Binding Energy Distributions Inference on Interstellar Ice Models

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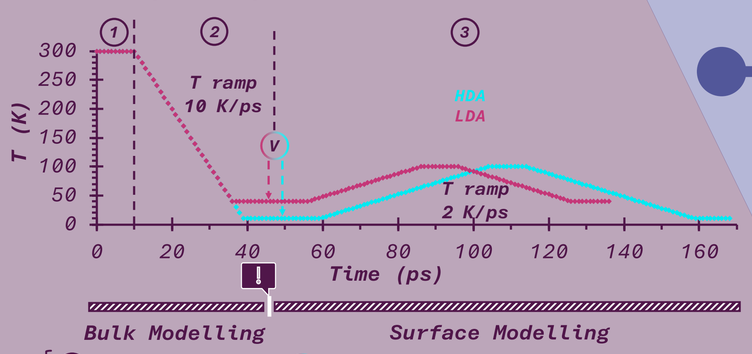
MD-simulated ices

Two interstellar ice analogues have been built, with

- ρ ~ **0.94** g/cm³ for Low density Amorphous Solid Water (**LDA**)
- ρ ~ **1,13** g/cm³ for High density Amorphous Solid Water (**HDA**)

Heat & quench protocol

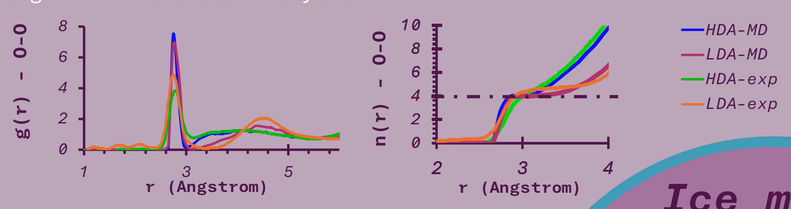


① Equilibration to 300 K
② Quenching
→ *Periodic Boundary Conditions* (**PBC**)
Ⓥ Addition of a slab of ***void*** in the z-direction - ***"2D" PBC***
③ Re-heating to 100 K and new quenching

The bulk structure reliability has been checked through

- *Comparison to experimental O-O, O-H and H-H Radial Distribution Functions (**g(r)**)/Running Coordination Number (**n(r)**)*

E.g. O-O distances analysis



- *H-bonds analysis*

Both check-up gave constistant results

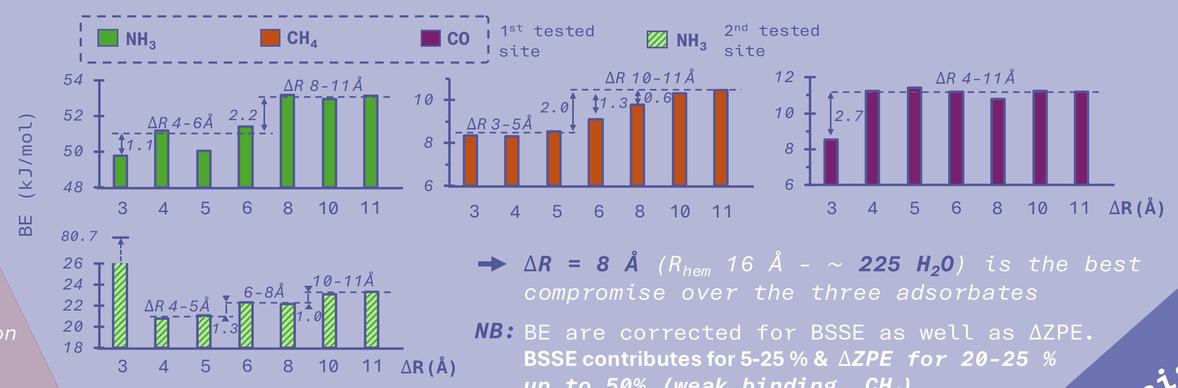
High-level method design

A DFT-functionnal benchmark on quadrumeric structures (1 adsorbate + 3 H_2O) has been performed, with **6-311+G(d,p)** as basis set.

	Mean absolute relative difference (%) w.r.t. CCSD(T) over the three adsorbate test cases		Mean absolute relative difference (%) w.r.t. CCSD(T) over the three adsorbate test cases
B3LYP-D3BJ	**14.3**	**B3PW91-D3BJ**	**26.0**
PBE0-D3BJ	**51.3**	**B3PW91**	**84.9**
PBE0	**22.8**	**CAMP-B3LYP**	**18.6**
BMK-D3BJ	**145.0**	**M06-2X**	**22.7**
BMK	**89.0**	**ωB97XD**	**17.8**

Low-level size benchmark *with a high-level of 8 Å (~ 20 H_2O)* [4]

Curently, very **few studies** have addressed the **impact** of the **system size** on the **inferred BE** and its stability… However, **long-range interractions** are expected to have large contributions to BE values, especially on amorphous systems. The low level size **Δ*R*** has therefore been benchmarked, with **GFN2-xtb** [5] as low level method.



→ ***ΔR = 8 Å*** (*R_{hem} 16 Å - ~ **225 H_2O***) *is the best compromise over the three adsorbates*

NB: BE are corrected for BSSE as well as ΔZPE.
BSSE contributes for 5-25 % & *ΔZPE for 20-25 % up to 50% (weak binding, CH_4)*

Retro-checking on the high and low level sizes

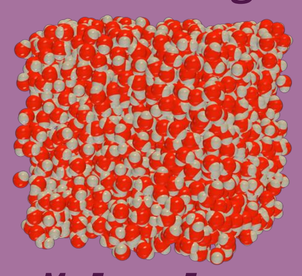
BE values have been re-computed with R_{High-L} of 12 Å for a ΔR_{low-L} *of 13* Å.

→ Very **consistent** with the converged values from the low-level size benchmark with relative discrepencies < 6 %

High-Level Basis Set & Functional check
High-Level Size 8 Å
Low-Level Size benchmark
Retro-check

Ice model building

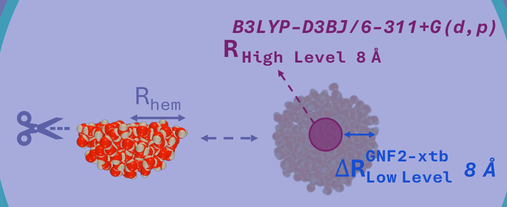
2000 H_2O
TIP4P/2005
Heat & quench
NVT



Molecular Dynamics
NAMD 2.14 [2]

NH_3, CO & CH_4

Binding energy inference



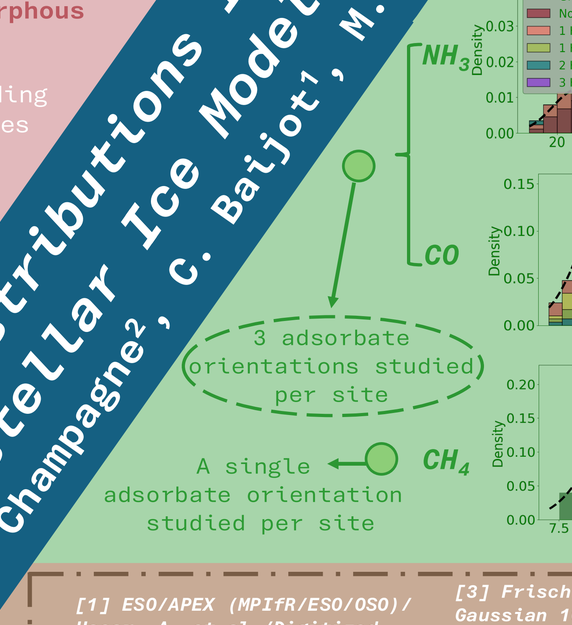
ONIOM-2 framework design
Gaussian 16 [3]

Scientific context

Dense molecular clouds:

- Birthplace of ★★ and
- Astrochemically very efficient

→ *Great **interest** in the investigation of the **exogenous origin** of **prebiotic molecules***



[1]

Dust grains

With T of 10-20 K, densities of 10^3-10^6 part./cm³, & almost complete UV extinction within the cloud interior… How can they be efficient chemical factories under such conditions?

Slow gas phase kinetics BUT presence of **dust grains** (1 %w/w w.r.t gas) surrounded by an **icy mantle** (molecular clouds & outer regions of protoplanetary disks)

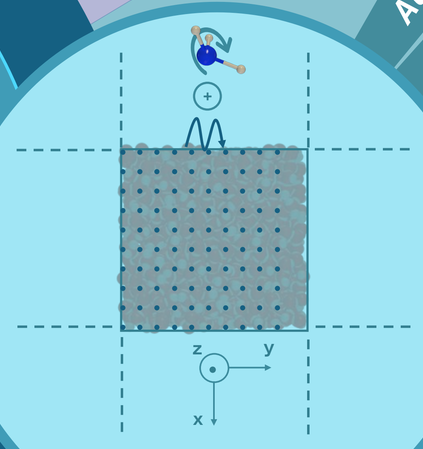
→ *Heterogeneous catalyst; third body (energy excess) & hub to put in close proximity potential reaction partners*

Icy mantles have been proven to be **water-rich** & **amorphous** in molecular clouds

- **Distribution** of Binding Energies (**BE**) per species required
- **Unique value** used in most current **codes**
- **No consensus** on the structure of the ice model nor the BE inference scheme

BE sampling

Automated
Two-fold sampling



What are the main sources of BE diversity?

① Complexity of the substrate typology (amorphicity)

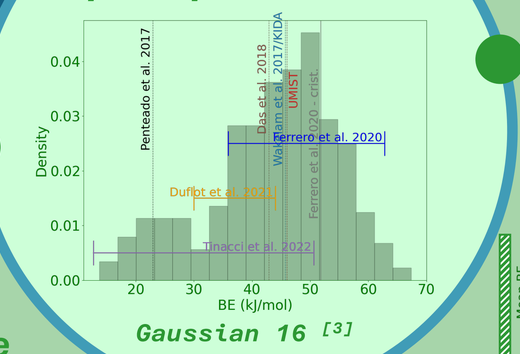
② Adsorbate orientation & local roughness of the potential energy landscape at a given binding site (in-site reorientation, metastable states with kinetic locking under a given T_{cutoff})

In practise-automated workflow

1
- I. *Replication* of the box in x-y plane (***PBC***)
- II. *Grid* of ***100*** equally spaced hemispheric centers
- III. *First starting guess* for the *adsorbate barycenter* position at ***2 Å in z*** from each grid point
- Sampling of *locally distinct* binding *sites*

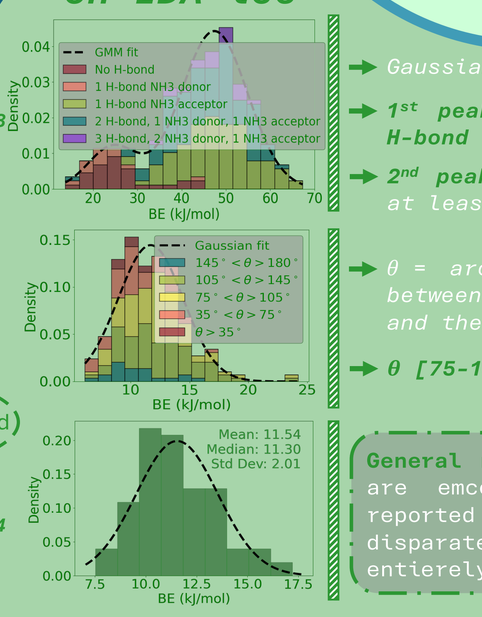
2
- IV. Definition of the *substrate-to-adsorbate* starting *orientation*(s) based on the adsorbate symmetry
  - → 3 starting orientations for NH_3 & CO
  - → Unique starting orientation for CH_4 (very symmetric)
- Sampling of the *local PES* within each locally distinct site
- V. Atoms grouped by *ONIOM layers*
- Input written + submitted

Results & perspectives



Gaussian 16 [3]

PDFs on LDA ice



→ *Gaussian Mixture Model (**GMM**)*

→ *1st peak - config. **without** H-bond*

→ *2nd peak - config. with NH_3 at least H-bond **acceptor***

→ *θ = arc-cos of the angle between the C-O bond axis and the z-reference vector*

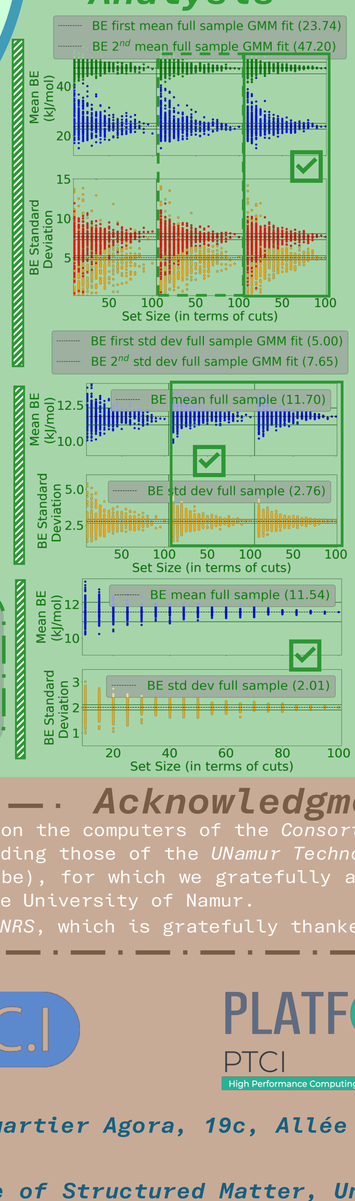
→ *θ [75-145]° favored*

3 adsorbate orientations studied per site

A single adsorbate orientation studied per site

General note - These results are emcompassing previously reported results, which where disparate or presenting non entierely overlapping ranges.

Convergence Analysis



Influence of the ice model density

The same sampling has been applied on the **HDA** model. Global statistics are conserved, even for the NH_3 GMM profile.

→ *Results are **well-reproducible**, with **high stability** w.r.t. the **ice density**.*

Perspectives

→ From vibrationnal frequency results, exact the desorption ***pre-exponential factors*** ($k_{des} = A.e^{-BE/RT}$)

→ What about such distributions on ***CO ices***?

→ Inclusion in an ***astrochemical model***

[1] ESO/APEX (MPIfR/ESO/OSO)/ Hacar, A. et al./Digitized Sky Survey 2.

[2] Phillips, JC. et al., 2020, J. Chem. Phys.,153

[3] Frisch, M.J. et al.,2016, Gaussian 16

[4] Tinacci, L. et al., 2022, ACS Earth Space Chem, 6

[5] Bannwarth, C. et al., 2019, WIRESs Comput. Mol. Sci., 11

Acknowledgments

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