FORMATION OF MOLECULES ON COLD INTERSTELLAR DUST GRAINS
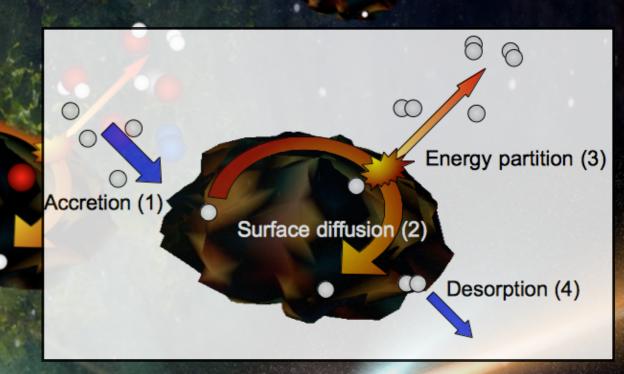
(c) « The colour of hydrogen » . E. Congiu

François Dulieu, LERMA
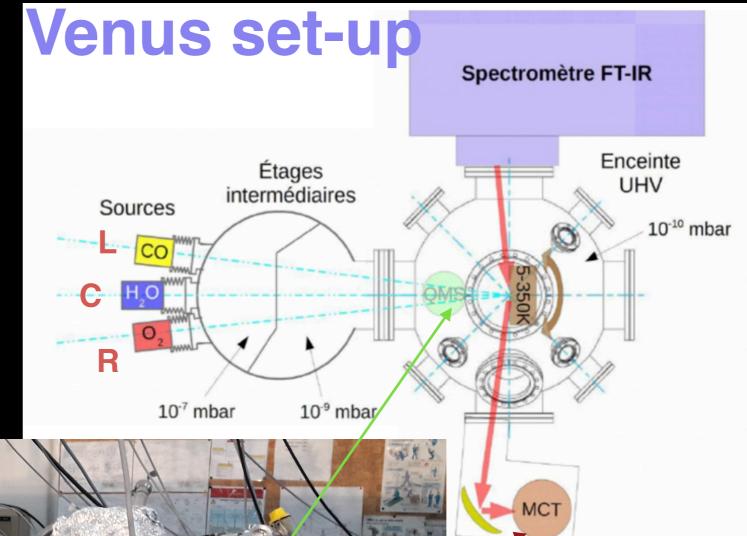
Cergy's team purpose:

- starting from atoms or small radicals/molecules

- without external energy

- **on** *surfaces*

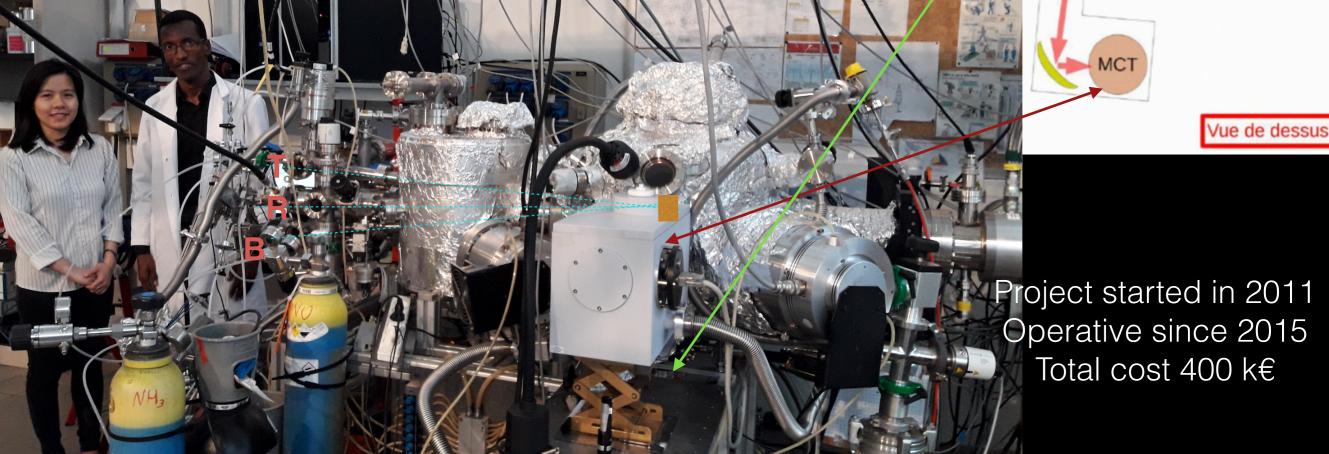- Understand processes, like the return in the gas phase, or the diffusion

Accretion (1)

Surface diffusion (2)

Energy partition (3)

Desorption (4)

The chemical tree, (c) FD

Ve**r**s de **No**u**v**elles **S**ynthèses

5 sources/ beams
Left, **R**ight **C**enter
Top and **B**ottom

Venus set-up

Spectromètre FT-IR

Sources
L — CO
C — H_2O
R — O_2

Étages intermédiaires

Enceinte UHV

10^{-10} mbar

5-350K

QMS

MCT

10^{-7} mbar 10^{-9} mbar

Vue de dessus

Project started in 2011
Operative since 2015
Total cost 400 k€

Thanh Nguyen and Abdellahi Sow in front of VENUS - Juin 2017

ASTRONOMY
AND
ASTROPHYSICS

Model Calculations of the Molecular Composition of Interstellar Grain Mantles

A. G. G. M. Tielens* and W. Hagen**

Laboratory Astrophysics Group, Rijksuniversiteit, 2300 RA Leiden, The Netherlands

Let's read together !

ASTRONOMY AND ASTROPHYSICS

Model Calculations of the Molecular Composition of Interstellar Grain Mantles

A. G. G. M. Tielens* and W. Hagen**

Laboratory Astrophysics Group, Rijksuniversiteit, 2300 RA Leiden, The Netherlands

Summary. The chemical composition of mantles accreting on interstellar grains has been calculated numerically with a chemical reaction scheme which comprises gas phase as well as grain surface reactions. The equilibrium abundances of the molecules in the gas are calculated using gas phase reactions except for H_2 formation. The composition of the growing grain mantle is determined on the basis of the relative accretion rates of the gas phase molecules and diffusion controlled surface reactions.

The results show that in most circumstances grain mantles consist of the molecules H_2O, H_2CO, N_2, O_2, CO, CO_2, H_2O_2, and NH_3. The relative concentrations of these species depend strongly on the physical conditions in the gas. The formation of H_2 on grain surfaces is examined in detail. We conclude that it proceeds through hydrogen abstraction from molecules like H_2CO, H_2S, N_2H_2, and N_2H_4. In essence these molecules act as enhanced binding sites for H atoms.

The infrared characteristics of the calculated grain mantles are discussed with an emphasis on the observed 3250 cm^{-1} "ice"
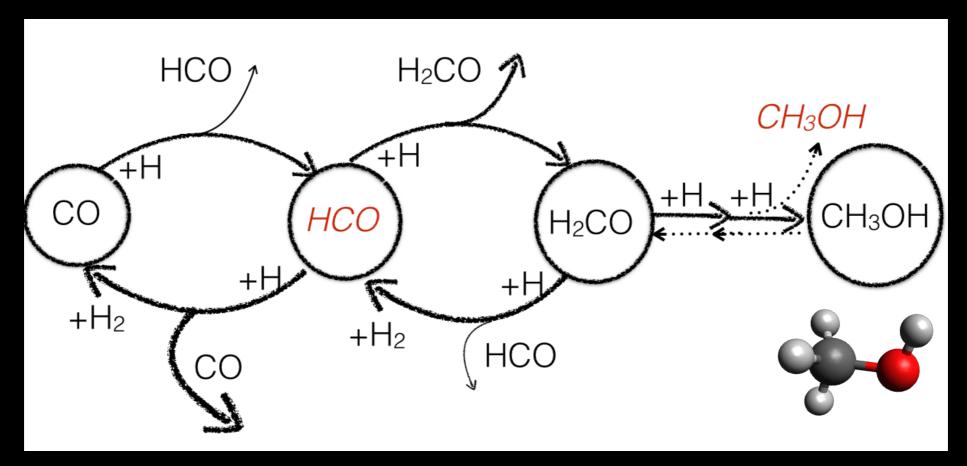
H_2 formation first !

H abstraction : very trendy

See also work by Oba, Watanabe and al …
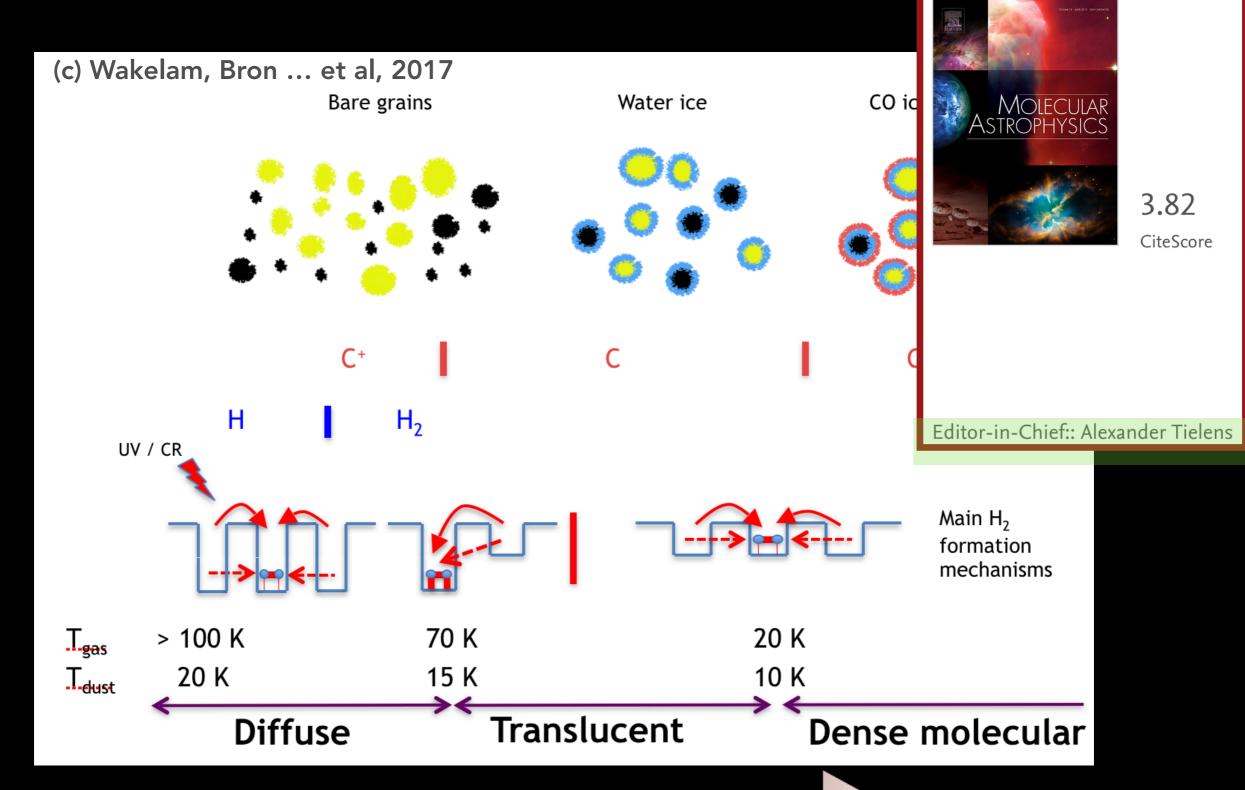
Chemistry of H_XCO

Minissale et al, MNRAS 2016

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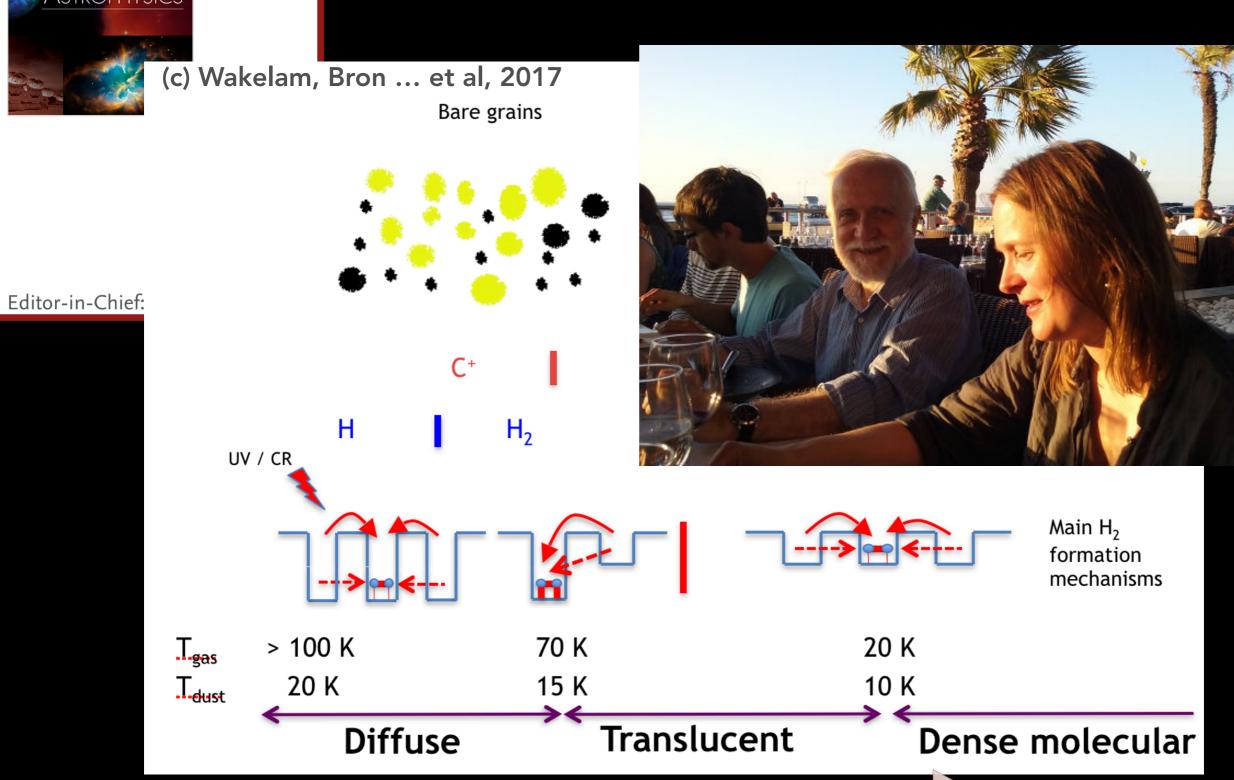inducing chemical desorption, 'small' barrier

see also Hiraoka+ 2004, Watanabe+ 2007, +++, poster 05 G. Fedoseev

(c) Wakelam, Bron ... et al, 2017

Density
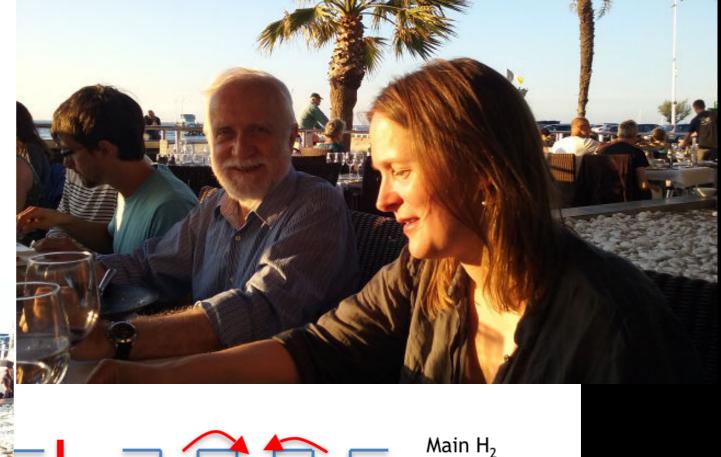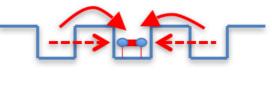
(c) Wakelam, Bron ... et al, 2017

Bare grains

C^+

H H_2

UV / CR

Main H₂ formation mechanisms

T_{gas} > 100 K   70 K   20 K
T_{dust} 20 K   15 K   10 K

Diffuse   **Translucent**   **Dense molecular**

Density

(c) Wakelam, Bron ... et al, 2017

Density

Model Calculations of the Molecular Composition of Interstellar Grain Mantles
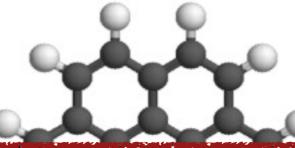
A. G. G. M. Tielens* and W. Hagen**

Laboratory Astrophysics Group, Rijksuniversiteit, 2300 RA Leiden, The Netherlands

1949). 750 cm^{-1} and may therefore escape detection because of atmospheric absorption (Hagen and Tielens, 1982; Hagen et al., 1982). The identification of interstellar solid H_2O can therefore be considered reliable. Recent spectra of the 3500 cm^{-1} to 1250 cm^{-1} region show broad absorption lines due to molecules in the solid phase

negligible (Gillett et al., 1975; Merrill et al., 1976). It is now generally accepted that graphite, silicate and "dirty ice" grains are present in the interstellar medium. However the relative importance of each material is still controversial. A bimodal dust model has been proposed in which large

in our scheme we have chosen to perform a time-independent calculation of the molecular abundances in dense interstellar clouds. An equilibrium solution is possible since for all the molecules at least one formation and one destruction reaction is included in the network. The assumption of chemical equilibrium is justified for the following reason. The observations with which the model calculations will be compared are made towards

schemes have been proposed (Watson and Salpeter, 1972a, b; Herbst and Klemperer, 1973; Mitchell et al., 1978; Black and Dalgarno, 1976; Prasad and Huntress, 1980; Allen and Robinson, 1977). Because of the large number of free parameters and the uncertainty in the reaction rates involved it is difficult to estimate the importance of the different processes. However, at intermediate densities the observed abundances of most of the simple gas phase

principle on the ion-molecule scheme of Herbst and Klemperer (1973). We have made minor modifications, mainly by updating reactions with new rate measurements. In total we have 1520 reactions involving 139 species. Only a quarter of these reactions have been studied in the laboratory. The rates and products of the remaining reactions are estimated by analogy with reactions involving chemically similar species. A detailed discussion of the gas phase chemistry is given in Prasad and Huntress (1980).

A. G. G. M. Tielens and W. Hagen: Molecular Comp

gro...ing grain mantle is then calculated from relativ rate. using diffusion controlled surface reactions.

a perfect H_2O surface. The surface scanning time on a realistic grain surface will be much longer. It will however still be much smaller than the evaporation time scale of an H atom ($2\,10^2$ s). Consequently an H atom can scan the grain surface many times before it evaporates.

Because the timescale for tunneling depends strongly on the surface structure. The surface potential will vary more or less periodically due to the discrete positions of the mantle molecules. For a particle adsorbed in a potential minimum (site) to move to a n neighbouring minimum an energy barrier of about half the binding energy has to be surmounted. The quantum mechanical tunneling time through a rectangular barrier with height E and
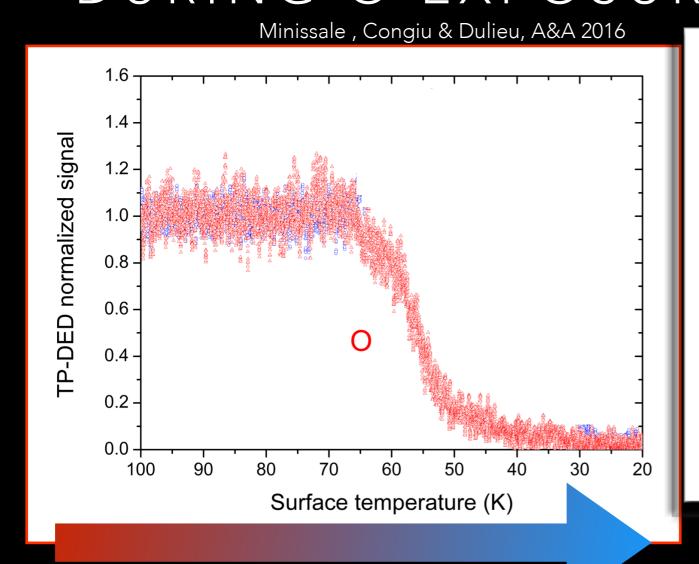
to estimate the binding energy of other molecules from their polarizabilities using the measured binding energy of H_2 and H_2O. For the atoms C, N, and O the binding energy will be about 800 K while for larger molecules, like O_2, it is about 1500 K (Watson and Salpeter, 1972a). For H_2O the binding energy is much higher. This is partly due to its strong dipole moment and partly to its ability to form hydrogen bonds. The binding energy
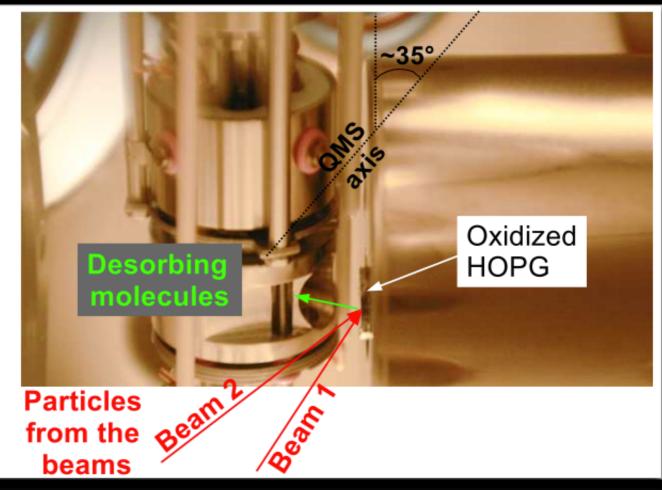
Binding energies (so diffusion) of O N and C are similar
They are less than CO N2 or O2

Because of its smaller mass and polarizability the binding energy of an H atom on the surface is lower than for H_2. Typically E_b is about 350 K for H. The thermal evaporation timescale for H atom is then about $2 \cdot 10^2$ s. This is much smaller than the time between H atom-grain collisions in a molecular cloud (10^5 s). This

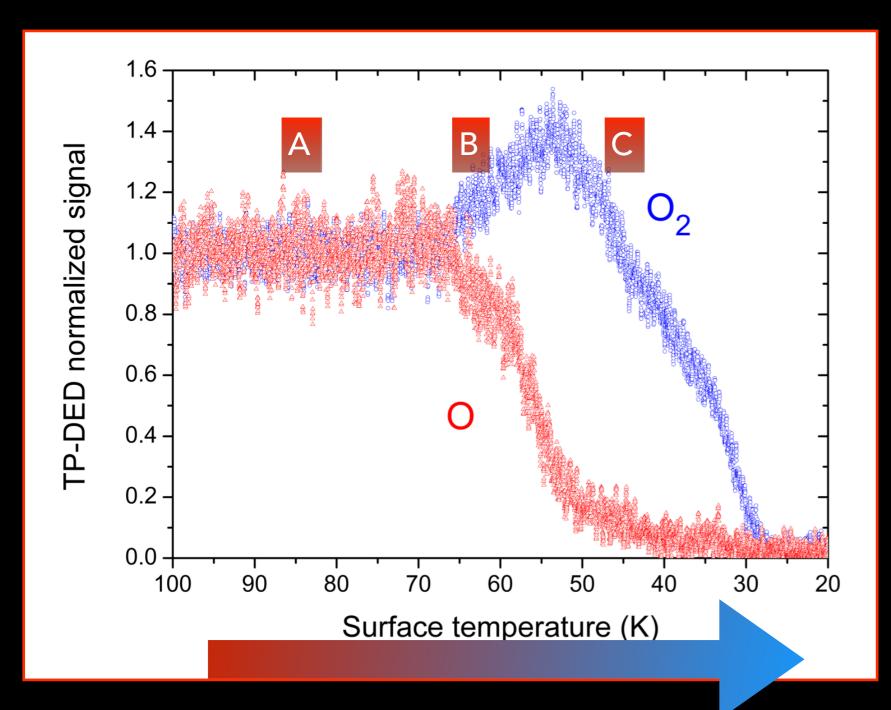# DIRECT GAS PHASE O MEASUREMENT DURING O EXPOSURE
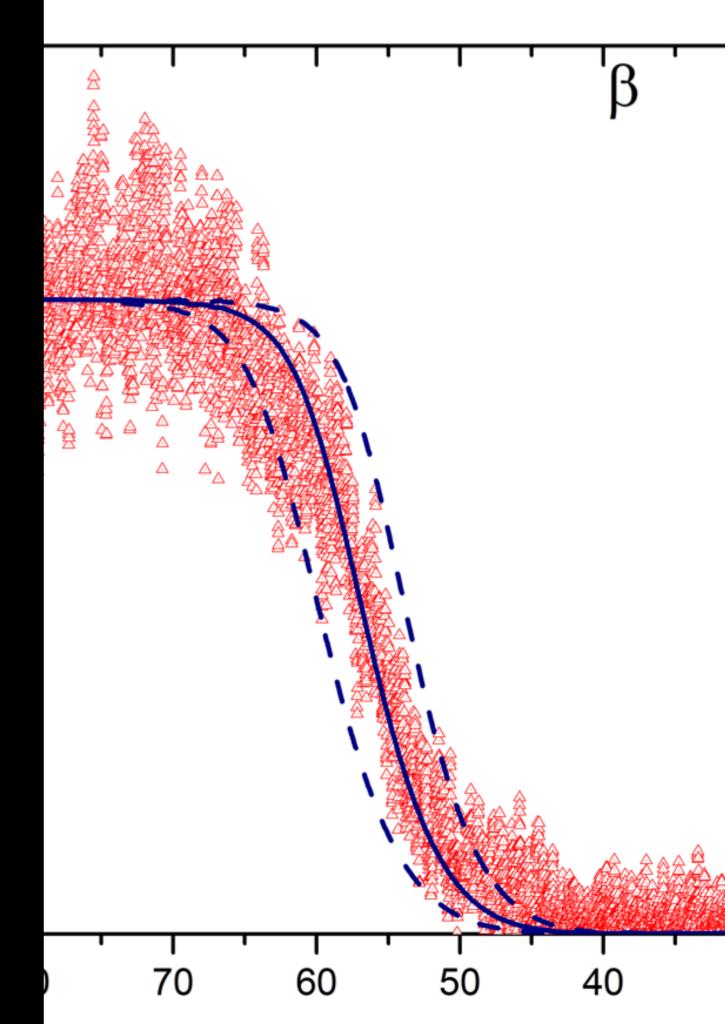
Minissale , Congiu & Dulieu, A&A 2016
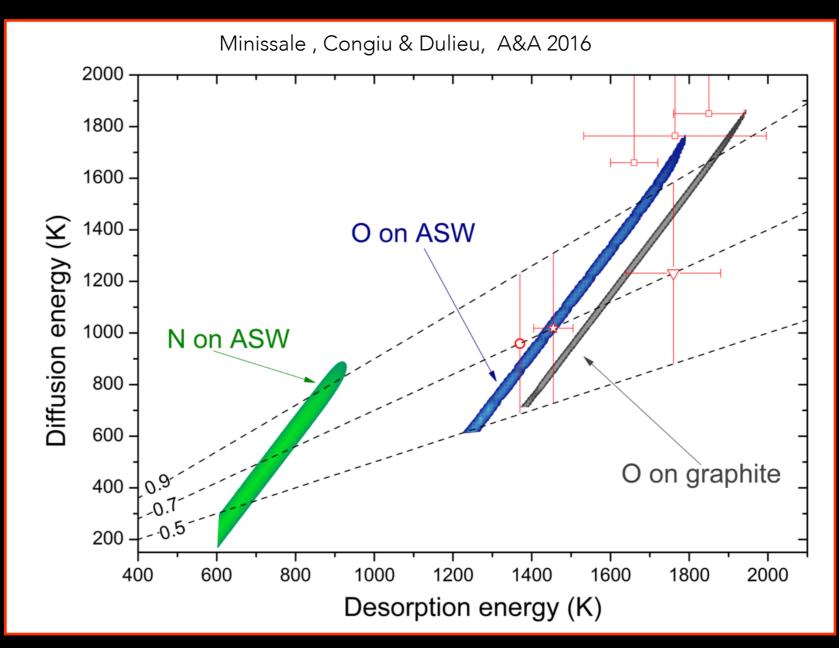
Disappearance of O : Residence time on the surface is increasing with the T-Decreasing ==> allows reactions to proceed ?

O TP-DED MODEL

- Assuming thermal (Arrhenius) regime

- Desorption and diffusion (followed by reactivity)

- Fast reactivity can compensate low binging energy
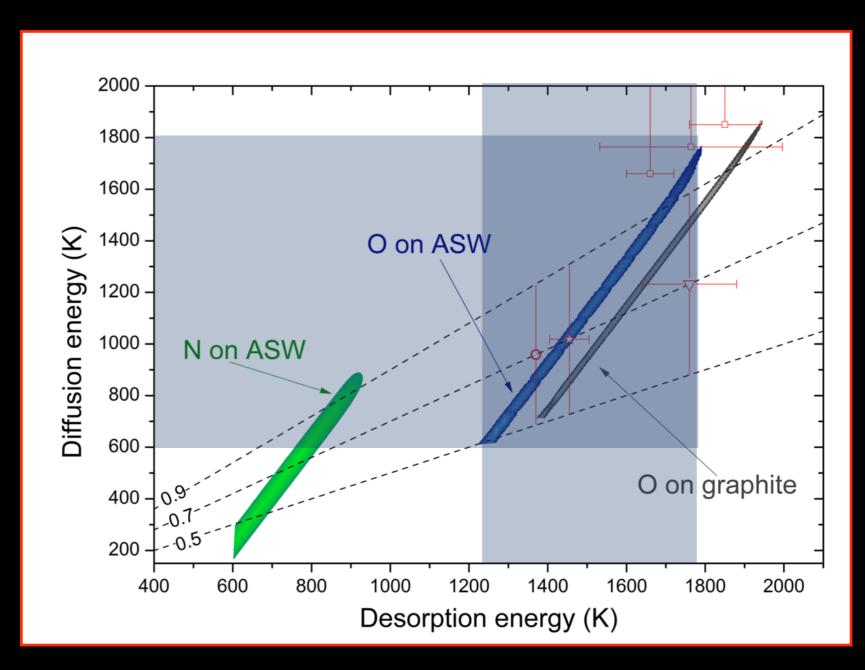
- ==> Couples of solutions (Desorption, Diffusion)

DIFFUSION VS DESORPTION

Minissale , Congiu & Dulieu, A&A 2016

Couples of best fit
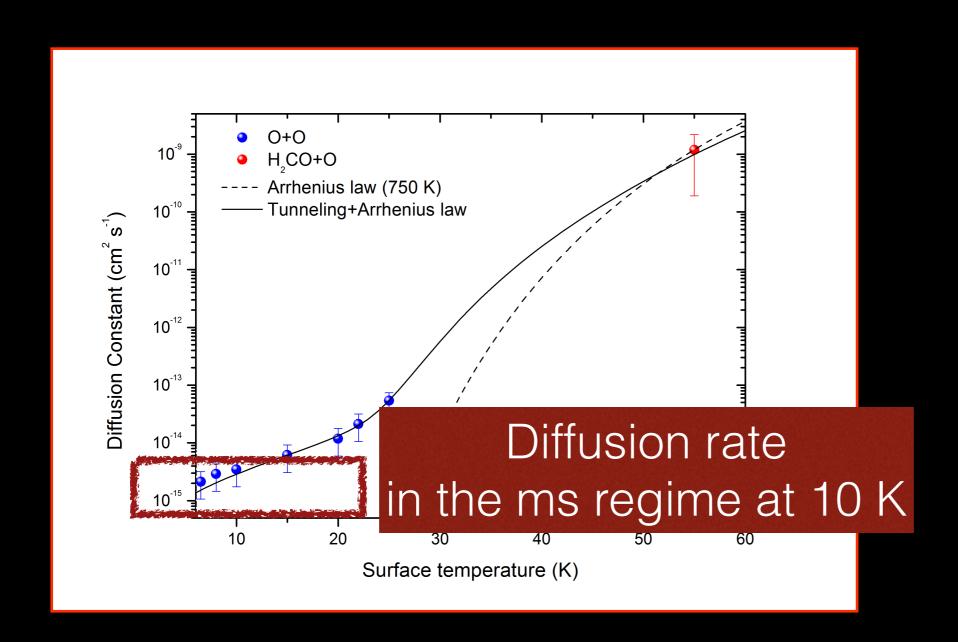
+ Previous calculations or measurements (indicating only binding energies)

DIFFUSION VS DESORPTION

Couples of best fit

Unfortunately (?) Binding energy is better constrained than diffusion

DIFFUSION BELOW THE DESORPTION TEMPERATURE

Diffusion rate
in the ms regime at 10 K

Etunn=520 K, Atunn=0.7 A°, Eclass=750 K
Mass effect

SUMMARY

- O and N binding couples of binding and diffusion energies can be derived.

- Ratio Ediff/Ebinding of 0.5-0.9 is possible, even other experiments tend to favor 0.5-0.6 (see H. Cuppen for comparison with molecules).

- Typical values for binding energies for O [1300-1700K] and [600-900K] for N

- **This is larger than the binding energy of CO**

- At low T, Quantum tunneling dominates over thermal hopping for O atoms

The barrier against diffusion, E_d, can be estimated from laboratory experiments employing matrix isolation techniques (Paper I). In this way the classical hopping time scale for atoms from the second period of the periodical system on a H_2O surface at 10 K has been estimated to be 10^{-3} s. For third period atoms this timescale is about 10 s. For molecules this timescale will be very long. The timescale to scan the whole surface is now given by (Paper I):
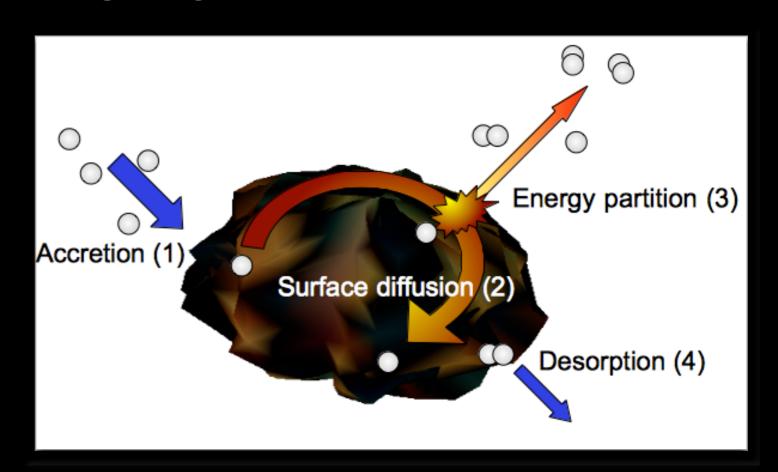
Comparing these timescales for scanning the whole surface with the collision timescale of radicals with a grain, about 10^5 s at a density of 10^4 cm^{-3}, shows that only H, H_2, C, N, and O can undergo appreciable migration on a grain surface within an accretion or evaporation timescale. The other species remain trapped in their site. We have therefore selected only reactions of species with the migrating species H, H_2, C, N, and O. The diffusion of these species ends when they recombine with each

COMMON KNOWLEDGE ?

And polarisability argument for H/H$_2$?
still valid ?

Cergy's team purpose:
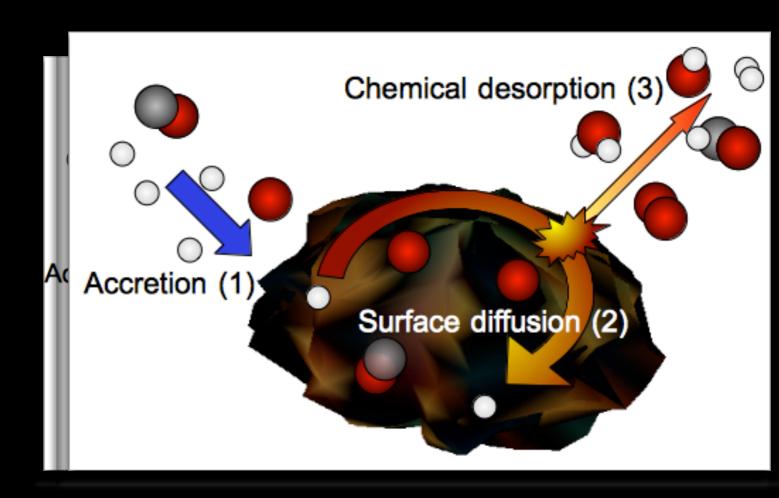
HOW FAR CAN MOLECULAR COMPLEXITY GROW ?

- starting from atoms or small radicals

- without external energy

- **on** *surfaces*

- Understand processes, like the return in the gas phase, the diffusion, the nuclear spin conversion or the reactivity

Accretion (1)
Surface diffusion (2)
Energy partition (3)
Desorption (4)

Diffusion & desorption of O,H
Chemical desorption
H_2O, H_2, O_2 CO_2 formation…
Desorption & transformation

Here we focus iCOMs synthesis

Chemical desorption (3)

Accretion (1)

Surface diffusion (2)

Diffusion & desorption of O,H

Chemical desorption

H_2O, H_2, O_2 CO_2 formation…

Desorption & transformation
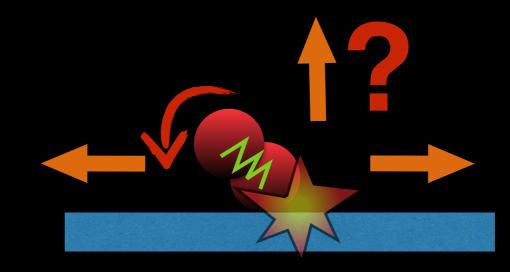
What could be the mechanism of chemical desorption ?
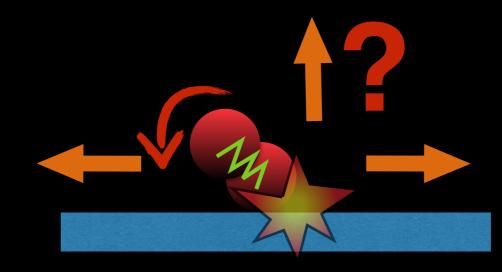
Source of energy: Enthalpy of formation (50,000 K)

Chem
- Chemi
- Adsorp
- Degree
- Energy transfer to the substrate (or neighbor)

will be transferred to neighbouring molecules through multipolar-multipolar interaction, will flow into local rotational modes or will be radiated away. Since only a small amount of energy goes to local center-of-mass translational motion, only a small fraction of all newly formed molecules will evaporate (Paper I).
(2) A fraction of the formation energy will be converted into heat. The resulting temperature rise depends on the size of the

Minissale&Dulieu JCP 14
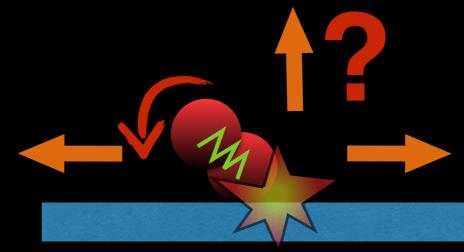
Key point: how the initial energy is converted in ⬆ ?

And the chemical network…

and (16). If $N_{cor} = 1$ then all H atoms has a 50% chance of tunneling through an activation barrier of about 4000 K and reacting with that species. If $N_{cor} = 10^4$ (e.g. 1% surface coverage) then a H atom has a 50% chance of tunneling through an activation barrier of 8000 K and reacting with that species. Consequently the reactions of H listed in Table 2 are by of importance on interstellar grain surfaces. This mechanism is not effic

R_{ph} whe pho o, spec
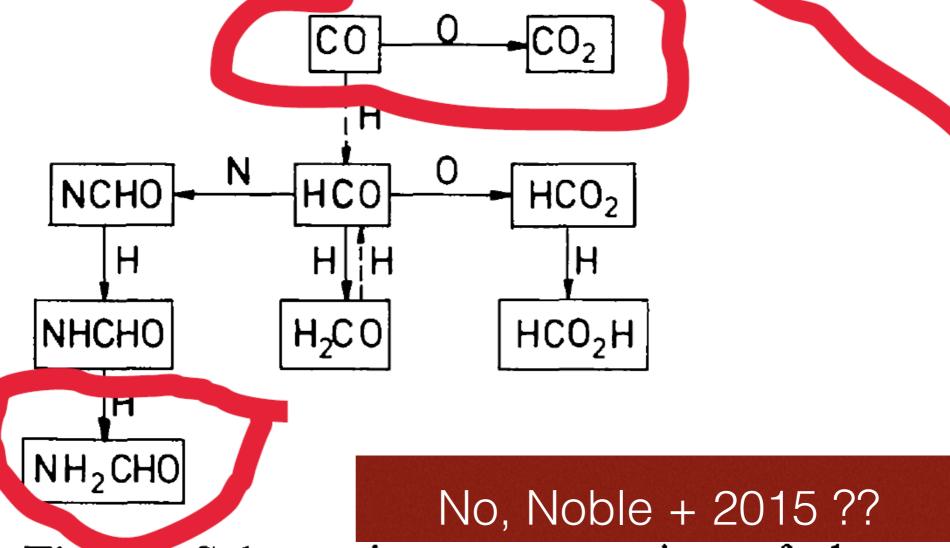
With hydrogenation, no matter the barrier ?

Fig. 3. Schematic representation of the most im
surface reactions involved in the carbon chemi
arrows indicate reactions with activation barriers of
molecules (see Table 2)

Yes, but barrier Minissale + 2014

No, Noble + 2015 ??

activation energy of $\sim 15,0$

2) safely be disregarded (Tully,

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

is of statistical importance.

(Schiff. 1973). We have take

Yes, Oba + 2014

see also the discussion of H2 coverage,
and read Amiaud + 2006, Amiaud+2007,Amiaud+2015

Some molecules synthetized in my lab
10K, no photon…

H2 O2 O3 OH H2O H2O2

N2 NO HNO HNOH NH2OH

NH2CHO CO H2CO CH3OH
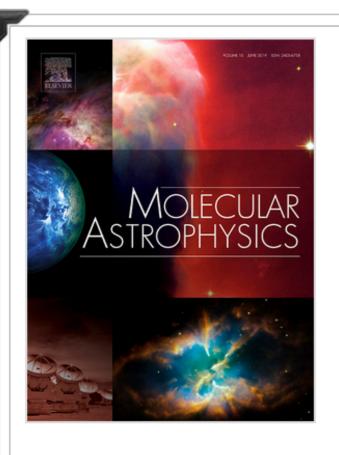
CH4 NH3 N2O NO2 N2O2

H2S HS H2CS OCS CS2

CH3CH2CN NH2CH3CHO

NH2CH3OH HCOCH2OH …

IN TIELENS&HAGEN 1982 ???

+ salts

1. Both gas phase and surface reactions are important in determining the composition of mantles accreted on interstellar grains.

2. Molecules like HCO, HS, N_2H, and N_2H_3 act as enhanced binding sites for molecular hydrogen formation on interstellar grain surfaces.

3. The bulk composition of grain mantles consists of H_2O, H_2CO, N_2, CO, O_2, CO_2, H_2O_2, and NH_3 in varying ratios, plus other trace constituents. The exact composition reflect the physical conditions in the gas phase.

4. The observed $3250\ cm^{-1}$ "ice" band can be explained by mantles accreted at a density of $n_0 \sim 10^3$–$10^4\ cm^{-3}$. The low frequency wing on this feature is then mainly due to absorption by H_2CO. In some circumstances absorption of H_2O hydrogen bonded to NH_3 may also contribute appreciably to this wing. Moderate resolution spectra of the $3250\ cm^{-1}$ band could discriminate between these two possibilities and yield further insight into cloud evolution.

5. The observed $1670\ cm^{-1}$ band is attributed to absorption by H_2O and H_2CO. The observed $1475\ cm^{-1}$ band is too strong to be due to absorption by H_2CO and H_2O_2.

6. Many of the molecules present in the calculated grain mantles have concentrations too low or absorption strengths too small to make them detectable with present day techniques. However it is expected that when the signal to noise ratio and frequency resolution are improved even the weaker interstellar features should become measurable. These observations are expected to yield a wealth of information on the chemical history of the grains and the gas.

MOLECULAR ASTROPHYSICS
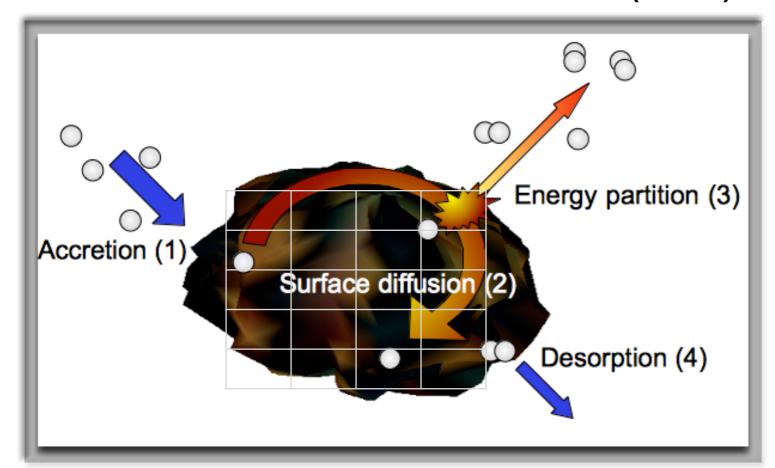
3.82 CiteScore

Editor-in-Chief:: Alexander Tielens

Thank you !

This was not a talk sponsored by X. T.

2 PHD positions available in Cergy, please contact me !

Tienlens' formalism (2D)

Accretion (1)
Surface diffusion (2)
Energy partition (3)
Desorption (4)

Reality (1.5 D)

Accretion (1)
Surface diffusion (2)
Energy partition (3)
Desorption (4)