How micron-sized dust particles determine the chemistry of our Universe

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In the environments where stars and planets form, about one percent of the mass is in the form of micro-meter sized particles known as dust. However small and insignificant these dust grains may seem, they are responsible for the production of the simplest (H2) to the most complex (amino-acids) molecules observed in our Universe. Dust particles are recognized as powerful nano-factories that produce chemical species. However, the mechanism that converts species on dust to gas species remains elusive. Here we report experimental evidence that species forming on interstellar dust analogs can be directly released into the gas. This process, entitled chemical desorption (fig. 1), can dominate over the chemistry due to the gas phase by more than ten orders of magnitude. It also determines which species remain on the surface and are available to participate in the subsequent complex chemistry that forms the molecules necessary for the emergence of life.

Eighty years ago, dust was first identified in the interstellar space as the “something” which is obscuring the light coming from stars1. For several decades, dust grains were thought to be only passive and annoying entities present towards any astrophysical objects that astronomers wanted to observe. Only in the 60 s, the real nature of dust was revealed and it appeared that dust is a powerful interstellar catalyst2. The presence of several chemical species that cannot form efficiently in the gas only highlighted the need to explore the chemistry occurring on interstellar dust. At first, the use of chemistry occurring on dust to palliate the failure of gas phase chemistry was qualified as the refuge of the scoundrels3. However, while the role of dust as interstellar catalyst is now well recognized, the mechanism that allows the formed species on the surface to populate the gas phase is still unknown. This is a real paradox and issue of modern astrochemistry: to reconcile almost non-observable solid phase catalysis to observable products in the gas phase. Observations of deeply embedded protostars show that the disappearance of CO in the gas (because CO sticks on the dust) leads to a high abundance of CH3OH in the gas4. This anti-corelation demonstrates that CO converts into CH3OH on dust and is released into the gas phase through an efficient mechanism. It appears that many reactions occurring on dust grains are accompanied with an excess energy which is too large to dissipate. Consequently, the formed species are ejected in the gas phase upon formation. This process, called chemical desorption, implies that the chemistry occurring on interstellar dust affects the composition of the gas. Whereas the existence of this process, first suggested one decade ago5, has been shown theoretically6–10, it has been experimentally observed only for H2 molecules11–14 which is the most favorable expected case (very light, weakly bounded, very exothermic). In this work, we present the first experimental evidence of this process for several reactions occurring on dust analogs. We show that chemical desorption is very important (more than 90% of water formed through OH + H on the dust is released in the gas phase) and has been considerably underestimated by previous assumptions. We discuss the importance of this mechanism in comparison with the chemistry in the gas, and show that it can dramatically change the chemical composition of the interstellar medium. In this sense, because the chemical composition of a medium is one of the main observational tool used to determine physical conditions, we show that current astrochemical models have to account for the catalytic role of dust due to chemical desorption in order to properly describe/predict observations. This new result also affects our current understanding of star formation. By changing the abundances of molecules present in the gas of a cloud that undergoes gravitational collapse to form a star, the gas cools more or less rapidly, which impacts the efficiency and characteristics (mass, binarity) of star formation.
Results

We study experimentally the formation of water on silicate surfaces. For this purpose, we deposit O₂ molecules on silicates, and deposit D atoms in a second step. The surface chosen in this study is usually used as interstellar dust analogs. After deposition at 10 K, the surface temperature is increased up to 200 K and molecules are measured in the gas with a mass spectrometer. The results of these experiments are presented in fig. 2. The solid lines represent the thermal desorption spectra of O₂ (mass 32), the dashed lines the signal for D₂O (mass 20), while dotted lines the signal of D₂O₂ (mass 36), as the temperature of the surface is increased at 0.04 K/s. The thermal desorption spectra of the 3 different species on silicate surfaces are represented in red. For comparison, we also report our experimental results for the formation of water on graphite (green), and non-porous ice (blue).

The black line represents the thermal desorption spectrum when only O₂ is deposited on silicate surfaces. It desorbs as a single peak at around 35 K and the integrated signal corresponds to 1.0 monolayer (1 ML, 10¹⁵ atoms/cm²). The red lines (solid for O₂, dashed for D₂O and dotted for D₂O₂) represent the thermal desorption spectra when O₂ is similarly deposited, and is exposed to 4 x 10¹⁵ atoms/cm² of D. In this case, the desorption of O₂ around 35 K is very weak compared to the deposition of O₂ only, meaning that most (≥90%) of the initial O₂ molecules have disappeared. D₂O and D₂O₂ desorption features are observed at 150 K, and before 200 K, respectively. The location of these peaks in temperature allow to derive the binding energies of the different species on the substrate. These binding energies are reported in table 1. Previous studies showed that O₂ reacts quickly with D, forming O₂D, D₂O₂ and finally D₂O₁₆⁻¹₈. The area of the desorbed peaks indicates that only 35% of the oxygen has been included in the D₂O and D₂O₂ molecules, meaning than around 65% of the O₂ molecules are missing from the surface.

The O₂ molecules missing in the desorption spectra are believed to be ejected into the gas phase during exposure with D atoms, following chemical reaction. In this sense, once new species are formed, and are unable to thermalize on the surface, they are released into the gas phase (the so called chemical desorption). To prove the existence of this process, we monitor the mass signal during D irradiation, with the quadrupole mass spectrometer placed in a position remote from the sample. The measurements are reported in the inset of fig. 2 before and during D irradiation for D₂O (mass 20), DO₂ (mass 34) and D₂O₂ (mass 36). We observe a direct D₂O signal far above the

| Table 1 | TPD desorption peaks and associated binding energies of the molecules on the silicate surface |
|-----------------|-----------------|-----------------|-----------------|
| Species      | TPD peak | Binding energy (K) | ref.            |
| H₂            | 12 K     | 300              | [11]            |
| H             | 500      |                  | [20]            |
| O             | 1100     |                  | This work       |
| O₂            | 40 K     | 1255             | [15]            |
| O₃            | 67 K     | 2100             | Minisale et al. submitted |
| O₂H           |          | 4000             |                |
| OH            | 140 K    | 4600             |                |
| H₂O           | 145 K    | 4800             | This work and [21,22] |
| H₂O₂          | 180 K    | 6000             |                |

Figure 2 | Experimental evidence of chemical desorption. Desorption peaks of O₂ (solid), D₂O (dashed) and D₂O₂ (dotted) species after the exposure of D atoms on 1 ML coverage of O₂ ice deposited on different substrates (silicates SiOₓ in red, graphite in green and np-ASW ice in blue) held at 10 K. Inset: D₂O, D₂O₂ and D₂O monitored with the QMS during the exposure of D atoms on 1 ML coverage of O₂ ice deposited on the silicate substrate at 10 K.
noise level, indicating that D₂O is chemically desorbed. On the other hand, we do detect a very small increase of the DO₂ signal (in the noise) but no increase of the D₂O₂ signal. OD (mass 18) and O₂ (mass 32) are also monitored, but the presence of H₂O (mass 18) and O₂ as minor contaminants in the vacuum decreases the signal to noise ratio, allowing only a one sigma detection of O₂. The measurement before/during irradiation provides clear evidence of the chemical desorption, and that the product concerns mainly D₂O. The signal before and during irradiation cannot be directly compared since the QMS is not located at the same place during these experiments. For the TPDs, it is placed in front of the sample to maximize the signal. In the irradiation configuration, it is placed closed to the surface, but with an angle of about 45°.

Our experimental results show that in the case of water formation on a silicate substrate, 65% of the O₂ molecules initially on the substrate are no longer present after D irradiation. By measuring the amount of species desorbing before/during the irradiation of O₂ with D atoms, we show that repulsive addition of D to O₂ leads to the detection of D₂O in the gas phase. The possible reactions routes are the following:

reaction1 : O₂ + D → D₂O + D → D₂O₂ + D → D₂O + OD

reaction2 : O₂ + D → D₂O + D → OD + OD

The branching ratio of these two reactions are k and (1-k).

The table 2 reports the reactions involved in our experiment as well as their exothermicities. The reaction O₂ + D leading to D₂O is slightly exothermic (2.3 eV) but we only see a slight increase of the mass signal (mass 34) when O₂ is exposed to D atoms (this signal is in the noise). The reaction D₂O + D leading to D₂O₂ has an exothermicity of 3.7 eV, but D₂O₂ is not detected in the gas phase during irradiation. Previous studies showed that H₂O₂ (D₂O₂) can easily decompose in H₂O (D₂O) on the wall of chamber™, meaning that the H₂O (D₂O) signal obtained is due to molecules bouncing on the wall. In our experimental configuration, the number of bounces molecules that are detected are less than 10% (see Ref. 13), and can be neglected in our analysis. We know that D₂O₂ leaving in the gas phase cracks into D₂O (for ~40%) but that ~60% stays under the form of D₂O₂. The cracking pattern of D₂O₂ is estimated during the TPD after 160 K, where we see a signal at the masses 20 (D₂O) and 36 (D₂O₂) simultaneously. Therefore, if D₂O₂ is chemically desorbed into the gas phase, we should see an increased signal during irradiation. The reaction OD + D can also lead to OD + OD, and has an exothermicity of 1.6 eV. However, we are not able to detect OD molecules since their mass coincide with H₂O (mass 18) which is contaminating the mass spectra. We are therefore not able to derive the fraction that is chemically desorbed for this reaction. The reaction D₂O₂ + D → D₂O + OD is exothermic with an energy of 3.1 eV, and the reaction OD + D → D₂O has an exothermicity of 5.2 eV. Since D₂O is observed in the gas phase during exposition of O₂ with D atoms, we can not differentiate which of these two routes are responsible for the important chemical desorption of D₂O which is observed.

Table 2 | Chemical desorption efficiency of different reactions

| Reaction                  | Exothermicity (eV) | Fraction released in gas phase |
|---------------------------|--------------------|-------------------------------|
| OD + D → D₂O             | 5.2                | >90%                          |
| O₂ + D → D₂O             | 2.3                | <10%                          |
| D₂O + D → D₂O₂            | 3.7                | <10%                          |
| D₂O₂ + D → OD + OD       | 1.6                | <10%                          |
| D₂O₂ + D → OD + OD       | 3.1                | <10%                          |
| O + O₂ → O₃             | 5.2                | 60% Dulieu et al. in prep.    |
| O + O₂ → O₃             | 1.1                | ≈10% Minissale et al. in prep.|

Figure 3 | Desorption spectra of water after its formation via 1 ML of O₂ followed by 7 × 10¹⁵ atoms/cm² on silicas held at 10 K (blue); 1 ML of O₃ followed by 7 × 10¹⁵ atoms/cm² on a surface held at 10 K (red) and at 45 K (green).

We perform complementary TPD experiments to address the origin of the very important chemical desorption of D₂O. Here we use hydrogen instead of deuterium. Figure 3 represents the desorption spectra of water after its formation via 10¹⁵ atoms/cm² of O₂ followed by 7 × 10¹⁵ atoms/cm² of H atoms on a surface held at 10 K (blue); 10¹⁵ atoms/cm² of O₃ followed by 7 × 10¹⁵ atoms/cm² of H atoms on a surface held at 10 K (red) and 45 K (green). We can see that in the case of O₃, there is a lower production of H₂O, because the formation of water is made of two sub-routes O₂ + H → OH + O₂. Performing experiments at 45 K, where O₂ is evaporating at a high rate, almost forbid the O₂ + H sub-route, so the O₂ + H at 45 K is almost like observing the OH + H reaction. We can see clearly that there is almost no water produced that way, indicating a very strong chemical desorption during exposure through the reaction OH + H. To check that the disappearance of the water signal for O₂ + H at 45 K is not due to the fact that the reaction does not proceeds, we measure the amount of O₂ present on the surface as O₂ is exposed to H atoms. We see that the peak of O₂, located at 67 K in the TPD, decreases as the exposure with H atoms increases. This shows that even if the residence time of H atoms on the surface is short at 45 K, it is long enough to proceed radical-radical reactions, as observed here for the reaction O₂ + H and also observed for NO + H². To summarize, we show that the OH + H route is the one responsible for the important amount of water during exposure of O₂ with H or D. Since most of the water formed through this route is ejected in the gas phase, this allows us to bring further constrains on our first TPD experiment. The reaction O₂ + D leads to the formation of D₂O₂ and then D₂O + OD, or to the formation of 2 OD. Since OD on the surface reacts with a D to form D₂O and is ejected in the gas, D₂O and D₂O₂ observed in the TPD are the results of the reaction 1. This implies that the 35% of O₂ found on the surface come from the reaction 1, and that the branching ratio is k = 0.35. The reactions occurring in our experiment, as well we the fraction of species chemically desorbed are reported in table 2.

Similar experiments have been performed on graphitic surface and on water ice substrate (Dulieu et al. in prep). For graphite, 80% of the O₂ molecules initially on the substrate are no longer present after D exposure. For the water ice as a substrate, this percentage strongly depends on the morphology of the ice, and can vary from almost 0% in the case of porous ice, to 40% in the case of non porous amorphous ice. These percentages are the fraction of the newly formed species that are ejected into the gas phase upon formation due to the high
exothermicity of the reaction. Coupling to the substrate (phonons) is believed to be the source of the different rates observed for different substrates. Therefore, our results show (table 2) that the fraction of species released into the gas phase upon formation do not depend directly on the exothermicity of the reaction and on the binding energy of the products. The mass of the formed species also plays a fundamental role, as well as the type of substrate that is considered. Many follow-up experimental studies using different reactions/substrates are envisaged to understand the nature of the chemical desorption process.

Discussion

To estimate the impact of chemical desorption on the gas phase composition of astrophysical environments, we use a theoretical model\textsuperscript{10,24}, but include the chemical desorption yields derived from the experiments presented in the previous section. In this sense, we quantify the direct impact of the chemistry on dust on the gas phase. For some reactions occurring on the surface, an important amount of the formed species are ejected in the gas phase. Therefore, within the parameter range at which these reactions dominate the chemistry on the dust surface, an important contribution in the gas phase is expected. Figure 4 illustrates the chemical desorption of H\textsubscript{2}O, OH and O\textsubscript{2} as a function of the dust temperature. The calculations of these efficiencies are reported in the methods section. These efficiencies are the amount of O that is converted to OH, H\textsubscript{2}O and O\textsubscript{2} on the dust and directly released into the gas phase. In this sense, the calculated efficiencies directly provide the conversion rate of gas phase fundamental role, as well as the type of substrate that is considered. Many follow-up experimental studies using different reactions/substrates are envisaged to understand the nature of the chemical desorption process.

In the gas phase, the formation routes of water (OH + H\textsubscript{2}) and OH (O + H\textsubscript{2}) are associated with barriers of 1736 K, 3150 K, respectively\textsuperscript{25}. While the gas phase formation rate of O\textsubscript{2} through OH + O, is still subject to debates (no barrier until T\textsubscript{gas} \sim 150 K see references in\textsuperscript{26}). The rates k\textsubscript{OH,gas}, k\textsubscript{H\textsubscript{2}O,gas} (in cm\textsuperscript{3} s\textsuperscript{-1}) are reported in the supplementary material.

If we compare the formation rates of species via gas or dust routes, we need to compare R\textsubscript{gas} = n\textsubscript{X} \cdot \nu\textsubscript{gas} \cdot k\textsubscript{dust} to R\textsubscript{dust} = n\textsubscript{X} \cdot n\textsubscript{H} \cdot k\textsubscript{dust}. In our case, X is oxygen, since we are dealing with the formation of oxygenated species.

The formation of OH (and water) on dust surfaces dominates by 12 (9) orders of magnitude the gas phase route for a gas at 100 K, while this becomes of 0 (2) for a gas at 500 K. These estimations are made considering the dust temperature in the range (0–15 K) for OH and (0–25 K) for water (and with the density of gas phase O and OH as n\textsubscript{O} = 10\textsuperscript{−4} n\textsubscript{H}, n\textsubscript{OH} = 10\textsuperscript{−7} n\textsubscript{H}).

Searches of O\textsubscript{2} with ground based telescopes and space missions such as SWASS and ODIN indicated that O\textsubscript{2} has a widespread low abundance. O\textsubscript{2} remained unseen allowing to derive some upper limits (X(O\textsubscript{2}) \leq 10\textsuperscript{−7} \textsuperscript{27,28}). However, while recent Herschel observations confirmed the general trend that O\textsubscript{2} has very low abundances (detection of O\textsubscript{2} towards \rho\textsubscript{Oph}, X(O\textsubscript{2}) \sim 10\textsuperscript{−6} \textsuperscript{29}), one isolated high abundance of O\textsubscript{2} has been reported towards ORION\textsuperscript{29}. This high abundance has been attributed to the presence of warm dust, or to shocks. In this work, our model shows an alternative efficient way to form O\textsubscript{2} in the gas phase through chemical desorption from dust. This efficiency is important only for very specific conditions (T\textsubscript{dust} \sim 30–40 K and high UV field), which could explain why the detection of O\textsubscript{2} is seen only in isolated cases. This will be investigated in a forthcoming paper.

Figure 4 | Efficiency of chemical desorption as a function of dust temperature. This efficiency represents the fraction of oxygen released into the gas as OH, H\textsubscript{2}O and O\textsubscript{2}. The first three reactions are computed for a UV field of G\textsubscript{0} = 1, while the final three are for G\textsubscript{0} = 100. Note that the amount of O\textsubscript{2} released into the gas is significantly enhanced in the presence of a strong UV field.
In summary, we report the first experimental evidence that species which form on the surface of interstellar dust grains can subsequently be released into the gas phase due to the exothermicity of the reaction. By depositing O$_2$ molecules on several types of surfaces, and depositing D atoms in a second step, we show that an important fraction of the newly formed species are released into the gas phase during their formation, therefore confirming the existence and importance of the chemical desorption process. We also show that chemical desorption is sensitive to the type of surface upon which the formation reaction occurs. We derive canonical expressions for the formation of water, OH and O$_2$ in the gas phase due to chemical desorption. These expressions can be implemented in any astrophysical model to properly account for the chemistry occurring in space. We show that this process, that covers gas phase species to another though dust, dominates by many orders of magnitude gas phase chemistry in the typical astrophysical environments where water and water ice are forming.

The process highlighted in this study, chemical desorption, has an important impact on the chemistry and thermodynamics of our Universe. In regions where stars are forming, the presence of dust dramatically influences the gas phase composition, changing the abundances of molecules available to cool the gas. Therefore, a cloud that undergoes gravitational collapse to form a star will cool more or less rapidly, depending on the available coolants, and this impacts the efficiency and characteristics (mass, binarity) of star formation. In this sense, the existence of chemical desorption, illustrated in this study, not only impacts the chemical composition of our Universe, but affects the way stars form.

**Methods**

**Experimental setup.** Experiments were performed using the FORMOLISM set-up$^{13}$. In an ultra high vacuum chamber, a gold mirror covered with amorphous silicate (or a graphite substrate) is held at 10 K. All the experiments are performed in the sub-monolayer regime (1 monolayer means that the surface is covered at 100%), to ensure that the interactions of the species with the surface is not perturbed by layering effects. The surface coverage is determined using the specific desorption properties of the second layer$^{12}$. One layer (or less) of O$_2$ molecules is deposited at 10 K. Coincidently, or just after O$_2$ deposition, a D beam (with a dissociation efficiency of 70%) is aimed at the solid sample covered with O$_2$. In a second phase, the surface temperature is increased and the desorption flux is monitored using a movable quadrupole mass spectrometer, placed 3 mm away from the surface.

**Microscopic model.** To estimate the impact of chemical desorption on the gas phase composition of astrophysical environments, we use the chemical network presented in previous studies$^{11,12}$, but include the chemical desorption reactions derived from the experiments presented in this work (Table 1). We solve this chemical network using the rate equations method. We follow the evolution of the species on the surface in monolayers, and calculate the amount of newly formed species that desorb into the gas phase (and vice versa) until $T_{dust} = 25$ K.

The formation of OH, H$_2$O and O$_2$ are insured by several reactions routes on the dust but only the reactions O + H, OH + H and O + O see their products (OH, H$_2$O and O$_2$) released in the gas phase. The different gas phase efficiencies due to the chemistry on dust can be written as follows:

$$
\begin{align*}
\frac{d(N_i)}{dt} &= R_{acc}(X_i) - R_{des}(X_i) - R_{diss}(X_i) - R_{phot}(X_i) - R_{chem}(X_i) - R_{evap}(X_i),
\end{align*}
$$

where $N_i$ are the species on the surface. The six terms of this equation represent (1) the accretion of species $X_i$ from the gas phase, (2) the formation of new species that involve species $X_i$, (3) the creation of species $X_i$ by the encounter of species $X_i$ and $X_j$ that are present on the surface, (4) the evaporation of species $X_i$ (5) the photodissociation of species $X_i$ on the dust, and (6) the creation of $X_i$ by photo-dissociation of species $X_j$.

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$$
\begin{align*}
\frac{d(N_i)}{dt} &= R_{acc}(X_i) - R_{des}(X_i) - R_{diss}(X_i) - R_{phot}(X_i) - R_{chem}(X_i) - R_{evap}(X_i),
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\[ \text{den} = 1.5 \times 10^{22} \frac{n_{\text{H}_2}}{100} \left( \frac{T_{\text{gas}}}{1000} \right)^{3/2} \exp \left( \frac{143}{T_{\text{dust}}} \right) + \exp \left( \frac{-1076}{T_{\text{dust}}} \right) + \exp \left( \frac{-500}{T_{\text{dust}}} \right) \]

With OH the approximate of the OH surface species on the dust:

\[ \text{OH} = 0.26 \frac{n_{\text{H}_2}}{n_{\text{H}_2}} \left( \frac{T_{\text{gas}}}{1000} \right)^{3/2} \exp \left( \frac{-143}{T_{\text{dust}}} \right) + 0.6 \times 10^{6} \exp \left( \frac{-143}{T_{\text{dust}}} \right) \]

As the temperature increases, some reactants evaporate and we enter a stochastic regime where the system should be treated with stochastic methods (Monte Carlo). Therefore, the rates we derive here overestimate the actual rates at temperatures greater than 30 K (when the rates decrease exponentially). Note that the value of \( T_{\text{dust}} \) for the validity of our estimates is higher at higher densities.

**Formation rates in the gas phase.** In the gas phase, the formation routes of water (OH + H2) and OH (O + H2) are associated with barriers of 1736 K, 3150 K, respectively. These rates can be written as:

\[ k_{\text{OH}} = 3.14 \times 10^{-10} \frac{T_{\text{gas}}}{100}^{2.70} \exp \left( -\frac{1350}{T_{\text{gas}}} \right) \text{cm}^3 \text{s}^{-1} \]

\[ k_{\text{H}_2O} = 2.05 \times 10^{-11} \frac{T_{\text{gas}}}{300}^{1.52} \exp \left( -\frac{1736}{T_{\text{gas}}} \right) \text{cm}^3 \text{s}^{-1} \]

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**Author contributions**

S. Cazaux and F. Dulieu wrote the main manuscript. The experiments were performed by E. Congiu, J. A. Noble, S. Baucoche, H. Chaabouni, A. Moudens, M. Minissale and F. Dulieu. S. Cazaux developed the theoretical model. All authors reviewed the manuscript.

**Additional information**

**Competing financial interests:** The authors declare no competing financial interests.

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