Multi-basis-set TDDFT methods for predicting electron attachment energies

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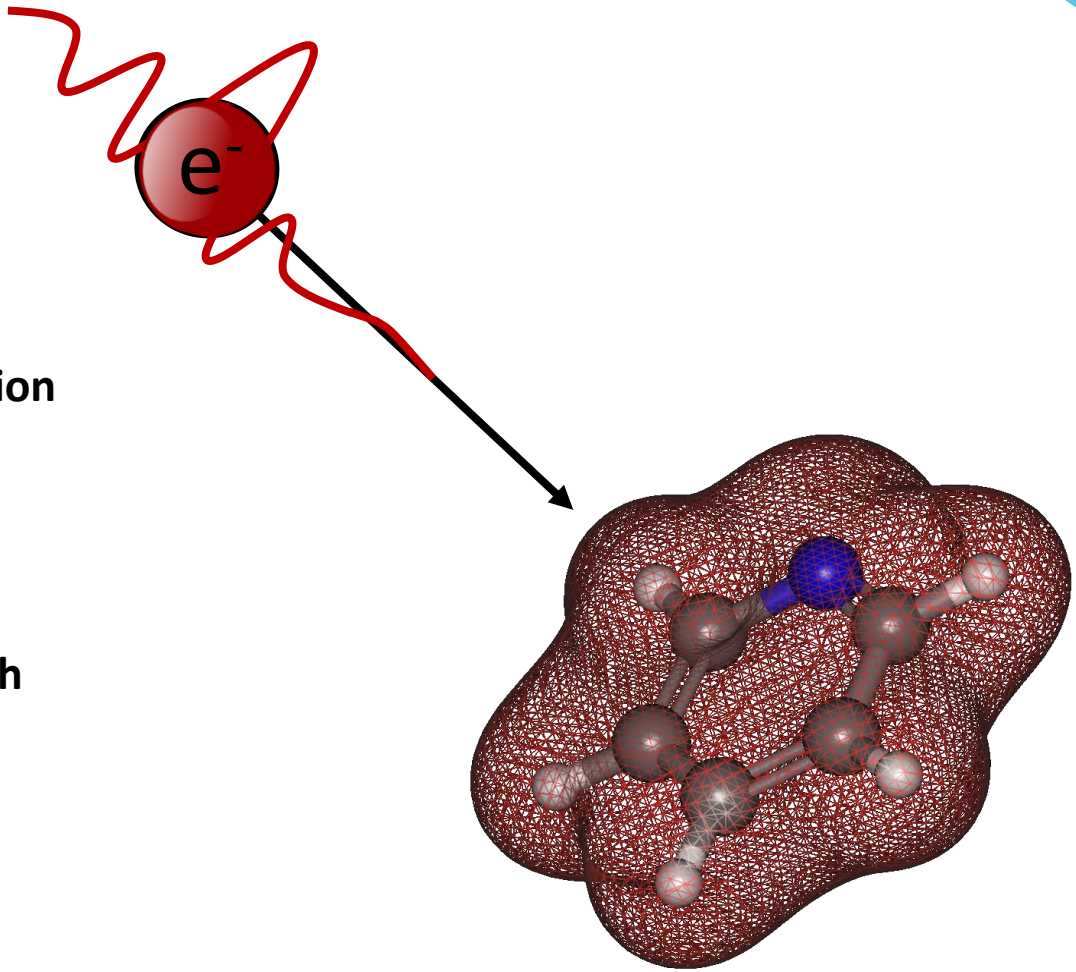
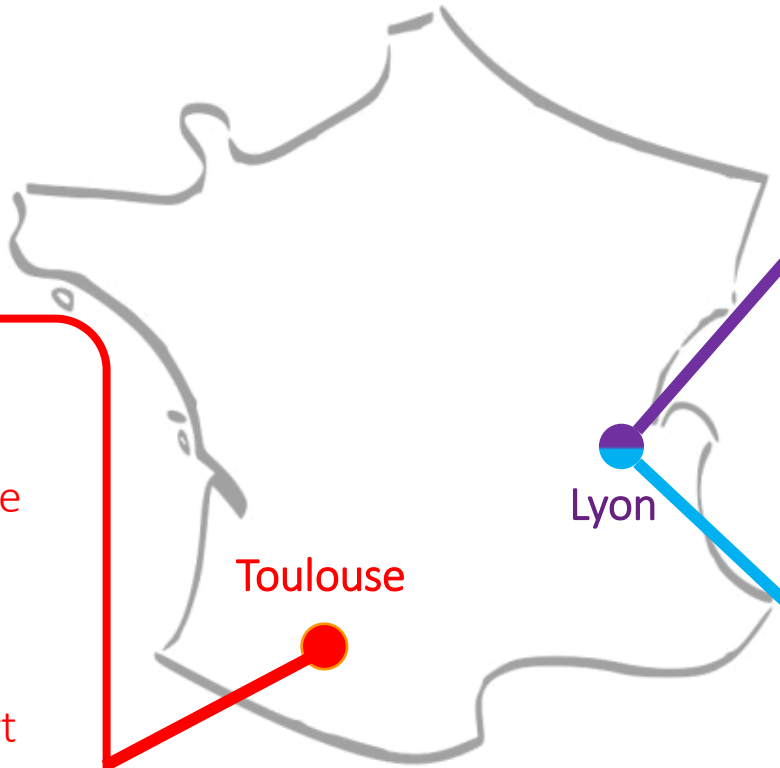
OUTLINE



- I- Motivations and context
- II-Electron-molecule interaction
  - Electron-attachment
  - Empirical method
  - Stabilization method
  - Multi-Basis-Set approach
- III-Results
- IV-Conclusions

Funding: ANR BAMBI

BAMBI : Beta-particle Attachment to Molecules of Biological Interest



ILM
Calculation of static properties

Ab initio methods
DFT, TD-DFT

LPT
Laboratoire de Physique Théorique

Mai DINH

Calculation of short time dynamical processes
Real Time TD-DFT

IP2I
Institut de Physique des deux infinis

Hassan ABDOUL-CARIME

Experiments

ANR AGENCE NATIONALE DE LA RECHERCHE

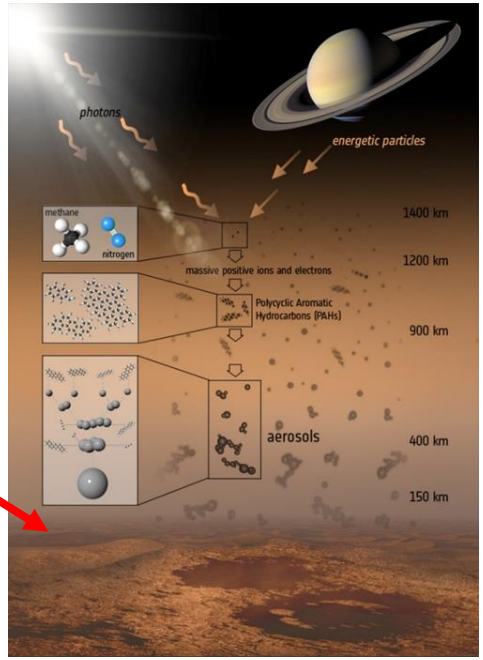
Funding: MITI/Projet Origines

SMOOTIE :

Synthesis of complex organic molecules on Titan induced by slow electrons

- **Titan** (Saturn's satellite) : Has a thick and misty atmosphere that could be analogous to atmosphere of the pre-biotic earth.
- **SMOOTIE** project aims at studying reactional mecanism induced by slow electrons, that could generate complex molecules on Titan

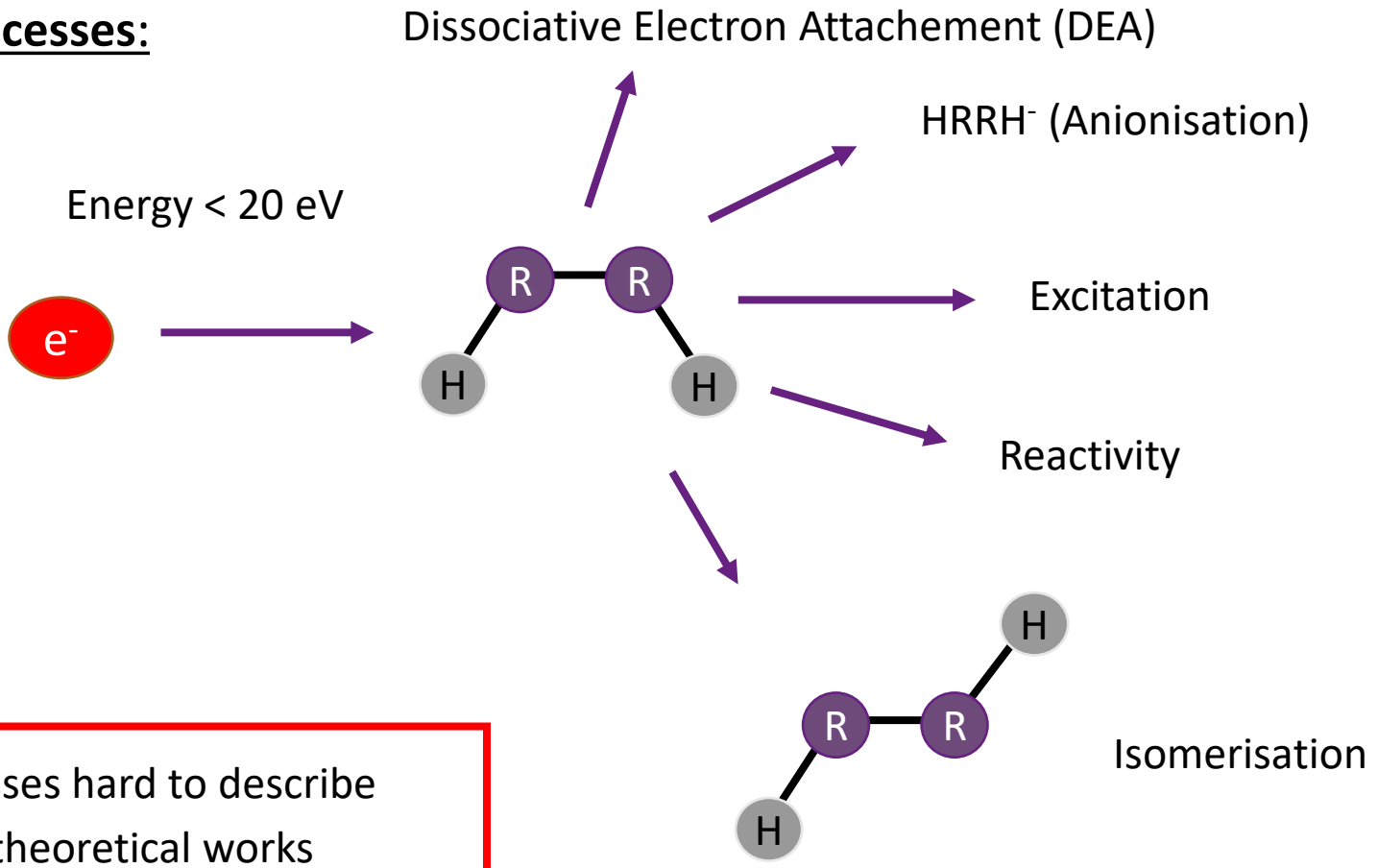
- High density of secondary electrons (E < 20 eV)
- Temperature of 90K on the ground and 70 to 130K in low atmosphere



Keith Cooper, *Astrobiology Magazine*

Electron-molecule interaction

Multiple processes:

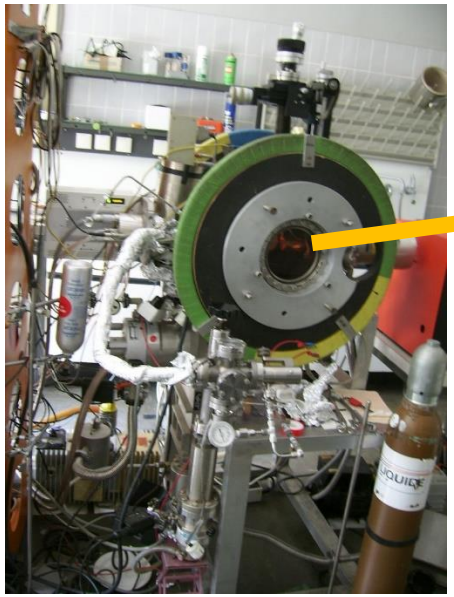


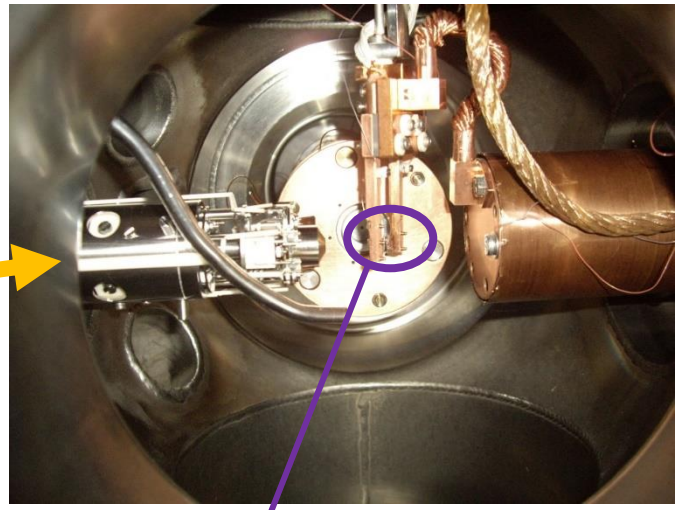
- Processes hard to describe
- Need theoretical works

Electron-molecule interaction

H.Abdoul-Carime

Reaction in thin molecular films by electron impact





Electron-molecule interaction

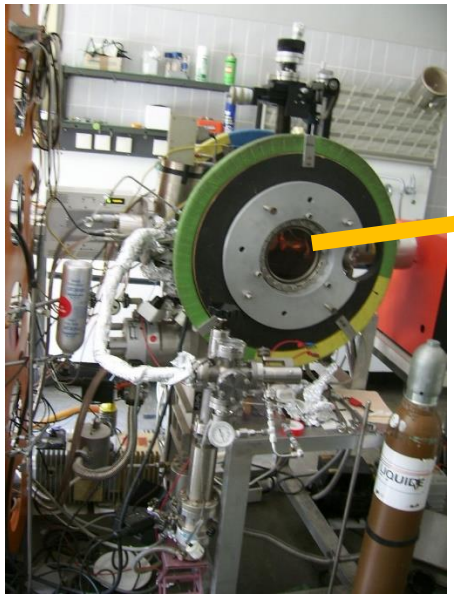
H.Abdoul-Carime

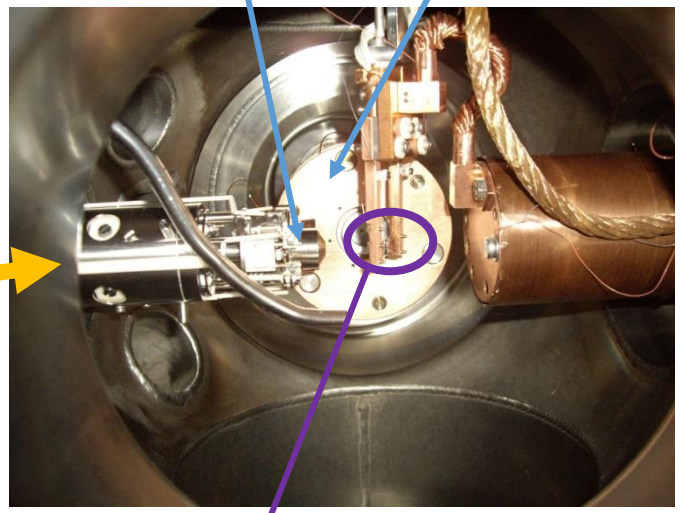
Reaction in thin molecular films by electron impact

Mass Spectrometer

detects ions or neutrals after ionisation by electrons at 70 eV

Electron gun





Measurements:

- Neutrals = f(T)
- Neutrals = f(e^- Energy)
- Neutrals = f_E(e^- dose)
- Ions = f(e^- Energy)
- Ions = f_E(e^- dose)

Neutral species Desorption

Electron beam

Thin film (4 – 5 layers)

Gold Substrate (T~90K)

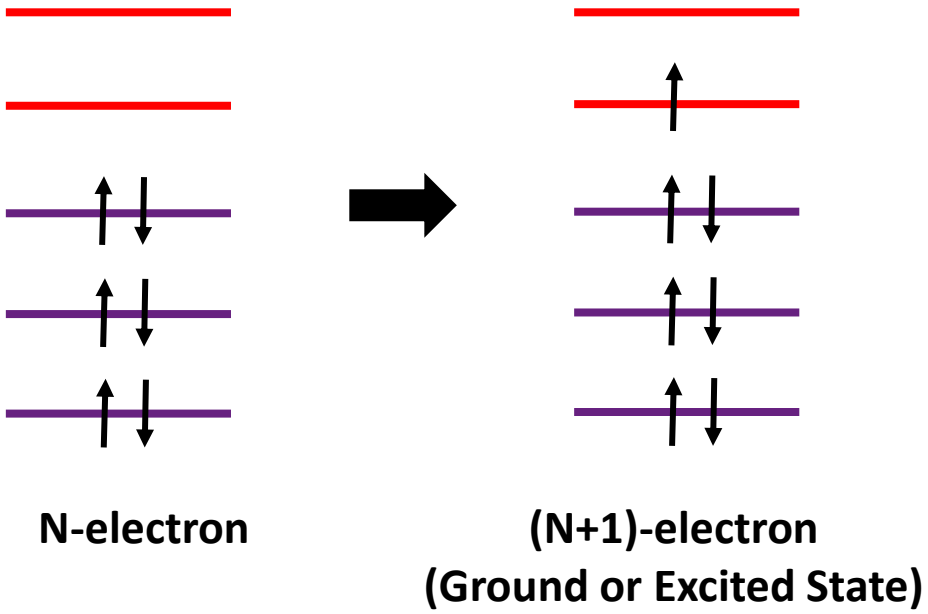
Heating

Describing electron attachment

- **Describing a molecular system with an additional electron**

Several methods:

- **Empirical methods**
- **Stabilization method**
- **R-matrix**
- **Schwinger Multi-Channel**



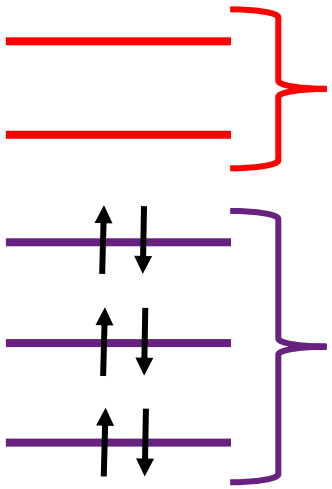
N-electron

(N+1)-electron
(Ground or Excited State)

Empirical methods (empirical correlation in litterature)

$$E_{resonance} = q\, E_{virtual\ orbitals} + k$$

- **Resonance energies are extrapolated from the energies of the virtual orbitals (Hartree-Fock or Kohn-Sham)**
- ***q*, *k* coefficients are optimized with a large data set of experimental resonances**



Virtual orbitals

N-electron neutral molecule

N-electron

Describing an anion within DFT/TD-DFT framework

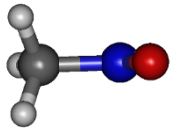
- **The XC-Functional**
  - XC-Functional that can describe an anion
    - Hybrid Long-range corrected functional (1/r behaviour, exchange correction)

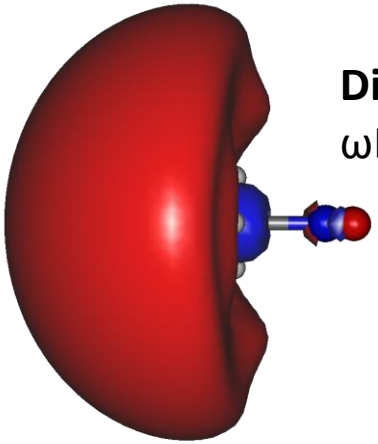
- **Existence of long distance bound states**

- **Influence of the basis-set : calculation with finite size simulation box**

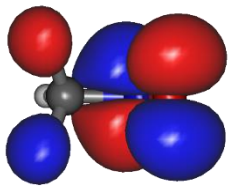
  - Calculation using different basis-set can converge toward a different state

  - Ex : **Nitromethane CH_3NO**



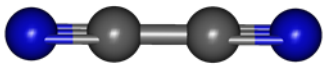


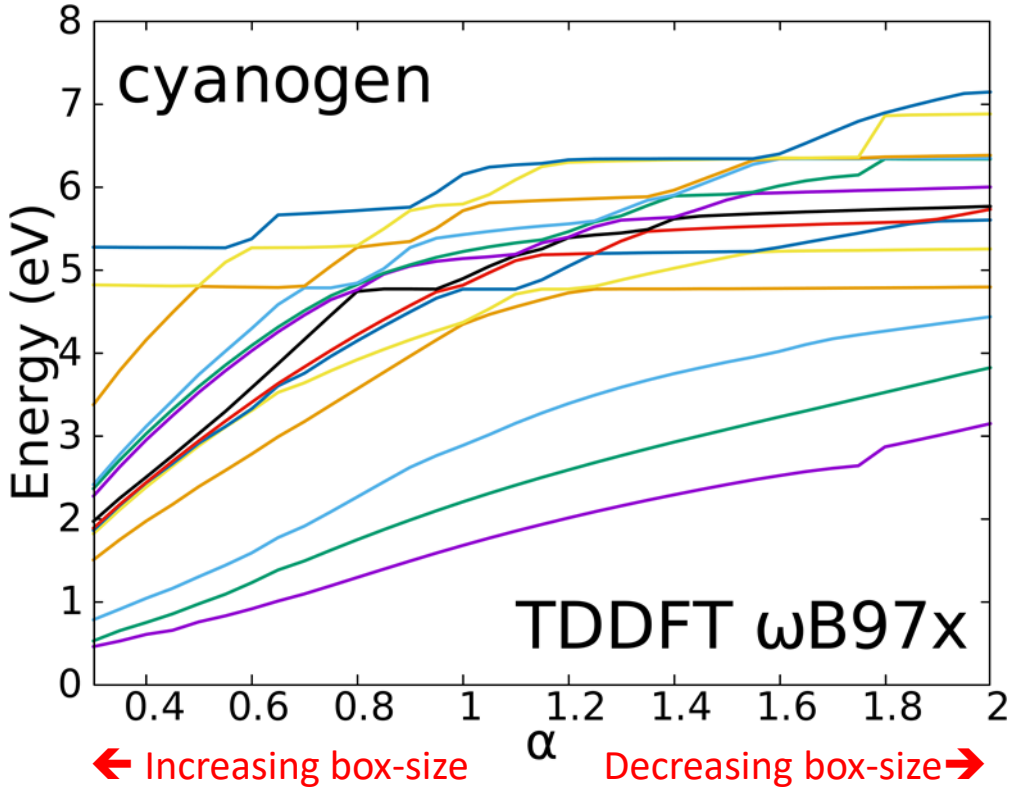
Dipole bound state
ωB97x/aug-cc-pvtz



Valence state
ωB97x/cc-pvtz

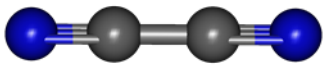
Stabilization method (Cheng, Phys. Chem. Chem. Phys. (2014), **16**, 26306)

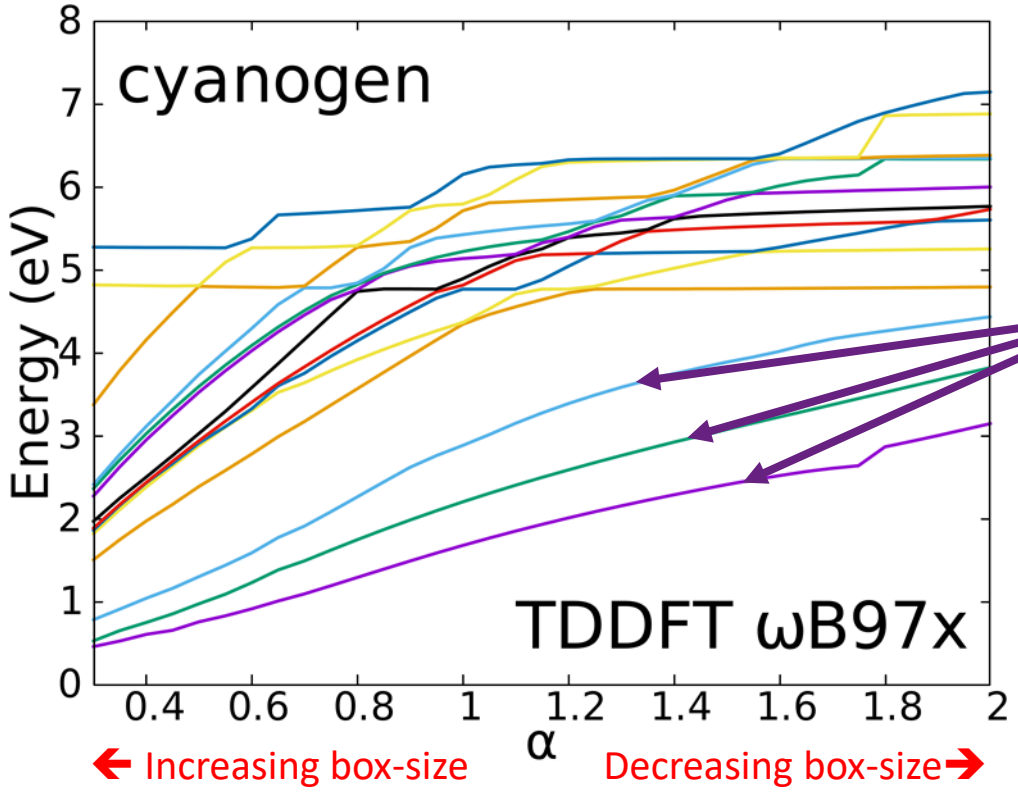




Stabilization method (Cheng, Phys. Chem. Chem. Phys. (2014), **16**, 26306)

➡ Varying the size of the box using a **scaling factor α** to discriminate **bound states** from **discrete continuum** ones





Discrete continuum states:
E ↗ when box size ↘
E → ~0 when box size ↗

Stabilization method (Cheng, Phys. Chem. Chem. Phys. (2014), **16**, 26306)

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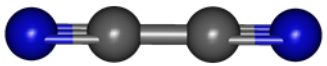
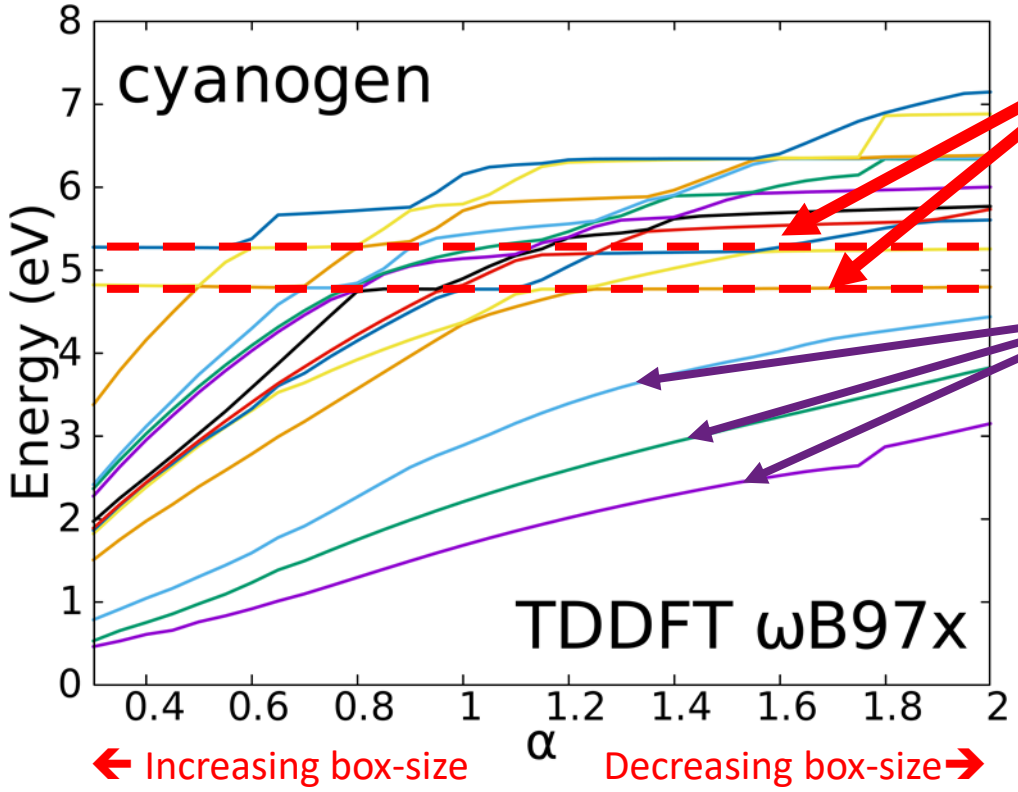




Bound states:

➡ **Energy independent from the size of the box**

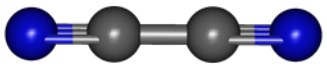
Discrete continuum states:

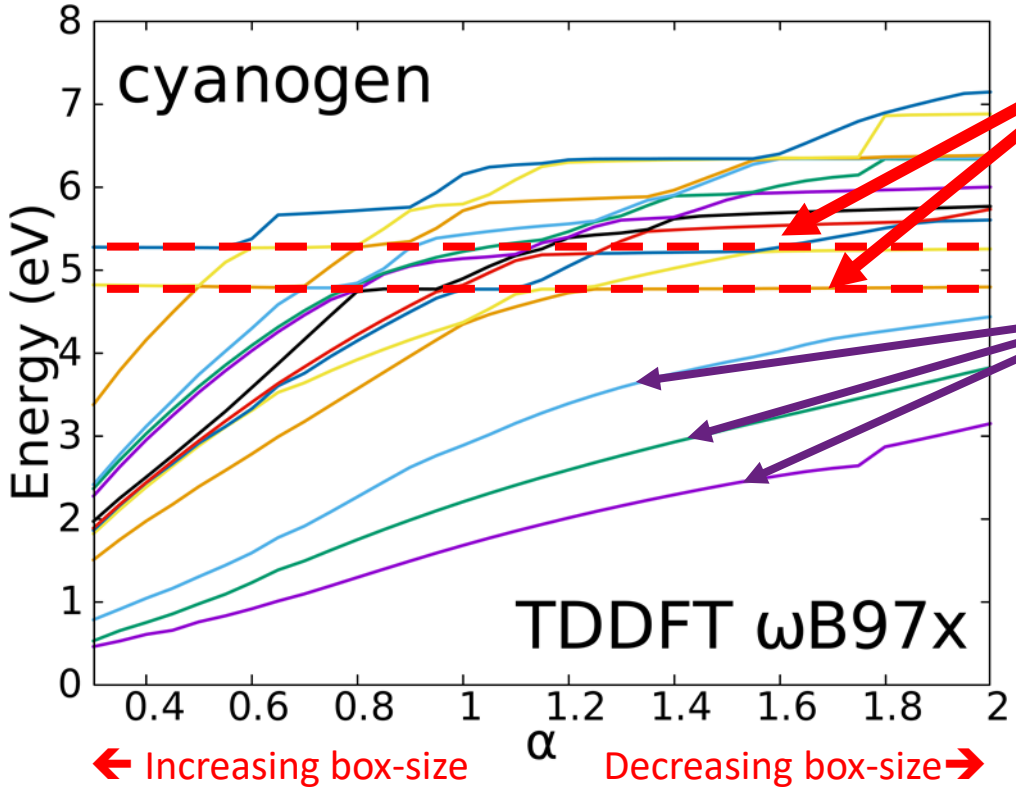
E ↗ when box size ↘

E → ~0 when box size ↗

Stabilization method (Cheng, Phys. Chem. Chem. Phys. (2014), **16**, 26306)

➡ Varying the size of the box using a **scaling factor α** to discriminate **bound states** from **discrete continuum** ones





Bound states:

➡ **Energy independent from the size of the box**

Discrete continuum states:

E ↗ when box size ↘

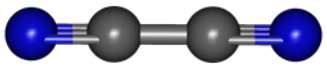
E → ~0 when box size ↗

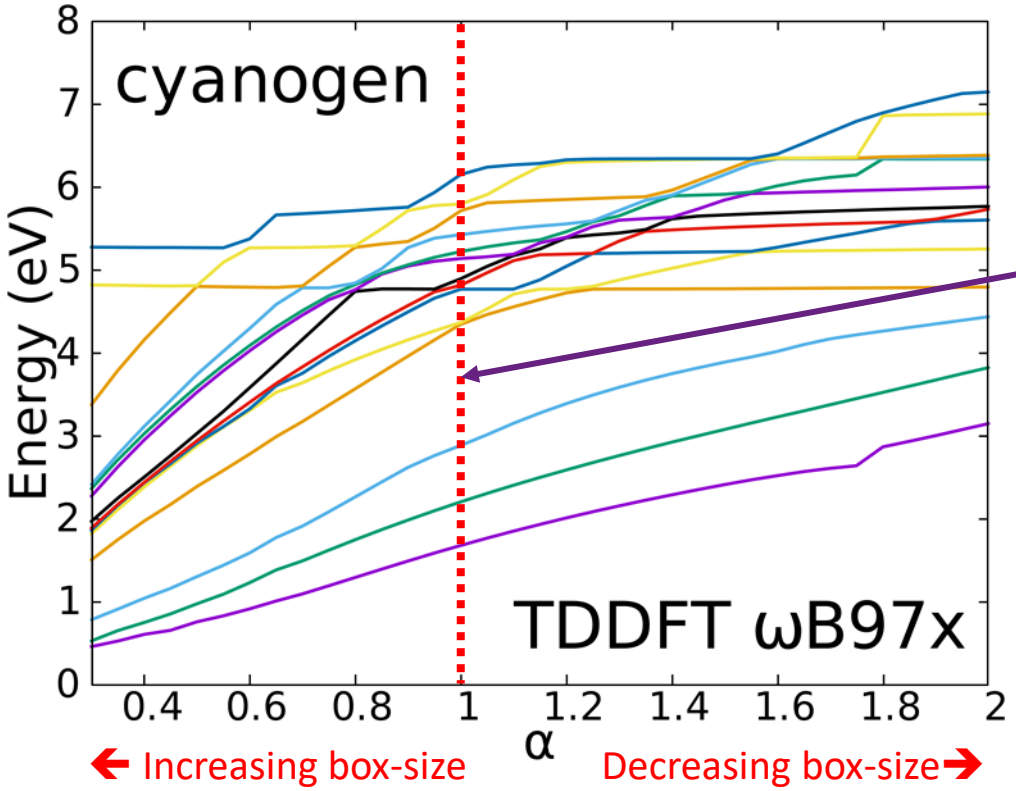
Difficulties

- **Hybrid states**
- **Nature of states**
- **Nature of the ground state**

Stabilization method (Cheng, Phys. Chem. Chem. Phys. (2014), **16**, 26306)

➡ Varying the size of the box using a **scaling factor α** to discriminate **bound states** from **discrete continuum** ones





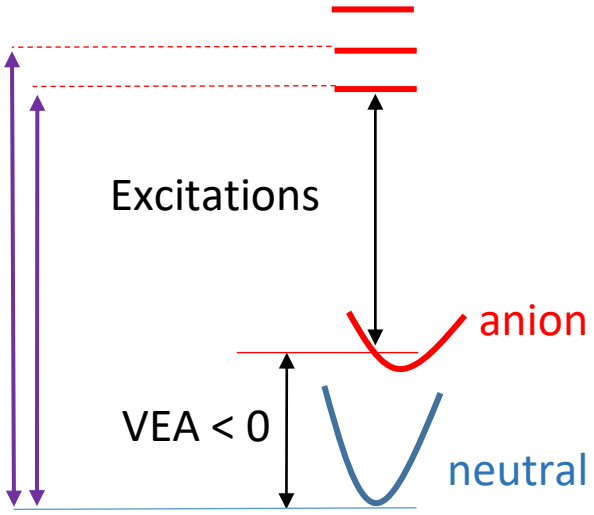
For a given value of α several parasite states

➡ **Varying the size of the box is necessary to exclude discrete continuum states**

Another Methodology

- **Neutral system → Neutral system + 1 additional electron**
- Resonances correspond to excited states of the anion at the optimized geometry of the neutral

Vertical Electron Attachment Energies



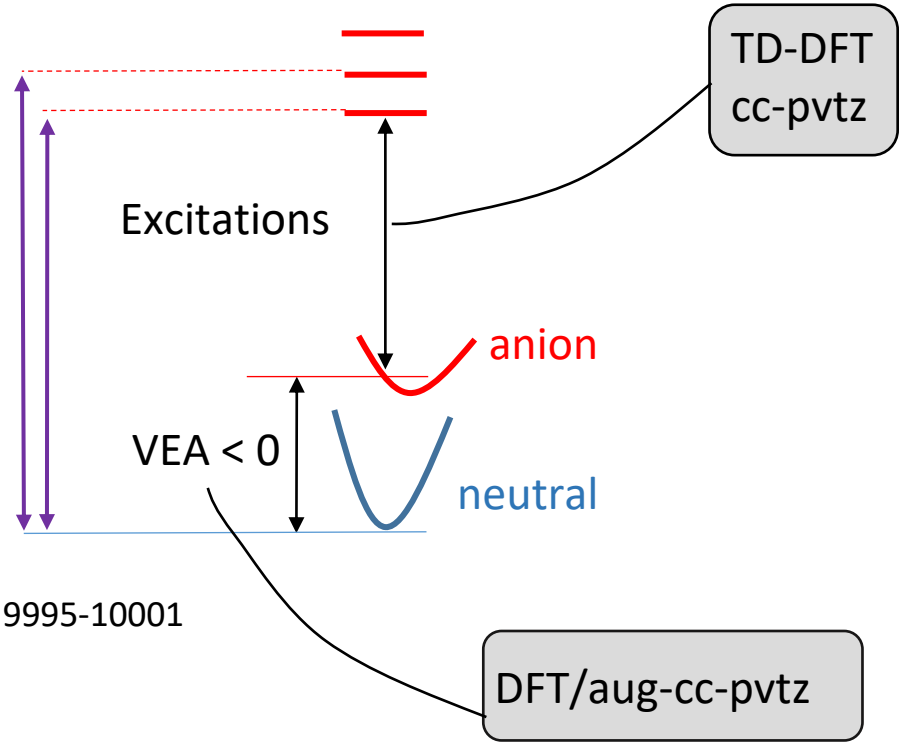
G.Thiam & F. Rabilloud – J. Phys. Chem. Lett. (2021) **12**, 9995-10001

Multi-Basis set TD-DFT/DFT method

- **Multiple basis-set are used to exclude the discrete continuum states**

  - **Neutral** state calculation using **DFT**
  - **Anion excited states calculation** at the geometry of the neutral using **TD-DFT**
  - **Tested upon 19 molecules** of different types (simple, double, triple C-C bound, cycles)
  - **53 electronic states** compared with **experiment**

Vertical Electron Attachment Energies



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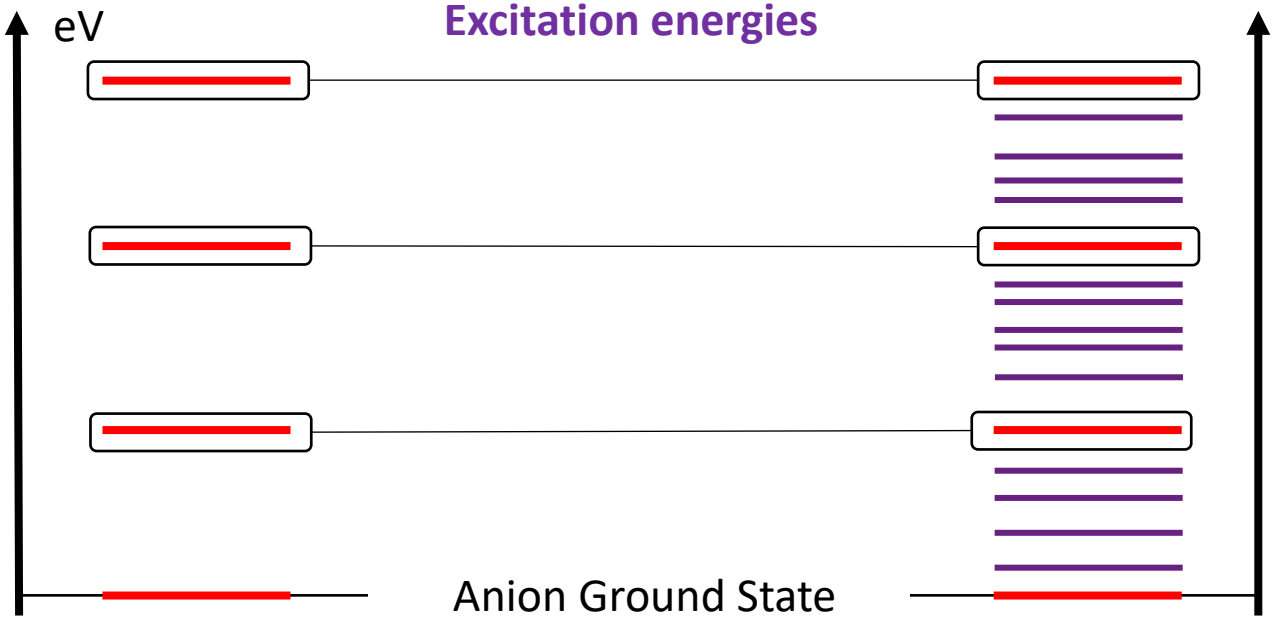
Excitation energies with respect to the anion

TD-DFT/cc-pvtz vs TD-DFT/aug-cc-pvtz:

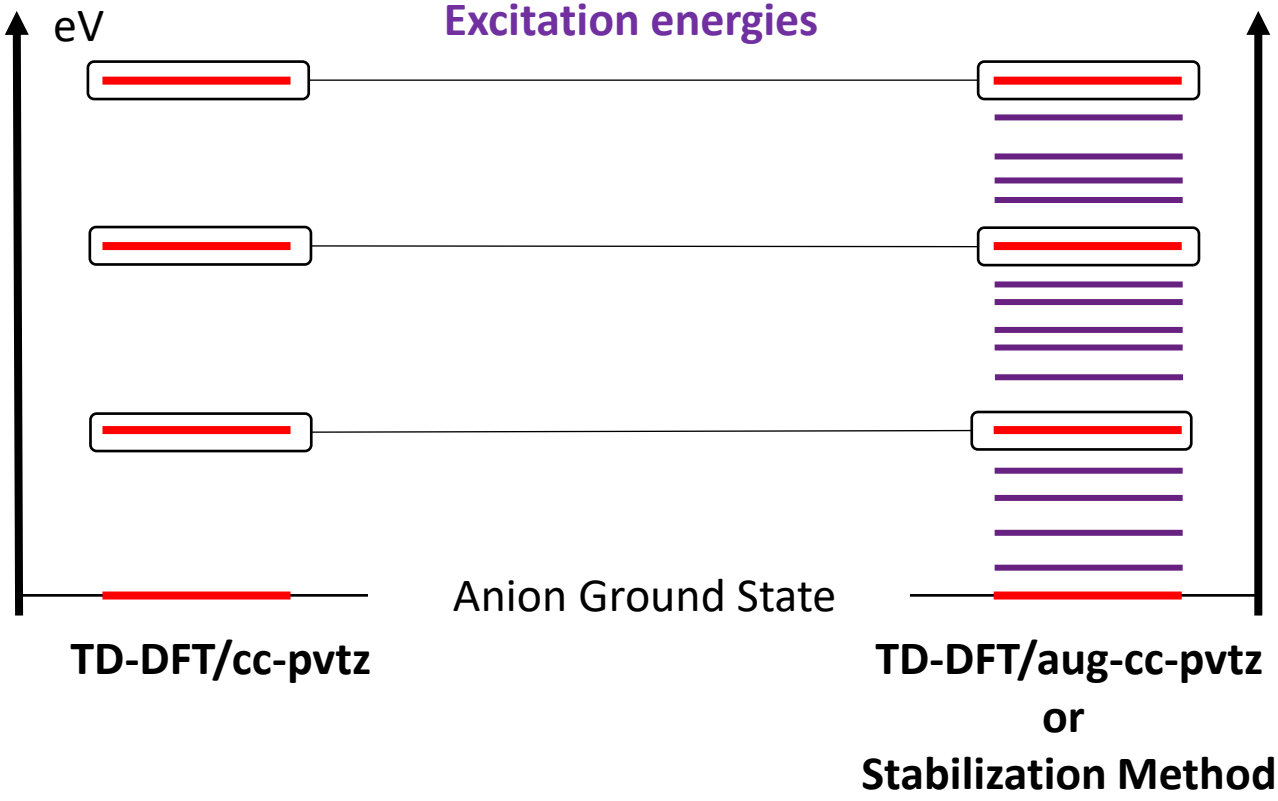


- **Anions** are usually **described** using **large basis-sets**
- Only **valence type states** are of **interest** here

→ Need to **ensure** that the **calculated excitation** energies **are the consistent** when calculated in a large or small basis-sets

Excitation energies with respect to the anion

TD-DFT/cc-pvtz vs TD-DFT/aug-cc-pvtz:

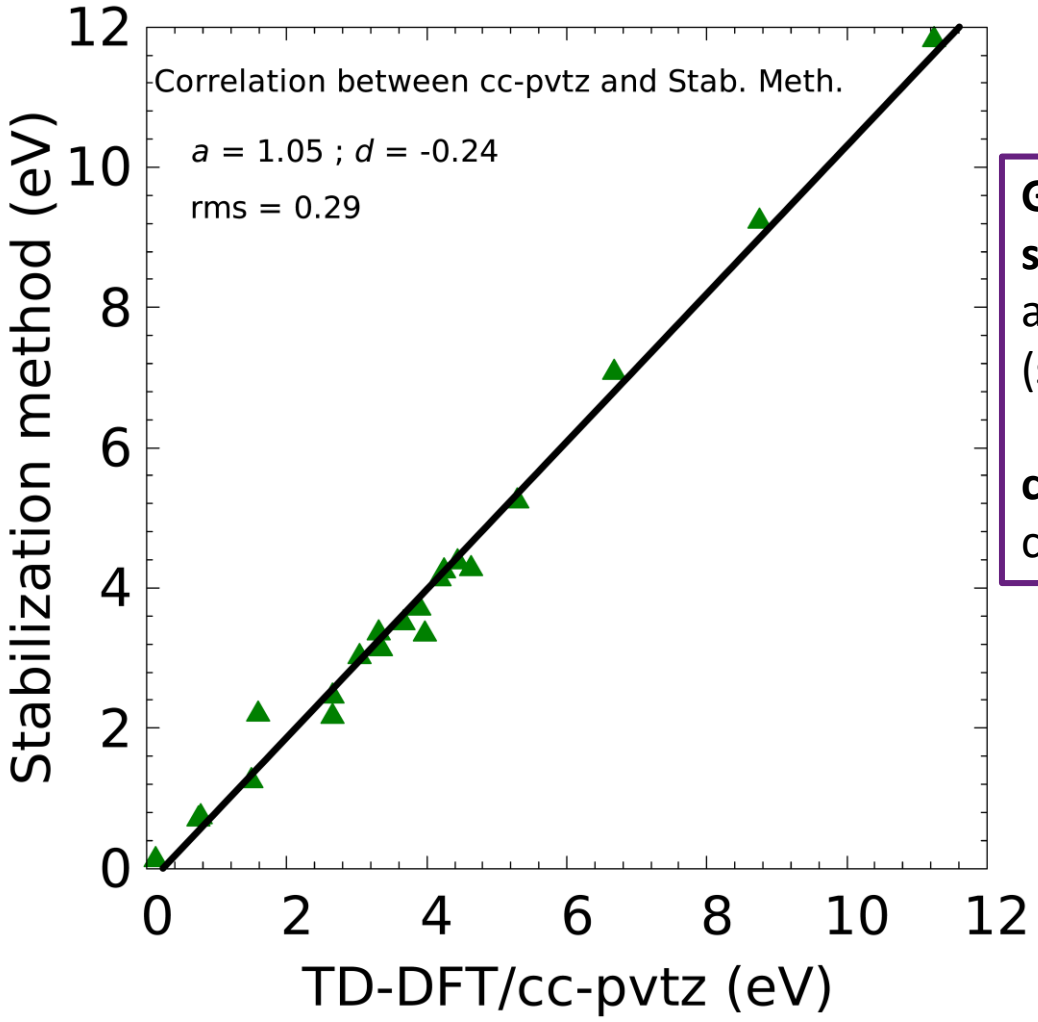


- **Anions** are usually **described** using **large basis-sets**
- Only **valence type states** are of **interest** here

➡ On the **selected sample**, calculations with **large and small** basis-sets were **consistent**

Excitation energies with respect to the anion

TD-DFT/cc-pvtz vs Stabilization method:



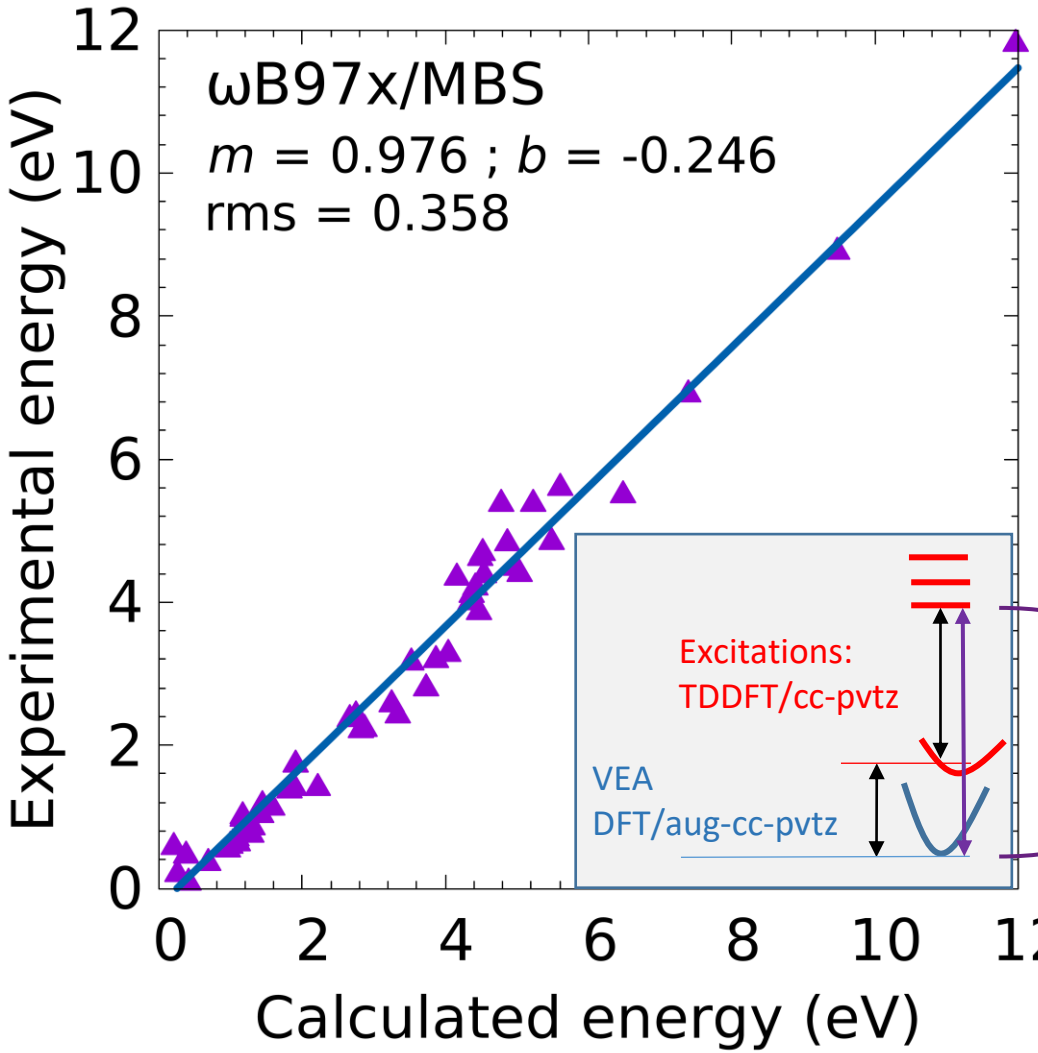
Good agreement between **stabilization method** excitation energies and **TD-DFT/cc-pvtz**
(same with TD-DFT/aug-cc-pvtz)

cc-pvtz basis-set is a **reliable** choice to calculate valence type **excitation energies**

Electron attachment energies

MBS : Multi-Basis-Set (G.Thiam & F. Rabilloud – J. Phys. Chem. Lett. (2021) **12**, 9995-10001)

ωB97x:TD(cc-pvtz) + vEA DFT(aug-cc-pvtz)

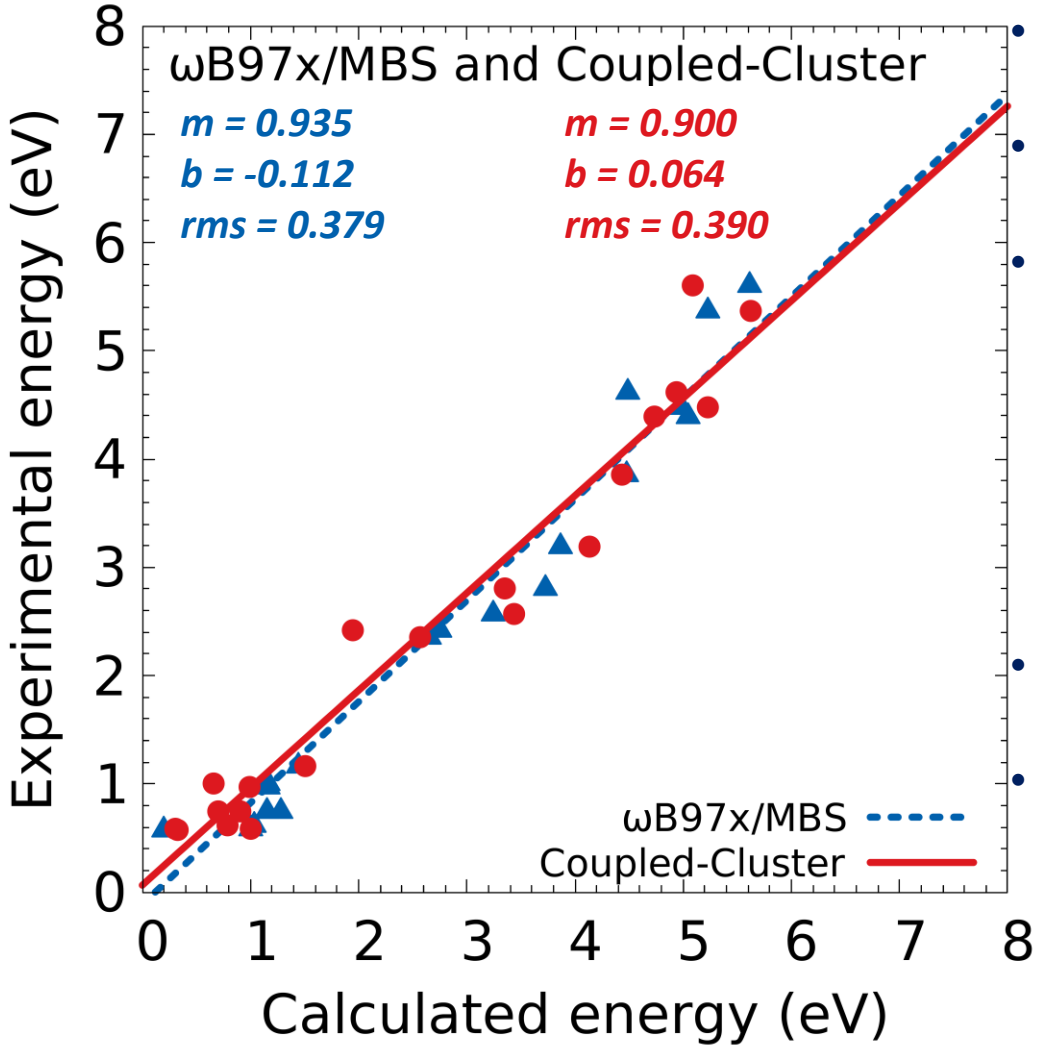


- **These results show good agreement with experimental data**
- **This method predict both shape and core exited resonances**
- **Analysis easier to do than with stabilization method**

Vertical Electron Attachment Energies

Electron attachment energies

Comparison with Coupled-Cluster



- **Reduced sample**
- EOM-CCSD/cc-pvtz + CCSD(T)/aug-cc-pvtz
- **Previous results**
  Coupled-Cluster/cc-pvtz**:**
  m = 0.857, **b = -0.397**
  rms = 0.63 eV for **63 pts**
  Sommerfeld
  J. Phys. Chem. A, 2011, 115, 6675-6682
- **Two basis-sets** are necessary
- **DFT** compares well to more computationally expensive methods

Sample

- Pyrazine (C4H4N2)
- P-benzoquinone (C6H4O2)
- Benzene
- benzonitrile (C7H5N)
- Buta-13-diene
- pyridine (C5H5N)
- Dichdifluromethane (CCl2F2)
- Chlorobenzene (C6H5Cl)
- Nitrobenzene (C6H5NO2)
- H2O
- Nitromethane
- Furan
- Benzaldehyde
- Phenyl-isothiocyanate
- Butadiyne
- Cyanogene
- GeCl4
- C8H6

Conclusion and perspectives

- **Stabilization method** and **multi-basis-set method**: **efficient** and **complementary** tools to predict **electron attachment energies***

- **In the future**
  - Application to electron-induced reactivity in **Titan's atmosphere**
    Binary **H_2O - CH_3CN film or H_2O – benzene film**

  - Computation of **electron attachement cross sections** from stabilization graphs
    *J.S.Y. Chao, M.F. Falcetta, and K.D. Jordan, JCP **93**, 1125 (1990)*
    *V.A. Mandelshtam, T. R. Ravuri and H.S. Taylor Phys. Rev. Lett. **70**, 13, 1932, (1993)*

  - Testing the method using **GW/BSE** formalism

*(G.Thiam & F. Rabilloud – J. Phys. Chem. Lett. (2021) **12**, 9995-10001)

Acknowledgement

- Jean-Zay supercalculator from IDRIS

- PSMN clusters from ENS Lyon

- CNRS for the various fundings

Thanks for your attention!