Radiationless Transitions

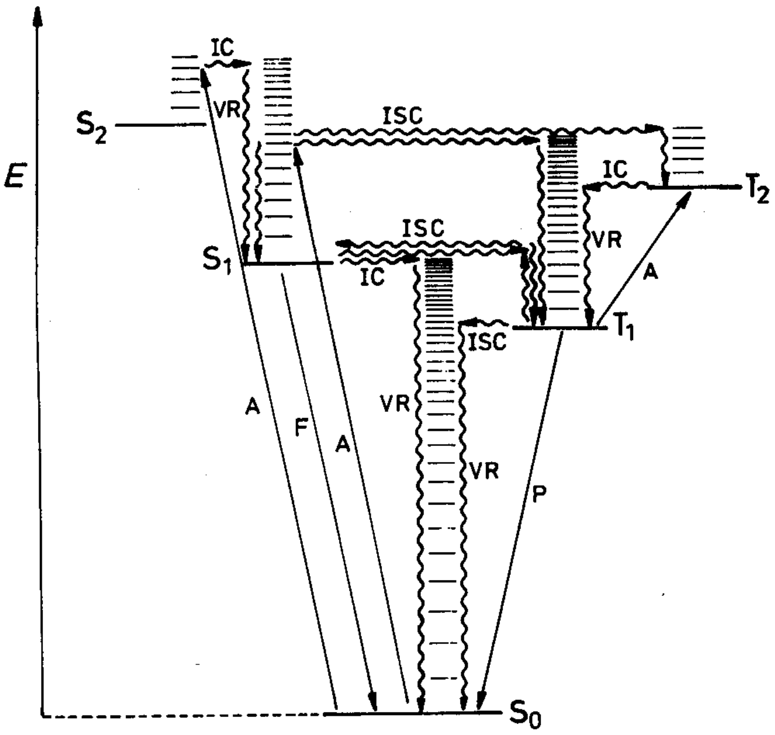
- Spin allowed
- Spin forbidden

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?

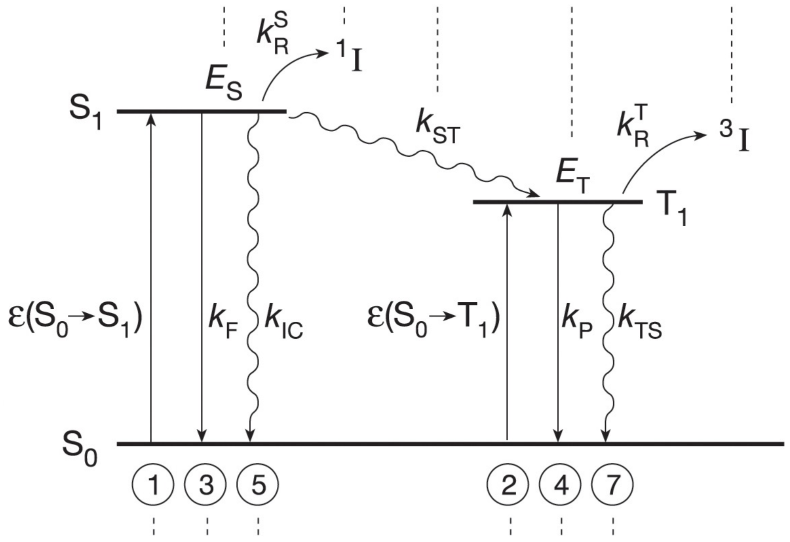
Competes with fluorescence and phosphorescence

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

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

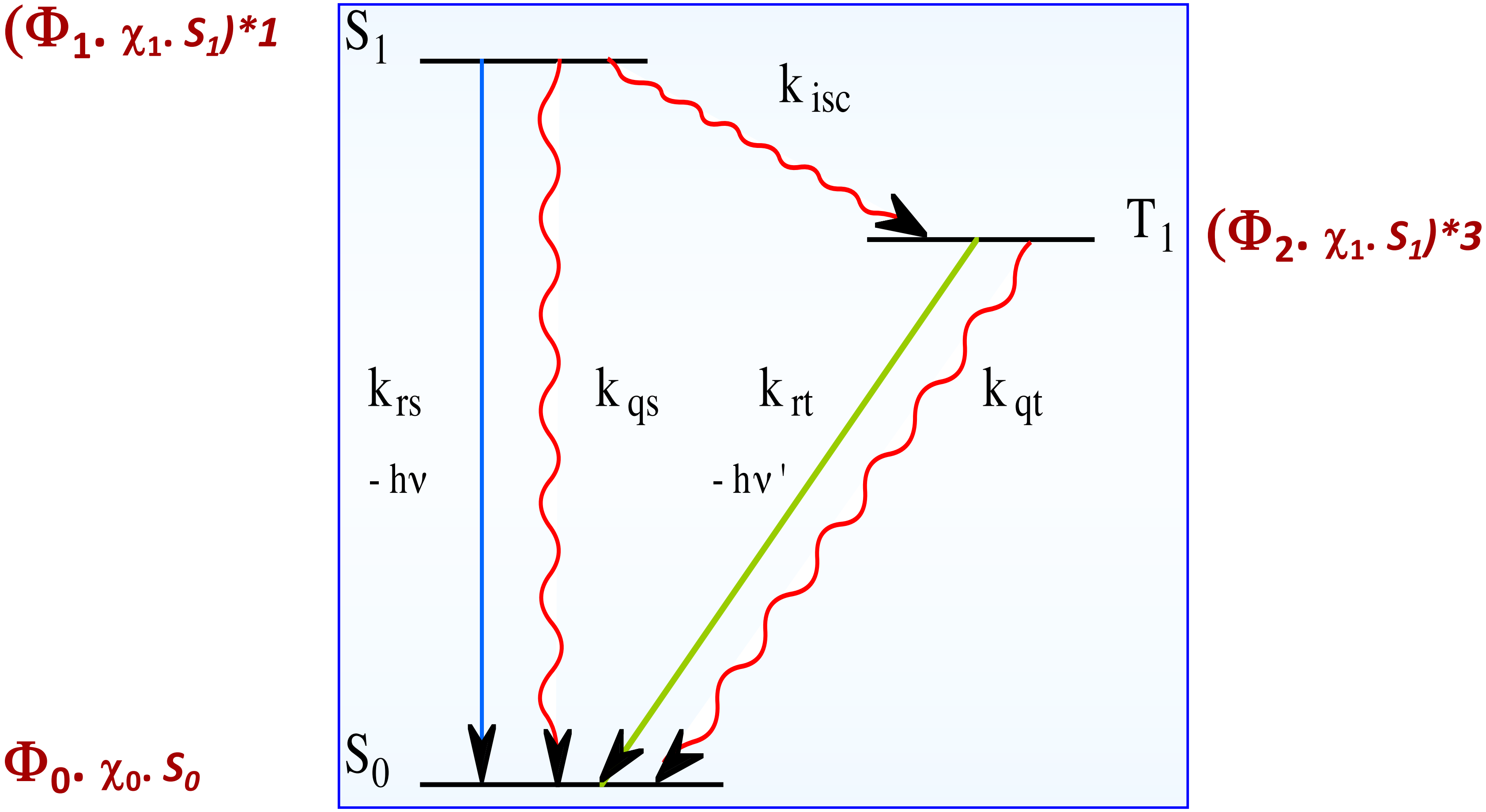
$$S_1 \xrightarrow{k_{isc}} T_1$$

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



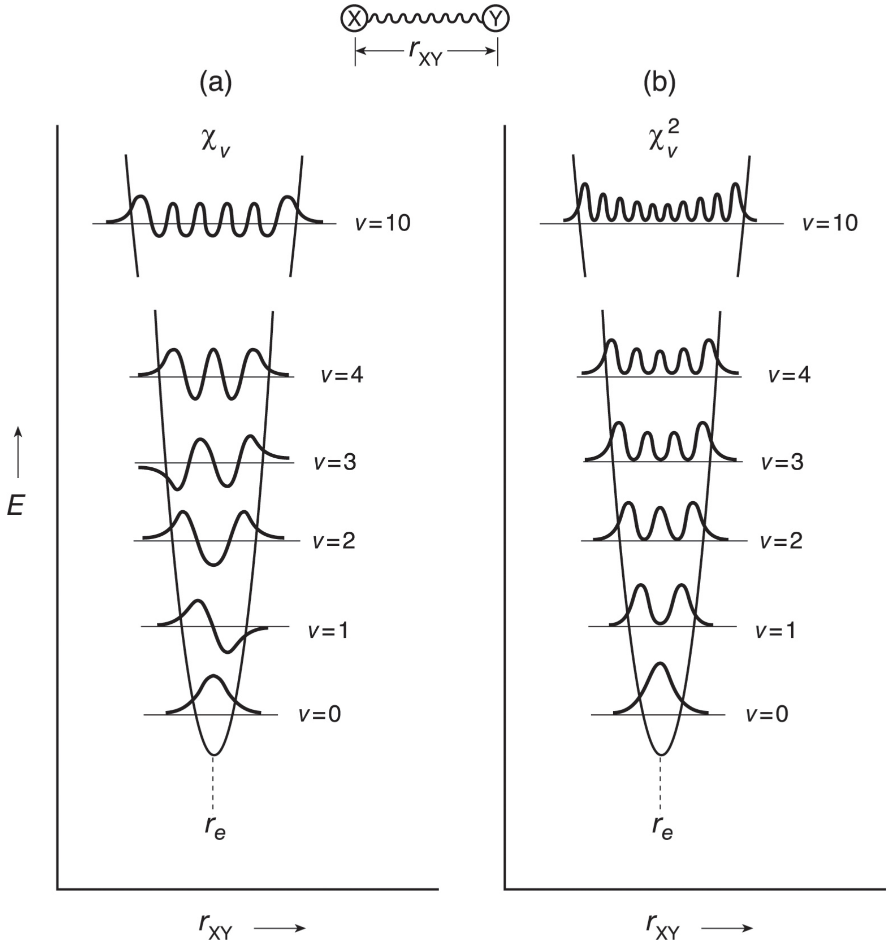
$$\phi_f = \frac{k_f[S_1]}{(k_f + k_{isc} + k_{ic} + \ldots)[S_1]}$$

Radiationless Transitions

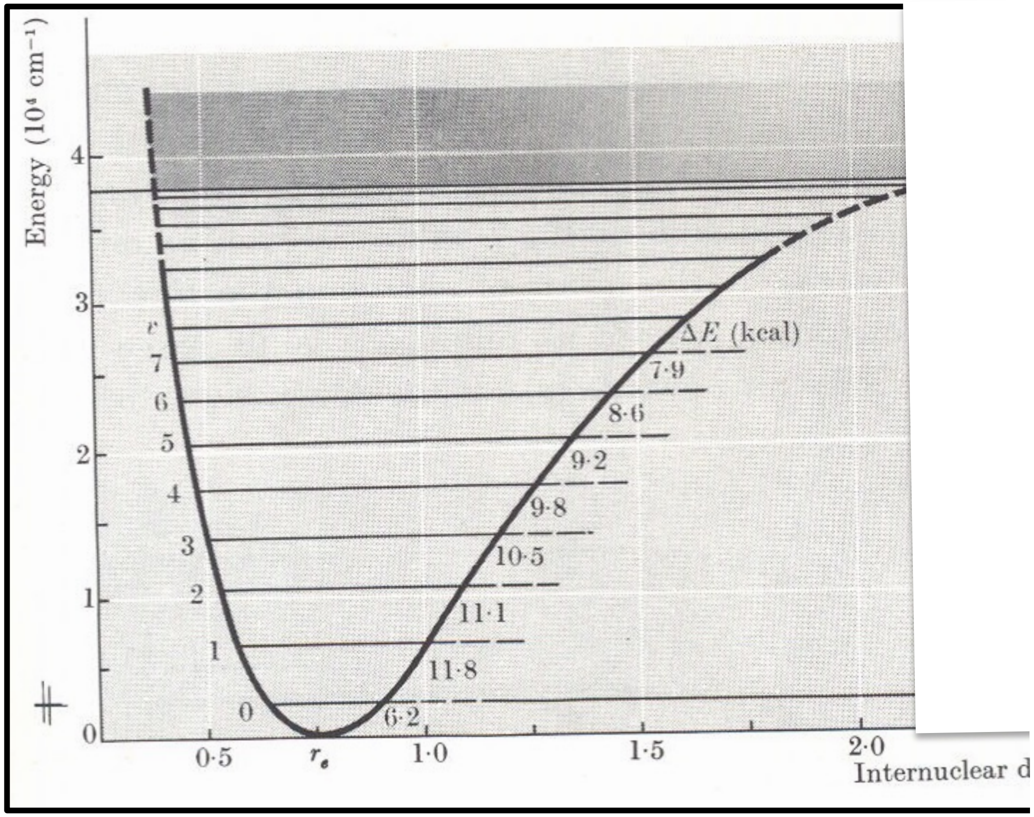


- **Changes in electronic, vibrational and spin configurations without the help of a photon**
- **Energy redistribution--electronic to vibrational**

Visualization of vibrational levels within an electronic energy surface

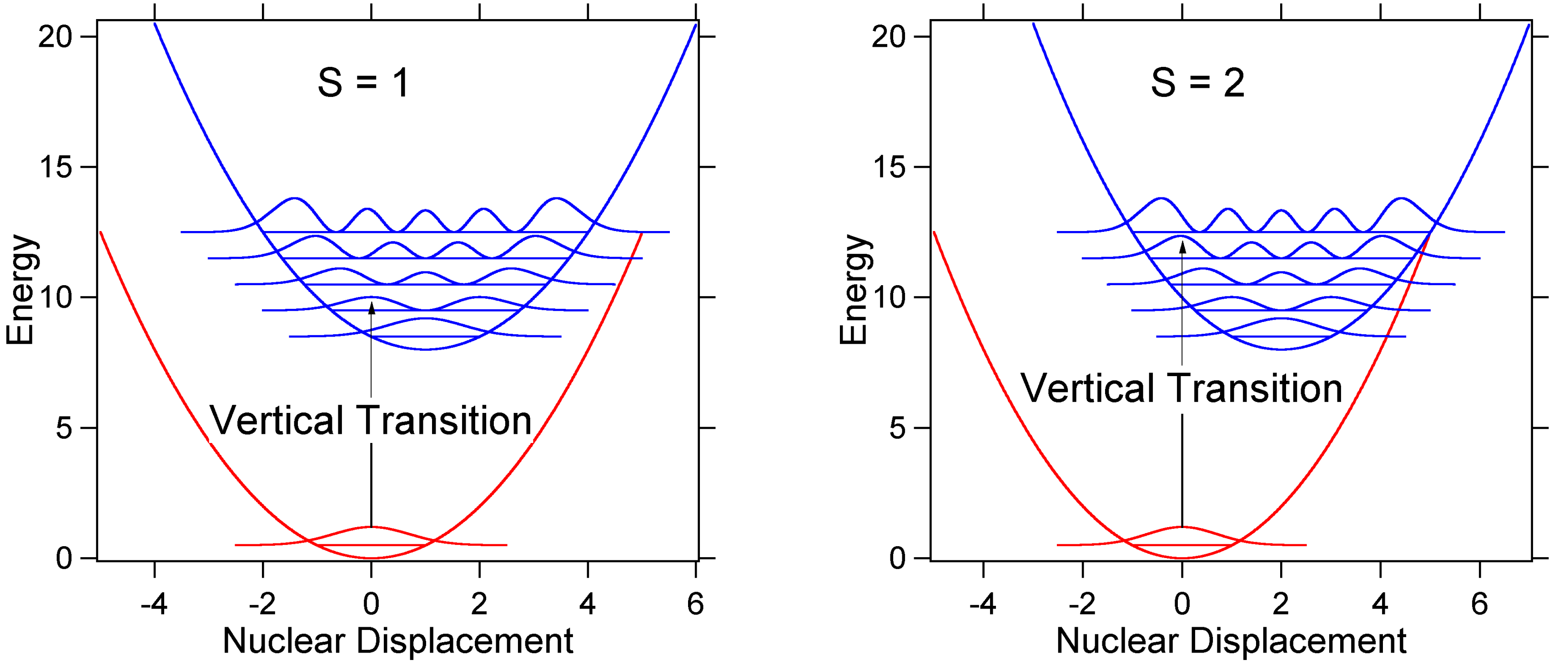


Harmonic

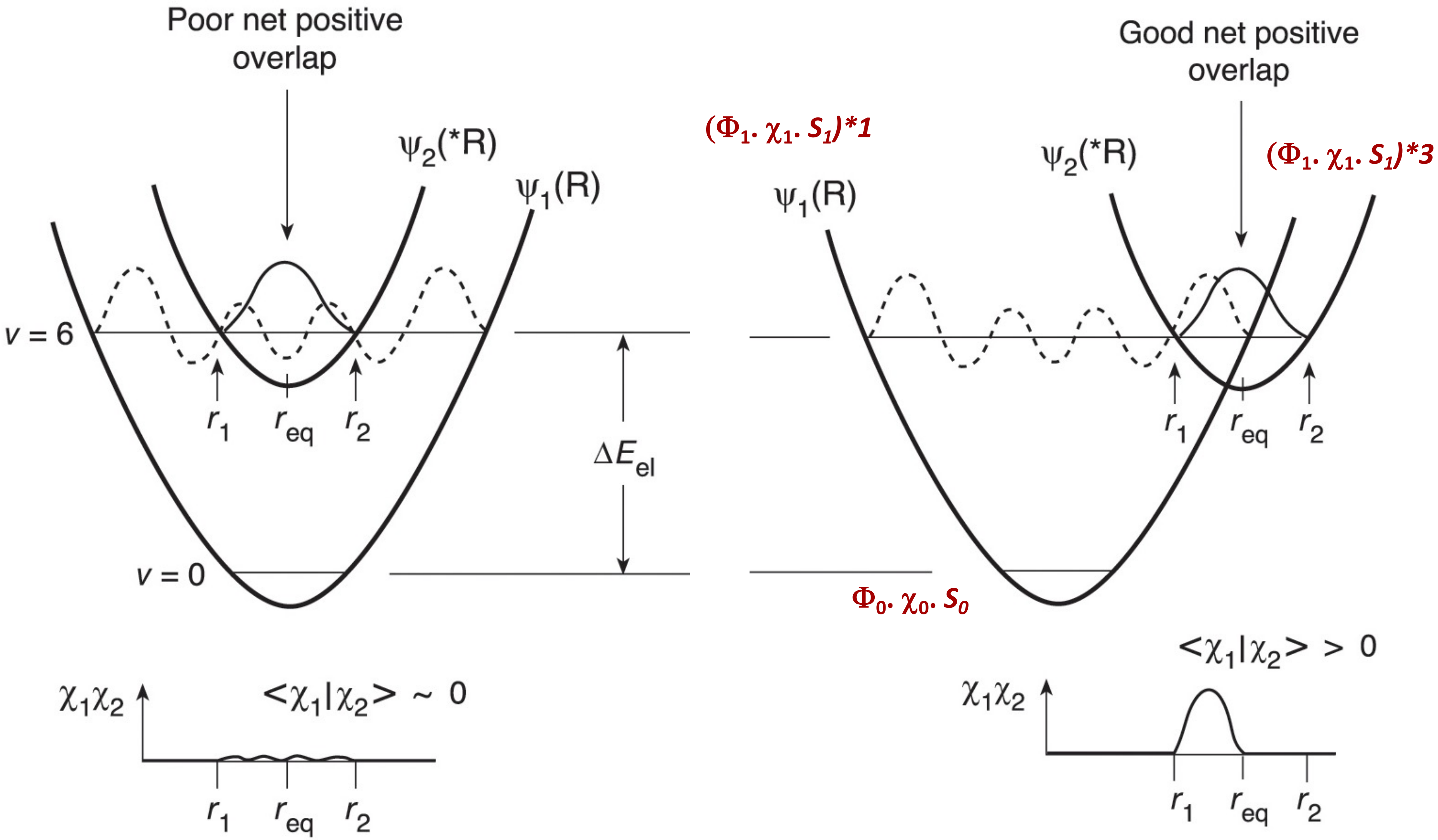


Anharmonic

Relative position of energy surfaces

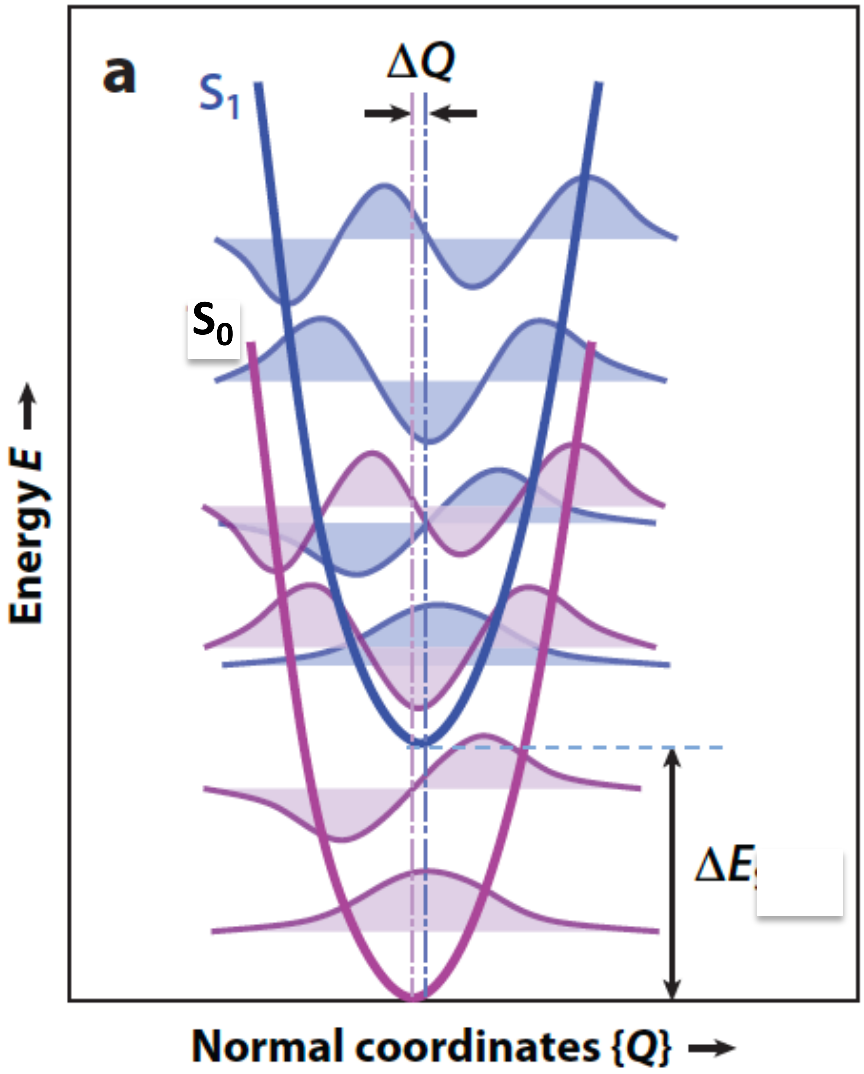


Matching *vs.* Crossing Surfaces



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

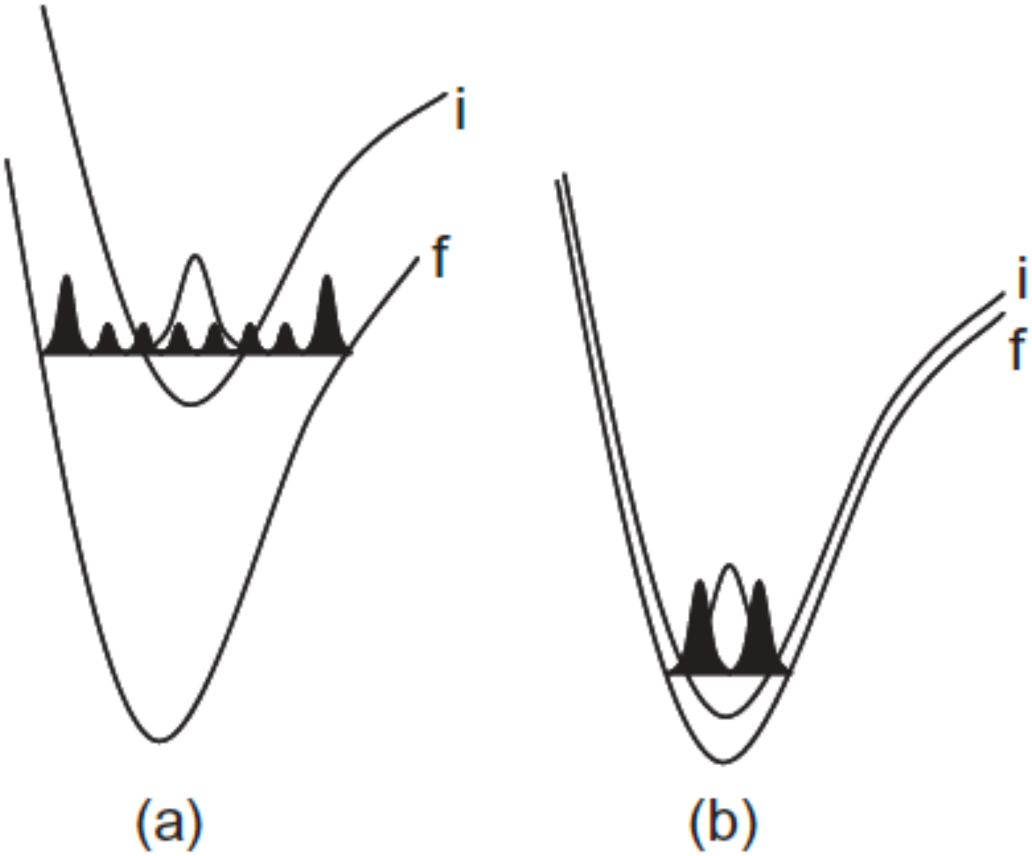
Matching surfaces (e.g., polyaromatics)



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

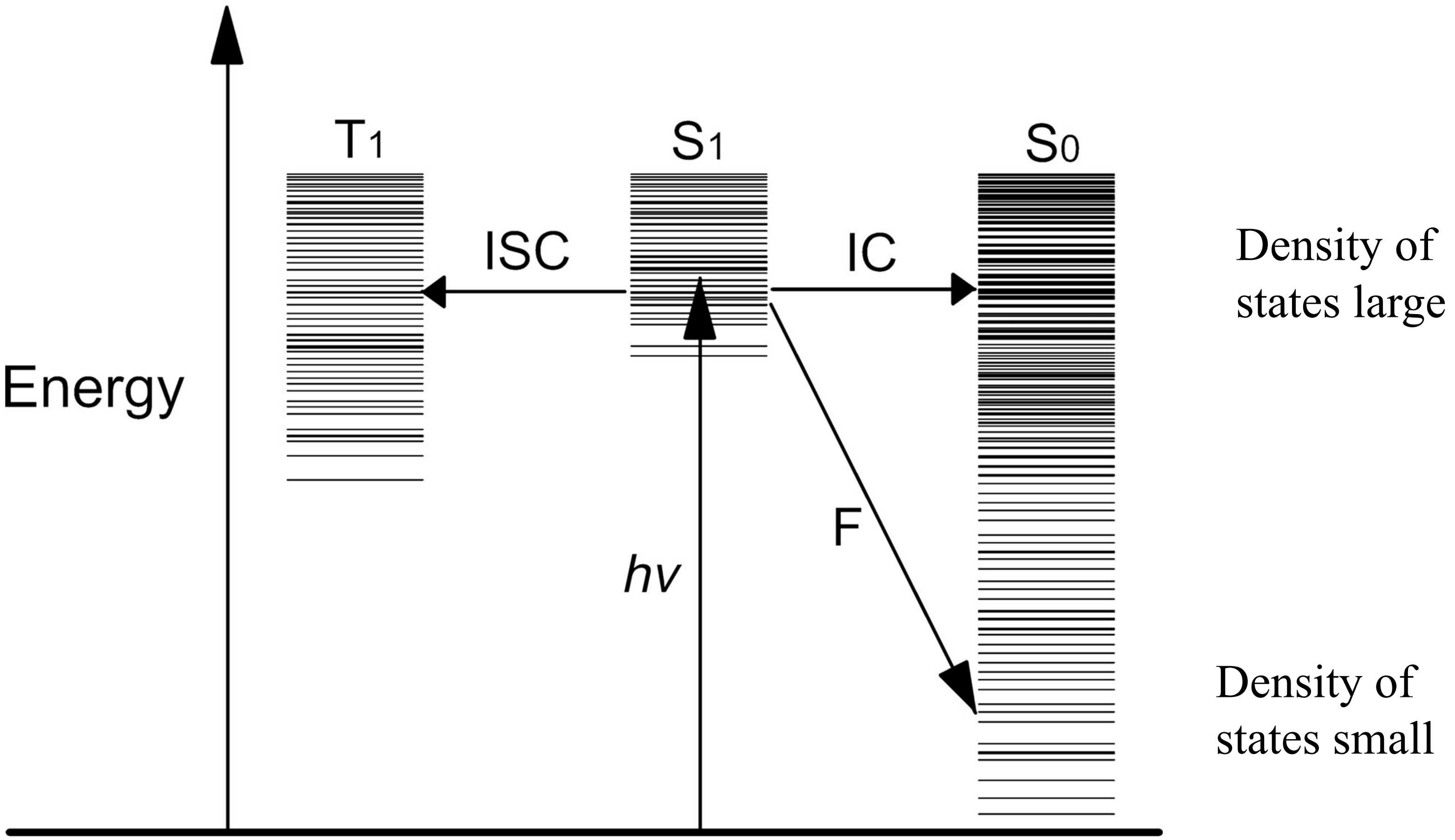
$$\boldsymbol{f \sim \exp^{-\Delta E}}$$

$$k_{IC} \sim 10^{13} f_{\nu}$$

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

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

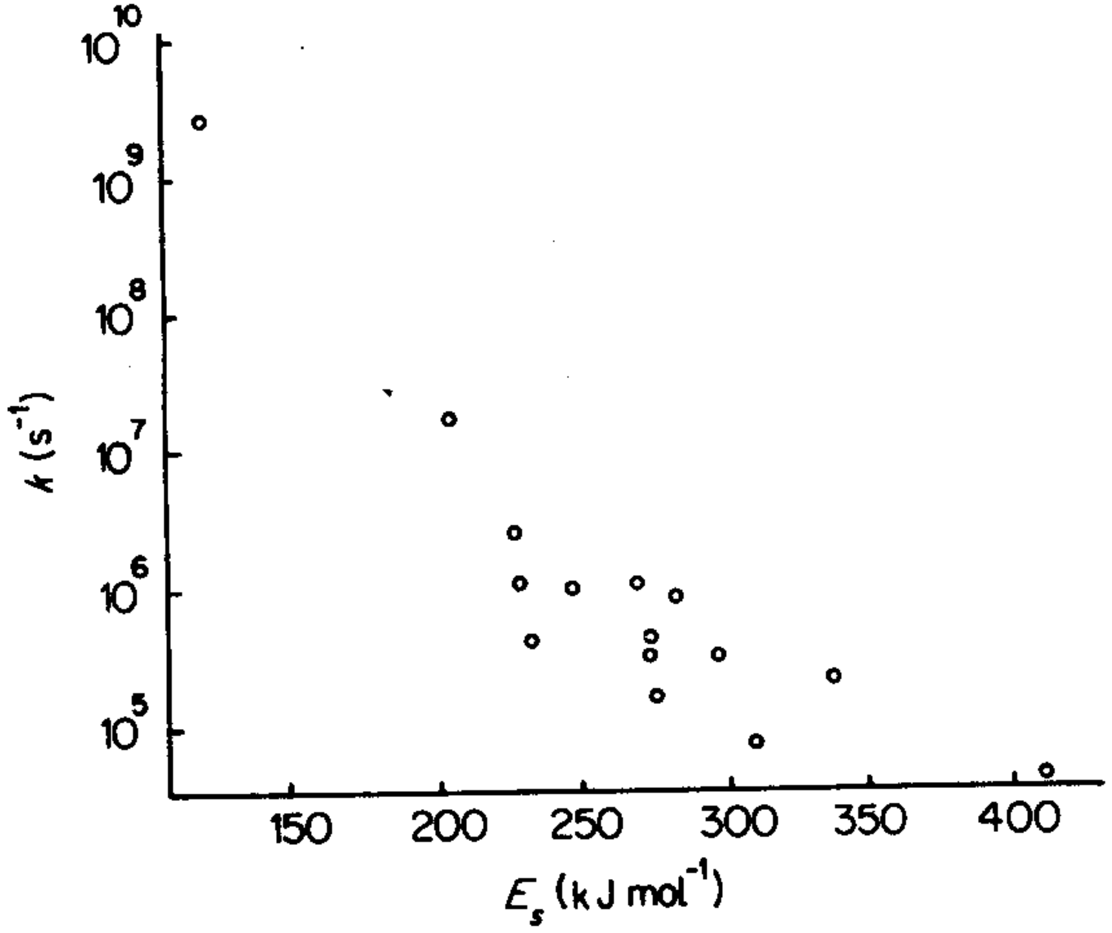
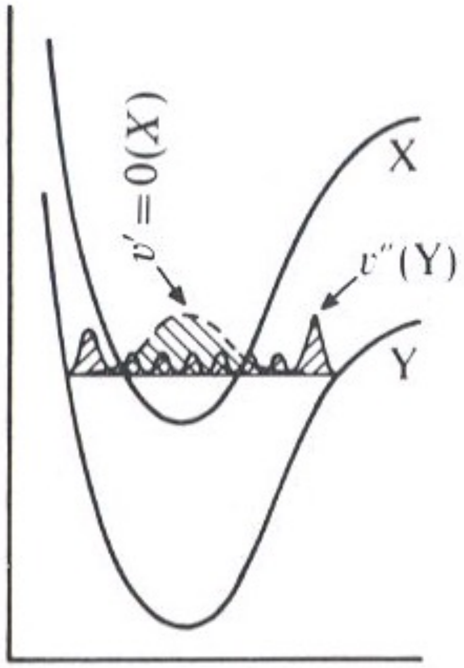
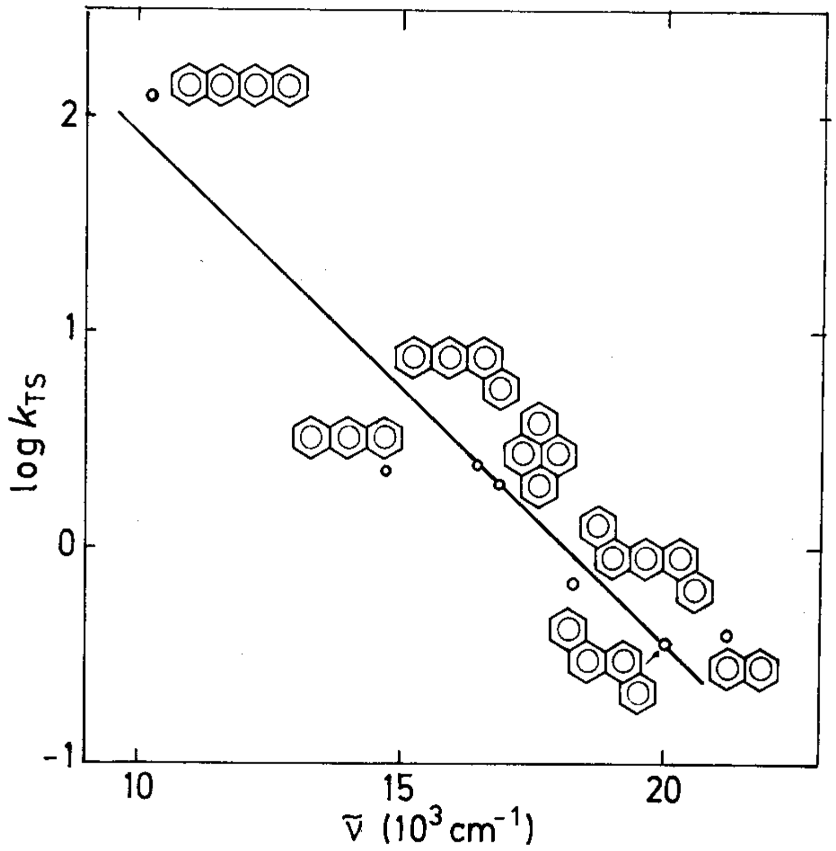


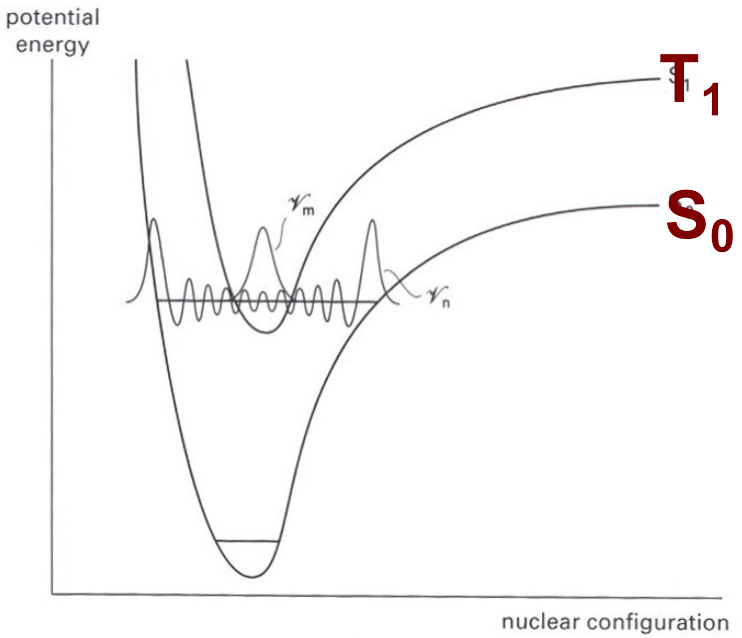
Figure 3.25. Singlet decay rate constants (k) of aromatic hydrocarbons plotted against the singlet energy (E_S). (From data in J. B. Birks, *Photophysics of Aromatic Molecules*, (1970), Wiley)



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

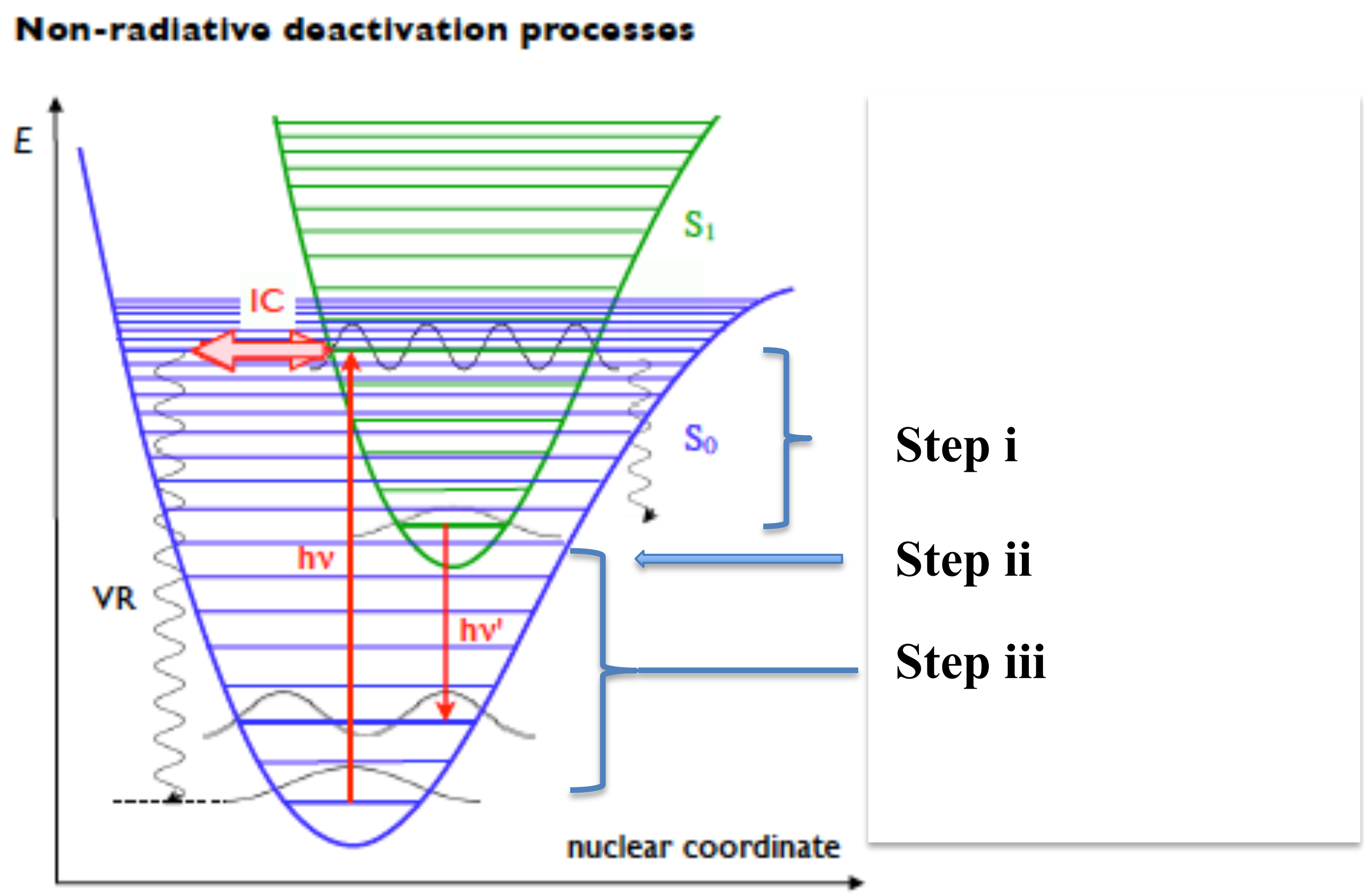


igure 5.5. Relationship between the energy gap $\Delta E(T_1 - S_0)$ and the logarithm of he rate constant k_{TS} of intersystem crossing in aromatic hydrocarbons (data from irks, 1970).



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

Conversion of electronic to vibrational energy



Step i

Step ii

Step iii

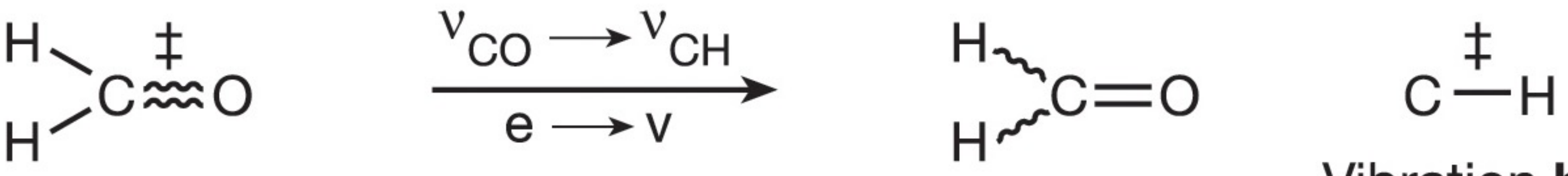
Three step process: (i) upper vibrational to lower vibrational level in excited state

(ii) lower vibrational level to upper vibrational of the lower state

(iii) upper vibrational of the lower state to lowest vibrational level

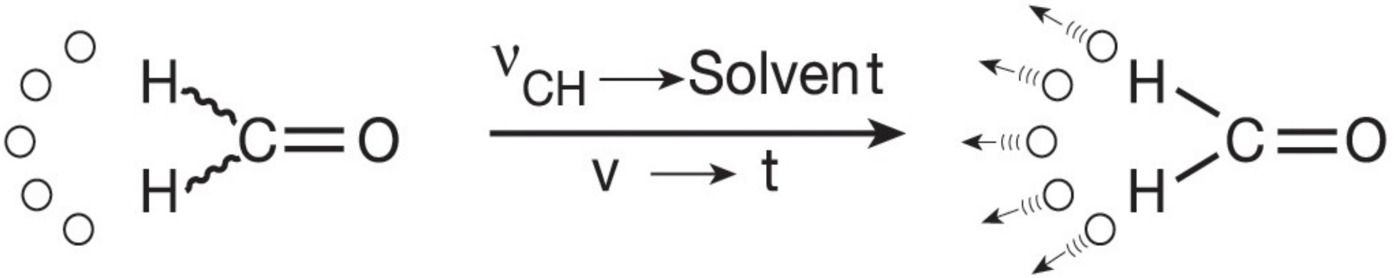
Visualization of
Electronic Energy to Vibrational Energy Transfer

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



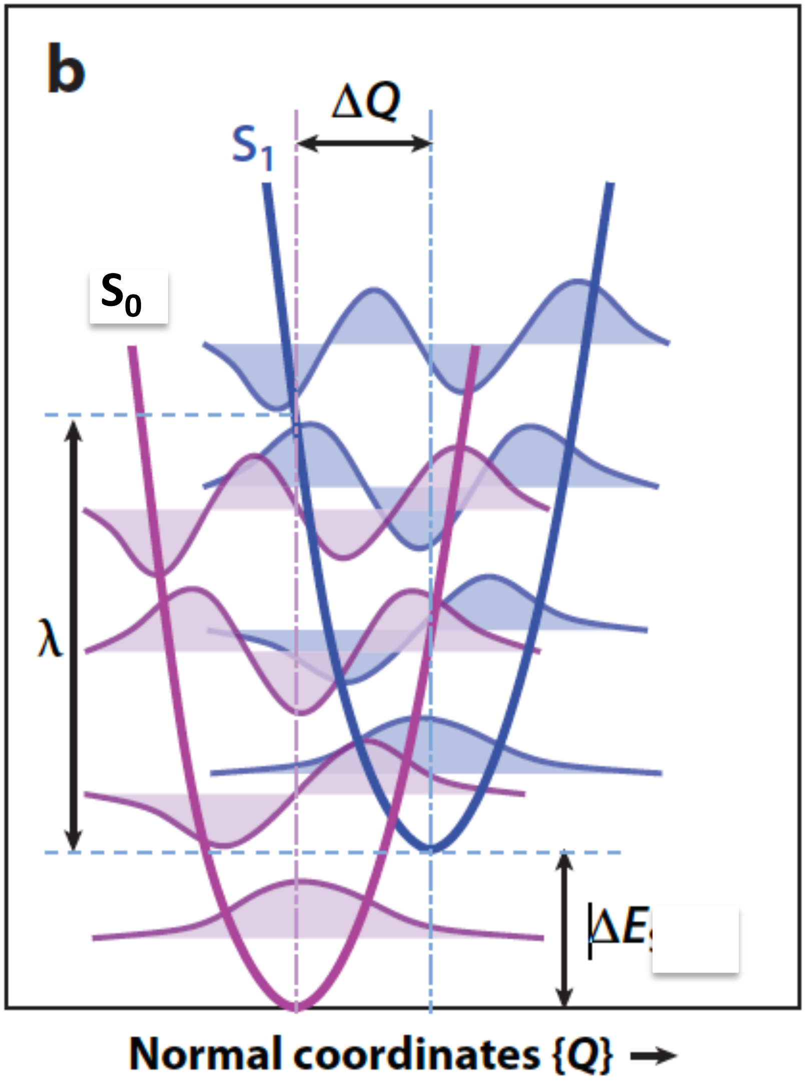
Vibration **hot**

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

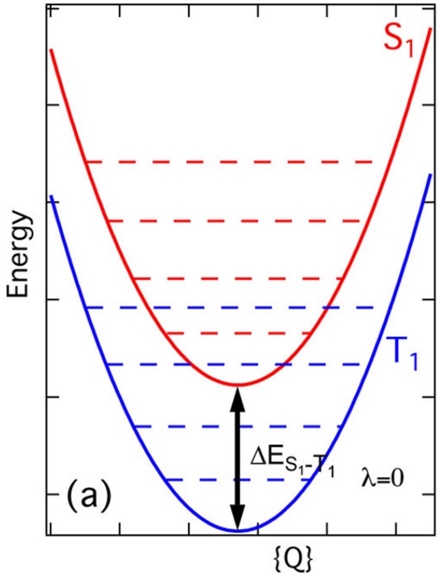


Solvent is **hot**
(translations and
vibrations)

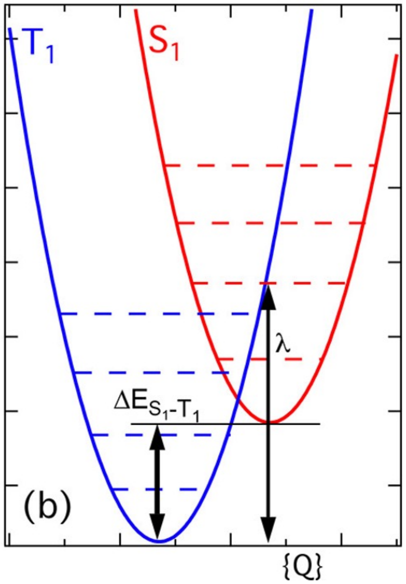
Crossing surfaces



Equilibrium geometries dissimilar

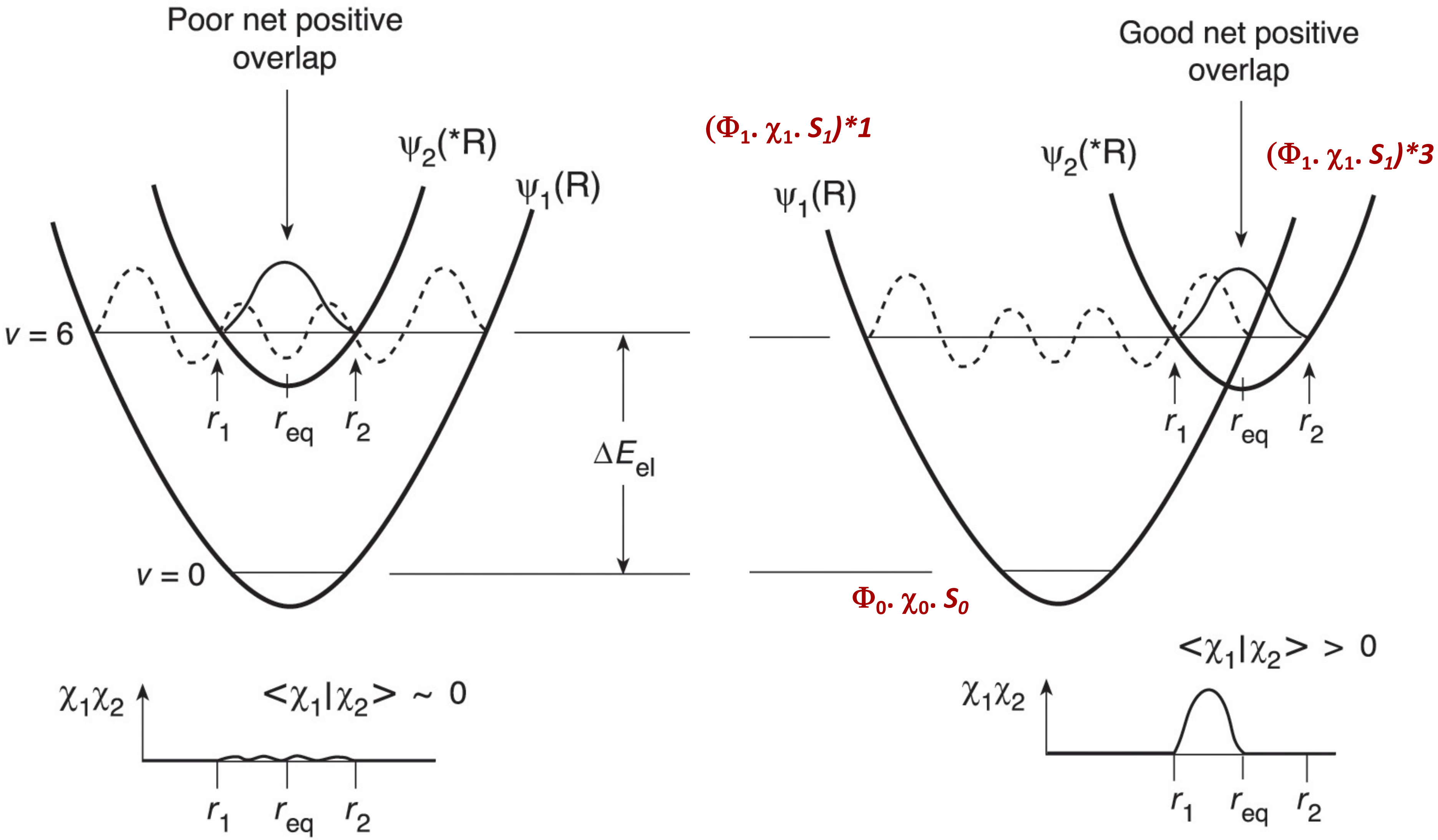


Weak Coupling



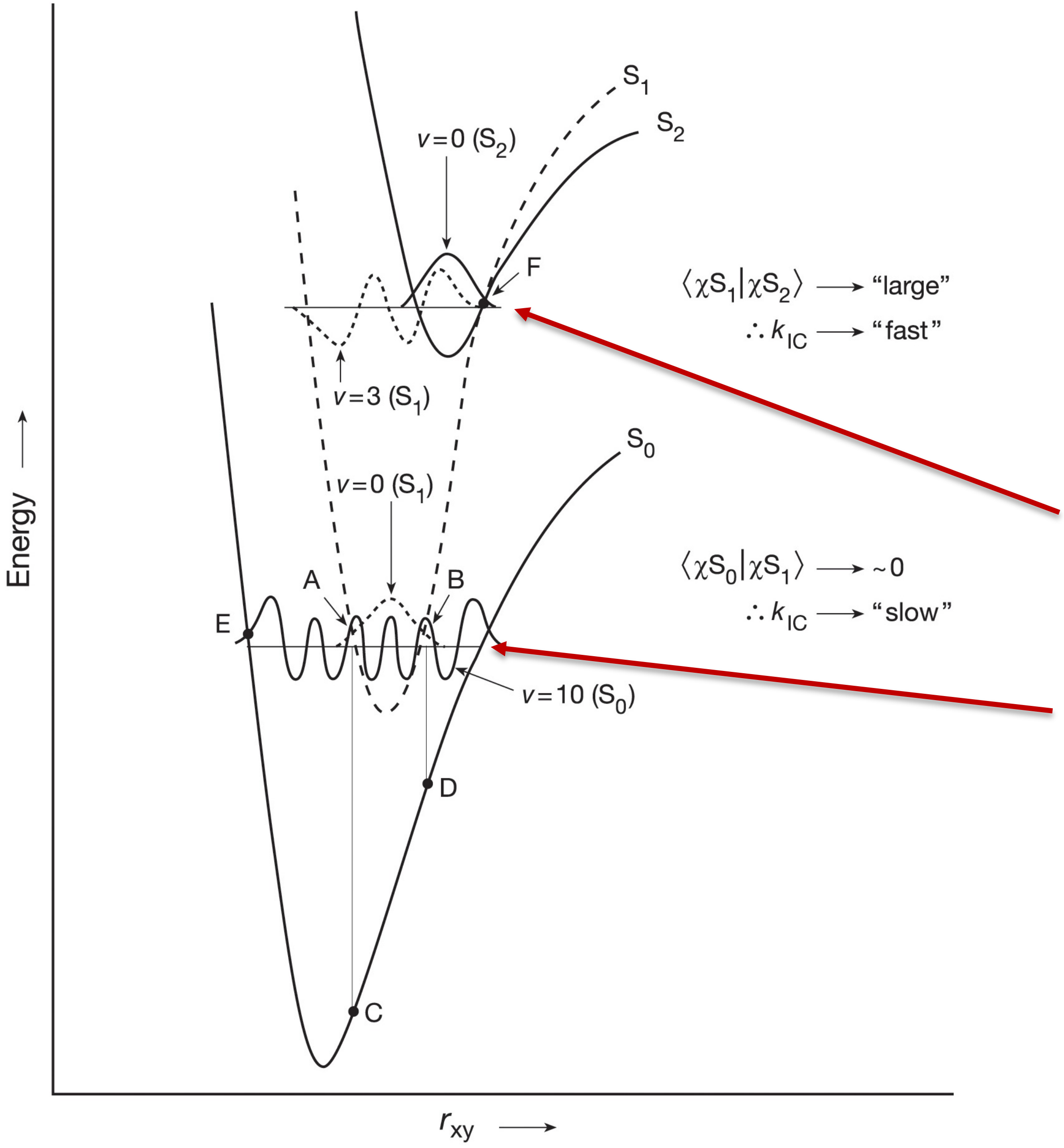
Strong coupling

Matching *vs.* Crossing Surfaces



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.

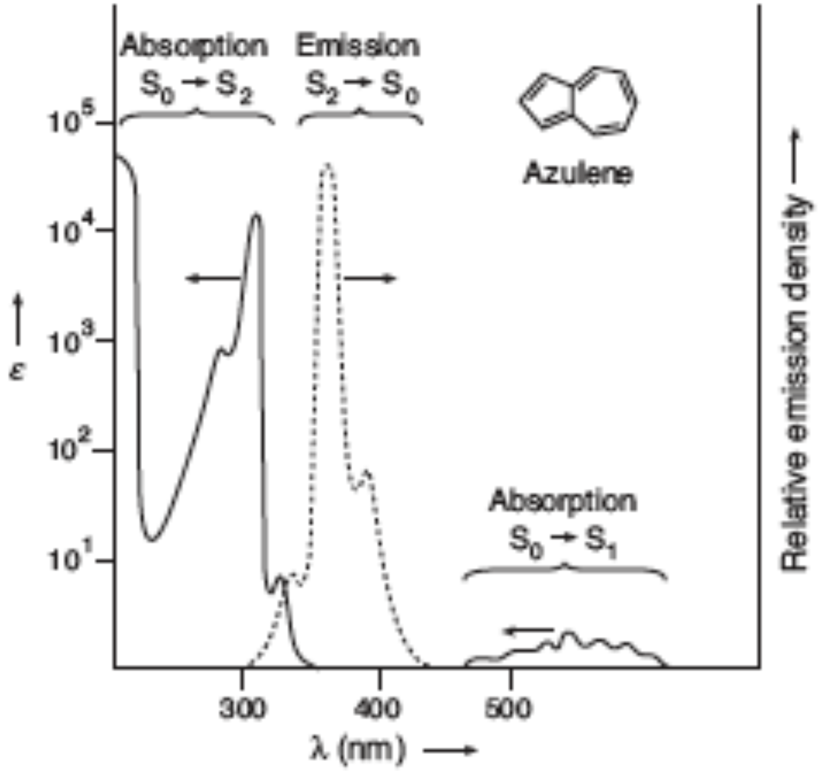
S$_2$ to S$_1$ IC is fast due to possible surface crossing and smaller gap

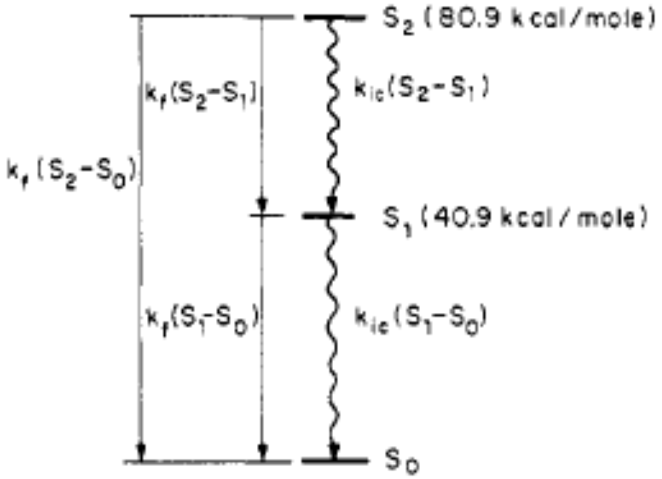
S$_1$ to S$_0$ IC is slow due to matching surface and larger gap

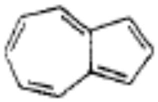
S$_2$ to S$_1$ IC can be slow if gap is larger and the surfaces don't cross

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).







$k_f(S_2-S_0) = 1.4 \times 10^7$ ←

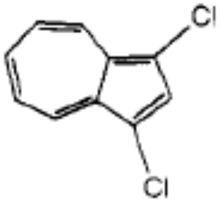
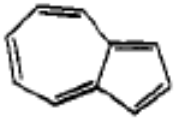
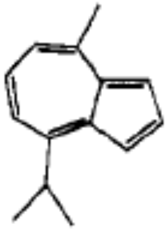
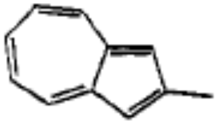
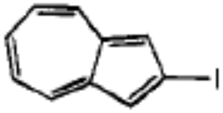
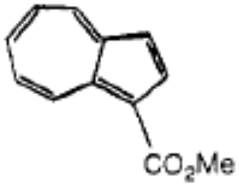
$k_f(S_2-S_1) \approx 1.4 \times 10^4$

$k_f(S_1-S_0) = 1.3 \times 10^6$

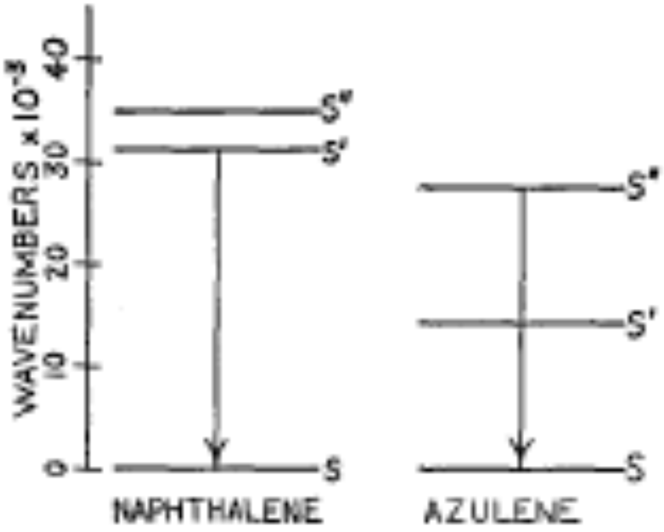
$k_{ic}(S_2-S_1) = 7 \times 10^8$ ←

$k_{ic}(S_1-S_0) = 1.2 \times 10^{11}$

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

S_2 to S_1 rate vs Energy Gap



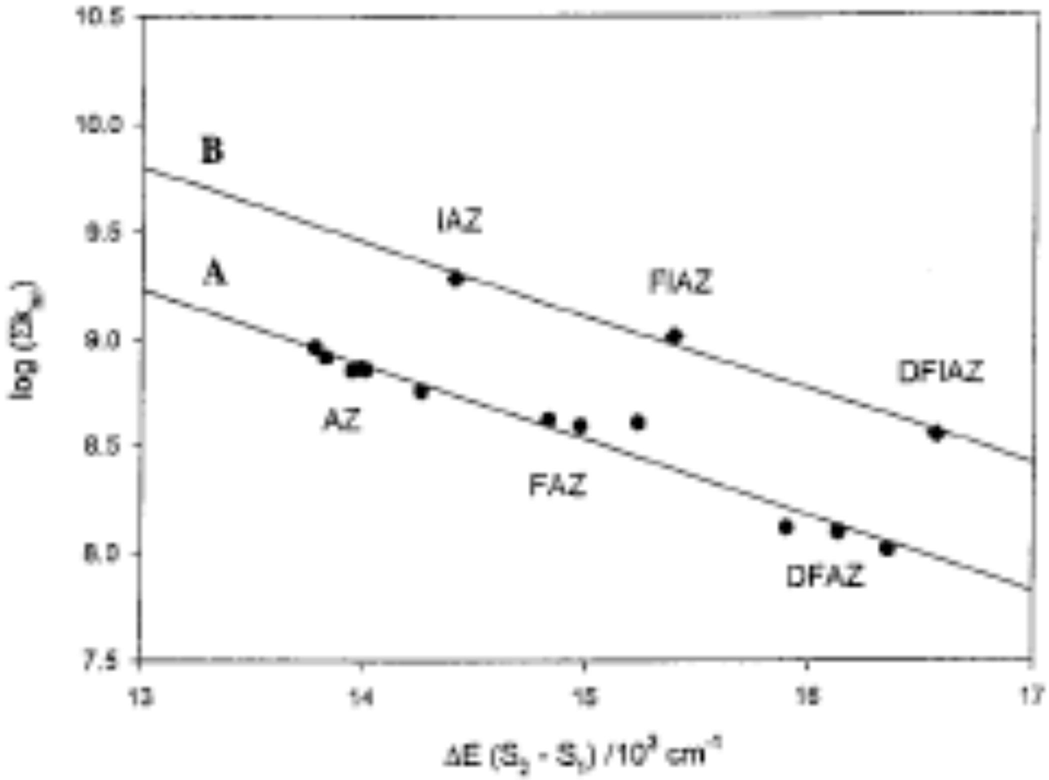
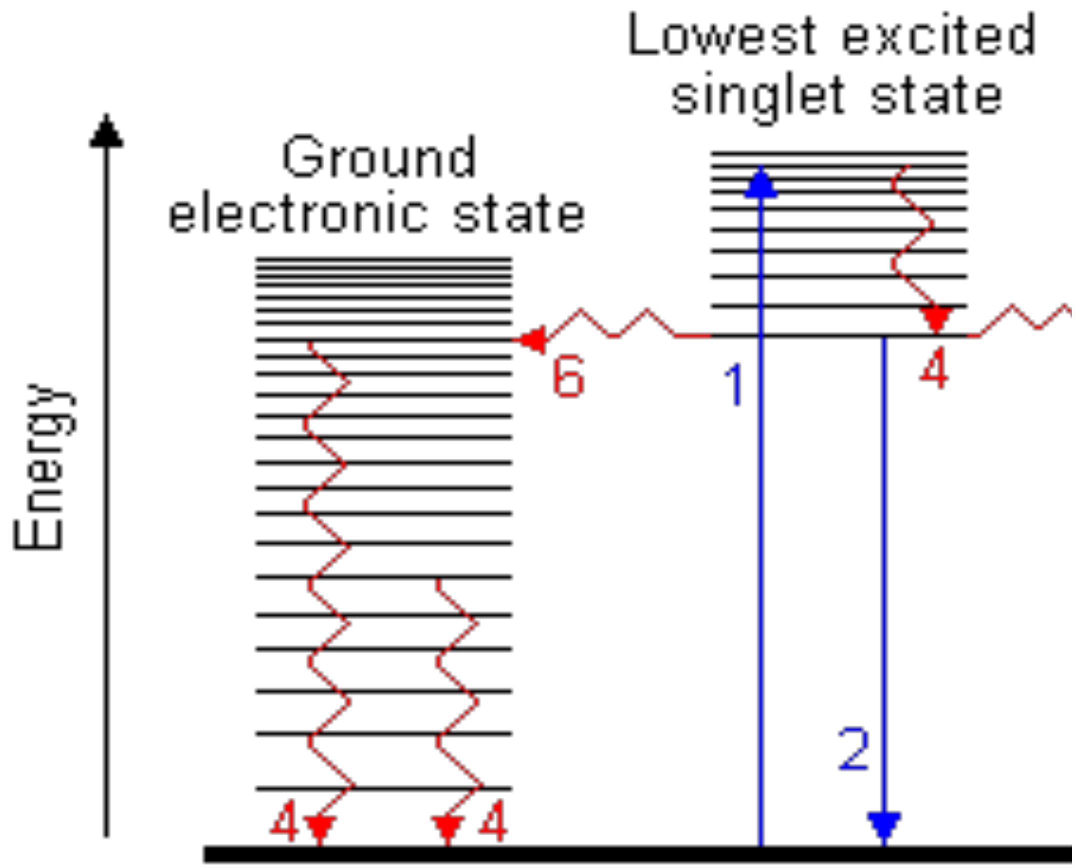
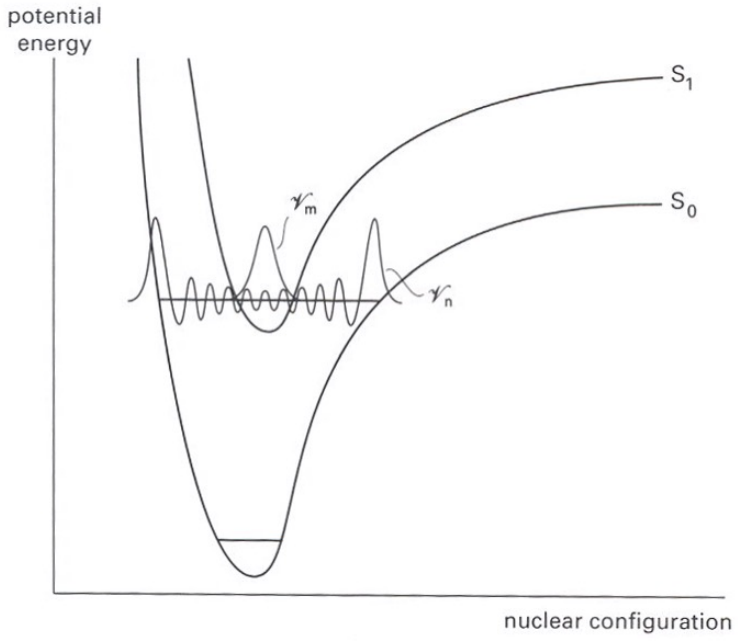


Figure 3. Log–linear energy gap law plots (see text) for azulene (AZ), 1-fluoroazulene (FAZ), and 1,3-difluoroazulene (DFAZ) in several solvents (line A), and for 6-isopropylazulene (IAZ), 1-fluoro-6-isopropylazulene (FIAZ), and 1,3-difluoro-6-isopropylazulene in *n*-hexane (line B). The data for AZ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

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.

Isotope Effect on Rate of T_1 to S_0

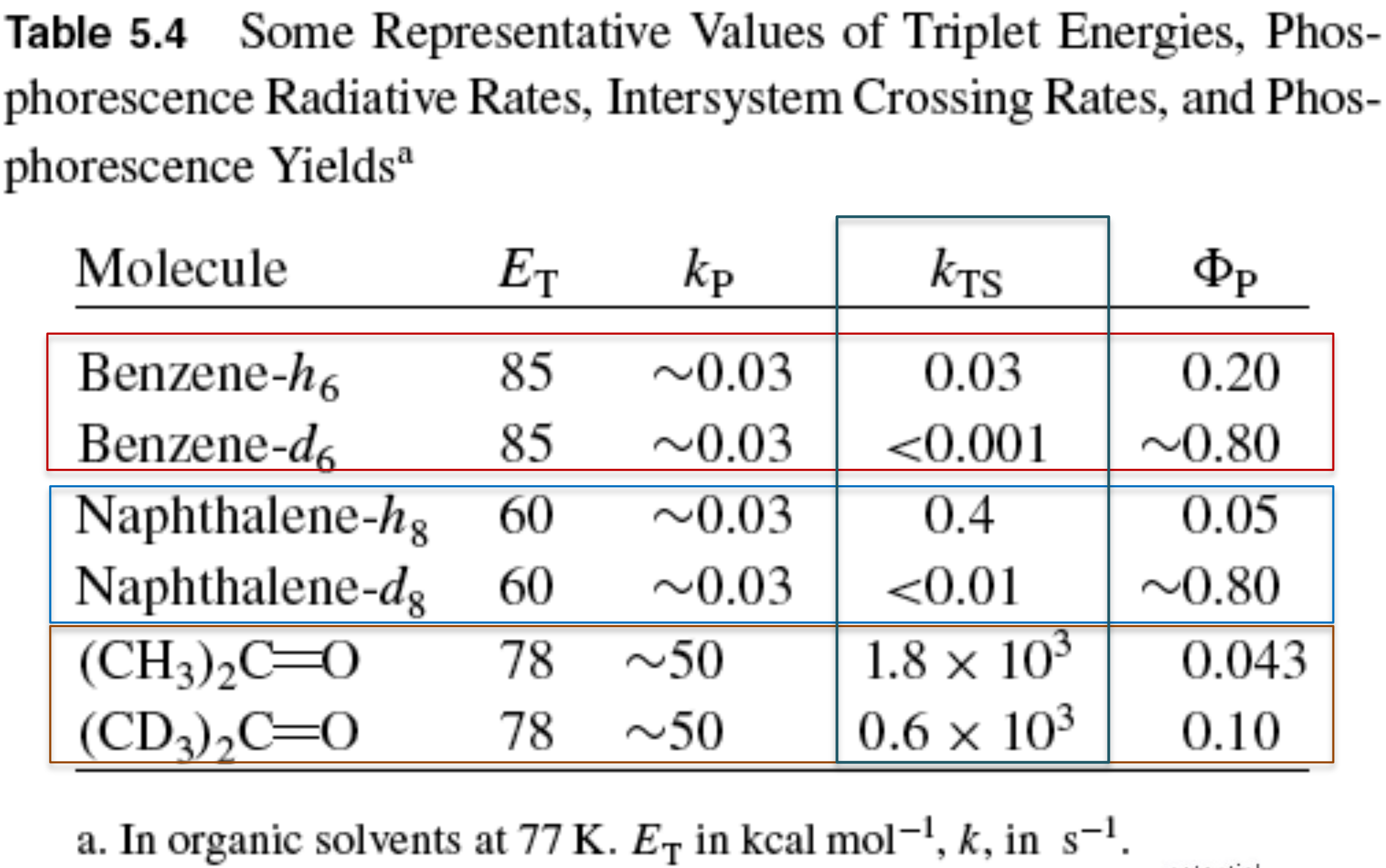


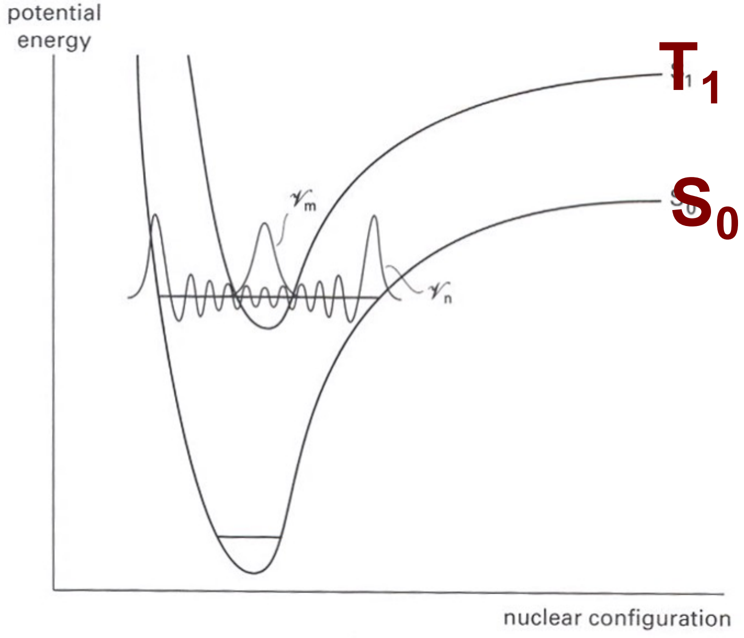
Table 5.4 Some Representative Values of Triplet Energies, Phosphorescence Radiative Rates, Intersystem Crossing Rates, and Phosphorescence Yields[a]

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

a. In organic solvents at 77 K. E_T in kcal mol^{-1}, k, in s^{-1}.

C-H stretch	**3000 cm^{-1}**
C-D stretch	**2100 cm^{-1}**

Higher vibrational level needed to match; poor overlap, slow decay, large Φ_P



Effect of deuteration on radiationless process (T_1 to S_0)

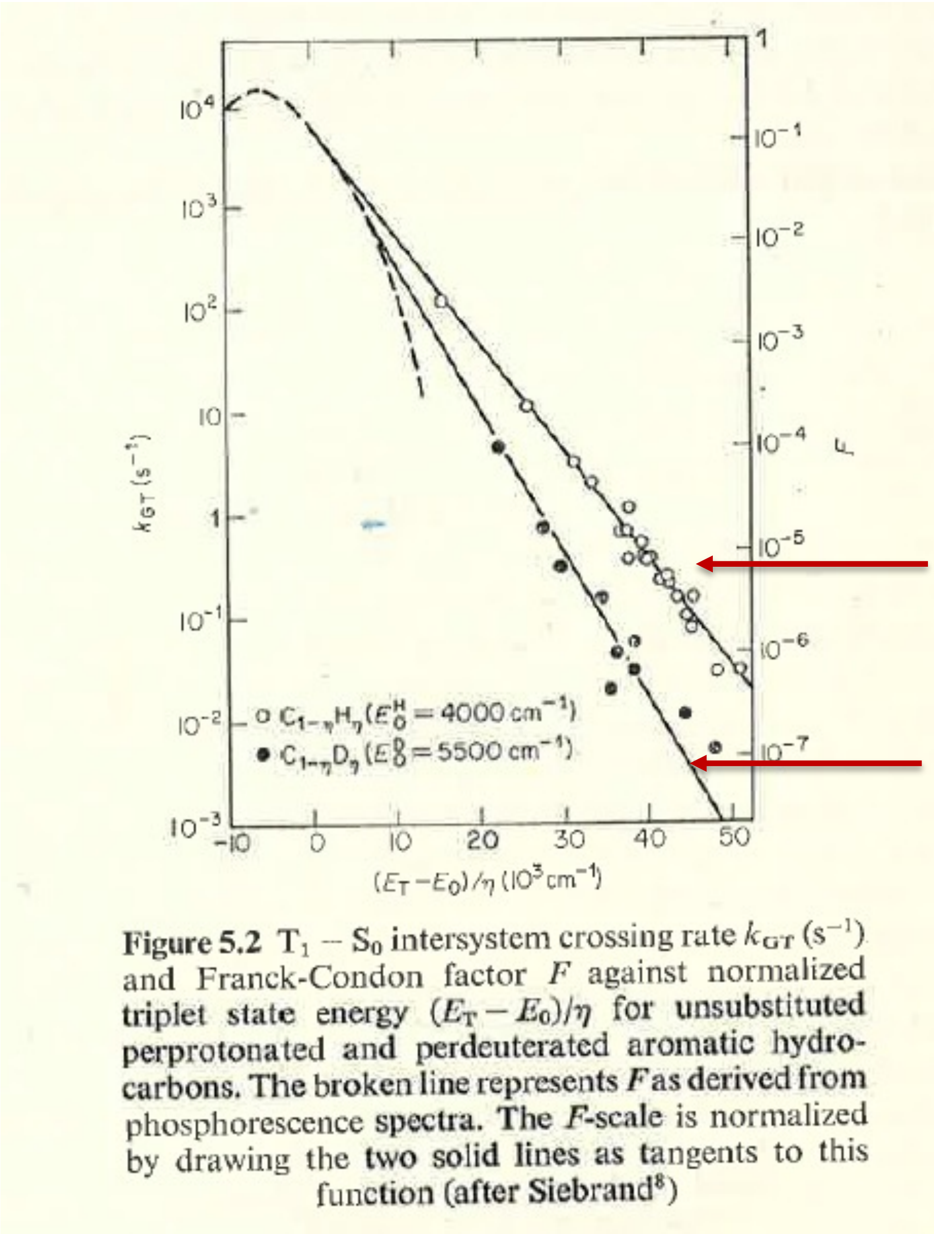


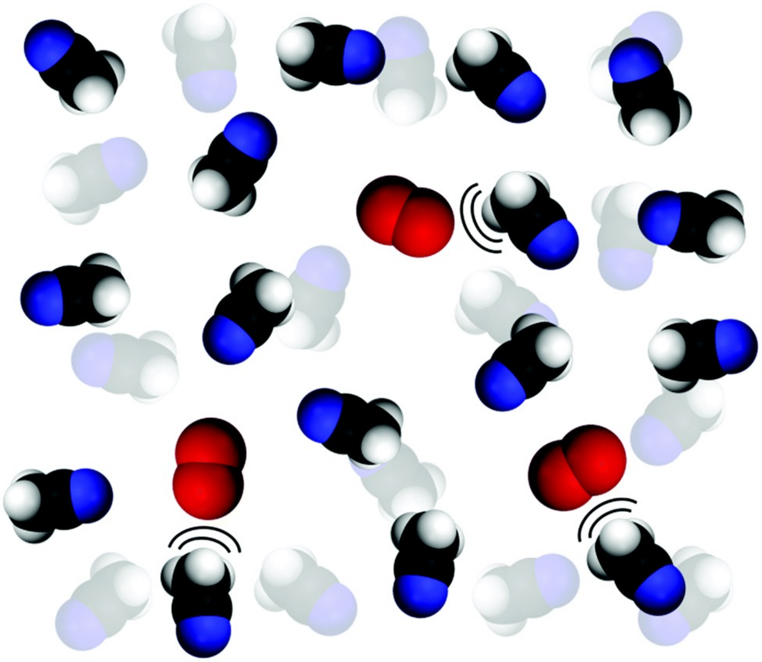
Figure 5.2 $T_1 - S_0$ intersystem crossing rate k_{GT} (s^{-1}) and Franck-Condon factor F against normalized triplet state energy $(E_T - E_0)/\eta$ for unsubstituted perprotonated and perdeuterated aromatic hydrocarbons. The broken line represents F as derived from phosphorescence spectra. The F-scale is normalized by drawing the two solid lines as tangents to this function (after Siebrand[8])

perprotonated

perdeuterated

Birks book

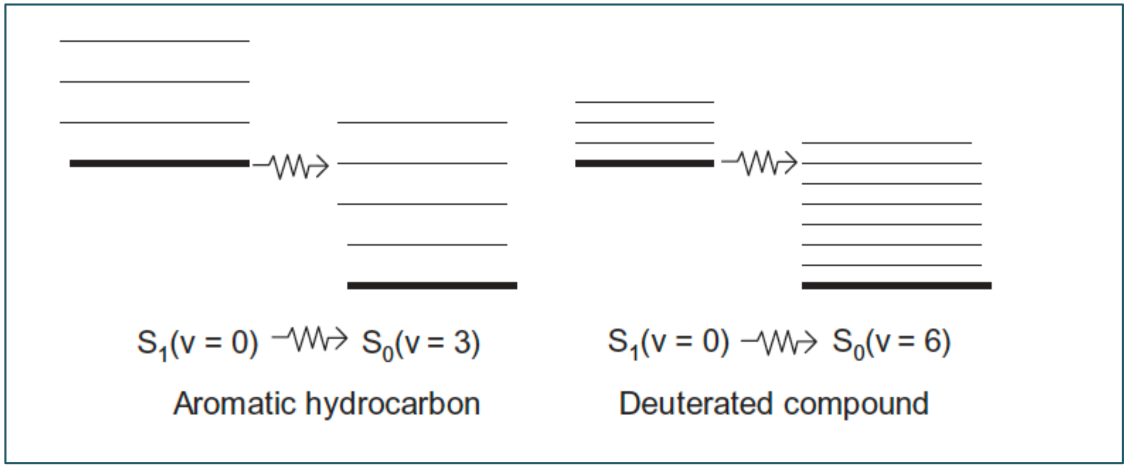
Decay of singlet oxygen depends on solvent and deuteration



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

	$\tau_\Delta/\mu s$	
Solvent	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



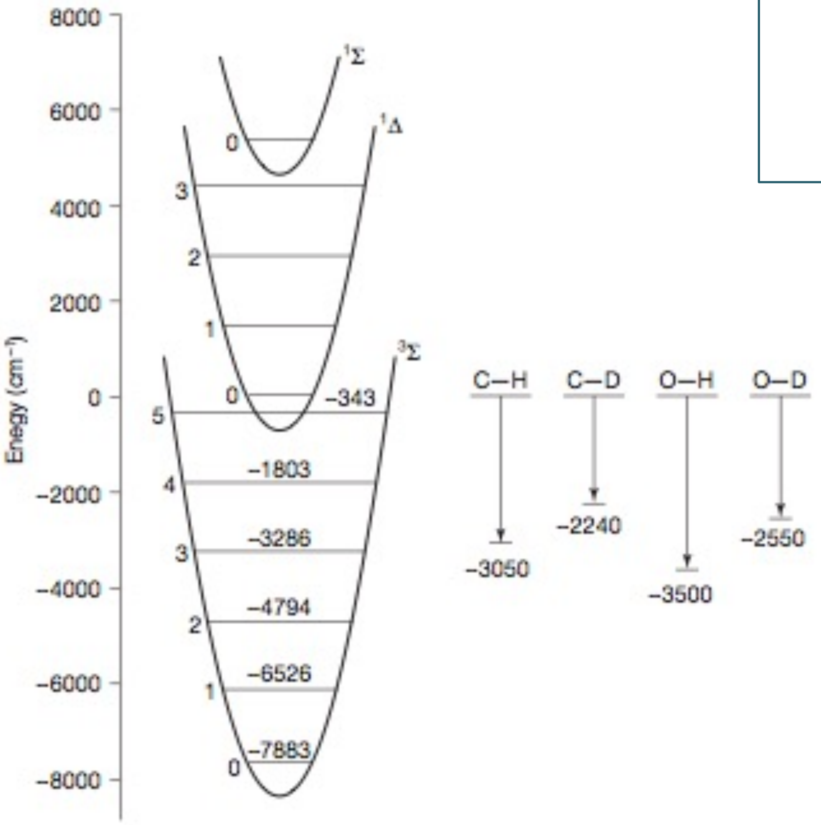


Figure 14.3 Comparison of the energy levels of $^1\Delta$ to common high frequency X—H and X—D vibrations of solvents. Energies in cm^{-1}.

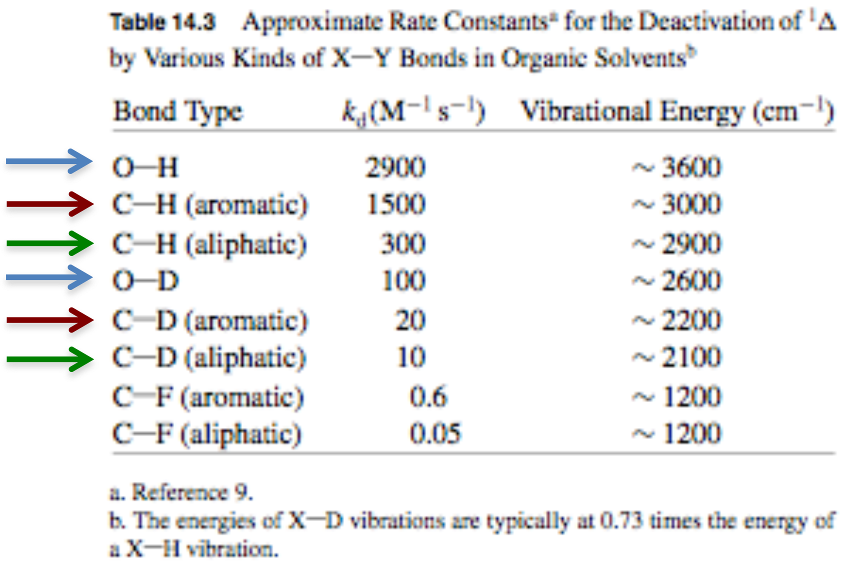


Table 14.3 Approximate Rate Constants[a] for the Deactivation of $^1\Delta$ by Various Kinds of X—Y Bonds in Organic Solvents[b]

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

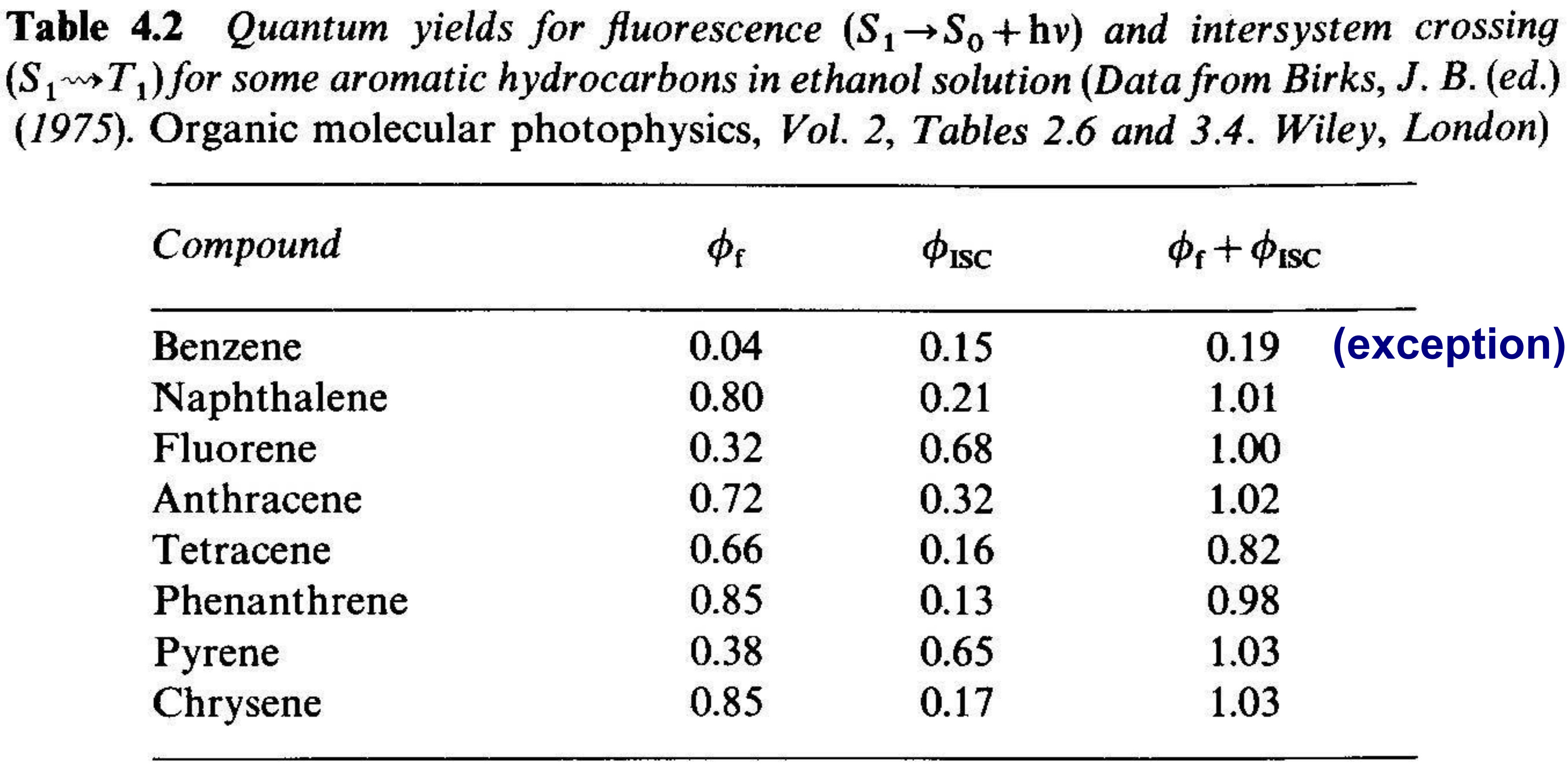
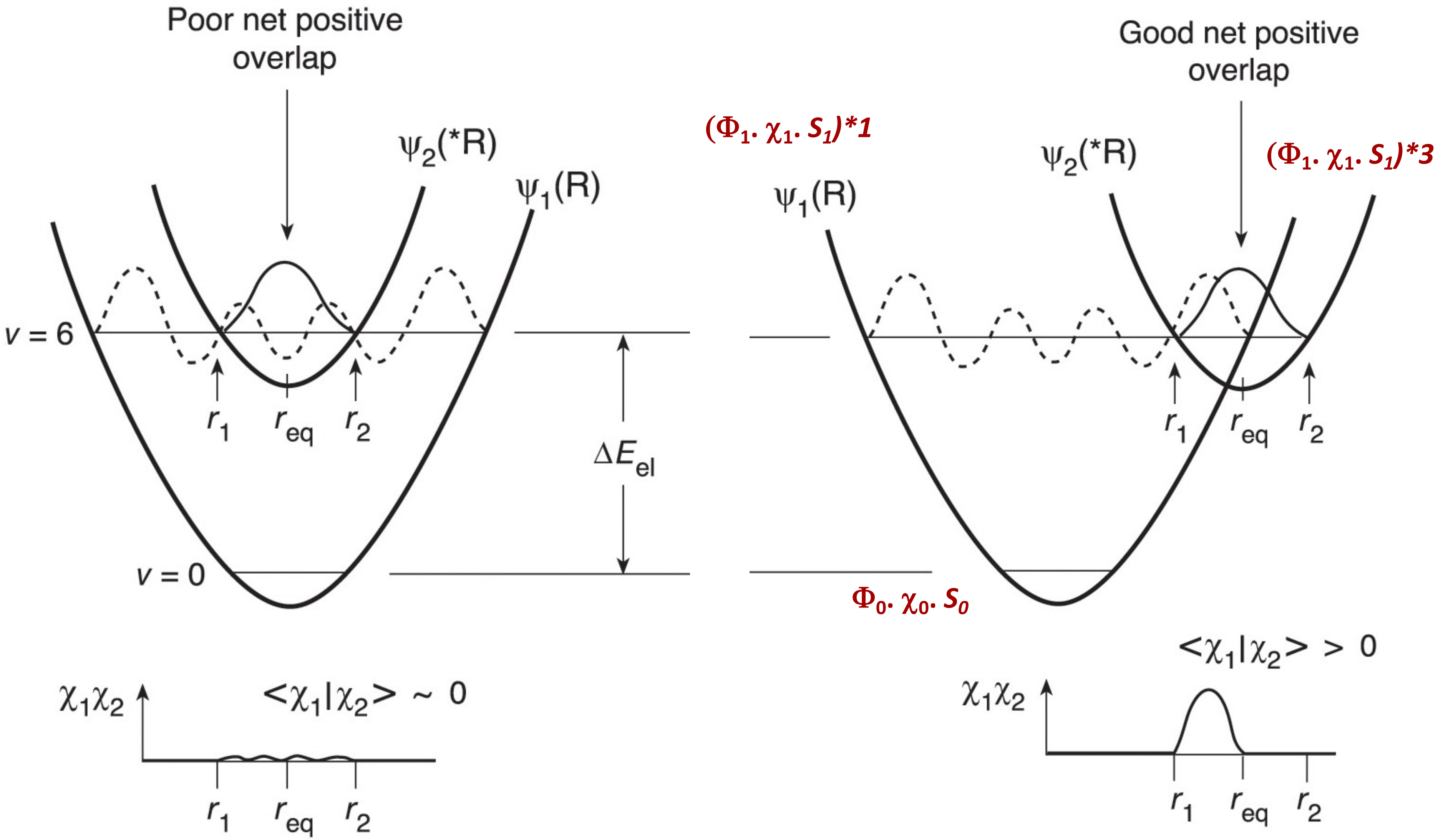


Table 4.2 *Quantum yields for fluorescence* ($S_1 \rightarrow S_0 + h\nu$) *and intersystem crossing* ($S_1 \rightsquigarrow T_1$) *for some aromatic hydrocarbons in ethanol solution* (*Data from Birks, J. B.* (*ed.*) (*1975*). Organic molecular photophysics, *Vol. 2, Tables 2.6 and 3.4. Wiley, London*)

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	

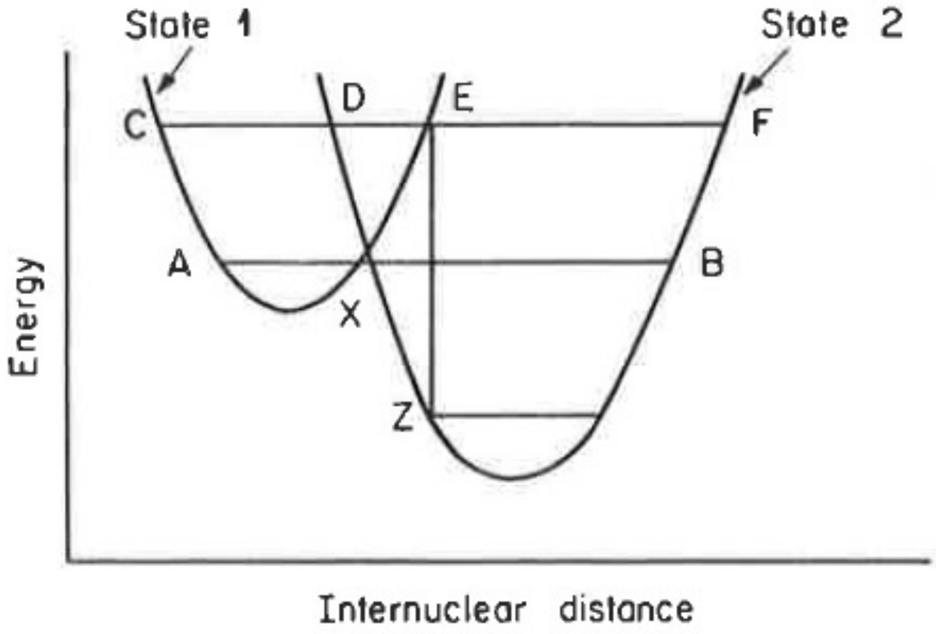
For large aromatic molecules the sum of the quantum yields of fluorescence and ISC is one i.e., rate of internal conversion is very slow with respect to the other two (**Ermolaev's rule**).

Internal conversion in matching *vs.* crossing surfaces



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

Why it is easier for molecules to move between surfaces at intersections?



Potential energy surfaces for two states (**1** and **2**) shown above.

The two surfaces cross at **X**.

At point E the molecule on state **1** is at rest (KE = 0). The same molecule at state **2** has KE equivalent to EZ.

Moving from state **1** to **2** is more likely at **X** and less probable at **E**.

Breakdown of Born-Oppenheimer Approximation

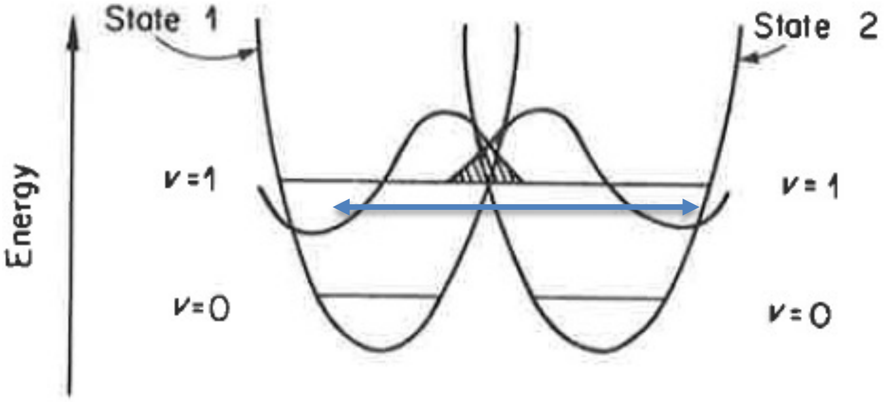


Figure 3.22. Large vibrational overlap at the crossing point of approximately degenerate electronic states

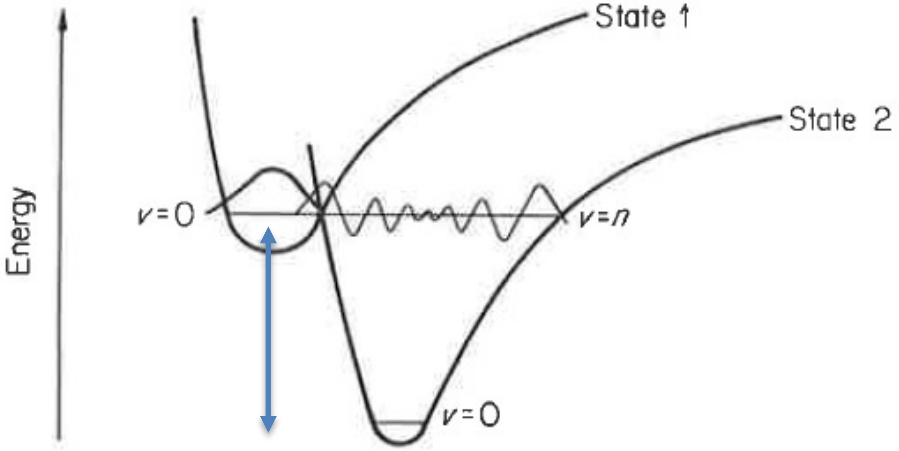


Figure 3.23. Vibrational overlap with a large energy difference between states

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.

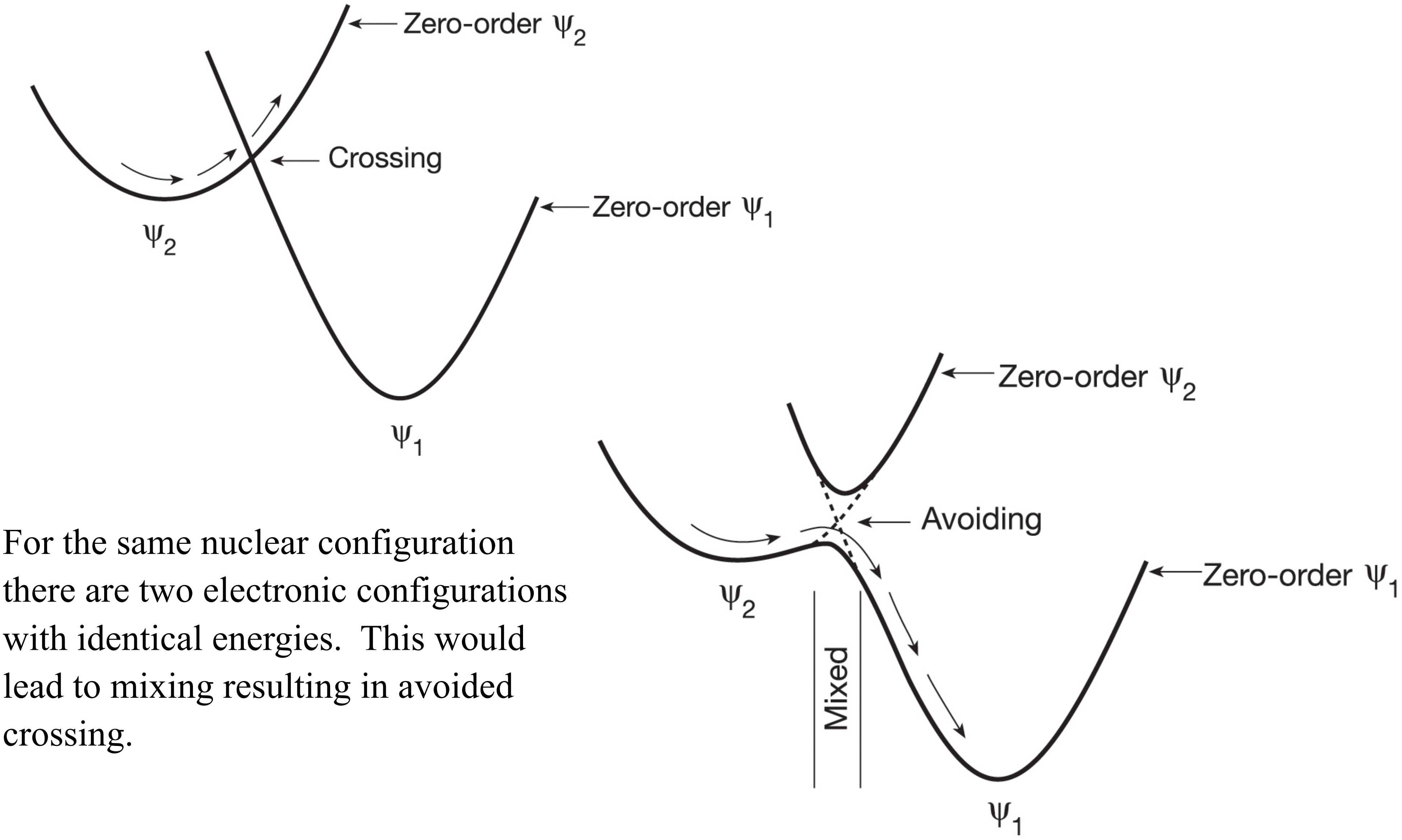
Energy gap law works even for crossing surfaces

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.

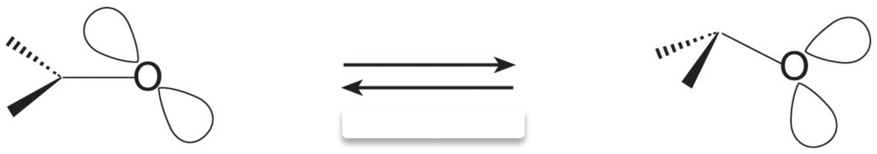
However, density of states is larger when the gap is larger. Higher vibrational levels would be closer. This would favor IC.

Breakdown of Born-Oppenheimer Approximation
Mixing of surfaces



For the same nuclear configuration there are two electronic configurations with identical energies. This would lead to mixing resulting in avoided crossing.

Breakdown of Born-Oppenheimer Approximation
Vibronic mixing enables surface mixing



Strictly planar

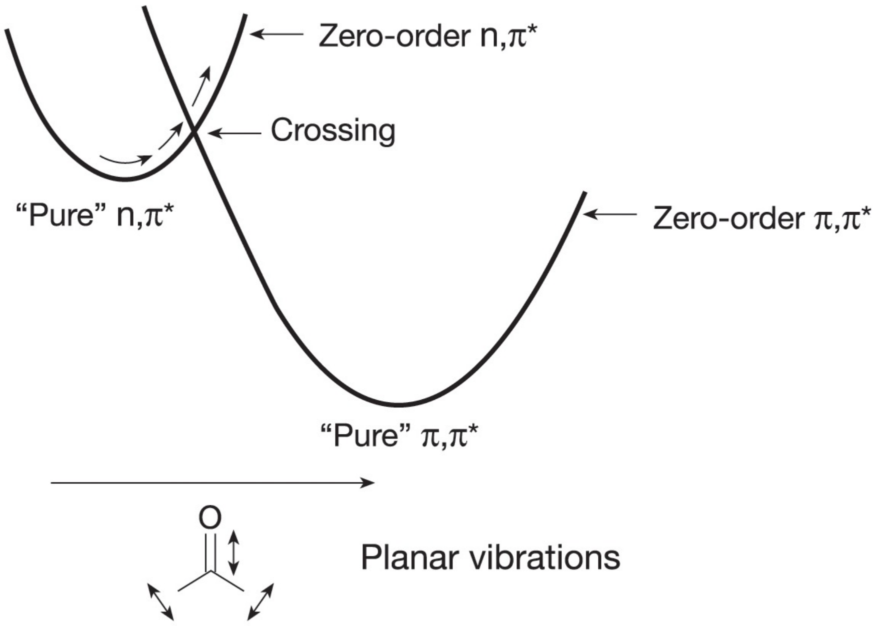
$n_0 = p_0$

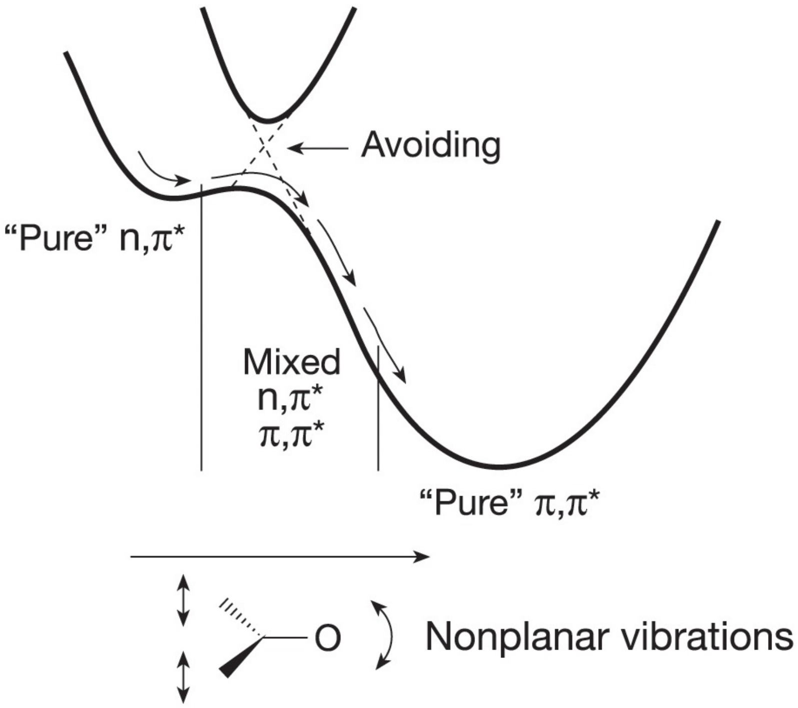
$\langle n_0 | \pi \rangle = 0$

Nonplanar

$n_0 = sp^n$

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





Energy is fine, but
orbitals don't overlap

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

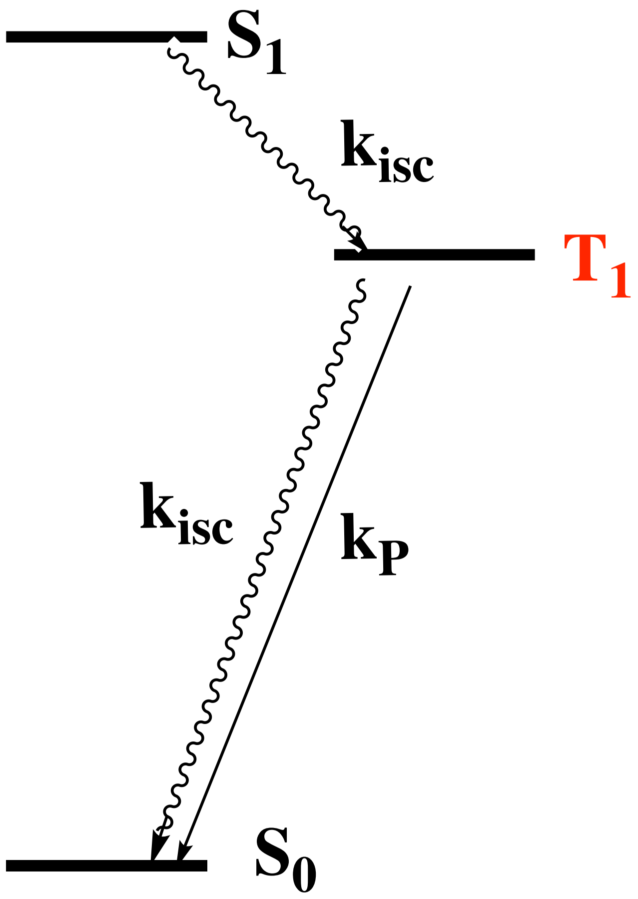
$R(S_0) + h\nu \rightarrow {}^*R(S_1)$

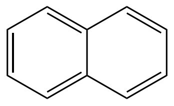
$R(S_0) + h\nu \rightarrow {}^*R(T_1)$

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

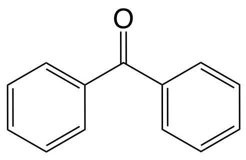
${}^*R(T_1) \rightarrow R(S_0) + \text{heat}$

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

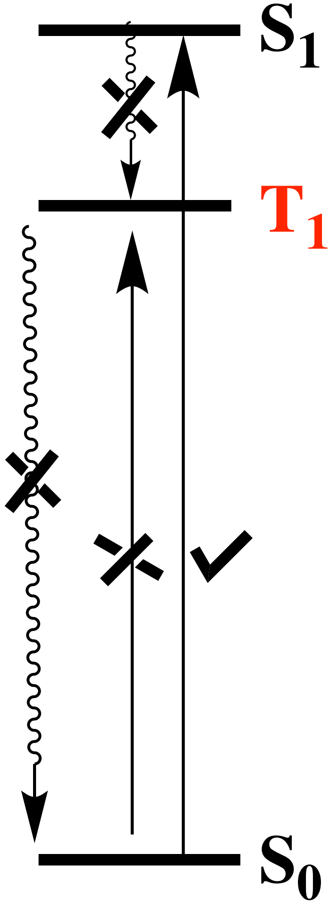


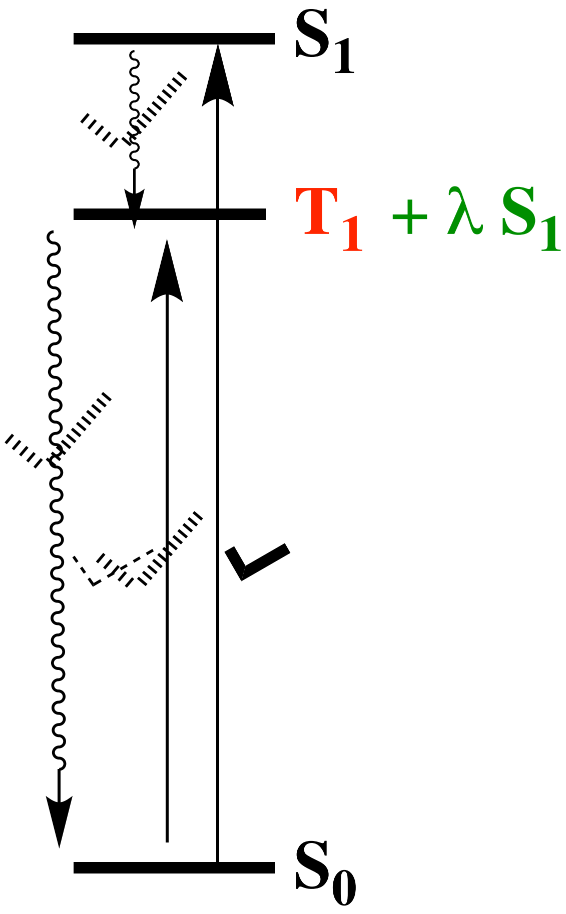


Intersystem crossing in molecules with nπ* and ππ* states



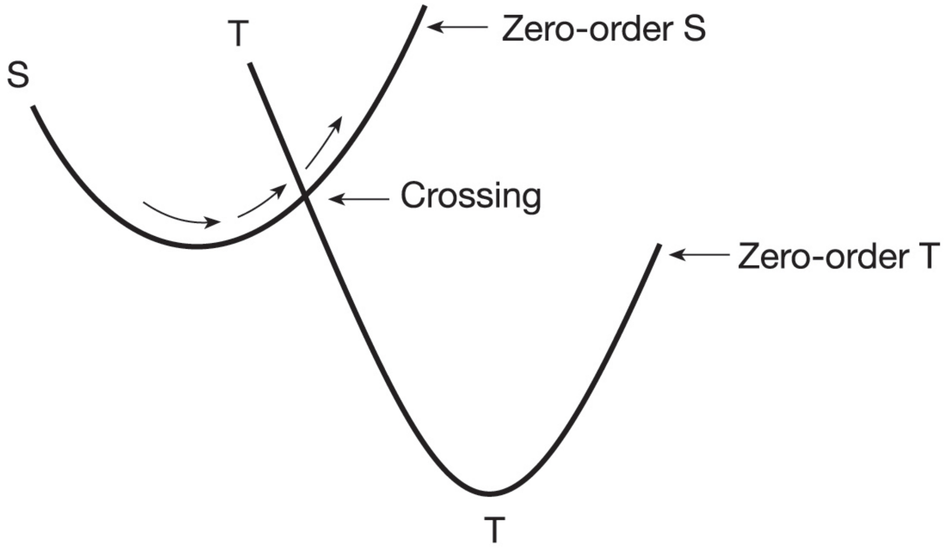
Singlet-Triplet Transitions
Role of Spin-Orbit Coupling





Spin-Orbit coupling mixes the states,
no longer pure states

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



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