Astrochemistry: Recent Successes and Current Challenges
Proceedings IAU Symposium No. 231, 2005
D.C. Lis, G.A. Blake & E. Herbst, eds.

doi:10.1017/S1743921306007344

H_2 Formation on Grain Surfaces

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Abstract. Molecular hydrogen is the most abundant molecule in the Universe and dominates the mass budget of the gas, particularly in regions of star formation. H_2 is also an important chemical intermediate in the formation of larger species and can be an important gas coolant when the medium lacks metals. Because of the inefficiency of gas-phase reactions to form H_2, this molecule is generally thought to form on grain surfaces. Observations of H_2 in a wide variety of objects showed that this molecule could form efficiently over a wide range of physical conditions. To understand the mechanism responsible for such an efficient formation, we developed a model for molecular hydrogen formation on grain surfaces. This model considers the interaction between atom and surface as beeing either weak (Van der Waals interaction—physisorption) or strong (covalent bound—chemisorption), as well as the mobility of the atom on a surface due to

quantum mechanical diffusion and thermal hopping. This model solves the time-dependent kinetic rate equation for the formation of molecular hydrogen and its deuterated forms. Our results have been benchmarked with laboratory experiments on silicates, carbonaceous and graphitic surfaces. This comparison allowed us to derive some characteristics of the considered surfaces. An extension of our model to astrophysical conditions gives an estimate of H_2 formation efficiency for a wide range of physical conditions. One of our main results is the efficient formation of molecular hydrogen for gas and grain temperatures up to several hundreds of kelvins. We also compared our predictions to observations in astrophysical objects such as photodissociation regions (PDRs). The addition of deuterium in our model for the formation of HD and D_2 molecules is also discussed.

Keywords. astrochemistry — ISM: molecules — molecular processes

1. Introduction

1.1. *H_2 Observations in Astrophysical Environments*

Molecular hydrogen is the most abundant molecule in the Universe and it constitutes the primary ingredient for astrochemistry. H_2 has been observed in a variety of galactic and extragalactic environments under varied physical conditions. The question of its formation is therefore of prime importance to understand the chemistry and the physics of astrophysical objects. In the Interstellar Medium (ISM), the formation of H_2 through gas-phase reactions is not efficient enough to explain its observed abundance in the Milky Way. Presently, in the ISM, H_2 forms on dust-grain surfaces and this process dominates gas-phase production by several orders of magnitude (Gould & Salpeter 1963).

Molecular hydrogen can be observed at mid- and near-infrared wavelengths in emission, but also in the far UV in emission and in absorption. A plethora of astrophysical observations testify that H_2 is present in environments with very different physical conditions.

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In diffuse interstellar clouds, with typical physical conditions of density $n(\mathrm{H})=50\ \mathrm{cm}^{-3}$, gas temperature of $\sim$ 100 K, and dust temperature of 15 K, the FUV absorption lines of H_2 have been observed (Spitzer & Jenkins 1975, with Copernicus; Gry *et al.* 2002, with FUSE). These detections showed that H_2 formation is very efficient with a rate of 1–3 $\times 10^{-17}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ (Jura 1974; Hollenbach, Werner, & Salpeter 1971).

When molecular clouds are irradiated by nearby stars, the molecules in the region closest to the source are photodissociated. These regions are called photodissociation regions (PDRs), and are that part of the molecular cloud where photons dominate the thermal and chemical balance of the gas. In these regions, the physical conditions represent a wide range of gas and grain temperatures (100 K $\leqslant T_{gas} \leqslant$ 1000 K; 10 K $\leqslant T_{grain} \leqslant$ 100 K). Habart *et al.* (2004) derive an H_2 formation rate in the range 3×10^{-17} to $1.5 \times 10^{-16}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ for the PDRs associated with Orion Bar, NGC 2023, S140, IC 63 and Oph W.

Jets, outflows and shocks in the surroundings of star-forming regions exhibit other sets of physical conditions where H_2 is detected. Many low-mass protostars drive C-shocks into their environment (velocity $\leqslant$ 40–50 km s^{-1}). Molecular hydrogen is not dissociated in these shocks and in the warm postshock gas is collisionally excited and radiates mainly in the v=1–0 ro-vibrational transitions. H_2 emission is also observed associated with fast dissociative J-type shocks (velocity $\geqslant$ 40–50 km s^{-1}), where the medium in the shock front is hot ($T_{gas} \sim 10^5$ K), highly ionized, and H_2 is collisionally dissociated. Nevertheless, H_2 molecules are efficiently reformed on grain surfaces in the postshock region, where the gas is cooler ($T_{grain} \sim$ 75 K and $T_{gas} \leqslant$ 2000 K; Hollenbach & McKee 1989; Neufeld & Dalgarno 1989).

Supernovae remnants also exhibit H_2 emission lines. In the region where the ejecta of the supernova remnant collides with a nearby molecular cloud, excited H_2 is detected. In IC443, H_2 is seen in a slow shock (C-shock with $v_s \sim 30\ \mathrm{km\,s}^{-1}$ and $n \sim 10^4\ \mathrm{cm}^{-3}$; Rho *et al.* 2001). In the Crab nebula, a younger supernova, H_2 is seen in emission in the complex and highly ionised filamentary structure of the nebula. H_2 has been observed in the core of the filaments, where it can be self-shielded enough to survive to the high UV flux (Graham *et al.* 1990). The physical conditions at which H_2 has been observed are $T_{grain} \sim$ 50 K (Davidson & Fesen 1985), $T_{gas} \leqslant$ 7000 K (Rudy *et al.* 1994), and a dust to mass ratio five to ten times higher than the normal ISM value (Sankrit *et al.* 1998). According to Graham *et al.* (1990), molecular hydrogen was formed after the explosion of the Supernova, when the density in the filaments was higher, and survived in the filamentary self shielded environments.

According to some observations discussed above, it appears that molecular hydrogen can be formed under almost all circumstances. H_2 can form on cold and warm grain surfaces, with various gas temperatures. Even when destroyed in shocked regions, it will reform again in the post-shock regions. Near strong UV or X-ray radiation fields, molecular hydrogen may even find some protected place to form and survive. The wide variety of these environments raises a key question in astronomy. *How does molecular hydrogen form in the Universe? Which physical and chemical processes can explain the presence of this molecule in such a wide range of physical parameters?*

2. H_2 Formation on Grain Surfaces

Many studies have aimed at understanding how molecular hydrogen could form on grain surfaces. Theoretically, Hollenbach & Salpeter (1970) developed a quantum mechanical model to calculate the mobility of the atoms on a grain surface. Because the interaction between atoms and grains involved in their calculations were weak, they found that H_2 formed only at low grain temperatures. To modify this result—in conflict with a variety of observations—they took the presence of lattice defects with enhanced binding into account (Hollenbach & Salpeter 1971). With this assumption, they could predict a very efficient H_2 formation for grain temperature $\leqslant 50$ K. In recent studies (Chang, Cuppen & Herbst 2005), various types of inhomogeneous and mixed surfaces are considered, allowing an efficient H_2 formation until grain temperatures of ~ 25 K.

Experimentally, Temperature Program Desorption (TPD) experiments at low temperatures revealed the weak interactions, also called physisorption, between the atoms and some surfaces of astrophysical interest. Pirronello *et al.* (1997a, 1997b, 1999) studied the formation of HD on olivine and carbonaceous surfaces at a range of surface temperatures between 5 and 25 K. These results allowed an estimate of the energy of physisorption of the atoms and molecules on the surface. Recent TPD experiments at high temperatures, performed by Zecho *et al.* (2002) on graphite, showed another type of interaction between the atoms and the surface. This interaction, also called chemisorption, is strong and allows the formation of H_2 at grain temperatures of hundreds of Kelvins.

Physisorbed atoms are weakly bound to the surface and are mobile at low grain temperatures (Ghio *et al.* 1980), whereas chemisorbed atoms are strongly bound to the surface and become mobile only at grain temperatures of a few hundred K (Barlow & Silk 1976; Aronowitch & Chang 1980; Klose 1992; Fromherz *et al.* 1993; Que *et al.* 1997; Jeloaica & Sidis 1999; Sha & Jackson 2002; Cazaux & Tielens 2002, 2004). By considering these two types of interactions between the atoms and the surface, H_2 can possibly form for a wide range of temperatures.

2.1. *Model of H_2 Formation*

We consider in our model two different interactions between the atoms and the surface, as shown in Figure 1. The formation of molecules at low surface temperatures involves atoms bound to the surface with a Van der Waals interaction, typically called physisorption (of the order of few meV), whereas formation of molecules at high surface temperature involves atoms strongly bound to the surface with an interaction called chemisorption (of the order of several eV). Therefore, these two ways of binding the atoms on a surface insure that molecules can form for a wide range of surface temperature. Another point considered in our model is the fact that atoms move on the surface by tunneling and thermal diffusion. This is essential for a comprehension of the formation of molecules at low grain temperatures where tunneling can dominate.

In order to characterise the surfaces that have been studied in the laboratory, we developed a rate equation model to follow the population of the physisorbed and chemisorbed H and D atoms, as well as the molecules. This model, benchmarked by experimental data, is used to derive the characteristics of the different surfaces. In our study, we considered in detail the experiments of Pirronello *et al.* (1997a, 1997b, 1999) made on carbonaceous and olivine surfaces at low temperatures. These TPD experiments consist of two steps: (1) in the first step the surface is set at a fixed temperature T_0, and is irradiated by H and D atoms during a time t_{irr}; (2) in a second step, the irradiation is stopped and the temperature of the surface is increased with a constant rate ($\beta = 1\ \mathrm{K\,s^{-1}}$).

The measurements, reported Figure 2, show the desorption peaks of HD molecules depending on the irradiation time. At high coverage ($t_{irr} \geqslant 33$ s for olivine), the peaks do not seem to shift at higher temperature with lower irradiation time. This phenomenon is called first-order desorption. When the coverage is high, the atoms find each other easily on the surface and form molecules. These molecules evaporate once an adequate surface temperature is reached and the binding energy of molecules on the surfaces is easily determined in this case (E0 is the binding energy of the molecules). At lower coverage,

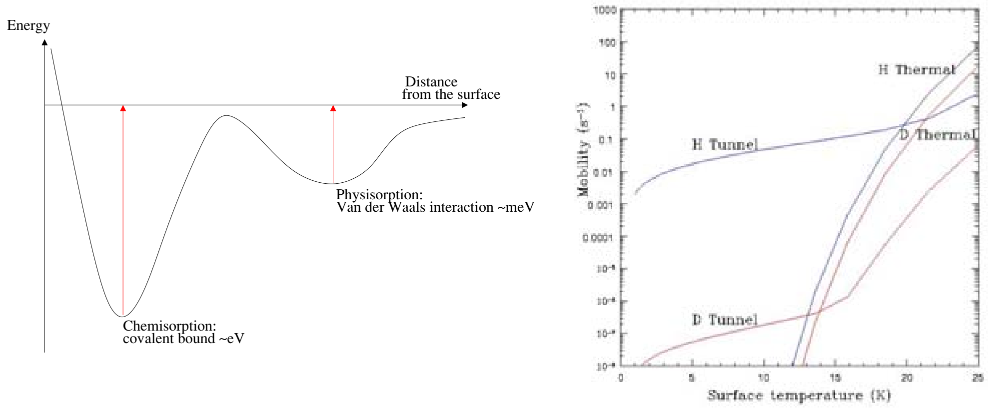

Figure 1. Two main points considered in our model. *Left:* The interaction between an atom and a surface can be either weak (physisorption) or strong (chemisorption). *Right:* The atoms move on the surface by tunneling and thermal diffusion. The mobility (in s^{-1}) to go from a physisorbed to a chemisorbed site is calculated here. Note the difference of mobility by tunneling between an H and a D atom due to the mass difference.

on the other hand, the atoms are far away from each other and need to scout the surface to associate with other atoms. The less the coverage, the more the atoms need higher mobility, and therefore higher grain temperatures to encounter another atom. This is called second-order desorption and is characterised by a shift of the desorption peaks to higher temperature with lower irradiation time. In this case, the binding energy of the atoms with the surface (E_{phys}, physisorption energy) can be determined, as well as an upper limit to the size of the barrier between two physisorbed sites (a_{pp}).

Another set of measurements performed during these TPD experiments is reported in Figure 3. These measurements represent the total HD formation efficiency during the entire experiments (irradiation + warming up). Therefore, the Y axis represents the percentage of the atoms sent on the surface that formed HD. These measurements are in fact a great tool to probe the existence of chemisorbed sites. Indeed, as reported in Figure 3, a model considering only physisorbed sites cannot reproduce the measurements. Inclusion of chemisorption sites explains the lower efficiency of HD formation because there is a leak of atoms from physisorbed sites to chemisorbed sites. Because these measurements are performed at low temperatures, the leak of the atoms from physisorbed to chemisorbed sites is governed by tunneling, and a constraint on the barrier between physisorbed and chemisorbed sites can therefore be determined. The rate of trapping in chemisorbed sites depends on the product of the width times the square root of the height of the barrier between physisorption and chemisorption ($a_{pc}\sqrt{E_a}$, where a_{pc} is the width of the barrier between physisorbed and chemisorbed sites and E_a its height). The structure of the surfaces considered here can have a physisorption-chemisorption barrier varying from a very high and thin barrier (Sha & Jackson 2002 and see discussion) to a very broad and low barrier (Parneix & Brechignac 1998). Because of these uncertainties, we consider two possible types of barrier, which we call type 1 and type 2, and assume that a realistic surface is intermediate between them.

An extension of our rate-equation model to steady state conditions is reported in Figure 4. The most important result of our model is that H_2 can form on carbonaceous and olivine dust grains for a large range of grain temperatures. This result is fundamental in order to explain the presence of H_2 molecules in almost all circumstances. The

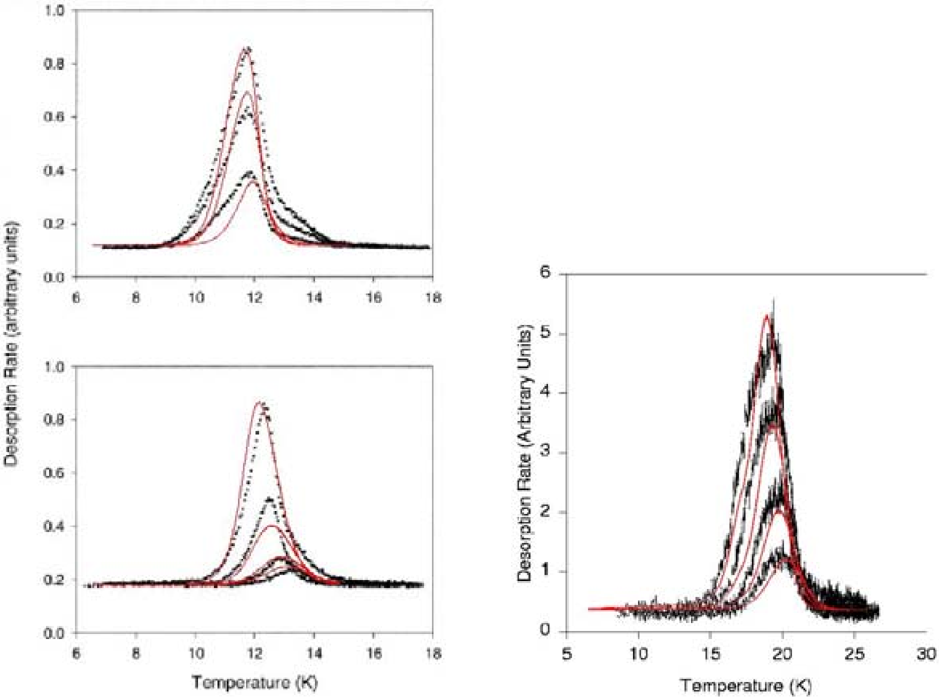

Figure 2. Temperature Program Desorption experiments from Pirronello et al (1997a,b, 1999). *Left:* The points represent the experiment performed on olivine surface for an irradition time of 480, 330 and 120 s (*top left*; from top to bottom), 33, 15, 6 and 4 s (*bottom left*; from top to bottom), benchmarked by our model (solid lines). *Right:* same experiment but on carbonaceous surfaces for an irradiation time of 192, 96, 48 and 24 s, benchmarked by our model (solid lines).

efficiencies of H_2 formation on olivine and carbonaceous grains are somewhat different but show the same behaviour. Our results show that H_2 formation efficiency is extremely sensitive to the physisorption-chemisorption barrier. Also, as discussed in previous work (Cazaux & Tielens 2004), this efficiency varies strongly with the temperature of the grains. When T_{grain} is very low ($\leqslant$ 10 K), a fraction of the newly formed molecules does not spontaneously desorb or evaporate, and therefore saturates the grain surface. The formation of molecules is then suppressed since the incoming atoms cannot stick to the grain. At higher grain temperatures ($\leqslant$ 20–25 K), the efficiency is extremely high, and is due to the association of physisorbed atoms. Because molecules have a lower surface binding energy than physisorbed atoms, the atoms stay on the grain and associate to form molecules, while molecules evaporate, bringing the efficiency of formation to 100 %. At higher T_{grain}, the physisorbed atoms also start to evaporate, and the formation of molecules is due to the association of physisorbed and chemisorbed atoms. Then, at high temperatures ($T_{grain} \geqslant$ 300 K), molecules form through the association of chemisorbed atoms. The differences of formation efficiency between the two types of grains depends strongly on how the atoms can chemisorb. In type 1 grains, the barrier between physisorption and chemisorption is high, preventing the atoms from becoming chemisorbed. Therefore, formation of molecules becomes inefficient at temperatures higher than $\sim$ 20 K, when the formation of molecules also involves chemisorbed atoms. In type 2 grains, on the other hand, the barrier between physisorbed and chemisorbed sites is low, and the atoms can easily become chemisorbed, allowing a more efficient formation of molecules for a large range of temperatures ($T_{grain} \sim$ 1000 K).

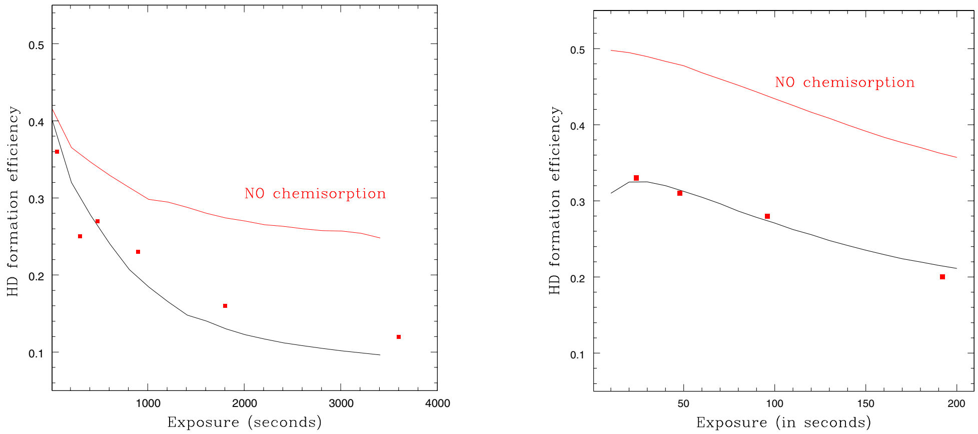

Figure 3. Total HD formation efficiency during the entire experiment (irradiation + warming up). Note that a model which doesn't take into account chemisorption cannot reproduce these measurements. *Left:* percentage of the atoms sent on olivine surface that form HD during the entire experiment (as a fonction of the irradiation time). *Right:* same but on carbonaceous surfaces.

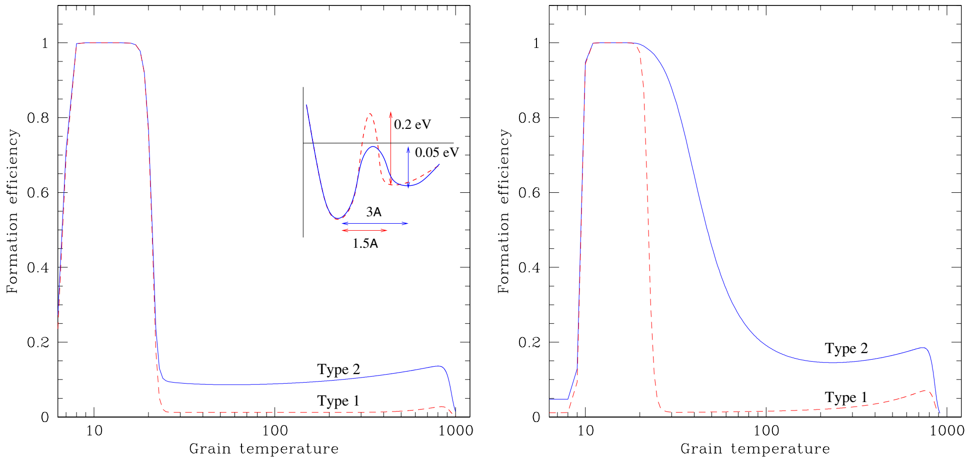

Figure 4. H_2 formation efficiency on olivine (*left*) and carbonaceous surfaces (*right*) and for type 1 (dashed lines) and type 2 (solid lines) grains.

2.2. *Formation Rate*

In astrophysical environments, the overall H_2 formation rate is written as:

$$R_d(\mathrm{H}_2) = \frac{1}{2} n(\mathrm{H}) v_{\mathrm{H}} n_{grain} \sigma S(T) \epsilon_{\mathrm{H}_2} \tag{2.1}$$

where $n(\mathrm{H})$ is the number density of H atoms, v_{H} the thermal velocity calculated as $\sqrt{\frac{8\pi kT}{m_H}}$ and ϵ_{H_2} the formation efficiency of H_2. We assume that the sticking coefficient, $S(T)$, decreases with T_{gas} and T_{grain} as $(1 + 0.4 \times \sqrt{(T_{gas} + T_{grain})/100})^{-1}$ (Burke & Hollenbach 1983). It is important to remember that $R_d(\mathrm{H}_2)$ is the overall rate of H_2 formation in units of $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$, whereas R, the rate coefficient of H_2 formation, commonly used in the literature, is in units of $\mathrm{cm}^3\,\mathrm{s}^{-1}$. These two rates are linked by the expression $R_d(\mathrm{H_2}) = R \times n \times n(\mathrm{H})$, where n is the abundance of H atoms in all forms. The H_2 formation rate can be indirectly measured in some astrophysical objects. In the next section we report the case of PDRs and their associate H_2 formation rate, in order to establish a comparison with our model. In the last section, we investigate the addition of deuterium in our model. We now concentrate only on carbonaceous grain surfaces, for which more studies have been dedicated to understand the nature of the barrier against chemisorption (Zecho *et al.* 2002; Sha & Jackson 2002; Klose *et al.* 1992; Aronowitz & Chang 1980, 1985; Parneix & Brechignac 1998).

3. Photodissociation Regions

The formation of H_2 has been observed in different PDRs at different physical conditions, as discussed by Habart *et al.* (2004). The grain and gas temperatures, as well as the densities and UV fluxes in these environments vary strongly from one PDR to another. For the PDRs associated with the Orion Bar, NGC 2023, S140, IC 63 and Oph W, these authors derived an H_2 formation rate in the range $3{\times}10^{-17}$ to $1.5{\times}10^{-16}$ $\mathrm{cm}^3\ \mathrm{s}^{-1}$.

In Figure 5, we compare our model with the H_2 formation rate derived for 5 PDRs (ISO observations; Habart *et al.* 2004) and a diffuse cloud (FUSE observations; Gry *et al.* 2002). In our model, we consider a grain size distribution as discribed in Weingartner & Draine (2001), which accounts for PAHs, small grains and big grains (grains with size from 5 Å to 0.8 μm). We calculate the H_2 formation rate for three different gas temperatures $T_{gas} = 100$ K, 300 K and 600 K, and a sticking coefficient decreasing with T_{gas} and T_{grain} (Burke & Hollenbach 1983). Our results show that grains with a low barrier between physisorbed and chemisorbed sites can better explain the high H_2 formation rate derived by Habart *et al.* (2004). Indeed, one needs to consider that the H atoms can "easily" cross the barrier against chemisorption in order to form H_2 in such an efficient way at high grain temperatures ($T_{grain} \geqslant 30$ K).

4. Addition of Deuterium to our Model

We reconsider our model of H_2 formation on grain surfaces, and include deuterium. We can therefore predict the formation efficiency of H_2, HD and D_2 on grain surfaces. As previously, the two different types of grains have some impact on the formation efficiency of molecules. The height and width of a barrier can segregate the H atoms from the D atoms because of their mass differences. Indeed, a very high and narrow barrier would be more easily crossed through tunneling by H atoms, whereas a low barrier, which favours mobility through thermal hopping, would not exhibit strong differences between the species. Figure 6 presents this result for the two types of grains, for a D/H of 2×10^{-5} and three different H fluxes $n(\mathrm{H}) = 10$ atoms cm^{-3} (dashed lines), $n(\mathrm{H}) = 100$ atoms cm^{-3} (solid lines) and $n(\mathrm{H}) = 10^3$ atoms cm^{-3} (dotted lines). 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. Also, the formation of D_2 is more important on type 1 grains than type 2. In the case of a high and narrow barrier against chemisorption (type 1 grains) H atoms can chemisorb easily by the tunneling effect, whereas D atoms stay physisorbed. In the case of a low and broad barrier against chemisorption (type 2 grains), tunneling is much less efficient and consequently less H atoms populate the chemisorbed sites, reducing the differences between H and D atoms. Therefore the formation of D_2, which occurs through the association of two physisorbed D atoms is enhanced when the physisorbed sites are mostly occupied by D atoms. In this case,

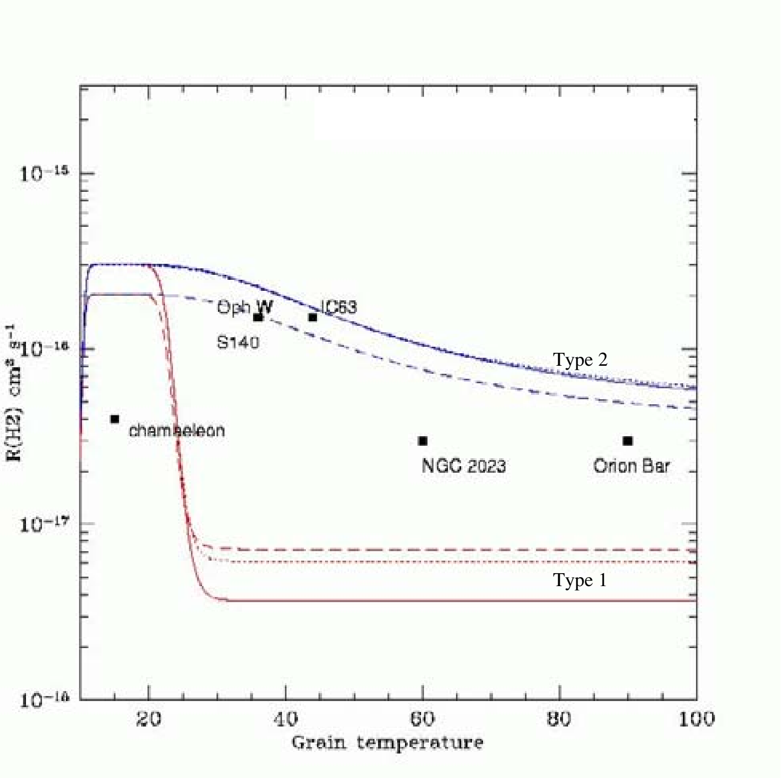

Figure 5. Comparison of our model with the H_2 formation rate derived for 5 PDRs (ISO observations, Habart *et al.* 2004) and a diffuse cloud (FUSE observations, Gry *et al.* 2002). Three different gas temperature are considerated here. Solid lines: $T_{gas} = 100$ K, dashed lines: $T_{gas} = 300$ K and dotted lines: $T_{gas} = 600$ K. The three higher curves correspond to our predictions with type 2 grains, and the three lower for type 1 grains. Note the discrepancy between the predicted and the observed formation rate for the Chamaleon point. Chamaleon is a diffuse cloud and the PAHs or very small grains could be less abundant, implying a lower H_2 formation rate.

type 1 grains which jail their H atoms in chemisorbed sites and let the D atoms free to recombine in physisorbed sites, are more efficient to produce D_2.

Gas-phase chemistry has been included in our grain-surface model in order to study the formation of H_2 and its deuterated forms in diffuse clouds. A study by Le Petit *et al.* (2002) concentrates on the H/H_2 and D/HD fronts in the cloud, using the PDR model of Le Bourlot *et al.* (1993). Because this model concentrates on the gas-phase chemistry, but does not follow the evolution of the populations of the different species on the grains, we reexamine the importance of the gas-phase and grain surface chemistry and follow the population of the different species on the grain as well as in the gas phase. The H_2 formation rate derived from observations of diffuse clouds is $\sim 3 \times 10^{-17}$ cm^3 s^{-1}, as discussed by Jura (1974). In order to scale our model to these observations, we adapt the mean cross section for collisions between grains and atoms as $\frac{n_{\rm grain}}{n_{\rm H}}\sigma \sim 10^{-21}$ cm^2. Then, we calculate the populations and formation rates of H_2 HD and D_2 until the system reaches steady state for each step towards larger Av.

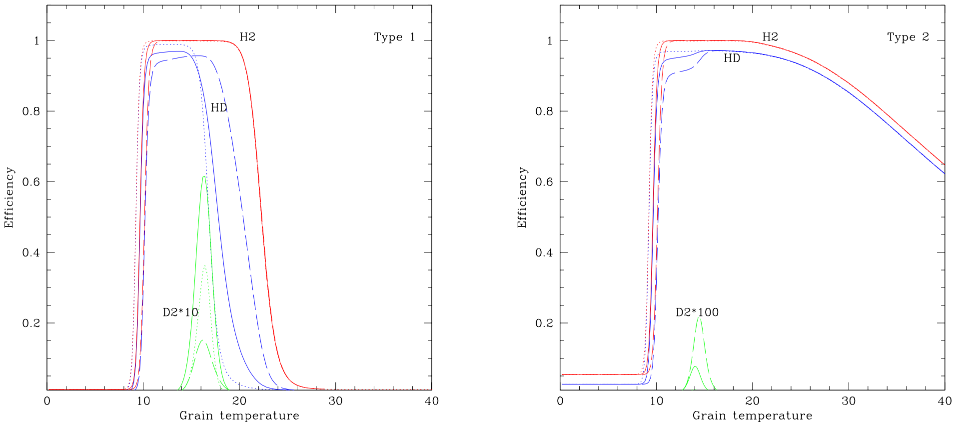

Figure 6. H_2, HD and D_2 formation efficiencies on carbonaceous grain surfaces, as a function of grain temperature, for different densities $n(\mathrm{H})$. Dotted lines: $n(\mathrm{H}) = 10$ atoms cm^{-3}, solid lines $n(\mathrm{H}) = 100$ atoms cm^{-3} and dashed lines $n(\mathrm{H}) = 1000$ atoms cm^{-3}. We consider in our calculation a gas temperature of 100 K and a D/H ratio is set as 2×10^{-5}. *Left:* Efficiencies for type 1 grains, when the characteristics of the surface are such that the barrier between physisorption and chemisorption is very high and narrow. *Right:* Efficiencies for type 2 grains, when the characteristics of the surface are such that the barrier between physisorption and chemisorption is low and broad.

We consider clouds with a density of 10–10^4 atoms cm^{-3}, a gas temperature of 50 K and we choose a grain temperature ∼15 K. We predict the H I, H_2, HD and D_2 column densities as a function of the extinction for type 1 grains in order to estimate the highest D_2 column density that could be observed (see Fig. 7). Our results show that D_2 should be observable in dense environments ($n(\mathrm{H}) \geqslant 10^3$ atoms cm^{-3}). Also, if the density of the medium is known and D_2 is observed, a constraint on the grain structure could be derived. Indeed, for a type of grain considered, D_2 formation is more or less enhanced and therefore observations of D_2 could constrain which type of grains are present in the observed environment. Therefore, D_2 molecules could be a good probe of grain structure.

References

Aronowitz, S. & Chang, S. 1980, *Ap. J.* 242, 149
Aronowitz, S. & Chang, S. 1985, *Ap. J.* 293, 243
Barlow, M.J. & Silk, J. 1976, *Ap. J.* 207, 131
Burke, J.R. & Hollenbach, D.J. 1983, *Ap. J.* 265, 223
Cazaux, S. & Tielens, A.G.G.M. 2004, *Ap. J.* 604, 222
Cazaux, S. & Tielens, A.G.G.M. 2002, *Ap. J.* 575, L29
Chang, Q., Cuppen, H.M., & Herbst, E. 2005, *A&A* 434, 599
Davidson, K. & Fesen, R.A. 1985, *ARA&A*, 23, 119
Fromherz, T., Mendoza, C., & Ruette, F. 1993, *MNRAS* 263, 851
Ghio, E., Mattera, L., Salvo, C., Tommasini, F., & Valbusa, J.U., 1980, *Chem. Phys.* 73(1), 556
Gould, R.J. & Salpeter, E.E. 1963, *Ap. J.* 138, 393
Graham, J.R., Wright, G.S., & Longmore, A.J. 1990, *Ap. J.* 352, 172
Gry, C., Boulanger, F., Nehmé, C., Pineau des Forêts, G., Habart, E., & Falgarone, E. 2002, *A&A* 391, 675
Habart, E., Boulanger, F., Verstraete, L., Walmsley, C.M., & Pineau des Forêts, G. 2004, *A&A* 414, 531
Hollenbach, D. & McKee, C.F. 1989, *Ap. J.* 342, 306

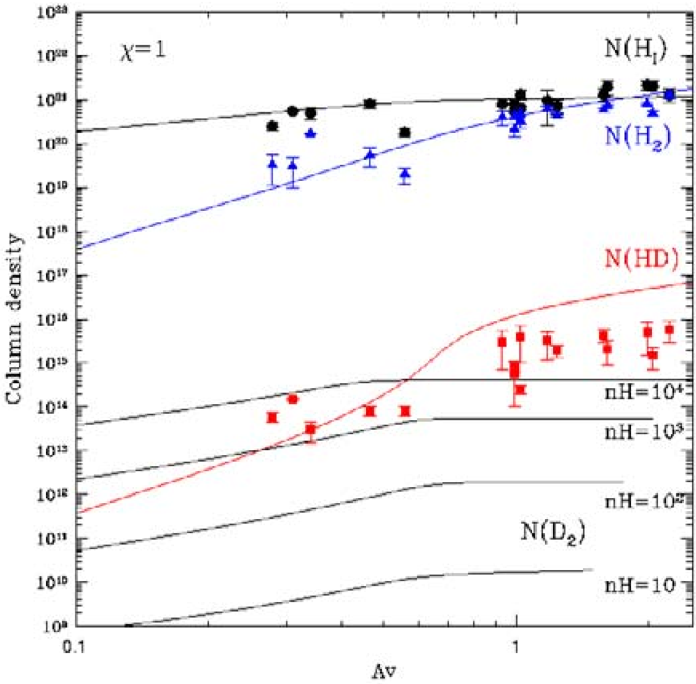

Figure 7. Column densities of H, H_2 and HD for a density $n(\mathrm{H}) = 10$ atoms cm^{-3} compared with the FUSE/Copernicus measurements towards translucent clouds (Lacour *et al.* 2005). D_2 column densities for type 1 grains are predicted for $n(\mathrm{H}) = 10$, 10^2, 10^3 and 10^4 atoms cm^{-3}. It seems that D_2 can be observed only in shielded environments with a density $\geqslant 10^3$ cm^{-3}. In our model, we assume a UV field of $\chi = 1$, a D/H ratio of 2×10^{-5} and a gas temperature of 50 K.

Hollenbach, D. & Salpeter, E.E. 1970, *J. Chem. Phys.* 53, 79
Hollenbach, D. & Salpeter, E.E. 1971, *Ap. J.* 163, 155
Hollenbach, D.J., Werner, M.W., & Salpeter, E.E. 1971, *Ap. J.* 163, 165
Jeloaica, L. & Sidis, V. 1999, *Chem. Phys. Lett.* 300, 157
Jura, M. 1974, *Ap. J.* 191, 375
Klose, S. 1992, *A&A* 260, 321
Lacour, S., *et al.* 2005, *A&A* 430, 967
Le Bourlot, J., Pineau Des Forets, G., Roueff, E., & Flower, D.R. 1993, *A&A* 267, 233
Le Petit, F., Roueff, E., & Le Bourlot, J. 2002, *A&A* 390, 369
Neufeld, D.A. & Dalgarno, A. 1989, *Ap. J.* 340, 869
Parneix, P. & Brechignac, P. 1998, *A&A* 334, 363
Pirronello, V., Liu, C., Roser, J.E., & Vidali, G. 1999, *A&A* 344, 681
Pirronello, V., Biham, O., Liu, C., Shen, L., & Vidali, G. 1997a, *Ap. J.* 483, L131
Pirronello, V., Liu, C., Shen, L., & Vidali, G. 1997b, *Ap. J.* 475, L69
Que, J.-Z., Radny, M.W., & Smith, P.V. 1997, *Surface Sci.* 391, 161
Rho, J., Jarrett, T.H., Cutri, R.M., & Reach, W.T. 2001, *Ap. J.* 547, 885
Rudy, R.J., Rossano, G.S., & Puetter, R.C. 1994, *Ap. J.* 426, 646
Sankrit, R., *et al.* 1998, *Ap. J.* 504, 344
Sha, X. & Jackson, B. 2002, *Surface Sci.* 496, 318

Spitzer, L. & Jenkins, E.B. 1975, *ARA&A* 13, 133
Weingartner, J.C. & Draine, B.T. 2001, *Ap. J.* 548, 296
Zecho, T., Güttler, A., Sha, X., Jackson, B., & Küppers, J. 2002, *J. Chem. Phys.* 117, 8486

Discussion

TAPPE: What happens with the formation enegy of H_2 in your model? Is it possible to include, phenomenologically, a free parameter to account for this energy and fit the experiments?

CAZAUX: We do not take into account, in our model, the energy of the newly formed molecules. In order to account for this energy when we fit the experiments, we need to include a parameter (that we call μ) which is the amount of molecules spontaneously released from the surface when formed. This corresponds to about 60–70% of the newly formed molecules.

PAPADOPOULOS: Is the H_2 formation rate of 1.5×10^{-16} to be believed for H_2 formation in PDR-type of conditions? This is 5 times higher than the canonical value of 3×10^{-17} $\mathrm{cm}^3\,\mathrm{s}^{-1}$.

CAZAUX: The H_2 formation rate was estimated using the H_2 line intensity ratios as a diagnostic. Habart *et al.* (2004) used the ratio of the 0–0 S(3) to the 1–0 S(1) line, which increases strongly with R_f. (Steady state PDR models were used to examine the sensitivity of different H_2 line ratios to the H_2 formation rate R_f.) Then for each PDR, from comparison of PDR model results with ISO and ground-based data of the vibrational ground (0–0 S(3)) and excited state (1–0 S(1)) lines of H_2 a value of R_f was estimated.

BAURICHTER: I have a comment on the modelling of your type 1 grain surfaces. The calculations of Sha & Jackson you are referring to show a barrier of 0.2 eV with respect to a hydrogen atom at infinite distance to the surfaces and not in a 0.05 eV physisorption well as you assumed.

CAZAUX: I misunderstood the calculations of Sha *et al.* (2002) in this case, and this should be corrected. Our problem is that by reproducing the experiments on carbonaceous and olivine surfaces, we determined a value for the width times the square root of the height of the barrier between physisorption and chemisorption. In this case, the barrier calculated by Sha *et al.* (2002) has too large a value. This problem needs further investigation.


WARNING