Effect of porosity and non-planarity on icy grains chemistry in molecular clouds

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The recent observation by the Rosetta probe of large amounts of O_2 in the coma of comet 67P (3.8 % wrt water on average) was unexpected. The large amount of O_2 and its strong correlation with water indicates that it was incorporated in the comet during its formation when icy grains agglomerated to form the cometary nucleus. This suggests that the production of O_2 in icy grains in molecular clouds or in the protosolar nebula is much higher than predicted by models. Molecular cloud and protosolar nebula chemistries involve a strong interaction between the gas phase and the solid phase consisting in icy grains. Icy grains are made of a silicate nucleus on which an icy layer grows due to surface chemistry and exchanges with the gas phase. This icy layer is highly porous and uneven. We investigate the effect of surface non-planarity and porosity on icy grain chemistry. With a simple model we estimate its effect on atomic and molecular exchange between the solid and gas phases. These results suggest that hydrogen is more likely to out-diffuse from the grain than heavier species like O or O_2 on uneven or porous surfaces. We estimate the impact of this enhanced hydrogen escape and of the resulting enrichment of the grains in radiolytic oxygen on the composition of the grain icy mantle and by extension on the composition of comets.

O_2 detection @ comet 67P

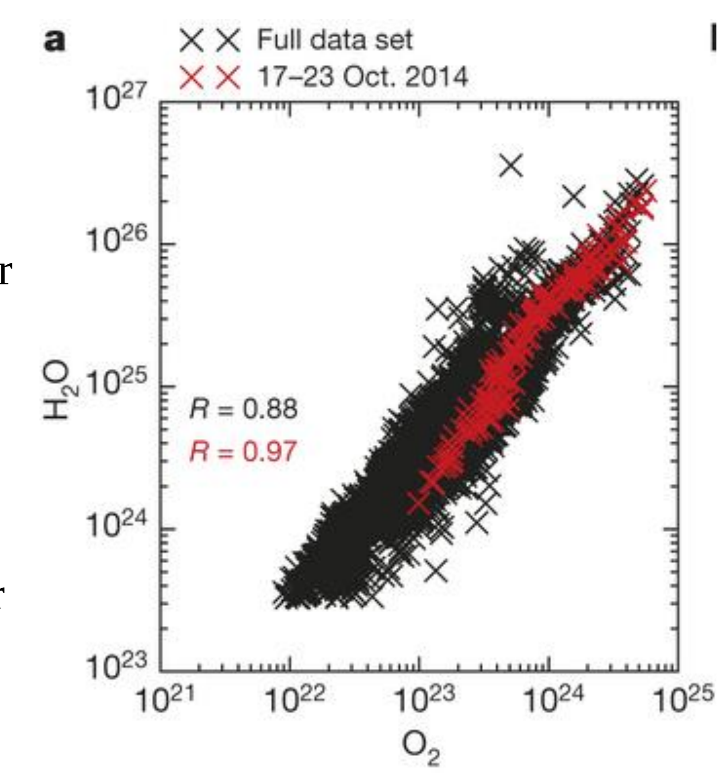
The ROSINA mass spectrometer onboard Rosetta detected significant amounts of O_2 in the coma of comet 67P (Bieler et al. Nature 2015)

The amount of O_2 is correlated to the amount of H_2O, the average O_2/H_2O being ~3.8 %

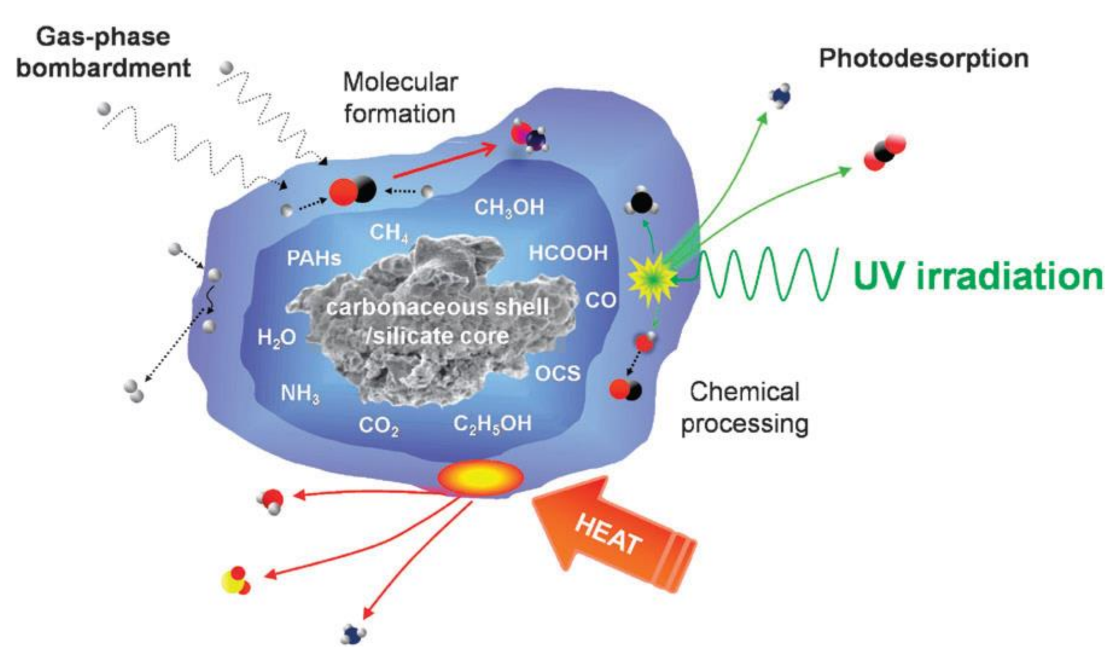
These observations suggest that O_2 is primordial, i.e. incorporated in the comet during its formation and thus produced inside molecular clouds or proto-solar nebulae.

Several formation processes have been invoked including:

- Water radiolysis inside the icy grain matrix in molecular clouds (Mousis et al. ApJ 2016). Pb: radiolysis should produce significant amount of H_2O_2, O_3 and HO_2 which is incompatible with ROSINA measurements
- Non-energetic surface chemistry (Taquet et al. MNRAS 2016). Pb: molecular clouds models didn't predict significant O_2 formation in the solid phase before its detection on 67P. To obtain amounts of O_2 compatible with ROSINA observation, the molecular cloud from which we formed has to be warmer than typical low-mass pre-stellar cores (20-30 K instead of 10 K).



From Bieler et al. Nature, 2015



From Burke and Brown, Physical Chemistry Chemical Physics 2010

Molecular cloud chemistry

- Chemistry in interstellar clouds is complex. It involves gas phase chemistry and solid phase chemistry on icy grains that act as catalysts.
- Exchange between the gas phase and solid phase via desorption or adsorption is a key process

Exchanges between icy grain surfaces and the gas phase

- **Adsorption**: gas phase atoms or molecules can stick on grain surfaces where they can further react
- **Desorption**: due to cosmic ray impacts, photodesorption, or exothermic surface reactions

Desorption rates are estimated from laboratory experiments or models with significant error/uncertainty

In this study we make a qualitative investigation of the effect of grain geometry (non-planarity of the surface and porosity of the ice matrix) on O and H desorption and discuss its possible implications on gas-grain chemistry, focusing on O_2 production

Causes of non planarity and porosity

Icy layer growth and molecules re-arrangement

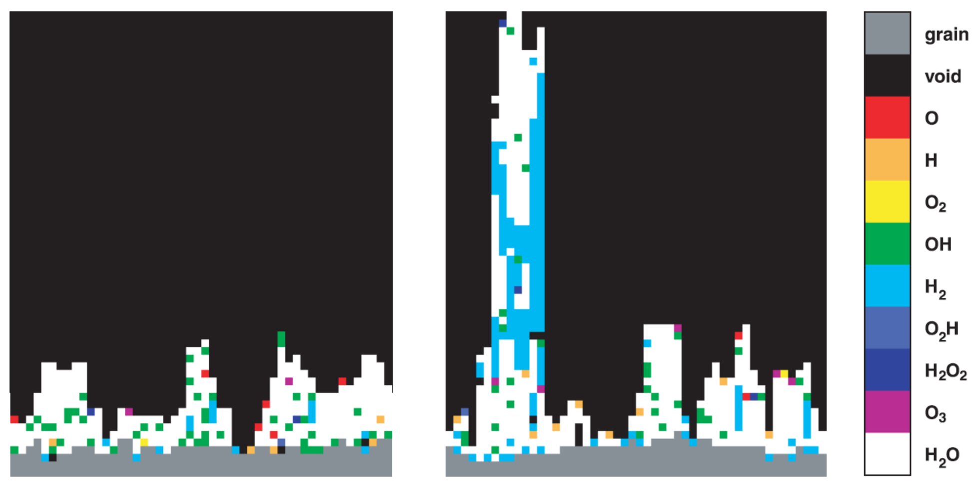
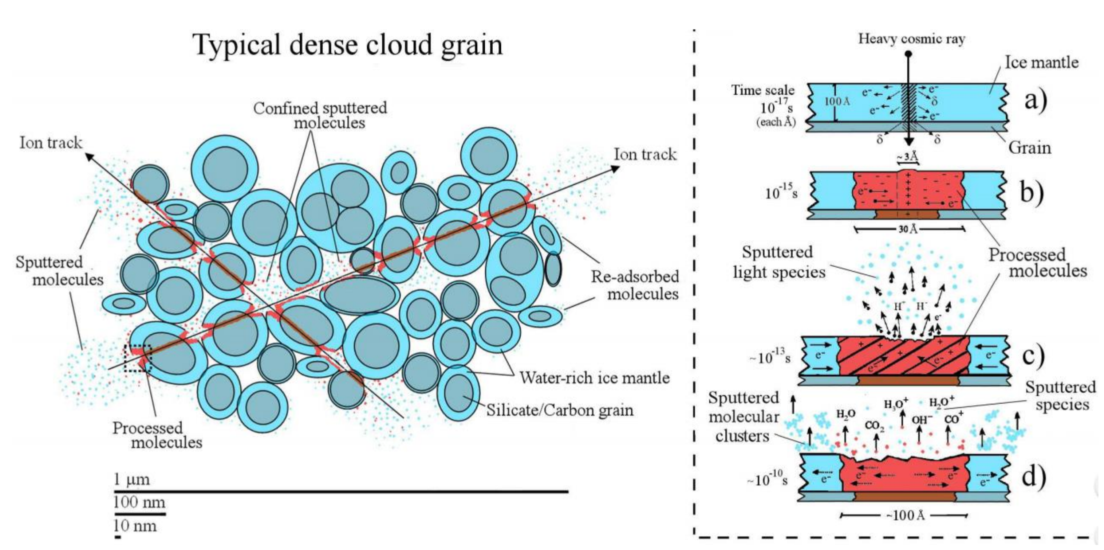


Fig. 5.—Vertical cross sections of the ice mantles after 1×10^5 yr for two different dense-cloud physical conditions. *Left panel* (*E2*): $A_V = 5$, $T_{gr} = 12$ K, $T_{gas} = 20$ K, and $n_H = 5 \times 10^3$ cm^{-3}. *Right panel* (*F2*): $A_V = 10$, $T_{gr} = 10$ K, $T_{gas} = 10$ K, and $n_H = 2 \times 10^4$ cm^{-3}. The molecules are color coded.

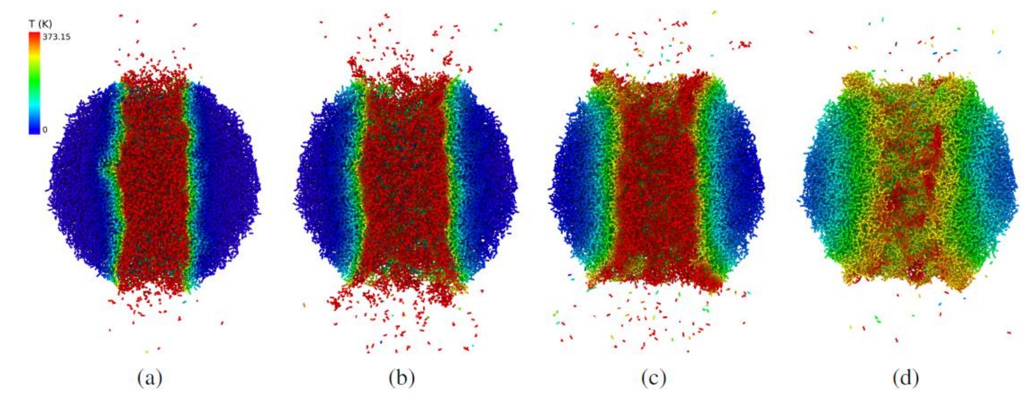
From Cuppen and Herbst, ApJ 2007

Aggregation of grains



From Pilling et al. A&A 2010

CR track



From Mainitz et al. A&A 2016

Fig. 2. Meridional cut through the irradiated grain at times of **a)** 1.6 ps, **b)** 6.4 ps, **c)** 19.2 ps, **d)** 49.4 ps after track formation. Color denotes the local temperature. Figure prepared with OVITO (Stukowski 2010).

Porosity and non planarity impact on O and H desorption

Non planarity and porosity implies that a large proportion of desorbed atoms and molecules won't directly escape into the gas phase but will experience collisions with the ice surface beforehand. During these collisions they have a significant probability to be recaptured on the grain surface, which is equivalent to a reduction of the desorption rate

Estimate of the sticking probability in the litterature

- ***H and D, Burch and Zhang ApJ 1991***

  $\mathbf{S(E)} = \alpha\, e^{-E/E_0}$, with $\alpha = 1$ and E_0 = 102 K for H and 200 K for D

  $\Rightarrow E_{O(D)}/E0_{(H)} \approx 2 = m_D/m_H$

- ***H, Al-Halabi and Van Dishoeck J. Chem. Phys. 2007***

  $\mathbf{S(E)} = \alpha\, e^{-E/E_0}$, with $\alpha = 1$ and E_0 = 300 K for H

- ***CO, Al-Halabi et al. J. Chem. Phys. 2004***

  $\mathbf{S(E)} = \alpha\, e^{-E/E_0}$, with $\alpha = 1$ and E_0 = 10800 K for CO

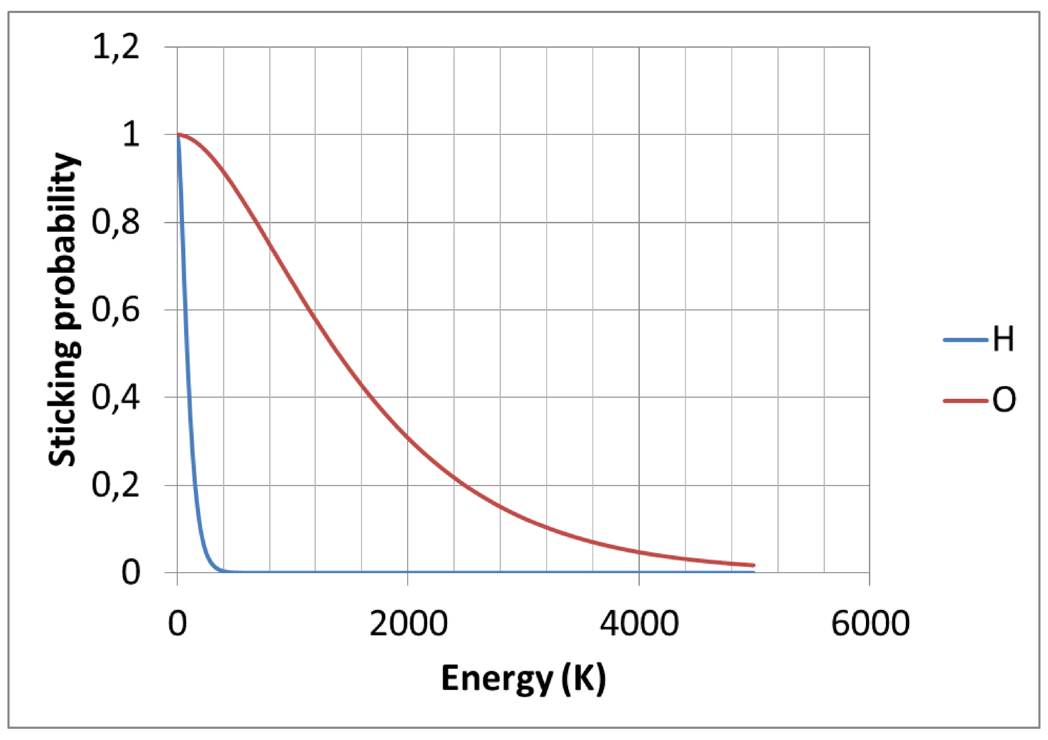
  $\Rightarrow E_{O(CO)}/E_{0(H)} \approx 36$, comparable with $m_{CO}/m_H = 28$

- ***H and D, Matar et al. J. Chem. Phys. 2010***

  $$\mathbf{S(E)} = \boldsymbol{S_0}\,\left(\mathbf{1} + \frac{\boldsymbol{E}}{\boldsymbol{E_0}}\right) e^{-E/E_0}$$, with $\alpha = 1$ and $E_{0(D)}/E_{0(H)} = 2$

  $\Rightarrow E_{O(D)}/E_{0(H)} \approx 2 = m_D/m_H$

$\Rightarrow$ To our knowledge, no estimate of the sticking probability of O is available in the literature. In a first approximation, the sticking probability of a particle with an energy E and a mass m depends on $E/mE_{0(H)}$. We use an extrapolation of the Matar et al. 2010 formula for O.



Sticking probability for H from the Matar et al. 2010 formula and for O from an extrapolation of this formula.

Energy in K	Energy in eV	O velocity in m/s	H velocity in m/s
100	8.6 10-3	320	1283
500	4.3 10-2	717	2868
1000	8.6 10-3	1014	4056
5000	4.3 10-2	2267	9070

Correspondence between energy in K and in eV with the kinetic energy of O and H

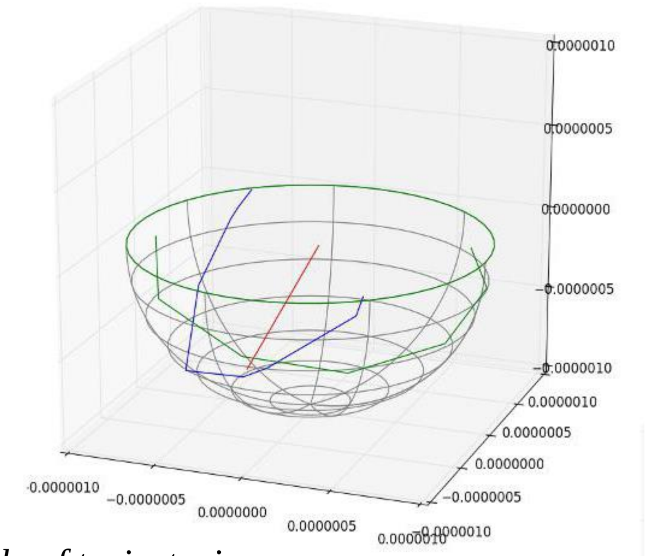
Modeling O and H recapture

We compute the trajectory of H and O ejected from icy grains and estimate the number of contacts with the surface and the probability of recapture in order to answer the following questions:

1- Is recapture due to non-planarity significant?

2- Can the mass dependent sticking probability lead to composition changes in cavities?

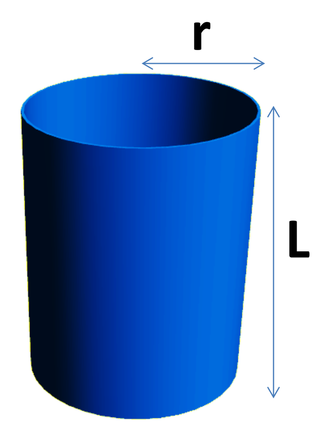
- We use the sticking probability extrapolated from Matar et al. 2010.
- We consider two simple geometries, partially open spheres to simulate surface irregularities and cylinders to simulate cosmic ray tracks. The particles are launched from the inner surface at random locations and in random directions but with a fixed speed. In between the contact with the surfaces the particles follow straight lines.
- We consider mirror bounces at the surface; considering bounces in random directions doesn't change our conclusions.
- We don't take into account energy losses during bounces while it would increase the sticking probability in configurations where the number of contact with the surface is significant.
- For each temperature and surface parameter, the displayed values are averages obtained using 50,000 test particles.

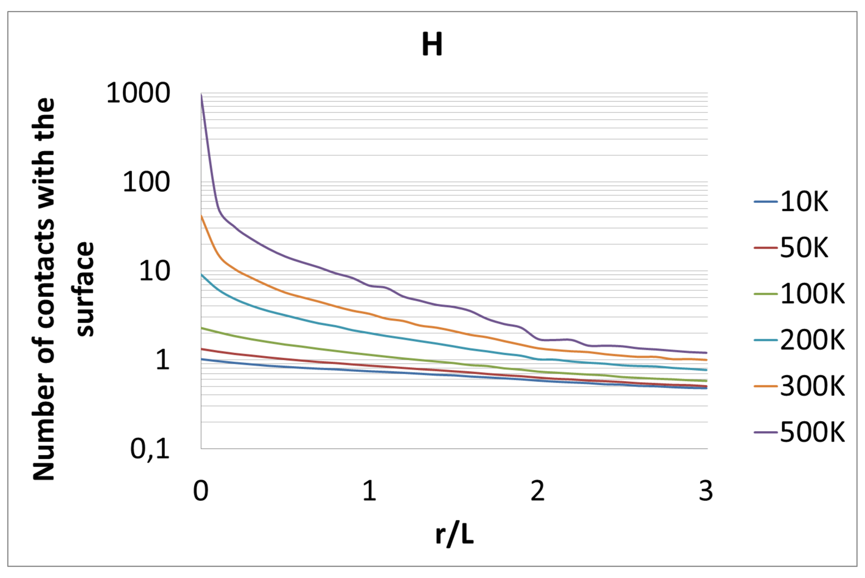


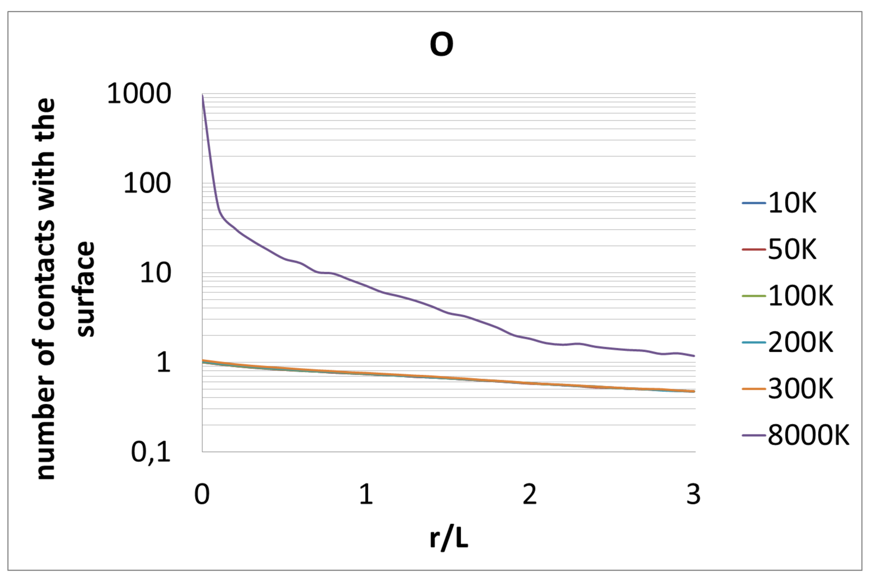
Example of trajectories:
- *red: direct escape*
- *blue: escape after contact(s) with the surface*
- *green: recaptured particle*

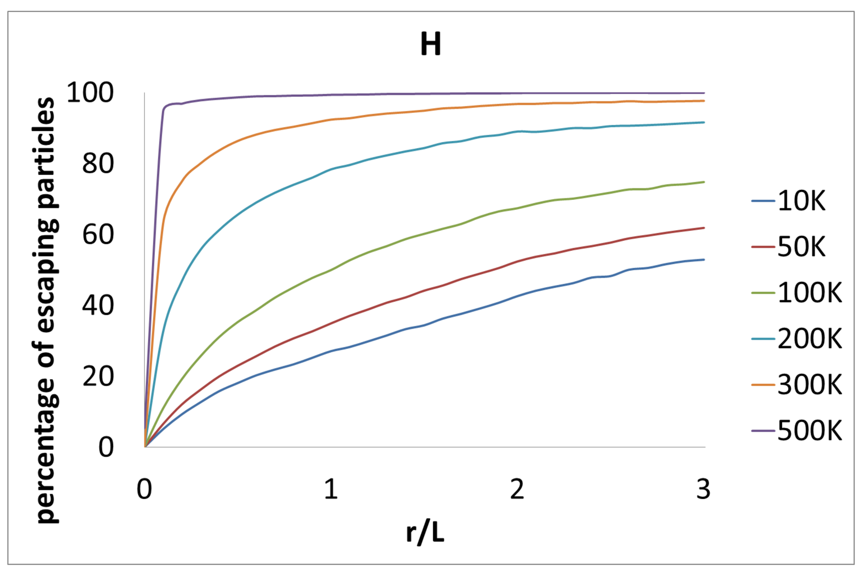
Results

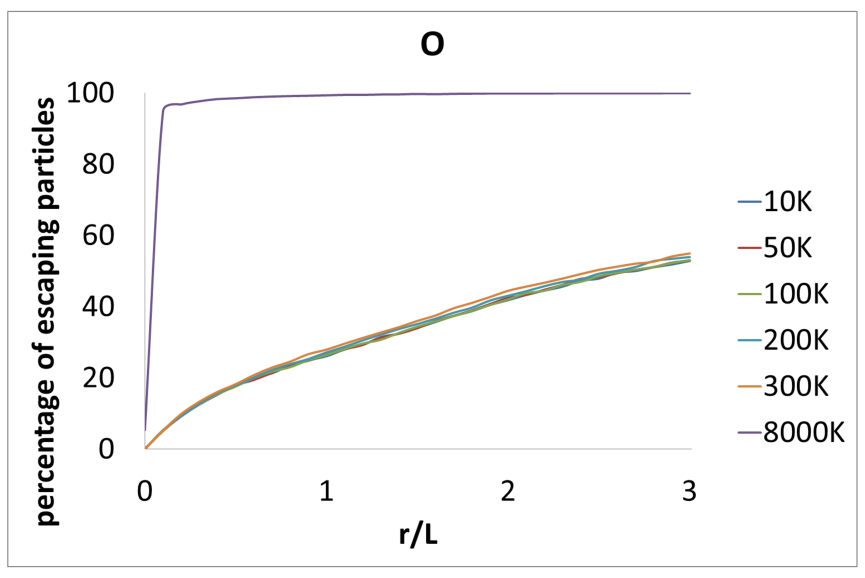
Cylinder: We vary the r/L ratio between 0.01 to 3 for various particles velocities (expressed in K). The bottom of the cylinder is closed.

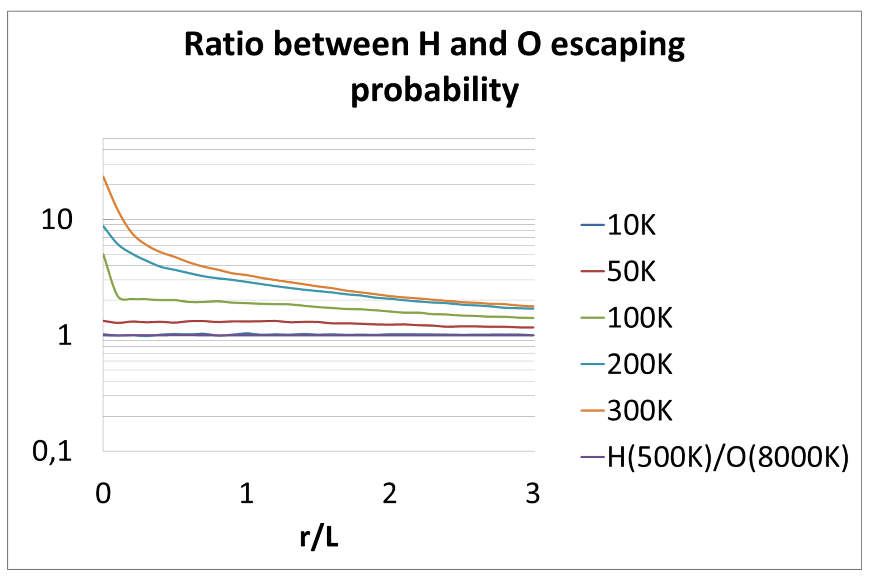




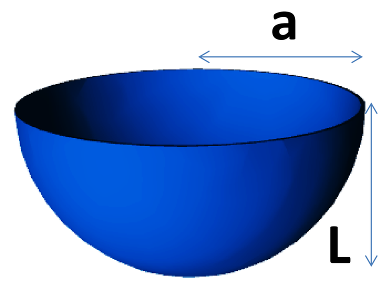




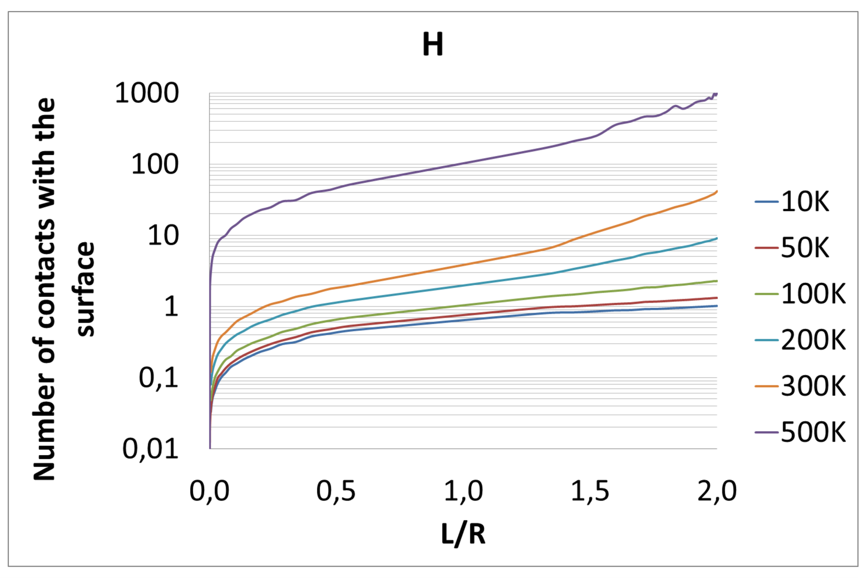


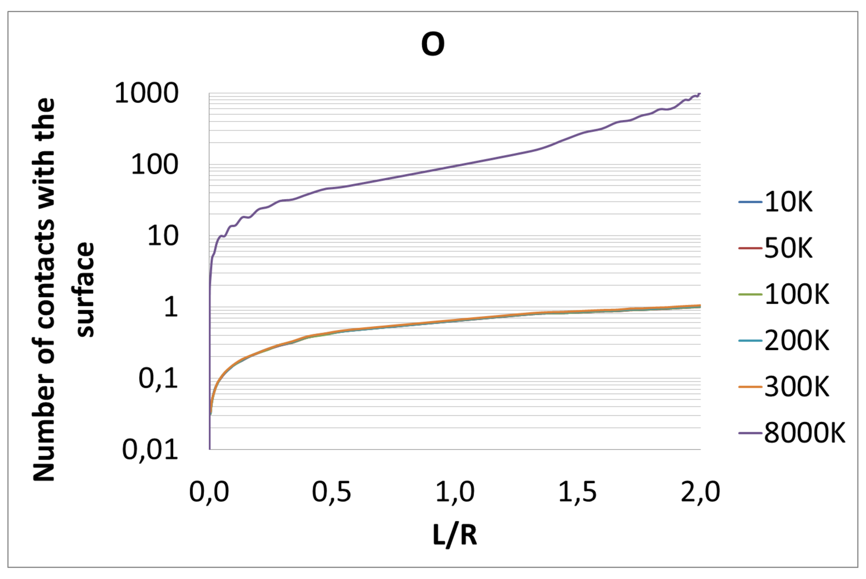


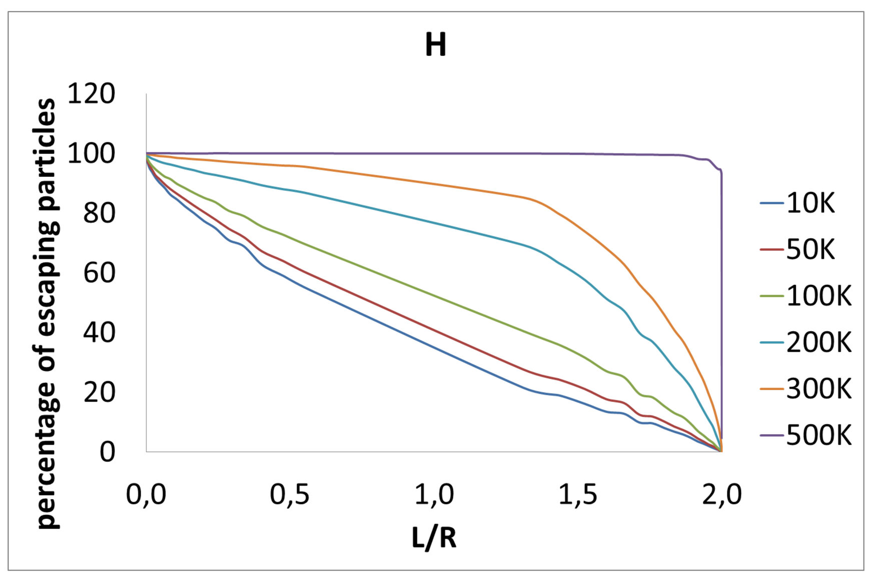
Sphere: We consider a partially open sphere with a radius R for various particles velocities (expressed in K). L corresponds to the height where the aperture is located (L=0 equivalent to a planar surface and L=D to a fully closed sphere).

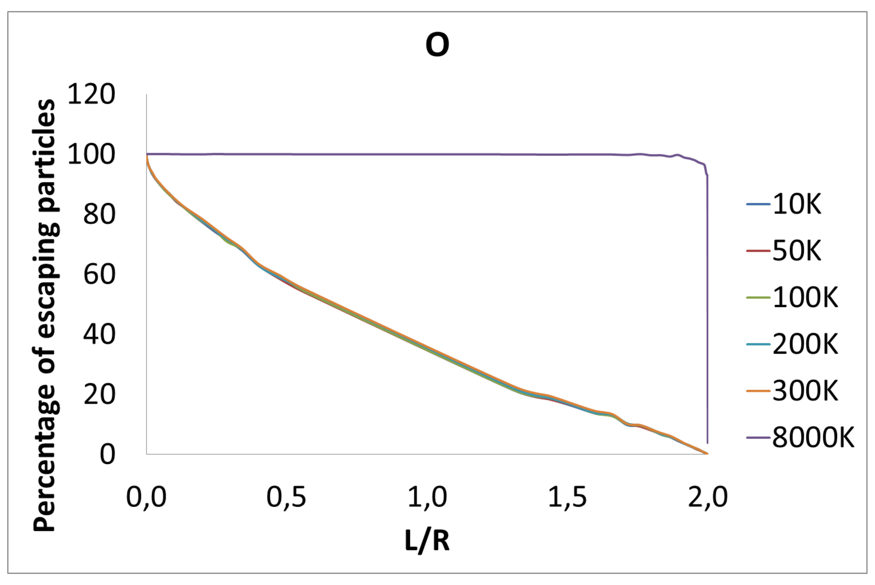


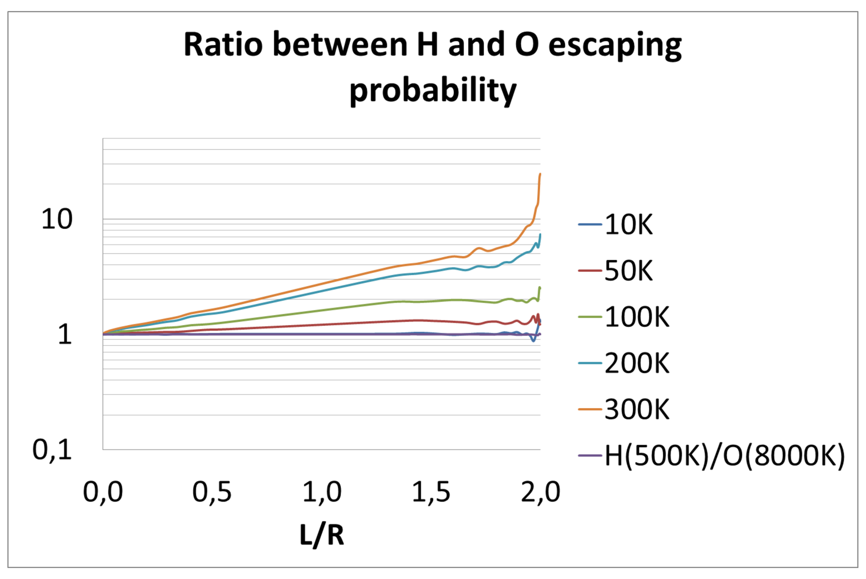
a: radius of the aperture
L: height of the partial sphere
R: radius of the sphere











For low r/L and large L/D (highly uneven surfaces)
The number of contacts is high. The probability of recapture is high, in particular for O

For large r/Land low L/D (smooth surfaces)
The probability of escape without contact is high. The probability of recapture is low and similar for O and H

⇒ For smooth surfaces, direct escape without bounce is highly probable so the escaping probability is similar for O and H

⇒ In cavities, the probability of hitting the surface is high, so O has much more chances than H to be recaptured

At low energy (< 100 K), both H and O have a high probability to stick to the surface and their probability of recapture is similar, even for low r/L

At intermediate energies, the probability of recapture strongly differs between O and H

At high energies (above ~ 500 K for H and ~8000 K for O) both have a negligible probability to stick to the surface and both are unlikely to be recaptured.

This values are obtained without considering any energy loss during bounces. Taking it into account would increase the probability of recapture, in particular in cavities for energetic particles.

⇒ At low energies, the probability of recapture is significant, even for limited surface irregularity
⇒ There should be an intermediate energy range for which O has a much higher probability of being recaptured than H
⇒ At very high energy, both O and H have a high probability of escaping without being recaptured.

Implications

Production of O and H

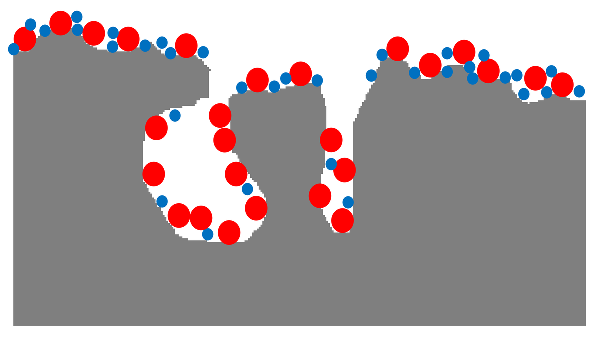
Water dissociation upon electron impact, Makarov et al. JGR 2004

- Mean kinetic energy of H atoms: 1 population with mean energy of ~ 2300 K for all electron impact energies + 1 population with mean energy of ~ 23000 K (for 35 eV electrons) or of ~ 81000 K (for 100 eV electrons): **at these energies the sticking probability of H is negligible.**
- O atom kinetic energy is very small with an upper limit of ~ 12000 K for all electron impact energies**: O atoms with significant sticking probability should be produced.**

Water photodissociation

- Mean kinetic energy of H atoms originating in the first bilayer show a peak at 3700 K, 2300 K for the second and third bilayers (Andersson et al. Chem. Phys. Lett. 2005): **at these energies the sticking probability of H is negligible.**
- Mean kinetic energy of O atoms ~ 4300 K; mean kinetic energy of OH radicals ~ 2200 K (Lai et al. Earth, Moon and Planets 2016): **O atoms and OH radicals with significant sticking probability should be produced.**

⇒ Both photodissociation and electron impact dissociation of H_2O produce H with higher kinetic energy than O, which further favors the preferential recapture of O compared to H



Schematic sketch of an icy grain depleted in H in cavities

Production of O_2 and oxygen rich species

The present results have implications on the formation of oxygen-rich molecules such as CO_2 or O_2 in the interstellar medium. The *in situ* photodissociation of water molecules in the icy mantle combined with the high escape probability of the hydrogen atoms produced through this process will induce a locally oxygen-enriched pore that will push the equilibrium of surface chemistry towards the formation of these oxygen-rich molecules.

For instance, O_2 formation and trapping can occur at the surface of icy grains through the O + O → O_2 reaction. However, molecular oxygen ice is destroyed by

$$O_2 \xrightarrow{H} HO_2 \xrightarrow{H} H_2O_2 \xrightarrow{H} H_2O + OH$$

While favorable conditions (low cosmic-ray ionisation rates, high densities and slightly warmer temperatures) can explain the amounts of O_2 observed in cometary ices (Bieler et al. 2015, Rubin et al. 2015) through a low adsorbed H/O ratio (Taquet et al. 2016), they also overproduce O_2 in the gas phase (Taquet et al. 2016, Hincelin et al. 2011). **The solid phase photodissociation of water presented here can locally lower the H/O ratio without the need for specific physicochemical conditions and without high O_2 abundances in the gas phase, which is in agreement with the low amounts of O_2 observed in e.g. the ½ Ophiuchi cloud (Larsson et al. 2007)**. Additionally, O_2 ice formation through water ice irradiation is more efficient during the condensation of the water ice itself (Teolis et al. 2006), which means **the presented mechanism can induce an enrichment of molecular oxygen in the icy mantles of grains in molecular clouds specifically**, where water ice is being formed, and which is able to subsist through the latter star formation stages all the way to comet formation (e.g. Taquet et al. 2016 and Mousis et al. 2016).

⇒The higher escape probability of H compared to O will induce a depletion in H which can enhance the production of oxygen rich molecules in the solid phase but not in the gas phase.

Others

-Depletion in H compared to heavier atoms or molecules can have consequences on the production of other species like CO_2, not only on the oxygen rich molecules.
-Recapture due to non planarity and porosity can also enhance the D/H ratio in grains compared to the gas phase as D has a higher probability of recapture. This remains to be quantified.