Effects of H$_2$ coating of grains on depletion of molecular species

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ABSTRACT

Physical conditions in dense and cold regions of interstellar clouds favour the formation of ice mantles on the surfaces of interstellar grains. It is predicted that most of the gaseous species heavier than H$_2$ or He will adsorb onto the grains and will disappear from the gas-phase, changing its chemistry, within $\sim 10^9/\eta_{H_2}$ years. Nonetheless, many molecules in molecular clouds are not completely depleted in timescales of $10^7$ yr. Several speculative mechanisms have been proposed to explain why molecules stay in the gas phase, but up to now none are fully convincing. At the same time, these mechanisms are not mutually exclusive and we can still explore the effects of other possible processes. We speculate on the consequences of H$_2$ coating of grains on the evaporation rates of adsorbed species. More experiments and simulations are needed to calculate the evaporation rate $E_{\text{evap}}(X-H_2)$.

Key words: astrochemistry — ISM: abundances — ISM: molecules — molecular processes

1 INTRODUCTION

Icy mantles on dust grains have been long detected in cold and dense regions of the interstellar medium (Williams et al. 1992). These mantles are the result of the accumulation of heavy molecules on grain surfaces due to the low temperature and high density conditions of the environment. The collisions between the dust grains and the neutral component of the gas lead to the retention of the gas phase particles on the grain surface, because their thermal energy is lower than the typical adsorption energies and because the excess kinetic energy can be transferred rapidly to the surface (Herbst & Millar 1991). Calculations have shown (Leitch-Devlin & Williams 1985) that $\sim 30$–$100\%$ of the collisions result in retention, depending on the species and the nature of the surface. Moreover, the widespread detection of molecular mantles in dense regions of molecular clouds indicates a high efficiency of the sticking of heavy atoms and molecules on the surfaces of cold dust grains.

The main observed component of the mantles is water ice (Tielens & Hager 1982; Whittet et al. 1998), but it is thought that most of the gaseous species heavier than H$_2$ or He will adsorb onto the grains and will disappear from the gas-phase, changing its chemistry, in a relatively short “freeze-out” time. The freeze-out rate is $\sim 10^9/\eta_{H_2}$ years (Leitch-Devlin & Williams 1985), where $\eta_{H_2} = n(H) + 2n(H_2)$ is the total hydrogen nucleon number density. For densities as low as $\sim 10^3$ cm$^{-3}$, the freeze-out timescale is much less than the expected lifetime of a typical molecular cloud ($\sim 10^7$ yr), so it would be expected that, contrary to the observational result, the majority of observations would not show evidence for heavy gas-phase species. Tielens (1977) showed that for non-zero sticking efficiency, when no desorption processes act to remove mantle material, the accretion of gas-phase species on to the dust dominates the chemical evolution and the total freeze-out of gas is inevitable.

Thus, some mechanism is preventing the growth of mantles in grains and maintains an equilibrium between molecules in the gas and solid phases by producing the desorption of molecular species from the surface of dust grains. The finding of a convincing desorption mechanism that explains the observed molecular gas-phase abundances has proved to be rather elusive in the last 20 years. It is not yet precisely known how this desorption takes place and several different continuous desorption processes have been proposed, either working simultaneously or separately (Roberts et al. 2007):

- Classical thermal evaporation (Leger et al. 1985), which is negligible at the temperatures of dense clouds, $\sim 10$ K
- Desorption by direct impact of cosmic rays (or X-rays) onto grains, which causes local heating that lead to the evaporation of weakly bound molecules, such as CO (Willacy & Williams 1993; Leger et al. 1985; Hasegawa & Herbst 1993)
- Cosmic ray-induced photo-desorption (Hartquist & Williams 1993; Willacy et al. 1994)
- Exothermic mantle reactions, such as the formation of H$_2$, which can result in a local “hotspot” heating of the grain mantle (Willacy et al. 1994; Duley & Williams 1993)
- Grain-grain collisions or chemical explosions (Langer et al. 2000; Leger et al. 1985; Tielens et al. 1994)
- If the cloud is composed of clumpy molecular gas layers, interstellar UV radiation can penetrate two or three times deeper than in the case of a homogeneous cloud and can produce orders of magnitude more photo-ionisation and photo-desorption even at modest extinctions, $A_V \sim 2$ (Boisse 1990; Bethell et al. 2007).

The feedback from the star formation processes, which
eventually disrupt the dense cores from which stars form, will also limit the growth of ice mantles or force the return of the adsorbed species to the gas phase, in a sporadic or intermittent manner, through a variety of mechanisms: by sublimation of icy mantles from warm grains near bright stars in a more or less gradual way (Viti & Williams 1992; Rodgers & Charnley 2005; Garrod et al. 2008), by destruction or sputtering of grain cores and mantles by passing shocks (Charnley et al. 1988; Flower & Pineau des Forêts 1994; Bergin et al. 1998; van Dishoeck & Blake 1998), or by ice sublimation due to UV radiation originating in shocks (Viti et al. 2003; Christie et al. 2011).

All the mechanisms above are not mutually exclusive, but no proposed non-thermal mechanism convincingly explains the presence of molecules such as CO in dark clouds or it is widely accepted as a reliable desorption mechanism (e.g. Frederking et al. 1982; Duvert et al. 1986; Dickman & Herbst 1990). In this paper, we propose to explore another possible mechanism: the consequences of the variation of the adsorption energies due to the different properties of the substrate and, in particular, the effect that the coating of dust grains by molecular hydrogen has on the evaporation rates of adsorbed molecules.

2 EFFECTS OF H₂ COATING OF GRAINS ON ADSORPTION ENERGIES

Once a molecular species sticks to a grain, the time it stays on the surface before it evaporates depends on the surface temperature and the binding (adsorbing) energy of the adsorbate species on a given substrate. The desorption rate, in s⁻¹, is described by Hasegawa et al. (1992)

\[ R_{\text{evap}} = \nu_0 \exp(-E_D/T) \]  

(1)

where \( T \) is the temperature surface of the grain, \( E_D \) the adsorption energy in K, and \( \nu_0 \) is the characteristic vibrational frequency for the adsorbed species, \( \nu_0 = (2n_1E_D/\pi^2m)^{1/2} \), where \( n_1 \) is the surface density of sites (\( \approx 10^{15} \) cm⁻²) and \( m \) is the mass of the adsorbing particle. Typically \( \nu_0 \approx 10^{12} - 10^{13} \) s⁻¹. The adsorption energies, \( E_D \), of molecules onto the grains depends on the properties of the substrate. Table 1 shows the adsorption energy, in K, of several fundamental species on different substrates that can be found in molecular clouds. Table II also shows the evaporation time expected for each adsorption energy for two relatively close grain surface temperatures, \( T_{\text{dust}} = 10 \) and 15 K. It is easily visible the large differences between the different molecular species and substrates and the influence of temperature.

When modelling the accretion of gas-phase molecular species onto the grain surfaces, many adsorption energies are needed to describe the complex interacting system thus created (Cuppen & Herbst 2007). Ideally, we would need to know the adsorption energies of the species onto the carbonaceous substrate, but also the energies between the species and ice (or different ice structures) and with other adsorbed species. Unfortunately, many of these energies are poorly known, if at all (see Cuppen & Herbst 2007 and references therein). The lower half of Table II also shows some estimates of the adsorption energies of several molecular species when the substrate is H₂. Most of these values were calculated assuming, for demonstration purposes and following Allen & Robinson (1977), a scaling value of 1/5 of the adopted standard value of \( E_D \). The adsorption energies for H₂ surfaces are considerably reduced when compared with the ones for silicate or H₂O ice surfaces. For instance, the adsorption energy for H₂ on H₂O ice, \( E_D = 350 \) K, while on H₂ ice, \( E_D = 100 \) K. The adsorption energies of other accreting heavy molecules behave in a similar way. Once \( E_D \)'s are reduced to 1/5 of the silicate surface values, evaporation timescales would be shorter than freezing timescales, \( t_{\text{evap}} \sim 40 \) minutes for CO on H₂ at 10 K (see Table 1).

2.1 Coating of grains by H₂

By definition, H₂ is the most abundant gas-phase species in molecular clouds and several authors have long suspected that it could be an important component of the grain surfaces (Tielens & Hagen 1982; Govers et al. 1980). At the same time, the adsorption energies of H₂ indicate that it is a rather volatile molecule. Table II shows that the evaporation time for H₂ on H₂O ice can go from a few seconds at a grain surface temperature of 15 K to 0.5 years for 10 K.

The surface coverage of H₂ molecules will depend on the balance between their evaporation and accretion rates. The number of accreting H₂ molecules per unit of time can be calculated from Tielens & Hagen (1982)

\[ R_{\text{ac}} = s_d(V_{H_2})n(H_2)S = 0.10193 \left[ \frac{n(H_2)}{10^4 \text{cm}^{-2}} \right] \text{s}^{-1} \]  

(2)

where \( n(H_2) \) is the abundance of gas-phase H₂ molecules, \( V_{H_2} \) is the mean velocity of H₂ molecules (\( \sim 1.026 \times 10^4 \sqrt{T_k} \) cm s⁻¹, where \( T_k \) is the gas kinetic temperature). \( s_d \) is the grain geometrical cross-section (\( \sim 3.14 \times 10^{-10} \) cm²), and \( S \) is the sticking coefficient, which we will assume equal to 1. In practical terms, for a dense gas density, \( \sim 10^4 \) cm⁻³, a H₂ molecule should hit a grain every 10 s.

The number of H₂ molecules that evaporate from the surface of a grain per unit of time can be expressed as

\[ R_{\text{evap}} = N(H_2) \nu_0 \exp(-E_D(H_2)/T) \]  

(3)

where \( N(H_2) \) is the number of H₂ molecules on the grain surface. If the number of grain sites, \( N_s = 10^6 \), the accretion time is \( \sim 10^7 \) s or \( \sim 0.3 \) yr. For a dust temperature of 10 K, and \( E_D(H_2 - H_2O) = 450 \) K, the evaporation time is \( \sim 1.47 \times 10^7 \) s or \( \sim 0.5 \) yr. The time needed for the system to reach steady state can be calculated as

\[ \frac{dN(H_2)}{dt} = R_{\text{ac}} - R_{\text{evap}} = 0 \]  

(4)

and the number of H₂ molecules on the grain surface will be

\[ N(H_2) = 1.5 \times 10^6 \left[ \frac{n(H_2)}{10^4 \text{cm}^{-2}} \right] \]  

(5)

For a number of grain sites, \( N_s = 1-3 \times 10^6 \), and \( n(H_2) > 10^4 \text{cm}^{-2} \), all the exposed sites will be occupied by H₂ molecules in \( \sim 0.5 \) yr at \( n_H > 10^4 \text{cm}^{-2} \) (Tielens & Hagen 1982). The evaporation of H₂ from an H₂ ice surface is very fast, leaving no possibility of multiple layers of H₂ ice.

Given the possibility that grains in molecular clouds are covered by a layer of H₂ molecules and, as Table II shows, this can greatly reduce the adsorption energies of heavy molecules, it is relevant to explore how much do the changes in the adsorption ener-
gases used in the chemical models change the values of molecular depletion in the gas.

3 RESULTS OF THE CHEMICAL MODELLING

We used our gas-grain chemical model based on the gas-grain chemistry of Hasegawa et al. (1992) to explore the evolution of gas- and solid-phase abundances of species after assuming that the grains are coated with H₂ molecules. The chemical model contained 3768 gas and surface reactions involving 503 species, but we only took into account adsorption and evaporation of species from the grain surfaces, with no other chemical reaction on them apart from the formation of H₂. We ran several models at different gas densities (2 × 10⁴, 2 × 10⁵, and 2 × 10⁶ cm⁻³), at a gas and dust temperature of 10 K, and cosmic ray ionisation rate $\zeta = 1.3 \times 10^{-17}$ s⁻¹. All models used initial elemental ‘low metal’ atomic abundances (Ruffle & Herbst 2000).

We assumed a crude approach to simulate the effects of the coating of grains by H₂ molecules and the subsequent modification of the adsorption energies, $E_D$. We ran three different sets of models: a fiducial one with no modification of $E_D$, and two models where all $E_D$, except for H, H₂ and He, were reduced by either a factor of 1/2 or 1/3, a conservative value still far away from the scaling factor used by Allen & Robinson (1977) to estimate the change in the adsorption energy of molecules landing on H₂-coated grains. Figure [1] shows the results for two different number densities, 2 × 10⁴ and 2 × 10⁶ cm⁻³, and three different sets of adsorption energies: standard values, 1/2 of the standard $E_D$ values, and 1/3 of the standard $E_D$ values.

The upper row of Fig. [1] shows the results of a fiducial case. For a gas density of 2 × 10⁴ cm⁻³, the gas-phase molecular abundances begin to suffer from depletion at a few times 10⁸ yr, at which point the gas and grain-phase abundances are approximately similar, and most of the molecular species disappear from the gas-phase at a few times 10⁹ yr. This effect is accelerated by about a factor of 10 for a higher density, $2 \times 10^6$ cm⁻³.

The middle row of Fig. [1] shows the results of the case where the adsorption energies are half of the standard values. There is still some degree of depletion (larger than 90%) for some molecules, at a density of $2 \times 10^5$ cm⁻³, but total depletion is never reached. Some molecules, such as NH₃, do not have so high a depletion and the gas-phase abundance remains higher than the solid-phase abundance at all times. The level of depletion is much larger for higher densities, but even in this case there is not an almost total disappearance of the gas-phase molecules as in the standard case. On the other hand, the times when the solid-state abundances become larger than the gas-phase abundances do not seem to change that much.

The case where the molecular adsorption energies have been reduced by a factor of 3 (bottom row of Fig. [1]) shows the more dramatic changes. Many molecules, such as CO, CS (prime candidates for depletion) or NH₃, show little or insignificant depletion, even at high densities, measured as the fraction of molecules in the gas and solid phases. This is not the case for CN, which still shows high depletion in this case. One must be cautious in this case, though, because the presence of CO in the gas at all times clearly affects the abundance of many molecules, such as CN and N₂H⁺.

4 DISCUSSION AND CONCLUSIONS

We have shown how the modelling of the depletion of heavy molecular species in dense and cold regions of molecular clouds depends on the determination of accurate adsorption energies, $E_D$. Different values of $E_D$ affect the time molecular species reside on the grain surfaces and can provide a way to help explain the incomplete freeze-out of molecules from the gas phase. In particular,
we argue that the adsorption energies of molecules on a substrate of H₂ ice can be several times lower than the ones commonly used in current chemical models. We also showed that H₂ could occupy all the available grain sites in a relatively short time, ~ 0.5 yr, which could produce a change in the adsorption rates of molecules on grain surfaces.

We ran a few simple gas-grain models to test how much relatively small changes in the adsorption energies of molecular species affect the gas-phase abundances. We find that if we use values of $E_D$ half of the standard values, the depletion of most of the molecules is greatly reduced, although it is still at levels of a factor of 10. A further reduction of the molecular adsorption energies, down to a factor of 0.3$E_D$, which would be a conservative value of how much the adsorption energies can be changed, shows that molecules show very little or no depletion even at relatively high densities, $2 \times 10^6$ cm$^{-3}$. Thus, lower evaporation energies of heavy molecular species due to the coating of grains by H₂ molecules may explain the presence of CO and other heavy molecules in the gas in average dark clouds.

As we indicated in Sect. 2.1, we do not expect to have more than one monolayer of H₂ molecules due to the almost instantaneous evaporation of any H₂ landing on H₂-ice (see Table 1). On the other hand, we estimate that a CO molecule landing on a grain completely covered by H₂ will be able to scan the $N_s$ sites on the surface of the grain in a time, ~ 0.2 s, much shorter than the expected evaporation time, $t_{\text{evap}}(\text{CO}) \sim 40$ min. If the grain surface is only partially covered by H₂-ice, the effect will be that any CO molecule landing on H₂-ice will be able to find a free site outside of the H₂-ice, at which point it will remain trapped on the surface. This will reduce the number of available sites to be covered by H₂ molecules by about 500 in a year, as we expect about one CO molecule landing on the surface per day at a gas density of $10^4$ cm$^{-3}$, and should not have any effect on the basic mechanism we discussed.

In the calculations shown in Sect. 2.1 we assumed a “flat” or homogeneous grain surface, represented by just one value of the absorption energy, $E_D$, seen by the H₂ molecules. But grain surfaces are thought to be rough, with an inhomogeneous structure of valleys, protrusions, cavities, and with a certain degree of porosity. Landing H₂ molecules will be then subject to a variety
of binding energies. Results of the effects of surface roughness on the formation rate of \( \text{H}_2 \) on grains (Cuppen & Herbst 2005, 2007, Cuppen et al. 2006) show that irregularities affect the binding energies of the surface molecules, effectively increasing the binding energy “seen” by each molecule. We expect that \( \text{H}_2 \) molecules will tend to fill the valleys of the surface and, probably, help to build, locally, more than one layer of \( \text{H}_2 \) ice.

We realise that there are several objections that could be raised against this approach. There were some experimental results that show that the surface coverage of \( \text{H}_2 \) might be \( \sim 20\% \) for a binding energy of 450 K (Govers et al. 1980, Schutte et al. 1976). Additionally, in the simulations of Cuppen & Herbst (2007), \( \text{H}_2 \) molecules pile up with CO in it. The potential dislocation of (almost completely) coating \( \text{H}_2 \) molecules with the surface below it, there is no doubt that \( \text{H}_2 \) molecules must be located all over the grain surfaces, due to the ubiquity of \( \text{H}_2 \) in molecular clouds. This should have some, maybe substantial, effect on the effective adsorption energy value of molecular species that in the right environment makes this mechanism relevant. Particularly, after proving that some relatively small changes can affect a lot the depletion rate of heavy molecules.

At the same time, the present mechanism and the several previously proposed desorption mechanisms could very well work simultaneously. It is yet to be seen which process dominates in a certain environment, how effective the \( \text{H}_2 \) coating can be or in which kind of environments it would be dominant.

The presence of a monolayer of \( \text{H}_2 \)-ice on the surfaces of grains in molecular clouds could be observationally tested. Unfortunately, there is no clear evidence yet of the detection of solid \( \text{H}_2 \) on interstellar grains. Sandford & Allamandola (1993b) showed that solid \( \text{H}_2 \) could be detected by an infrared absorption band at 2.417 \( \mu \text{m} \) (4137 cm\(^{-1}\)) attributed to the \( Q_1(1) \) pure vibrational transition of \( \text{H}_2 \). This band has never been detected and Sandford & Allamandola (1993b) argue that it would probably trace the \( \text{H}_2 \) trapped in water ices. Schaefer (2003) proposed six pure para-hydrogen pair transition bands as candidates to explain unidentified emission features in ISO-SWS spectra of the NGC 7023 nebula. If any \( \text{H}_2 \)-ice absorption band was detected, it would be a combination of existing surface and mantle solid \( \text{H}_2 \). Infrared spectroscopy studies of dust have found visual extinction thresholds of \( \approx 3 \) for \( \text{H}_2 \text{O} \) ice (Whittet et al. 1988), \( \approx 5 \) for CO ice (Whittet et al. 1989), and \( \approx 4 \) for \( \text{CO}_2 \) ice (Whittet et al. 2007), which roughly correspond to very few monolayers of ice, probably between 2 and 5 (Hassel et al. 2010). The detection of only one monolayer of \( \text{H}_2 \) ice, in the absence of any solid \( \text{H}_2 \) in the mantle, may not be yet feasible.

Finally, it is interesting to consider if the \( \text{H}_2 \)-coating mechanism proposed here can have any influence on the determination of the visual extinction thresholds discussed above. As Table 1 shows, the evaporation time of \( \text{H}_2 \) on \( \text{H}_2 \)-ice is highly sensitive on temperature, \( t_{\text{evap}, \text{H}_2} \sim 4.5 \) s at 15 K. Thus, at the expected temperatures of the grains at those visual extinction thresholds (between 12 and 20 K, Draine & Lee 1984, Smith et al. 1993), \( \text{H}_2 \) molecules do not have time to build up on the grain surfaces and we do not expect them to play any relevant role. Only when the grain temperatures go down to about 10 K will this mechanism delay the growth of ices.

Our simple modelling of the chemistry, changing the values of the adsorption energies, also proves how important it is to obtain reliable estimates of evaporation energies, either laboratory measurements or theoretical calculations, for heavy molecules on \( \text{H}_2 \) ice, or, for that matter, in different kinds of substrate. A simplified experiment could be the study of \( 
\text{H}_2 \) adsorption on various types of pure ice (\( \text{H}_2 \text{O}, \text{NH}_3, \text{SO}, \text{SO}_2, \text{H}_2\text{CO}, \ldots \)) to estimate the interaction potential between the \( \text{H}_2 \) molecules and other heavier molecules.

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