Molecular Hydrogen formation on grain surfaces

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Abstract. We reconsider H_2 formation on grain surfaces. We develop a rate equation model which takes into account the presence of both physisorbed and chemisorbed sites on the surface, including quantum mechanical tunnelling and thermal diffusion. In this study, we take into consideration the uncertainties on the characteristics of graphitic surfaces. We calculate the H_2 formation efficiency with the Langmuir Hinshelwood and Eley Rideal mechanisms, and discuss the importance of these mechanisms for a wide range of grain and gas temperatures. We also develop a Monte Carlo simulation to calculate the H_2 formation efficiency and compare the results to our rate equation models. Our results are the following: (1) Depending on the barrier againt chemisorption, we predict the efficiency of H_2 formation for a wide range of grain and gas temperatures. (2) The Eley-Rideal mechanism has an impact on the H_2 formation efficiency at high grain and gas temperatures. (3) The fact that we consider chemisorption in our model makes the rate equation and Monte Carlo approaches equivalent.

1. Introduction

H_2 formation is a process which has been studied extensively in the past decades, but which is still not well understood. In the interstellar medium, H_2 formation occurs on grain surfaces due to three-body reactions which are much more efficient than gas phase formation mechanisms (Gould & Salpeter 1963).

Observations of H_2 in several astrophysical environments has shown that this molecule can be produced in various physical conditions (Jura 1974, Hollenbach & McKee 1979, Tielens & Hollenbach 1985a, 1985b, Habart et al. 2004). 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 shocks regions. Even in strong UV or X-ray radiation field, H_2 may find some protected place to form and survive. The wide variety of these environments raises the question of how H_2 can form in such a wide range of physical conditions.

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 palliate 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 $\leq$ 50K.

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 25K. 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 temperature 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. Surfaces characteristics.

In this section, we consider carbonaceous surfaces. Olivine surfaces have been the subject to experimental studies only at low temperatures (Pirronello et al. 1997a, 1997b), making a characterisation of the strong interaction between the atoms and the surface impossible. Because of our lack of knowledge concerning chemisorption of atoms on olivine, we will concentrate on carbonaceous surfaces. These surfaces so called carbonaceous in amorphous form, and graphitic in crystalline form, have been the subject of a variety of experimental and theoretical studies (Morisset et al. 2003, Zecho et al 2002, Sha & Jackson 2002, Mennella et al. 1999, 2002, Pirronello et al. 1997a, 1997b, 1999, Klose et al 1992, Aronowitch & Chang 1980, 1985, Parneix & Brechignac 1998). Whereas the experiments performed at low temperatures on carbonaceous surfaces do not allow an evaluation of the energy of chemisorption, other studies performed at high temperatures on graphitic surfaces reveal high interactions involved between the atoms and the surface. One of the main question remaining is the nature of the barrier between physisorbed and chemisorbed sites, and therefore, the barrier against chemisorption. As shown by Zecho et al. (2002), with TPD experiments performed at high surface and gas temperatures, the atoms from the gas phase can, if their energy is high enough, cross the barrier against chemisorption and occupy a chemisorbed site. Theoretically, Sha & Jackson (2002) and Jeloaica & Sidis (1999), determined a high barrier between physisorption and chemisorption of 0.2 eV. This barrier has been determined for graphitic surfaces, and make H_2 formation at intermediate and high grain temperatures negligible. On the other hand, it seems that these numerical values differ greatly depending on the methods used. Indeed, in different theoretical studies made by Fromhertz (1993) and Parneix & Brechignac (1998), the barrier against chemisorption on graphite surface is estimated to be 0.03-0.09 eV.

Finally, at elevated temperatures, H can also be chemically bonded to a graphitic surface. The carbon atom converts then from sp^2 to sp^3 and the hydrogen is bound by some 4 eV. Mennella et al (2002), in a study devoted to the 3.4um aliphatic CH feature, showed that a H/C ratio of 60 % can be attained this way.

In a previous article, we used our model to benchmark experiments at low temperatures (Cazaux & Tielens 2004) and characterise the weak interactions between atoms and surface. Also, we determined a constraint on the barrier between physisorption and chemisorption by estimating the number of H atoms that directly chemisorbed at low temperatures. This constraint defined only the product of the width times the height of the barrier, but cannot separate the two (At low temperatures, H atoms populate chemisorbed sites through tunneling effect. This rate is a function of $a \times \sqrt{(E)}$, where a is the width and E the height of the barrier

between physisorbed and chemisorbed sites). In the next sections, we therefore will consider two extreme possibilities: (1) That described by Sha & Jackson (2002) and Jeloaica & Sidis (1999) who found 0.2 eV height and suppress the formation of H_2 at intermediate and high temperatures. (2) That discussed in a previous work (Cazaux & Tielens 2004), ~ 0.05 eV height, which is consistent with the calculations of Parneix & Brechignac (1998) and Fromhertz (1993), and allows a high H_2 formation efficiency, even at high gas and grain temperatures.

3. Model for H_2 formation: Langmuir-Hinshelwood kinetics

We developed a rate equation model describing the formation of H_2 on grain surfaces. This approach is based on two main assumptions: (i) Atom can bind to the surface in two energetically different sites: a physisorption site (weak Van der Waals interaction) or a chemisorption site (strong covalent bound). We assume the number of physisorbed and chemisorbed sites on a grain to be identical. (ii) The atoms can move from site to site by quantum tunneling or thermal diffusion.

In our model, an atom from the gas phase can accrete onto a grain only into physisorbed sites. If the physisorbed site is already occupied, the incoming atom bounces back to the gas phase. The accreted atoms can scout the surface, going from site to site, and a H_2 molecule is formed where two atoms encounter in the same site. This process of forming H_2 molecules follows Langmuir-Hinshelwood kinetics. Of these newly formed molecules, a fraction is spontaneously released in the gas phase, and another fraction remains on the grain and evaporates if the surface temperature is sufficiently high.

We used this model to benchmark the experimental data of Pirronello et al (1997a, 1997b, 1999). These TPD experiments probe the interactions between the surface and the adsorbed species. Indeed, by irradiating a surface with H atoms, and measuring the desorption of the newly formed molecules, it is possible to characterise the interactions involved between the atoms, the molecules and the surface. Because these experiments were performed at very low surface temperatures (from 5 to 25 K), only the weak interactions between the atoms, the molecules and the surface can be determined. In a previous study, we deduced the strength of the physisorbed bounds, the nature of the barrier between two physisorbed sites, and also gave a constraint on the barrier between physisorbed and chemisorbed sites. Once some characteristics of the surface under consideration are defined, it becomes possible to calculate the H_2 formation efficiency at steady state. In fig 1, left panel, we report the H_2 formation efficiency for the two extreme barriers between physisorption and chemisorption.

The H_2 formation efficiency at intermediate and high temperatures remains uncertain. At very low grain temperatures, H_2 formation efficiency is extremely small because only a certain percentage of the molecules formed on the grain are released in the gas phase (60 %), and the dust temperature is too low to allow evaporation of the molecules remaining on the surface. Thus, the grain is saturated with H_2 molecules, suppressing adsorption of H, and becomes "passive" for H_2 formation. Actually, some H atoms might bind to this "sea of H_2" and lead to H_2 formation. This aspect of H_2 formation has not further been investigated here. At slightly higher temperatures, H_2 formation efficiency rises to 100 % because the molecules remaining on the surface can evaporate whereas the physisorbed atoms, more strongly bound to the surface, can travel on the grain surface until they find another H atom. Then, as temperature increases, the physisorbed H atoms become able to evaporate before encountering another atom. The H_2 formation efficiency decreases, and H_2 forms through the association of physisorbed and chemisorbed atoms, at intermediate temperatures, and then through association of chemisorbed atoms at high temperatures.
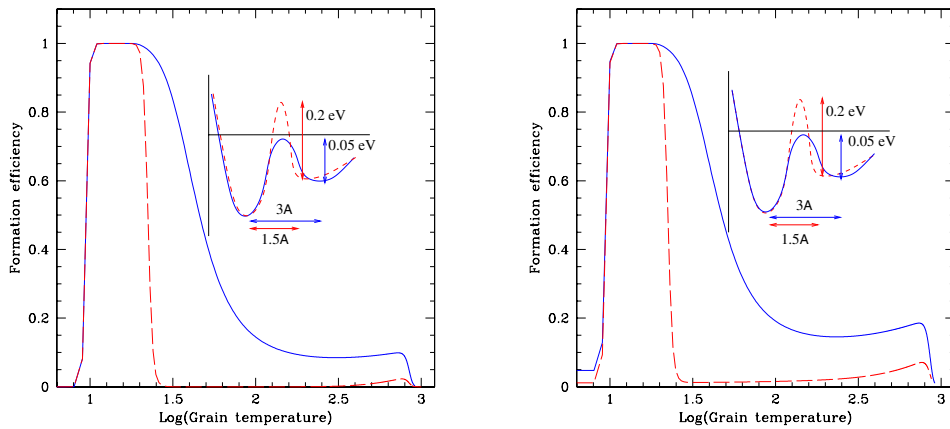
Figure 1. H_2 formation efficiency with the rate equation model for a grain radius of 0.1 μm and a density of H atoms of 10^2 atoms/cm^3. Two extreme possible barriers between physisorption and chemisorption are presented here, and demonstrate that the H_2 efficiency is either suppress if the barrier is high, or enhance if it is low. Left: H_2 formation efficiency considering only Langmuir-Hinshelwood kinectics. Right: H_2 formation efficiency considering direct chemisorption as well as the Langmuir-Hinshelwood and Eley Rideal mechanisms (solid lines).

4. Langmuir Hinshelwood VS Eley Rideal

In this section, we consider another possible way to form H_2 molecules on grain surfaces: the Eley Rideal mechanism which is relevant at high grain temperatures (Parneix & Brechignac 1998, Zecho et al. 2002) and when the collision energy of the incoming atom is high enough (Morrisset et al. 2003). In this approach, the H_2 molecules can be formed if an atom coming from the gas phase arrives in an already occupied site. Also, we consider possible direct chemisorption: if an incoming atom possesses enough energy to directly cross the barrier against chemisorption, it can directly be chemisorbed. Both mechanisms increase the H_2 formation efficiency at high temperatures.

In fig 1, right panel, we report the H_2 formation efficiency considering direct chemisorption as well as Langmuir-Hinshelwood and Eley-Rideal mechanisms, when the rate equation system reach a steady state equilibrium. The importance of the barrier between physisorbed and chemisorbed sites is striking. If this barrier is high (0.2 eV height and 1.5 Å width), the H_2 formation efficiency is almost suppressed, even considering both Langmuir-Hinshelwood and Eley Rideal mechanisms. If, on the contrary, the barrier is low (0.05 eV and 3 Å width), the H_2 formation efficiency is enhanced considerably. In our calculations, we consider the gas and grain temperatures coupled. Obviously, an increased of the gas temperature will enhance the Eley Rideal mechanism as well as the direct chemisorption.

Fig 2 shows at which temperatures which mechanisms are predominant for H_2 formation. It is clear that the Eley Rideal mechanism is important at low and intermediate temperatures. This mechanism stops when the chemisorbed atoms become mobile enough to scout the grain surface and associate with another H atom. The Langmuir-Hinshelwood mechanism is predominant in the H_2 formation. At high temperatures, the H atoms populate the chemisorbed sites by direct chemisorption, scout the surface of the grain, and associate through Langmuir-Hinshelwood mechanism. The gas temperature, as shown in fig 2 left and right panels, changes slightly the efficiency of the different mechanims.
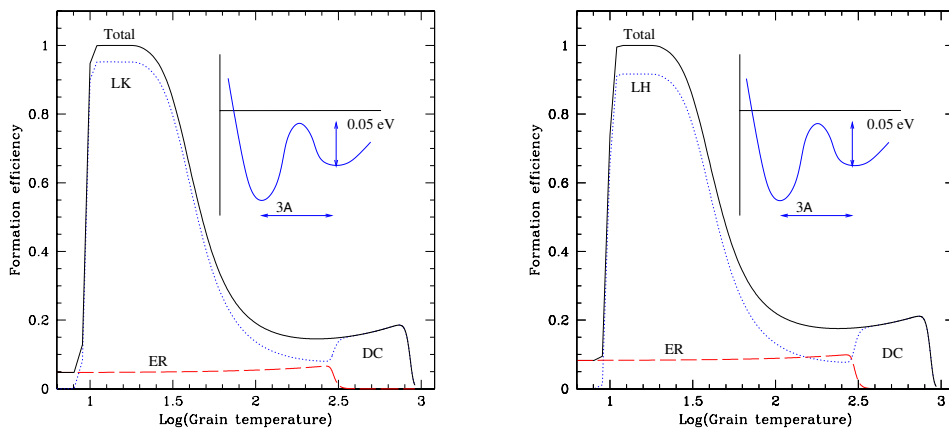
Figure 2. H$_2$ formation efficiency due to Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) mechanisms are reprensented. The direct chemisorption (DC) mechanism populates the chemisorbed sites and increases the efficiency of the Langmuir-Hinshelwood mechanism at high grain temperature. The temperature of the gas and the grains are set as: Left: T$_{gas}$ = T$_{dust}$. Right: T$_{gas}$ = T$_{dust}$ + 500K.

5. Monte Carlo simulation

We have developed a Monte Carlo simulation to describe H$_2$ formation on grain surfaces. The grain is seen as a squared grid, with, at each of its points, the possibility to have a chemisorbed and physisorbed atom. We consider as before direct chemisorption as well as Langmuir-Hinshelwood 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 into the gas phase. 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. As we did previously with the rate equation model, we report the H$_2$ formation efficiency when the Monte Carlo model reach the steady state equilibrium. In fig 3, we consider grains with a radius of 100 Å (left panel) and with a radius of 20 Å (right panel). We compare the H$_2$ formation efficiency in steady state equilibrium obtained by the rate equations and Monte Carlo methods. The two methods give identical results until quite high temperatures (∼400K). At very high temperatures we expect the two models to differ because we arrive in a regime where the grain has 1 atom or less. As a conclusion, for a large range of physical conditions, the presence of chemisorbed sites on the grain surface insures the coverage to be high enough that the Monte Carlo and rate equations approachs are equivalent.

6. Conclusions

We reconsidered the model of H$_2$ formation developed in Cazaux & Tielens (2004). We discussed the uncertainties on the characteristics of grain surfaces and the nature of the barrier between physisorbed and chemisorbed sites. A barrier which is too high prevents the atoms entering into chemisorbed sites, and therefore supresses H$_2$ formation at high grain temperatures. A low barrier, on the contrary, allows the atoms to populate these sites, and enhances H$_2$ formation at high temperatures through the recombination of chemisorbed atoms. We also compared two mechanisms of H$_2$ formation, the Langmuir-Hinshelwood and Eley Rideal processes. The Eley Rideal mechanism gives a small contribution to the H$_2$ formation efficiency at low and
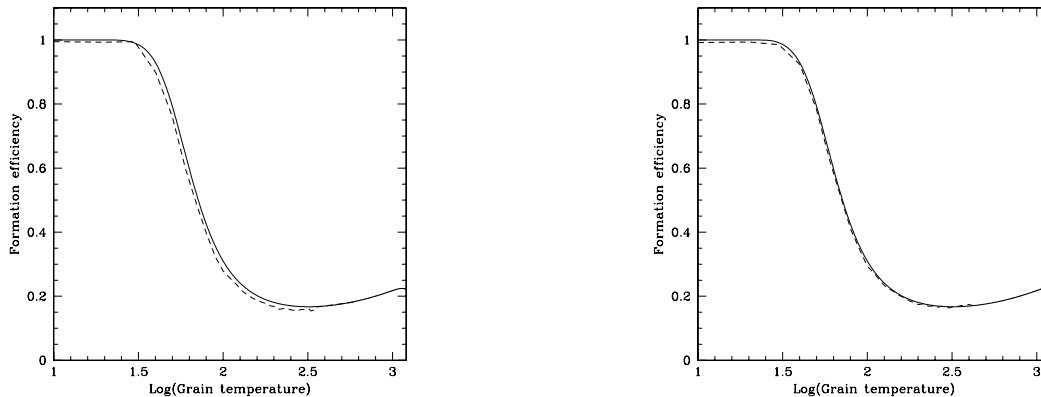
Figure 3. Comparison of the H$_2$ formation efficiency in steady state equilibrium obtained with a rate equations (solid line) and a Monte Carlo (dashed lines) approachs. These efficiencies are calculated for a grain with a radius of 100Å(left panel), and with a radius of 20 Å(right panel).

intermediate temperatures (T$_{grain}$ $\leq$ 300K). At high temperatures, the chemisorbed atoms become mobile and Langmuir-Hinshelwood mechanism dominates completly. We developed a Monte Carlo simulation to calculate H$_2$ formation efficiency on small grains. These results are in perfect agreement with the rate equations model until the regime where the grain possess 1 or less atom is reached. Thus, the inclusion of chemisorption in our model makes the H$_2$ formation efficiency through rate equations or Monte Carlo simulations equivalent.

7. References

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