The role of carbon grains in the deuteration of H$_2$

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ABSTRACT

Aims. The production of molecular hydrogen and its deuterated forms onto carbonaceous dust grains is investigated in detail. The goal of this study is to estimate the importance of the chemistry occuring on grain surfaces for the deuteration of H$_2$. Furthermore, we aim to find a robust and general surface chemical model which can be used in different astrophysical environments.

Methods. Surface processes are described for the cases of graphitic and amorphous–carbon grains, where laboratory work is available. Langmuir–Hinshelwood as well as Eley–Rideal surface chemistries are included in the model and their relative contributions are highlighted. Analytic expressions are derived for H$_2$, HD, and D$_2$ formation efficiencies for both type of grains. Rate equations are tested against stochastic methods.

Results. As expected, rate equations and stochastic methods diverge for grain sizes lower than a critical value $a_{\text{crit}}$. For grain sizes below this critical value, D$_2$ formation decreases to favour HD formation. The formation efficiencies of H$_2$ and D$_2$ can be calculated by adding a correction factor to the rate equations methods (this factor is a simple exponential factor that becomes unity when $a > a_{\text{crit}}$). We found that because of the presence of chemisorbed sites, which can store atoms to form molecules up to high grain temperatures, the formation efficiency of HD and D$_2$ is very high compared to models where only physisorption sites are taken into account. When considering a realistic distribution of dust grains, we found that the formation rate of H$_2$ and HD is enhanced by an order of magnitude if small grains are taken into account. The formation of D$_2$, on the other hand, is due to a contribution of small ($\leq 100\,\text{Å}$) and big ($\geq 100\,\text{Å}$) grains, depending on the D/H ratio, the grain temperature and the volume density. The processes described in this paper, that allow a strong enhancement of the deuterated forms of molecular hydrogen, could explain the high degree of deuterium fractionation observed in protostellar environments.

Key words. dust, extinction - molecular hydrogen - ISM: molecules
1. Introduction

Formation of molecular hydrogen has been studied since decades but is still the subject of polemics. Because of its importance to establish the time scale of molecular cloud formation (e.g. Bergin et al. 2004), as a coolant in low metallicity environments (Tegmark et al. 1997), or as the primary ingredient for astrochemistry, the formation of H$_2$ occurring through grain surface reactions (Gould & Salpeter 1963), is the most studied surface reaction. However, there are considerable uncertainties associated with this simple reaction mainly caused by our ignorance concerning dust grain constitution (see the review by Hollenbach & Tielens 1999, where one also finds references to much of the earlier work). Because of this, recent investigations have focused on the structure of dust grains, the interaction between grain surfaces and accreting atoms, as well as the theoretical approach to treat surface chemistry and to couple it with gas–phase chemistry (Chang, Cuppen & Herbst 2007). Interaction between H atoms and dust grains has been extensively studied theoretically (Sha & Jackson 2004, Sha & Jackson 2002, Jeloaica & Sidis 1999, Parneix & Brechignac 1998, Klose 1992) as well as experimentally (Pirronello et al. 1997a,b; 1999, Dulieu et al. 2005, Zecho et al. 2002, Hoenekaer et al. 2003), allowing a better understanding of the morphology of dust grains.

The past discussion and also much recent work have centred on the fact that for the case (Langmuir Hinshelwood mechanism) where the two H atoms are physisorbed (attached to the surface by Van der Waals forces), one predicts efficient H$_2$ formation in a very small temperature range. This specificity is backed up by laboratory studies (Pironnello 1997a,b; 1999). Although the predicted temperature range for significant formation of H$_2$ is close to the observed interstellar grain temperatures (Boulanger et al. 1996; Dwek et al. 1997; Rawlings et al. 2005) of around 15-18 K, it seems unlikely that this coincidence happens everywhere. Moreover, there are cases where the grain temperature is much higher and yet the H$_2$ formation rate appears high (Duley & William 1984; Tielens & Hollenbach 1985a, 1985b; Habart et al. 2004; Allers et al. 2005). Molecular hydrogen has been observed in the Universe under various physical conditions. In diffuse clouds, that typically have a density of 50 cm$^{-3}$, a gas temperature of $\sim$ 100 K, and a dust temperature of 15 K, H$_2$ forms with a rate of $1 - 3 \times 10^{-17} n_o n(H) \, \text{cm}^{-3} \, \text{s}^{-1}$ where $n_o$ is the total density and $n(H)$ is the density of H-atoms (Jura 1974; Hollenbach, Werner, & Salpeter 1971). In molecular clouds and PDRs, the physical conditions at which H$_2$ has been observed can cover a wide range of gas and grain temperatures (100K $\leq$ T$_{\text{gas}}$ $\leq$ 1000K; 10K $\leq$ T$_{\text{dust}}$ $\leq$ 100K). H$_2$ formation rate varies from $3 \times 10^{-17}$ to $1.5 \times 10^{-16}$ cm$^{-3}$ s$^{-1}$ for the PDRs associated with Orion Bar, NGC 2023, Chamaeleon, S140, IC 63 and Oph W (Habart et al. 2004, Allers et al. 2005). In Active galaxies, i.e. in galaxies hosting an active galactic nucleus (AGN), H$_2$ emission originates from a region with a gas temperature $\leq$ 2000K (in NGC 1068, Rigopoulou et al. 2002), and from a region with two dust components: one cold at 15-30 K and one warm at 50-70 K (Barthel & van Bemmel 2003). Molecular hydrogen is also present in the early Universe, as testified by Damped Lyman Alpha systems (DLAs). Ledoux, Petitjean & Srianand (2003) detected absorption lines of H$_2$ toward several DLAs at high redshift ($z_{\text{abs}} \geq 1.8$), showing that H$_2$ could form even in low metallicity objects where the dust to gas ratio is as low as 1/20 to 1/4 of the Milky Way (Fall, Pei, & McMahon 1989). All these observations show that molecular hydrogen forms with a high rate under various physical conditions. This
have led to various attempts to examine the circumstances under which the efficiency $\epsilon(T_{dust})$ could be close to 1 over an extended temperature range (Morisset et al. 2004, 2005; Cazaux & Tielens 2002, 2004; Chang et al. 2005; Cuppen & Herbst 2005).

The most recent approaches deal with the inhomogeneities of the interstellar grain surfaces. The interactions between the atoms and these surfaces are supposed to be only weak (Van der Waals) and are distributed in energy. An approach adopted by Chang et al. (2005) showed that on inhomogeneous surfaces with distributions of H–atom diffusion barriers and (physisorption) binding energies, as well as on mixed surfaces of olivine and carbon, the $\text{H}_2$ formation efficiency remains large at dust temperatures relevant for diffuse clouds. More recently, Cuppen & Herbst (2005) considered in their Monte Carlo simulations $\text{H}_2$ formation on rough surfaces (where, unlike flat surfaces, there are height differences of at least several monolayers), based on the structure of olivine and amorphous carbon studied in laboratory experiments. Their results show an $\text{H}_2$ formation efficiency large until $T_{dust} \sim 40$ K depending on the poorly known strengths of lateral bonds between H atoms and the (rough) surface. In their work, the presence of surface irregularities enhances the binding energy of hydrogen atoms but ignores a possible barrier for the H atoms to enter in these sites, as it is the case for strong interactions.

The approach of Cazaux and Tielens (2002, 2004) considers that in addition to physisorption sites on the grain, there are also sites where H (or D) atoms can be chemisorbed with well depths of a large fraction of an electron volt. The presence of these two interactions between an atom and a surface has been calculated and measured by several authors since decades (Physisorption: Ghio 1980; Pirronello et al. 1997a, 1997b, 1999 and chemisorption: experimentally: Gütter et al. 2004; Zecho et al. 2002; Theoretically: Aronowitch & Chang 1980; Klose et al. 1992; Fromherz et al. 1993; Jeloaica & Sidis 1999; Sha & Jackson 2002; Sha & Jackson 2005). By considering these two interactions, one might have formation of $\text{H}_2$ due to association of a physisorbed H atom with a chemisorbed H atom. Since the chemisorbed H atom is more tightly bound will be less susceptible to evaporation, one can thus maintain $\text{H}_2$ formation at grain temperatures higher than the 15-18 K mentioned above. Cazaux & Tielens (2004) examined this possibility and found that one could indeed keep a high $\text{H}_2$ formation efficiency up to temperatures of 20-30 K with moderate efficiency up to several hundreds of Kelvins. This seems more satisfactory though this efficiency depends strongly (for $T_{dust} \geq 20$-30K) on how easy an atom can chemisorb on an interstellar grain, and therefore, on the nature of the barrier against chemisorption. This uncertainties will be discussed in this paper.

More laboratory work on olivine and carbonaceous grains will definitely help in better constraining dust properties, but the actual structure of interstellar dust grains cannot be completely defined if model predictions cannot be tested against observations. As discussed above, the $\text{H}_2$ formation process alone cannot be used for these purposes, given that a large variety of models can reproduce the $\text{H}_2$ abundance observed in diffuse clouds. We need to go one step forward and make other predictions besides the formation of $\text{H}_2$. The simplest next step is to concentrate on the deuterated forms of molecular hydrogen (HD and $\text{D}_2$) and this is the topic of the present paper. This has traditionally been considered unimportant because HD can form in the gas phase from $\text{H}_2$ via ion-molecule reactions (and analogously $\text{D}_2$ from HD). The gas phase route is expected to be more efficient than direct formation on grains if the $\text{H}_2$ molecular fraction $f_{mol} = \frac{2n(\text{H}_2)}{n_H}$ is larger than roughly 0.1 (Watson 1973). In a future paper, we will examine under which circumstances this
is true and whether formation on dust grains makes an appreciable contribution to the observed HD in diffuse clouds. D\textsubscript{2} has not been observed to date and we study its formation on grains as well as the possibility that it might be observable. The present paper focuses on surface processes, whereas in a future paper, surface chemistry will be coupled with gas phase chemistry and the model will be applied to different astrophysical environments.

In section 2 of this paper, we describe the properties of dust surfaces, concentrating on Graphitic and amorphous carbon grains, for which laboratory work is available. In Section 3 our model of surface chemistry is described, including the H and D rates of evaporation and mobility, rate equations, formation efficiencies. We also give some analytic approximations which reasonably reproduce our computed efficiencies for a limited range of grain temperature. In Section 4, we check the validity of the rate equation method against the Monte Carlo approach and compare with previous work. A general discussion can be found in Section 5, whereas the main conclusions are listed in Section 6.

2. Properties of the dust surface

We concentrate here on Graphitic (Gr) and Amorphous Carbon (AC) grains since Olivine surfaces have been experimentally studied only at low temperatures (Pirronello et al. 1997a, 1997b), making a characterisation of the strong interaction between the atoms and the surface very doubtful (Cazaux & Tielens 2002). Grains rich in carbon, usually called carbonaceous in amorphous form, and graphitic in crystalline form, have been the subject of a variety of experimental and theoretical studies. Graphite surfaces have been favoured for their simplest structures in order to perform ab-initio calculations as well as experiments. Theoretically, studies agree in saying that there is a barrier between physisorbed and chemisorbed sites of 0.2 eV (Jeloaica & Sidis 1999; Sha & Jackson 2002), making the filling of the chemisorbed sites very unlikely if the incoming atoms have low energies. Experiments at high temperatures on graphite confirmed the presence of a high barrier against chemisorption (Zeche et al. 2002). Carbonaceous surfaces, on the other hand, present a very small barrier against chemisorption. Experiments, performed by Menella et al. (2001), show that for nano-sized carbon grains, low energies H atoms can efficiently be bound to the surface (C-H bonds 6%), showing that the barrier against chemisorption is small. Recent experiments from Zeche (private communication) proved that amorphous carbon surfaces present almost no barrier against chemisorption. Theoretically, Sha & Jackson (2004) determined a very small activation barrier for the adsorption of H atoms on the edges of Graphitic nanostructures, and proved that H atoms can easily be chemisorbed on amorphous carbon surfaces.

It seems that carbon grains in the diffuse medium are a mixture of aliphatic and aromatic compounds (Pendleton & Allamandola 2002). Big dust grains are thought to be under the form of carbonaceous grains, whereas small dust grains are under the form of PAHs. In this work, we consider two types of carbon grains as illustrated in Fig.1: (1) Small grains (≤ 100 Å), also called PAHs, have a surface similar to graphite. This surface present a barrier against chemisorption of 0.2 eV height and suppress the formation of H\textsubscript{2} at intermediate and high temperatures. (2) Bigger grains, have a surface similar to Amorphous Carbon surface. This surface presents a small (or none) barrier against chemisorption.
3. Surface chemistry

The formation of H$_2$ and its deuterated forms on cold grains ($T_{\text{dust}} \leq 20K$) has been discussed by many authors, and is still a controversial subject. While the Langmuir–Hinshelwood kinetics – the association of two atoms moving on the surface – is one of the main processes for the formation of these molecules at low grain temperatures (Pirronello et al. 1997a, 1997b, 1999; Katz et al. 1999; Chang et al. 2005; Cuppen & Herbst 2005), the Eley–Rideal mechanism – the association of an atom from the gas phase with a physisorbed atom – seems not negligible (Morrisset et al. 2003). We consider in our model these two mechanisms, and discuss in Sect. [5.3.1] their relative importance.

3.1. Interaction between H, D atoms and the dust surface

An atom from the gas phase hits the grain surface with a certain energy $kT_{\text{gas}}$, and, if stuck on the grain, it can either become physisorbed or chemisorbed. The probability for an atom to directly arrive in a chemisorbed site is given by the transmission coefficient (to pass the barrier against chemisorption) integrated over an energy range described by the Boltzmann law (for details see Cazaux & Tielens 2004). We call this probability $T_{\text{pc}}(H_{\text{gas}})$ and $T_{\text{pc}}(D_{\text{gas}})$ for H and D atoms, respectively. Once on the surface, the atom can go from its site to another site with a rate $\alpha_{ij}$, where $i$ is the initial site, and $j$ is the next site which can be occupied. These rates, which describe the mobility of atoms on the surface, are calculated similarly to the $T_{\text{pc}}(H_{\text{gas}})$ and $T_{\text{pc}}(D_{\text{gas}})$, but they are multiplied by the oscillation factor of the atoms. Also, the Boltzmann energy distribution of an atom on a grain is centered on $T_{\text{dust}}$, while it is centered on $T_{\text{gas}}$ for an atom in the gas phase. The atom on the grain can evaporate with a rate $\beta(H_P)$ and $\beta(D_P)$ for physisorbed H and D atoms, and $\beta(H_C)$ and $\beta(D_C)$ for chemisorbed H and D atoms. Figure 2 shows the various rates adopted in our model as a function of dust temperature and for the two different types of grains considered (see Sect. [2]). $\alpha_{\text{pc}}$ and $\alpha_{\text{pp}}$ are the mobility rates of H or D to move from a physisorbed to a chemisorbed site and between two physisorbed sites, respectively. $\beta$ is the evaporation rate for physisorbed deuterium and hydrogen, exponentially dependent on the temperature. $T_{\text{pc}}$ is the fraction of the H and D atoms coming from the gas phase, with a temperature of 100K, that directly chemisorb (1 % on an amorphous carbon surface, and 0.02 % on graphitic surfaces). The first thing to note in the figure is the huge difference between $\alpha_{\text{pc}}$ for Gr and AC grains at $T_{\text{dust}} > 20$ K, which shows weak dependence with dust temperature when tunnelling dominates ($T_{\text{dust}} < 20$ K for AC and < 100 K for Gr), whereas the dependence becomes exponential when thermal hopping dominates. We also note the steep rise of $\alpha_{\text{pp}}(D)$ at $T_{\text{dust}} > 11$ K and $\alpha_{\text{pp}}(H)$ at $T_{\text{dust}} > 14$ K for Gr and AC grains.

3.2. Rate equations

The model described in Cazaux & Tielens (2004) is reconsidered here, with the addition of deuterated species. H$_2$, HD and D$_2$ formation mechanisms on grain surfaces are studied with the rate equation method based on the following assumptions:

1) The interaction atom/surface can be either weak (Van der Waals interaction, also called physisorption) or strong (covalent bound also called chemisorption), with the assumption that for
each physisorbed site, there is a chemisorbed site.

2) An atom on the grain moves from one site to another by tunnelling effect or thermal hopping, according to its energy.

3) Two atoms can associate to form a molecule following the Langmuir–Hinshelwood and Eley–Rideal mechanisms.

In this study, we add deuterium in our rate equation model and follow the population of physisorbed H (H\textsubscript{p}) and D (D\textsubscript{p}), chemisorbed H (H\textsubscript{c}) and D (D\textsubscript{c}), and the H\textsubscript{2}, HD and D\textsubscript{2} molecules, which are physisorbed. The rate equations are written as follow:

\[
\dot{H}_p = F_p(1 - T_{pc}H_{gas})(1 - H_p - D_p - HD - H_2 - D_2) \\
- F_p(1 - T_{pc}H_{gas})H_p - F_D(1 - T_{pc}D_{gas})H_p \\
- \alpha_{pp}(H)H_p - 2\alpha_{pp}(H)H_p^2 - \alpha_{pp}(H)H_pD_p - \alpha_{pp}(D)D_pH_p \\
- \beta_{H_p}H_p
\]  

(1)

\[
\dot{D}_p = F_D(1 - T_{pc}D_{gas})(1 - H_p - D_p - HD - H_2 - D_2) \\
- F_D(1 - T_{pc}D_{gas})D_p - F_H(1 - T_{pc}H_{gas})D_p \\
- \alpha_{pp}(D)D_p - 2\alpha_{pp}(D)D_p^2 - \alpha_{pp}(D)D_pH_p - \alpha_{pp}(H)H_pD_p \\
- \beta_{D_p}D_p
\]  

(2)

These two equations describe the fractional population of H and D atoms in physisorbed sites, when a flux F\textsubscript{p} and F\textsubscript{D} of H and D atoms is sent on the surface. The first two lines of these equations describe the fraction of H and D atoms coming from the gas phase that physisorb on the grain. A fraction T\textsubscript{pc}H\textsubscript{gas} and T\textsubscript{pc}D\textsubscript{gas}, of H and D atoms goes directly in chemisorbed sites. These fractions are the amount of H and D atoms, coming from the gas phase with an energy T\textsubscript{gas}, that can cross the barrier against chemisorption. Also, a part of the incoming atoms going to physisorb arrive in an already filled physisorbed site and can either form directly a molecule (Eley-Rideal mechanism, 2\textsuperscript{nd} lines of eq. 1 and 2) if the site is occupied by an atom, or bounce back to the gas phase if the site is occupied by a molecule. The third line of these equations are dealing with Langmuir kinetic processes where the atoms diffuse on the surface from a site i to a site j with a rate \(\alpha_{ij}(H)\) and \(\alpha_{ij}(D)\). On these third lines, the first terms are the rate of atoms going to chemisorbed sites, the second, third and fourth terms are the association of the physisorbed atoms with other physisorbed atoms and the last term is the evaporation rate of the physisorbed atoms.

The equations describing the fractional population of H and D atoms in chemisorbed sites are:

\[
\dot{H}_c = F_H T_{pc}H_{gas} (1 - H_c - D_c) - F_H T_{pc}H_{gas} H_c - F_D T_{pc}D_{gas} H_c \\
\alpha_{pp}(H)H_p(1 - H_c - D_c) - \alpha_{pp}(H)H_pH_c - \alpha_{pp}(D)D_pH_c \\
- \beta_{H_c}H_c
\]  

(3)

\[
\dot{D}_c = F_D T_{pc}D_{gas} (1 - D_c - H_c) - F_D T_{pc}D_{gas} D_c - F_H T_{pc}H_{gas} D_c \\
\alpha_{pp}(D)D_p(1 - D_c - H_c) - \alpha_{pp}(D)D_pD_c - \alpha_{pp}(H)H_pD_c \\
- \beta_{D_c}D_c
\]  

(4)
The first lines represent the fraction of the H and D atoms that cross the barrier against chemisorption and populate directly the chemisorbed sites (with probability $T_{pc}(H)$ and $T_{pc}(D)$, respectively). One part of these atoms arrive in some already occupied sites and form a molecule (Eley-Rideal mechanism, 2nd and 3rd terms of the first lines). In the second lines, the first terms account for physisorbed atoms arriving in empty chemisorbed sites, the second and third terms for the association of incoming physisorbed atoms with chemisorbed atoms, and the last term accounts for the evaporation of chemisorbed atoms.

The fractional population of $H_2$, $D_2$ and HD on grain surfaces is described by the following three equations:

$$\dot{H}_2 = +\mu(\alpha_{pp}(H)H^2_P + \alpha_{pc}(H)H_PH_C) - \beta_{H_2}H_2$$ (5)

$$\dot{D}_2 = +\mu(\alpha_{pp}(D)D^2_P + \alpha_{pc}(D)D_PD_C) - \beta_{D_2}D_2$$ (6)

$$\dot{HD} = +\mu(\alpha_{pp}(H)H_PD_C + \alpha_{pp}(D)D_PH_C + \alpha_{pc}(H)H_PD_C + \alpha_{pc}(D)D_PH_C) - \beta_{HD}HD$$ (7)

When a molecule is formed, because of the energy released during formation, a fraction $\mu$ stays on the grain surface, while a fraction $1-\mu$ spontaneously desorbs in the gas phase. The value of $\mu$ has been estimated from experiments (Katz et al. 1999; Cazaux & Tielens 2002), and is considered to be identical for the different species (based on the experiments of HD desorption from Pirronello et al. 1997). The terms multiplied by $\mu$ describe the total formation rate of species remaining on the surface, whereas the last terms correspond to their evaporation rate. We consider in our approach that the molecules formed through the Eley-Rideal mechanism directly desorb in the gas phase. In the next section, we show that this approximation is reasonable for grain temperatures higher than 10K.

In order to estimate the coverage of the different atoms and molecules on the grain, one needs to solve the 7 rate equations above, which are coupled. We point out here that the rate equation approach is valid when grains are covered by 1 or more of each species considered. This point is discussed in Sect. 4 of this paper.

### 3.3. Formation rates and formation efficiencies

The formation rate on dust surface of $H_2$, HD and $D_2$ that are released in the gas phase can be written as:

$$R_d(H_2) = F_H(1 - T_{pc}H_{gas})H_P + F_H T_{pc}H_{gas} H_C + (1-\mu)(\alpha_{pp}(H)H^2_P + \alpha_{pc}(H)H_PH_C) + \beta_{H_2}H_2$$ (8)

$$R_d(D_2) = F_D(1 - T_{pc}D_{gas})D_P + F_D T_{pc}D_{gas} D_C + (1-\mu)(\alpha_{pp}(D)D^2_P + \alpha_{pc}(D)D_PD_C) + \beta_{D_2}D_2$$ (9)

$$R_d(HD) = F_H(1 - T_{pc}H_{gas})D_P + F_H T_{pc}H_{gas} D_C + F_D(1 - T_{pc}D_{gas})H_P + F_D T_{pc}D_{gas} H_C$$

In these expressions, the terms with $F_H$ and $F_D$ represent the association of gas phase atoms with adsorbed atoms to form molecules via the Eley–Rideal mechanism. The other terms involve the association of two adsorbed atoms through the Langmuir-Hinshelwood kinetic. The formation efficiencies of the different molecules are: 

$$
\varepsilon(H_2) = \frac{2 \times R_d(H_2)}{P_H}, \quad \varepsilon(D_2) = \frac{2 \times R_d(D_2)}{P_D} \quad \text{and} \quad \varepsilon(HD) = \frac{R_d(HD)}{P_D}.
$$

### 3.3.1. Eley–Rideal vs Langmuir–Hinshelwood

The efficiency of formation of $H_2$, HD and $D_2$ for graphitic and amorphous carbon surfaces are shown in Fig. 3 for a density of H atoms of 100 atoms cm$^{-3}$, a gas temperature of 100K, and a D/H ratio of $2 \times 10^{-5}$. The different mechanisms involved in the formation of these molecules are presented. The Langmuir–Hinshelwood mechanism (LH) is the dominant process at any dust temperatures for amorphous carbon grains and at low grain temperatures ($T_{dust} \leq 25$K) for graphitic grains. Then, only in the case of graphitic grains, and at higher grain temperatures ($T_{dust} \geq 25$K), the Eley-Rideal (ER) mechanism becomes important because most of the physisorbed atoms evaporate before populating the chemisorbed sites. The formation of molecules is then assured by the association of those atoms that chemisorb with the atoms from the gas phase that cross the barrier against chemisorption.

We consider in our model that molecules formed through the Eley–Rideal mechanisms are directly released into the gas phase. There is actually no experimental prove of such a behaviour, but because the Eley-Rideal mechanism is efficient for grain temperatures higher than 25K, if some newly formed molecules remain on the surface, they will evaporate immediately. Therefore, considering $\mu = 0$ for the Eley-Rideal mechanism is actually a reasonable approximation. In the case of very cold grains $\leq 9$K, this approximation can not be applied and a factor $\mu \neq 0$ should be considered.

A striking result is the enhanced $D_2$ formation for a very narrow range of grain temperatures, while $H_2$ and HD form efficiently for a much broader range. This $D_2$ enhancement is much more important on graphitic surfaces than on amorphous carbon surfaces. Indeed, in the case of graphitic surfaces, at low surface temperatures, the high and narrow barrier against chemisorption allows H atoms to chemisorb through tunnelling, whereas most of the D atoms stay physisorbed. The H atoms, imprisoned in chemisorbed sites, free the physisorbed sites and let the physisorbed D atoms meet other physisorbed D atoms. This process makes the formation of $D_2$ very efficient (for $T_{dust} \leq 20$K), but for higher grain temperatures, the physisorbed D evaporate and no chemisorbed D can insure the formation of $D_2$. Therefore the $D_2$ efficiency drops for grain temperatures higher than 20K. In the case of carbonaceous grains, the barrier against chemisorption is smaller, and H and D atoms present similar mobilities (see Fig. 2) making the physisorbed sites also populated by H atoms. The formation of $D_2$ is slightly enhanced around $T_{dust} \sim 15$K and follows the same behaviour than $H_2$ and HD at higher grain temperatures.

The grain temperature at which $D_2$ formation reaches its maximum also varies with the type of grain. In fact, the formation of $D_2$ depends on the amount of physisorbed D atoms, which decreases with the physisorption–chemisorption mobility and evaporation rates, $\alpha_{pc}(D)$ and $\beta_{D_p}$, both strongly dependent on $T_{dust}$ (see Fig. 2). For graphitic grains, at the highest $D_2$ formation effi-
ciency, the physisorbed D atoms evaporate more easily than they move into a chemisorbed site ($\alpha_{pc}(D) \leq \beta_{Dp}$). For amorphous carbon grains, on the other hand, the physisorbed D atoms disappear by getting trapped in chemisorbed sites (for low H densities ~ 1 cm$^{-3}$) or by associating with a physisorbed H atom (only for high H densities ~ $10^4$ cm$^{-3}$). Therefore, the decrease of D$_2$ efficiency, due to the disappearance of physisorbed D, occurs at lower grain temperatures for Gr than for AC grains.

The effect of the variation of gas temperature and H density is shown in Fig. 4 with a grain temperature set at 15K. The gas temperature does not have a big impact on the formation of H$_2$, HD and D$_2$ with the Langmuir–Hinshelwood mechanism. On the other hand, the gas temperature strongly increases the formation of the different molecules through the Eley-Rideal mechanism because the atoms can cross more easily the barrier against chemisorption.

As shown in Fig. 4 the H$_2$ and HD formation efficiencies are constant with H density, while D$_2$ formation efficiency is sensitive to its variation. The Langmuir–Hinshelwood kinetic is strongly affected by the density of H atoms. Indeed, for low H densities, the physisorbed sites are mainly populated with D atoms, and D$_2$ formation is enhanced, while for high H densities, physisorbed sites are also populated by H atoms, making easier the formation of an HD molecule then of a D$_2$ molecule. This effect is very different for the two types of grain since the barrier between physisorption and chemisorption sets the migration time of the atoms to go to a chemisorbed site, $1/\alpha_{pc}(H)$ and $1/\alpha_{pc}(D)$. If the physisorbed D atoms go to a chemisorbed site easier than they evaporate ($\alpha_{pc}(D) \geq \beta_{Dp}$), or than they meet a physisorbed H atom ($\alpha_{pc}(D) \geq \alpha_{pp}(H) F_H$ where this expression represents the flux of H atoms in physisorbed sites), then D atoms transit to chemisorbed sites, and less D$_2$ forms. If, on the other hand, the physisorbed D atoms have more chance to meet another physisorbed D than to chemisorb ($\alpha_{pc}(D) \geq \alpha_{pp}(D) F_D$ becomes $\geq \alpha_{pc}(D)$) or to meet a physisorbed H ($\alpha_{pc}(D) F_H$ becomes $\geq \alpha_{pp}(H) F_H$), then D$_2$ is formed more efficiently. For the two types of grains considered here, the D$_2$ efficiency reaches its maximum at different H densities (nH=100 atoms cm$^{-3}$ for Gr grains and nH=$10^4$ atoms cm$^{-3}$ for AC grains).

The effect of the variation of the D/H ratio on the formation efficiencies of the different molecules is reported in Fig. 5 with a grain temperature set at 15K, a gas temperature at 100K and a density of 100 atoms cm$^{-3}$. H$_2$ does not depend on the D/H ratio, while HD and D$_2$ efficiencies show very different behaviours for Gr and AC grains. As discussed before, Gr grains, which have a very high barrier against chemisorption, segregate the H and D atoms by having most of its H chemisorbed and D physisorbed. This segregation favours deuteration.

### 3.3.2. Analytic expressions

Between dust temperatures of 10K and 25 K, as discussed previously, the Eley-Rideal mechanism can be neglected. The formation efficiency of H$_2$, HD and D$_2$ are calculated by setting the rate equations to zero (steady state conditions), and can be approximated as:

$$
\epsilon_{H_2} = 2 \times \frac{(\alpha_{pp}(H)H_p^2 + \alpha_{pc}(H)H_pH_C)}{F_H}
$$

$$
\epsilon_{D_2} = 2 \times \frac{(\alpha_{pp}(D)D_p^2 + \alpha_{pc}(H)H_pD_C)}{F_D}
$$

$$
\epsilon_{HD} = \frac{\alpha_{pp}(H) + \alpha_{pp}(D))H_pD_p + \alpha_{pc}(H)H_pD_C + \alpha_{pc}(D)D_pH_C}{F_D}
$$

(11)  
(12)  
(13)
These equations show that the formation of $H_2$ occurs mainly through the association of a physisorbed and a chemisorbed atom. HD can be formed through the association of 2 physisorbed atoms, when the H atoms populate the physisorbed sites (high H densities of the medium, and low grain temperatures) or through the association of physisorbed and chemisorbed atoms. In the same way, $D_2$ can be formed through the association of two physisorbed atoms when physisorbed sites are mostly populated by D atoms, or through the association of a physisorbed and a chemisorbed D atom. The population of physisorbed H ($H_P$) and D ($D_P$), as well as chemisorbed H ($H_C$) and D ($D_C$) and $H_2$, HD and $D_2$ are determined in steady state conditions as:

$$H_P = \frac{F_H}{\alpha_{pc}(H) + \beta_{H_P}} \quad (14)$$

$$D_P = \frac{\alpha_{pc}(D) + \alpha_{pp}(H)H_P + \sqrt{(\alpha_{pc}(D) + \alpha_{pp}(H)H_P)^2 + 4F_D\alpha_{pp}(D)}}{2\alpha_{pp}(D)} \quad (15)$$

$$H_C = \frac{1}{2} \quad (16)$$

$$D_C = \frac{\alpha_{pc}(D)D_P}{2\alpha_{pc}(H)H_P} \quad (17)$$

$$H_2 = \frac{\mu\alpha_{pc}(H)H_P H_C}{\beta_{H_2}} \quad (18)$$

$$HD = \frac{\mu(\alpha_{pp}(H) + \alpha_{pp}(D))H_P D_P + \alpha_{pc}(H)H_P D_C + \alpha_{pc}(D)D_P H_C}{\beta_{HD}} \quad (19)$$

$$D_2 = \frac{\mu(\alpha_{pp}(D)D_P^2 + \alpha_{pc}(D)D_P D_C)}{\beta_{D_2}} \quad (20)$$

Half of the chemisorbed sites are occupied by hydrogen atoms because at low temperatures, the rate of physisorbed atoms to become chemisorbed is higher than their evaporation rate (as shown in fig. 2). Therefore physisorbed atoms, after visiting a number of $\frac{\alpha_{pc}}{\alpha_{pp}}$ of physisorbed sites, will become trapped in chemisorbed sites. Above a certain temperature (20K for graphite and 50 K for amorphous carbon), this sites are filled through direct chemisorption.

The formation efficiencies of the different species, for grain temperatures between 10 and 25 K, can be written:

$$\epsilon_{H_2} = \left[ \frac{\alpha_{pc}(H) + \beta_{H_P}}{\alpha_{pc}(H)} \right] \quad (21)$$

$$\epsilon_{D_2} = 2 \frac{D_P^2}{F(D)} \left[ \frac{\alpha_{pp}(D) + \alpha_{pc}(D)^2}{2F(H)} \right] \quad (22)$$

$$\epsilon_{HD} = D_P \left[ \frac{(\alpha_{pp}(H) + \alpha_{pp}(D))H_P + \alpha_{pc}(D)}{F_D} \right] \quad (23)$$

In Fig. 6 we show the validity of these approximations with our model. As discussed above, we consider a range of grains temperatures ($10K \leq T_{dust} \leq 25K$) in which the Eley Rideal mechanism can be neglected. Because we are using a rate equation approach to calculate the formation rate of the different molecules, we need to define for which circumstances our approach is not valid. Indeed, rate equations cannot be used if the grain is covered by less than 1 species (Biham et al. 2001, Green et al. 2001, Caselli et al. 1998). In the case of hydrogen, rate equations are always valid because half of the chemisorbed sites are filled with hydrogen atoms. The problem is different for deuterium since most of the small grains are covered by less than 1 D atom.
4. Validity check of the Rate Equation method

For very small grains, while the number of hydrogen on the surface (half of the chemisorbed sites) is always larger than one, and therefore the rate equation method is always appropriate to describe H\(_2\) formation, the number of D atoms on the grain can be less than 1. In figure 7 we calculate the “critical” size of a grain for which one deuterium is present on its surface. These calculations have been performed for a density of nH=100 cm\(^{-3}\), a grain temperature of 15K, and for three different D/H ratio: 2\(\times\)10\(^{-5}\), 2\(\times\)10\(^{-3}\) and 2\(\times\)10\(^{-1}\) for graphitic grains (left panel) and amorphous carbon grains (right panel).

4.1. Monte Carlo and approximations

For grains below the critical size, the rate equation method cannot be used to follow the formation of HD and D\(_2\) on very small grains. We developed a Monte Carlo model in order to follow the formation of HD and D\(_2\) on these grains. In our model, the grain is seen as a squared grid, with, at each intersection, the possibility to have a chemisorbed and a physisorbed atom. We consider as before direct chemisorption as well as Langmuir and Eley-Rideal mechanisms. When an atom comes from the gas phase onto this grid, depending on its energy, it can become physisorbed or chemisorbed. If the site is already occupied, it can form a molecule which is released in the gas phase (we consider \(\mu=0\), which is a valid approximation for a range of temperature at which newly formed molecules staying on the surface thermally desorb). The position of the incoming atom on the grid is chosen randomly. Once on the grid, the atom can move from site to site according to its energy and follows a random walk. If two atoms arrive in the same site, they associate to form a molecule which is released in the gas phase. As discussed before, small grains (\(\leq 100\)Å) are considered to have surfaces similar to graphite, and big grains similar to amorphous carbon.

Because the accretion of D on the grain is very low compared with the accretion of H, the calculation times to form a HD and a D\(_2\) molecule are very important. To deal with this problem, we performed the Monte Carlo simulation for a D/H ratio from 10 to 1000 times higher than the standard value 2\(\times\)10\(^{-5}\), and extrapolate these results for small D/H ratios. The calculations are performed here for T\(_{\text{dust}}\)=15K, T\(_{\text{gas}}\)=100K and nH=100 cm\(^{-3}\). Fig. 9 show the HD and D\(_2\) efficiencies for graphitic grain from 100 sites (\(\sim 30\) Å) to 10\(^7\) sites (\(\sim 1\) µm) and for a D/H ratio that varies from 2\(\times\)10\(^{-4}\) to 2\(\times\)10\(^{-1}\). Fig. 9 shows these efficiencies for carbonaceous grains for a D/H ratio of 2\(\times\)10\(^{-1}\) and 2\(\times\)10\(^{-3}\). For big grains, steady state and Monte Carlo simulations give the same results. As expected, when the number of physisorbed deuterium on the grain is less than one, the two methods diverge. This happens for a grain smaller than a critical size as determined in Fig. 7. Below this critical size, with decreasing grain sizes, the efficiency of D\(_2\) decreases, while the efficiency of HD increases. Indeed, on big grains, the number of physisorbed deuterium is higher or equal to 1, and a D atom coming from the gas phase on the grain can meet another physisorbed deuterium. On small grains, on the other hand, the number of physisorbed deuterium can be less than 1, and a deuterium atom coming from the gas phase on the grain can scout the surface before getting trapped in a chemisorbed site without meeting another deuterium. When getting chemisorbed, the deuterium can meet a H atom already present, or can wait for a H atom coming in the chemisorbed site. According to our calculations, as shown in fig. 9 (right) and in fig. 10 (right), association of physisorbed atoms on grain surfaces are dependent on the size of the grains,
while association of physisorbed and chemisorbed atoms are independent of size. We derived an empirical formula in order to reproduce the formation efficiencies of HD and D$_2$ with grain sizes:

\[ e(D_2) = \epsilon_{SS}(D_2)_{P+C} + \epsilon_{SS}(D_2)_{P+P} \exp \left( \frac{-1}{\sqrt{D/H \times n_{sites}}} \right) \quad (24) \]

\[ e(HD) = \epsilon_{SS}(HD) + \epsilon_{SS}(D_2) - e(D_2) \]

\[ = \epsilon_{SS}(HD) + \epsilon_{SS}(D_2)_{P+P}(1 - \exp \left( \frac{-1}{\sqrt{D/H \times n_{sites}}} \right)) \quad (25) \]

where $\epsilon_{SS}$ is the total formation efficiency in steady state (see Fig. 5). $\epsilon_{SS}(P+C)$ is the formation efficiency through the association of physisorbed and chemisorbed atoms and $\epsilon_{SS}(P+P)$ the formation efficiency through the association of two physisorbed atoms. Efficiencies due to the formation of molecules through the association of 2 physisorbed atoms decreases with decreasing grain size. These approximations are compared to our Monte Carlo simulation in fig. 8 and 9. The error bars in our Monte Carlo simulations are obtained by repeating the calculations at least twice, depending on the CPU times required. The mean values are calculated together with the standard deviation. This latter quantity is multiplied by the appropriate student variable and the result represents the half confidence interval at the critical risk of 5% (95% confidence interval).

4.2. Comparison with previous work

Recently, Lipshtat et al. (2004) studied the formation of HD and D$_2$ on grain surfaces. Their work differs from ours in several respects. First, their study considers only physisorbed sites and, as a consequence, they find H$_2$ formation to be relatively inefficient at temperatures as low as 18 K (though note the efficiency is close to 1 below 16K). Second, they consider the formation of H$_2$, HD and D$_2$ on grains as small as 50 Å with a master equation approach, and integrate over a realistic grain size distribution. Their conclusions are that the production of the different molecules decreases with grain sizes. Also, when integrated over a large range of grain sizes, the ratio of the production of HD over that of H$_2$ $R(\text{HD})/R(H_2)$ and D$_2$ over H$_2$ $R(D_2)/R(H_2)$ can be enhanced by a factor as high as 44 (78) for HD (D$_2$) (but sensitively dependent on $T_{\text{dust}}$). This enhancement is due to a decrease of production of H$_2$.

Our results differ in that, as a consequence of the presence of chemisorbed sites, we find almost 100 percent efficiency in both H$_2$ and HD formation (see Fig. 5), as long as the formation is made through the association of physisorbed and chemisorbed atoms. With our model, H$_2$ formation is independent of the size of the grains. D$_2$, which is mostly formed through the association of physisorbed atoms, has an efficiency which is grain size dependant. The efficiency of D$_2$ formation from Figs. 3 and 4 can be enhanced by 3000 for graphitic grains and a factor of 100 for carbonaceous grains. Also, using a Monte Carlo simulation, we show that the formation of D$_2$ decreases with decreasing grain sizes, while the formation of HD increases. The production of these molecules integrated over a range of grain sizes is discussed in the next section.

5. Discussion

Density Functional Theory (DFT) calculations, showed that an H atom get chemisorbed on graphitic surfaces atop a C atom which has to move from the surface towards this adsorbate
S. Cazaux, P. Caselli, V. Cobut, J. Le Bourlot: H\textsubscript{2}, HD and D\textsubscript{2} (Jeloaica & Sidis 1999, Sha & Jackson 2002). This phenomenon is called puckering, and creates a barrier against chemisorption of 0.2 eV. Recent studies from Rougeau et al. (2006) and Hornekaer et al. (2006) showed that once an H atom is chemisorbed on graphite, and therefore that a C atom has puckered out of the plane, the next coming H atom can chemisorb in certain neighbouring site (para site) without barrier. Another study by Bachellerie et al. (2007) shows that once an H atom is chemisorbed in a para site, a second H atom can also chemisorb in the same site without barrier and form a molecule. These results are of main importance for the formation of molecules when the chemisorbed atoms are involved. Because rate equations do not take into account the detailed structure of the surface, we could not take this phenomenon into account. In this study, we developed a Monte Carlo simulation in order to understand how the formation of H\textsubscript{2}, HD and D\textsubscript{2} changes with the size of the grain. We compared these simulation to the rate equations model, and therefore had to consider the same surface without taking into account the properties of the para sites. In a future work we will incorporate these properties in our Monte Carlo simulations and see how the formation efficiencies of H\textsubscript{2} and its deuterated forms differ if we take into account the para sites. The first effect of the inclusions of the para sites in our model should be a more efficient H\textsubscript{2} formation rate temperatures higher than 20K.

To summarise the results obtained so far for D\textsubscript{2}, figure 11 shows the variation of the D\textsubscript{2} formation efficiency with dust temperature for the following parameters: \( n(H\textsubscript{2}) = 1000 \text{ cm}^{-3} \) and D/H = \( 2 \times 10^{-5} \). The efficiency of D\textsubscript{2} formation varies strongly from one kind of surfaces to another. If we consider surfaces where only physisorption is possible, the formation of D\textsubscript{2} is very low, as discussed in Lipshtat et al. 2004. The inclusion of chemisorbed sites in our model increases the formation efficiency of D\textsubscript{2} because of the different behaviour of H and D on grain surfaces. H atoms are more mobile and will get easily trapped on chemisorbed sites, whereas D will mostly stay in physisorbed sites. Therefore, the surface structure has a big impact on the formation of D\textsubscript{2}. Surfaces, such as graphitic surfaces, present a very high barrier against chemisorption. H atoms will overcome this barrier by tunnelling, while D will tunnel much less efficiently, and stay in the physisorbed sites. Since D\textsubscript{2} forms mostly through the association of physisorbed atoms, this segregation favours the formation of D\textsubscript{2}. Carbonaceous grains, on the other hand, present a very low barrier against chemisorption, making the behaviour of H and D similar. The formation efficiency of D\textsubscript{2} present a small enhancement. Therefore, deuteration will be more efficient on graphitic surfaces (small grains) than on amorphous carbon surfaces (big grains).

We consider a grain size distribution, as described by Weintgartner & Draine (2001), in order to predict the formation rate of H\textsubscript{2}, HD and D\textsubscript{2} (in cm\textsuperscript{-3} s\textsuperscript{-1}). This distribution is represented figure 12. We calculated the total cross section of the grains, for graphitic grains and carbonaceous grains. We considered that PAHs and very small grains (\( \leq 100 \text{ Å} \)) have surfaces similar to graphitic surfaces, and that bigger grains have surfaces similar to carbonaceous surfaces. Then, we integrated the efficiencies for the formation of the different molecules, with our correction for small sizes, over the range of grain sizes, following the distribution of Weintgartner & Draine (2001). Figure 13 shows how the formation of these species depends on the D/H ratio for graphitic surfaces (solid lines) and for carbonaceous grains (dashed lines), for a grain temperature of 15K, a gas temperature of 100 K and a density of 100 cm\textsuperscript{-3}. The formation of H\textsubscript{2} and HD under these circumstances comes mostly from the contribution of small grains (Gr grains). On the other hand, D\textsubscript{2} is mostly formed on big grains (AC grains), for low D/H ratios (D/H \( \leq 10^{-4} \)), and on small grains (Gr grains) for higher
D/H ratio. Figure 14 presents the same results as a function of the density, for a grain temperature fixed at 15K and a gas temperature of 100K. While the formation of H₂ and HD is mostly due to the small grains contribution for any n(H), D₂ is mainly produced on small grains at low densities and on big grains at high densities. Figure 15 presents the formation rate of the different species as a function of the grain temperature, for a gas temperature of 100 K, a density of 100 cm⁻³ and a D/H ratio of 2×10⁻⁵. First, it seems clear that the formation of H₂ comes from the contribution of small grains at low grain temperature, and of big grains at higher grain temperature. These two contributions, added together, reproduce quite well the formation rates observed in different PDRs, as described by Habart et al. (2003). Small grains contribute strongly on the formation of H₂ and HD at low grain temperatures. Then, for temperatures higher than ~ 20K, these molecules are formed mostly on big grains. At these higher temperatures, the rate of H₂ formation drops to 10⁻¹⁷ nH n(H) cm⁻³ s⁻¹. This value is similar to the one observed in PDRs where warm dust grains are present as in NGC 2023 and the Orion Bar (Habart et al. 2004, Allers et al. 2005). For the case of D₂, for standard D/H, its formation comes from the big grains.

In the interstellar medium, dust is heated by photons. Dust grains receive a short heat impulse, resulting in temperature fluctuations, especially for small grains. This phenomenon has been described by Draine & Li (2001) who showed that grains of the size of 50 Å can fluctuate from 5 to 40 K, but still spend most of their life (90%) at temperatures below 20K. For smaller grains (25Å), the fluctuations are even more important (from few K to 50 K), but the grain spend 95% of its life at temperatures below 20K. In this study we did not consider the temperature fluctuations of small grains. The limiting factor in the formation of molecules on very small grains is the accretion. In environments with a density of 100 cm⁻³, a small grain of 10 Å (30 Å) will receive a H atom from the gas phase every 7 10⁶ (7 10⁵) seconds and a D atom every 3 10¹¹ (3 10¹⁰) seconds. Once the atom arrives on the grain, it can evaporate (if T_dust ≥ 20K for graphitic surface, and for very high temperatures for amorphous carbon surface, see fig.??), or become chemisorbed in a few hundreds of seconds (on graphitic surfaces) and a few tens of seconds (on amorphous carbon surfaces). This time can be estimated by 1/α_p, and the number of physisorbed sites that the atom will visit can be estimated by the ratio α_p/α_c. Therefore, in most cases an atom coming on a grain will become chemisorbed in an empty or in a filled chemisorbed site. In the latter case, a molecule will be formed. If the grain is at temperatures higher than 20K, then the atom will evaporate and no molecule will be formed. Therefore, the temperatures fluctuations of dust grains should reduce the efficiency of the formation of the molecules by a maximum of 10% for grains lower than 100 Å (which spend 90% of their life at temperatures below 20K). A recent study by Cuppen, Morata & Herbst (2006) shows that when considering grains that possess only physisorbed sites, the efficiency depends both on the modal temperature (the most frequent temperature of the grain) and its fluctuations. In this case, these fluctuations shuts down the formation of H₂ on grains smaller than 100 Å when rough surfaces are considered. In our case, because we consider chemisorbed atoms, the formation of H₂ will just slightly decrease by a maximum 10% (for graphitic surfaces) or will not decrease at all (for amorphous carbon surface).

Another important process that we did not take into account in this study is the so-called “Hot Atom Mechanism”. An atom that becomes physisorbed on a dust grain is not directly in thermal equilibrium with the grain. In most cases, the atom comes from the gas phase with a higher energy, and once on the grain surface, it bounces against potential walls and looses slowly its energy. Such a
process has been described by Buch & Zhang (1991), and shows how many sites an atom can scout before being in thermal equilibrium with the grain. In our study, the efficiencies of the formation of the different molecules is lower at low grain temperatures. Indeed, at grain temperatures less than 10K, atoms visit grain surfaces through tunnelling and when they encounter to form molecules, a fraction of the newly formed molecules stay on the grain. Therefore, the reason of a low formation efficiency is that dust grains are saturated with molecules. In this study, the Hot Atom Mechanism will not increase the efficiency of the formation of molecules at low grain temperature.

6. Conclusions

We developed a rate equation model for the formation of H\textsubscript{2} and its deuterated forms on carbonaceous surfaces. This model takes into account the structure of carbonaceous surfaces in order to describe the formation mechanism of the different molecules. Small carbonaceous grains (≤ 100Å), also called PAHs, possess surfaces that are similar to graphite, while big grains have surfaces similar to amorphous carbon. One or the other type of grain, and therefore of the surface, will have a big impact on the chemistry and on the deuteration of H\textsubscript{2}.

Small grains present surfaces characteristics similar to graphitic surfaces which show a high barrier against chemisorption. Big grains, on the other hand, have surfaces similar to amorphous carbon that present no barrier against chemisorption. Because of their mass differences, H and D atoms will overcome high barriers against chemisorption with different efficiencies. H atoms can tunnel through the barrier to populate the chemisorbed sites, while D atoms, with higher mass, tunnel much less efficiently and therefore mostly populate physisorbed sites. This segregation leaves the D atoms free to travel and associate on physisorbed sites, while the H atoms are trapped in chemisorbed sites. In this sense, small grains (graphitic surface) favour deuteration.

The rate equation method is applicable only when there is at least one species on the grain. For molecular hydrogen, this method is always valid since a H\textsubscript{2} molecule is formed through the association of a physisorbed and a chemisorbed H atoms. Because half of the chemisorbed sites are filled with hydrogen, there is always more than one H on the surface, and therefore rate equations are always valid.

In the case of deuterium, because of the low D/H ratio in the ISM, it is common that a grain possesses less than 1 D atom on its surface. To understand the formation of HD and D\textsubscript{2} in this case, we developed a Monte Carlo simulation. Our results show that HD formation efficiency increases with smaller grain sizes, while D\textsubscript{2} decreases. Indeed, with decreasing grain sizes, the number of physisorbed D decreases, and therefore a D atom on a grain will easily get trapped in a chemisorbed site, and form HD, instead of finding another physisorbed D, and form D\textsubscript{2}. We propose an approximation to describe the formation of HD and D\textsubscript{2} as a function of grain sizes.

We calculated the formation rate of H\textsubscript{2} and its deuterated forms when the grain sizes follow the Weintgartner & Draine (2001) distribution. We differentiated the contribution of small (≤ 100Å; Gr Grains) and big grains (AC grains) in the formation of the different species. Our results show that H\textsubscript{2} and HD are formed at low grain temperature (≤ 25K) mostly on small grains (Gr grains), and on big grains at higher grain temperatures (AC grains). The formation of D\textsubscript{2}, on the other hand, can be dominated by the contribution of big grains, for high densities, and of small grains for low densities.
At last, this paper shed some light on the chemistry of species on realistic dust grains, that possess physisorbed as well as chemisorbed sites. On big grains certain molecules form through the association of 2 physisorbed atoms. On small grains, the physisorbed atoms are much less abundant and become chemisorbed before finding another physisorbed atom on the surface. Therefore, small grain will favour the formation of molecules through the association of physisorbed and chemisorbed atoms.

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Fig. 1. Two possible types of carbonaceous grains.
Fig. 2. Mobility and evaporation rate of the H (solid lines) and D (dashed lines) atoms on the graphitic surfaces (Gr) and amorphous carbon surfaces (AC).
Fig. 3. $\text{H}_2$ (solid lines), HD (dashed lines) and $\text{D}_2$ (dotted dashed lines) formation efficiencies on graphitic surfaces (left) and amorphous carbon surfaces (right). LH: Langmuir–Hinshelwood kinetic and ER: Eley–Rideal mechanism.

Fig. 4. $\text{H}_2$, HD and $\text{D}_2$ formation efficiencies on graphitic (solid lines) and amorphous carbon surfaces (dotted dashed lines). Left: Efficiencies as a function of the gas temperature, with a density of $100 \text{ cm}^{-3}$. Right: Efficiencies as a function of the density $n_H$, with a gas temperature set at $100 \text{ K}$. 
Fig. 5. HD and D$_2$ formation efficiencies on graphitic (left panel) and amorphous carbon surfaces (right panel), as a function of the D/H ratio. The grain temperature is set at 15 K, the gas temperature at 100 K and the density at 100 cm$^{-3}$.

Fig. 6. H$_2$, HD and D$_2$ formation efficiencies on graphitic (left) and amorphous carbon (right) surfaces compared to our approximations (dashed lines).
Fig. 7. Critical grain size for which a grain possess at least one deuterium physisorbed and chemisorbed for graphitic (left panel) and carbonaceous (right panel) grains.
Fig. 8. Monte Carlo (solid lines) compared to rate equations (dashed lines) simulations and our approximations (dotted lines) for the HD and D₂ formation efficiencies on graphitic surfaces. D/H ratio at 0.2 (top left), 2 \times 10^{-2} (top right), 2 \times 10^{-3} (bottom left) and 2 \times 10^{-4} (bottom right). The error bars represent the 95% confidence intervals.
**Fig. 9.** Monte Carlo (solid lines) compared to rate equations simulations (dashed lines) and our approximations (dotted lines) for the HD and D$_2$ formation efficiencies on amorphous carbon grains. The D/H ratio is $2 \times 10^{-1}$ (left) and $2 \times 10^{-3}$ (right). The error bars represent the 95% confidence intervals.

**Fig. 10.** Monte Carlo (solid lines) compared to rate equations simulations (dashed lines) for the HD and D$_2$ formation efficiencies at higher grain temperatures. Left panel: graphitic surfaces at 20K. Right panel: carbonaceous surfaces at 25K. The error bars represent the 95% confidence intervals.
Fig. 11. Formation efficiency of D$_2$ molecules for graphite and amorphous carbon and for surfaces without chemisorption sites, such as icy grains.
Fig. 12. Grain size distribution for carbon and silicate grains, as estimated by Weintgartner & Draine (2001). Small grains (≤100Å) are similar to PAHs, and big similar to amorphous carbon grains.
Fig. 13. Formation rate of H$_2$, HD and D$_2$ on small grains and PAHs (solid lines) and big grains (dashed lines) as function of the D/H ratio.
Fig. 14. Formation rate of H$_2$, HD and D$_2$ on small grains and PAHs (solid lines) and big grains (dashed lines) as function of the density.
Fig. 15. Formation rate of $\text{H}_2$, HD and $\text{D}_2$ on small grains and PAHs (solid lines) and big grains (dashed lines) as function of grain temperatures.