FORMATION OF MOLECULES ON COLD INTERSTELLAR DUST GRAINS

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

François Dulieu, LERMA

CELEBRATING THE FIRST 40 YEARS OF ALEXANDER TIELENS’ CONTRIBUTION TO SCIENCE:
THE PHYSICS AND CHEMISTRY OF THE ISM, Avignon Sept. 2019
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

**How far can molecular complexity grow?**

**The chemical tree, (c) FD**
Vers de Nouvelles Synthèses

5 sources/ beams
Left, Right Center
Top and Bottom

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

Received February 1, accepted May 19, 1982

Let’s read together!
Model Calculations of the Molecular Composition of Interstellar Grain Mantles

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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$_2$O, H$_2$CO, N$_2$, O$_2$, CO, CO$_2$, H$_2$O$_2$, and NH. 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$_2$CO, H$_2$S, N$_2$H$_2$, and N$_2$H$_4$. 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" stretching band.
Chemistry of H\textsubscript{x}CO

From CO to CH\textsubscript{3}OH with chemical loops inducing chemical desorption, ‘small’ barrier

see also Hiraoka+ 2004, Watanabe+ 2007, +++, poster 05 G. Fedoseev
H₂ FORMATION ON GRAINS, SCHEMATIC VIEW

Bare grains

Water ice

CO ice

Main H₂ formation mechanisms

Density

T_{gas} > 100 K
T_{dust} 20 K

T_{gas} 70 K
T_{dust} 15 K

T_{gas} 20 K
T_{dust} 10 K

Diffuse

Translucent

Dense molecular

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

Molecular Astrophysics

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H$_2$ FORMATION ON GRAINS, SCHEMATIC VIEW

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

Bare grains

C$^+$

UV / CR

H

H$_2$

$T_{\text{gas}}$ > 100 K

$T_{\text{dust}}$ 20 K

70 K

20 K

15 K

10 K

Diffuse

Translucent

Dense molecular

Density

Main H$_2$ formation mechanisms
FORMATION ON GRAINS, SCHEMATIC VIEW

Bare grains

Main $\text{H}_2$ formation mechanisms

20 K
10 K

Density

Diffuse Translucent Dense molecular
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its an... However, in H$_2$O (as) this absorption feature occurs around 1949). 750 cm$^{-1}$ and may therefore escape detection because of atmospheric absorption (Hagen and Tickens, 1962; Hagen et al., 1982). The identification of interstellar solid H$_2$O can therefore be considered reliable.

Recent spectra of the 2500 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 model that accounts for the variability of which the emission of different
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 reasons. 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 of 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 1528 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-
growing grain mantle is then calculated from rel-
rate, using diffusion controlled surface reactions.

REFERENCES? COMMON KNOWLEDGE?

a perfect H$_2$O surface. The surface scanning time on a realistic
a grain surface will be much longer. It will however still be much
smaller than the evaporation time scale of an H atom ($2 \times 10^2$ s).
Consequently an H atom can scan the grain surface many times
before it evaporates.

Because the timescale for tunneling depends strongly on the
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
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
(Pa)
Binding energies (so diffusion) of O N and C are similar. They are less than CO N2 or O2.
Disappearance of O: Residence time on the surface is increasing with the T-Decreasing $$\Rightarrow$$ allows reactions to proceed?
Temperature is slowly reduced (-1K/min)

Direct gas phase O measurement during O exposure

A: O accommodation and desorption compensate each other

B: O is staying long enough to form O$_2$ which is desorbing

C: O$_2$ is staying long enough to form O$_3$ which is staying on the surface

Residence time is increasing with the T-Decreasing
OTP-DED MODEL

- Assuming thermal (Arrhenius) regime
- Desorption and diffusion (followed by reactivity)
- Fast reactivity can compensate low binding energy
- ==> Couples of solutions (Desorption, Diffusion)
DIFFUSION VS DESORPTION

Couples of best fit

Previous calculations or measurements (indicating only binding energies)
Unfortunately (?) Binding energy is better constrained than diffusion
DIFFUSION BELOW THE DESORPTION TEMPERATURE

$E_{\text{tunn}} = 520 \text{ K}$, $A_{\text{tunn}} = 0.7 \text{ Å}^2$, $E_{\text{class}} = 750 \text{ K}$

Minissale et al, *PRL*, 2013
Minissale, Congiu & Dulieu, *JCP*, 2014
Congiu et al, *FD*, 2014

**Diffusion rate in the ms regime at 10 K**

$E_{\text{tunn}} = 520 \text{ K}$, $A_{\text{tunn}} = 0.7 \text{ Å}^2$, $E_{\text{class}} = 750 \text{ K}$

Mass effect
SUMMARY

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

• Ratio $E_{\text{diff}}/E_{\text{binding}}$ 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 periodic table on a H$_2$O 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 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
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

Diffusion & desorption of O,H
Chemical desorption
H₂O, H₂, O₂, CO₂ formation...
Desorption & transformation

Here we focus iCOMs synthesis
Diffusion & desorption of O,H

Chemical desorption

H₂O, H₂, O₂, CO₂ formation...

Desorption & transformation

DULIEU+2013, MINISSALE+2016
CAZAUX +2016, OBA+2018
What could be the mechanism of chemical desorption?

Source of energy: Enthalpy of formation (50,000 K)

Chemical desorption: 4 parameters?
- Chemical energy available
- Adsorption energy of products
- Degree of freedom
- Energy transfer to the substrate (or neighbor)

Key point: how the initial energy is converted in the...
What could be the mechanism of chemical desorption?

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Key point: how the initial energy is converted in ?
What could be the mechanism of chemical desorption?

**Source of energy:** Enthalpy of formation (50,000 K)

**Chemical desorption:** 4 parameters:
- Chemical energy available
- Adsorption energy of products
- Degree of freedom
- Energy transfer to the substrate (or neighbor)

(2) A fraction of the formation energy will be converted into heat. The resulting temperature rise depends on the size of the...
With hydrogenation, no matter the barrier?

and (16). If $N_{\text{cor}} = 1$ then an H atom has a 50% chance of tunneling through an activation barrier of about 4000 K and reacting with that species. If $N_{\text{cor}} = 10^4$ (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 3 are emblematic of such conditions, as they are of significant importance on interstellar grain surfaces. This mechanism is not efficient...
Fig. 5. Schematic representation of the most important surface reactions involved in the carbon chemistry. Black arrows indicate reactions with activation barriers of molecules (see Table 2).
activation energy of $\sim 15,000$ kcal/mol can safely be disregarded (Tully, 1973). For comparison, the activation energy of $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ is of statistical importance. We have taken

$$\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$$

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  H2O2
N2  NO  HNO  HNOH  NH2OH
NH2CHO  CO  H2CO  CH3OH
CH4  NH3  N2O  NO2  N2O2

H2S  HS  H2CS  OCS  CS2
CH3CH2CN  NH2CH3CHO
NH2CH3OH  HCOCH2OH  …

+ salts

IN TIELENS & HAGEN 1982 ???
1. Both gas phase and surface reactions are important in determining the composition of mantles accreted on interstellar grains.

2. Molecules like HCO, HS, N₂H, and N₂H₃ act as enhanced binding sites for molecular hydrogen formation on interstellar grain surfaces.

3. The bulk composition of grain mantles consists of H₂O, H₂CO, N₂, CO, O₂, CO₂, H₂O₂, and NH₃ in varying ratios, plus other trace constituents. The exact composition reflects 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 H₂CO. In some circumstances absorption of H₂O hydrogen bonded to NH₃ 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 H₂O and H₂CO. The observed 1475 cm⁻¹ band is too strong to be due to absorption by H₂CO and H₂O₂.

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.
This was not a talk sponsored by X. T.

2 PHD positions available in Cergy, please contact me!
Tienlens’ formalism (2D)

Reality (1.5 D)