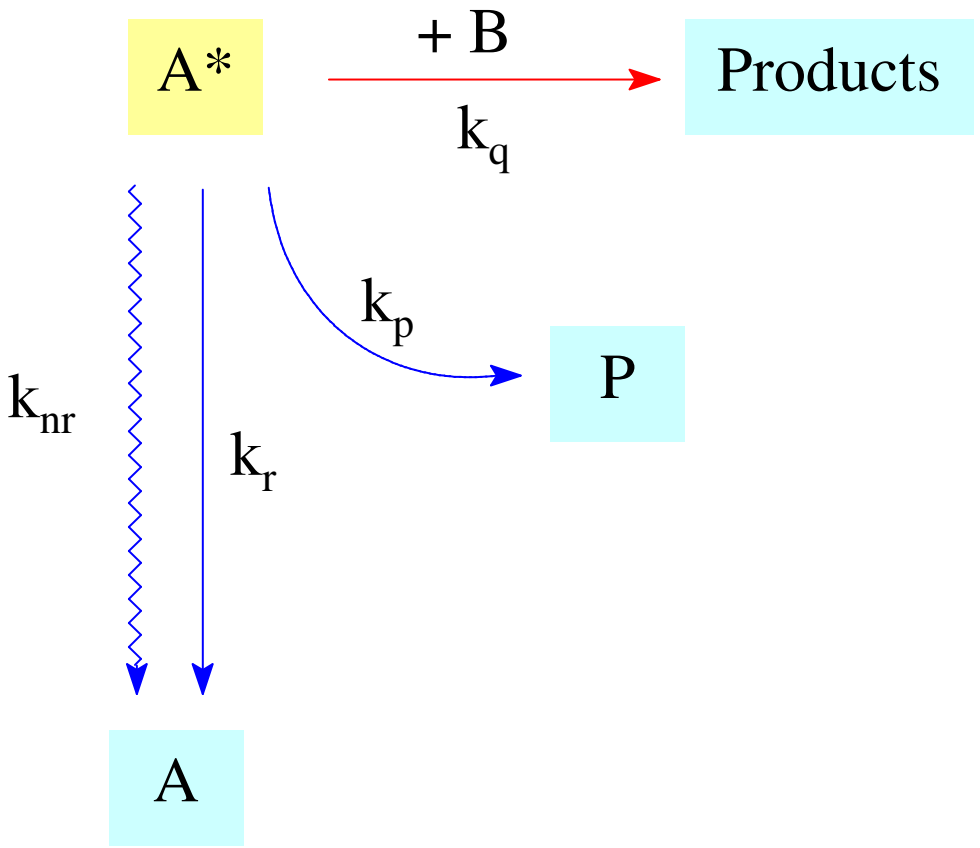
Excited-State Processes



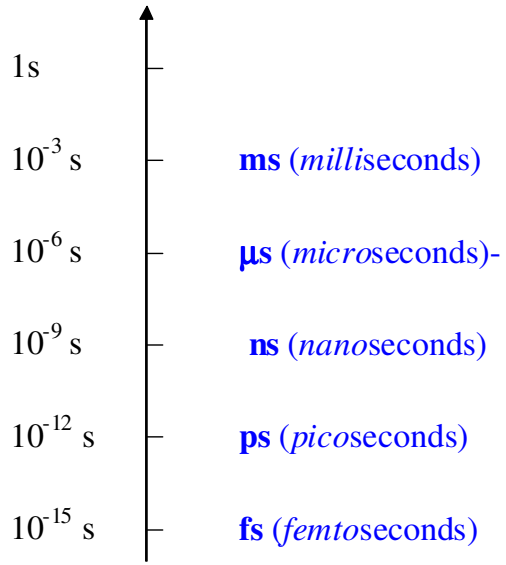
Unimolecular Processes:

k_r: radiative deactivation (emission)
k_{nr}: radiationless deactivation
k_p: chemical reaction

Bimolecular Processes:

k_q: bimolecular quenching of A*
("products" include energy, electron, and proton transfer between A and B)

The timescale of photochemical events



- **fs** is the lower limit of the chemistry time scale.

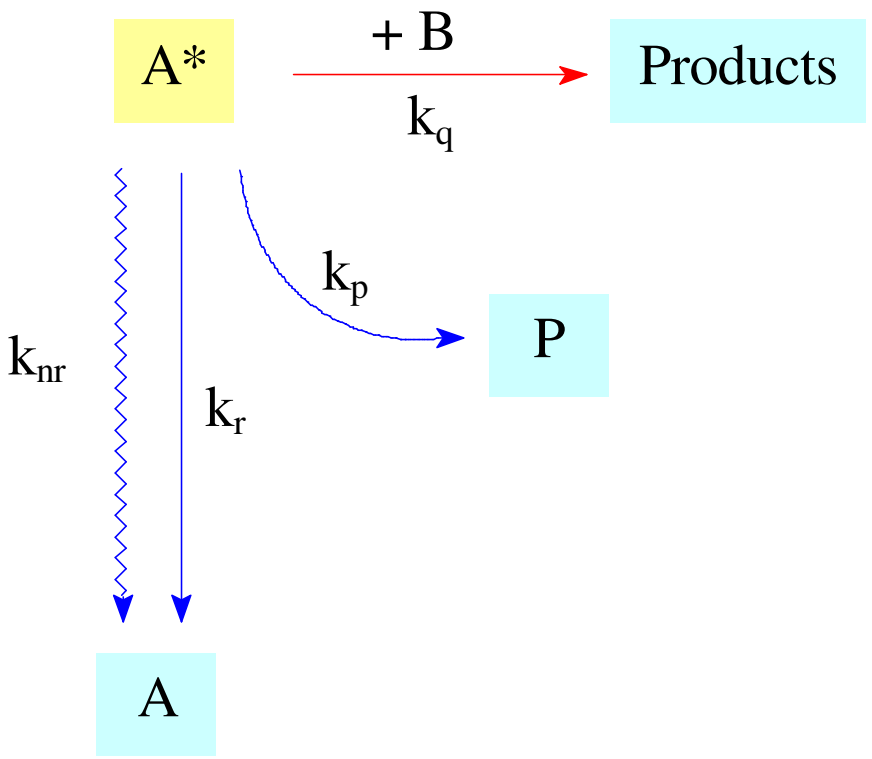
- electron motion in molecules takes place in **fs**.

- photon absorption (excitation) take place in **fs**.

The time scale

Power	Units		e.g.,	Light travels…
18	Exasecond	31.7 10^9 years	age of universe	31.7 billion light-years
17				
16				
15	Petasecond	31.7 10^6 years	oligocene	31.7 million light-years
14				
13				
12	Terasecond	31.7 10^3 years	entering prehistory	31.7 thousand light-years
11				
10				
9	Gigasecond	31.7 years	1 human generation	31.7 light-years
8				
7				
6	Megasecond	11.6 days	1 generation of Drosophila	0.32 light-years
5				
4				
3	Kilosecond	16.7 min	coffee break	300 million Km
2				
1				
0	second		heartbeat	300 thousand Km
-1				
-2				
-3	millisecond		camera shot	300 Km
-4				
-5				
-6	microsecond		free radicals	300 m
-7				
-8				
-9	nanosecond		electr. excited molecules	30 cm
-10				
-11				
-12	picosecond		energy/electron transfer	0.3 mm
-13				
-14			mol. vibrations	
-15	femtosecond			0.3 µm
-16				
-17			electron motion in atoms	
-18	attosecond			3 Å

Excited-State Processes



Unimolecular Processes:

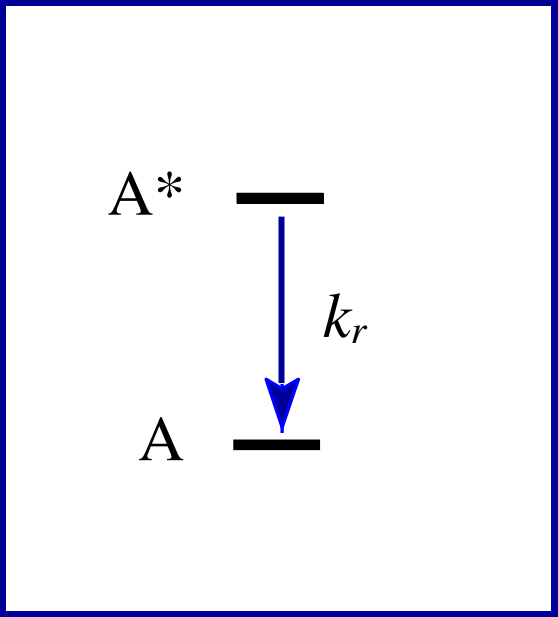
- k_r: radiative deactivation (emission)
- k_{nr}: radiationless deactivation
- k_p: chemical reaction

Radiative deactivation (Emission)

$$A^* \xrightarrow{k_r} A + h\nu$$

$$k_r = \frac{64\pi^4 \nu^3}{3h^2} \left| \mu_{12}{}^2 \right|$$

$$\mu_{12} = \int \Psi_1 \mu \Psi_2 dq \int S_1 S_2 d\xi \sum_n X_1{}^0 X_2{}^n dQ$$

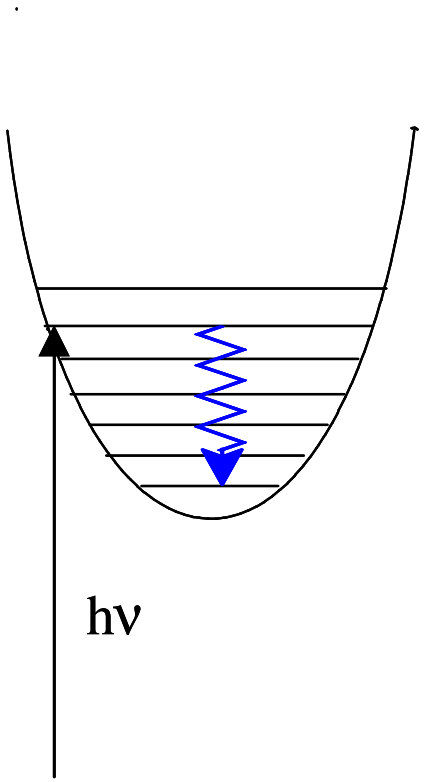


Same selection rules as for absorption. In particular,

spin-allowed emission	**Fluorescence**
spin-forbidden emission	**Phosphorescence**

Again, Franck-Condon factors do not affect k_r, but determine the **shape** of the emission band.

Rilassamento vibrazionale (“termalizzazione”) degli stati eccitati



10^{-12} s

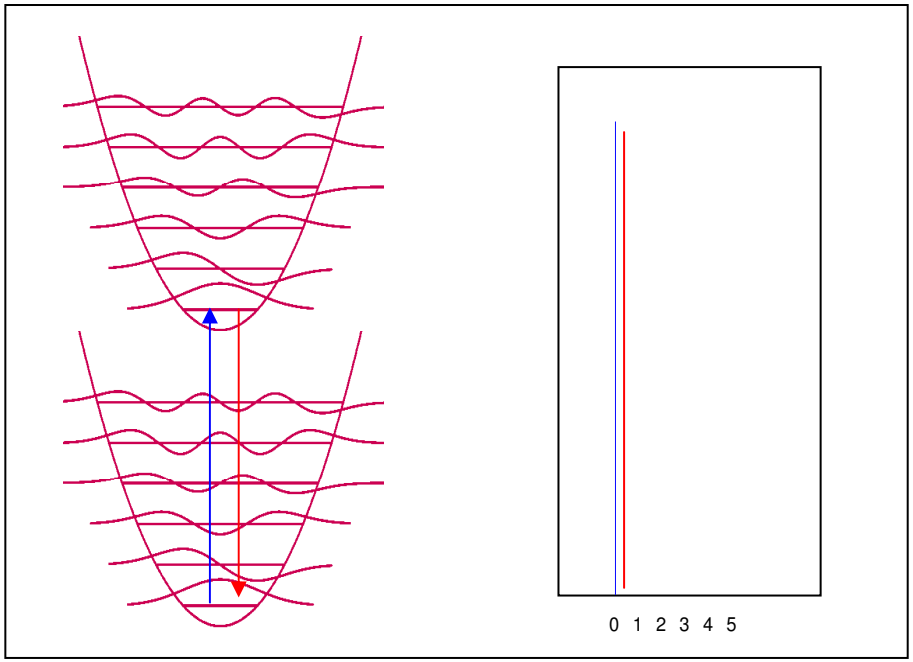
per Franck-Condon, le molecole elettronicamente eccitate vengono spesso formate con un eccesso di energia vibrazionale rispetto all’ambiente circostante (cioè sono “calde” rispetto alla T del mezzo).

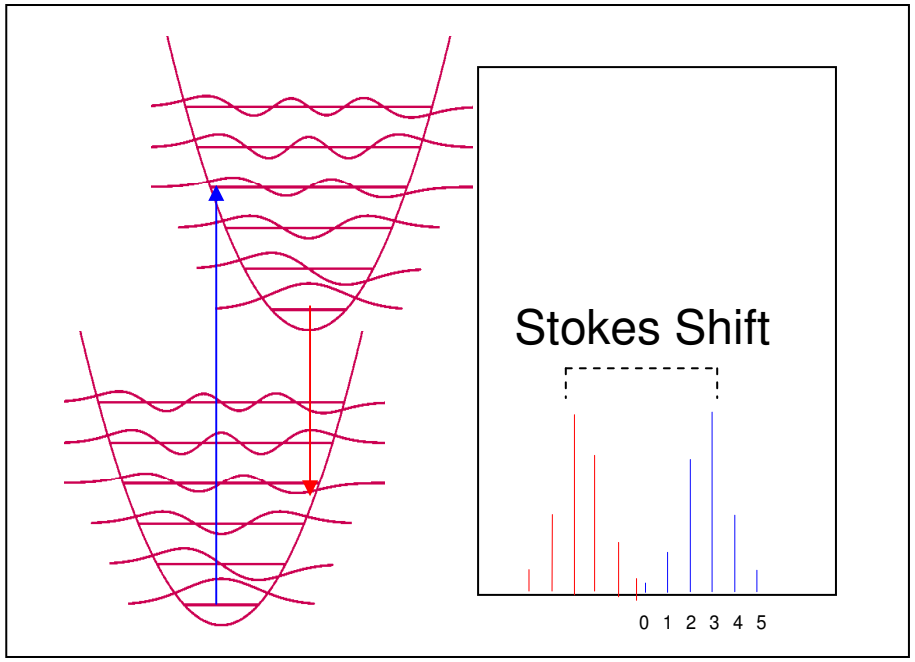
In fase condensata, le molecole perdono il loro eccesso di energia per collisione con il mezzo in tempi dell’ordine di pochi picosecondi (qualche vibrazione).

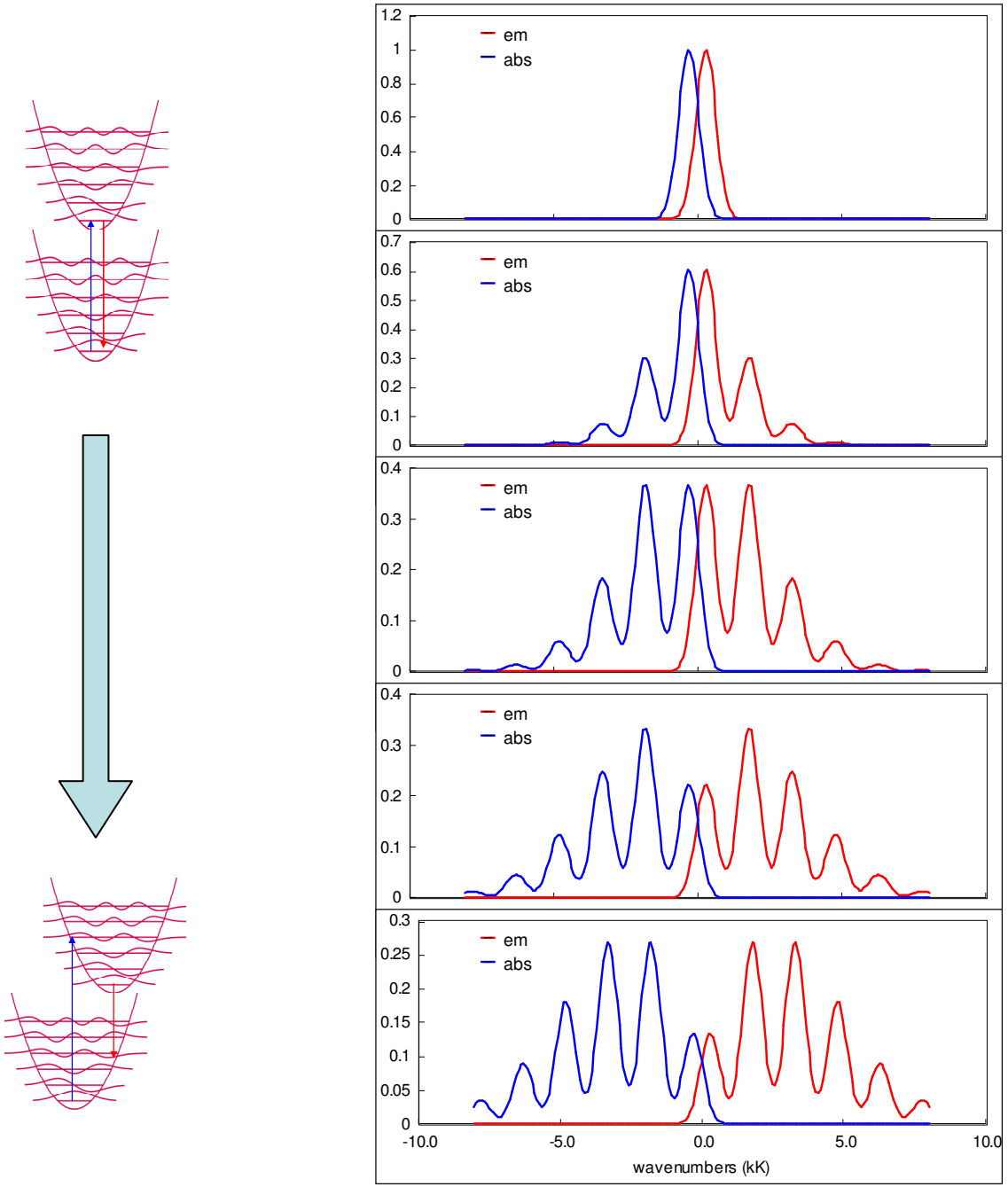
La maggior parte dei processi fotochimici e fotofisici di interesse avvengono in tempi > 10^{-11}s . Perciò gli stati eccitati, indipendentemente dalla loro formazione, si possono considerare a tutti gli effetti sul livello $v = 0$.

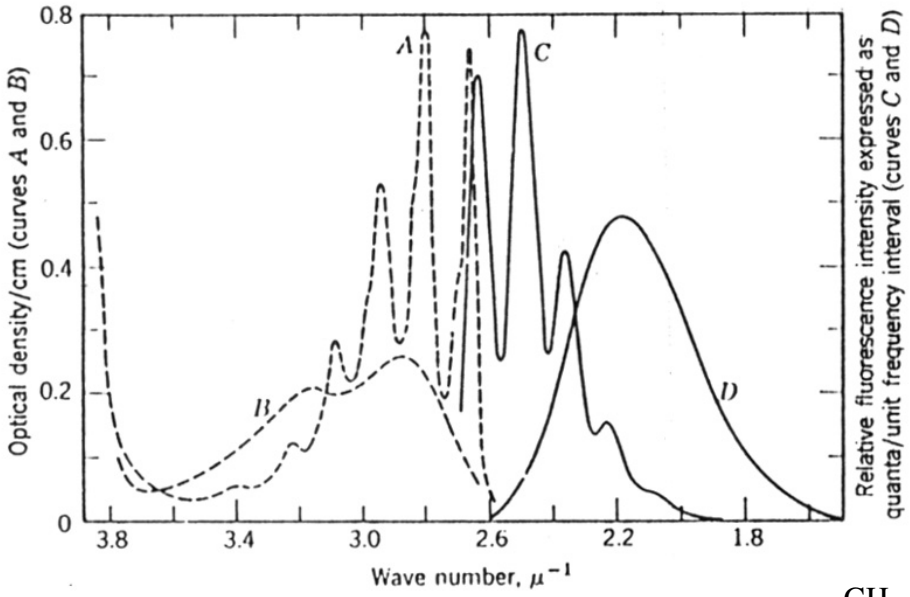
Franck-Condon Factors and Absorption/Emission Bandshape

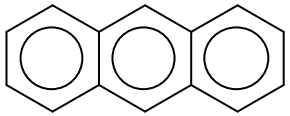
Stokes Shift and Excited-State Distortion



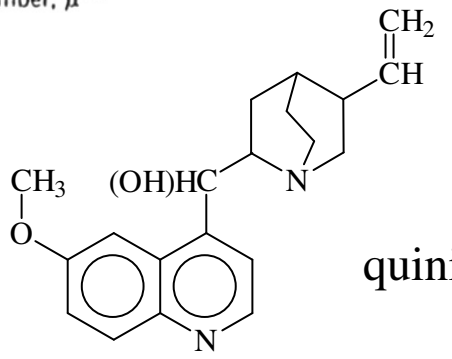



em
abs
wavenumbers (kK)



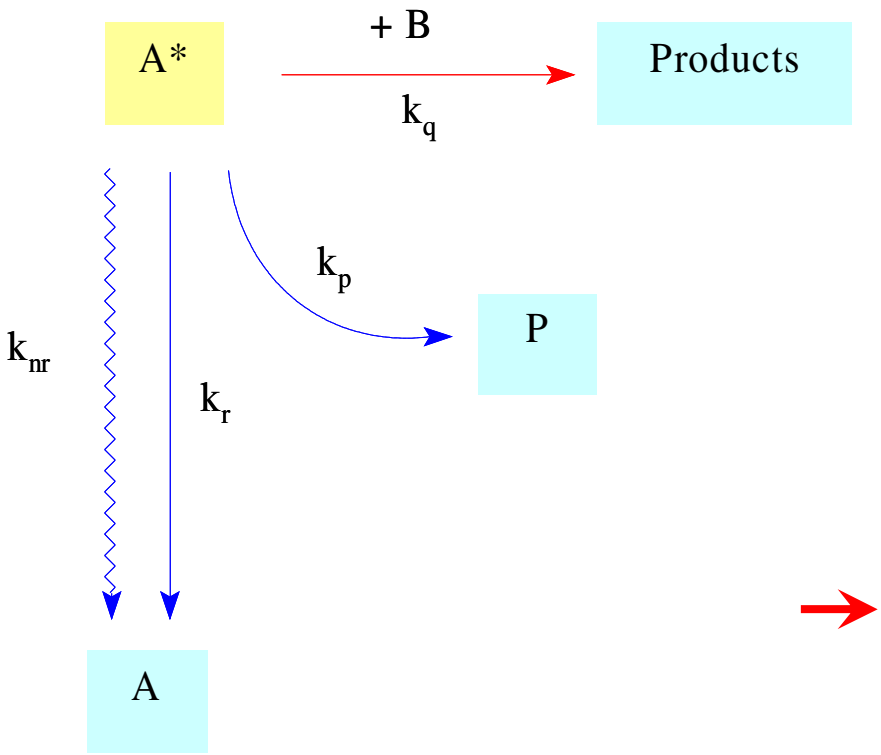


anthracene



quinine

Excited-State Processes



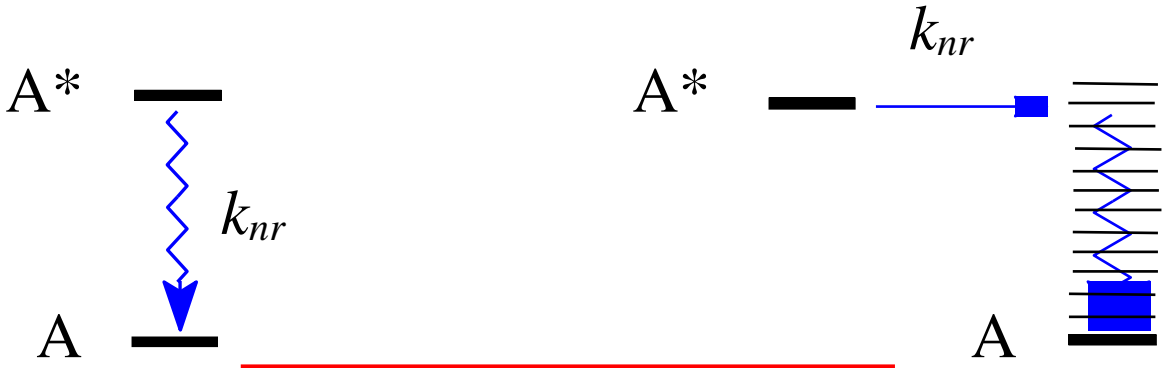
Unimolecular Processes:

k_r: radiative deactivation (emission)

→ k_{nr}: radiationless deactivation

k_p: chemical reaction

Radiationess Transitions



$$k_{nr} = \frac{2\pi}{\hbar}\left\langle \Psi_1 H' \Psi_2 \right\rangle^2 \rho_2$$

Fermi's golden rule

$$k_{nr} = \frac{2\pi}{\hbar}\left|\int \Psi_1 S_1 H' \Psi_2 S_2 dq d\xi \int X_1^0 X_2^n dQ\right|^2$$

H' is that part of the Hamiltonian responsible for driving the process.

- spin orbit coupling operator for spin-forbidden transitions
- nuclear kinetic energy (vibronic coupling) for spin-allowed

$\rho_f(E)$ is the density of vibrational states of A isoenergetic with A*

$$k_{nr} = \frac{2\pi}{h}\left|\int \Psi_1 S_1 H \Psi_2 S_2 dq d\xi \int X_1^0 X_2^n dQ\right|^2$$

Electronic factors: Spin Selection Rule

spin-allowed	***internal conversion***
spin-forbidden	***intersystem crossing***

Table 4.3. *Effect of halogen substitution in naphthalene on the rates of spin-forbidden processes (Data from Ermolaev, V. L. and Svitashev, K. K. (1965). Opt. Spectrosc. 7, 399)*

Compound	A_p (s^{-1}) $T_1 \rightarrow S_0 + h\nu$	k_t (s^{-1}) ISC $T_1 \rightsquigarrow S_0$	ϕ_p/ϕ_f
Naphthalene	0.05	0.39	0.09
1-Fluoronaphthalene	0.23	0.42	0.07
1-Chloronaphthalene	1.10	2.35	5.2
1-Bromonaphthalene	13.5	36.5	169
1-Iodonaphthalene	190	310	>760

El Sayed Rule:

ISC allowed if change of orbital configuration (rotation of charge density)

M	Type of transition[a]	k_{ISC}/s^{-1}
	"Forbidden"	
Anthracene	$S_1(\pi,\pi^*) \rightarrow T_1(\pi,\pi^*)$	1.4×10^{8}[b]
Acetone	$S_1(n,\pi^*) \rightarrow T_1(n,\pi^*)$	5×10^{8}
Benzil	$S_1(n,\pi^*) \rightarrow T_1(n,\pi^*)$	5×10^{8}
Biacetyl	$S_1(n,\pi^*) \rightarrow T_1(n,\pi^*)$	7×10^{7}
	"Allowed"	
9-acetoanthracene	$S_1(\pi,\pi^*) \rightarrow T_1(n,\pi^*)$	10^{10}
Benzophenone	$S_1(n,\pi^*) \rightarrow T_1(\pi,\pi^*)$	10^{11}

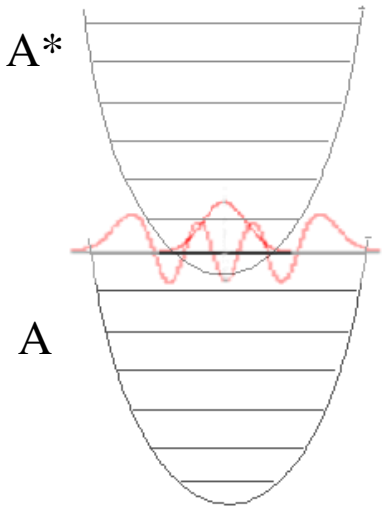
Franck-Condon factor

Radiative case, $k_r = \frac{2\pi}{\hbar}\left|\int \Psi_1 S_1 H \Psi_2 S_2 dq d\xi\right|^2 \left|\sum_n \int X_1^0 X_2^n dQ\right|^2$ → = 1

Radiationless, $k_r = \frac{2\pi}{\hbar}\left|\int \Psi_1 S_1 H \Psi_2 S_2 dq d\xi\right|^2 \left|\int X_1^0 X_2^n dQ\right|^2$

FC factor extremely important in determining k_{nr}.

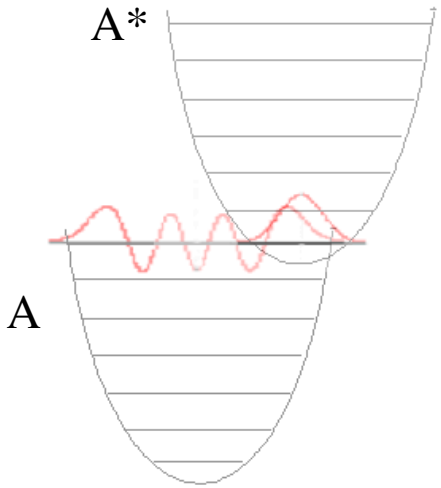
Radiationless transitions.
Role of the Franck-Condon factor



“Nested” states.

Bad Franck-Condon factor. Classically, abrupt change in nuclear kinetic energy.

Slow process. Rate decreases with increasing “energy gap”.

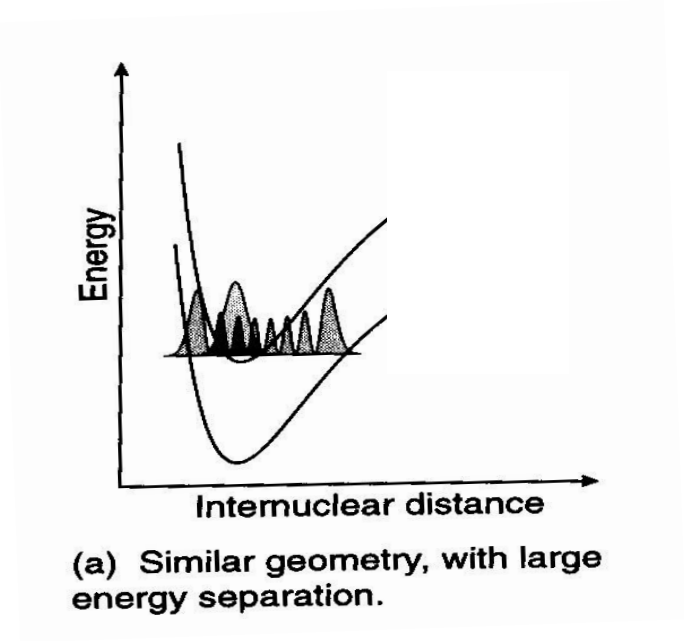


“Crossing” states.

Good Franck-Condon factor. Classically, nuclear kinetic energy is conserved.

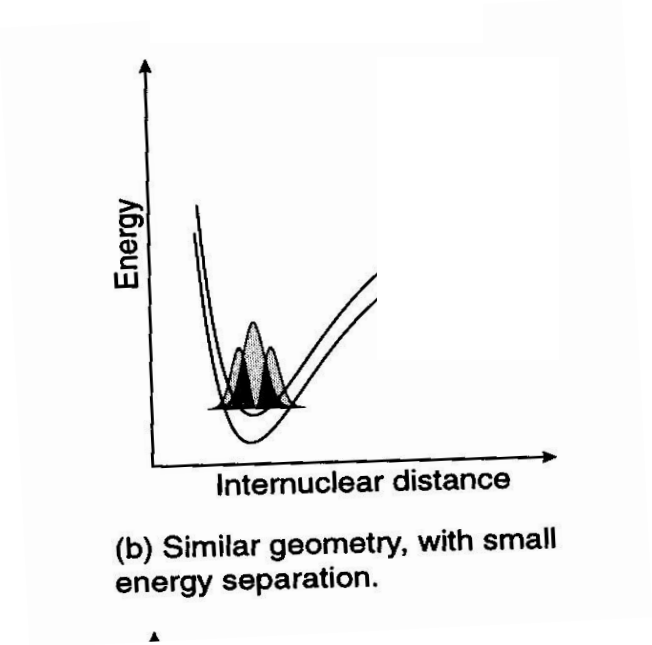
Very fast process

Energy Gap Law



(a) Similar geometry, with large energy separation.

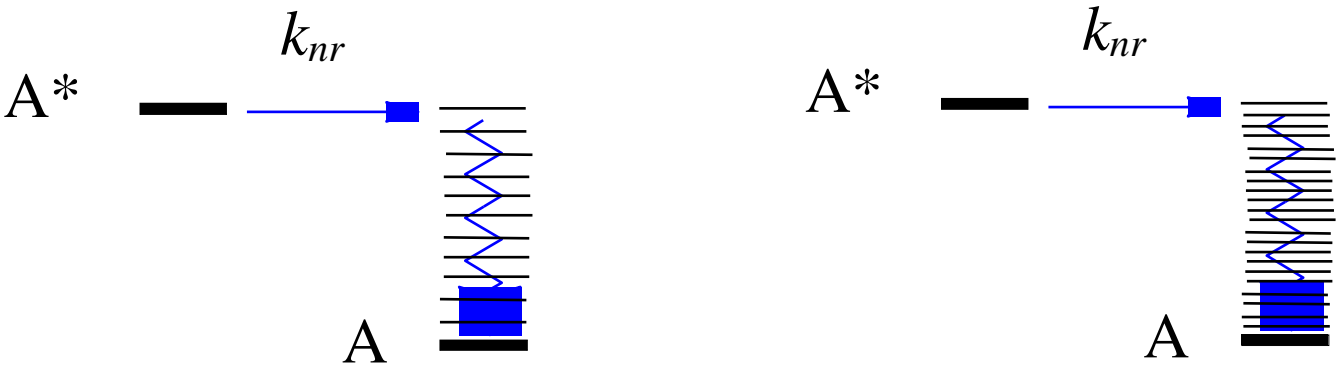
Poor overlap



(b) Similar geometry, with small energy separation.

Better overlap

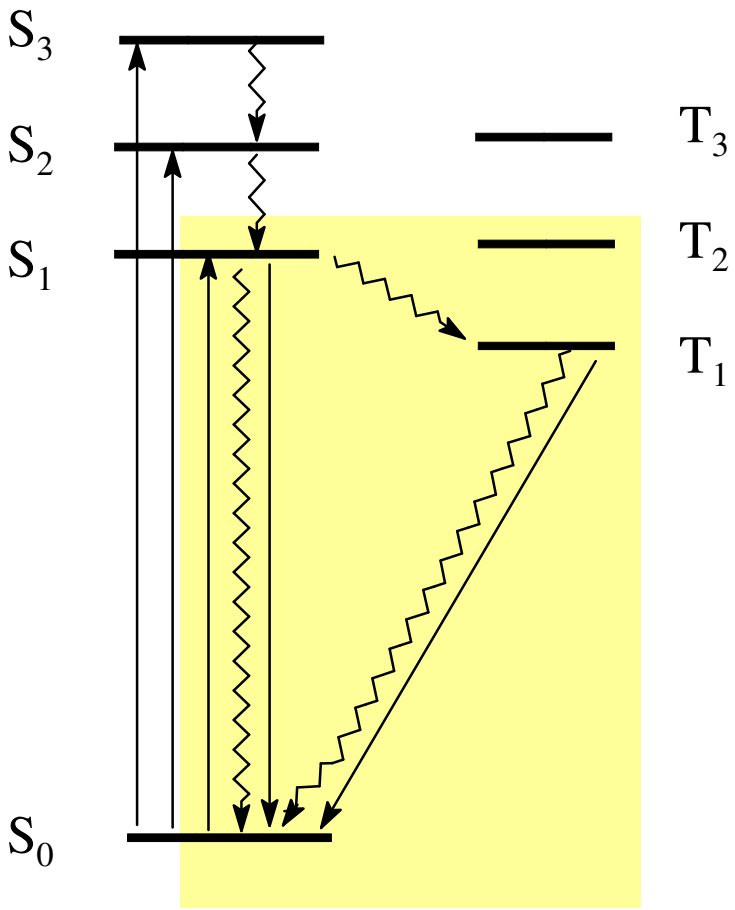
Deuteration Effect



C-H C-D

M	$10^{-4}k''_{ISC}/s^{-1}$	τ_p/s
Benzene	17.6	4.75
Benzene-d_1	16.0	5.15
Benzene-d_5	7.1	9.50
Benzene-d_6	3.7	14.1

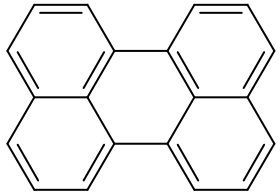
Kasha's Rule:
Radiative (and most other intersting) processes always occur from S_1 or T_1, independent on the energy of initial excitation

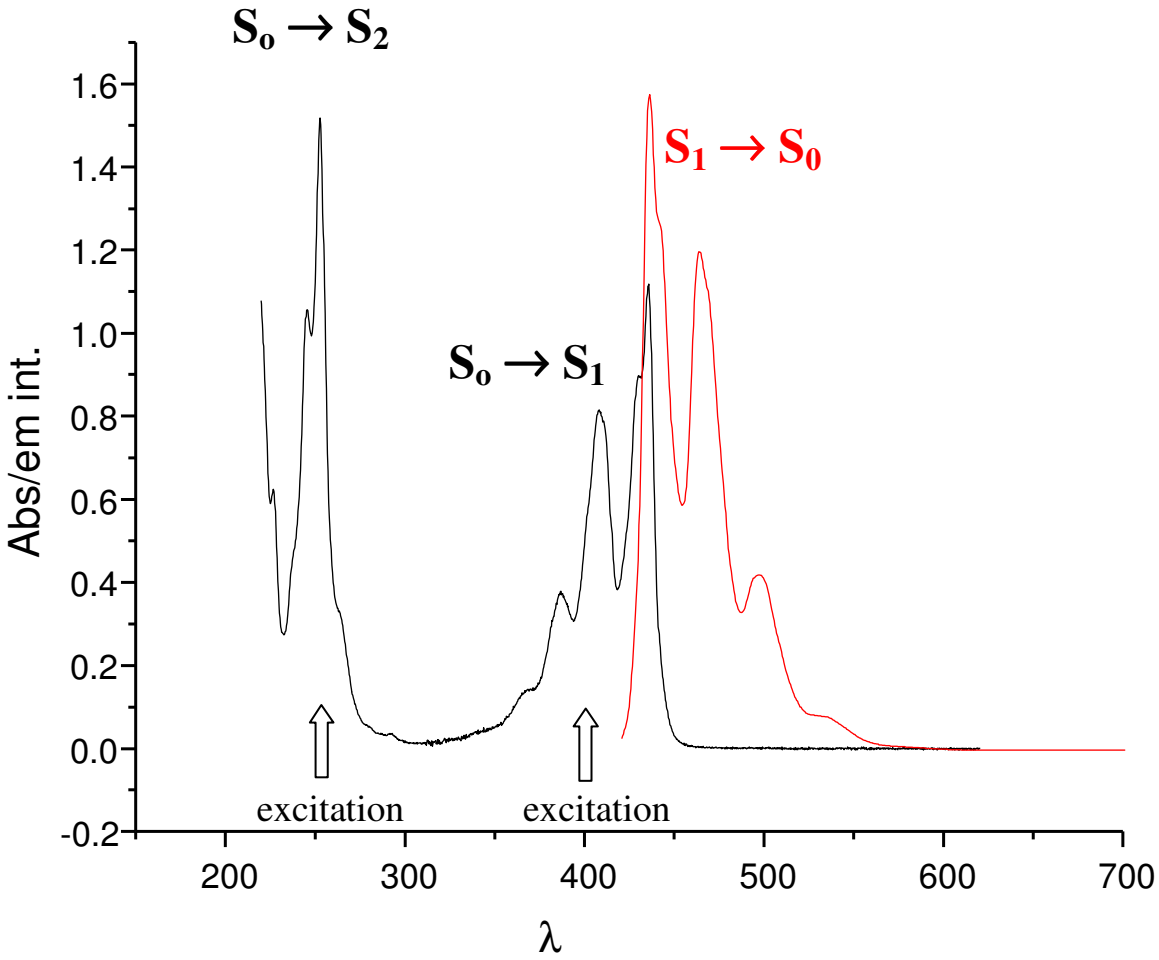


Rationale: Small energy gaps between excited states, large energy gap between S_1 and the ground state. **Very fast, 100% efficient radiationless deactivation from upper states to S_1.**

Consequence: Simplified effective Jablonski diagram

e.g., perylene

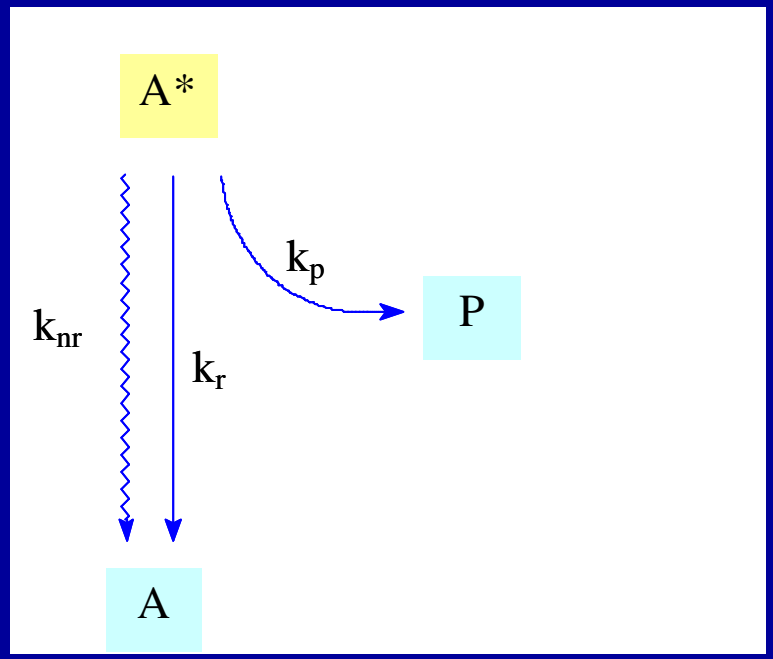


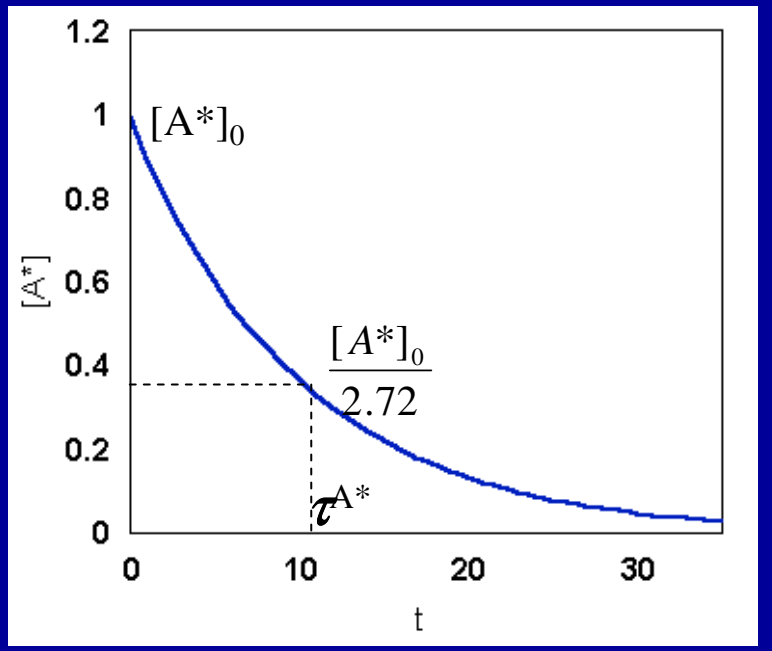


Emission = Fluorescence from S_1

Independent (constant Φ) on excitation wavelength

Excited State Kinetics





$$-\frac{d[A^*]}{dt} = (k_r + k_{nr} + k_p)[A^*] = \sum_i k_i [A^*]$$

excited-state decay kinetics

$$\tau^{A^*} = \frac{1}{(k_r + k_{nr} + k_p)} = \frac{1}{\sum_i k_i}$$

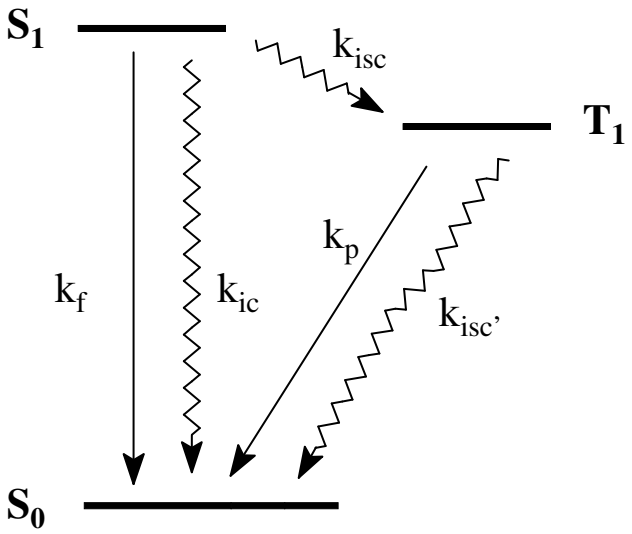
excited-state lifetime

efficiency of process i $\quad \eta_i = \frac{k_i}{\sum_i k_i}$

Quantum yield of process i $\quad \Phi = \eta(\rightarrow A^*)\eta_i = \frac{k_i}{\sum_i k_i}$

Kinetic Scheme

Dependence of experimental parameters τ_S, Φ_f, τ_T, Φ_p on rate constants of individual processes



$\tau_S = 1/(k_F + k_{IC} + k_{ISC})$

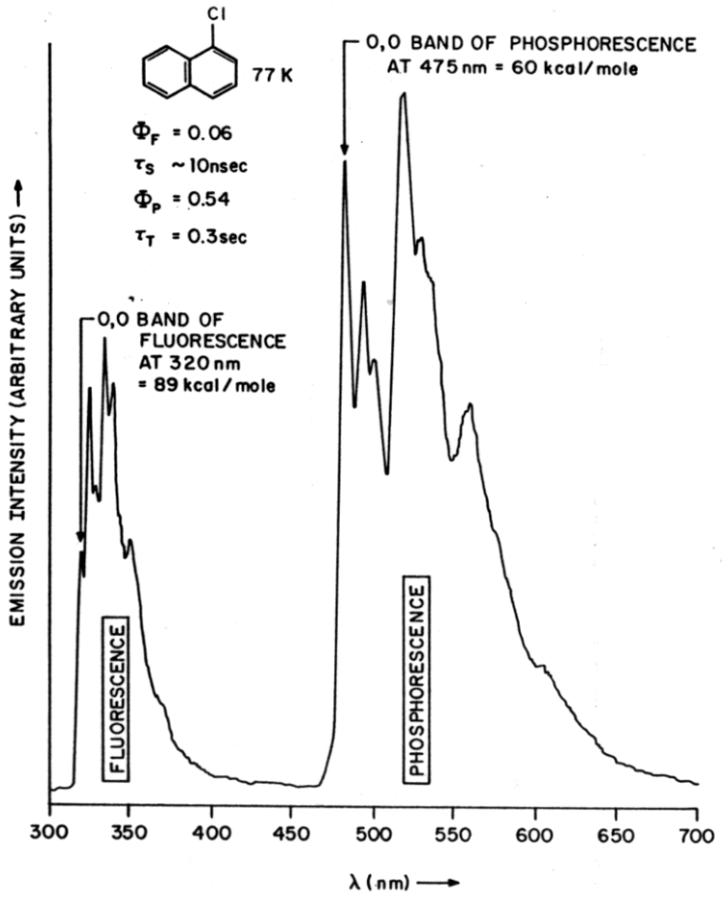
$\Phi_f = \eta_f(S_1) = k_f/(k_f + k_{ic} + k_{Iisc}) = k_f\tau_S$

$\tau_T = 1/(k_P + k_{ISC'})$

$\Phi_p = \eta_{isc}(S_1) \times \eta_r(T_1) = \eta_{isc}(S_1) \times [k_p/(k_p + k_{isc'})] = \eta_{isc}(S_1)\ k_p\tau_T$

$\eta_{isc}(S_1) = k_{isc}/(k_f + k_{ic} + k_{Iisc}) = k_{isc}\tau_S$

Example:
Lowest π–π* state



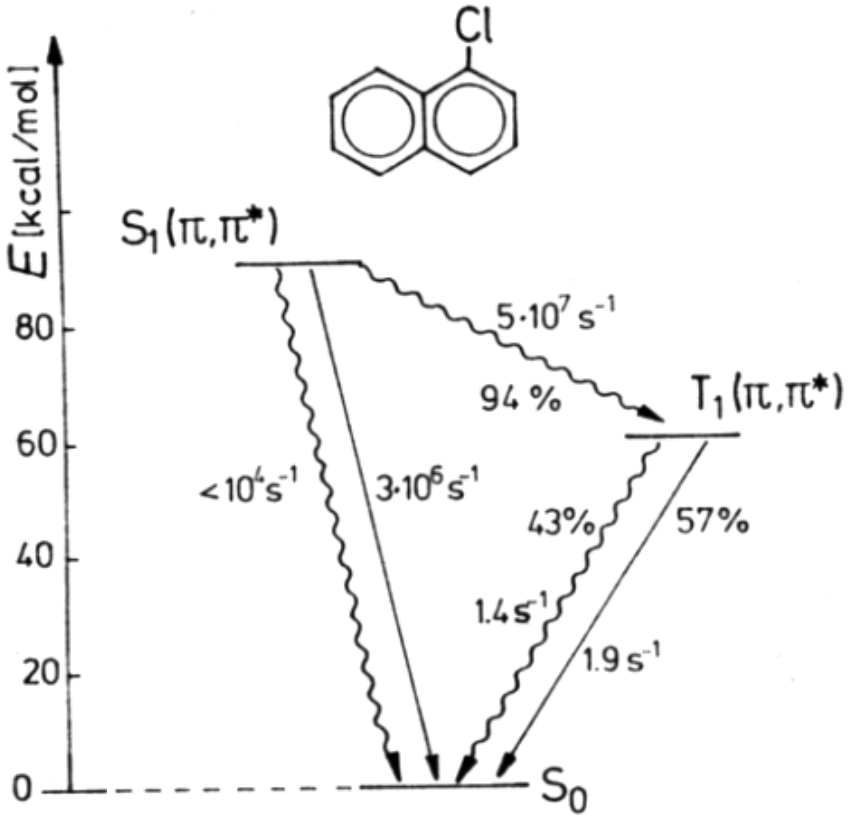
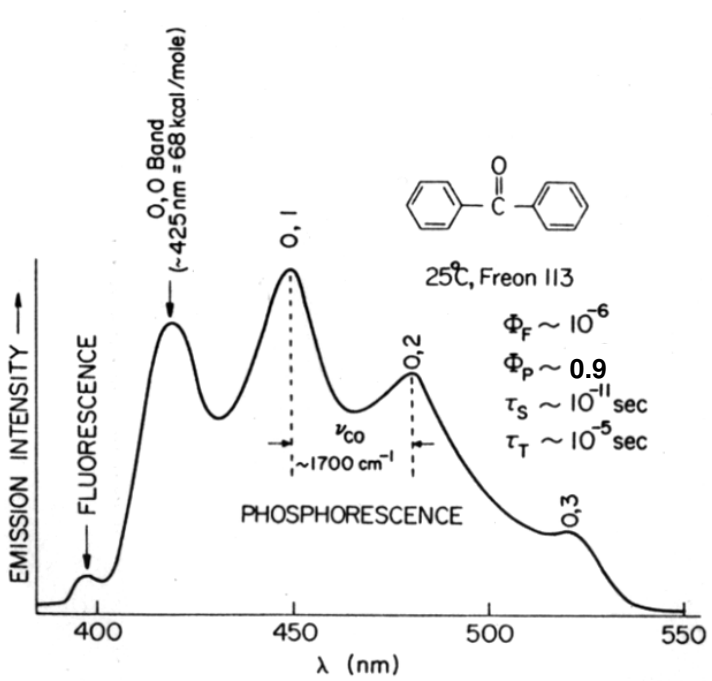
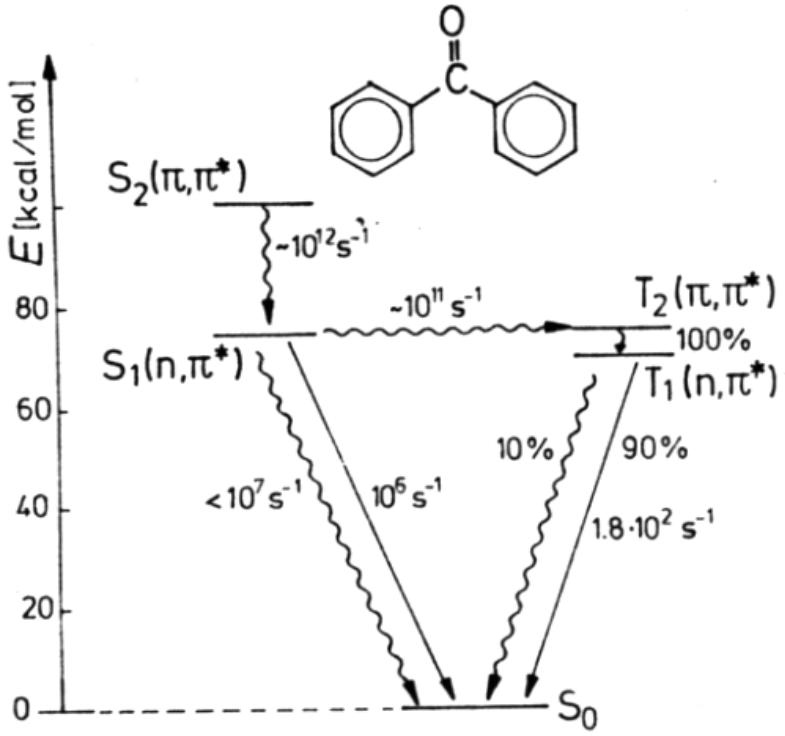


Table 4.2 *Quantum yields for fluorescence* ($S_1 \rightarrow S_0 + h\nu$) *and intersystem crossing* ($S_1 \rightsquigarrow T_1$) *for some aromatic hydrocarbons in ethanol solution* (*Data from Birks, J. B. (ed.) (1975).* Organic molecular photophysics, *Vol. 2, Tables 2.6 and 3.4. Wiley, London*)

Compound	ϕ_f	ϕ_{ISC}	$\phi_f + \phi_{ISC}$
Benzene	0.04	0.15	0.19
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

Example:
Lowest n–π* state





Organic chromophores

"typical" behavior

Lowest π–π^* states

– $\tau(S_1)$, ns

– Φ_F = 0.1-1.0

–$\eta_{ISC} < 1$

–$\Phi_F + \eta_{ISC} \approx 1$

– $\eta_{IC} = 0$

– $\tau(T_1)$, ms-s

Lowest n–π^* states

– $\tau(S_1)$, ps

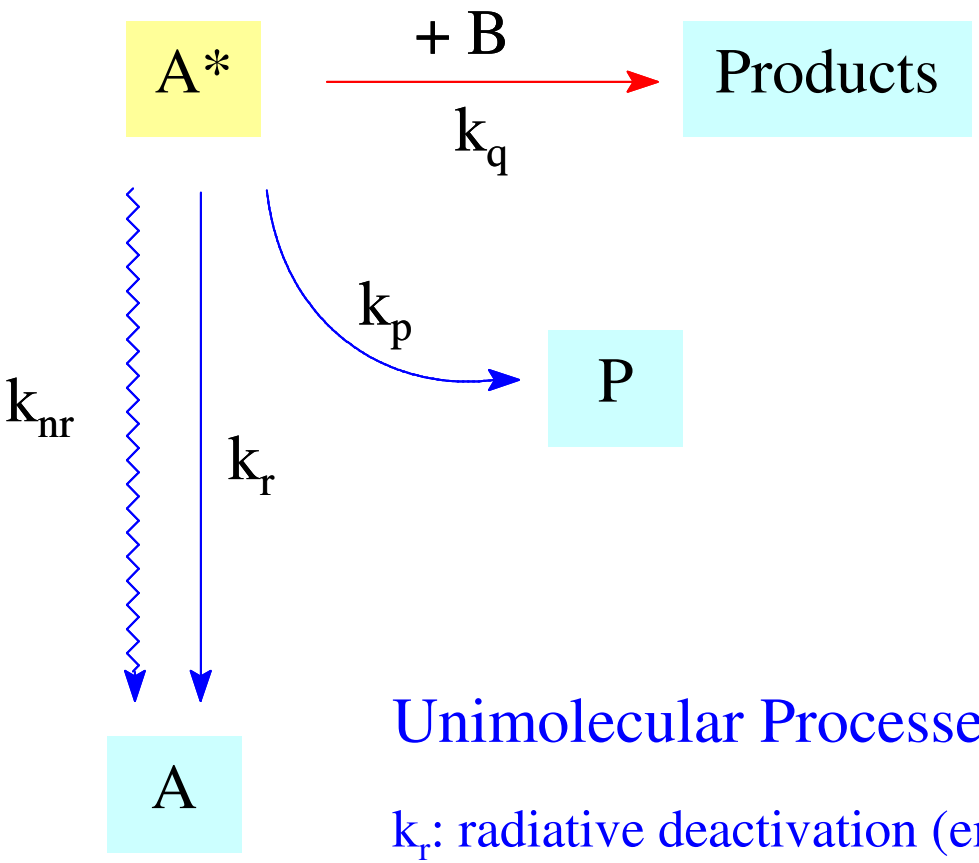
– $\Phi_F = 0$

– $\eta_{ISC} = 1$

–$\eta_{IC} = 0$

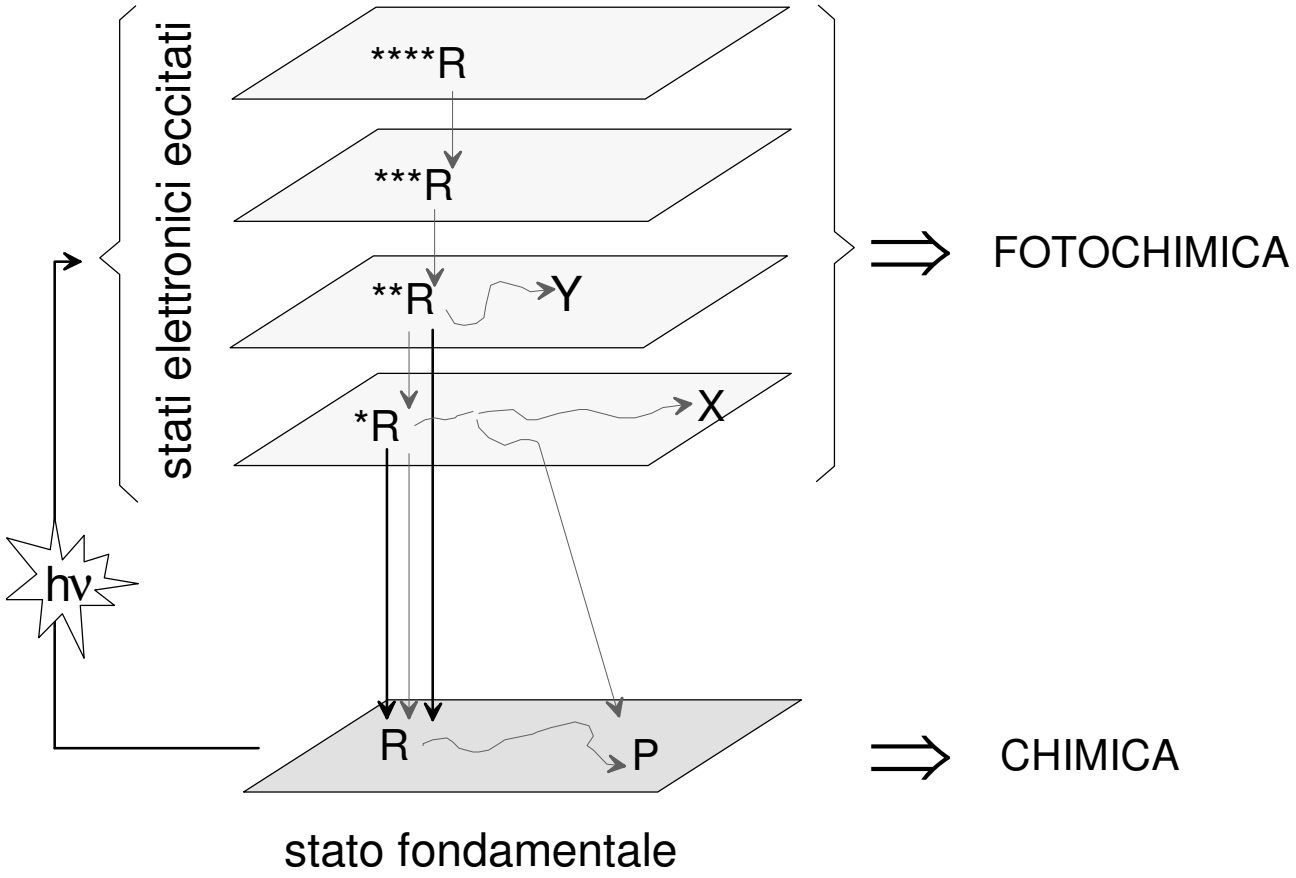
– $\tau(T_1)$, μs-ms

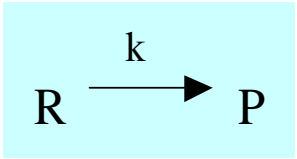
Excited-State Processes

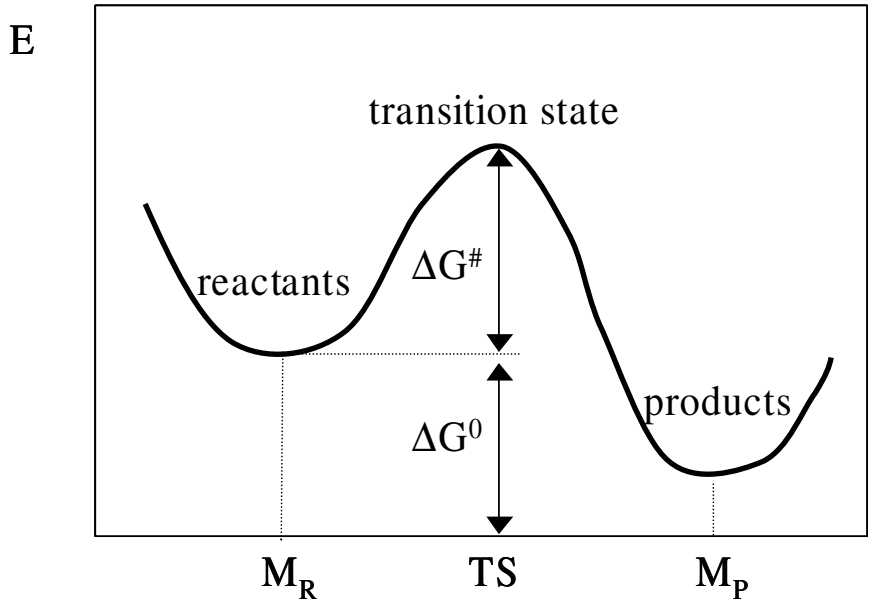


Unimolecular Processes:

k_r: radiative deactivation (emission)
k_{nr}: radiationless deactivation
k_p: chemical reaction


stati elettronici eccitati
****R
***R
**R
Y
*R
X
hν
R
P
FOTOCHIMICA
CHIMICA
stato fondamentale

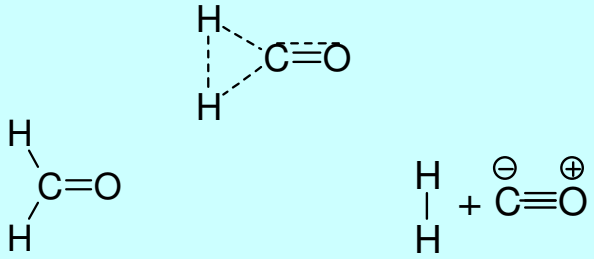


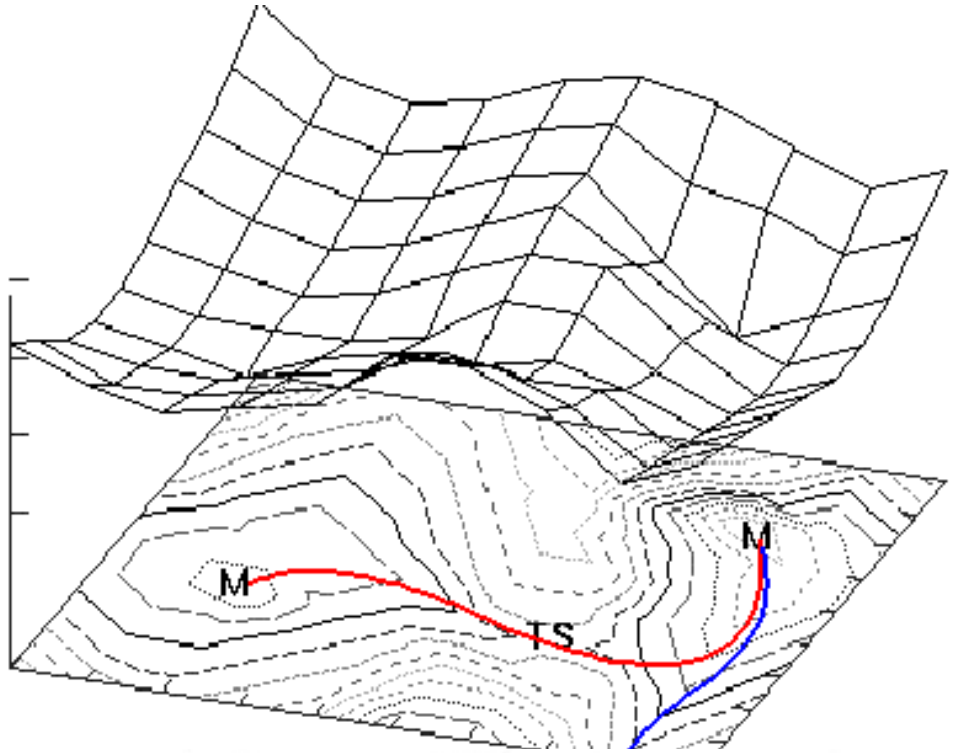


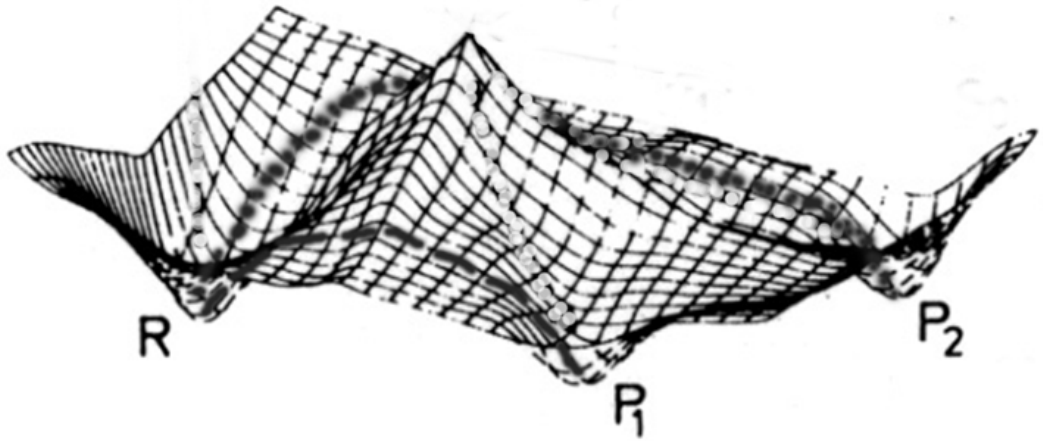
$k = (k_B T/h) \exp(-\Delta G^{\#}/RT)$

e.g.,

$HCHO \rightarrow H_2 + CO$



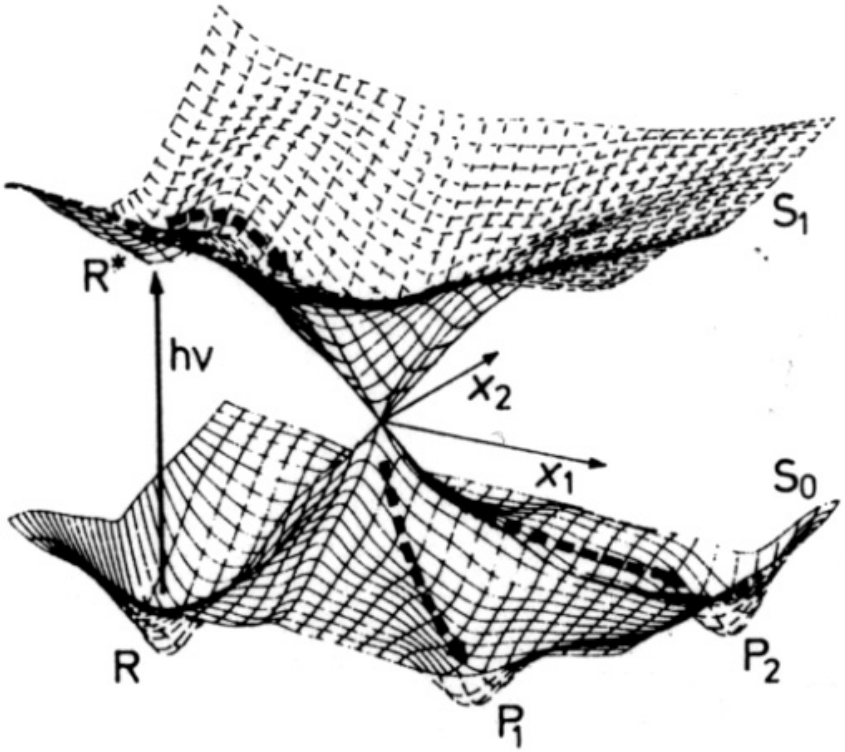

M
TS
M


R
P1
P2

Excited states are short-lived

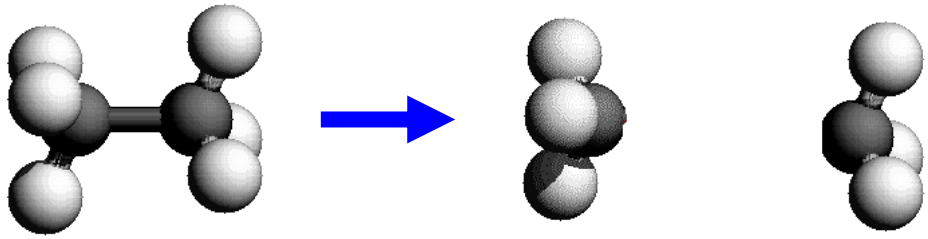
⇓

to be efficient, excited-state reactions must be very fast: i.e., activationless or downhill

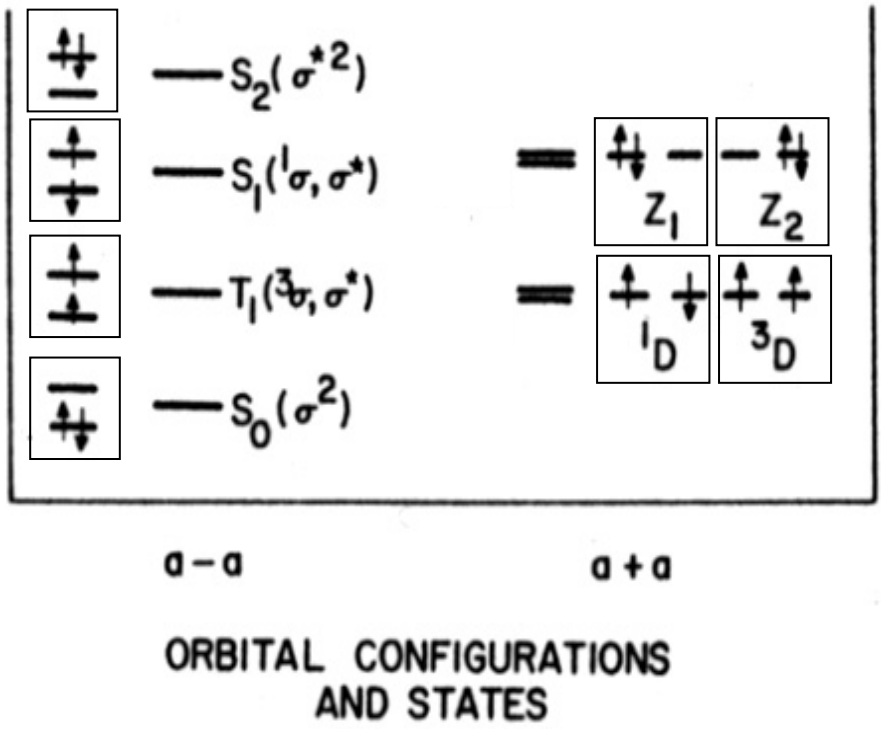


prototype reaction:

breaking (stretching) of a σ bond



Stretching of a σ Bond
e.g., H-H, CH_3-CH_3



ORBITAL CONFIGURATIONS
AND STATES

Correlation of states:
- Same spin
-Same symmetry
-No state crossing between states of same spin&symmetry

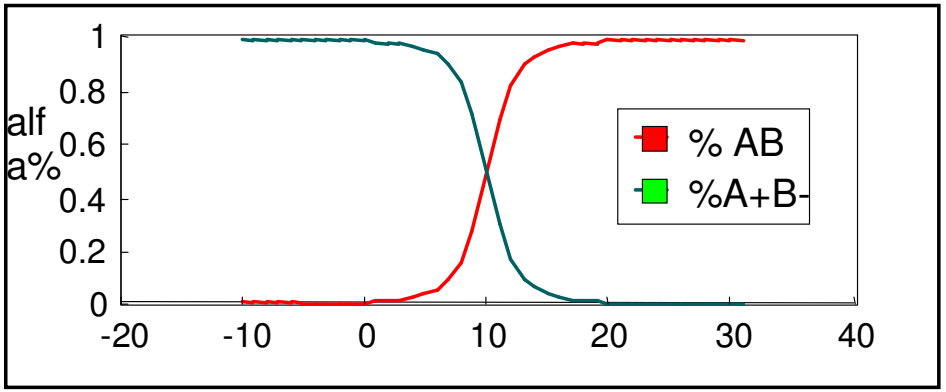
Rules for the correlation of states
between different molecular geometries

- must have the same spin
- must have the same symmetry
- states of same symmetry and spin can never cross

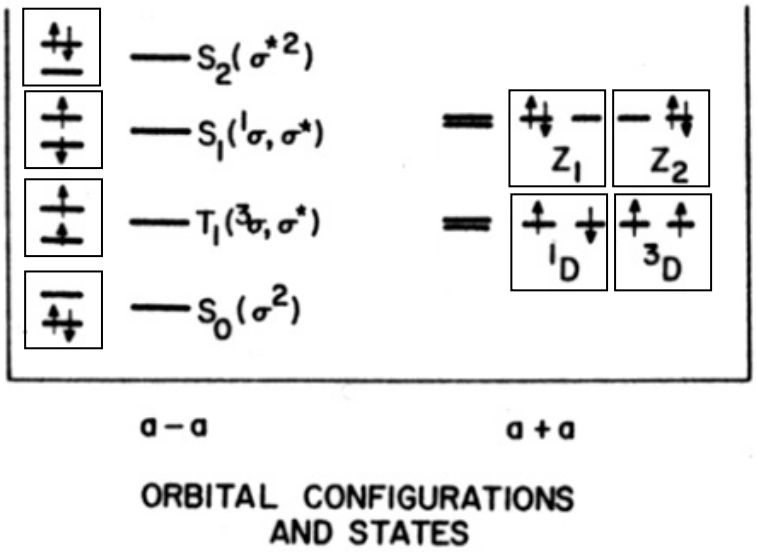
$$\Psi = c_1 \Psi_1^0 + c_2 \Psi_2^0$$

$$E = \frac{E_1 + E_2}{2} \mp \frac{\sqrt{(E_1 - E_2)^2 - 4H_{12}{}^2}}{2}$$

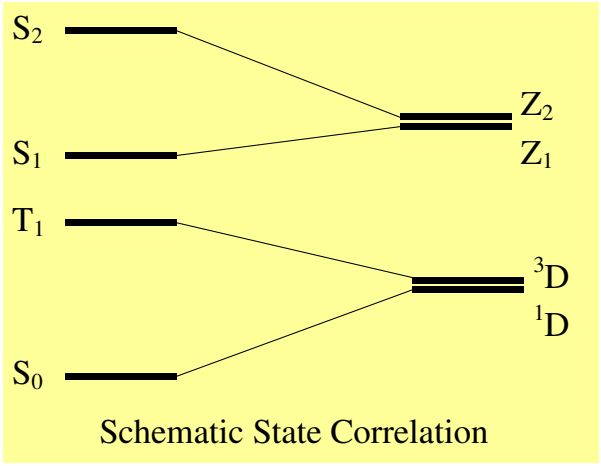
$$\left\{ \begin{array}{l} c_1(E_1 - E) + c_2 H_{12} = 0 \\ c_2 H_{12} + c_2(E_2 - E) = 0 \end{array} \right\}$$



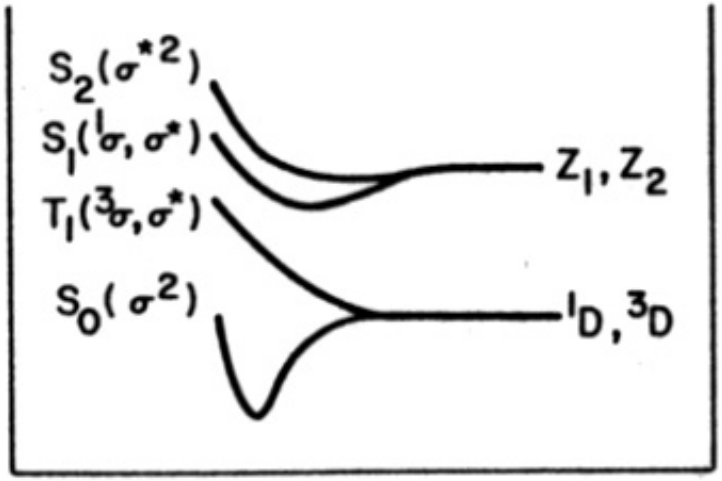
Stretching of a σ Bond
e.g., H-H, CH_3-CH_3



ORBITAL CONFIGURATIONS AND STATES



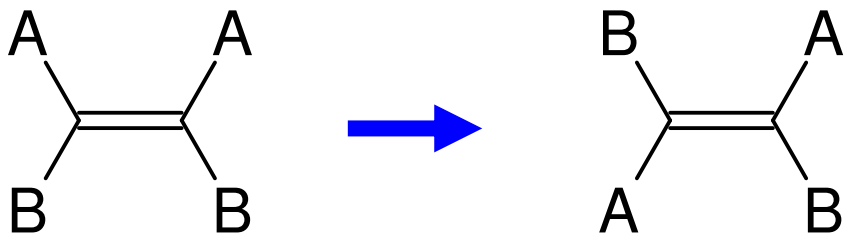
Schematic State Correlation

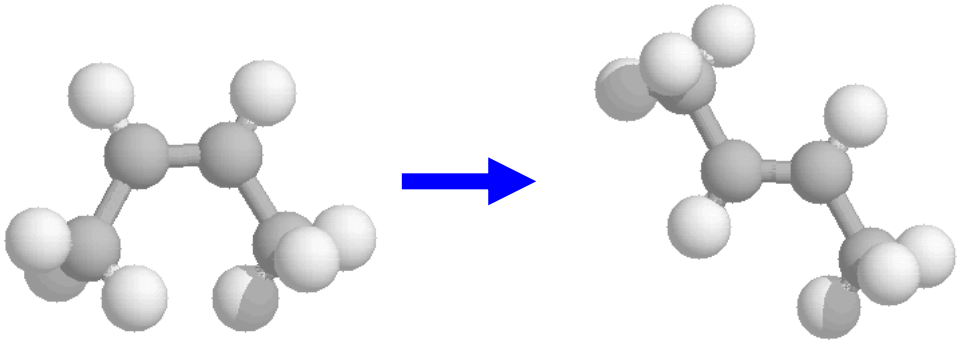


STATE CORRELATION

prototype reaction:

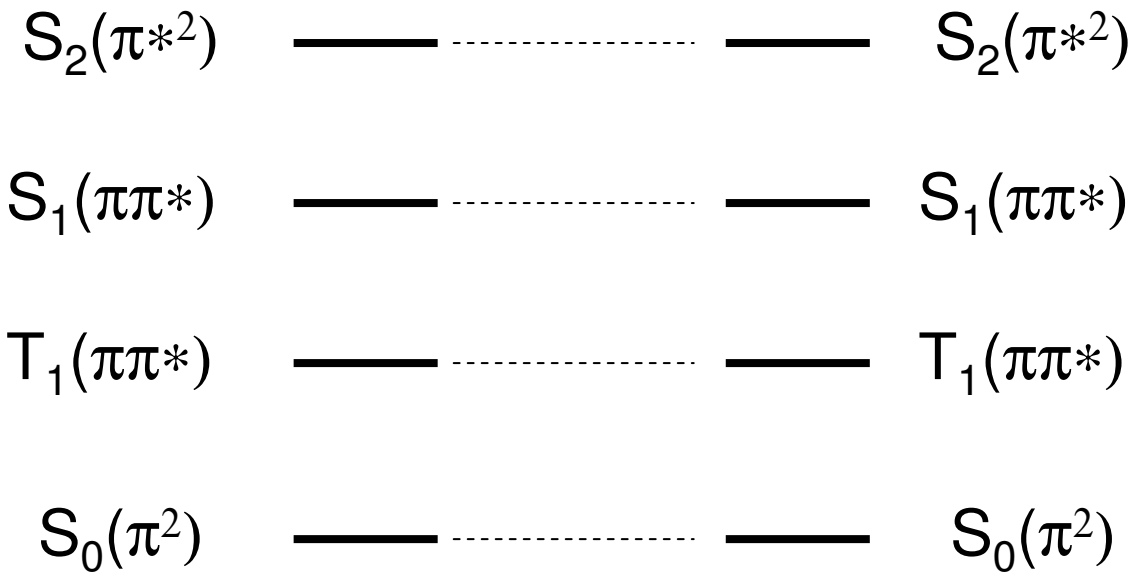
twist around a double bond
(*cis-trans* isomerization)

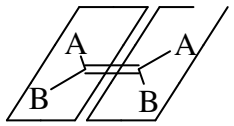




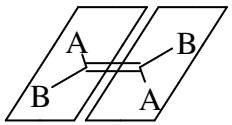
State correlation diagram

(no inforamtion)

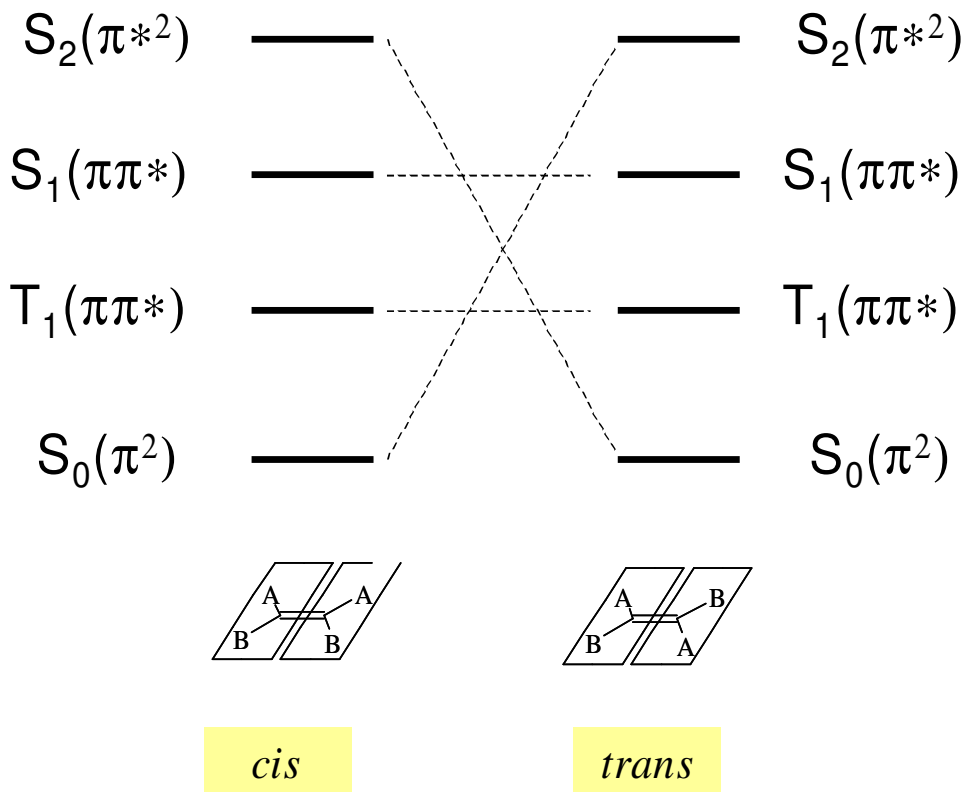




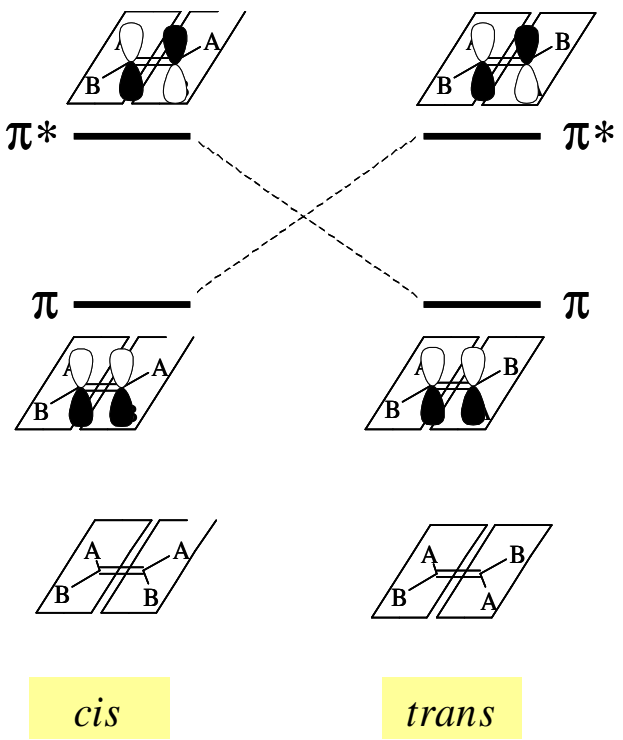
cis



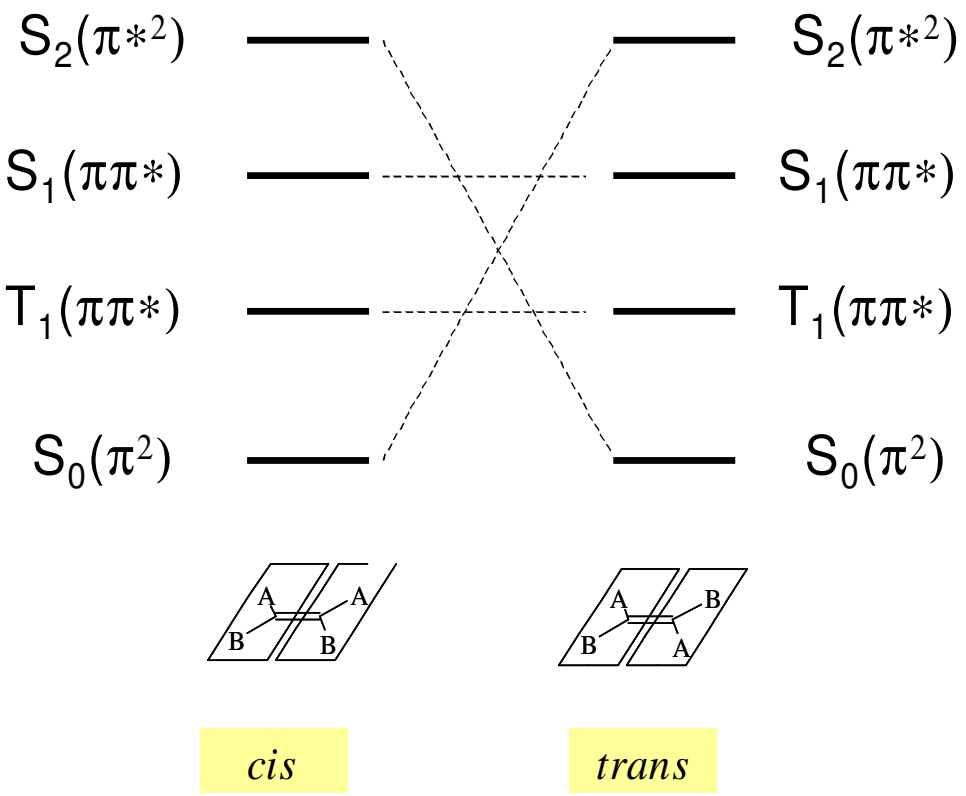
trans

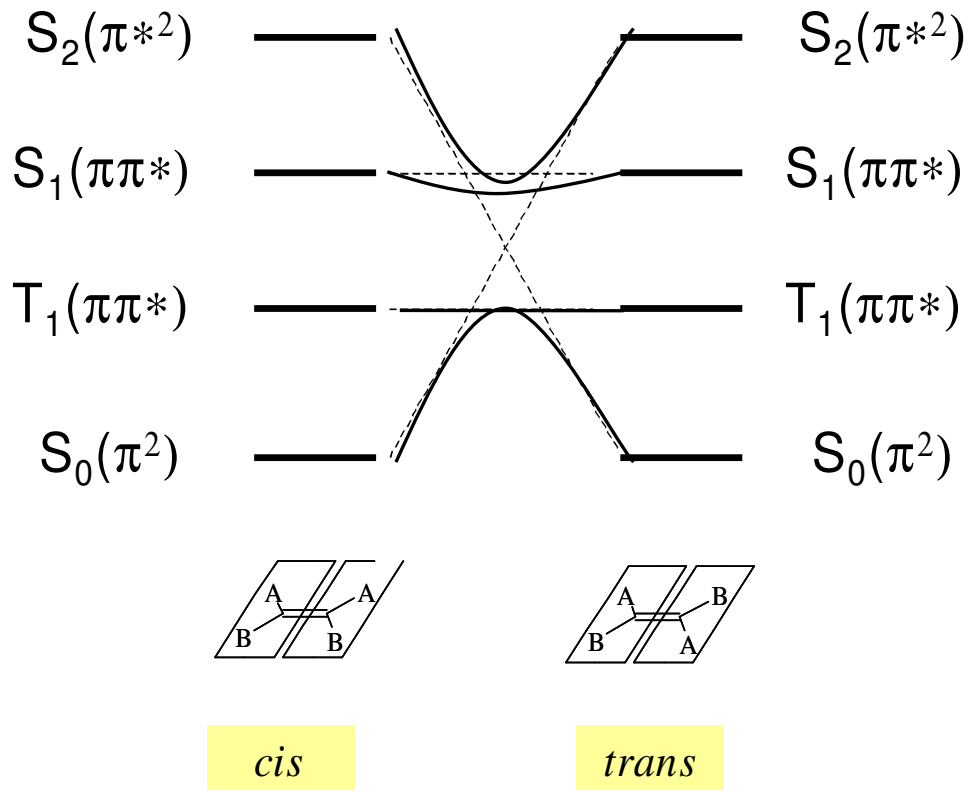

$S_2(\pi^{*2})$
$S_1(\pi\pi^*)$
$T_1(\pi\pi^*)$
$S_0(\pi^2)$
$S_2(\pi^{*2})$
$S_1(\pi\pi^*)$
$T_1(\pi\pi^*)$
$S_0(\pi^2)$
A
A
B
B
A
B
B
A
cis
trans

orbital correlation



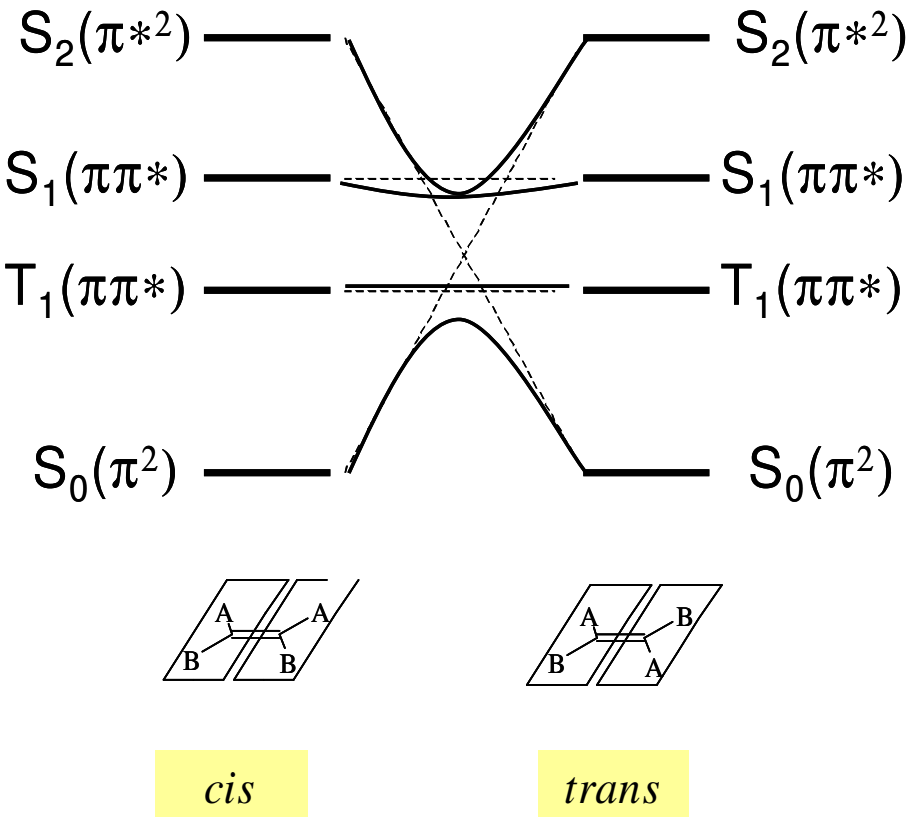
state correlation



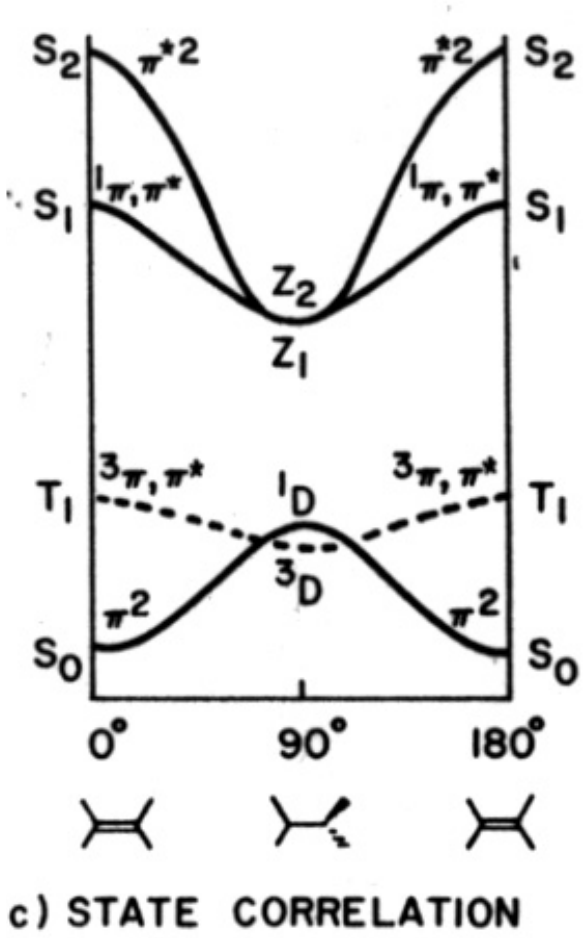

$S_2(\pi^{*2})$
$S_1(\pi\pi^*)$
$T_1(\pi\pi^*)$
$S_0(\pi^2)$
$S_2(\pi^{*2})$
$S_1(\pi\pi^*)$
$T_1(\pi\pi^*)$
$S_0(\pi^2)$
A
A
B
B
A
B
B
A
cis
trans

state correlation

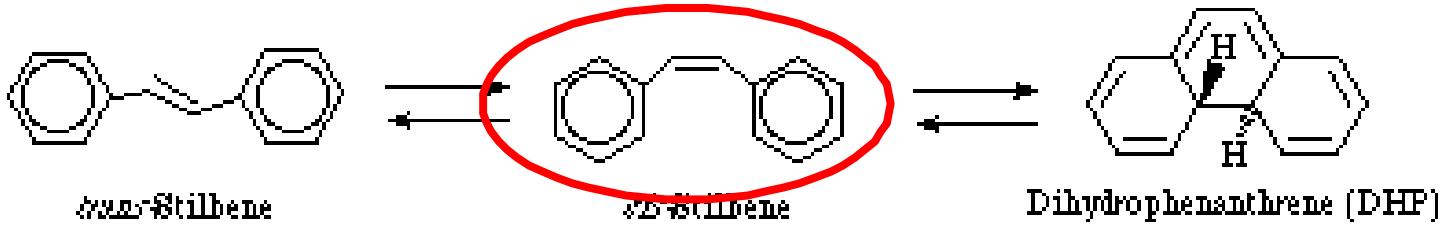
real potential energy

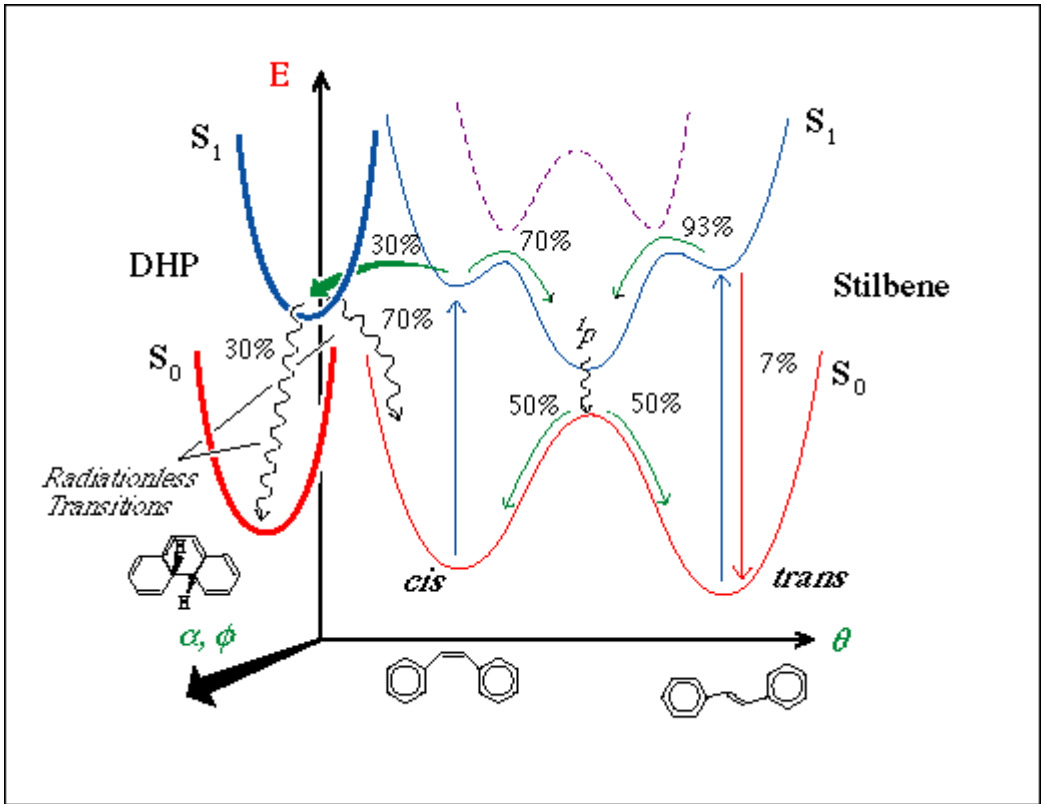


cis *trans*

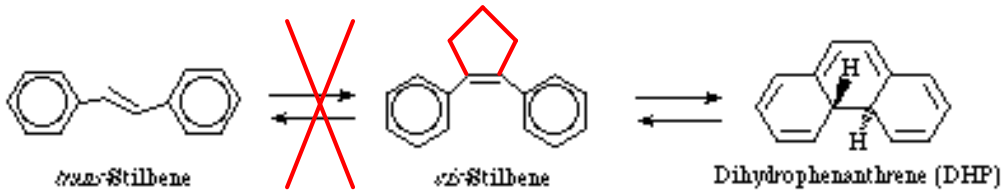


c) STATE CORRELATION

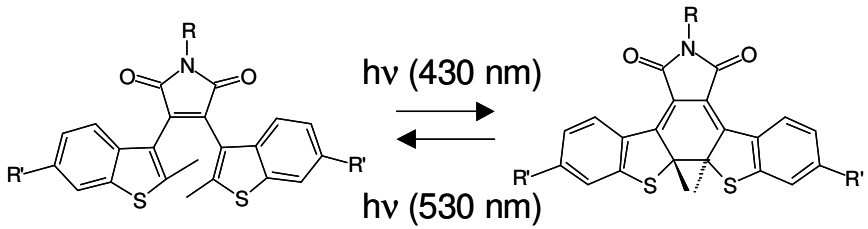

H
H
trans-Stilbene
cis-Stilbene
Dihydrophenanthrene (DHP)

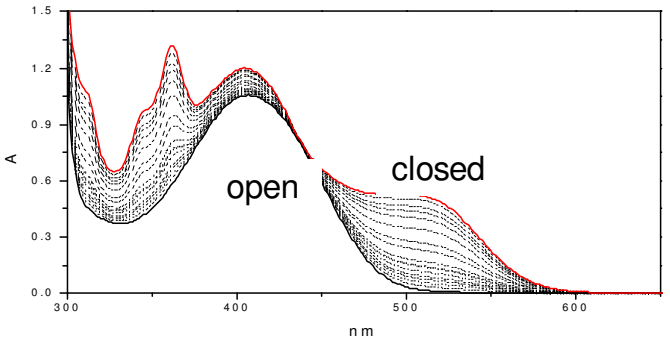

E
S1
S1
DHP
30%
70%
93%
Stilbene
70%
30%
S0
S0
7%
50%
50%
Radiationless
Transitions
cis
trans
α, ϕ
θ

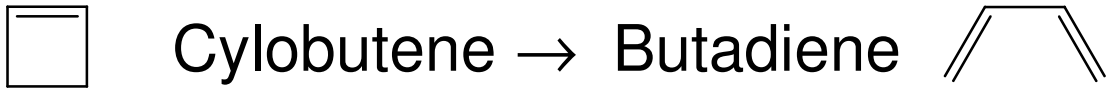
Photochromic Diarylethenes

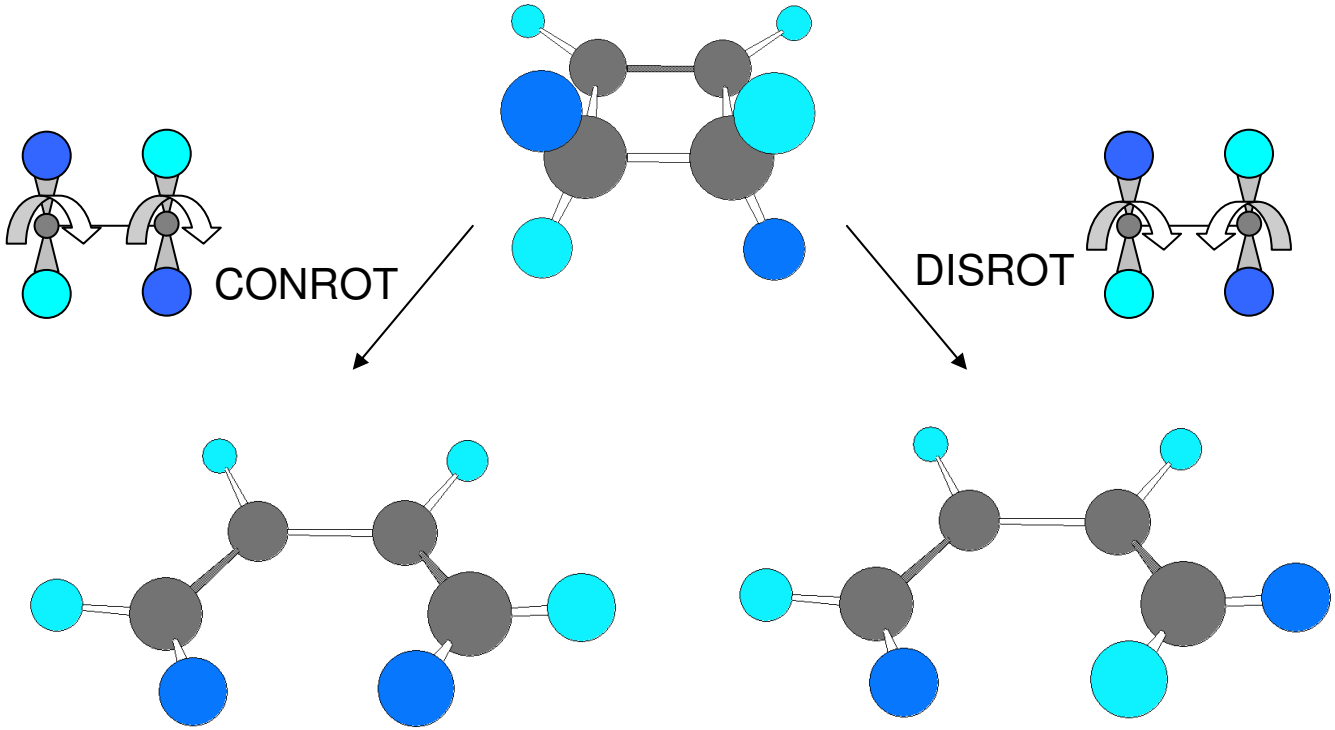


e.g.,





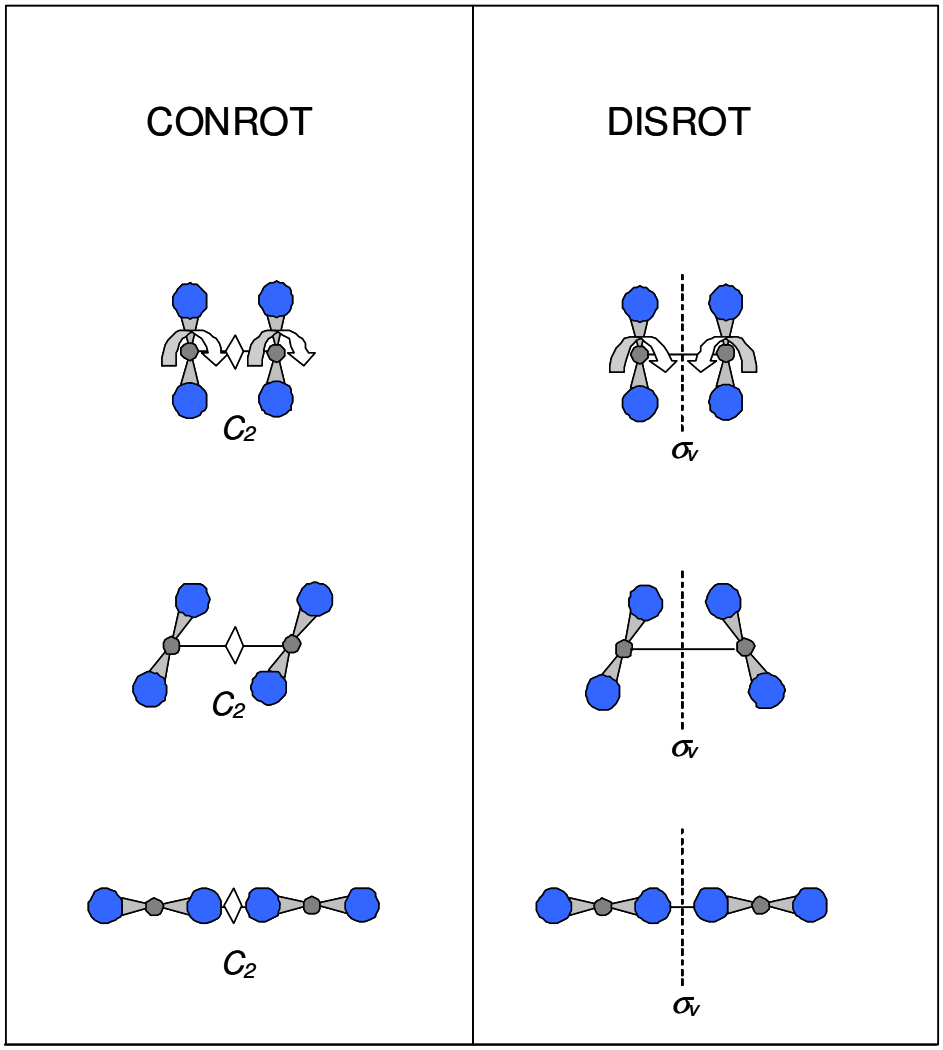




Ground vs excited states: different reactivity?

Answer: correlation of MOs and states between reactant and products.

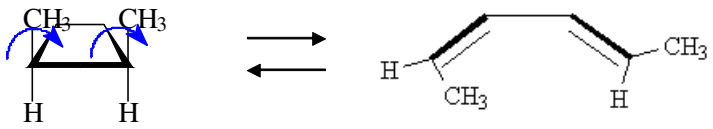
Relevant symmetry element: C_2



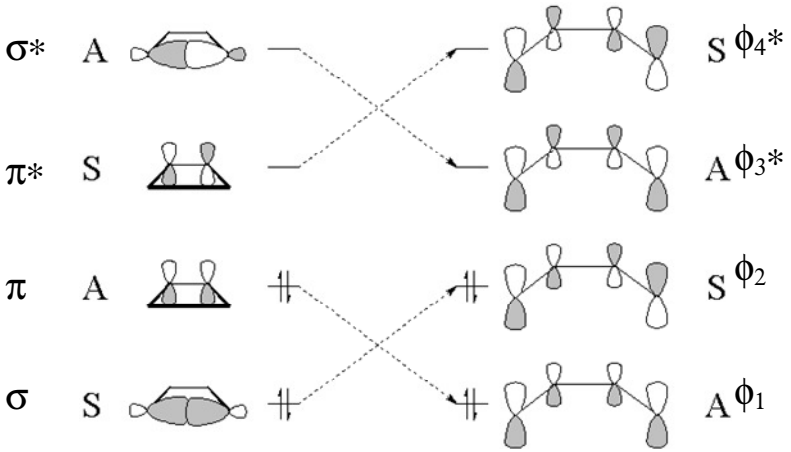
Relevant symmetry element: σ_v

Symmetry must be maintained along the reaction coordinate

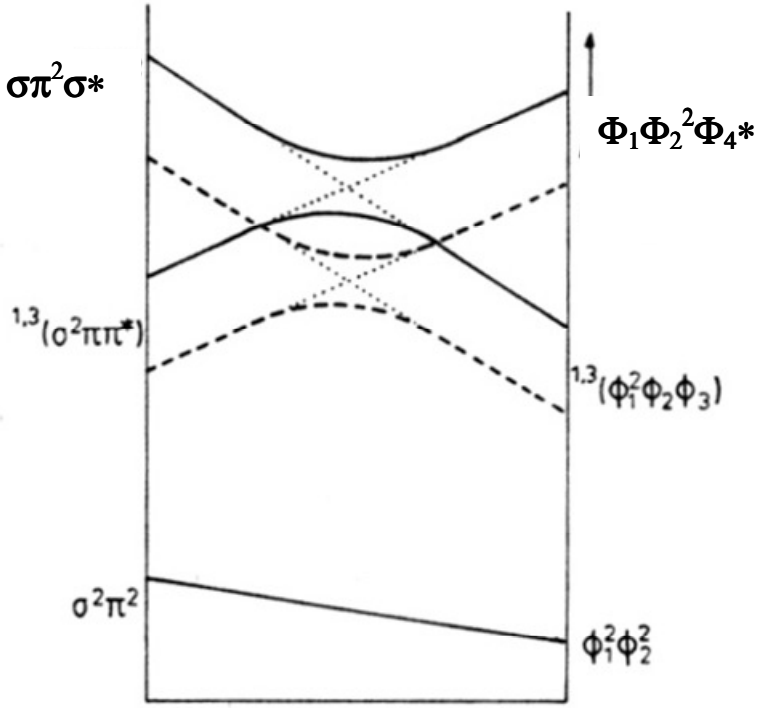
Cyclobutene – Butadiene
conrotatory ring opening/closure



Orbital Correlation:

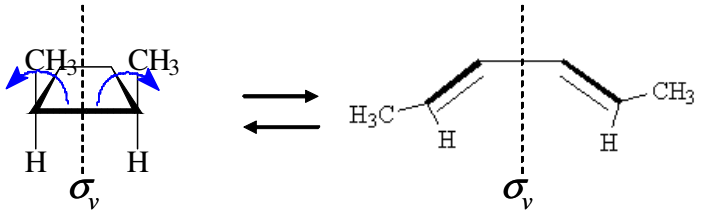


State Correlation:

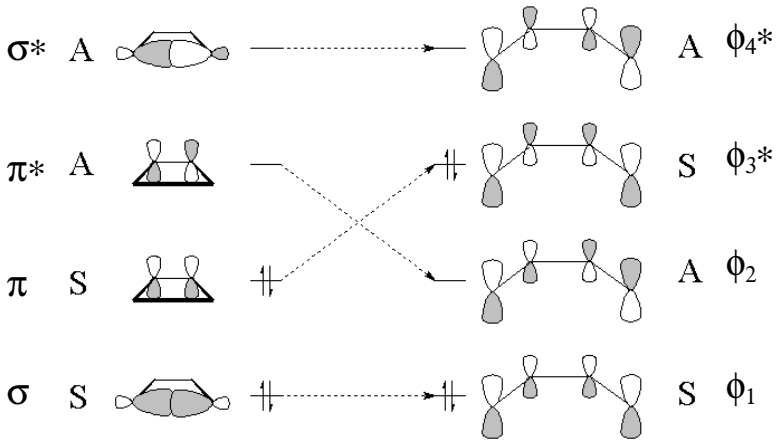


-thermally allowed
-photochemically forbidden

Cyclobutene – Butadiene
disrotatory ring opening/closure

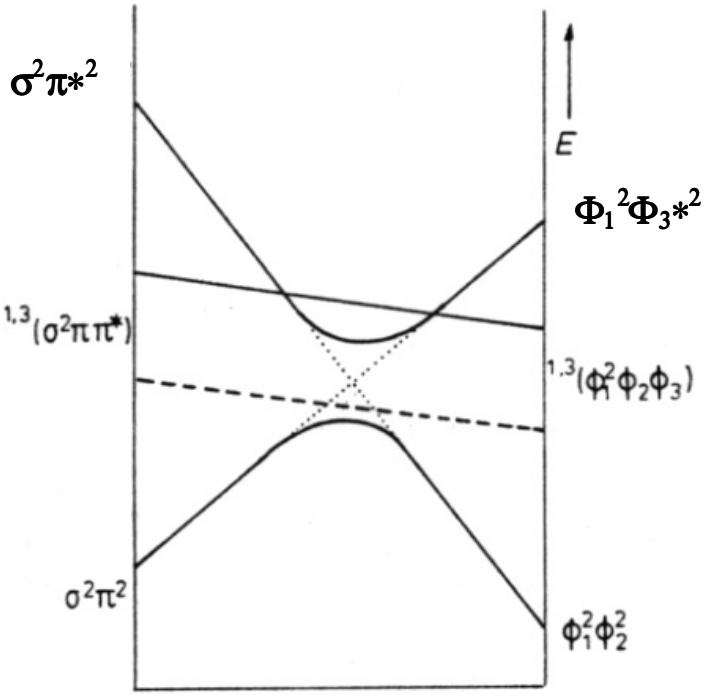


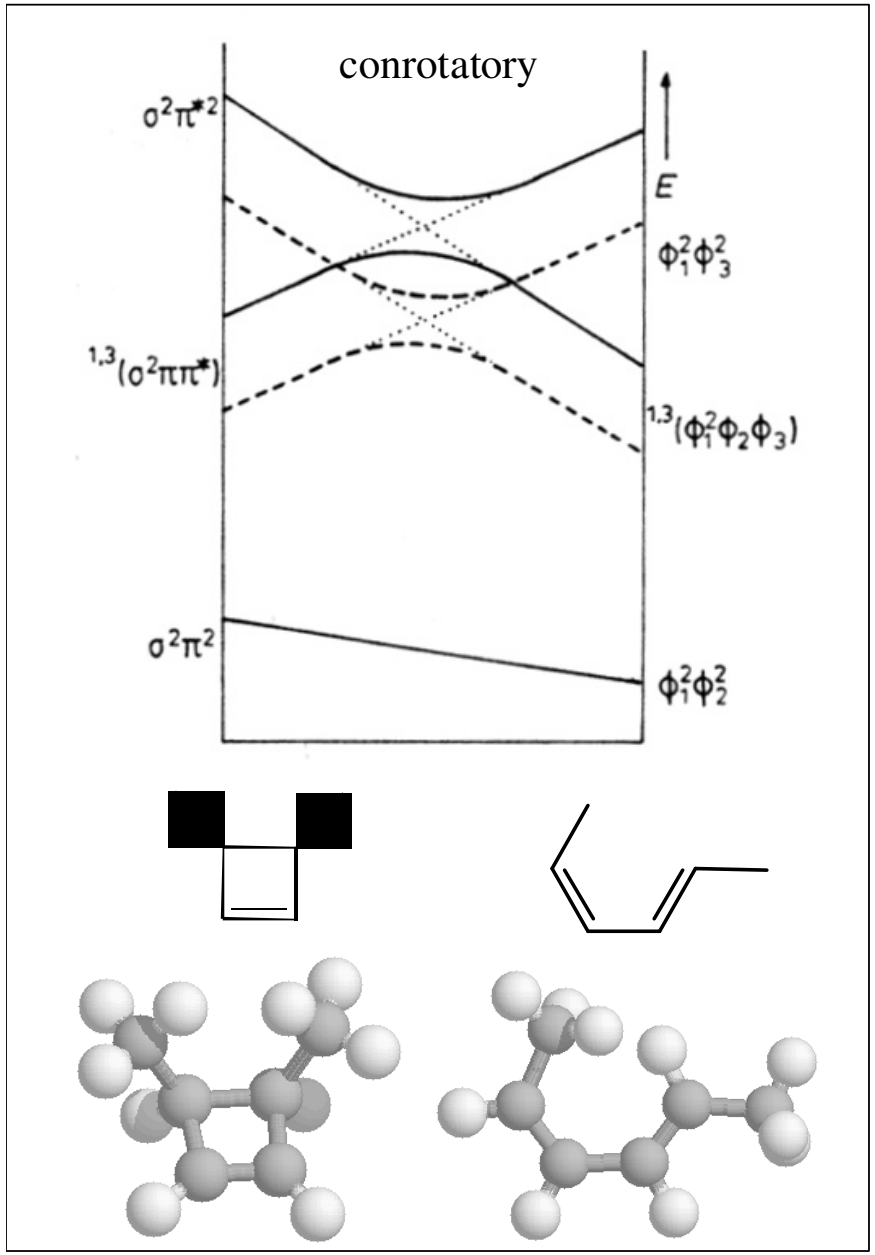
Orbital Correlation:

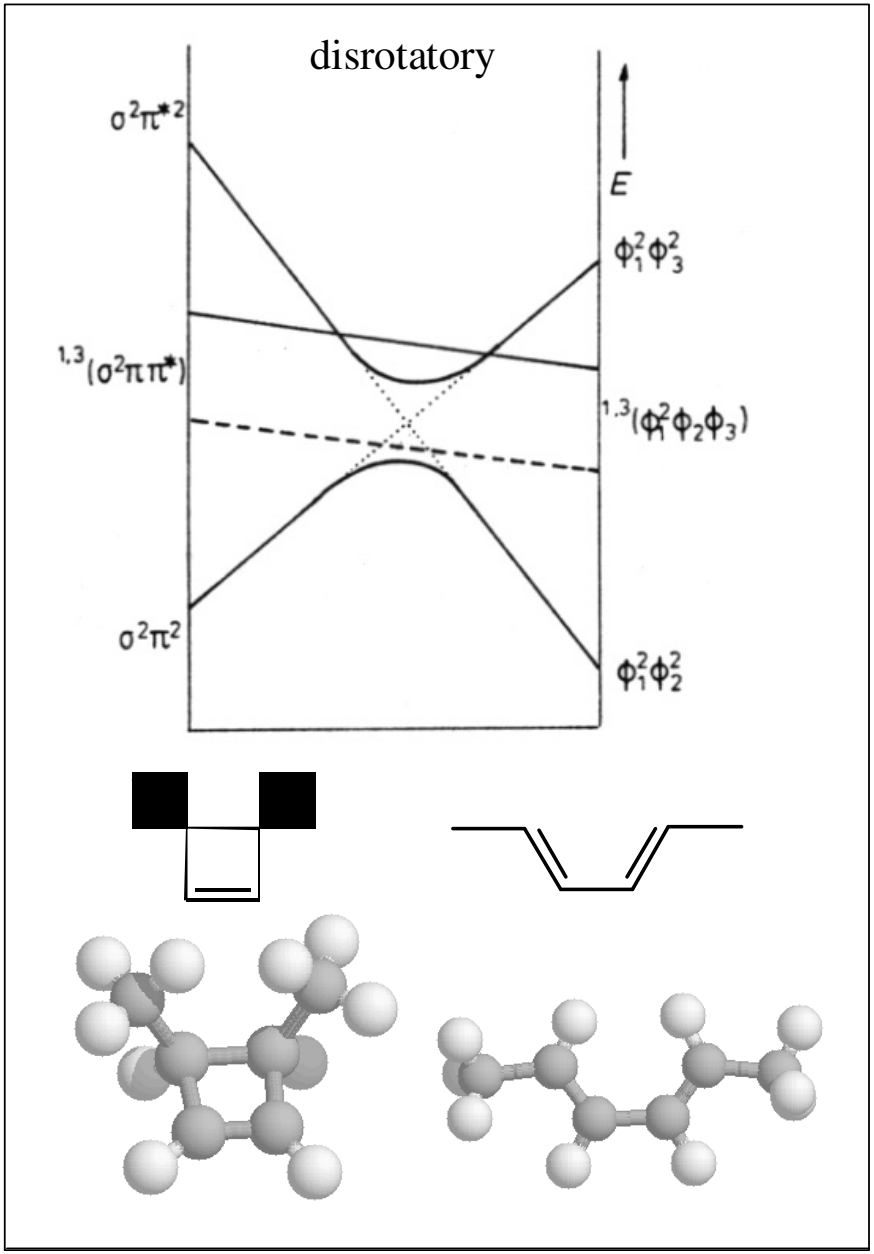


-thermally forbidden
-photochemically allowed

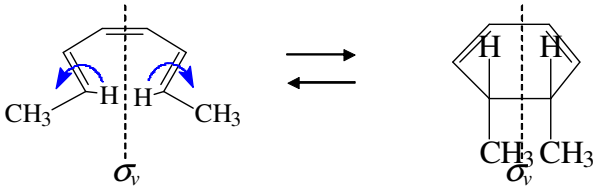
State Correlation:

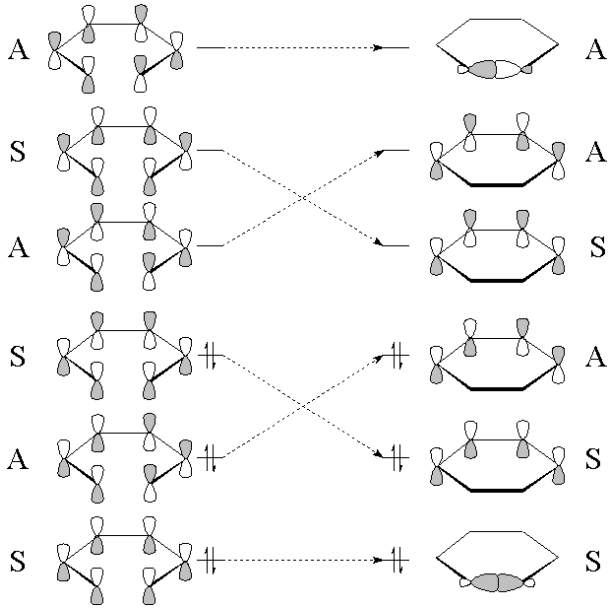



conrotatory
$\sigma^2\pi^{*2}$
$^{1,3}(\sigma^2\pi\pi^*)$
$\sigma^2\pi^2$
E
$\phi_1^2\phi_3^2$
$^{1,3}(\phi_1^2\phi_2\phi_3)$
$\phi_1^2\phi_2^2$


disrotatory
$\sigma^2\pi^{*2}$
$^{1,3}(\sigma^2\pi\pi^*)$
$\sigma^2\pi^2$
E
$\phi_1^2\phi_3^2$
$^{1,3}(\phi_1^2\phi_2\phi_3)$
$\phi_1^2\phi_2^2$

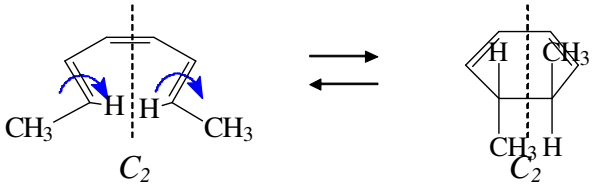
Hexatriene-Cyclohexadiene
disrotatory ring closure/opening

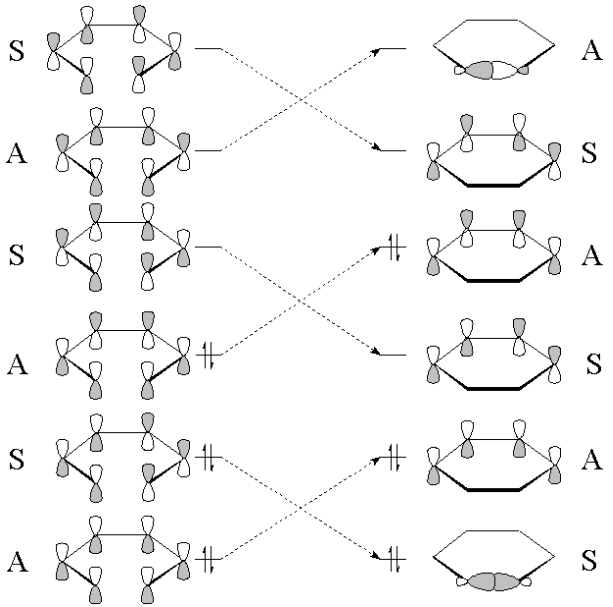




- thermally allowed
- photochemically forbidden

Hexatriene-Cyclohexadiene
disrotatory ring closure/opening





- thermally forbidden
- photochemically allowed