Modelling Reactivity At The Interstellar Ice Interface: Exploring HCN Isomerization For The Identification Of Accurate Methods.

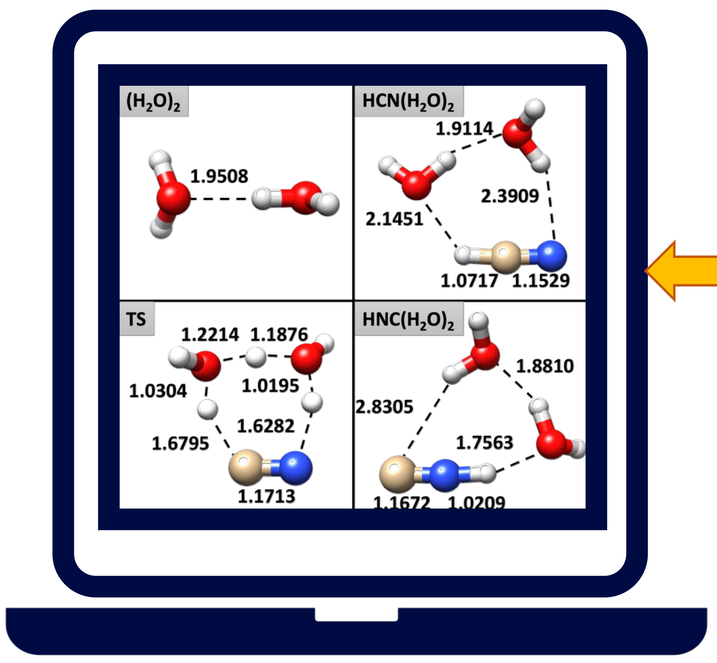
C. Baiano [1]*, J. Lupi [1], V. Barone [1] and N. Tasinato [1]

[1] Scuola Normale Superiore, Pisa, Italy

***carmen.baiano@sns.it**

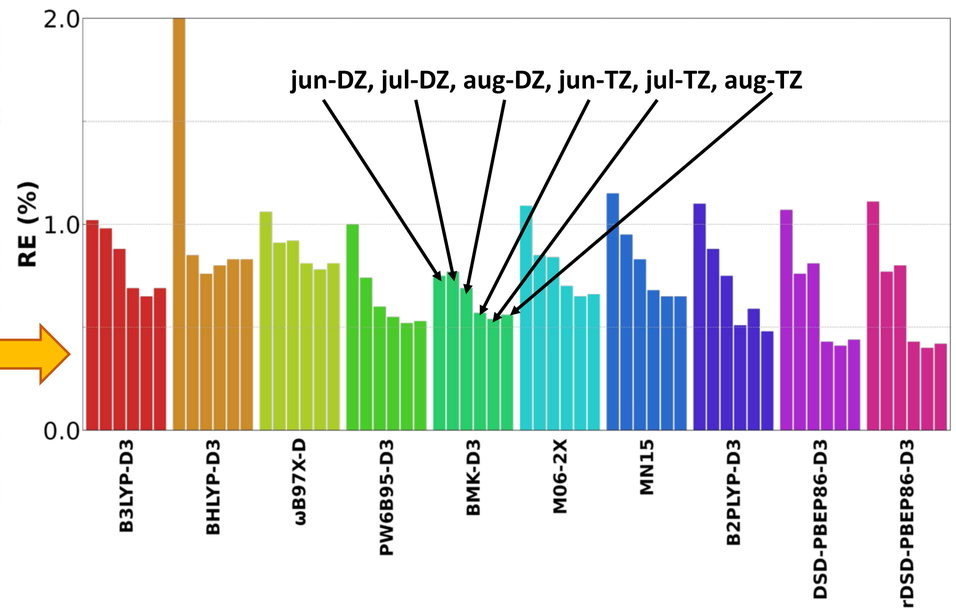
Introduction

No previous study systematically assessed the performances of **state-of-the-art density functional theory (DFT)** methods for investigating the reactivity on **interstellar water ice analogues**. We performed a comprehensive study focusing on both reaction/activation energies and geometries using HCN ⇌HNC isomerization which seems to be relevant in the Strecker synthesis for amino acids precursors formation.[1-2] Ices catalyse intermolecular H-transfers lowering the energy barrier to the formation of the transition state (TS).



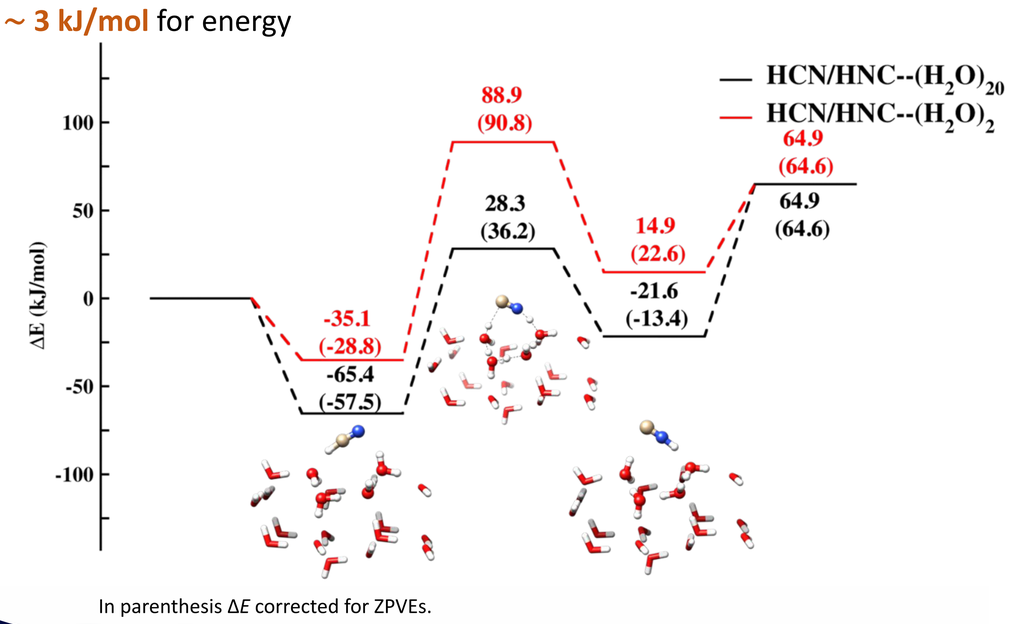
On our way to the DFT methods with the best computational cost/accuracy trade-off:

1. Setting an accurate reference: **geometries and energies at jun-ChS[3-4] level.**
2. Statistical analysis: **how common functionals and basis perform with respect to our standard?**
3. Scale up the system size: **implement the results in a ONIOM framework.**



Best performer:

- PW6B95-D3/jul-cc-pVDZ
  RE ~ 0.7% on structural parameters
  RE ~ 6 kJ/mol on energy
- DSD-PBEP86-D3/jul-cc-pVTZ
  RE ~ 0.4% on structural parameters
  RE ~ 3 kJ/mol for energy



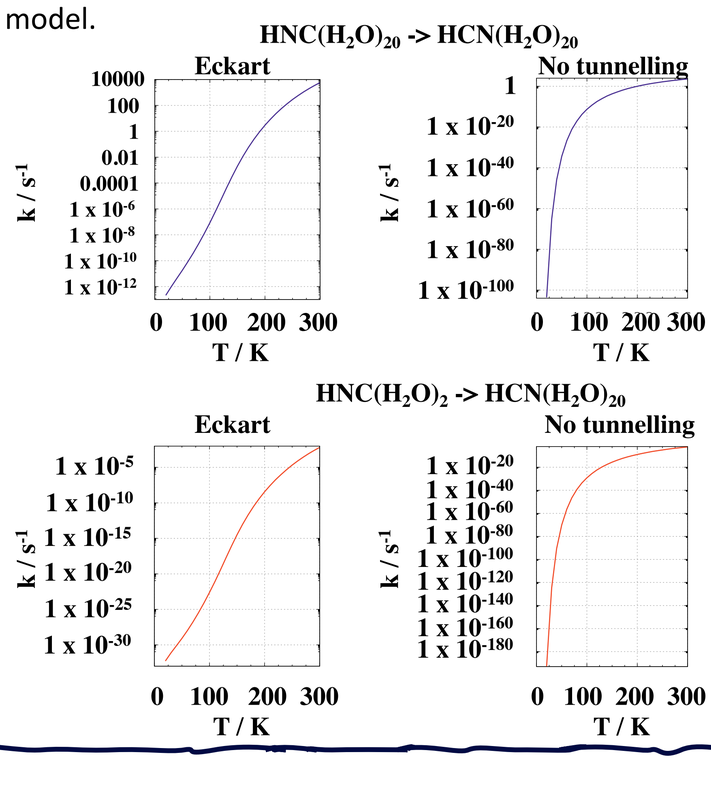
In parenthesis Δ*E* corrected for ZPVEs.

ONIOM:

- HCN ⇌HNC isomerization at $(H_2O)_{20}$
- Geometry and energy:
  DSDPBEP86/jul-cc-pVTZ:PW6B95-D3/jul-cc-pVDZ
- Refined energies:
  jun-ChS:PW6B95-D3/jul-cc-pVDZ

RATE CONSTANTS:

Multiwell one-dimensional master equation with eigenvalues method. Conventional TST within the rigid-rotor harmonic-oscillator approximation. Tunneling and nonclassical reflection effects by the Eckart model.



Going bigger with ONIOM:

HCN⇌HNC @$(H_2O)_{192}$

DSDPBEP86/jul-TZ:PW6B95-D3/jul-DZ:Amber

- HCN isomer stabilized by ~4 kJ/mol with respect to HNC
- Negligible effect on the energy barrier (less than 0.4 kJ/mol).

Conclusion

PW6B95-D3/jul-cc-pVDZ and **DSDPBEP86/jul-cc-pVTZ** have been selected as the best methods for the simulation of astrochemical reactions catalysed by interstellar icy mantles.

Passing from $(H_2O)_2$ to $(H_2O)_{20}$ lowers the barrier of HCN⇌HNC isomerization since **four water molecules** assist the intermolecular H-transfer.

For the HNC@$(H_2O)_{20}$ model, only **tunnelling** allows for an effective isomerization of HNC in the harsh conditions of the ISM.[5]

Currently, we are working on a more adequate modelling of interstellar ice surfaces considering the **amorphous** nature of icy mantles.

References

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