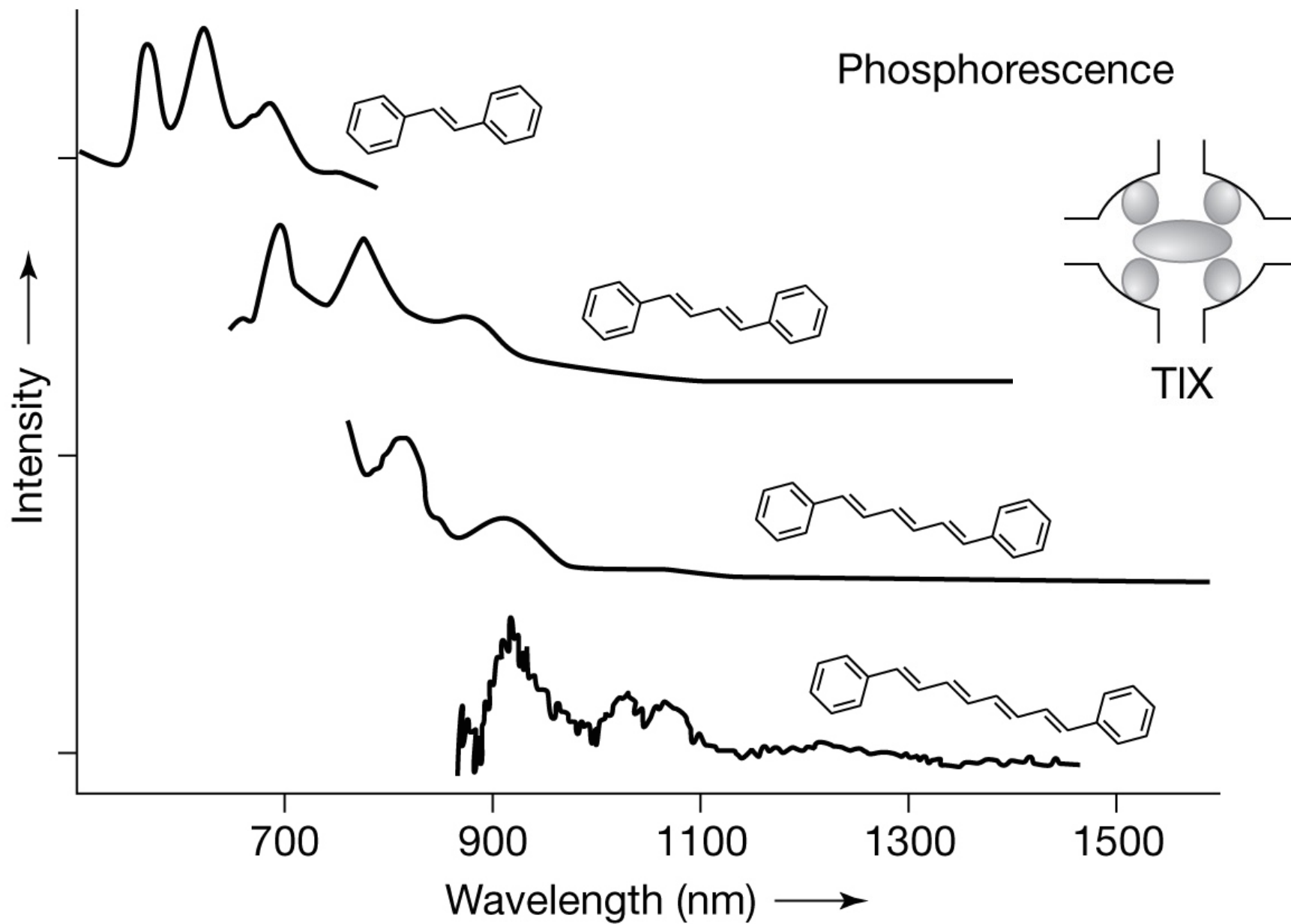# Heavy Cations Enhance the S_1 to T_1 Crossing

Emission Spectra of Naphthalene Included in MY Zeolites

Room temperature phosphorescence

Phosphorescence from Diphenyl Polyenes

Phosphorescence from Azo Compounds in TlY at 77 K nπ*–nπ* crossing

a)

b)

b)