Monte Carlo simulations of H$_2$ formation on grains of varying surface roughness

H. M. Cuppen$^1$* and Eric Herbst$^2$

$^1$Department of Physics, The Ohio State University, Columbus, OH 43210, USA
$^2$Departments of Physics, Astronomy, and Chemistry, The Ohio State University, Columbus, OH 43210, USA

ABSTRACT

Continuous-time random-walk Monte Carlo simulations of H$_2$ formation on a variety of grain surfaces of varying roughness based on olivine and amorphous carbon have been performed. With these inhomogeneous surfaces, we find that the temperature range over which efficient H$_2$ formation occurs in the interstellar medium is larger than it is for flat surfaces characterized by single values of the energy parameters for hydrogen-atom adsorbates. Our results show, in particular, that the formation of H$_2$ on non-flat interstellar grains can occur efficiently at typical surface temperatures in diffuse interstellar clouds, although the results are dependent on the strength of lateral bonds between H atoms and the surface.

Key words: molecular processes – ISM: molecules.

1 INTRODUCTION

Although the formation of molecular hydrogen in diffuse and dense regions of the neutral interstellar medium (ISM) occurs by the recombination of hydrogen atoms on the surfaces of dust particles, the detailed mechanisms by which this process occurs are still not clear (Chang, Cuppen & Herbst 2005). Experimental studies using a technique known as temperature-programmed desorption (TPD) indicate that for olivine and amorphous carbon, H$_2$ is formed by the so-called Langmuir–Hinshelwood mechanism, which involves the diffusion of one or both H atoms to find one another on a given granular surface (Pirronello et al. 1997a,b, 1999). The situation on various forms of amorphous ice is more controversial and less clear (Hornekaer et al. 2002; Roser et al. 2002; Perets et al. 2005). Based on laboratory measurements and a flux of H atoms relevant for diffuse interstellar clouds, it was deduced that the surface temperature range over which efficient H$_2$ formation occurs is very small for olivine (6–10 K) and amorphous carbon (13–17 K) (Katz et al. 1999). Considering that the surface temperature for interstellar grains in unshielded regions is probably closer to 20 K (Li & Draine 2001), it appears that if the experimental results and inferences are correct, then olivine and amorphous carbon are not realistic candidates for granular surfaces in diffuse clouds, where H$_2$ formation is known to be efficient. The model of Katz et al. (1999), used to analyse the experimental results of Pirronello et al. (1997a,b, 1999), considered only a single barrier for diffusion and a single low binding energy between physisorbed H atoms and the surface, and did not distinguish between the H and D atoms used in the experiments. Cazaux & Tielens (2004) show that molecular hydrogen can be produced over a larger temperature range in the ISM with olivine and amorphous carbon if chemisorption sites and a difference between H and D atoms are included in the analysis of the experimental data. They found the temperature range to be strongly dependent on the width and the height of the barrier between sites of physisorption and chemisorption. In their fits to the experimental data, however, Cazaux & Tielens (2004) were only able to constrain the product of the two quantities. In the limiting case of a small width and a large barrier, the H atoms cannot enter a chemisorbed site at low temperatures, and a similar small temperature range for high efficiency as the one found by Katz et al. (1999) was obtained. Since quantum chemical calculations by Sha & Jackson (2002) on the interaction between H and a relaxed graphite (0001) surface indicate that there is probably a small width and a high barrier, chemisorption may not explain H$_2$ formation on olivine and carbonaceous grains in the ISM at surface temperatures larger than that deduced by Katz et al. (1999).

We have recently developed a method for simulating H$_2$ formation on different types of surfaces (Chang et al. 2005). Based on the continuous-time random-walk (CTRW) Monte Carlo procedure (Montroll & Weiss 1965), it allows us to follow individual H atoms as they undergo random walk on a planar square lattice with periodic boundary conditions. Reaction occurs when two H atoms arrive at the same lattice site. Both adsorption and desorption of H atoms are also followed. If an H atom lands atop one already adsorbed, the assumption is made that it is rejected. The details of the Monte Carlo procedure are discussed in Chang et al. (2005), in which we used the method for surfaces with some degree of irregularity. The study of surface chemical reactions on ‘non-uniform’ surfaces was initially championed by Halsey Jr (1949). The irregularity, for which we coined the adjective ‘inhomogeneous’, refers to surfaces containing mixtures of olivine and carbon, and surfaces, both pure and mixed, in
which the binding energy and diffusive barrier for adsorbing \( \text{H} \) atoms follow distributions that are either exponential or Gaussian. The distributions are governed by a normalized variance \( \sigma \), which indicates the width divided by the mean energy. With the diffusive and evaporation energy parameters taken from the analysis of the TPD experiments (Katz et al. 1999) and the assumption of diffuse cloud conditions, the major result of the calculation was the finding that \( \text{H}_2 \) formation on either olivine or amorphous carbon is efficient over a larger temperature range if these substances have \( \sigma \) larger than zero; i.e. if these substances show ranges of binding energies and diffusive barriers rather than the single values deduced via the analysis of the TPD data using simple models. In fact, the larger the value of \( \sigma \), the larger the temperature range. A secondary finding of the research is that the efficiency of \( \text{H}_2 \) formation declines for small grains compared to large ones, but that the declination is less strong for inhomogeneous structures compared with simple olivine and carbon.

Although our work in the previous paper indicates that \( \text{H}_2 \) formation in diffuse clouds can occur on sufficiently inhomogeneous grains, we did not cover the most common types of surface irregularities studied by surface scientists, which are grouped under the term ‘roughness’. In this paper, we remedy the deficiency. To avoid further confusion, it is first necessary to define different types of surfaces and irregularities, some of which are illustrated in Fig. 1.

(i) Regular surface: A surface that can be generated by translational symmetry from its smallest unit, known as a surface unit cell.

(ii) Flat surface: A surface with height differences within one monolayer only. Adsorption onto the surface will have the same potential function for sites that are equivalent. Inequivalent sites can have different binding energies [Fig. 1(a)].

(iii) Smooth surface: A surface with height differences within a few monolayers obtained by removal of surface units from and addition of surface units to a flat surface. Both Figs 1(b) and (c) show examples of smooth surfaces. Often the surface is covered with large additions known as ‘islands’ such as the lighter areas in Fig. 1(c). Adsorption onto the surface will have stronger binding near ‘irregular’ sites where there are valleys and ridges. Examples of irregularities are steps, kinks, vacancies and adatoms.

(iv) Rough surface: A surface with height differences of at least several monolayers. No distinct islands can be observed. The valleys are deeper and the ridges are higher for this type of surface [Fig. 1(d)].
(v) Amorphous surface: The surface atop an amorphous solid, containing no long-range order. The surface can also be rough. Adsorption onto the surface will generally involve a continuous distribution of binding energies.

(vi) Inhomogeneous surface: A self-coined term used earlier to refer to surfaces comprising two species (e.g. carbon and olivine) and/or amorphous surfaces.

(vii) Adatoms: Single-surface units atop a locally completely flat piece of grain surface. The units are not in the immediate vicinity of a surface irregularity. The lighter spots in Fig. 1(b) are examples of adatoms. We use this term as it is commonly used in surface science. One should not confuse the term with H atoms deposited on the surface.

With the definitions here, most of the surfaces studied in our previous paper would be described as amorphous, although we used the adjective ‘inhomogeneous’ to avoid confusion with the use of the adjective ‘amorphous’ to characterize not the surface but the actual solid. Molecular hydrogen formation on amorphous carbon used in this latter sense of the word was actually analysed by Katz et al. (1999) in terms of a single desorption energy and a diffusive barrier for H atoms, which would make the surface ‘flat’ and ‘regular’ in our lexicon.

In this paper, we first consider how surface roughness affects H₂ formation on olivine and carbonaceous grains in diffuse interstellar clouds, and then consider its formation on surfaces that are both non-flat and amorphous. Although we do not know much about the surface topologies of real interstellar grains, we do know that interstellar grains are likely to have a fluffy and irregular shape with surfaces that possess a high degree of roughness, and are also likely to be amorphous. The flat regular surface topology in Fig. 1(a) is used as a reference and gives the same results as the homogeneous surfaces in our previous paper.

We conclude, as we did earlier for flat amorphous surfaces, that the larger the degree of irregularity and non-uniformity, the larger the temperature range over which molecular hydrogen can be formed efficiently. Although the relationship between the laboratory surfaces used in the olivine and amorphous carbon studies and true interstellar grain surfaces is not obvious, it is also interesting to see if a small degree of surface roughness affects the previous laboratory analysis of Katz et al. (1999). In the Appendix, we consider a new interpretation of the laboratory TPD results for olivine with the assumption, based on actual microscopic data, that the surface used possesses irregularities to a small degree.

2 GENERATION OF SURFACES AND BASICS OF MODEL

To study H₂ formation, we constructed four surfaces with different topologies. The first surface is entirely flat, the second surface is of minimal roughness and has only adatoms atop the major surface layer and vacancies, the third surface has a combination of individual adatoms and islands, while the fourth surface is exceedingly rough. On all the surfaces, the formation of H₂ is expected to occur instantly when two H atoms occupy the same site. In other words, possible activation energy barriers caused by enhanced binding of H atoms at irregularities are not considered.

To generate a surface numerically, we used the procedure of Gilmer & Bennema (1972). Starting from a flat surface, new particles are created and particles in the surface layer are removed by using a Metropolis probability scheme (Metropolis et al. 1953) with the probability P given by

\[ P = \min\{\exp\left[-(\Delta E - \Delta\mu)/T\right], 1\}, \]

where \( \Delta E \) is the energy difference between the predecessor and subsequent states, \( \Delta\mu \) is the driving force for solidification defined by the difference in chemical potential of the material making up the grain between the gas phase and the solid state and \( T \) is the temperature. Thus, if a new, randomly created state has a high energy, the probability is low, but if it has a low energy compared to its predecessor, the probability is unity. The result is a ‘relaxation’ to a state of lower energy. The degree of roughness achieved is controllable by the ratios of the bond strength \( \phi \) between two surface units to the temperature \( T \) and the driving force. Essentially, the smaller the ratio \( \phi/T \), the larger the degree of roughness eventually achieved because the individual binding units are bound more weakly and do not mind making irregular configurations. A higher value of \( \Delta\mu/T \) also promotes a higher surface roughness, since it lowers the energy of all unfavourable configurations with the same value. Large islands on the surface are only formed if \( \Delta\mu/T > 0 \).

For a detailed description of the influence of the parameters \( \phi \) and \( \Delta\mu \) on the roughness, see Gilmer & Bennema (1972) or Cuppen et al. (2003).

Fig. 1 shows pictures of the four surfaces; the rough one (d) is obtained with \( \phi/T = 0.8 \) and \( \Delta\mu/T = 0.5 \), while the two smooth surfaces (b, c) are formed under the conditions \( \phi/T = 1.3 \) and \( \Delta\mu/T = 0 \), and \( \phi/T = 1.4 \) and \( \Delta\mu/T = 0.5 \), respectively. The flat one (a) corresponds to a surface at \( \phi/T \to \infty \) and \( \Delta\mu/T = 0 \).

Adsorption of H atoms onto these surfaces is assumed to occur with unit sticking efficiency onto the bare substrate. The flux of H atoms, relevant to diffuse interstellar clouds, is given by \( 1.8 \times 10^{-9} \) atoms per lattice site per second (Biham et al. 2001). The number of lattice sites is related to the radius \( r \) of a spherical grain by the expression

\[ N = 4\pi r^2 s, \]

where \( s \) is the surface lattice density, which is \( 2 \times 10^{14} \) cm⁻² for olivine (Katz et al. 1999). Thus, an olivine grain of radius 0.06 \( \mu \)m can be represented by a lattice of \( 1 \times 10^5 \) sites, or a square lattice of dimension \( 316 \times 316 \), which is the size of the surfaces presented in this paper. The results in our previous paper (Chang et al. 2005) indicated that these surfaces are large enough to be in the asymptotic regime, where the efficiency of the H₂ formation is no longer size dependent. On a rough surface, one must imagine the lattice to consist of the topmost sites of the granular structure at any particular position. A hydrogen atom landing on a lattice site next to an upward step edge is adjacent to a horizontal neighbour of the lattice and can form a bond with this neighbour in addition to the bond with the lattice vertical neighbour below it. Clearly such a situation and others involving more than one horizontal bond will slow down both desorption and diffusion, as quantified below.

For the rate coefficients for desorption and diffusion (hopping) of the H atoms on the surfaces, expressions are adopted that are generally used within the field of crystal growth to describe the movement of adsorbates on surfaces (Gilmer & Bennema 1972). The rate coefficient for desorption of an H atom from a site with \( i \) horizontal lattice neighbours, \( k_{\text{d},i} \) (s⁻¹), is given by the equation

\[ k_{\text{d},i} = v \exp\left(-\frac{E_D + iE_i}{T}\right), \]

where \( v \) is the attempt frequency, typically taken to be \( 1 \times 10^{12} \) s⁻¹ (Biham et al. 2001), \( E_D \) is the binding, or desorption, energy of the adsorbed H atom and \( E_i \) is the lateral interaction of the H atoms.
with the grain. If an H atom is adsorbed on a flat bit of surface, and sees no horizontal (raised) neighbours of the lattice, then \( i = 0 \) and the effective binding energy is simply \( E_D \). If there is one horizontal neighbour, as might occur at a step edge, then \( i = 1 \) and the effective binding energy is \( E_1 \) higher. For a square lattice with four neighbouring sites, \( i \) can adopt all values from 0 to 4. Fig. 2 shows some possible configurations with the corresponding values for \( i \). The desorption of H\(_2\) is not considered since evaporation is expected to occur efficiently at all temperatures but the lowest ones considered.

The rate coefficient \( k_{b,i} \) (s\(^{-1}\)) for hopping from one site with \( i \) neighbours to a nearest neighbour is given by the expression

\[
k_{b,i} = v \exp \left( -\frac{E_b}{T} \right) \exp \left( -\frac{iE_1}{T} \right),
\]

where \( E_b \) is the diffusive barrier. The rate of hopping is slowed down by horizontal neighbours. For example, if \( i = 1 \), there is an additional Boltzmann factor involving the binding energy of the H atom because in order to hop in a given direction, the H atom must also extricate itself from its binding energy to another site on the surface. For simplicity, we use \( E_1 = E_D \) in most cases in this paper. Since this limit may exaggerate the effect, we consider in Section 4 systems for which \( E_1 < E_D \).

Fig. 3 shows the distribution of sites \( \beta_i \) amongst the five possible bonding environments for each of the surfaces (a), (b), (c) and (d) discussed above. The graph clearly indicates that an H atom hitting one of the surfaces (a), (b) or (c) has a chance of landing initially on a site without any lateral neighbours of more than 0.9.

**Figure 2.** A portion of a surface with a square lattice, showing differing surface irregularities with their corresponding values of \( i \). The spheres represent H atoms atop the surface.

**Figure 3.** The fraction \( \beta_i \) of surface sites with configuration \( i \). Surface (a) has sites with configuration \( i = 0 \) only.

### 3 OLIVINE AND CARBON SURFACES

To study the effect of surface roughness on the formation of molecular hydrogen, a number of simulations involving the surface topologies shown in Fig. 1 were performed based on the \( E_D \) and \( E_b \) values determined for olivine and amorphous carbon (Katz et al. 1999), as shown in Table 1. For each simulation, the recombination efficiency was calculated. The efficiency \( \eta \) is defined as the ratio between the flux of incoming H atoms and twice the rate at which molecular hydrogen is formed

\[
\eta = \frac{2R_{H_2}}{F}.
\]

Since the CTRW Monte Carlo method uses discrete numbers and not rates, as in rate equation methods, the formation rate cannot be directly determined. For this reason, we approximate the efficiency by

\[
\eta = \frac{2N_H}{N_{H_2}},
\]

where \( N_H \) is the number of H atoms that approach the surface in a given time interval and \( N_{H_2} \) is the number of molecules formed in that interval. If the efficiency does not change over time, this gives the same result as equation (5). We monitor \( N_H \) and \( N_{H_2} \) for \( 6 \times 10^6 \) depositions after a steady state is achieved. Under steady-state conditions, the H atom population simply fluctuates around an average value. To determine whether this state has been attained, the number of atoms on the surface is checked every 1000 depositions. If the new number does not exceed the old number by 1 per cent a steady-state situation is assumed.

Fig. 4 shows the recombination efficiency on all the four surface topologies as a function of temperature for surfaces based on olivine and carbon. For the flat surface (a), there is only a small temperature range in which the recombination efficiency is high, in agreement with previous studies (Katz et al. 1999; Bham et al. 2001; Chang et al. 2005). For the rougher surfaces, the temperature range becomes much larger. Even though surface (b) has only a limited surface roughness, since it contains only adatoms and vacancies, the large temperature range over which the recombination efficiency remains high is comparable to surface (c), which has many islands. For these surfaces, the efficiency drops to 0.5 at a temperature of 16–17 K for olivine and 28–29 K for carbon. Surface (d), the roughest surface, has the largest temperature range, in which the efficiency is still 0.50 at surface temperatures of 29 K for olivine and 50 K for amorphous carbon. This general increase in temperature range towards higher temperatures can be explained in terms of mobile and immobile H atoms. Because the total binding energy is much higher at sites with \( i > 0 \), many mobile H atoms move across the surface until they become immobilized at such sites, where they remain available for reaction with more rapidly diffusing atoms. Since rougher surfaces contain more sites where atoms can be immobilized, the chance of

<table>
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<th>Parameter</th>
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<tr>
<td>( E_D )</td>
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<tr>
<td>( E_D )</td>
<td>658 K (carbon)</td>
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<tr>
<td>( E_b )</td>
<td>287 K (olivine)</td>
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<tr>
<td>( E_b )</td>
<td>511 K (carbon)</td>
</tr>
<tr>
<td>( v )</td>
<td>( \times 10^{12} ) s(^{-1})</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>( 1.8 \times 10^{-9} ) atoms per lattice site per second</td>
</tr>
<tr>
<td>Array size</td>
<td>( 316 \times 316 ) unit cells</td>
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Monte Carlo simulations

Figure 4. The recombination efficiency as a function of the temperature for (a) olivine and (b) carbon surfaces of varying roughness.

Figure 5. The average number of H atoms on the surface during the simulations as a function of the surface temperature. The graphs show a sudden decrease in the number of atoms at distinct temperatures, which corresponds to the temperatures at which there is enough thermal energy to overcome the binding energies of the different binding configurations. For example, for olivine, the atoms on the smooth terraces \(i = 0\) desorb first. Since surface (a) only contains atoms in this configuration all atoms have evaporated by \(T > 11\) K. Surface (b) also contains adatoms with \(i = 1\) and vacancies with \(i = 4\), which causes the more or less constant number of atoms between 17 and 40 K. Surfaces (c) and (d) contain all the five different configurations, and their five drops can be observed. Note the particularly large number of H atoms on surface (d) at low temperatures, comprising nearly 30 per cent of the total. This large number actually begins to inhibit molecular hydrogen formation since H atoms approaching occupied sites are rejected. The large number of surface sites occupied by H atoms and the fact that there are only five distinct configurations indicates that for these topologies a rate equation treatment might be adequate (Chang et al. 2005). Calculations indeed show that the results of calculations with the rate equation approach do resemble closely with those of the more detailed Monte Carlo method. This approach can be seen in the Appendix, where it is used to simulate the laboratory olivine surface, where large numbers of atoms participate.

Given the high surface coverage at low temperatures, the Eley–Rideal process, in which physisorbed atoms react with approaching gas-phase atoms to produce molecular hydrogen, should be considered as a possible mechanism. We make the assumption that the process involves no activation energy, and so the rejection of H atoms approaching occupied lattice sites, in our previous simulations, is replaced by reaction. Fig. 6 shows the results for simulations performed under the same circumstances as in Figs 4 and 5, but now including both the Langmuir–Hinshelwood and Eley–Rideal mechanisms. A small decrease in the average number of H atoms can be observed. The major effect is that surface (d) now shows a higher efficiency at lower temperatures. Since we do not know if the Eley–Rideal reaction will actually occur, we present all results in the remainder of the paper both with and without this mechanism.
Figure 6. The recombination efficiency and the average number of H atoms on the surface at steady state as a function of the temperature for (a,b) olivine and (c,d) carbon surfaces. The Eley–Rideal mechanism is included.

4 THE INFLUENCE OF $E_l$ ON THE TEMPERATURE RANGE

In the absence of quantum chemical studies that explore the actual binding of H atoms at sites of irregularity, it is of interest to see how our results are changed by a reduction in the strength of the horizontal bonds made between adsorbed H atoms and the surface. That horizontal bonds might not be as strong as vertical bonds is indicated by studies such as Perets et al. (2005), which can be interpreted to indicate that for H$_2$ on low-density amorphous ice, the horizontal interactions are only one-fourth to one-third of the vertical ones. In addition, since sites of physisorption may not be specific lattice sites in all cases, the horizontal interactions may not represent specific directed bonds. Fig. 7 gives the upper bound of the temperature range where an efficiency of $>$50 per cent is reached as a function of the lateral interaction for (a) olivine and (b) amorphous carbon.

Figure 7. The upper bound of the temperature range in which an efficiency of $>$50 per cent is reached as a function of the lateral interaction for (a) olivine and (b) amorphous carbon.
in which an efficiency of $>50$ per cent is reached as a function of the lateral interaction for surfaces (a)–(d). The lateral interaction is expressed in terms of the vertical interaction, $E_D$. The left panel is for olivine; the right for amorphous carbon. Since surface (a) only contains sites with $i = 0$ the temperature range is not influenced by the strength of $E_l$. For the other surfaces a clear correlation between the temperature range in which molecular hydrogen is efficiently produced and the strength of $E_l$ can be observed, although all surfaces have a different dependence.

The results show an increase in temperature range for high $H_2$ formation efficiency as compared with the flat surface in the whole lateral bond regime studied. Even for the case where $E_l = 0.1 E_D$, an efficiency of $>50$ per cent occurs up to 11.6 K for olivine and 20.4 K for carbon with surface (d). The conclusion that surface roughness helps to explain the formation of $H_2$ in the diffuse ISM is thus still secure, although the degree of roughness needed depends on assumptions about bond strengths. In the remainder of the paper we use $E_l = E_D$ to study the effect of altering the surfaces in different ways. These effects will be most clearly visible for $E_l = E_D$.

5 MORE COMPLEX SURFACES

5.1 Mixed surfaces

Mixed surfaces are those that contain both olivine and carbon sites, with compositions in which the carbon sites occupy 2 per cent, 20 per cent and 40 per cent of the total. We consider topologies in which either the carbon sites are all situated at one large square island in the lattice or at many small square islands ranging in size from $1 \times 1$ to $10 \times 10$ that are randomly distributed. Both distributions are independent of the local surface topology.

Fig. 8 shows results for the three different compositions and two different topologies. For each composition/topology arrangement, simulations have been undertaken for our four surfaces of varying roughness. The black lines represent the simulations in which only the Langmuir–Hinshelwood mechanism is considered. The other lines also include the Eley–Rideal mechanism. The most important feature of the curves is the temperature range over which $H_2$ formation is efficient. If we focus on the upper temperature at which the efficiency drops to 0.50, we see that this temperature increases with increasing carbon content. For surface (b), for example, the temperatures range from 16 to 20 K as the percentage of carbon is increased; these values lie in between that of pure olivine (16 K) and 28 K (pure amorphous carbon). For surface (c), the analogous temperatures range from 17 to 22 K, and for surface (d), from 29 to 32 K. The inclusion of the Eley–Rideal mechanism has little effect on this temperature, since it is mainly important in the lower temperature ranges.

5.2 Amorphous surfaces

In reality, interstellar grains are amorphous and it is likely that the interactions between $H$-atom adsorbates and the surfaces of such amorphous particles show continuous distributions of diffusive (hopping) barriers and desorption energies. It was concluded in our earlier paper (Chang et al. 2005) that an increase in the normalized variance of these energy distributions results in an increase in the temperature range over which molecular hydrogen is efficiently produced. This result was found for both Gaussian and exponential distributions.

To simulate amorphous particles with the irregularities considered here, we utilize a Gaussian distribution. For an adsorbate at a site with $i$ horizontal neighbours and $i + 1$ interactions with the surface, the desorption and hopping rate coefficients are given by the expressions

$$k_{d,i} = v \exp\left(-\frac{(i + 1)E_D + \sum_{n=0}^{i} x_n \sigma E_D}{T}\right)$$

and

$$k_{h,i} = v \exp\left(-\frac{E_b + x_0 \sigma E_s}{T}\right) \exp\left(-\frac{i E_D + \sum_{n=1}^{i} x_n \sigma E_D}{T}\right),$$

where $\sigma$ is the normalized variance and $x_0, \ldots, x_i$ are numbers picked from a Gaussian distribution with average 0 and variance 1. Normalized variances of 0.1 and 0.2 are utilized.

Fig. 9 shows the recombination efficiency as a function of temperature for the two different values of $\sigma$. Three different compositions are used: pure olivine, pure carbon and a mixture of the two. The lighter lines represent again the Eley–Rideal results. Our results show, when compared with earlier figures, that the recombination efficiency of surface (a) gives larger temperature ranges for efficient $H_2$ formation for larger values of $\sigma$, as expected on the basis of the results of Chang et al. (2005). The other surfaces show little additional effect in temperature range beyond that caused by surface irregularities.

6 DISCUSSION AND CONCLUSION

It is likely that interstellar grains have a fluffy shape with a very rough surface structure. The influence of the surface roughness of interstellar grains on the efficiency of molecular hydrogen formation has been studied with the CTRW Monte Carlo method (Chang et al. 2005). This approach allows us to include regular and irregular surface structure in our computer models explicitly and to follow individual $H$ atoms deposited on the surface as they diffuse over a surface and react with one another. Four surfaces with varying surface roughness were constructed by a well-known computer algorithm and used in the calculations: one flat (surface a), one smooth, or with minimal roughness (surface b), one with minimal roughness and large islands (surface c) and one exceedingly rough (surface d). The surface materials considered are based on the olivine and amorphous carbon studies of Pirronello et al. (1997a,b, 1999) as analysed by Katz et al. (1999), in which individual values of the binding energy $E_D$ and diffusive barrier $E_b$ of $H$ atoms were derived, corresponding to what we would regard as pertaining to flat surfaces. The various irregularities considered affect the binding of $H$ atom adsorbates because the atoms are assumed to bind not only with the surface underneath them, but also horizontally with the surface at step edges (see Fig. 2). Five different configurations of different total binding energy and diffusive barrier are utilized. The binding energies range from a minimum value $E_D$, which pertains to flat regions of the surface (terraces), to a value five times this amount, which pertains to an atom that has fallen into a vacancy in the surface.

With flat surfaces of olivine and amorphous carbon, we reproduce the results of previous studies (Katz et al. 1999; Biham et al. 2001), which show that under diffuse cloud conditions, the efficiency of molecular hydrogen formation is limited to small temperature ranges. For the case of olivine, the temperature range is well below that of even cold dense clouds, whereas for amorphous carbon, the temperature range lies somewhat below the typical surface temperature (20 K) estimated for diffuse clouds with little
extinction. Thus, these surfaces are poor candidates for interstellar dust particles because of the widespread high abundance of molecular hydrogen. The inclusion of even a minimal amount of surface roughness changes the picture dramatically by raising the temperature range of high efficiency (>50 per cent) significantly. For pure olivine grains, surfaces (b) and (c) raise this temperature from 9 K for smooth olivine to over 16 K and for amorphous carbon from 16 K to almost 30 K. For our very rough surface (d), the corresponding temperatures are near 30 and 50 K, respectively. Mixed surfaces involving various percentages of carbon in a mainly olivine lattice show temperature ranges in between that of olivine and amorphous carbon. The amount with which the temperature range is increased is not only determined by the surface roughness, but also by the bond strength of the lateral bond. The previous temperatures are for the situation in which the lateral bond is the same as the vertical interaction. Probably, the lateral interaction is weaker, since the vertical bond is the sum of the interactions of the atom with several atoms in the grain, whereas there is only one ‘grain atom’ in each lateral

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Figure 8. The recombination efficiency as a function of temperature for mixed olivine–carbon surfaces. The percentage of carbon sites is 2 (panels a,b), 20 (panels c,d) and 40 (panels e,f). In the simulations shown in panels (a), (c) and (e), the carbon is present in one large square island, while in panels (b), (d) and (f), small square islands of carbon sites ranging in size from $1 \times 1$ to $10 \times 10$ are randomly distributed across the surface. The lighter curves represent the results including the Eley–Rideal mechanism.
direction. However, even if the lateral interaction is reduced to a quarter of the vertical one, the temperature at which molecular hydrogen is still efficiently produced rises to 14.2, 13.3 and 15.6 K for olivine surfaces (b), (c) and (d), respectively. For the carbon surfaces, the corresponding temperatures are 24.5, 22.9 and 27.8 K.

We have also considered amorphous surfaces, in which Gaussian distributions of binding energies and diffusive barriers are included, as discussed in Chang et al. (2005). Although the inclusion of these distributions increases the temperature range of high H$_2$ efficiency for flat olivine and amorphous carbon, the effect is minimal for the rougher surfaces. The overall conclusion is, as was made in our earlier paper, that surface irregularities, if sufficient, can easily explain the high efficiency of surface formation of H$_2$ in diffuse interstellar clouds and possibly even in warmer photon-dominated regions.

The main reason for the increase in efficiency of hydrogen formation at higher temperatures for surfaces (b), (c) and (d) is the...
increase in the population of H atoms on the surface. Atoms landing
on sites of low binding energy migrate to the irregular sites, where
the binding energies exceed $E_D$. They are then available for reaction
in our model since they do not evaporate until much higher tempera-
tures. This picture includes the tacit assumption that the increased
binding does not result in any chemical activation energy when reac-
tion occurs between a rapidly migrating H atom and a more strongly
bound one. Clearly, chemical activation energies may indeed occur
if the binding becomes large enough to be in the range normally
described as chemisorption. For olivine, the binding energies of our
five types of binding sites are at most $(i + 1) \times 373$ K for $E_i =
E_D$, where $i$ goes from 0 to 4. The highest binding energy consid-
ered is thus $1865$ K ($0.23$ eV) which, although weaker than typical
chemisorption bonds, is still significant. The sites of high binding
energy change our previous picture of interstellar grains in which
for most temperatures only a few weakly bound H atoms are present
at a time. It is ironic that the use of stochastic methods such as the
master equation and Monte Carlo techniques (Biham et al. 2001;
Green et al. 2001; Charnley 2001) originated to combat the per-
ceived problem of low surface populations. In our current picture,
however, significant surface populations exist for large ranges of
temperature, and it is interesting to see if the simple rate equation
method can reproduce to a reasonable degree of accuracy the results
obtained here for non-amorphous grains with finite numbers of ir-
regular sites. Preliminary calculations indicate that this is indeed
the case. The rate equation method is utilized in the Appendix to
simulate the laboratory studies of $H_2$ formation.

In addition to the diffusive mechanism for reaction, known as
the Langmuir–Hinshelwood mechanism, we have considered the
Eley–Rideal process, in which a gas-phase atom strikes an H atom
stuck to the surface. This mechanism can be efficient if the sur-
face coverage is high, as occurs at low temperatures, especially
on our rough surface. The net effect of including the process is
to increase the efficiency of $H_2$ formation, especially on
surface (d), in the lower temperature range. We have no guar-
antee that the Eley–Rideal process occurs without activation energy,
however.

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APPENDIX A: COMPARISON WITH TPD EXPERIMENTS

A TPD experiment consists of two steps. In the first phase, atoms are deposited on a surface at a constant low temperature. During the second
step, the actual measuring of the TPD curves occurs. The atomic beams are switched off and the temperature of the surface is raised with a constant rate. After some time the temperature becomes high enough for the atoms to diffuse across the surface and to react with other atoms
they encounter. The number of molecules released from the surface is then measured as a function of temperature. For a detailed explanation
of the method see Vidali et al. (1998) and Fraser et al. (2001). Molecular hydrogen formed during the experiment is hard to distinguish from
the background $H_2$. In the experiments of Pirronello et al. (1997a,b, 1999) on olivine and amorphous carbon, two atomic beams were used,
one with H and one with D atoms, and HD was the measured product species.

As discussed in the Introduction, two groups have tried to fit the TPD curves measured by Pirronello et al. (1999). Katz et al. (1999)
assumed no differences between H and D atoms and considered only physisorption sites with one barrier and binding energy. Cazaux
& Tielens (2004) assumed both physisorption and chemisorption and distinguished between H and D atoms. We thought it of interest to see how
well our models with varying degrees of surface roughness could reproduce the laboratory data. Atomic force microscopic (AFM) images
taken from the olivine surface used in the TPD experiments show surface structures similar to our surface (c) (Vidali, private communication).
Below, we discuss how this type of surface reproduces the data although we did not attempt an actual least-squares fit. It is important to realize
that whether or not such a model fits the laboratory data has little to do with our results for the models of interstellar dust. The actual TPD
data (dots) and the fit using the parameters and methodology of Katz et al. (1999) (solid lines) are shown in Fig. A1 along with our results,
as discussed below. It should be realized that this fit is a good, but not perfect, representation of the TPD data. These fits all resulted from
direct integration of rate equations, in contrast with the results in the rest of this paper which were all obtained using CTRW Monte Carlo
simulations that take into account the spatial structure of the surface.

Monte Carlo simulations

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Figure A1. TPD curves on an olivine slab. Irradiation times are (a) 0.07, 0.10, 0.25 and 0.55 min (bottom to top) and (b) 2.0, 5.5 and 8.0 min (bottom to top). The superimposed curves come from the fit of Katz et al. (1999) (solid lines), Model 1 (dashed lines) and Model 2 (dash-dotted lines). All curves are normalized to the curves with the longest irradiation times (0.55 and 8.0 min).

To model the laboratory formation of H$_2$ on a rough surface, we employed the following rate equations (using the notation of Katz et al. (1999)):

\[ \dot{N}_{H,i} = (1 - N_{H,i} - N_{H_2,i}) F - k_{d,i} N_{H,i} - N_{H,i} \left( \sum_{j=0}^{4} \beta_j k_{h,i} N_{H,j} \right) - k_{h,i} N_{H,i} \left( \sum_{j=0}^{4} \beta_j N_{H,j} \right) \]

\[ -k_{h,i} N_{H,i} \left( \sum_{j=0}^{4} \beta_j (1 - N_{H,i} - N_{H_2,j}) \right) + (1 - N_{H,i} - N_{H_2,i}) \left( \sum_{j=0}^{4} \beta_j k_{h,i} N_{H,j} \right) \]

\[ \dot{N}_{H_2,i} = -k_{d,2,i} N_{H_2,i} + \mu N_{H,i} \left( \sum_{j=0}^{4} \beta_j k_{h,2,i} N_{H_2,j} \right) - k_{h,2,i} N_{H_2,i} \left( \sum_{j=0}^{4} \beta_j (1 - N_{H,i} - N_{H_2,j}) \right) \]

\[ + (1 - N_{H,i} - N_{H_2,i}) \left( \sum_{j=0}^{4} \beta_j k_{h,2,i} N_{H_2,j} \right), \]

where $N_{H,i}$ and $N_{H_2,i}$ are the fractions of sites with environment $i$ occupied by H atoms and H$_2$ molecules, respectively, $F$ is the flux in atoms per site per second, and $\mu$ is the fraction of molecular hydrogen not immediately released into the gas after the reaction. The rate coefficients $k$, in units of s$^{-1}$, have two subscripts: the first referring to the rate of desorption ($d$) or hopping ($h$) and the second referring to the number of horizontal neighbours. For molecular hydrogen, we use the subscripts $d2$ and $h2$. The rate coefficients $k_{d,2,i}$ and $k_{h,2,i}$ are obtained using expressions similar to equations (3) and (4) with binding energy $E_{D2}$ and diffusive barrier $E_{h2}$. The first term in equation (A1) describes the deposition. The so-called Langmuir rejection term is utilized (Katz et al. 1999), although it is not clear to us that this term pertains to physisorption. The second term is due to evaporation, the third and fourth terms describe the loss of H atoms due to the recombination to
molecular hydrogen and the last two terms describe the hopping to and from differing types of sites. The terms in equation (A2) are respectively the evaporation, recombination and two hopping terms. The rate of gas-phase hydrogen production, measured in the experiment, is given by

\[ R = \left( \sum_{i=0}^{4} \beta_i k_{d2,i} N_{H_2,i} \right) + (1 - \mu) \left[ \sum_{i=0}^{4} \beta_i N_{H,i} \left( \sum_{j=0}^{4} \beta_j k_{H,j} N_{H,j} \right) \right]. \]  

(A3)

This rate is given in atoms per site per second, MLs\(^{-1}\).

The molecular hydrogen formation rate curves can be obtained as follows. First, the amount of atomic and, if any, molecular hydrogen that accumulates on the surface during the deposition time is determined by the integration of 10 differential equations with respect to time. In the second stage, these differential equations are integrated with respect to temperature assuming a constant heating rate (6 K s\(^{-1}\)). Simultaneously, the production rate of gas-phase H\(_2\) as a function of temperature is determined.

Equations (A1) and (A2) have 12 parameters: \( F, E_D, E_{D2}, E_b, E_{b2}, E_1, E_{12}, \mu \) and \( \beta_i \). The flux \( F \) is taken to be the same as in the previous models (2.7 \times 10^{-4} \text{ atoms per site per second}). As a first guess, we set \( E_1 \) and \( E_{12} \) to \( E_D \) and \( E_{D2} \), respectively. Since the AFM images taken from the olivine surface used in the TPD experiments showed surface structures similar to our surface (c) (Vidali, private communication), we fix the parameters \( \beta_i \) at the values for surface (c). This leaves us with five remaining variables: \( E_D, E_{D2}, E_b, E_{b2} \) and \( \mu \). Setting these variables to the values obtained by Katz et al. (1999) and assuming a hopping energy for molecular hydrogen of 243 K (Ruffle & Herbst 2000) allow us to compare curves with similar shapes to the ones obtained using the equations and parameters of Katz et al. (1999), but with peaks at a lower temperature. If we multiply all variable energies by 1.07, we obtain better agreement with the solid curves, as can be seen from Fig. A1. These slightly increased energies are given in Table A1 under the column labelled Model 1. For this model, we made the standard assumption in this paper that the lateral bond energies are the same as the desorption energies. The curves obtained using Model 1 are plotted in Fig. A1 as dashed lines.

In this figure, all curves are normalized to the curve with the longest irradiation time. Model 1 needs a larger normalization factor than the reproduced fit of Katz et al. (1999), however, since it otherwise gives curves with significantly lower peaks. Although both the treatments reproduce the peak widths and peak positions approximately equally well, the peak heights are less well described by Model 1. In addition, if Model 1 is applicable, many H atoms are still bound to the olivine surface at sites with one or more horizontal neighbours at 19 K. If the temperature is raised further, these atoms will also recombine to form H\(_2\), which will be released from the surface and lead to weak secondary peaks. We do not know if these weak secondary features were searched for.

We have also run a model that contains lower binding energies for the lateral bonds than for the vertical bonds. By choosing the parameters in this way, only one peak during which all hydrogen is released is found. The optimal setting for this model has quite weak lateral bonds of the H atoms, approximately 9 per cent of the vertical interaction. Designated Model 2, with parameters also listed in Table A1, this approach gives slightly broader peaks compared with the other two treatments, as can be seen in the dash-dotted lines of Fig. A1. The peak heights and positions are still a bit different from the solid curves, but they describe the experimental data approximately equally well. None of the models can explain the shoulder in the experimental peaks in Fig. A1(b).

If we assume that interstellar grains also have \( E_1 \approx 0.1 E_D \) and consider rough surface (d), high H\(_2\) formation efficiency extends to 11.6 K for olivine and 20.4 K for carbon.