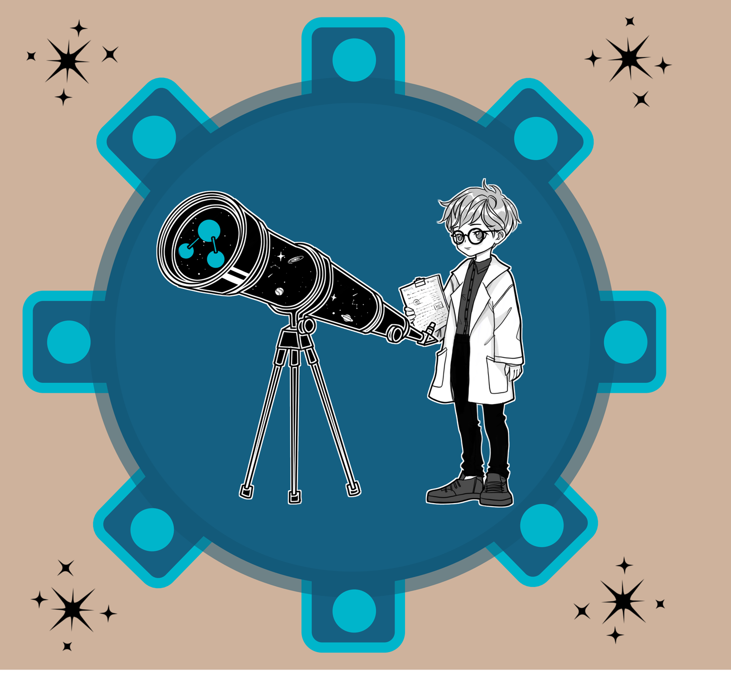

Astrochemistry – A game of spatial & temporal scales

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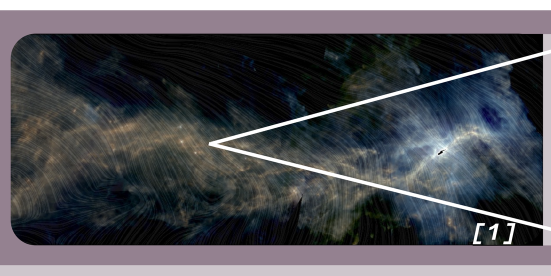
Observationnal Astrochemistry



Interstellar matter – mix of
- gas (99%) - ~ 74 wt.% H; 24 wt.% He
- dust grains (1%)- solid particles

Molecules? In cold molecular clouds

Dense molecular clouds-dark cores
- 10^3-10^6 part./cm^3
- Birthplace of stars

- First detected molecule – CH (UV-vis, 1937) ; now detections mostly in radio + recently IR (JWST)
- *In this work* – **theoretical study** of the chemistry of ***dense clouds***, **no observationnal studies** Still, necessary **source of data** for the development & improvement of the two other sub-fields

Who is there? Which species should be integrated in the network?

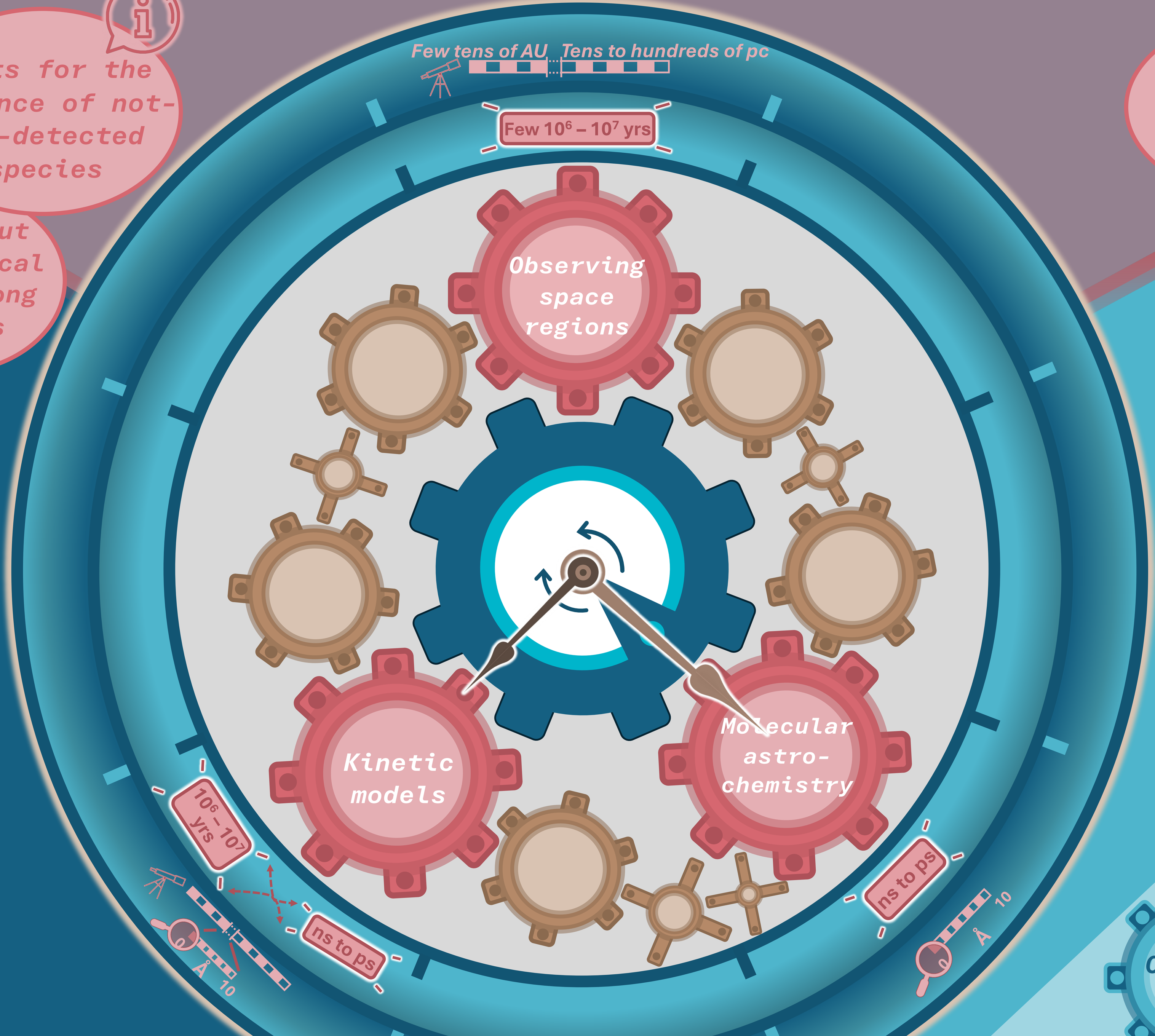
Ref data for real column density

Hints for the presence of not-yet-detected species

Info about the chemical links among species

Ref data for the processing of observationnal spectra

Who is there? On which species should we focus?



Molecular Astrochemistry

What can be explored within this sub-field?

Smallest scales investigations

- Both computationnal chemistry and empirical studies
- Allows for the generation of **reference data** both for spectroscopic & kinetic purpose

Focus in this work

- Interior of dense molecular clouds – **icy mantle** surrounding dust grains (grains ~ 1% in mass of gas phase) → **rich chemistry**, interesting for the molecular complexity (surface acting as **third body**) & **Amorphous** water-rich ices dominate – no unique binding sites/configurations
- Desorption and diffusion parameters poorly constrained[2] → **theoretical focus**

Kinetic astrochemical modelling

Filling the scale gap

Astrochemical models – **time evolution** over **billions years** of the abundances of species in astrophysical stuctures from kinetic parameters (molecular properties)

Physical param. target astro object → Code ← Chemical network

Multi-Phase Astrochemical Modelling

Ultimate goal of this work & current reasonings

I. Generalities

Different types of models built so far in the literature …

- Purely **gas-phase** VS **gas-grain** (2 or 3 phases)
- Dynamical (astrochemical timescale $\tau_{astrochem}$ > dynamical timescale $\tau_{dynamic}$ of the simulated object) VS **non-dynamical** ($\tau_{astrochem}$ < $\tau_{dynamic}$) models in terms of physical parameters describing the source
- 0, 1, or 2 Dimensionnal models

Here focus on **Multi-Phase** models under **non-dynamical**, time- and space-independant (**0D**) physical conditions – targetted astrophysical object: interior of **dense molecular clouds** *(extinct external radiation field - dust & self-shielding)*

Main challenges?

- An astrochemical system – hundreds of species, thousands of reactions & very different evolution behaviors/timescales ↔ cumbersome treatment, set of ***stiff Ordinary Differential Equations (ODE)*** to be solved
- The treatment of ***solid-phase*** astrochemistry differs among current codes (based on ***different assumptions*** with diverse extents) & is highly ***challenging*** (high ***number*** of required input ***kinetic parameters*** with intrinsic current strong ***uncertainties***)

Gas-phase treatment
- Deterministic approach – **rate eq. method** (ODE solver)
- Illustrative eq. – 2 bodies system

$$\frac{dn_i}{dt} = \sum_l \sum_j k_{lj}\, n(l)n(j) - n(i) \sum_l k_{il}\, n(l) + k_{diss}(j)n(j) - k_{diss}(i)n(i)$$

II. Future Focus

Solid–phase – grain chemistry
- Deterministic VS stochastic approach (Monte Carlo) – Which?
- Inclusion of **BE Distributions** – **branching ratio**
- ΔPenetration depth CR VS UV

Full coupling

Ref kinetic parameters feeding astrochemical networks

Which routes are the most impacting? – great care on their kinetic parameter accuracy

Current Focus

Work in progress …

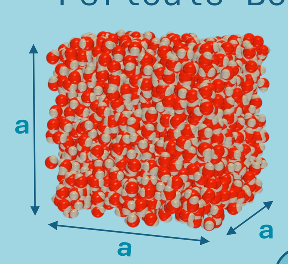
Binding, Desorption & Diffusion Parameters on Amorphous Solid Water (ASW)

Theoretical Multi-scale Molecular Investigations

I. ASW models building through Molecular Dynamics (NAMD 2.14)[3]

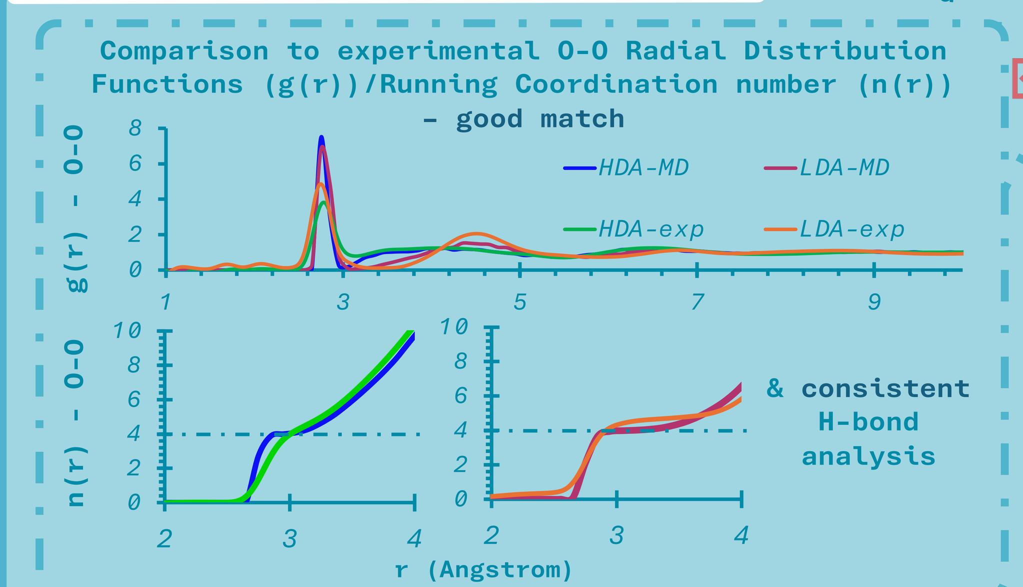
Bulk modelling

2000 H_2O molecules in a **box** (*Packmol*)[4]
- a – 40 Å for Low Density (~ 0.94 g/cm^3) ASW (**LDA**) ; 37.5 Å for High Density (~ 1.13 g/cm^3) ASW (**HDA**)
- **NVT** ensemble – **TIP4P/2005** Force Field – Full Periodic Boundary Conditions (**PBC**)



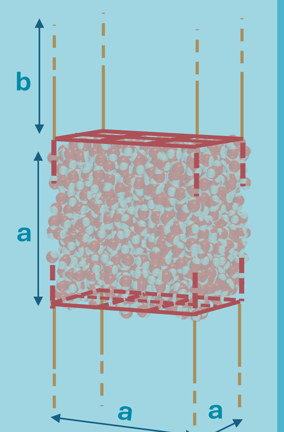
1. **Equilibration to 300 K – 10 ps**
2. **Quenched to 40** (LDA) **& 10 K** (HDA) – T ramp of **10 K/ps** ⊕ **equilibration – 10 ps**

2.1 **Check of the structure reliability**



Surface modelling

3. Towards surface modelling – From 2 → "2D" PBC – slab of 100 Å of vacuum (**b**)
4. **Re-heating to 100 K & New quench to 40 K** (LDA) **& 10 K** (HDA) in "2D" PDC – T ramp of **2 K/ps** ⊕ **equilibration – 10 ps**

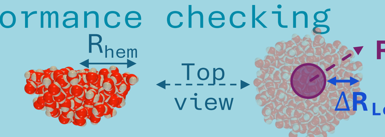


II. Binding energy (BE) inference through ONIOM-2 computations (Gaussian16)[5]

- → ΔR 8 Å (R_{hem} 16 Å – ~ 225 H_2O) seems to be the best compromise
- → ONIOM(B3LYP-D3/6-311+G**:xtb) convergent with (B3LYP-D3/6-311+G**: B3LYP-D3/6-31G(d,p)) within < 1 kJ/mol from ΔR 8 Å and higher

ONIOM-2 (DFT:xtb) scheme design

5. **Hemispheric cuts**
6. Low level size **benchmark** & *xtb* performance checking



7. **High Level Basis Set Checking** – 6-311+G** VS Def2TZVPP – ΔBE < 1.4 kJ/mol
8. **Retro-checking** of the **ONIOM zones setup (size)** – R_{hem} 25 Å, R_{High} 12 Å, ΔR_{Low} 13 Å

Binding sites sampling

9. **Sampling of both modelled surfaces** – replication of 4 in xy plane & grid of **100** hemispheres centers
10. **Adsorbate orientation randomization**
11. **BE distribution** – BE corrected for **BSSE & ΔZPE**

Perspectives

- *At short terms: reproduce a basic pure gas-phase code – include simple freezing out and desorption processes*
- *At medium terms: fully include the solid-phase treatment with the proper inclusion of nanoscale details (e.g. BE distribution) – simplified Kinetic MC?*
- *At longer terms – gold objective: couple solid-phase treatment to a neural network & dynamically link it to the gas-phase modelling*

Perspectives

Continuing to focus on the solid phase fundamental parameters
- *Inferring BE distributions for a growing set of relevant interstellar species*
- *From the thermochemistry computations, computing desorption/diffusion pre-exponential factor (Statistical Thermodynamics & Transition State Theory)*
  - *Processes parameterized as Arrhenius-like functions in kinetic codes*
- *What about such parameters on CO-ices?*
- *To longer terms – problematic of universal binding-to-diffusion (energy barriers) ratio*

References

[1] ESA/Herschel/Planck; J. D. Soler, MPIA
[2] Minissale et al.,2022,ACS Earth Space Chem, 6
[3] Phillips et al.,2020, J.Chem.Phys.,153
[4] Martinez et al., 2009, J.Comp. Chem., 30
[5] Frisch et al.,2016, Gaussian 16
[6] Tinacci et al., 2022, ACS Earth Space Chem, 6

Acknowledgments

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Top left drawing inside the gear - Courtesy of Lucy Panier.

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