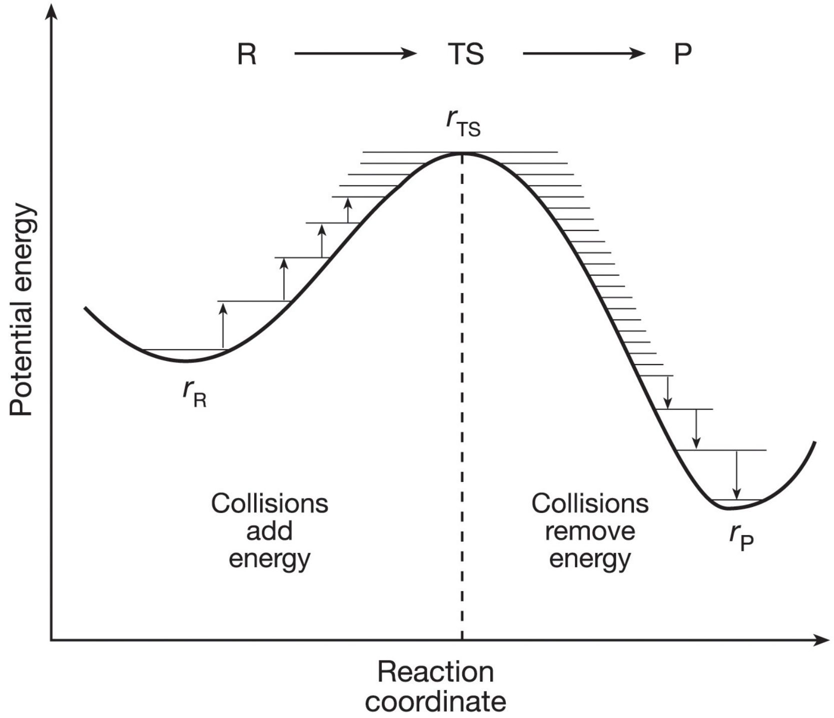
Dynamics of molecules on excited state surfaces

Chapter 6

Principles of Molecular Photochemistry: An Introduction

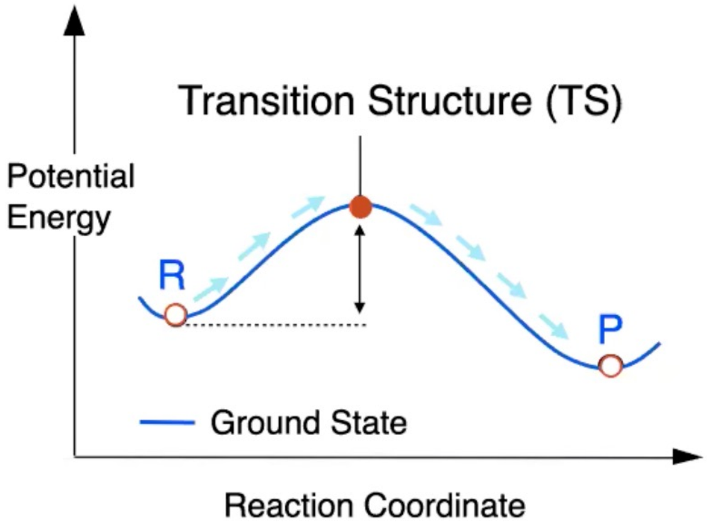
NJT, VR and JCS

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.

An Elementary Thermal Reaction Path

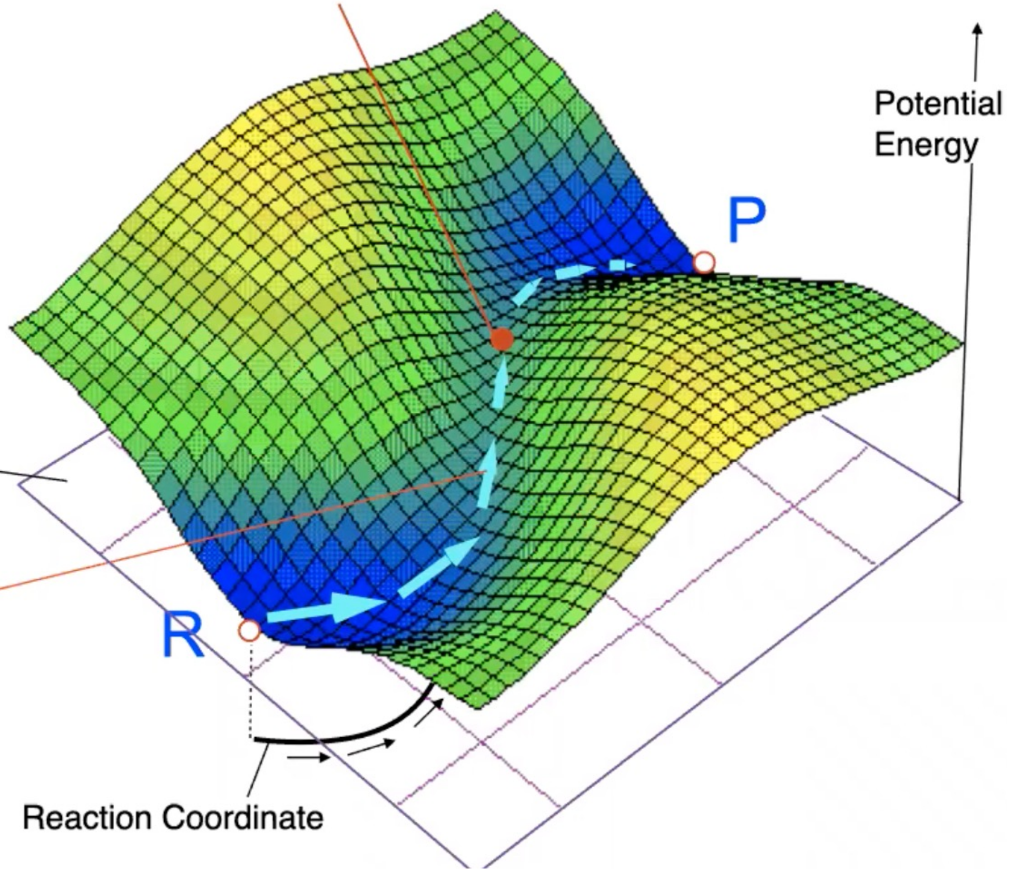


TS or "activated complex"

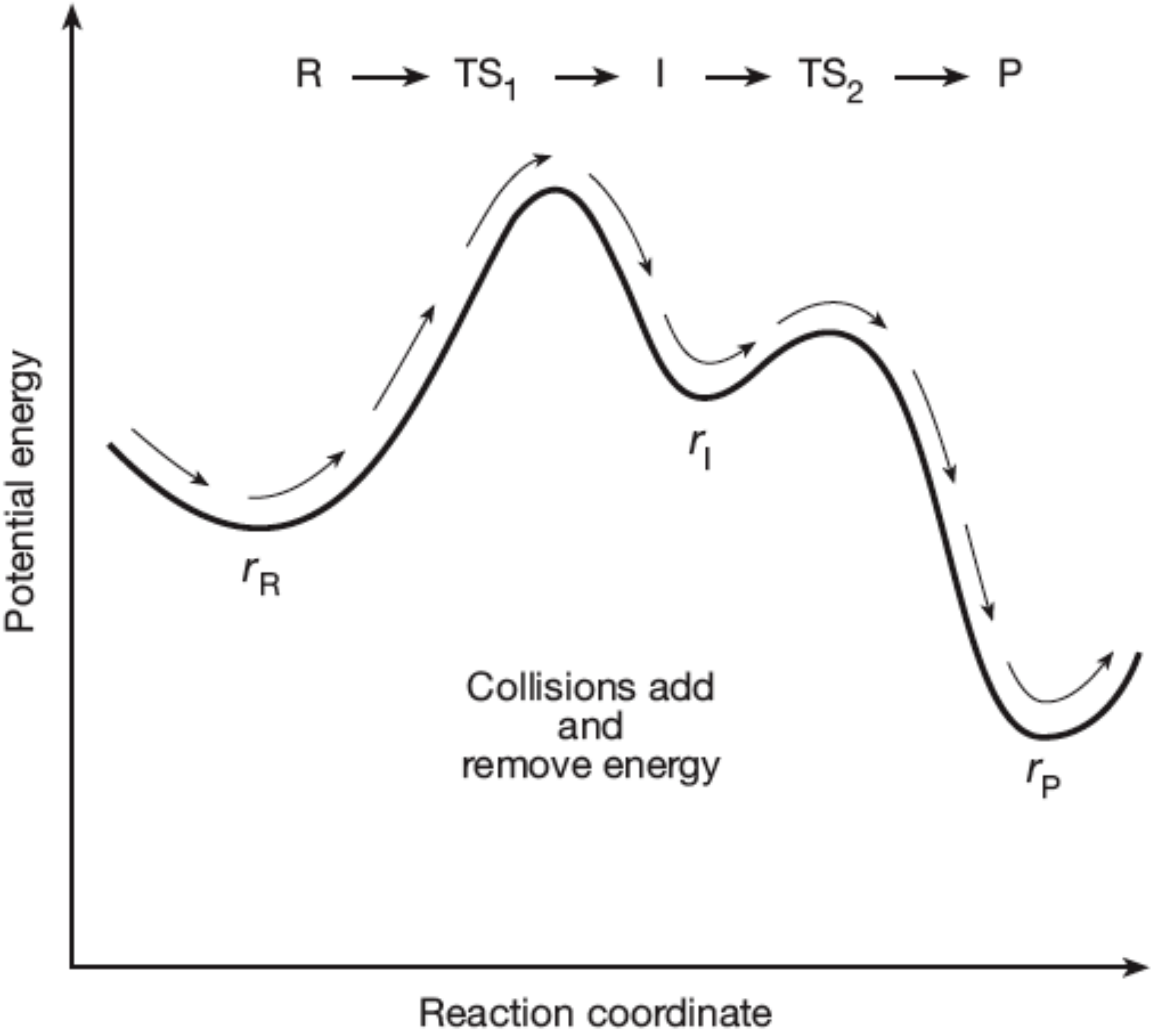
1935 Eyring, Evans and Polanyi

3N-6 dimensional coord. space

Minimum Energy Path

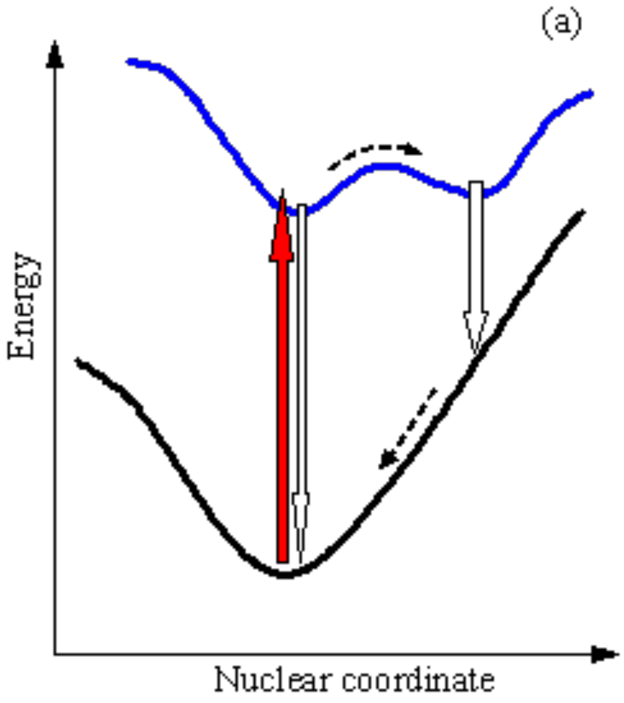


Visualization of Thermal Reactions

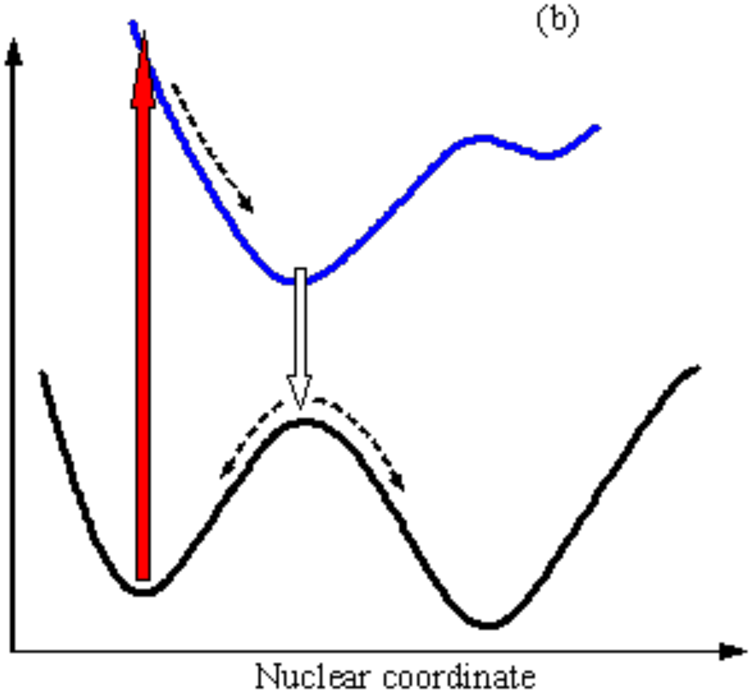


Radiative transition *vs* Reaction

How do molecules move on surfaces?
How molecules navigate between surfaces?

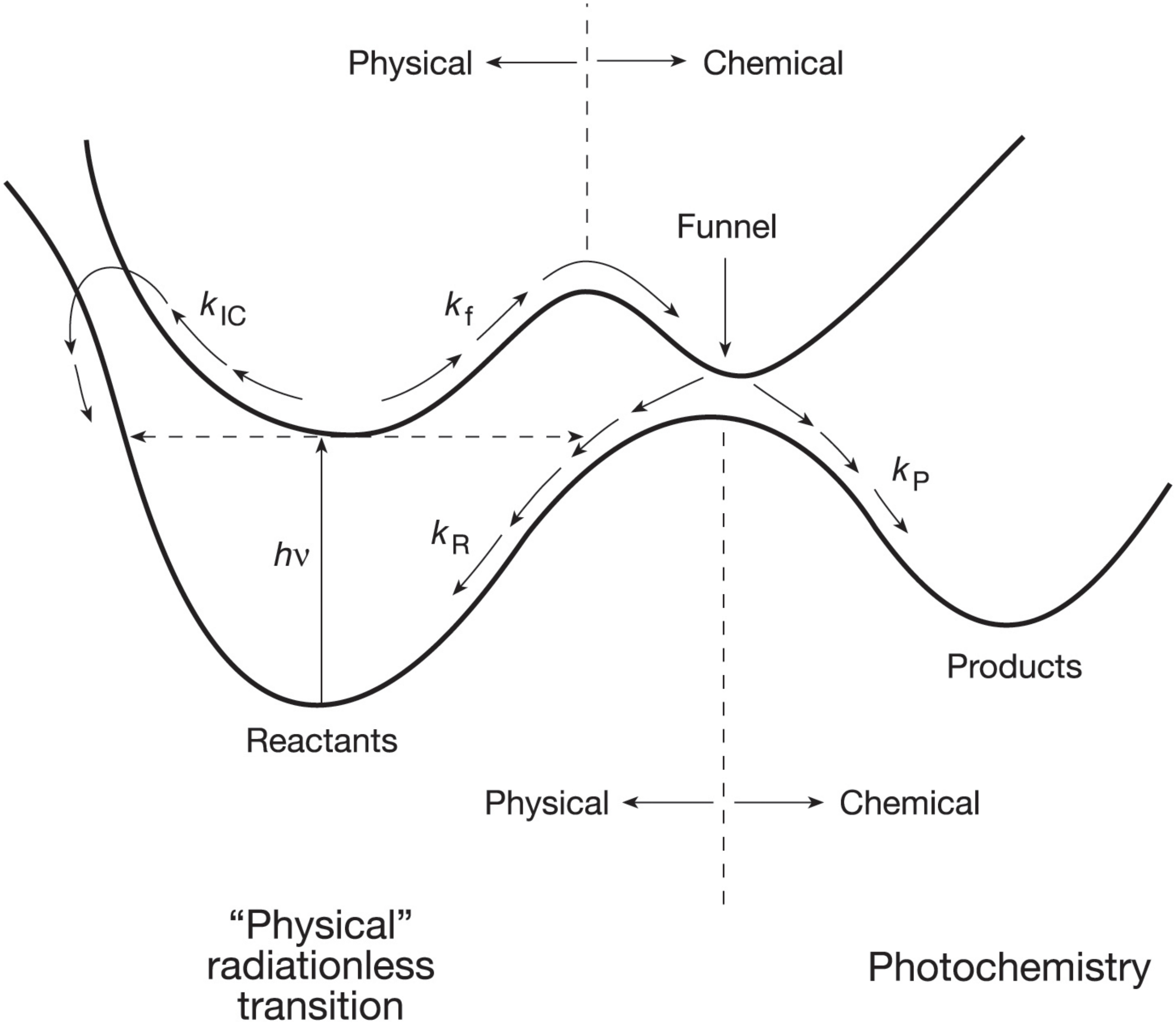


Radiationless Transition

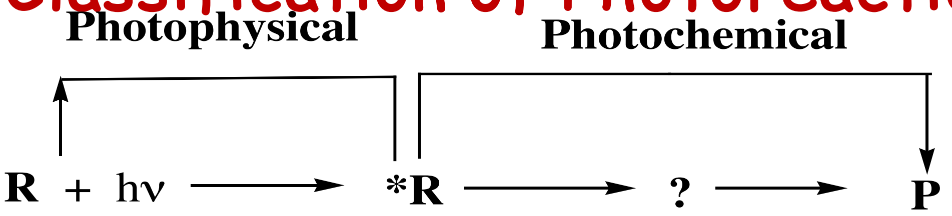


Photoreaction

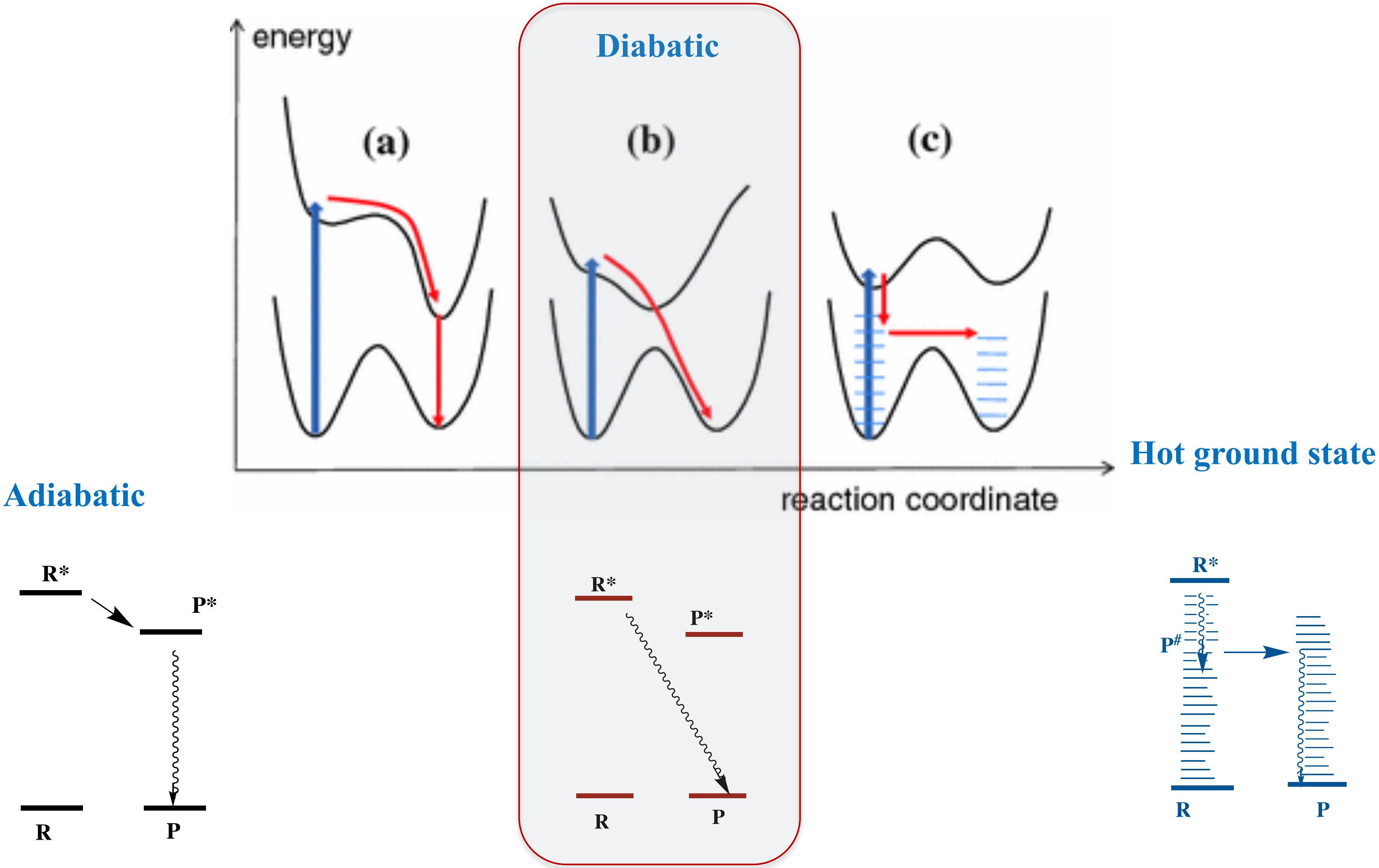
A Model for Photochemistry and Photophysics of Organic Molecules



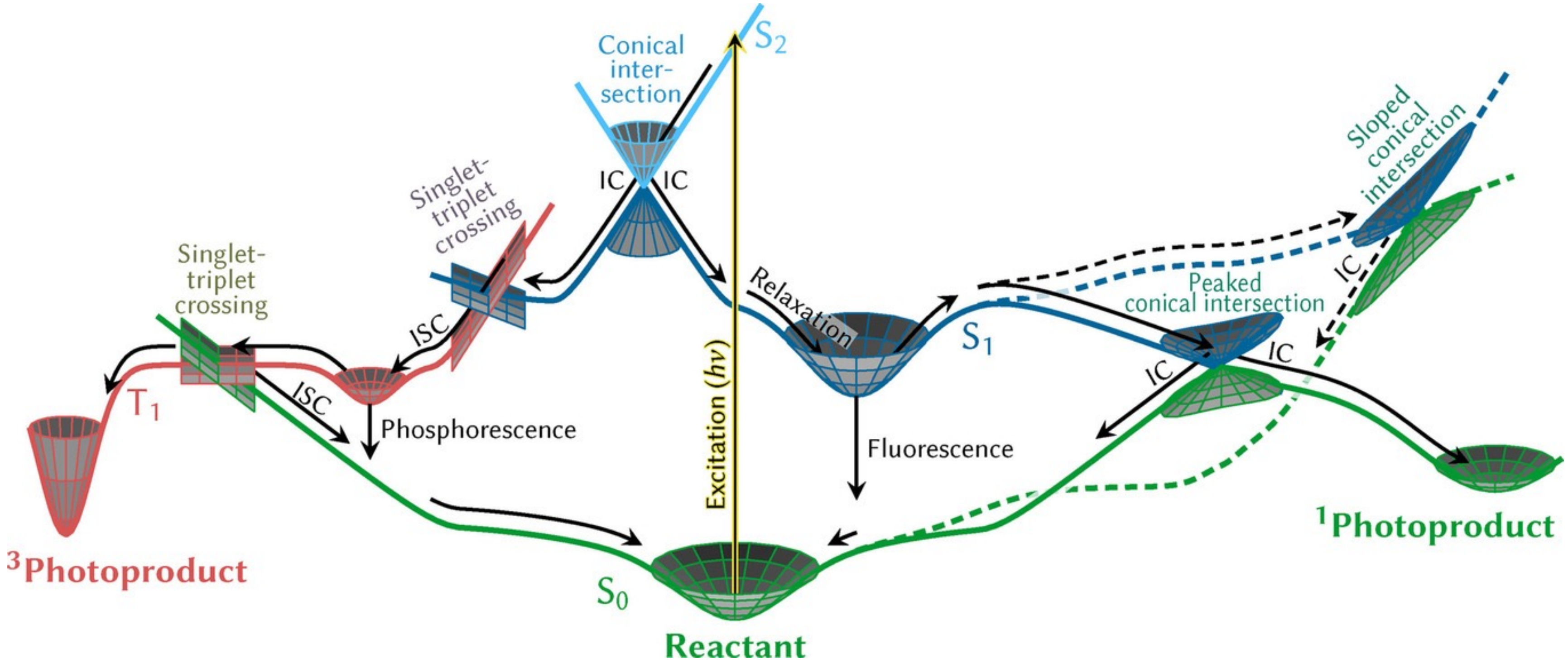
Classification of Photoreactions



$$R + h\nu \longrightarrow {}^*R \longrightarrow ? \longrightarrow P$$



A fancier way of drawing the actions on excited surfaces



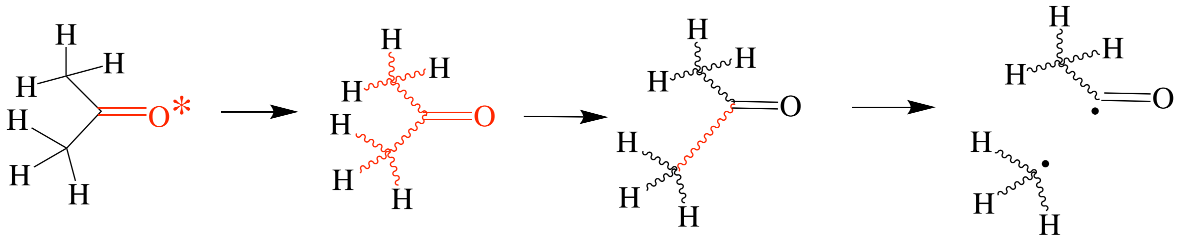
Molecular Photochemistry: Recent Developments in Theory, S. Mai and L. Gonzalez, *Angew. Chem. Int. Ed.* **2020**, *59*, 16832 – 16846

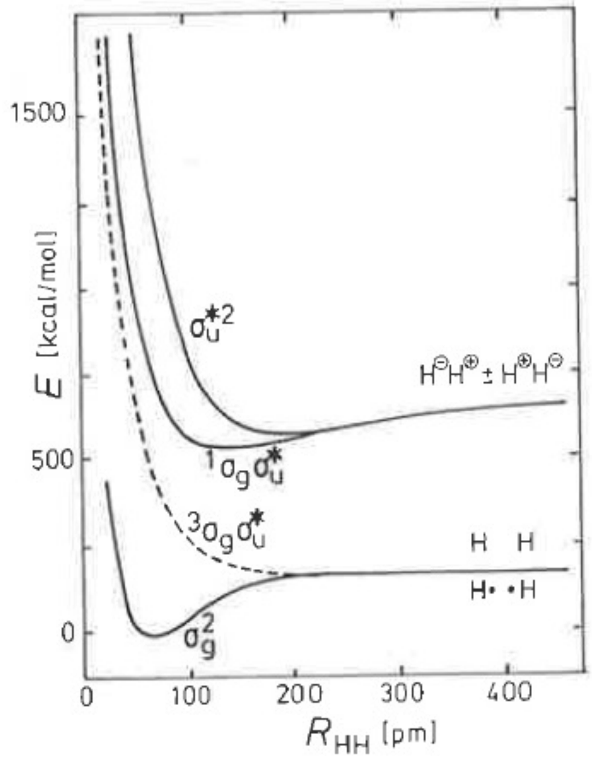
Models used to understand reactions on excited surfaces

- Adiabatic and diabatic surfaces
- Crossing and avoided crossing
- Funnel
- Conical intersection
- Energy gap law / Fermi's golden rule
- Wave packets vs particles (marbles)

Photodissociation of σ bond

$$H{-}H \longrightarrow H \quad H$$





H_2

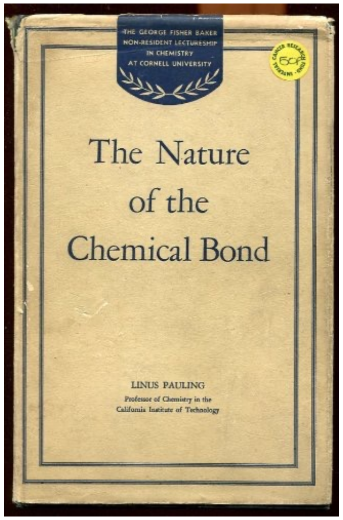
- E. Schrödinger developed the famous Φ equation in 1926
- Based on E.Sch. eq. Heitler and London developed the concept of bonding for H_2 molecule in 1927.
- L. Pauling extended this to the concept of valence-bond theory.

W. Heitler

F. London

These formed the basis of energy diagrams for photodissociation.

Potential energy curves for dissociation of NaCl



THE GEORGE FISHER BAKER
NON-RESIDENT LECTURESHIP
IN CHEMISTRY
AT CORNELL UNIVERSITY

The Nature
of the
Chemical Bond

LINUS PAULING
Professor of Chemistry in the
California Institute of Technology

Linus Pauling, 1938

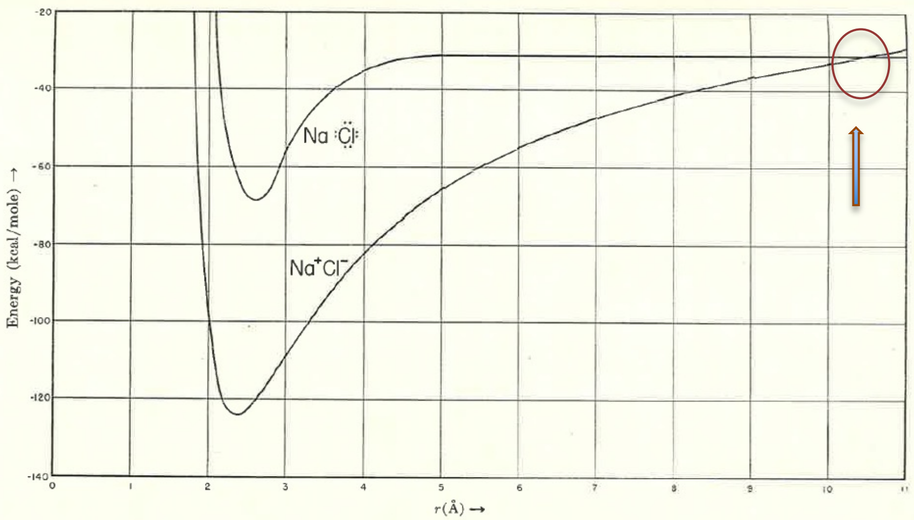
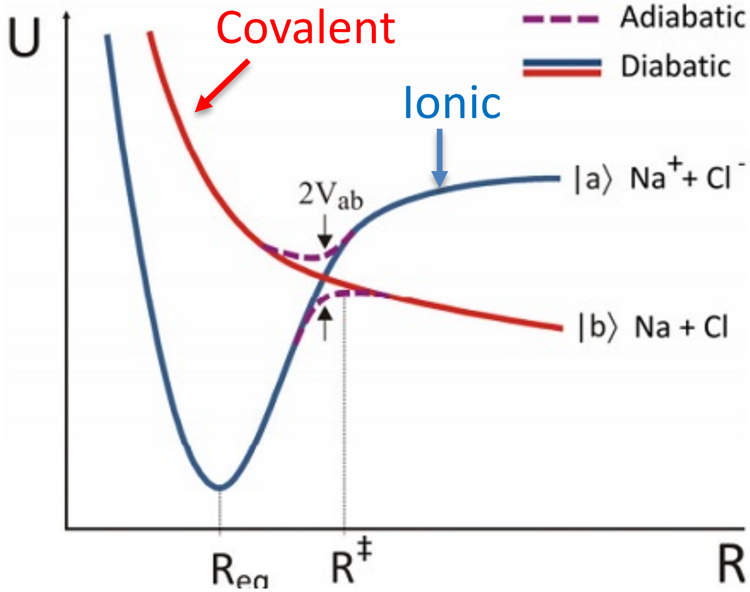
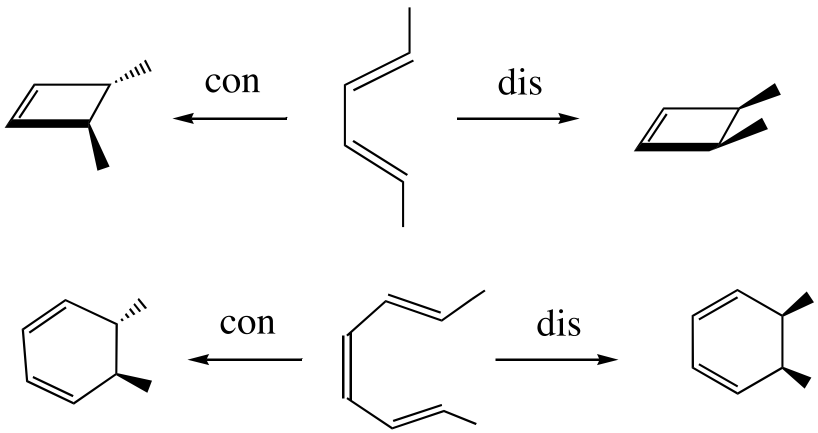
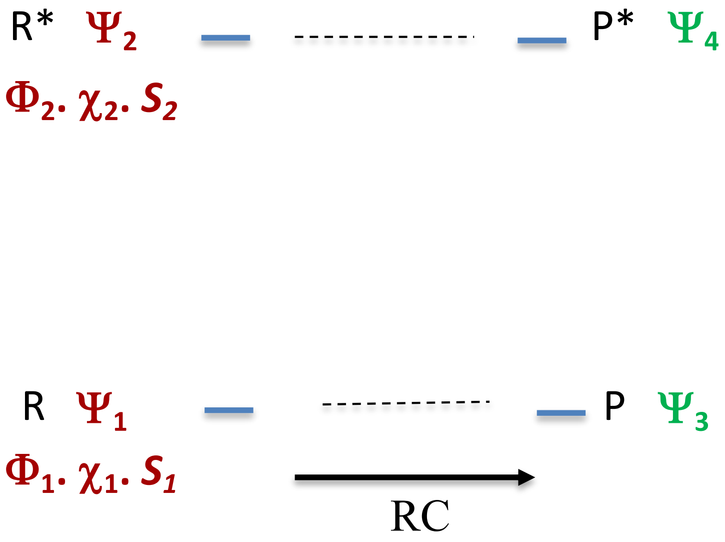


FIG. 3-5.—Energy curves for the sodium chloride molecule. At very large internuclear distances the curve for the ionic structure lies above that for the covalent structure. The curves cross at 10.5 Å, and at smaller internuclear distances the ionic structure is the more stable one.



Electronic correlation diagram for a given reaction co-ordinate




R* Ψ_2

$\Phi_2 . \chi_2 . S_2$

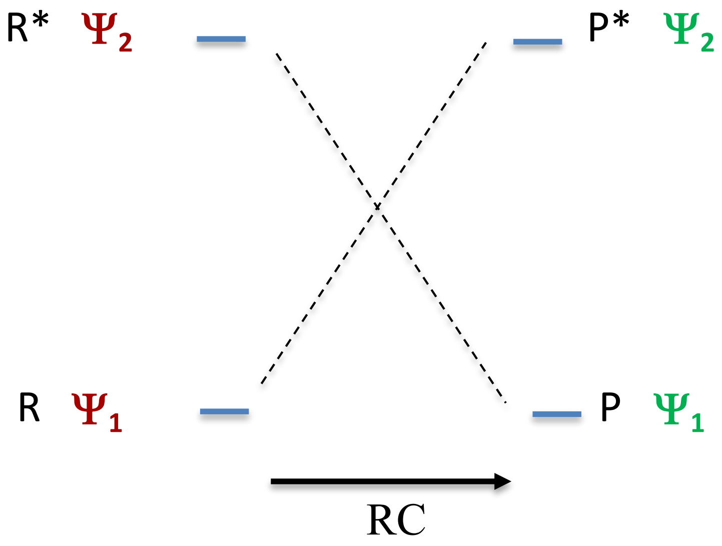
P* Ψ_4

R Ψ_1

$\Phi_1 . \chi_1 . S_1$

P Ψ_3

RC


R* Ψ_2

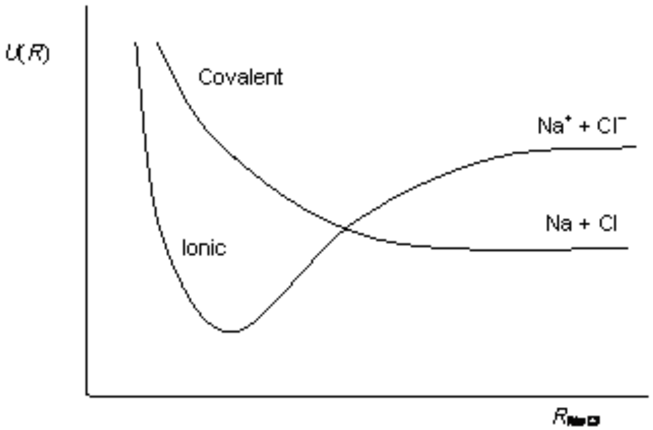
P* Ψ_2

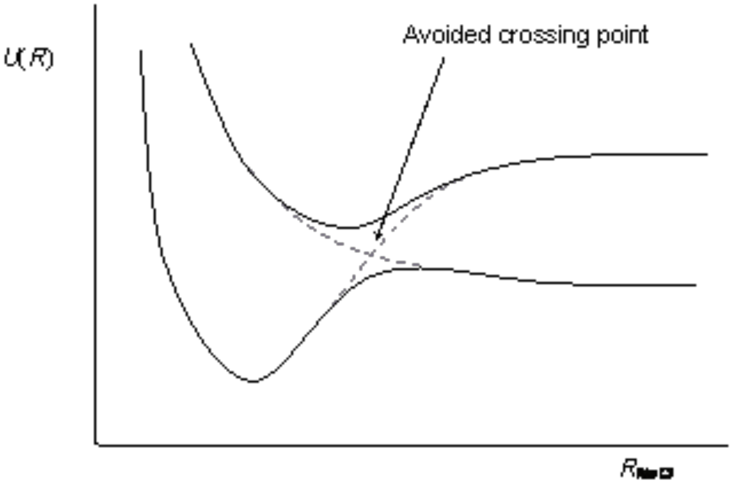
R Ψ_1

P Ψ_1

RC

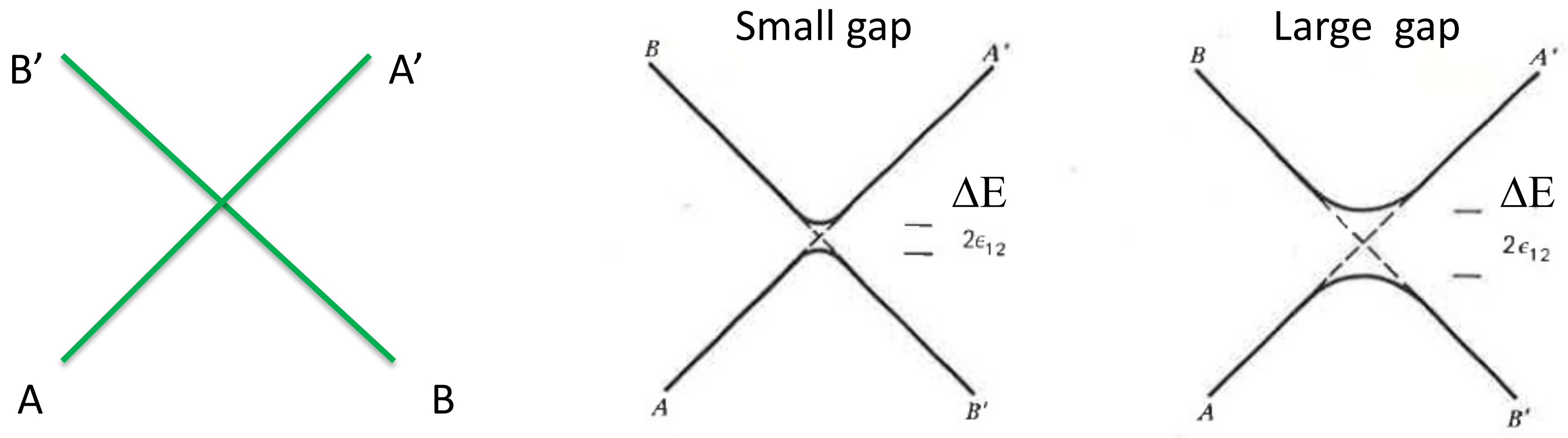
Crossing and avoided crossing





The curves are based on simple coulombic attraction between charged spheres (of which there is zero for the covalent model), and repulsion of nuclear charge and physical interaction between hard spheres.

To obtain the best wavefunctions and energies at any particular point, we must mix the ionic and covalent wavefunctions. The resulting energies repel each other. Therefore, at every internuclear separation, the energies of the original wavefunctions are "split apart." At the crossing point, the new energies (which will be closer to the true energies than the original ionic and covalent wavefunction energies) split apart and the curves no longer cross. This point of nearest approach is called an avoided crossing point



Landau-Zener-Stuecktberg equation

$$\mathbf{P = \exp(-\Delta E^2/v\Delta s)}$$

Probability of jump from lower to upper or the reverse

- Energy gap (ΔE)
- Velocity (v)
- Slope difference (Δs)

A Bit of History
Molecular Physics

- E. Teller *Isr. J. Chem.* 7, 227, **1969**

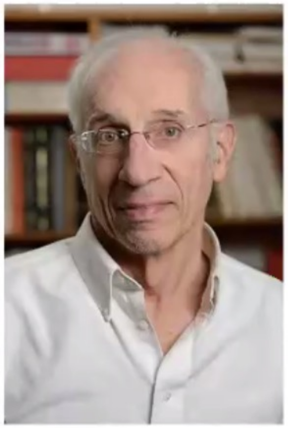
"…in a polyatomic molecule the non-crossing rule, which is rigorously valid for diatomics, fails and two electronic states, even if they have the same symmetry, are allowed to cross at **a conical intersection**..".

"…radiationless decay from the upper to the lower intersecting state occurs **within a single vibrational period** when the system "travels" in the vicinity of such intersection points…"

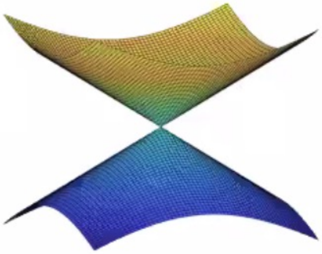
- H.C. Longuet-Higgins, "The Intersection of Potential Energy Surfaces in Polyatomic Molecules", *Proc. R. Soc. Lond. Ser. A.*, 344, 147-156, **1975**

"…thereby disposing of a recent claim that the non-crossing rule for diatomic molecules applies also to polyatomic molecules...".

Conical Intersection

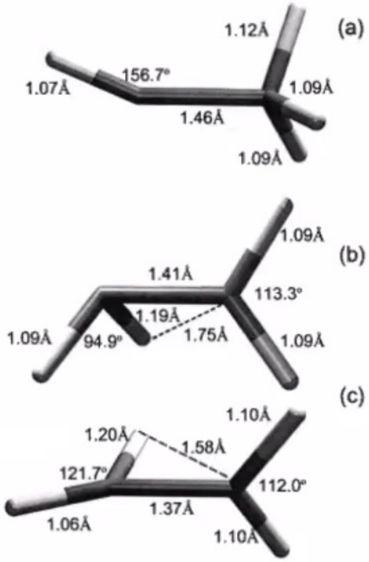


$$\hat{H}\Psi_I(\mathbf{r};\mathbf{R}) = E_I(\mathbf{R})\Psi_I(\mathbf{r};\mathbf{R})$$



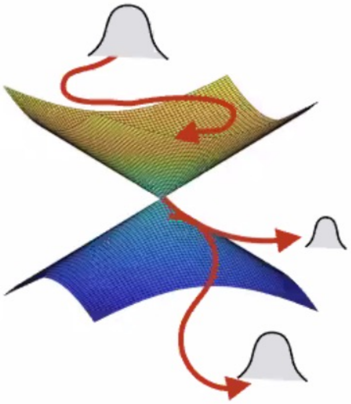
$$f_{IJ}(\mathbf{R}) = \langle \Psi_I(\mathbf{r};\mathbf{R}) | \nabla \Psi_J(\mathbf{r};\mathbf{R}) \rangle$$

David Yarkony



Todd Martinez

John Tully



A Bit of History

Photochemistry

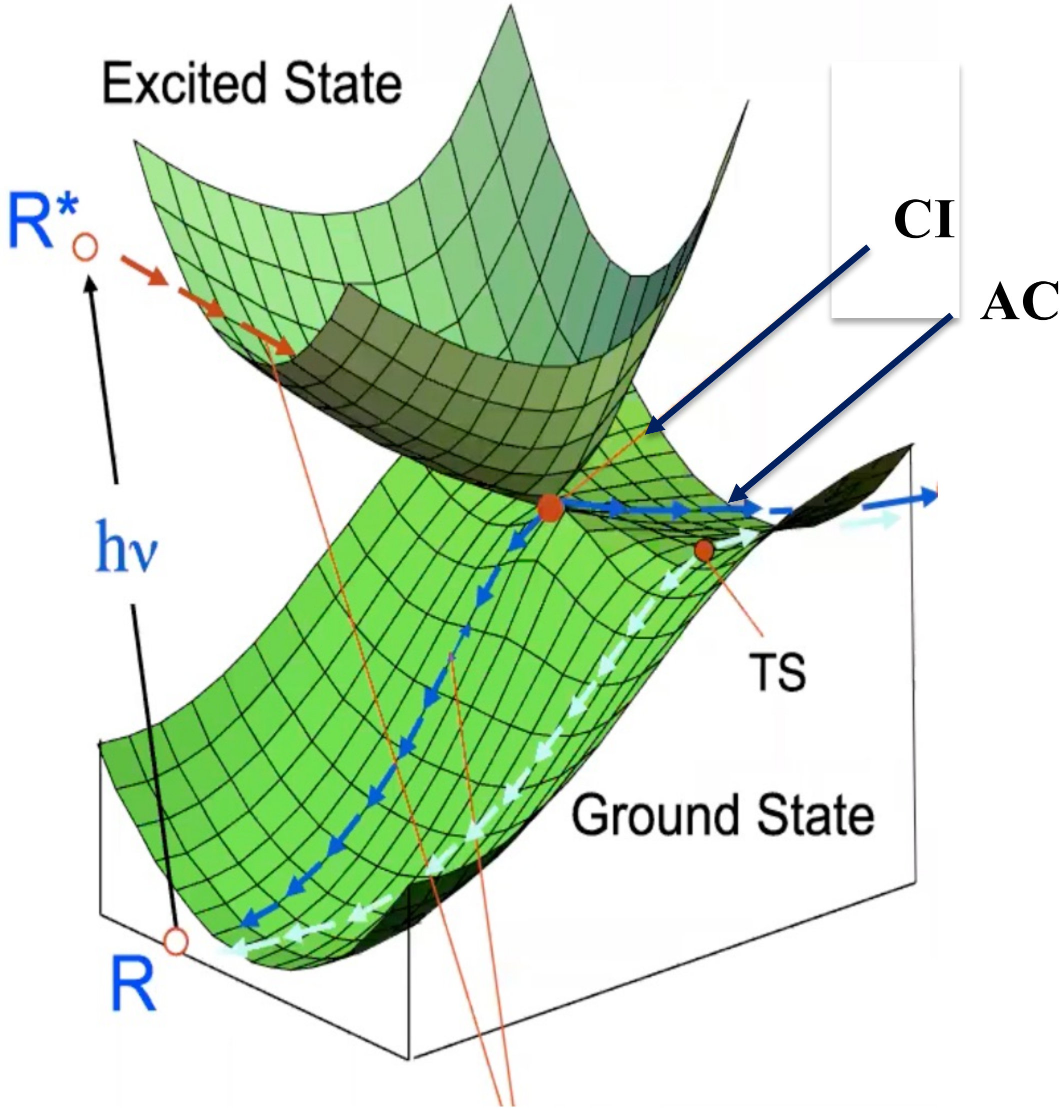
- Zimmerman, Michl and Salem were the first to suggest that, in photochemical organic reactions, the point of return M* may correspond to a conical intersection. Zimmerman and Michl call it photochemical funnel.

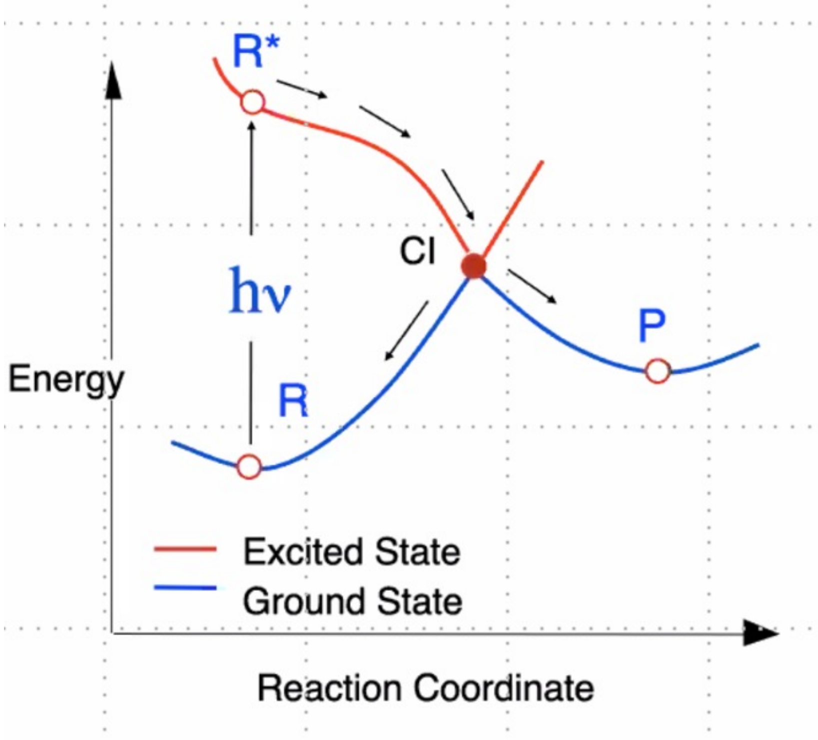
- **1966, Howard Zimmerman**

- **1970, Josef Michl**

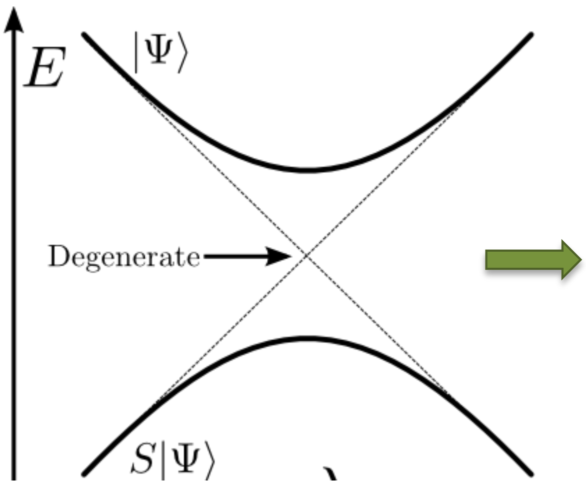
- **1974, Lionel Salem**

Minimum at Avoided Crossing & CI may not be at the same place

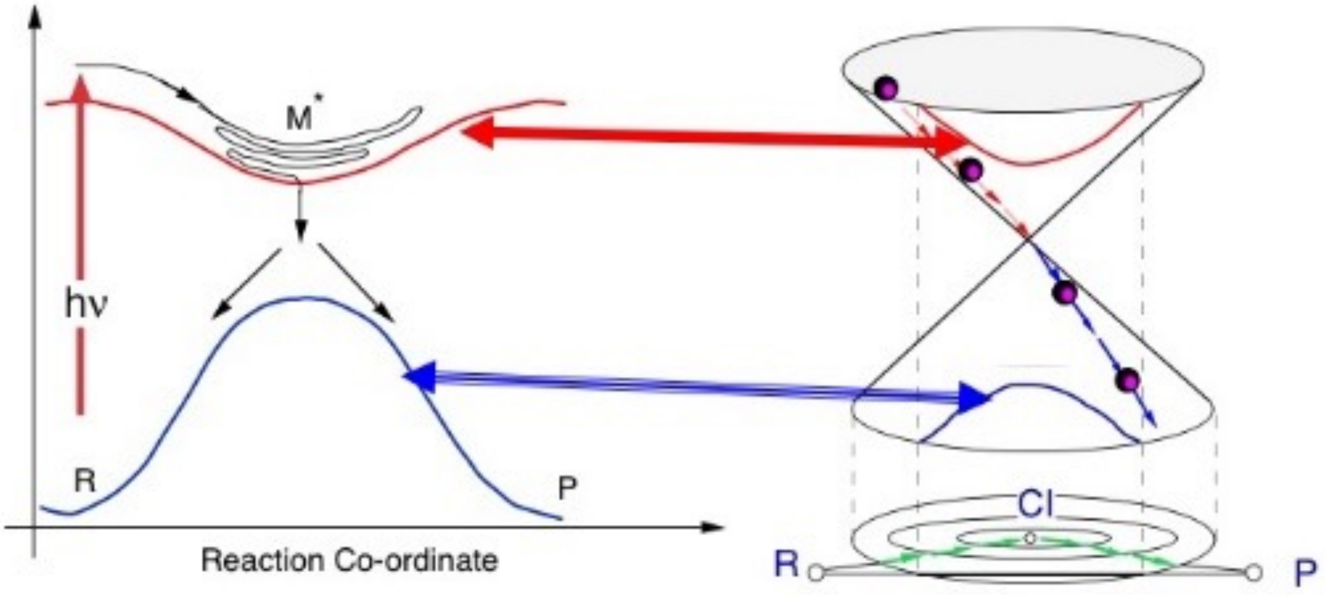




Avoided crossing, true crossing and conical intersection



Diatomic



Avoided crossing
in two dimensions

Product appears in ns

Allowed crossing in higher dimensions (polyatomic molecules); Conical intersection

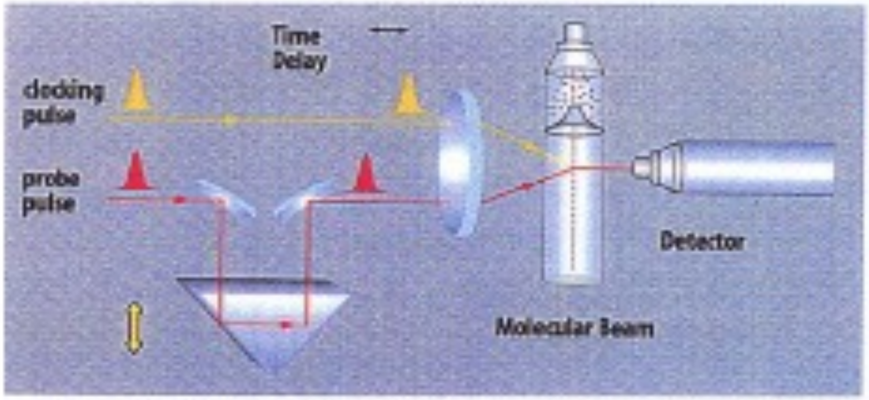
Product appears in ps-fs

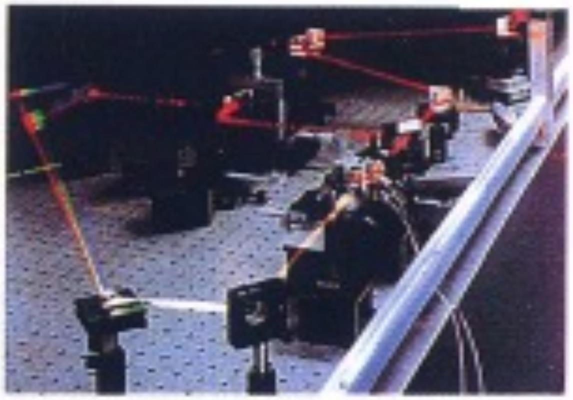
10^{-15} sec time resolution (1980s)

Ahmed H. Zewail

The Nobel Prize in Chemistry 1999

"for his studies of the transition states of chemical reactions using femtosecond spectroscopy."





Chem. Eng. News., **1988**, Nov 7, 24

Physics Today, May **1990**, 24

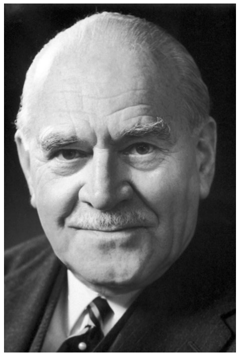
J. Phys. Chem. C., **1996**, 100, 12701

Angew. Chem. Int. Ed., **2000**, 39, 2586

J. Chem. Edu., **2001**, 78, 737

10^{-6} sec time resolution (1960s)

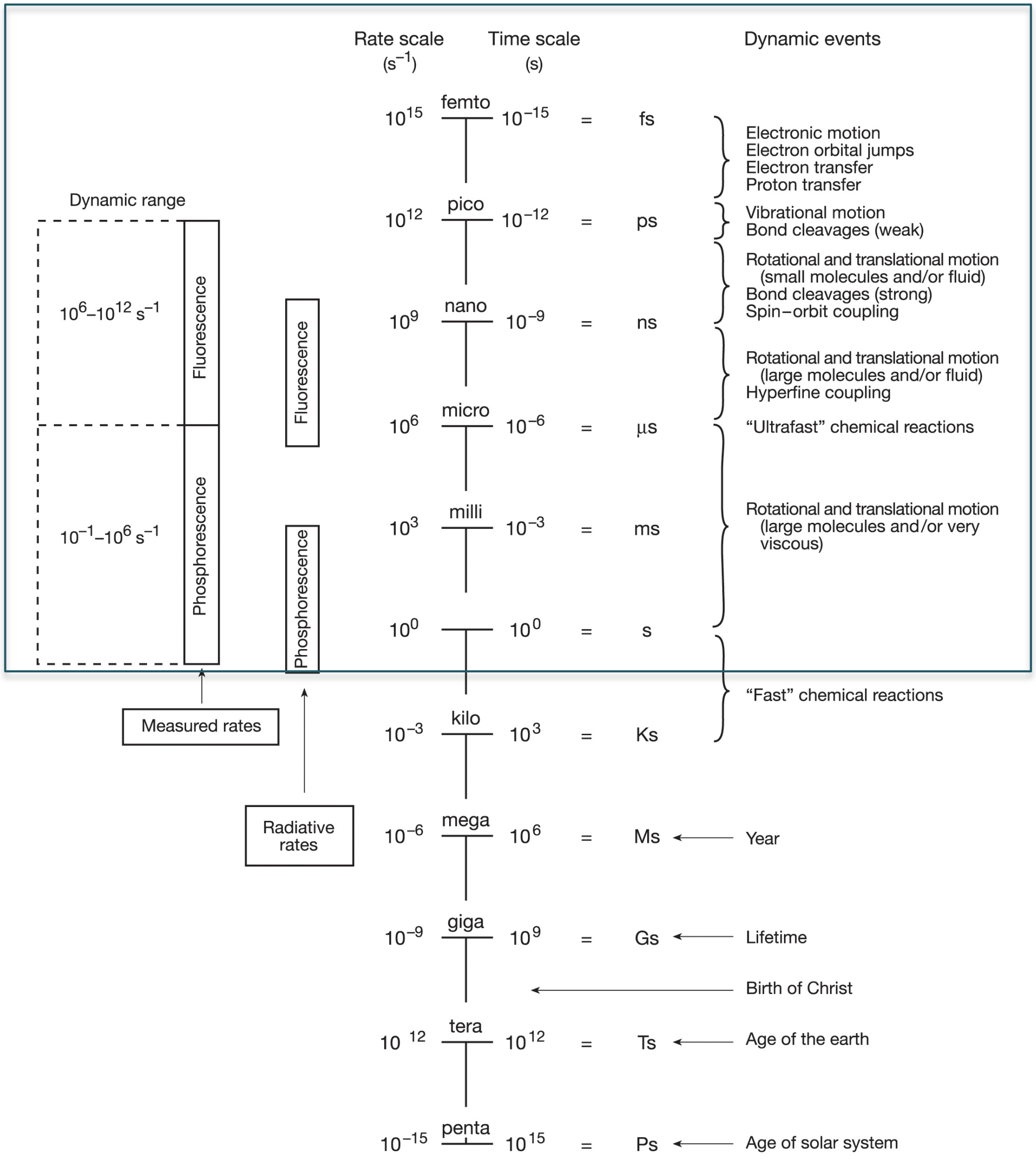
M. Eigen



R. G. W. Norrish

G. Porter

The Nobel Prize in Chemistry 1967 was divided, one half awarded to M. Eigen, the other half jointly to R. G. W. Norrish and G. Porter "*for their studies of <u>extremely fast chemical reactions</u>, effected by disturbing the equilibrium by means of very short pulses of energy*."



Rate scale (s^{-1})		Time scale (s)			Dynamic events
10^{15}	femto	10^{-15}	=	fs	Electronic motion Electron orbital jumps Electron transfer Proton transfer
10^{12}	pico	10^{-12}	=	ps	Vibrational motion Bond cleavages (weak) Rotational and translational motion (small molecules and/or fluid) Bond cleavages (strong) Spin–orbit coupling
10^{9}	nano	10^{-9}	=	ns	Rotational and translational motion (large molecules and/or fluid) Hyperfine coupling
10^{6}	micro	10^{-6}	=	µs	"Ultrafast" chemical reactions
10^{3}	milli	10^{-3}	=	ms	Rotational and translational motion (large molecules and/or very viscous)
10^{0}		10^{0}	=	s	"Fast" chemical reactions
10^{-3}	kilo	10^{3}	=	Ks	
10^{-6}	mega	10^{6}	=	Ms	Year
10^{-9}	giga	10^{9}	=	Gs	Lifetime Birth of Christ
10^{12}	tera	10^{12}	=	Ts	Age of the earth
10^{-15}	penta	10^{15}	=	Ps	Age of solar system

Dynamic range

10^{6}–10^{12} s^{-1} Fluorescence

10^{-1}–10^{6} s^{-1} Phosphorescence

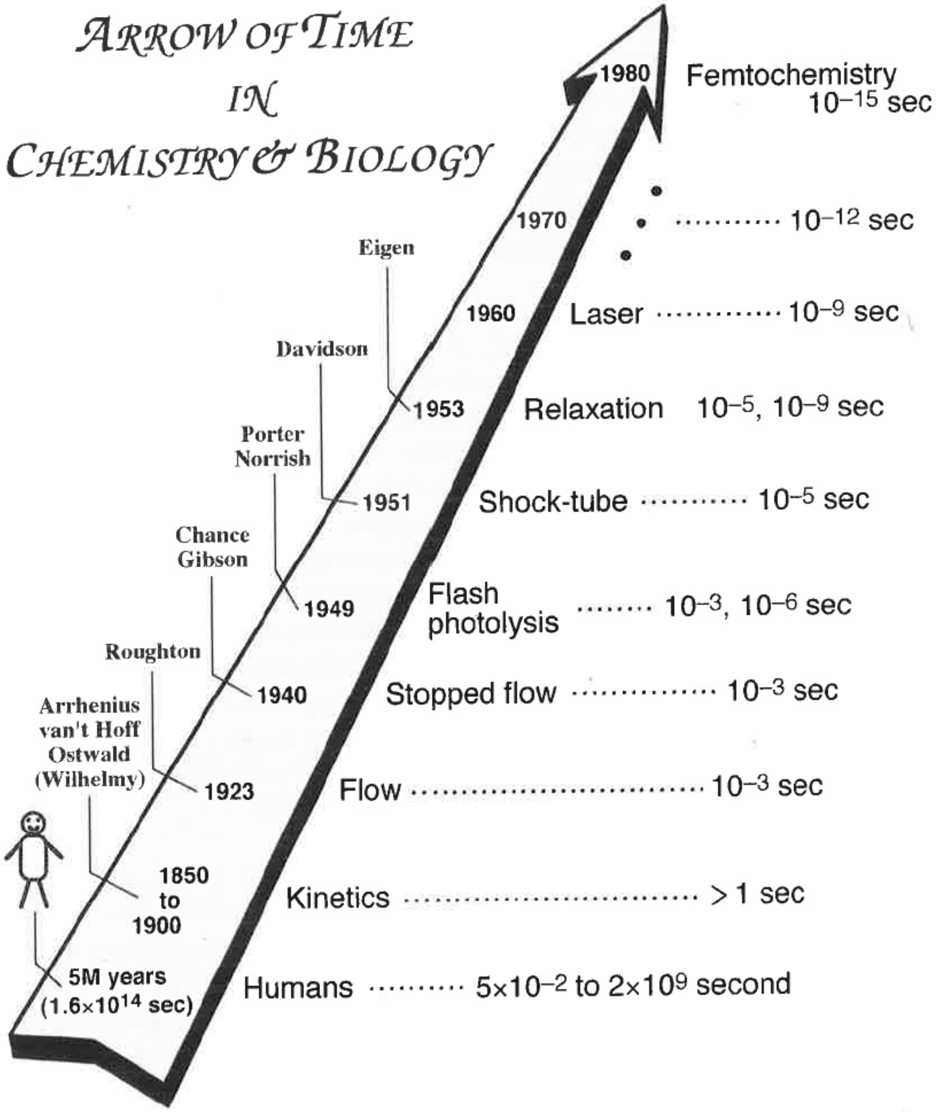
Measured rates

Fluorescence

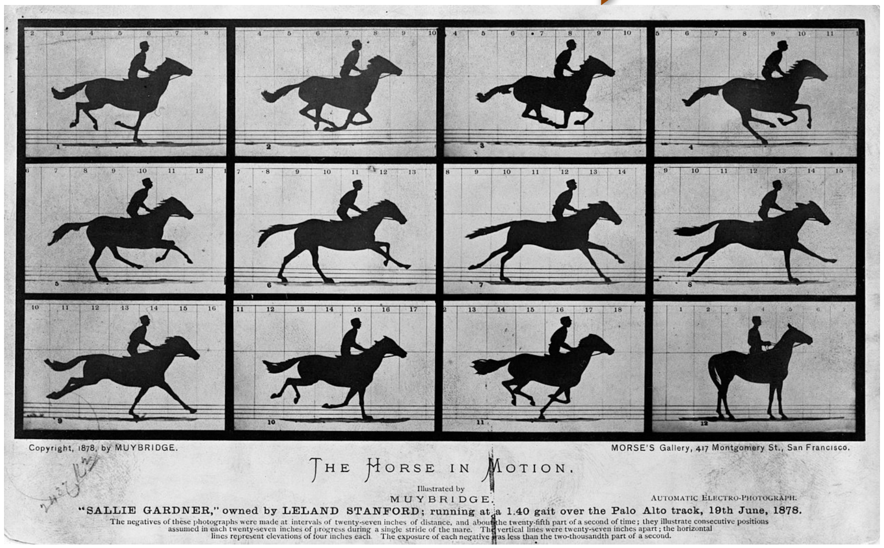
Phosphorescence

Radiative rates

The birth of high-speed camera



Can a horse fly



"SALLIE GARDNER," owned by LELAND STANFORD; running at a 1.40 gait over the Palo Alto track, 19th June, 1878.

The negatives of these photographs were made at intervals of twenty-seven inches of distance, and about the twenty-fifth part of a second of time; they illustrate consecutive positions assumed in each twenty-seven inches of progress during a single stride of the mare. The vertical lines were twenty-seven inches apart; the horizontal lines represent elevations of four inches each. The exposure of each negative was less than the two-thousandth part of a second.

Photo series by Eadweard Muybridge, 1870

Can a horse fly

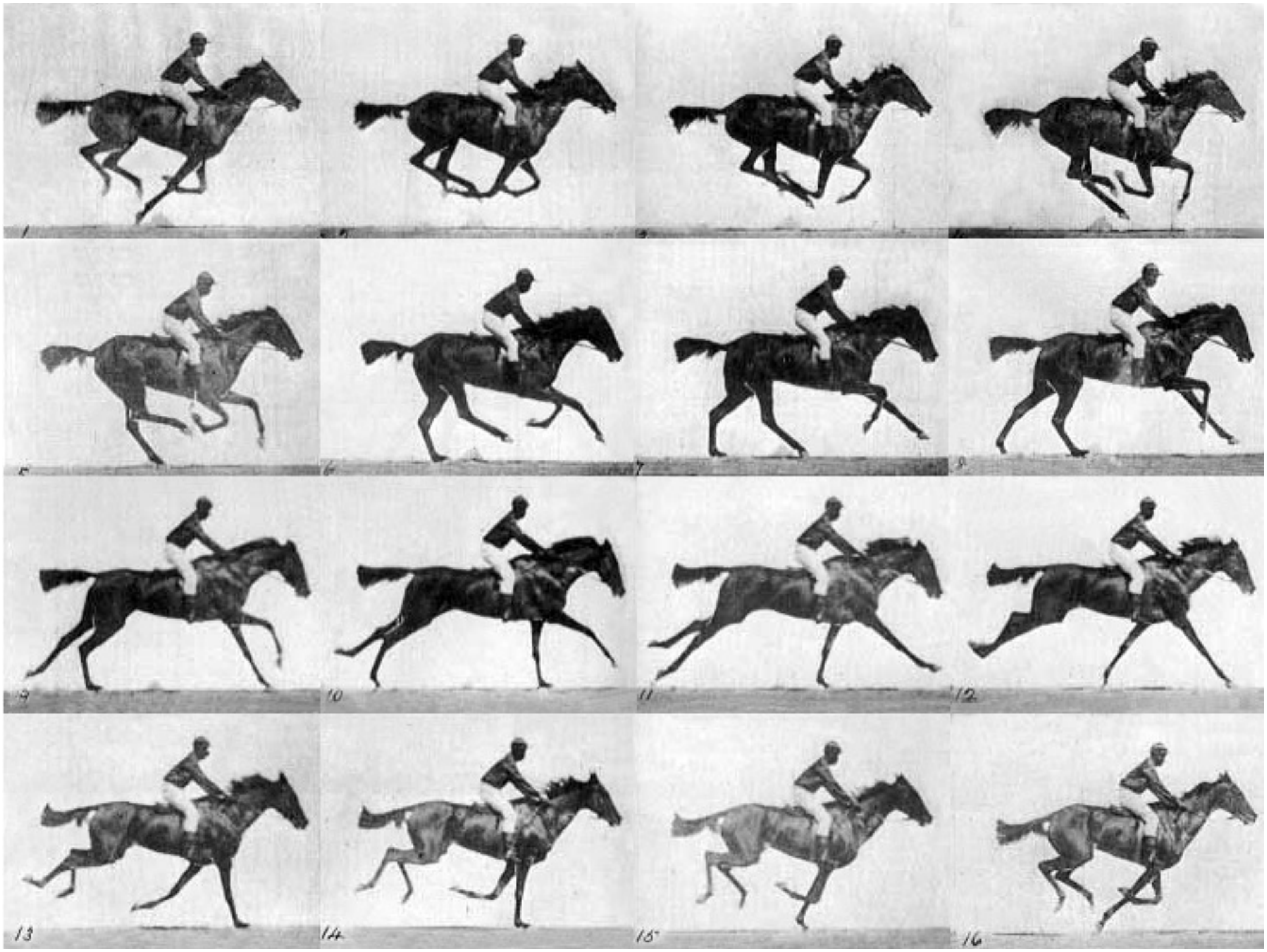


Photo series by Eadweard Muybridge, 1870

Coherence

Incoherence

Partial Coherence

Millions of molecules are reacting

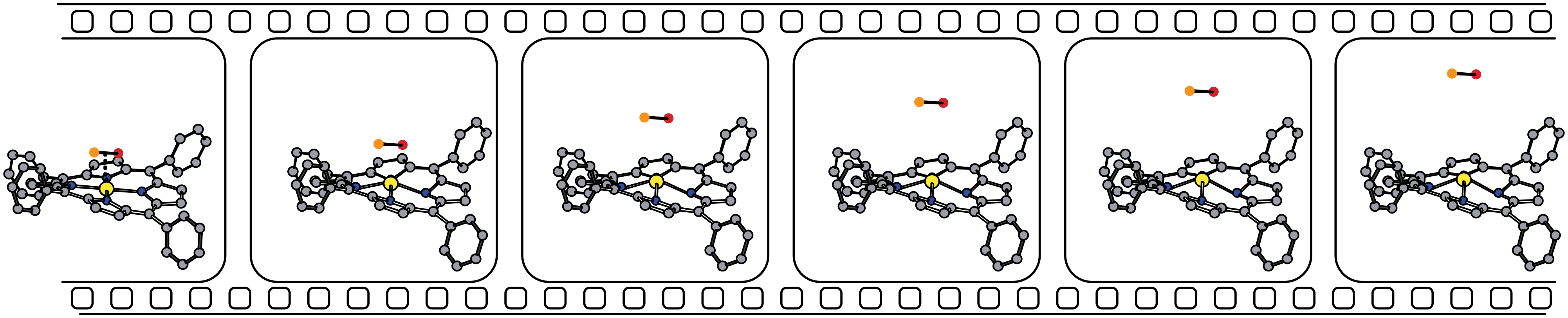
Although same reaction – they don’t run in lock-step

How to synchronize ?

As if a whole herd of horses in lock-step in one camera

Coherence

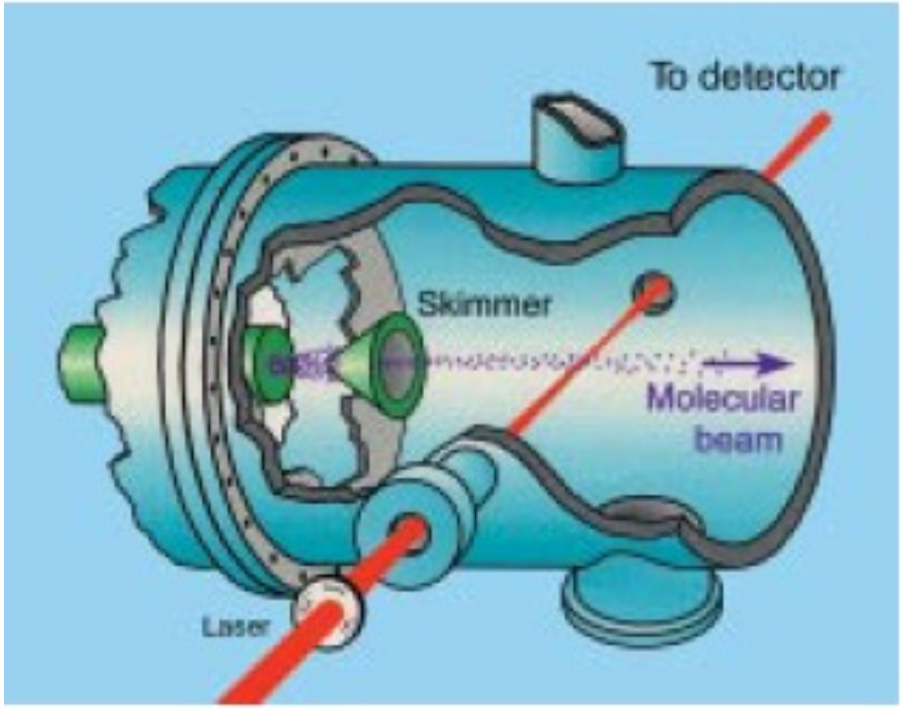
- Millions of molecules could march in lock-step from a common starting point
- A series of pictures can be taken at different times
- Equivalent to a movie of a chemical reaction

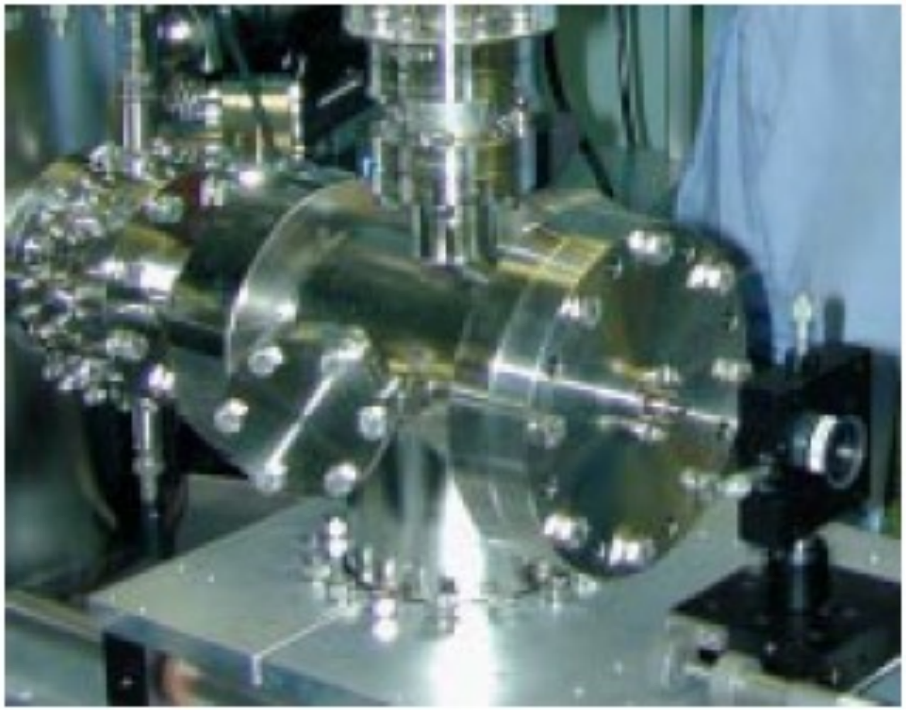


Coherence

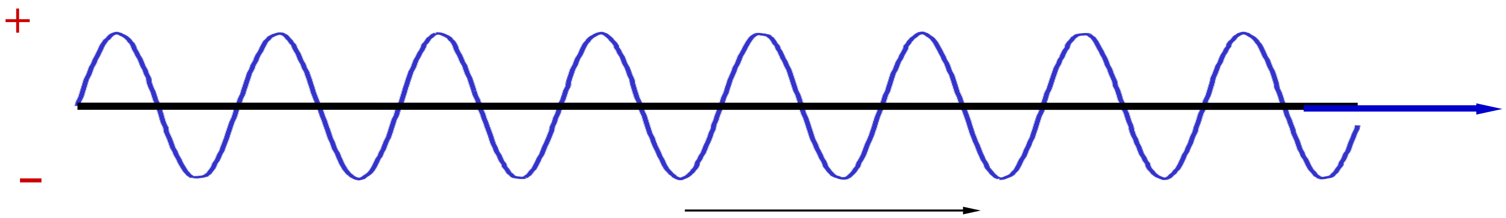
Coordinated fashion or acting together.
How to achieve this?

Molecular beam

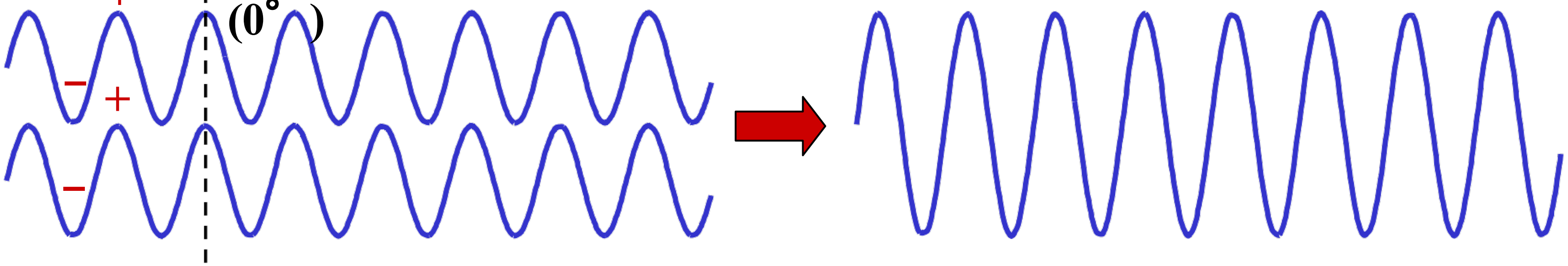




Waves oscillate positive and negative and travel

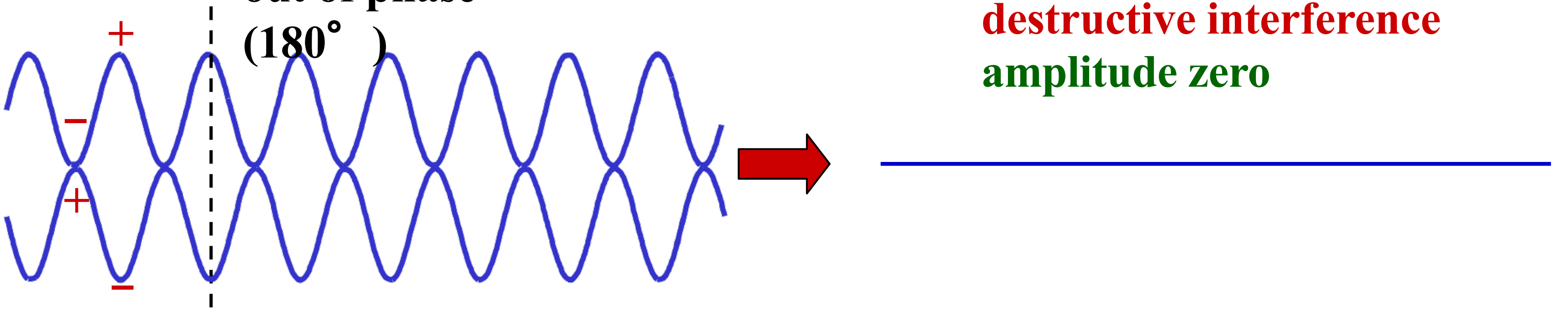


Waves can be added.



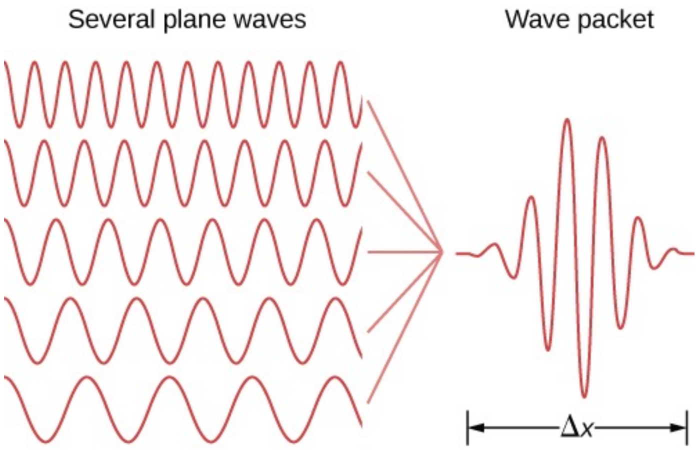
in phase
(0°)

constructive interference
amplitude doubled

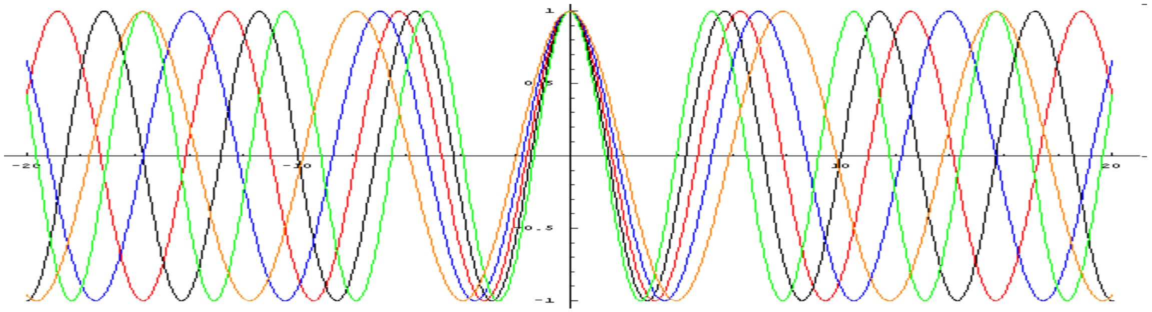


out of phase
(180°)

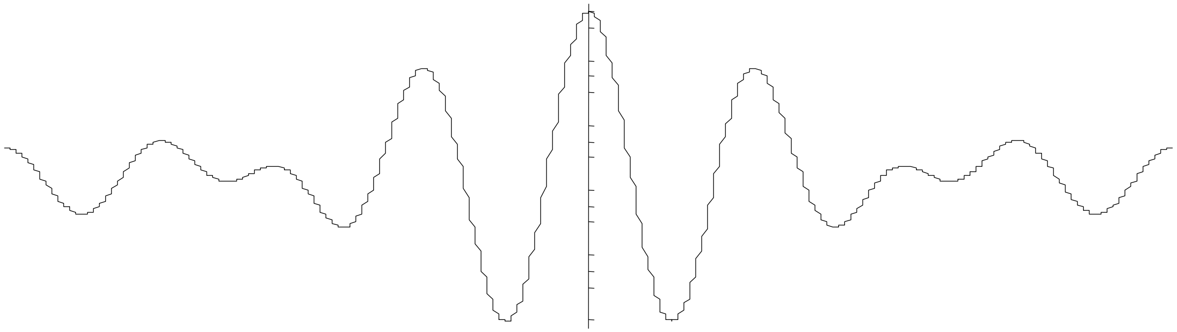
destructive interference
amplitude zero



Waves of different wavelengths can be added. Add 5 waves.
λ = 1.2, 1.1, 1.0, 0.9, 0.8



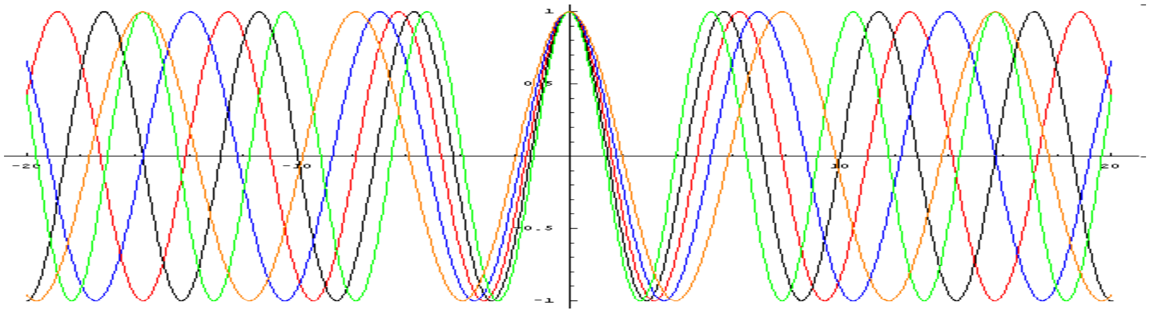
Superposition
Sum of the 5 waves



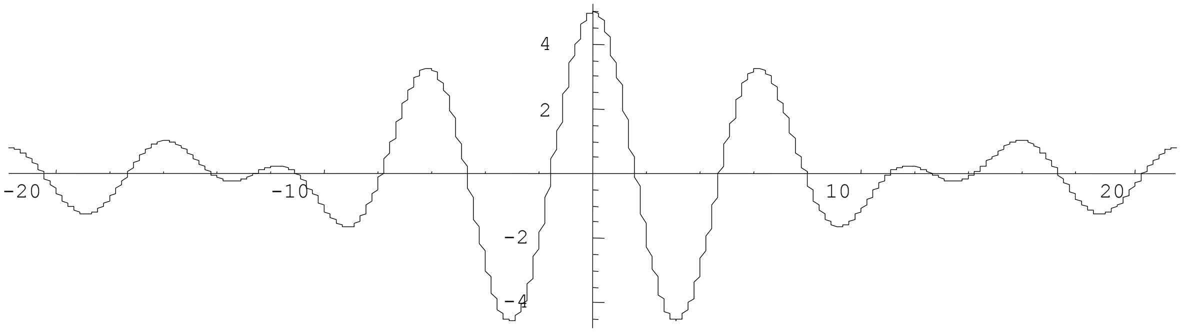
Classical – can know momentum p and position x exactly at the same time.

Quantum – know p exactly, x completely uncertain. Equal probability of finding particle anywhere.

Waves of different wavelengths can be added. Add 5 waves.
λ = 1.2, 1.1, 1.0, 0.9, 0.8

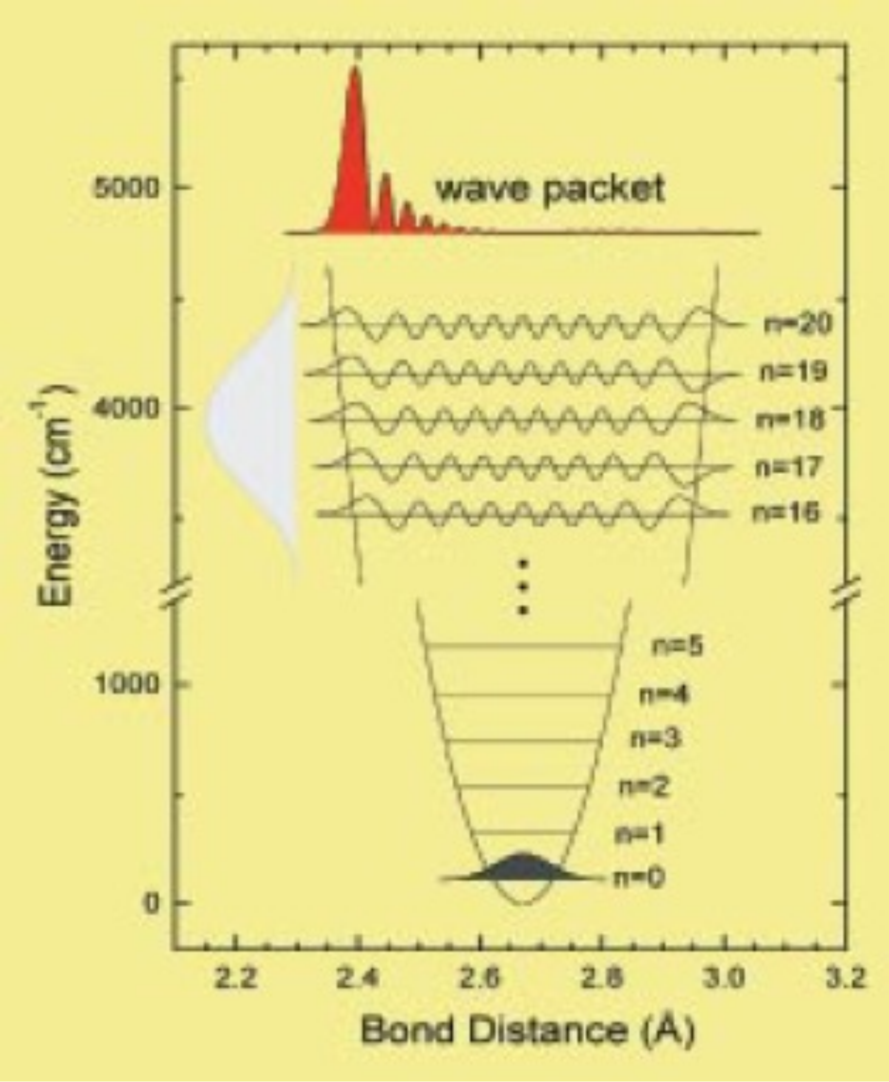


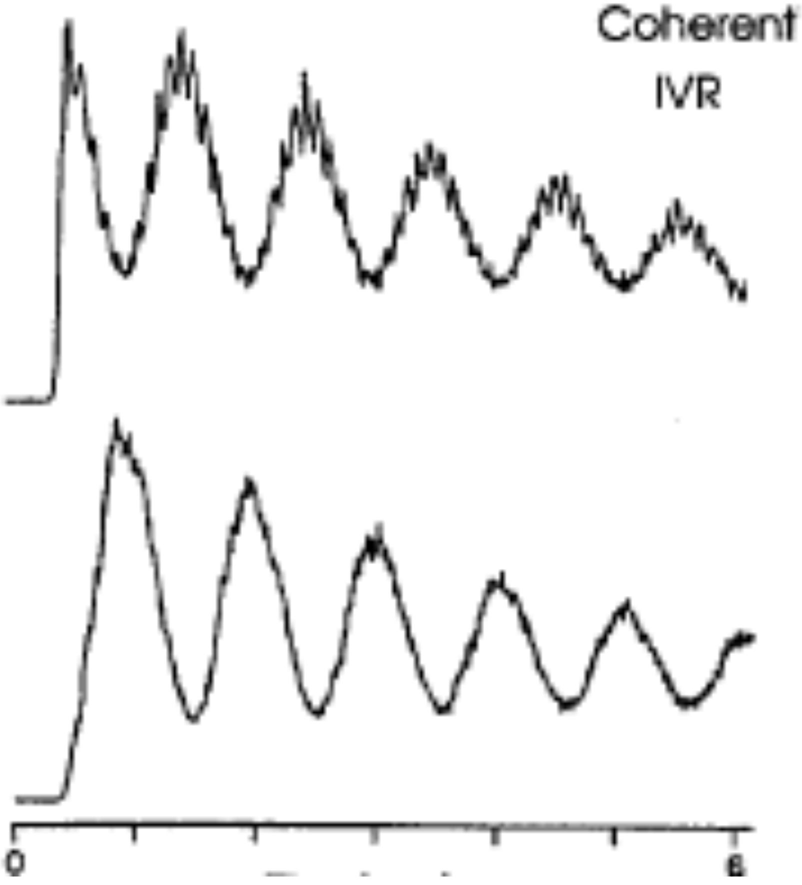
Superposition
Sum of the 5 waves



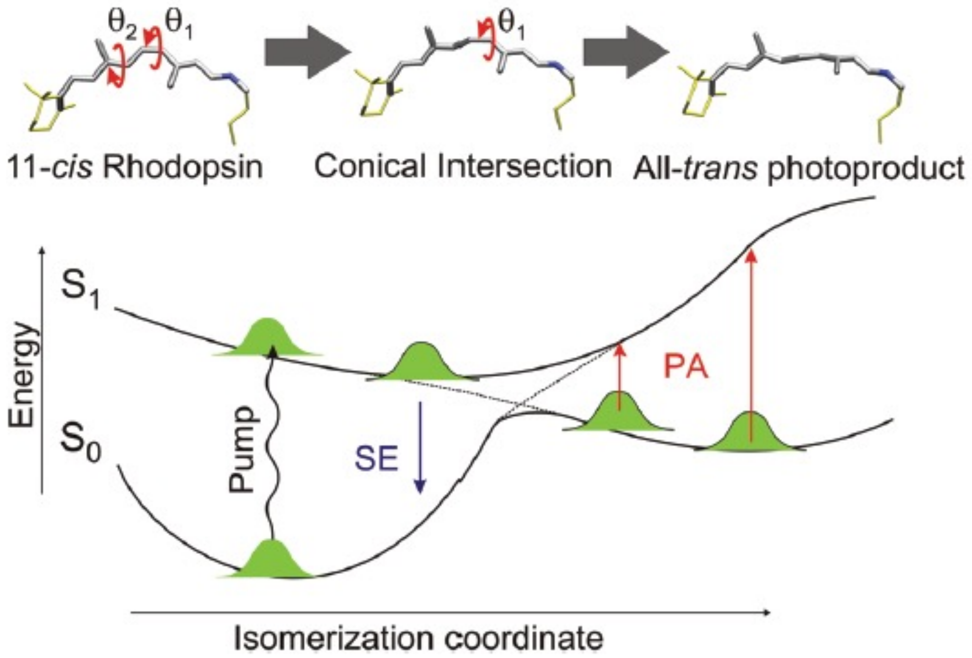
Superimposing 5 waves concentrates probability in a region of space, but now there are 5 values of the momentum.

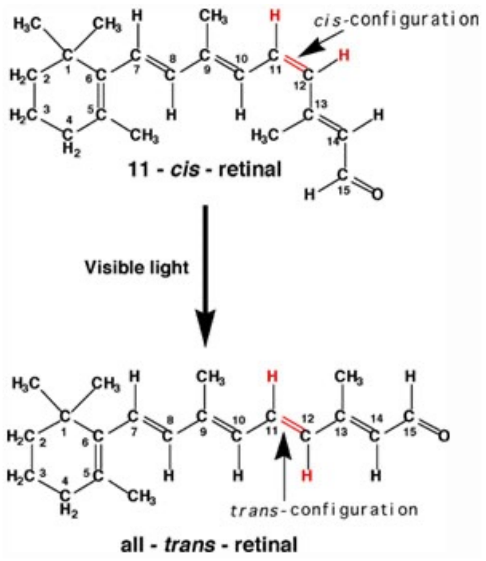
Wave packets





Ultrafast time resolution (fs) has changed the way we visualize reactions on excited surfaces





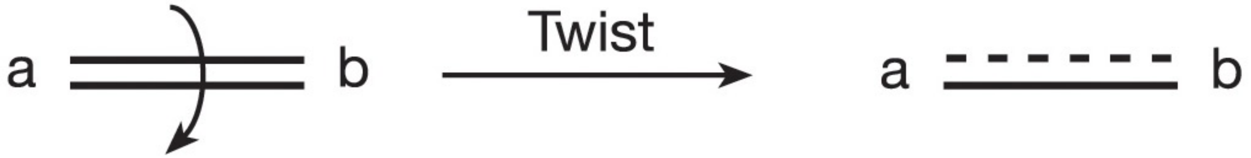
The **wavepacket** initially created in the **FC region** of the excited state of the reactant rapidly evolves along the reaction pathway towards the **conical intersection**, and the stimulated emission (SE) progressively shifts to the red as the band gap between the excited and ground states narrows. Near the conical intersection region, which is reached in **~80 fs** according to both experiments and simulations, the SE signal vanishes as the two surfaces approach each other. Following the "jump" to the hot ground state of the photoproduct, a symmetric photo-induced absorption (PA) signal is formed. This PA band rapidly shifts to the blue as the surfaces move away from each other energetically and the wavepacket relaxes to the bottom of the photoproduct well.

Photochem. Photobiol. Sci., **2015**, *14*, 213

Classification of photoreactions

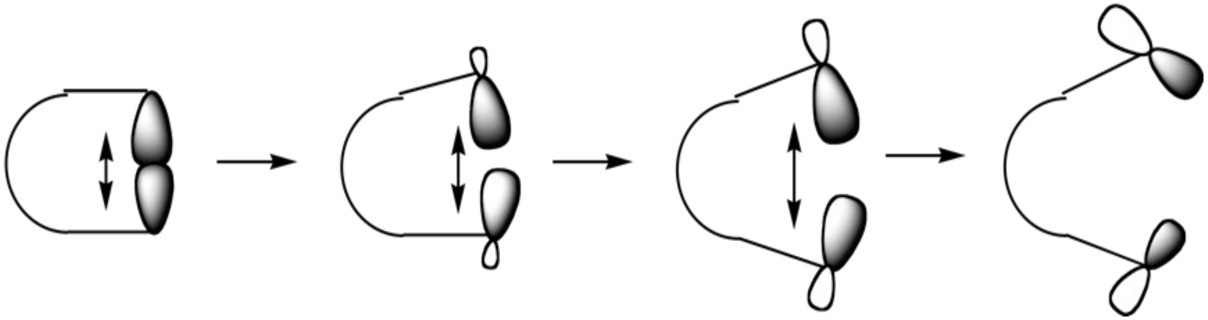
- Bond breaking----cleavage reactions
- Bond twisting-----geometric isomerization
- Addition at one end----abstraction, substitution
- Addition at two ends-----cycloaddition
- Concerted pericyclic reactions---electrocyclization
- Rearrangement

How do bonds break?: Stretching and twisting



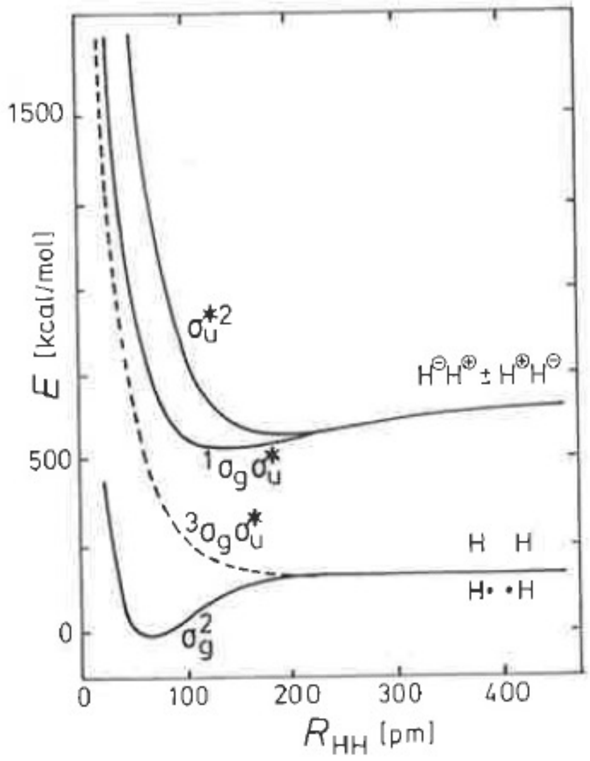
π-bonds break upon twisting

σ-bond break upon stretching



A model for breaking σ bond by stretching

$$H{-}H \longrightarrow H \quad H$$



H_2

- E. Schrödinger developed the famous Φ equation in 1926
- Based on Sch. Eq. Heitler and London developed the concept of bonding for H_2 molecule in 1927.
- L. Pauling extended this to the concept of valence-bond theory.

W. Heitler

F. London

These formed the basis of energy diagrams for photodissociation.

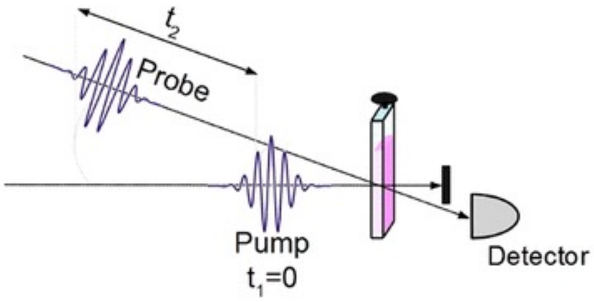
Homolytic photodissociation of I_2, ICN, IBr, CH_3I etc.

Exemplars for σ bond cleavage in the excited state

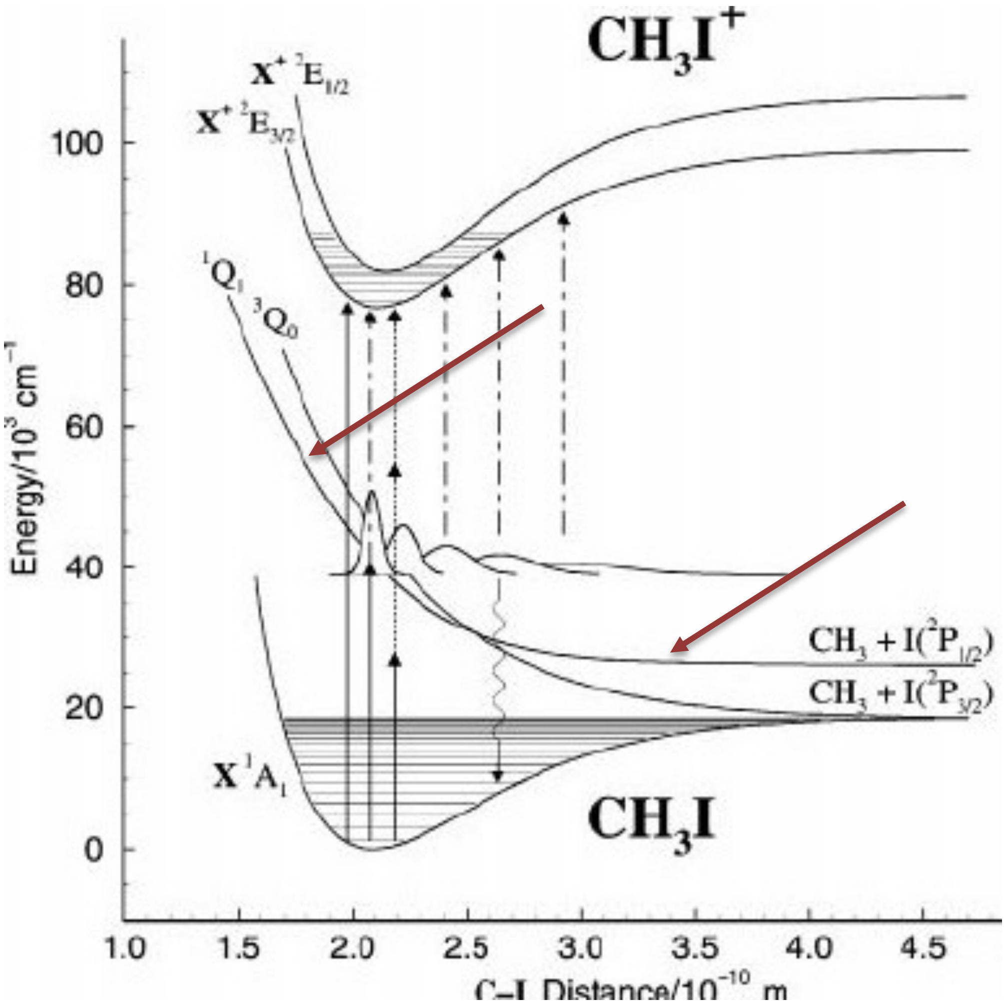
- Photodissociation of CH_3 I
  - Zewail et. al., *J. Chem. Phys.*, *83*, 1996, **1985**
  - Zewail et. al., *Chem. Phys. Lett*, *142*, 426, **1987**
- Photodissociation of ICN
  - Zewail et. al., *J. Chem. Phys.*, *87*, 2395, **1987**
  - Zewail et. al., *Science*, *241*, 4870, **1988**
  - Zewail et. al., *J. Chem. Phys.*, *89*, 6128, **1988**
  - Zewail et. al., *J. Chem. Phys.*, *90*, 829, **1989**
- Photodissociation of NaI
  - Zewail et. al., *Chem. Phys. Lett.*, *146*, 175, **1988**
  - Zewail et. al., *J. Chem. Phys.*, *88*, 6672, **1988**
  - Zewail et. al., *J. Chem. Phys.*, *91*, 7415, **1989**
  - Zewail et. al,. *Nature*, *348*, 225, **1990**
- Photodissociation of I_2
  - Zewail et. al., *Chem. Phys. Lett*, *161*, 297, **1989**

J. C. Polanyi
D. Hersbach
Y. T. Lee
R. Bershon
R. Zare
James L. Kinsey

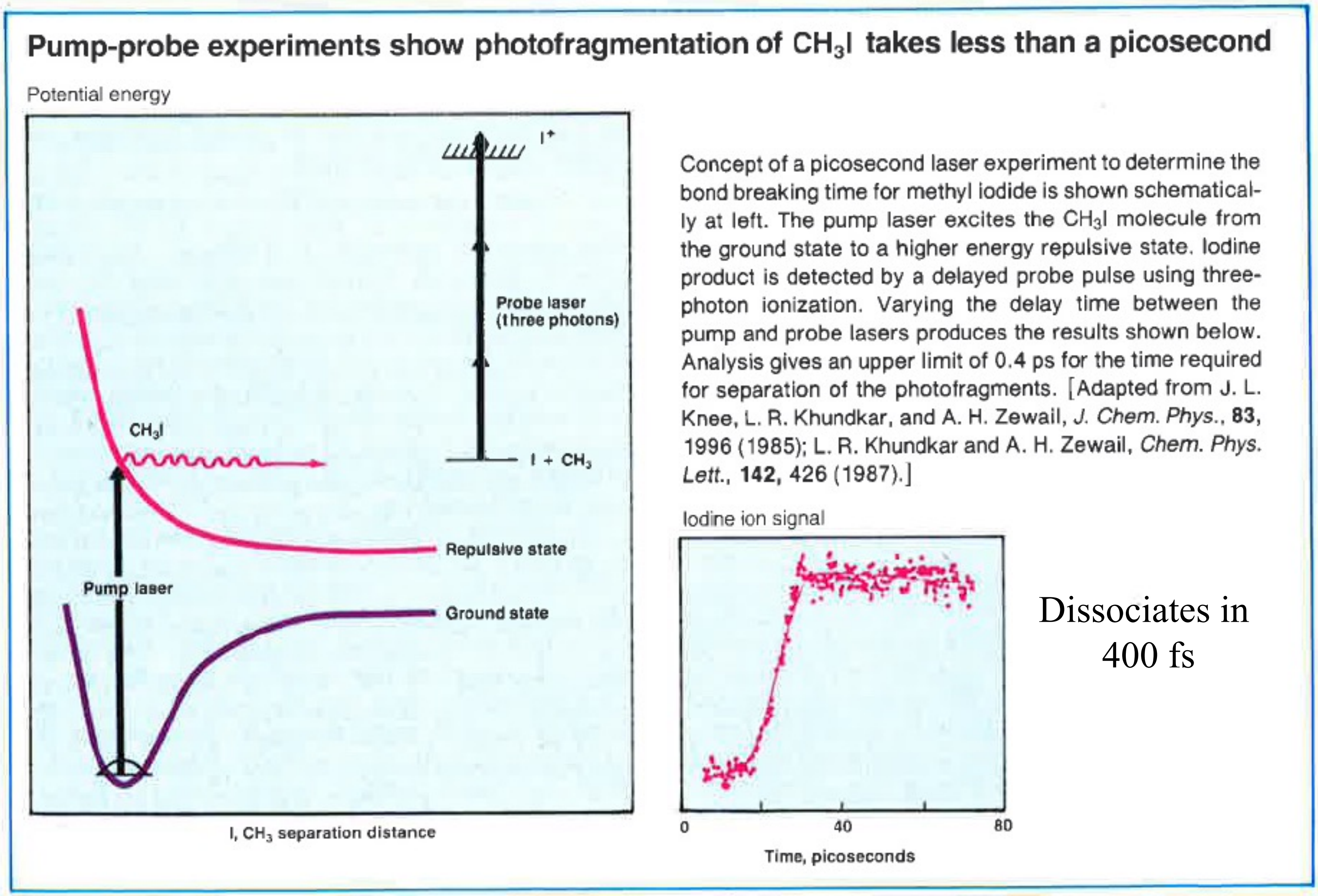
Pump-Probe-Detect in fs time scale



Potential energy curves for dissociation of CH_3I



The first study on photodissociation by Zewail (1985)

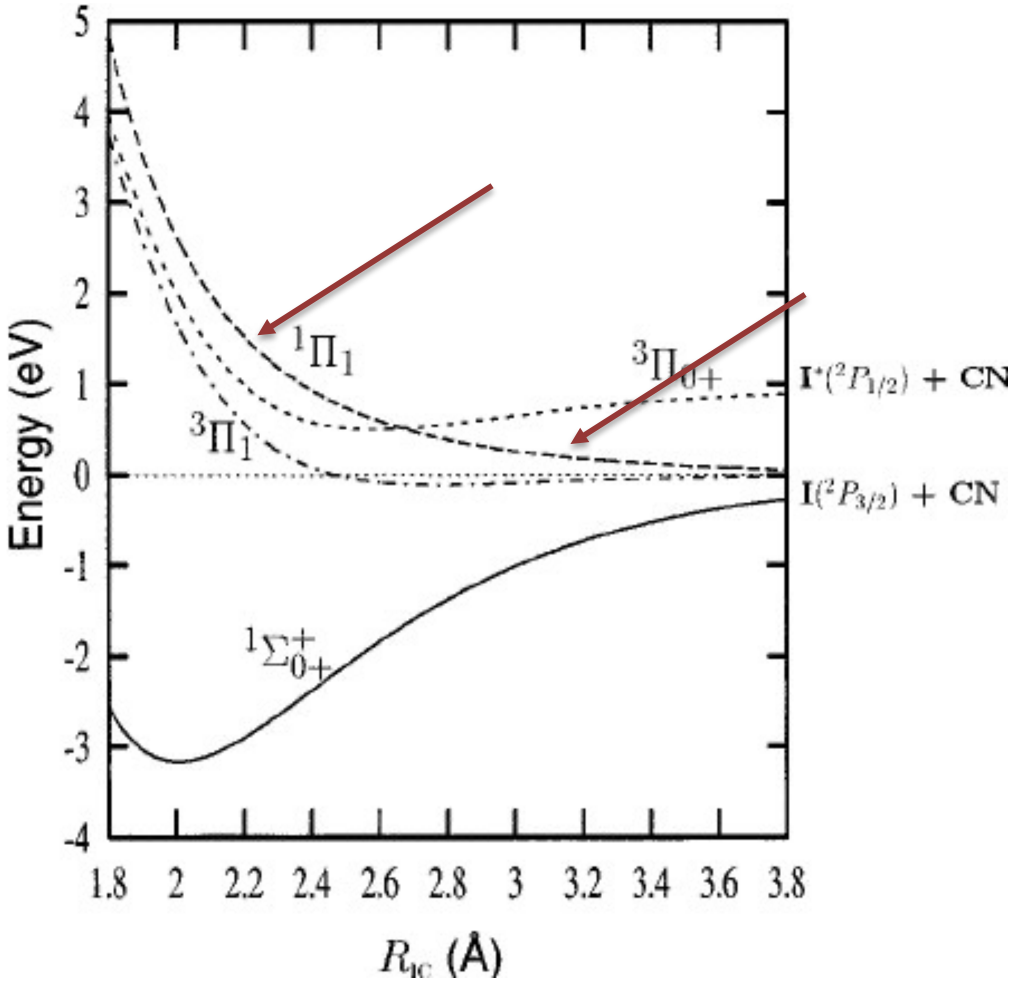


Pump-probe experiments show photofragmentation of CH_3I takes less than a picosecond

Concept of a picosecond laser experiment to determine the bond breaking time for methyl iodide is shown schematically at left. The pump laser excites the CH_3I molecule from the ground state to a higher energy repulsive state. Iodine product is detected by a delayed probe pulse using three-photon ionization. Varying the delay time between the pump and probe lasers produces the results shown below. Analysis gives an upper limit of 0.4 ps for the time required for separation of the photofragments. [Adapted from J. L. Knee, L. R. Khundkar, and A. H. Zewail, *J. Chem. Phys.*, **83**, 1996 (1985); L. R. Khundkar and A. H. Zewail, *Chem. Phys. Lett.*, **142**, 426 (1987).]

Dissociates in 400 fs

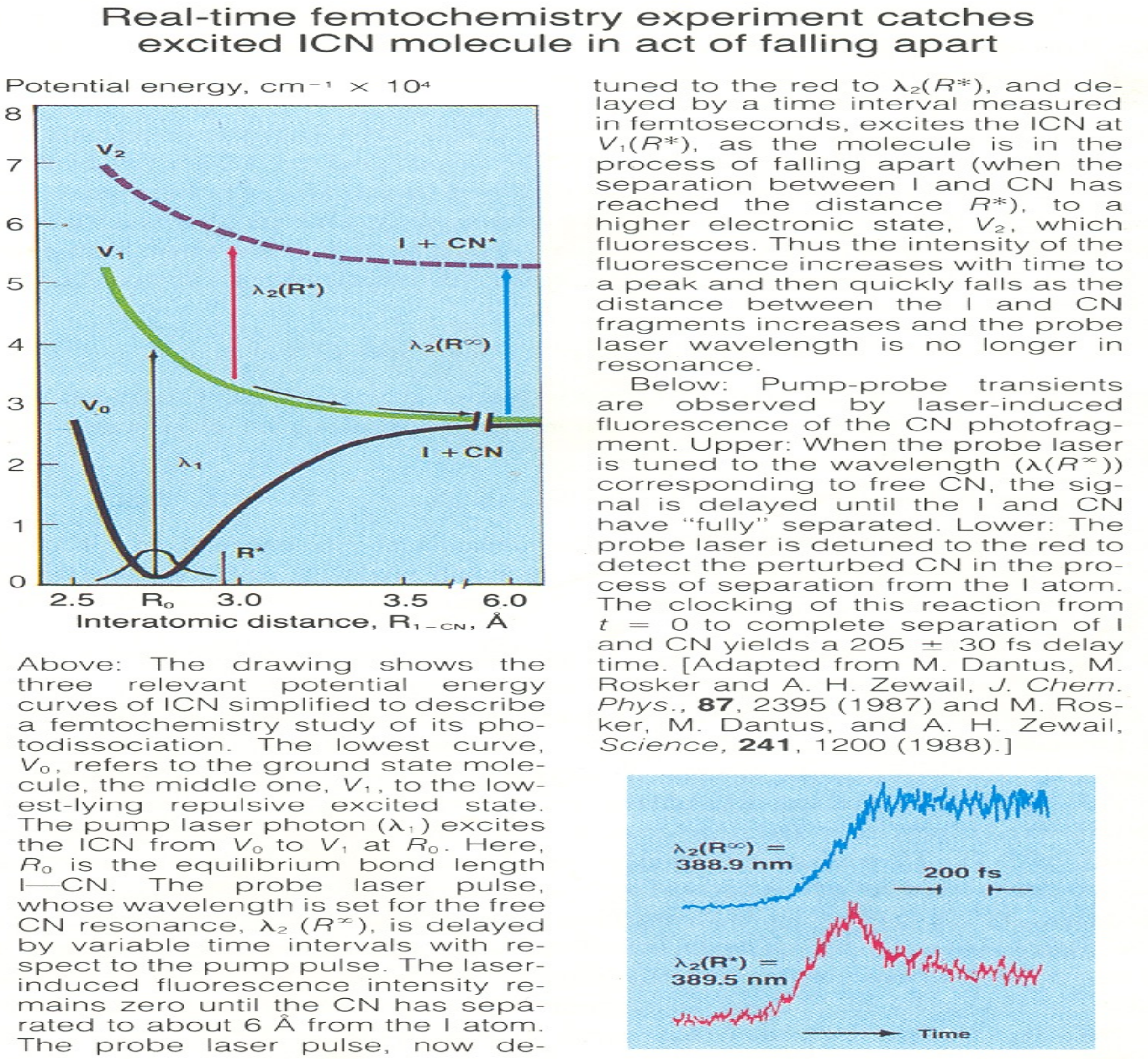
Potential energy curves for dissociation of ICN



Y. Amatatsu, S. Yabushita and K. Morokuma, *J. Chem. Phys*. 100, 4894 **1994**

J. Qian, D. J. Tannor, Y. Amatatsu and K. Morokuma, *J. Chem. Phys*. 101, 9597 **1994**

Photodissociation of ICN (1987)



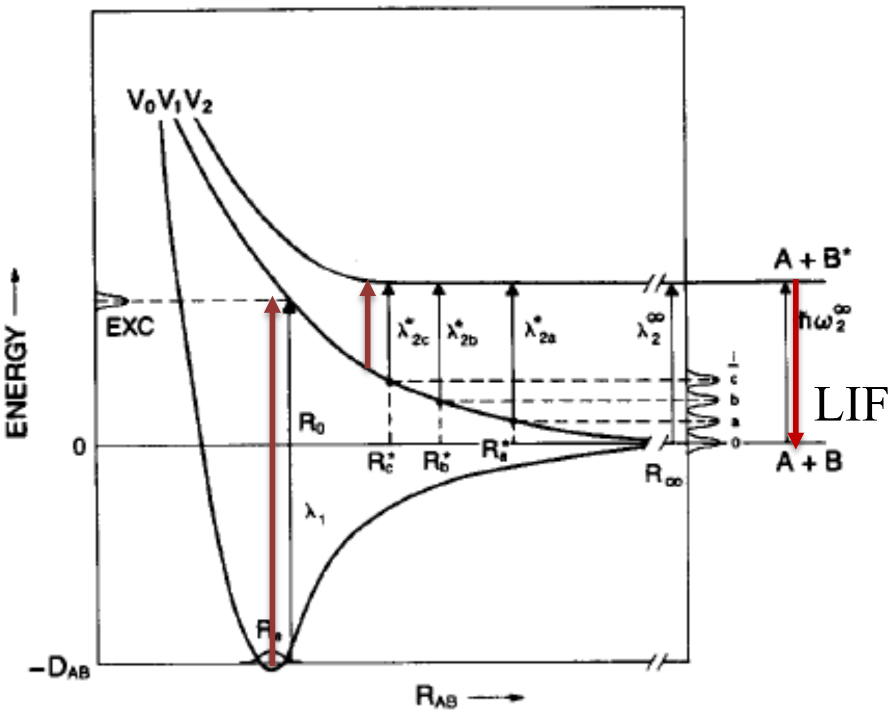
Real-time femtochemistry experiment catches excited ICN molecule in act of falling apart

Above: The drawing shows the three relevant potential energy curves of ICN simplified to describe a femtochemistry study of its photodissociation. The lowest curve, V_0, refers to the ground state molecule, the middle one, V_1, to the lowest-lying repulsive excited state. The pump laser photon (λ_1) excites the ICN from V_0 to V_1 at R_0. Here, R_0 is the equilibrium bond length I—CN. The probe laser pulse, whose wavelength is set for the free CN resonance, λ_2 (R^∞), is delayed by variable time intervals with respect to the pump pulse. The laser-induced fluorescence intensity remains zero until the CN has separated to about 6 Å from the I atom. The probe laser pulse, now detuned to the red to $\lambda_2(R^*)$, and delayed by a time interval measured in femtoseconds, excites the ICN at $V_1(R^*)$, as the molecule is in the process of falling apart (when the separation between I and CN has reached the distance R^*), to a higher electronic state, V_2, which fluoresces. Thus the intensity of the fluorescence increases with time to a peak and then quickly falls as the distance between the I and CN fragments increases and the probe laser wavelength is no longer in resonance.

Below: Pump-probe transients are observed by laser-induced fluorescence of the CN photofragment. Upper: When the probe laser is tuned to the wavelength ($\lambda(R^\infty)$) corresponding to free CN, the signal is delayed until the I and CN have "fully" separated. Lower: The probe laser is detuned to the red to detect the perturbed CN in the process of separation from the I atom. The clocking of this reaction from t = 0 to complete separation of I and CN yields a 205 ± 30 fs delay time. [Adapted from M. Dantus, M. Rosker and A. H. Zewail, *J. Chem. Phys.*, **87**, 2395 (1987) and M. Rosker, M. Dantus, and A. H. Zewail, *Science*, **241**, 1200 (1988).]

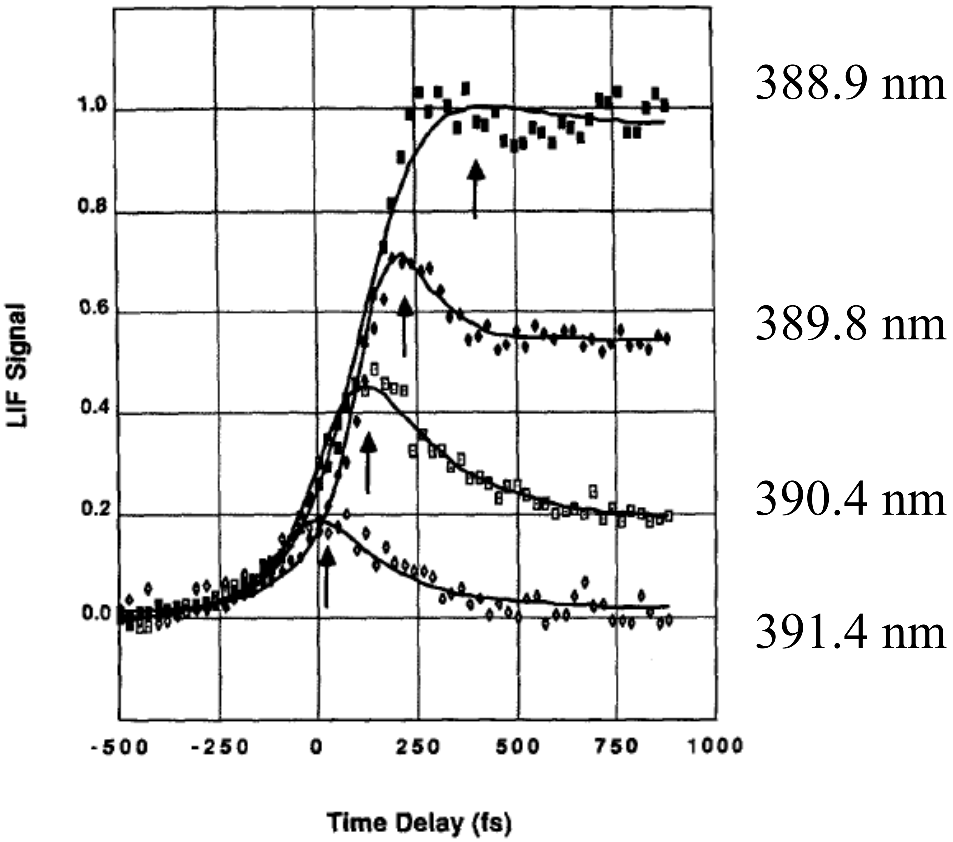
Photodissociation of ICN
Tracing the unbound surface (1987)

ICN → I + CN → I + CN*



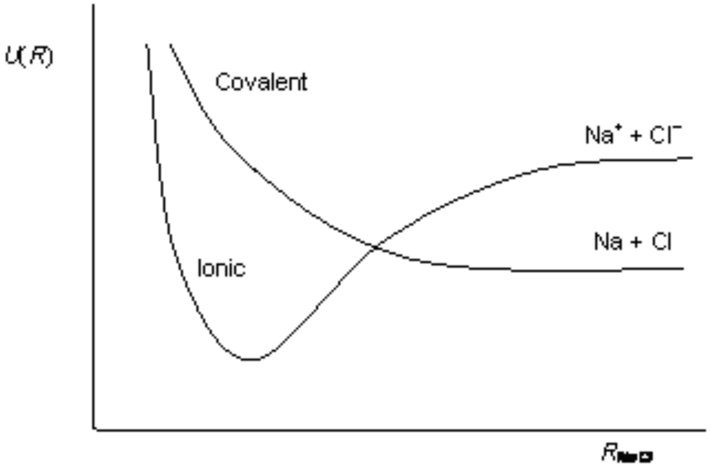
Goal (map the surface)
Experiment (pump & probe)

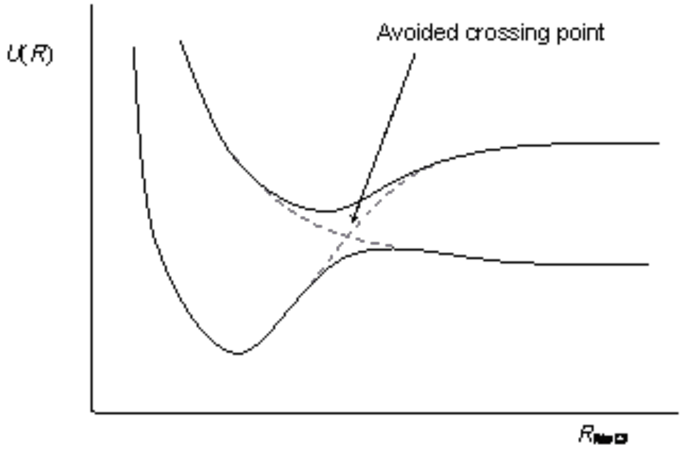
Rise and decay of laser induced fluorescence signal of CN*

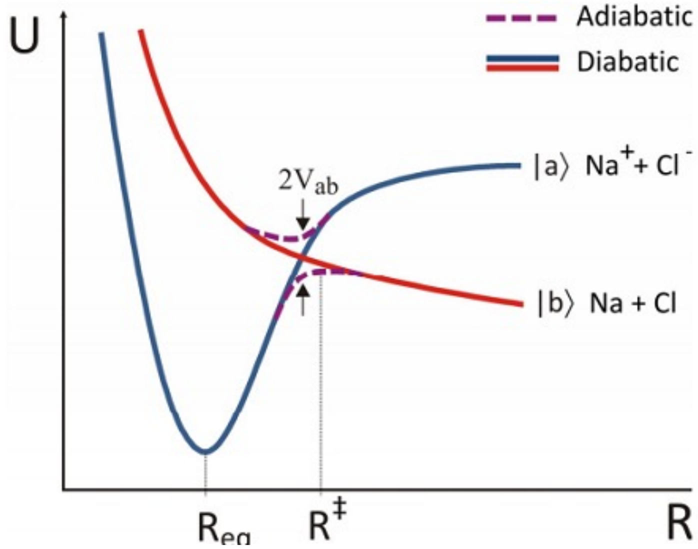


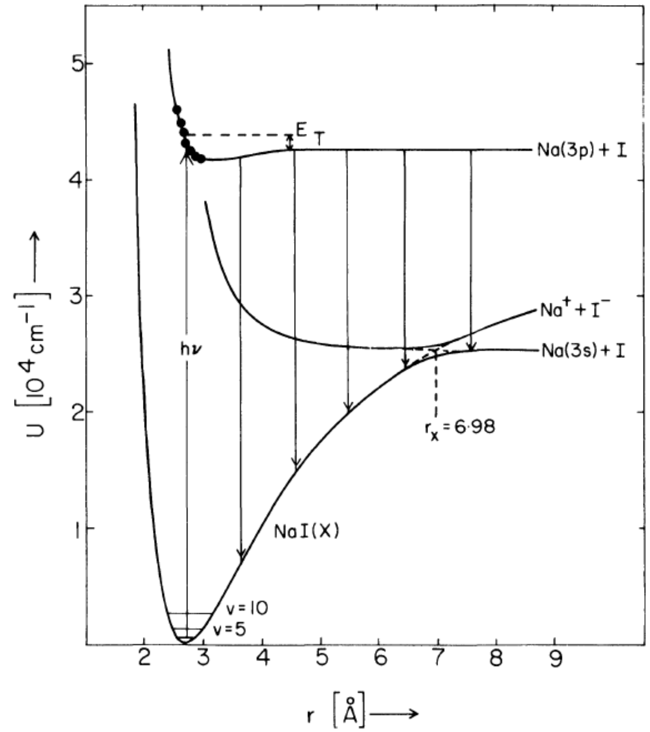
- **Excited state surface of ICN is dissociative, not bound (no oscillation)**
  - **ICN dissociates within 205 ± 30 fs (~0.2 ps)**

Potential energy curves for dissociation of NaCl



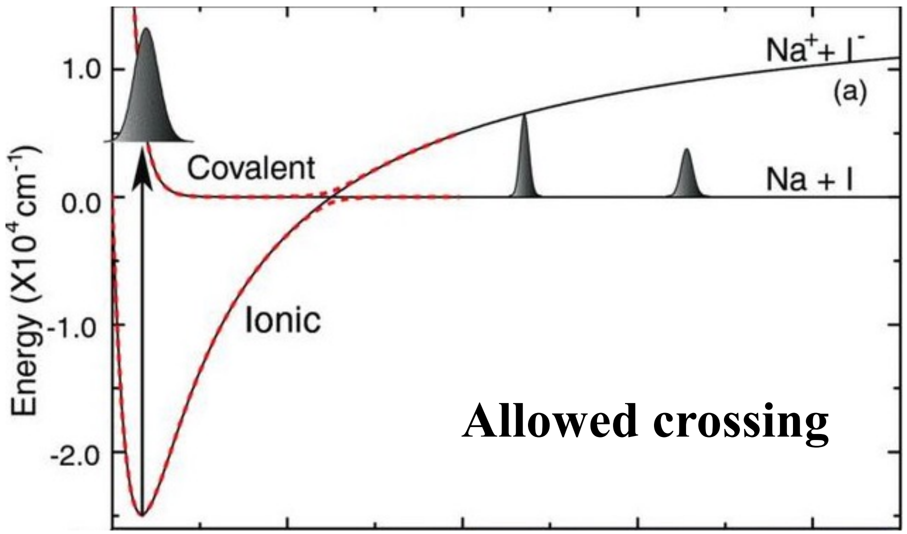


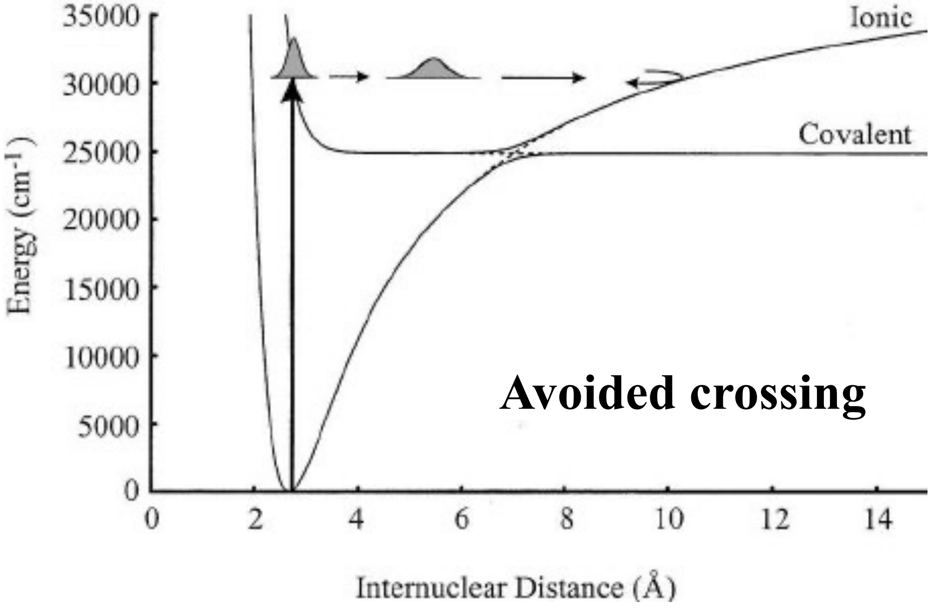




Detection of crossing and avoided crossing

Resonance





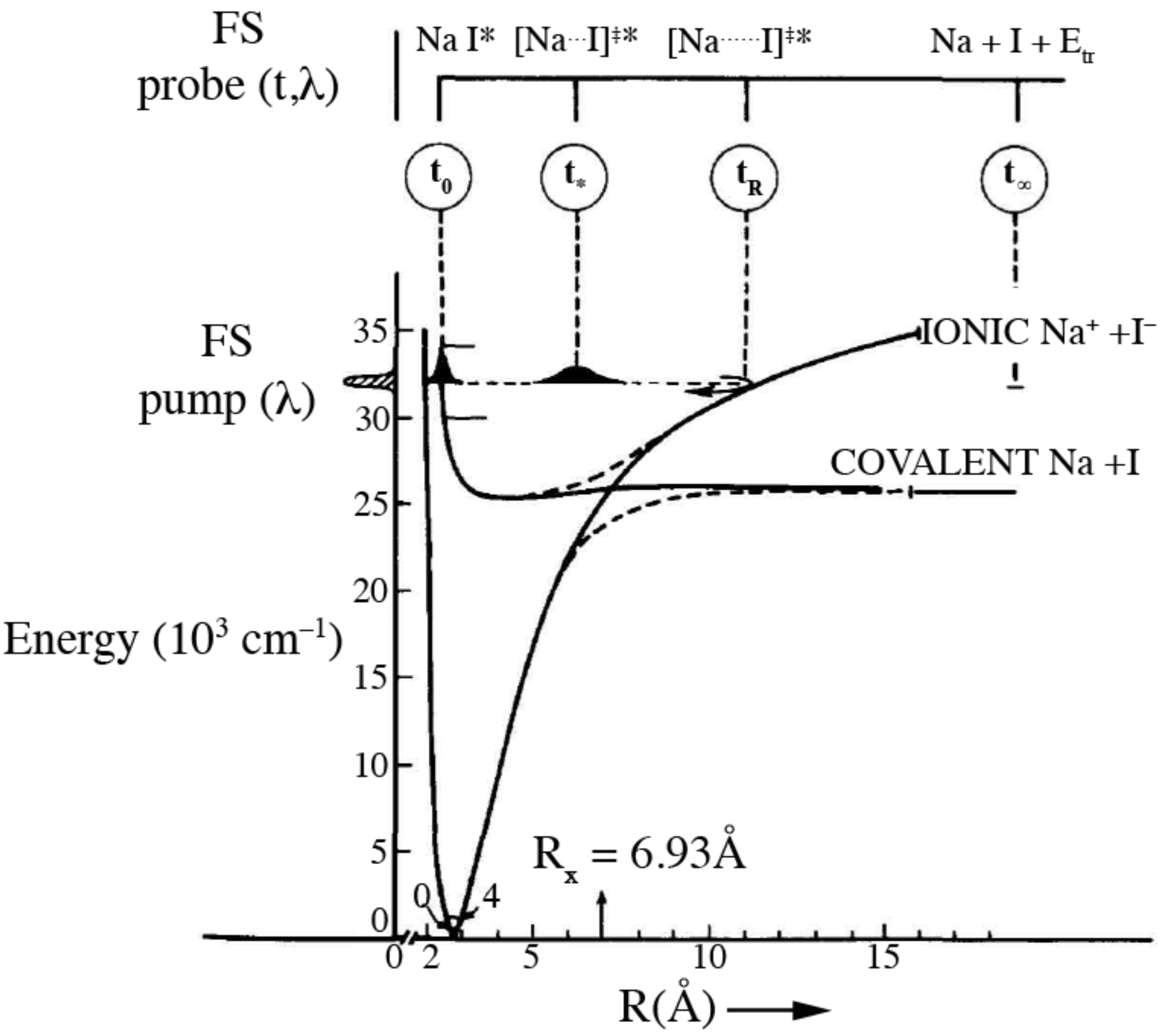
- If there is no mixing, the two curves would remain separate and the excited NaI will retain covalent character and dissociate like CH_3I and ICN.

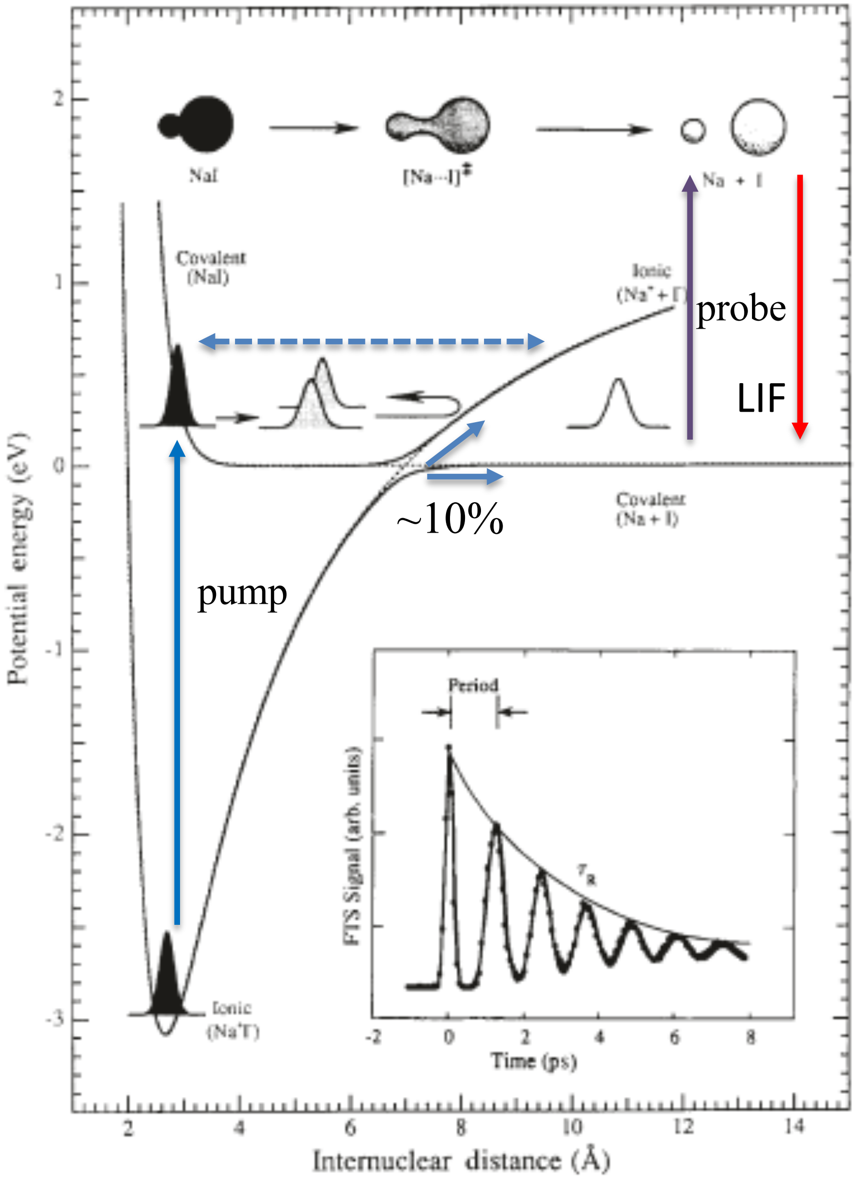
- If the two first order curves mix the crossing will become avoided.

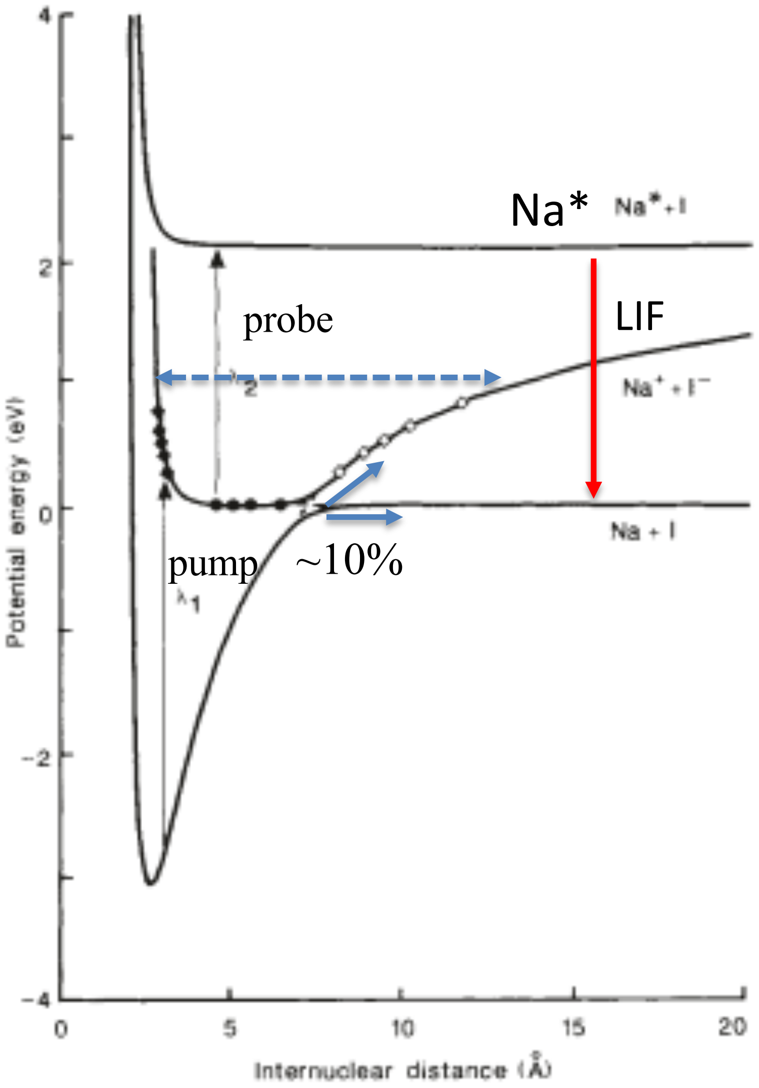
- The avoided crossing will lead to a ‘well’ where the excited NaI will get trapped and establish a resonance (oscillation) between covalent and ionic character.

- The molecule resonates between two electronic configuration

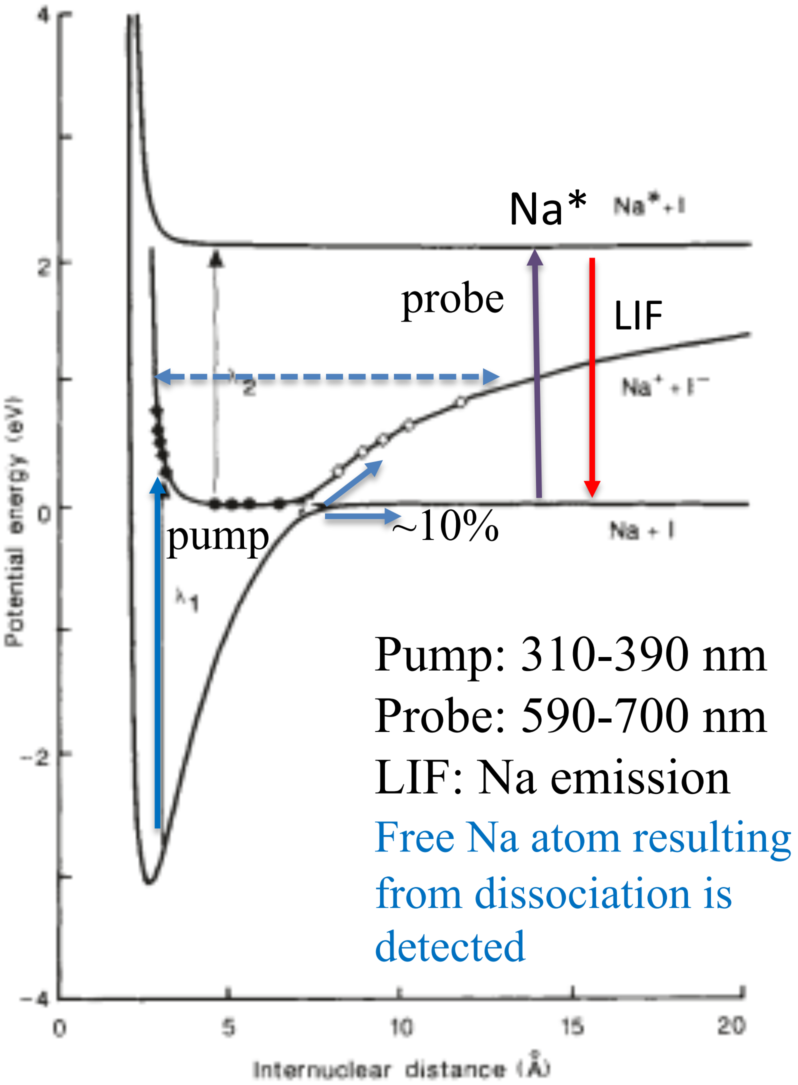
Experimental demonstration for curve crossing (1988)




NaI
[Na--I]‡
Na + I
Covalent (NaI)
Ionic (Na⁺ + I⁻)
probe
LIF
~10%
Covalent (Na + I)
pump
Ionic (Na⁺I⁻)
Period
FTS Signal (arb. units)
τ_R
-2
0
2
4
6
8
Time (ps)
Potential energy (eV)
2
1
0
-1
-2
-3
2
4
6
8
10
12
14
Internuclear distance (Å)

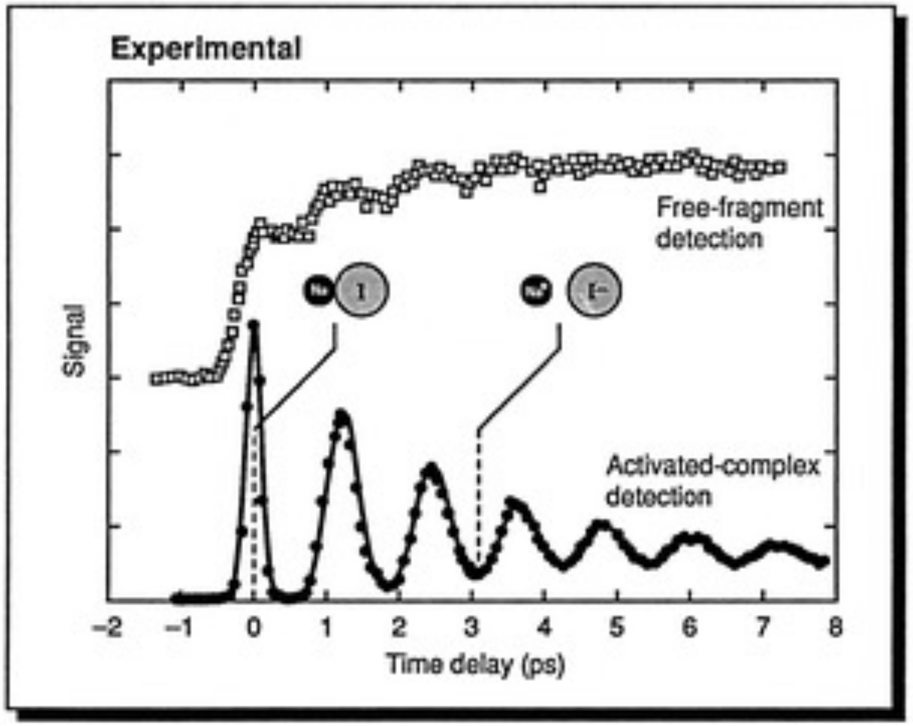

Na*
Na*+I
probe
λ2
LIF
Na⁺ + I⁻
pump
λ1
~10%
Na + I
Potential energy (eV)
4
2
0
−2
−4
0
5
10
15
20
Internuclear distance (Å)

Ultrafast (fs) photodissociation of NaI: Consequences of surface crossing



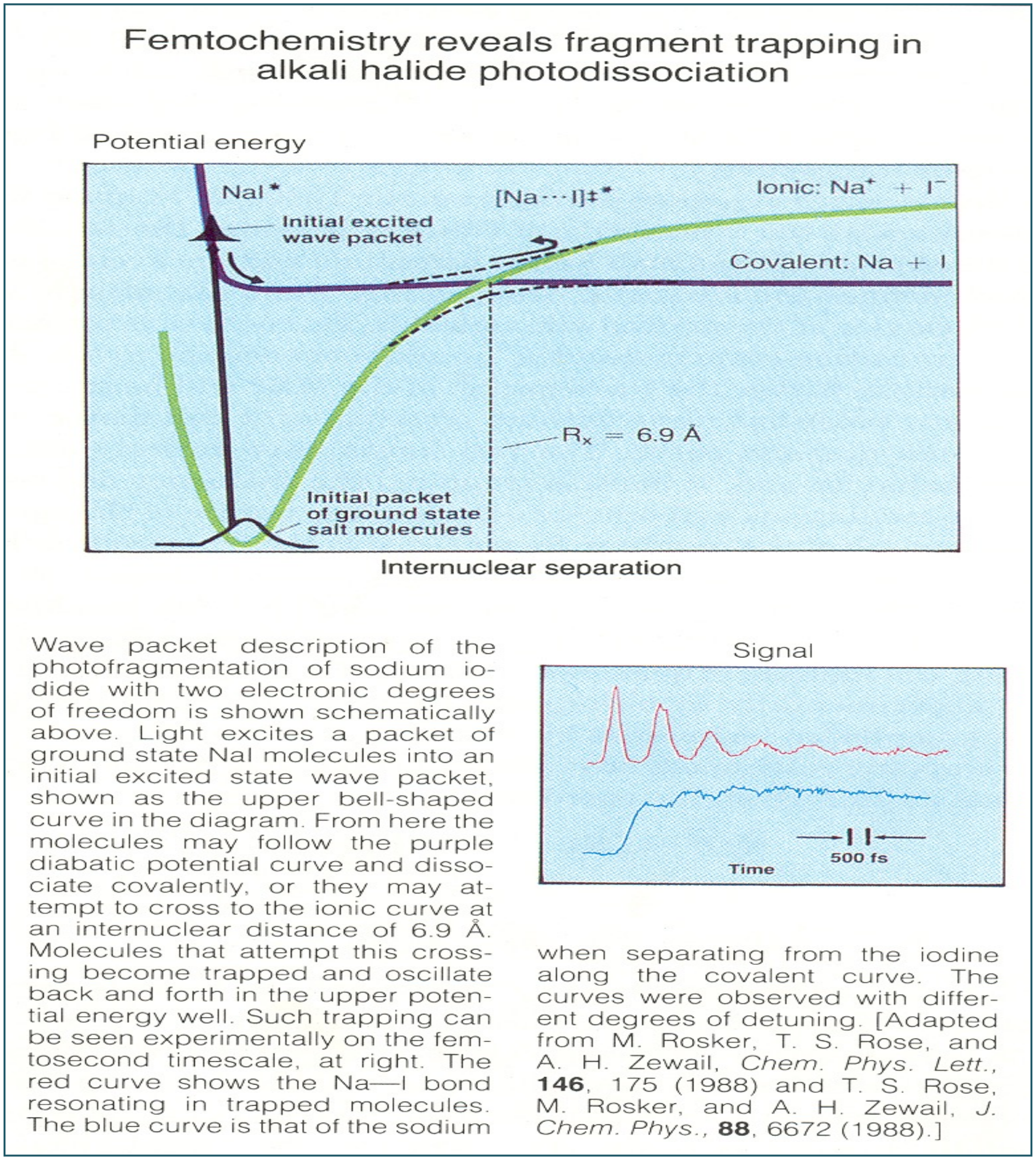
Pump: 310-390 nm
Probe: 590-700 nm
LIF: Na emission

Free Na atom resulting from dissociation is detected



Every time the wave packets hit the outer potential wall, some tunneling occurs and a little puff of products, Na + I, comes out.

Photodissociation of NaI (1988)



Femtochemistry reveals fragment trapping in alkali halide photodissociation

Wave packet description of the photofragmentation of sodium iodide with two electronic degrees of freedom is shown schematically above. Light excites a packet of ground state NaI molecules into an initial excited state wave packet, shown as the upper bell-shaped curve in the diagram. From here the molecules may follow the purple diabatic potential curve and dissociate covalently, or they may attempt to cross to the ionic curve at an internuclear distance of 6.9 Å. Molecules that attempt this crossing become trapped and oscillate back and forth in the upper potential energy well. Such trapping can be seen experimentally on the femtosecond timescale, at right. The red curve shows the Na—I bond resonating in trapped molecules. The blue curve is that of the sodium when separating from the iodine along the covalent curve. The curves were observed with different degrees of detuning. [Adapted from M. Rosker, T. S. Rose, and A. H. Zewail, *Chem. Phys. Lett.*, **146**, 175 (1988) and T. S. Rose, M. Rosker, and A. H. Zewail, *J. Chem. Phys.*, **88**, 6672 (1988).]

Can we get experimental support for avoided crossing?

Zewail et. al.

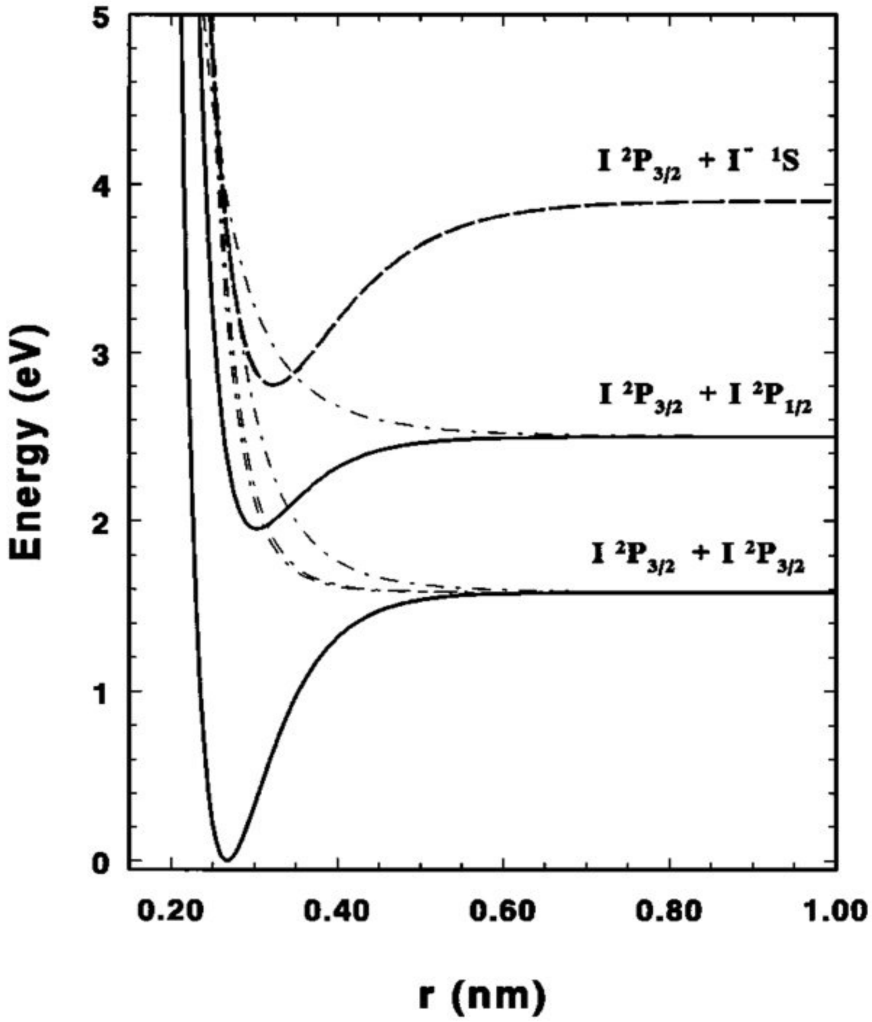
Chem. Phys. Lett., *146*, 175, **1988**

J. Chem. Phys., *88*, 6672, **1988**

J. Chem. Phys., *91*, 7415, **1989**

Nature, *348*, 225, **1990**

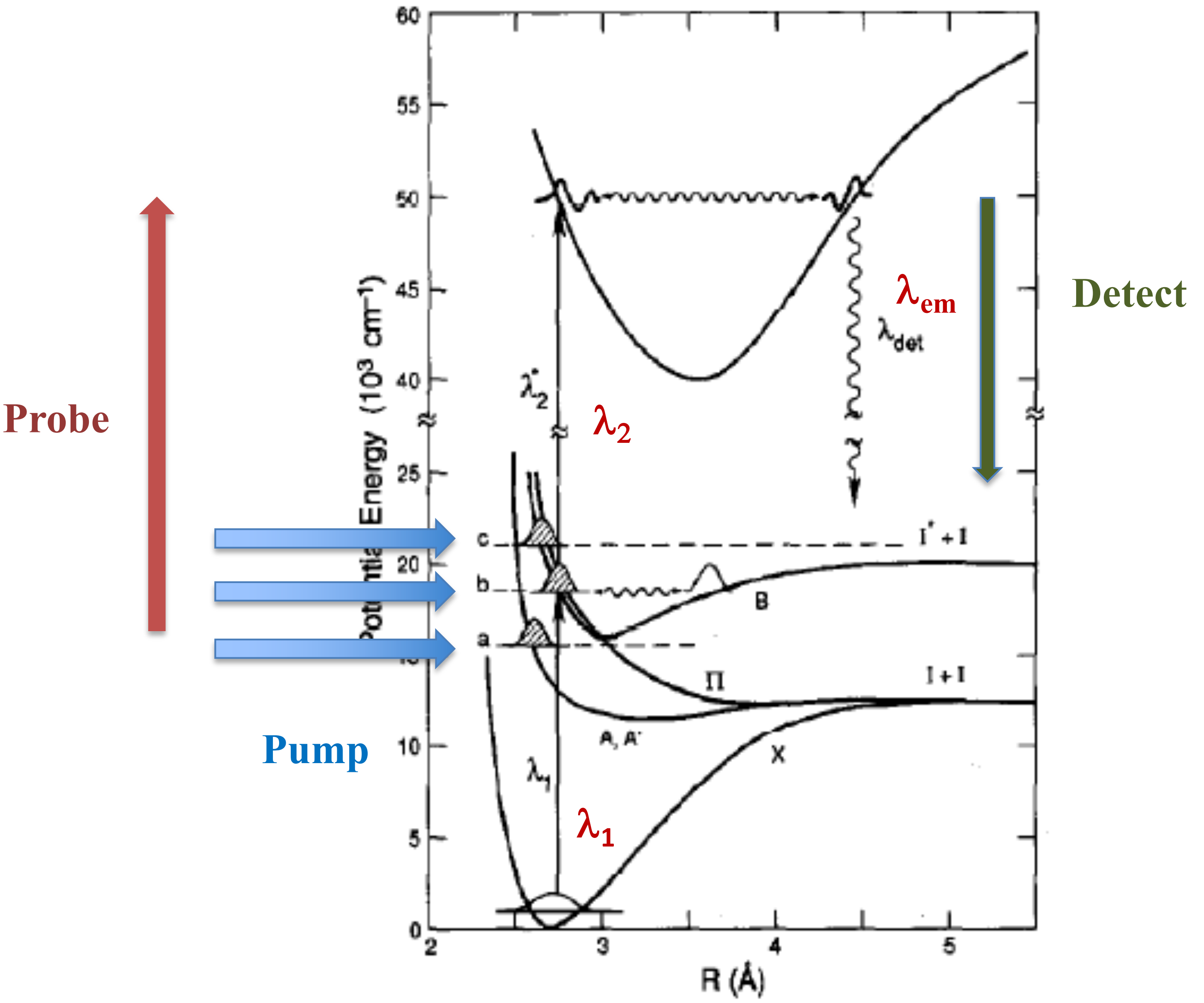
Photodissociation of Iodine (1989)



I_2

R. S. Mulliken, *J. Chem. Phys*, *55*, 288, **1971**

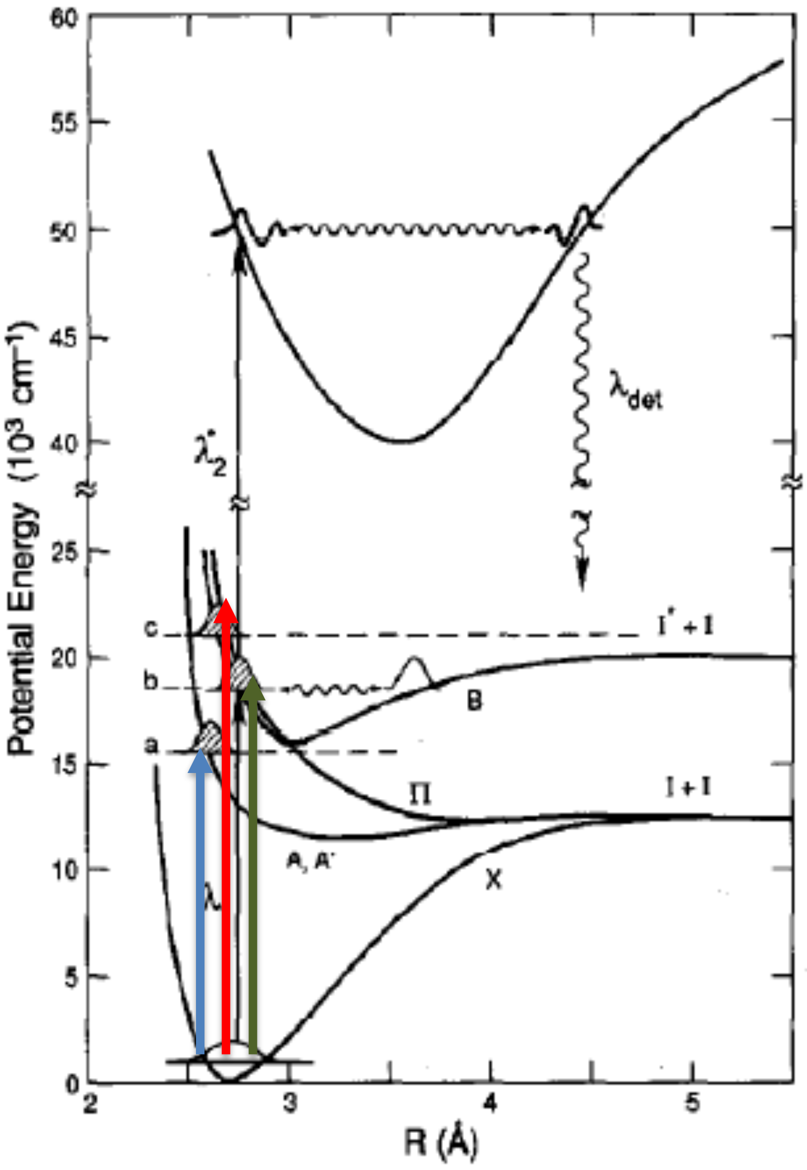
Photodissociation of I_2: A model for cleavage reactions

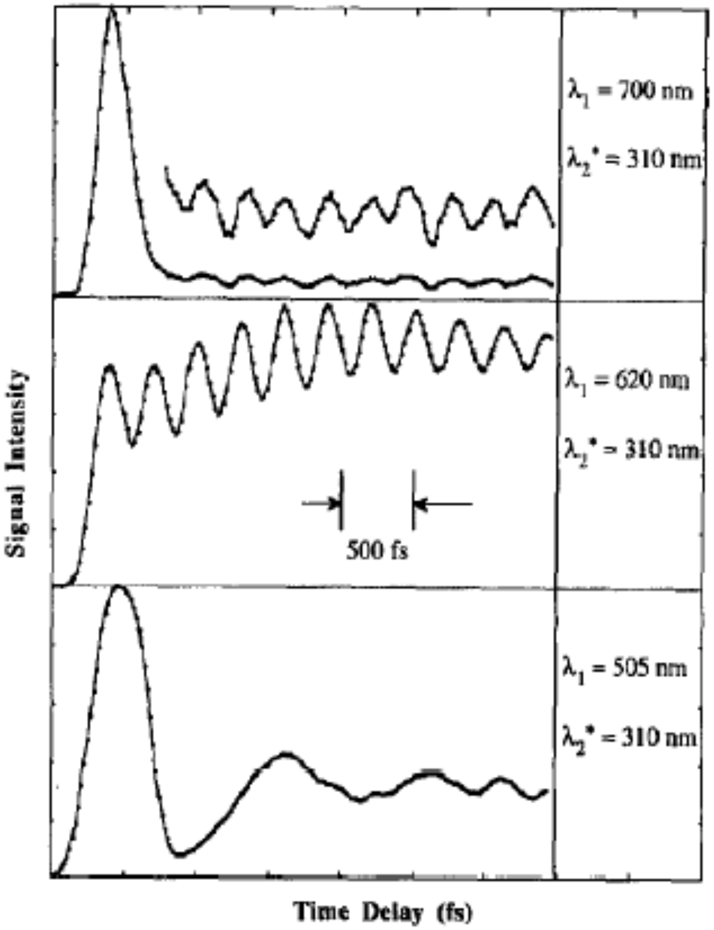


R. S. Mulliken, *J. Chem. Phys*, *55*, 288, **1971**

Photodissociation of Iodine (1989)

Tracing the unbound and the bound surfaces (a, b & c)





700/310/ (a state)

620/310/ (b state)

Time of oscillation

500 fs

505/310/ (c state)

Conclusions based on ultrafast experiments

> *"The study of chemical events that occur in the femtosecond time scale is the ultimate achievement in half a century of development and, although many future events will be run over the same course, chemists are near the end of the race against time"*
>
> George Porter, 1993

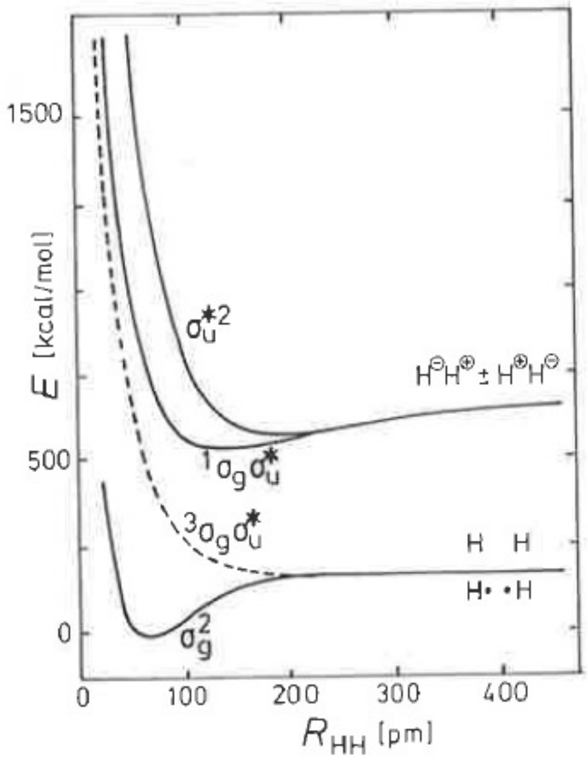
- Considering molecules as particles (classical mechanics) or wave packets (quantum mechanics) lead to similar results. Wave packets can leak through a barrier (tunneling) while particles cannot.

- Surfaces generated based on electronic correlation diagrams help predict reaction dynamics

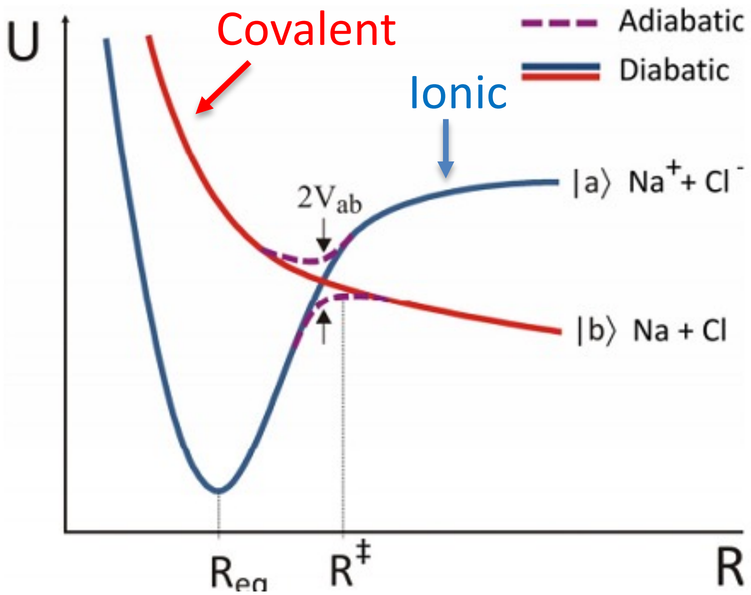
- Crossing of surfaces are common and these could lead to 'real', 'avoided' and conical intersections

- On excited state surfaces oscillation (resonance) of electronic structures occurs in fs time scale.

Models for photodissociation of covalent and ionic σ bond



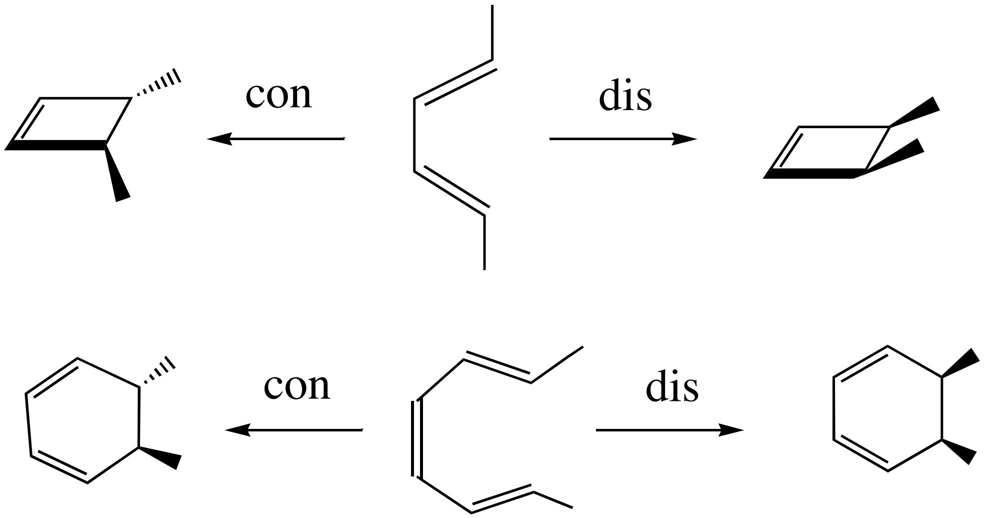
H_2

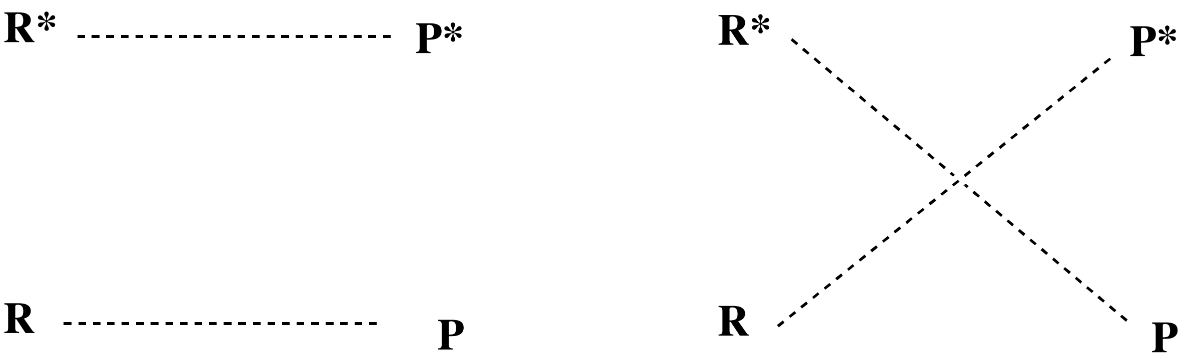


NaCl

Energy surfaces generated by following the electrons as the nuclei move along the reaction co-ordinate.

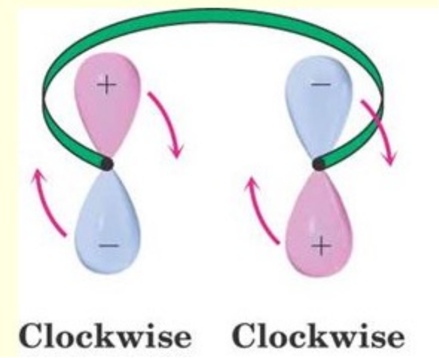
Concerted (pericyclic) reactions: Cyclization

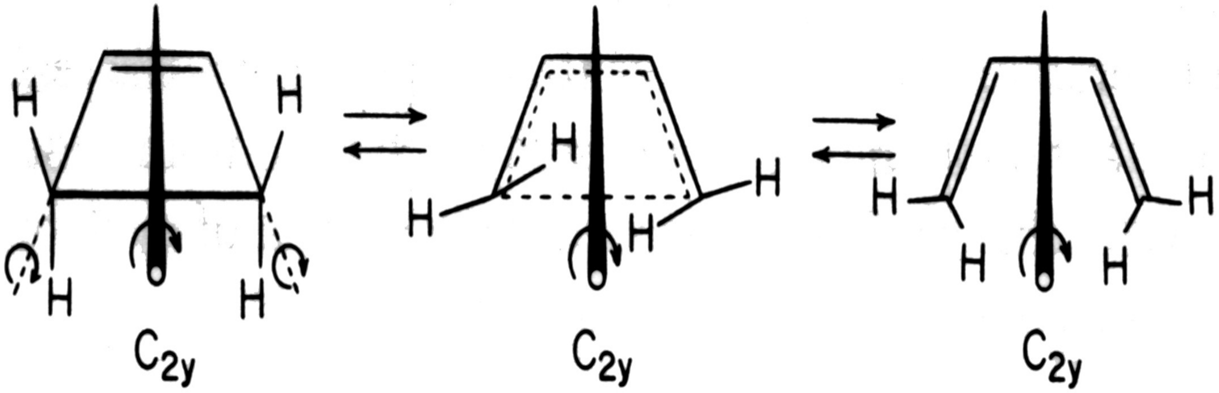




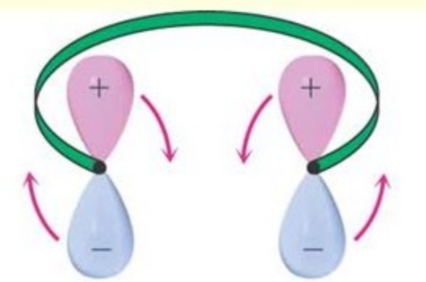
Assigning symmetry to relevant orbitals

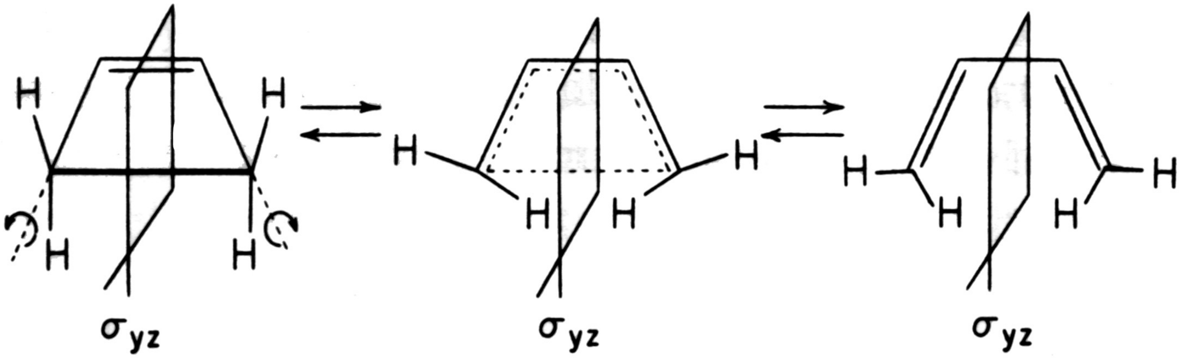
Conrotatory



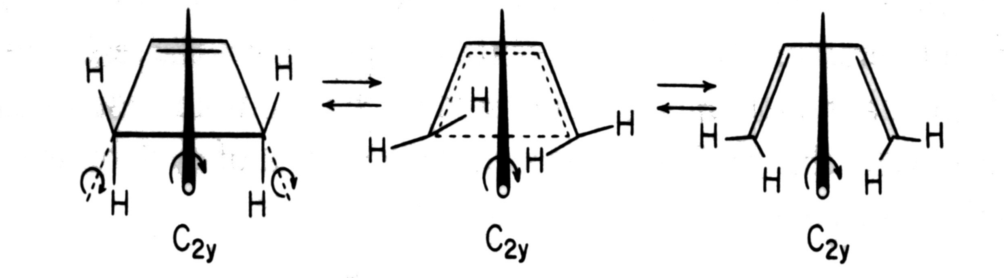


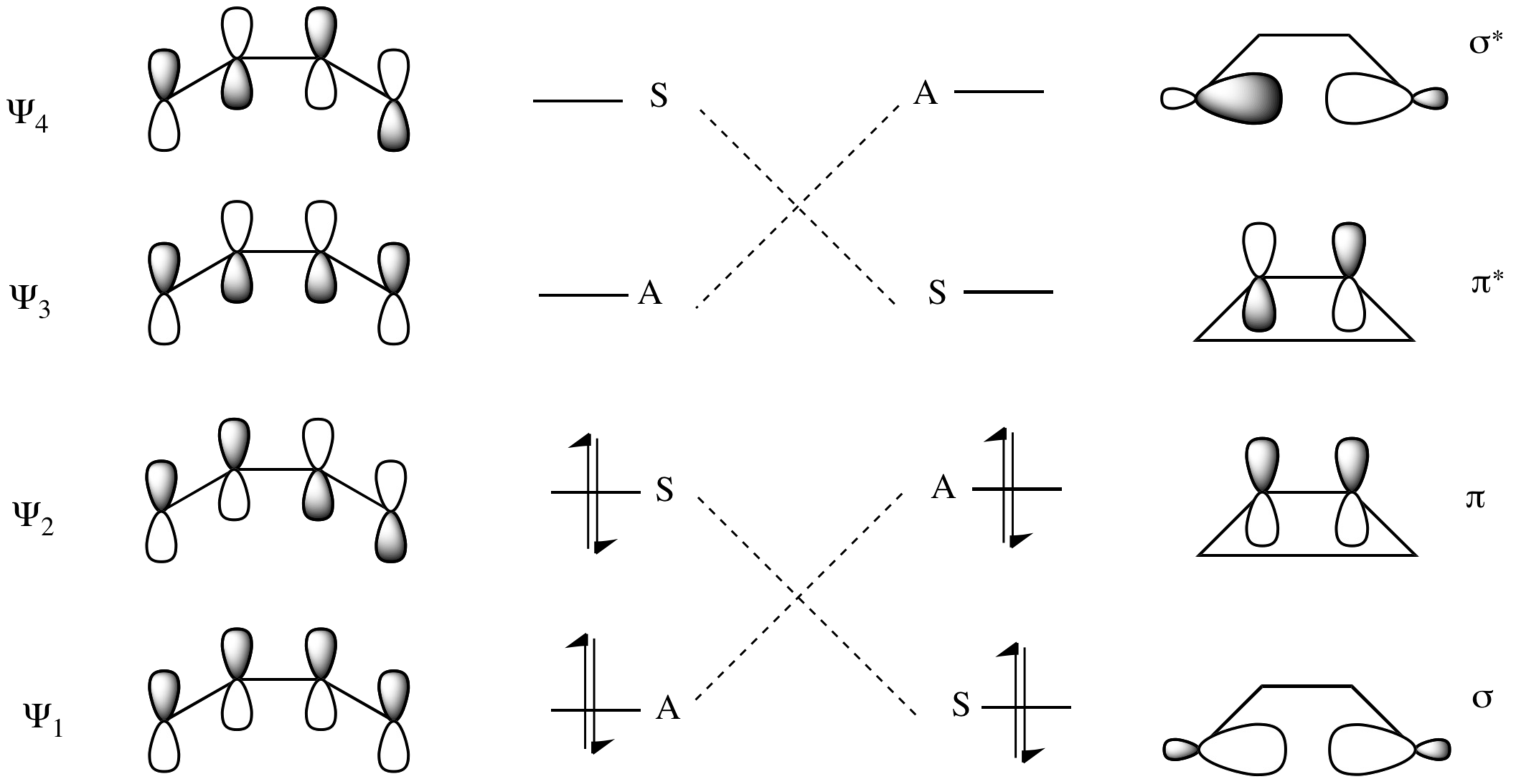
Disrotatory





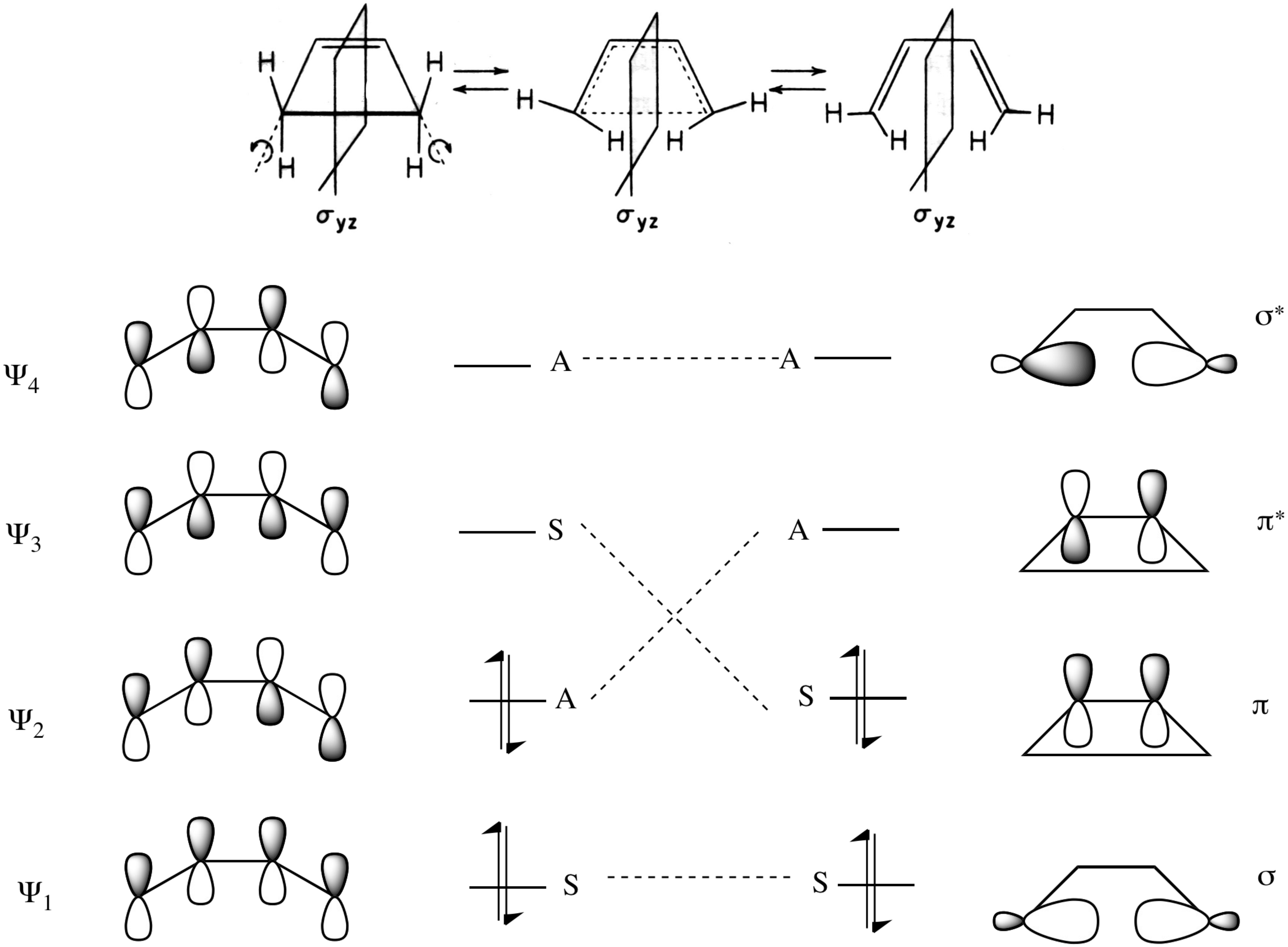
Conrotatory Orbital Correlation Diagram





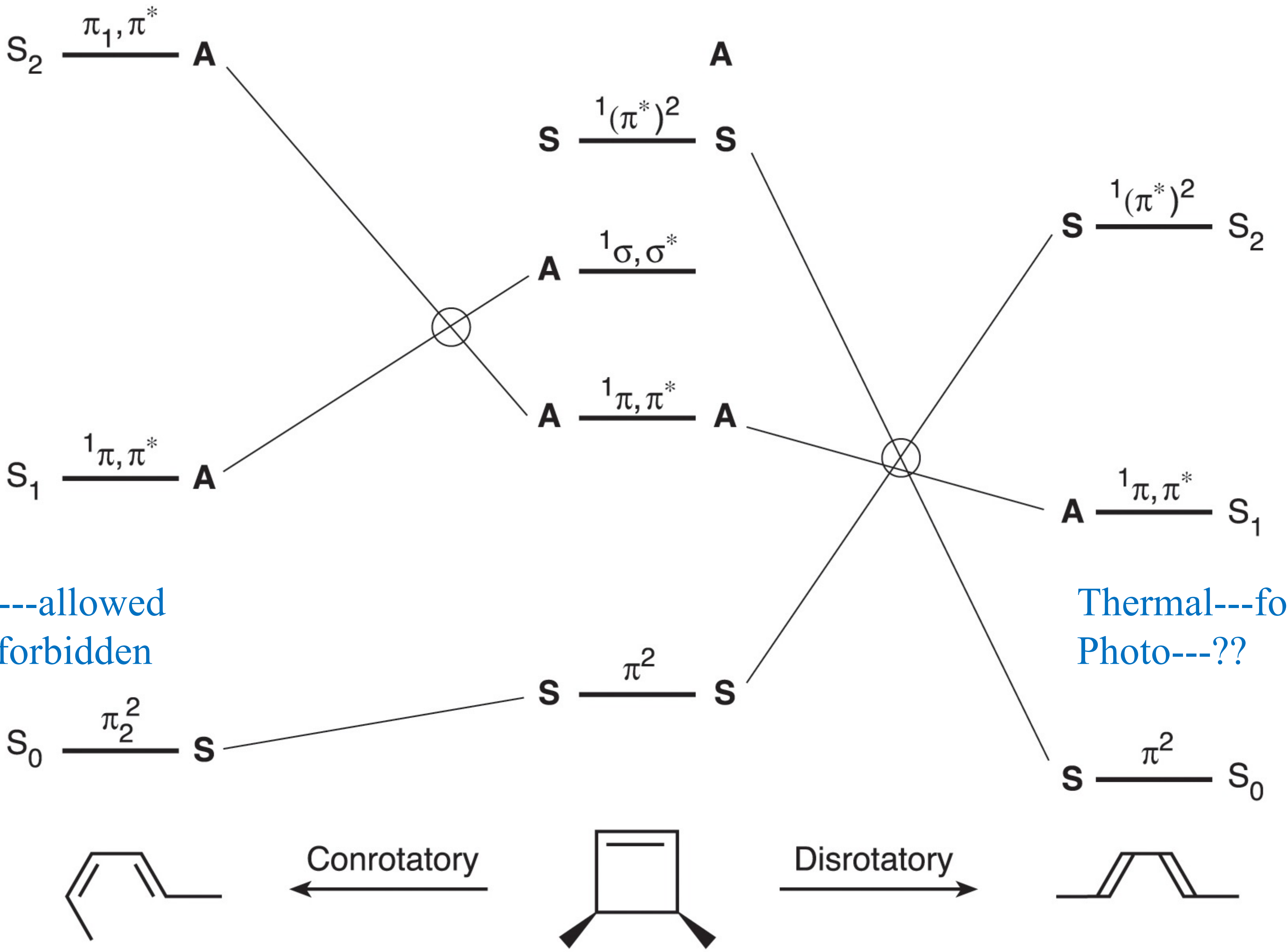
R. B. Woodward, R. Hoffmann, JACS, 87, 396,1965

Disrotatory Orbital Correlation Diagram



R. B. Woodward, R. Hoffmann, JACS, 87, 396,1965

State correlation diagram for an electrocyclic reaction

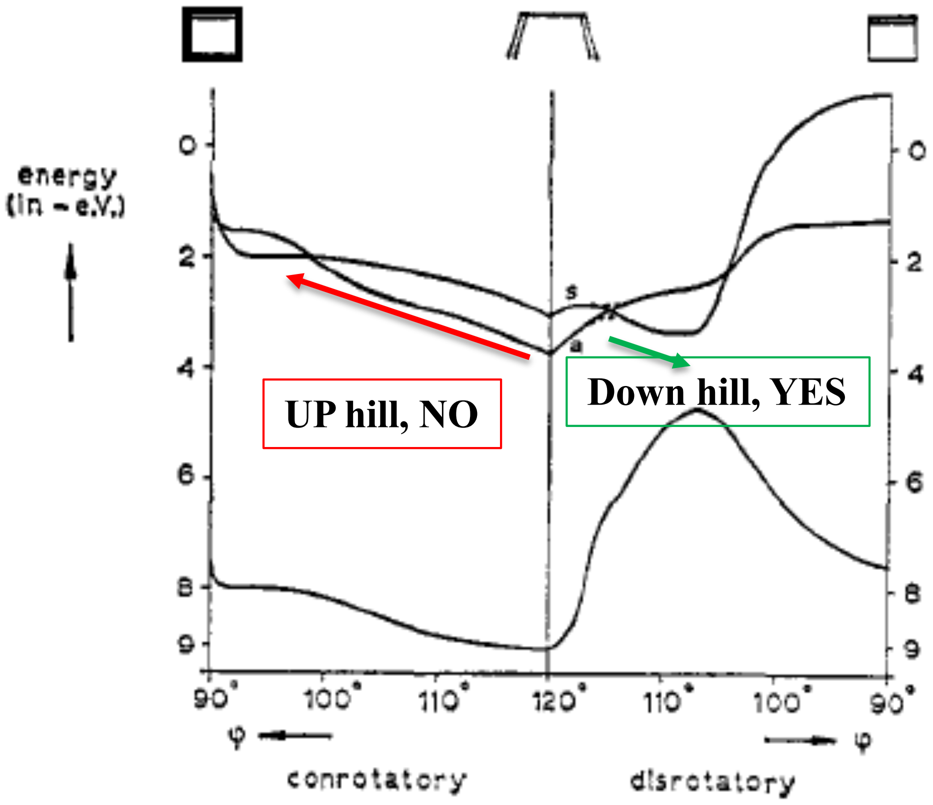


Thermal---allowed
Photo---forbidden

Thermal---forbidden
Photo---??

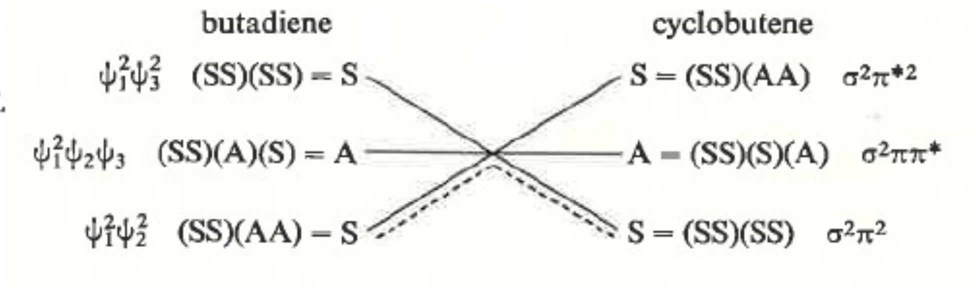
H. C. Longuet-Higgins, E. W. Abrahamson, JACS, 87, 2045,1965

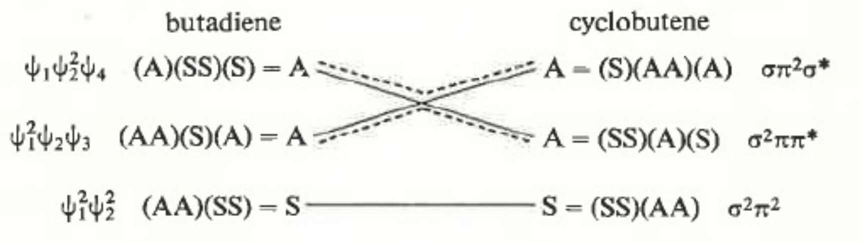
The photochemical reaction is facilitated by crossings of surfaces in the excited state



UP hill, NO

Down hill, YES





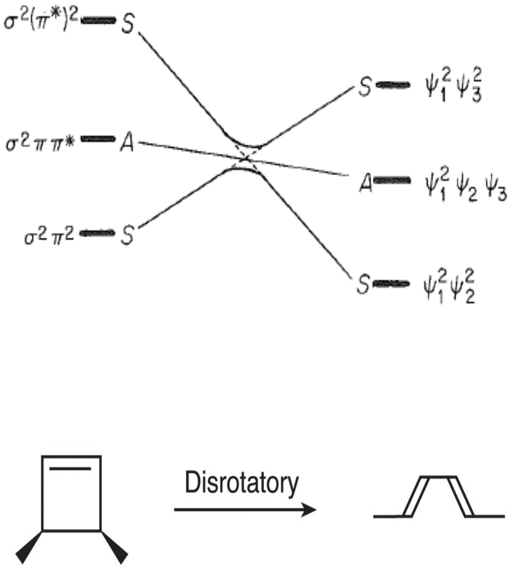
H. C. Longuet-Higgins, E. W. Abrahamson, *J. Am. Chem. Soc.*, *87*, 2045, **1965**

W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Am. Chem. Soc.*, *91*, 6041, **1969**

The photochemical reaction is facilitated by crossings of surfaces

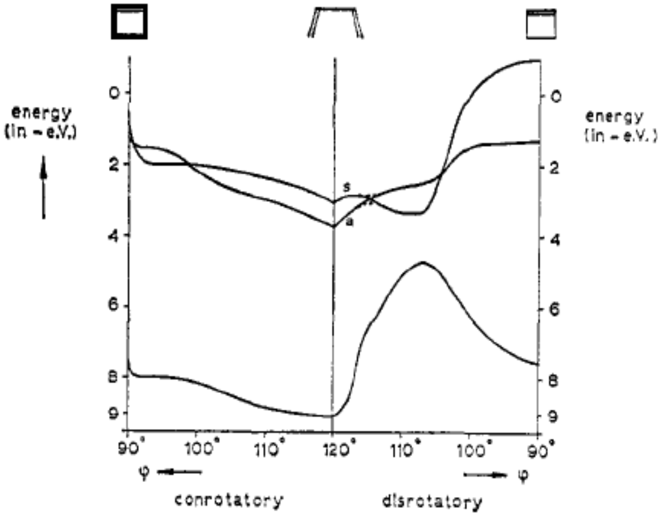
in the excited state

1965



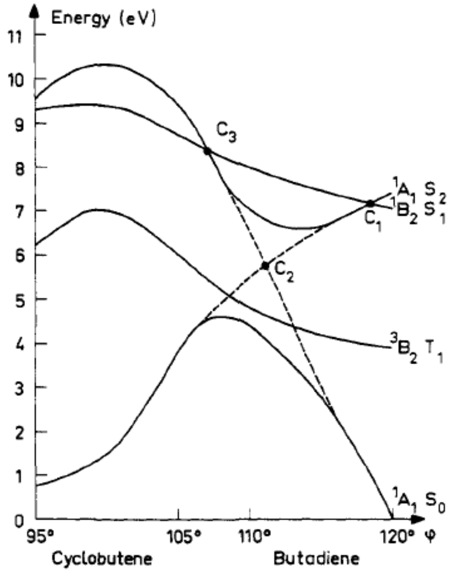
Longuet-Higgins and Abrahamson,
J. Am. Chem. Soc., *87*, 2045, **1965**

1969



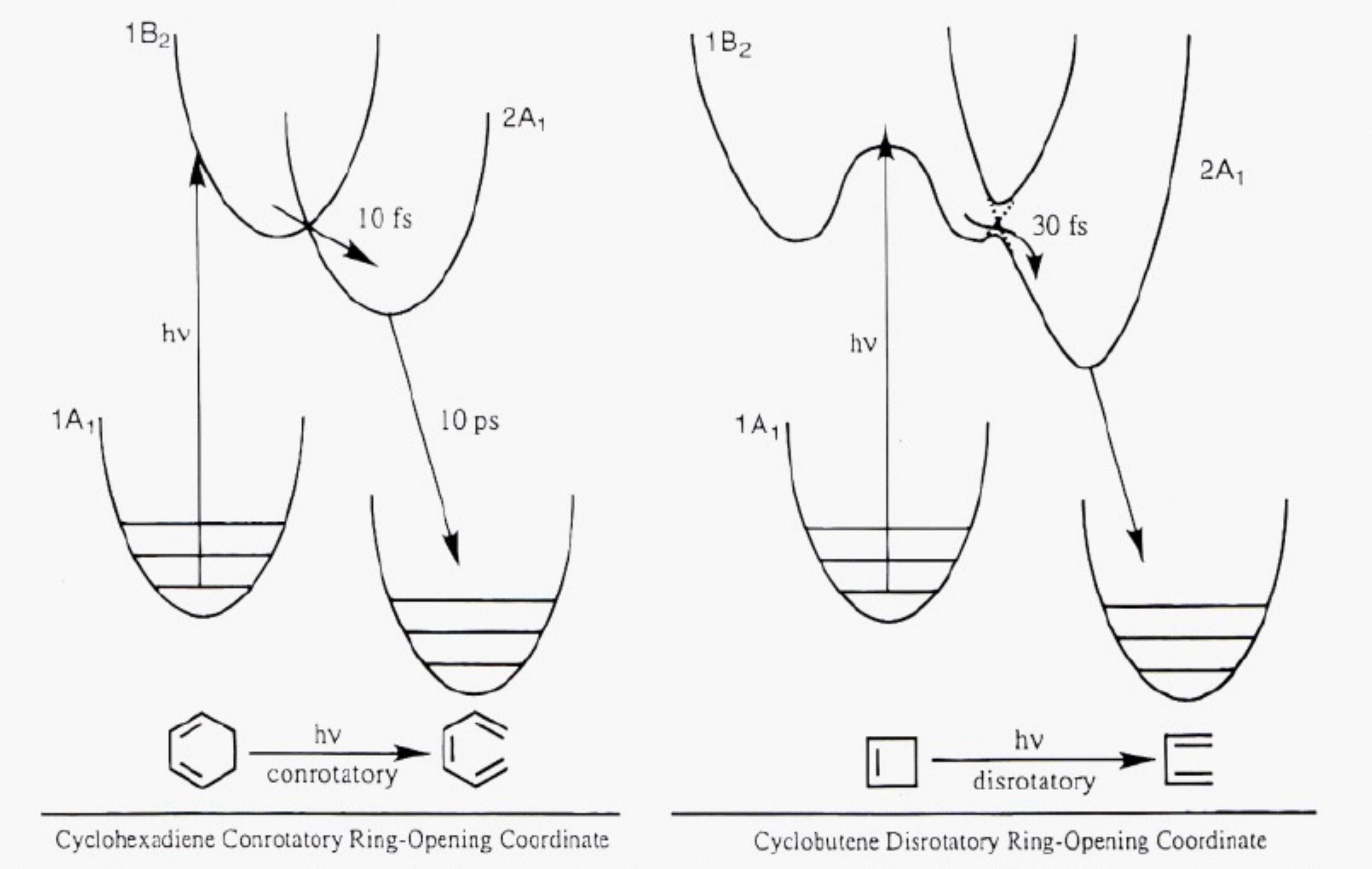
van der Lugt and Oosterhoff,
J. Am. Chem. Soc., *91*, 6041, **1969**

1975



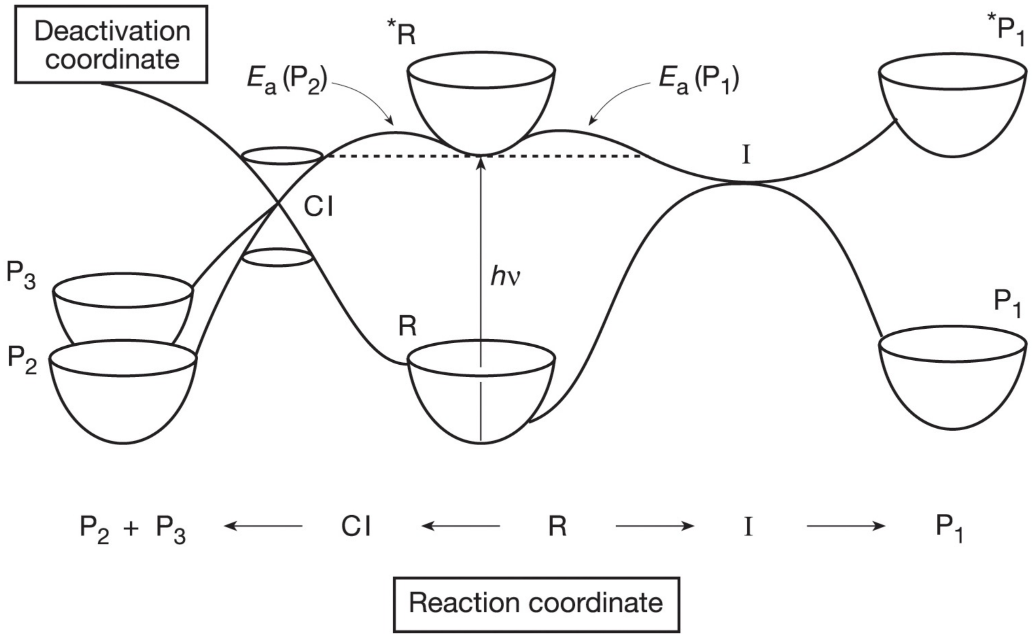
D. Grimbert, G. Segal, and A. Devaquet,
J. Am. Chem. Soc., *97*, 6629, **1975**

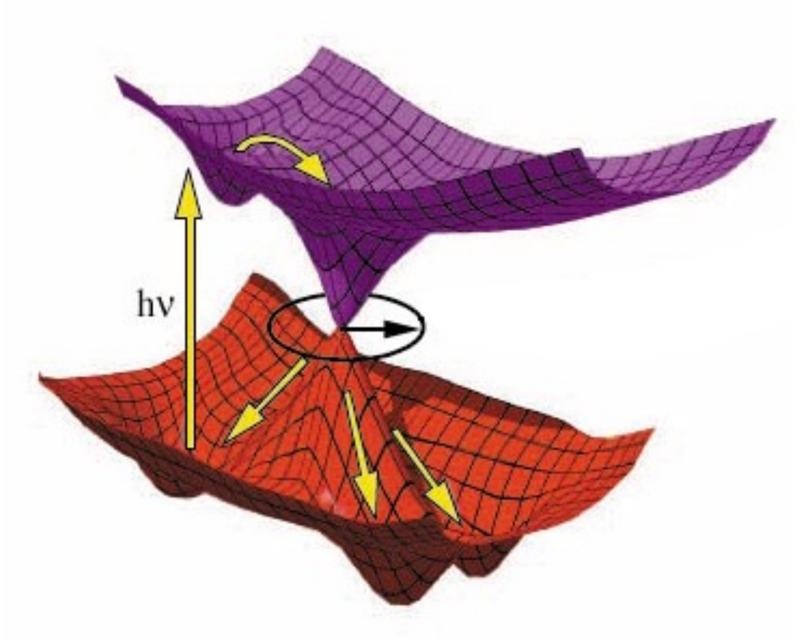
Ultrafast dynamics studies



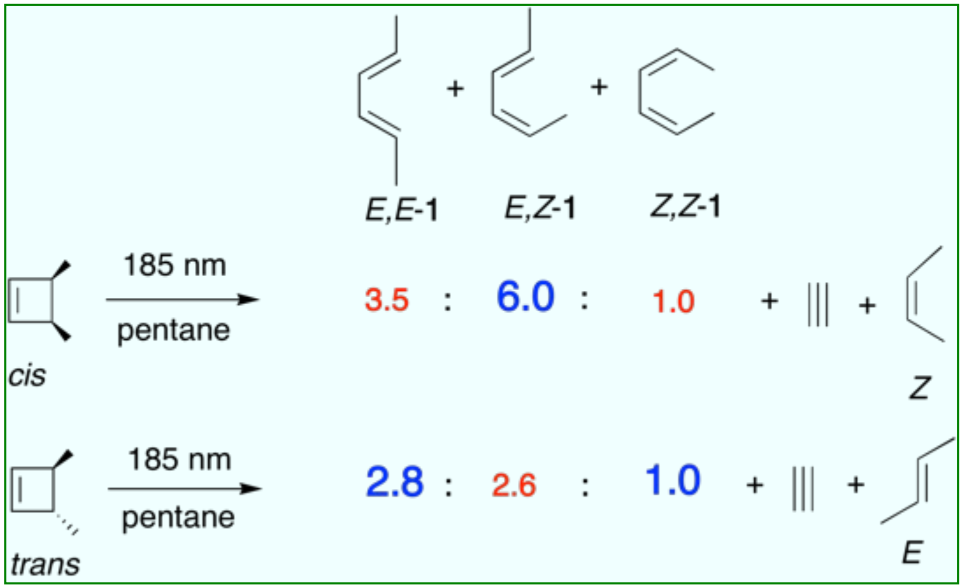
R. Mathies *et.al*, *Acc. Chem. Res*. **28**, 493, **1995**

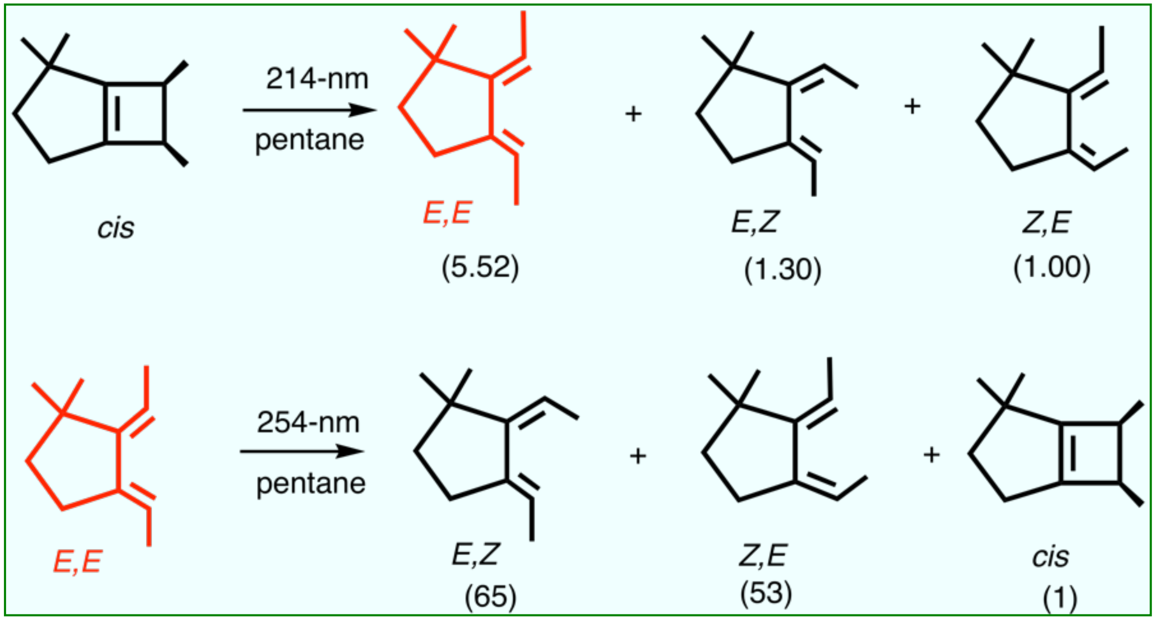
Conical Intersection and Multiple Products



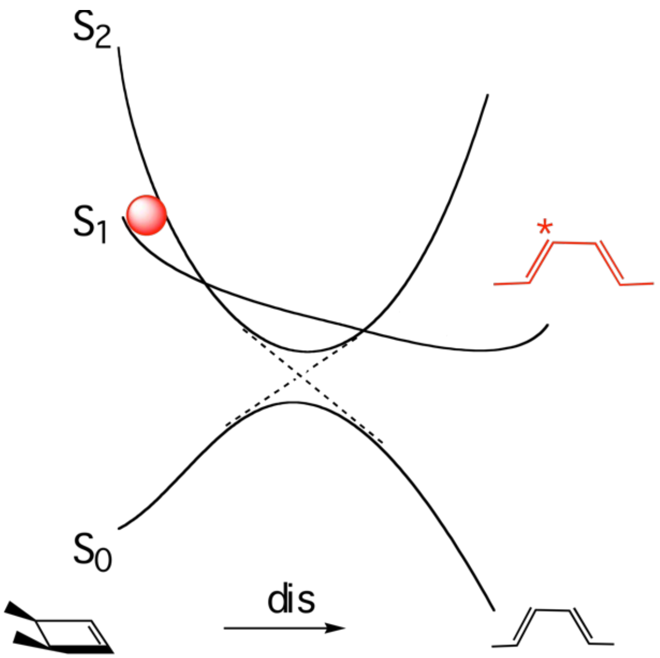


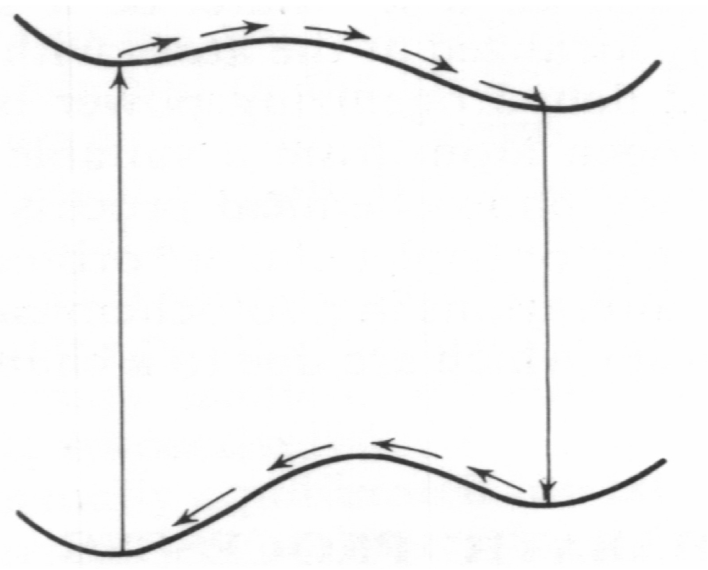
Cyclobutene ring opening is not stereospecific?

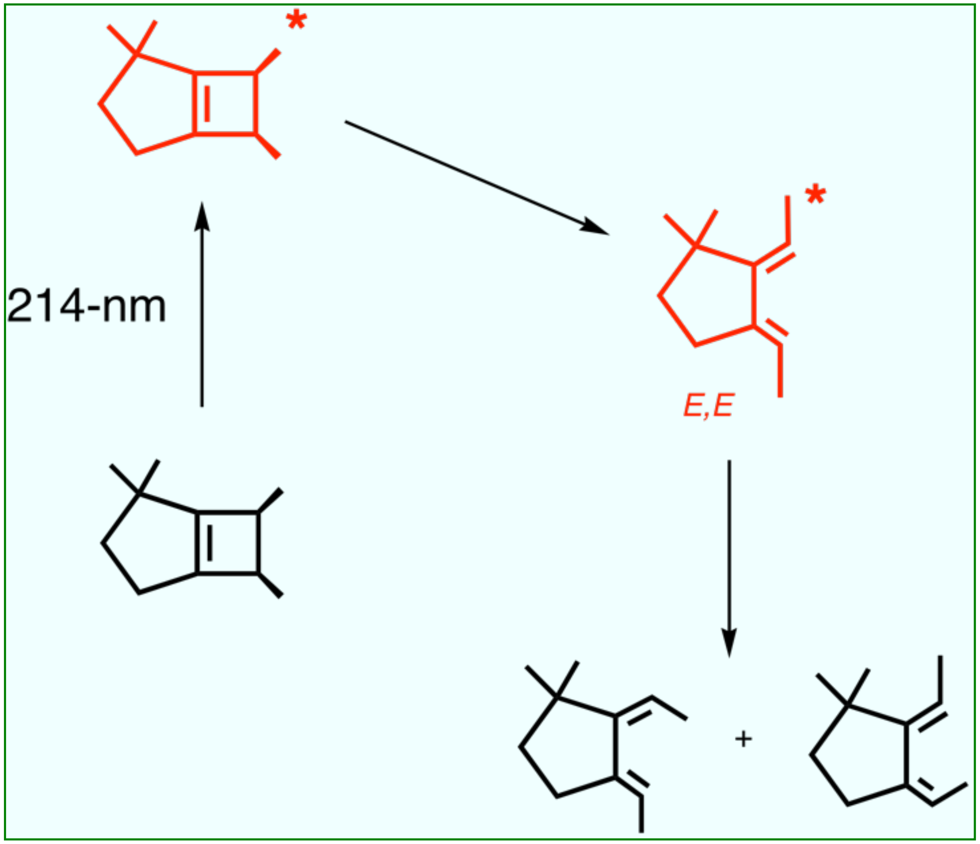




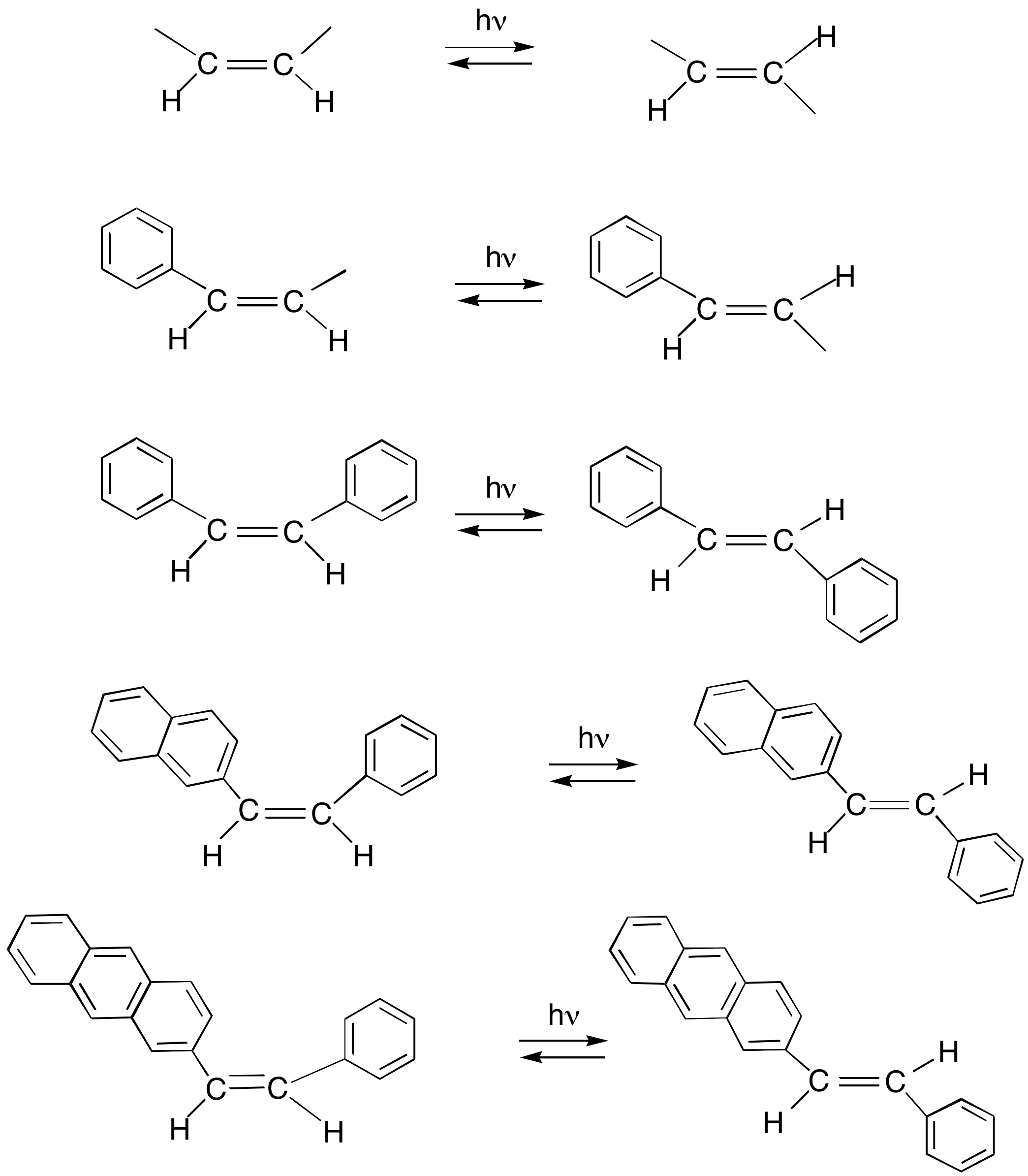
Adiabatic Photochemistry?
Conical intersection with multiple exits?



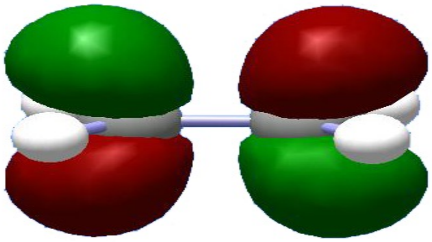




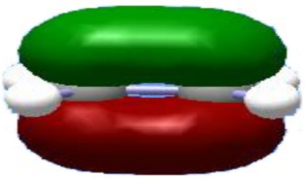
Geometric Isomerization



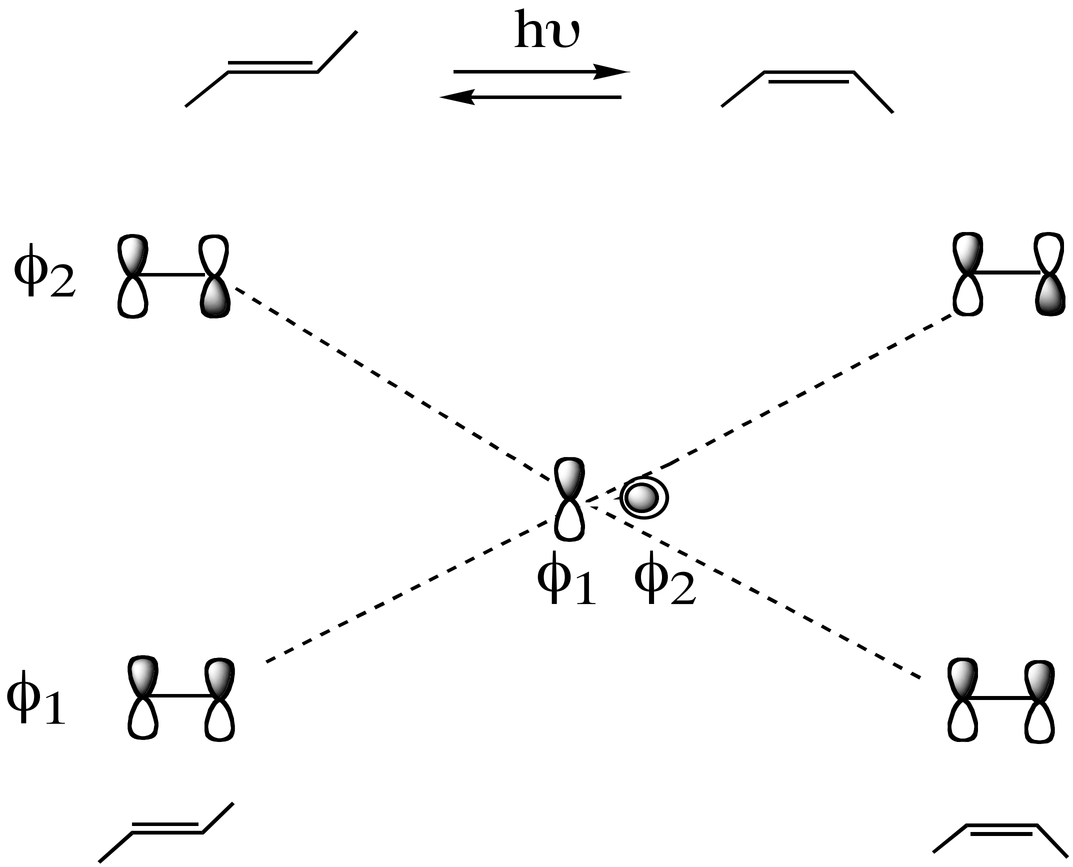
Geometric Isomerization: Twisting of a C=C π Bond

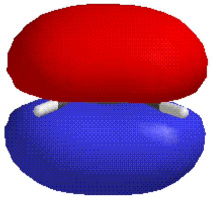


Ethylene - LUMO

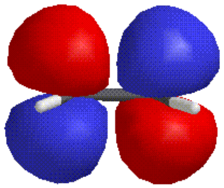


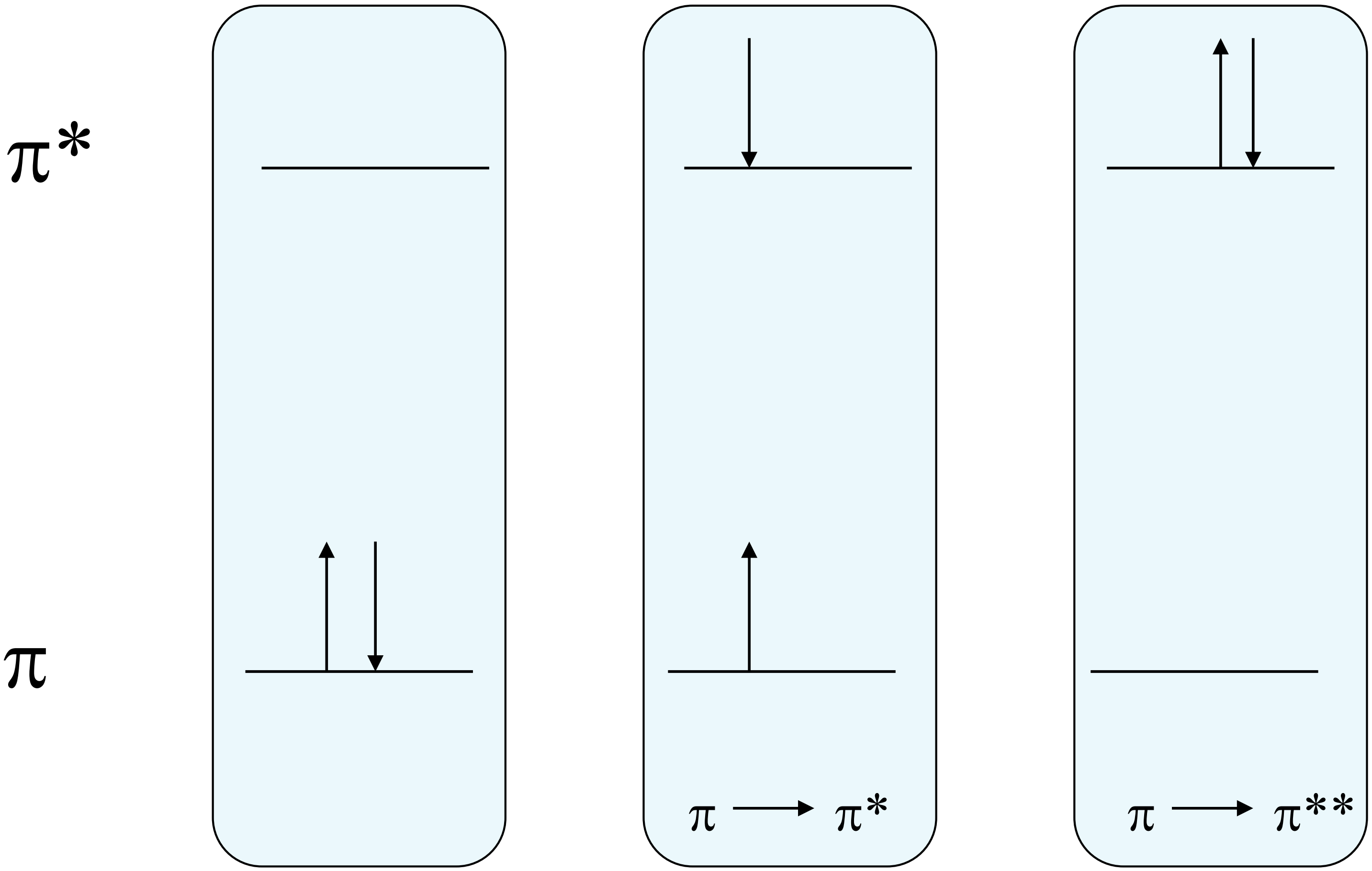
Ethylene - HOMO





Ethylene





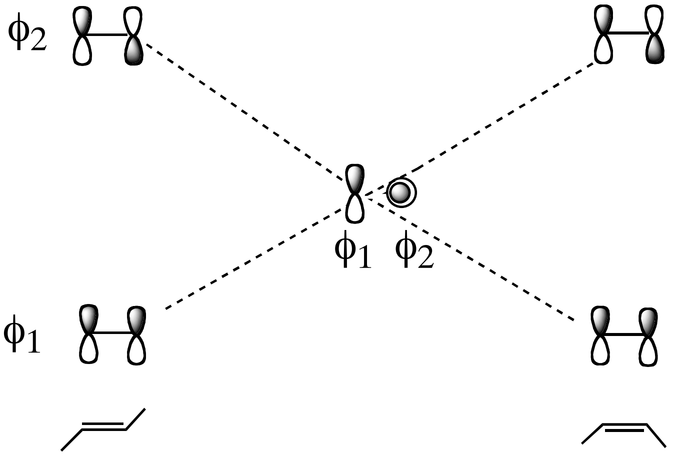
π^*

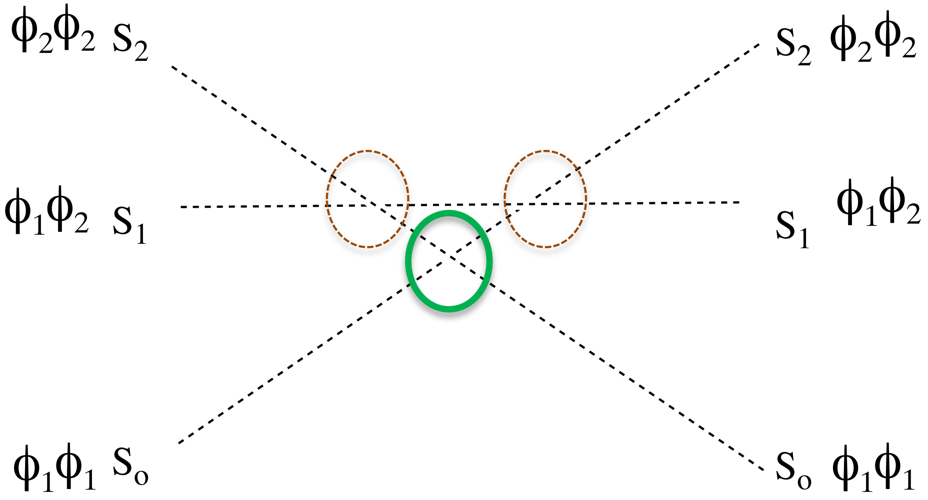
π

$\pi \rightarrow \pi^*$

$\pi \rightarrow \pi^{**}$

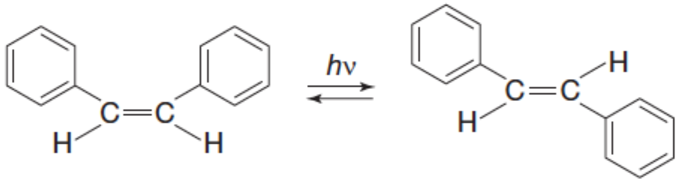
Correlation Diagram for Geometric Isomerization

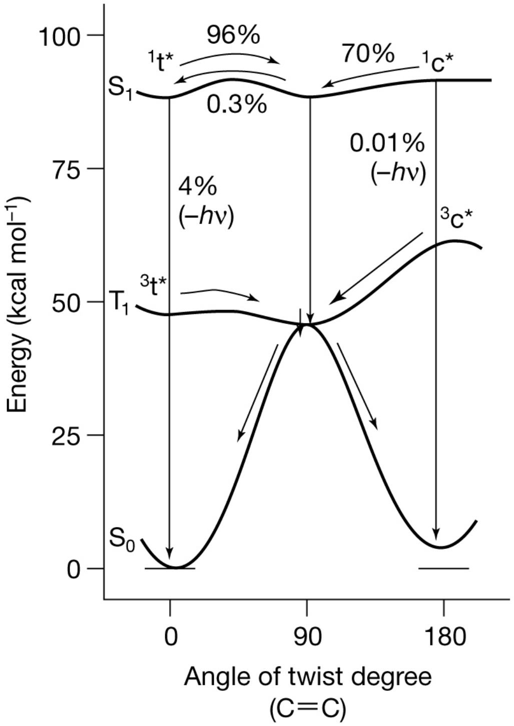


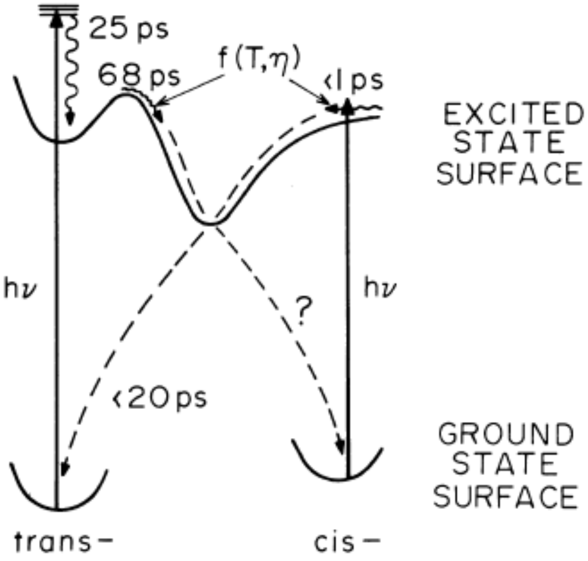


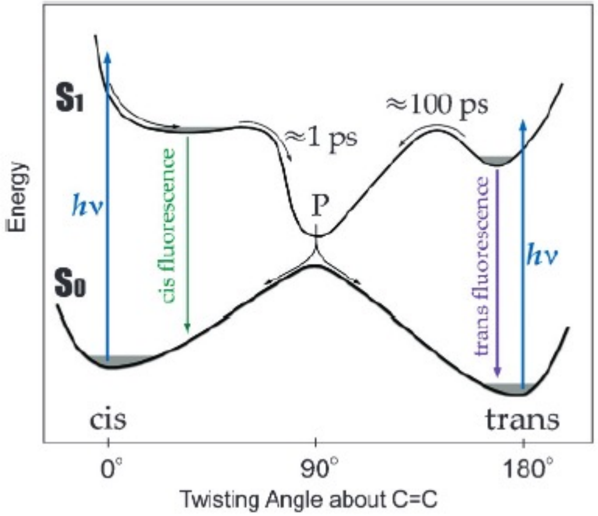
Note the similarity between this diagram and WH diagram for electrocyclization

Energy surface for the isomerization of stilbene







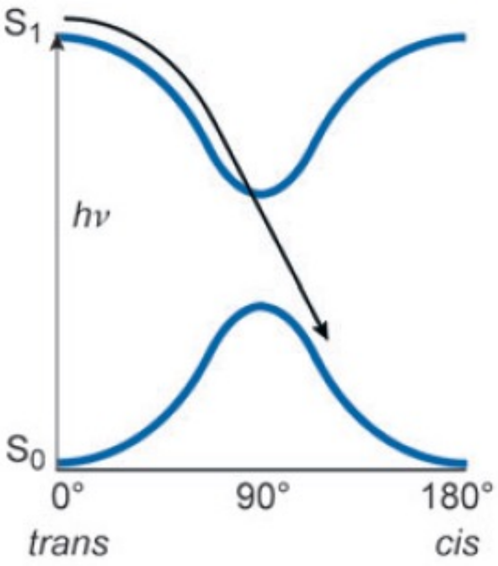


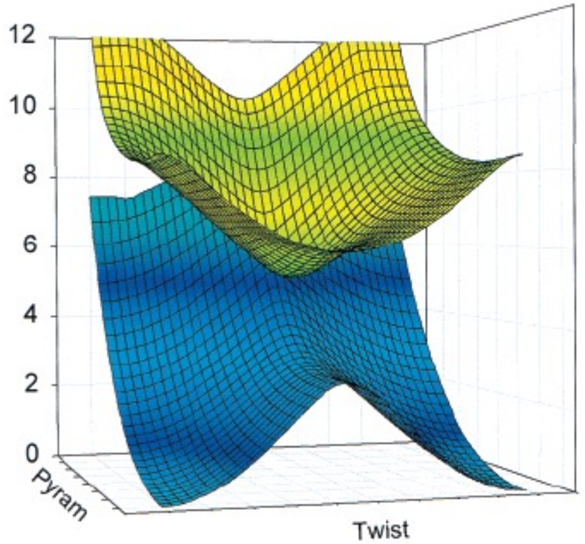
J. Saltiel, et. al., *J. Photochem. Phobiol A, Chem*. **1992**, *65*, 29

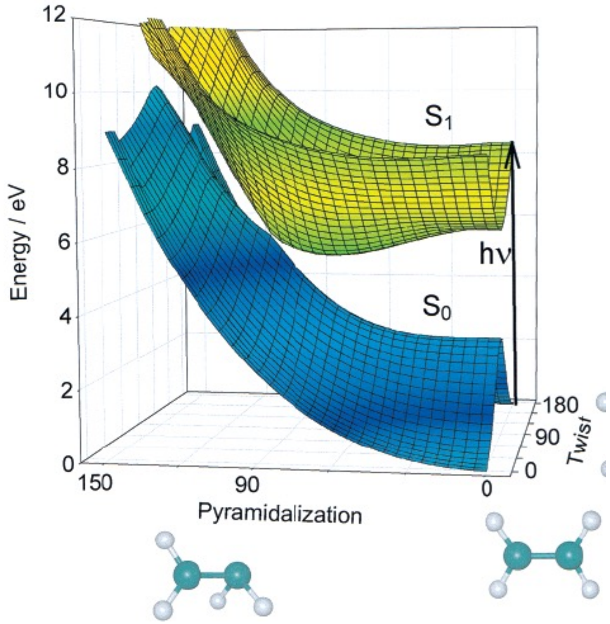
R. Hochstrasser, *Pure & Appl. Chem*., **1980**, *52*, 2683

T. Tahara et. al., *Phys. Chem. Chem. Phys*., **2012**, *4*, 6225

Geometric Isomerization of Ethylene
Conical Intersection is a Possibility



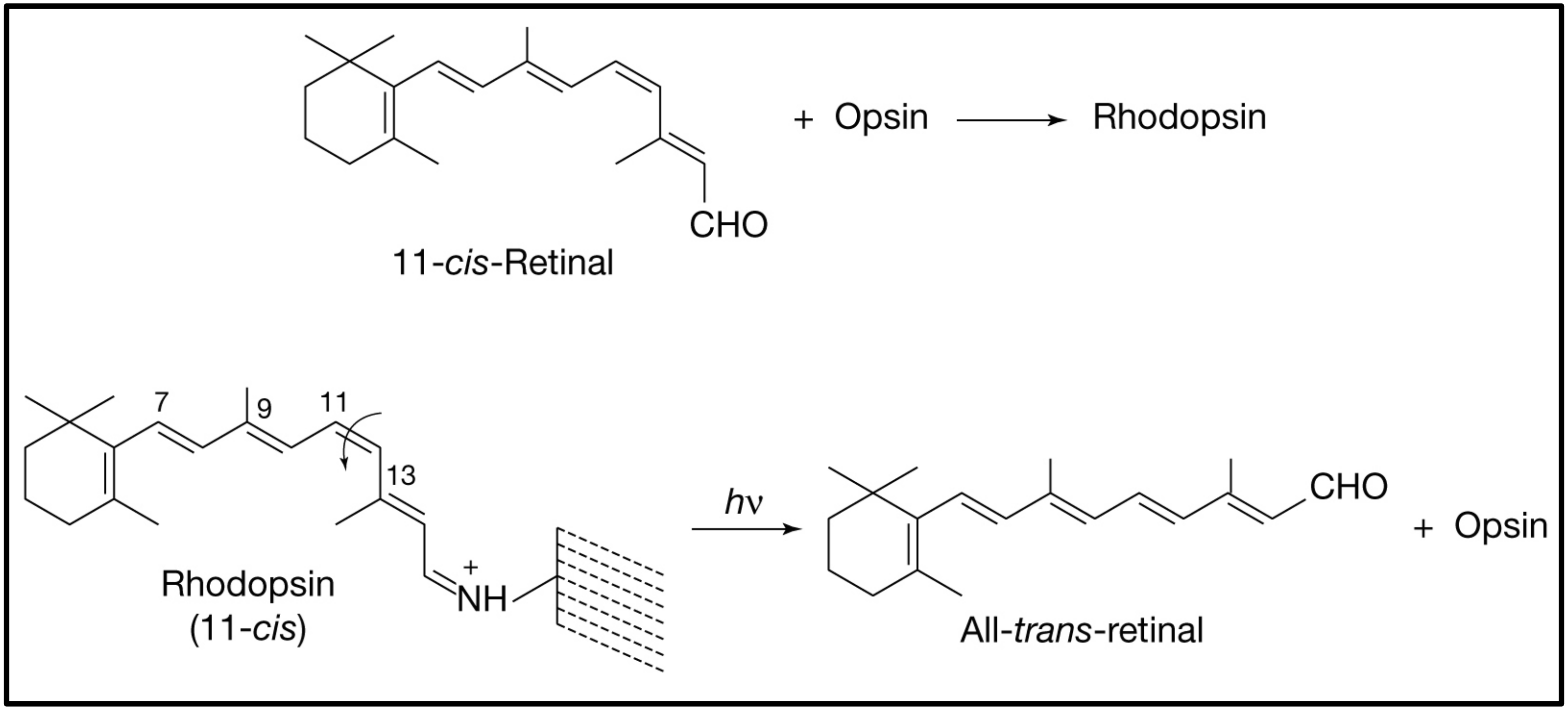


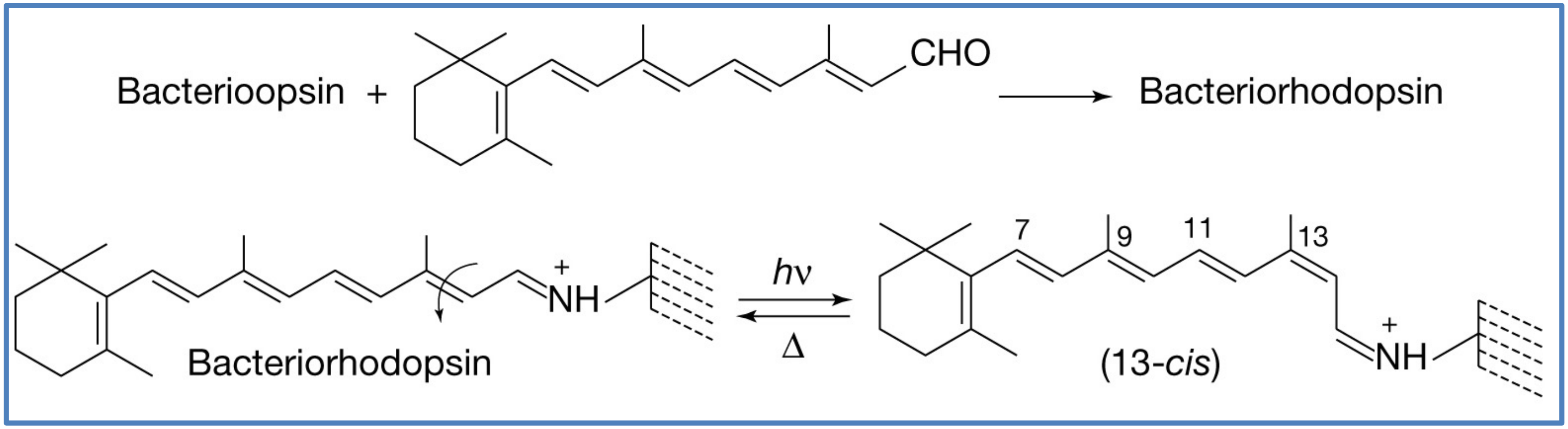


Ethylene decays with a lifetime of 20±10 fs (2 x 10^{-14} sec); computed

Conical intersection at a twisted, mono-pyramidalized geometry suggested through computation.

T. J. Martinez et. al., *Annu. Rev. Phys. Chem*. **2007,** *58*, 613.
T. J. Martinez et. al., *Chem. Phys*., **2000**, *259*, 237.


CHO
11-cis-Retinal
+ Opsin
Rhodopsin
7
9
11
13
Rhodopsin
(11-cis)
NH
+
hν
CHO
All-trans-retinal
+ Opsin


Bacterioopsin +
CHO
Bacteriorhodopsin
Bacteriorhodopsin
+
NH
hν
Δ
7
9
11
13
(13-cis)
+
NH

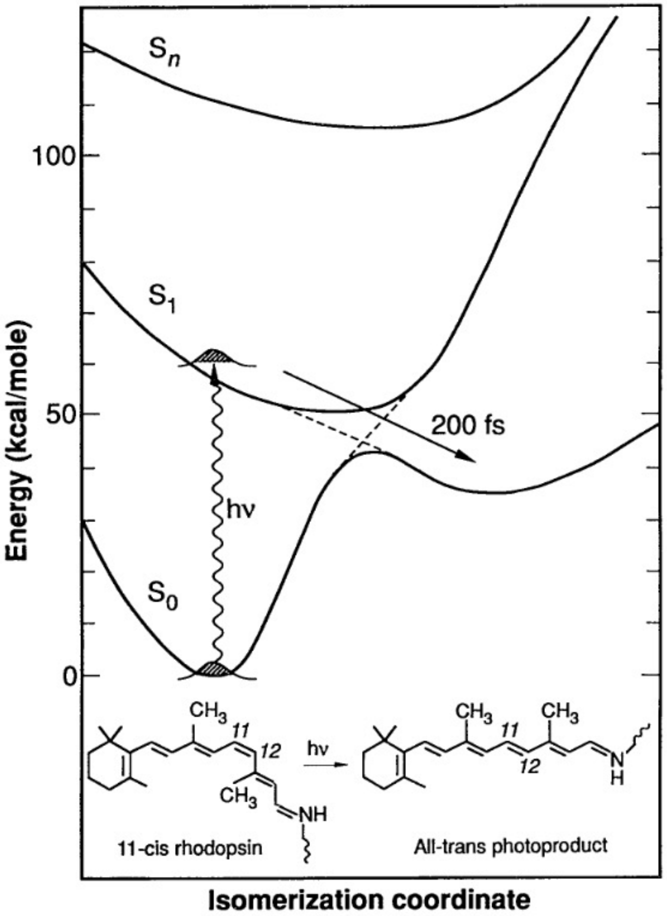


Fig. 1. Schematic ground-state and excited-state potential energy surfaces for the 11-*cis* → 11-*trans* isomerization in rhodopsin, adapted from (*14*). The reaction path of the photoisomerization is indicated by the nonadiabatic potential surfaces (broken lines).

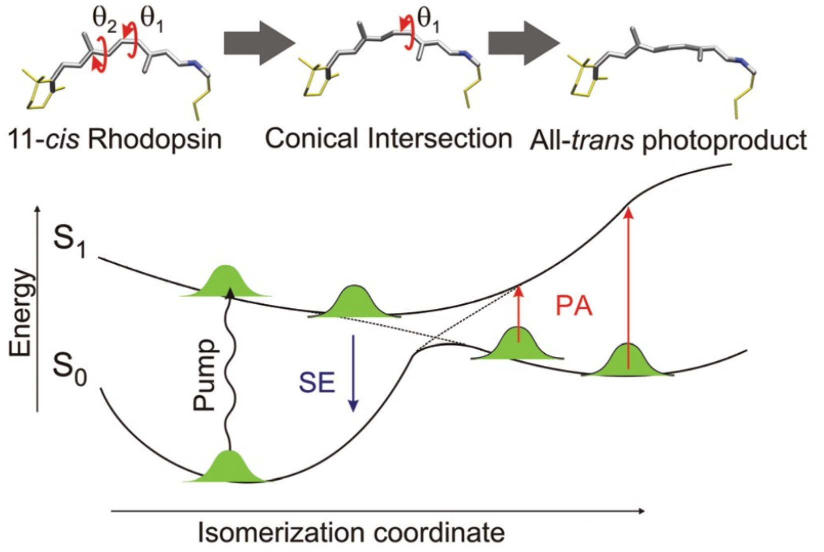


Fig. 7 Sketch of the ground- and excited-state PES of the retinal chromophore in Rh as a function of the isomerization coordinate. It shows that SE from the excited state of the parent molecule and PA from the hot photoproduct can monitor the wavepacket dynamics through the conical intersection. On top averaged structures of the chromophore at the initial 11-*cis*, conical intersection and final all-*trans* configurations; gray/yellow colours indicate the chromophore QM/MM mobile regions in the simulations.

Suggested references on excited state surfaces, crossings, avoided crossings, conical intersections etc.

E. Teller, THE CROSSIKG OF POTENTIAL SURFACES, *J. Phys. Chem* , **1937**, *41*, 109.

E. Teller, INTERNAL CONVERSION IN POLYATOMIC MOLECULES, *Isr. J. Chem*. **1969**, *7*, 227

C. Zener, Non-Adiabatic Crossing of Energy Levels, *Proc. Roy. Soc. London* **1932**, *137A*,696

T. J. Martinez et. al., *Annu. Rev. Phys. Chem*. **2007,** *58*, 613.

T. J. Martinez el. al., *J. Phys. Chem. A*, **2000**, *104*, 5161

M. Robb et. al., *Rev. Computational Chemistry*, **2000**, *15*, 87-146.

Oliviucci, *Photochem. Photobiol. Sci*., **2011**, 10, 867.--- Rev on CI

Domcke and Yarkony, *Annu. Rev. Phys. Chem*., **2012,** *63*, 325–52

Yarkony, *Chem. Rev*., **2012**, *112*, 481–498

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F. F. Crim, *J. Phys. Chem.*, **1996**, *100*, 12725-12734J.

Watch two videos by Oliviucci in this site (Murthy group); search, they are at the end

https://chemistry.as.miami.edu/research-groups/ramamurthy-group/video-lectures/video-lectures-miami/index.html

Michl, J. "Photochemical Reactions of Large Molecules. I. A Simple Physical Model of Photochemical Reactivity", Mol. Photochem. 1972, 4, 243.

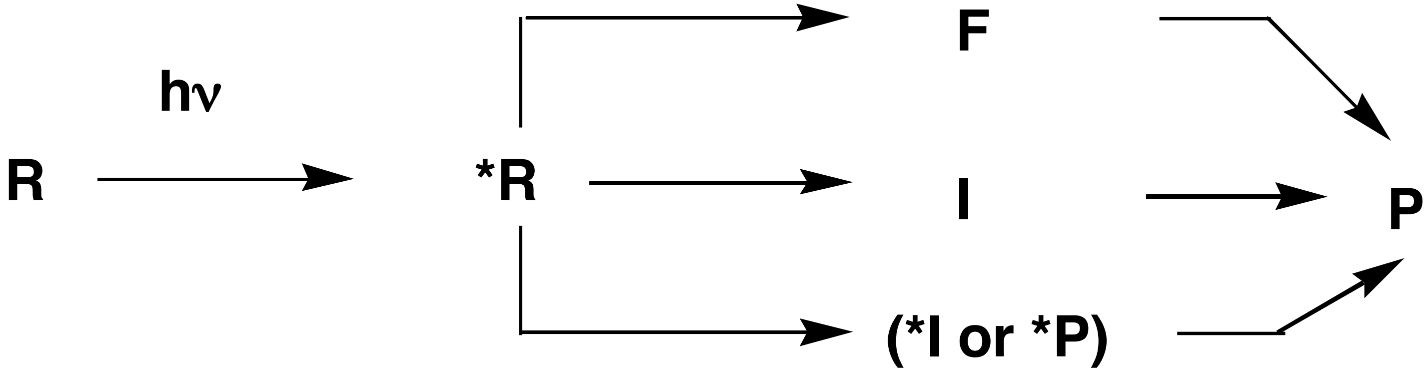
Michl, J. "Photochemical Reactions of Large Molecules. II. Application of the Model to Organic Photochemistry", Mol. Photochem. 1972, 4, 257.

Michl, J. "Photochemical Reactions of Large Molecules. III. Use of Correlation Diagrams for Prediction of Energy Barriers", Mol. Photochem. 1972, 4, 287.

J. Michl, *Topics Curr. Chem*., **1974**, *46*, 1

M. Klessinger and J. Michl, *Excited States and Photochemistry of Organic Molecules*, VCH, **1995**, pp. 179-241

Mechanistic Possibilities



$$\begin{tikzcd}
 & & F \arrow[dr] & \\
R \arrow[r, "h\nu"] & {*R} \arrow[ur] \arrow[r] \arrow[dr] & I \arrow[r] & P \\
 & & (*I \text{ or } *P) \arrow[ur] &
\end{tikzcd}$$

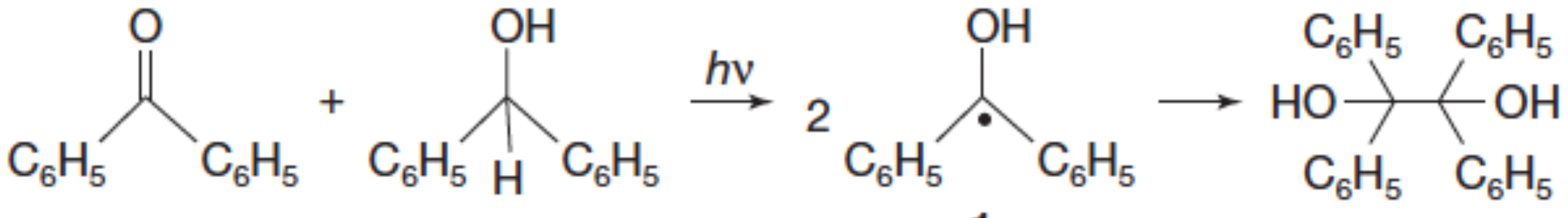
F = funnel from excited to ground state surface

I = ground state reactive intermediate

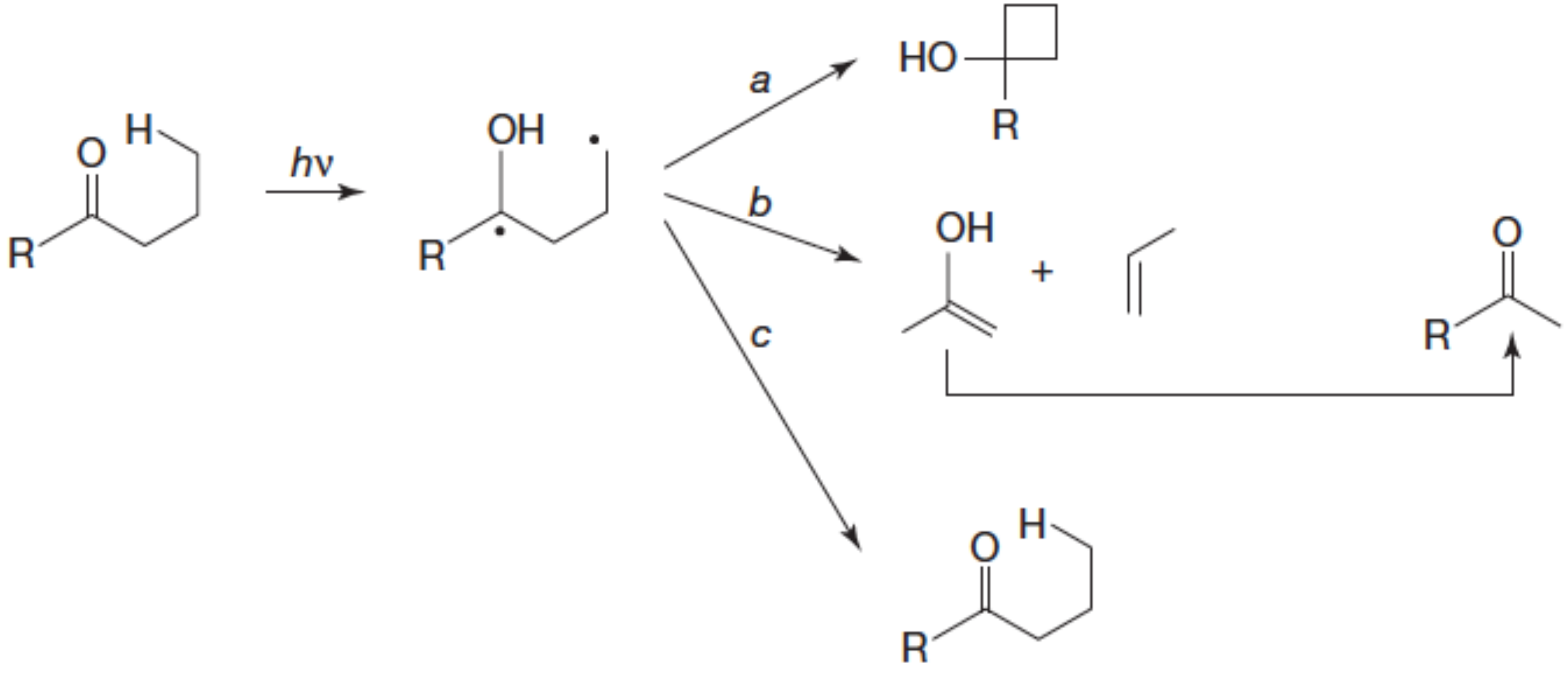
***I = excited state of a reactive intermediate**

***P = excited state of product**

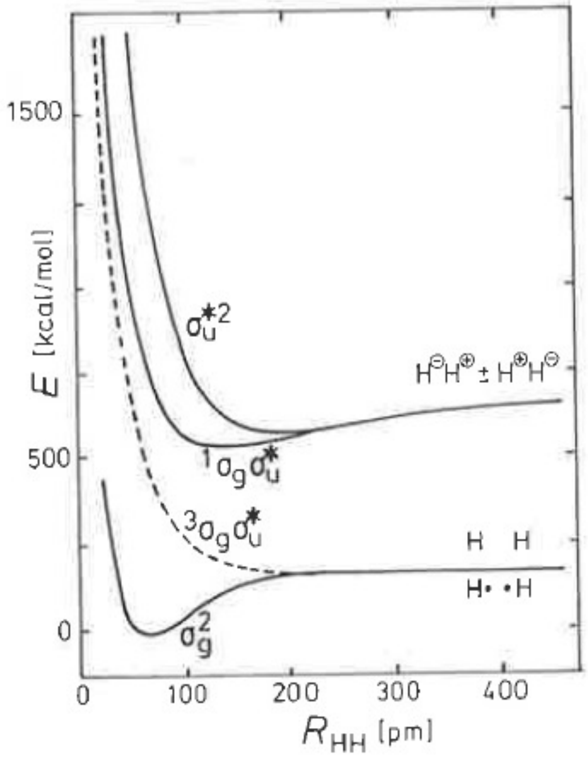
Hydrogen abstraction is a common photoreaction



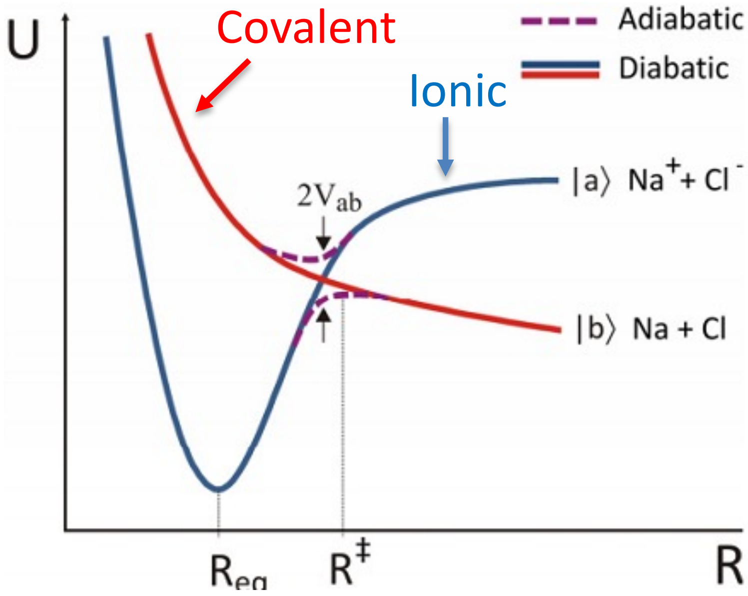
1



Models for photodissociation of covalent and ionic σ bond



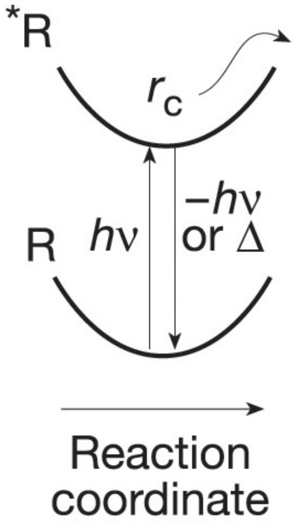
H_2

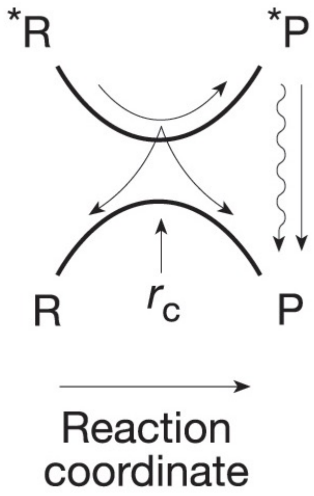


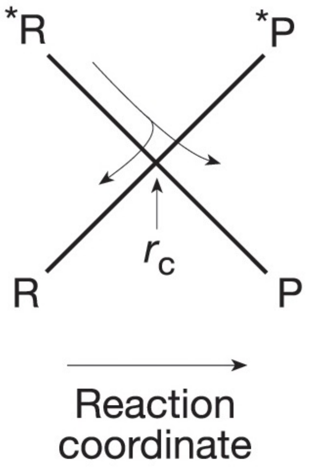
NaCl

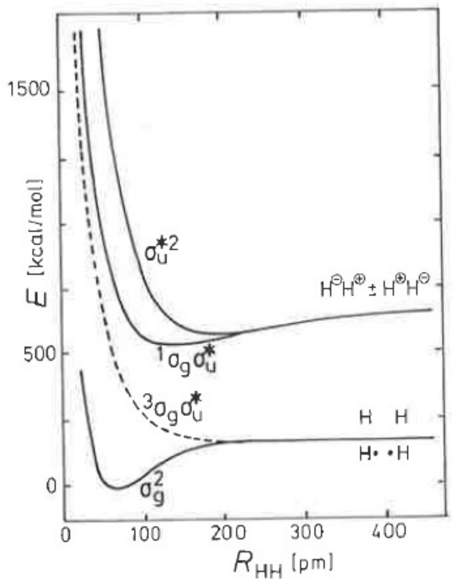
Energy surfaces generated by following the electrons as the nuclei move along the reaction co-ordinate.

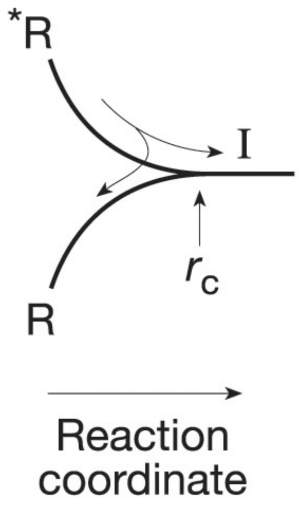
Types of surfaces

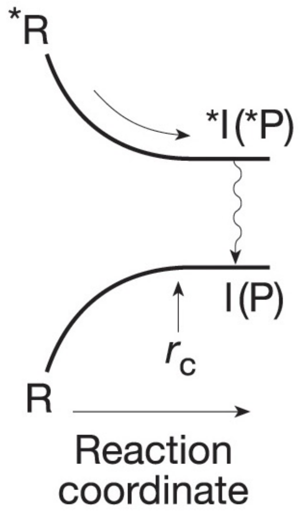




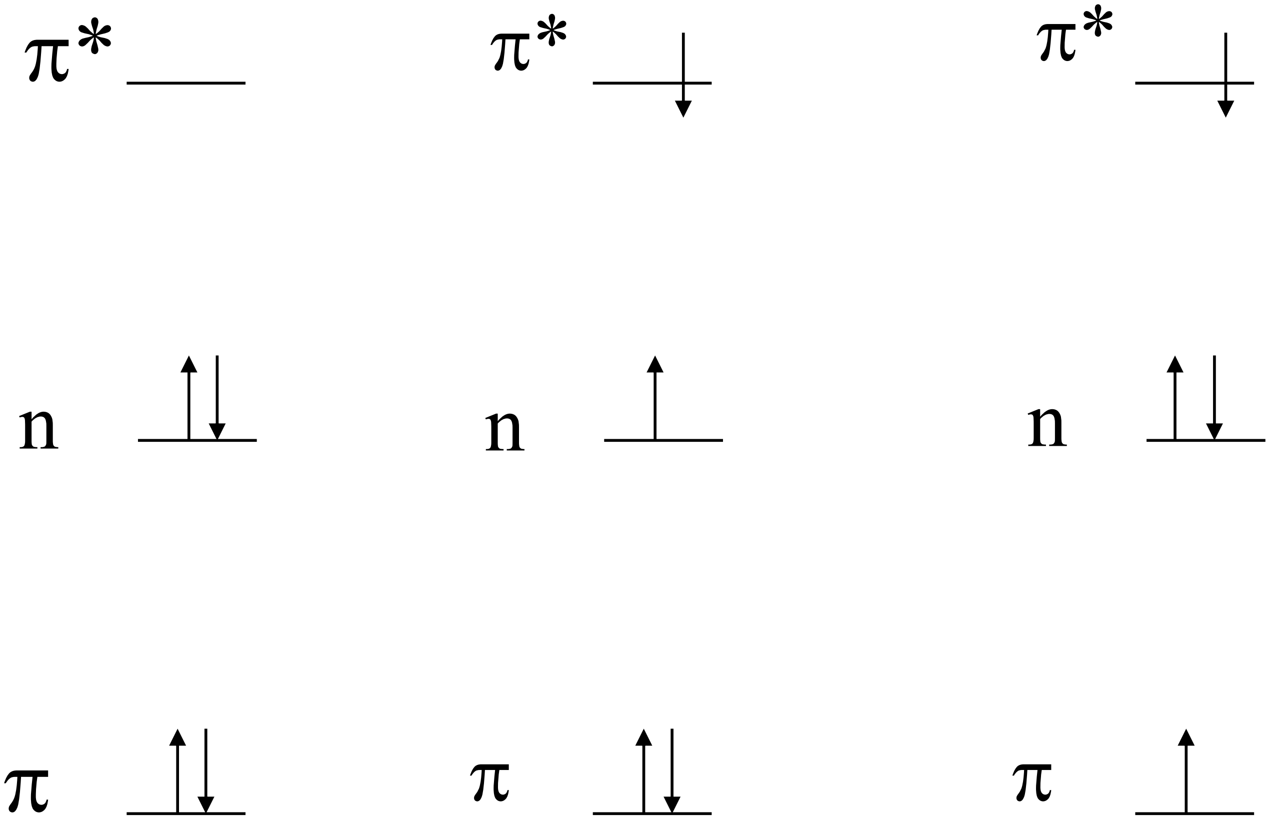






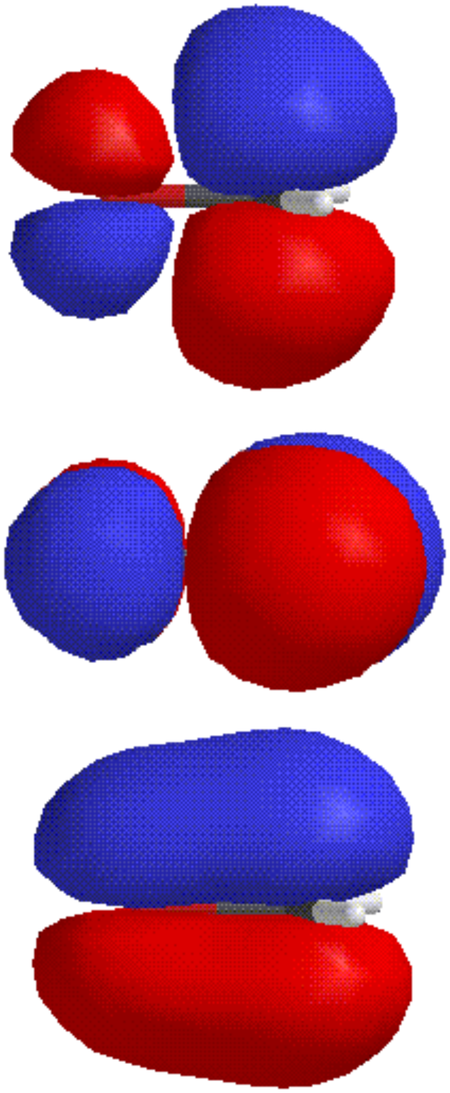


Electronic States of Carbonyl Compounds



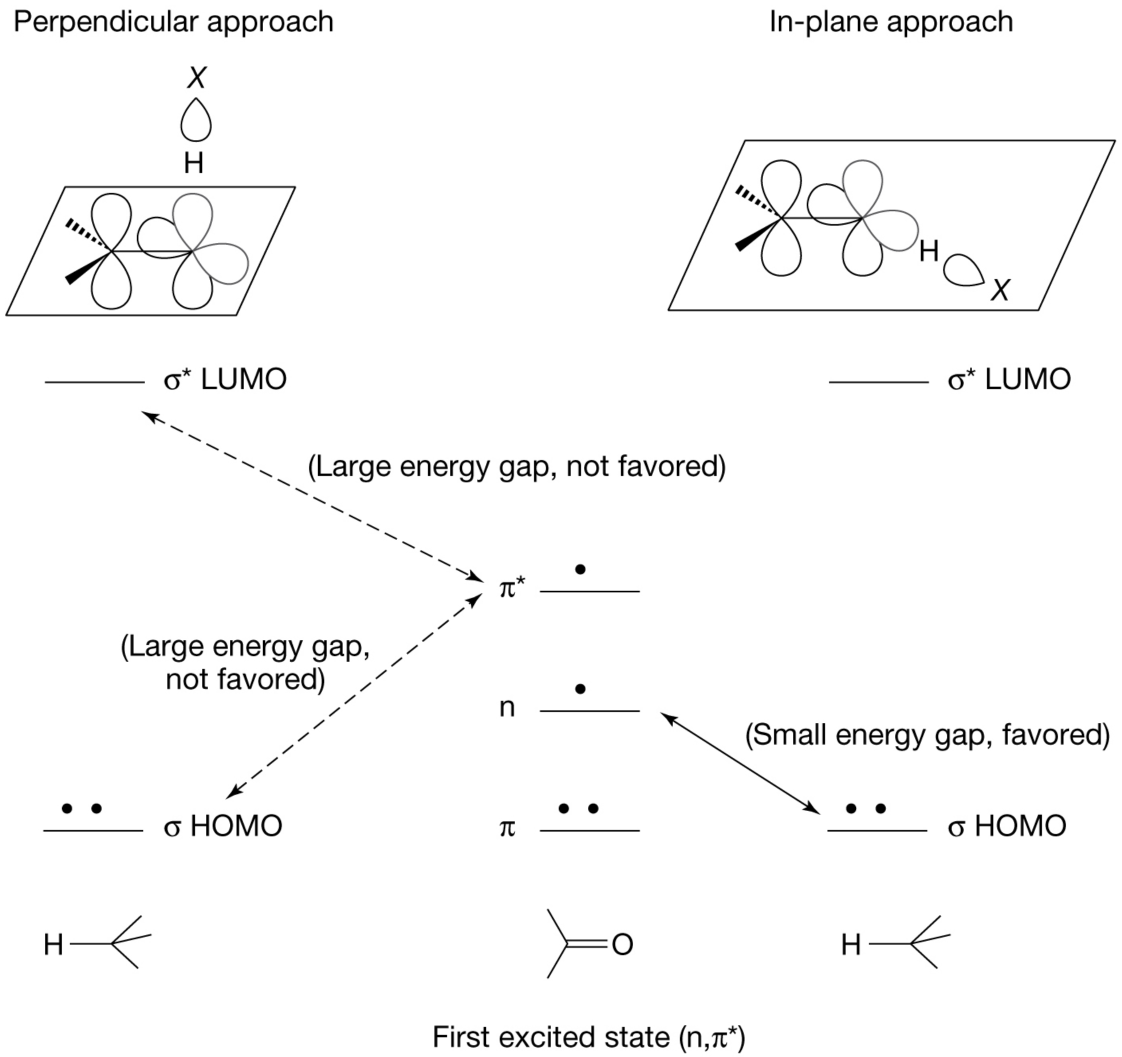
$n \longrightarrow \pi^*$

$\pi \longrightarrow \pi^*$



Frontier orbital view of hydrogen abstraction by carbonyl nπ* triplet

Geometry of orbital interaction



Perpendicular approach

In-plane approach

X

H

H

X

σ^* LUMO

σ^* LUMO

(Large energy gap, not favored)

Less likely

π^*

(Large energy gap, not favored)

n

(Small energy gap, favored)

More likely

σ HOMO

π

σ HOMO

H

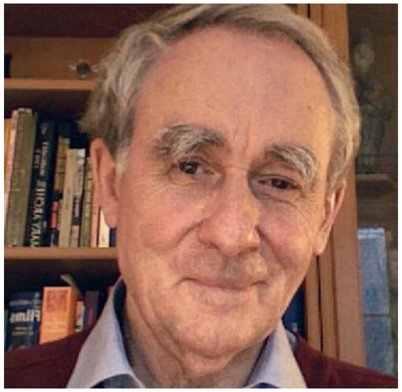
O

H

First excited state (n,π^*)

Non-concerted Photoreactions

Original publications on correlation diagrams, avoided crossings on reactions with intermediates



L. Salem
1937-

Salem Correlation Diagram

L. Salem, J. Am. Chem. Soc., 96, 3486, 1974

L. Salem, Israel. J. Chem., 14, 89, 1975.

L. Salem, Science, 191, 822, 1976

W. Dauben, L. Salem and N. J. Turro, Acc. Chem. Res., 8, 41, 1975

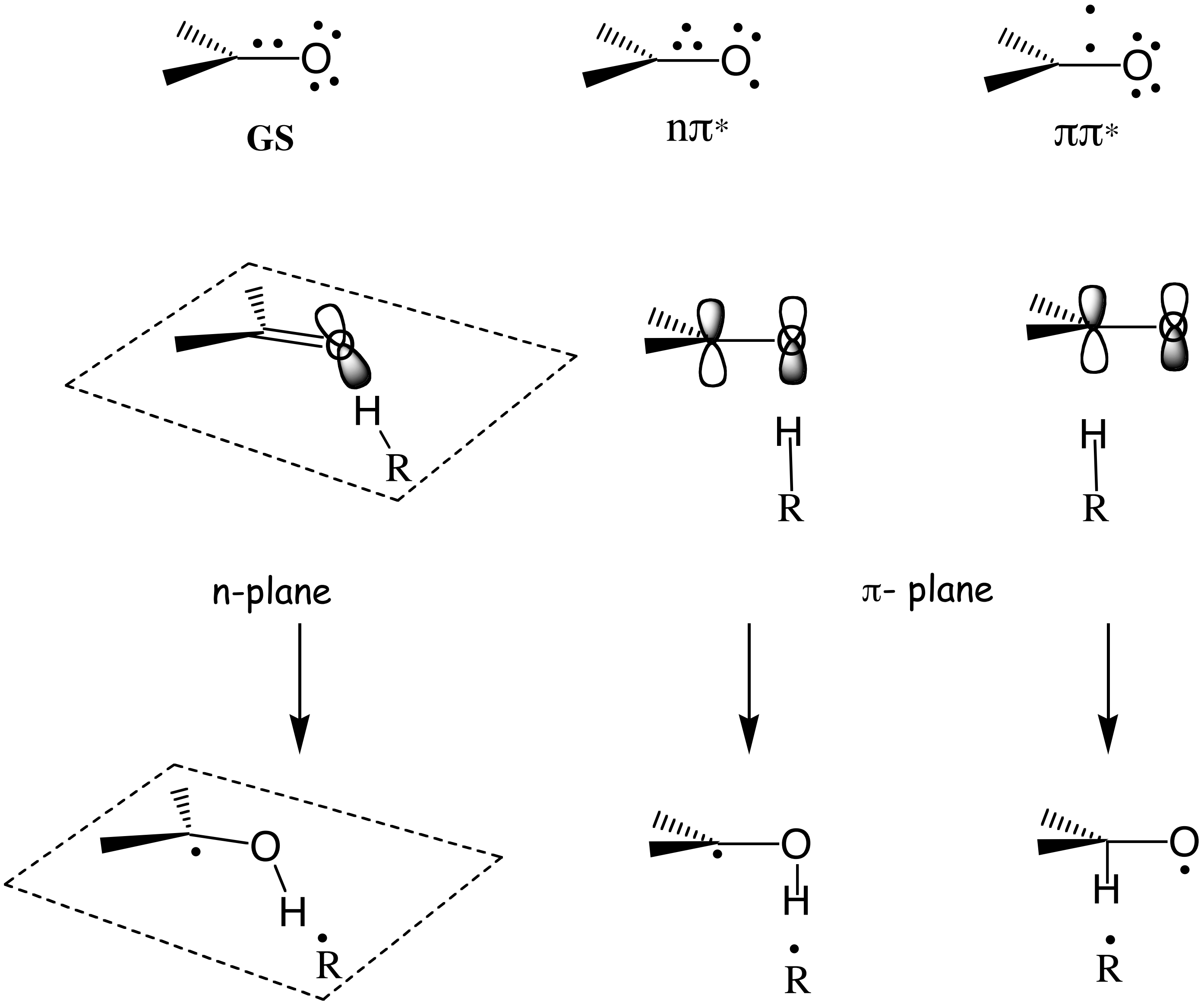
Allowed and Avoided Crossings

B. Bigot, A. Devaquet and N. J. Turro, J. Am. Chem. Soc., 103, 6, 1981

L. Salem, C. Leforestier, G. Segal and L. Salem, J. Am. Chem. Soc., 97, 479, 1975

Electrons in Chemical Reactions First Principles, L. Salem, Wiley, 1982, pp. 124-157

Constructing Salem Diagram



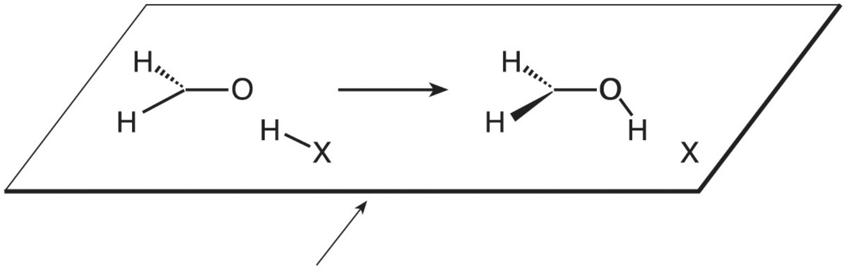
Relevant electronic states

Geometries of approach

Diradical intermediates formed

Constructing Salem diagram for n-plane attack

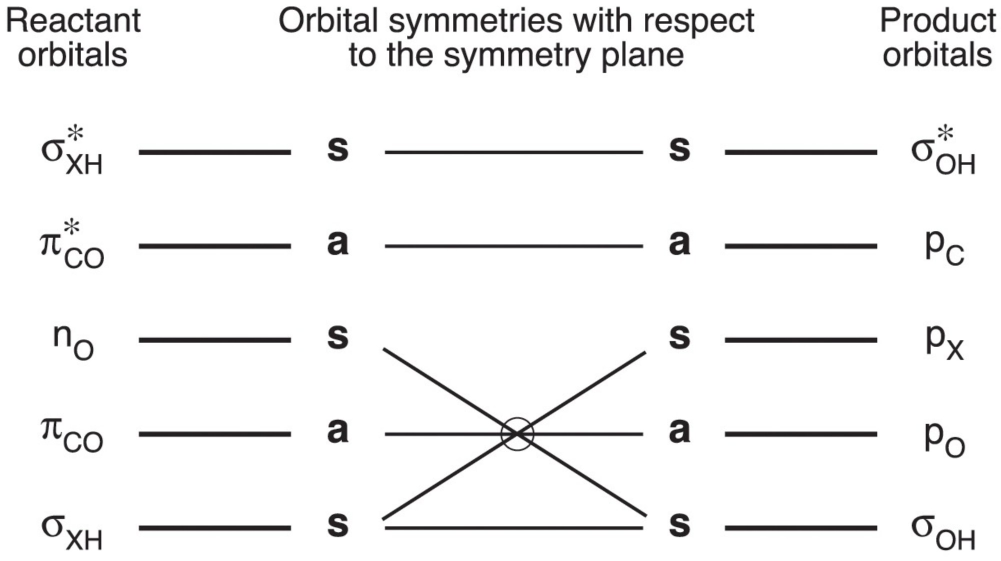
Identify a symmetry plane to which relevant orbitals are *s* or *a*



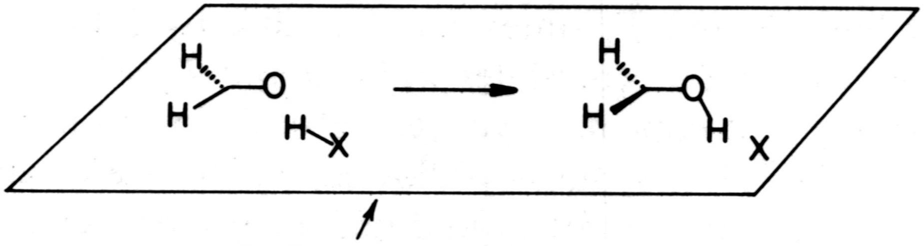
Symmetry plane
(contains atoms involved in reaction)

Enumerate the relevant orbitals of the reactant and the intermediate in the order of their energy.

Build the orbital correlation diagram based on energy and symmetry.

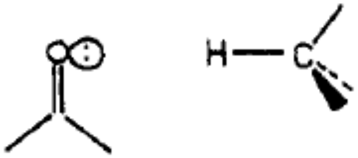


Salem correlation diagrams: L. Salem, *JACS*, **1974**, *96*, 3486; *Science*, **1976**, *191*, 822. Dauben, Salem and Turro, *Acc. Chem. Res*., **1975**, *8*, 41.



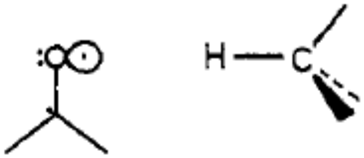
SYMMETRY PLANE
(contains atoms involved in reaction)

reactant ground state



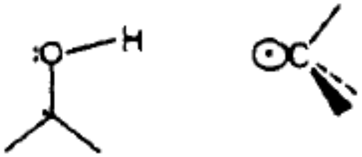
$4\sigma, 2\pi$ 4S 2A

reactant (n, π^*) excited state



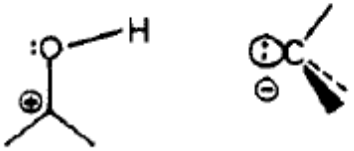
$3\sigma, 3\pi$ 3S 3A

ground state of primary product

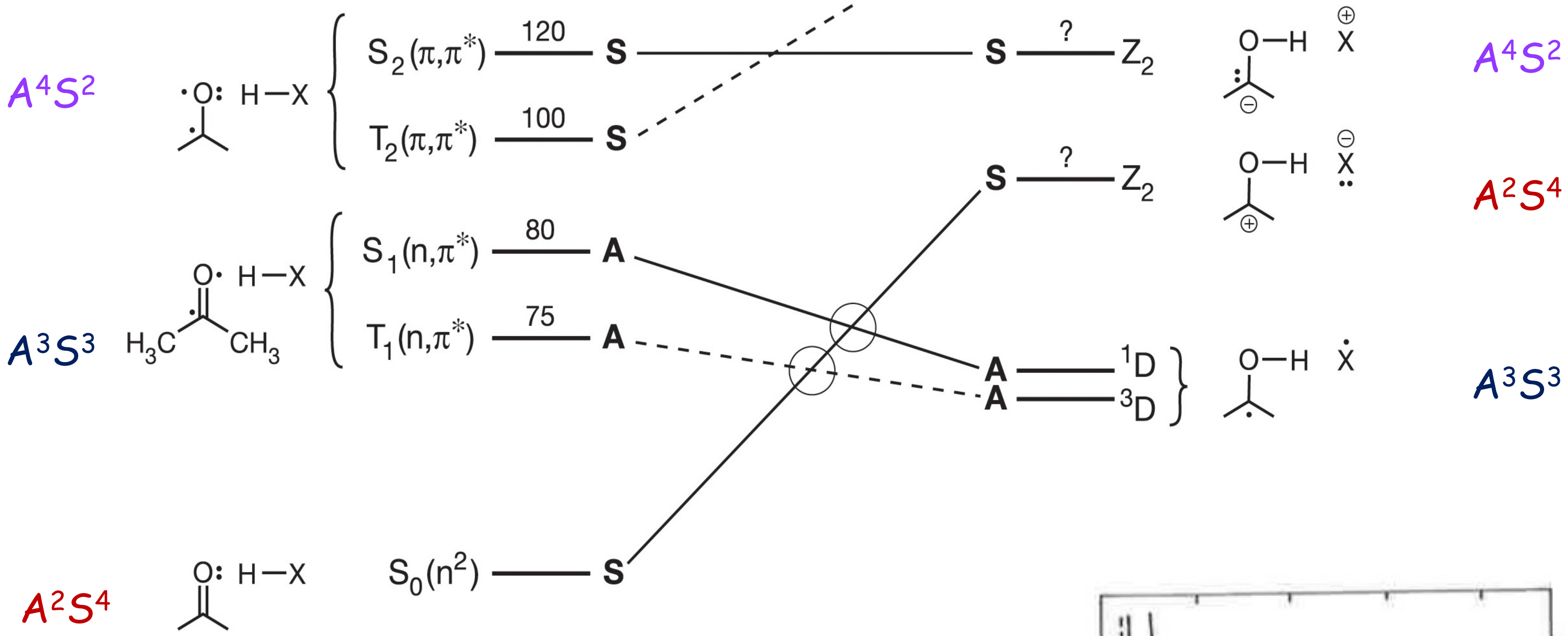


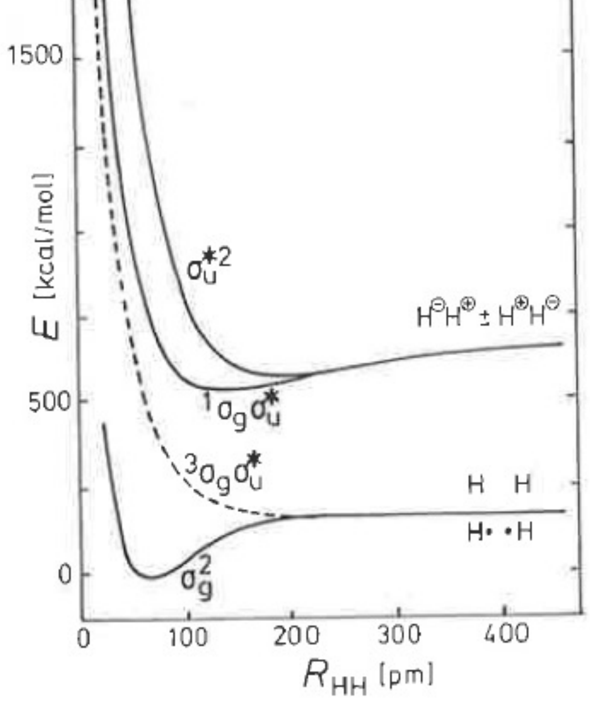
$3\sigma, 3\pi$ 3S 3A

excited state of primary product



$4\sigma, 2\pi$ 4S 2A

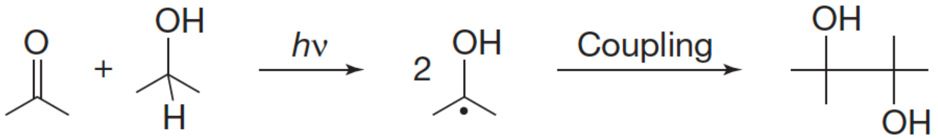


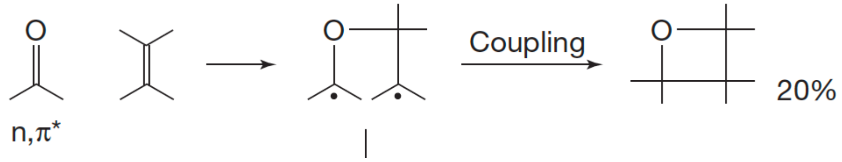


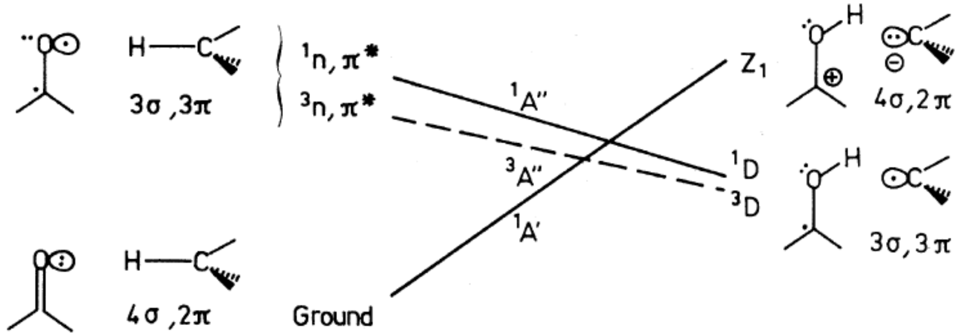
Hydrogen abstraction along n-plane is likely from nπ* state.

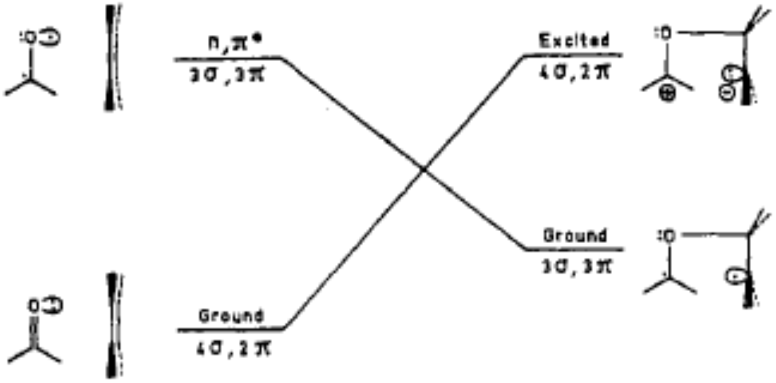
Reaction from T_1(nπ*) is likely to be more efficient than from S_1 (nπ*).

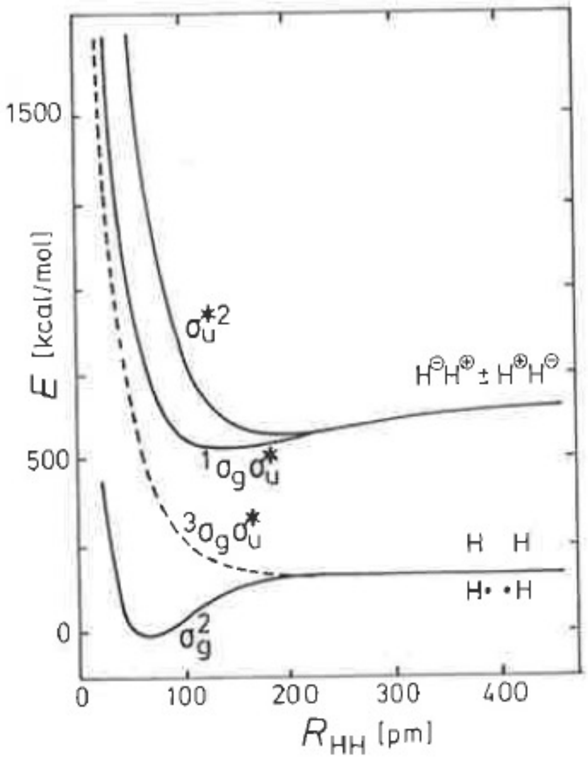
If T_1 is ππ* the reaction from n-face is unlikely.


O
OH
H
+
hν
2
OH
Coupling
OH
OH


O
n,π*
O
Coupling
O
20%


H—C
3σ ,3π
¹n, π*
³n, π*
Z₁
¹A''
³A''
¹A'
¹D
³D
H
4σ,2π
H
3σ, 3π
H—C
4σ ,2π
Ground


n,π*
3σ,3π
Excited
4σ,2π
Ground
3σ, 3π
Ground
4σ,2π


E [kcal/mol]
1500
500
0
0
100
200
300
400
R_HH [pm]
σ_u*²
¹σ_g σ_u*
³σ_g σ_u*
σ_g²
H⁻H⁺ ± H⁺H⁻
H H
H• •H

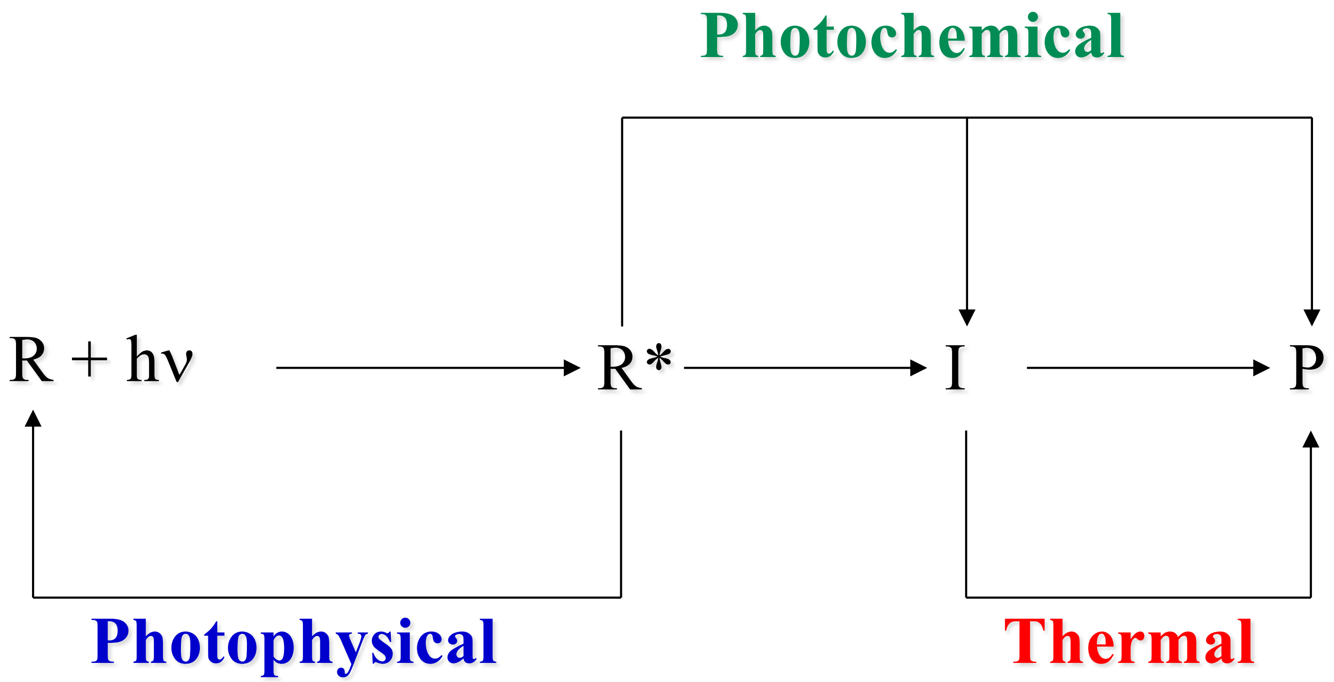
Mechanism of photoreactions involving intermediates

How do reactive intermediates in the triplet state transform to singlet products?

What is the mechanisms of intersystem crossing in diradicals?

Why excited singlet and triplet give different products?

Molecular Structure and Dynamics



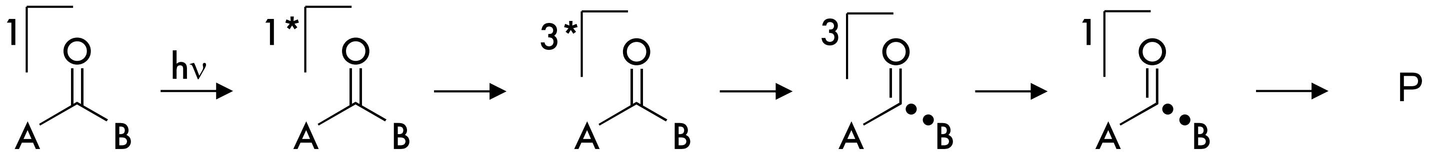
Photochemical

R + hν → R* → I → P

Photophysical

Thermal

Importance of intersystem crossing

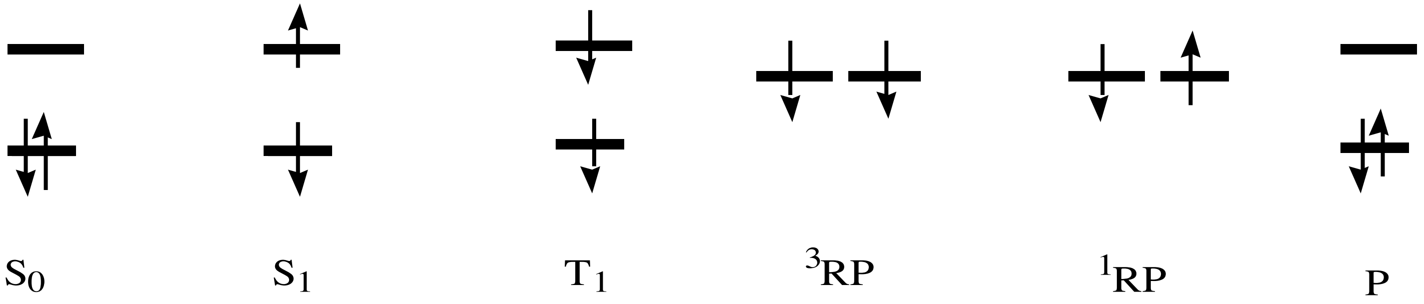


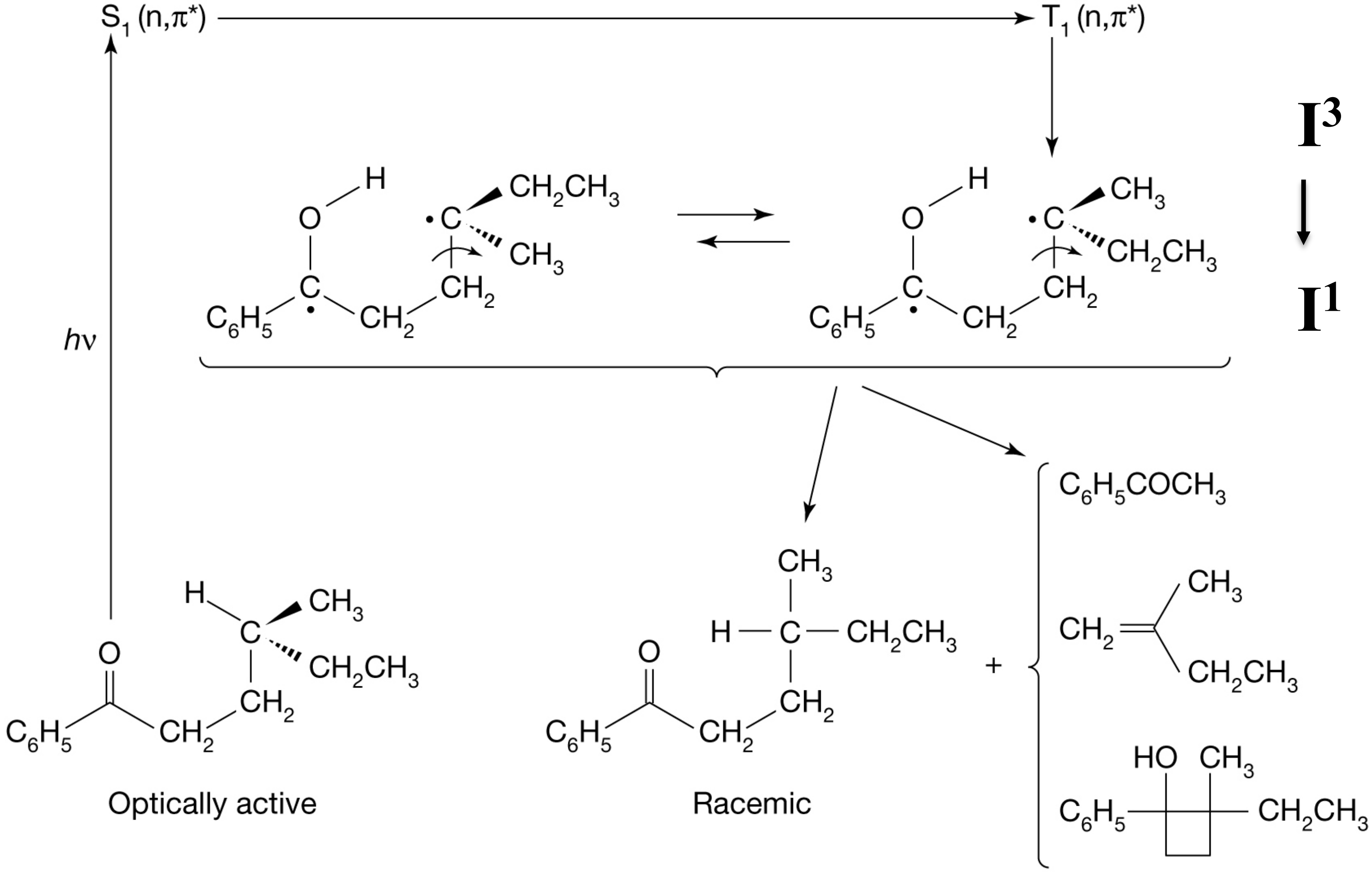
General Photochemical Paradigm

$$R \xrightarrow{h\nu} P$$

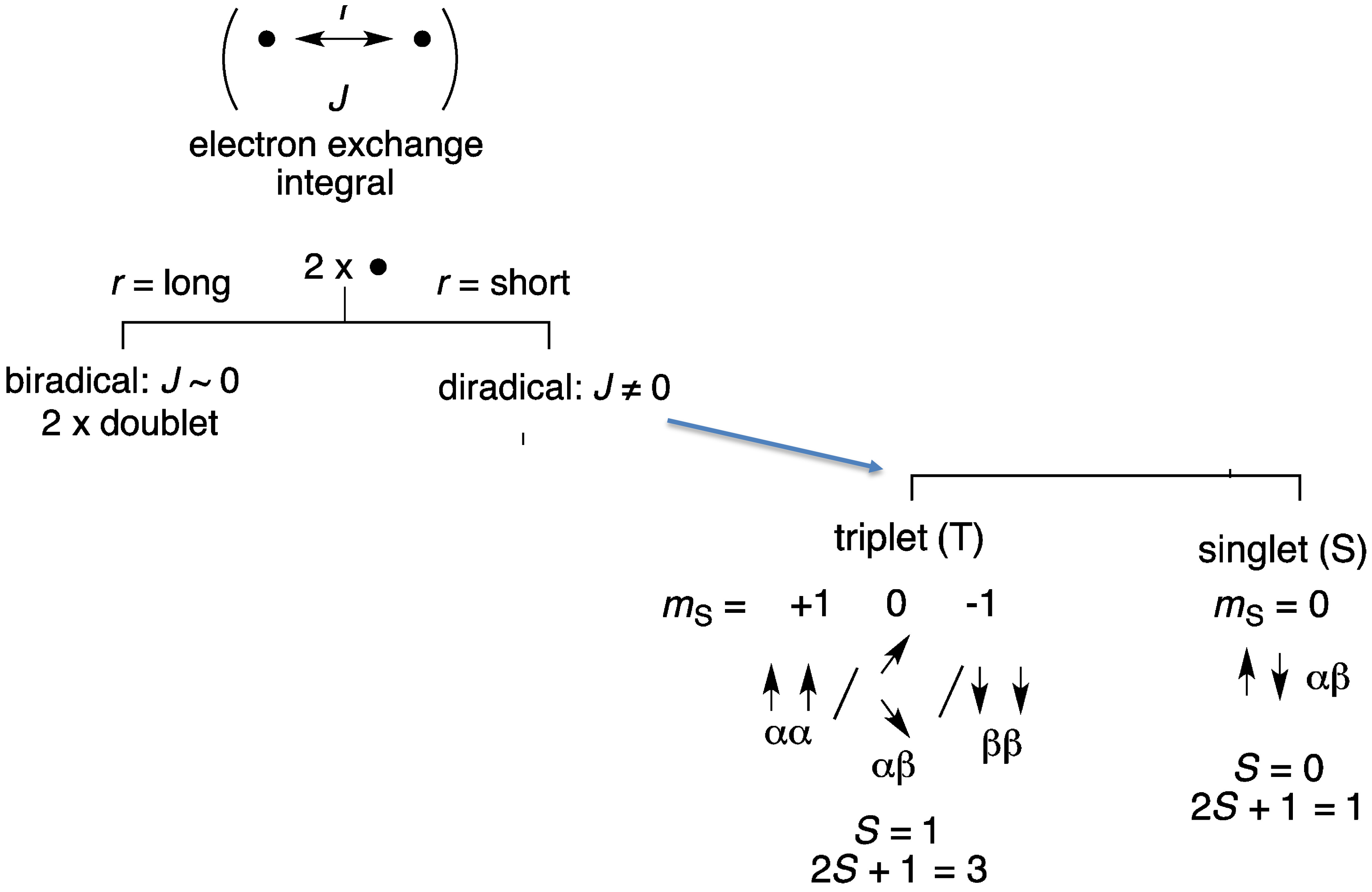
$$R \xrightarrow{h\nu} {}^*R \longrightarrow I \longrightarrow P$$

$$R \xrightarrow{h\nu} {}^{1*}R \xrightarrow{ISC} {}^{3*}R \longrightarrow {}^{3}I \xrightarrow{ISC} {}^{1}I \longrightarrow P$$




S₁ (n,π*)
T₁ (n,π*)
hν
I³
I¹
H
O
C
CH₂CH₃
CH₃
CH₂
C₆H₅
C₆H₅COCH₃
CH₂
HO
Optically active
Racemic
+

What is a diradical and a biradical?



r

J

electron exchange integral

2 x •

r = long

r = short

biradical: $J \sim 0$
2 x doublet

diradical: $J \neq 0$

triplet (T)

m_S = +1 0 -1

αα αβ ββ

$S = 1$
$2S + 1 = 3$

singlet (S)

$m_S = 0$

αβ

$S = 0$
$2S + 1 = 1$

The Electronic Properties of Diradicals, L. Salem *and C. Rowland*., *Angew. Chem. Internat. Edit*. *Eng*.,**1972**, *11*, 92.
L. Salem, Pure & Appl. Chem., **1973**, *33*, 317.

Concerted Reactions That Produce Diradicals and Zwitterions: Electronic, Steric, Conformational, and Kinetic Control of Cycloaromatization Processes, R. K. Mohamed, P. W. Peterson, and Igor V. Alabugin, *Chem. Rev*., **2013**, *113*, 7089.

Do Diradicals Behave Like Radicals? T. Stuyver, B Chen, T. Zeng, P. Geerlings, F. De Proft, and Roald Hoffmann, *Chem. Rev*., **2019**, *119*, 11291.

Diradicals, M. Abe, *Chem. Rev*., **2019**, *113*, 7011.

What controls the singlet-triplet energy gap in molecules and diradicals?

- **Molecules**
- **Intermediates (Diradicals)**

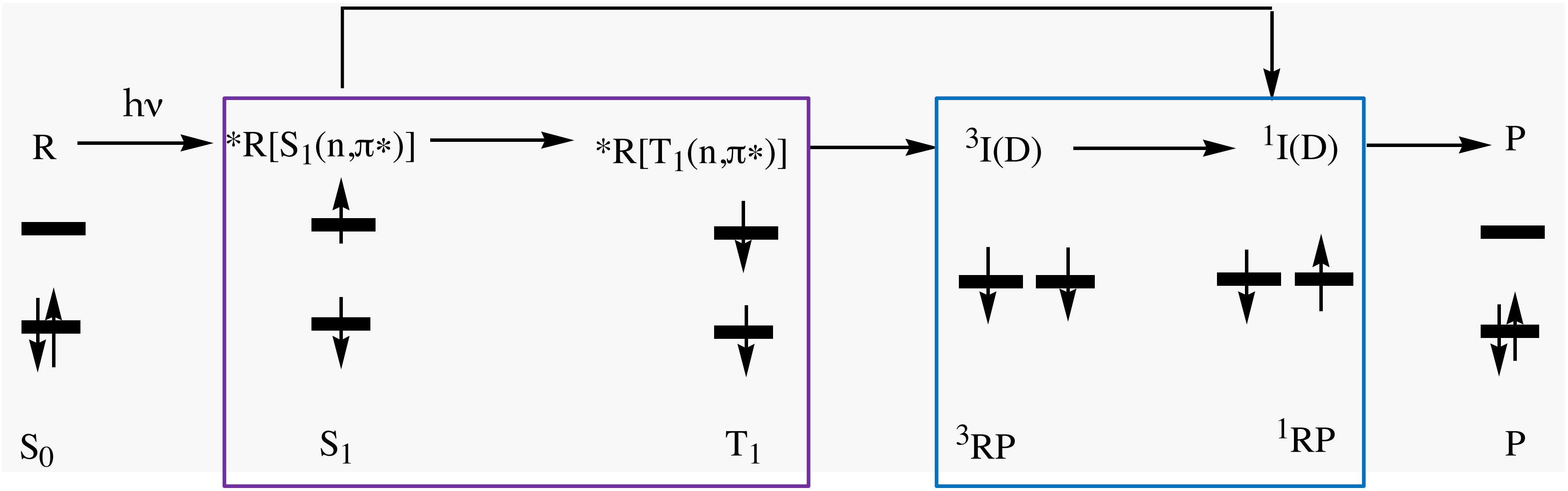
$\Delta E_{ST} = 2J$ in molecules where HOMO-LUMO gap is large

J: exchange integral, depends on the overlap of orbitals with one electron each

$\Delta E_{ST} = J - B$ in intermediates where HOMO-LUMO gap is very small

B: bonding interaction, interaction between nuclei due to the presence of two electrons in a bonding orbital

Electronic Energy Difference between Singlet and Triplet States in Diradical Reactive Intermediates, I(D)



R $\xrightarrow{h\nu}$ $^*R[S_1(n,\pi^*)]$ → $^*R[T_1(n,\pi^*)]$ → $^3I(D)$ → $^1I(D)$ → P

S_0

S_1

T_1

^3RP

^1RP

P

HOMO–LUMO gap large

Only J, no B

$$S_1 > T_1$$

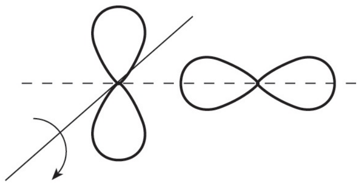
HOMO–LUMO gap small or equal energy

Only J

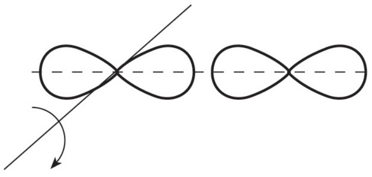
$$S_1 > T_1$$

Both J and B

$$S_1 < T_1$$



Perpendicular orientation

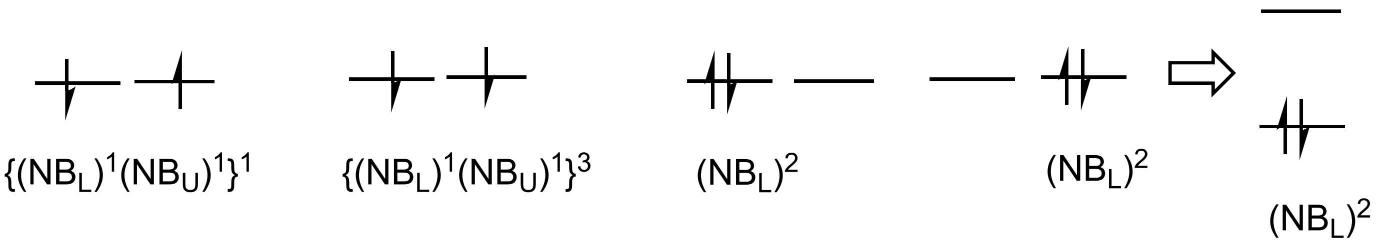


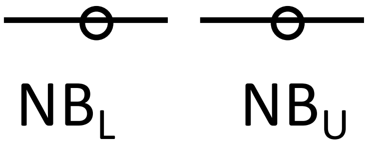
Parallel orientation

Singlet-triplet energy gap

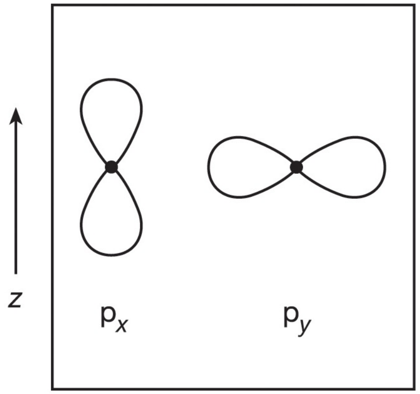
J will be proportional to the electron exchange integral for the $(NB_L)^1(NB_U)^1$ configuration

B will be proportional to the contribution of the $(NB_L)^2$ configuration. The latter corresponds to the bonding contribution.

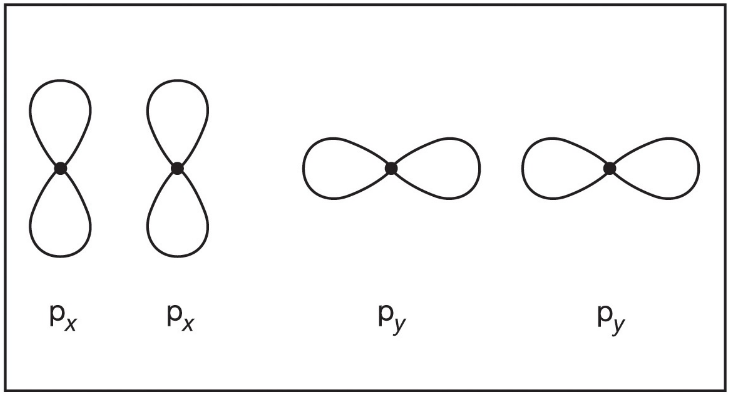




$$\Delta E_{ST} = J - B$$



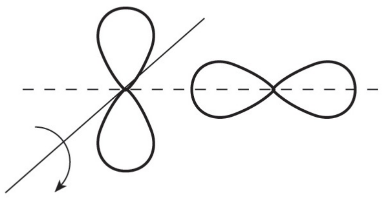
Good orientation for spin–orbit coupling



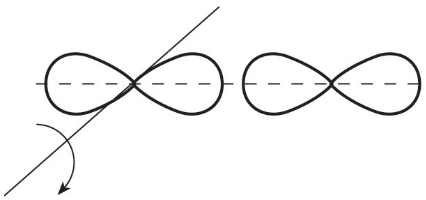
Poor orientations for spin–orbit coupling

Energy Ordering in Diradicals Depends on Values of J and B

$$\Delta E_{ST} = J - B$$



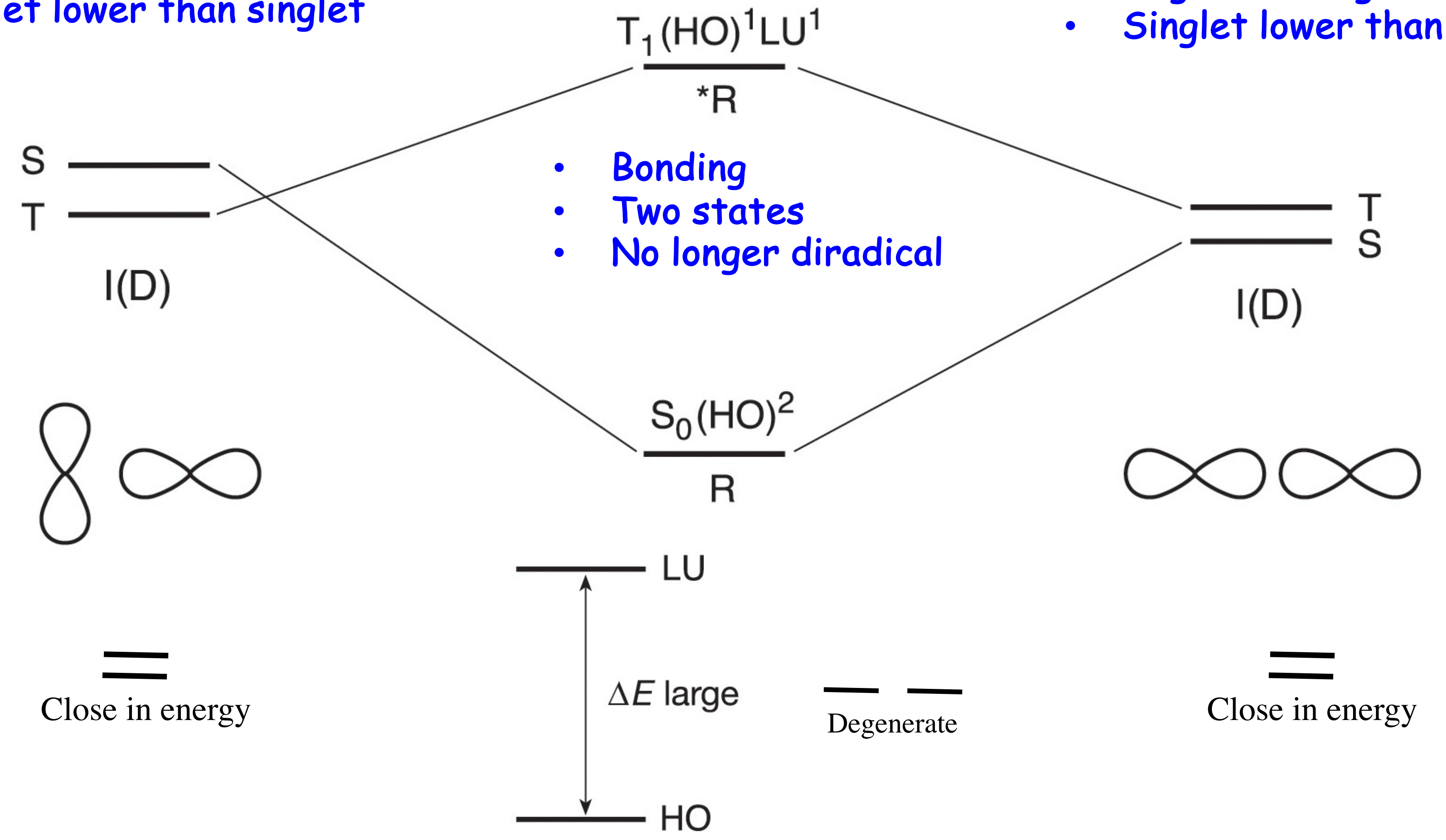
Perpendicular orientation



Parallel orientation

- No bonding
- Triplet lower than singlet

- Slight bonding
- Singlet lower than triplet

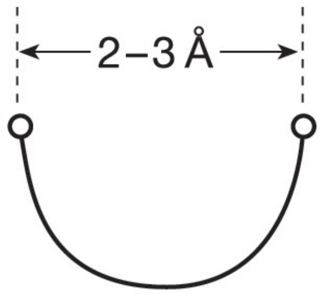


- Bonding
- Two states
- No longer diradical

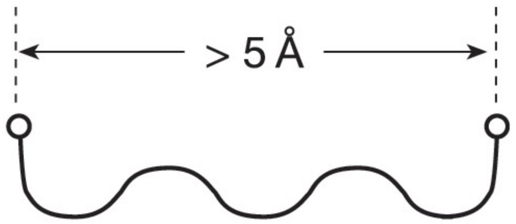
Salem's rules for ISC in diradicals-1

(1) The value of the exchange interaction, J, between the two radical centers is less than the strongest available magnetic coupling mechanism.

In order to mix the S and T states of I(D) effectively, <u>the two states must have essentially the same energy</u>, i.e., they must be very close to degenerate. Since J causes the energy of the S and T state to "split," the value of J must approach zero if the energies of the S and the T state of I(D) are to become degenerate and mix effectively.



J large, ISC slow

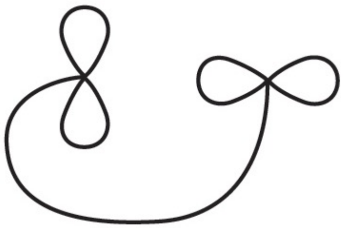


J small, ISC fast

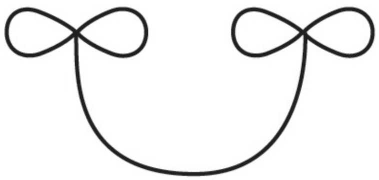
Salem's rules for ISC in diradicals-2

(2) The non-bonding orbitals of the diradical are in an orbital orientation that can interact to some extent and can create orbital angular momentum that couples with the spin angular momentum during the ISC step.

In order to generate angular momentum an orbital jump from a "$p_Z \rightarrow p_X$" type is required. The best orbital orientation for spin-orbit mixing is when the two non-bonded orbitals of the diradical are at a 90^0 orientation with respect to one another.



Good orientation for ISC at any separation

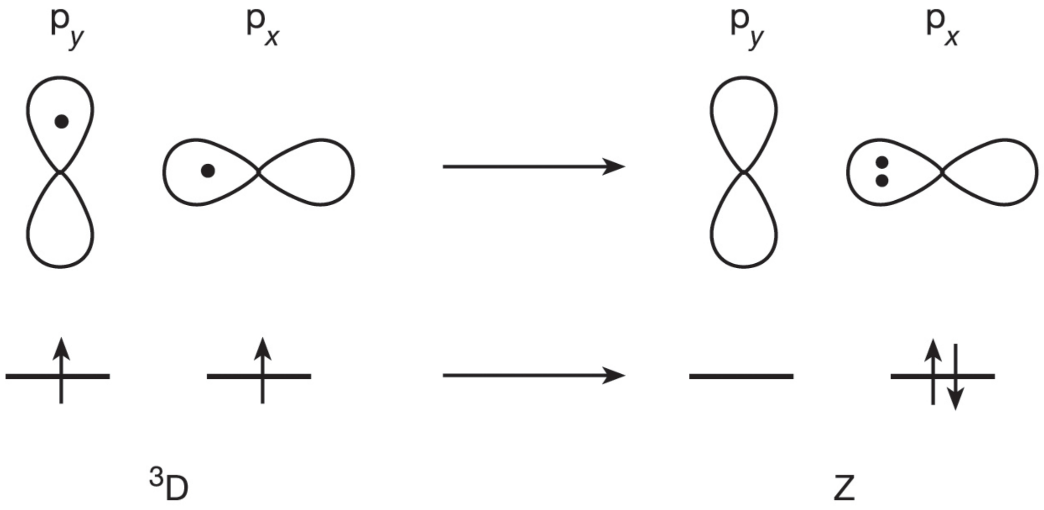


Poor orientation for ISC at any separation

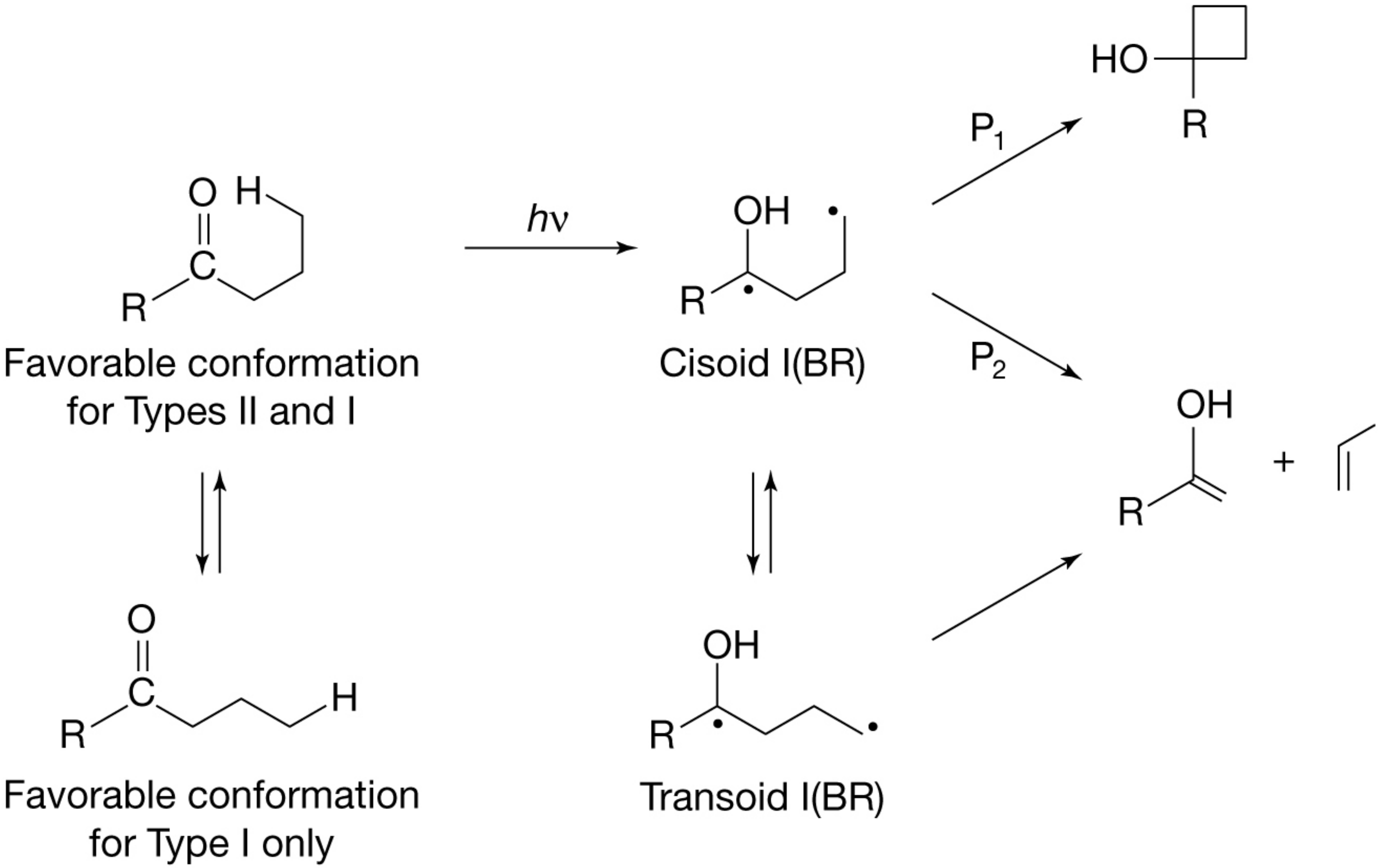
Salem's rules for ISC in diradicals-3

(3) The degree of electron pairing character in the singlet can become significant during the ISC step.

In order to effectively generate orbital angular momentum, the electron must jump from one orbital to the other half occupied orbital which is at a 90^0 orientation, as the singlet is created. This produces a situation for which there are two electrons in a non-bonding orbital to a "zwitterionic" structure (^{1}(Z)). Thus, for the most effective creation of angular momentum, the singlet must possess a certain amount of spin paired character.



Conformation dependent product formation



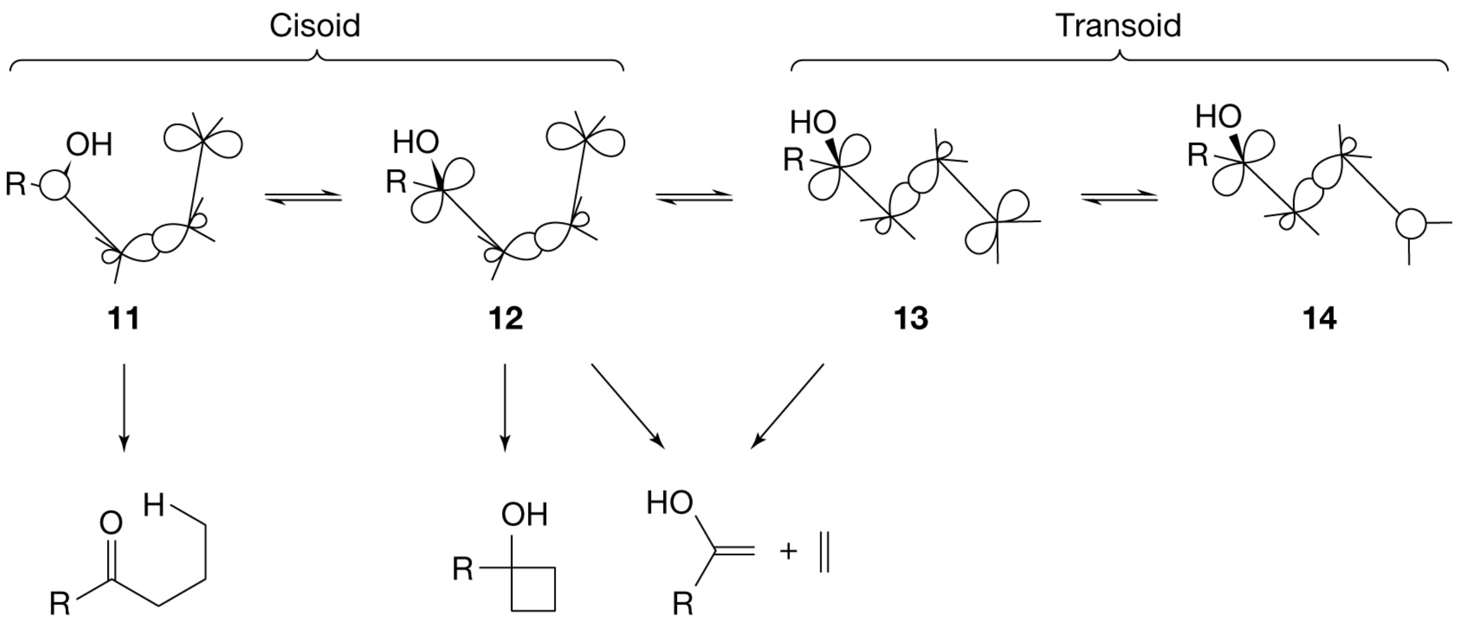
Favorable conformation
for Types II and I

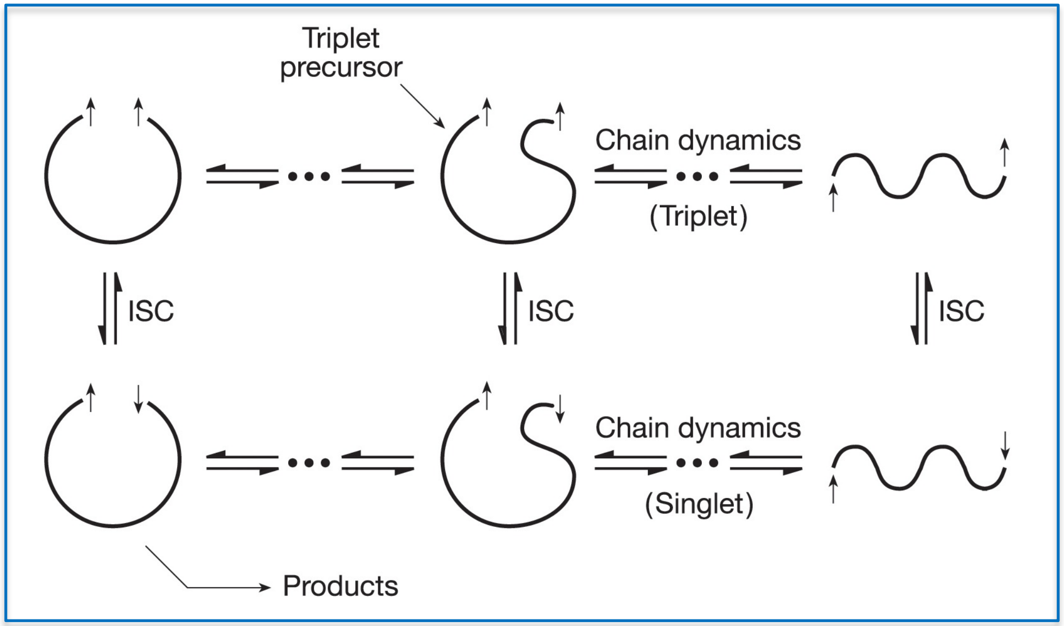
Cisoid I(BR)

Favorable conformation
for Type I only

Transoid I(BR)

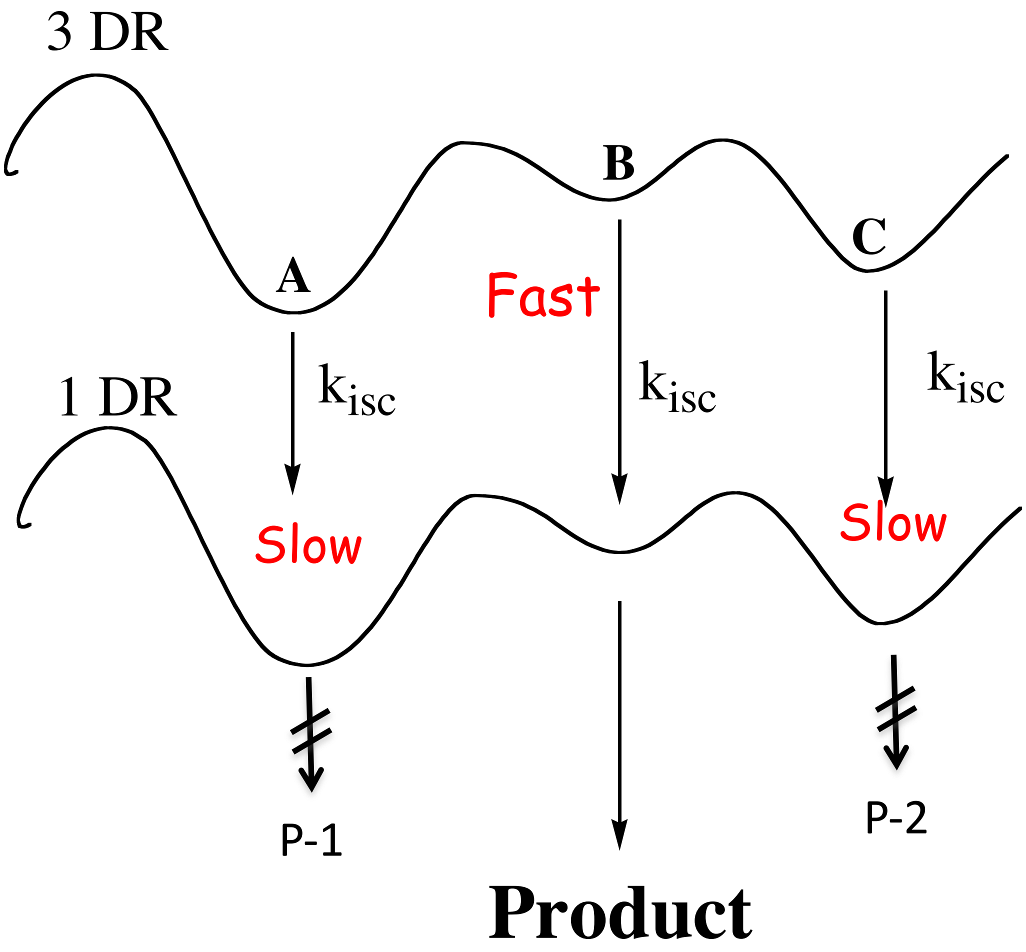
Conformation dependent ISC and its effect on product distribution



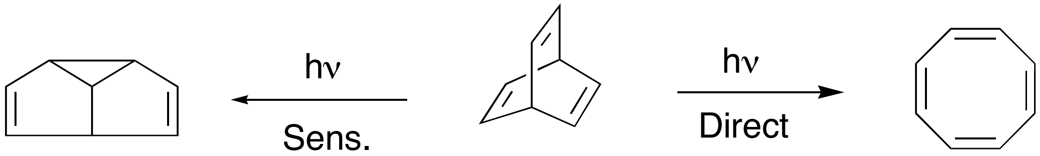


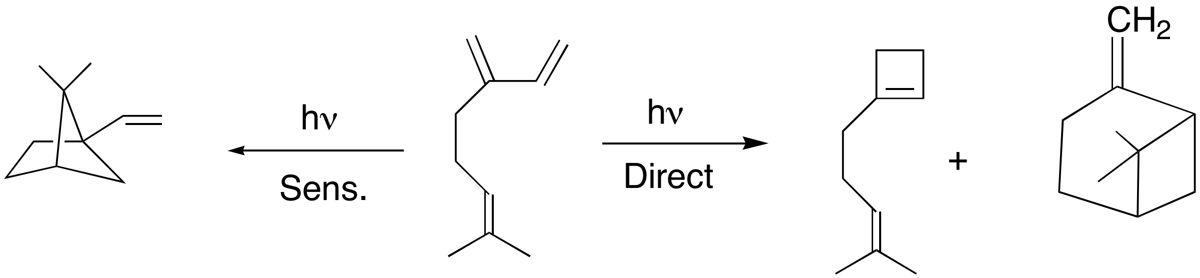
Not all conformations would have the same J, and orientation of the two p-orbitals

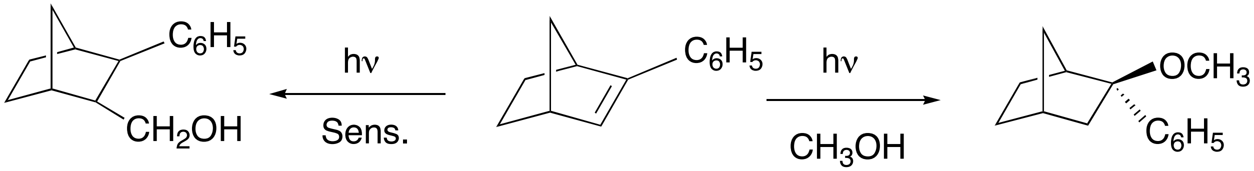
Conformation dependent ISC and its effect on product distribution

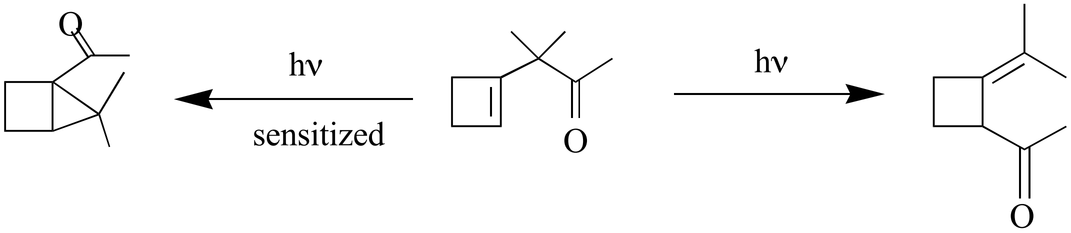


Excited Singlet and Triplet May Undergo Different Reactions



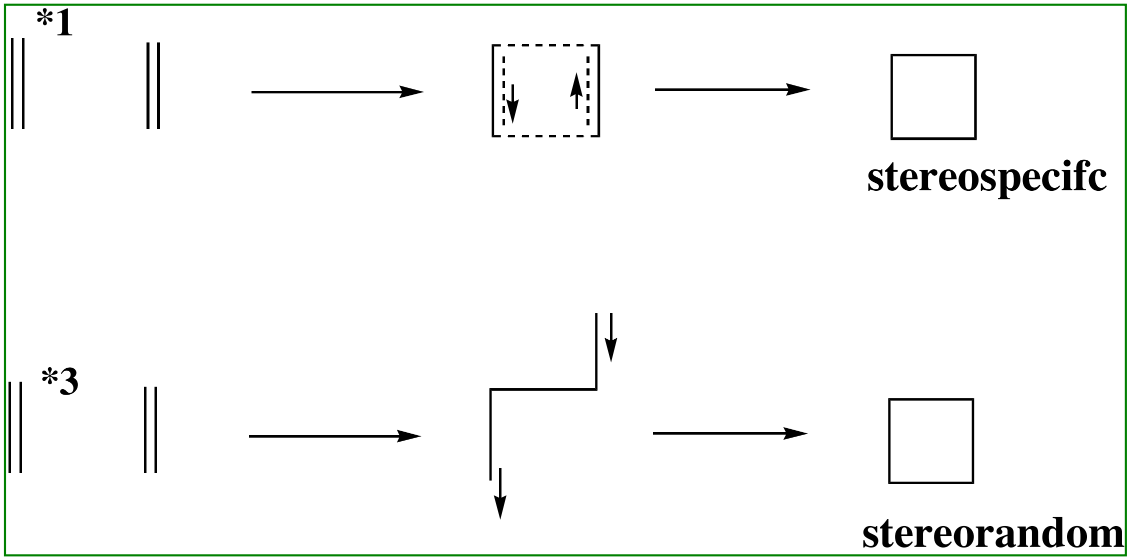


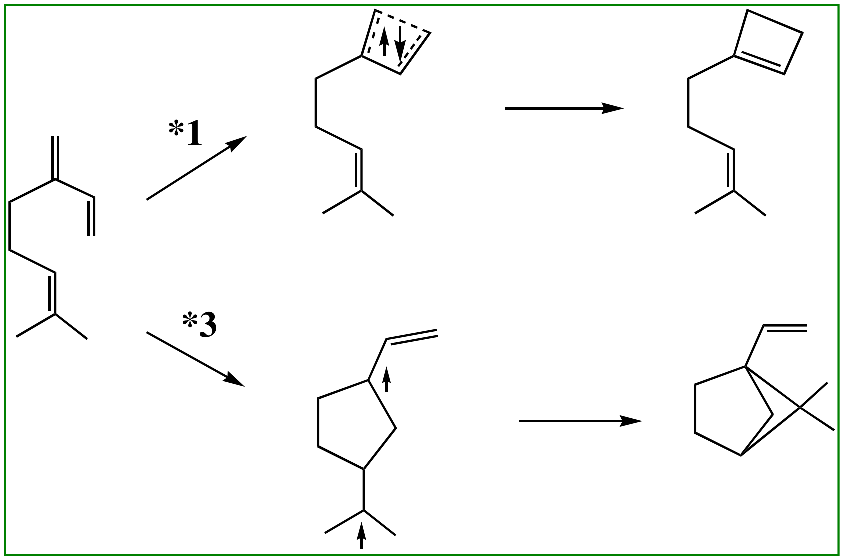




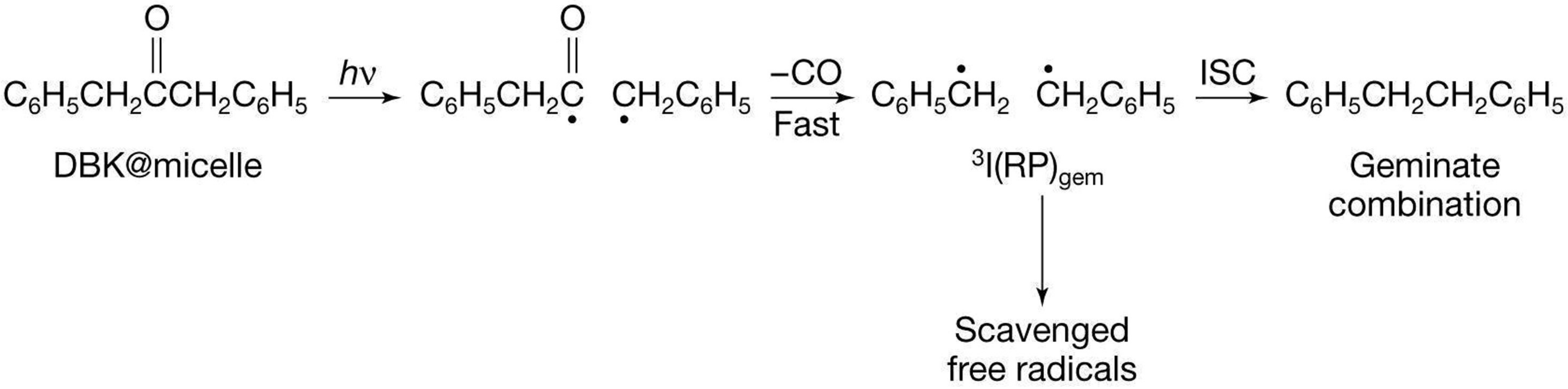
Why excited singlet and triplet give different products?

Loose and Tight Biradicals





Photochemistry of dibenzyl ketone as an exemplar of cage effect



$$C_6H_5CH_2\overset{O}{\overset{\|}{C}}CH_2C_6H_5 \xrightarrow{h\nu} C_6H_5CH_2\overset{O}{\overset{\|}{\underset{\bullet}{C}}}\quad \underset{\bullet}{C}H_2C_6H_5 \xrightarrow[\text{Fast}]{-CO} C_6H_5\dot{C}H_2\quad \dot{C}H_2C_6H_5 \xrightarrow{\text{ISC}} C_6H_5CH_2CH_2C_6H_5$$

DBK@micelle

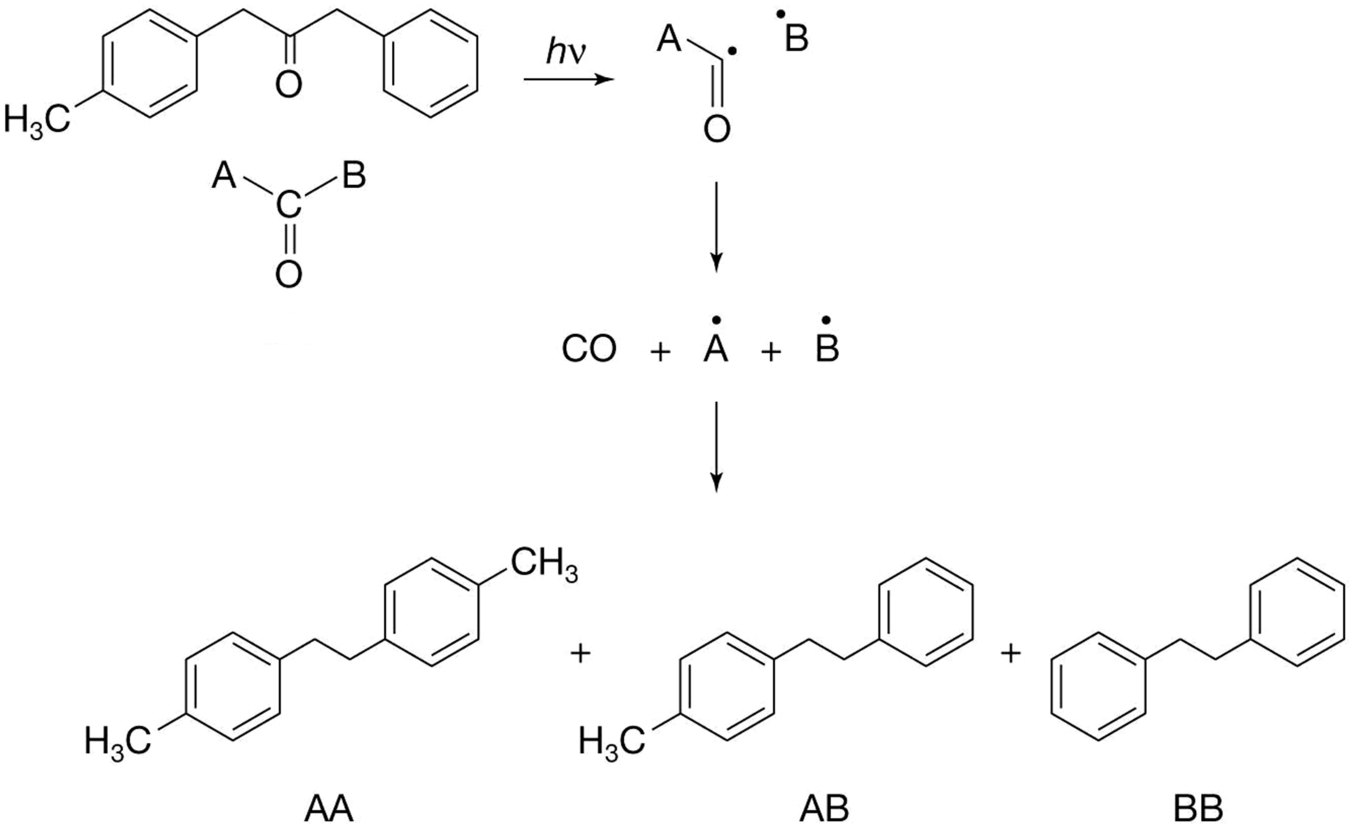
$^3I(RP)_{gem}$

$\downarrow$

Scavenged free radicals

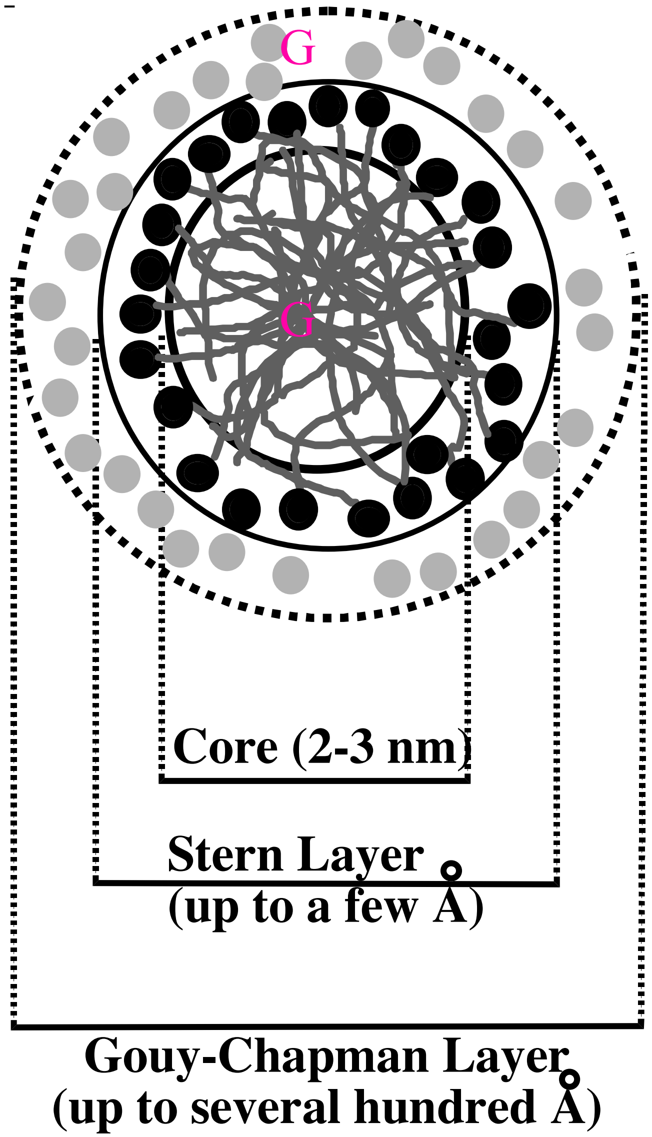
Geminate combination

Definition of cage effect



$$\text{Cage effect (\%)} = \frac{[AB] - ([AA] + [BB])}{([AB] + [AB] + [BB])} \times 100$$

Schematic representation of a guest@micelle complex

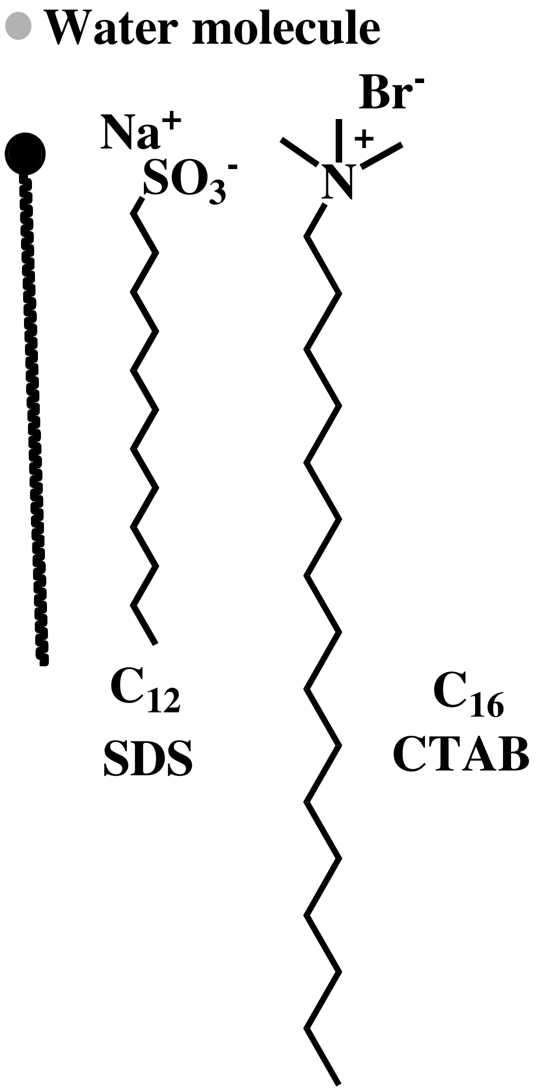


Core (2-3 nm)

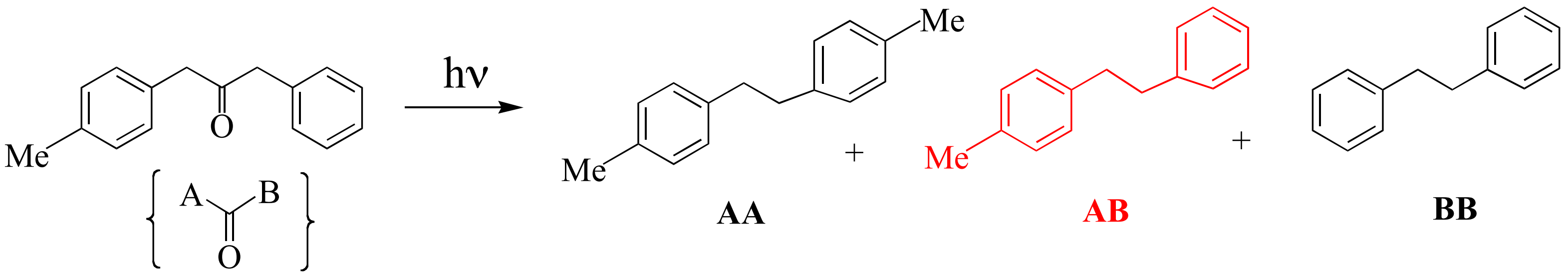
Stern Layer
(up to a few Å)

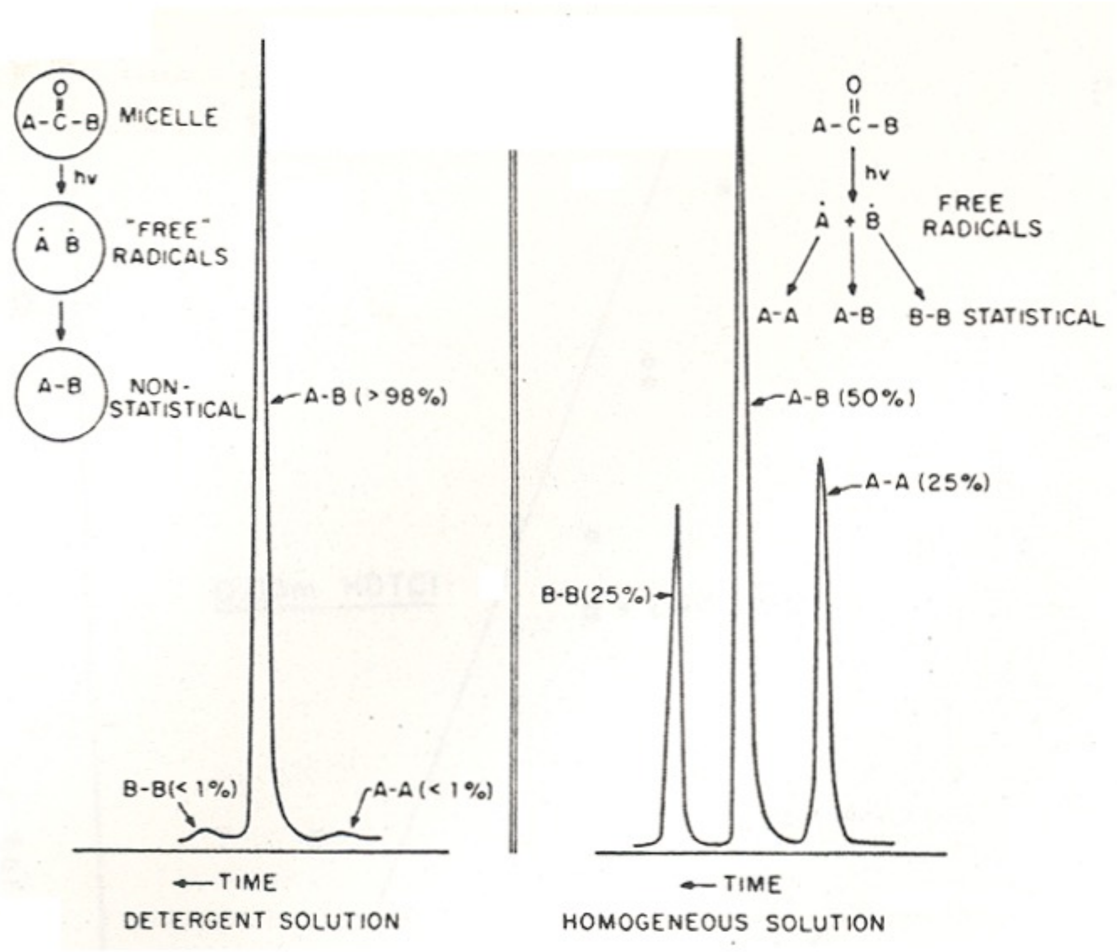
Gouy-Chapman Layer
(up to several hundred Å)

Surfactant monomers



A comparison between solution and micellar irradiations

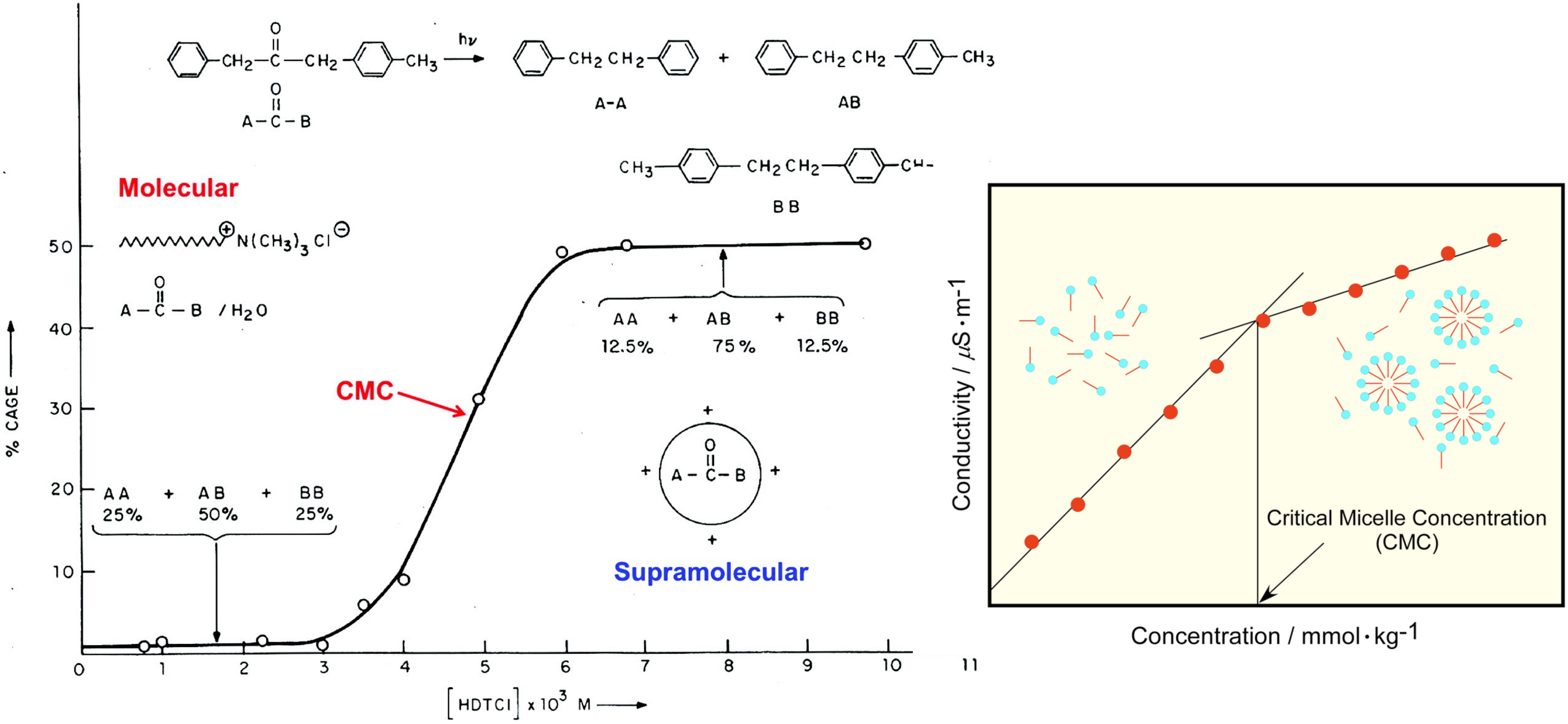




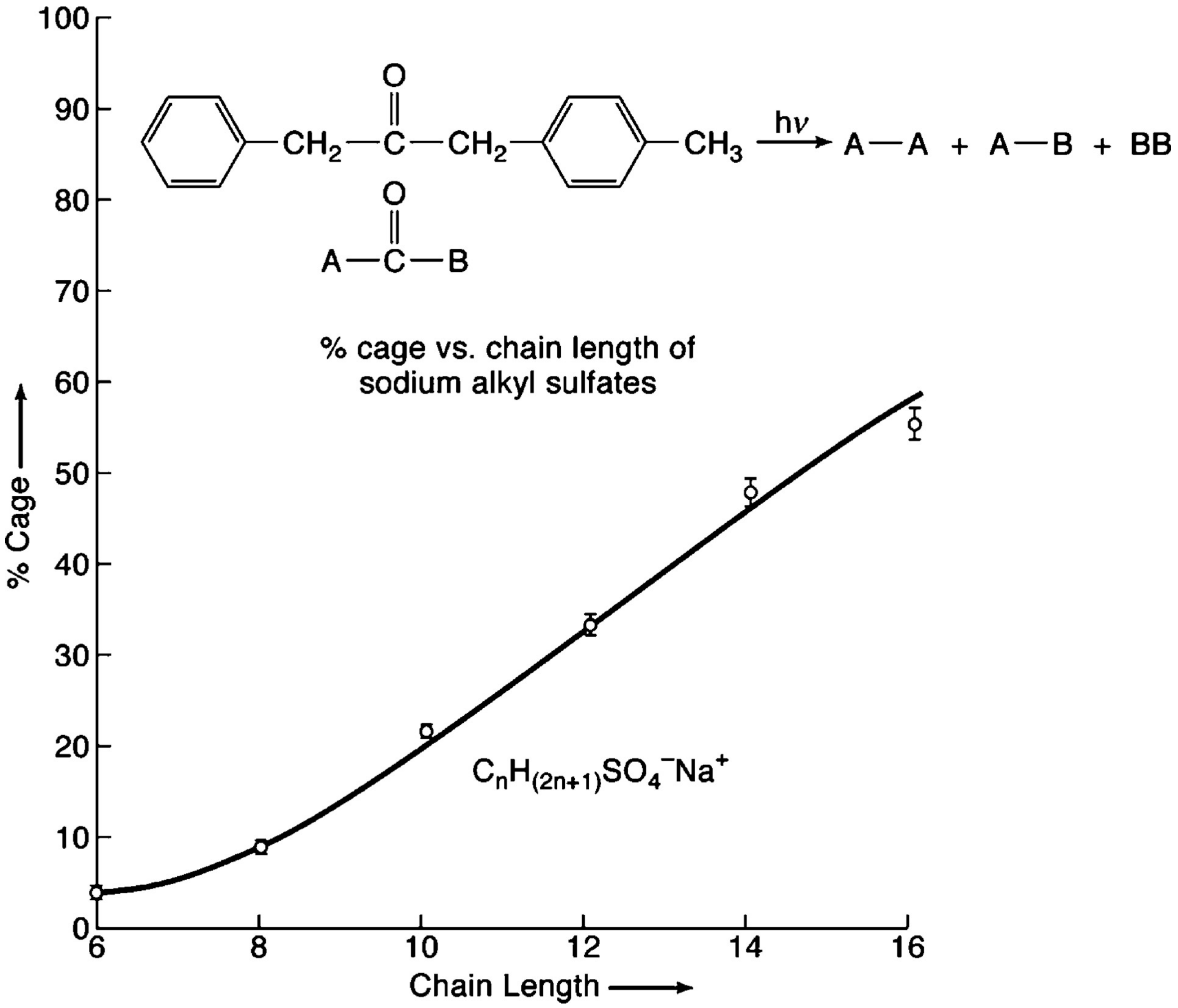
GC traces of product distributions upon irradiation in solution and in HDTCl micelle

In micellar solutions the % cage depends on the surfactant concentration

Cage effect dramatically increases at a certain concentration of surfactant



In micellar solutions the % cage depends on the the cage size



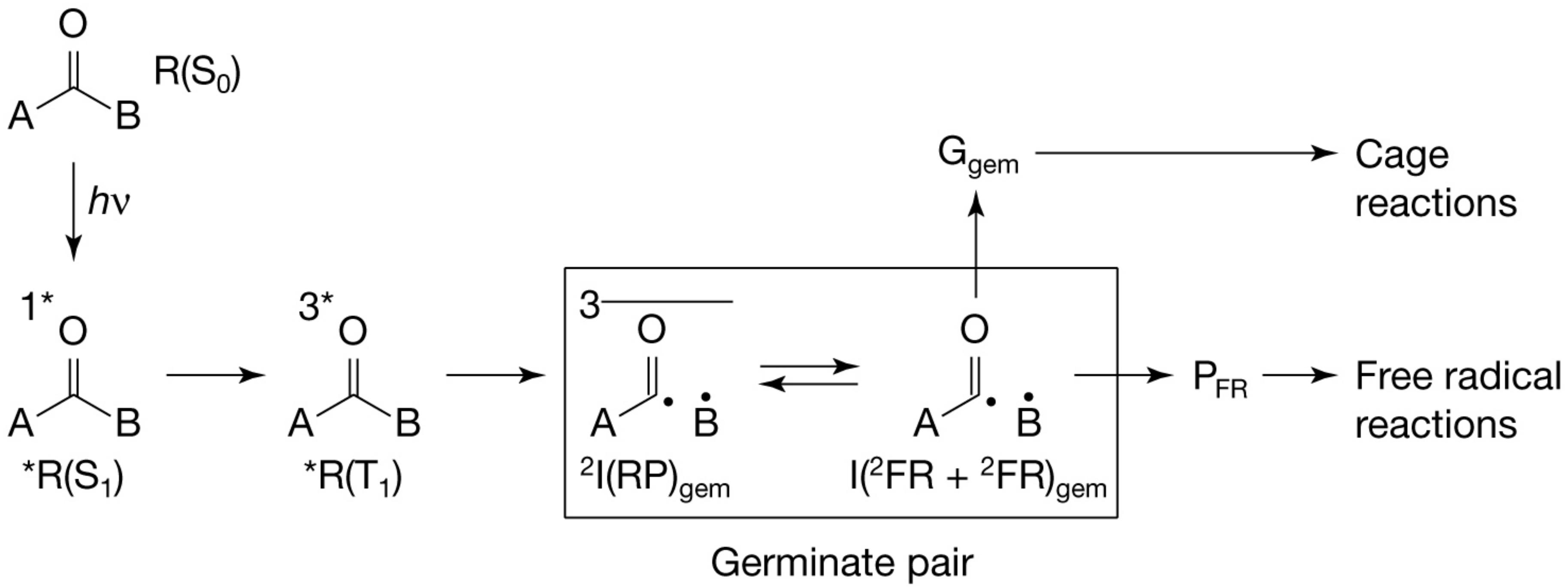
Sulfate surfactants

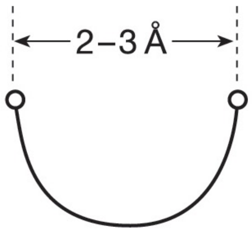
$CH_3(CH_2)_nOSO_3Na$

Reactive radicals escape from smaller cages more easily.

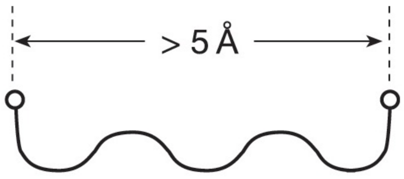
Bigger micelles,
more hydrophobic cage,
slower exit to water

Intersystem Crossing in Radical Pairs





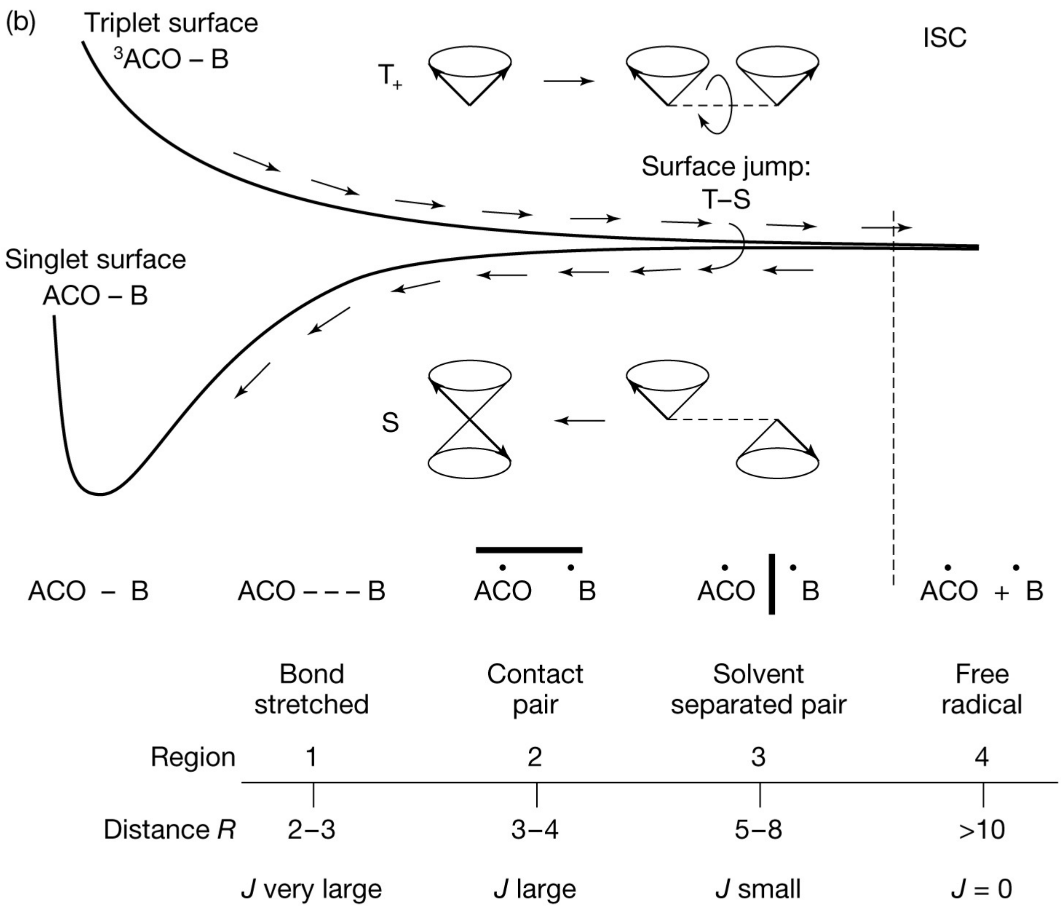
J large, ISC slow



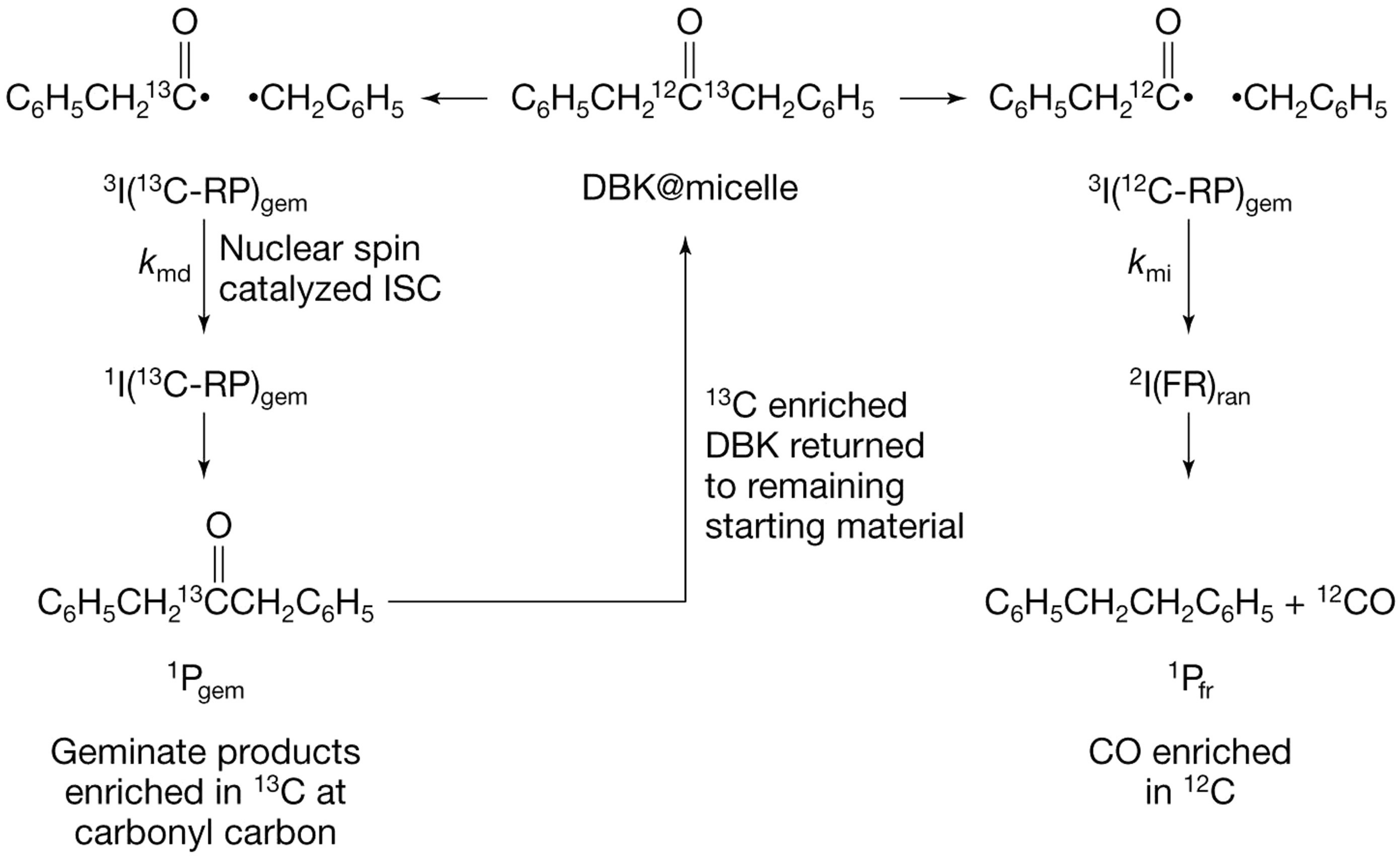
J small, ISC fast

Spin Dynamics - pictorial view

The system, in its T_1 state, slides down along the T_1 surface energy. This correspond to an increased distance between the two nuclei: the bond breaking step occurs.



Cage effect and nuclear isotope effect



$C_6H_5CH_2{}^{13}C(=O)\bullet \quad \bullet CH_2C_6H_5 \longleftarrow C_6H_5CH_2{}^{12}C(=O){}^{13}CH_2C_6H_5 \longrightarrow C_6H_5CH_2{}^{12}C(=O)\bullet \quad \bullet CH_2C_6H_5$

$^3I(^{13}C\text{-}RP)_{gem}$

DBK@micelle

$^3I(^{12}C\text{-}RP)_{gem}$

k_{md} Nuclear spin catalyzed ISC

k_{mi}

$^1I(^{13}C\text{-}RP)_{gem}$

$^2I(FR)_{ran}$

^{13}C enriched DBK returned to remaining starting material

$C_6H_5CH_2{}^{13}C(=O)CH_2C_6H_5$

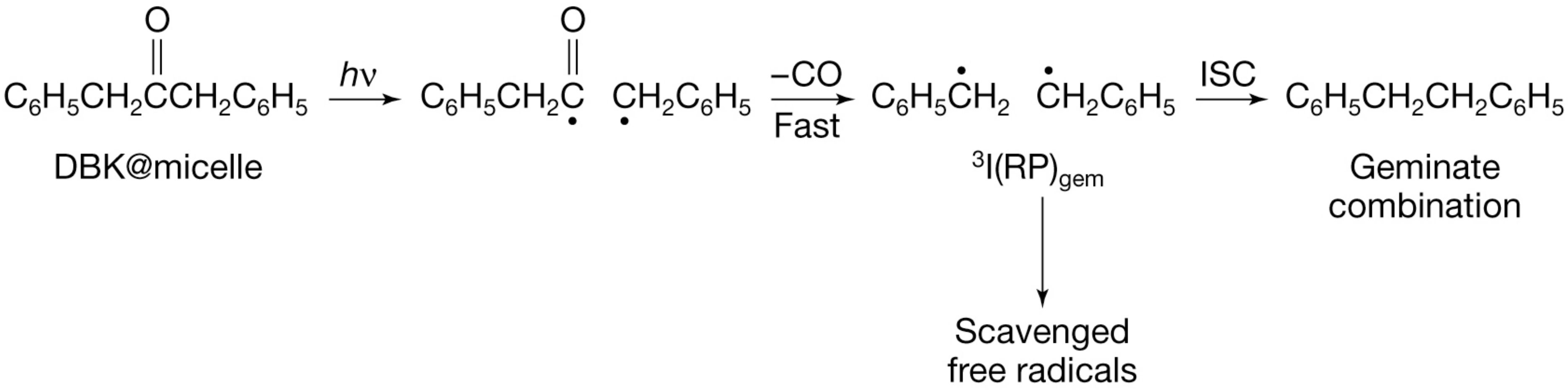
$C_6H_5CH_2CH_2C_6H_5 + {}^{12}CO$

$^1P_{gem}$

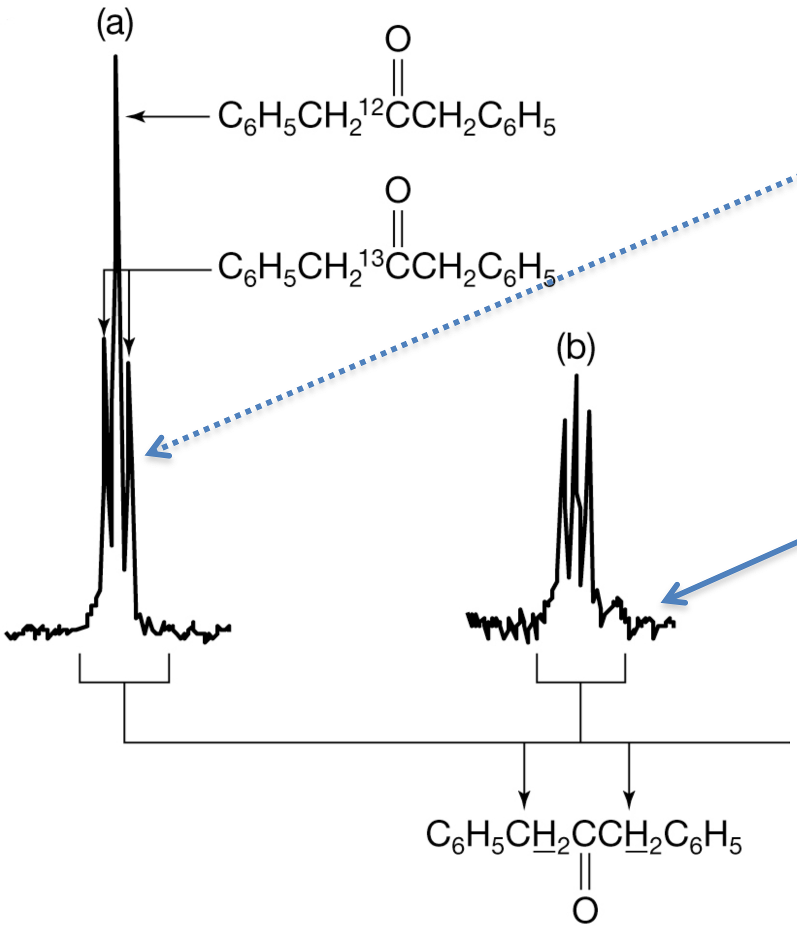
$^1P_{fr}$

Geminate products enriched in ^{13}C at carbonyl carbon

CO enriched in ^{12}C



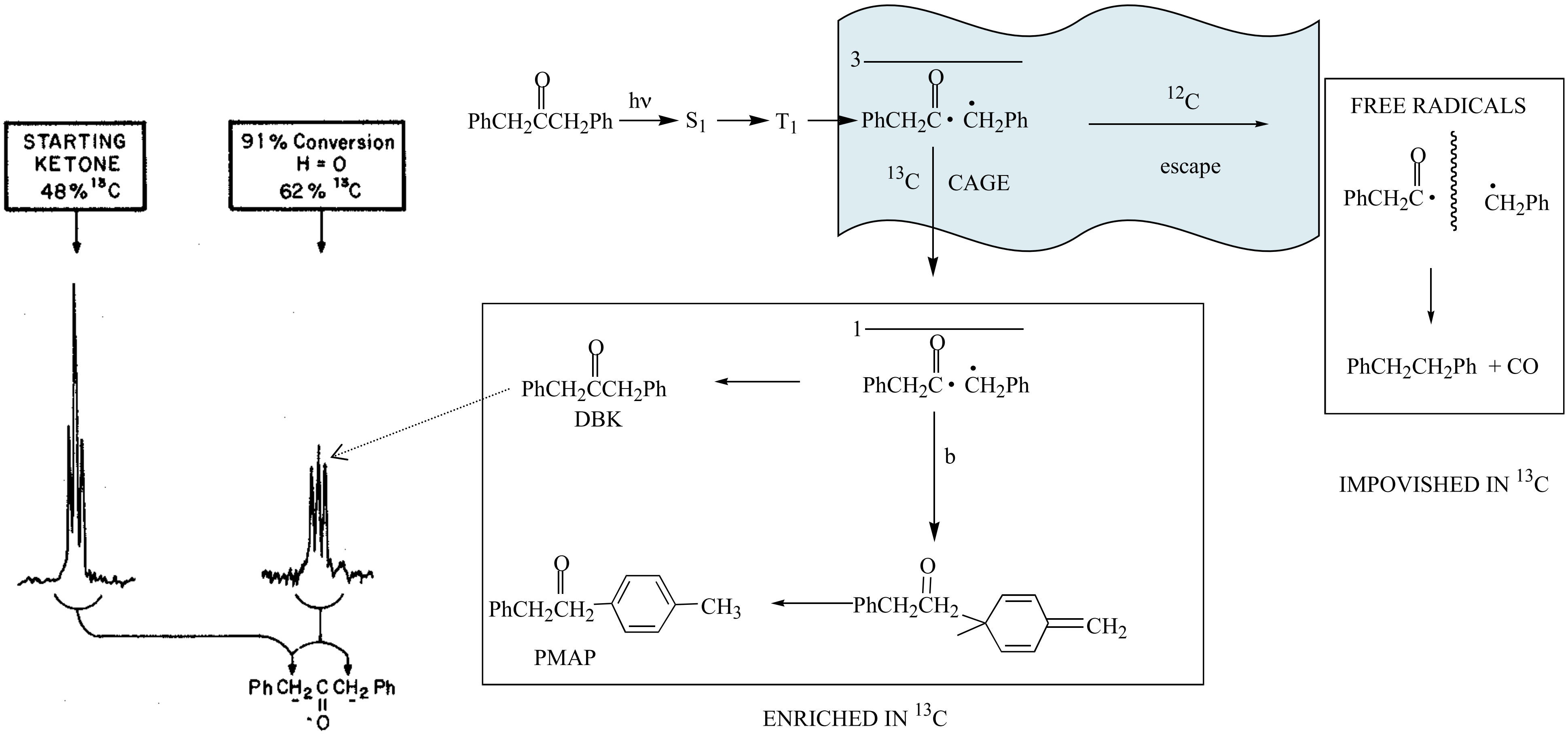
$$C_6H_5CH_2\overset{O}{\overset{\|}{C}}CH_2C_6H_5 \xrightarrow{h\nu} C_6H_5CH_2\overset{O}{\overset{\|}{\underset{\bullet}{C}}}\ \ \underset{\bullet}{C}H_2C_6H_5 \xrightarrow[\text{Fast}]{-CO} C_6H_5\dot{C}H_2\ \ \dot{C}H_2C_6H_5 \xrightarrow{\text{ISC}} C_6H_5CH_2CH_2C_6H_5$$



(a) Initial sample of $^{13}C=O$ enriched DBK

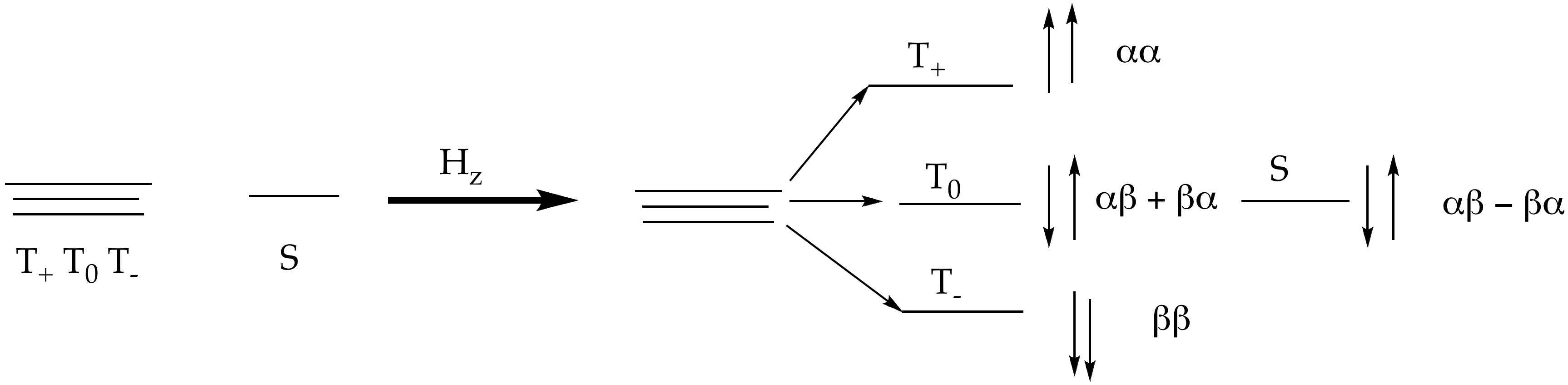
(b) The degree of $^{13}C=O$ in DBK increases with photolysis (90% conversion)

Cage effect can be utilized for isotope enrichment



The competion is between cage escape and hyperfine induced ISC

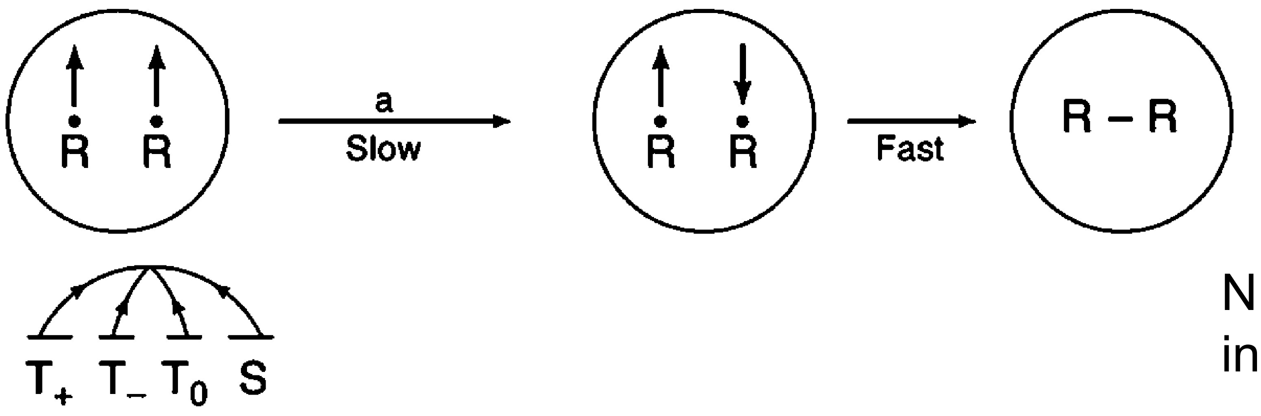
Effect of an applied magnetic field on the T splitting



T levels split apart, T_0 has the same energy as S

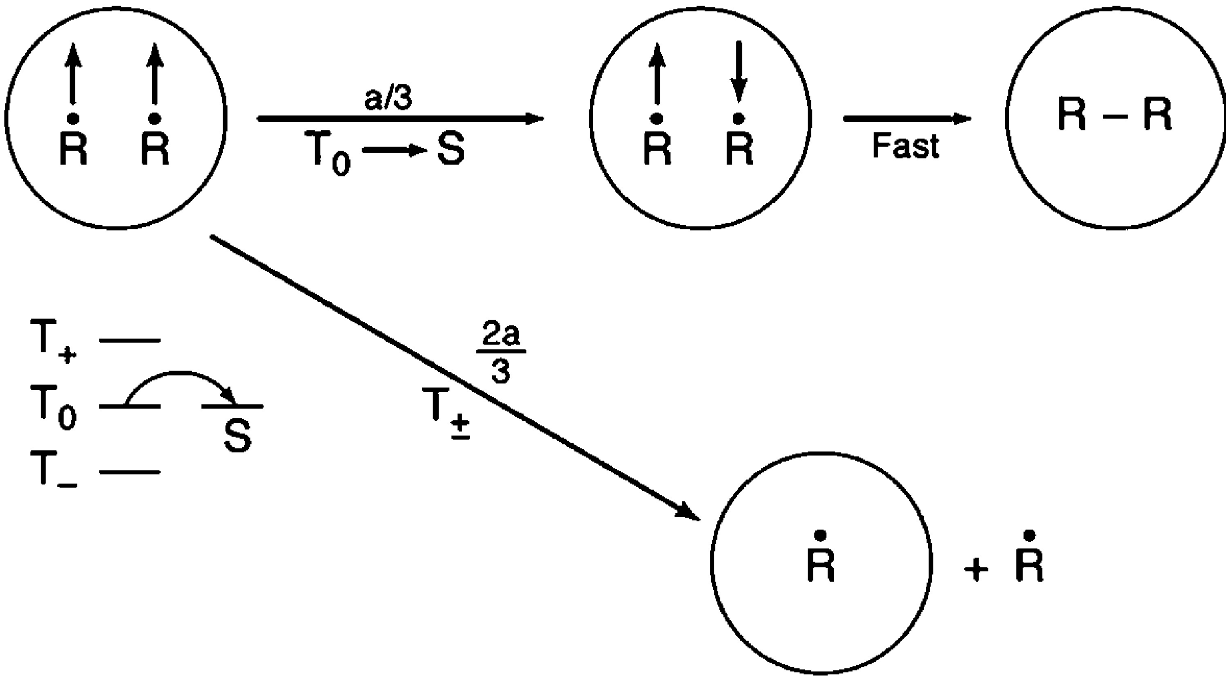
Only T_0 → S   ISC allowed

When $\underset{\sim}{H} = O$ (The earth's magnetic field)



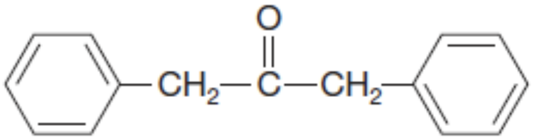
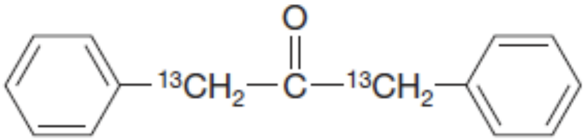
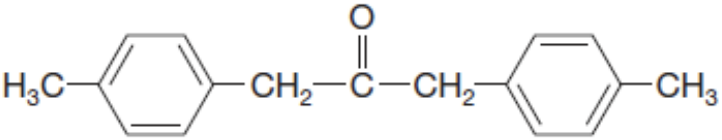
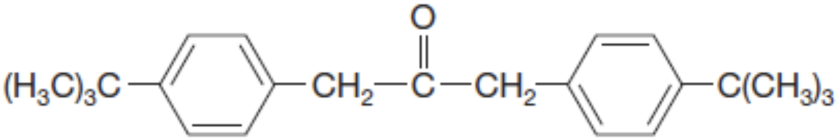
Nuclear isotope effect will increase cage reactions

When $\underset{\sim}{H} > a$



Magnetic field effect will decrease cage reactions

The effect of external magnetic field on the cage effect

Ketone	Cage Effect at 0 G	Cage Effect at 13,000 G
 DBK	31	16
 DBK-2,2′-^{13}C	46	22
 4,4′Di-MeDBK	59	31
 4,4′Di-*t*-BuDBK	95	76

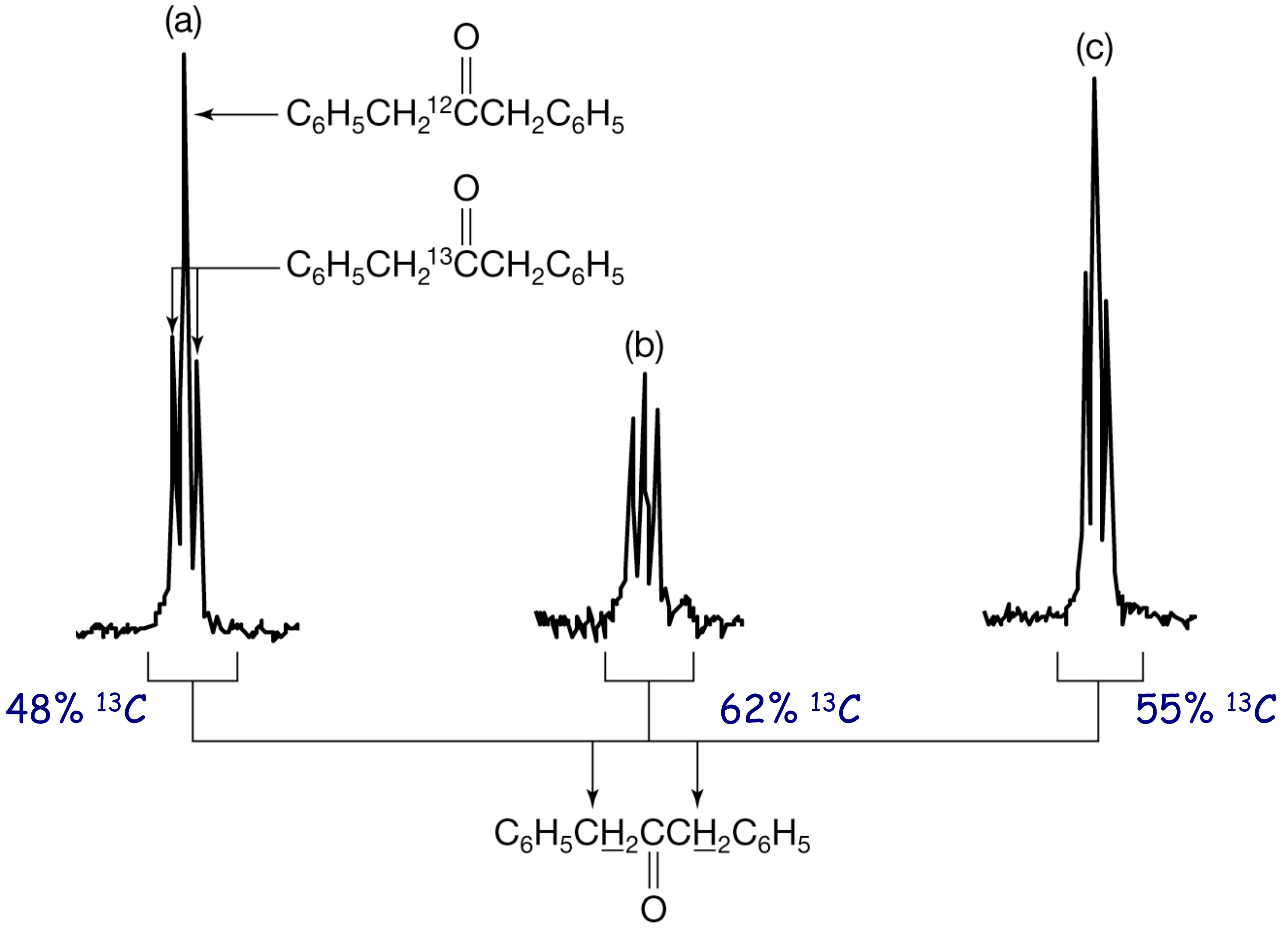
The cage effect decreases. More exit from host cage.

Isotope enrichment decreases in presence of applied magnetic field

Initial

90% photolysis
at 0 applied mag. field

90% photolysis
at 15,000 G applied
mag. field



$C_6H_5CH_2{}^{12}\overset{\overset{\Large O}{\|}}{C}CH_2C_6H_5$

$C_6H_5CH_2{}^{13}\overset{\overset{\Large O}{\|}}{C}CH_2C_6H_5$

$C_6H_5C\underline{H}_2\underset{\underset{\Large O}{\|}}{C}C\underline{H}_2C_6H_5$

48% ^{13}C

62% ^{13}C

55% ^{13}C

Thank You