Chemical bonding in excited states from topological frameworks: The case of [2+2] cycloaddition

Cristian Guerra[1], Leandro Ayarde[1], Mario Duque-Noreña[1], Eduardo Chamorro[1]

Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andrés Bello, Avenida República 275, Santiago, 8370146, Chile.[1]

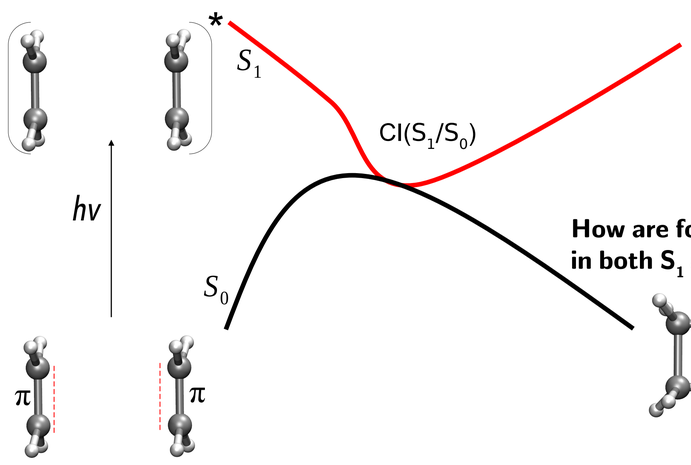
c.guerramadera@uandresbello.edu, layarde86@gmail.com, mduque@unab.cl, echamorro@unab.cl

INTRODUCTION

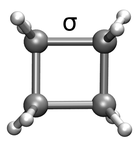
The [2+2] cycloaddition corresponds to a specific kind of pericyclic reaction has a synthetic route is mainly photochemical. From a mechanistic viewpoint, the electronic rearrangements associated to this reaction involved the breaking of two π-bonds forming two new σ-sigma bonds within a prototypical ethylene + ethylene reaction system. The most accepted reaction mechanism associated to these reactions was proposed by Bernardi et al., wherein the deactivation funnel to ground state is a conical intersection S_1/S_0.

How the C=C double bonds are broken in S_1 excited state?

Which electronic rearrangements accompanied the evolution of reacting system toward to conical intersection?



How are former the C-C bonds in both S_1 and S_0 states?

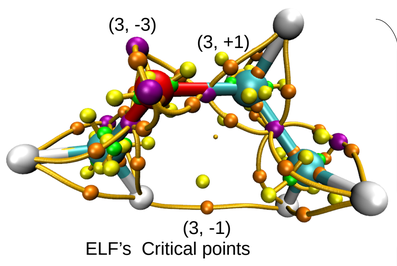


The aim of this work is to study the electronic rearrangements occurring in various mechanisms proposed for the [2+2] cycloaddition in S_1 excited state, from the Bonding evolution theory framework(BET).

$\eta(r)$

Electron localization Function

Localization of electron pairs.



ELF's Critical points

$\nabla\eta(r;R)=0$

The reaction system represented by the ELF along with nuclear displacements R, constitute a gradient dynamical system.

Rene Thom Classification.

Catastrophe

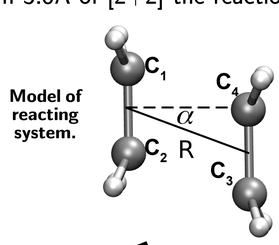
Appearance/annihilation of critical points.

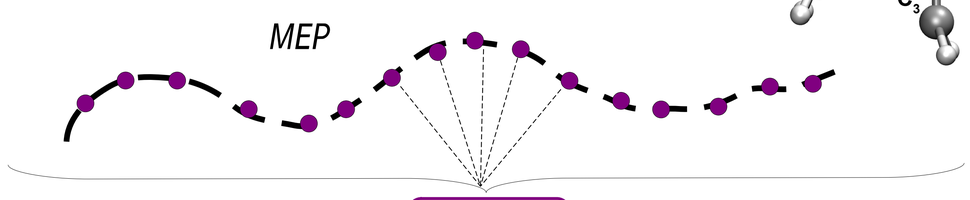
Key chemical bonding events.

- Formation and breaking of chemical bonds.
- Electron pair migration or appearance.

Computational details

All the Ab-initio calculations were performed within the MC-SCF theoretical background using the Gaussian09 and ORCA packages. The CASSCF calculations for the [2+2] reaction system were carried out with an active space of 4 electrons distributed in 4 orbitals. The composition of active space includes the orbitals in both ethylene fragments (HOMO-LUMO pair), which has been reported as the most relevant in this kind of calculation. The molecular modeling of [2+2] reaction path was carried out employing the Nudged Elastic Band method (NEB). The reaction path was generated means by NEB calculations mapping the energy surface from 3.8Å of [2+2] the reaction center distance to the optimized cyclobutane product in each of the states S_0, S_1.





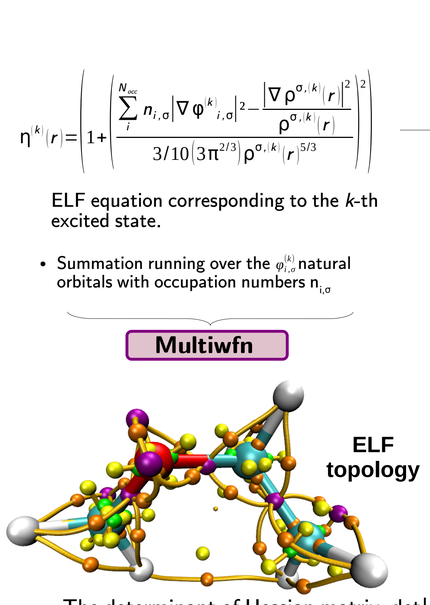
Ψ_{CASSCF}

$$\eta^{(k)}(r)=\left(1+\left(\frac{\sum_{i}^{N_{occ}} n_{i,\sigma}\left|\nabla\varphi^{(k)}_{i,\sigma}\right|^2-\frac{\left|\nabla\rho^{\sigma,(k)}(r)\right|^2}{\rho^{\sigma,(k)}(r)}}{3/10\left(3\pi^{2/3}\right)\rho^{\sigma,(k)}(r)^{5/3}}\right)^2\right)$$

ELF equation corresponding to the *k*-th excited state.

- Summation running over the $\varphi^{(k)}_{i,\sigma}$ natural orbitals with occupation numbers $n_{i,\sigma}$

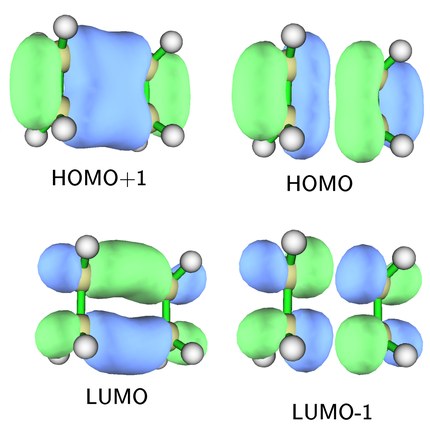
Multiwfn



ELF topology

The determinant of Hessian matrix, det|H_{ij}|, at the ELF critical points was used for the characterization of catastrophes.

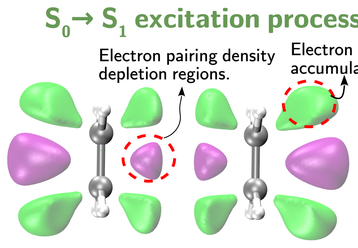
$det|H_{ij}|$



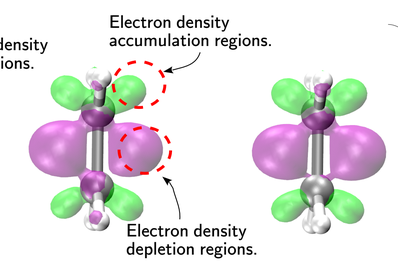
NEVPT2 Energies

RESULTS

$S_0 \rightarrow S_1$ excitation process



$\Delta\eta(r)_{S_0\rightarrow S_1}$

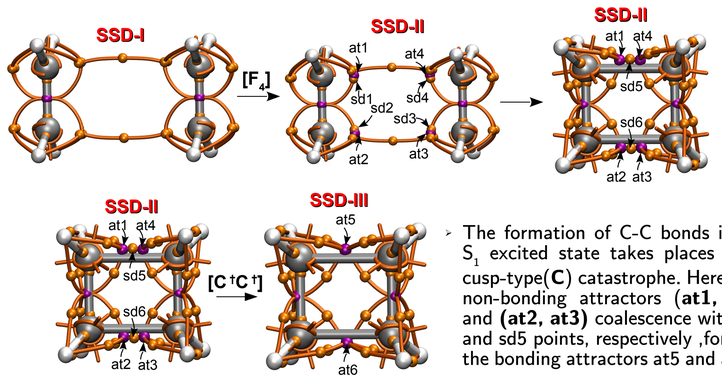


$\Delta\rho(r)_{S_0\rightarrow S_1}$

- Double bond weakening
- Accumulation of pairing and electron density on carbon centers.

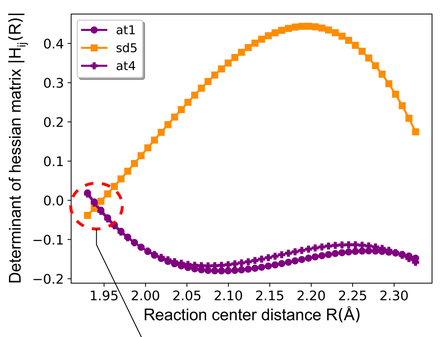
S_1-Reaction path

The fist reaction stage is the accumulation of pairing density on C carbon atoms, this rearrangement is characterized by four simultaneous fold (**F**) catastrophes.



The formation of C-C bonds in the S_1 excited state takes places via a cusp-type(**C**) catastrophe. Here, the non-bonding attractors (**at1, at4)** and **(at2, at3)** coalescence with sd1 and sd5 points, respectively ,forming the bonding attractors at5 and at6.

C: at + sd+ at→at

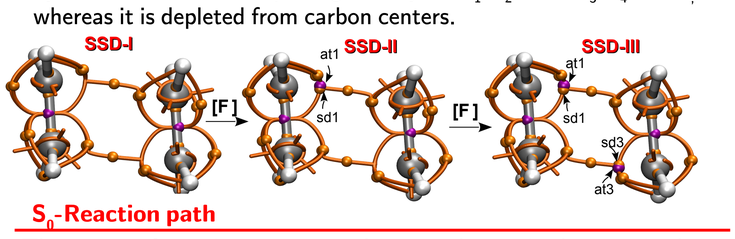


Degeneration of at1,sd5, and at4 critical points.

S_1-S_0Reaction path

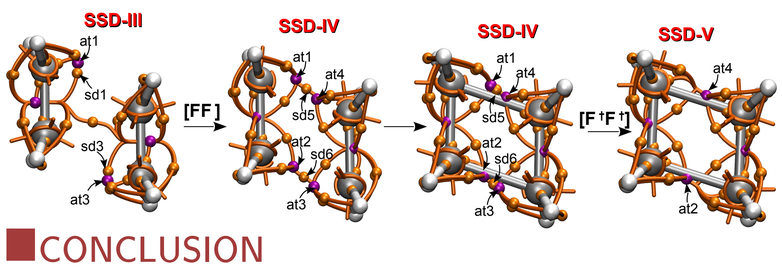
S_1-Reaction path

In the case of rhomboidal reaction path, the accumulation of pairing density occurs on C_1 and C_3 centers, via a fold-type catastrophe, instead of the over whole reaction center. The minimal energy conical intersection point (MECI) is characterized by the concentration of pairing density on C_1-C_2 and C_3-C_4 bonds, whereas it is depleted from carbon centers.

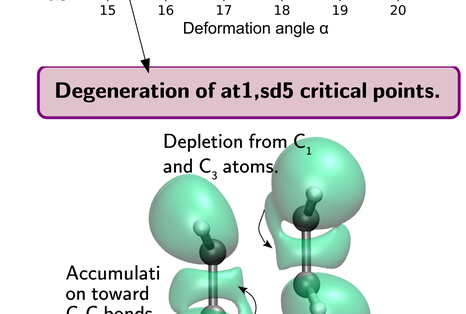


S_0-Reaction path

The return of reacting system to the ground state is characterized by the full reduction of C=C bonds to single type ones. Besides, carbon atoms accumulate higher pairing density than in the case of the S_1 excited state. The new C-C bonds formed in ground state are originated through fold-type catastrophes ocurring at both C_1 and C_3 carbon atoms.



F: at + sd→ wp



Degeneration of at1,sd5 critical points.

MECI(S_1/S_0)

CONCLUSION

- The excitation process ($S_0 \rightarrow S_1$) leads to weakening of double bonds in each reactant ethylene, as well as to the accumulation of pairing density on carbon atoms.
- The activation of the reaction center in [2+2]-type cycloaddition in the S_1 excited state takes place at comparatively long interaction distances and through ***fold-type*** catastrophes.
- The return to reacting system to ground state is featured by the formation of C-C bonds via ***fold-type*** catastrophes.
- The formation of the C-C bonds in the S_1 excited state for [2+2] type cycloaddition, via **cusp-type catastrophes**, where two electron density centers of equally charged pairs and one saddle point fused.
- Elementary catastrophes can explain electronic rearrangements occurring in excited electronic states. So far, only fundamental state bifurcation catastrophes have been reported in reactions such as Diels-Alder, or the Cope rearrangement. This work showed that the bonding evolution theory can be applied to reactions in excited states such as [2+2]-type cycloaddition, explaining key bonding events.

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ACKNOWLEDGMENTS

The authors acknowledge the continuous support provided by Fondo Nacional de Ciencia y Tecnologia (FONDECYT-Chile) through project no. 1181582. E.R.