Adapting heterogeneous catalysis calculations to the astrochemistry world

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Presence of solids in astrochemistry

- ISM : grains, bare or icy, all over the place .
- Solar system: a number of objects (moons and comets) covered with ices (H_2O, CO, CO_2, NH_3…).

Role of solids in astrochemistry

- Trapping by adsorption : distortion of the observed abundances; reservoir of potential reactants.
- Energy provider or adsorber for reactions at surface; catalytic role by providing H radicals (case of water).
- Protection of species into the bulk

Solid state approach

Quantum chemistry calculations:

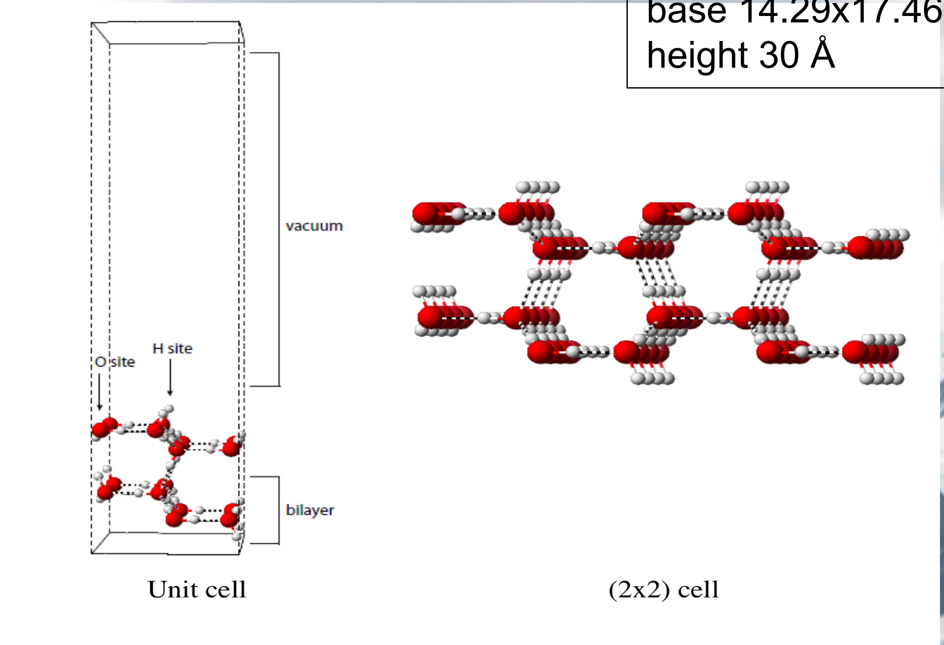
- Density functional theory
- Periodic representation in three dimensions

Characteristics

- « Real solid »
- Kind of rigidity
  but can be accomodated
- Pay attention
  to base cell dimensions
  for no lateral interaction
  No edge effect as in cluster
- Pay attention
  to the vacuum dimension
  for surfaces studies
  (expensive)

The ice model

Working cell:
base 14.29x17.46 Å^2
height 30 Å



View of the hexagonal apolar ice based on two bi-layers.

Molecular crystals with solid state approach

- Periodic DFT (density functional theory) :
  - Exchange-correlation functional (PBE)
  - Hybrid functional : part of HF exchange
    question relevant for periodic as non periodic (cluster) approaches
- Example 1: adsorption energies on water ices for atoms & molecules

- Weak interactions: long-range van der Waals interactions and hydrogen bonding
  - Corrective scheme for dispersion by Grimme (2010): function D2 D3
  - Cluster: same problem
- Example 2: adsorption energies on water ices for atoms

- Basis functions: code VASP plane wave basis sets
  - Avoid the correction of BSSE (basis set superposition error)
  - Not the case for local basis sets (atomic basis sets)

Example 1:
Dispersion versus Exchange interactions

Building an hybrid function

(PBE-D2) +	0% HF	25%HF	50%HF	Exp.
C	1.42	1.19	1.08	
N	0.10	0.06	0.05	0.062
O	0.73	0.12	0.11	0.121
Si	1.10	0.98	0.87	
P	0.10	0.05	0.04	
S	0.61	0.30	0.20	
O2	0.127	0.113	0.107	0.092
N2	0.132	0.135	0.131	0.096

Adsorption energies (eV) on water ices

Example 2:
Taking care of dispersion effects

(PBE+50% HF) +	No D	With D2	With D3	Exp.
C	0.974	1.08	1.21	
N	0.017	0.05	0.05	0.062
O	0.059	0.11	0.12	0.121

Adsorption energies (eV) on water ices

I- ADSORPTIONS on surfaces

Collaboration and check with experiments (TPD)

Example: CH3CN/CH3NC

Trapping by adsorption : distortion of the observed abundances; reservoir of potential reactants.

Example: selective depletion of isomers

Application: search for chiral molecules

Surface modeling versus experiment

Surface	CH3CN	CH3NC
α-quartz Experiment	**460 ± 60**	**430 ± 50**
α-quartz Theory	**460**	**414**
Crystalline water Exper.	**565 ± 50**	**540 ± 30**
Crystalline water Theory	**558**	**545**

Energies in meV

Bertin et al 2017, A&A 598, A18

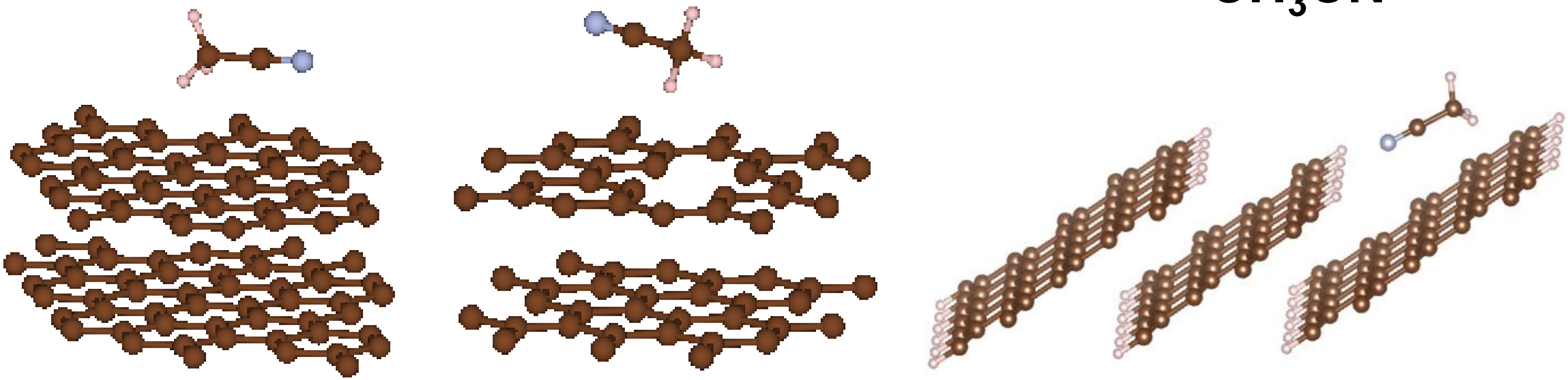
Graphite surface	CH3CN	CH3NC
Experiment	**440 ± 25**	**430 ± 25**
Perfect HOPG	**275 ± 30**	**255 ± 30**
Damaged (holes)	**310 ± 40**	**300 ± 40**
Damaged (hydrog. holes)	**390 ± 50**	**350 ± 50**
Steps	**480**	**440**

Experiment: Temperature programmed desorption (TPD)

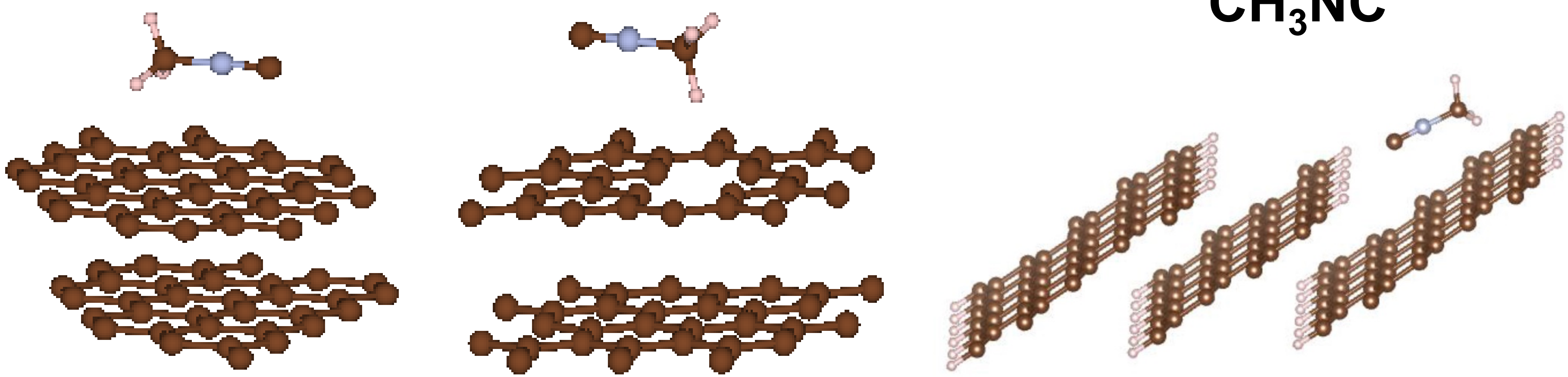
Bertin et al 2017, A&A 608, A50

Nitrile versus Isonitrile on graphite

CH_3CN



CH_3NC



M. Bertin, M. Doronin, et al; A&A, 608, A50 (2017)

Selective depletion of isomers at ice surfaces

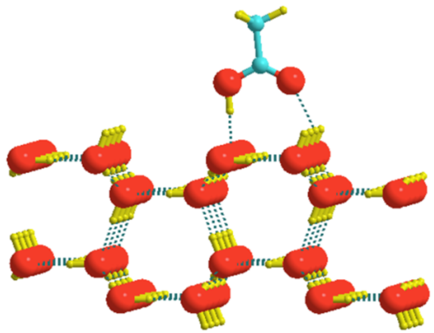
Acetic acid CH3COOH / Methylformate HCOOCH3 pair

E(kcal.mol^{-1})

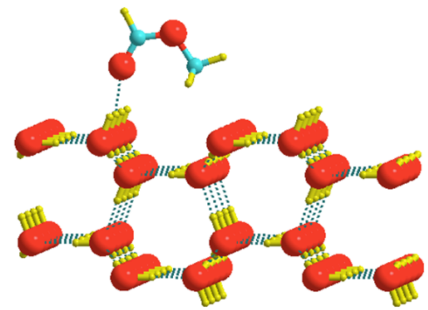
17 — $HCOOCH_3$

0 — CH_3COOH

Relative stability



E_{ads} = 16,2 kcal.mol^{-1}
2 adsorption points



E_{ads} = 9,2 kcal.mol^{-1}
1 adsorption point

Observed relative abundance: CH_3COOH / $HCOOCH_3$ = 0,01 – 0,1

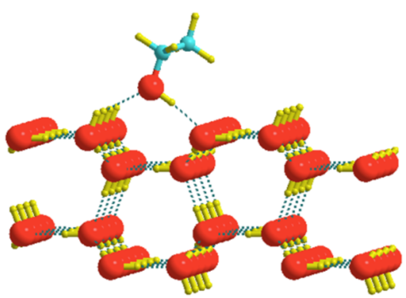
Ethanol CH3CH2OH / Dimethylether CH3OCH3 pair

E(kcal.mol^{-1})

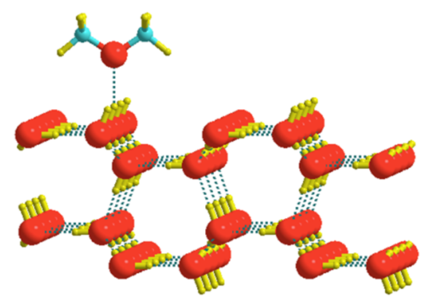
12 — CH_3OCH_3

0 — CH_3CH_2OH

Relative stability



E_{ads} = 13,5 kcal.mol^{-1}
2 adsorption points



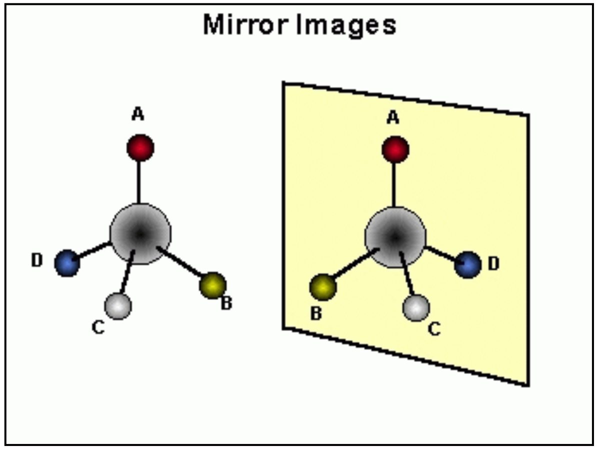
E_{ads} = 8,4 kcal.mol^{-1}
1 adsorption point

Observed relative abundance: CH_3CH_2OH / CH_3OCH_3 = 0,03 – 2.0

The most stable isomer is the one with the strongest adsorption energy, i.e. the most responsive to depletion, hence a biaised observation

M. Lattelais, M. Bertin et al. A&A, 532, A12 (2011)

Homochirality: a signature of life, …



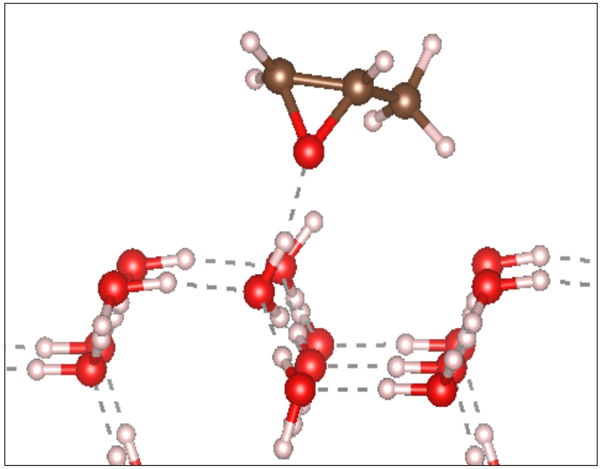
I call any geometrical figure, or group of points,«chiral», and say it has «chirality», if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself. [Kelvin (1904)]

Life as we know it: Sugars D + Amino-acids L

Only one chiral molecule identified in the ISM (2016)

Although several of them are common in carbonaceous chondrites

Search for chirality: stability versus adsorption



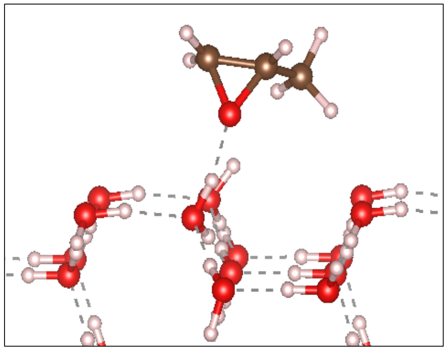
Methyl-oxirane	
30.	ΔE
2.0	μ
10.	Eads

Energy (to acetone) in kcal/mol
Dipole moment in Debye

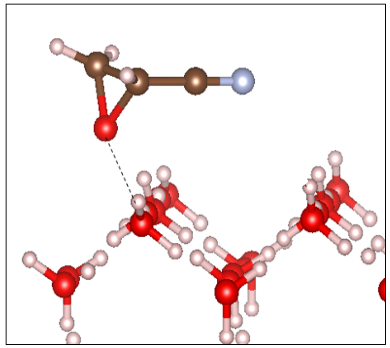
The only chiral molecule observed to-day in the ISM
is not the most stable isomer of its family
but has only 1 point of attach to the ice covering the grains,
implying an adsorption energy of 10. kcal/mol

Predictions

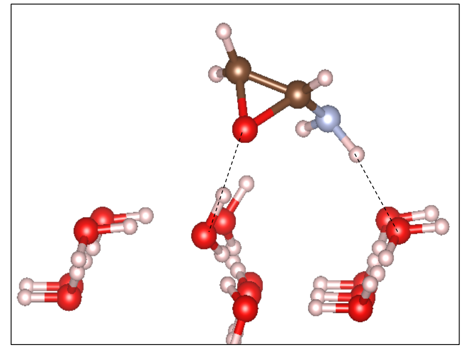
Oxirane daughters



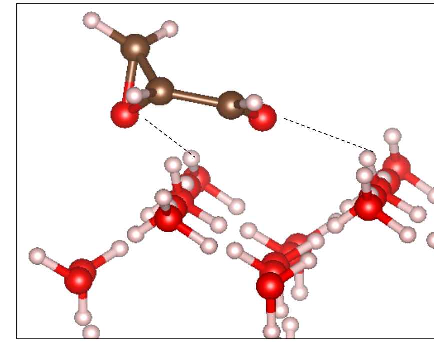
(I)



(II)



(IV)



(V)

(I)methyl	(II)cyano	(III)ethyne	(IV)amino	(V)formyl	-oxirane
30.	28.	59.	47.	38.	**ΔE**
2.0	3.8	1.8	1.0	2.6	**μ**
10.	11.	12.	15.	13.	**Eads**

(Energy in kcal/mol Dipole moment in Debye)

This suggests that (II) could be a good candidate for radio-detection

II- REACTIVITY on ices surfaces

- Provider of H or electrons:

  catalysis and cooperative effect

  Example: HCN/HNC isomerisation

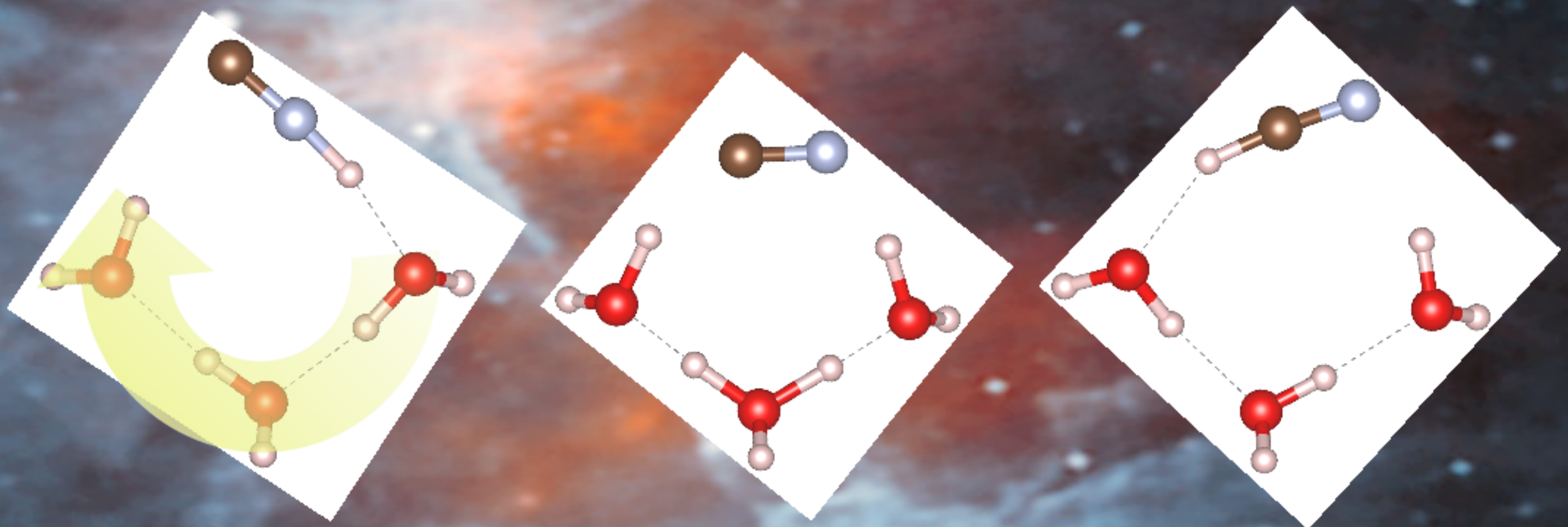
- Provider/adsorber of energy and/or reactants

  Example: reconstruction of H_2O by $OH + H_2$

HCN/HNC isomerization

Cluster approach: water catalysis trend

Gas phase isomerization : barrier above 30 kcal/mol



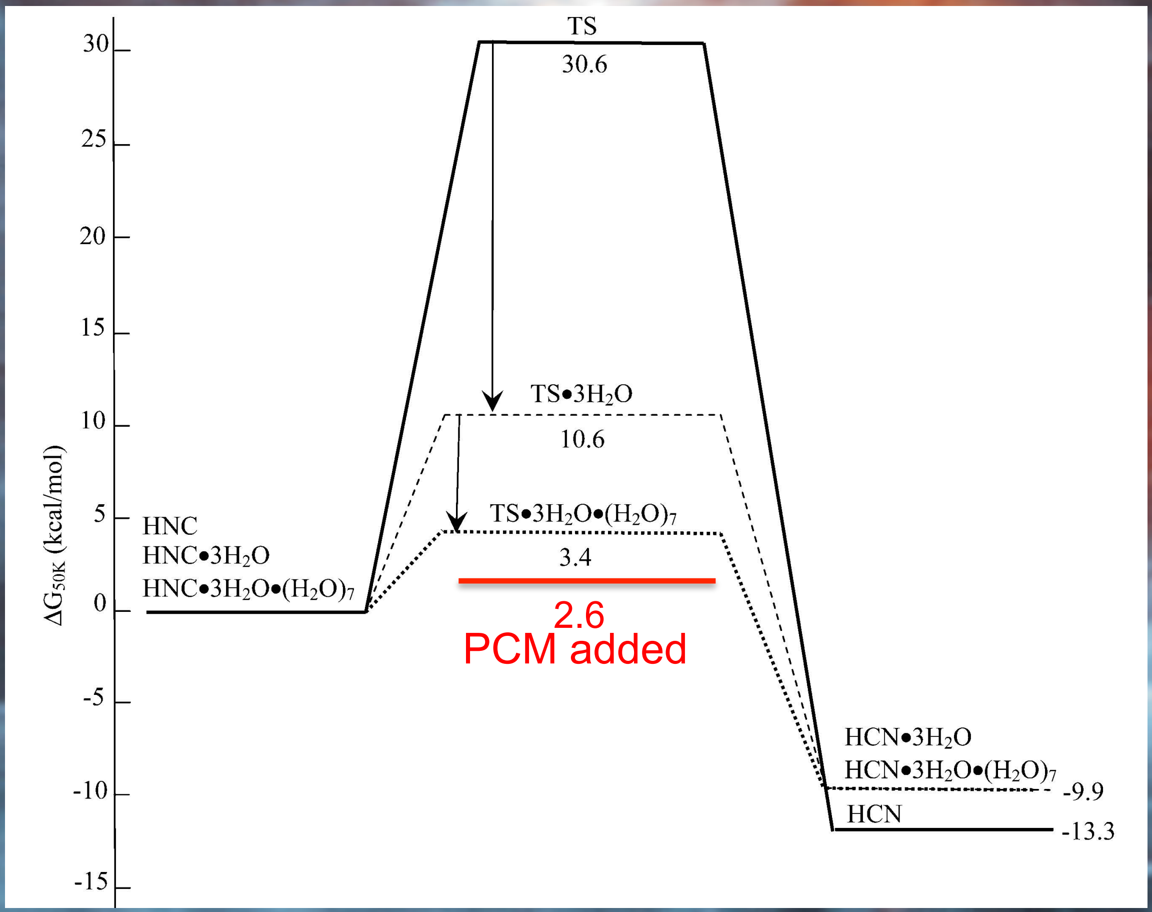
Oxygens are almost motionless

	PBE	Hybrid	Ref[1]	Ref [2]
barrier (kcal/mol)	4.2	9.7	9.6	10.5

[1] Fabrice Gardebien and Alain Sevin J. Phys. Chem. A 2003, 107, 3925-334 Opt. MP2, E(CCSD(T)/6+31G(d,p))

[2] Denise M. Koch, Céline Toubin at al. J. Phys. Chem. C 2007 111, 15026-15033 B3LYP//6+31G(d,p) (OPT BSSE ZPE)

From cluster to « solid »

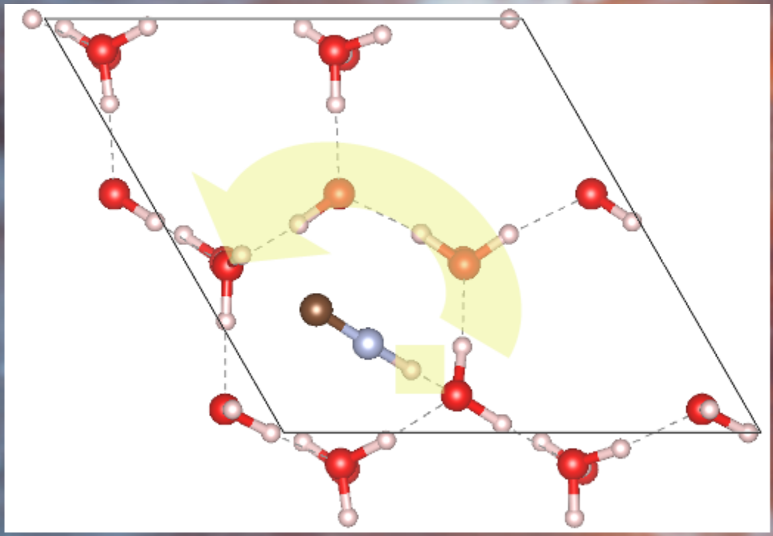


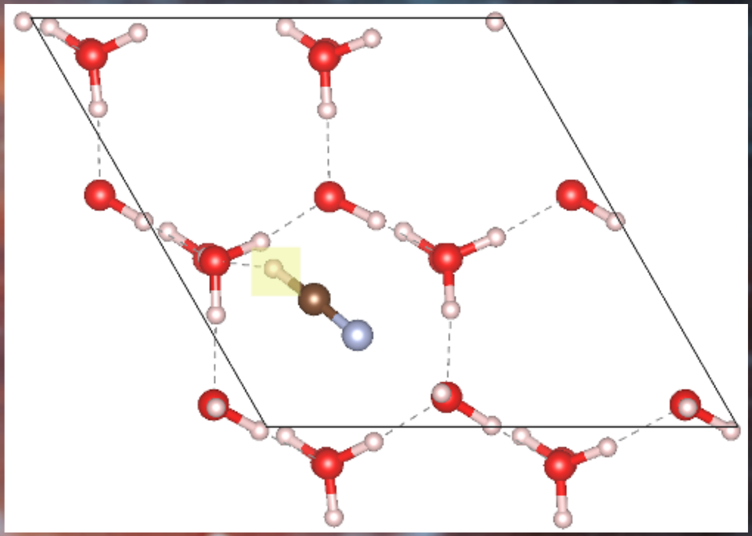
PCM:
polarizable continuum model

Adapted from D. Koch et al. J. Phys. Chem. C 2007 111, 15026

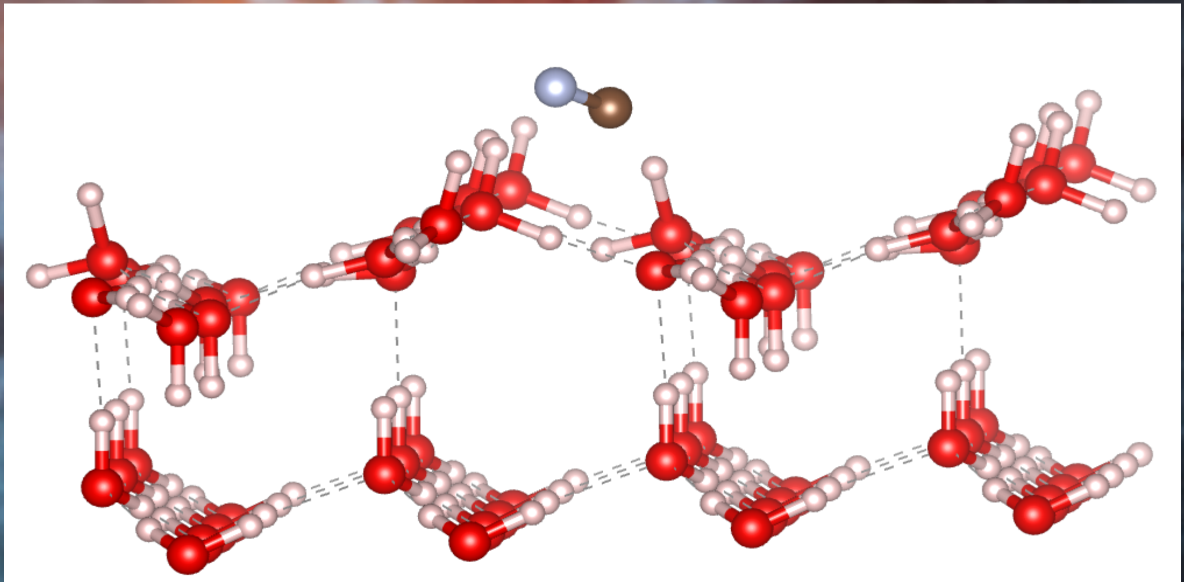
HCN/HNC isomerization

Periodic approach: water catalysis confirmation





ΔE_{TS} = 2.5 kcal/mol



Cooperative effect visible

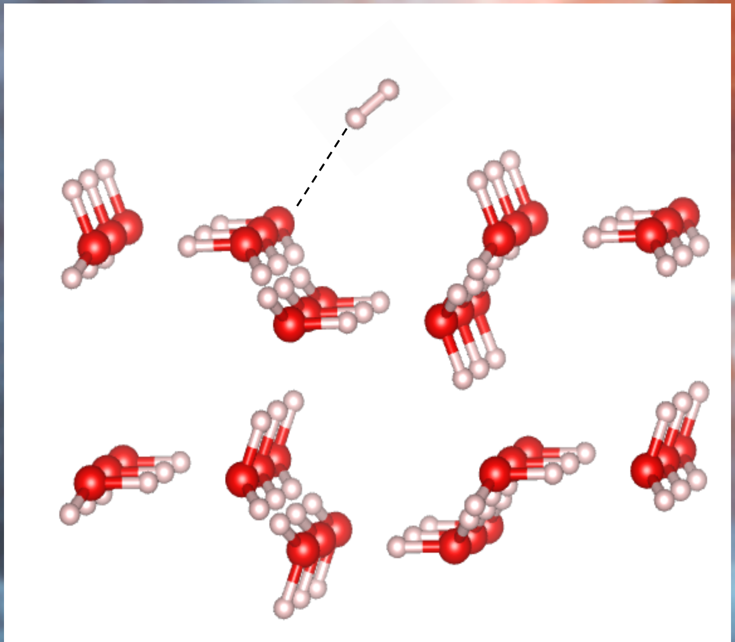
Reactivity with dissymetric reactants

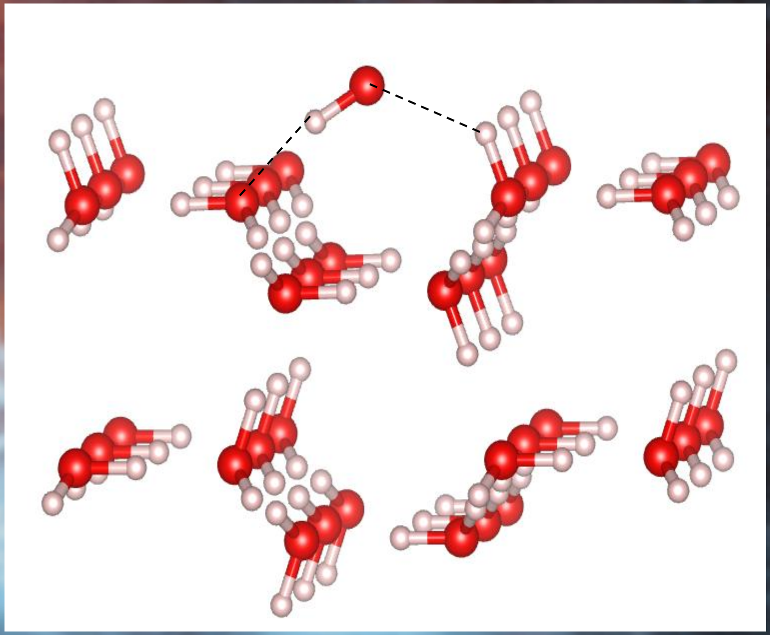
Intervention of the medium to orientate the first step through adsorption of one or the other of the reactants

→ Dependant of environment

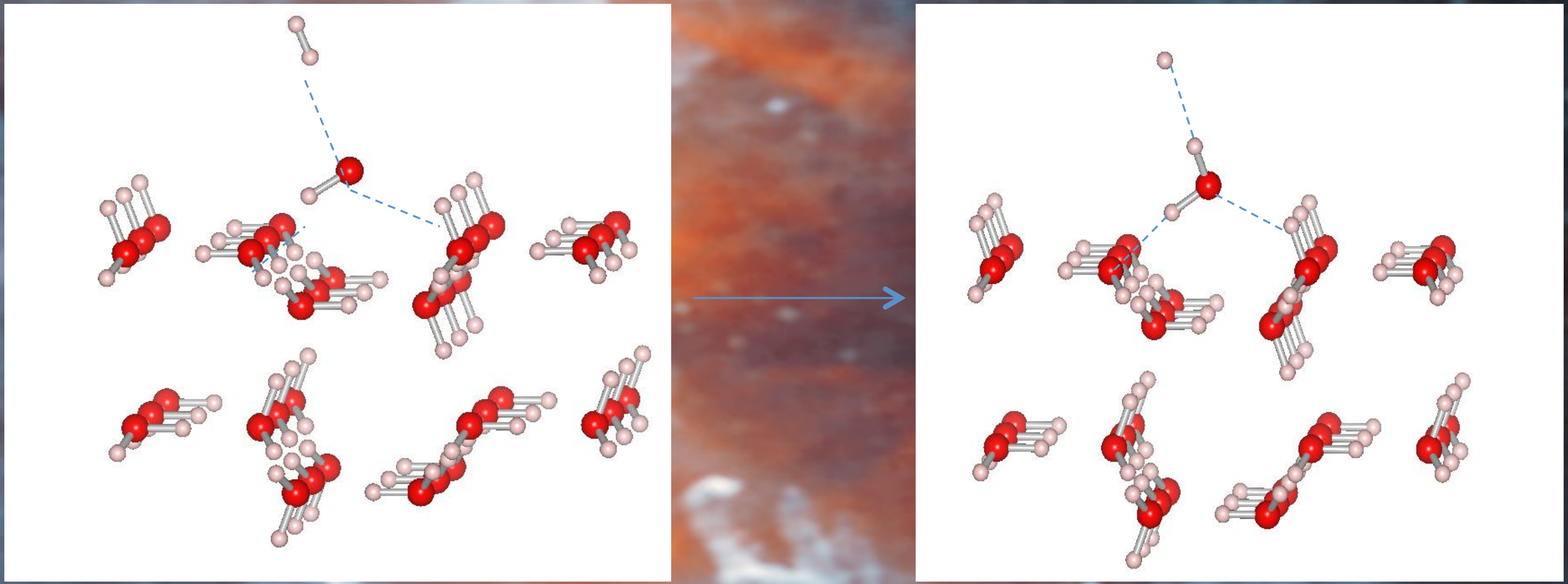
Example: OH +H2

Step1: adsorption





Step2: reactivity



OH attached	Gas phase	cluster	solid
barrier	5.7/4.8	4.8	4.1
exothermicity	15.0/15.3	16.9	16.2

Kcal/mole

→ Tunnel effect

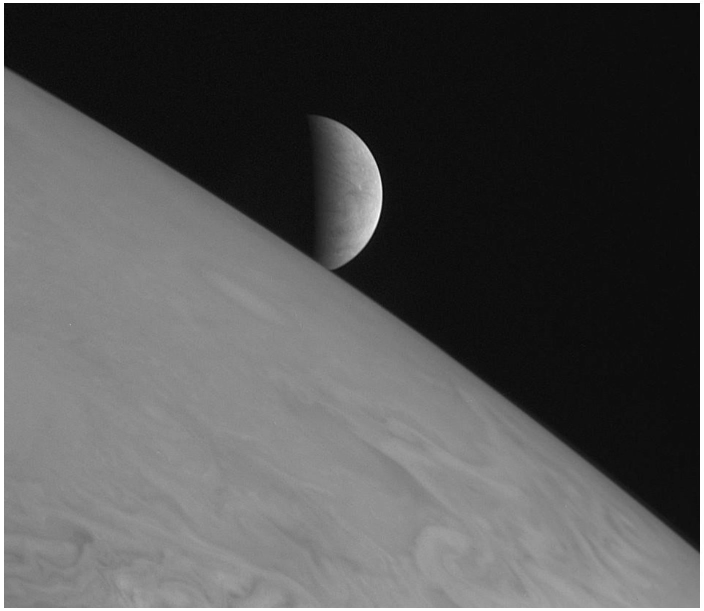
H2 attached	a no barrier reaction

III-Inside the icy BULK

1

Alcali in Europa's exosphere: an endogenous scenario

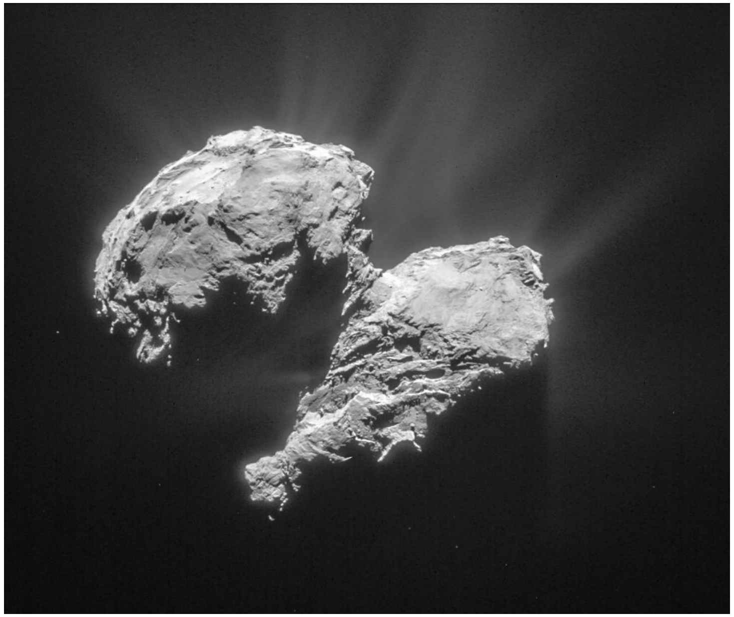
Ö. Özgürel et al. ApJ Letters, 865,2,L16 (2018)



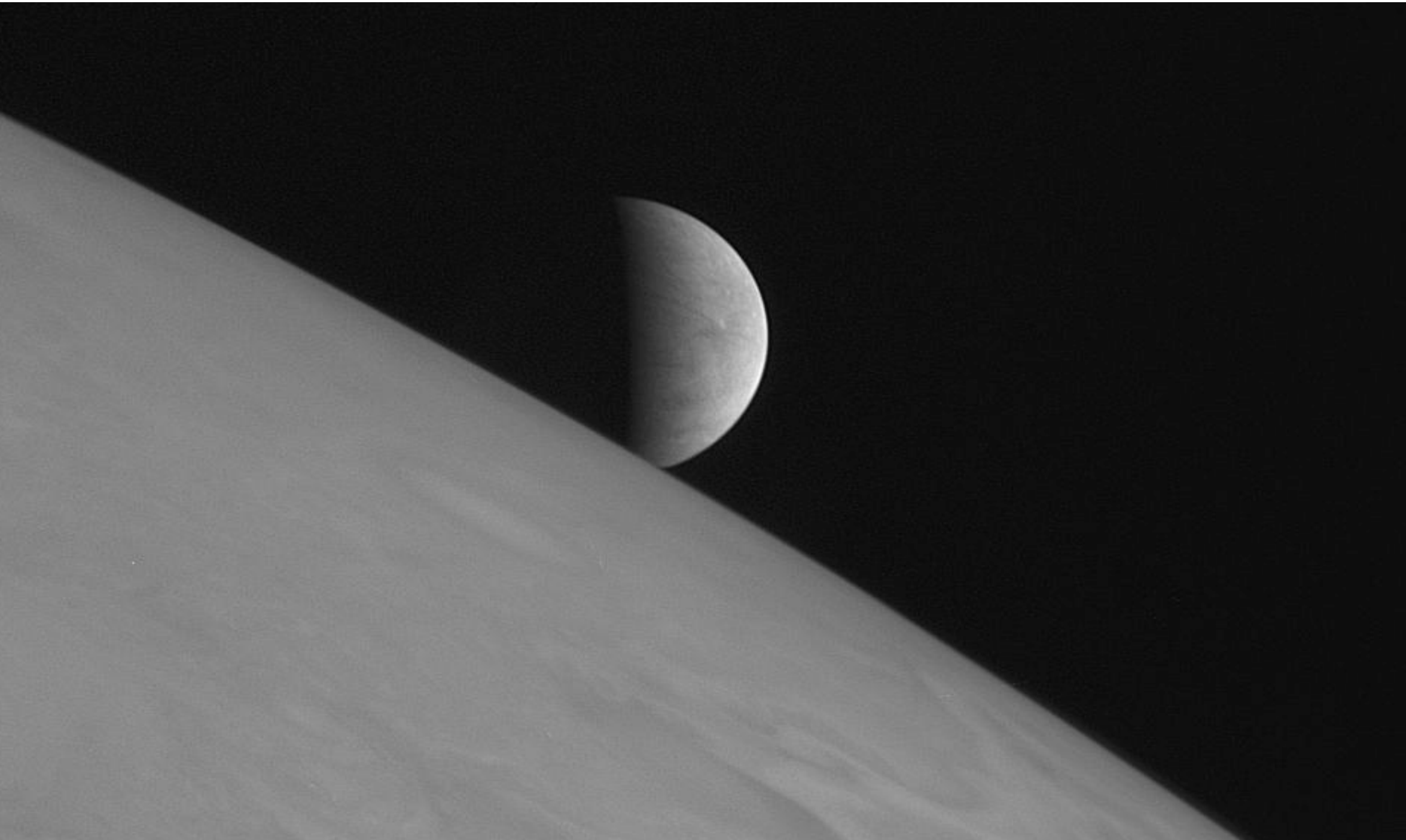
2

Origin of O_2 in comet 67P/ Churyumov-Gerasimenko

O. Mousis et al. ApJLetters 823, L41 (2016)



Alcali in Europa's exosphere
an endogenous scenario



Detections and conjectures

Simultaneous detections in Europa exosphere
➔ Na/K = 25 ± 2 (Brown, 2001)
≈ 30 (Trafton, 1981)

Cosmic abundances Na/K = 20

Exogenous sources:

Volcanism of Io Na/K (Io) = 10 ± 3

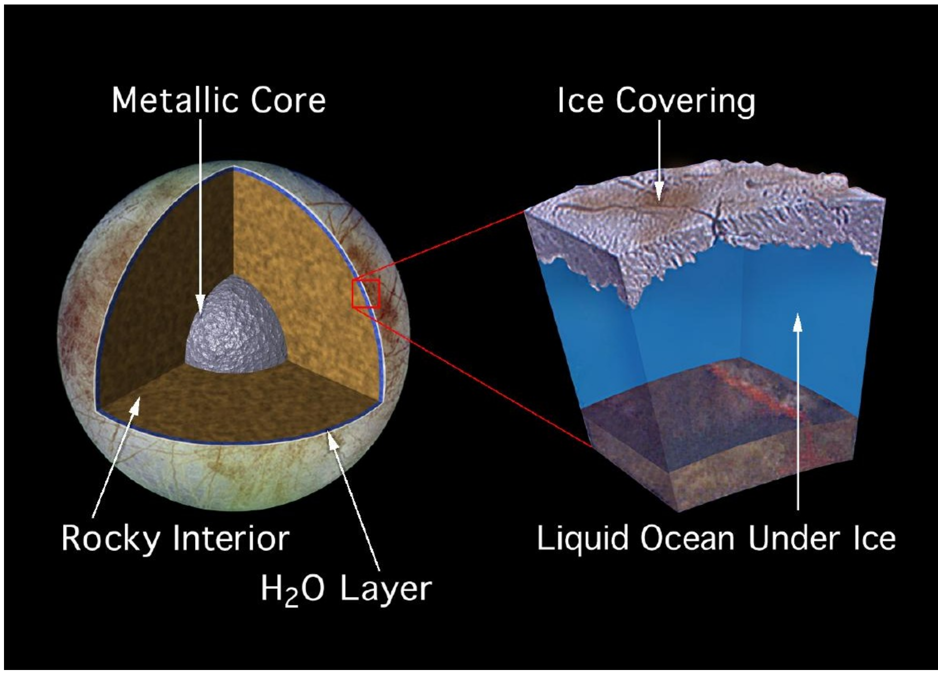
Meteoritic bombardment Na/K = 13 ± 3

Endogenous sources:

Earth seawater Na/K = 45

Io & Europa transit Jupiter

From rocks to surface:
a surprising journey in time and space

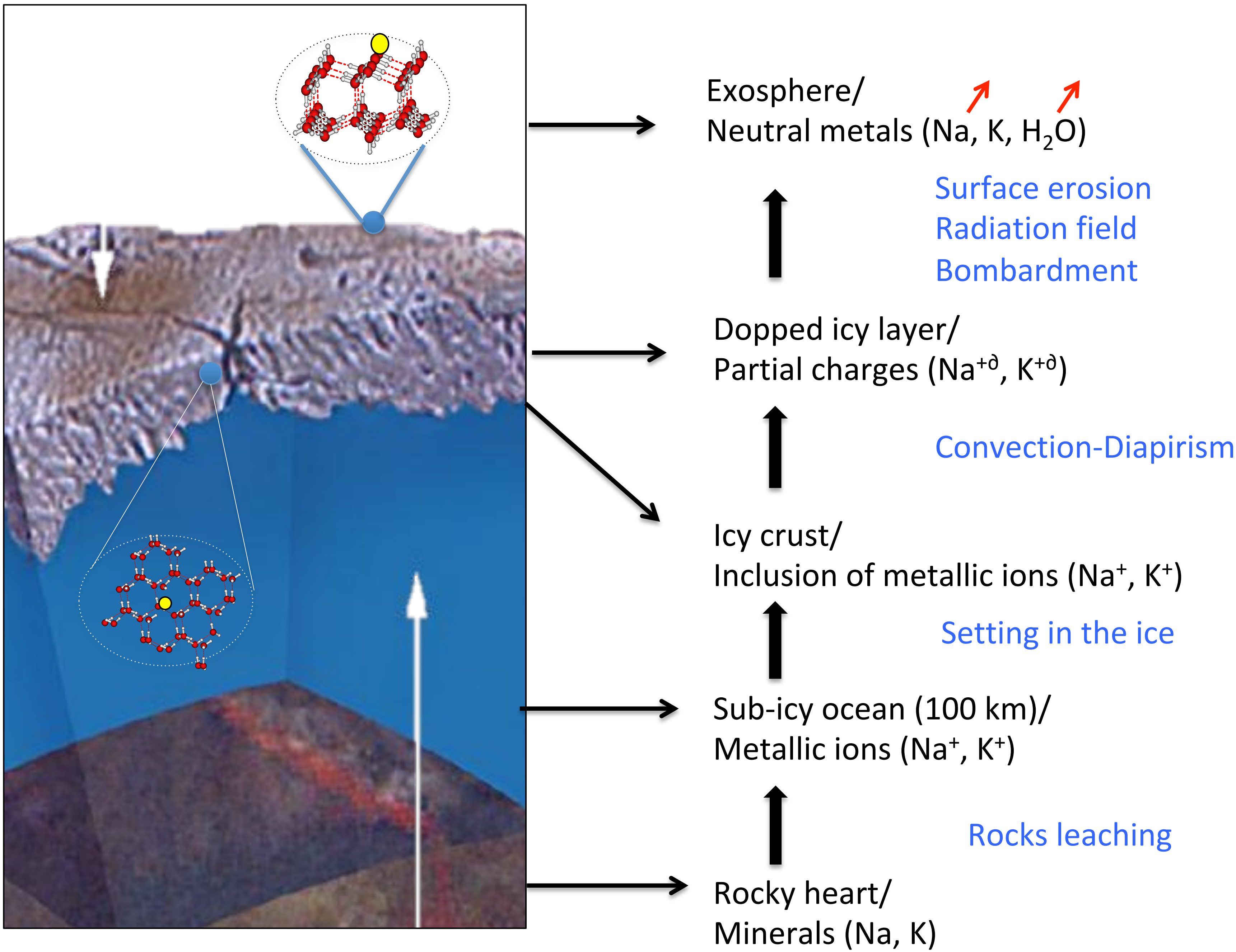


Na, K , H_2O

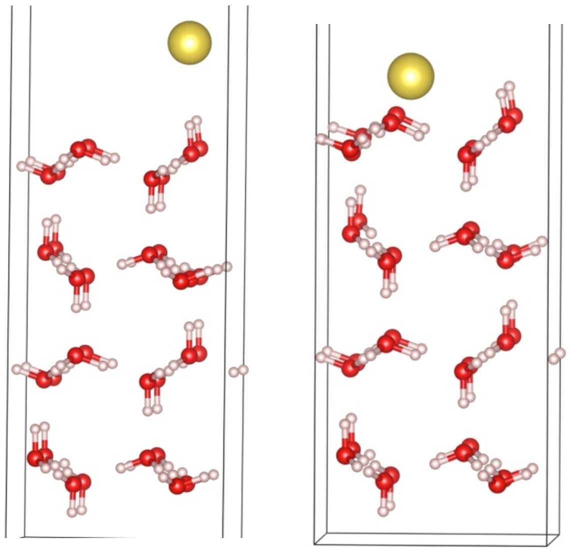
$Na^{(+)}$,$K^{(+)}$/water ice

Na^+,K^+/liquid water

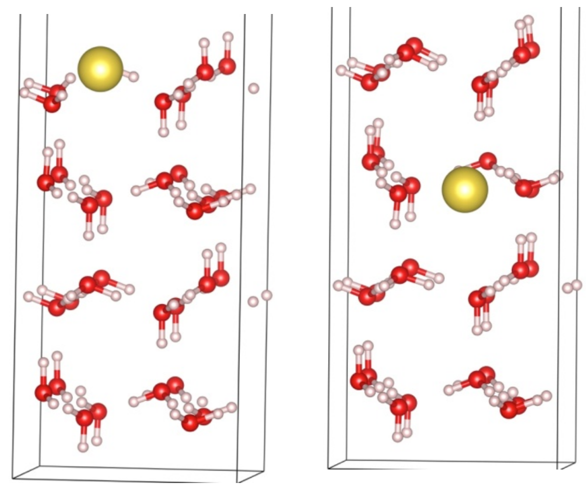
Na^+,K^+/minerals


Exosphere/
Neutral metals (Na, K, H2O)
Surface erosion
Radiation field
Bombardment
Dopped icy layer/
Partial charges (Na+∂, K+∂)
Convection-Diapirism
Icy crust/
Inclusion of metallic ions (Na+, K+)
Setting in the ice
Sub-icy ocean (100 km)/
Metallic ions (Na+, K+)
Rocks leaching
Rocky heart/
Minerals (Na, K)

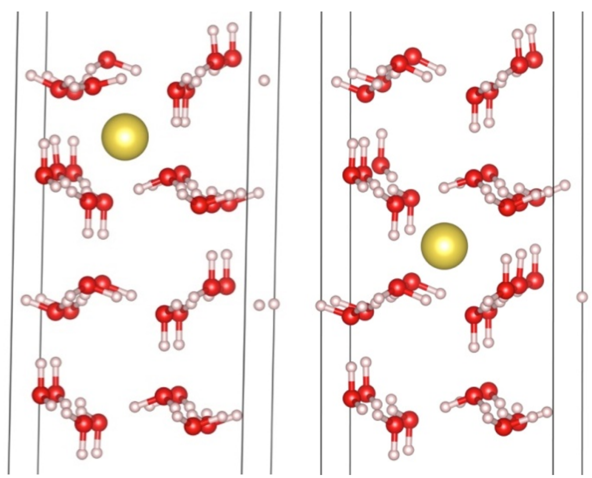
Definitions



Adsorption

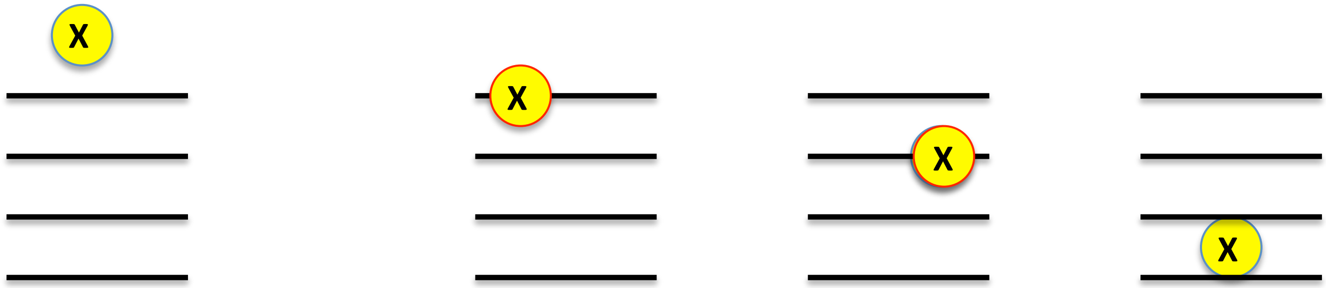


Substitution



Inclusion

From charged to neutral



Atom	Adsorption (over H)	Adsorption (over O)	Substitution (surface)	Substitution (bulk)	Inclusion
Na	**0.10 / 0.2**	**0.41 / 0.3**	**0.86 / 0.54**	**1.02-1.10 / 0.8**	**0.06 / 0.9**
K	**0.16 / 0.2**	**0.60 / 0.4**	**0.86 / 0.55**	**0.91-1.17 / 0.8**	**0.22 / 0.9**
Ca	**0.20 / 0.2**	**0.98 / 0.3**	**1.41 / 0.70**	**1.54-1.71 / 0.9**	**0.26 / 1.31**

Stabilization energies in eV / Charges in electron
Bader charge analysis

Conclusion

- Na & K :
  - similar behaviors in water ice
  - different concentrations in liquid water

→ **Na/K ~ 30**

- Ca :
  - very stable in ice
  - lower concentration than Na but higher than K

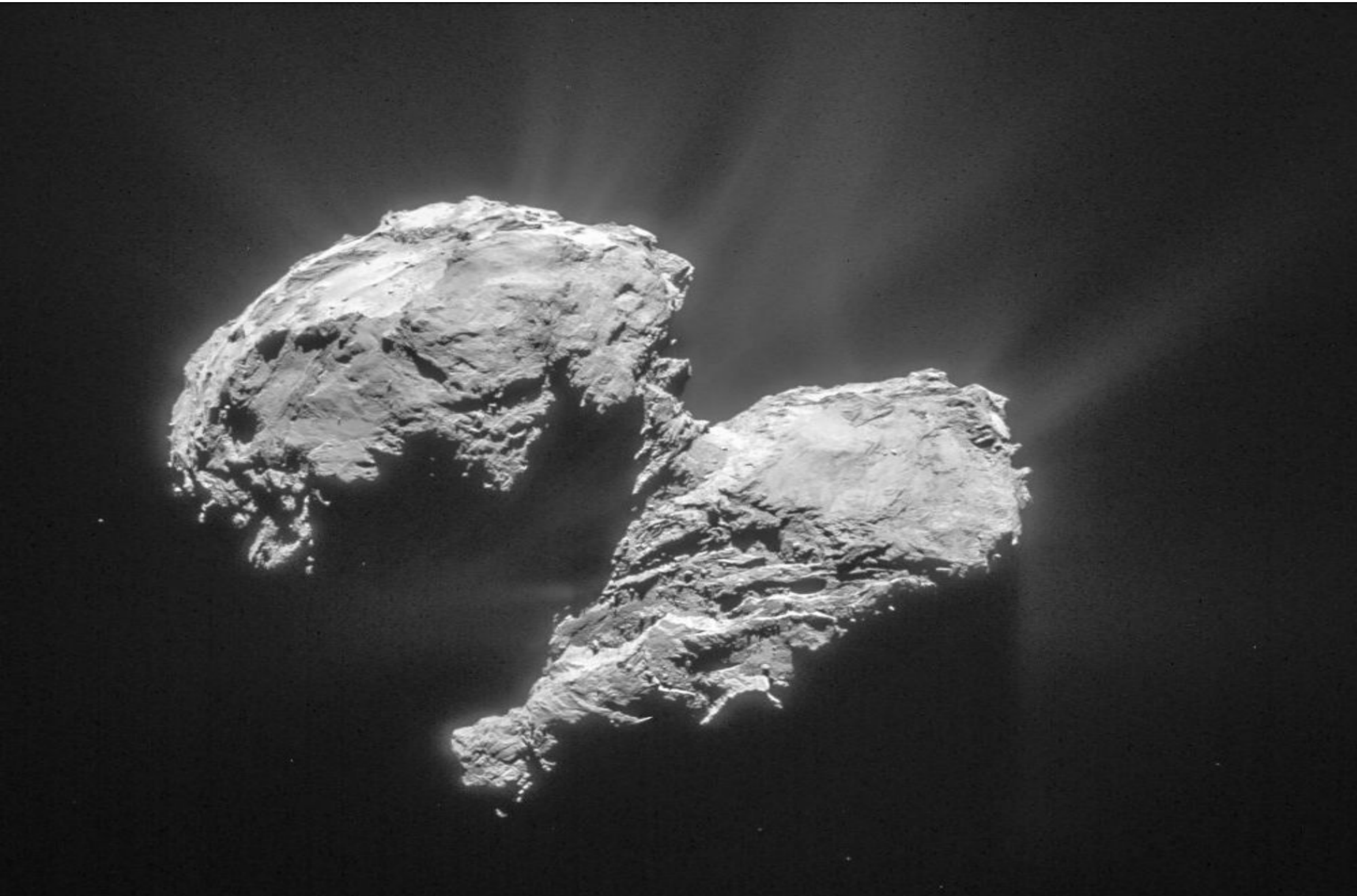
→ **Na/Ca ~ 8**

- Presence of subsurface ocean

No need for exogen contamination (Io)

Process based on metal ions saturation in the deep ocean

Comet 67P



Observational context

Detection of O_2 in comet 67P/C-G by ROSINA on board of ROSETTA (Bieler et al. 2015)

local O_2/H_2O abundances in the 1%–10% range
a mean value of 3.80 ± 0.85%

Re-analysis of the **1P/Halley** data from Giotto Neutral Mass Spectrometer
(Rubin et al. 2015)
O_2 with abundance of 3.7 ± 1.7% with respect to H_2O

Both observations → O_2 might be a rather common parent species in comets

No significant variation observed for O_2/H_2O ratio in the coma during the time of the mission
→ primordial origin

Correlation with H_2O release for O_2 emissions

Computational results

Presence of O2 should not perturbate the ice structure until it is ejected in the coma

No vacancy: with no H2Oremoved we found **no stabilization** for the inclusion of O2 in the hexagonal lattice

One vacancy: with one H2O removed and replaced by **one O2**, we have a substitution structure with a meaningless stabilization (0.001 eV)

Two ad more vacancies: with 2,3 and 4 adjacent H2O removed from the lattice, we obtain the formation of well-defined cavities of different shapes, able to accomodate **one O2** with stabilization energies of **0.2-0.3 eV**

Dimers of O2 can also remain embedded in such cavities with stabilization energies of **0.4-0.5 eV**

Accordance with observations

Strong interaction between O_2 and the water bulk surrounding

→

O_2 trapped inside durably

→

Strongly-correlated escape of O_2 and H_2O

Average proportion of about 4%

calculated as a ratio of the number of neighboring H_2O molecules to one O_2 molecule considering the minimum dimension holes necessary to keep O_2 trapped into the bulk

Can be less, depending on the occupation by O_2

For holes containing a **dimer of O_2**, the proportion doubles to **8% close to the maximum 10% observed**

(Mousis et al. ApJL 823, L41, 2016)

Message to go:

Solid state methods and codes (VASP, CRYSTAL, QuantumExpresso, CP2K……) are quite helpful for understanding astrochemistry mechanisms related to ices and other interstellar surfaces as silicated and carbonaceus ones

but

As these codes are being used in conditions quite different from the ones they have been set up for, be careful in their interpretation and extension to unusual situations!