On the automatic computation of global (intermolecular) potential energy surfaces for quantum dynamical simulations

Ramón L. PANADÉS-BARRUETA

30^{th} Summer School and International Symposium on the Physics of Ionized Gases

(SPIG2020)

August 27, 2020

Outline

PhLAM Physique des Lasers Atomes et Molécules

1. Environmental and physicochemical problem
   - Interaction of soot particles with atmospheric molecules
2. Theoretical modeling of the system
   - Automatic topographical characterization of the PES
     - vdW-TSSCDS
   - Computation of the PES
3. The Pyrene-NO_2 system
   - LL trajectories and sampling
   - HL stationary points
   - Reaction network
4. Conclusions and future perspectives

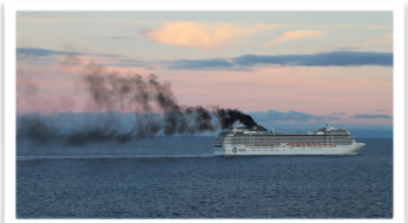
Outline

Environmental problem

Incomplete combustion products

https://californiaac.wordpress.com/2015/02/19/what-is-soot/

https://www.quora.com/Why-is-the-exhaust-from-my-diesel-engine-black-smoke



http://www.dw.com/en/hoping-for-a-fresh-sea-breeze-aboard-a-cruise-ship-better-hold-your-nose/a-37284464

http://www.co2offsetresearch.org/aviation/Particulates.html

What is the interaction between a "soot" particle and a (small) molecule?

Soot particles are *second* to CO_2 in their contribution to global warming

Ramanathan *et al.* Nat. Geosci. 1.4 (2008): 221.

REVIEW ARTICLE

Global and regional climate changes due to black carbon

Soot particles are substrate to heterogeneous reactions leading to the production of radicals...

Monge *et al.* PNAS 107.15 (2010): 6605-6609.

Light changes the atmospheric reactivity of soot

Maria Eugenia Monge[a], Barbara D'Anna[a,1], Linda Mazri[a], Anne Giroir-Fendler[a], Markus Ammann[b], D. J. Donaldson[c], and Christian George[a]

Suspected neurotoxicity of traffic related pollution

Sunyer *et al.* PLOS Med. 12.3 (2015): e1001792.

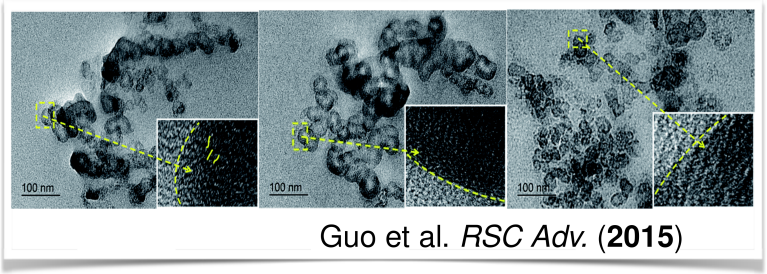
RESEARCH ARTICLE

Association between Traffic-Related Air Pollution in Schools and Cognitive Development in Primary School Children: A Prospective Cohort Study

Jordi Sunyer[*1,2,3,4], Mikel Esnaola[1,2,3], Mar Alvarez-Pedrerol[1,2,3], Joan Forns[1,2,3],

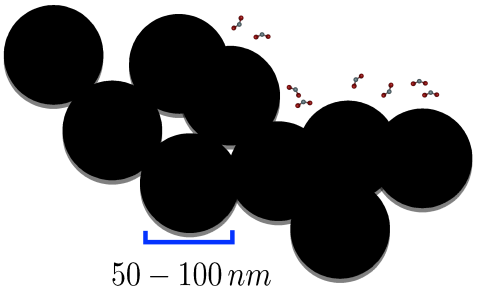
Modeling of the system

Modeling the molecule-soot (M-S) system

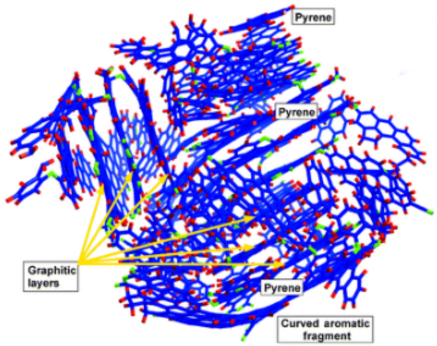


Guo et al. *RSC Adv.* (**2015**)

ns-soot

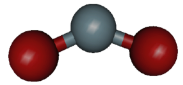


P. R. Buseck *et al.*, *Atmos. Chem. Phys. Discuss.* (**2012**)

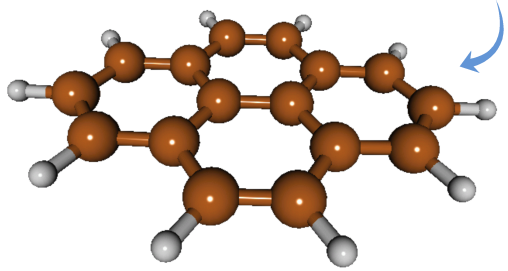


J. D. Kubicki, Geochem. Trans., 1, 41-46 (2000)

M = NO_2, NO, OH, O_3,...



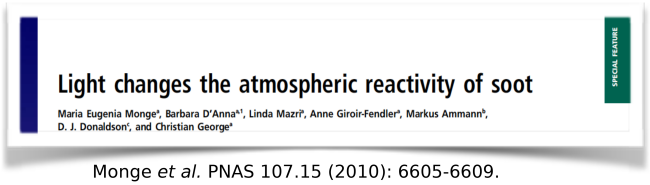
S = PAH



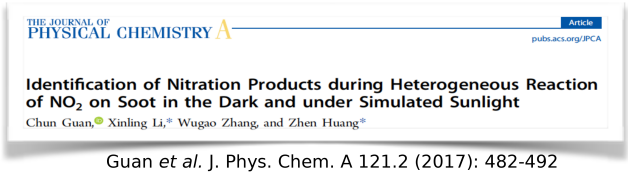
81D

Full Dimensional topographical analysis

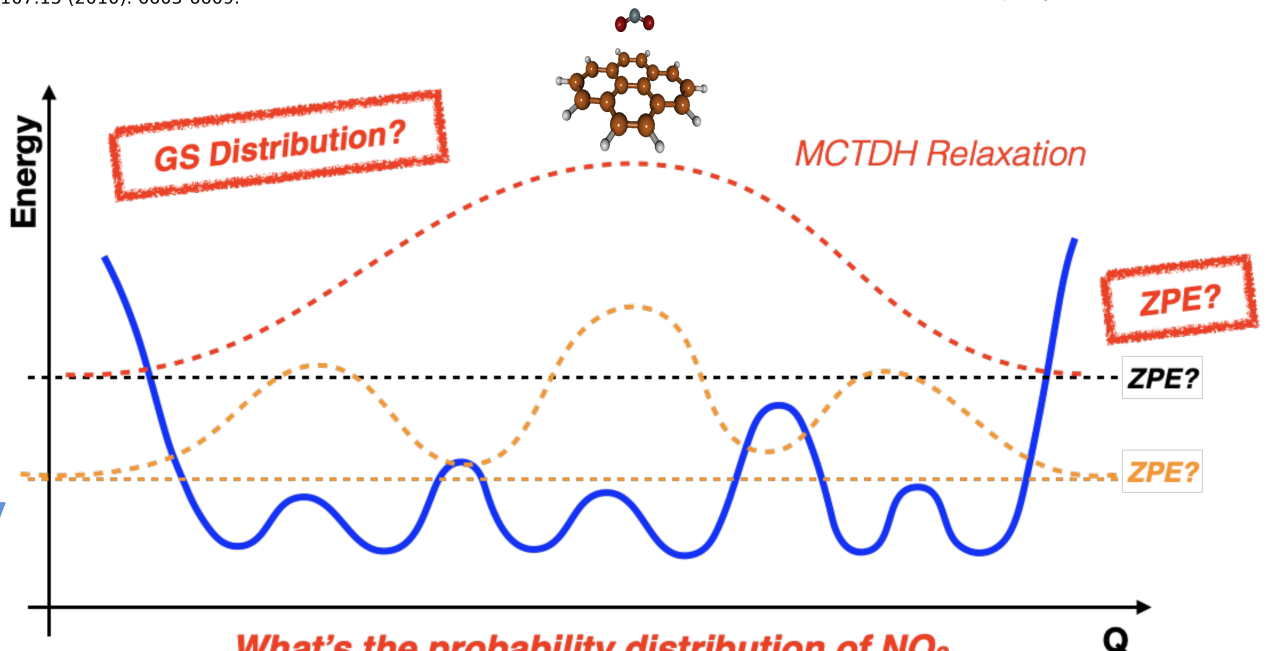
Ground state of the Pyrene NO_2 system



Monge *et al.* PNAS 107.15 (2010): 6605-6609.



Guan *et al.* J. Phys. Chem. A 121.2 (2017): 482-492

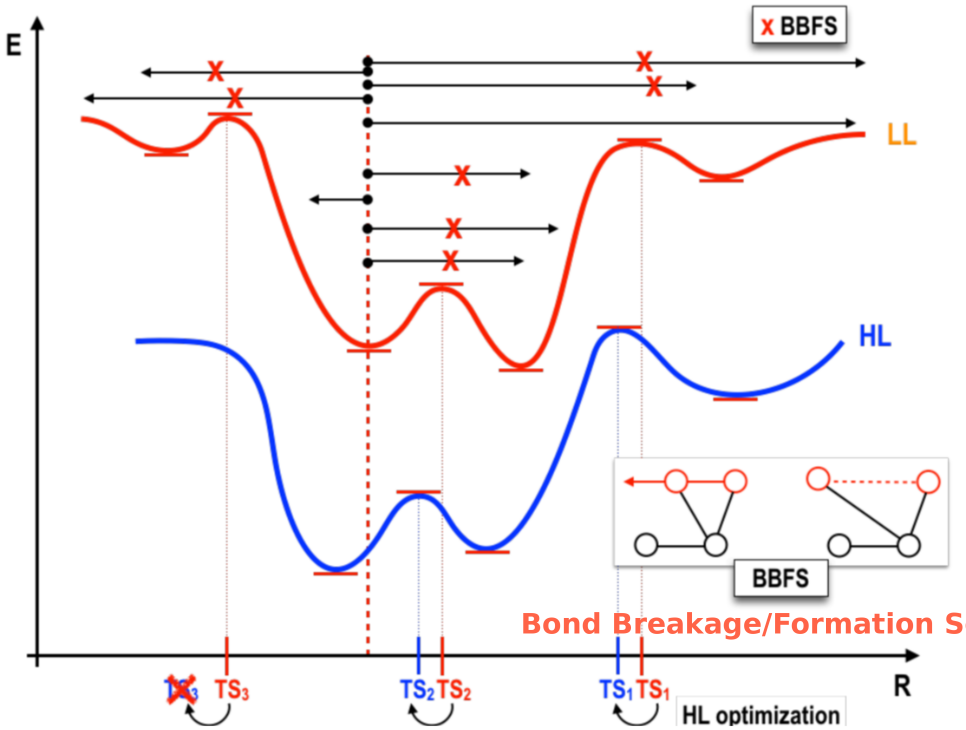


MCTDH
Multiconfiguration Time-Dependent Hartree

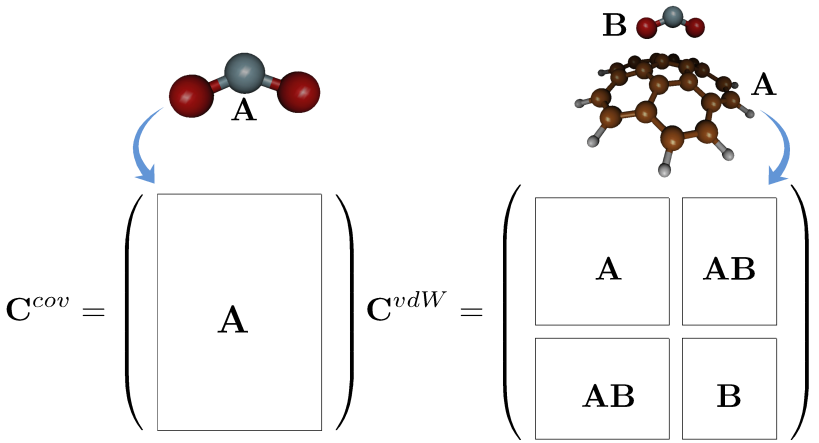
Nuclear Quantum Dynamics
(in reduced dimensionality)

Outline

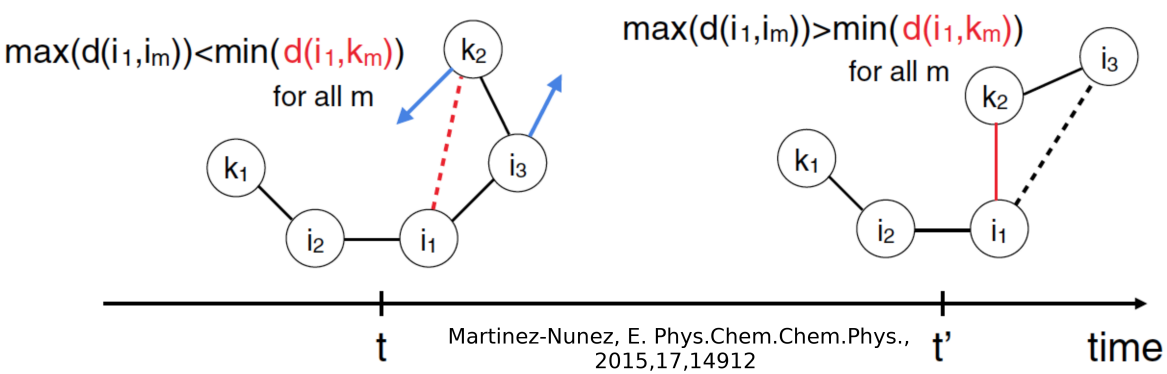
The vdW-TSSCDS method



Single input geometry!



Kopec, S., Martinez-Nunez, E., Soto, J. M., and Peláez, D.
Int. J. Quantum Chem. e26008. 2019

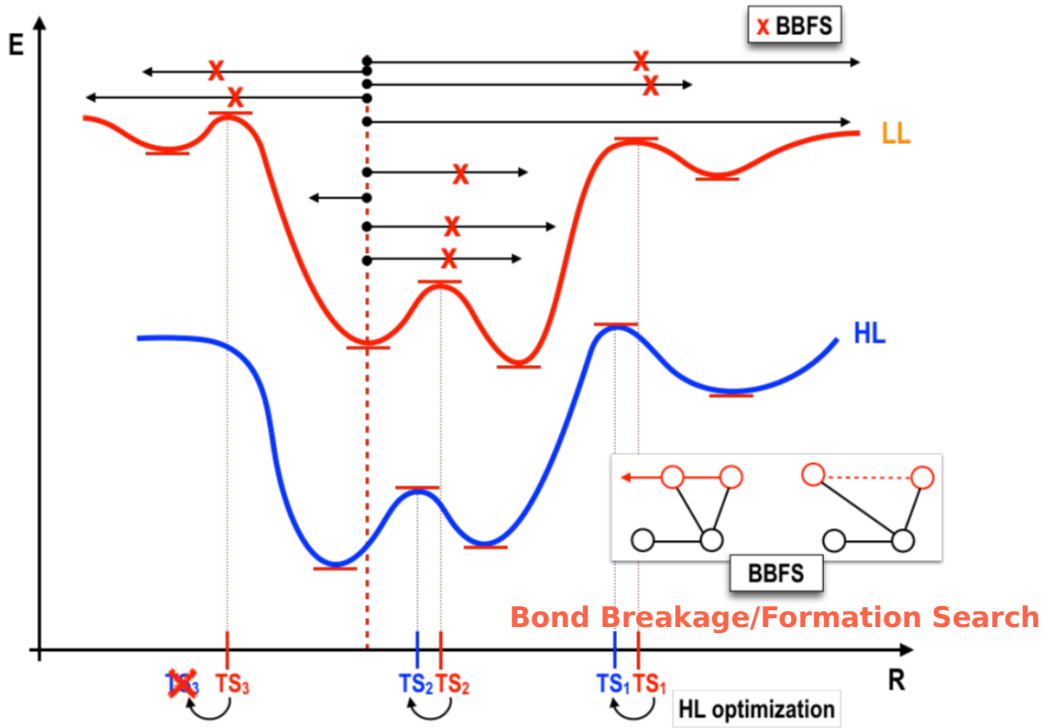


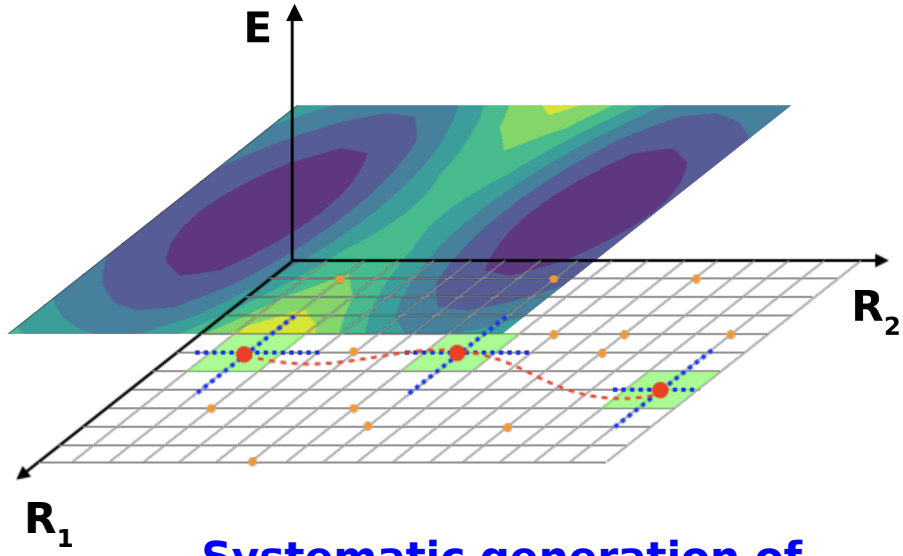
Martinez-Nunez, E. Phys.Chem.Chem.Phys., 2015,17,14912

$$c_{ij} = \begin{cases} 1 & \text{if } \delta_{ij} < 1 \\ 0 & \text{otherwise} \end{cases} \quad \text{, with } \delta_{ij} = \frac{d_{ij}}{d_{ij}^{ref}}$$

$$d_{ij}^{ref} = \begin{cases} A, B & \text{covalent radii} \\ AB & \text{van der Waals radii} \end{cases}$$

The vdW-TSSCDS method





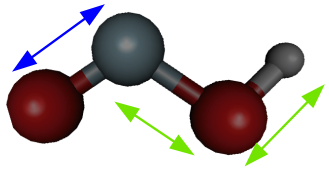
Systematic generation of PES reference data

Many body expansion:

$$R_i + R_{ij} + R_{i...n} + R_{IRC} + R_{\Delta IRC}$$

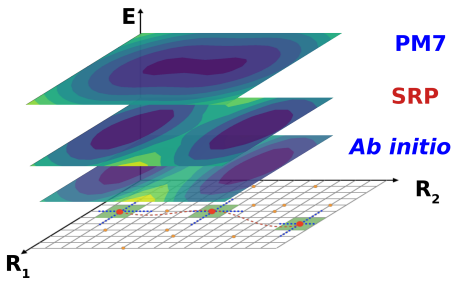
Panadés-Barrueta R., Martínez-Nuñez E. and Peláez D. Front. Chem. 7:576. 2019

Example:



- SP (vdW-TSSCDS)
- 1D grids
- 2D grids
- $rnd(6D)_{SP}$
- IRC

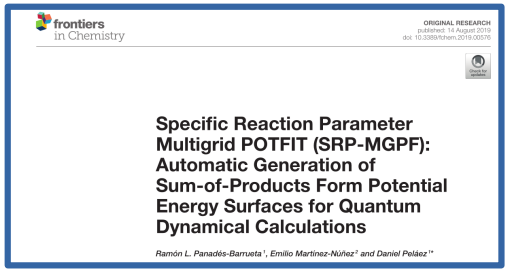
Computation of the PES



Automated generation of electronic structure level of theory

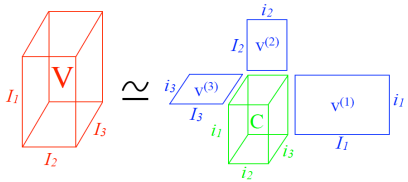
SRPTucker

SciPy



Specific Reaction Parameter Multigrid POTFIT (SRP-MGPF): Automatic Generation of Sum-of-Products Form Potential Energy Surfaces for Quantum Dynamical Calculations

Panadés-Barrueta R., Martínez-Nuñez E. and Peláez D. Front. Chem. 7:576. 2019



Tensor decomposition algorithm interfacing to nuclear quantum dynamical software

MGPF

f(or)tr[an]

The multigrid POTFIT (MGPF) method: Grid representations of potentials for quantum dynamics of large systems

Peláez, D., and Meyer, H. D. J. Chem. Phys. 138(1), 014108. 2013

$$V(q_1,\ldots,q_f)=\sum_{j_1}^{m_1}\cdots\sum_{j_f}^{m_f}C_{j_1,\ldots,j_f}\prod_{\kappa}^{f}\Big(\sum_{\mu}^{M}c_{\mu}^{(\kappa)}T(q^{(\kappa)})\Big)_{j_\kappa}$$

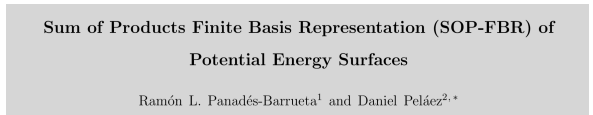
SOP-FBR

R.L. Panadés-Barrueta, D. Peláez, *article in preparation* (**2020**)

Automatic direct computation of the PES in Sums of Products form

SOP-FBR

f(or)tr[an]



Sum of Products Finite Basis Representation (SOP-FBR) of Potential Energy Surfaces

Ramón L. Panadés-Barrueta[1] and Daniel Peláez[2,*]

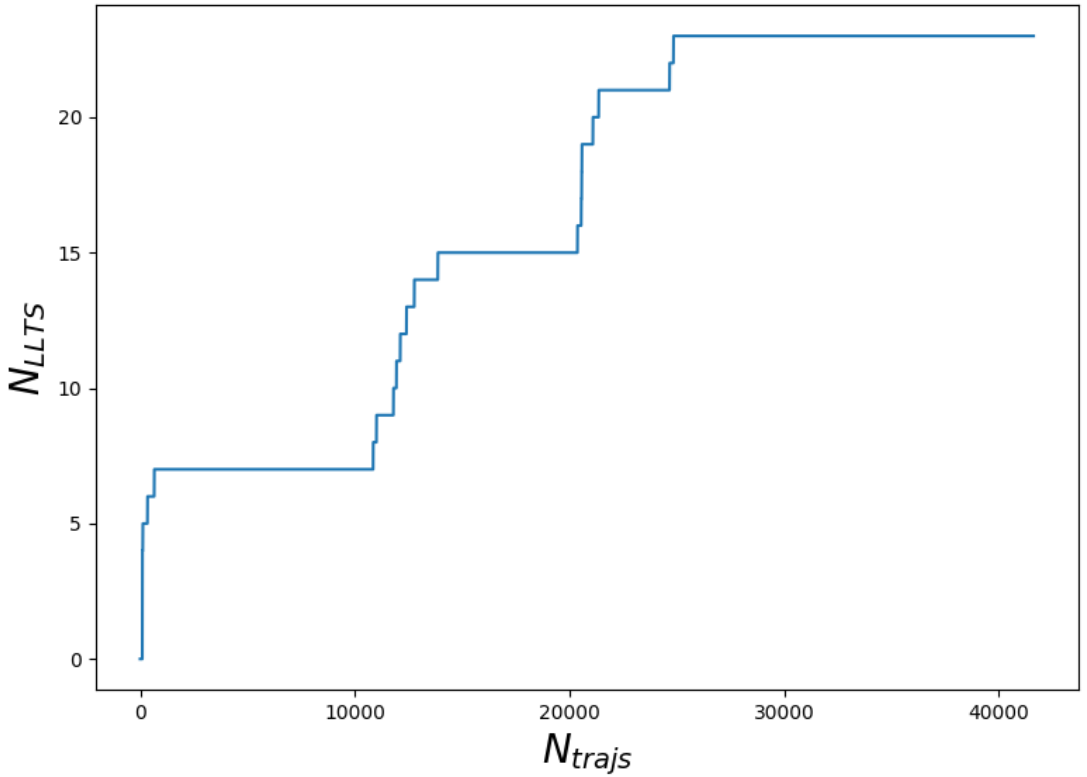
Panadés-Barrueta R., and Peláez D. (in preparation)

Needed for Nuclear Quantum Dynamics with MCTDH!

Outline

LL trajectories and sampling

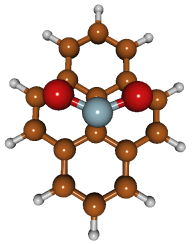
40000 microcanonical trajectories of E_{max} = 200 kcal/mol
CPU time ~ 78 s



Convergence of the number of unique LL TS (PM7)

Guess

4 x

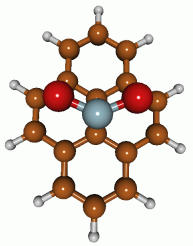


Propagation 500 fs

BBFS

TS

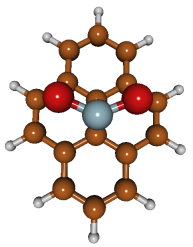
70 x



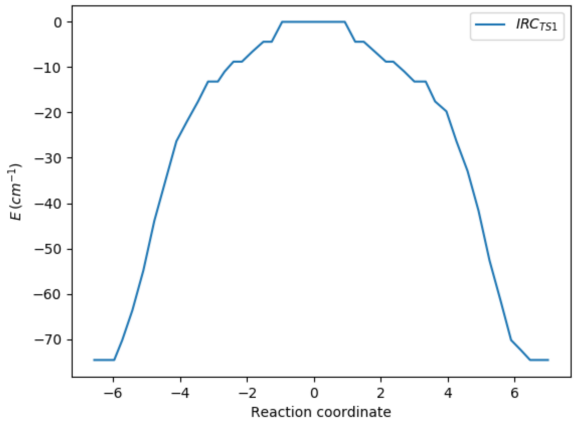
Screening (SVD, CMAT)

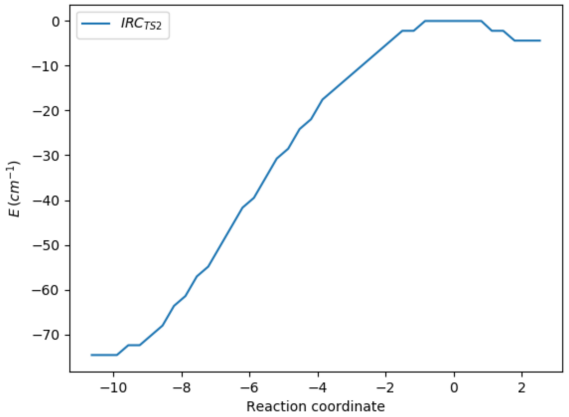
TS

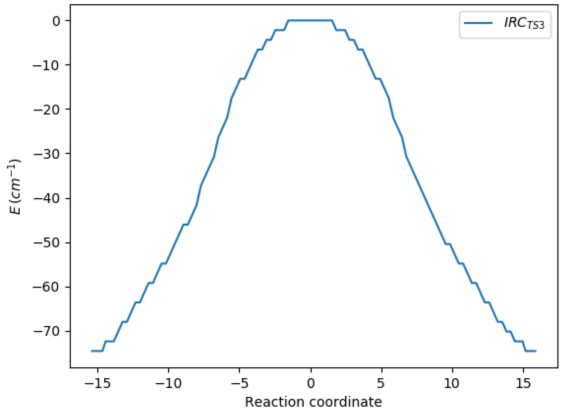
22 x

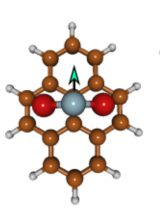


HL Transition States and Minimum Energy Paths

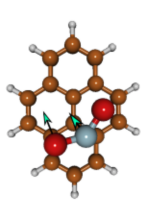




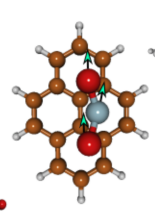




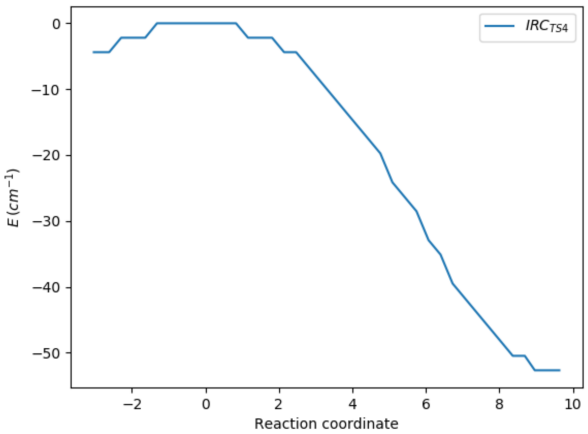
TS1
R_{CM} = 3.114 Å
ω = -30.35 cm^{-1}

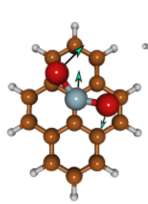


TS2
R_{CM} = 3.291 Å
ω = -17.03 cm^{-1}

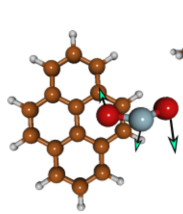


TS3
R_{CM} = 3.283 Å
ω = -10.62 cm^{-1}

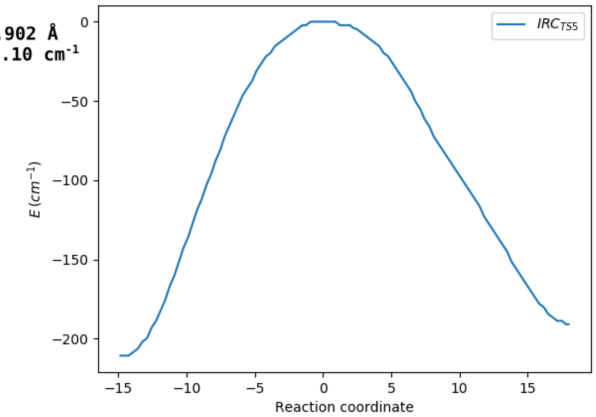




TS4
R_{CM} = 3.252 Å
ω = -13.39 cm^{-1}



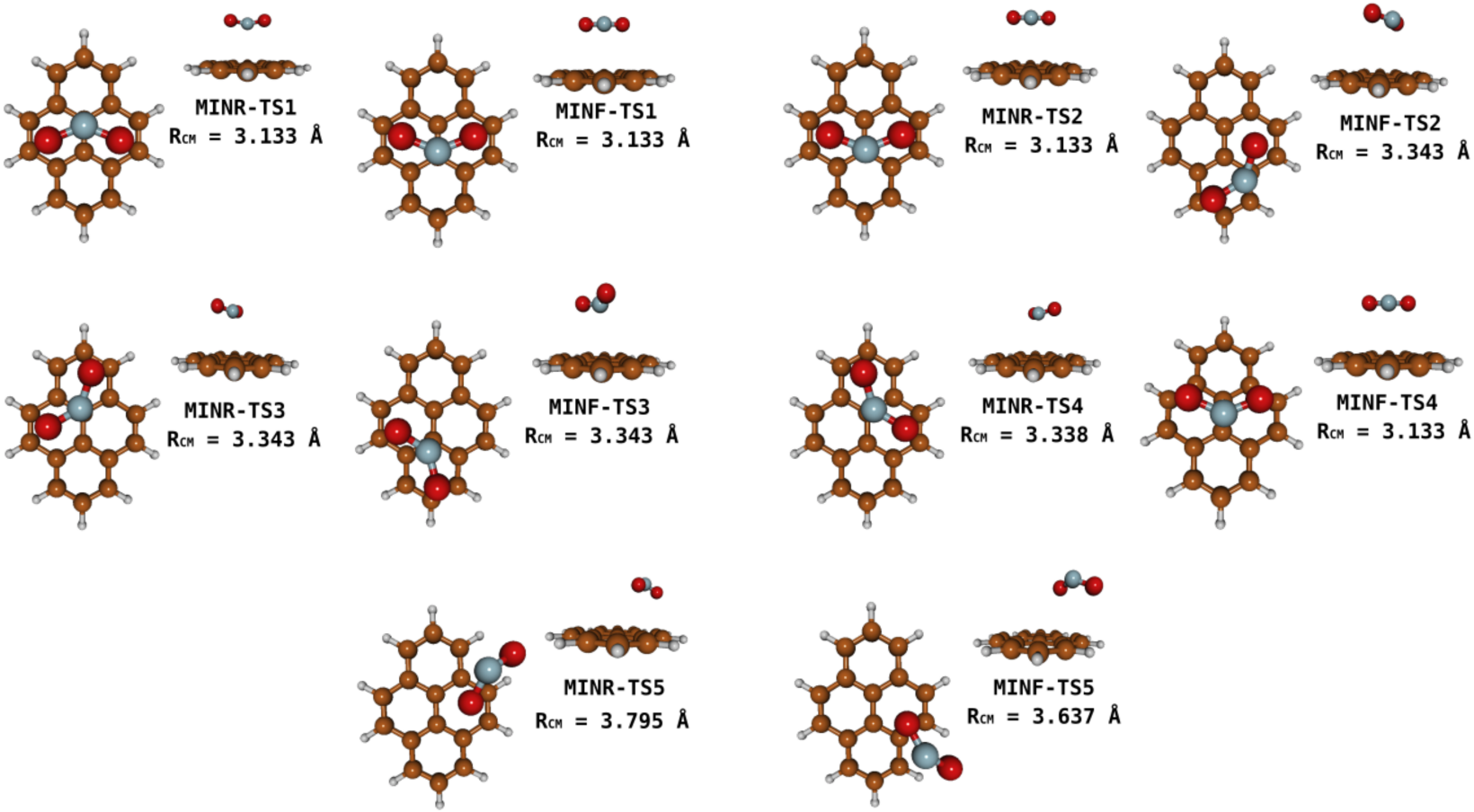
TS5
R_{CM} = 3.902 Å
ω = -17.10 cm^{-1}



ωB97XD/cc-pVDZ
Integral(SuperFineGrid)

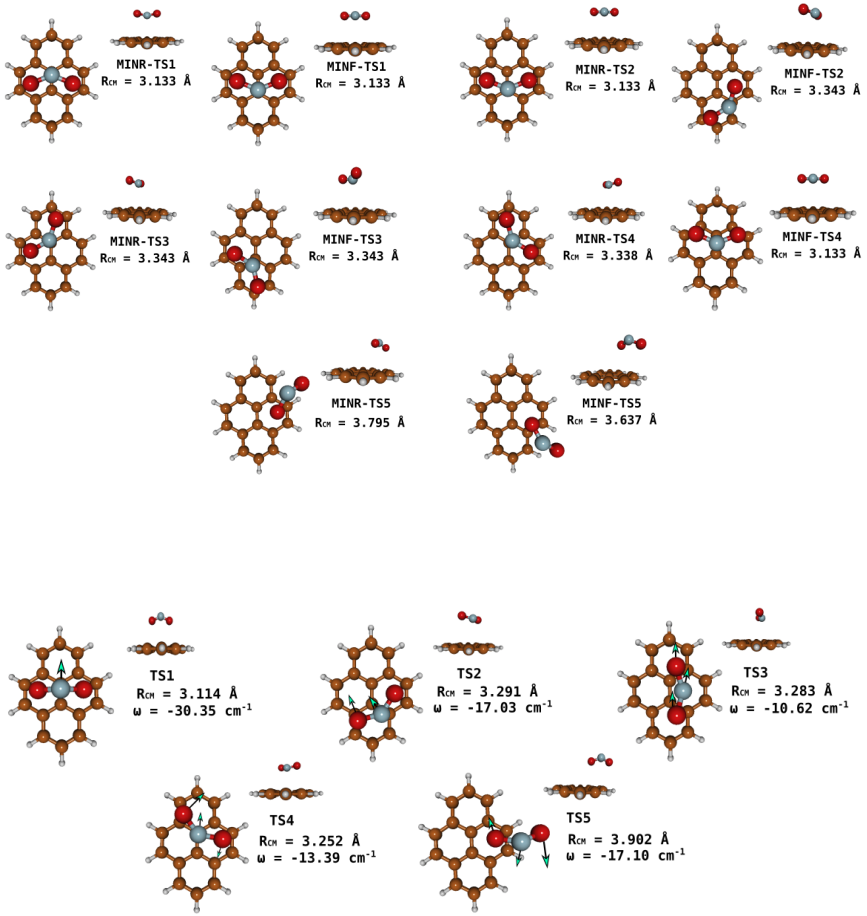
Panadés-Barrueta R., Dembele K., Duflot D. and Peláez D. (in preparation)

HL Minima obtained from IRCs



Panadés-Barrueta R., Dembele K., Duflot D. and Peláez D. (in preparation)

Energies of the Stationary Points



Energies of the HL Stationary Points

Structure	$\Delta E(cm^{-1})$
MINR-TS1	4.3894e-04
MINR-TS2	4.3894e-04
MINR-TS3	6.4751e+01
MINR-TS4	3.8800e+01
MINR-TS5	7.6236e+01
TS1	7.4973e+01
TS2	7.4372e+01
TS3	1.3858e+02
TS4	5.1983e+01
TS5	2.8805e+02
MINF-TS1	4.3894e-04
MINF-TS2	6.4752e+01
MINF-TS3	6.4753e+01
MINF-TS4	0.0000
MINF-TS5	9.7619e+01

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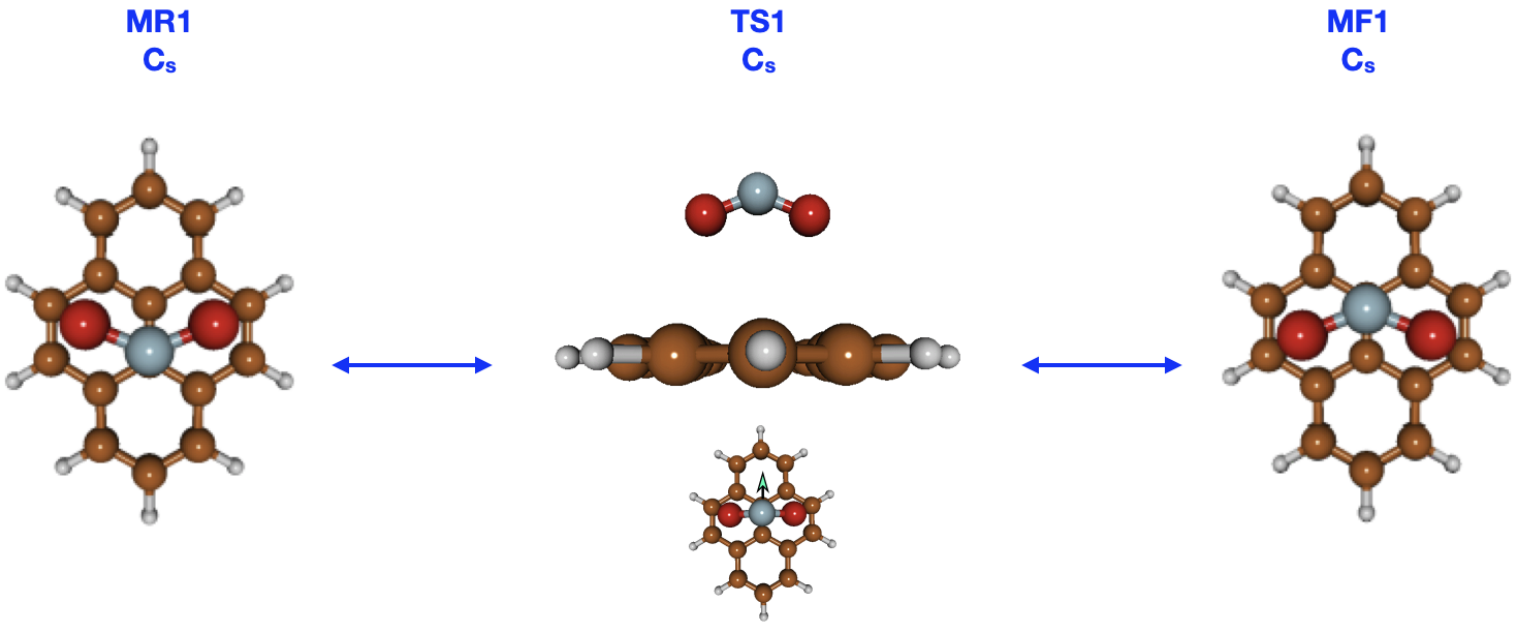
Reaction network



Panadés-Barrueta R., Dembele K., Duflot D. and Peláez D. (in preparation)

Reaction network

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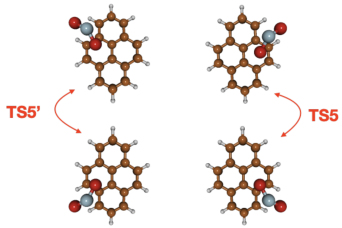
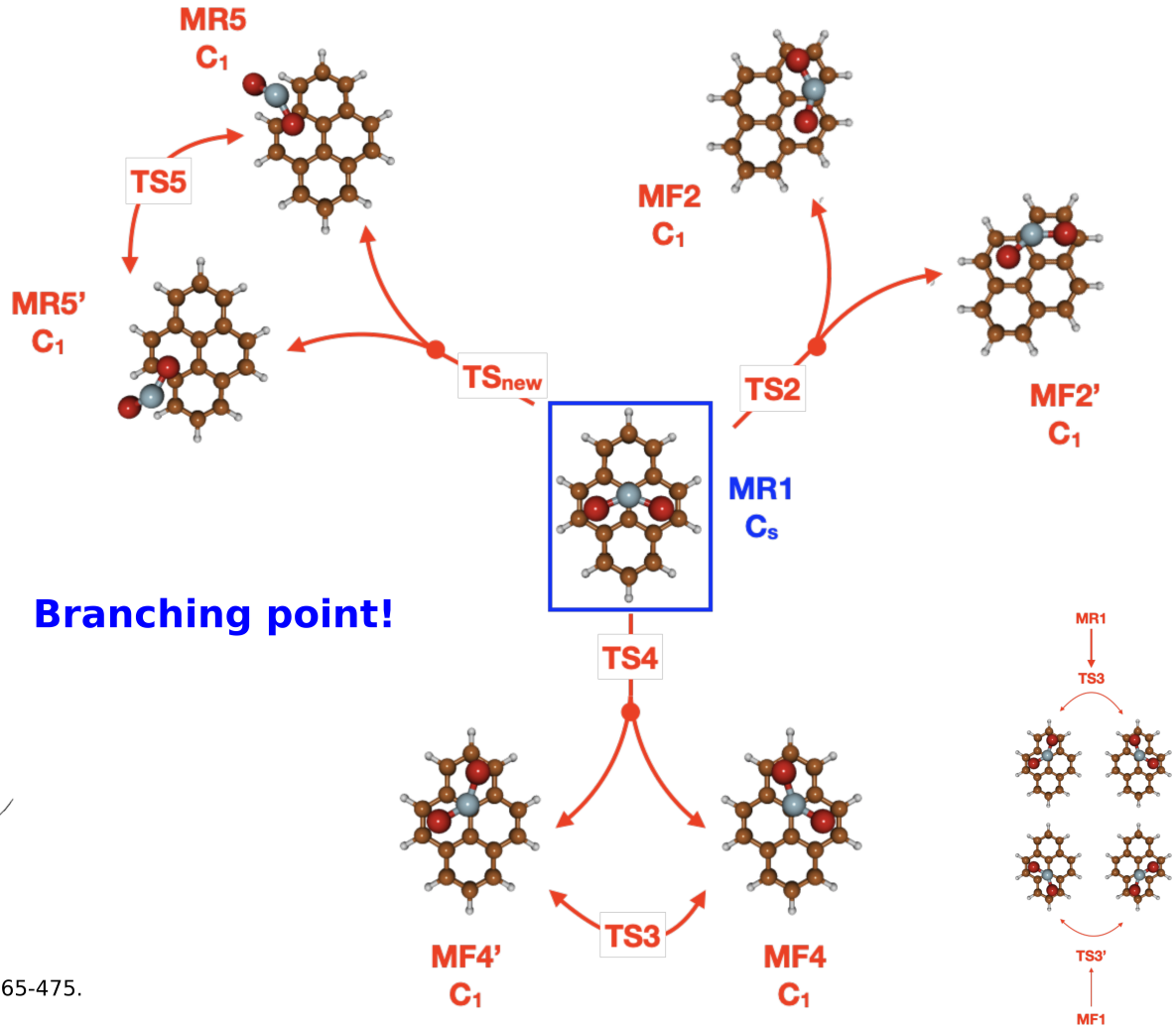
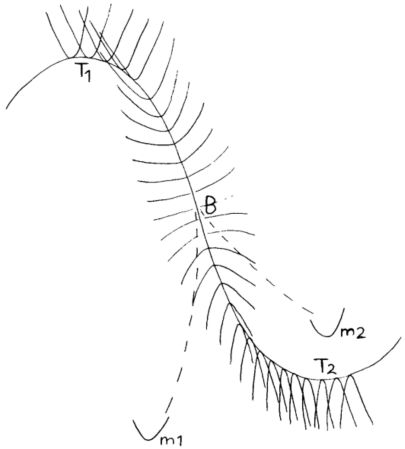


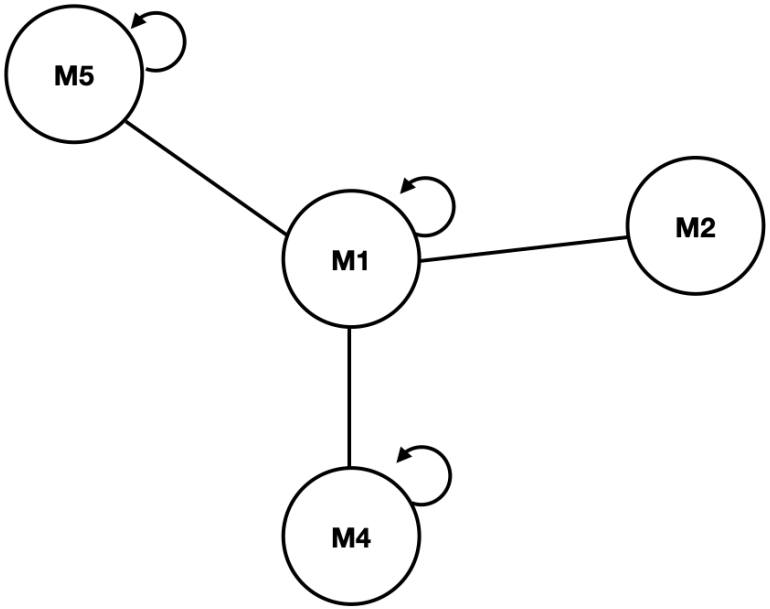




Baker, J., and P. M. W. Gill, JCP 9.5 (1988): 465-475.

Reaction network

The missing stationary point cannot be found with PM7!



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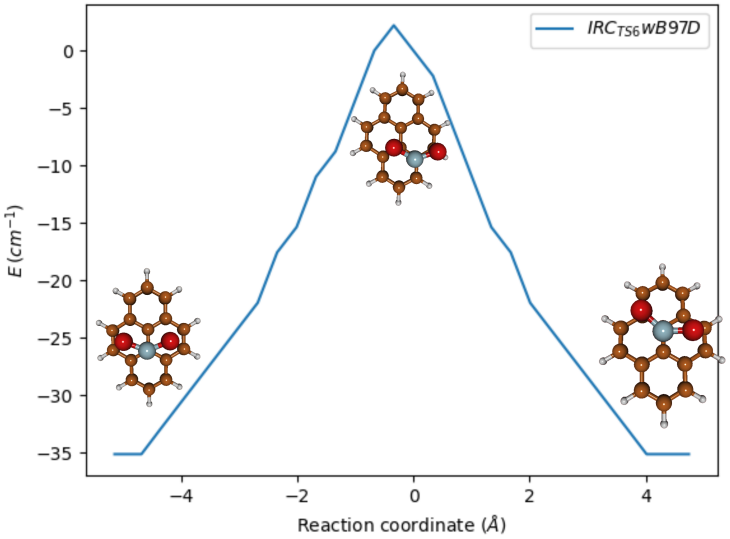

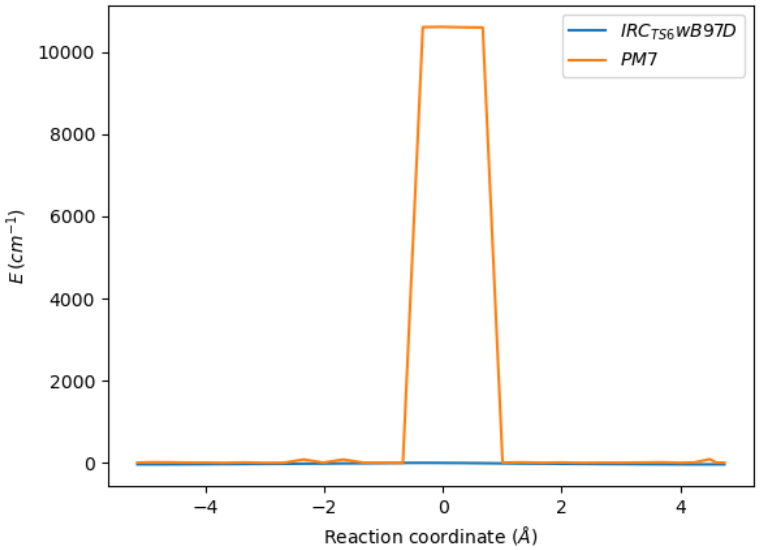

Outline

Conclusions and future perspectives

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- The present study constitutes the first application to weakly bound clusters of the recently developed vdW-TSSCDS method
- The topography of the intermolecular PES of the Pyr-NO_2 has been automatically characterized
- The reaction network of the system has been elucidated. Some problems in the LL of theory have been detected.

Perspectives: Pyr-NO_2

- Obtain the global interaction potential (article in preparation)
- Determination of the ground state
- Study the electronic excitations
- Use SRPs to improve LL stage (Panadés-Barrueta *et al*, Front. Chem. 7:576. 2019)

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PhD supervisor:

Daniel Peláez-Ruiz (ISMO)

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