

**Adsorption selectivity  
on  
interstellar surfaces:  
Computational experiments**

*Local versus global approach*

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# ***Astrophysical Context***

1) Increasing diversity and complexity of molecules observed in the Interstellar Medium (ISM)

2) Untangled mix between what occurs on the surfaces and in the gas phase:

*Gas phase reactions as solid-gas reactions and chemical/physical processes involving adsorbed partners*



*The equilibrium between the molecules on the surface and those in the gas phase depending on the adsorption/desorption energies **critically***

# *Selective adsorption phenomenon*

In cold molecular clouds, the grains are most probably covered with ice and molecules are trapped on and in these ices.

As the temperature increases, the less bound molecules are first released in the gas phase, followed by H<sub>2</sub>O and the strongly bound species.

The bare grain underneath is revealed as a different kind of surface on which some molecules may re-adsorb and be ready for a new kind of reactivity.



*mechanism of recycling*

*implying adsorption on different types of interstellar surfaces  
and strongly depending on the physical conditions*

with a direct impact on the relative abundances of molecules, in particular of isomers, observed in the gas phase.

# ***Computational Context***

***Quantitative*** results for adsorption energies are hard to get, experimentally as well as theoretically, taking into account that both, nature of the surface and nature of the molecule, intervene in their own way.

*We rely on numerical simulations based on the methods of quantum chemistry, namely Density Functional Theory (DFT) that proved efficient in the periodic approach to this category of phenomena.*

*Note: solid model versus cluster model*

# ***Methodology***

The Vienna ab initio simulation package (VASP) was used to carry out all the calculations using the PW91/PW91 functional.

*Kresse and Hafner, Phys. Rev. B, 49, 14251 (1994)*

Grimme (PBE+D2) correction included for dispersion effects.

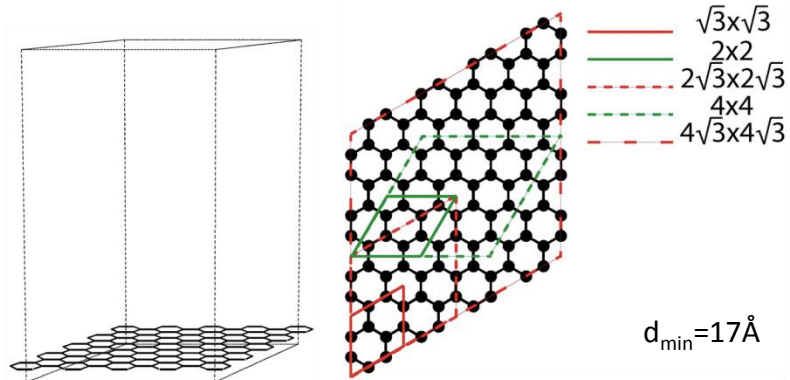
*S. Grimme et al. J. Chem. Phys., **132**, 154104 (2010)*

The core electrons are kept frozen and replaced by pseudo-potentials generated by the plane augmented wave method (PAW).  
Energy cut off = 500 eV.

The basal and the vertical dimensions of the unit cell have been determined to avoid any spurious interactions due to replication in the three directions of space.

# Modeling of surfaces

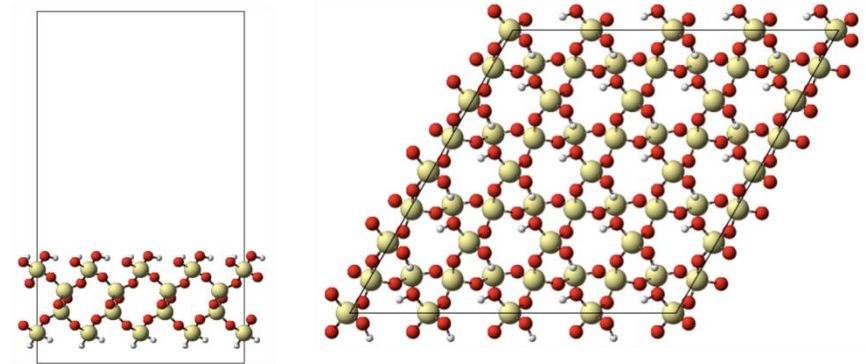
## The graphene model



Left: Side view of the  $(4\sqrt{3} \times 4\sqrt{3})$  graphene cell with a  $30 \text{ \AA}$  height.  
 Right: Top views of the different cells considered in this work

Working cell: base  $4\sqrt{3} \times 4\sqrt{3}$ , height  $30 \text{ \AA}$

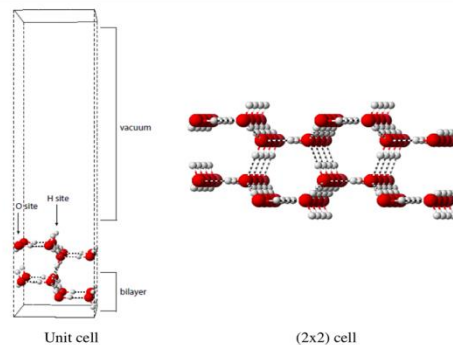
## The silica model



Views of the  $(4 \times 4)$  silica slabs: (top) the  $(0001)$  silica slab  
 (surface  $(10\bar{1}0)$  not shown)

Working cell: base  $19.664 \times 19.664 \text{ \AA}^2$ , height  $30 \text{ \AA}$

## The ice model



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

Working cell: base  $14.29 \times 17.46 \text{ \AA}^2$ , height  $30 \text{ \AA}$

M.Lattalais, F. Pauzat, Y.Ellinger &  
 C.Ceccarelli, A&A (2015)

# ***Determining adsorption energies***

We present several examples  
of increasing complexity  
by mixing

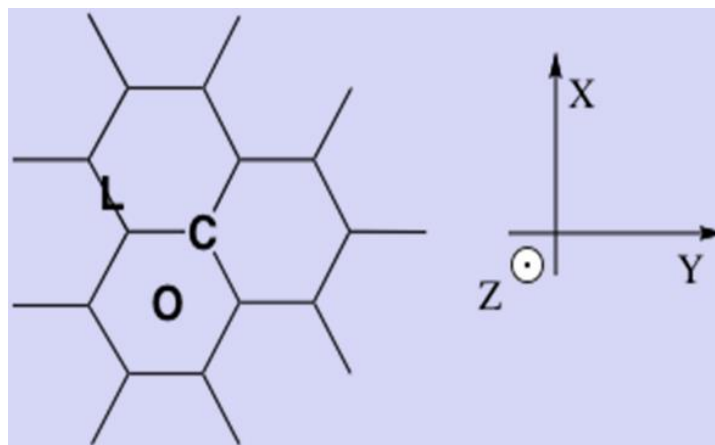
***adsorbates***

going from atoms to prebiotic molecules,

***and surfaces***

as graphene, water ices and silica.

# $H_2$ on graphene



site	$H_2$ // surface (Average X/Y)	$H_2$ $\perp$ surface
O: center of ring	0.74	0.74
C: carbon atom	0.72	0.72
L: middle of bond	0.70	0.70

Adsorption:  
weak and **quasi-independent** of  
orientation and site

$H_2$  able to roll on the surface

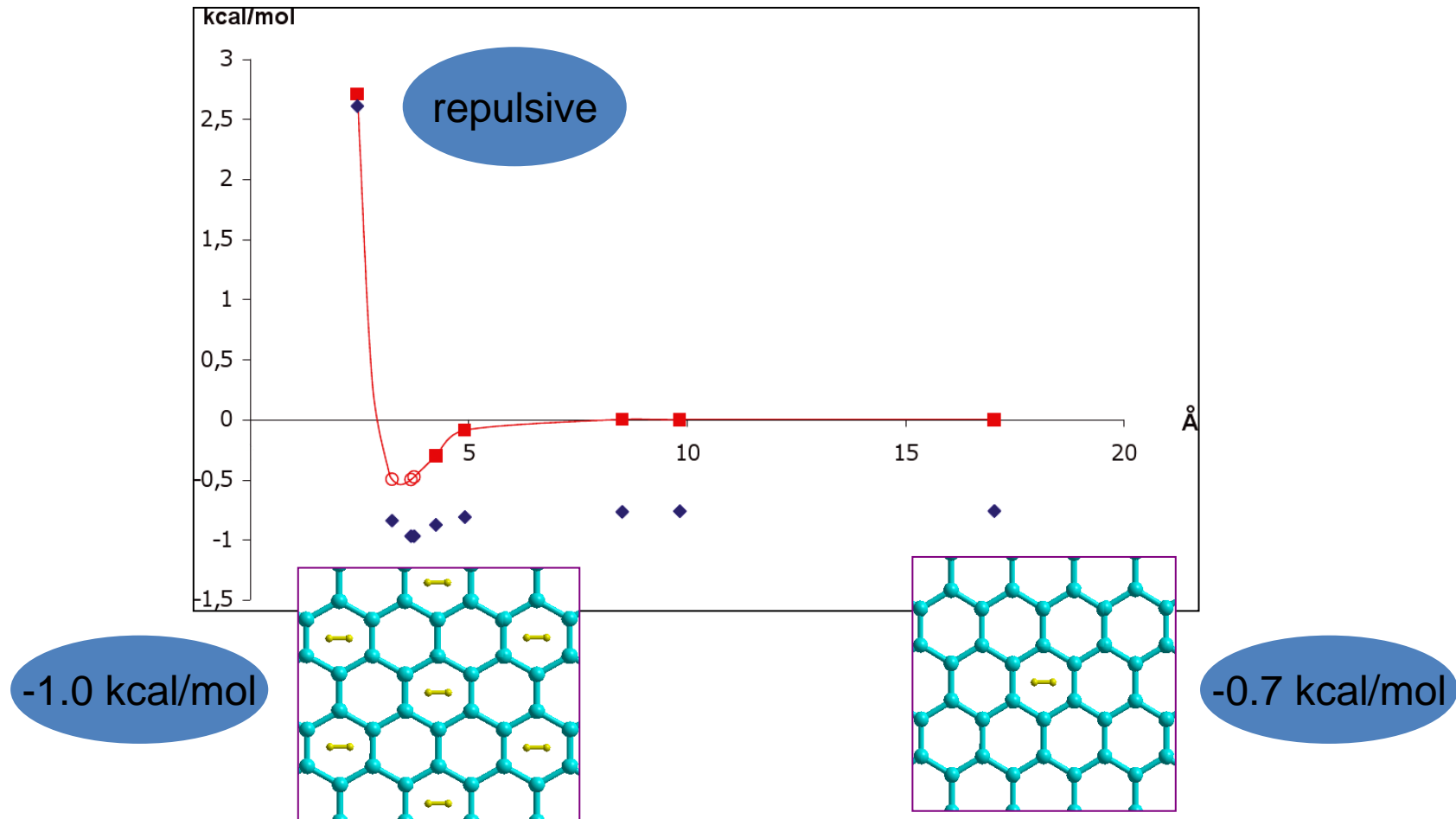
*F. Pauzat, M. Lattalais, Y. Ellinger &  
C. Minot, MNRAS, (2011)*

*Adsorption energies (kcal/mol)*

*Note: Studies for ice and silica lead to stronger adsorption but preferential orientation according Z ( $\perp$  surface) and/or in the direction of the oxygen lone pair*



# $H_2$ : dependence with the coverage



*Red curve*: lateral interaction for  $H_2$  as a function of the distance to its nearest neighbors.

*Blue diamonds*: total interaction energy between  $H_2$  and graphene as a function of the distance between  $H_2$  molecules in the monolayer.

**Difference between H.C. and L.C. : 30%**

# Noble gases on water ice

Crystalline ice hexagonal system (chair)

site	1	2	3	4	5	6
Argon	2.66	1.97	2.67	1.53	2.54	2.75
Krypton	3.36	2.33	3.43	2.24	3.20	3.53
Xenon	4.05	3.12	4.17	2.33	3.86	4.31

*Adsorption energies (kcal/mol)*

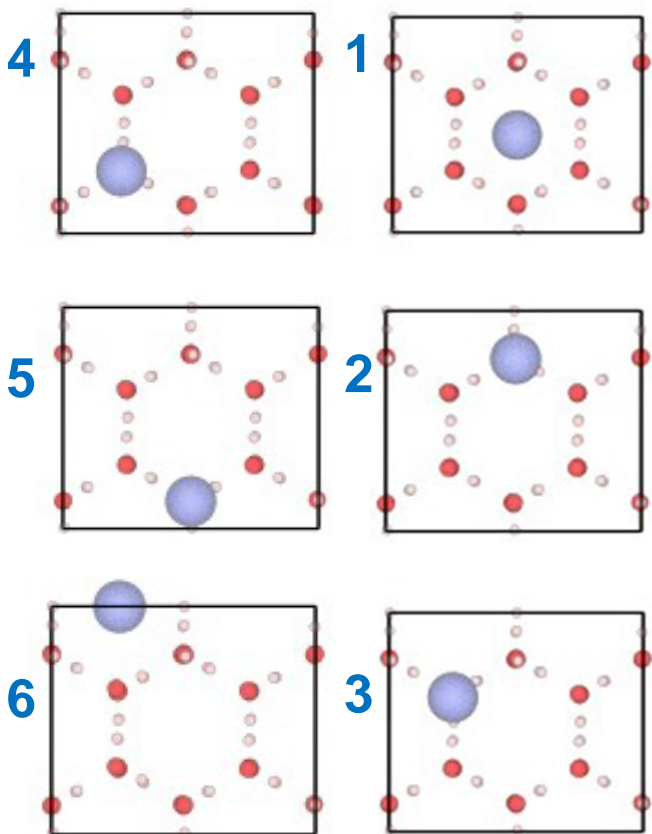
**Theoretical maximum**

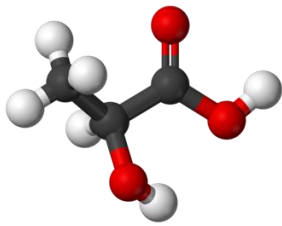
2.75 (Ar) / 3.53(Kr) / 4.31 (Xe) kcal  
0.119 (Ar) / 0.153(Kr) / 0.187 (Xe) eV

**Theoretical average**

2.35 (Ar) / 3.01(Kr) / 3.64 (Xe) kcal  
0.102 (Ar) / 0.128(Kr) / 0.158 (Xe) eV  
*(20% lower)*

*(Doronin et al : to be published 2015)*



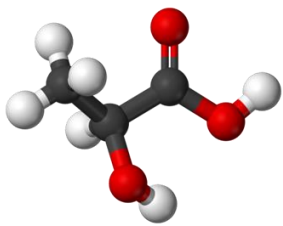


## ***Lactic acid enantiomers on active surface of silica {1010}***

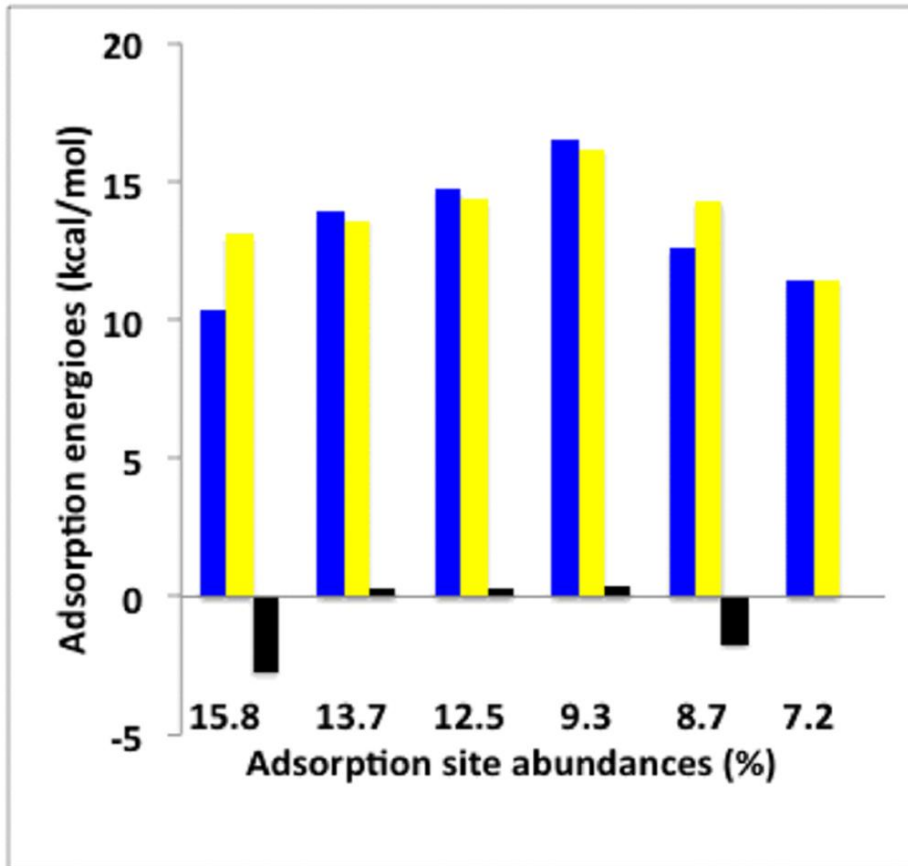
Two enantiomers have identical internal energies. However, when adsorbed on a same chiral surface, the complexes obtained are no longer enantiomers, but diastereoisomers and these *diastereoisomers do not have the same energy*.

Assuming that we have a chiral interstellar surface at hand, we can consider the possibility to *adsorb selectively one of the two enantiomers* and thus engage a process of enantiomeric enhancement (homochirality and life).

*Adsorption of simple molecules have shown different adsorption energies for different adsorption points on the surface. As we are aiming at small differences, we consider that the complexity of the  $\alpha$ -quartz surface could potentially generate different adsorption sites with opposite selectivity for chiral molecules.*



# Variability of adsorption



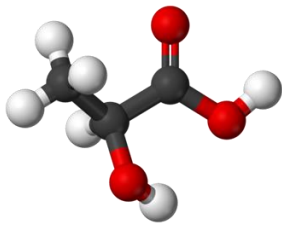
*A local adsorption is not representative and may lead to erroneous conclusions.*

*We propose that the selectivity of the surface should be considered as a global property and be determined by a statistical approach.*

*Colour code:*

*Blue: R-enantiomer; Yellow: S-enantiomer;*

*Black: R vs S adsorption selectivity*



# Procedure

## ❑ Extensive search on the surface for all adsorption sites

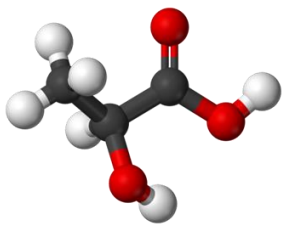
A first screening is performed starting from a dense mesh of initial guesses of adsorption points (molecule + interacting atoms on the surface) : *n = 1680 initial sites*. The structure of each of them is optimized using the semi-empirical DFTB+ method (Tight Binding approximation).

## ❑ Determination of typical adsorption sites

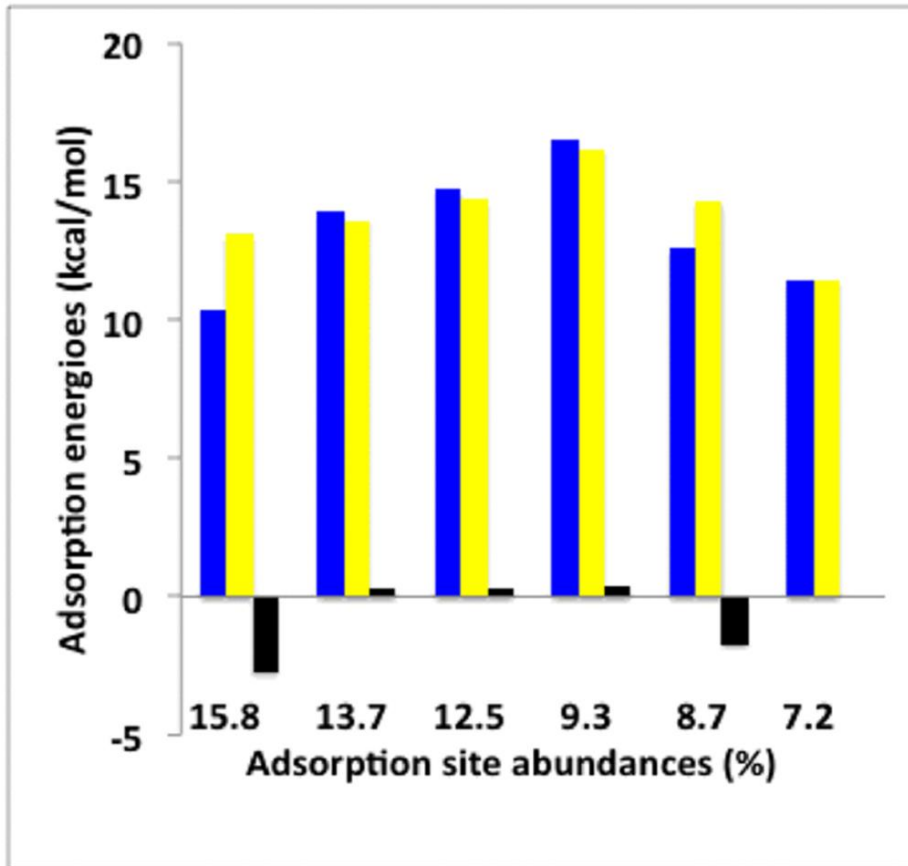
By means of geometric criteria, we determine groups of k points considered as identical within periodic constraints and affect a statistical weight of k/n to each one: *15 groups with 6 major*. The geometries of each representative of the most populated sites (total  $\geq 70\%$ ) are re-optimized in the periodic “first principle model” to obtain reliable final adsorption energies.

## ❑ Calculation of the average selective adsorption energy

The adsorption energy that is characteristic of the couple adsorbate/surface is obtained as the sum of the adsorption energies of the most significant sites weighted by their occurrence numbers normalized to 100%.



# Statistical budget for lactic acid adsorption



Colour code:

**Blue:** R-enantiomer; **Yellow:** S-enantiomer;

**Black:** R vs S adsorption selectivity

F. Pauzat, G. Marloie, A. Markovits &  
Y. Ellinger, IJA, (2015)

- For one molecule, *adsorption is specific of the enantiomer.*  
Here S favored by 0.7 kcal/mole

But the energy differences are found small, mostly *around 1Kcal/mole* (which corresponds to 500K).

- *Adsorption depends strongly on the site on the surface.*

Different adsorptions energies are found according to the topology of the adsorption sites, showing the possibility of an opposite selectivity.

**Statistics needed**

# ***Conclusion***

**Adsorption may depend strongly on the site especially for complex surfaces and complex molecules.**

**The question of the suitability of a statistic treatment could arise according the degree of complexity, the coverage of the surface and the precision needed.**

*For a low coverage, the energetically most favored position could be the only one to consider if the radiation flux onto the surface is sufficient to induce non destructive photo-desorption allowing re-adsorption on opportune positions.*

*For a coverage close to a monolayer, all sites will most probably be occupied and a statistical behavior should be observed.*

*If the complexity of the molecule allows a reorganization of the topology of the adsorption site, the larger will be the differences between sites and the more a statistics treatment will be necessary to get the global behavior of the surface.*

# ***Situation complex but not that desperate***

Example of the pairs of isomers  
CH<sub>3</sub>COOH/HCOOCH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>OH/CH<sub>3</sub>OCH<sub>3</sub>

*M. Lattalais, M. Bertin, and al. A&A (2011)*

Example of the CHON isomers

*M. Lattalais, F. Pauzat, Y. Ellinger & C. Ceccarelli A&A (2015)*

Example of CH<sub>3</sub>CN/CH<sub>3</sub>NC

*see poster 2 by M. Doronin*



# About CHON

- The CHON generic chemical formula covers four different isomers, [isocyanic acid \(HNCO\)](#), [cyanic acid \(HO CN\)](#), [fulminic acid \(HCNO\)](#) and [isofulminic acid \(HONC\)](#), the first three being identified in a large variety of interstellar environments. Relative abundance ratios in various environments are crucial data for constraining astrochemical models.
- For most of the species observed so far in the interstellar medium (ISM), the most abundant isomer of a given generic chemical formula is the most stable one (*minimum energy principle – MEP*). The few exceptions have been linked to different pathways of formation and destruction involving gas phase and/or to surface processes.

*Remember the two pairs of isomers [Acetic acid / Methylformate](#) and [Ethanol / Dimethylether](#) where the most stable isomer was the one with the strongest adsorption energy, i.e. the most responsive to depletion on ices, which challenges the usual order of MEP (M. Lattalais, M. Bertin, H. Mokrane, et al., A&A, (2011)).*

# Adsorption of CHON

*No averaging. No statistics. Value retained: the most strongly bonded  
→ Adsorption energies (kcal-mole<sup>-1</sup>/ eV)*

Surface/isomer	HCNO	HNCO	HONC	HOCN
Graphene	3.7/0.16	4.4/0.19	7.9/0.34	8.1/0.35
Hexagonal Ice (apolar)	10.5/0.46	<b>13.9</b> /0.60	26.6/1.15	29.9/1.30
Silica 0001	3.0/0.13	5.5/0.24	9.2/0.40	10.2/0.44
Silica 1010	3.7/0.16	5.5/0.24	12.7/0.55	14.3/0.62

## *Whatever the nature of the surface*

The adsorption energies are in the order **HOCN > HONC > HNCO > HCNO**  
whereas the relative stabilities are **HNCO > HOCN > HCNO > HONC**

There are two different classes of isomers:

one weakly bound (HNCO-HCNO) and one strongly bound (HOCN-HONC)

*HNCO, the most abundant observed isomer has an adsorption energy of -13.9 kcal/mol equal to that of H<sub>2</sub>O on the water ice. It will not be released in the gas phase until the ice sublimates.*

*HOCN, the second most abundant isomer with the largest adsorption energy may remain on the grain until the ice is totally vaporized.*

We should observe more of the less bound molecules in the outer (colder) regions and more of the strongly bonded species in the inner (warmer) parts.

**Isomers cannot be given equal adsorption energies in chemical models.**

