Modèles et données de l’astrochimie de surface

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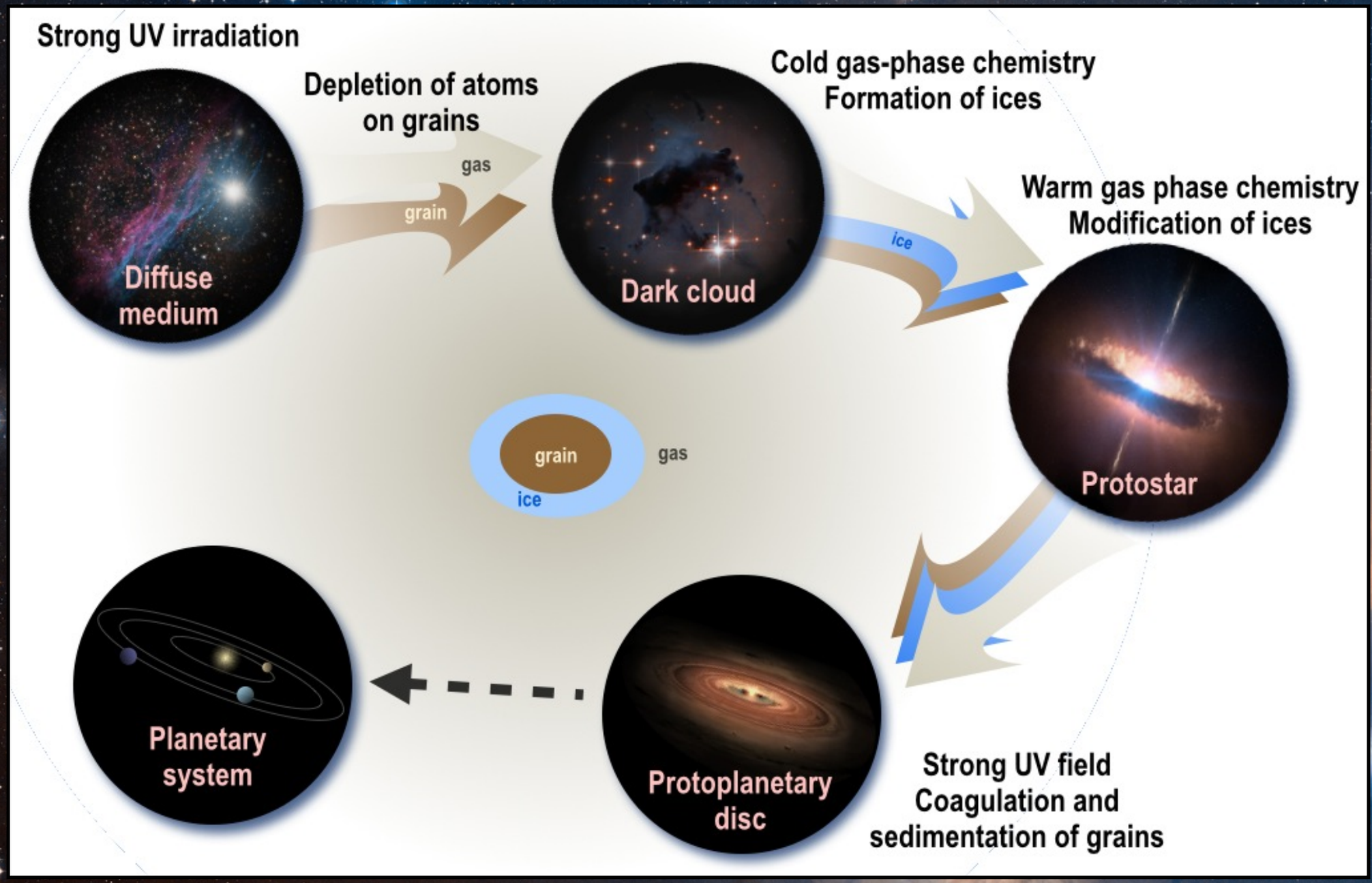
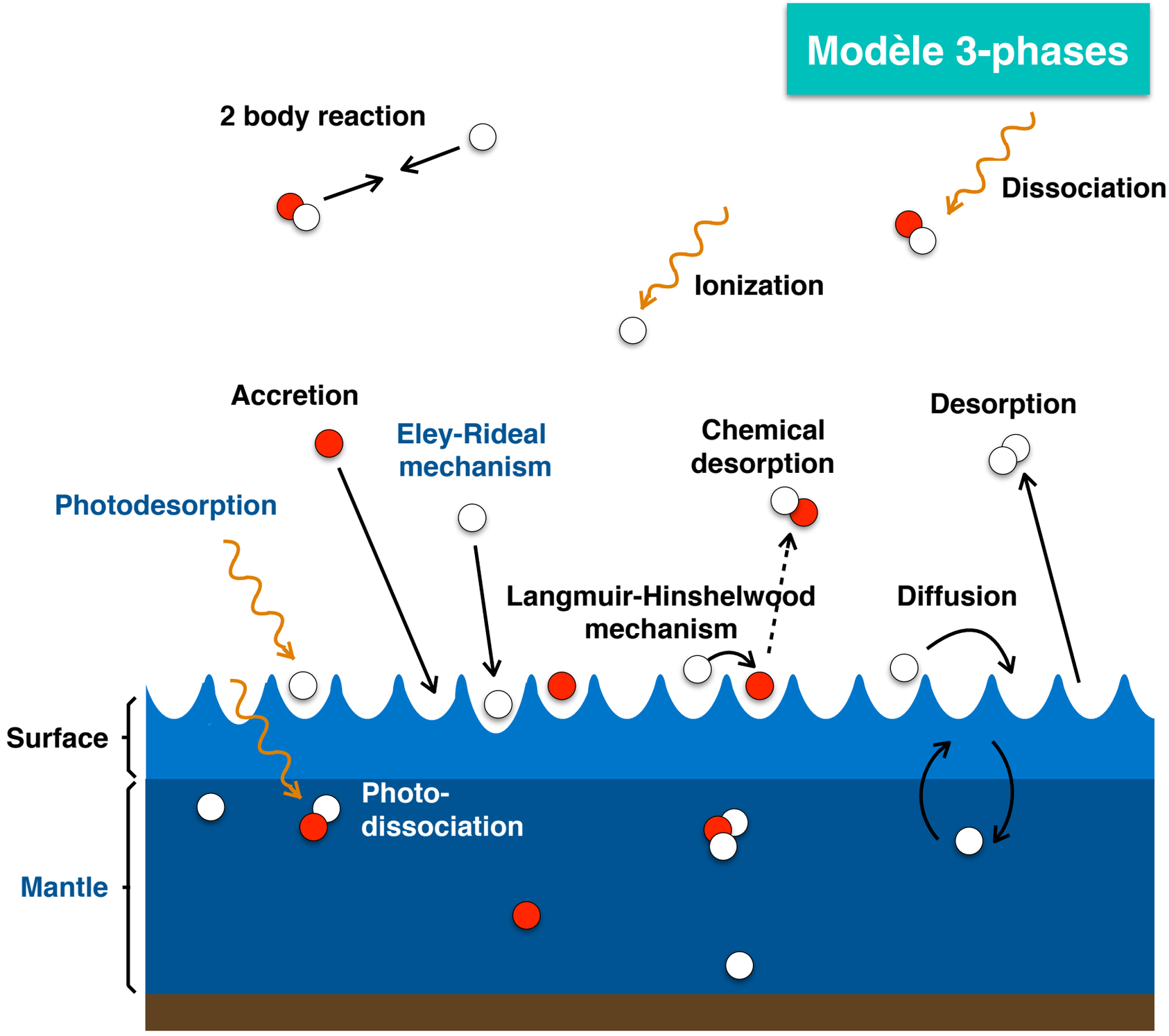


Chemical models compute the gas-phase composition and the abundance of chemical species at the surface of dust grains assuming a budget of elements and a set of parameters.

The Nautilus gas-grain model

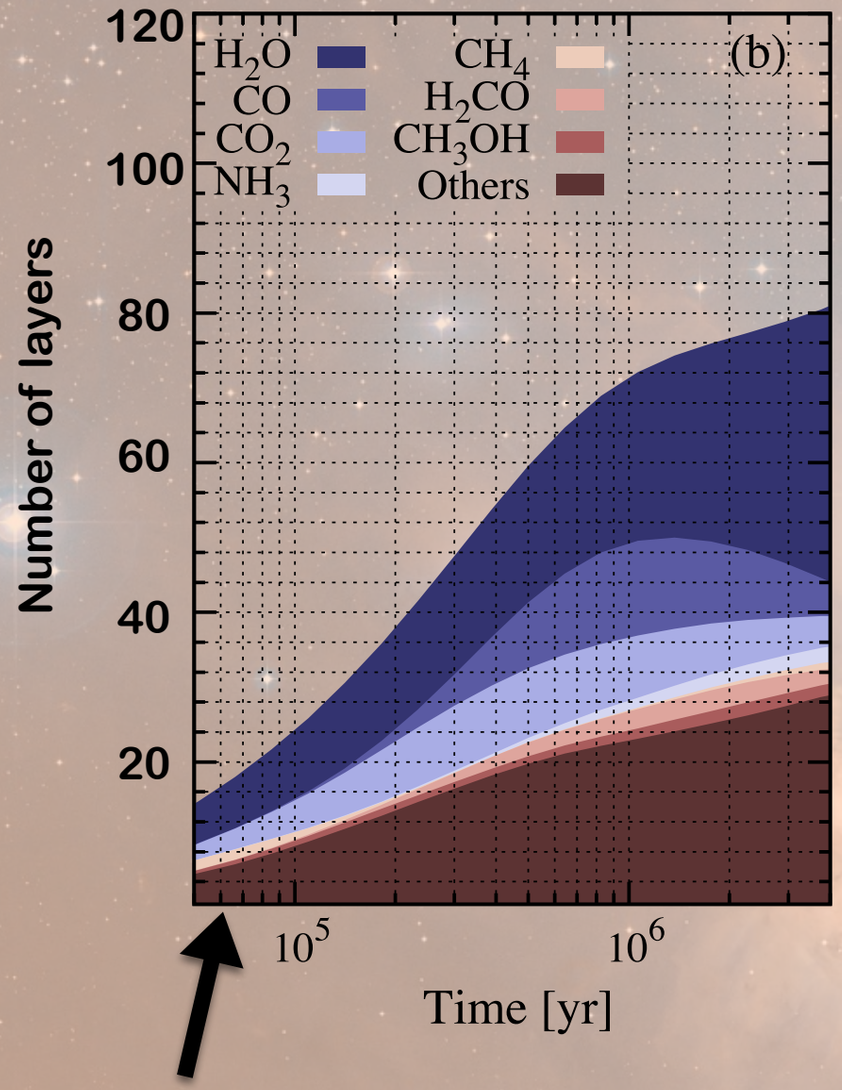
Processes included:

- Diffusion:
  - Thermique
  - Tunneling effect
- Reaction:
  - Langmuir-Hinshelwood
  - Eley-Rideal
- Desorption:
  - Thermique
  - Chemical
  - Cosmic-ray induced
  - Photodesorption
- Dissociation:
  - Photons
  - Secondary photons



Ruaud et al. 2016

Predictions of ice composition



HCN, N_2, CH_3CHO, HCOOH, HCO, CH_3O,…

Ruaud et al. (2016)

Numerical limitations of the diffusion formalism:

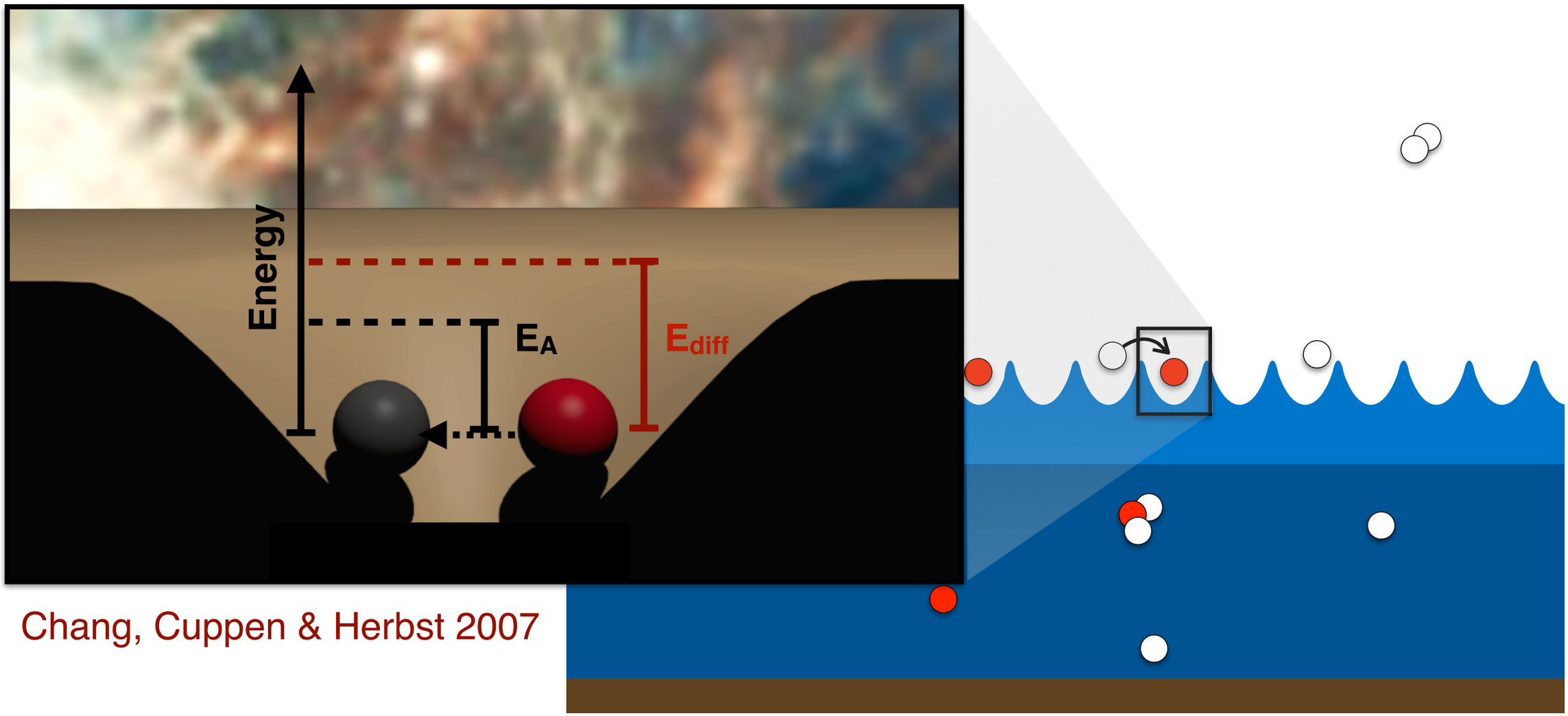
Random walk
Our models do not take into account the random nature of the diffusion of species on grains. We usually assume that all species will automatically scan the grain surface without coming back on its trail.
-> study from Willis & Garrod (2017)

Competition reaction-diffusion
Our models do not take into account the fact that a species does not necessarily hop from its site each time.
-> numerical trick to include such effect

Reaction-diffusion competition:

→ **For reactions with activation barrier**

if $E_A < E_{diff}$, the reaction has a higher probability to occur than the diffusion of one of the two reactants.



Chang, Cuppen & Herbst 2007

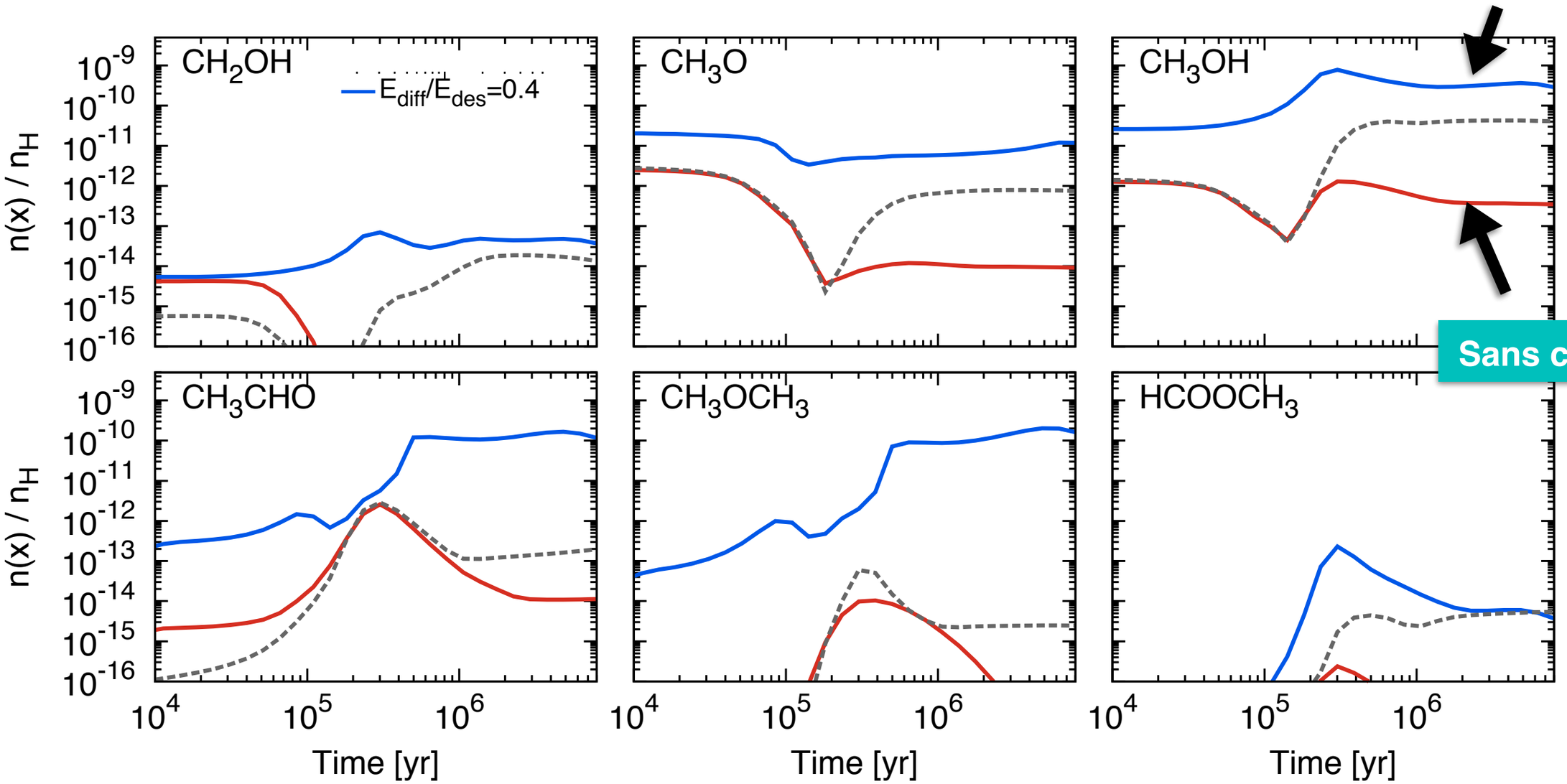
Transparent - thèse M. Ruaud

Effect of the reaction-diffusion competition on the formation of COMs :

→ HCO is more easily produced: H+CO (E_A=2500K)
→ CH_3O as well: H+H_2CO (E_A=2200K)

CH_3+HCO → CH_3CHO
CH_3O + HCO → $HCOOCH_3$

With competition



Sans compétition

→ Gas phase abondances
→ Medium diffusivity

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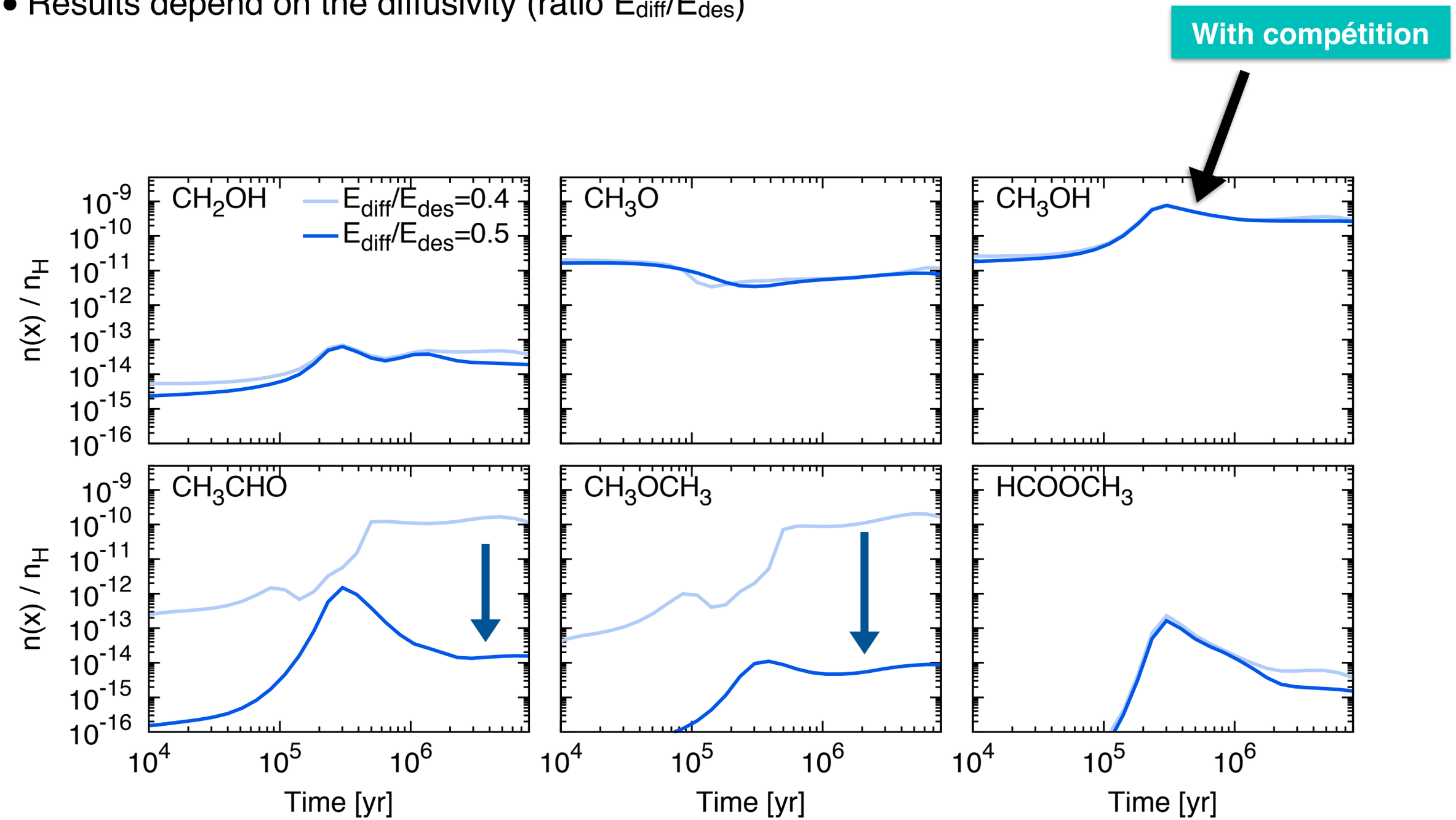
Ruaud et al. 2016

Effect of the reaction-diffusion competition on the formation of COMs :

- Results depend on the diffusivity (ratio E_{diff}/E_{des})



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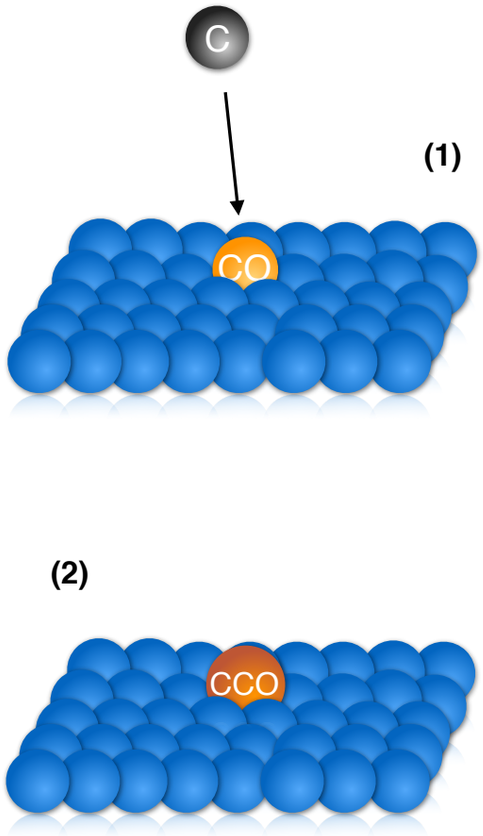
Ruaud et al. 2016

Surface reactivity

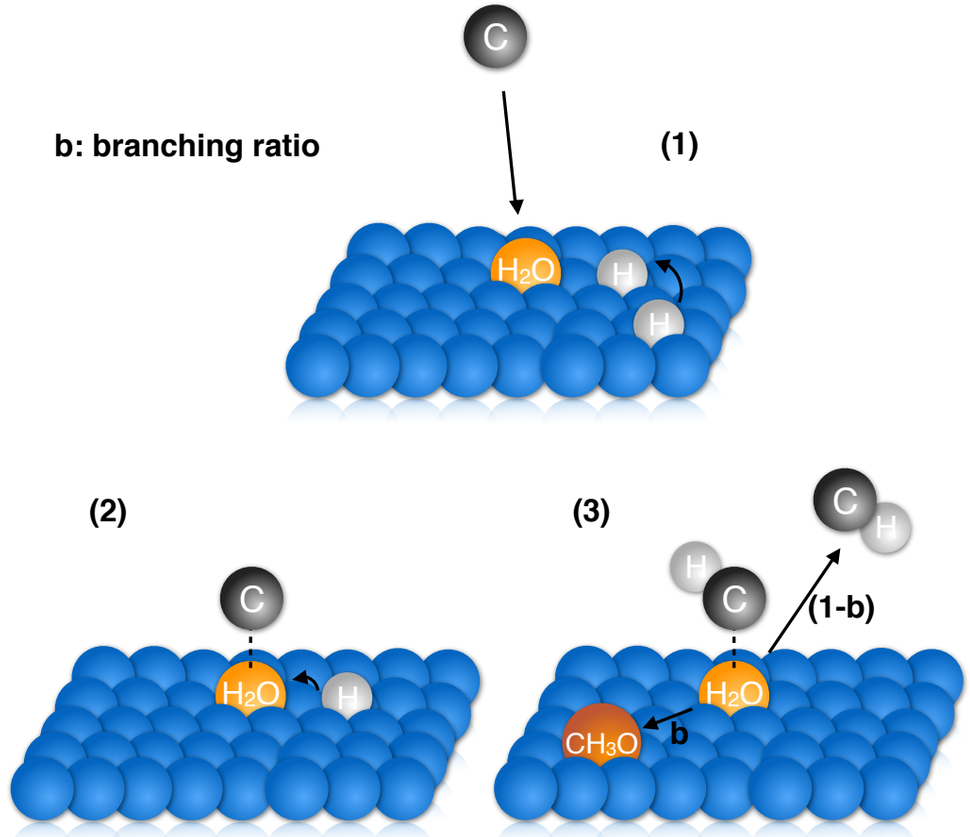
Taking into account the nature of the surfaces

Reaction†		
C + s-X	→	s-CX
	→	s-C...X
s-C...X + s-H	→	s-CHX
	→	s-CH...X
	→	CH + s-X
s-O...CO + s-H	→	s-HOCO
	→	s-OH + s-CO
	→	s-H + s-CO_2
	→	OH + s-CO

Eley-Rideal mechanism and formation of complexes with the surface (Ruaud et al. 2015)



Reactions without barriers
(H_2, CO, H_2CO)



Reactions with barriers
(H_2O , CO_2, CH_3OH, CH_4, NH_3)

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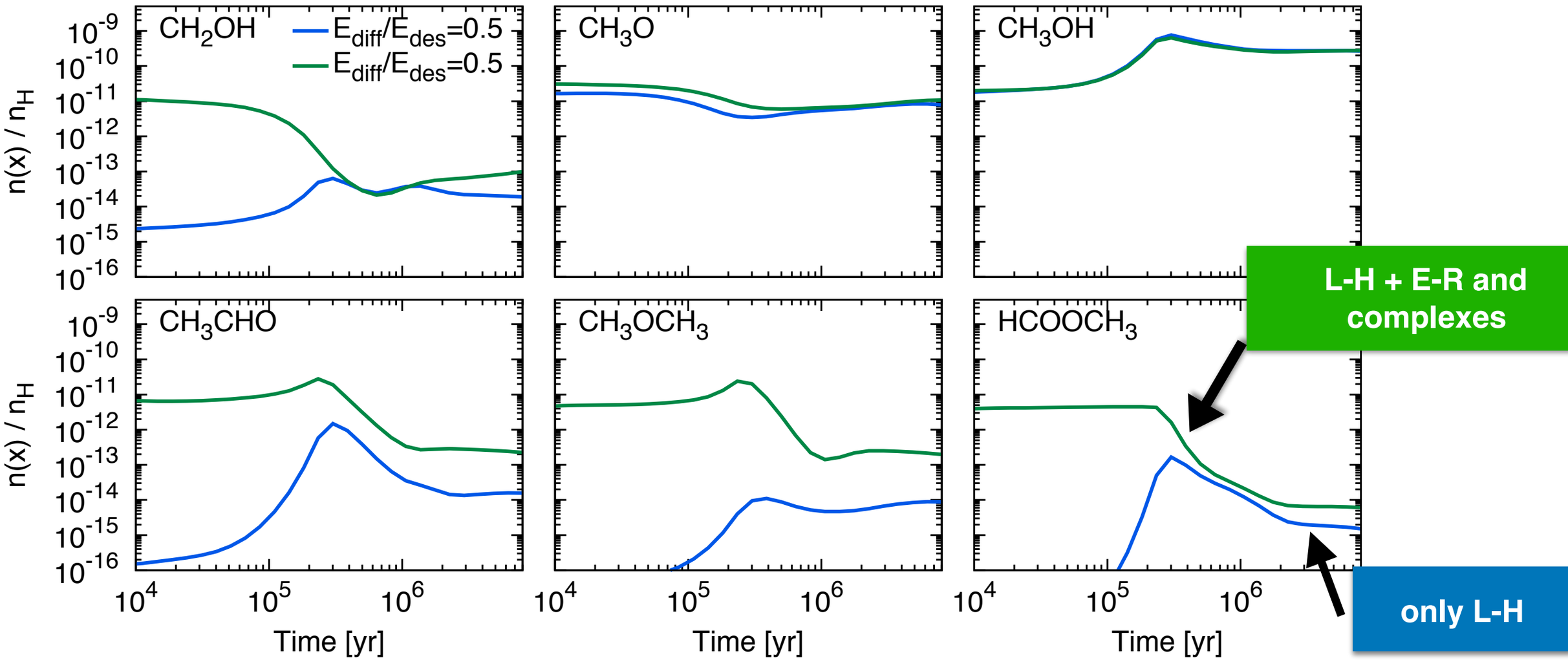
Surface reactivity

Taking into account the nature of the surfaces

Eley-Rideal mechanism and formation of complexes with the surface

- Boosts the formation of COMs at the surface of the grains



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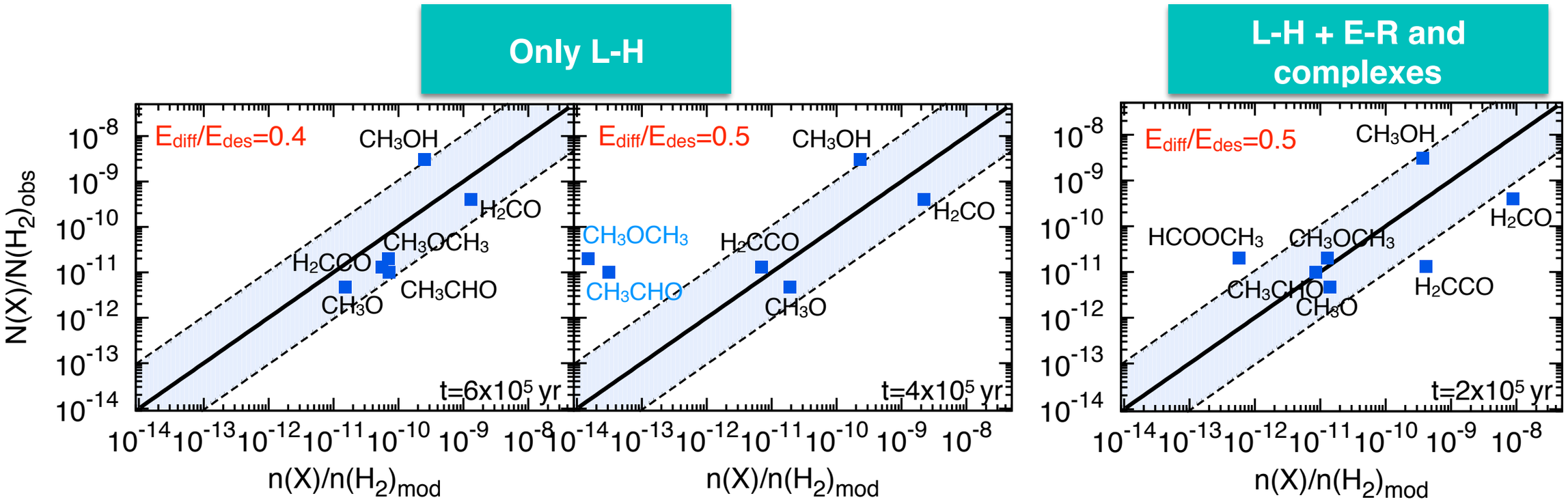
Ruaud et al. 2015

Formation of complex organic molecules at low temperature: Comparison to observations in B1-b



- Modeling with E_{diff}/E_{des} = 0.4: good agreement with observations

- Modeling with E_{diff}/E_{des} = 0.5 : low production only by diffusion
  → Eley-Rideal mecanisme and formation of surface complexes

(Refs. Obs. : Cernicharo et al. (2012), Marcelino et al. (2005), Öberg et al. (2010))

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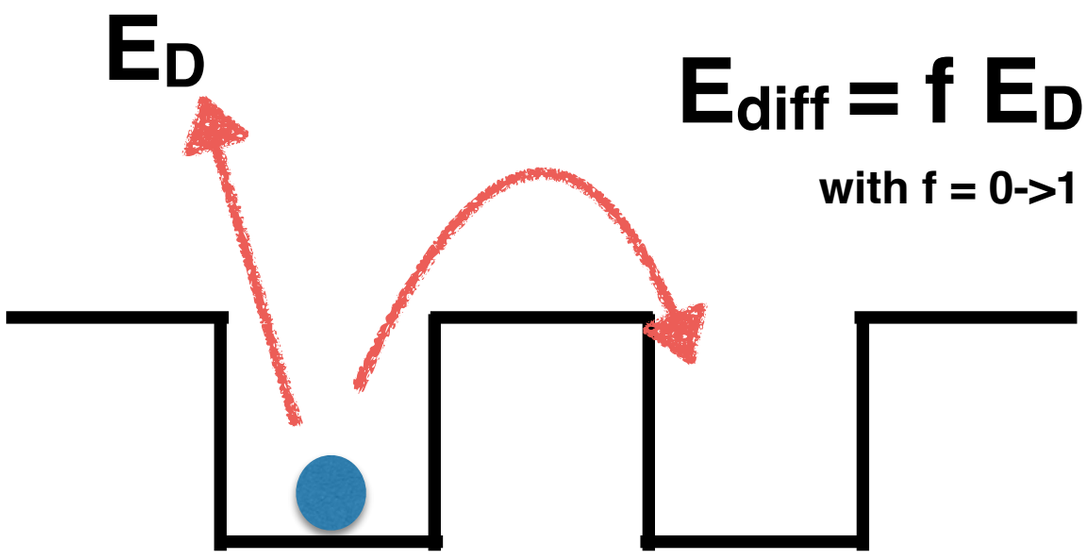
Binding energies : keys for diffusion (for the moment) and desorption

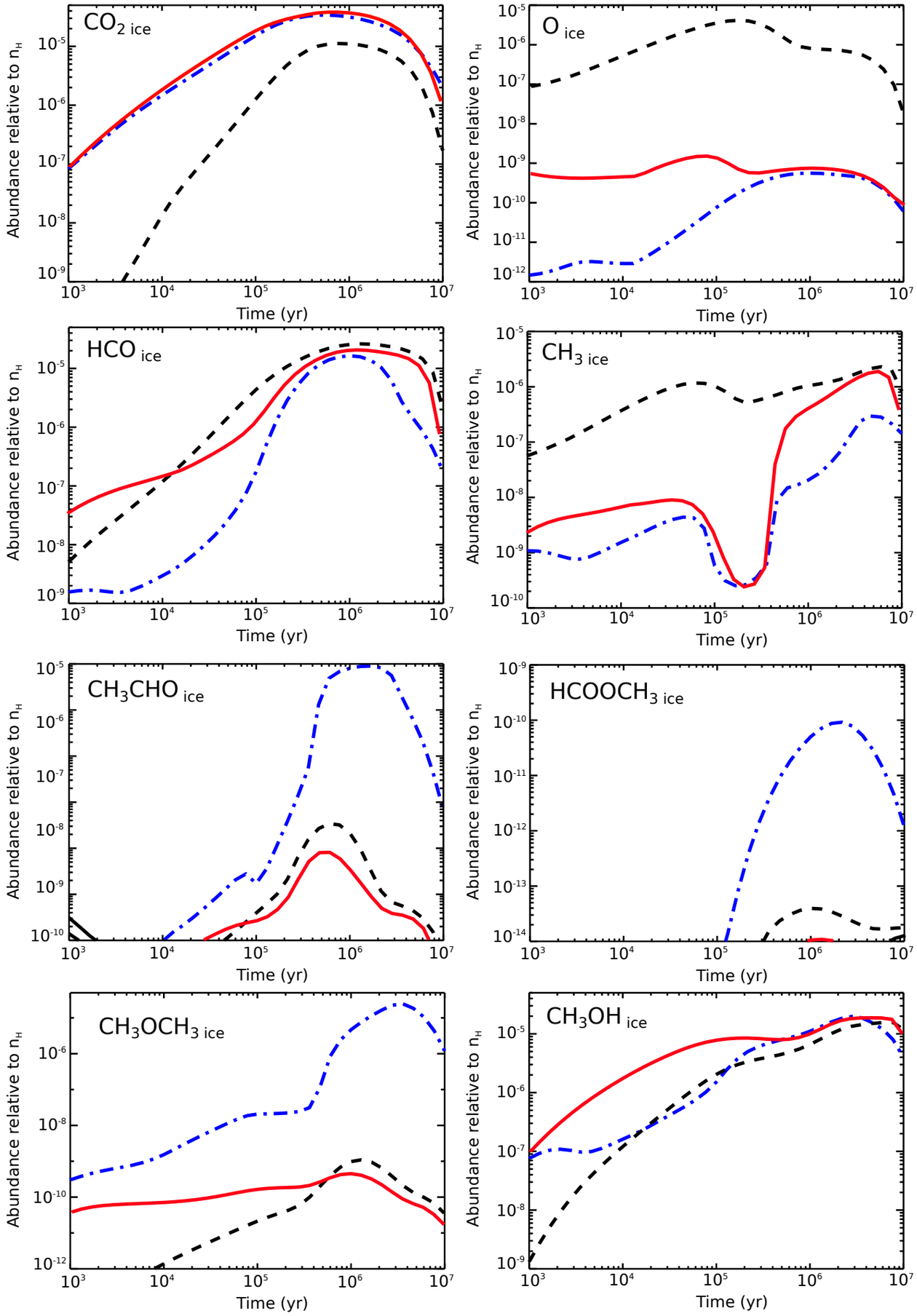


Simple method to estimate the binding energies (E_D) for missing data (mostly radicals) + other updates from the literature (Wakelam et al. 2017).

79 modified values (important in some cases).

Strong impact on the model predictions from:

- O (**800K** Tielens & Hagen (1982) **-> 1600K** experiements from He et al 2005, Ward et al 2012, Kimber et al 2014, Minissale et al 2016),
- CH_3 (**1175K** C+(3/4)*(CH4-C) **-> 1600K** Wakelam et al.)
- HCO (**1600K** CO+H -> **2400K** Wakelam et al.)



Old E_D

New E_D

New E_D + diffusion of by tunneling effect O (Minissale et al. 2013)

Chemical desorption

Garrod et al. (2007) - based on the Rice-Ramsperger-Kessel theory (Rice & Ramsperger 1927, Kassel 1928).

Desorption probability

$$P = \left(1 - \frac{E_D}{E_{reac}}\right)^{s-1}$$

Fraction of molecules to evaporate

$$f = \frac{aP}{1 + aP}$$

With a unknown taken between 0.01 and 0.1.

Minissale et al. (2016) - based on experimental measurements of simple systems (O+H, CO+H, O+O and N+N)

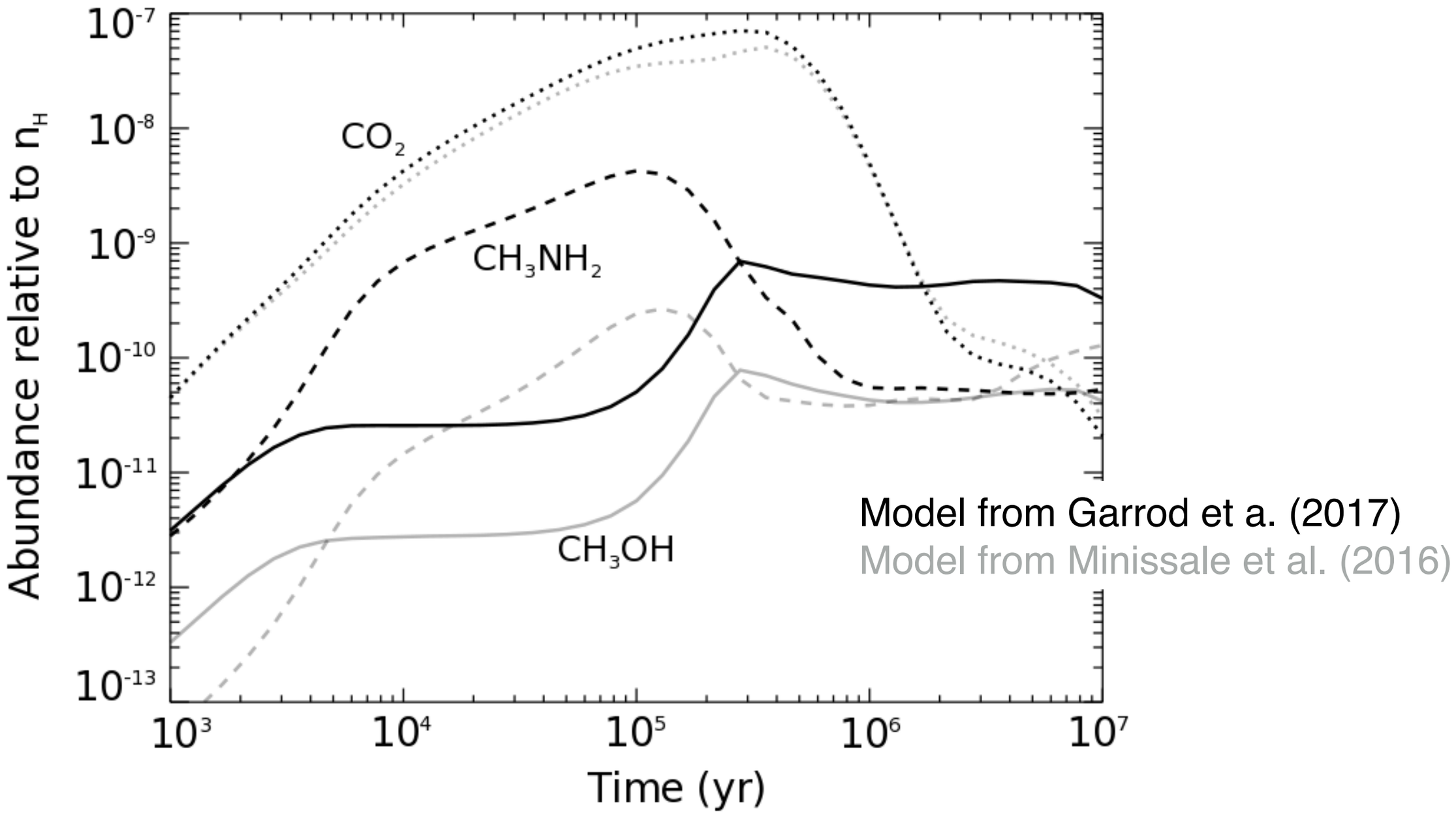
Fraction of molecules to desorb $$f = e^{-\frac{E_D}{\epsilon E_{reac}/N}}$$

ϵ unknown for ice surfaces.

Measurements show an efficient process of bare grains but probably not on ices for big systems.

Chemical desorption

Efficiency of the Minissale's chemical desorption much smaller **on water ice than the Garrod's one. No COMs in the gas-phase anymore.**



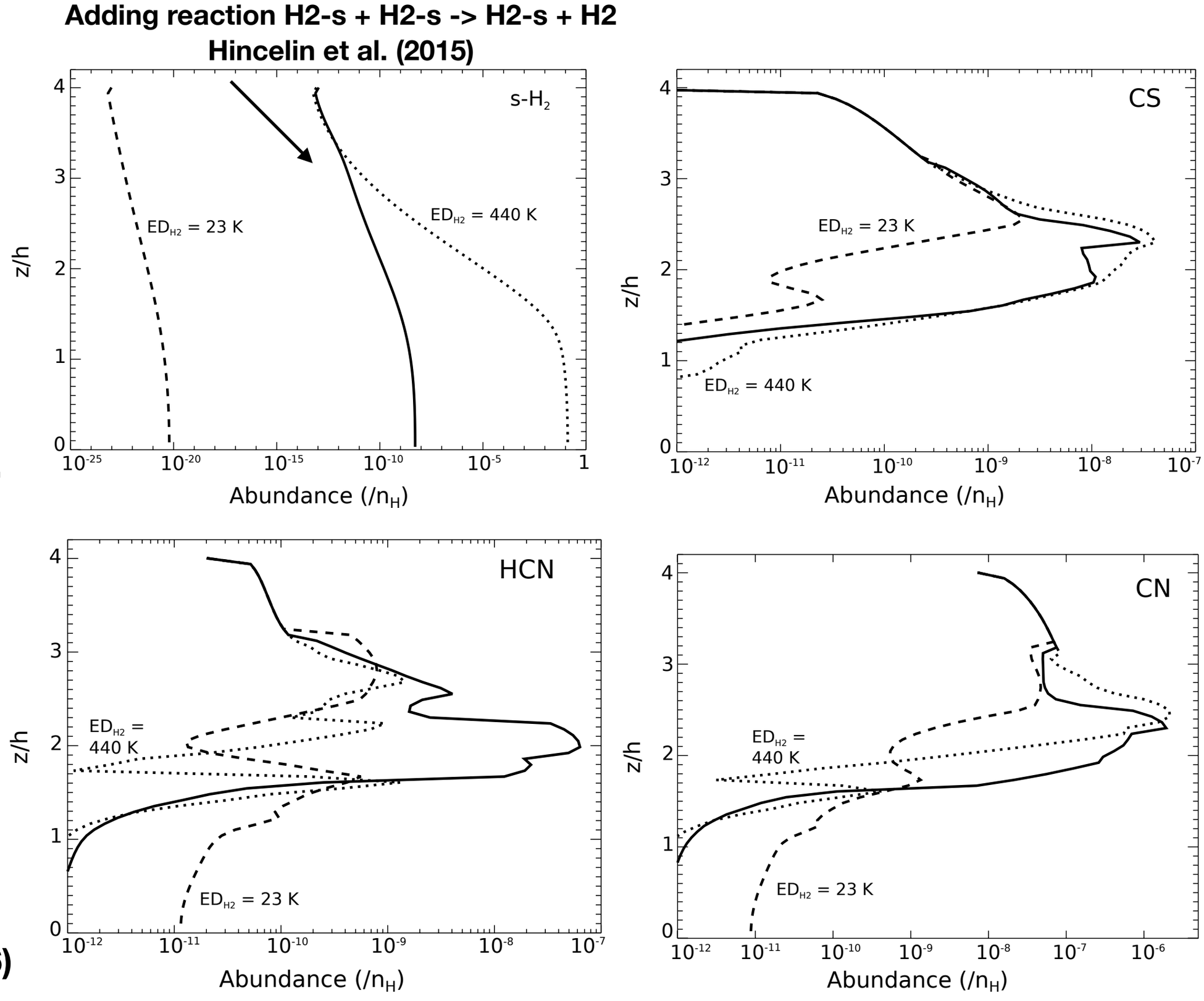
Model from Garrod et a. (2017)

Model from Minissale et al. (2016)

Detailed sticking of H_2: effect on the disk molecular column densities

Time scale of H_2 depletion is small. The sticking of H_2 needs to be treated with care.

Wakelam et al. (2016)



Many other types of processes that need to be included or better included

- **Photo desorption (many studies - still under investigation)**
- **Sputtering induced by cosmic-rays (Dartois et 2019)**
- **Radiolysis by cosmic-rays (Shingledecker & Herbst 2018)**
- **Ro-thermal desorption from rotating grains (Hoang & Day Tung 2019)**
- **Characteristics of the grains (multi-grain sizes and surface natures)**

Conclusion + résumé

- Le modèle 3-phases aura tendance à produire plus d'espèces variées sur les surfaces (notamment des radicaux car peu de réactions dans le manteaux.

- La compétition réaction/diffusion permet de produire plus de COMs tant que le rapport E_{diff}/E_D est inférieur ou égal à 0.4.

- Pour des diffusions plus lentes, le mécanisme Eley-Rideal + complexation permet de produire les COMs.

- Si les E_D des précurseurs CH_3 et HCO est plus grande alors on ne forme plus de COMs (à moins d'avoir une super diffusion et ce malgré le processus Eley-Rideal + complexation).

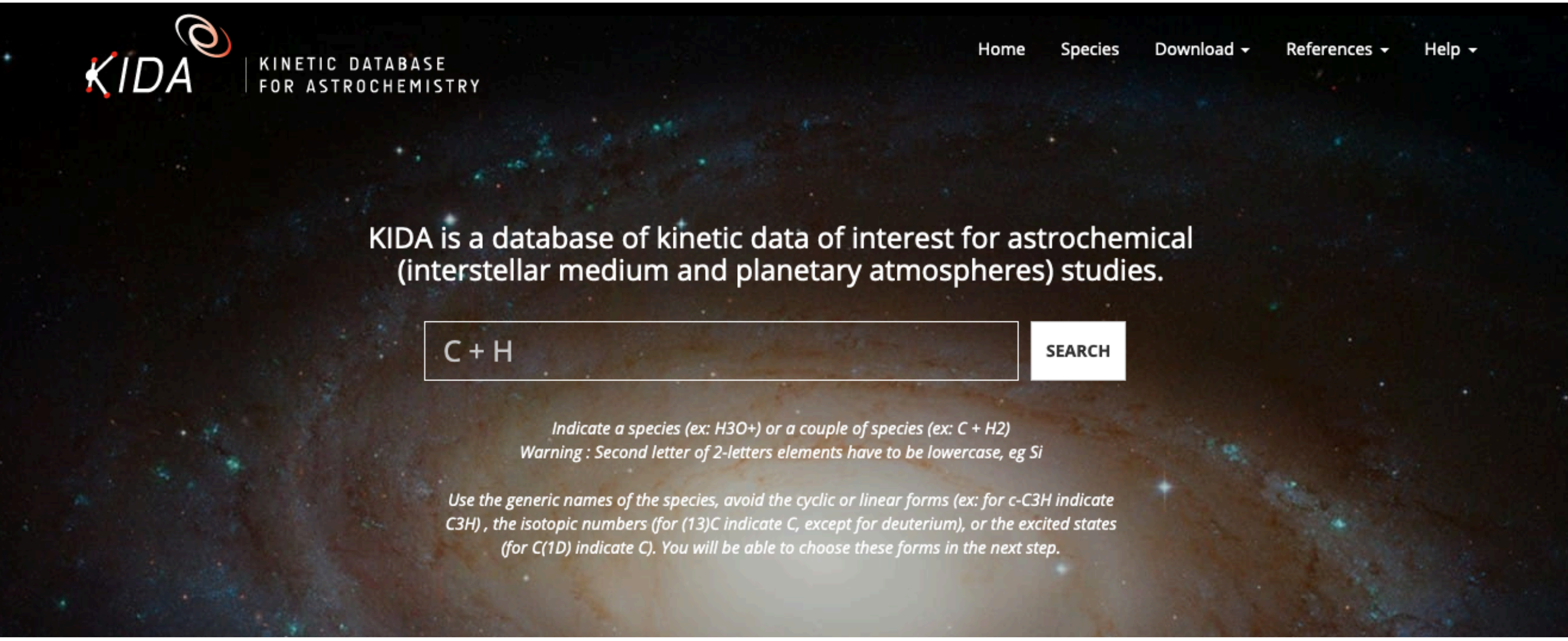
- Avec le nouveau modèle d'évaporation chimique de Minissale -> on n'évapore plus rien.

-> plus à venir avec le travail de fond de JC

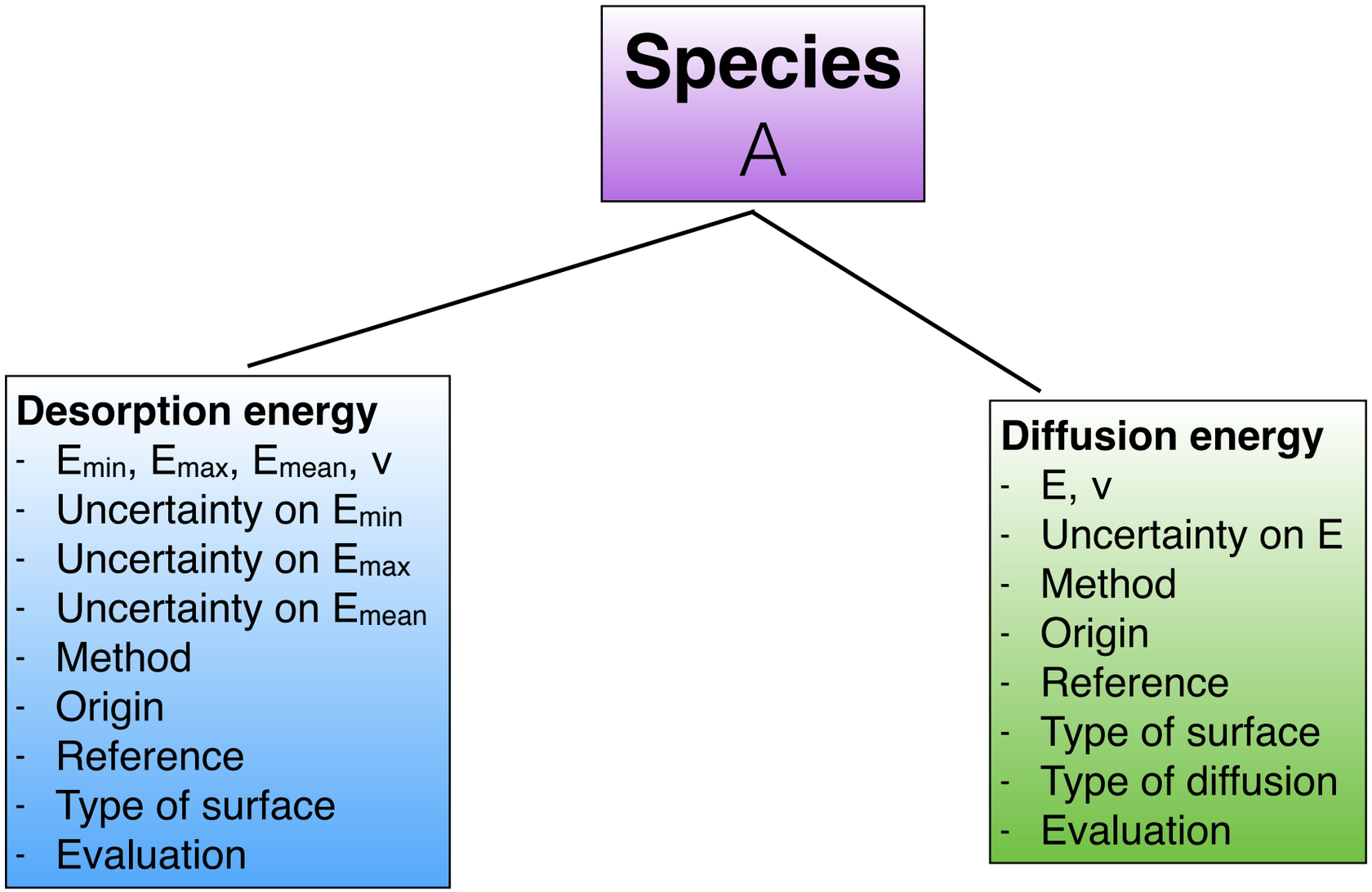
Surface data in KIDA

http://kida.obs.u-bordeaux1.fr/

KIDA
KINETIC DATABASE FOR ASTROCHEMISTRY



Data model for surfaces reactions



Data model for surfaces reactions

Reaction

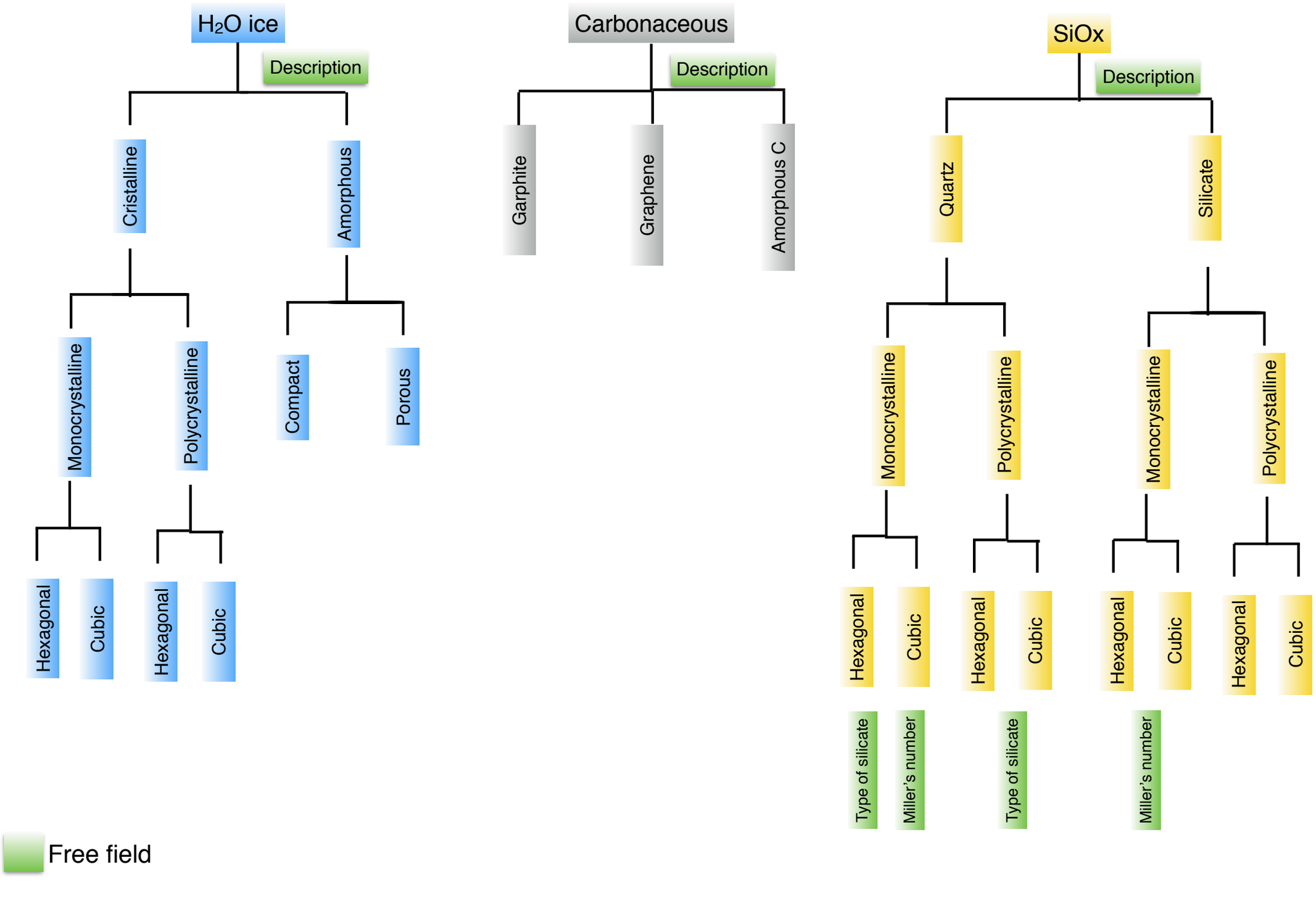
$A + B \rightarrow C + D$

Branching ratio
- Value
- Uncertainty on BR
- Method
- Origin
- Reference
- Type of surface
- Evaluation

Activation energy
- EA
- Pre-exponantial factor
- Uncertainty on EA
- Method
- Origin
- Reference
- Type of surface
- Evaluation

Barrier width for tunneling
- Value
- Uncertainty
- Method
- Origin
- Reference
- Type of surface
- Form of the barrier
- Evaluation

Data model for substrate



Data model for surface reactions

Remarks:

1) Little reliable data available.
2) Difficulty to characterize the nature of the surface.
3) Data strongly influenced by the nature of the surface, which is not homogeneous.
4) The data are not direct measurements but fitted by a model (necessity to homogenize the experimental methods). -> example of the pre-exponential factor for the fitting of diffusion and binding energies.
5) Many processes are just not yet understood and cannot be simply translated by a few parameters.

My opinion: not ready for a standard.

Bordeaux astrochemical tools

KInetic Database for Astrochemistry
http://kida.obs.u-bordeaux1.fr/

InterStellar Abundance database
http://isa.obs.u-bordeaux1.fr/

AstroChemical Newsletter
http://acn.obs.u-bordeaux1.fr/

Nautilus gas-grain code
http://perso.astrophy.u-bordeaux.fr/~vwakelam/Nautilus.html

Funding