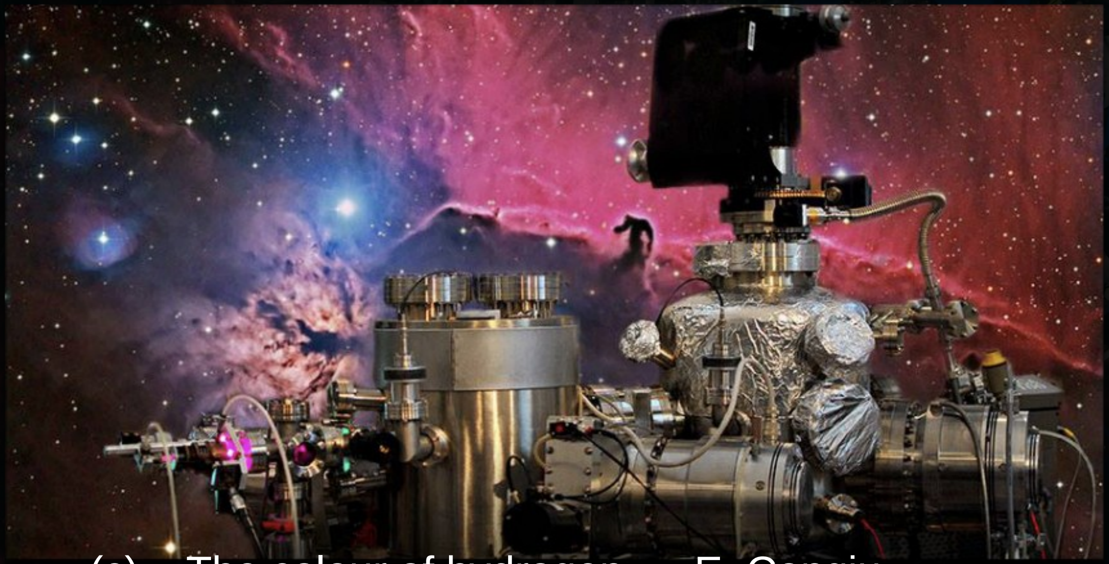
Experimental study of the formation of the molecular mantle at the surfaces of cold dust grains

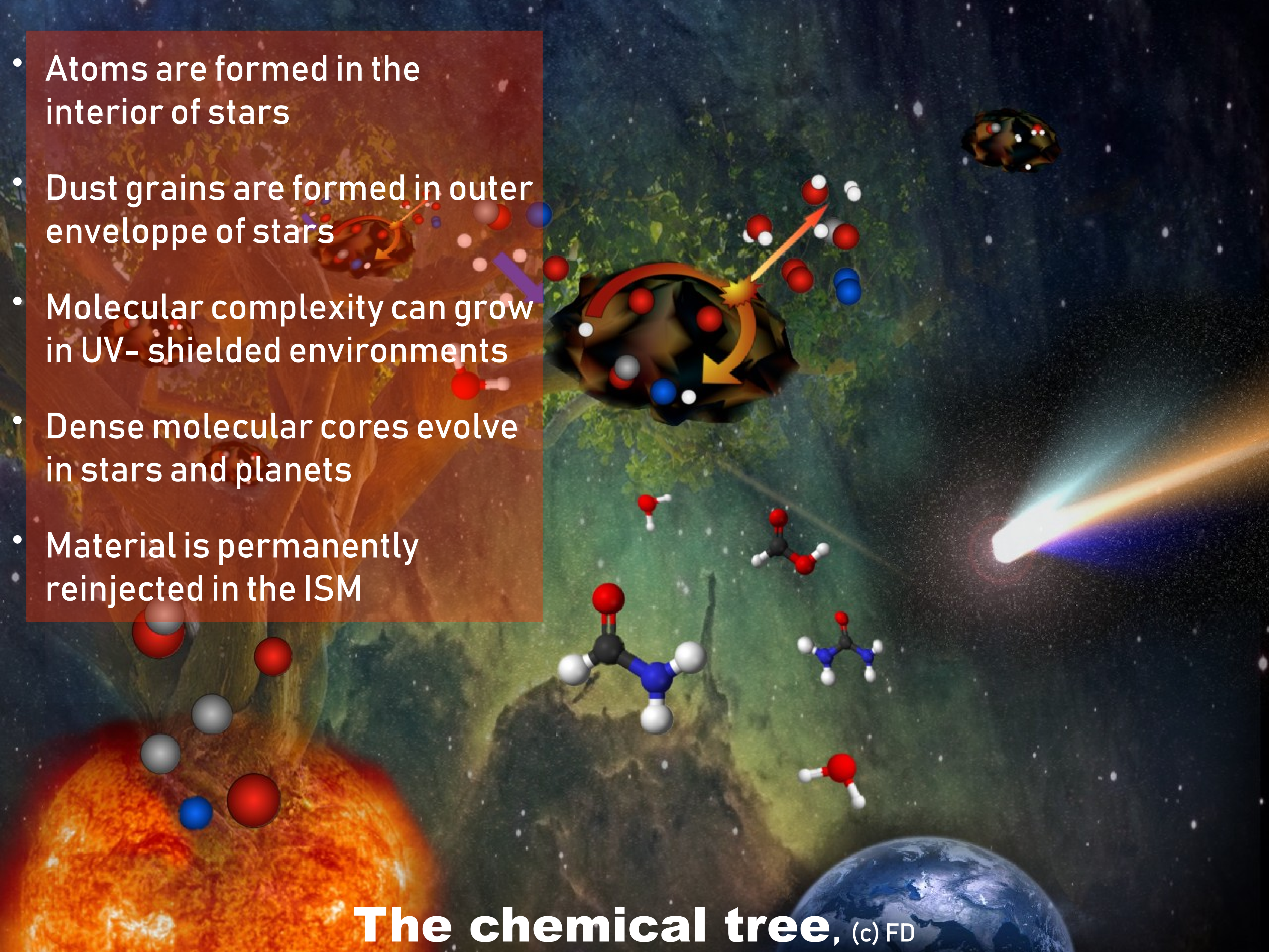


(c) « The colour of hydrogen » . E. Congiu

François Dulieu,

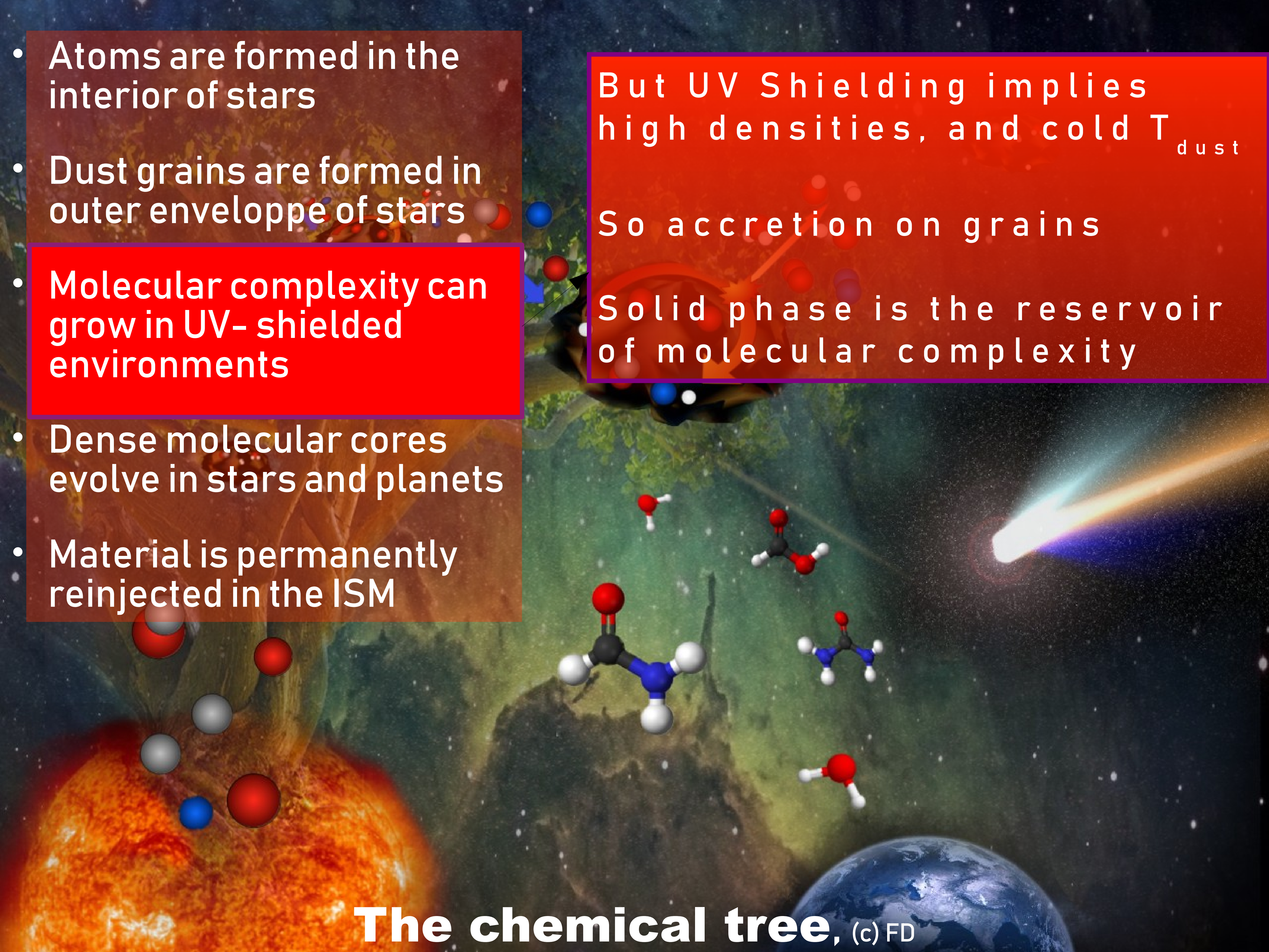
Thanh Nguyen, Emanuele Congiu, Saoud Baouche, Marco Minissale, Abdellahi Sow, Abdi-Salam Ibrahim Mohamed, Stephan Diana et al
LERMA, Université de Cergy Pontoise, Observatoire de Paris, Sorbonne Université, PSL, CNRS.

Paris, Atelier Glaces Octobre 2019



- Atoms are formed in the interior of stars
- Dust grains are formed in outer enveloppe of stars
- Molecular complexity can grow in UV- shielded environments
- Dense molecular cores evolve in stars and planets
- Material is permanently reinjected in the ISM

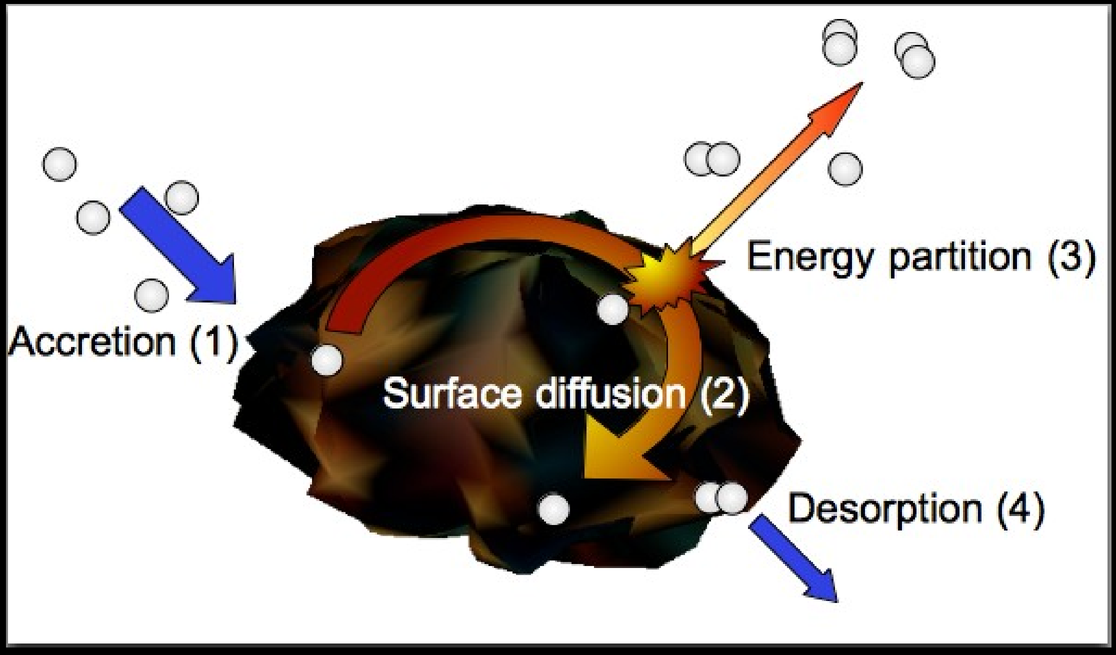
The chemical tree, (c) FD


Atoms are formed in the interior of stars
Dust grains are formed in outer enveloppe of stars
Molecular complexity can grow in UV- shielded environments
Dense molecular cores evolve in stars and planets
Material is permanently reinjected in the ISM
But UV Shielding implies high densities, and cold T dust
So accretion on grains
Solid phase is the reservoir of molecular complexity
The chemical tree, (c) FD

Cergy's team purpose:

How molecular complexity can develop ?

- starting from atoms or small radicals
- without external energy
- ***on*** *surfaces*



Understand processes, like the return in the gas phase, the diffusion, the isotopic effects or the reactivity

Par déposition de la phase gaz

Formation de la glace

Par transformation de la phase solide

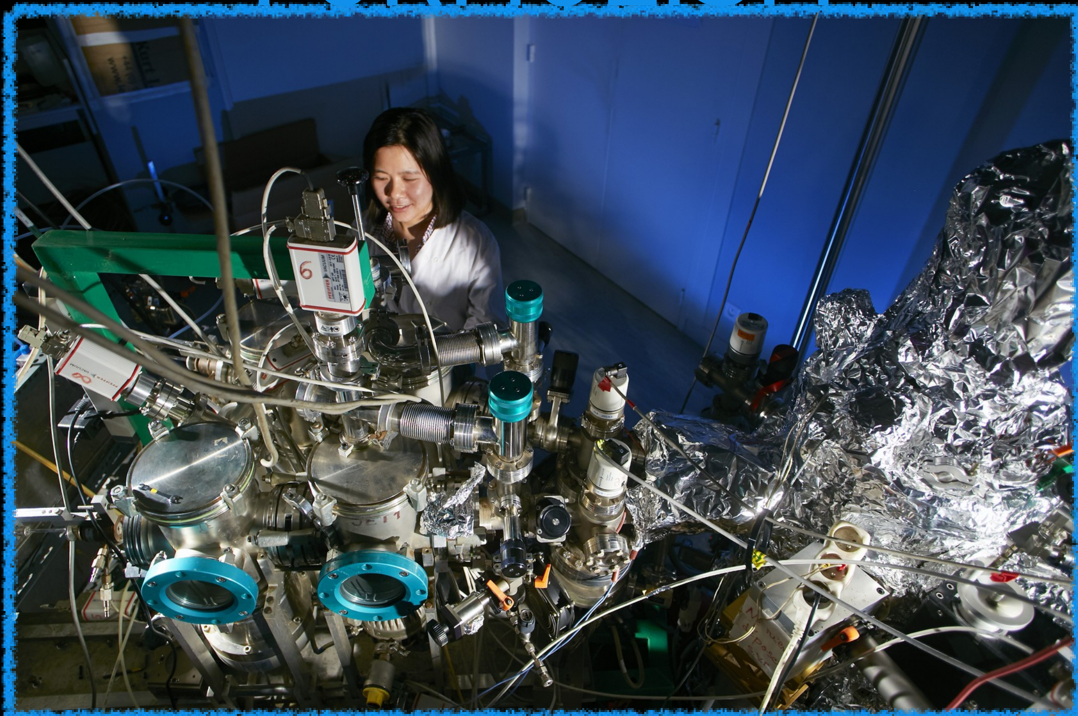
Transformation ‘initiale’ (chimie de surface)

Transformation ‘énergétique’ continue (bulk)

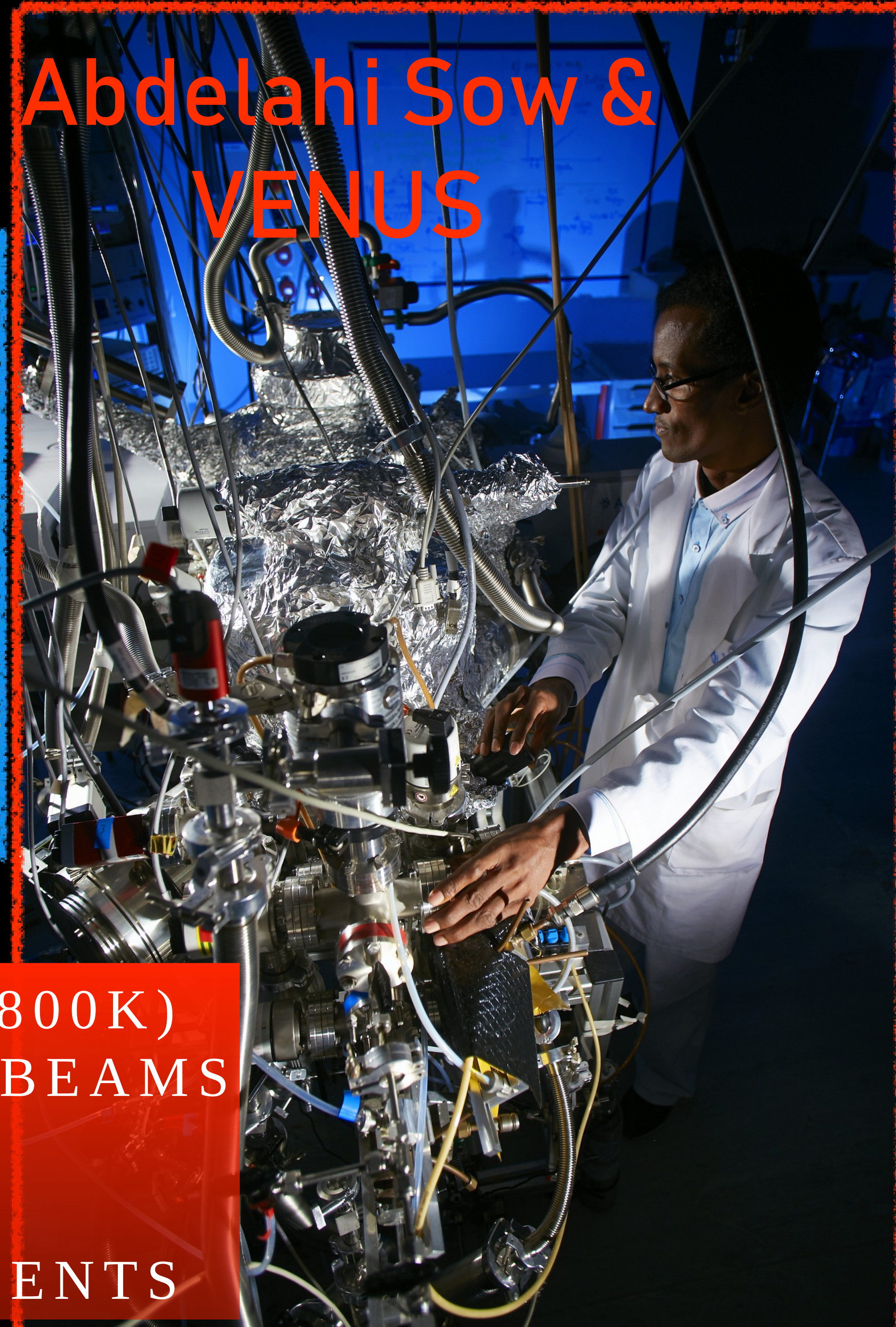
(cf collègues : Dartois, Boduch,Bertin...)

Formation de la glace → Par déposition de la phase gaz

Thanh Nguyen & FORMOLISM



Abdelahi Sow & VENUS

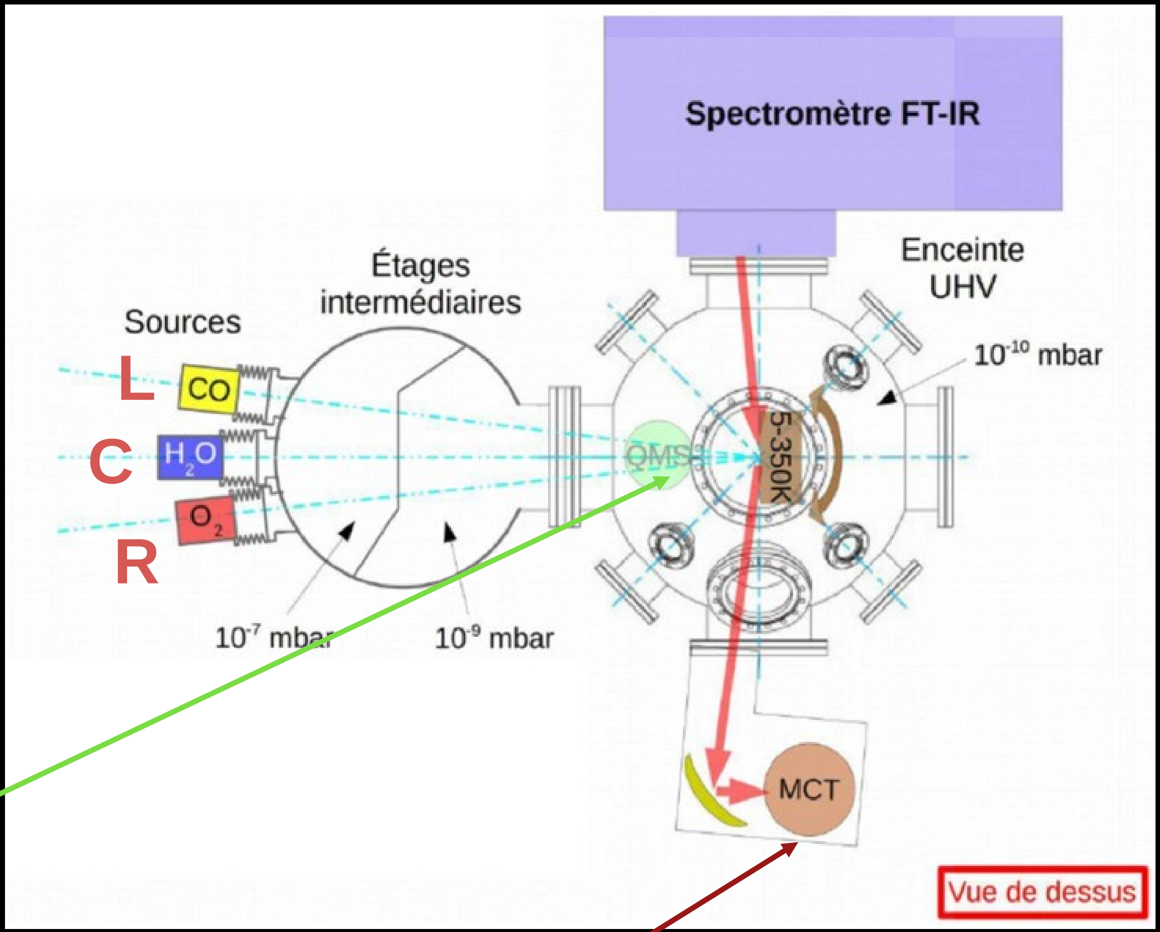


UHV + COLD SURFACES (8-800K)
2 (4) ATOMIC MOLECULAR BEAMS
FT-IR, QMS, LASERS
SUB MONOLAYERS
QUANTITATIVE MEASUREMENTS

Vers de Nouvelles Synthèses

Venus set-up

5 sources/ beams
Left, Right Center
Top and Bottom



QMS :
Phase gaz
Précis-sensible (0.01 ML)
mesure entrées et sorties

FT RAIRS
Phase solide (in situ)
Moins sensible (0.2 ML)
Dépend des espèces et environnement

Formation de la glace → Par déposition de la phase gaz

Méthanol déposé par jet, de 0,5 à 3 ML (monocouches)

Mesure IR surface, temps reel

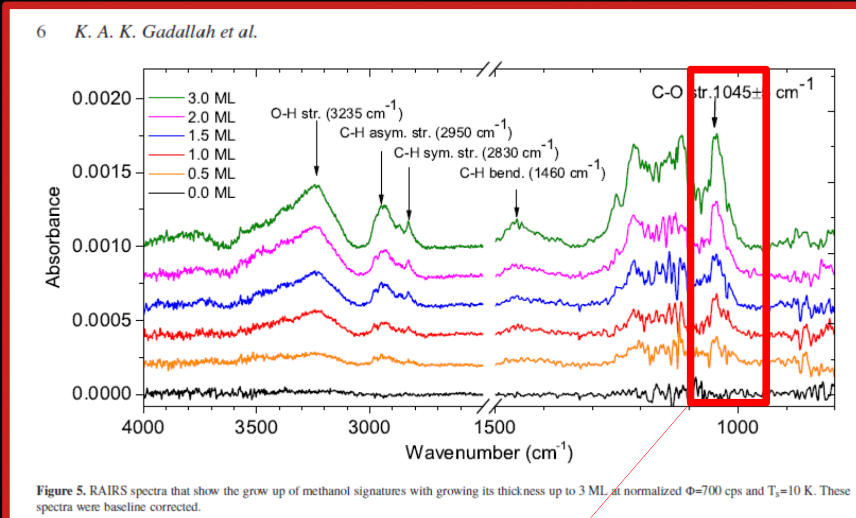
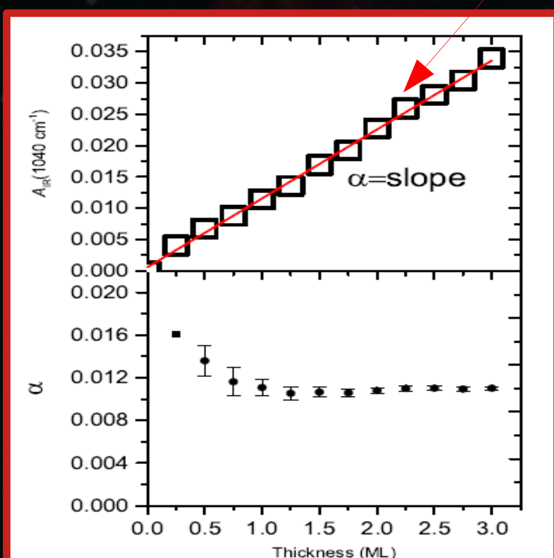
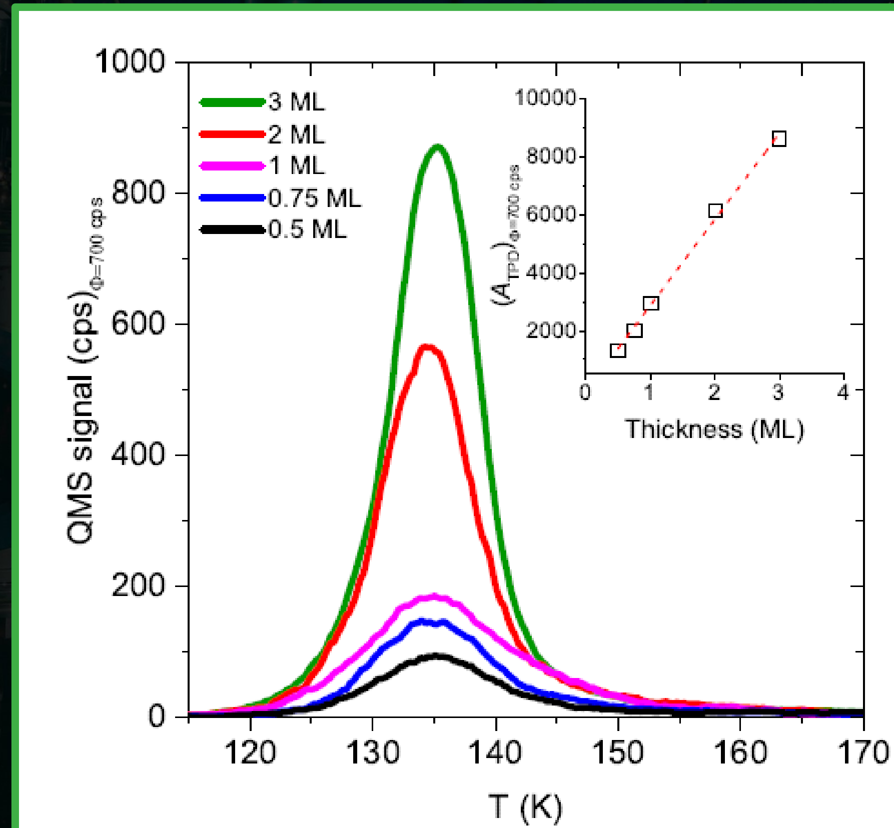


Figure 5. RAIRS spectra that show the grow up of methanol signatures with growing its thickness up to 3 ML at normalized Φ=700 cps and T_s=10 K. These spectra were baseline corrected.



Mesure TPD a posteriori, QMS



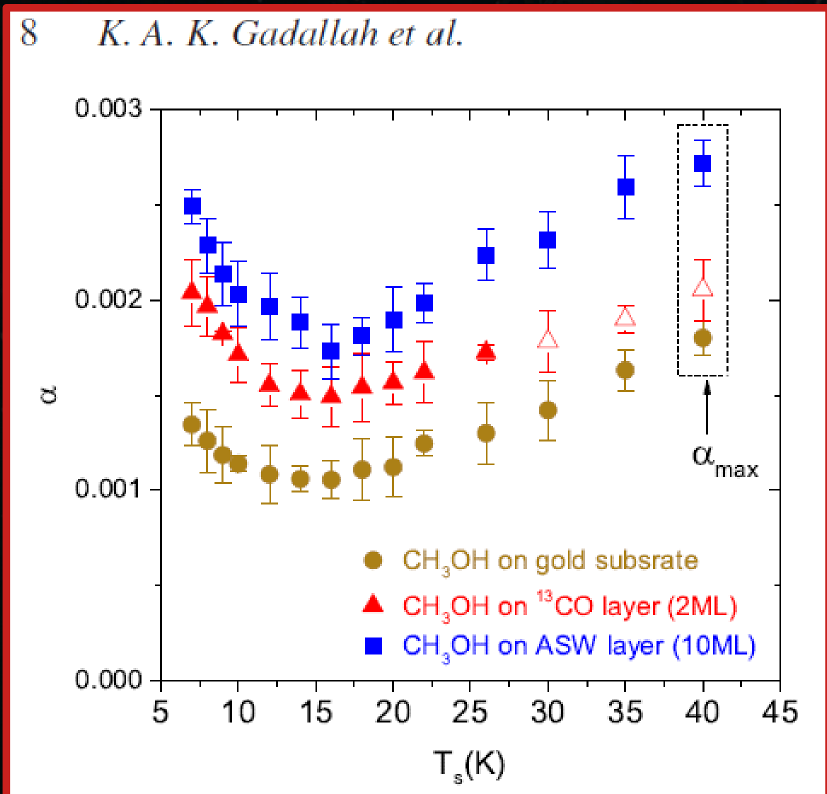
Signal proportionnel au temps de dépôt
Résultats TPD et IR convergents

Soutenance de la thèse de A. Sow le 4 novembre 2019
Travail réalisé avec K. Gadallah de l'univ. du Caire

Formation de la glace → Par déposition de la phase gaz

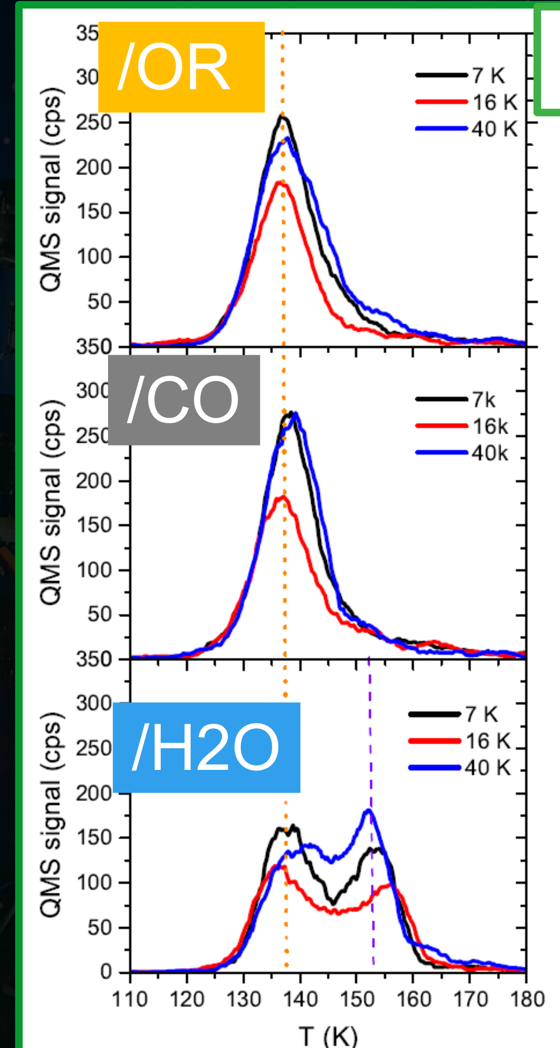
Méthanol déposé par jet 1 ML sur 3 surfaces à Ts Variable

Mesure IR surface, temps reel



Force de bandes variables !

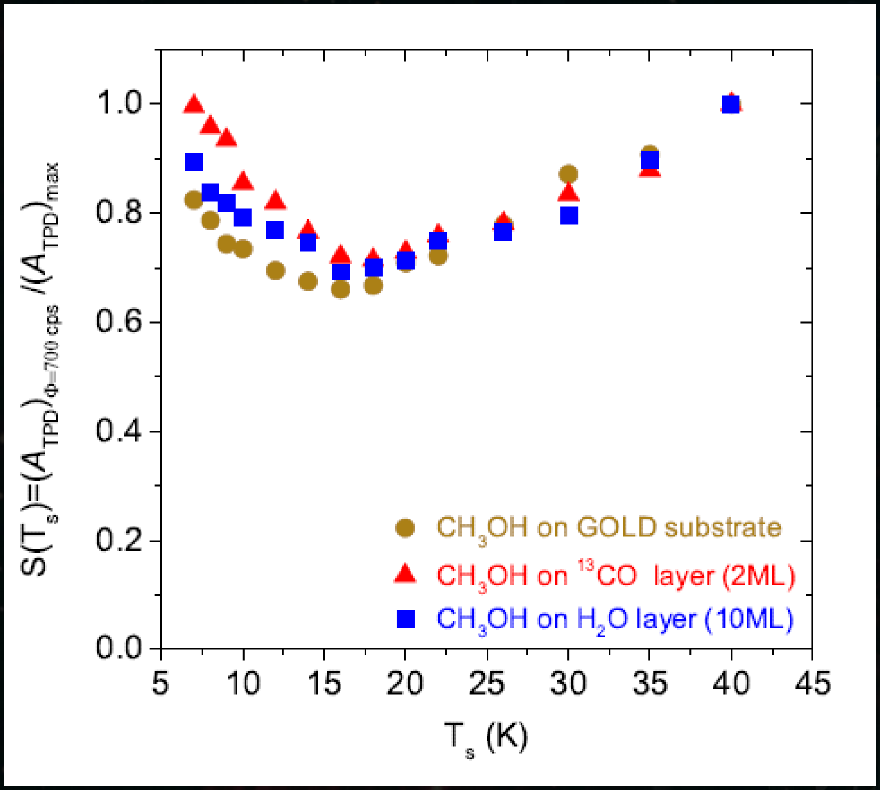
QMS



Quantité déposée ou désorbée minimale à 16 K

Formation de la glace → Par déposition de la phase gaz

Méthanol déposé par jet 1 ML sur 3 surfaces à Ts Variable



Le collage du méthanol varie de 30 % avec la température de surface
Il est moins sensible au substrat (variation de 10%)

Y-a-t-il une barrière d'entrée pour l'adsorption ?
Si oui, de quel type ?

Expérience gaz 300 K sur surface froide
Et pour un gaz froid sur une surface froide ?
Le collage pourrait-il être une raison du maintien des molécules en phase gaz ?

Formation de la glace → Par déposition de la phase gaz

Les snowlines ou transition de phase sont définies comme des zones ou l'accrétion égale la désorption

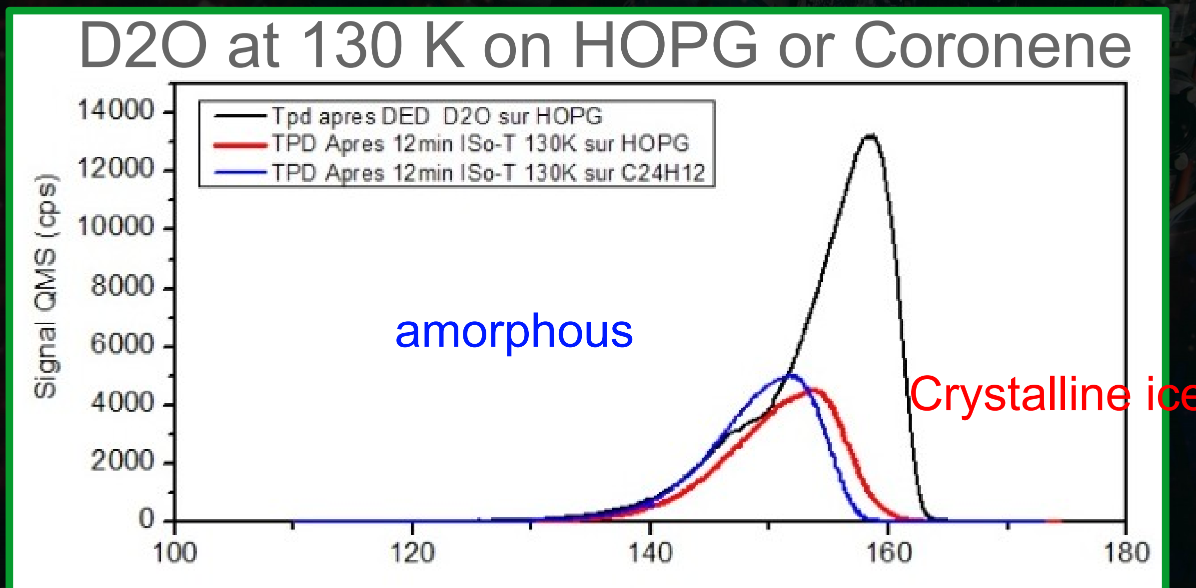
Binding energies can greatly vary depending on the surface ice layer : CO is able to prevent N_2 adsorption by shifting donwn its binding energy (Nguyen et al 2018)

Formation de la glace → Par déposition de la phase gaz

Les snowlines ou transition de phase sont définies comme des zones ou l'accrétion égale la désorption

Binding energies can greatly vary CO vs N2 (Nguyen et al 2018)

Water ice morphology can change with the substrate at low deposition rates.



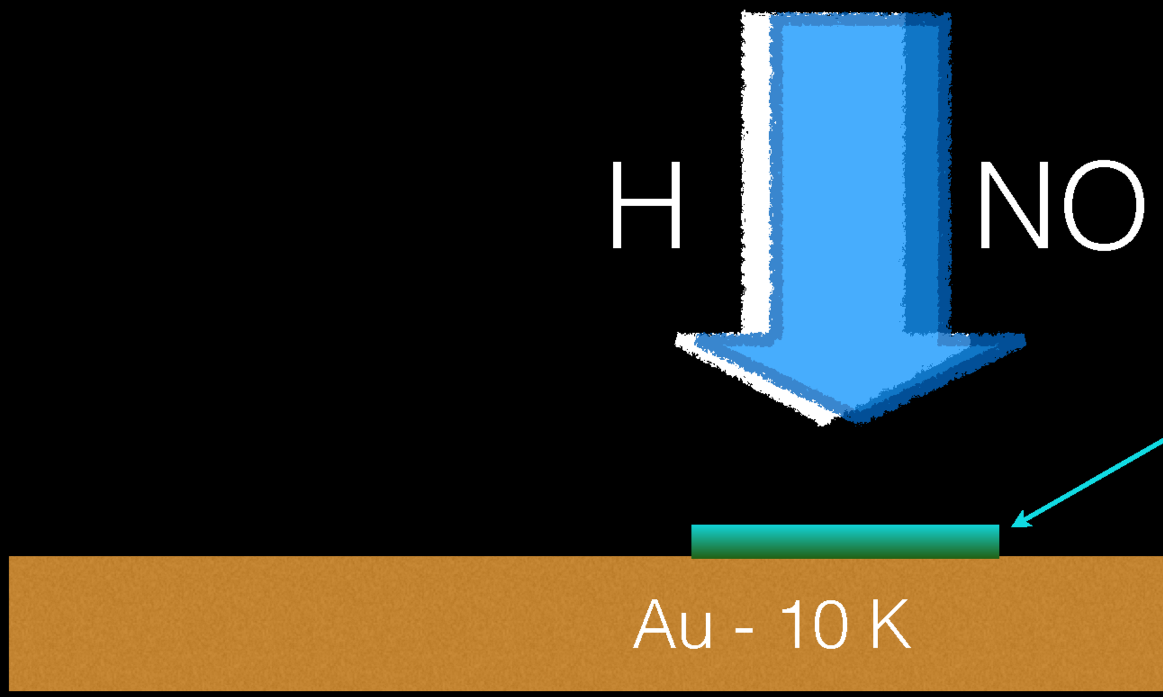
Black : Reference curve, the shoulder corresponds to the cristalisation
Blue : From coronene film , Red : From graphite

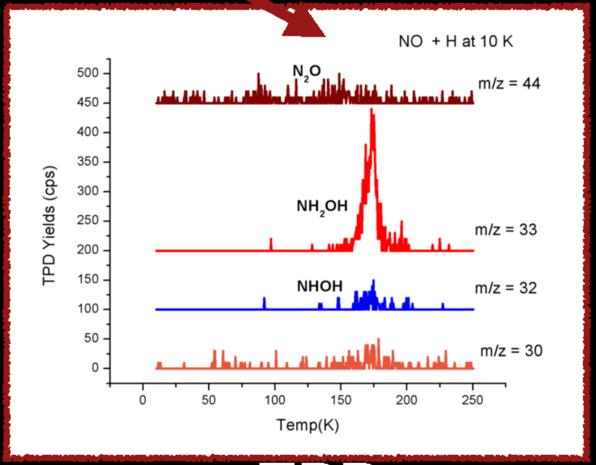
Thèse de Abdi Salam Ibrahim Mohamed en décembre 2019

co-deposition experiment

0 - On a specific substrate : e.g. Au held at 10 K
A - Co-deposition of NO and H - monitor by IR
B - Remove the products and monitor by TPD

$\{NO+H\}_{10K}$





TPD

NH_2OH, N_2O, H_2O

(c) Congiu + 2012

Par déposition de la phase gaz

Formation de la glace

Par transformation de la phase solide

Transformation 'initiale' (chimie de surface)

Transformation 'énergétique' continue (bulk)

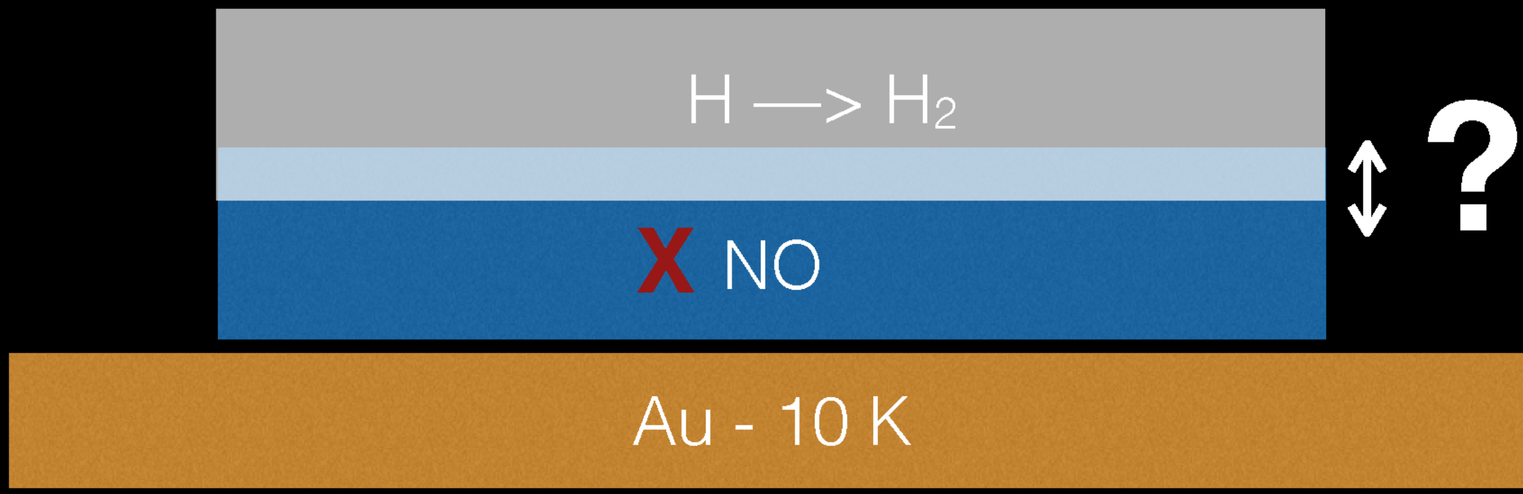
(cf collègues : Dartois, Boduch,Bertin...)

One typical layered experiment

0 - On a specific substrate : e.g. Au held at 10 K
A - Deposit ***X*** ML of NO - monitor by IR
B - Expose to 3 ML of H - monitor by IR
C - Remove the products and monitor by TPD

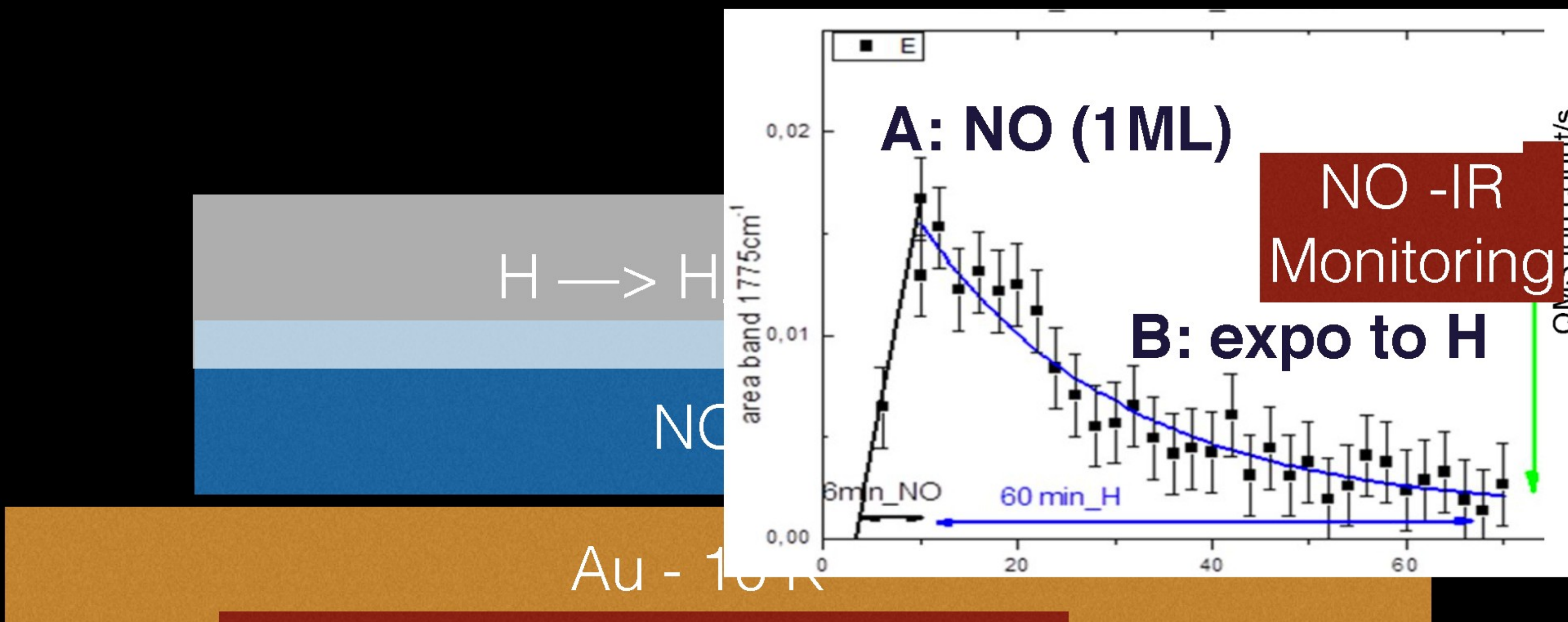
$$_{Au10K\ X\ ML}\{NO\} + \{H\}_{10K}$$

ML = Mono layer



One typical layered experiment

0 - On a specific substrate : e.g. Au held at 10 K
A - Deposit 1 ML of NO - monitor by IR
B - Expose to H - monitor by IR in real time
C - Remove the products and monitor by TPD

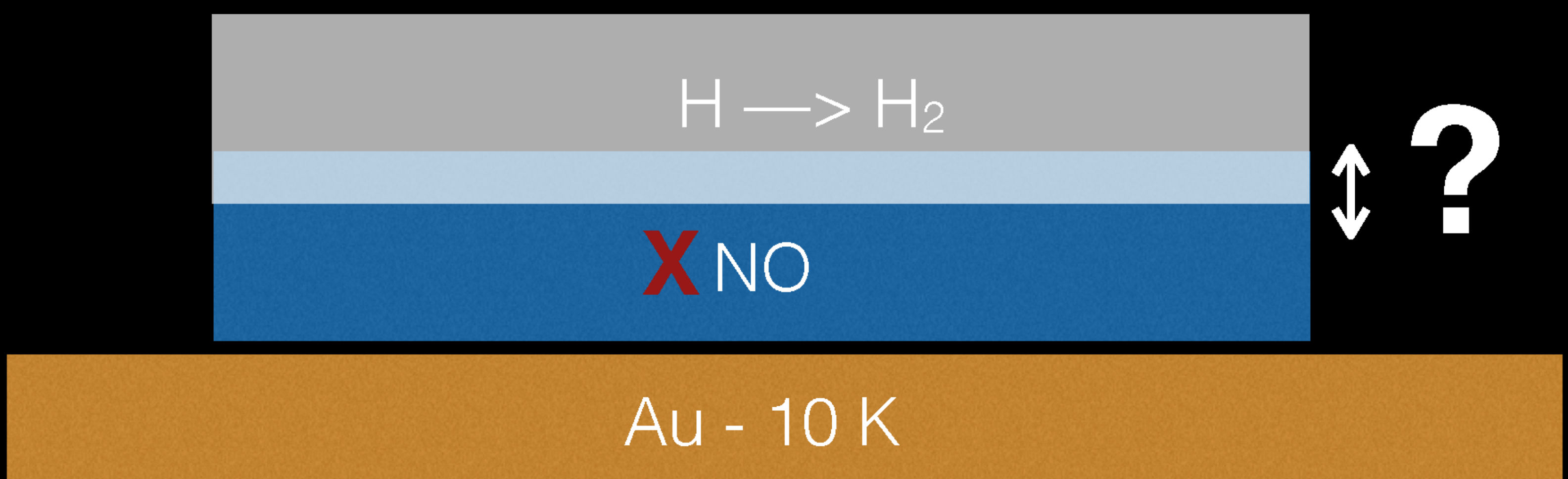


For 1 ML all the NO is reacting

One typical layered experiment

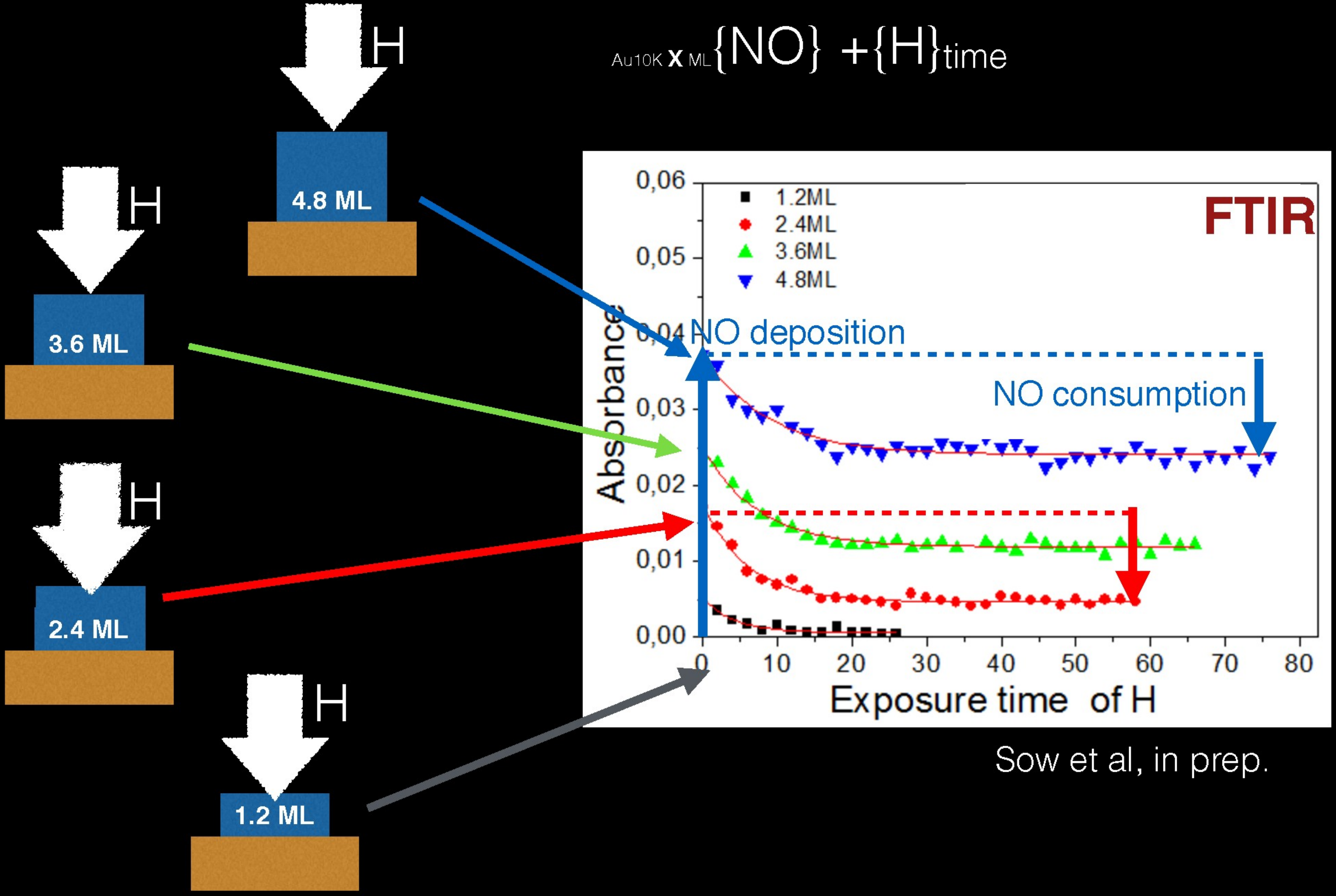
0 - On a specific substrate : e.g. Au held at 10 K
A - Deposit **X** ML of NO - monitor by IR
B - Expose to H - monitor by IR
C - Remove the products and monitor by TPD

$$ {}_{\mathrm{Au\,10K\,3ML}}\{\mathrm{NO}\} + \{\mathrm{H}\}_{\mathrm{10K\,3ML}} $$



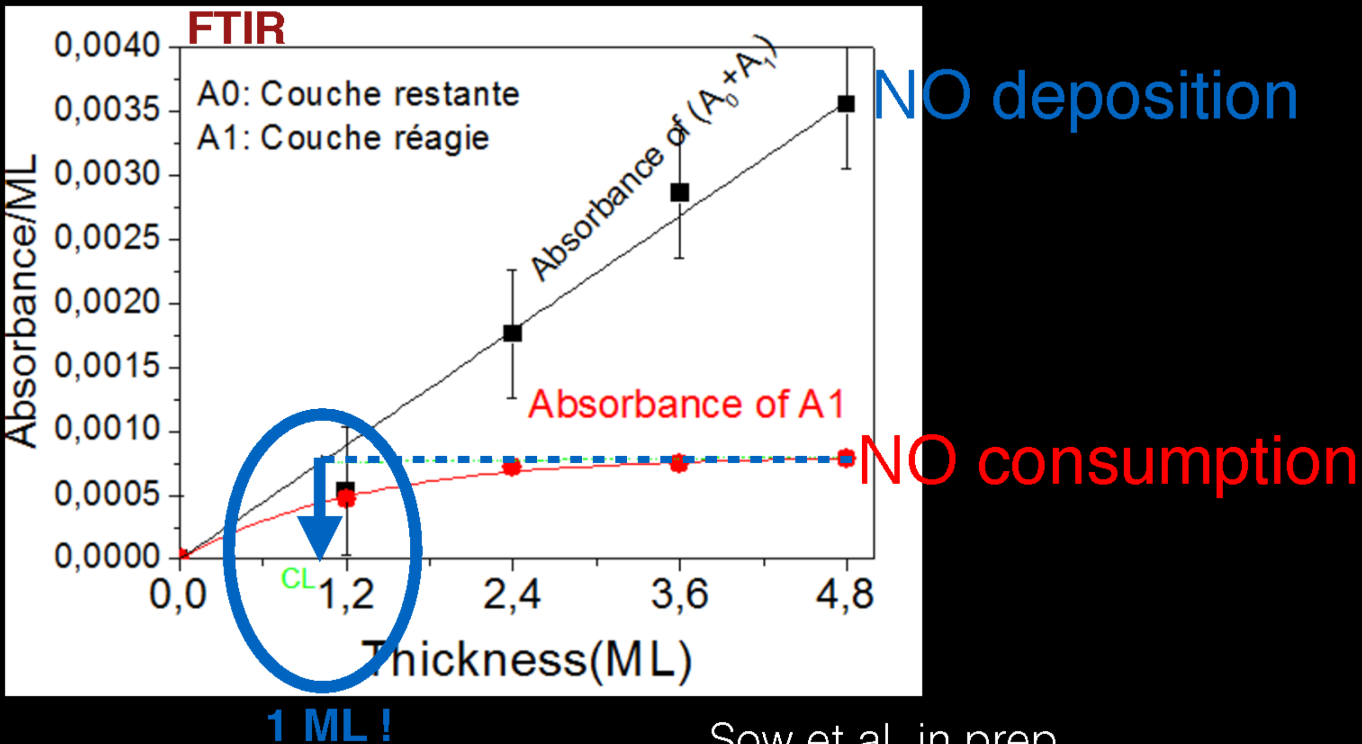
The chemical penetration depth

$_{Au10K}\ \mathbf{X}\ _{ML}\{NO\} + \{H\}_{time}$



Sow et al, in prep.

The chemical penetration depth



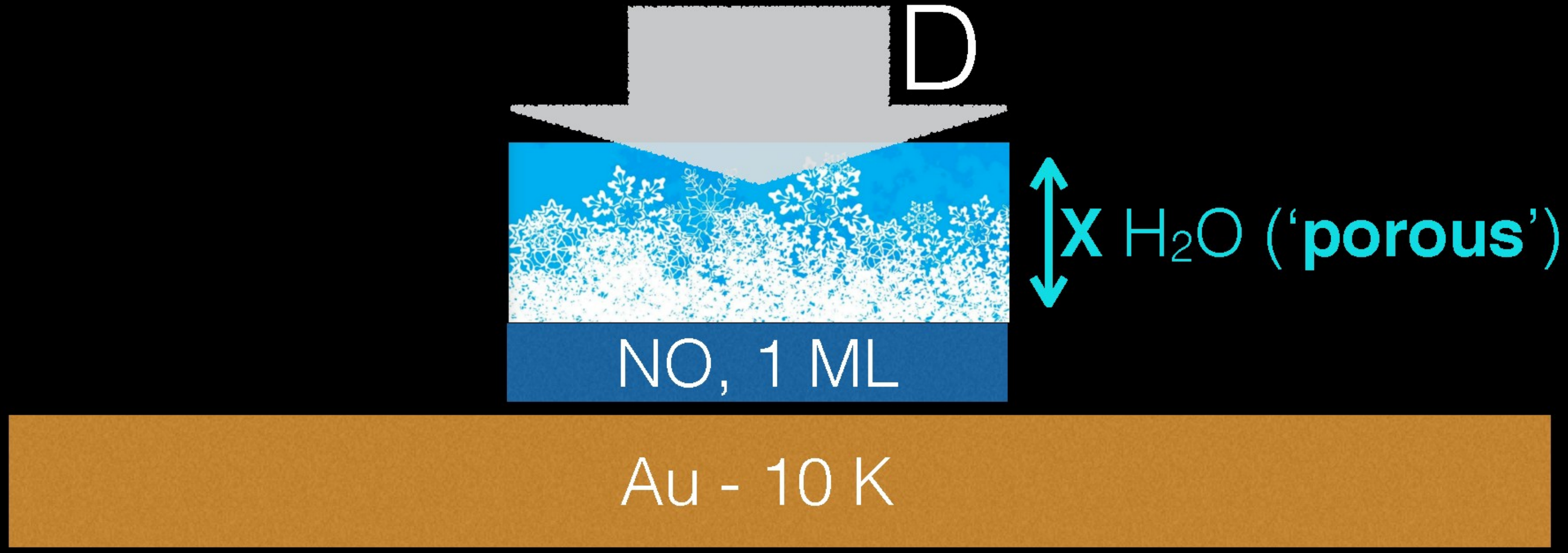
Sow et al, in prep.

- only on the first outer layer is reacting
- The physical layer is the same than the chemical layer
- There is no penetration of H below the first layer of NO,
- It is the same for H_2CO ices

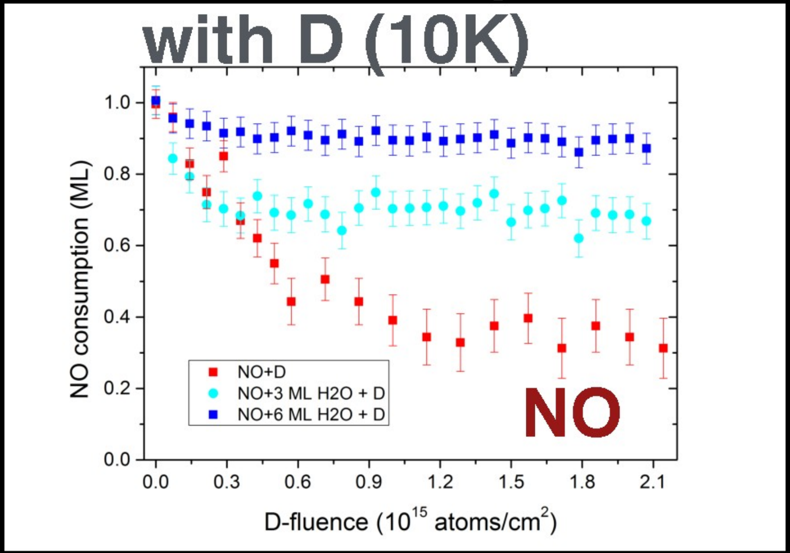
D/O penetration in ice

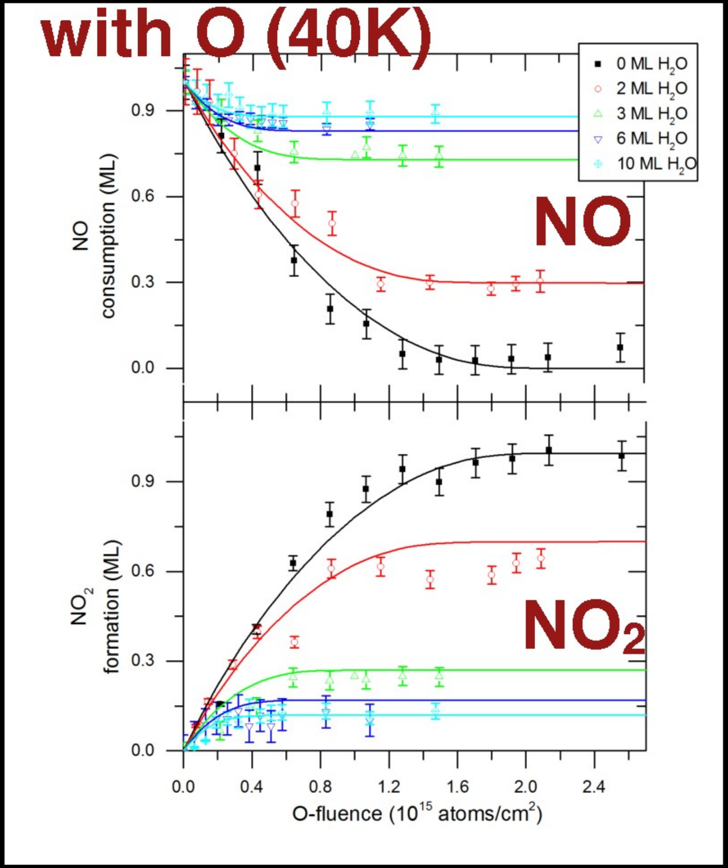
1 - On a specific substrate : e.g. Au held at 10 K
2 - Deposit 0.5 ML of NO - monitor by IR
3 - Depose to **X** ML of H_2O @ 40 K - monitor by IR
5 - Expose to H (or **O**)
4 - Remove the products and monitor by TPD

$$_{Au10K\ 0.5\ ML}\{NO\}+\{H2O\}_{40K}+\{D\}_{10K}$$



D/O penetration in ice



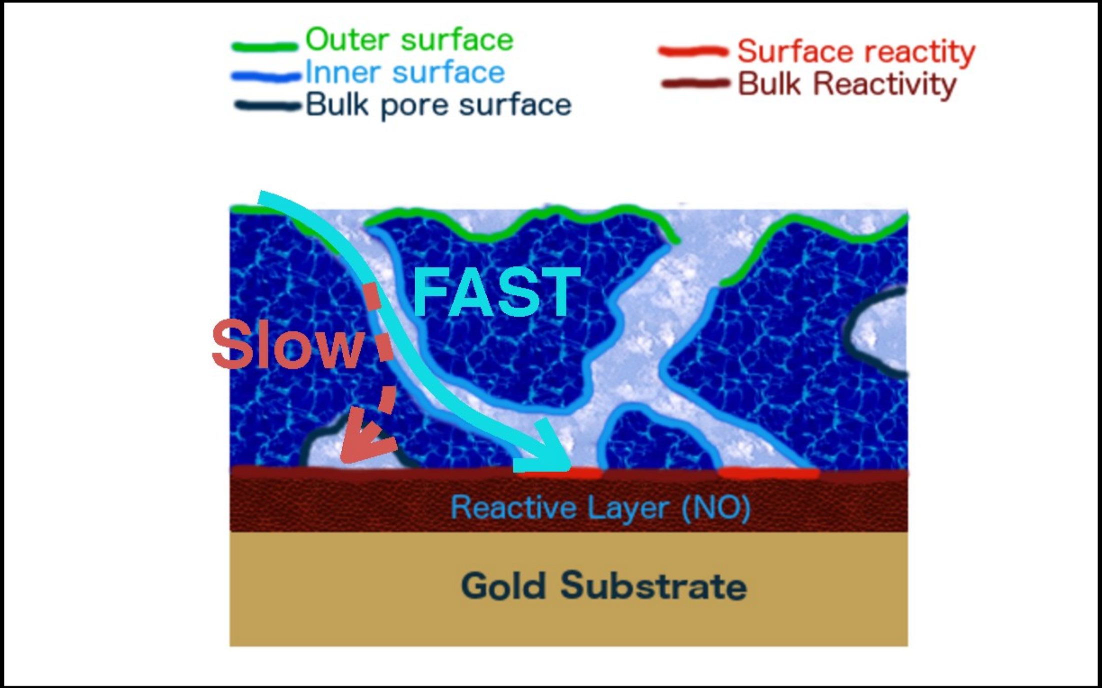


Minissale et al, submitted

- Kinetics of D (10K) and O (40K) are quite similar
- There is no penetration of D or O through H2O
- The water bulk is hermetic to D (in our experimental conditions)

First conclusions

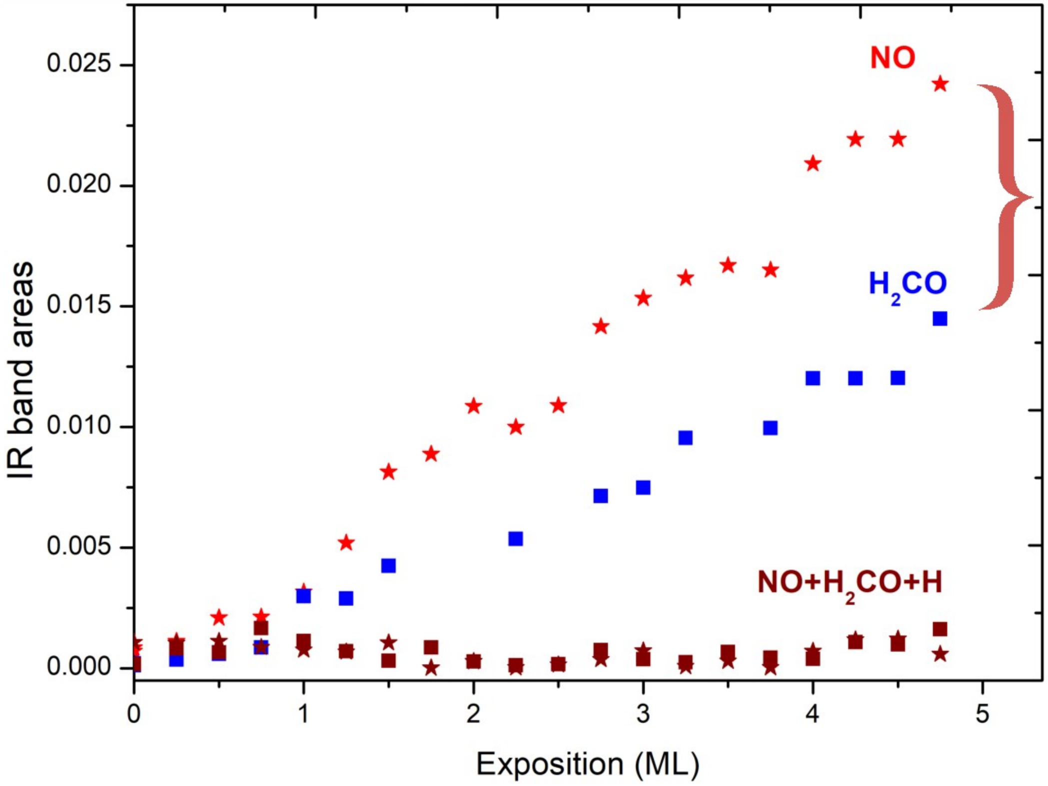
- Surface chemistry is much faster that penetration
- *In our experimental conditions* one molecular layer is hermetic to H
- Only porosity allows to access to deeper layers



$\{NO_1 + H_2CO_{0.8} + H_4 + H_2O_{1.5}\}$ 4 ML 10K

IR monitoring

Both NO and H2CO are reacting

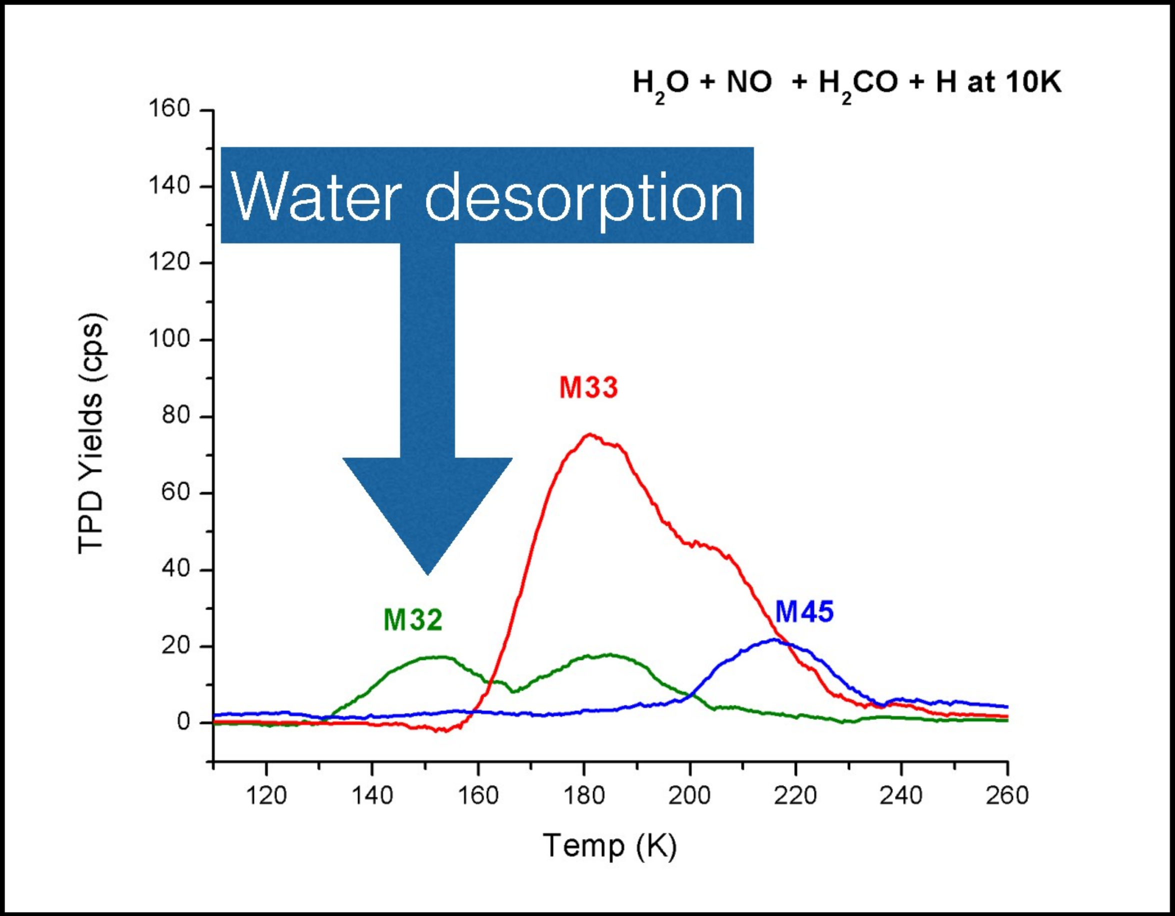


without H

with H

There is ***no more*** NO or H_2CO after the deposition ***at 10 K***

$\{NO_{1}+H_2CO_{0.8}+H_{4}+H_2O_{1.5}\}$ 4 ML10K

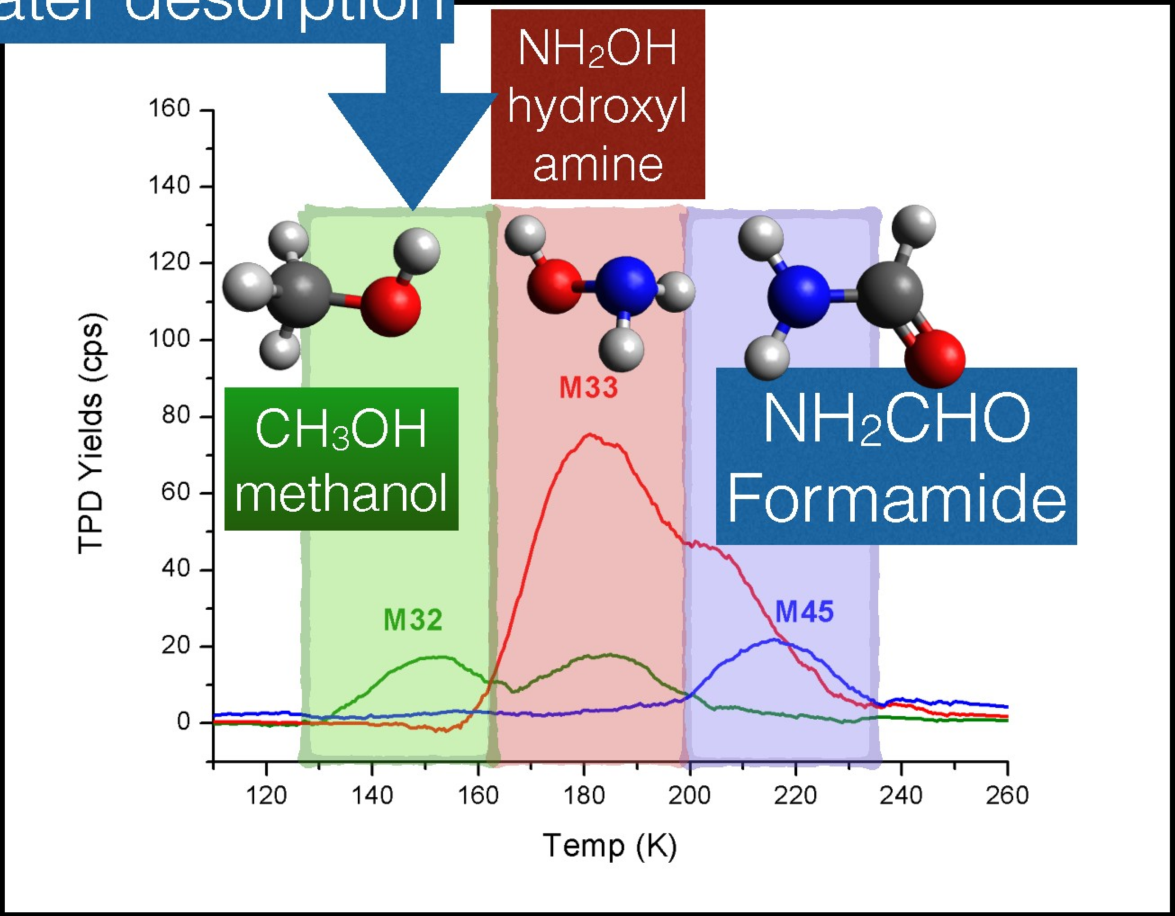


Three main species desorbing at 3 different temperatures

$\{NO+H_2CO+H+H_2O\}$ 4 ML10K

1 0.8 4 1.5

Water desorption

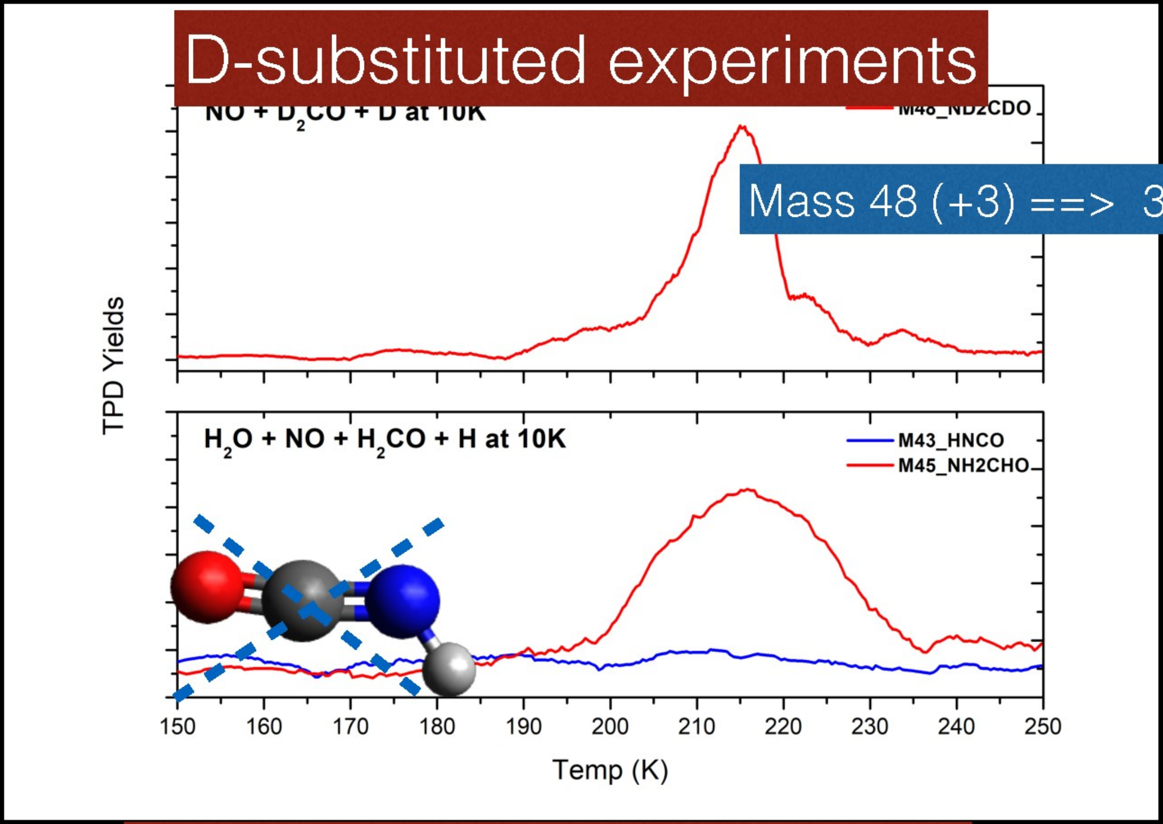


Three main species desorbing at 3 different temperatures

The problem of side reactions !

Nguyen et al, to be submitted

{$NO+H_2CO+H$} 4 ML10K



Formamide NH_2CHO

Dulieu et al, submitted

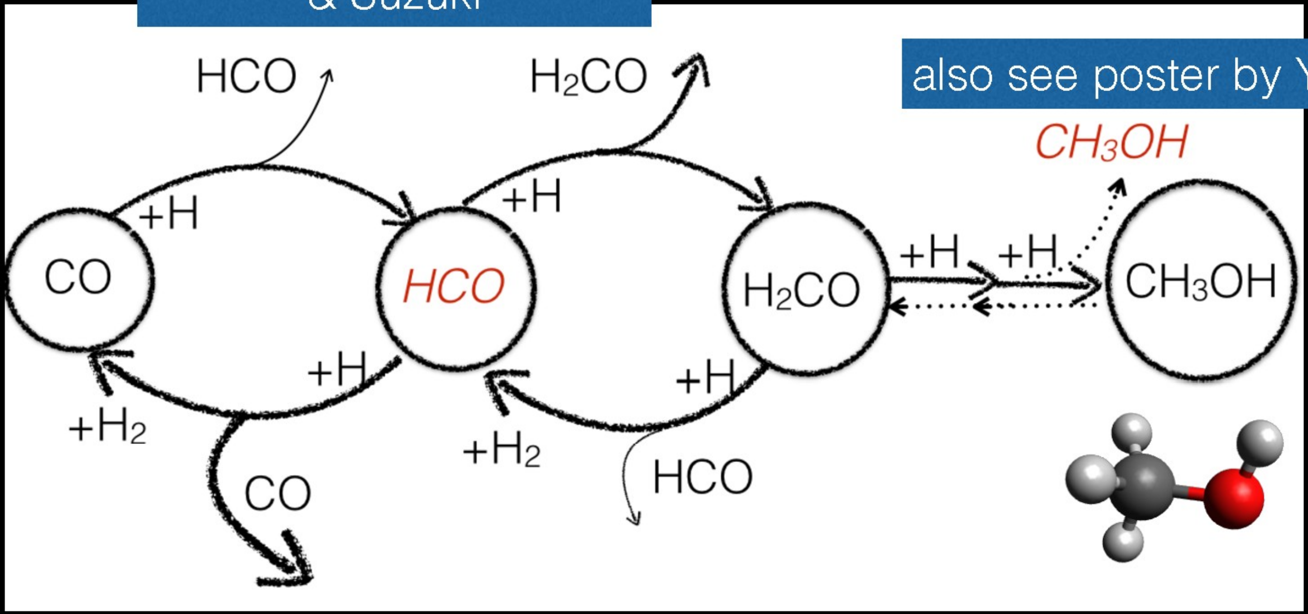
Only Formamide: no HNCO

- Formamide : prebiotic precursor (Saladino et al 2012)
- Not formed via {HNCO+H} (Noble et al 2015)
- see Lopes-Sepulcre et al 2015 for possible observational correlations
- No obvious chemial link on the solid phase

Chemistry of H_xCO

also see poster Komatsu & Suzuki

also see poster by Yarnall et al

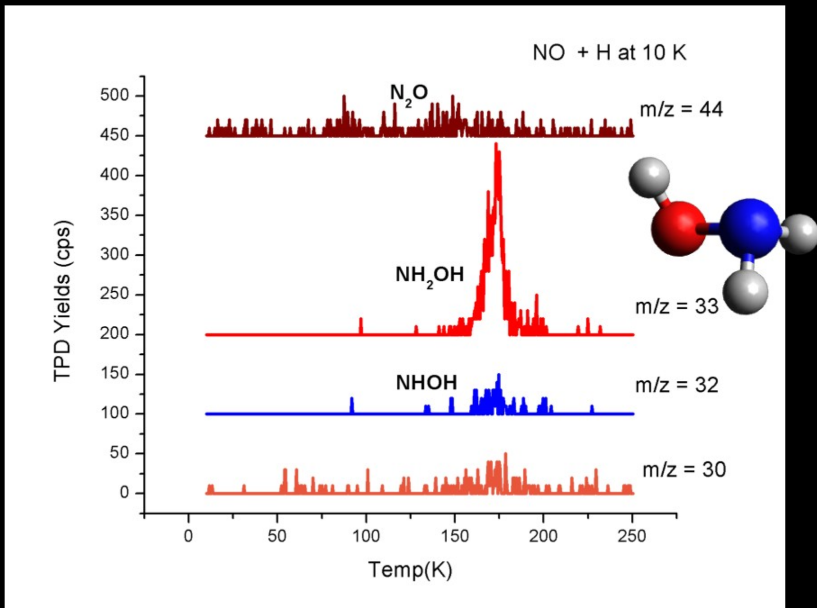


Minissale et al, MNRAS 2016

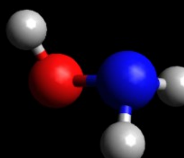
From CO to CH_3OH with chemical loops inducing chemical desorption, ‘small’ barrier

see also Hiraoka+ 2002/2004, Watanabe+ 2002/2007, +++,

$\{NO + H\}_{4\ ML\ 10K}$



$$NO \xrightarrow{+H} HNO \longrightarrow H_2NO \xrightarrow{+H} NH_2OH$$



$HNO \xrightarrow{+NO} N_2O + OH\ (\longrightarrow H2O)$

$HNO \xrightarrow{+HNO} N_2O + H_2O$

Congiu+2012, Congiu+2012, Ioppolo+2012, Ioppolo+2014

Possible *(first order side)* reactions

Chemistry of $H+H_2CO$

Chemistry of $H+NO$

	CO	HCO	H_2CO	CH_3O	CH_3OH
NO	R1A	R1B	R1C	R1D	R1E
HNO	R2A	R2B	R2C	R2D	R2E
H_2NO	R3A	R3B	R3C	R3D	R3E
NH_2OH	R4A	R4B	R4C	R4D	R4E
H_2O	R5A	R5B	R5C	R5D	R5E
OH	R6A	R6B	R6C	R6D	R6E
N_2O	R7A	R7B	R7C	R7D	R7E

at least 35 reactions ?

Example:

R2C : H2CO+HNO —> HNCO+ H2O ??

R4E : H2CO+NH2OH —> NH2CHO +H2O

R3C : H2CO+H2NO —> NH2CHO + OH (+H—> H2O)

Possible *(first order)* reactions

	CO	HCO	H_2CO	CH_3O	CH_3OH
NO	~~R1A~~	R1B	~~[illegible]~~	R1D	R1E
HNO	R2A	R2B	R2C	R2D	R2E
H_2NO	R3A	R3B	R3C	R3D	R3E
NH_2OH	~~[illegible]~~	R4B	R4C	R4D	~~R4E~~
H_2O	~~[illegible]~~	R5B	~~[illegible]~~	R5D	~~[illegible]~~
OH	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~	~~[illegible]~~
N_2O	~~[illegible]~~	R7B	R7C	R7D	~~R7E~~

Trivial impossibilities

- Cannot form formamide : HO+HCO —> (no N…)
- Energetic consideration (need Exothermic reaction)

    H2O+ CH3OH —> ??? ; NH2OH+CH3OH

- Simple basic depositions

CO + NO; H2CO + NO —> H2CO+NO !

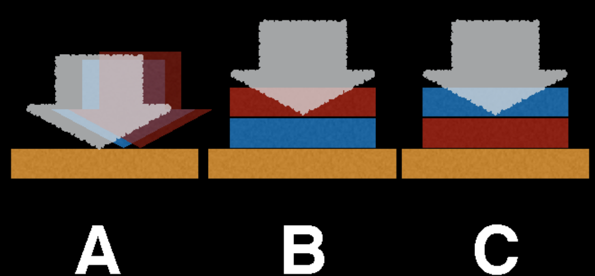
CO + N_2O…

Layered experiments: H_2CO on top of NO ***vs*** NO on top of H_2CO

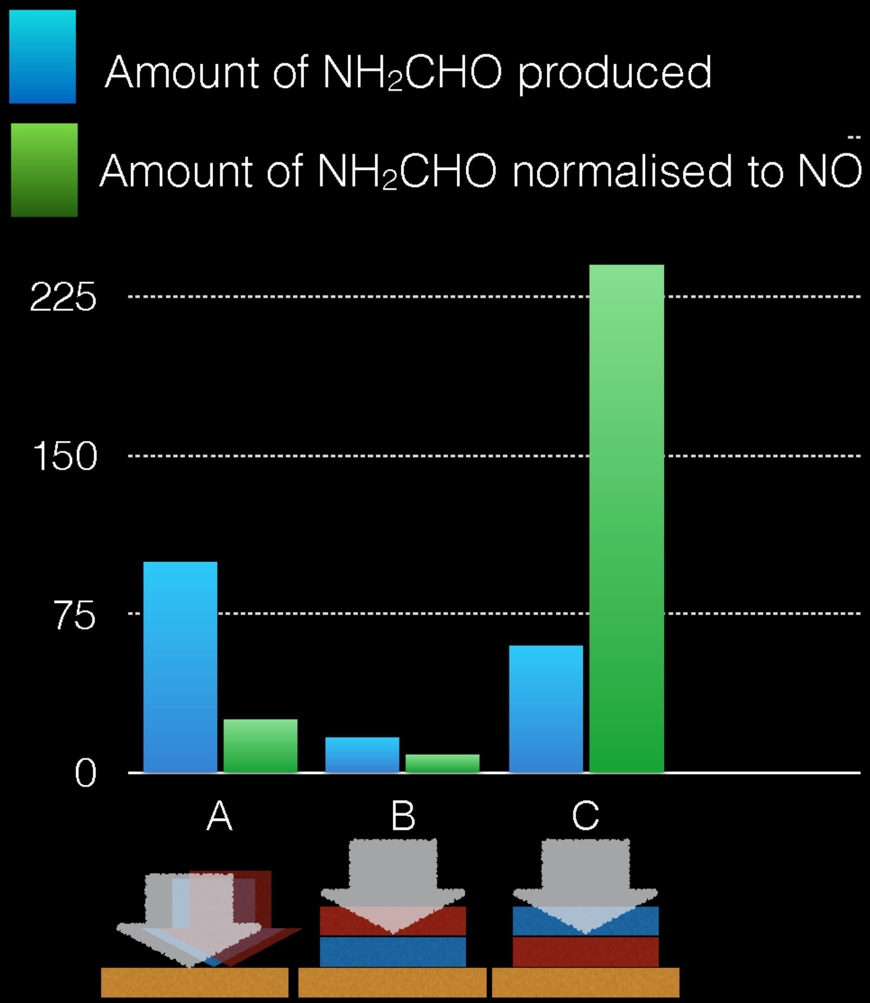
A $\{NO+H_2CO+H\}_{4\ ML 10K}$

B $\{NO\}_{2ML\ 10K}+\{H_2CO\}_{1ML\ 10K}+\{H\}_{5\ ML 10K}$

C $\{H_2CO\}_{2ML\ 10K}+\{N0\}_{1ML\ 10K}+\{H\}_{5\ ML 10K}$



Layered experiments:
H_2CO on top of NO ***vs*** NO on top of H_2CO



A $\{NO+H_2CO+H\}_{4\ ML 10K}$

B $\{NO\}_{2ML\ 10K}+\{H_2CO\}_{1ML\ 10K}+\{H\}_{5\ ML10K}$

C $\{H_2CO\}_{2ML\ 10K}+\{NO\}_{1ML\ 10K}+\{H\}_{5\ ML10K}$

Experiment B shows that the $\{H_2CO+H\}$ chemistry is not the driving force

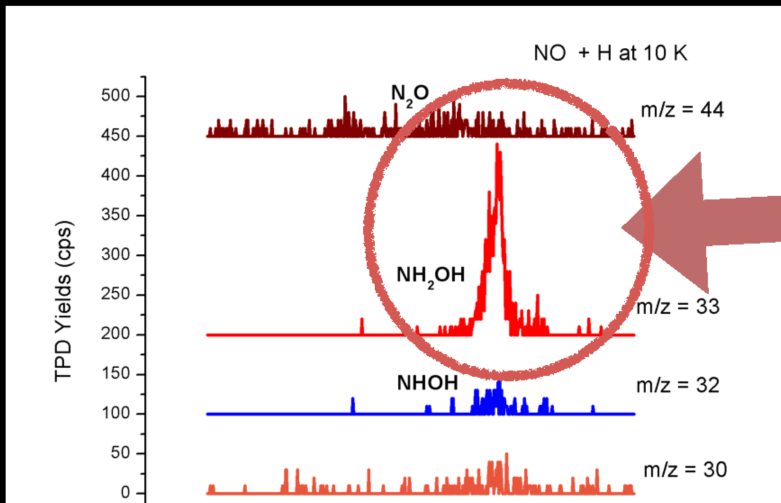
Experiment C shows that the $\{NO+H\}$ chemistry is the driving force

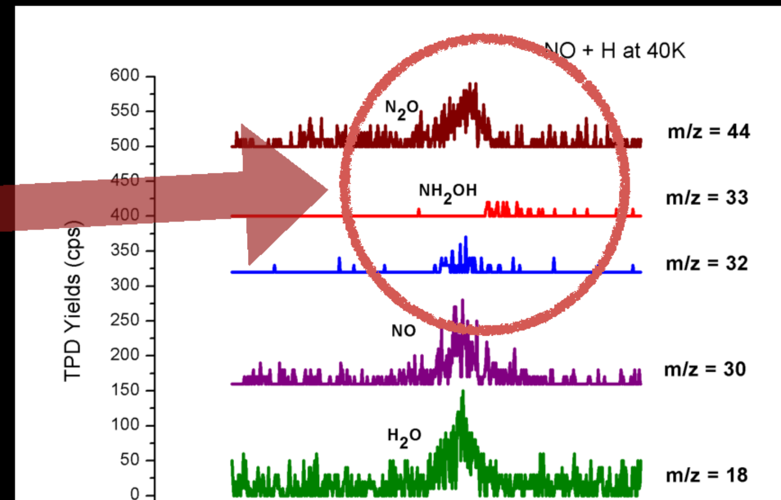
Possible *(first order)* reactions

	CO	HCO	H_2CO	CH_3O	CH_3OH
NO	R1A	R1B	R1C	R1D	R1E
HNO	R2A	R2B	R2C	R2D	R2E
H_2NO	R3A	R3B	R3C	R3D	R3E
NH_2OH	R4A	R4B	R4C	R4D	R4E
H_2O	R5A	R5B	R5C	R5D	R5E
OH	R6A	R6B	R6C	R6D	R6E
N_2O	R7A	R7B	R7C	R7D	R7E

Chemistry of H+NO

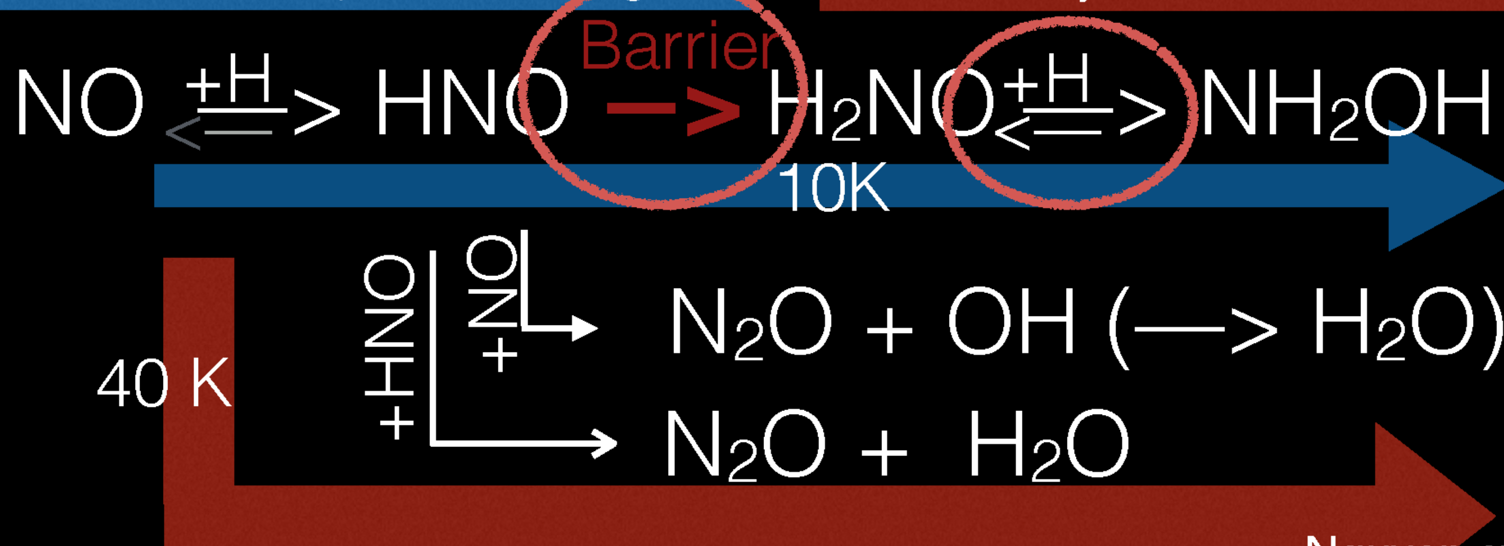
{NO +H}4 ML10K {NO +H}4 ML40K





10K: H long residence time
==> have time to proceed through QT

40K: residence time H very short
==> can only cross barrier-less reactions

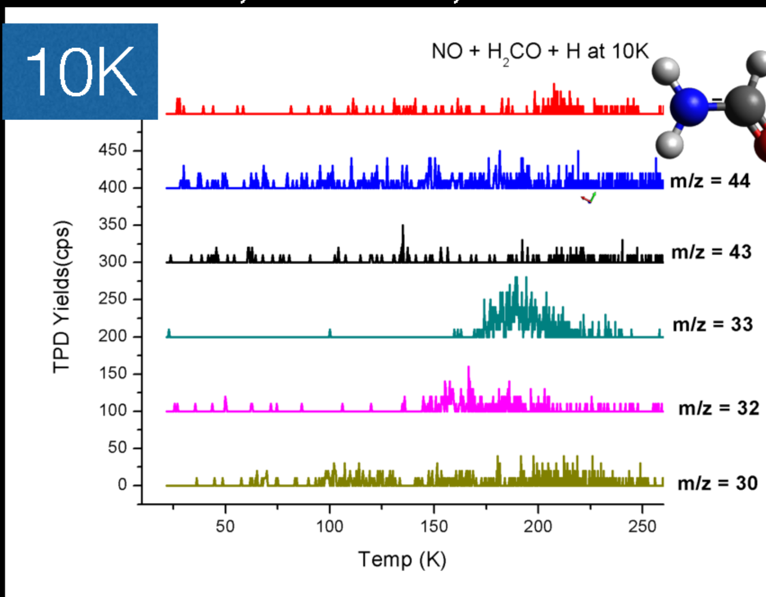


Nguyen et al B in prep.

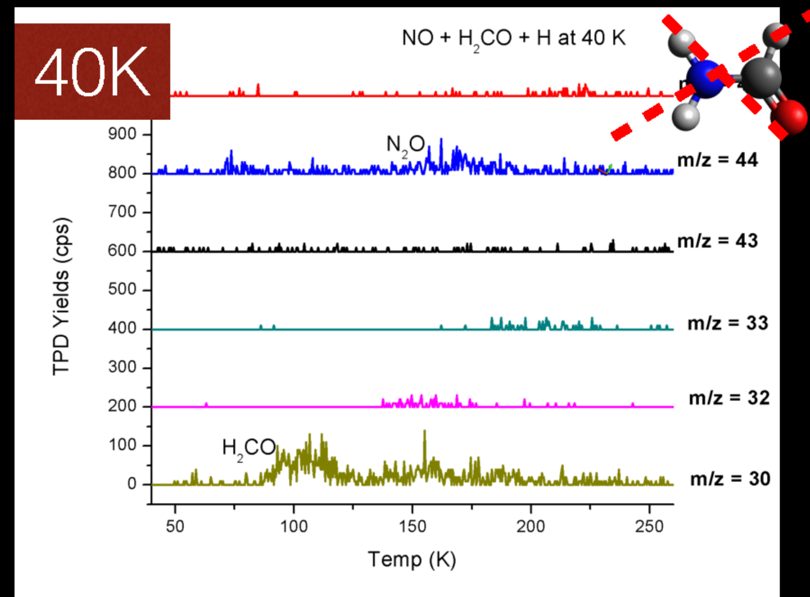
$\{H_2CO+NO+H\}_{4\ ML\ 10K}$

$\{H_2CO+NO+H\}_{4\ ML\ 40K}$

HNO, H_2NO, NH_2OH



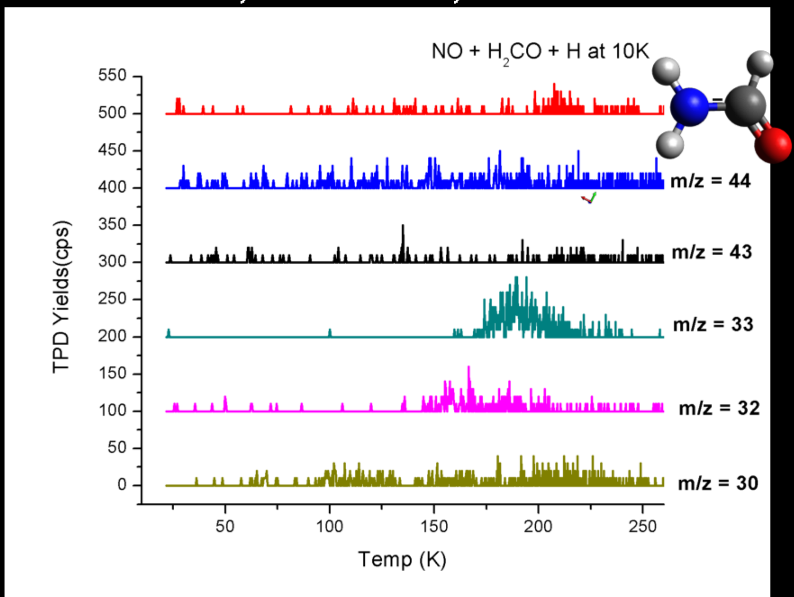
ONLY HNO



	CO	HCO	H_2CO	CH_3O	CH_3OH
NO	R1A	R1B	[illegible]	R1D	R1E
HNO	R2A	R2B	[illegible]	R2D	R2E
H_2NO	R3A	R3B	R3C	R3D	R3E
NH_2OH	R4A	R4B	R4C	R4D	R4E
H_2O	R5A	R5B	[illegible]	R5D	R5E
OH	R6A	R6B	[illegible]	R6D	R6E
N_2O	R7A	R7B	[illegible]	R7D	R7E

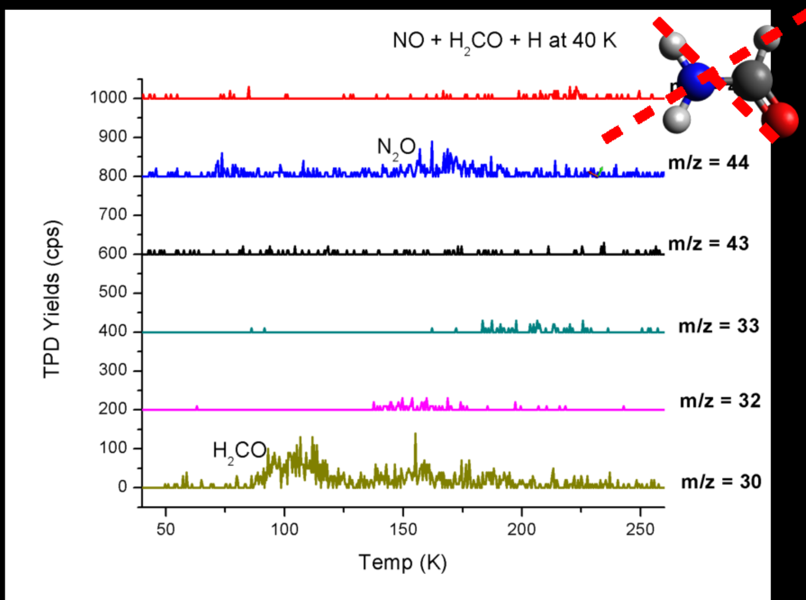
$\{H_2CO+NO+H\}_{4\ ML 10K}$

HNO, H_2NO, NH_2OH



$\{H_2CO +NO+H\}_{4\ ML 40K}$

ONLY HNO



	CO	HCO	H_2CO	CH_3O	CH_3OH
NO	R1A	R1B	[illegible]	R1D	R1E
HNO	R2A	R2B	R2C	R2D	R2E
H_2NO	R3A	R3B	R3C	R3D	R3E
NH_2OH	R4A	R4B	R4C	R4D	R4E
H_2O	R5A	R5B	[illegible]	R5D	R5E
OH	R6A	R6B	R6C	R6D	R6E
N_2O	R7A	R7E	[illegible]	R7D	R7E

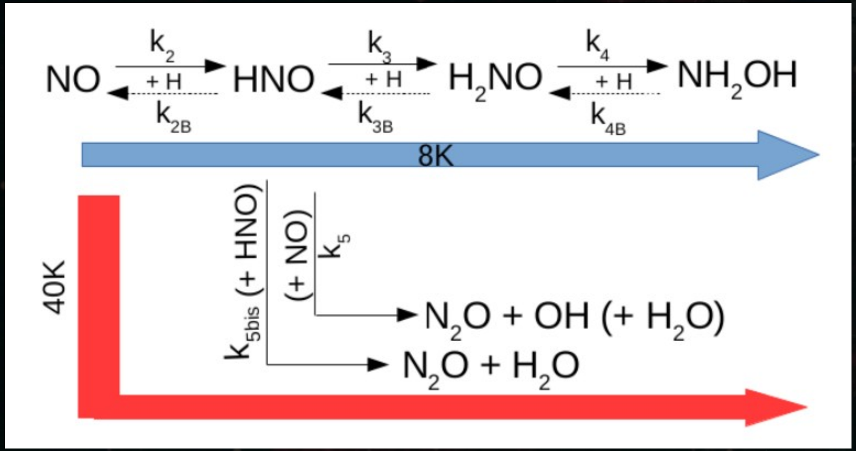
- Test $NH_2OH + H_2CO$ ==> weak
- 14 different set of conditions

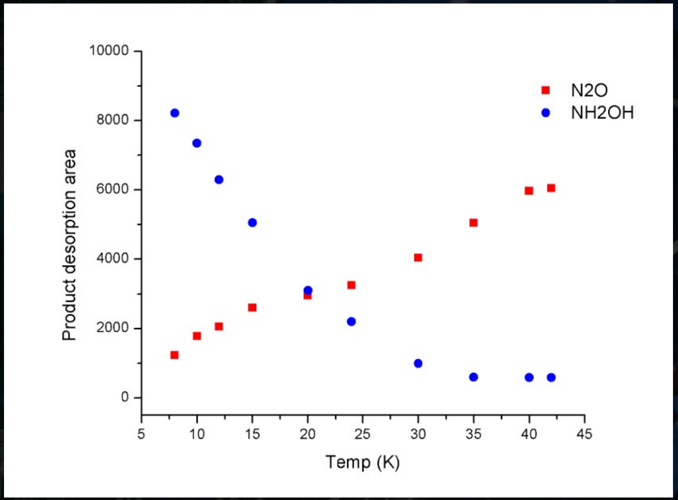
$H_2CO+NH_2O \longrightarrow NH_2CHO + OH$

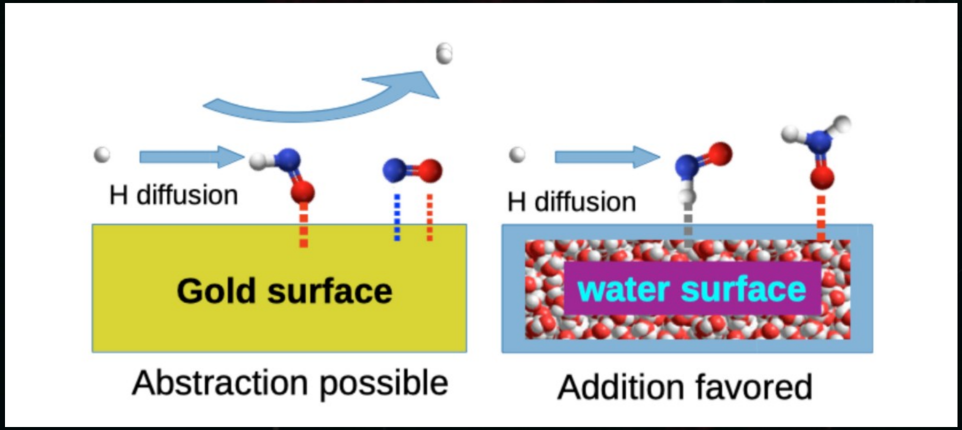
Nguyen et al in prep.

Le rôle de l'eau et l'importance des basses températures

{NO+H}







Calculs D. Talbi : orientation HNO empêche abstraction

Nguyen et al 2019

Par déposition de la phase gaz

Binding energies & environment)

Sticking may be not unity ?

Formation de la glace

Par transformation de la phase solide

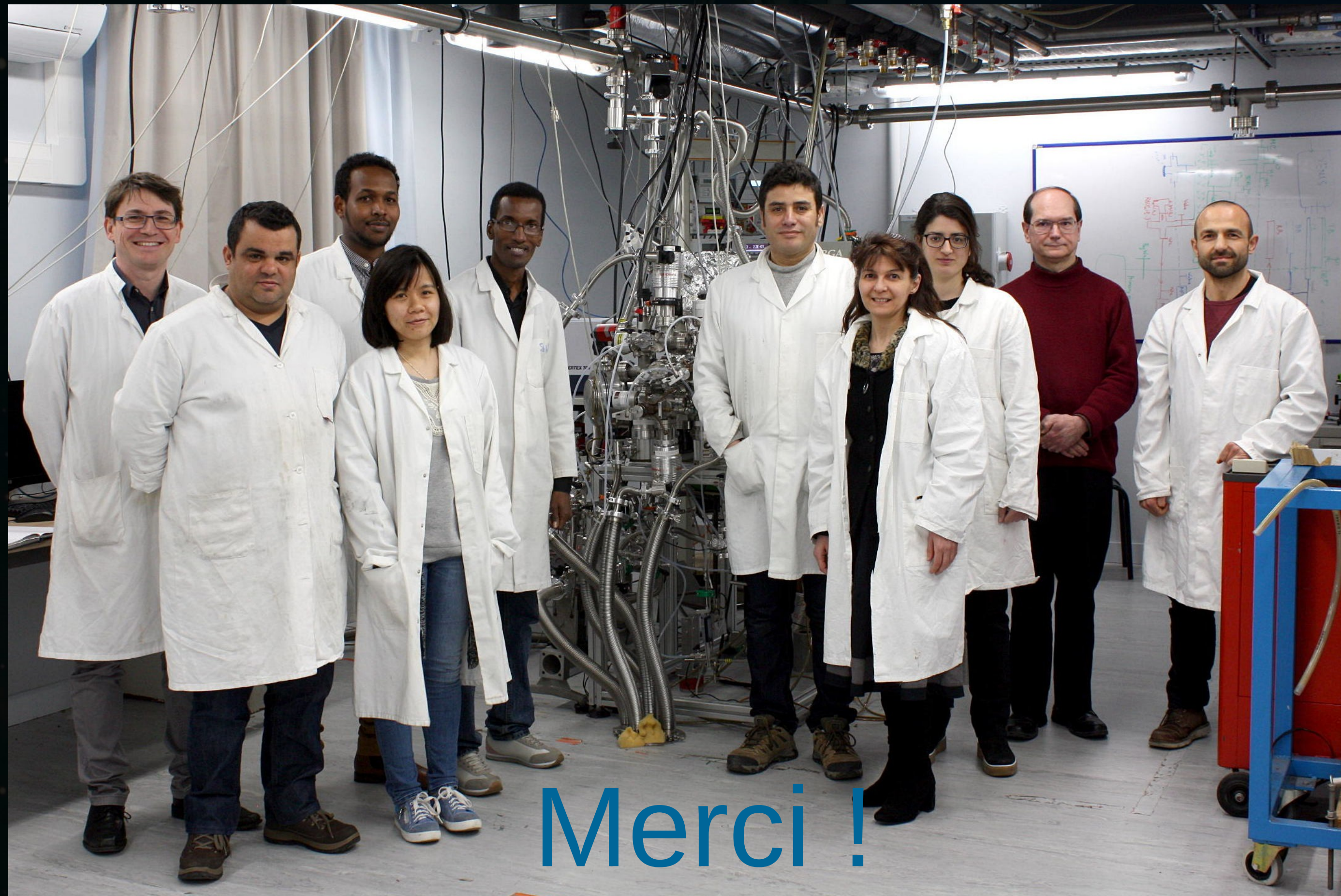
Transformation ‘initiale’ (chimie de surface)

Hydrogenation efficient at low T, but often in competition (abstraction)

Chemical loops provides radical that makes iCOMS

May lead to fragmentation, or chemical desorption…

Composition driven by gas composition, especially H/O



Et M. Minissale, V. Taquet, D. Talbi, J.C., Loison, S. Cazaux, S. Morisset et al, C. Fabre, Y. Ellinger et al.