CHM 535/635

Molecular and Supramolecular Photochemistry

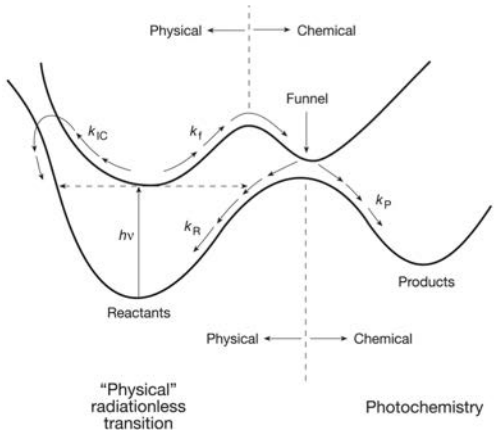
Dynamics of molecules on excited surface

Chapter 6

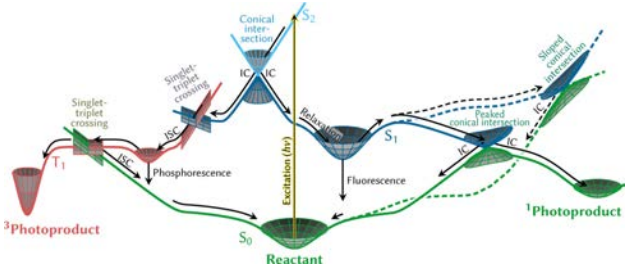
Principles of Molecular Photochemistry: An Introduction

NJT, VR and JCS

A Model for Photochemistry and Photophysics of Organic Molecules



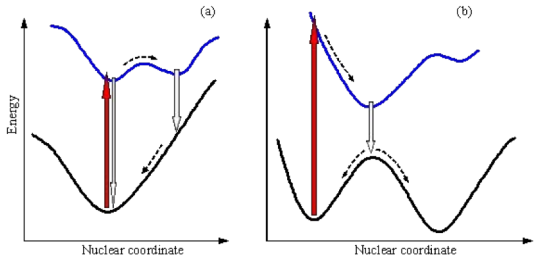
A fancier way of drawing the actions on excited surfaces



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

Radiative transition *vs* Reaction

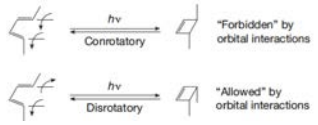
How do molecules move on surfaces?
How molecules navigate between surfaces

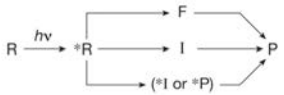


Radiationless Transition

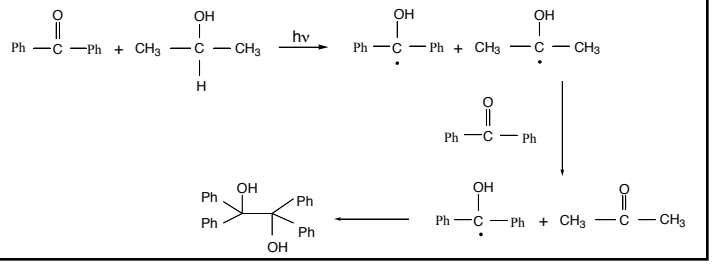
Photoreaction

Concerted; no intermediate involved

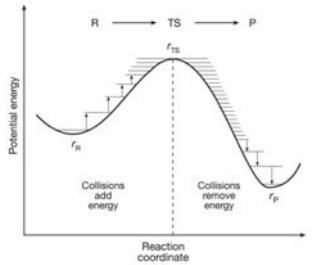




Stepwise; intermediate involved

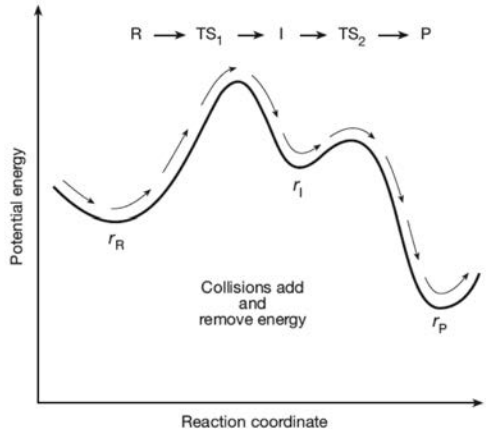


Visualization of Thermal Reactions

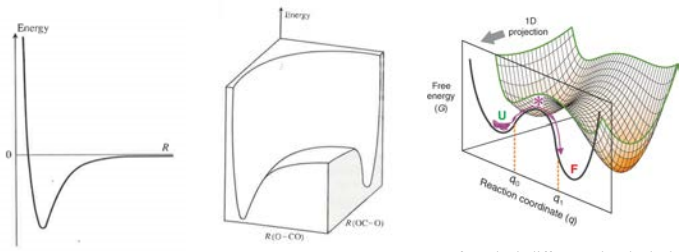


- Transition state connects a single reactant to a single product and it is a saddle point along the reaction course.
- Collisions are a reservoir of continuous energy (~ 0.6 kcal/mol per impact).
- Collisions can add or remove energy from a system.
- Concerned with a single surface.

Visualization of Thermal Reactions



Representation of molecules in more than one dimension

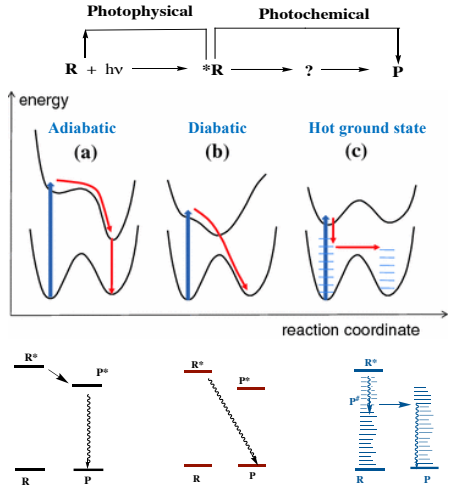


Surfaces look different when looked at and projected on two dimensional surface

To represent molecular motion with more than three atoms one needs 3N–6 space

However, generally polyatomic molecules are represented in two or three dimensional space. This leads to misinterpretation of dynamics.

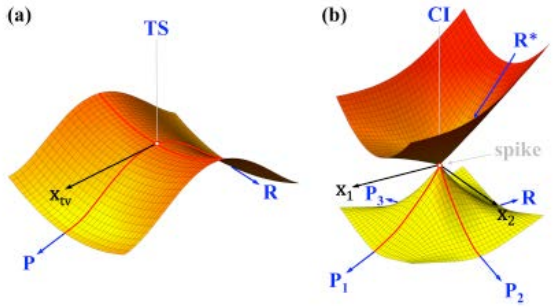
Classification of Photoreactions



Models used to understand reactions on excited surfaces

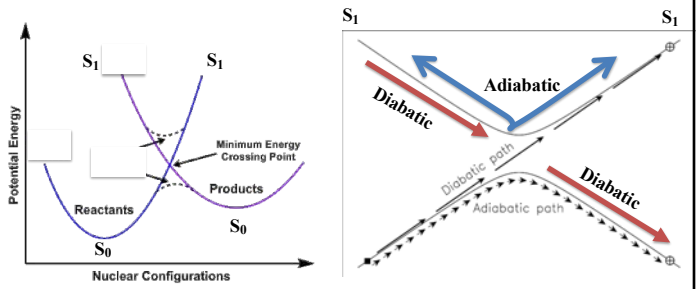
- Adiabatic and diabatic surfaces
- Crossing and avoided crossing
- Funnel
- Conical intersection
- Energy gap law and Fermi's golden rule
- Wave packets vs particles (marbles)

Ground State vs. Excited State Reactions



Thermal Photochemical

Adiabatic and diabatic curves and reactions

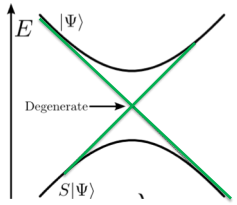


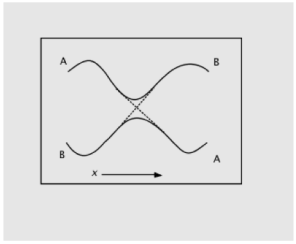
Note: the nomenclature change

Adiabatic: Change in electronic configuration as the reaction progresses

Diabatic: No change in electronic configuration as the reaction progresses

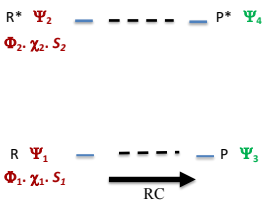
Crossing and avoided crossing

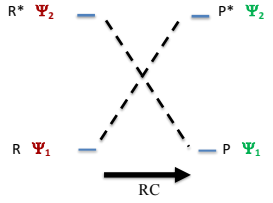


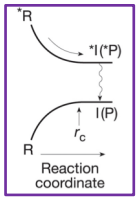


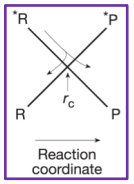
Frequently, two Born–Oppenheimer electronic states (ϕ and ϕ') change their energy as molecular geometry (x) is changed continuously along a path. In the process *their energies may become equal at some points (the surfaces are said to cross, dotted lines in the figure)*. If the electronic states are of the same symmetry, the surface crossing is always avoided in diatomics and usually avoided in polyatomics.

Electronic correlation diagram for a given reaction co-ordinate

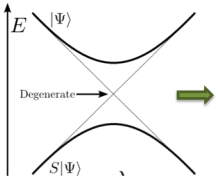


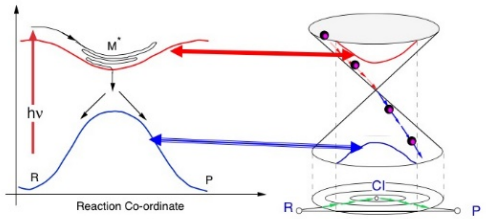






Avoided crossing, true crossing and conical intersection





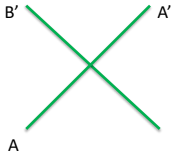
Diatomic

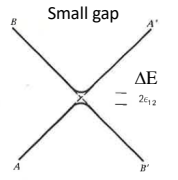
Avoided crossing in two dimensions

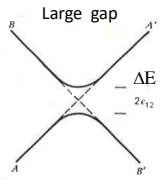
Product appears in ns

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

Product appears in ps-fs





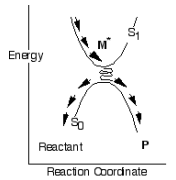


Landau-Zener-Stuecktberg equation

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

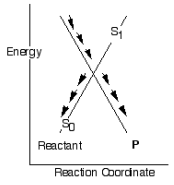
Probability of jump from lower to upper or the reverse

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



Avoided Crossing

Avoided crossing
Real crossing
Conical intersection



Crossing (Conical Intersection)

Wave packets and Particles (De Broglie, $h\nu = mc^2$)

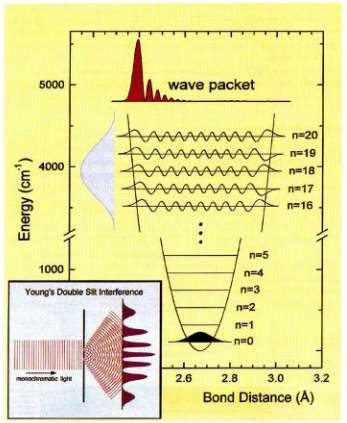
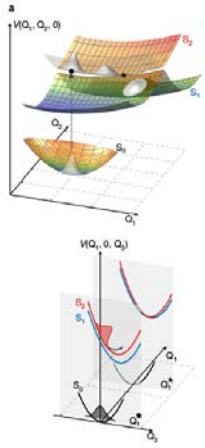


Figure A. The wave packet and wave function limits for molecular systems, in this case a diatomic molecule. The analogy with light interference is depicted – Thomas Young's experiment of 1801 [825].

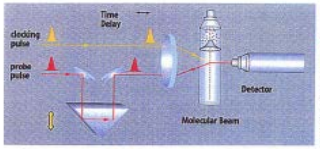


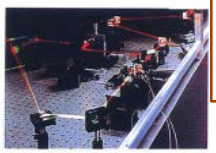
10^{-15} sec time resolution (1980s)

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

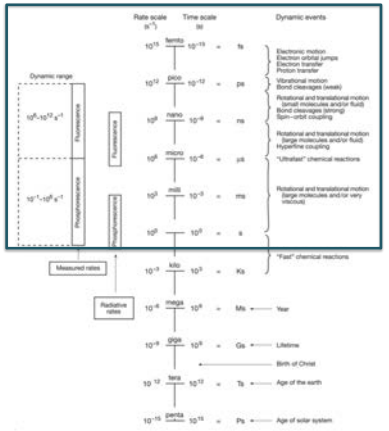
10^{-6} sec time resolution (1960s)

M. Eigen

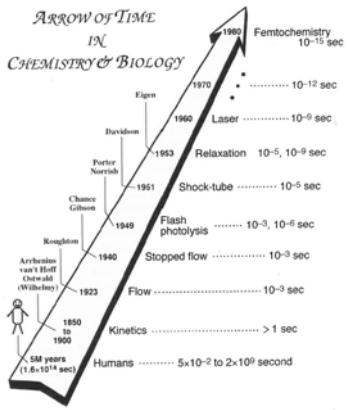
R. G. W. Norrish

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 extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short pulses of energy.*"



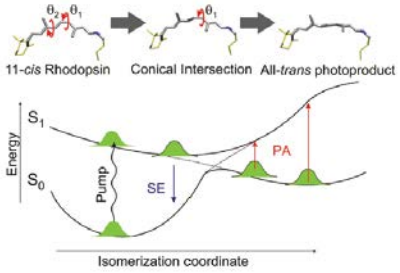
The birth of high speed camera

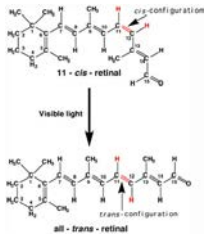


Can a horse fly

Photo series by Eadweard Muybridge, 1870

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





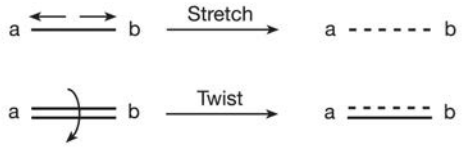
The **wavepacket** initially created in the **FC region** of the excited state of the reactant rapidly evolves along the reaction pathway towards the **conical intersection**, and the SE progressively shifts to the red as the band gap between the excited and ground states narrows. Near the conical intersection 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 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

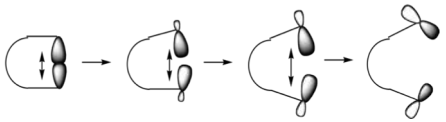
- Bond breaking----cleavage reactions
- Bond twisting-----geometric isomerization
- Addition at one end----abstraction, substitution
- Addition at two ends-----cycloaddition
- Concerted pericyclic reactions---electrocyclization
- Rearrangement

How do bonds break?: Stretching and twisting



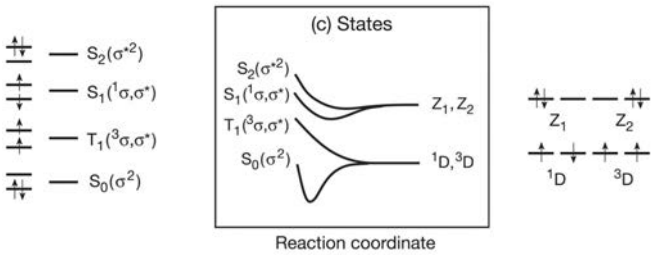
π-bonds break upon twisting

σ-bond break upon stretching

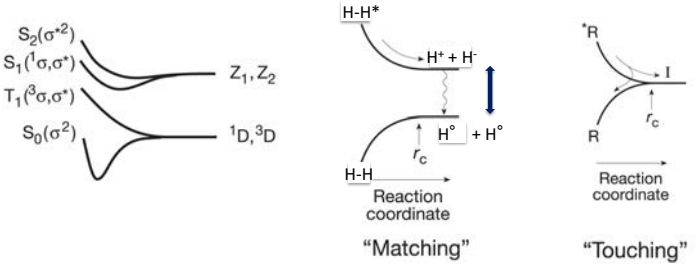


Visualizing photoreactions on surfaces
Photodissociation
A model for breaking σ bond by stretching

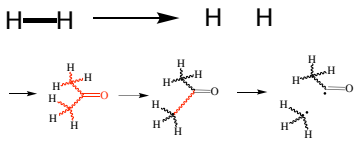
$H-H \rightarrow H + H$ **The Heitler-London model, 1927**

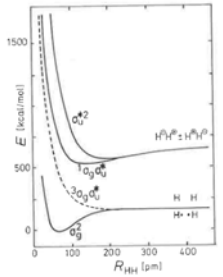


Homolytic photodissociation of I_2, ICN, IBr, CH_3I etc.



Photodissociation of σ bond





H_2

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


W. Heitler


F. London

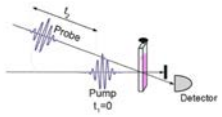
These formed the basis of energy diagrams for photodissociation.

Exemplars for σ bond cleavage in the excited state

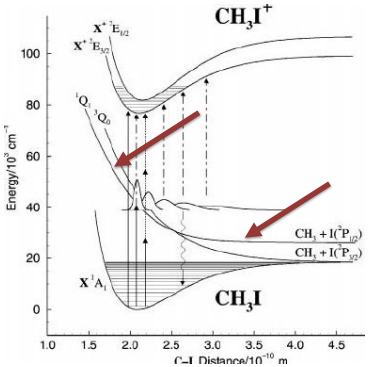
- Photodissociation of CH_3 I
  - Zewail et. al., *J. Chem. Phys*., *83*, 1996, **1985**
  - Zewail et. al., *Chem. Phys. Lett*, *142*, 426, **1987**
- Photodissociation of ICN
  - Zewail et. al., *J. Chem. Phys*., *87*, 2395, **1987**
  - Zewail et. al., *Science*, *241*, 4870, **1988**
  - Zewail et. 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

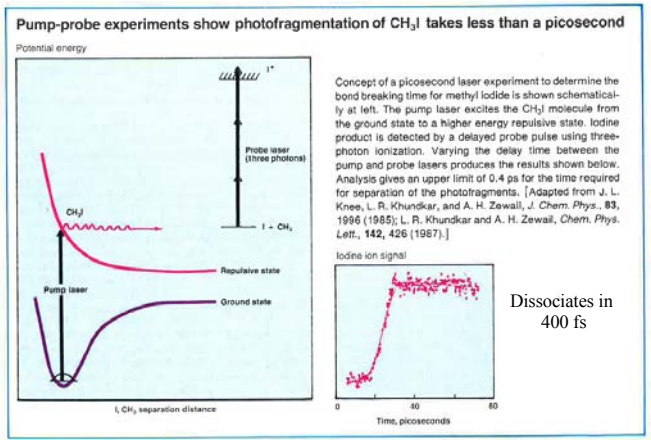
Pump-Probe-Detect in fs time scale



Potential energy curves for dissociation of CH_3I

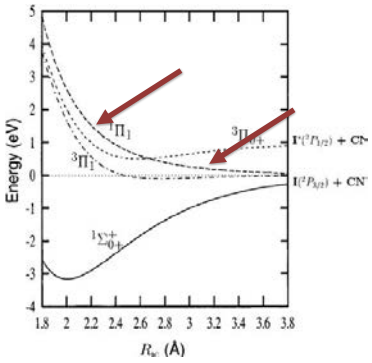


The first study on photodissociation by Zewail (1985)



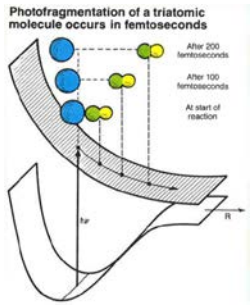
Dissociates in 400 fs

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**

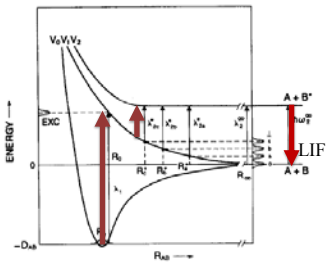
Photodissociation of ICN
Tracing the unbound surface (1987)



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**

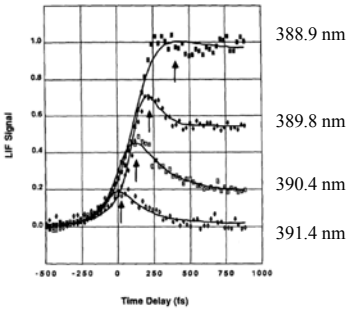
Probe excitation wavelength dependent emission from CN*

ICN → I + CN → I + CN*



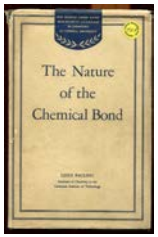
Goal (map the surface)
Experiment (pump & probe)

Rise and decay of laser induced fluorescence signal of CN*

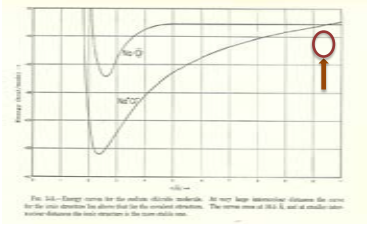


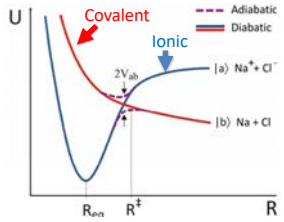
- **Excited state surface of ICN is dissociative, not bound (no oscillation)**
- **ICN dissociates within 205 ± 30 fs (~0.2 ps)**

Potential energy curves for dissociation of NaCl

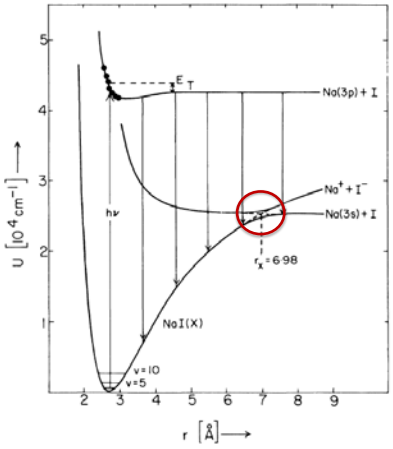


Linus Pauling, 1938





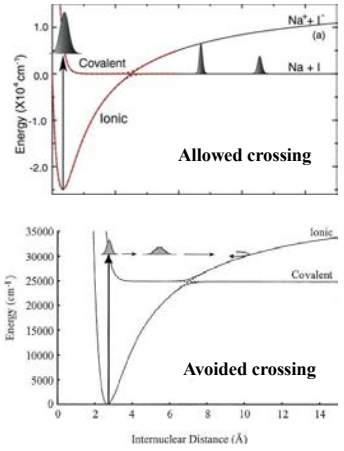
Experimental demonstration for curve crossing (1988)



Can we get experimental support for avoided crossing?

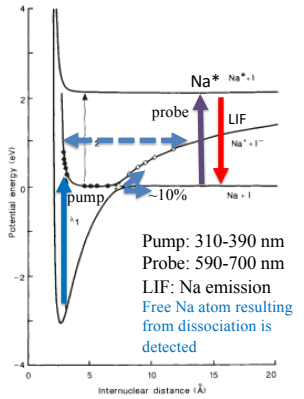
Zewail et. al.
Chem. Phys. Lett., *146*, 175, **1988**
J. Chem. Phys., *88*, 6672, **1988**
J. Chem. Phys., *91*, 7415, **1989**
Nature, *348*, 225, **1990**

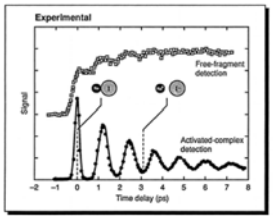
Detection of crossing and avoided crossing
Resonance

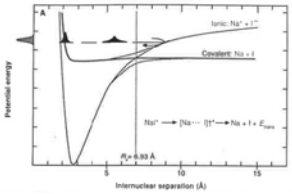


- If there is no mixing, the two curves would remain separate and the excited NaI will retain covalent character and dissociate like CH_3I and ICN.
- If the two first order curves mix the crossing will become avoided.
- The avoided crossing will lead to a 'well' where the excited NaI will get trapped and establish a resonance (oscillation) between covalent and ionic character.
- The molecule resonate between two electronic configuration

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

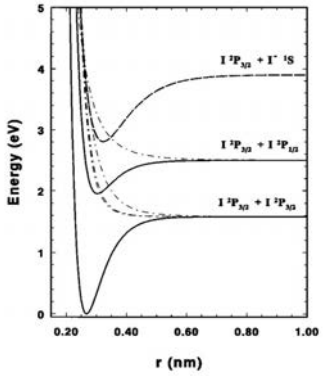






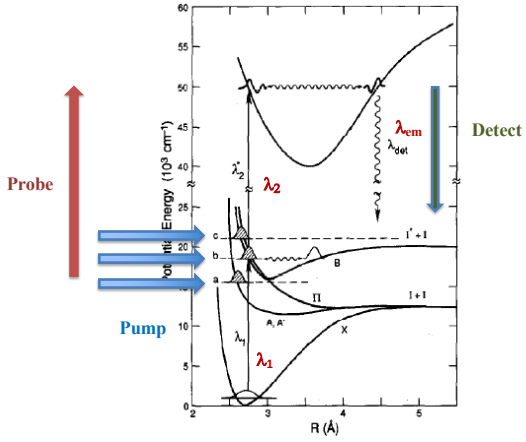
Pump: 310-390 nm
Probe: 590-700 nm
LIF: Na emission
Free Na atom resulting from dissociation is detected

Potential energy curves for dissociation of I_2



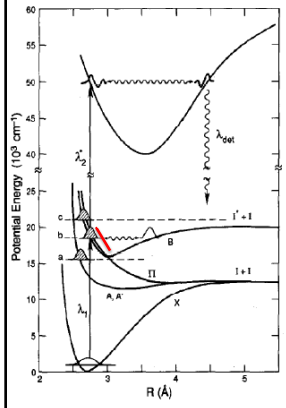
I_2

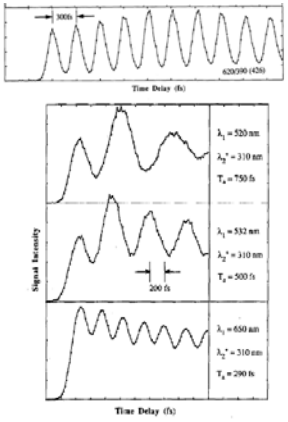
Photodissociation on I_2: A model for cleavage reactions



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

Photodissociation of Iodine (1989)
Tracing the bound and unbound surface





Pump/Probe/Detec
620/390/426

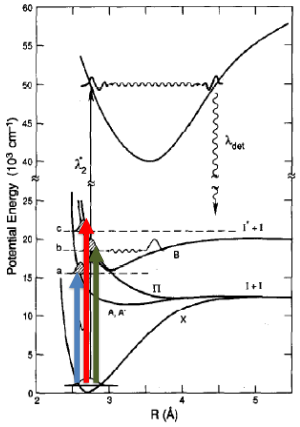
520/310/
Time of oscillation
750 fs

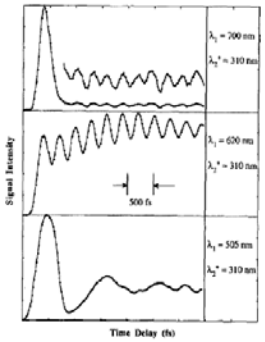
532/310/
Time of oscillation
500 fs

650/310/
Time of oscillation
290 fs

Zewail et. al., *Chem. Phys. Lett*, 161, 297, **1989**

Photodissociation of Iodine
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)

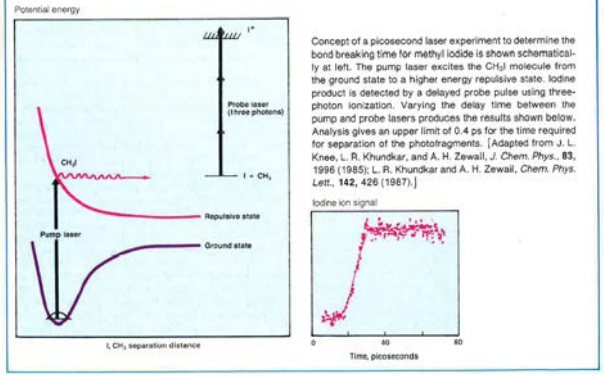
Conclusions based on ultrafast experiments

> *"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.

1985

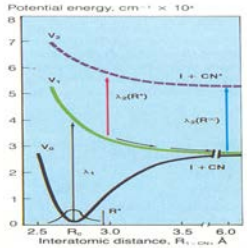
Pump-probe experiments show photofragmentation of CH_3I takes less than a picosecond



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).]

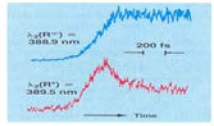
1987

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

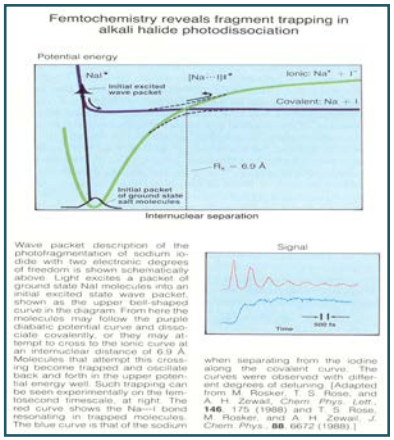


Above: The drawing shows the three relevant potential energy curves of ICN simplified to describe a femtochemistry study of its photodissociation. The lowest curve, V_0, refers to the ground state molecule, the middle one, V_1, to the lowest-lying repulsive excited state. The pump laser photon (λ_1) excites the ICN from V_0 to V_1 at R_e. Here, R_e is the equilibrium bond length I—CN. The probe laser pulse, whose wavelength is set for the free CN resonance, $\lambda_2(R^*)$, 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.

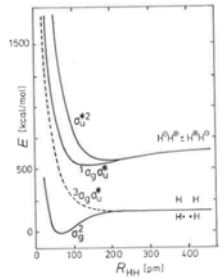
Below: Pump-probe transients are observed by laser-induced fluorescence of the CN photofragment. Upper: When the probe laser is tuned to the wavelength ($\lambda(R^{**})$) corresponding to free CN, the signal is delayed until the I and CN have "fully" separated. Lower: The probe laser is detuned to the 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).]



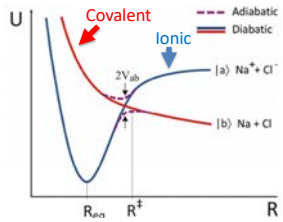
1988



Models for photodissociation of covalent and ionic σ bond



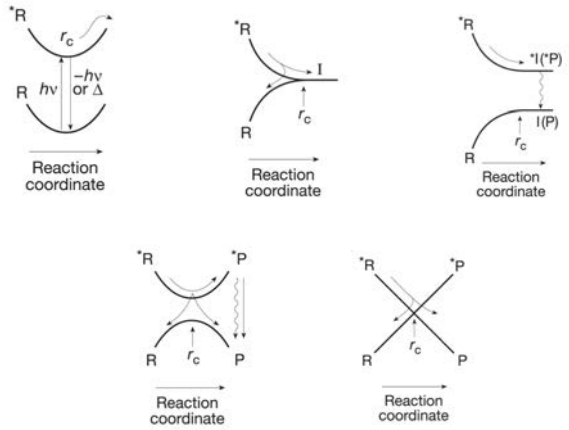
H_2



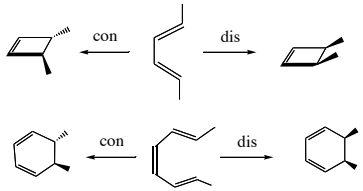
NaCl

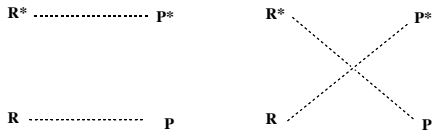
Energy surfaces generated by following the electrons as the nuclei move along the reaction co-ordinate.

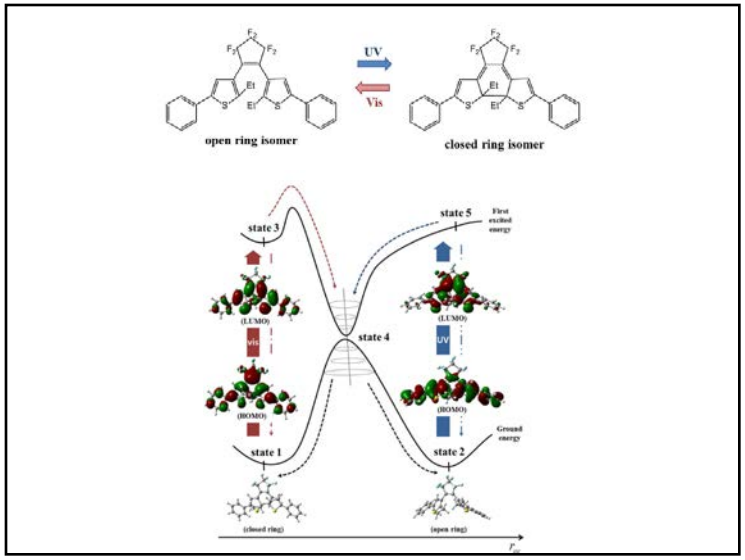
Types of surfaces

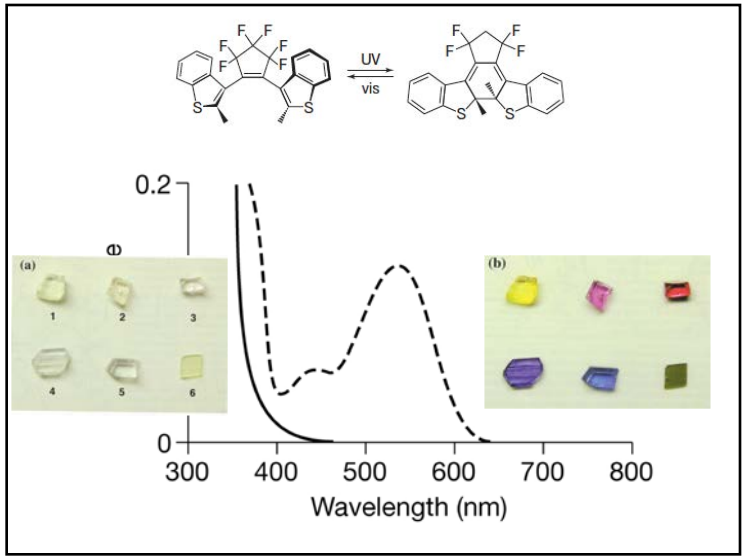


Concerted (pericyclic) reactions: Cyclization





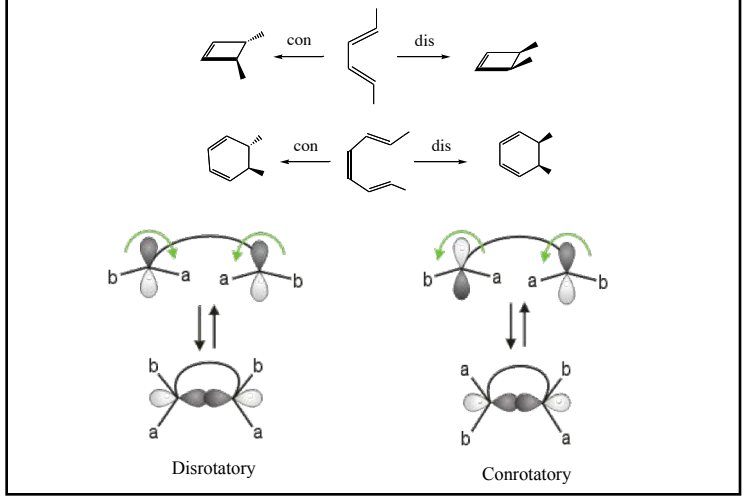




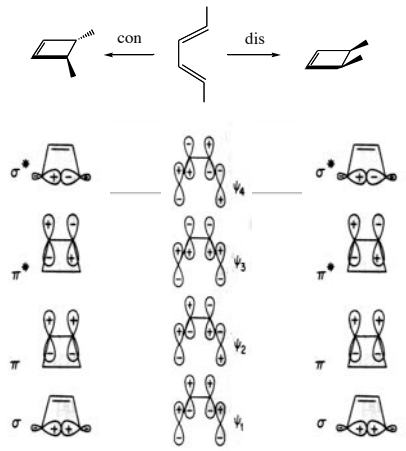
Suggested books on pericyclic (concerted) reactions

1. The Conservation of Orbital Symmetry, R. B. Woodward and R. Hoffmann, VCH, 1970; R. B. Woodward and R. Hoffmann, Angew. Chem. Engl. Ed., Int.,
2. Orbital Symmetry, A Problem Solving Approach, R. E. Lehr and A. P. Marchand, Academic Press, 1972.
3. Organic Reactions and Orbital Symmetry, T. L. Gilchrist and R. C. Storr, Cambridge University Press, 1972.
4. Frontier Orbitals and Organic Chemical Reactions, I. Fleming, John Wiley, 1976.
5. Molecular Orbitals and Organic Chemical Reactions, I. Fleming, Wiley, 2010.
6. Pericyclic Reactions-A Textbook by S. Sankararaman, Wiley, 2005
7. Lots of reviews

Nomenclature

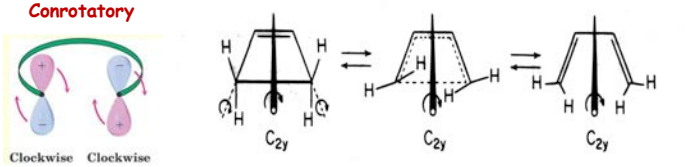


Orbitals involved in the transformation

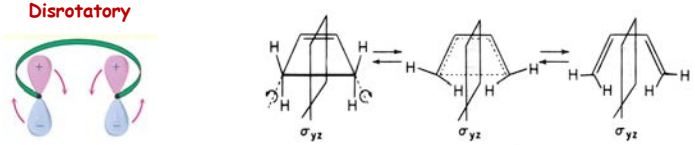


Assigning symmetry to relevant orbitals

Conrotatory



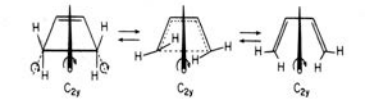
Disrotatory



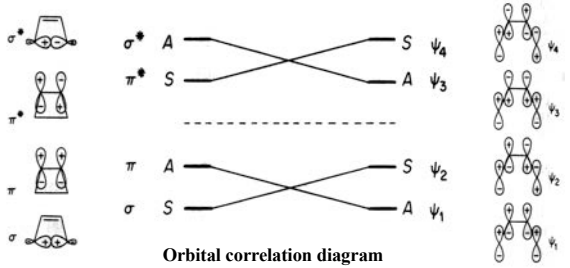
Conrotatory cyclization of 1,3-butadiene

R. B. Woodward, R. Hoffmann, JACS, 87, 396,1965
Nobel Prize 1981

R. B. Woodward
1917-1979

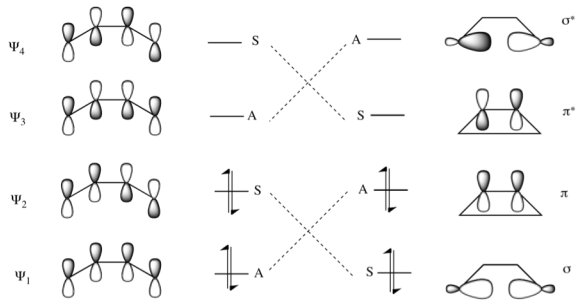


R. Hoffmann
1937-



Orbital correlation diagram

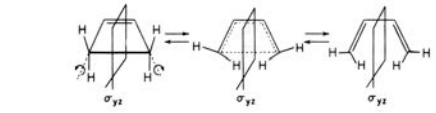
Orbital Correlation Diagram

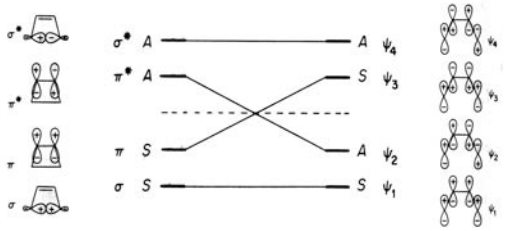


Conrotatory

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

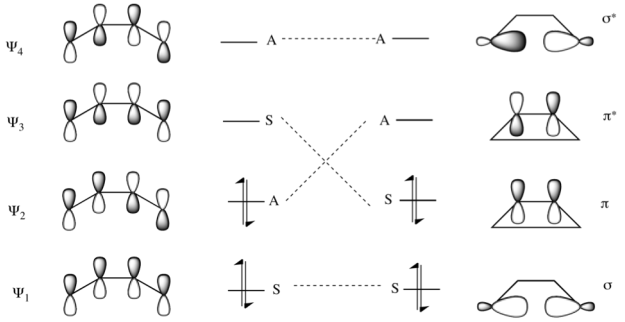
Disrotatory Cyclization of 1,3-Butadiene





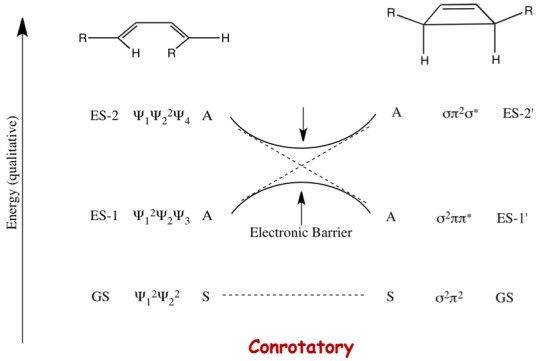
Orbital correlation diagram

Disrotatory
Orbital Correlation Diagram



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

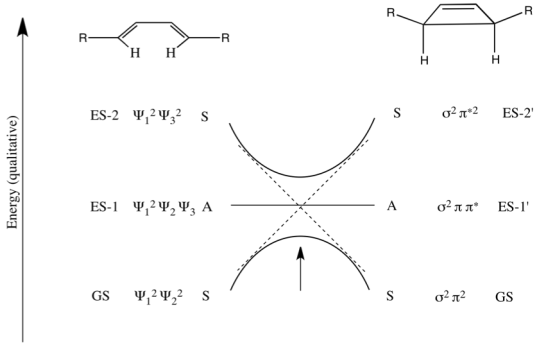
State Correlation Diagram



Conrotatory

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

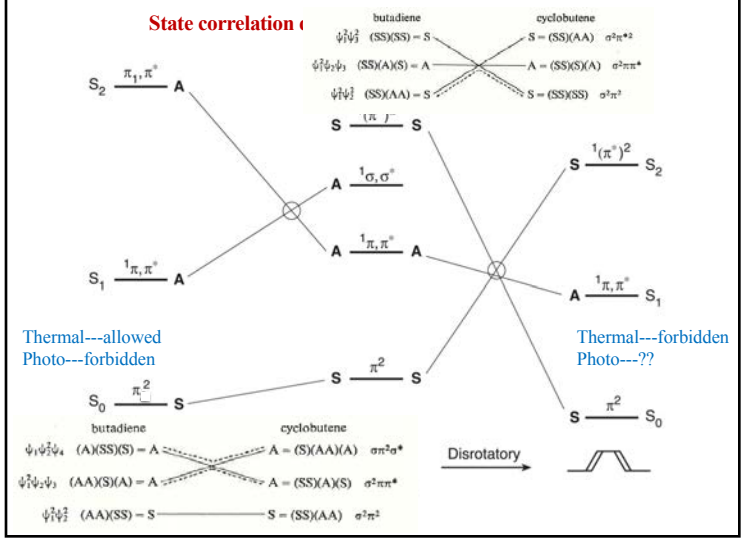
State Correlation Diagram



Disrotatory

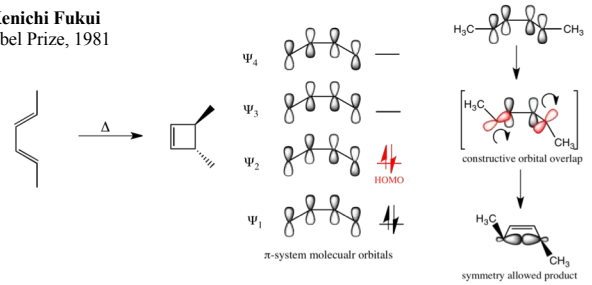
H. C. Longuet-Higgins, E. W. Abrahamson, JACS, 87, 2045,1965

State correlation



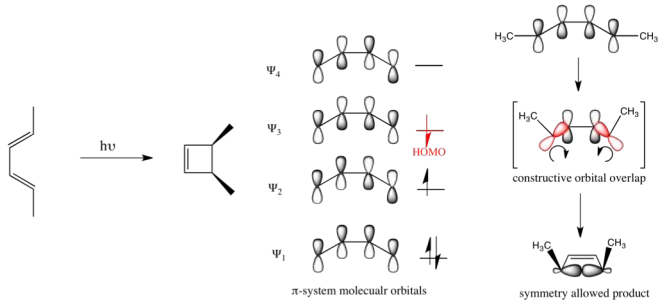
Kenichi Fukui
Nobel Prize, 1981

Frontier Orbital Approach (HOMO)



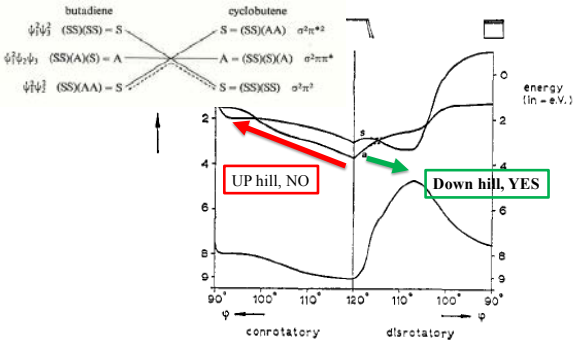
Thermally allowed

Frontier Orbital Approach (HOMO)



Photochemically allowed

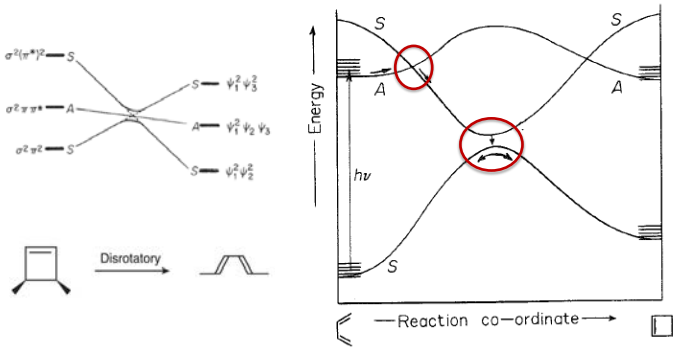
The photochemical reaction is facilitated by crossings of surfaces in the excited state



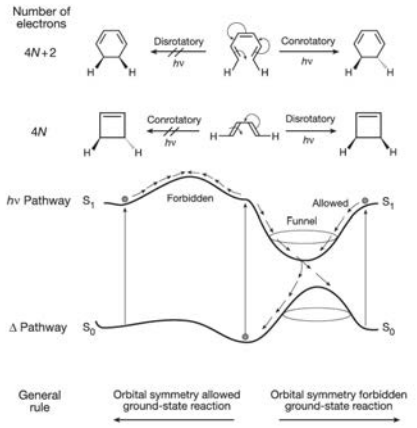
Details?

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

Energy surfaces with crossings

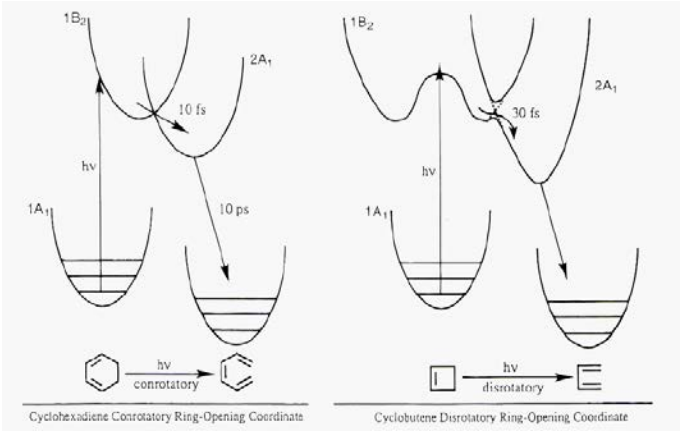


- No reaction from S_1
- Reaction from S_2 likely
- Multiple crossings involved
- Prediction in the excited state is not clear cut like thermal reaction

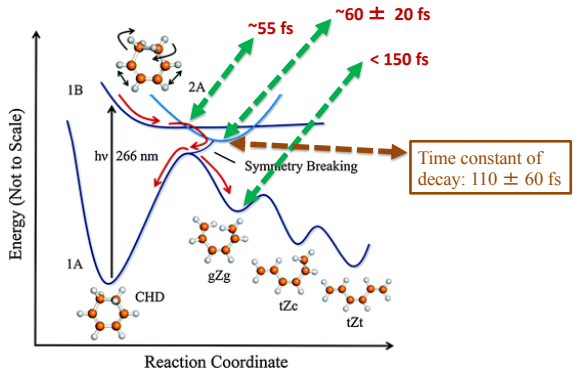


Turro book

Ultrafast dynamics studies



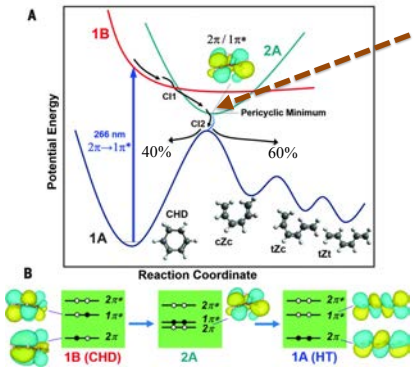
R. Mathies *et.al*, *Acc. Chem. Res.* **28**, 493, **1995**



Cartoon depicting the potential energy surface for the cyclohexadiene ring-opening and the hexatriene isomerization. The excited state undergoes an ultrafast relaxation through two conical intersections.

Femtosecond x-ray spectroscopy of an electrocyclic ring-opening reaction, A. R. Attar, A. Bhattacherjee, C. D. Pemmaraju, K. Schnorr, K. D. Closser, D. Prendergast, S. R. Leone, *Science* **2017**, *356*, 54-59

Femtosecond x-ray spectroscopy of an electrocyclic ring-opening reaction, A. R. Attar, A. Bhattacherjee, C. D. Pemmaraju, K. Schnorr, K. D. Closser, D. Prendergast, S. R. Leone, *Science* **2017**, *356*, 54-59

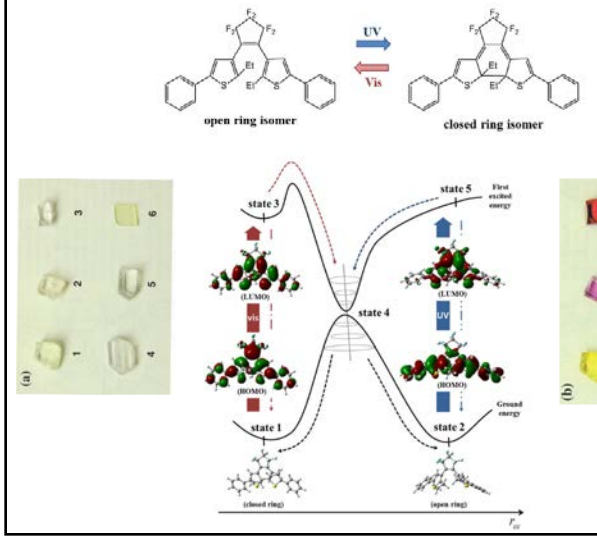


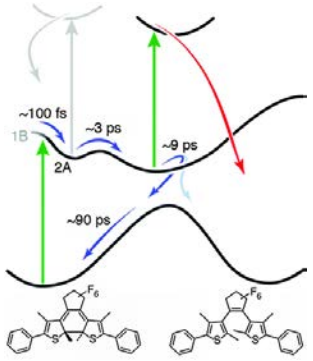
90-130 fs window probed for the structure of pericyclic minimum. The orbital natures looks like a mixture of HOMO-LUMO (2π and 1π*).

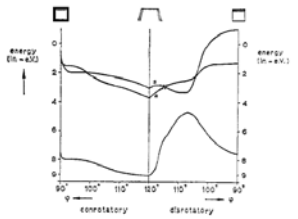
Further studies confirm the conclusions

M. Minitti, T. Martinez et.al., *Nature Chemistry*, **2019**, *11*, 504

P. M. Weber et. al., *Science Advances,* **2019**, 5, eaax6625







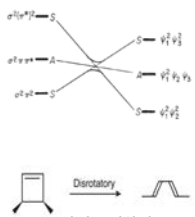
van der Lugt and Oosterhoff, *J. Am. Chem. Soc.*, *91*, 6041, **1969**

An ultrafast (100 fs) anisotropy change accounts for an initial change in electronic character from 1B to 2A. The molecule then traverses a barrier in 2A to reach a conical intersection with the ground state. Re-excitation of the molecule after the barrier is crossed results in maximization of the quantum yield for ring-opening.

C. L. Ward and C. G. Elles, *J. Phys. Chem. Lett.*, **2012**, *3*, 2995

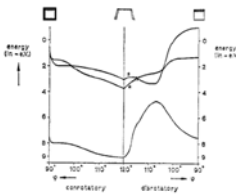
Ultrafast experimental studies support the original model

1965



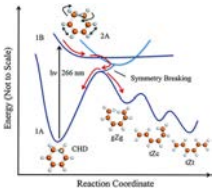
Longuet-Higgins and Abrahamson, *J. Am. Chem. Soc.*, *87*, 2045, **1965**

1969



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

2019



Minitti, Martinez et.al., *Nature Chemistry*, **2019**, *11*, 504

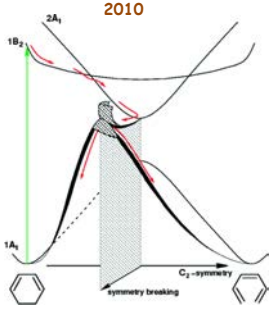
Weber et. al., *Science Advances,* **2019**, *5*, eaax6625

Leone et. al., *Science* **2017**, 356, 54

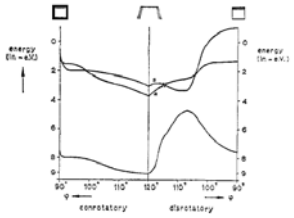
- Basic features remain the same
- Transformation occurs in subpicosecond (~200 fs) time scale
- Given the speed, all crossings are better considered as CI
- Energy surfaces developed based on orbital and state symmetry work

High level computation supports the original model

2010



1969



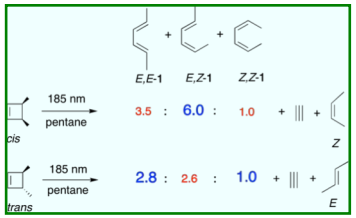
van der Lugt and Oosterhoff,
J. Am. Chem. Soc., *91*, 6041, **1969**

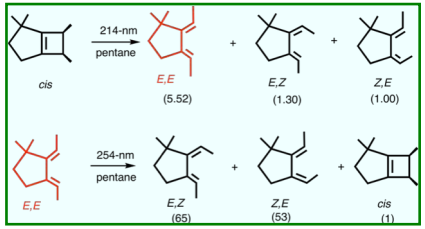
The excited state symmetry preserving path reflecting the ground state isomerization (as in the van der Lugt/Oosterhoff picture) leads to an avoided crossing with a large gap due to the electron correlation of both A_1 states. The S_1 minimum, as well as the CoIn, lie out of the drawing plane and are reached by symmetry breaking deformations, i.e., motions independent of the ones on the S_0 state. Acceleration in symmetry breaking direction is observed already at the $1B_2/2A_1$-CoIn.

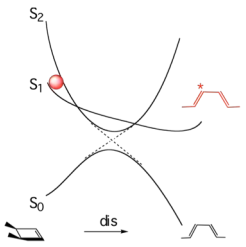
A.Nenov, P. Kolle, M. A. Robb and R. de Vivie-Riedle, *J. Org. Chem.*, 2010, **75**, 123–129

Cyclobutene ring opening is not stereospecific?

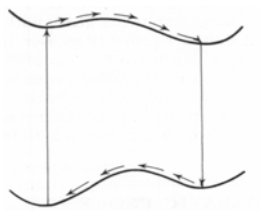
Cyclohexadiene ring opening is stereospecific!

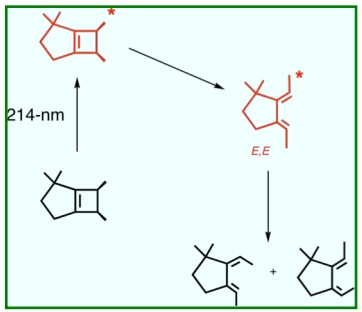






Adiabatic Photochemistry?
Conical intersection with multiple exits?

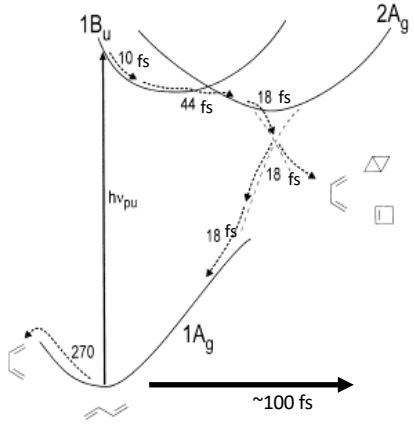


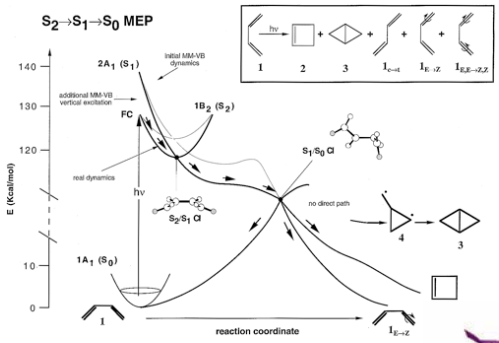


As per ultrafast studies the reaction is over within 100 fs.

Such a short time is not sufficient for molecules to jump to lower surface via the avoided crossing as per Fermi Golden Rule

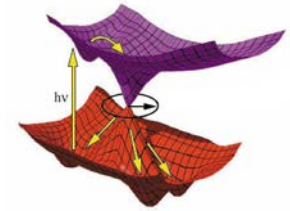
Computations suggest the presence of CI.



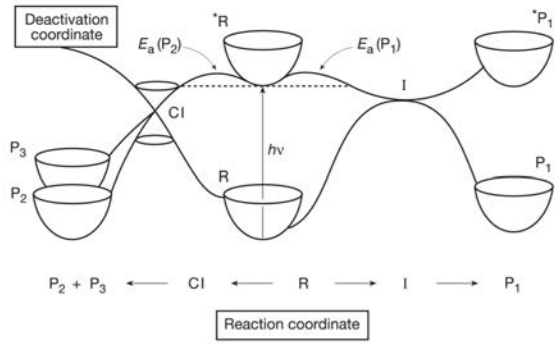


Conical intersection may connect multiple products.

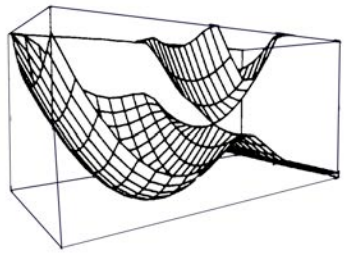
Prediction becomes impossible without the help of computations.



Conical Intersection and Multiple Products

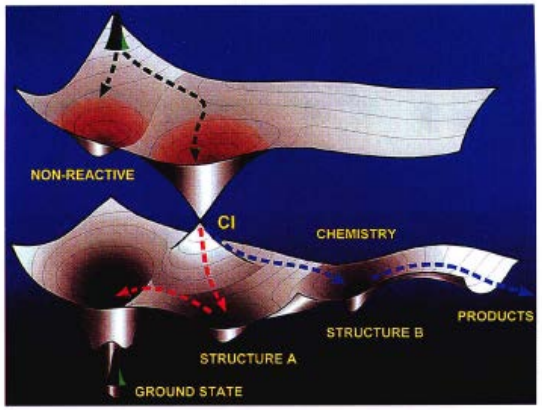


What is a conical intersection

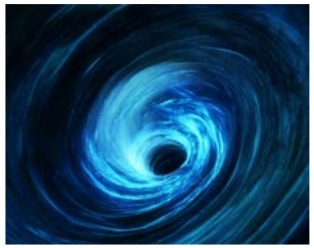
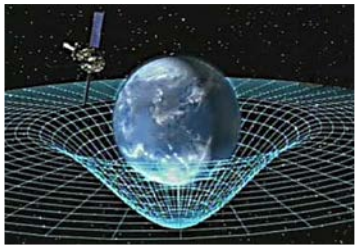


Two adiabatic potential energy surfaces cross. The interstate coupling is large facilitating fast radiationless transitions between the surfaces.

Pictorial description of conical intersection

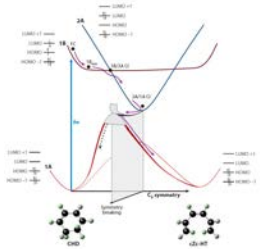


Analogy to conical intersection

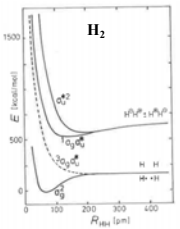

To think

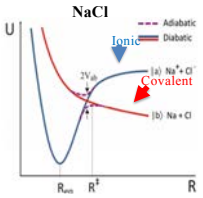
- What triggers a reaction upon light absorption?
- On the excited surface what triggers the reaction – electronic motion or nuclear motion?
- How do molecules jump between surfaces?
- What plays a role in the jump between surfaces – electronic or nuclear?
- Why orbital symmetry matters?



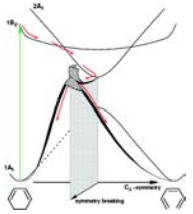
Models for photoreactions

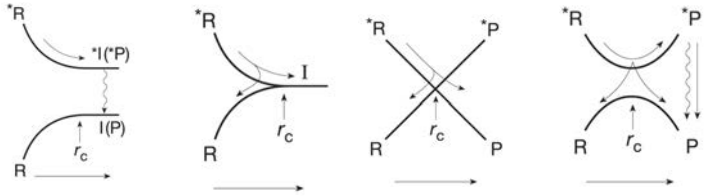
Photodissociation



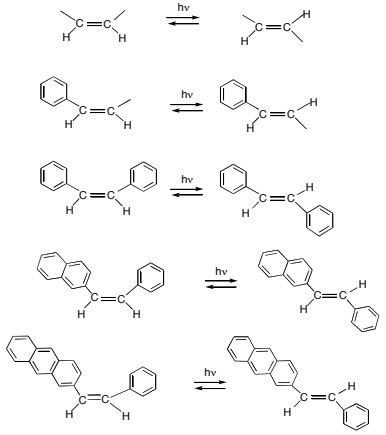


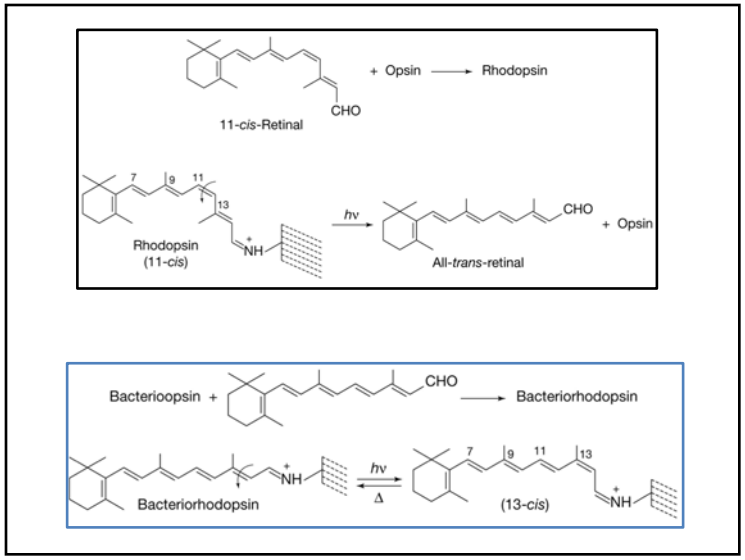
Photoelectrocyclization

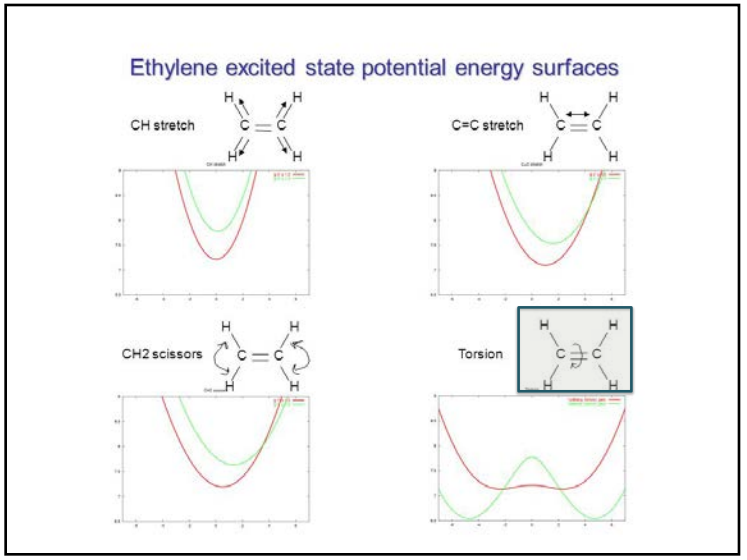




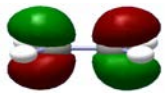
Geometric Isomerization





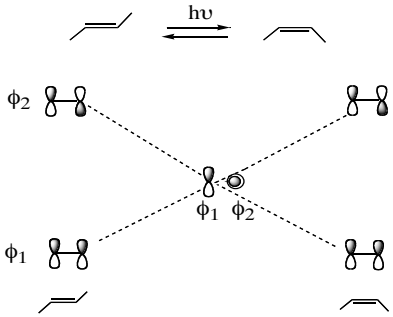


Geometric Isomerization: Twisting of a C=C π Bond

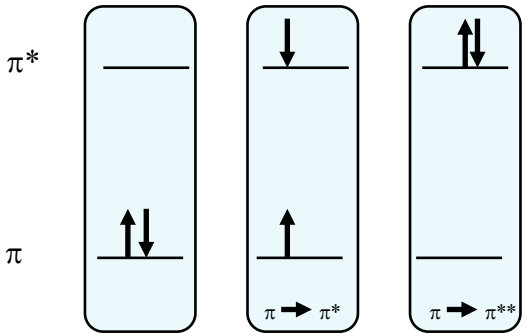


Ethylene - LUMO

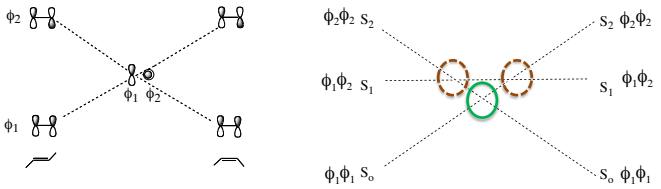
Ethylene - HOMO



Ethylene

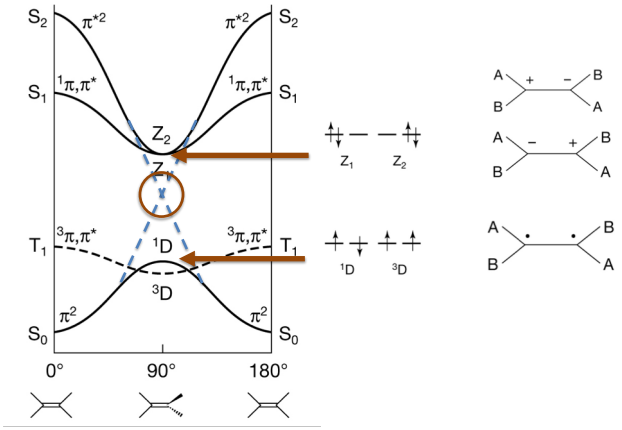


Correlation Diagram for Geometric Isomerization

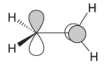


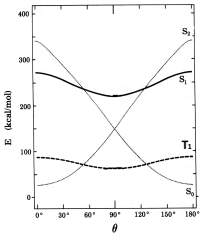
Note the similarity between this diagram and WH diagram for electrocyclization

Crossing becomes avoided and the point has two different electronic configurations

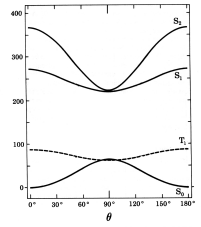


Geometric Isomerization of Ethylene

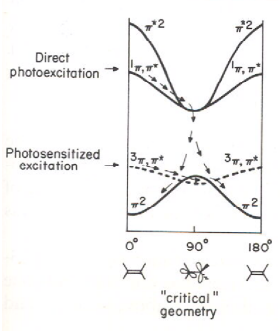




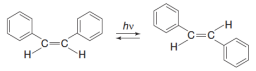
Allowed Surface Crossing

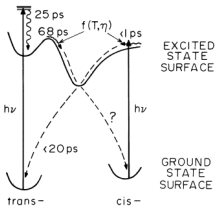


Avoided Surface Crossing

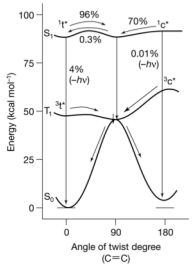


Energy surface for the isomerization of stilbene

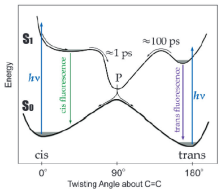




R. Hochstrasser, *Pure & Appl. Chem.*, **1980**, *52*, 2683

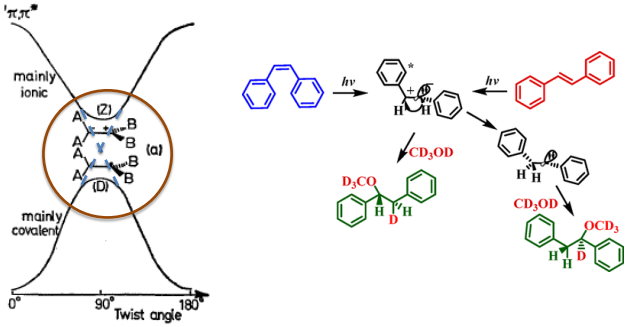


J. Saltiel, et. al., *J. Photochem. Phobiol A, Chem.* **1992**, *65*, 29



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

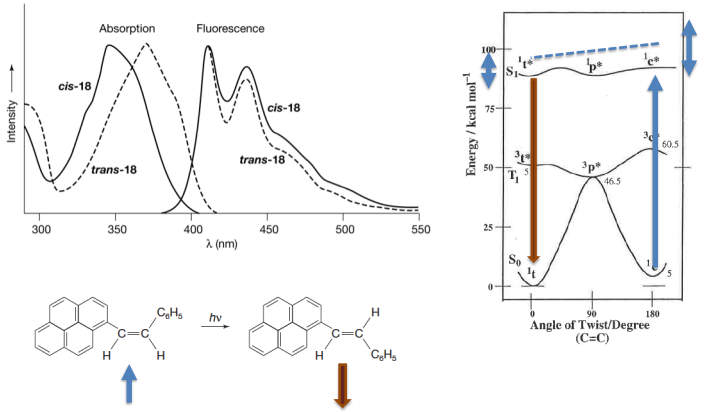
Sudden polarization

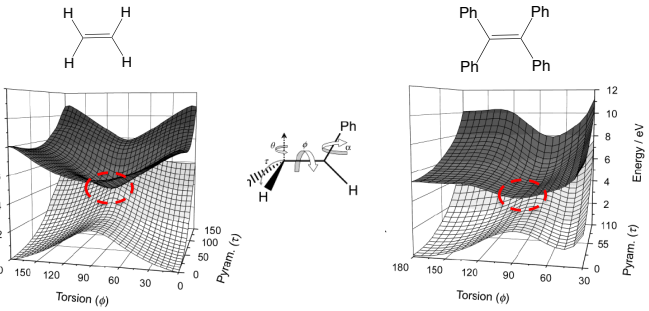


L. Salem, *Acc. Chem. Res.*, **1979**, *12*, 87

J. Saltiel et. al., . *J. Phys. Chem. A* **2018**, *122*, 29

Diagram works for most with some modifications
Adiabatic photoreaction

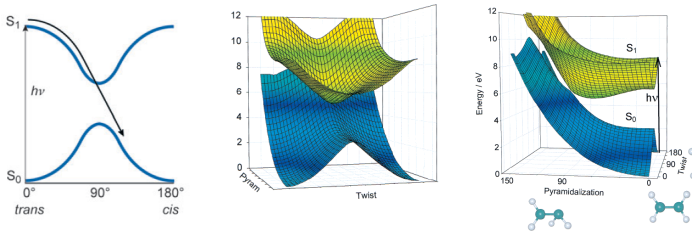




For both stilbene and ethylene, the twisted geometry represents a saddle-point on S_0. Accessing the minimal energy conical intersection from the purely twisted photoexcited molecule requires displacement along the pyramidalization coordinate.

Martinez et. al., *J. Phys. Chem. A* **2003**, *107*, 829

Geometric Isomerization of Ethylene
Conical Intersection is a Possibility

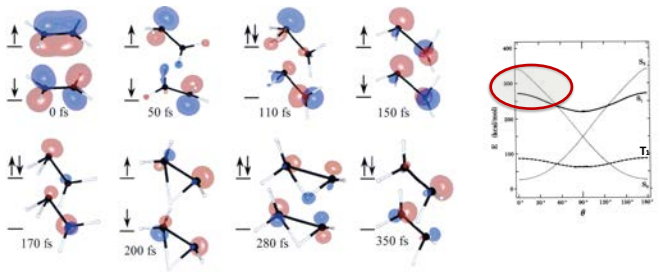


Ethylene decays with a lifetime of 20±10 fs (2 x 10^{-14} sec); computed

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.

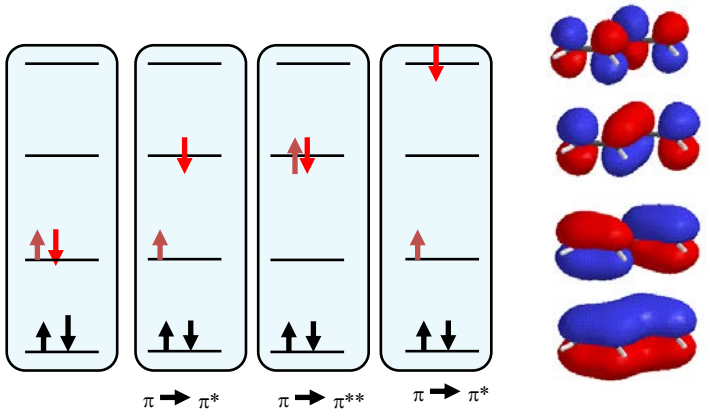
Change in electronic configuration upon twisting 0–350 fs (computed)



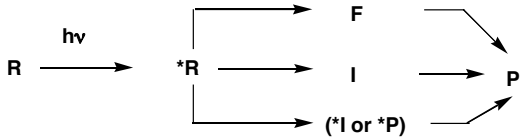
Snapshots of the π- and π*-like natural orbitals of an individual nuclear basis function traveling on the excited electronic state of ethylene. The calculation begins at a planar geometry where the excited state wave function has covalent ππ*character. During the course of the dynamics, the excited state wave function oscillates between covalent (50, 150, and 200 fs) and ionic (110, 170, 280, and 350 fs)forms.

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

1,3-Butadiene and higher polyenes



Mechanistic Possibilities



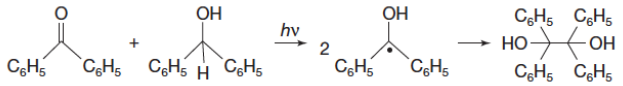
F = funnel from excited to ground state surface

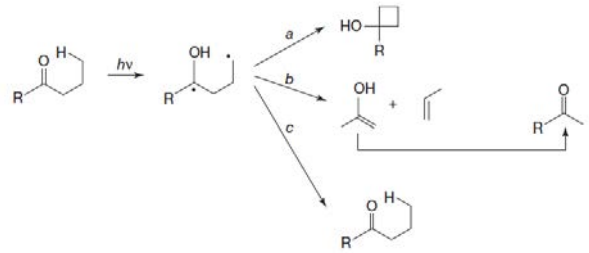
I = ground state reactive intermediate

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

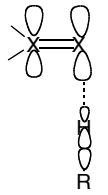
***P = excited state of product**

Hydrogen abstraction is a common photoreaction

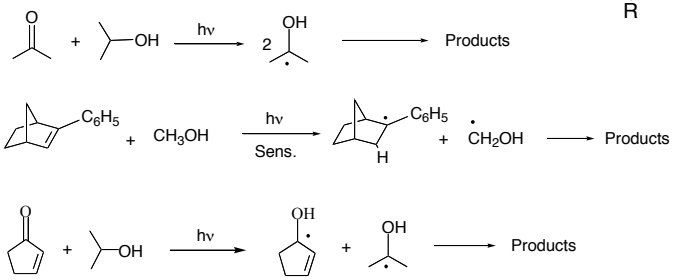




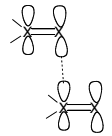
Primary Photoreactions



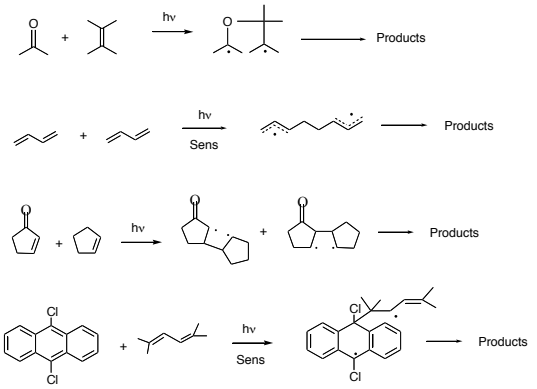
Hydrogen Abstraction



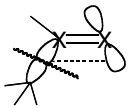
Primary Photoreactions



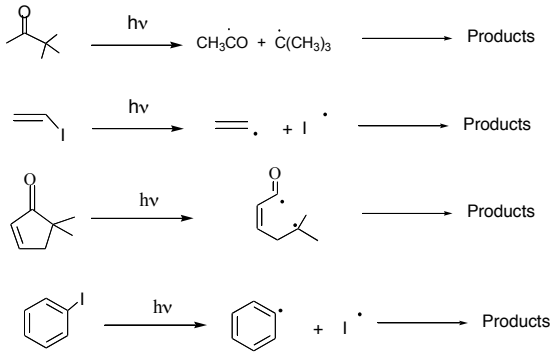
Addition to C=C bond, triplet, non concerted



Primary Photoreactions

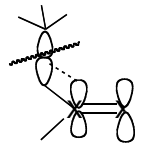


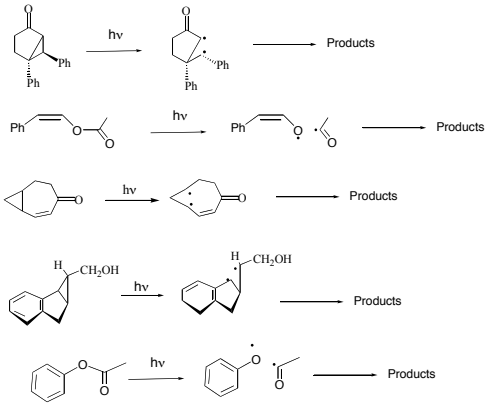
α-Cleavage



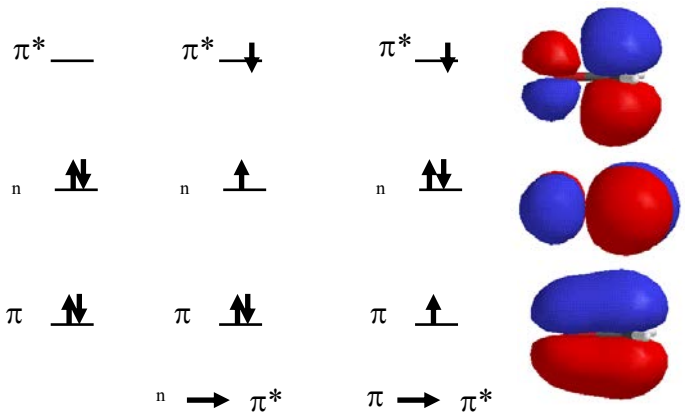
Primary Photoreactions

β-Cleavage



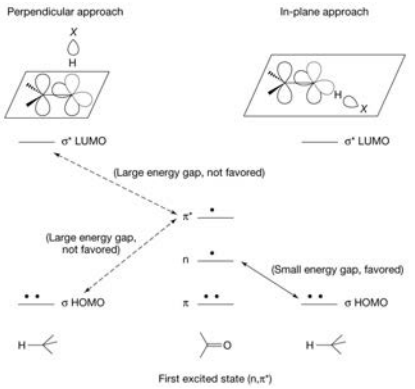


Carbonyl Compounds



Frontier orbital view of hydrogen abstraction by carbonyl nπ* triplet

Less likely

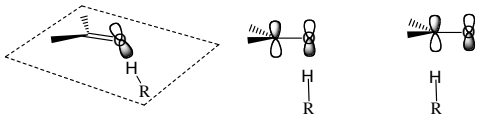


More likely

Constructing Salem Diagram

Relevant electronic states

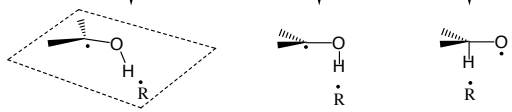
Geometries of approach



n-plane

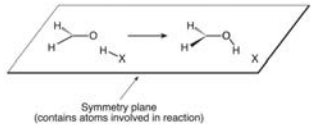
π- plane

Diradical intermediates formed



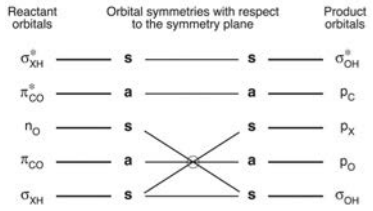
Constructing Salem diagram for n-plane attack

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

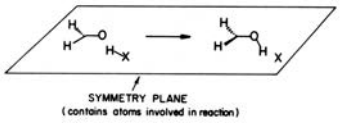


Enumerate the relevant orbitals of the reactant and the intermediate in the order of their energy.

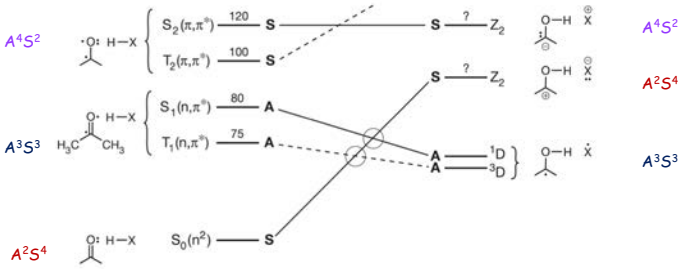
Build the orbital correlation diagram based on energy and symmetry.



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



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 2A
excited state of primary product	$4\sigma, 2\pi$	4S 2A

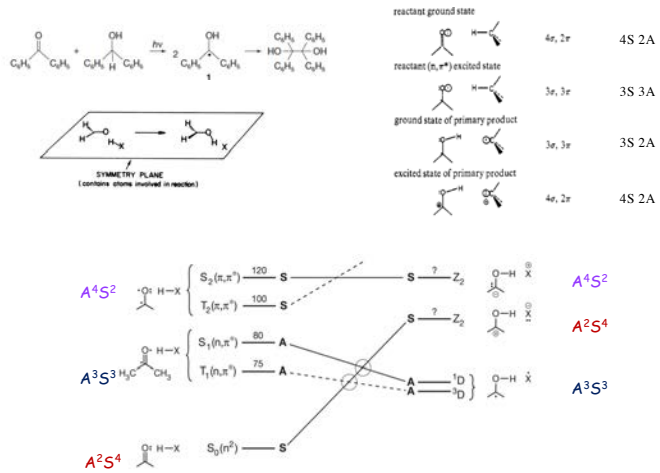


Hydrogen abstraction along n-plane is likely from nπ* state.

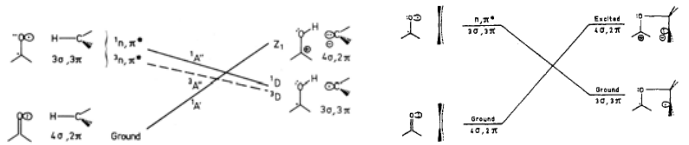
Reaction from $T_1(n\pi^*)$ is likely to be more efficient than from $S_1(n\pi^*)$.

If T_1 is $\pi\pi^*$ the reaction from n-face is unlikely.

Salem correlation diagram

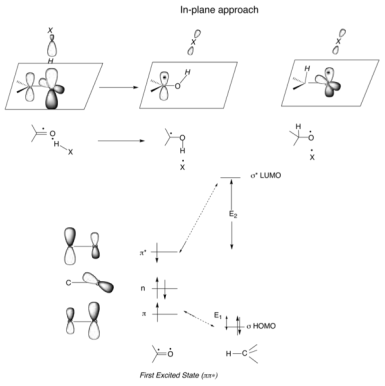


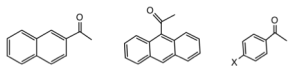
Dauben, Salem and Turro, *Acc. Chem. Res.*, **1975**, *8*, 41



Acknowledgments. The author is strongly indebted to Professors Bill Dauben and Nick Turro for a prolonged and stimulating exchange of correspondence, and for some very illuminating discussions. Paul de Mayo was the first to press on the author the question of the location of return from photoexcited state to ground state. He would like to thank Dr. Mrs. Poquet

Hydrogen abstraction from ππ*state is less common and occurs at a slower rate



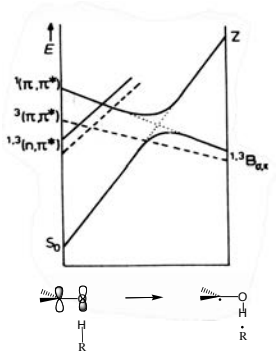


π* electron is diffused into the aryl ring.

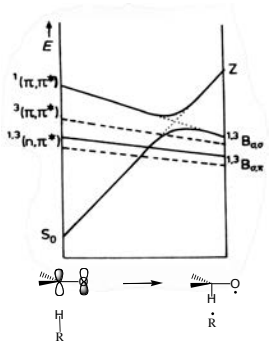
Leads to a less stable oxygen centered radical.

ππ* state in aryl carbonyl systems can abstract hydrogen but not at high rate.

Salem diagrams for π-plane attack

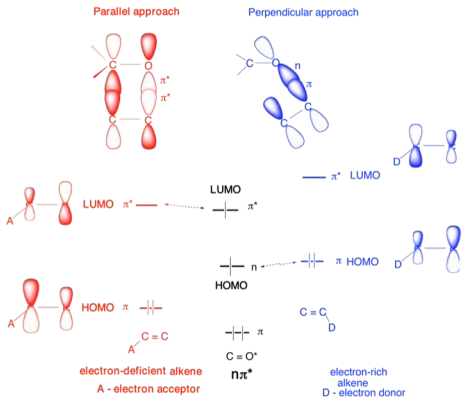


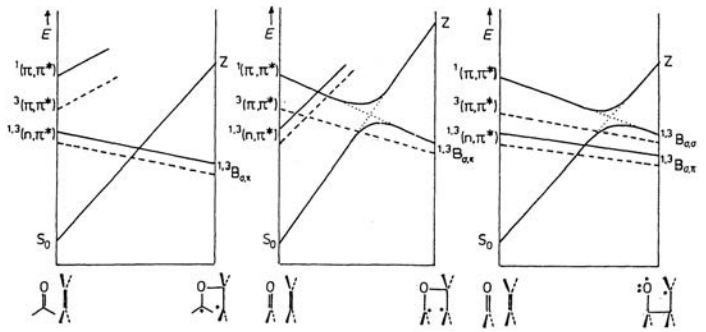
No reaction from nπ* state



Abstraction by carbon in the nπ* state favored

Difference Between Electron Rich and Electron Poor Olefins: Orbitals Involved in the Primary Interactions Are Different





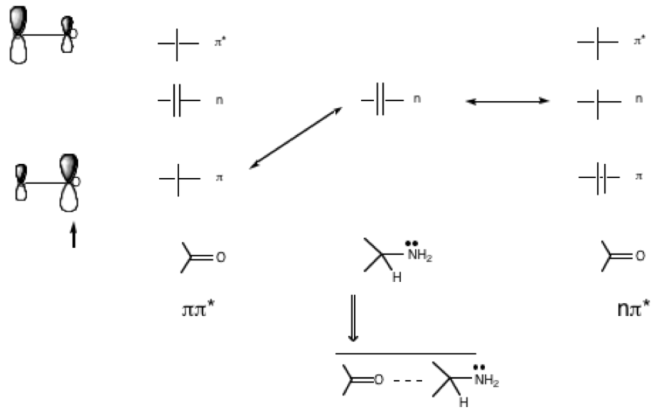
Electron rich olefin

Electron poor olefin
Addition to oxygen
BARRIER

Electron poor olefin
Addition to carbon
FAVORED
Reaction is likely to be less efficient.

Excited States and Photochemistry of Organic Molecules, Klessinger and Michl, VCH, **1995**, pp 424-432

Electron transfer would occur independent of the character of the triplet

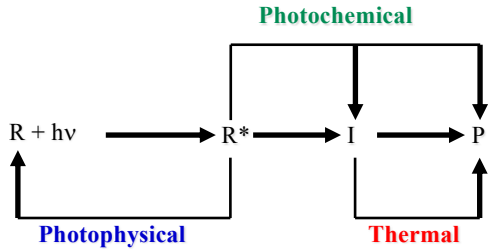


Why excited singlet and triplet give different products?

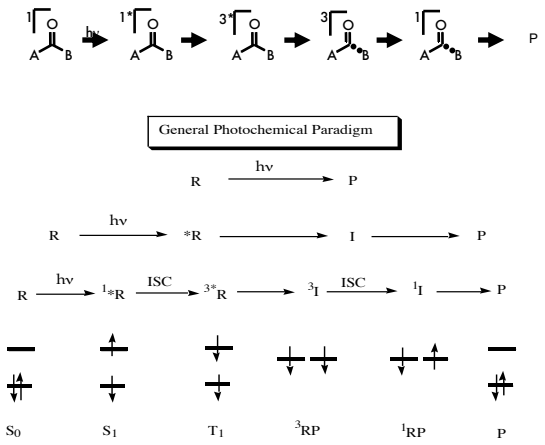
How do reactive molecules in the triplet state transforms to singlet product(s) or singlet intermediates?

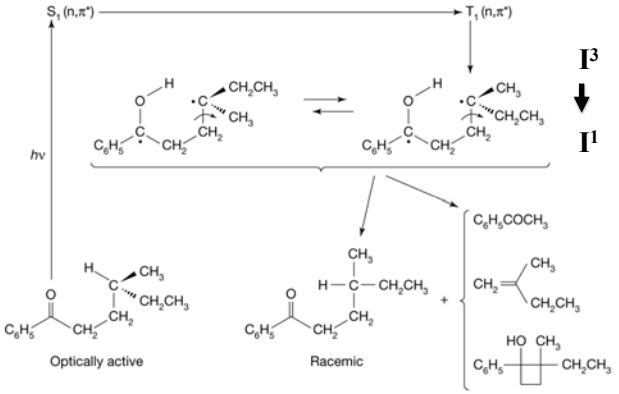
Intersystem crossing mechanisms?

Molecular Structure and Dynamics

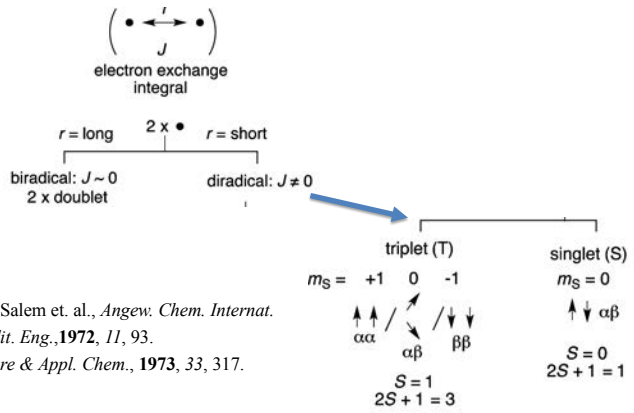


Importance of intersystem crossing





Diradical, Biradical



L. Salem et. al., *Angew. Chem. Internat. Edit. Eng.*,**1972**, *11*, 93.
Pure & Appl. Chem., **1973**, *33*, 317.

What controls the singlet-triplet energy gap?

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

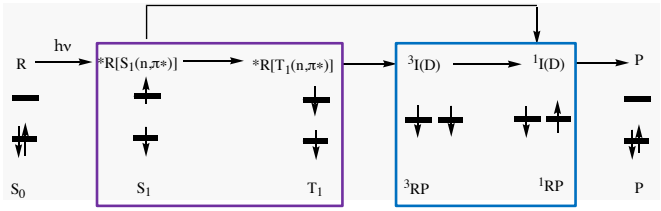
$\Delta E_{ST} = 2J$ in molecules where HOMO-LUMO gap is large

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

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

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)



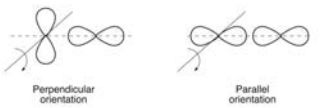
HOMO–LUMO gap large
Only J, no B

$S_1 > T_1$

HOMO–LUMO gap small or equal energy

Only J
$S_1 > T_1$

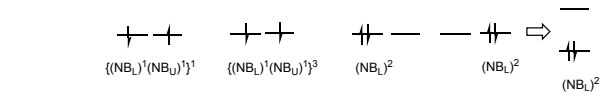
Both J and B
$S_1 < T_1$

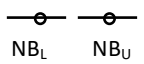


Singlet-triplet energy gap

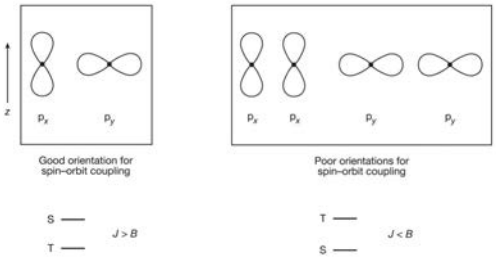
J will be proportional to the electron exchange integral for the $(NB_L)^1(NB_U)^1$ configuration

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





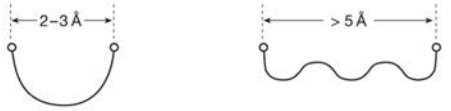
$\Delta E_{ST} = J - B$



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, the two states must have essentially the same energy, 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 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.

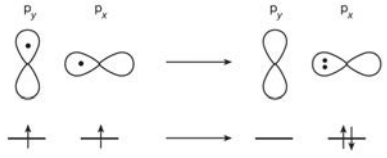
Good orientation for ISC at any separation

Poor orientation for ISC at any separation

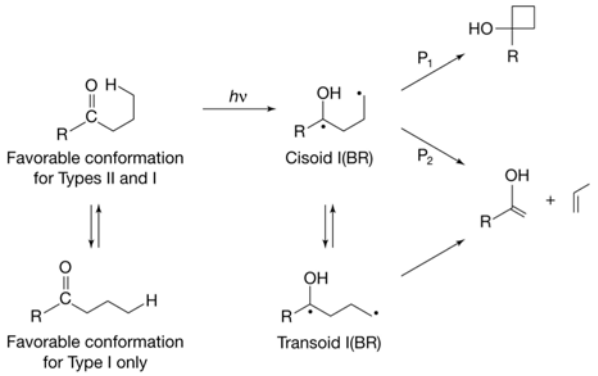
Salem's rules for ISC in diradicals-3

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

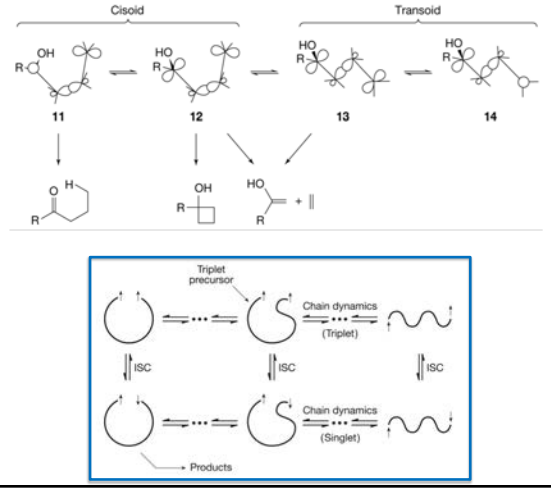
In order to effectively generate orbital angular momentum, the electron must jump from one orbital to the other half occupied orbital which is at a 90^0 orientation, as the singlet is created. This produces a situation for which there are two electrons in a non-bonding orbital to a "zwitterionic" structure (^{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

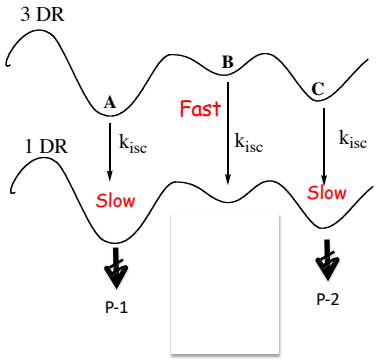


Conformation dependent ISC and its effect on product distribution

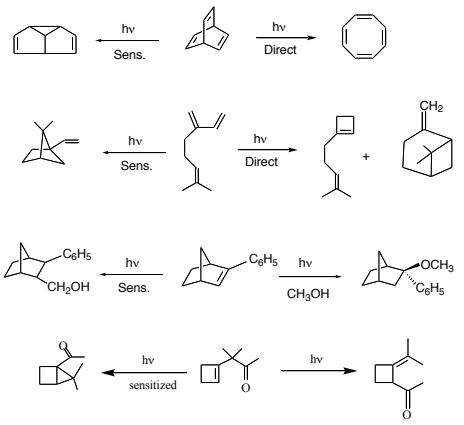


Not all conformations would have the same J, and orientation of the two p-orbitals

Conformation dependent ISC and its effect on product distribution

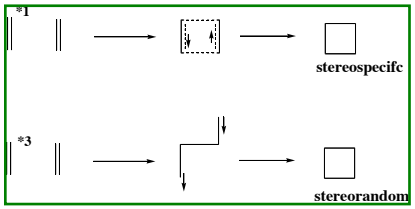


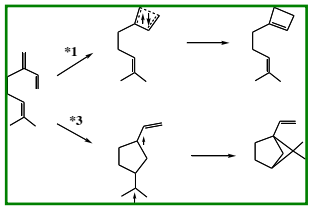
Excited Singlet and Triplet May Undergo Different Reactions



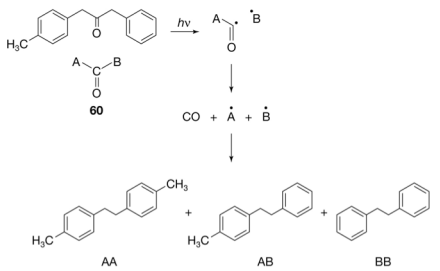
Why excited singlet and triplet give different products?

Loose and Tight Biradicals



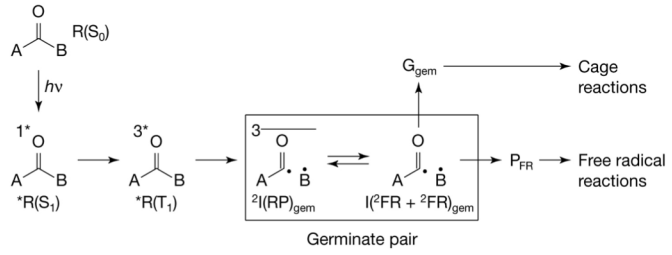


Definition of cage effect



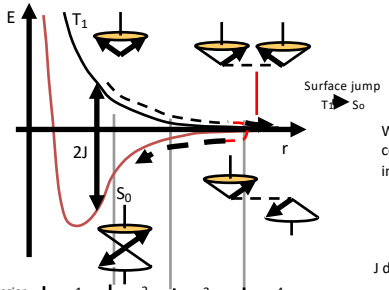
$$\text{Cage Effect} = \frac{[AB] - \{[AA] + [BB]\}}{\{[AB] + [AA] + [BB]\}}$$

Intersystem Crossing in Radical Pairs



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.



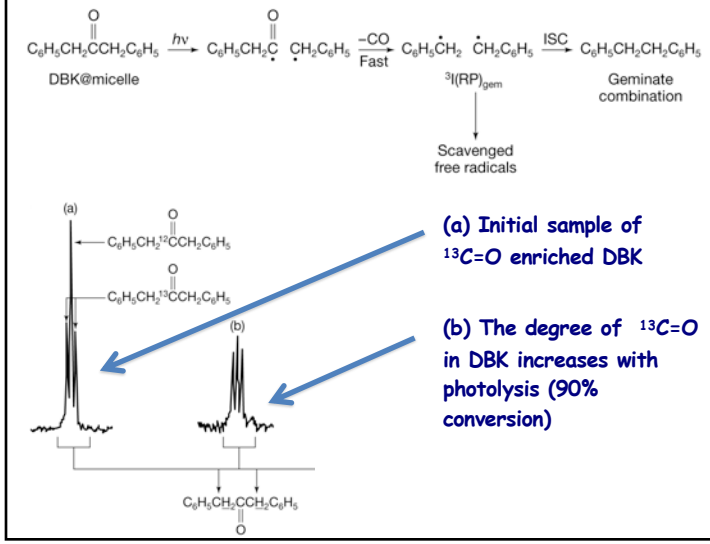
region	1	2	3	4
	bond stretching	contact pair	solvent separated pair	free radicals
distance	2-3Å	3-4Å	5-8Å	>10Å
J (G)	~10^{12}	~10^{8} -10^{9}	~ 10^{2}	~ 0

When J is large, the spins are strongly coupled together. The dipole-dipole interaction overwhelms the magnetic ones.

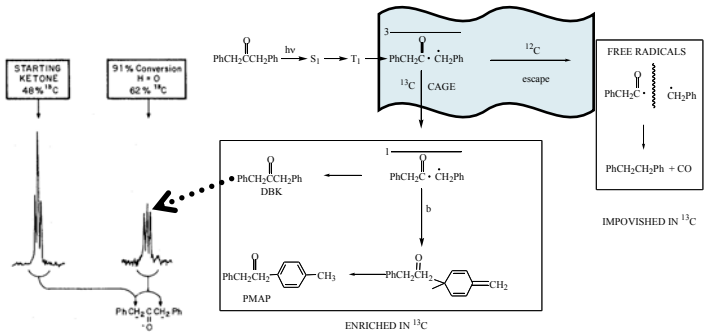
J decreases exponentially with distance

$$J \propto e^{-r}$$

and magnetic interactions, that generates torques responsible for rephasing or spin flipping (T_1 ▶ S_0), are effective.

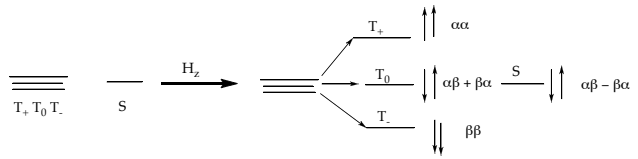


Cage effect can be utilized for isotope enrichment



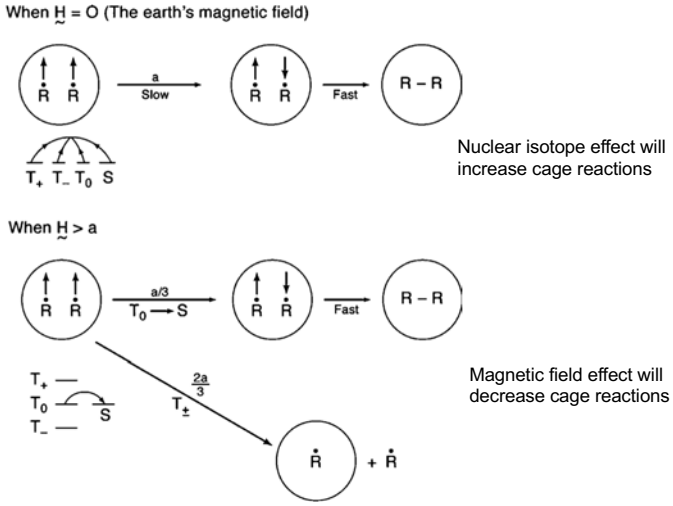
The competion is between cage escape and hyperfine induced ISC

Effect of an applied magnetic field on the T splitting

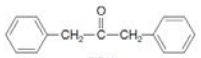
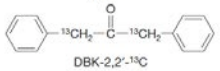
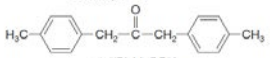
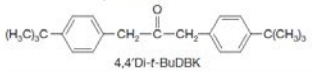


T levels split apart, T_0 has the same energy as S

Only $T_0 \rightarrow S$ ISC allowed

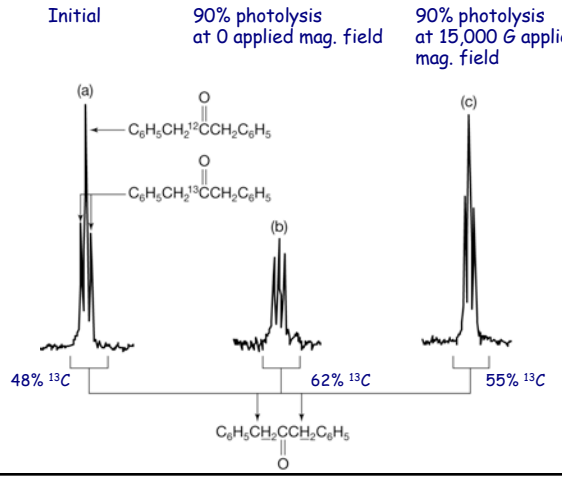


The effect of external magnetic field on the cage effect

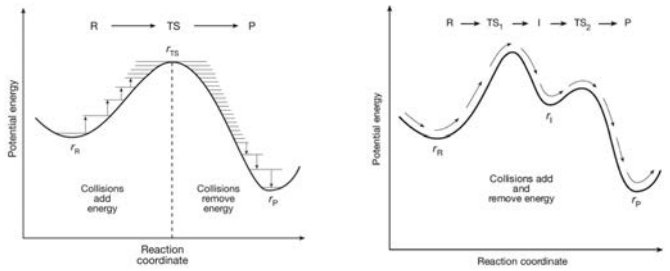
Ketone	Cage Effect at 0 G	Cage Effect at 13,000 G
 DBK	31	16
 DBK-2,2'-^{13}C	46	22
 4,4'Di-MeDBK	59	31
 4,4'Di-t-BuDBK	95	76

The cage effect decreases. More exit from host cage.

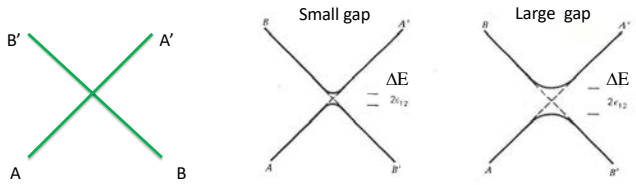
Isotope enrichment decreases in presence of applied magnetic field



Visualization of Thermal Reactions



Visualization of Photochemical Reactions



Landau-Zener-Stuecktberg equation

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