

Driving forces and momentum effects in photochemistry, as indicated by time-resolved spectroscopy

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Driving forces: pathway approach.

Driving forces and momentum effects have no equivalent in the traditional approach that uses matrix elements and densities of states.

Experimental observations suggest that

branching in a photochemical reaction does not only occur at the last conical intersection (S_1/S_0 CI)

but in addition also sometimes in the Franck-Condon (FC) region.

- Early branching can be induced by the initial slopes or curvatures of the potentials.
- A momentum acquired in the FC region can sometimes influence the later branching at the S_1/S_0 CI.
- Conservation of an initial momentum can also explain some wavelength dependences of photochemistry, i.e. deviations from the Kasha rule.

Always consider potentials, their slopes including their directions, and their (conical) intersections.

= Pathway approach [Fuß et al., Chem. Phys. 232 (1998) 161]

Note:

The slopes on the potential surfaces are forces (*driving forces*).

On each location on the potential, consider the driving forces!

Considering potentials etc. belongs to the basis of his summer school.

However, the previous approach is still widespread.

Tell the other people that the modern approach is better!

The previous approach

uses matrix elements, Franck-Condon factors and density of states, *tacitly assuming vertical transitions*.

But even ultrafast internal conversion is not vertical.

Traditional theory of internal conversion (IC):

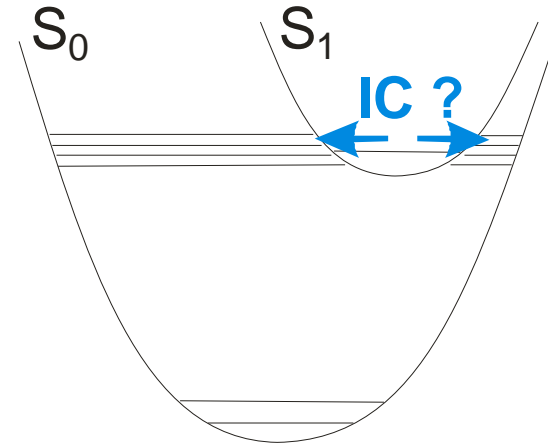
Use Fermi's Golden rule with electronic (V_{el}) and vibrational (FC = Franck-Condon factor) matrix elements and density of states ρ to calculate the rate k_{IC} :

$$k_{IC} = (4\pi^2/h) V_{el}^2 FC \rho$$

Tacit assumption: Vertical process

Probably based on the idea that electron motion can be faster than nuclear motion.

In this model, the IC can be interpreted as a tunnel process. The wave packet does not climb up to the intersection to cross over to the S_0 surface.



Cycloheptatriene, benzene and cyclopentadiene

- have similar size and excitation energies, hence similar densities of states,
- have similar S_1/S_0 FC factors (concluded from UV spectral widths),
- but have very different S_1 lifetimes !

	UV maximum	UV spectral width	S_1 lifetime
cycloheptatriene	4.8 eV	0.7 eV	70 fs
benzene	4.8 eV	0.62 eV	100 ns
cyclopentadiene	5.2 eV	0.9 eV	71 fs

Nonmonotonic variation by 6 orders of magnitude!

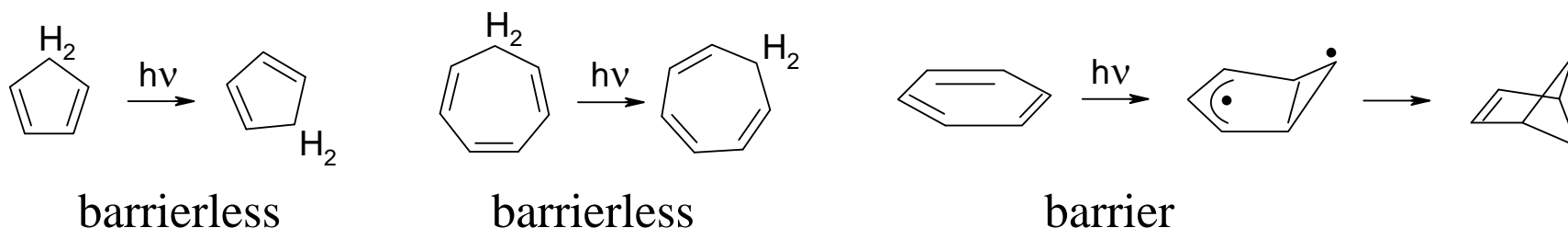
Obviously the traditional theory fails [Fuß et al, Chem. Phys. 316 (2005) 225].

$$k_{IC} = (4\pi^2/h) V_{el}^2 FC \rho$$

Obvious explanation:

The S_1/S_0 conical intersections (CI) of cycloheptatriene and cyclopentadiene are easily accessible. They belong to a barrierless H migration.

Benzene requires activation (nonplanar backbone deformation) to reach its last CI. Benzvalene forms from this CI. **But the reactants are also recovered from the last CI, corresponding to internal conversion.**



Ultrafast internal conversion is connected with an at least attempted photochemical reaction. The two processes have the initial path in common, branching only at the last CI.

Remarkable:

Just the fastest internal conversions are connected with large intermediate nuclear displacements!

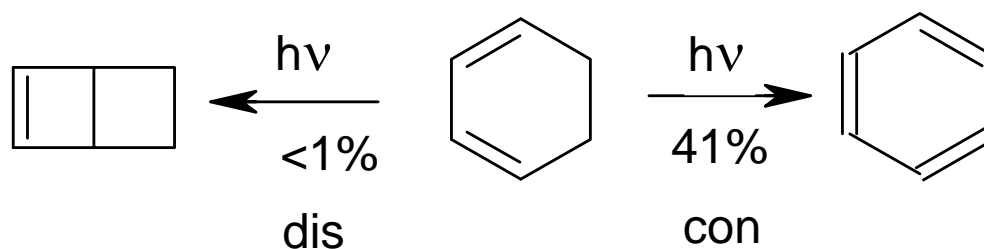
Instead of matrix elements and densities of states, consider potential surfaces, their slopes and intersections

Chemistry is not only a matter of matrix elements and density of states, but a matter of forces.

Early branching can be induced by the initial slopes:

1. Branching between conrotatory and disrotatory electrocyclic reactions.

Example:



Both reactions are Woodward-Hoffmann allowed.

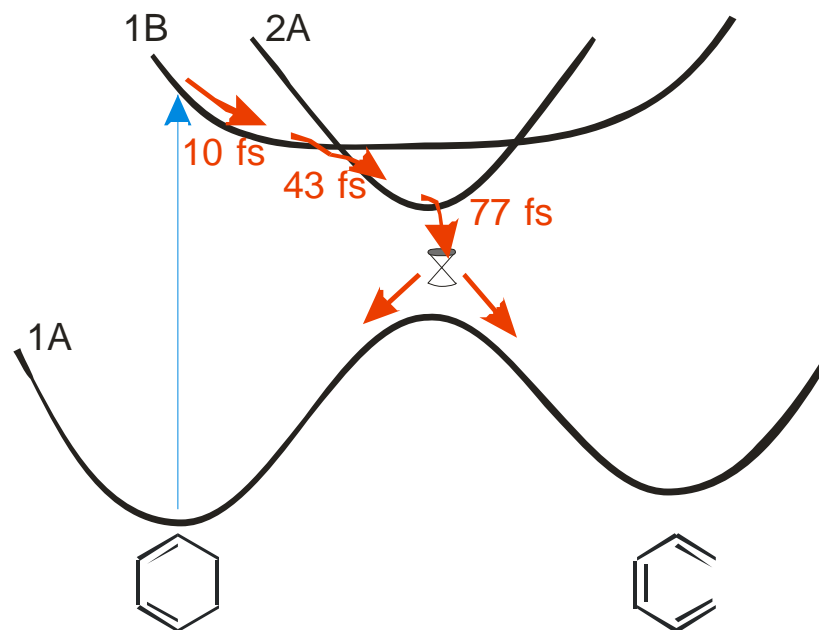
Why is the disrotatory reaction practically negligible versus the conrotatory reaction?

Suggestion:

This is not an electronic effect

but is induced by predistortion in S_0 in combination with the slopes in the FC region.

Cyclohexadiene ring opening: motion on the excited surfaces



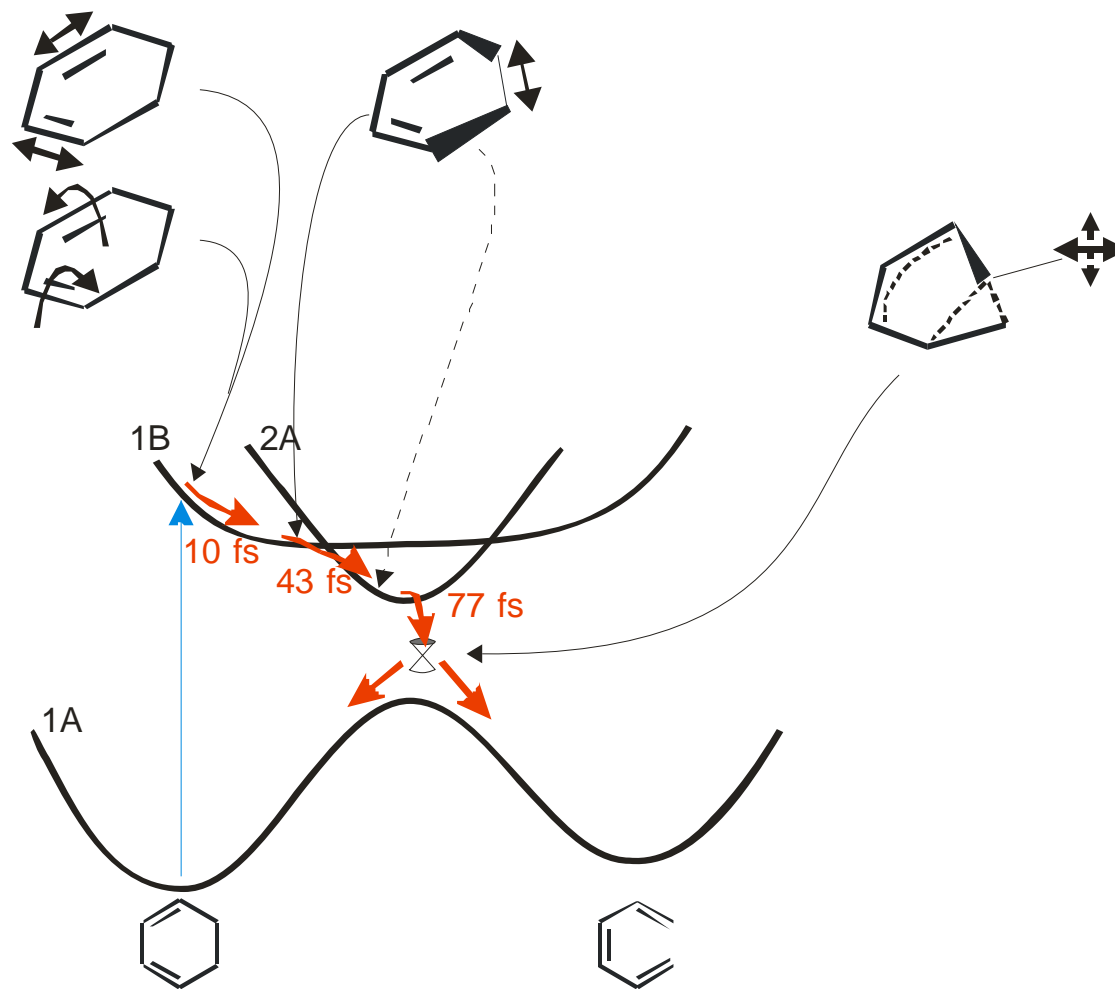
[Fuß et al., JCP 112 (2000) 8347]

Cyclohexadiene ring opening: motion on the excited surfaces

Calculated directions of motion, confirmed by substituent effects [Garavelli et al., JCP A 105 (2001) 4458].

C=C torsion in the FC region also distorts the backbone, erecting the CH₂CH₂ bond so that Woodward-Hoffmann interactions can set in. In the last CI: 3-electron 3-center bond.

Recently confirmed by observation of coherent oscillations (vibrations) at improved time resolution [Kosma et al., *subm. to PCCP*].



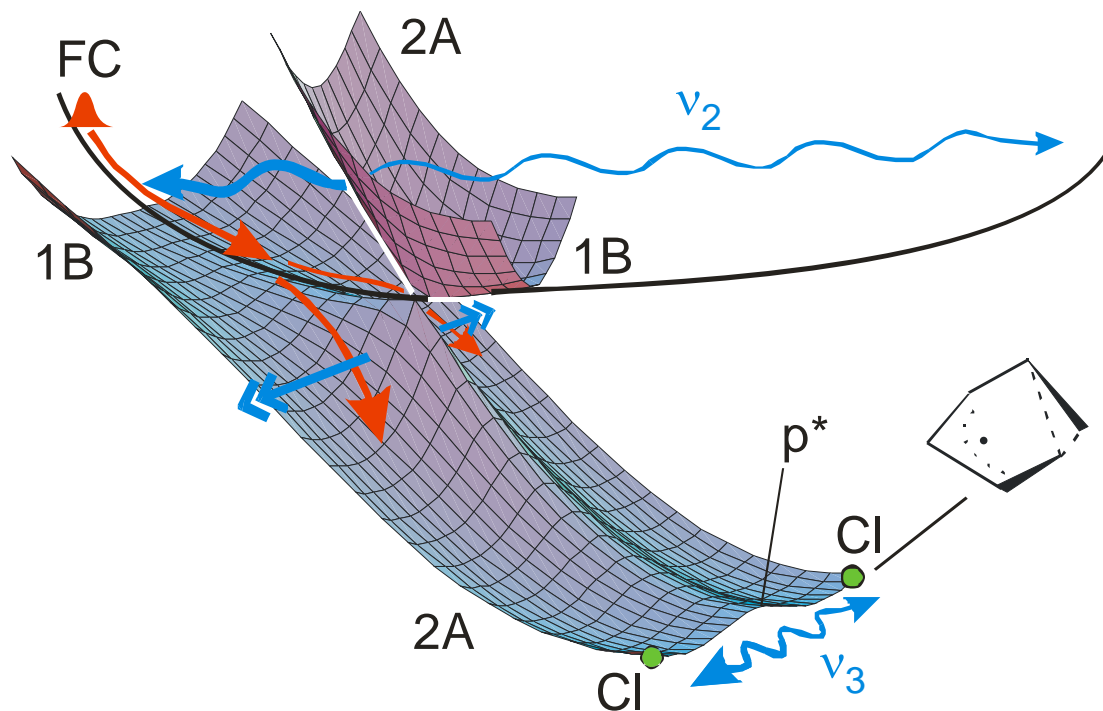
Every photochemical reaction begins with motion along Franck-Condon active coordinates.

The Woodward-Hoffmann rules are turned on only with delay, after leaving the Franck-Condon region.

Forces induced by

- (1) slopes along Franck-Condon active coordinates,
- (2) specific chemical interactions (pericyclic, cis-trans, proton transfer, ...)
- (3) slopes near conical intersections.

Cyclohexadiene: The path from the spectroscopic surface (1B) to the dark state (2A). Observed oscillations and (double arrows:) forces near the first CI.



Electronic symmetry change $1B \rightarrow 2A$ requires an antisymmetric (b-type) distortion on going around the lower cone of the first CI.

This is the origin of the steep negative curvature in this region, which later diminishes. The early force stimulates the antisymmetric vibration, which in turn indicates the direction of the force. (Similar with v_2 .)

The observed vibrations ($\nu_2 = 300 \text{ cm}^{-1}$, $\nu_3 = 140 \text{ cm}^{-1}$) correspond to ring puckering and are reduced compared to S_0 ($\nu_{18} = 506 \text{ cm}^{-1}$).
 \Rightarrow Ring opening begins on 1B, advances much more on 2A, but is only completed in S_0 .

A true photochemical reaction begins in an excited state but is only completed in the ground state.

Contrast: Hot-ground state reactions.

In ultrafast (more or less barrierless) reactions, the fate of the reaction is not controlled by thermodynamics but by the dynamics.

That is, the wave packet has no time to sample all parts of the potential that would be energetically accessible.

(Contrast to van der Lugt and Oosterhoff:

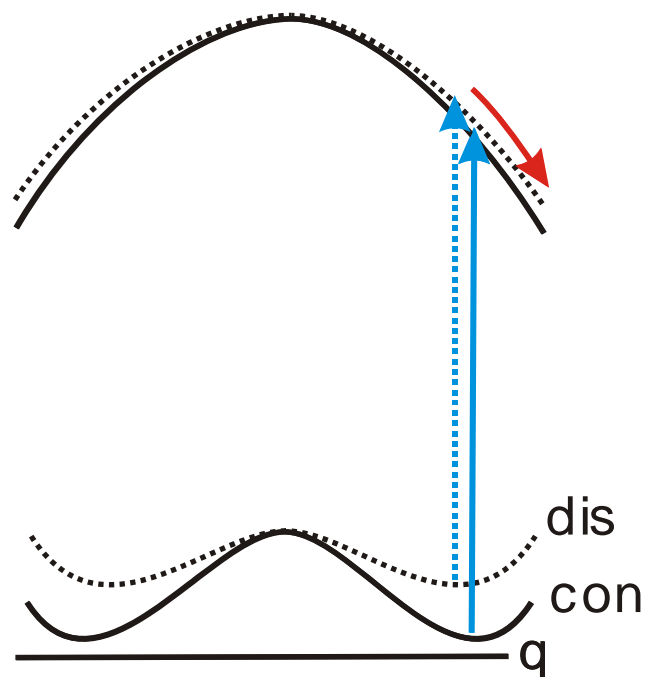
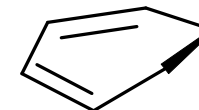
They said, the molecules, which initially went the wrong (anti-Woodward-Hoffmann) way, arrive at a late barrier (in the dark 2-el. excited state) and then will go back to try once more.)

The decision in favor of the WH-allowed (on expense of the WH-forbidden) path is taken in a different way.

(Still: Control by early branching)

Two degrees of freedom for C=C torsion in cyclohexadiene:

- in the 1B state probably similar in con- and dis- direction,
- in the ground state predistortion in conrotatory direction.



(Dotted lines: Cut perpendicular to the drawing plane)

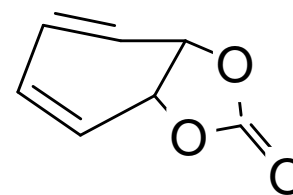
Vertical excitation leads to a down-slope in the direction of predistortion.

= Conformer control of a different kind than in the NEER principle.

Should work, if in the excited state the distortion is facilitated (or promoted) compared to S_0 .

In fact:

Substitution that causes disrotatory predistortion leads to (disrotatory) ring closure instead of (conrotatory) ring opening. Many examples!



The FC acceleration sends the molecule to one of two different regions.

In each, the forbidden path is blocked and the allowed one (which is different for the two regions) is taken.

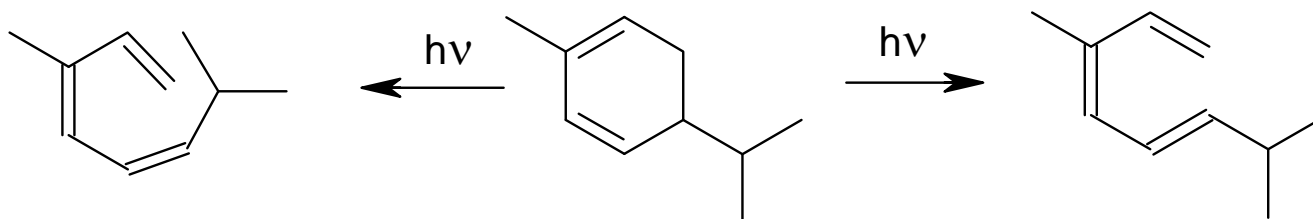
There is no necessity for the wave packet to return and try once more.

The FC acceleration selects between two allowed channels.

This mechanism can also be invoked to explain the principle of least motion.

Early branching can be induced by the initial slopes:

2. Principle of least motion. Example:

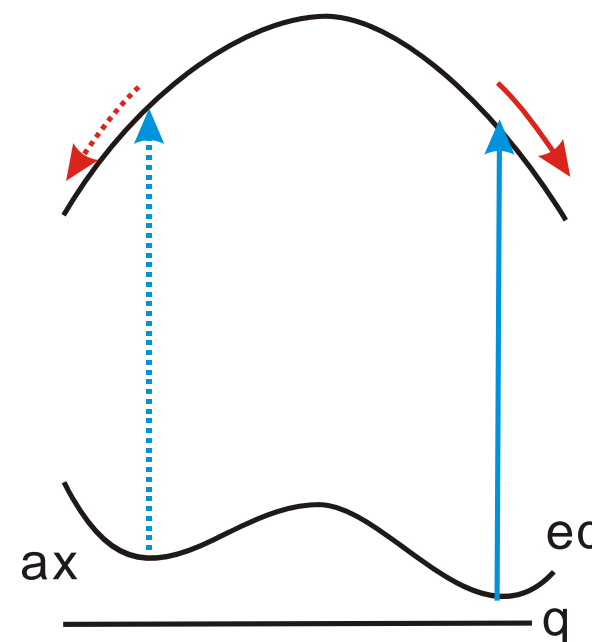


One of the two (axial/equatorial) conformers produces the cis-substituted triene, the other the trans isomer, such that least motion is involved.

Both are Woodward-Hoffmann allowed.

Electronic reasons have been invoked for the preference for least motion.

But the scheme with predistortion in S_0 and facilitated distortion in the excited state seems simpler.

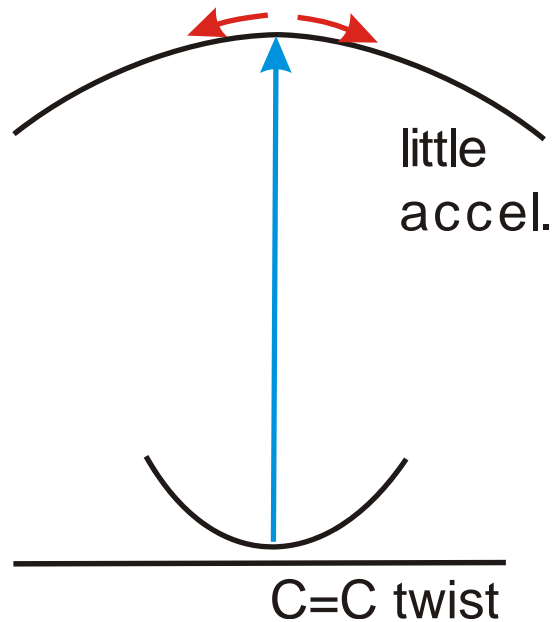


Early branching induced by the initial slopes

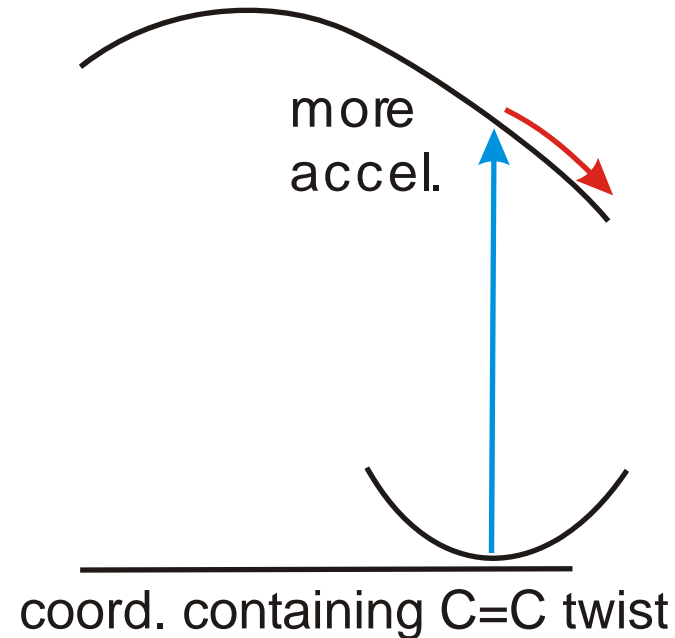
also in the case of the retinal chromophore in the opsin matrix?

In the matrix, the isomerization is (1) faster, (2) more efficient, (3) more selective. (1) and (2) are surprising in view of the steric hindrance.

free retinal-PSB



rhodopsin



Note: Initial change of bond lengths is not shown.

Explanation works, if momentum is conserved until reaching the S_1/S_0 CI.

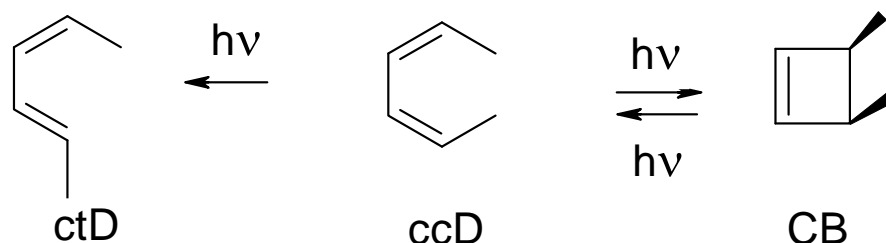
Momentum (memory) effects:

Ring closure/opening in the diene/cyclobutene system

(prototype of pericyclic reactions)

[Mol.Phys. 104 (2006) 1133, ChemPhysChem 8 (2007) 592]

(*cis,cis*-) diene \rightarrow (*cis*-) cyclobutene / cyclobutene \rightarrow diene

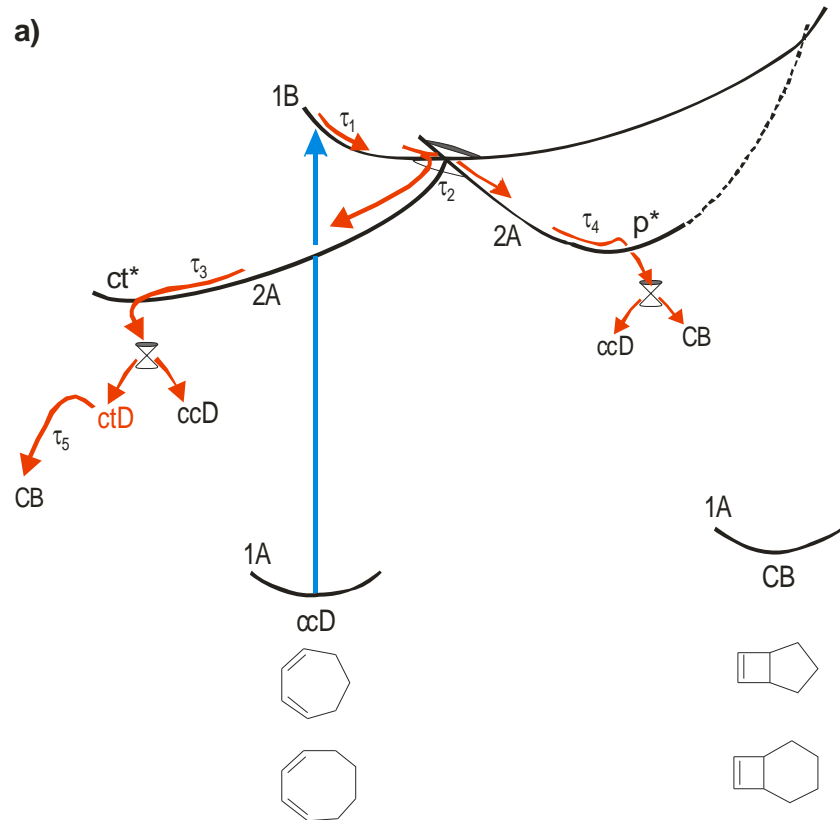


The forward reaction $ccD \rightarrow CB$ is **perfectly stereospecific** according to the Woodward-Hoffmann rules.

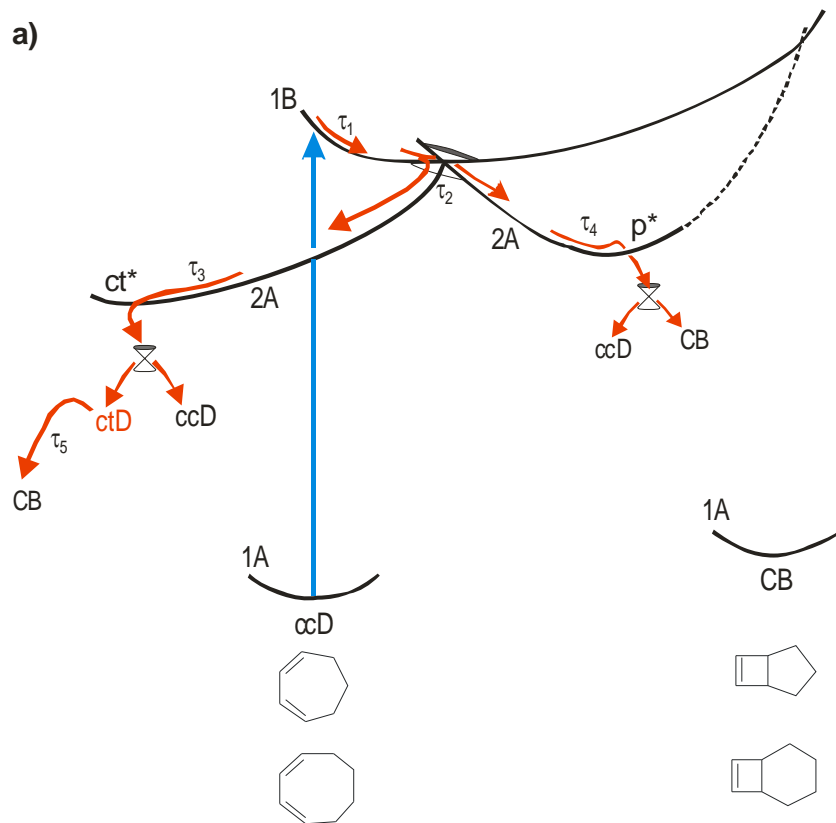
The backward reaction is **nonspecific**: $CB \rightarrow ccD + ctD$.

Seems incompatible with the idea of a common intermediate state.

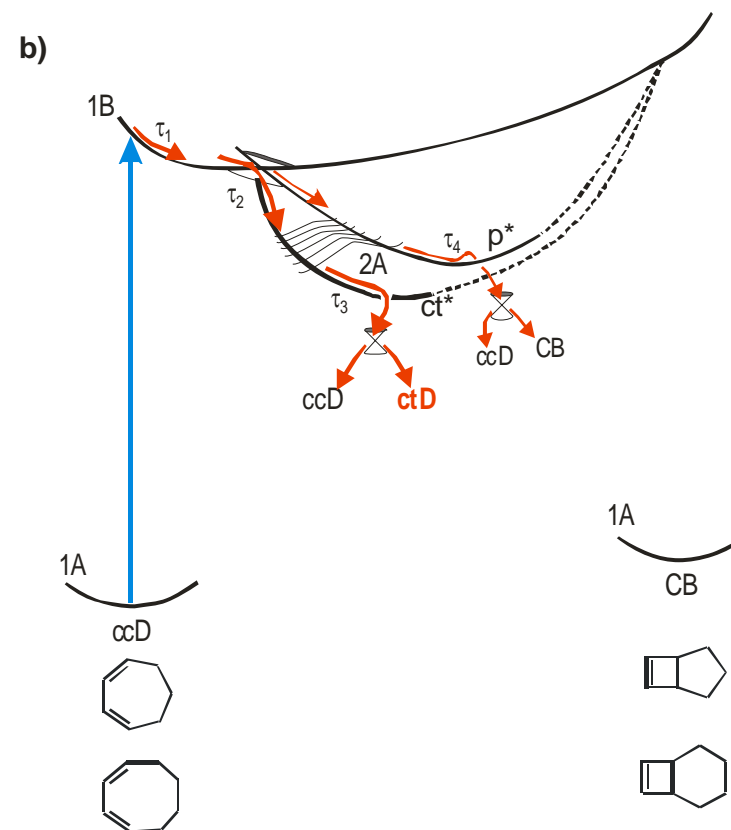
Olivucci et al. (1992): *The geometrical structures for the S_1/S_0 CI are very similar for the *cis-trans* (Hula-twist) isomerization and the 4e-electrocyclic reaction.*



Case that the coordinates for ring closure and cis-trans isomerization are *very different*

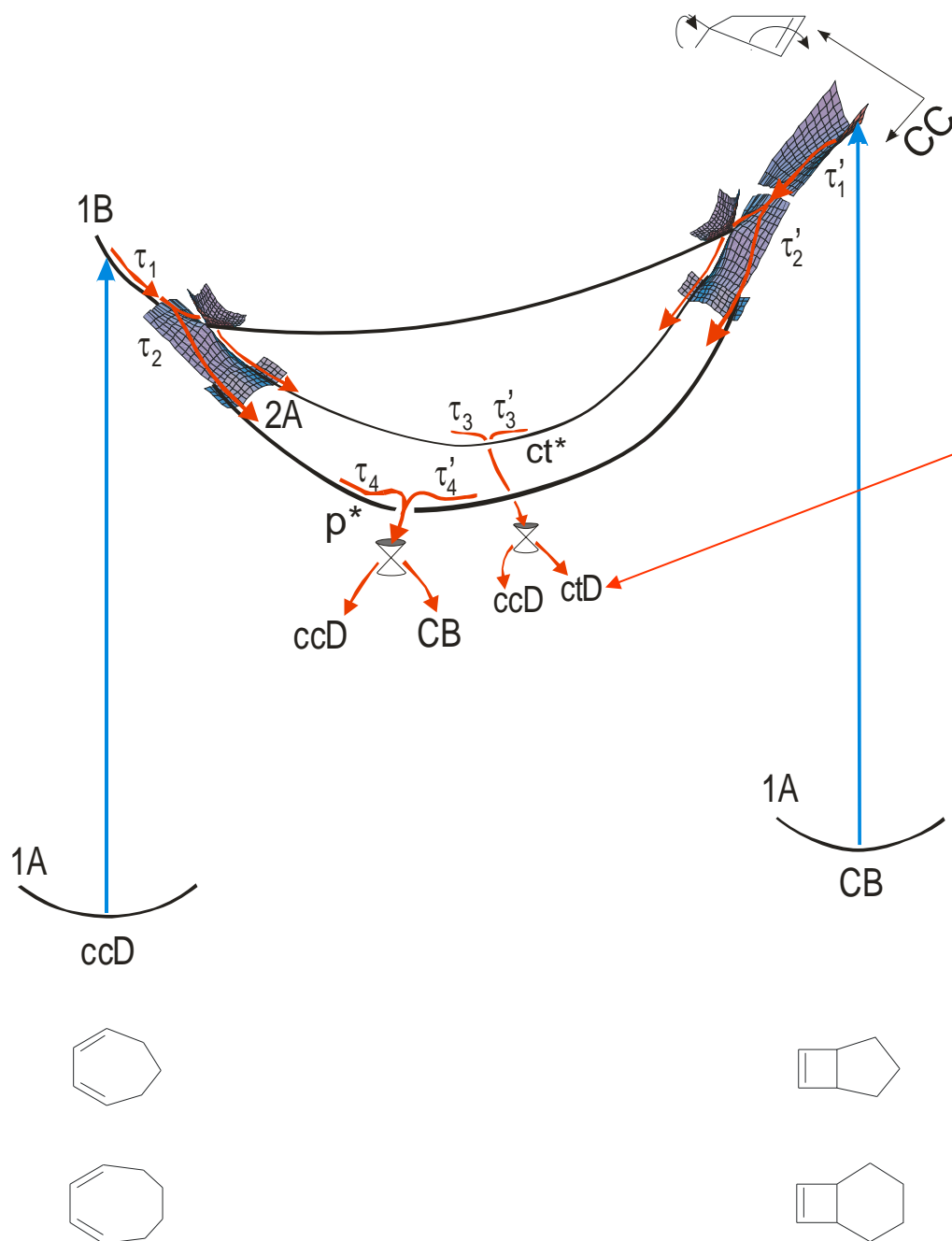


Case that the coordinates for ring closure and cis-trans isomerization are *very different*



Case that the coordinates for ring closure and cis-trans isomerization are *geometrically similar*.

In this case, the ct* minimum should also be accessible from the CB side!



Indeed, both channels are accessible also from the CB side. This explains the formation of the (forbidden) **ctD**.

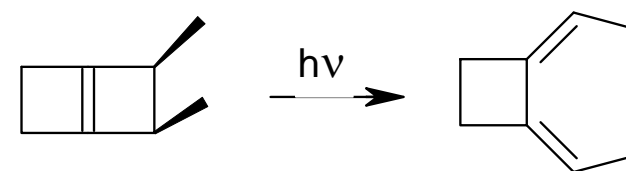
Evidence: $\tau_3' = \tau_3$ for two isomer pairs can hardly be accidental.

The allowed (disrotatory) path emanates out the front of the first CI and is energetically more favorable.

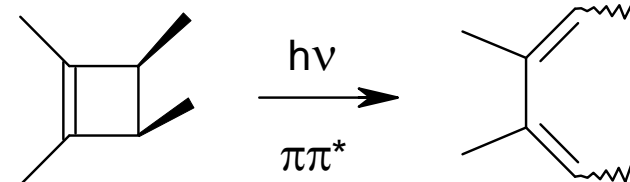
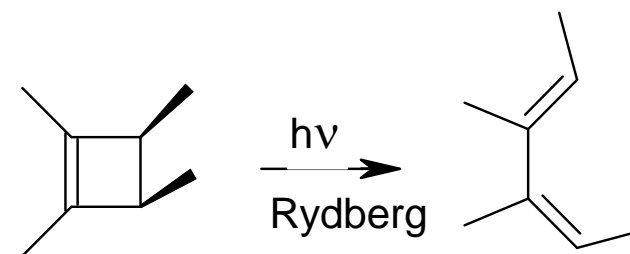
An initial (conrotatory) C=C twist renders the forbidden path competitive.

Additional evidence, that it is a momentum effect:

(1) One can *decrease* the initial (con = anti-WH) momentum by fusing CB with another small ring. Such systems indeed obey the WH rules [Leigh et al.] [Fuß et al., ChemPhysChem 8 (2007) 592].



(2) one can also *increase* the initial con momentum by exciting a Rydberg state, preceding the $\pi\pi^*$ band in 1,2-dialkyl-CB. In this case, ring opening is stereospecific in *anti-WH* direction, whereas on $\pi\pi^*$ excitation, the reaction is nonspecific! [Leigh et al.]

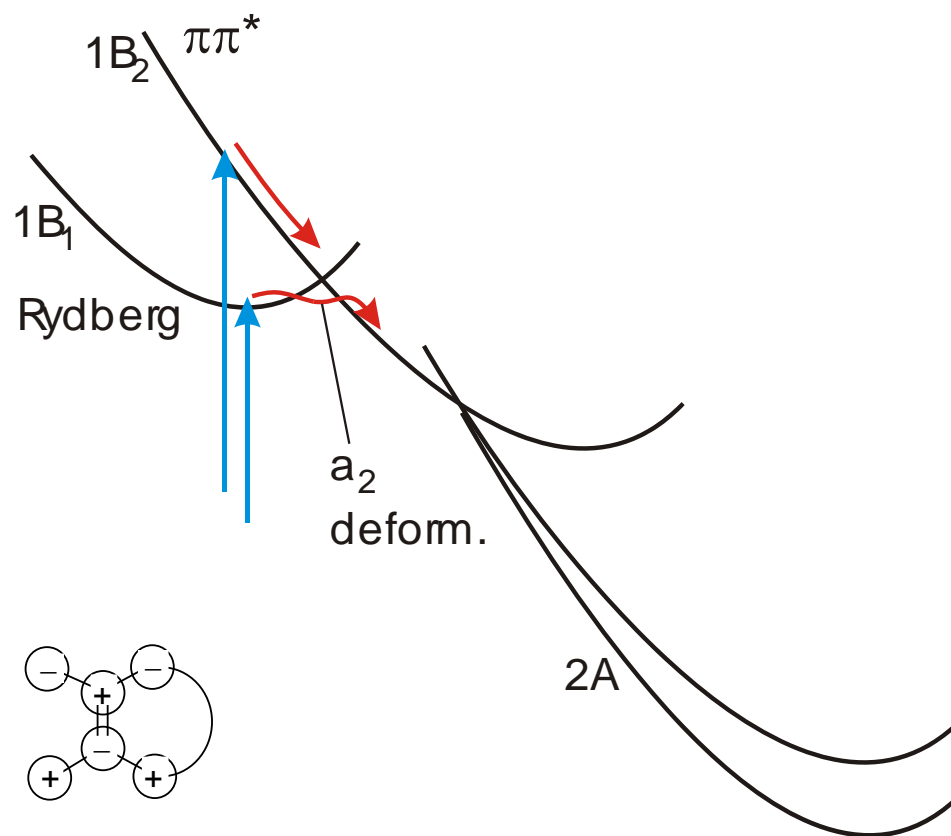


The molecule relaxes from the Rydberg state via the $\pi\pi^*$ state.

Because the two states have different symmetries, this relaxation is only possible with a temporary a_2 deformation.

An a_2 deformation is conrotatory (anti-WH)!

The a_2 momentum can influence a later branching between WH- and anti-WH-paths.



Note: At first sight, the potential and relaxation scheme seems to be compatible with the Kasha rule (“All paths merge in S_1 ”).

The observed anti-Kasha behavior (wavelength dependence) is here explained by the extra momentum.

This mechanism probably applies to many anti-Kasha cases.

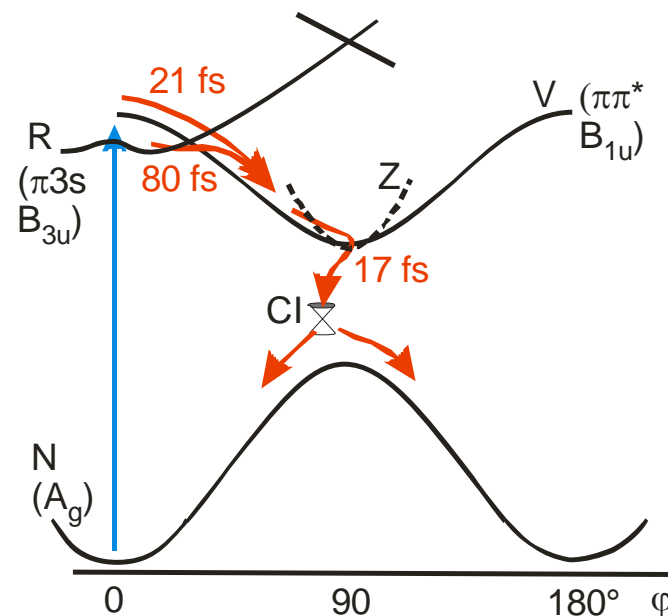
Momentum effects affect the final branching ratios.

⇒ Not only the dark states decide on the fate of the reactions.

We already applied this mechanism to the wavelength-dependent photochemistry (anti-Kasha behavior) of mono-olefins (cyclohexene ...): The yield ratio of carbene formation other isomers (cis-trans, pericyclic ...) is higher from the lowest Rydberg ($\pi\sigma^*$) state than from the $\pi\pi^*$ state. [JACS 123 (2001) 7101, JPC A 105 (2001) 10640].

But the two paths merge (as in the Kasha case); the Rydberg state is depleted into the $\pi\pi^*$ state. We measured this also in the case of ethylene:

The additional momentum of the wave packet coming from the Rydberg state is conserved over some time and influences the path near the last CI. Probably the region before the last CI is flat in several directions, and the intersection space probably too. (The CI is not a point, but extends over $f-2$ dimensions.)



Fast relaxation between energetically close-lying states (e.g. between excited states) (invoked to explain the Kasha rule):

Traditional rationalization: Exponential gap rule.

Better:

If two close-lying potentials have different curvature but different bonding properties (e.g. if a higher state is antibonding and a lower one (weakly) bonding in a certain direction) they will intersect, typically in an easily accessible CI. \Rightarrow Fast relaxation.

Also explains cases such as Rydberg \rightarrow $\pi\pi^*$ relaxation in C_2F_4 [ChemPhysChem 5 (2004) 1389], where in the FC region the $\pi\pi^*$ state is by 2 eV higher than the Rydberg state. The exponential gap rule would fail here.

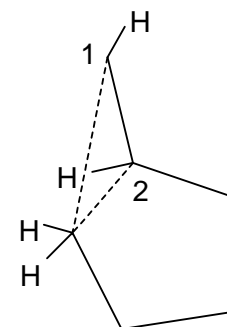
In alkylated olefins, cis-trans isomers are also formed from the same CI as carbenes. The latter often result mainly from alkyl migration, less so from H migration.

Cyclohexene, suggested CI structure.

[JACS123(2001)7101]

C1C2 = previous C=C bond, now perpendicularly twisted; CH₂ partially migrated from C1 to C2.

Note: **The σ backbone is strain-free!**



Cyclohexene forms not only a carbene but also a trans(oid) isomer, which is extremely strained.

Photochemistry often produces highly strained products.

The region of branching between strained products and the reactant (or other products), i.e. the S₁/S₀ CI, **must be practically strain-free**. When later a strain begins to develop, a barrier (ridge) must appear and separate the valleys. Otherwise the wave packet would decide to go back to the reactant.

Conclusion

To explain the course of photochemical reactions, in the early times people only considered the electronic structure in the Franck-Condon region. (Sometimes still done today.)

In the 1990s, conical intersections (far from the FC region) were recognized to be the most important branching regions in photochemical reactions (Olivucci, Robb, Domcke, Yarkony).

In many cases it seems worth while to consider all the path along the potentials, including also early branchings and momentum effects. This provides simple explanations of

- the choice of different WH allowed reactions,
- the principle of least motion,
- the lack (of species and wavelength dependence) of stereoselectivity in cyclobutene photochemistry,
- anti-Kasha behavior, and also Kasha conformity,
- formation of strained products.