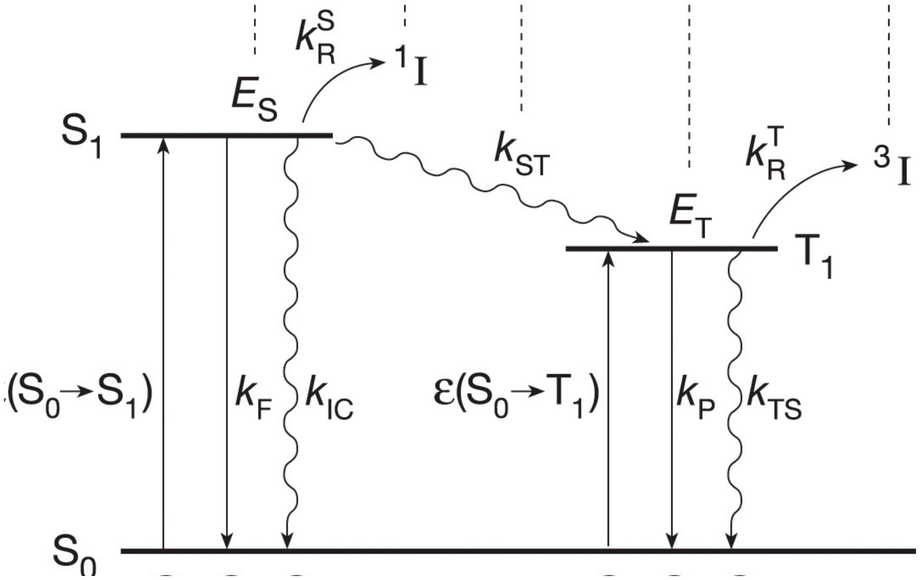
$$^{**}R(S_n) \longrightarrow {}^{*}R(S_1) + \Delta \text{ (Internal conversion)}$$

$$^{**}R(T_n) \longrightarrow {}^{*}R(T_1) + \Delta \text{ (Internal conversion)}$$

$$^{*}R(S_1) \longrightarrow R(S_0) + \Delta \text{ (Internal conversion)}$$

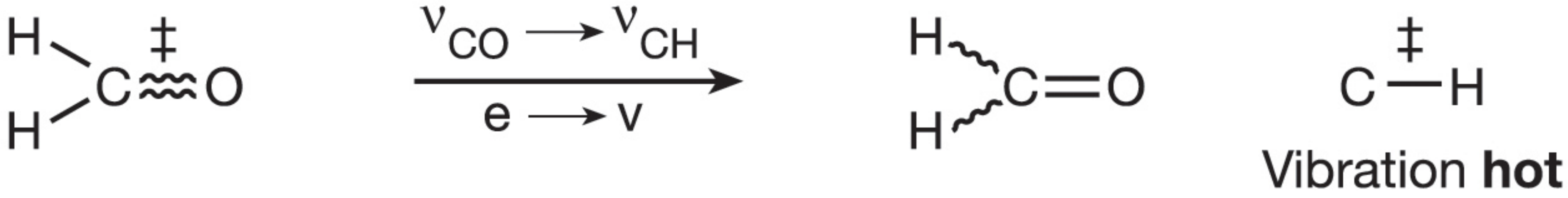
$$^{*}R(S_1) \longrightarrow {}^{*}R(T_1) + \Delta \text{ (Intersystem crossing)}$$

$$^{*}R(T_1) \longrightarrow R(S_0) + \Delta \text{ (Intersystem crossing)}$$

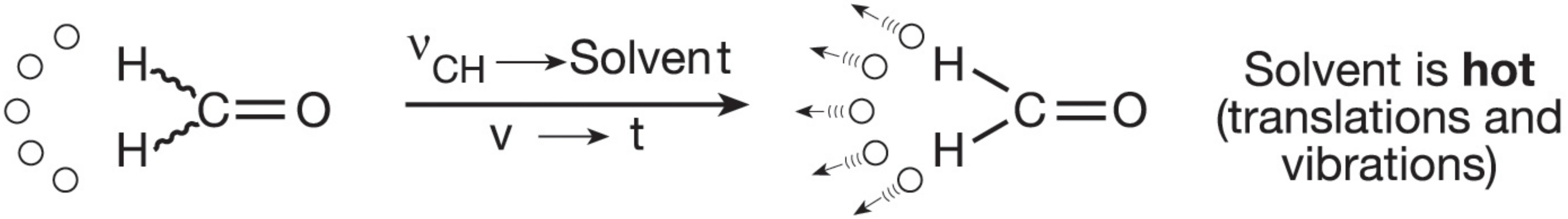


Electronic to Vibrational Energy Transfer

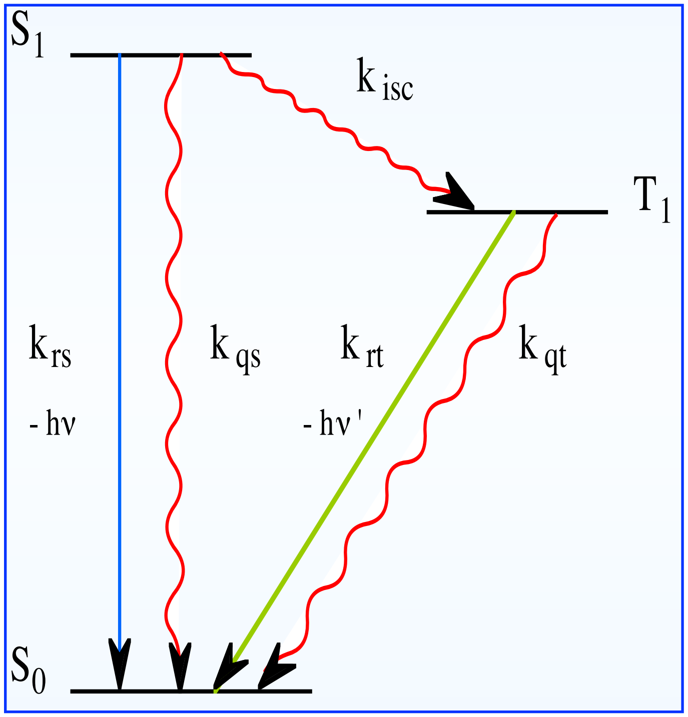
Intramolecular vibrational relaxation (IVR) occurs within 10 to 0.1 ps



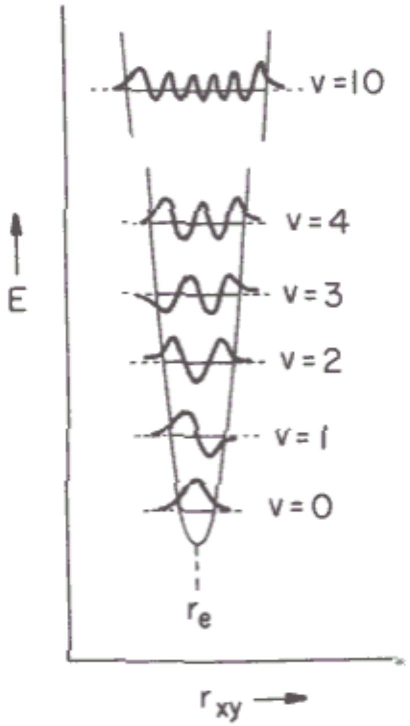
Intermolecular vibrational energy transfer (VET) from the molecule to the solvent occurs in the time range 100 to 10 ps



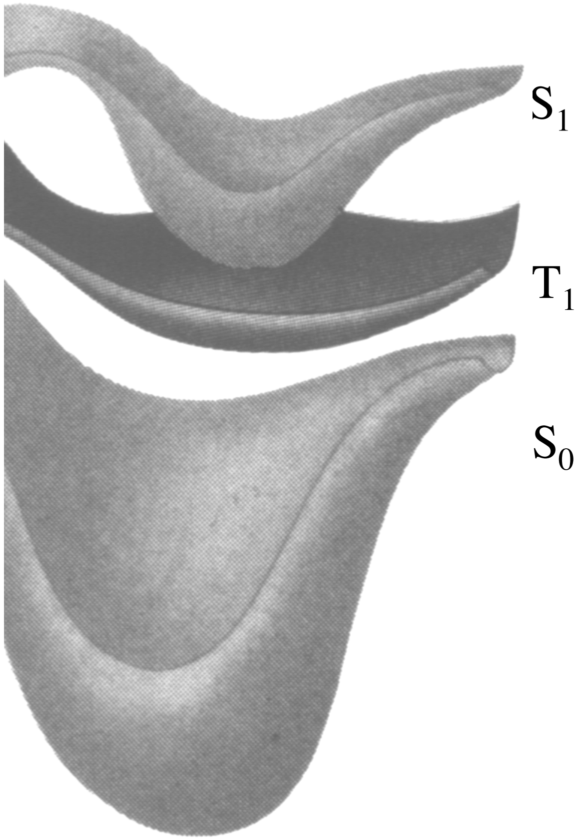
Visualizing molecules in ground and excited states



Molecule represented
in one dimension

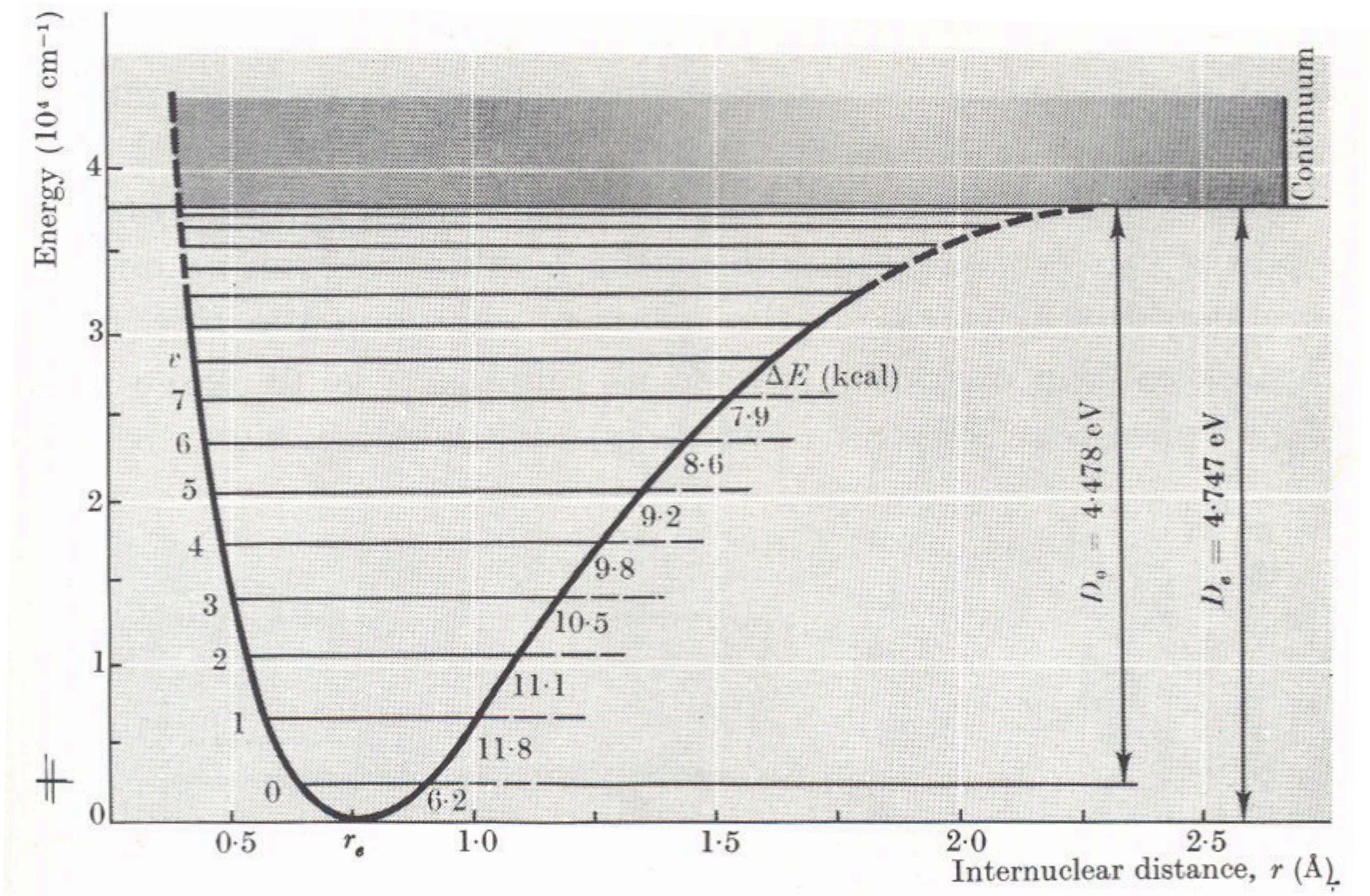


Molecule represented
in two dimensions



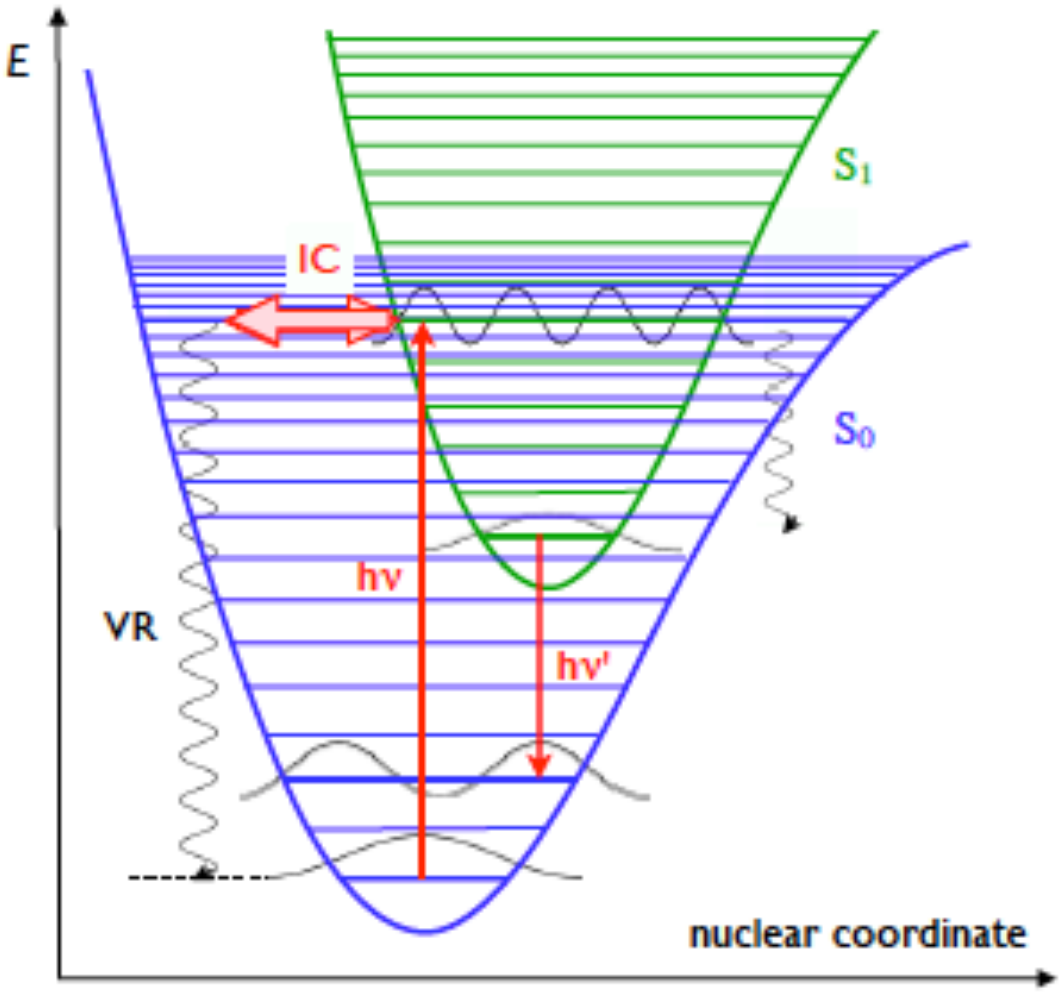
Molecule represented
in three dimensions

Visualizing vibrating molecules



Conversion of electronic to vibrational energy

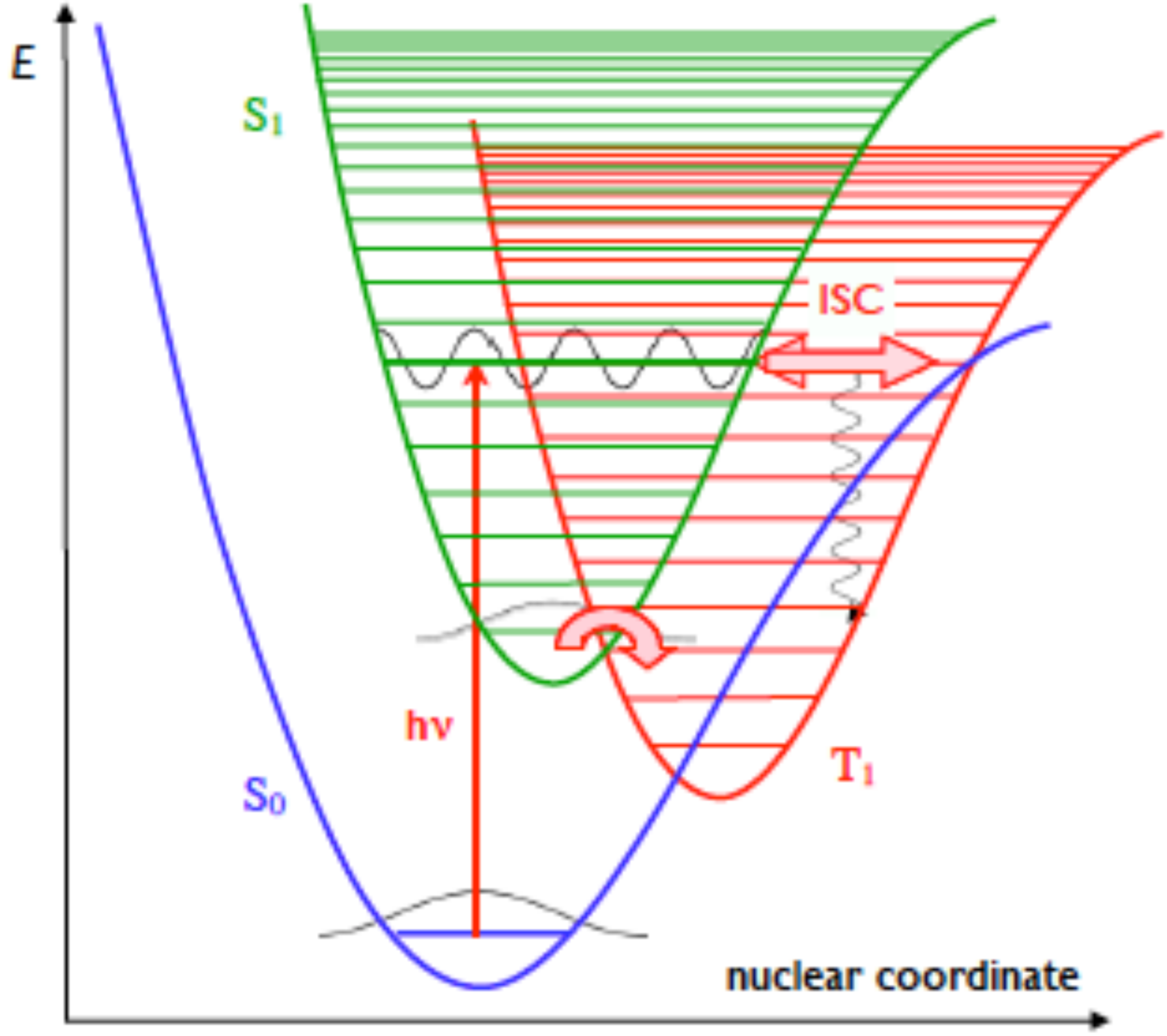
Non-radiative deactivation processes



Internal conversion (IC) implies the transformation of electronic excitation into vibrational energy. This process takes place through *nuclear tunneling* from the excited state potential surface to that of the ground state. Strong overlap of vibrational wave functions is necessary.

Since back-tunneling can also readily occur, fast vibrational relaxation (VR) is an important condition for this deactivation pathway.

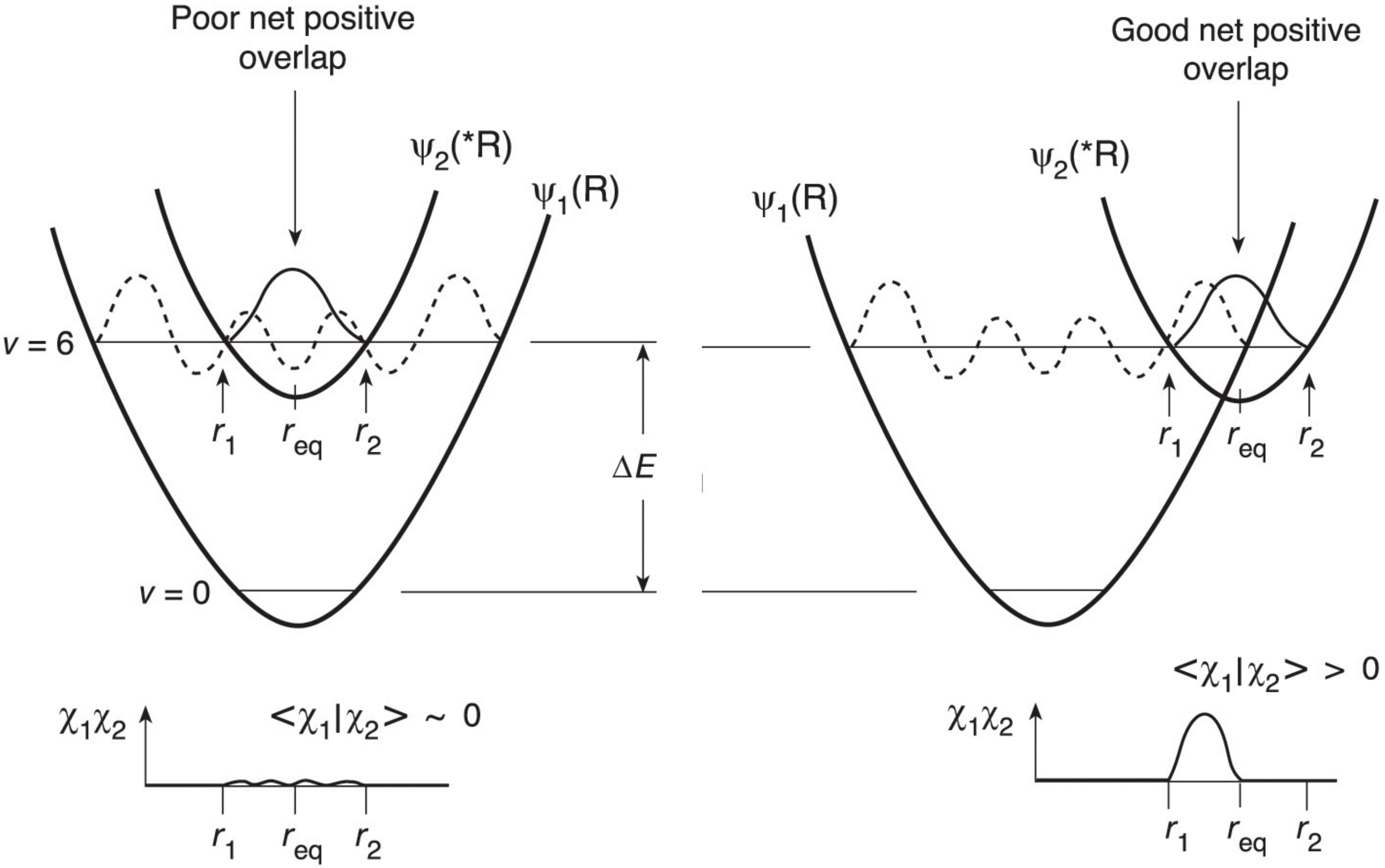
Non-radiative deactivation processes



Intersystem crossing (ISC) is a special case of internal conversion, which takes place between an electronic excited state and another excited state characterized by a different spin multiplicity ($S_1 \rightarrow T_1$, for instance). This process involves a simultaneous spin flip.

Vibrational relaxation is also necessary to avoid crossing back to the initial system.

Radiationless Process and Surface Crossing and Matching



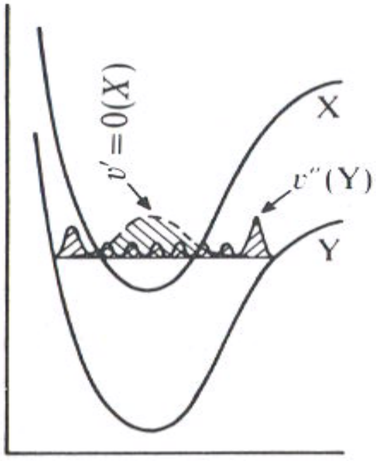
The Energy Gap Law for Internal Conversion

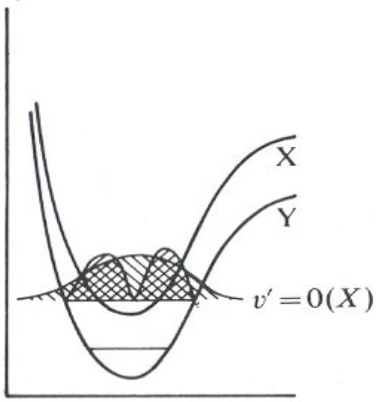
$$\boldsymbol{f \sim \exp\text{-}\Delta E}$$

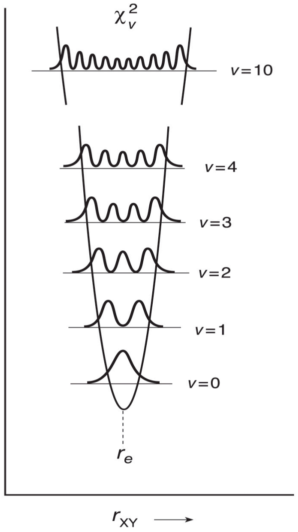
$$k_{IC} \sim 10^{13} f_{\nu}$$

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

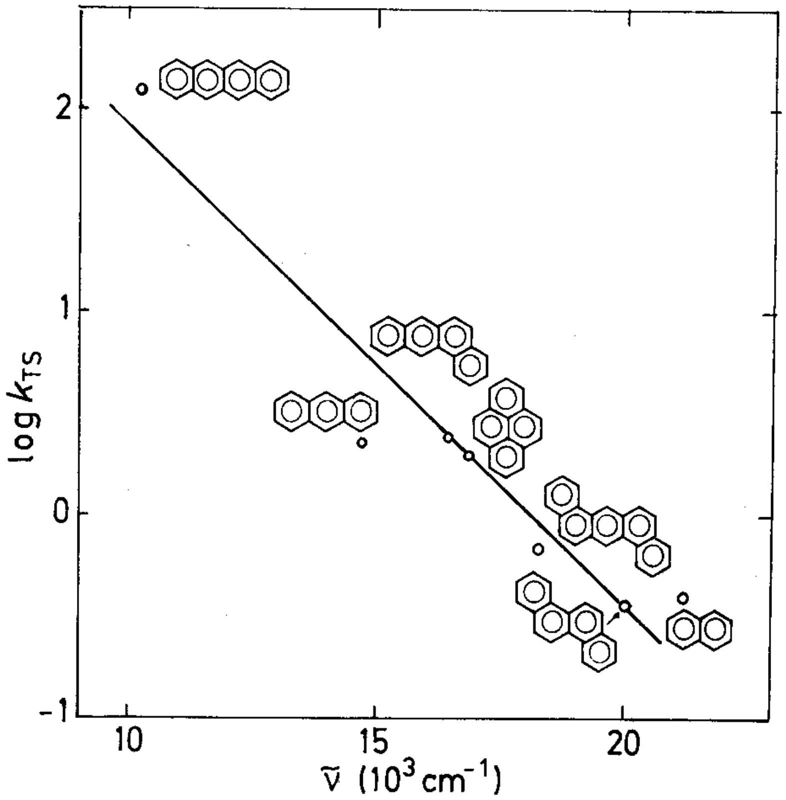
ΔE is the energy separation between the surfaces involved in the transition at the nuclear geometry r_c.



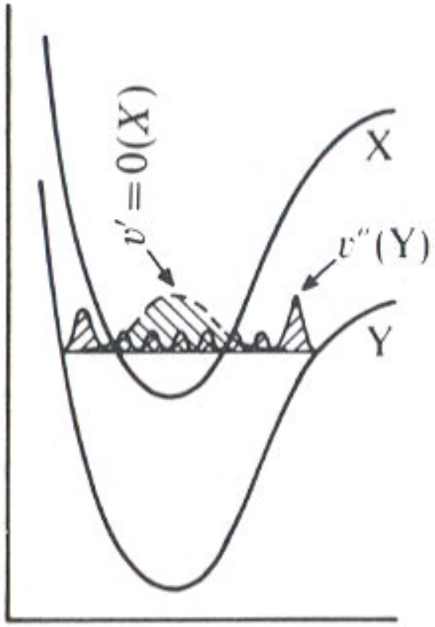




Dependence of rate of k_{ISC} T_1 to S_0 on energy gap



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).



In aromatics because of the large S_1 to S_0 energy gap internal conversion does not compete with ISC S_1 to T_1

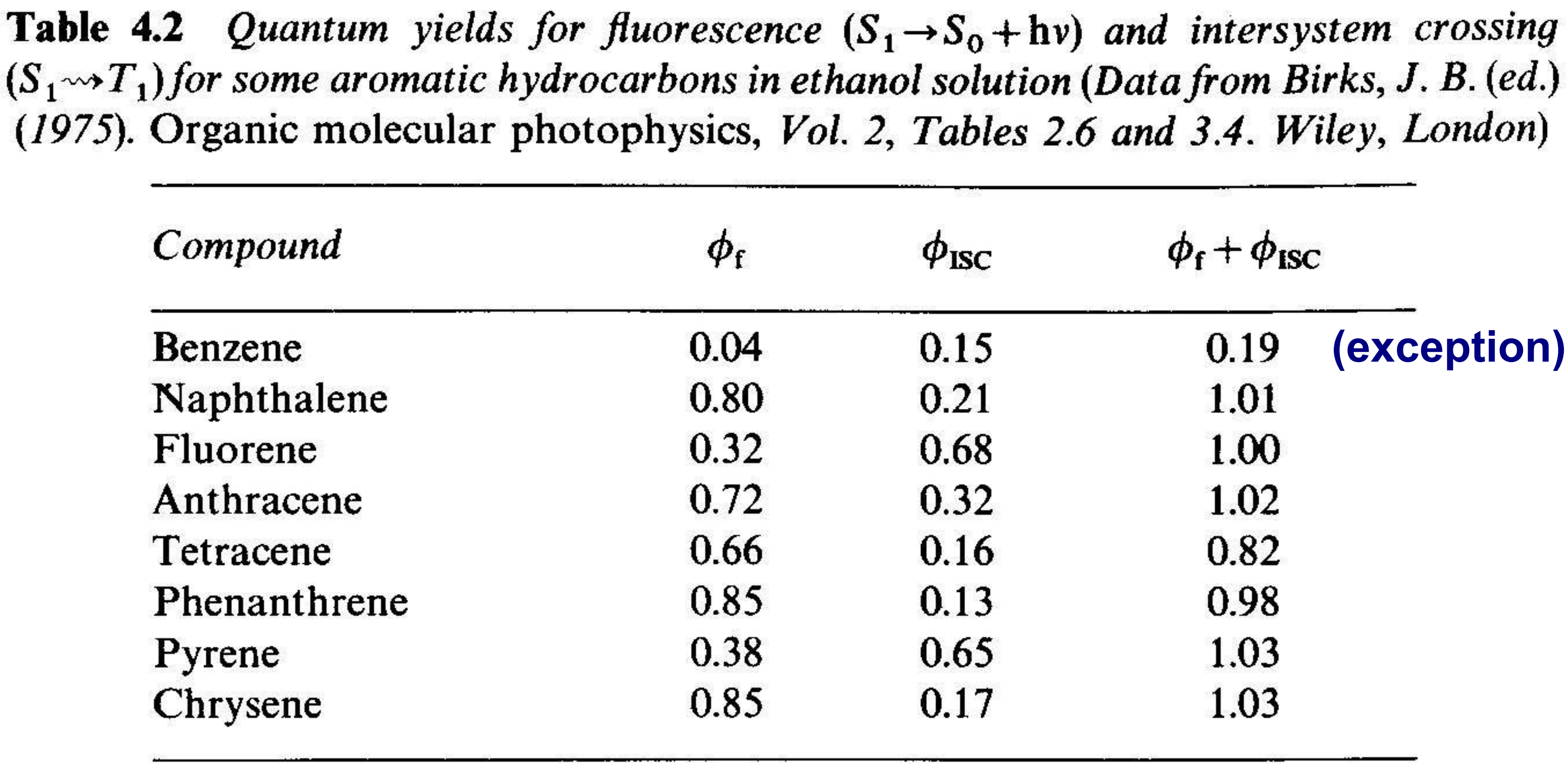


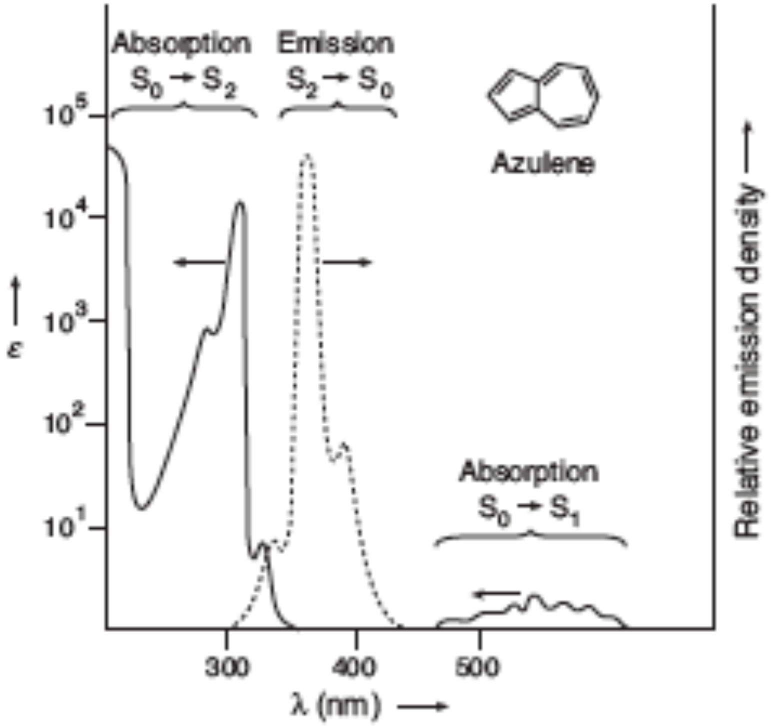
Table 4.2 *Quantum yields for fluorescence ($S_1 \rightarrow S_0 + h\nu$) and intersystem crossing ($S_1 \rightsquigarrow T_1$) for some aromatic hydrocarbons in ethanol solution* (*Data from* Birks, J. B. (ed.) (*1975*). Organic molecular photophysics, *Vol. 2, Tables 2.6 and 3.4. Wiley, London*)

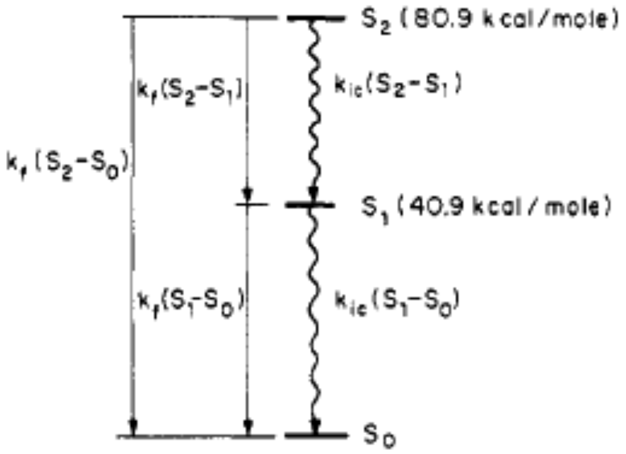
Compound	ϕ_f	ϕ_{ISC}	$\phi_f + \phi_{ISC}$	
Benzene	0.04	0.15	0.19	**(exception)**
Naphthalene	0.80	0.21	1.01	
Fluorene	0.32	0.68	1.00	
Anthracene	0.72	0.32	1.02	
Tetracene	0.66	0.16	0.82	
Phenanthrene	0.85	0.13	0.98	
Pyrene	0.38	0.65	1.03	
Chrysene	0.85	0.17	1.03	

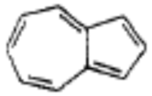
For large aromatic molecules the sum of the quantum yields of fluorescence and ISC is one i.e., rate of internal conversion is very slow with respect to the other two (Ermolaev’s rule).

Azulene Anamoly and Energy Gap Law

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







$k_f(S_2-S_0) = 1.4 \times 10^7$

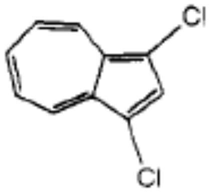
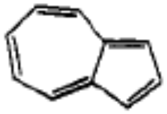
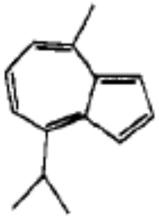
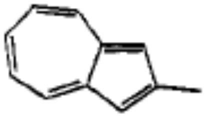
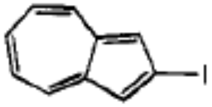
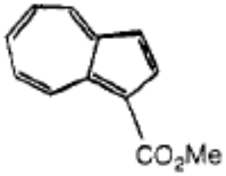
$k_f(S_2-S_1) \approx 1.4 \times 10^4$

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

$k_{ic}(S_2-S_1) = 7 \times 10^8$

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

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

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}**

Isotope Effect on Rate of T_1 to S_0

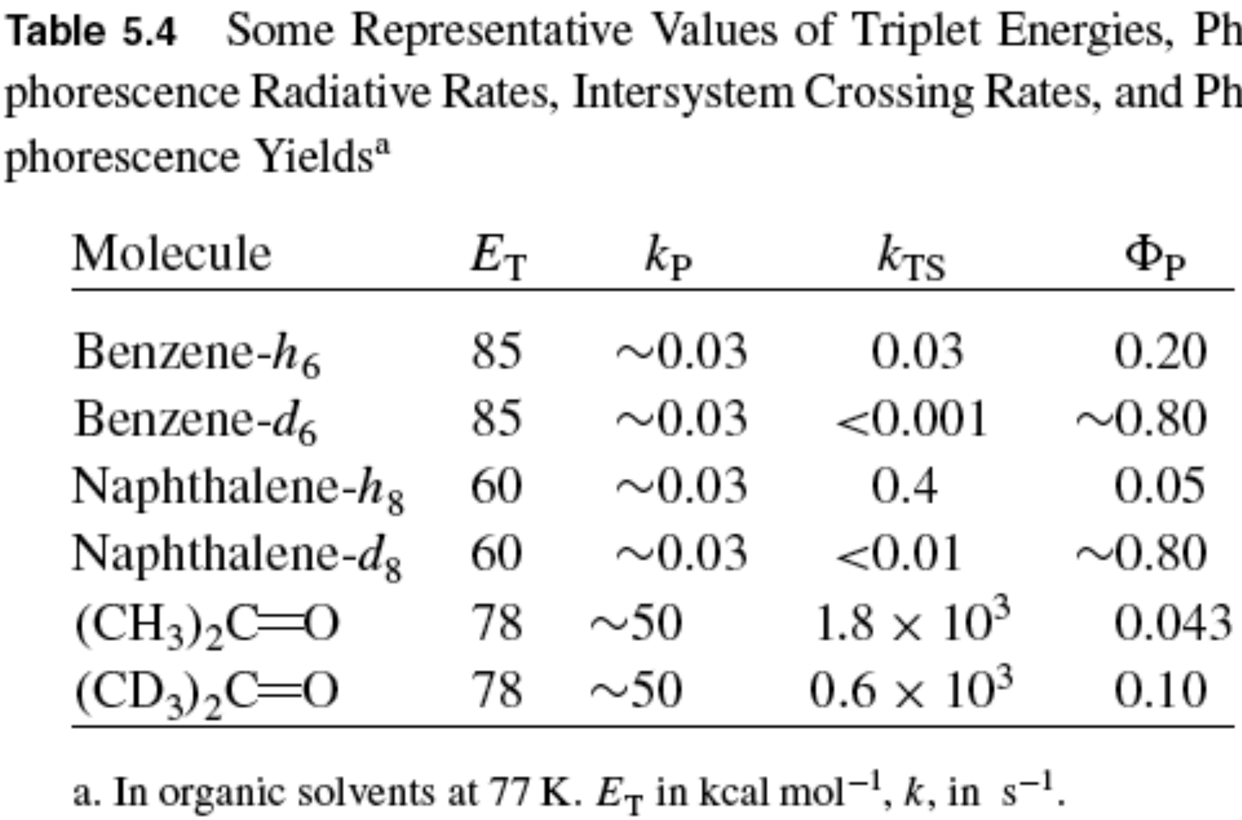
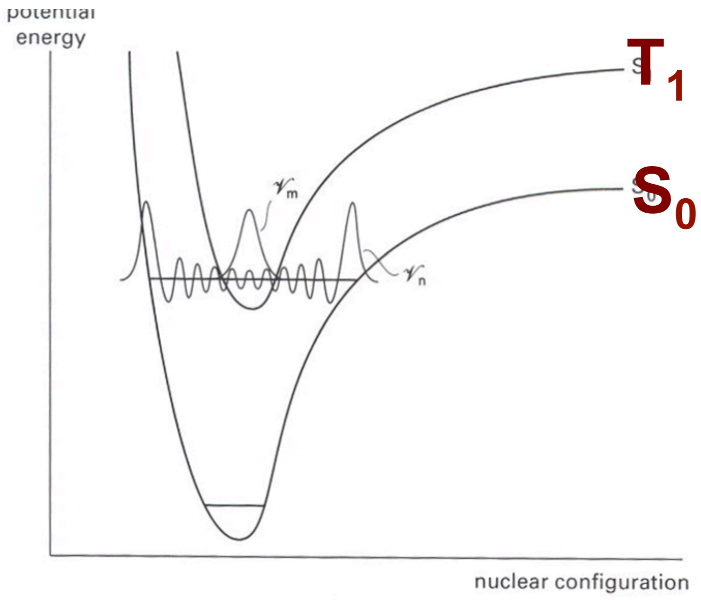


Table 5.4 Some Representative Values of Triplet Energies, Phosphorescence Radiative Rates, Intersystem Crossing Rates, and Phosphorescence Yields[a]

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}**



Vibrational effects on singlet oxygen lifetime

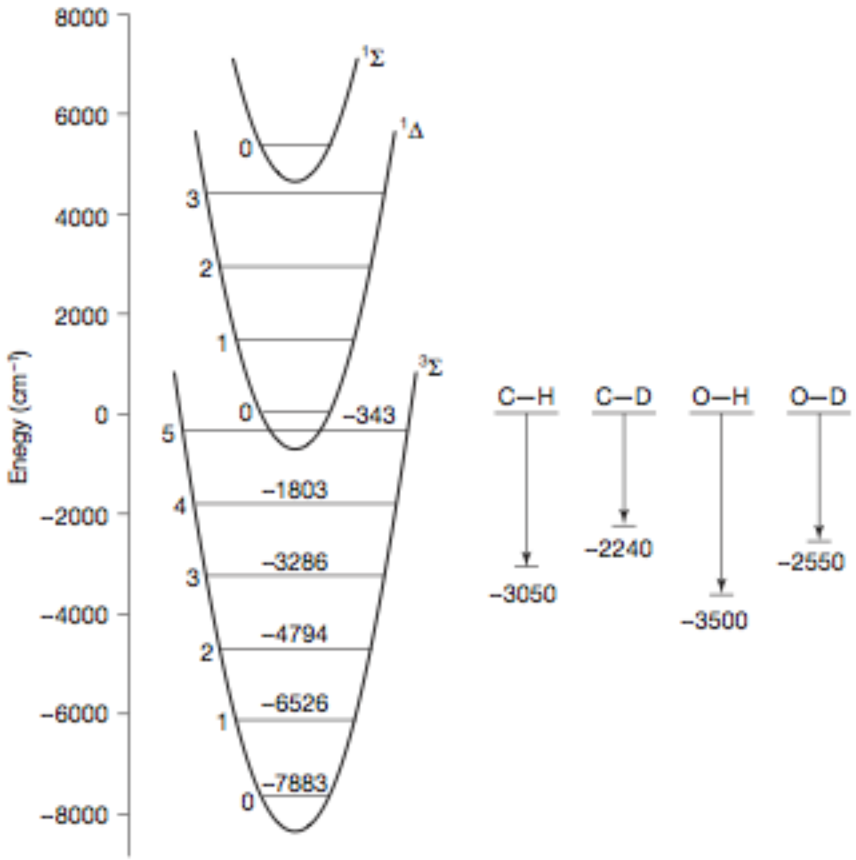


Figure 14.3 Comparison of the energy levels of $^1\Delta$ to common high frequency X–H and X–D vibrations of solvents. Energies in cm^{-1}.

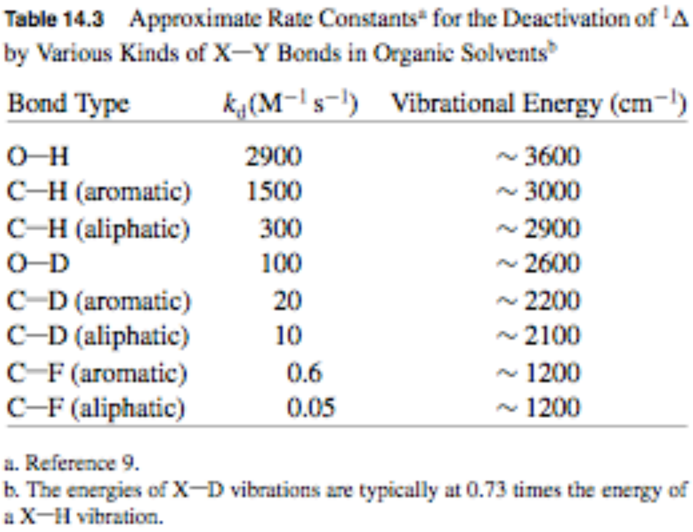
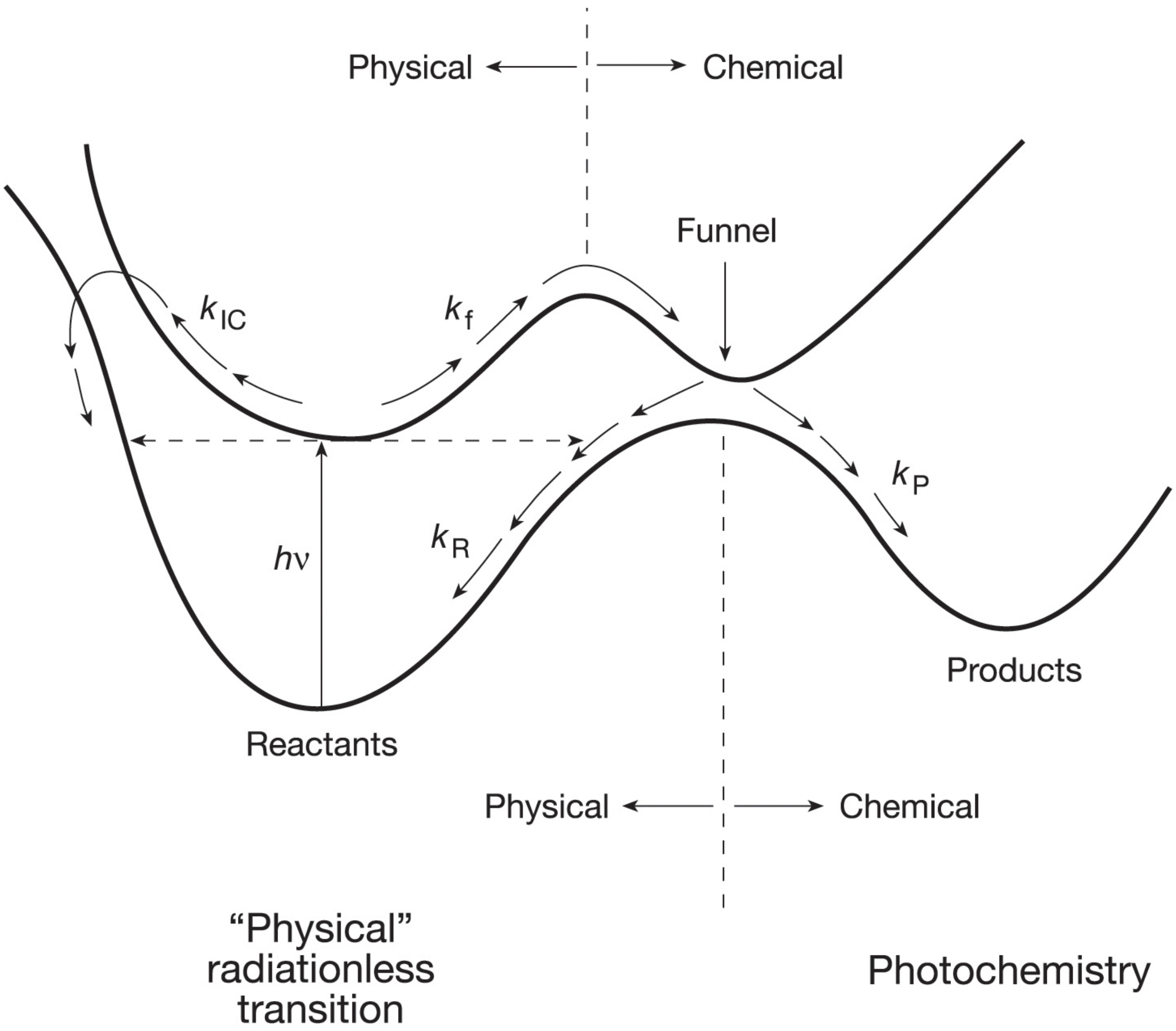


Table 14.3 Approximate Rate Constants[a] for the Deactivation of $^1\Delta$ by Various Kinds of X–Y Bonds in Organic Solvents[b]

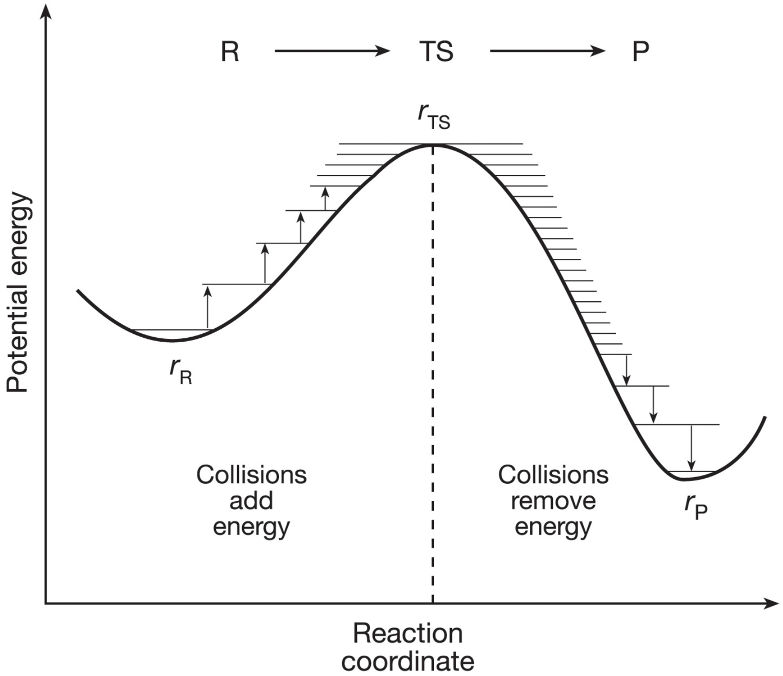
Bond Type	k_d (M^{-1} s^{-1})	Vibrational Energy (cm^{-1})
O–H	2900	~ 3600
C–H (aromatic)	1500	~ 3000
C–H (aliphatic)	300	~ 2900
O–D	100	~ 2600
C–D (aromatic)	20	~ 2200
C–D (aliphatic)	10	~ 2100
C–F (aromatic)	0.6	~ 1200
C–F (aliphatic)	0.05	~ 1200

a. Reference 9.

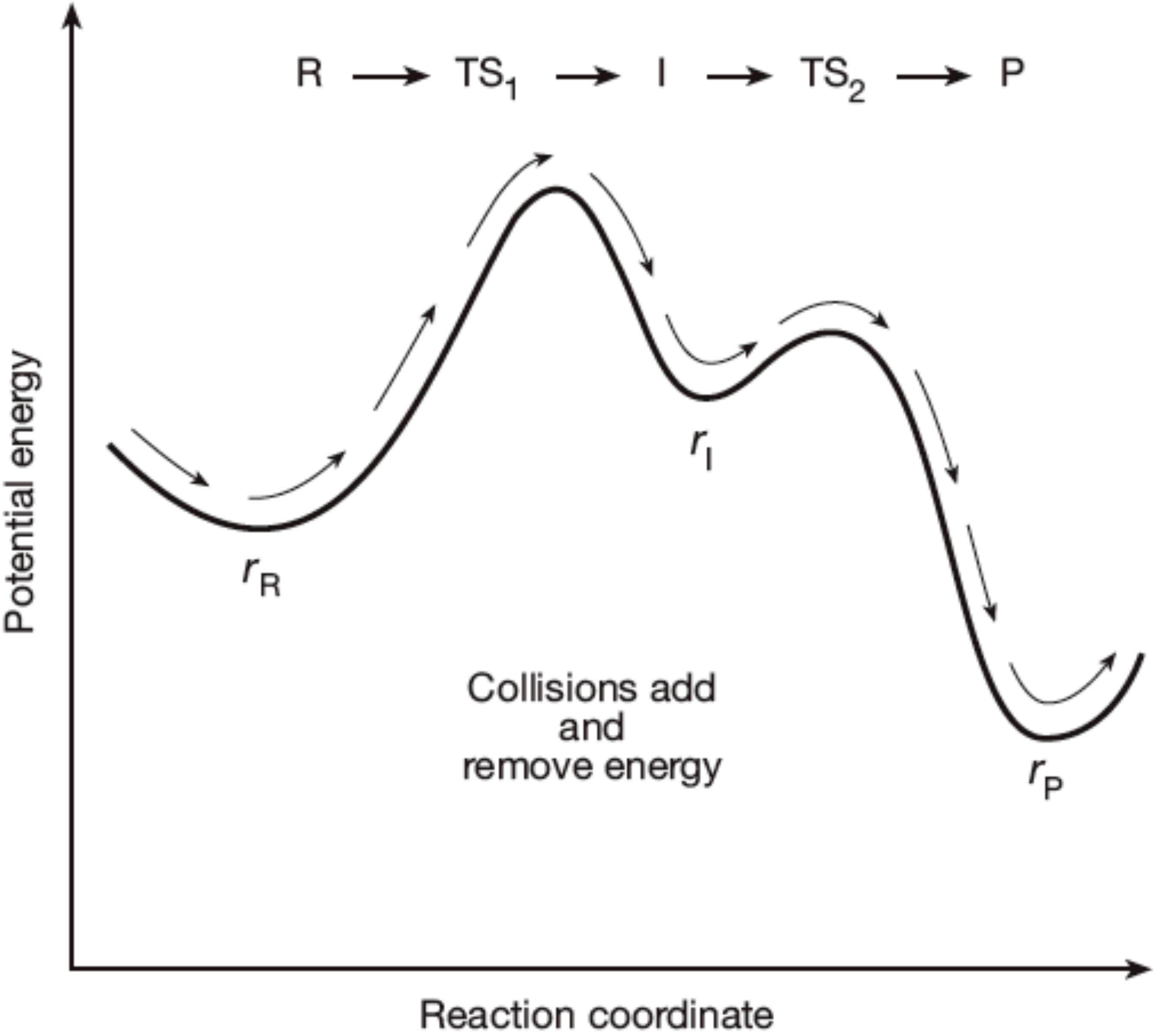
b. The energies of X–D vibrations are typically at 0.73 times the energy of a X–H vibration.


Physical
Chemical
Funnel
k_{IC}
k_f
k_P
k_R
$h\nu$
Reactants
Products
Physical
Chemical
“Physical” radiationless transition
Photochemistry

Visualization of Thermal Reactions



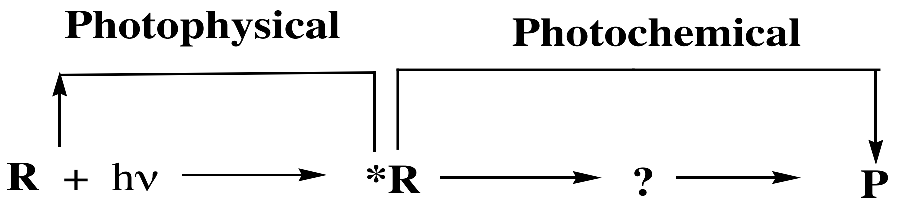
- Transition state connects a single reactant to a single product and it is a saddle point along the reaction course.
- Collisions are a reservoir of continuous energy (~ 0.6 kcal/mol per impact).
- Collisions can add or remove energy from a system.
- Concerned with a single surface.



R → TS1 → I → TS2 → P
Potential energy
r_R
r_I
r_P
Collisions add
and
remove energy
Reaction coordinate

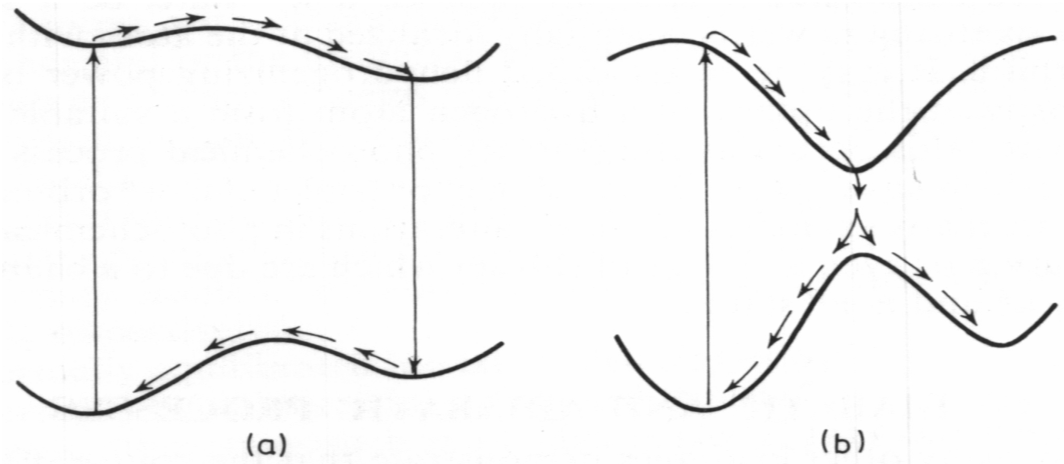
Photochemical Process-Horizontal (Non-vertical) Transition

We need to deal with two surfaces.

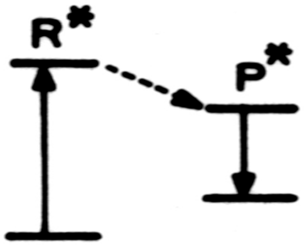


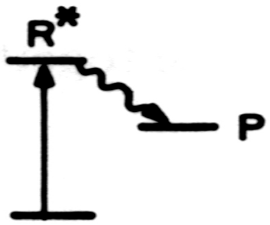
Adiabatic

Diabatic

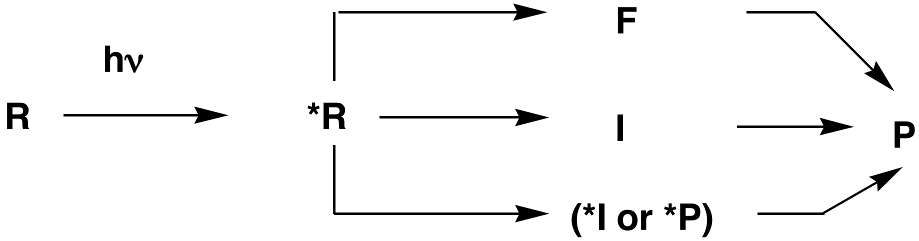


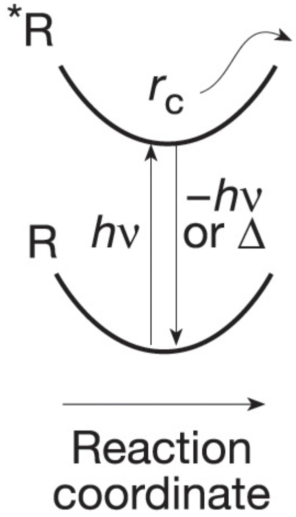
Pathways of photochemical reactions: (a) adiabatic, (b) diabatic.



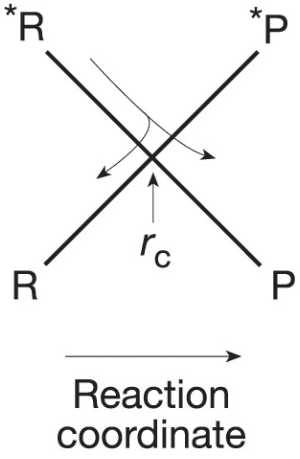


Photoreactions with and without intermediates: Two dimensional model



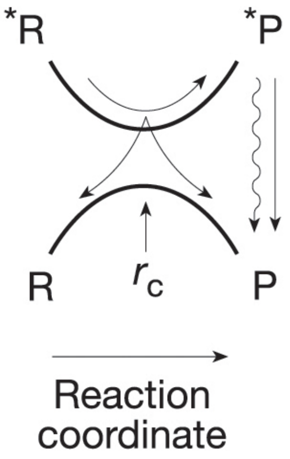


Spectroscopic states



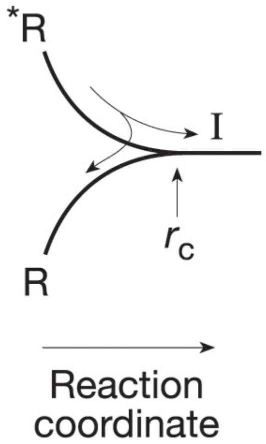
$^{*}\mathrm{R} \longrightarrow \mathrm{CI} \longrightarrow \mathrm{R,P}$

Pericyclic reacions



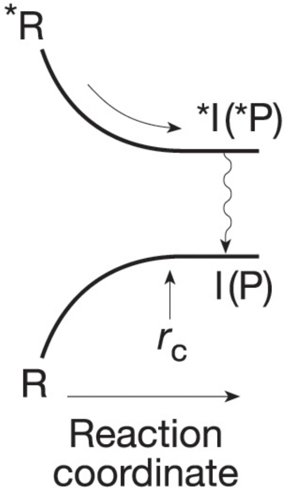
$^{*}\mathrm{R} \longrightarrow \mathrm{AC} \begin{array}{l} \nearrow {}^{*}\mathrm{P} \\ \searrow \mathrm{P} \end{array}$

Twist about a C=C bond



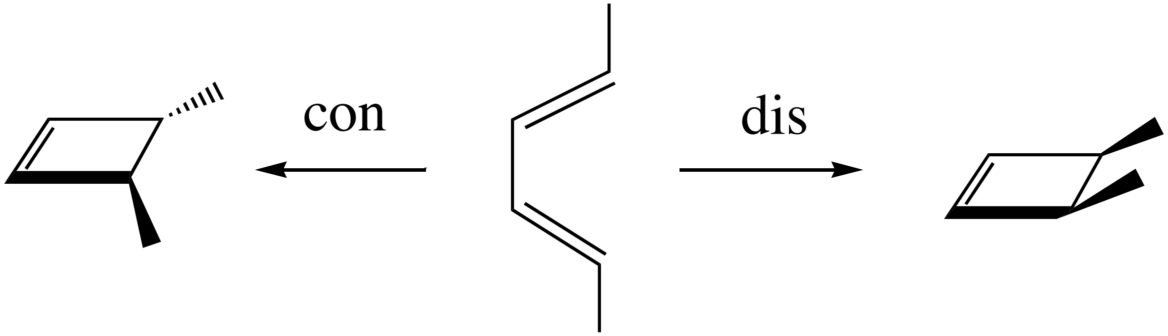
$^{*}\mathrm{R} \rightarrow \mathrm{ST} \rightarrow \mathrm{I,R}$

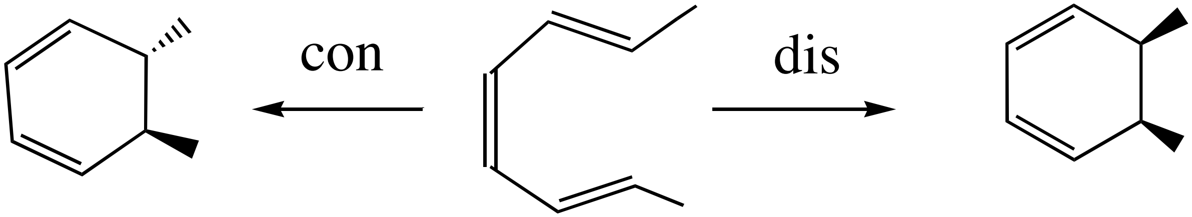
Reactions of n,π* states



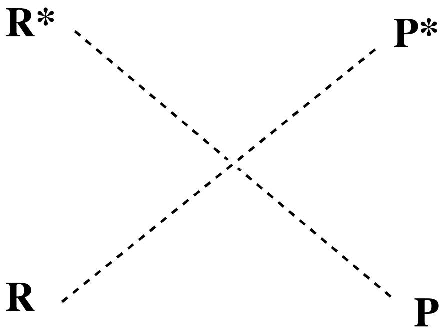
$^{*}\mathrm{R} \rightarrow \mathrm{SM} \rightarrow {}^{*}\mathrm{I}({}^{*}\mathrm{P})$

Exciplex/excimer formation

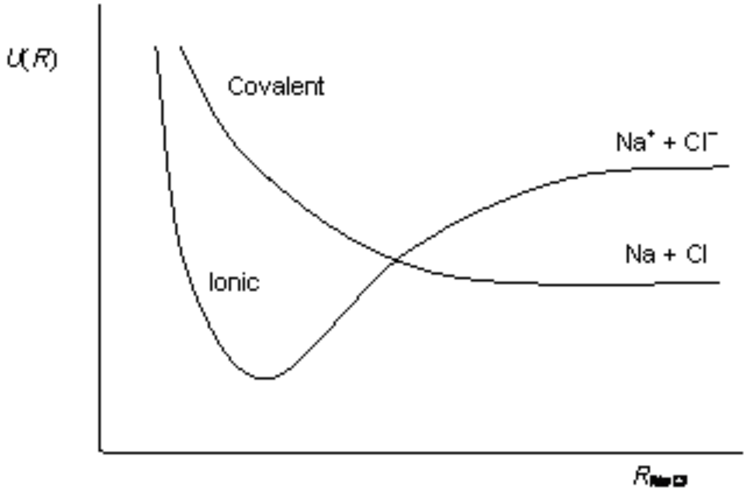

con
dis

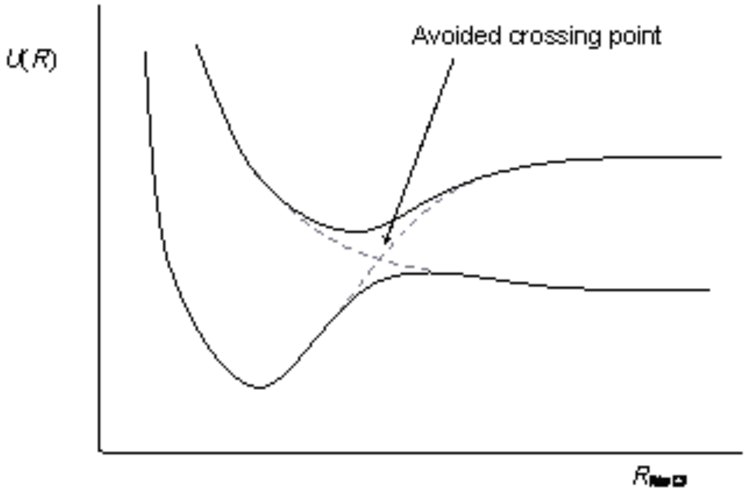

con
dis


R*
P*
R
P


R*
P*
R
P

Diatomic Molecules and Non-crossing Rule

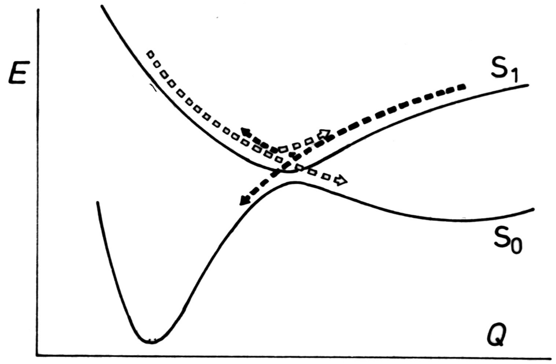




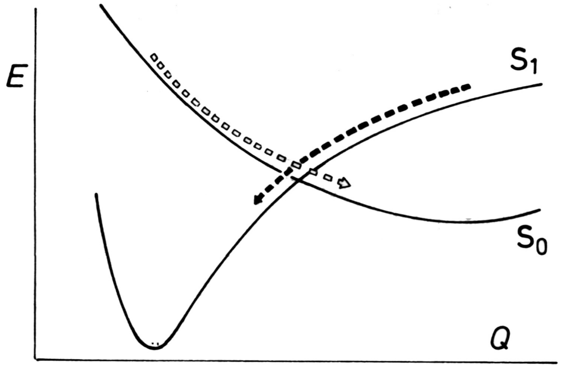
In diatomic molecules the two surfaces (e.g., ground and excited states) will only cross if the two states have different spatial and/or spin symmetry; i.e., the two surfaces will not cross if they have the same symmetry.

Polyatomic Molecules and Non-crossing rule

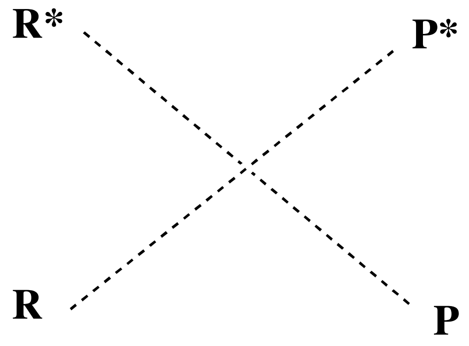
In **polyatomic** molecules the two surfaces (e.g., ground and excited states) **may cross** even if the two states have the same spatial and/ or spin symmetry.

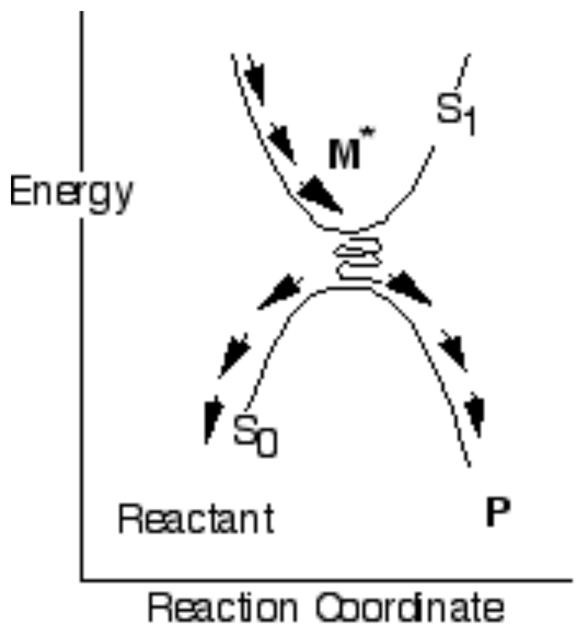


Avoided Crossing

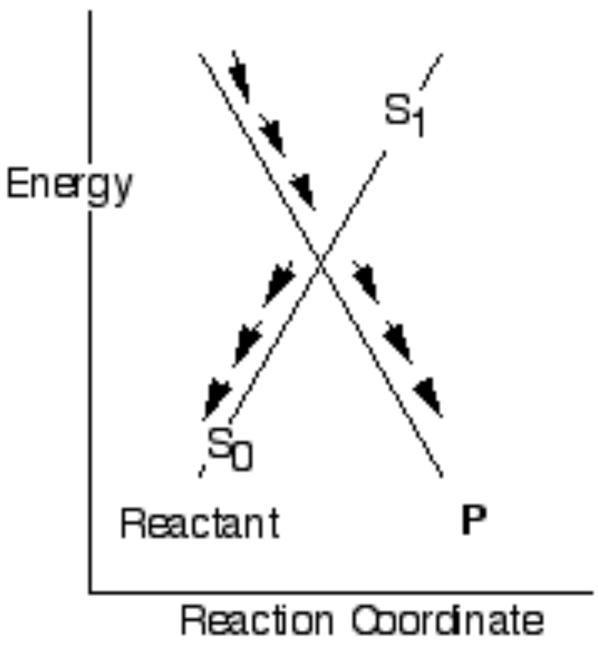


Allowed Crossing





Avoided Crossing



Crossing (Conical Intersection)

Allowed Crossing Follows Born-Oppenheimer Approximation

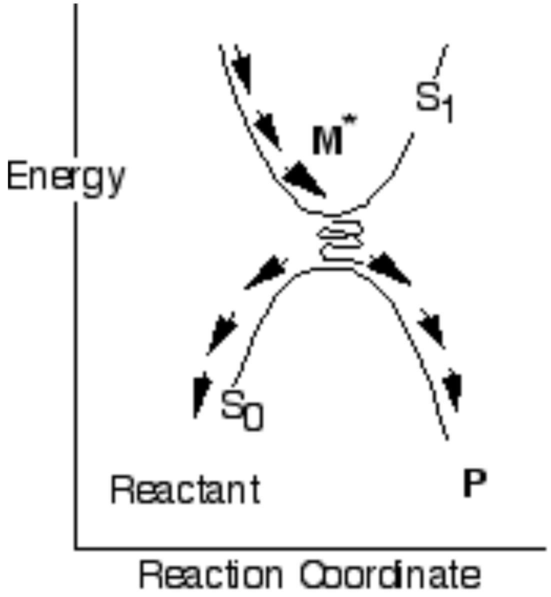
If the nuclei are assumed to move slowly, then the rate of jump is decided by Fermi Golden Rule

$$P \alpha e^{-(\Delta E)}$$

The rate of jump depends on the energy gap; smaller the gap faster the rate.

Expected time scale would be in the range of ns.

Longer time allows for equilibrium in the excited state.



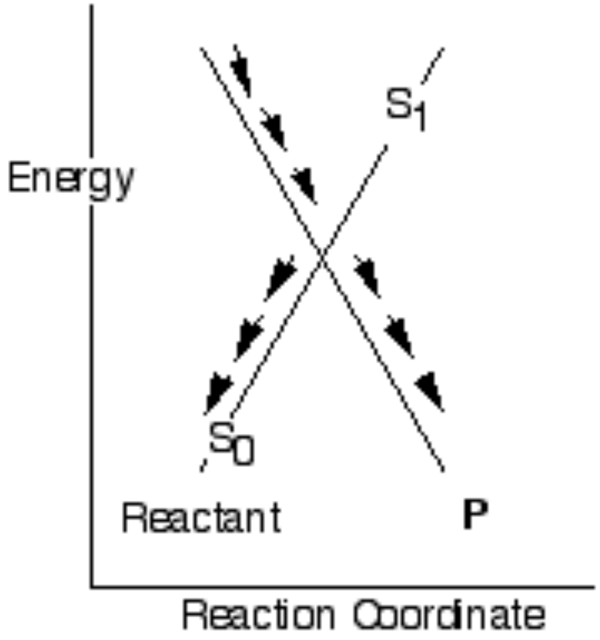
Avoided Crossing

Conical Intersections: Born-Oppenheimer Approximation Breaks Down

If the nuclei have sufficient velocity, the Born-Oppenheimer approximation breaks down and the there is no time for electronic configuration to respond to nuclear position changes.

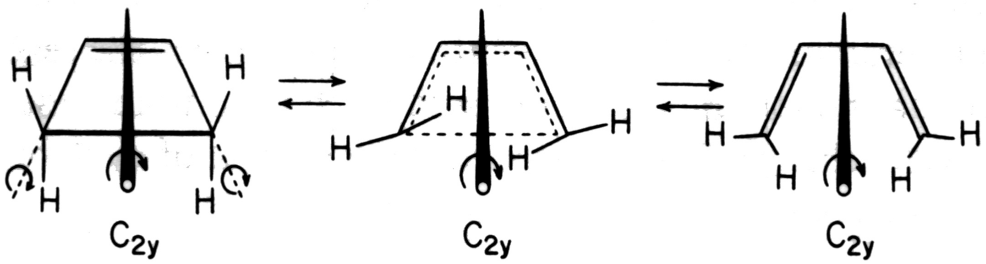
The same wavefunction may be classified as an excited state wavefunction in the region of energies higher than the crossing point and a ground state wavefunction in the region of lower energies than the crossing point.

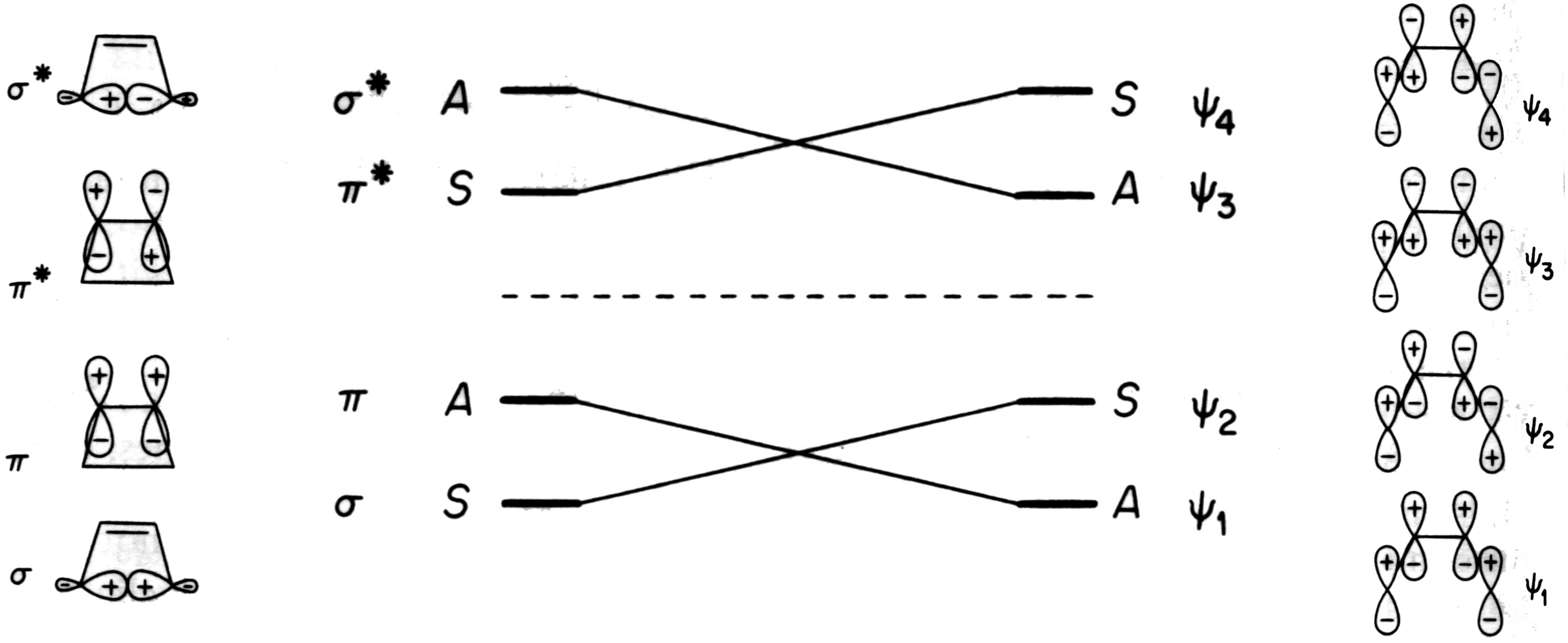
The rate of crossing is not controlled by Fermi Golden Rule since the energy gap between upper and lower surface is zero. The crossing is instantaneous.



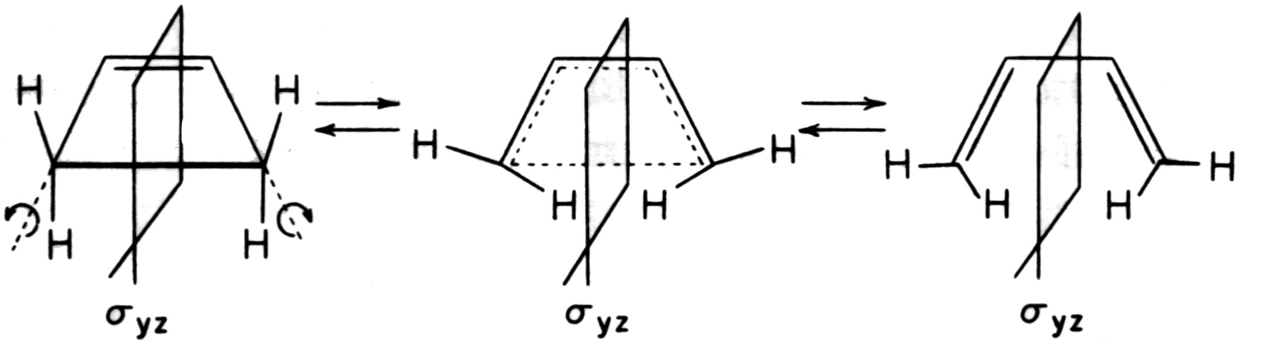
Crossing (Conical Intersection)

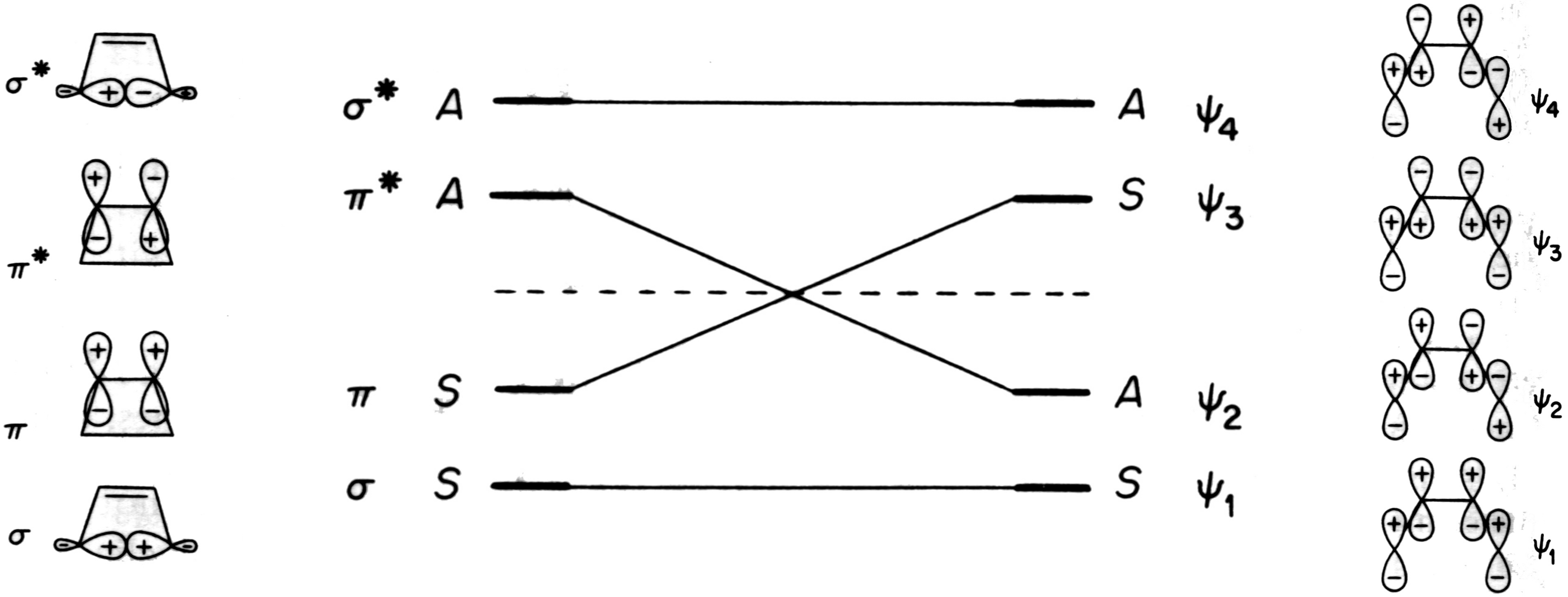
Conrototary Cyclization of 1,3-Butadiene



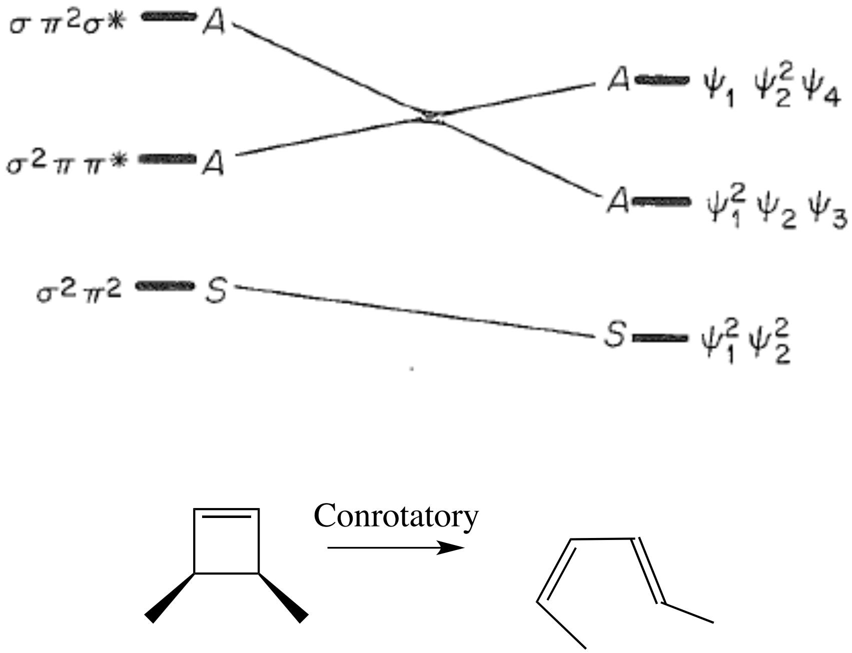


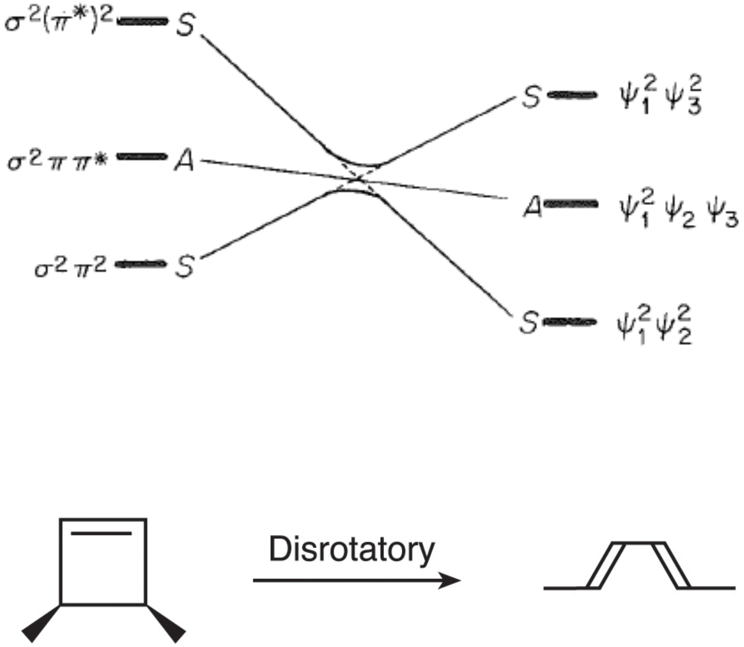
Disrototary Cyclization of 1,3-Butadiene

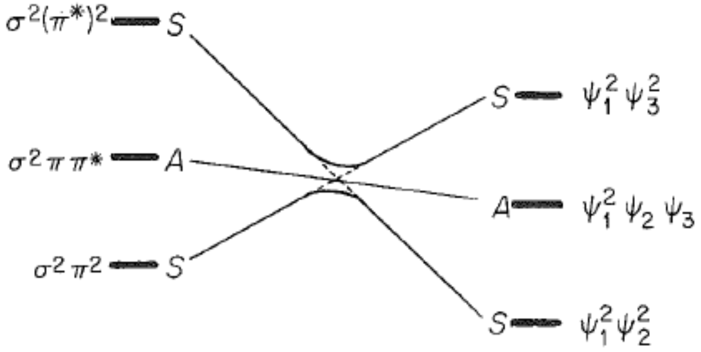


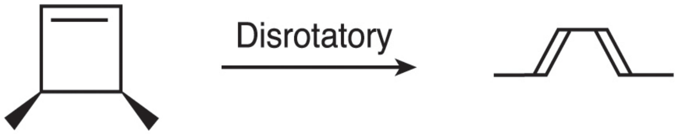


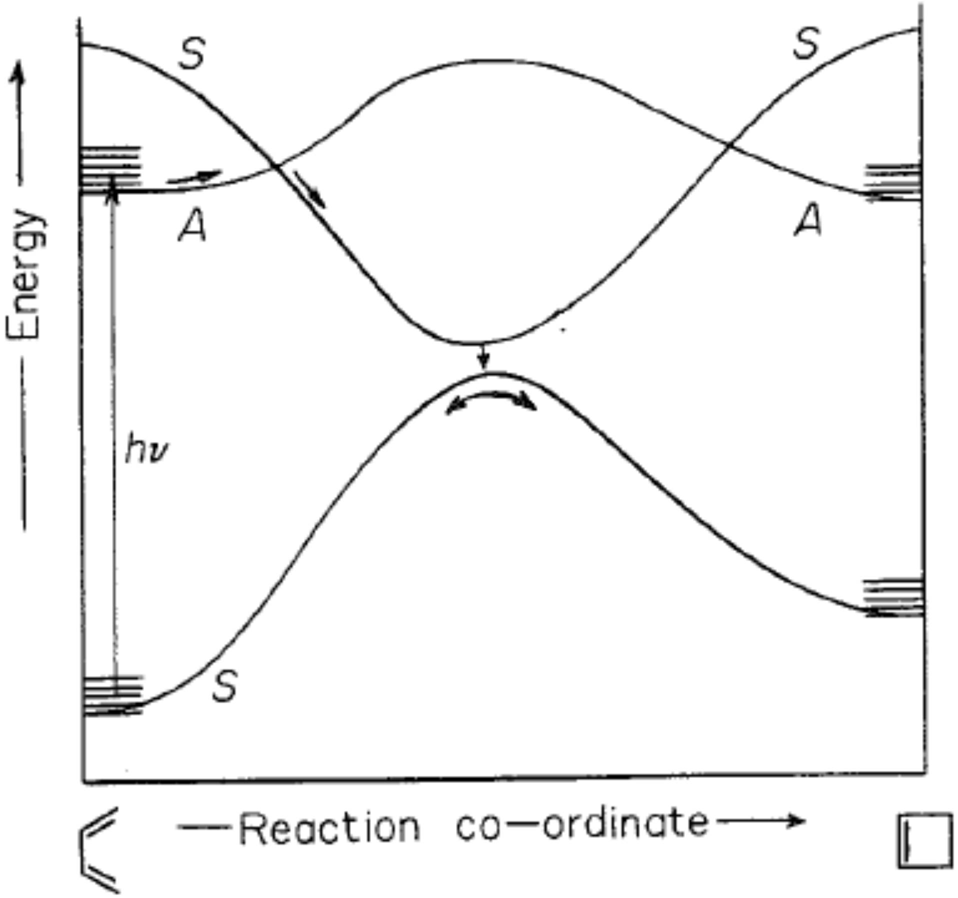
State Correlation Diagram

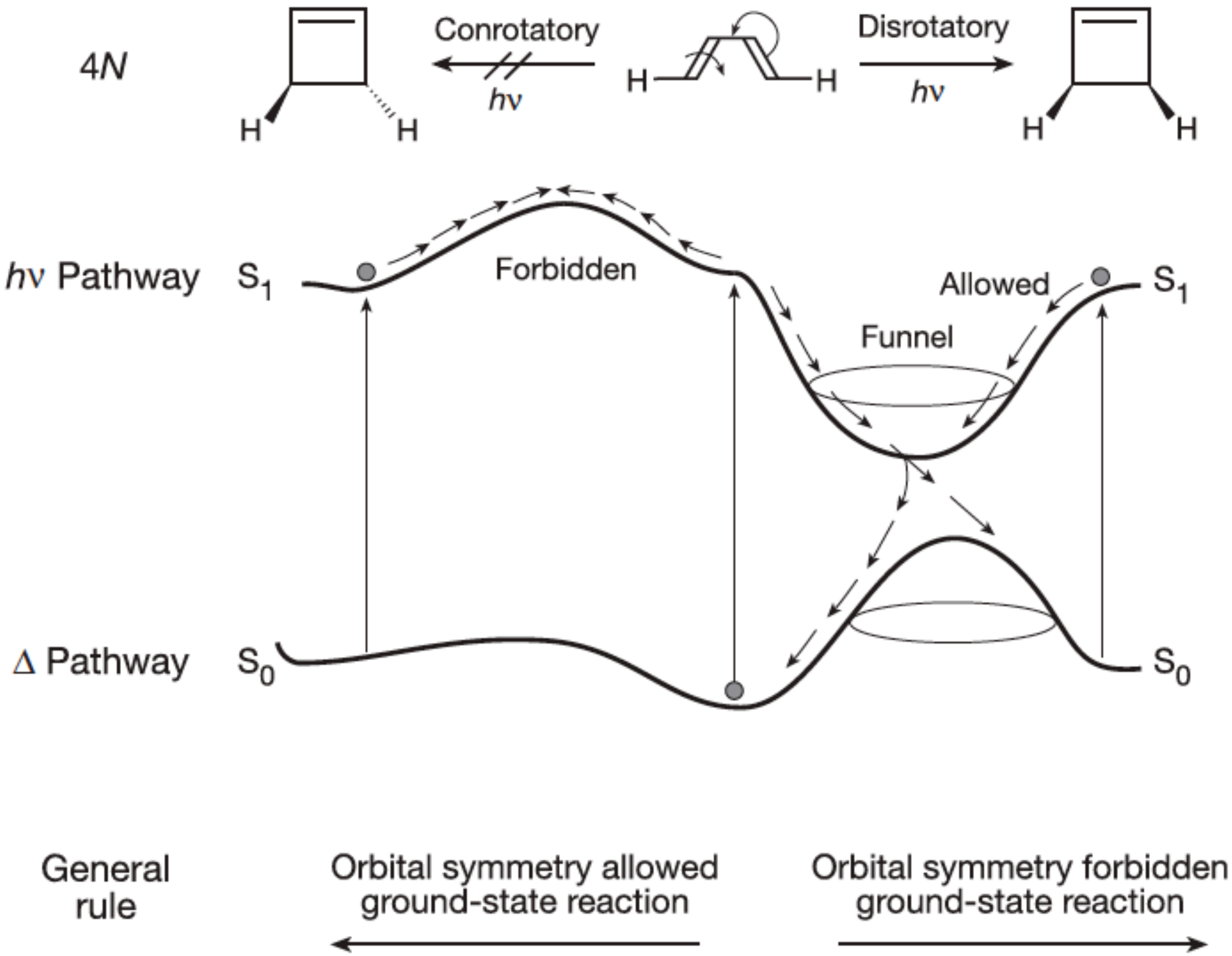




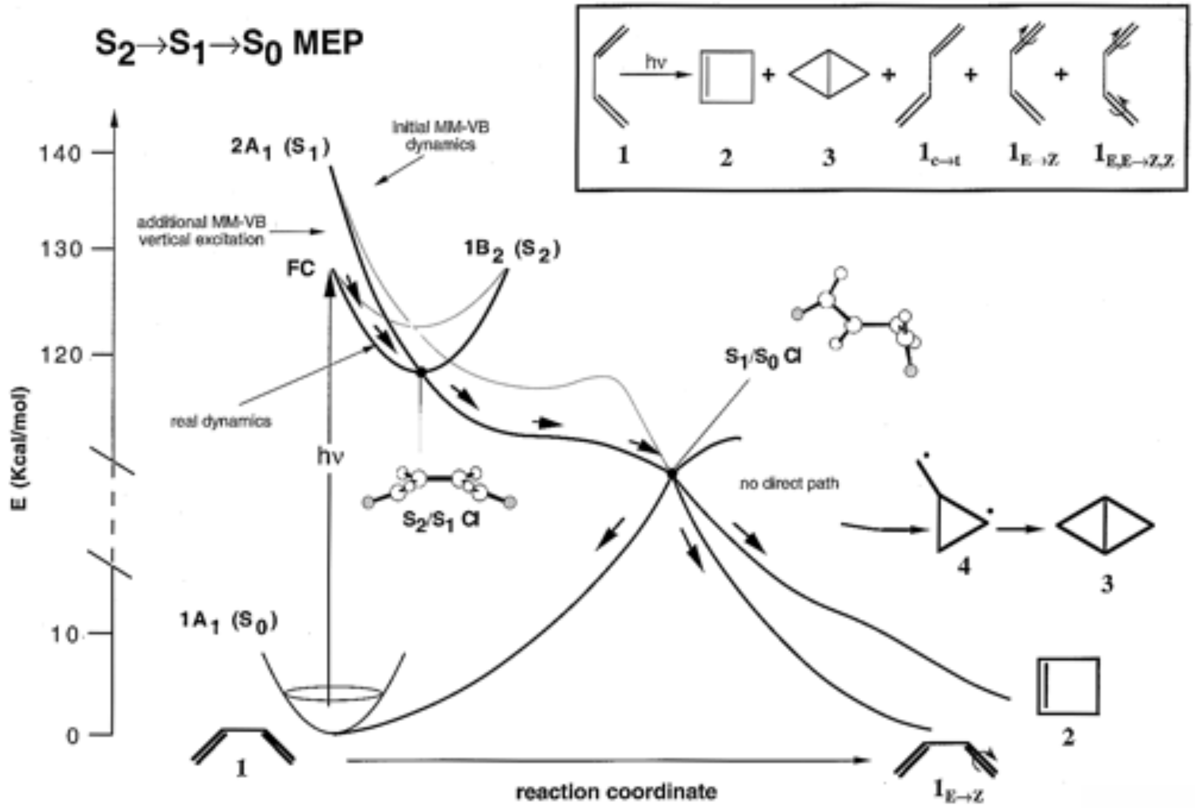

$\sigma^2(\pi^*)^2$ S
$\sigma^2\pi\pi^*$ A
$\sigma^2\pi^2$ S
S $\psi_1^2\psi_3^2$
A $\psi_1^2\psi_2\psi_3$
S $\psi_1^2\psi_2^2$


Disrotatory


S
S
A
A
S
Energy
$h\nu$
Reaction co-ordinate

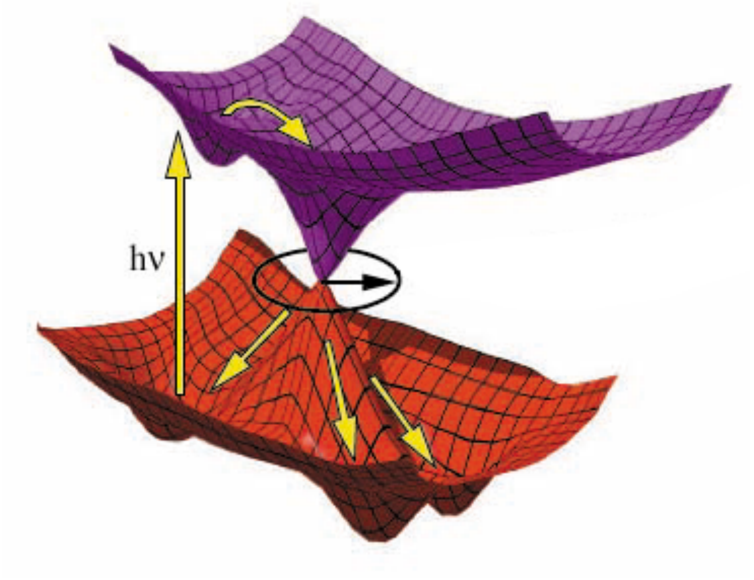


4N
Conrotatory
hν
H
H
H
H
Disrotatory
hν
H
H
hν Pathway
S1
Forbidden
Allowed
S1
Funnel
Δ Pathway
S0
S0
General rule
Orbital symmetry allowed ground-state reaction
Orbital symmetry forbidden ground-state reaction



Conical intersection may connect multiple products.

Prediction becomes impossible without the help of computations.



Presence of conical intersections leads to multiple products from a single 'funnel'