Damaged water ice: an opportunity for reactivity?

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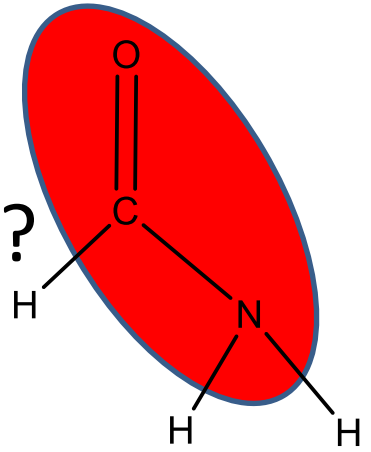
Formation of Formamide

Formamide: we just can't get enough:

3 talks, two posters at least

Formation in gas phase or on surfaces ?



Formation of Formamide

- $NH_2 + H_2CO$

No need to invoke grain-surface chemistry [1]

Not possible [2]

- H + HNCO [2]
- Gas phase reaction [3]
- Hydrogenation of NO and H_2CO in ice [4]

[1] V. Barone, C. Latouche, D. Skouteris, F. Vazart, N. Balucani, C. Ceccarelli and B. Lefloch MNRAS 2015 453, L31-L35

[2] L. Song and J. Kästner Phys. Chem. Chem. Phys. 2016 18, 29278-29285

[3] C. Codella , C. Ceccarelli, 1 , P. Caselli , N. Balucani, V. Barone, F. Fontani , B. Lefloch, L. Podio , S. Viti, S. Feng, R. Bachiller, E. Bianchi, F. Dulieu, I. Jiménez-Serra, J. Holdship , R. Neri, J. E. Pineda , A. Pon, I. Sims, S. Spezzano, A. I. Vasyunin, F. Alves, L. Bizzocchi, S. Bottinelli, E. Caux, A. Chacón-Tanarro, R. Choudhury , A. Coutens, C. Favre, P. Hily-Blant, C. Kahane, A. Jaber Al-Edhari, J. Laas, A. López-Sepulcre J. Ospina, Y. Oya, A. Punanova, C. Puzzarini, D. Quenard, A. Rimola, N. Sakai, D. Skouteris, V. Taquet, L. Testi, P. Theulé, P. Ugliengo, C. Vastel F. Vazart, L. Wiesenfeld, and S. Yamamoto Astro. Astrophys. 2017 605, L3

[4] F. Dulieu, T. Nguyen, E. Congiu, S. Baouche and V. Taquet MNRAS 2019 484 L119-L123

Formation of Formamide

- NH_2 + HCO:

OK but in competition with NH_3 + CO

- HCN: large barrier
- CN: OK

In the last scenario, water ice acts also as a reactant

A. Rimola, D. Skouteris, N. Balucani, C. Ceccarelli, J. Enrique-romero, V. Taquet and P. Ugliengo ACS Earth Space Chem. 2018, 2, 720-734

Role of water ice

- To concentrate reactants
- To help proton transer
- Energy transfer
- **Reactant (acting more than a catalyst).**

Tielens, A. G. G. M. & Hagen, W. 1982, A&A, 114, 245

Table 1. Reactions with negligible activation energy of atomic oxygen with molecules, containing an even number of electrons, included in the calculations

Reactions	Ref.
$O+CO \rightarrow CO_2$	Fournier et al. (1979), Mohammed et al. (1980)
$O+O_2 \rightarrow O_3$	Paper I
$O+CS \rightarrow OCS$	Paper I
$O+SO \rightarrow SO_2$	Paper I

Table 2. Hydrogen addition and abstraction reactions included in the calculations

Reaction	Activation energy (K)	Ref.
$H+CO \rightarrow HCO$	1000	Wang et al. (1973)
$H+H_2CO \rightarrow H_2+HCO$	1850	Klemm (1979)
$H+O_2 \rightarrow HO_2$	1200	Melius et al. (1979)
$H+H_2O_2 \rightarrow H_2O+OH$	1400	Klemm et al. (1975)
$H+H_2S \rightarrow H_2+SH$	860	Rommel et al. (1975)
$H+N_2H_4 \rightarrow H_2+N_2H_3$	650	Francis et al. (1971)
$H+N_2H_2 \rightarrow H_2+N_2H$	$\sim$ 650	Our estimate
$H+O_3 \rightarrow O_2+OH$	450	Lee et al. (1978)

It has been suggested that reactions of radicals with molecular hydrogen are also of importance, in particular $H_2+O \rightarrow H_2O$ (Watson and Salpeter, 1972b). It is expected that this type of reaction has a considerable activation barrier since a molecular bond has to be broken for these reactions to proceed. However because of the large number of H_2 molecules on the surface these reactions may still be of importance. The same kind of analysis applies as discussed above for atomic hydrogen. The limiting timescale for a reaction of a radical with H_2 is now the accretion time of an other radical. For an H_2 surface coverage of 20% and an accretion time of 10^5 s reactions with an activation barrier less than about 4500 K can occur. Theoretical calculations of the potential energy surface for the reaction of O plus H_2 give an activation energy of $\sim$15,000 K and this reaction can therefore safely be disregarded (Tully, 1980). We consider that the reaction

$$H_2 + OH \rightarrow H_2O + H$$

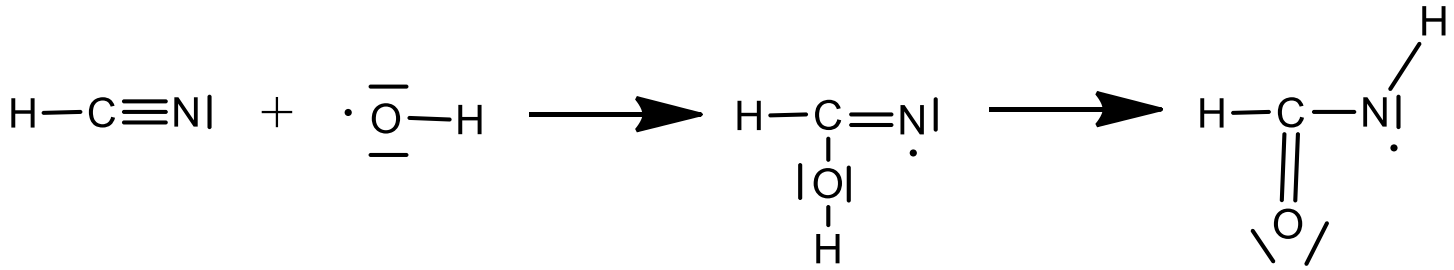
is of statistical importance. It has an activation barrier of 2600 K (Schiff, 1973). We have taken this reaction into account.

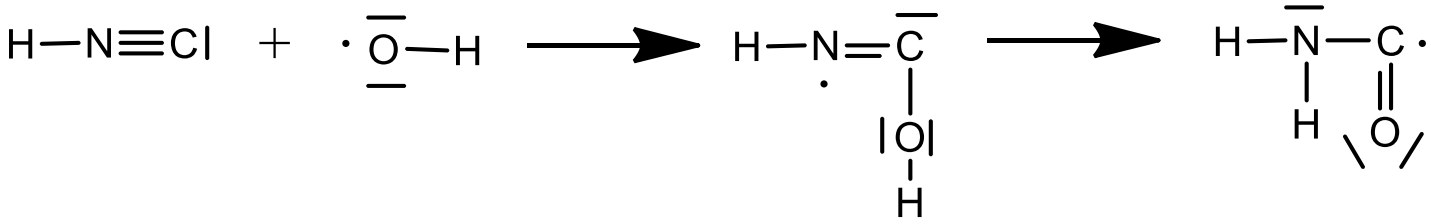
Formation of Formamide

Water ice is damaged by cosmic rays.

This yields $OH^{\cdot}$ and $H^{\cdot}$

Reaction of HCN or HNC with those radicals.

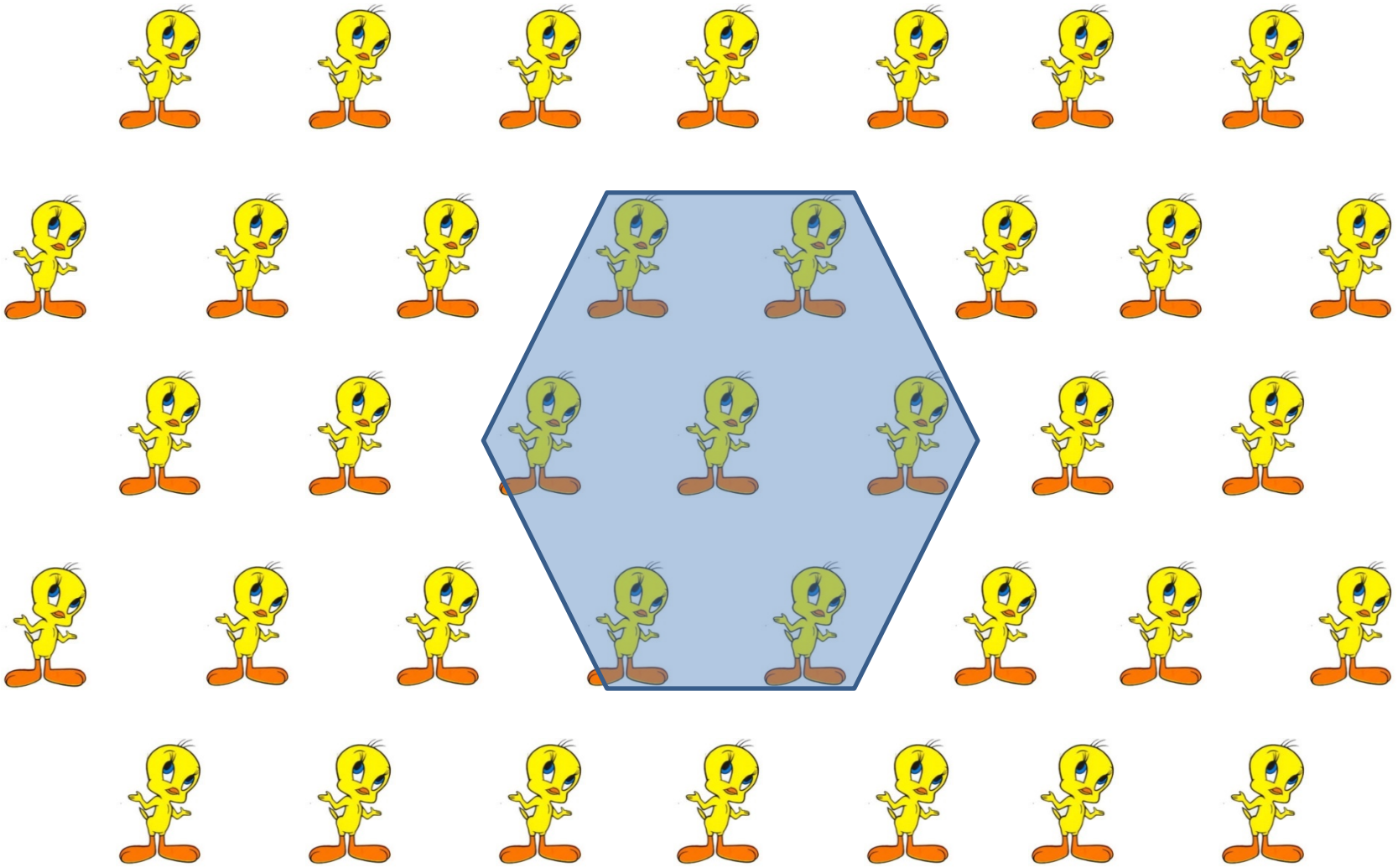




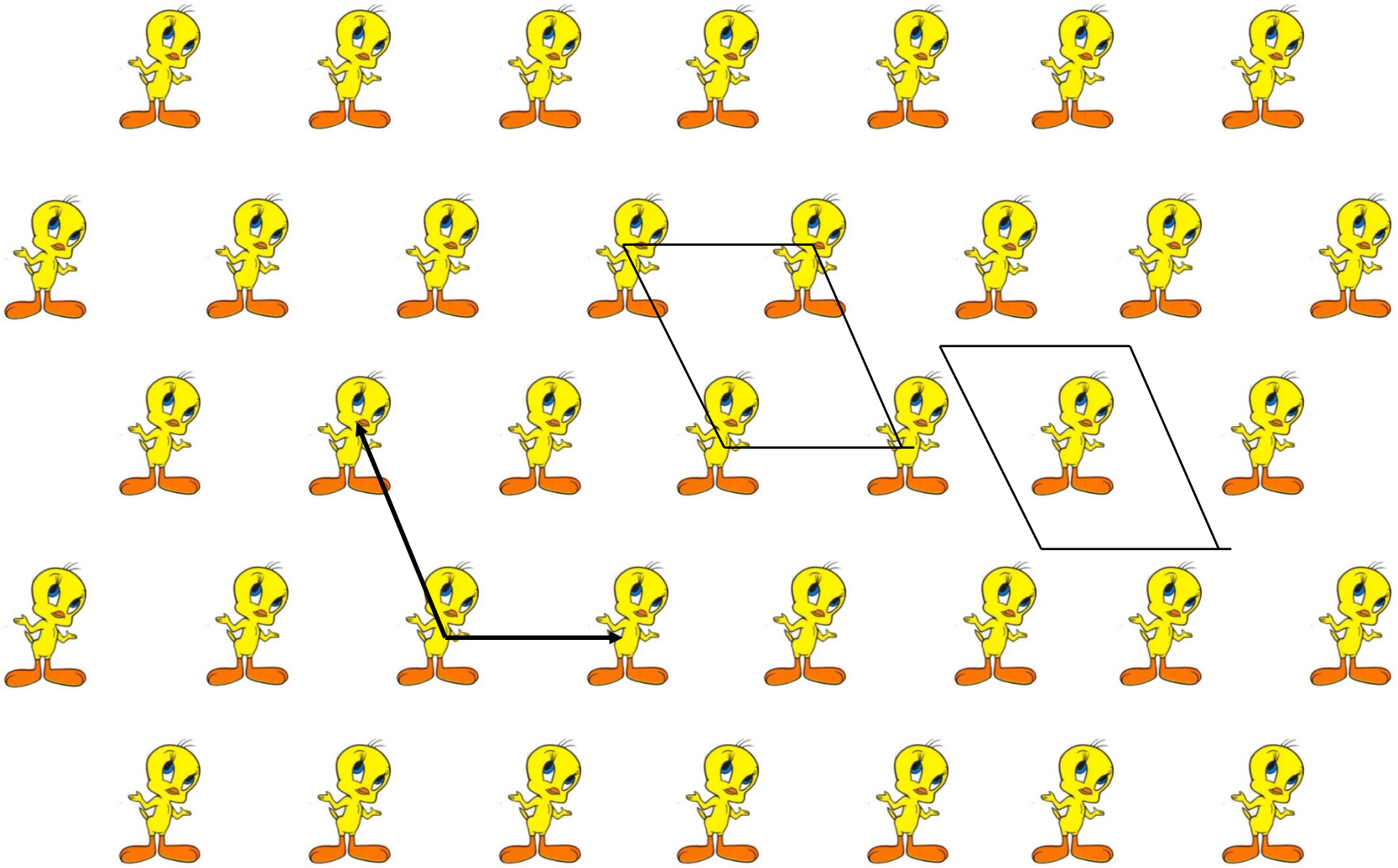
OUTLINE

- **Cluster and periodic approaches**
- HNC - HCN isomerization
  - Cluster modelling as a benchmark
  - Results with the periodic approach
- **HCN on water ice (cluster approach)**
- **HNC on water ice**
  - Results with the cluster approach
  - Results with the periodic approach
- **Conclusions**

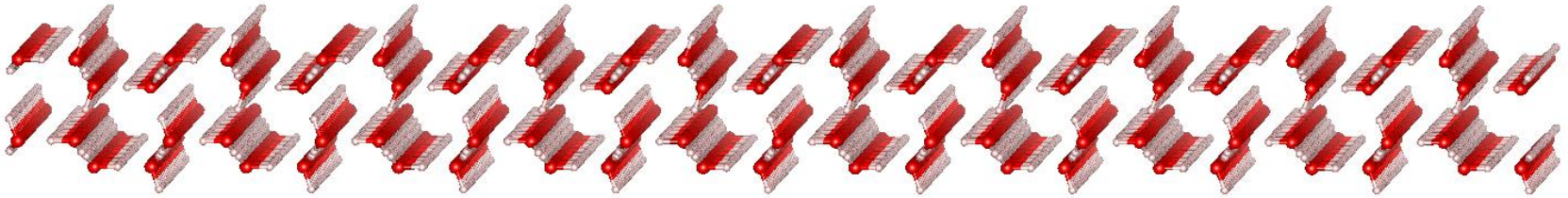
Cluster approach



Periodic approach

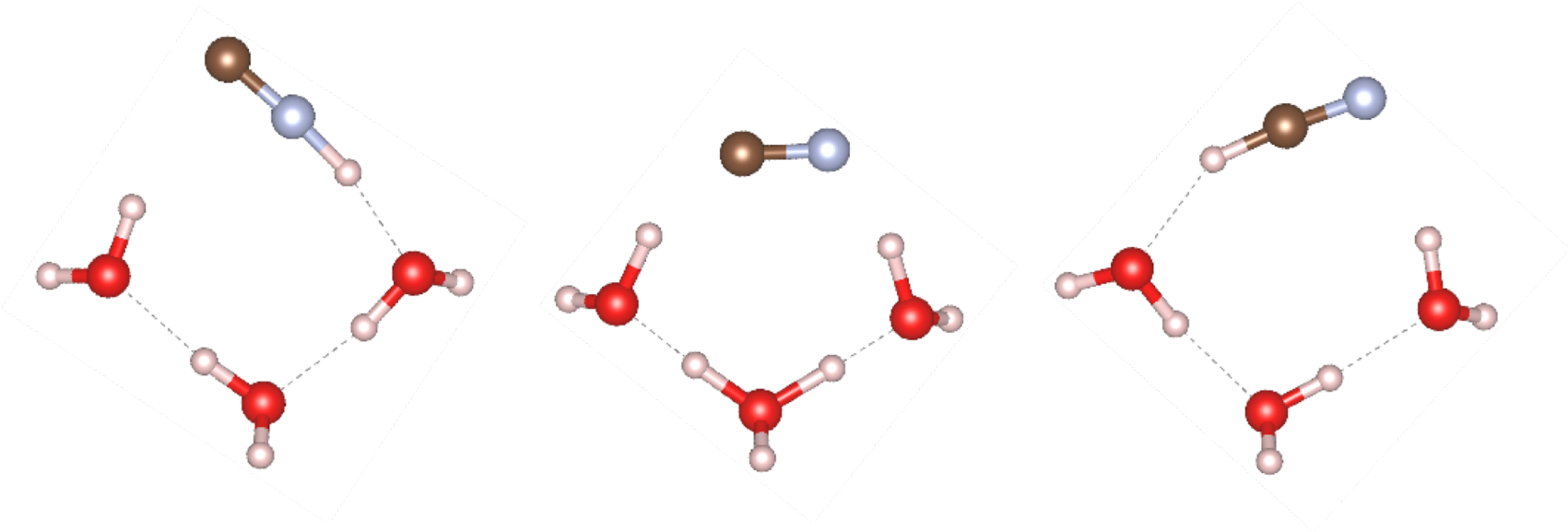


Periodic approach



HCN/HNC isomerization

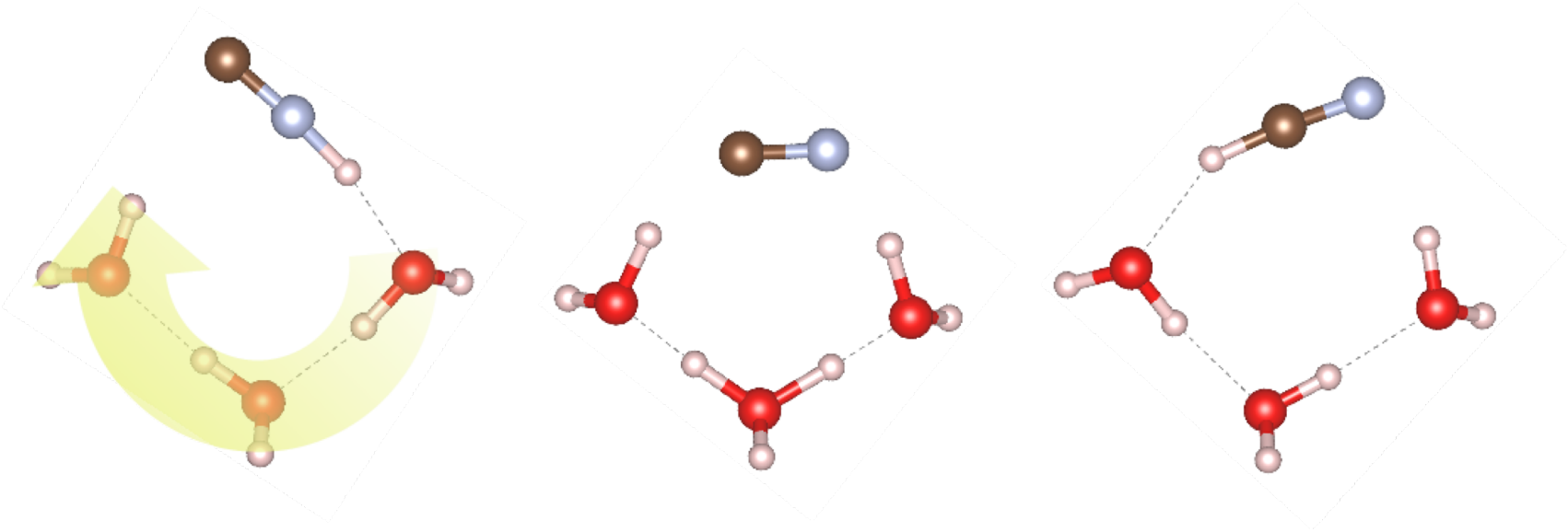
Cluster approach



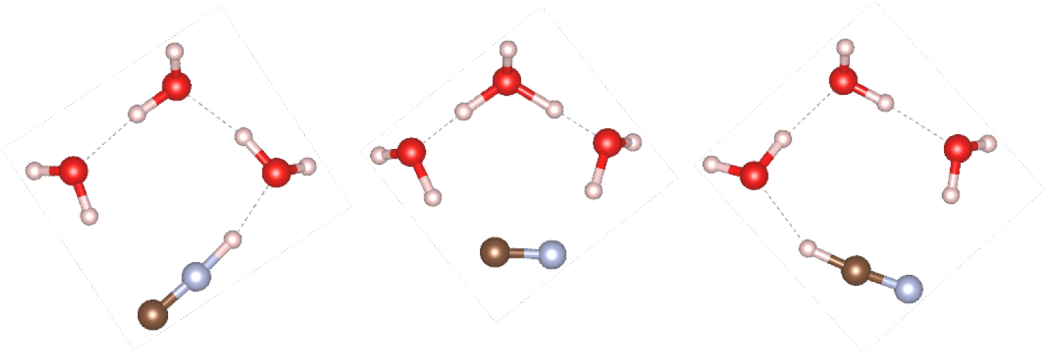
Fabrice Gardebien and Alain Sevin J. Phys. Chem. A 2003, 107, 3925-334

HCN/HNC isomerization

Cluster approach



Oxygen are almost motionless

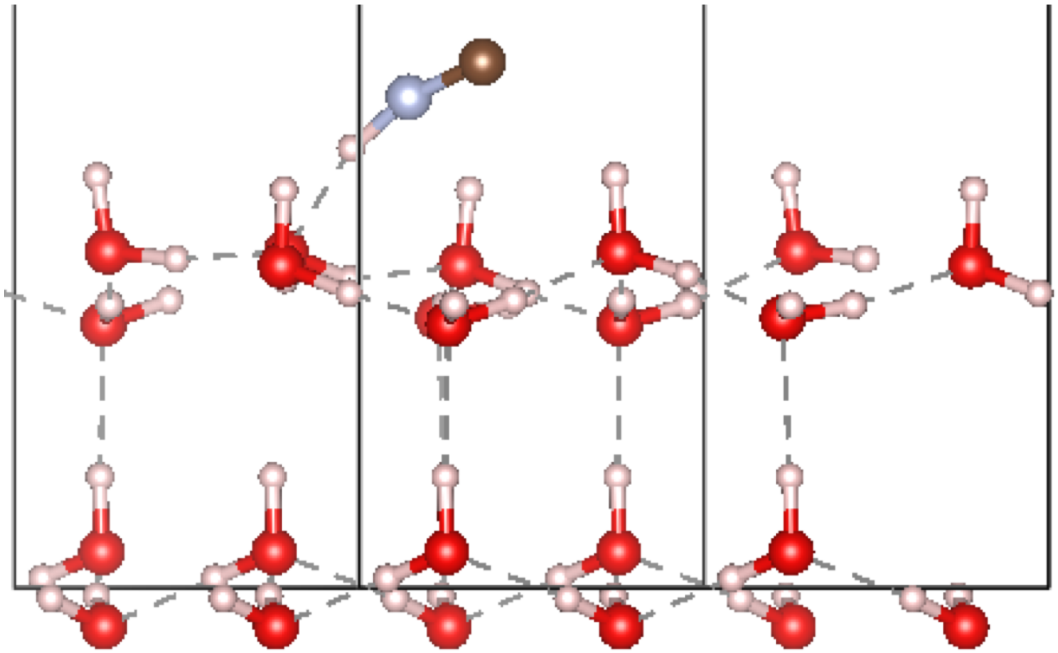


	PBE	Hyb	Ref[1]	Ref [2]
Ebarr (kcal/mol)	4,2	9,7	9,6	10,5

[1] Fabrice Gardebien and Alain Sevin J. Phys. Chem. A 2003, 107, 3925-334
Opt. MP2, $E_{CCSD(T)/6+31G(d,p)}$
[3] Denise M. Koch, James T. Hynes J. Phys. Chem. C 2007 111, 15026-15033
B3LYP//6+31G(d,p)

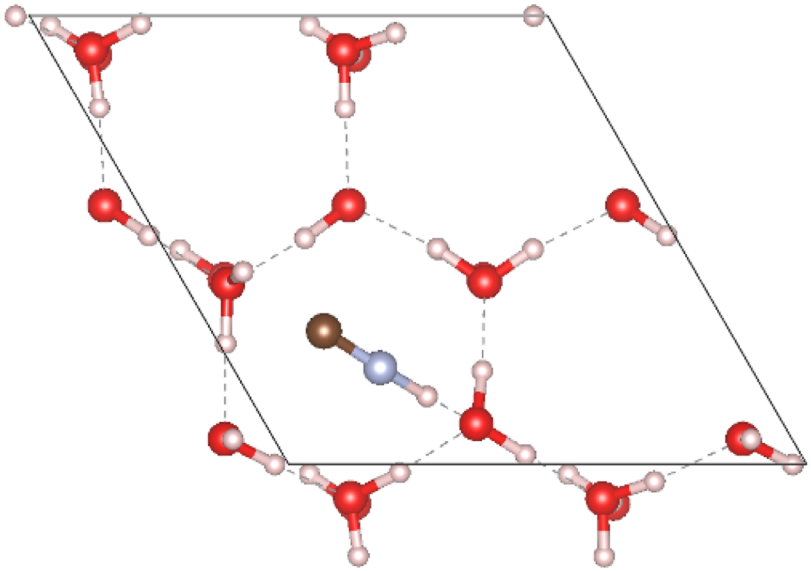
HCN/HNC isomerization

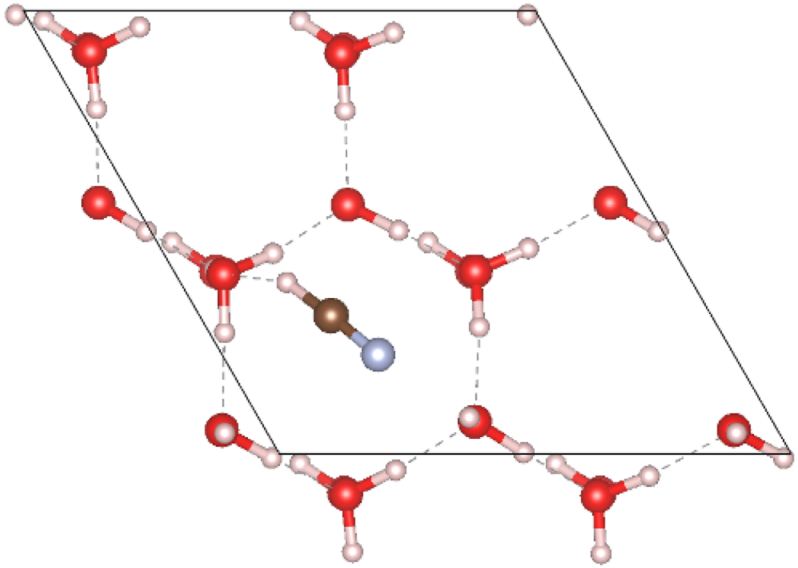
Periodic approach



HCN/HNC isomerization

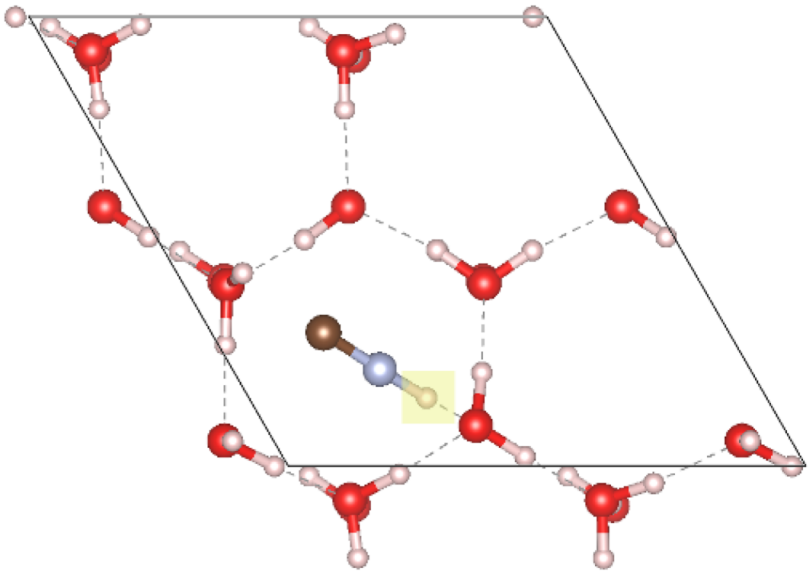
Periodic approach

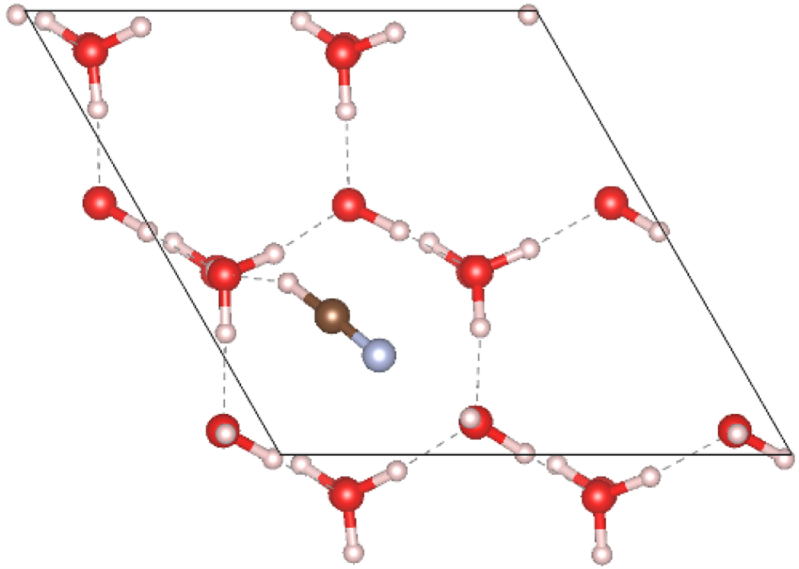




HCN/HNC isomerization

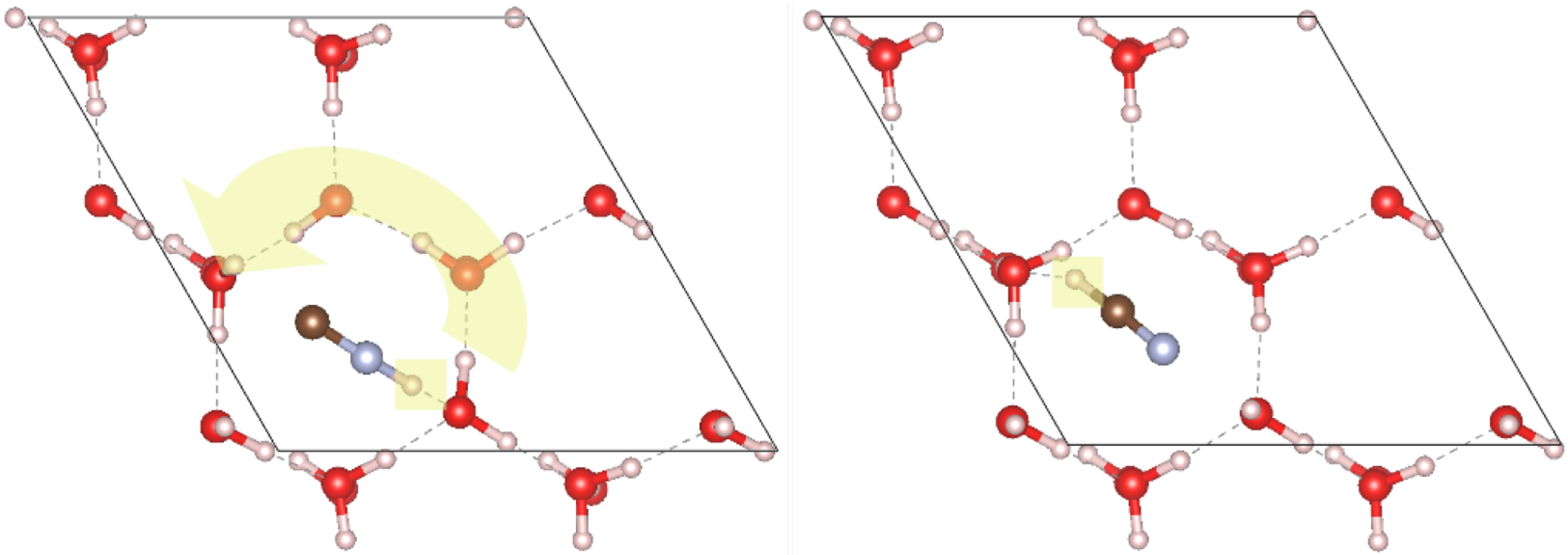
Periodic approach





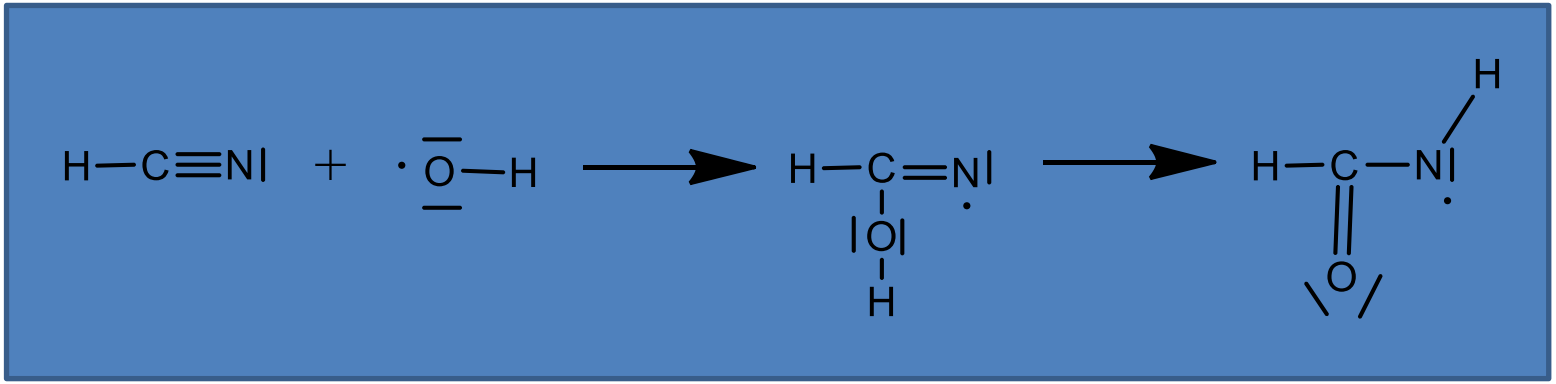
HCN/HNC isomerization

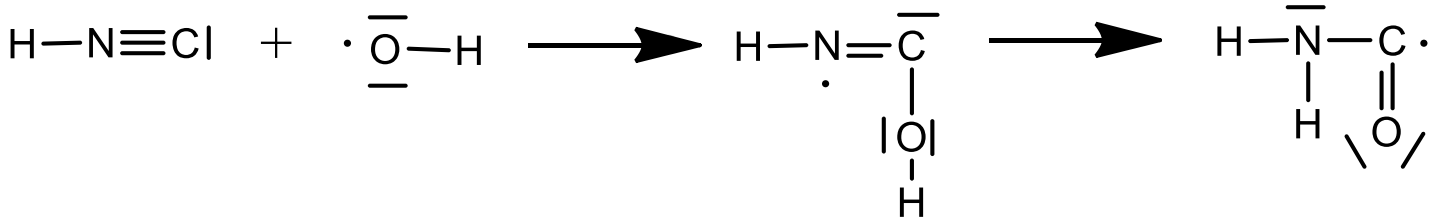
Periodic approach

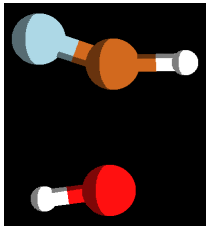


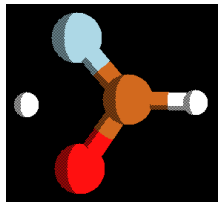
ΔE_{TS} = 2.5 kcal/mol

Formation of Formamide









0.00

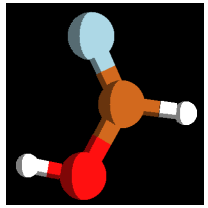
0.05

HCN + OH

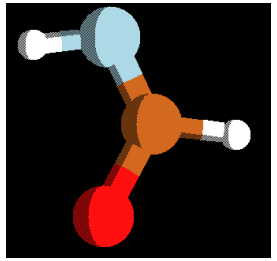
6.7

35.2

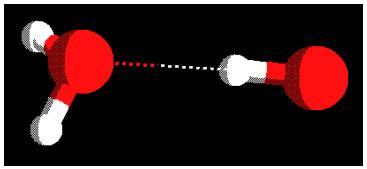
-27.0

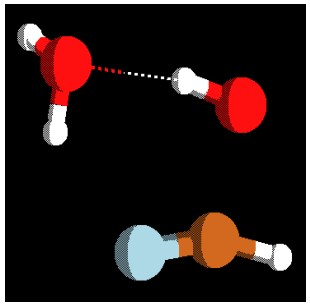


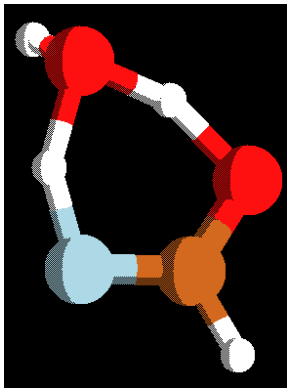
-28.5



Cc-pvtz/B3LYP (kcal/mol)







0.00

-3.8

-1.1

2.80

30.8

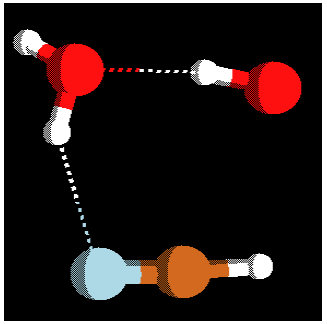
-31.9

-14.0

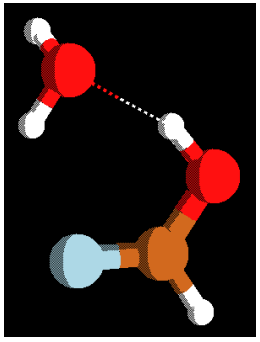
17.9

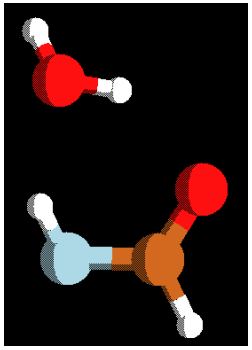
-27.7

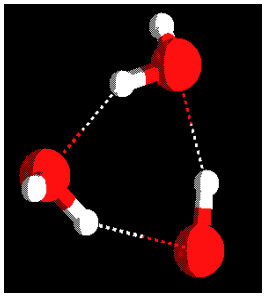
$HCN + H_2O…OH$



$HCN…H_2O…OH$







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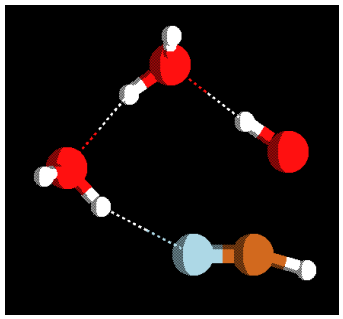
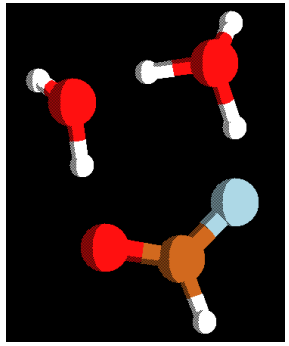


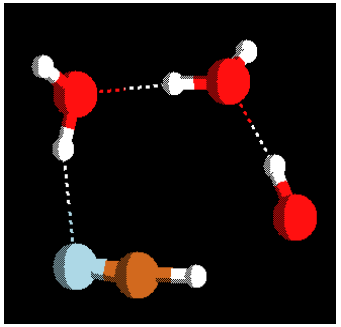
-0.7



HCN + $2H_2O$…OH

-6.8

5.9



33.6

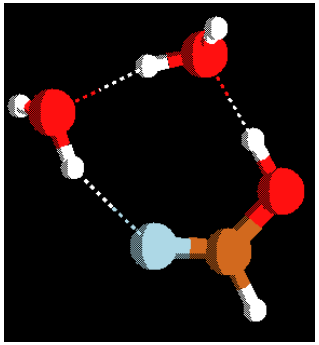
-19.5

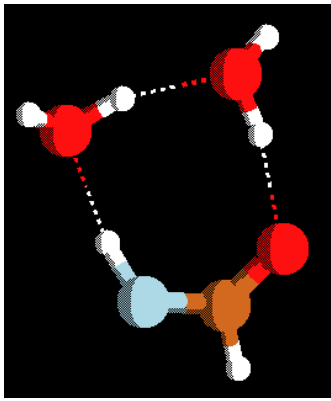
14.8

-28.9

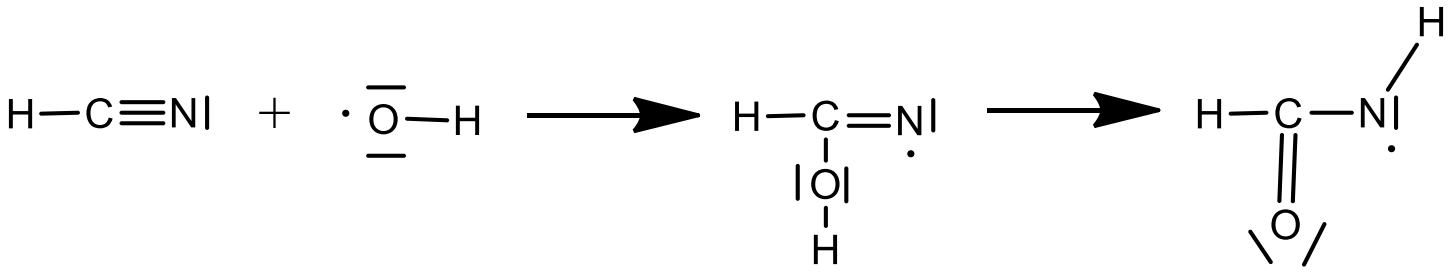
-34.3

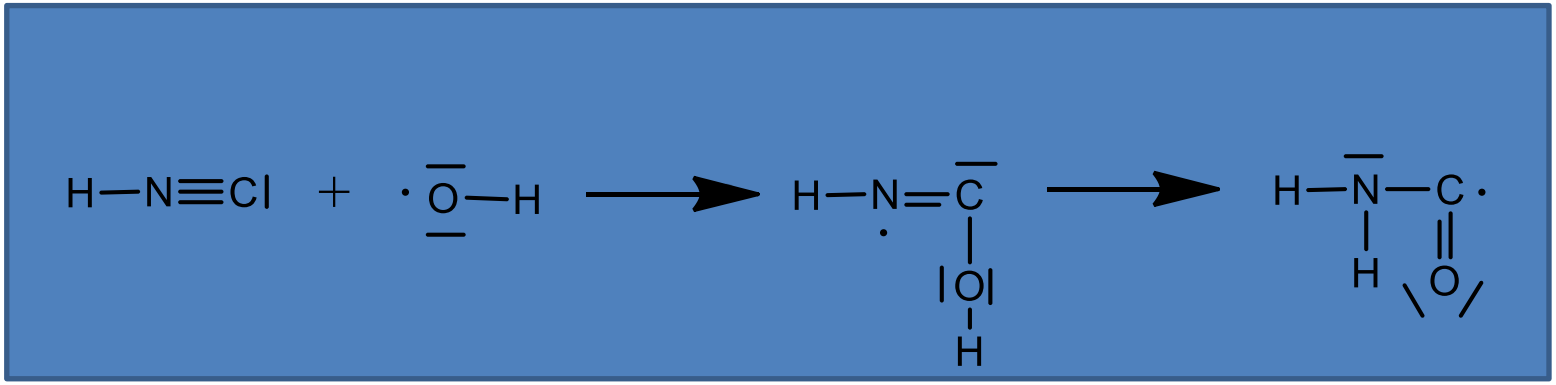
HCN…$2H_2O$…OH

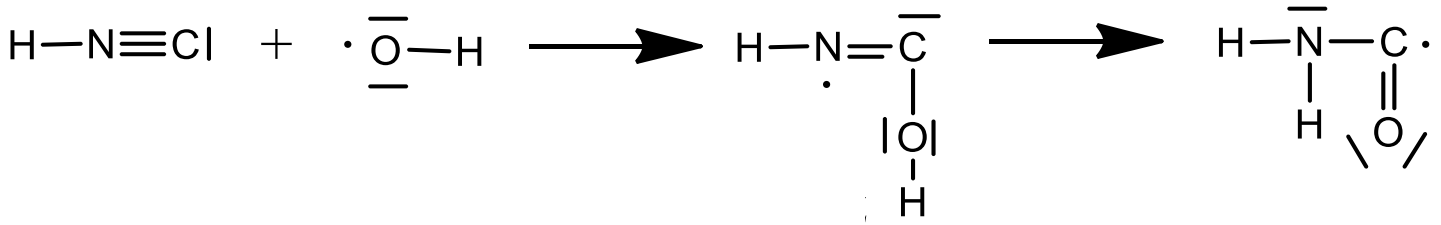


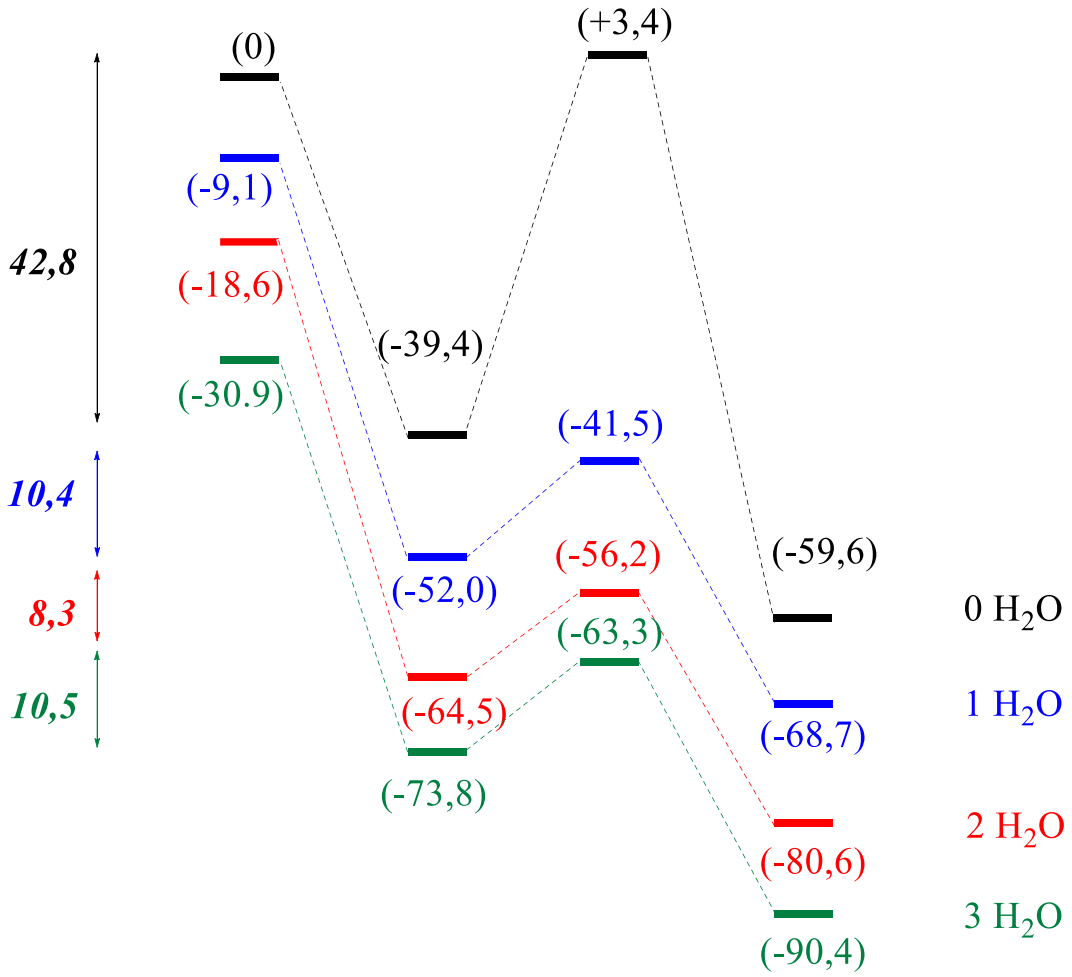


Formation of Formamide





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(+3,4)
(-9,1)
(-18,6)
(-30.9)
(-39,4)
(-41,5)
(-52,0)
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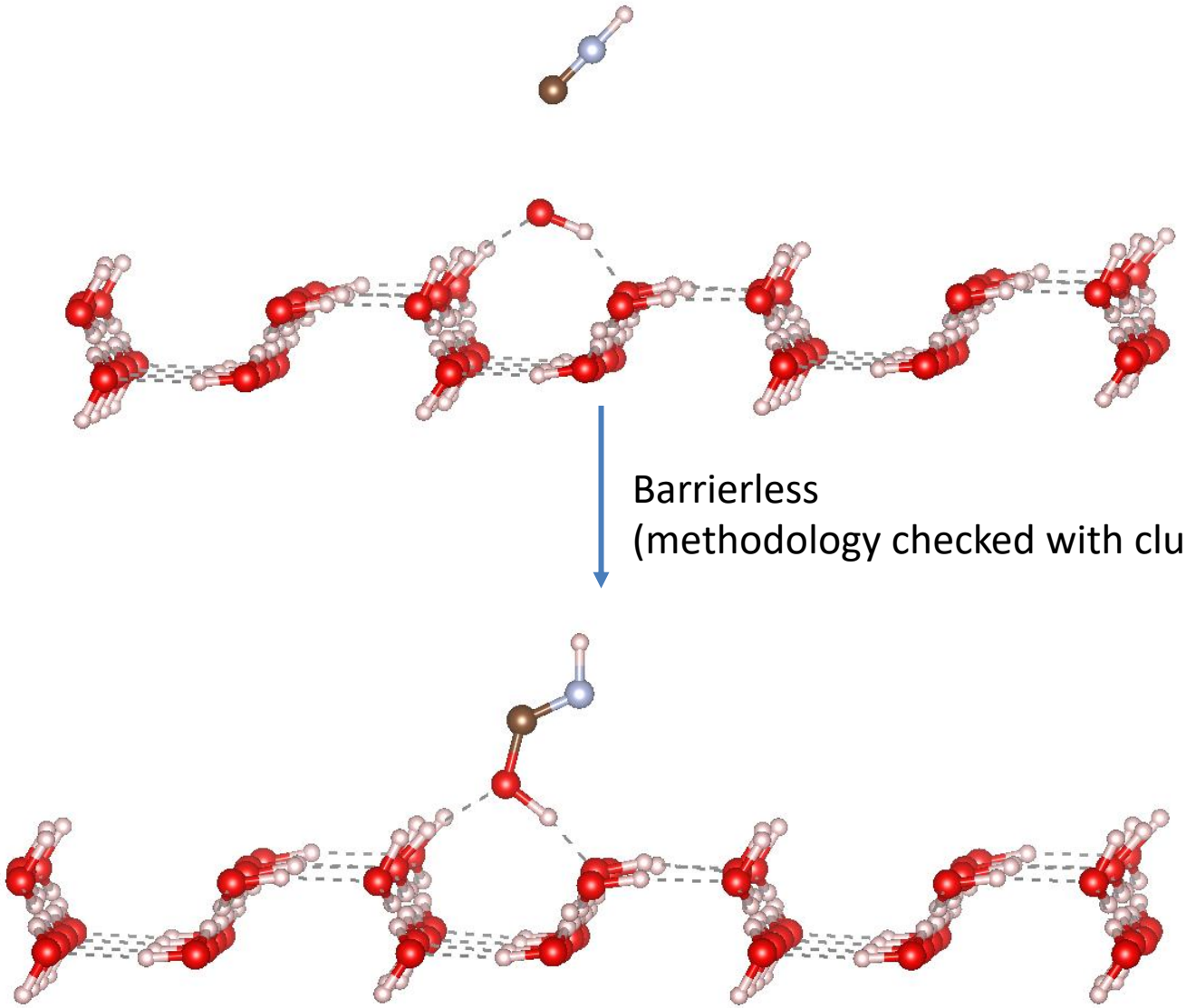
(-59,6)
(-63,3)
(-64,5)
(-68,7)
(-73,8)
(-80,6)
(-90,4)
42,8
10,4
8,3
10,5
0 H2O
1 H2O
2 H2O
3 H2O


Barrierless
(methodology checked with cluster calculations)

Conclusion and Perspective

- The ice is determinant for the prototropy
- The first step may occur in gas phase, the second one on solid
- HNC on damaged water ice could yield formamide

- Reactivity inside the bulk
- Interpretation *via* Molecular Orbital Theory

Cluster approach	Periodic approach
Border: artefact and what has to be optimized ?	Infinite
Environment may be small	Propreties convergence is fast
Amorphous	Cristalline
Methodology: sophisticated	Methodology: DFT

Modelling

- VASPCode *version 5.2.12*
- DFT PBE/Hybrid functional
- Pseudo-potentiels PAW
- MEP obtained with ci-NEB

- Boat surface of the hexagonal water ice
- Two bi-layers (or one…)
- Geometry optimization of one bi-layer