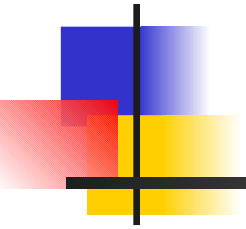
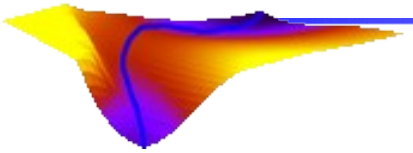


CARTE Half-Day

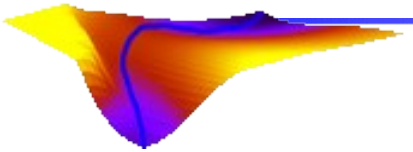
P. Fleurat-Lessard
Laboratoire de Chimie
Ecole Normale Supérieure de Lyon

Outline



- What CARTE is.
- What CARTE is not.
- How to describe a mechanism
- Some examples
- Conclusions

What CARTE is

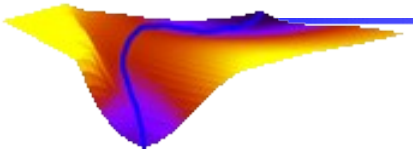


- Chemist are interested in reactions
  - Experimentalists
    - Give us reactants, products
    - Want to improve the yield, the enantioselectivity...
  - Mechanisms are the key to this

- On the theoretical side:
  - Quantum approach needed
  - Environment usually important: surface, protein, solvent, temperature, pressure...

  - One needs efficient methods ...

What CARTE is



- CARTE is there for you !

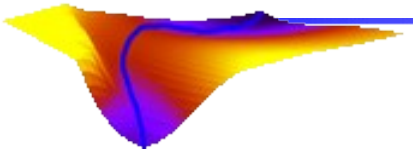
Chemins **A**utomatisés pour la **R**éactivité chimique incluant **T**empérature, pression et **E**nvironnement

Or

Construction-**A**utomatic of **R**eaction path with explicit **T**emperature, pressure, and **E**nvironment.

- Goal: Helping you to optimize reaction path
- Tools:
  - Initial path constructed using 'Computer Assisted Chemical Intuition'.
  - Path optimization using fast and efficient algorithms.

What CARTE is not



- A black box:
  - You do have to help it !
- A magic wand:
  - It cannot know what you really want
- A coffee machine !

How to describe a mechanism

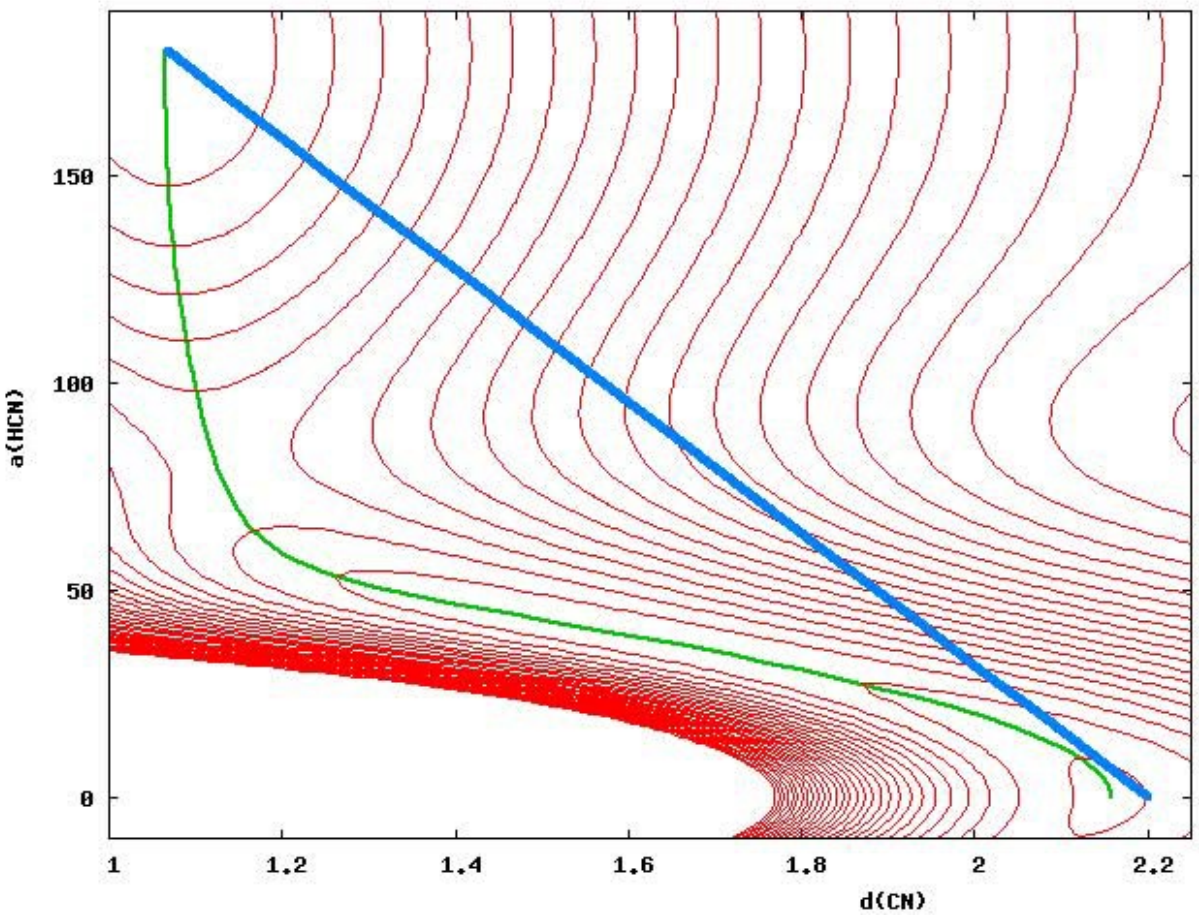
- Mechanism: a special path on the PES connecting reactants to products
- We are looking for the Minimum Energy Path (MEP)

- Working process:
  - •Construct an initial path
  - •Modify/Optimize it to reach the MEP

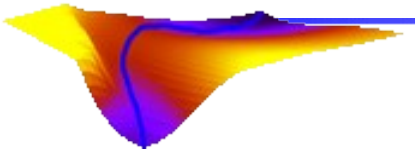
How to describe a mechanism

- Ex: HCN $\rightarrow$ CNH

- Result:



Description is discrete

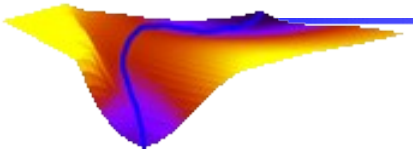


- How to choose the points ?
  - Equidistant: Fix number of points
- How to ensure good sampling of the path ?
  - String method:
    - Reparameterization from time to time

      W. E, W. Ren, E. Vanden-Eijnden PRB **2002**, 66, 052301

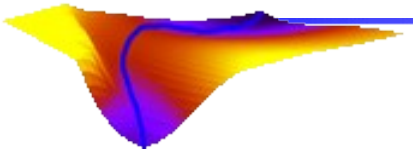
- We **really** need:
  - A good initial path: rough idea of the RCs
  - A good optimizer: we cannot afford 1000 iterations

Coordinates systems



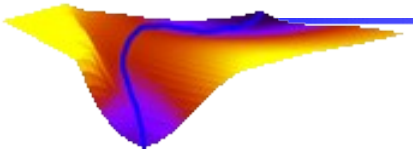
- Lots of discussions for geometries
- Mainly two families:
  - Cartesian coordinates
  - Internal coordinates:
    - Z-Matrix
    - Natural Coordinates
    - Redundant coordinates
    - Baker coordinates

Coordinates systems



- Lots of discussions for geometries
- Mainly two families:
  - Cartesian coordinates
  - Internal coordinates:
    - Z-Matrix
    - Natural Coordinates
    - Redundant coordinates
    - Baker coordinates

Cartesian coordinates



- Very general
- Easy to compute, store, manipulate

But

- No chemical meaning
- Overall rotation and translation not suppressed

Z-Matrix

- Based on internal coordinates:
  - bond distances, bond angles and dihedrals
- 3N-6 degree of freedom

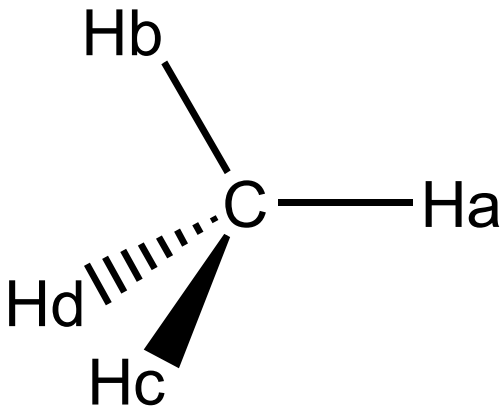
C

H_a C dCH_a

H_b C dCH_b H_a $\alpha H_a CH_b$

H_c C dCH_c H_a $\alpha H_a CH_c$ H_b DH1

H_d C dCH_d H_a $\alpha H_a CH_d$ H_b DH2



Z-Matrix

- Based on internal coordinates:
  - bond distances, bond angles and dihedrals
- 3N-6 degree of freedom

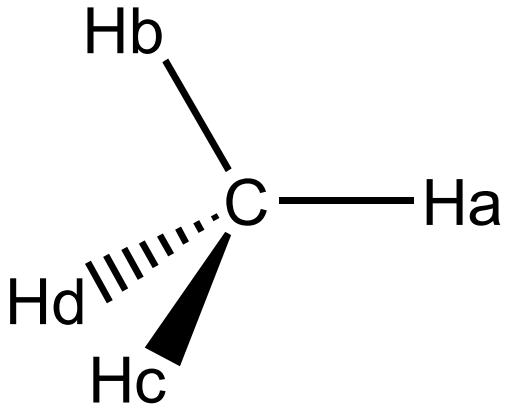
C ← Origin of the frame

H_a C dCH_a ← z axis

H_b C dCH_b H_a αH_aCH_b ← xz plane

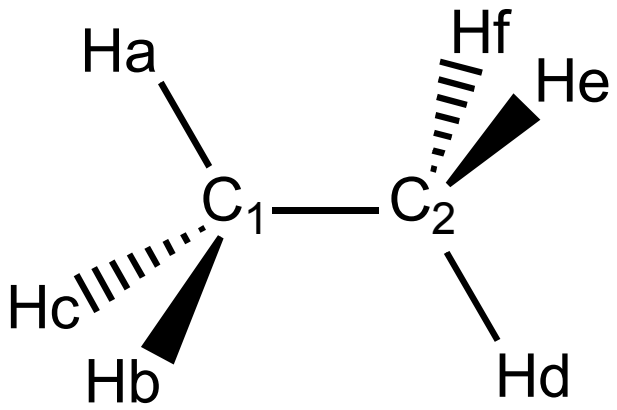
H_c C dCH_c H_a αH_aCH_c H_b DH1

H_d C dCH_d H_a αH_aCH_d H_b DH2



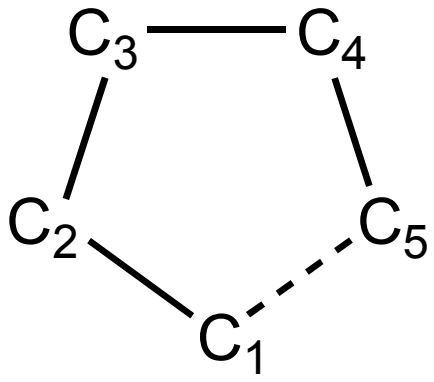
Z-Matrix

- But
  - Non unique
    - How to choose the order of the atoms ?

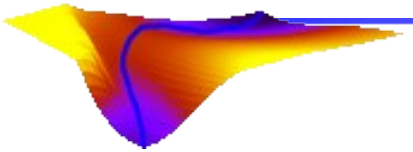


Z-Matrix

- But
  - Non unique
    - How to choose the order of the atoms ?
    - Problem for cycles



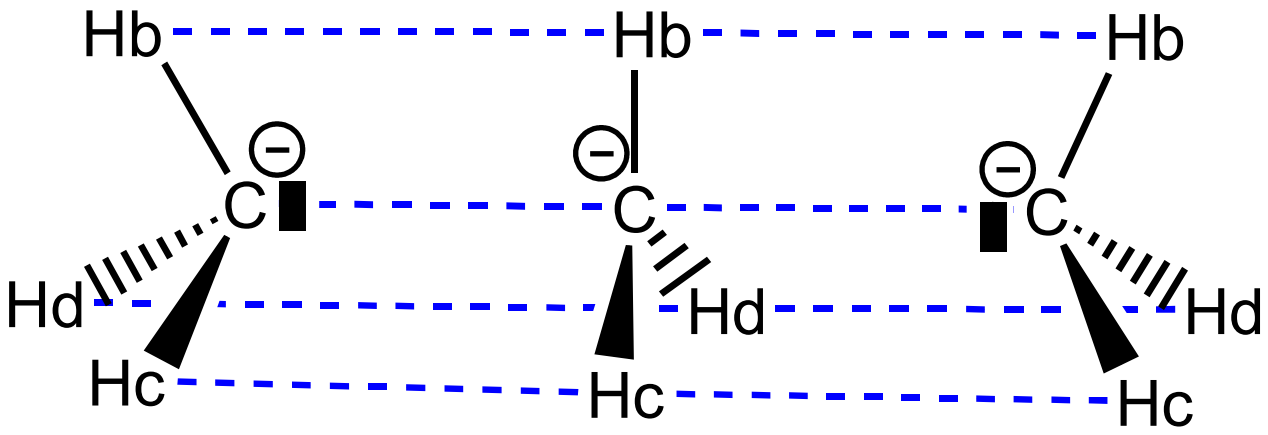
Z-Matrix



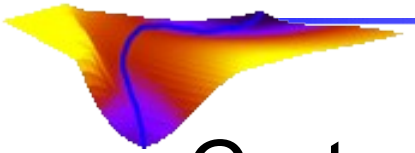
- But
  - Not unique
    - How to choose the order of the atoms ?
    - Problem for cycles
  - Not easy to compute
- Extension: Natural coordinates (Pulay), Redundant Coordinates (Pulay), Baker coordinates...
  - Redundant not yet in CARTE. Soon.

Reaction path coordinates

- Cartesian coordinates
  - Same description for all images
  - But
    - Problem of stretched/compressed bonds



Reaction path coordinates

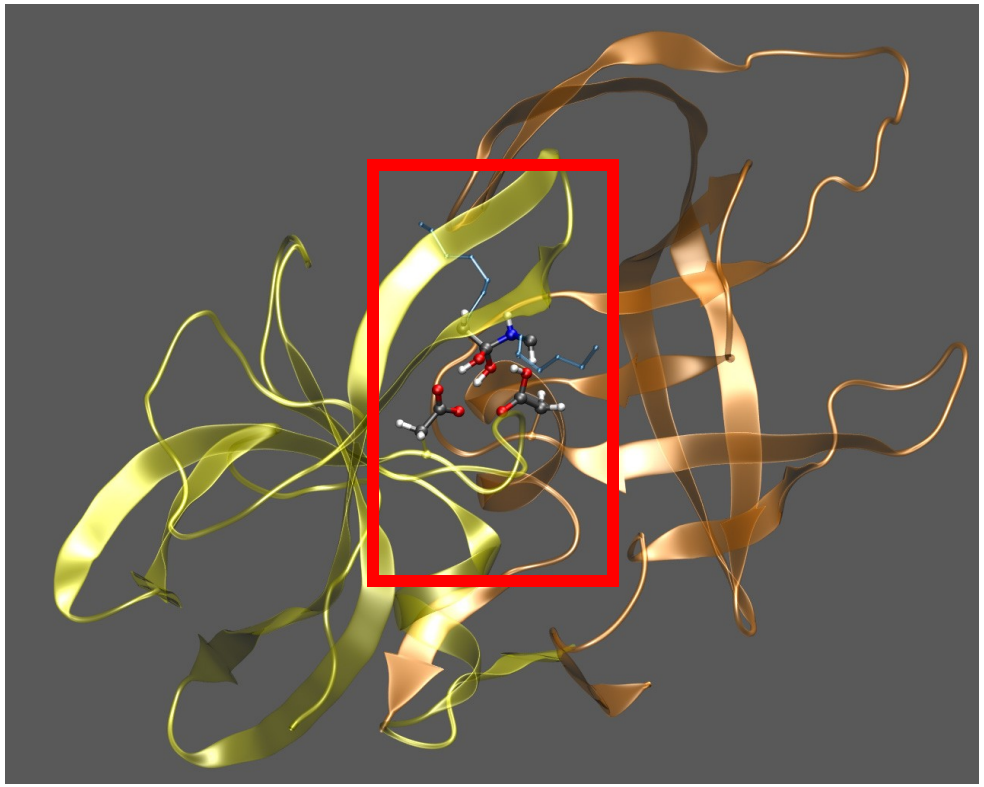


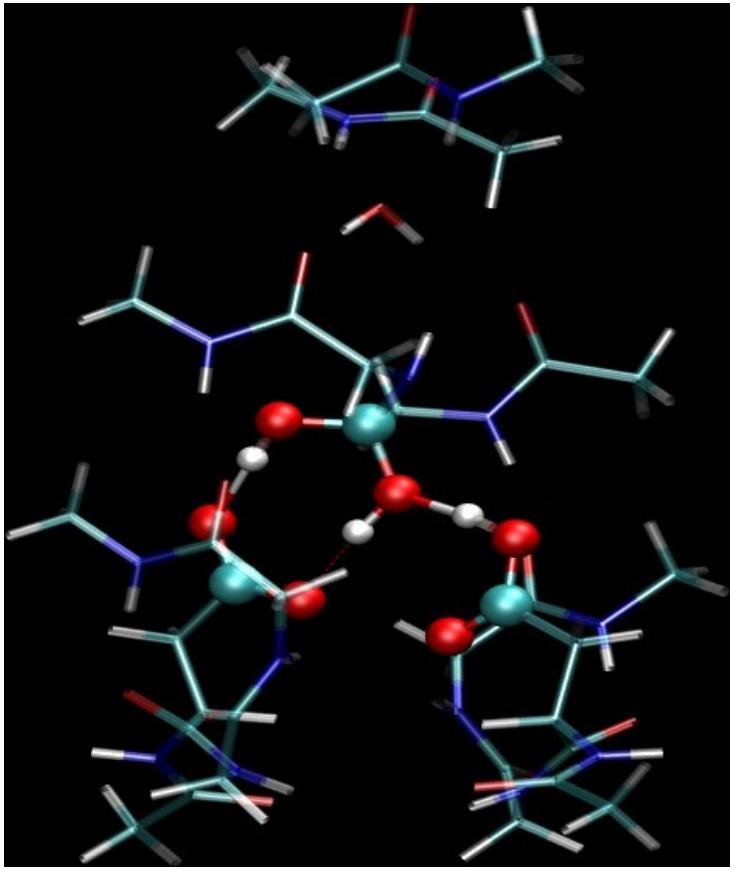
- Cartesian coordinates
  - Same description for all images
  - But
    - Problem of stretched/compressed bonds
    - Stupid path
    - HCN $\rightarrow$CNH might lead to

- Easy to check for HCN…

Reaction path coordinates

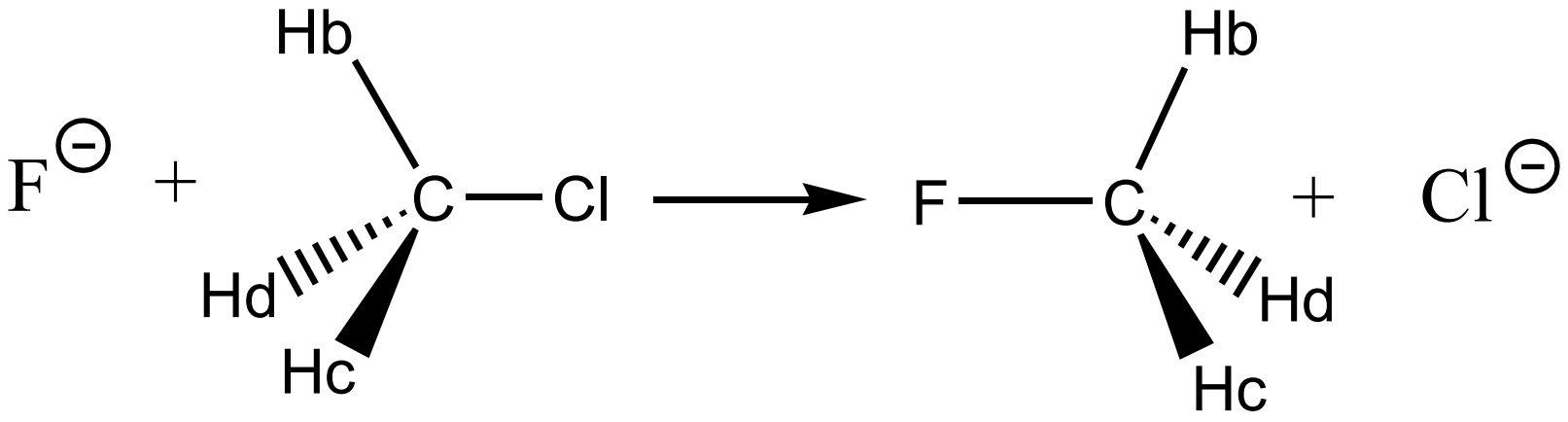
- Cartesian coordinates
  - But not in real life !



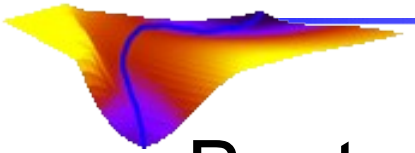


Reaction path coordinates

- Z-Matrix coordinates
  - Less problem of distorted bonds
  - But
    - Which Z-matrix ?

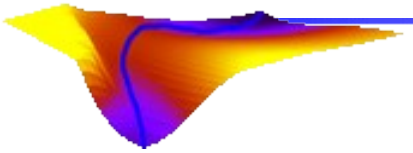


Reaction path coordinates

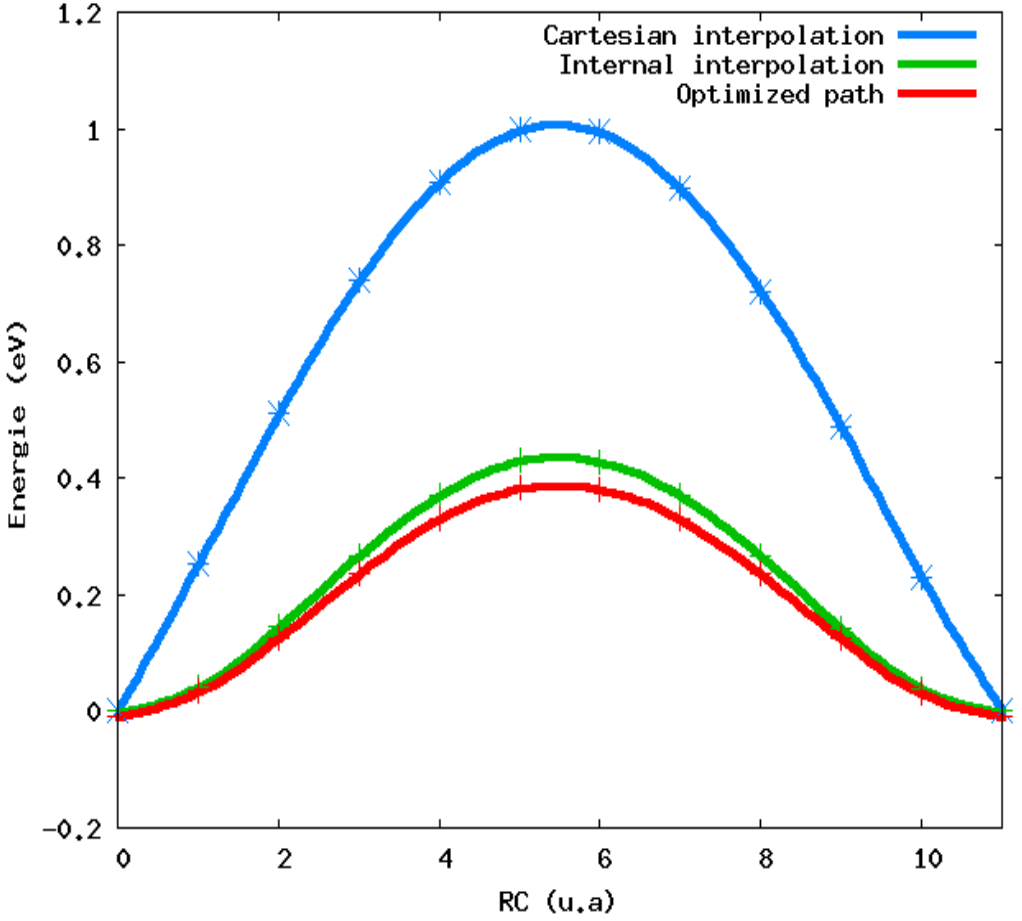


- Best compromise: mix cartesian and Zmat !
  - Atoms that are 'spectator' are described in cartesian
  - Reactive atoms are described in internal coordinates

CH_3^- inversion

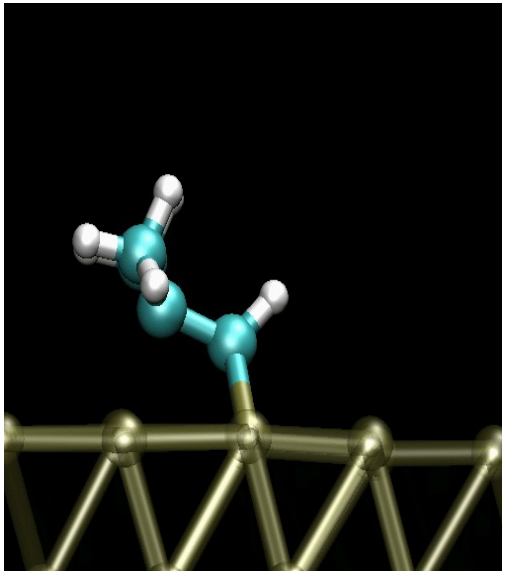
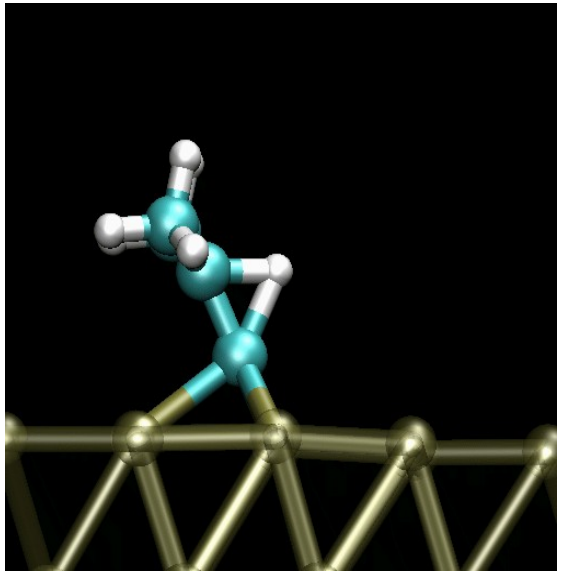
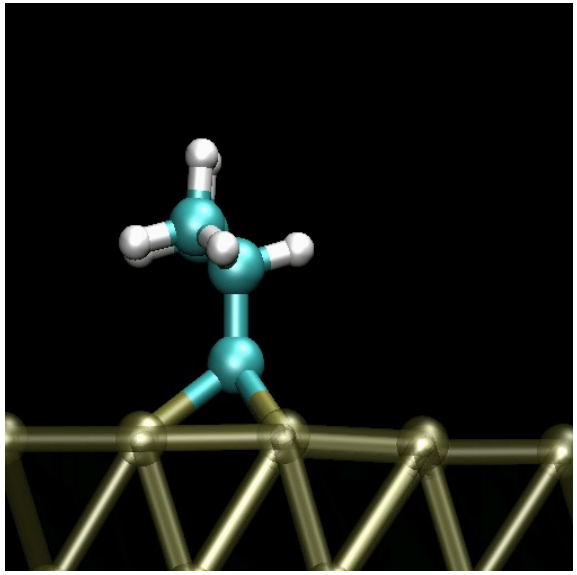


- Walden inversion:
  - Model of SN2 reactions
  - Floppy molecules
  - Cart vs Zmat
    - Initial path better in Zmat
    - Good optimizer
      - cart 8 iterations
      - Zmat 4

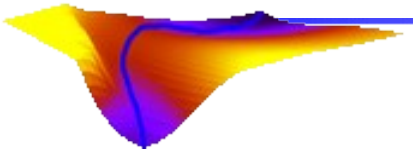


Catalytic hydrogenation on Pt

- Reaction:

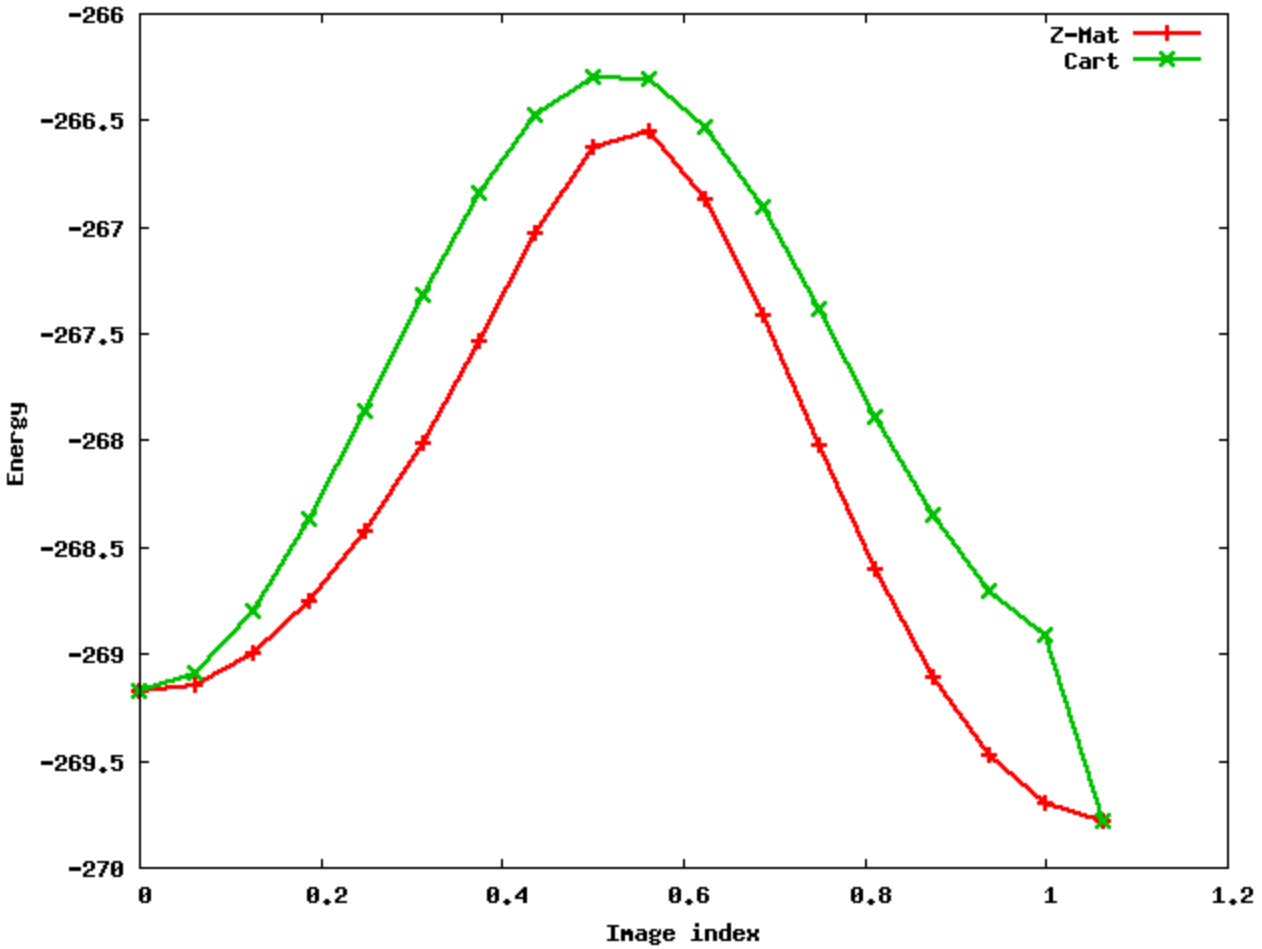




Catalytic hydrogenation



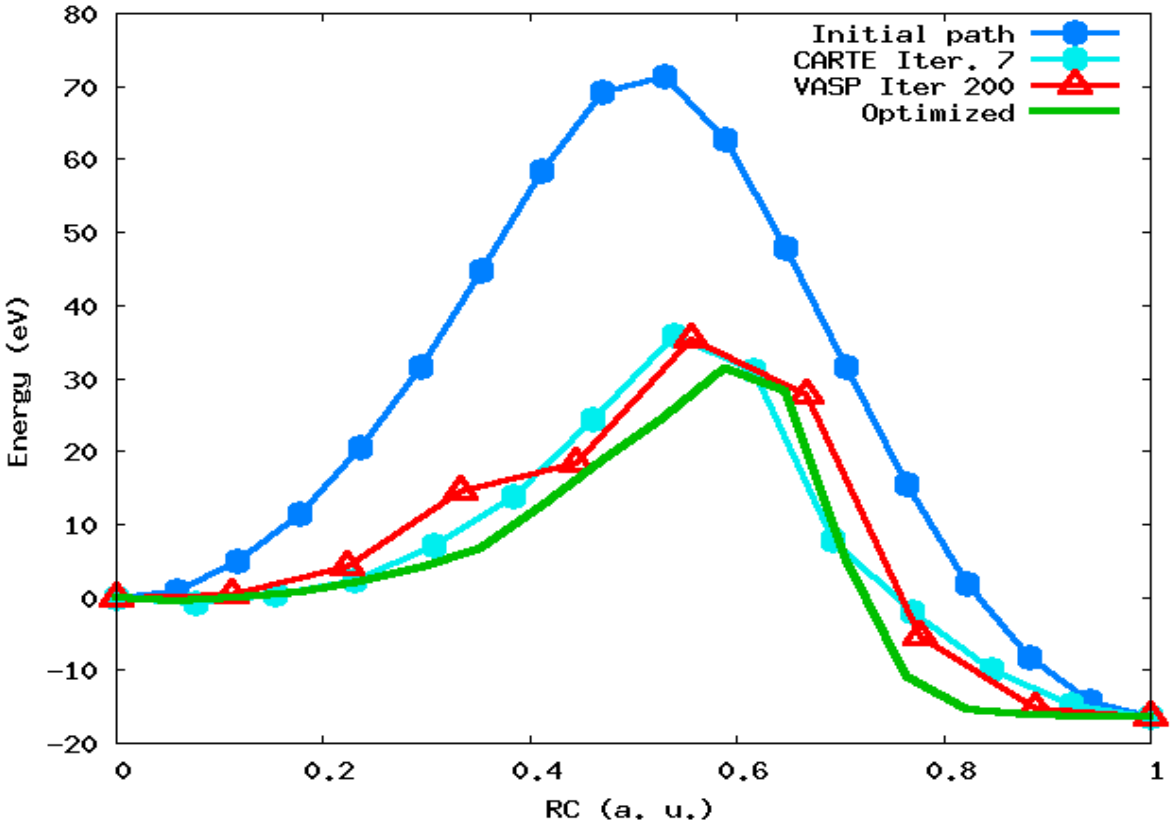
- Initial path

Energies



Catalytic hydrogenation

- Final results:



Acknowledgements

- People
  - P. Dayal: Baker coordinates
  - F. Delbecq, J. Garrec, N. Chéron, C. Dupont, N. Dinter, : beta testers.

- Money
  - ANR
  - Région Rhônes Alpes

ANR AGENCE NATIONALE DE LA RECHERCHE

CLUSTERS DE RECHERCHE RHÔNE-ALPES CHIMIE

… Thank you for your attention !