Molecular hydrogen formation during dense interstellar cloud collapse

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ABSTRACT

We study the evolution of molecular hydrogen on the grain surfaces and in the gas phase using both the rate equation (which tracks the average number of various species) and the master equation (which tracks the expectation values of various species). We show that above a certain critical accretion rate of H on the grains, the results from these two methods become identical. We used this result to follow the collapse of a dense interstellar cloud and studied the formation of molecular hydrogen for two different temperatures (T = 10 and 12 K) and two different masses (1 and 10M⊙) of the cloud when olivine grains were used. Because at higher temperatures, the recombination is very small for these grains, we also studied similar hydrodynamic processes at higher temperatures (T = 20 and 25 K) when amorphous carbon grains were used. We find that generally, for olivine grains, more than 90 per cent H is converted to H2 within ~105–7 yr whereas for amorphous grains it takes ~106–7 yr. H2 formed in this manner can be adequate to produce the observed complex molecules.

Key words: ISM: atoms – ISM: clouds – ISM: evolution – ISM: molecules.

1 INTRODUCTION

Over the last few years, several works have been carried out to investigate the formation of complex molecules in cool interstellar clouds (Prasad & Prasad 1980a,b; Leung, Herbst & Herbst 1984; Hasegawa, Herbst & Leung 1992; Hasegawa & Herbst 1993). One of the stumbling blocks has been to identify mechanisms to produce H2 molecules. It is has been realized that purely gas phase reactions are so improbable that one needs to invoke the grain chemistry (e.g. Biham et al. 2001; Green et al. 2001). The rate equation deals with the expectation value of the hydrogen number density. By comparing the H2 formation in two methods, we conclude that a significant H2 formation can be adequate to produce the observed complex molecules.

clouds where accretion rates may vary in the presence of a grain size distribution.

In the first paper of this series, we investigate precisely this problem. For concreteness, we concentrate on cool, dense interstellar clouds. We assume typical stationary models of protostellar collapse of these clouds and compute the formation of H2 molecules as the flow collapses. For number and size distributions of grains, we use the standard models of the grains (suitable for dense clouds) present in the literature. As far as the grain-surface chemistry goes, we compute using both the rate equation approach (e.g. Hasegawa et al. 1992) as well as the master equation (probabilistic) approach (e.g. Biham et al. 2001; Green et al. 2001). The rate equation deals with the variation of the number density of the particles and the probabilistic equation deals with the expectation value of the hydrogen number density. By comparing the H2 formation in two methods, we conclude that the results of these approaches become identical at extremely small accretion rates as well as at large accretion rates FH > FHc, where the exact value of the critical accretion rate FHc depends on the grain size. (For definition of FH, see equation 9 below.) Typically, as we show in Section 2.4, FHc ~ 0.1–2 s−1. For grains of smaller size, FHc is larger, i.e. rate equations can be used if the accretion rate is sufficiently large. The first procedure is computationally faster and is valid when the average number of each species on the grain is high. The second procedure is slower and is useful when the average number of species is low. In a realistic collapse, the value of FHc depends on the effective area of the grains, i.e. the sum of all the grain surfaces. After following such self-consistent procedures, we conclude that a significant H2

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is formed in the cloud during the collapse. Because H$_2$ is a precursor of more complex biomolecules, we believe that future works on biomolecule formation based on our present results would be more reliable.

The plan of the present paper is the following. In Section 2, we discuss the grain size distribution in a cloud. We also discuss the rate and the master equations. We show that the contribution of small grains towards the grain chemistry is more significant because their number density is much higher. We first compute recombination efficiency (Biham et al. 2001) as a function of temperature for two different activation barrier energies in order to select the suitable temperature range in which H$_2$ formation could become significant in the cold cloud condition. We compare the results H + H $\rightarrow$ H$_2$ on grains using both the rate equation and master equation approaches as a function of accretion rate of H and show that, at high and very low rates, the results from these two approaches merge. In Section 3.1, we first discuss our results for the case when the cloud is static, i.e. each shell starting with the same initial condition. We consider the cloud of high and low mass and of two different temperatures. We then show the variations of H and H$_2$ as functions of the radial coordinate. Because the cloud parameters are not very accurately known, we carry out the procedure for the cloud temperatures $T$ = 10 and 11 K respectively, as appropriate for a cold, dense cloud. In Section 3.2, we consider collapse of spherical shells. Here, the number densities are high, and thus the formation of H$_2$ on the grains and the subsequent desorption of H$_2$ to the gas are significant. We chose two types of grains such as olivine (at 10 and 12 K) and amorphous carbons (20 and 25 K, respectively) and use corresponding activation barrier energies. Finally, in Section 4, we make concluding remarks.

2 CLOUD AND GRAIN PROPERTIES

2.1 Cloud properties

A generic interstellar cloud may have several distinct regions (e.g. van Dishoeck et al. 1993). Diffused clouds have typical number density $\sim$100–800 cm$^{-3}$ and temperature $T$ $\sim$ 30–80 K and a mass could vary from 1 to 100 M$_\odot$. Translucent clouds are in the similar mass range, but have number density $\sim$500–5000 cm$^{-3}$ with a slightly lower temperature (15–50 K). Cold dark clouds have temperatures around 10–25 K, but the number densities are much higher (10–10$^4$ cm$^{-3}$) and the corresponding masses can vary from 0.3–10 M$_\odot$ at the core to 10–10$^3$ M$_\odot$ at the cloud region. In terms of extinction parameter $R_v$, it appears that a diffused cloud has $R_v$ $\sim$ 3.1, an intermediate dense region has $R_v$ $\sim$ 4.0 and a dense cloud has $R_v$ $\sim$ 5.5 (Weingartner & Draine 2001a). In contrast, the giant molecular clouds will have densities around 300 cm$^{-3}$ at the outer complex, 10$^2$–10$^3$ cm$^{-3}$ at the clouds, 10$^4$–10$^5$ cm$^{-3}$ in the warm regions while 10$^6$–10$^7$ cm$^{-3}$ in the hot cores. The typical size of a molecular cloud is around a parsec or so with an average lifetime $\sim$10–20 Myr. In the outer regions, the cloud may pass through an isothermal phase where the temperature is constant. Heat generated in this phase is radiated away through the optically thin region. As the cloud collapses, the radiation is trapped due to the high optical depth and the gas becomes more adiabatic (Hartmann 1998). Though our numerical approach is capable of handling temperature variation inside a cloud, in the absence of a suitable and satisfactory distribution, in the present work, we shall consider the clouds of constant temperatures for the sake of simplicity.

2.2 Size distribution of grains

A small fraction (in terms of the number density) of the interstellar cloud is in the form of dusts and grains. These grains play an important role in the formation of stars and planetary systems and in our context, causing chemical evolution of molecules. The degree of importance of the dust depends on the ratio of the number density of grains to gas atoms or molecules at each radius. Here, we discuss two models of grains, which we follow.

(i) The Mathis, Rumpl and Nordsieck (MRN) model: the simplest model that can reproduce functional dependence of the extinction with wavelength is due to Mathis, Rumpl & Nordsieck (1977). According to this so-called MRN model, the number density of grains having size between $a$ to $a + da$ is given by,

$$dn_g = Cn_g a^{-3.5} da, \quad a_{\text{min}} < a < a_{\text{max}},$$  \hspace{1cm} (1)

where, $n_g$ is the number density of hydrogen, $a$ is the grain radius in cm. This relation is strictly valid between the minimum and the maximum size of the grains $a_{\text{min}} = 50$ Å and $a_{\text{max}} = 2500$ Å. The grain constant, taken from Draine & Lee (1984) is given by $C = 10^{-2.5}$.

(ii) The Weingartner and Draine (WD) model: Weingartner & Draine (2001b, hereafter WDO1) revised the MRN distribution for the entire range of grain size that is applicable to the Milky Way, Large and Small Magellanic Cloud (LMC and SMC, respectively). This revision was needed to incorporate the real interstellar environment through which starlight passes. The parameters include reddening and carbon abundances. For instance, when the carbon abundance is negligible, this distribution becomes close to the MRN distribution. This distribution is valid for grains with $a > 3.5$ Å. If we take the weighted surface area (i.e. surface area of the grain $\propto a^2$) multiplied by the number density, that would give the effective surface area per unit volume contributed by the grains of a given size $a$. In Fig. 1, we present this plot for the parameters suitable for the dense interstellar cloud ($R_b^k = 5.5$ and Case A from table 1 of

Figure 1. Variation of the effective grain area $A_g$ as a function of the grain radius indicating that smaller grains have the highest contribution. Instead of choosing continuous distribution, three types of ‘average’ grains have been assumed having radii 10.4 (type 1), 33.8 (type 2) and 215.7 Å (type 3) respectively that have the same total number of grains. The arrows are drawn at humps of the Weingartner & Draine (2001b) distribution function.
WD01) used in the WD distribution. It is clear that the small sized grains contribute the most because of their large number density. It is also clear that there are three sizes of grains that are important: (i) the smallest one with $a \sim 10$ Å (Type 1), (ii) the intermediate one with $a \sim 35$ Å (Type 2) and (iii) the large grains with $a \sim 200$ Å (Type 3). The actual values, marked by arrows have been computed from the humps in the WD distribution. For simplicity of computation of the accretion rate on each type of grain and their catalytic effect, we assume that only these three types of grains exist. Their number densities are estimated self-consistently from the area under the curve given by WD distribution. See Acharyya, Chakrabarti & Chakrabarti (2002, 2004) for application of these considerations.

2.3 Equations governing the formation of molecular hydrogen

2.3.1 Rate equation method

Where the grain has a large number of reactant atoms or molecules, it is convenient to use this method. Here, one deals with the average number of reactants.

Let us consider $n_H$ to be the number of H atoms on a grain at time $t$ and let $n_{H_2}$ be the number of $H_2$ molecules at that instant, then the following equation gives the rate at which the number of H changes:

$$ \frac{dn_H}{dt} = F_H - W_H n_H - 2(A_{H}/S)n_H^2.$$  (2a)

Here, $F_H$ is the accretion rate of H, which increases the number of H on a grain by sticking to it. $W_H$ is the desorption coefficient of hydrogen, $v \exp (-E_1/k_bT)$, where $E_1$ is the activation barrier energy for desorption of the H atom, $k_b$ is the Boltzmann’s constant and $T$ is the temperature of the grain, assumed to be the same as the gas. Because in our case the number density is high, $\sim 10^8$ cm$^{-3}$ and above, such an assumption is justified. The second term causes a reduction of the number of hydrogen atoms on the grain, hence the minus sign. On the grain surface, mainly due to diffusive processes, two H atoms combine to form a single $H_2$ molecule. $A_{H} = v \exp (-E_0/k_bT)$, the hopping rate, gives the probability of this happening. Here, $v$ is the vibrational frequency:

$$ v = \frac{2s E_d}{\pi m_H},$$  (2b)

where $s \sim 10^{14}$ is the surface density of sites on a grain (Biham et al. 2001), $m_H$ is the mass of the H atom and $E_d$ is the binding energy for physical adsorption $E_d \sim 3E_0$. This is normally taken to be $10^{-12}$–$10^{-10}$ s$^{-1}$. $E_0$ is the activation barrier energy for diffusion of H atom. This term also reduces the number of H and is represented by the third term of equation (2a) with a the minus sign. The diffusion through tunnelling has not been taken into account as it could be less important (Katz et al. 1999). $S$ is the number of sites per grain:

$$ S = 4\pi r^2 s.$$  (2c)

It may be relevant to discuss the nature of the third term of equation (2a). If the fraction $f_H$ of grain sites occupied by any of the species is very small ($f_H \ll 1$), then in order to form an $H_2$, the incoming H has to hop, on average $S$ times to combine with another H located at an average distance of $S^{1/2}$ through a well-known ‘random-walk’ process. This accounts for the factor $S$ in the third term, which effectively reduces the diffusion rate. However, as $f_H$ becomes significant, any direction that the incoming H hops to would be useful for forming an $H_2$ and thus the factor may be reduced to $S^{1/2}$ or even less instead of $S$. In the present circumstance, $f_H$ is indeed very small and we use the factor $S$ in the denominator as in Biham et al. (2001) or Lipshat et al. (2004).

The following equation gives the rate at which the number of $H_2$ increases with time:

$$ \frac{dn_{H_2}}{dt} = \mu(A_{H}/S)n_H^2 - W_{H_2} n_{H_2}.$$  (2d)

where $W_{H_2}$ is the desorption coefficient of the hydrogen molecule given by $v \exp (-E_2/k_bT)$, $E_2$ is the activation barrier energy for desorption of the $H_2$ molecule. The parameter $\mu$ represents the fraction of the $H_2$ molecule that remains on the surface upon formation, while the (1-$\mu$) fraction is desorbed spontaneously due to the energy released in the recombination process. The $H_2$ production rate $R_{H_2}$ in the gas due to the grain is then given by

$$ R_{H_2} = (1 - \mu)(A_{H}/S)n_H^2 + W_{H_2} n_{H_2}.$$  (3)

However, the net production rate in the gas phase is obtained by the inclusion of the breakdown of $H_2$ by cosmic rays, the rate of which is assumed to be $10^{-17}$ s$^{-1}$ (Millar, Faquhar & Willacy 1997). The values for energy barriers $E_0, E_1, E_2$ and $\mu$ are taken from Katz et al. (1999). In our calculations, we used $E_0 = 24.7$ MeV, $E_1 = 32.1$ MeV, $E_2 = 27.1$ MeV and $\mu = 0.33$ for olivine, and $E_0 = 44$ MeV, $E_1 = 56.7$ MeV, $E_2 = 46.7$ MeV and $\mu = 0.413$ for amorphous carbon grains. Because of the difference in barrier energy, the recombination efficiencies (defined as $\eta = 2R_{H_2}/F_H$, see Biham et al. 2001) are high at completely different temperature ranges. In Figs 2(a) and (b), we show $\eta$ for (a) olivine and (b) amorphous carbon computed using the rate equation. Here, we also included the Langmuir and> Hinshelwood rejection term, which rejects the accretion of H and $H_2$ in the occupied sites. This term essentially reduces the efficiency at lower temperatures. The curves are drawn for three accretion rates $F_H = 10^{-8}$ (solid), $10^{-6}$ (dotted) and $10^{-4}$ s$^{-1}$ (dashed) respectively, which are appropriate for the dense clouds considered in this paper. It is to be noted that for olivine (Fig. 2a) the useful temperature range is around 7–13 K and for carbon (Fig. 2b) this range is around 13–25 K. We therefore select the low cloud temperatures ($T = 10$ and 12 K) for the first case and relatively higher temperatures ($T = 20$ and 25 K) for the second case. One could imagine having unusually high accretion rates in dense clouds, which might allow $H_2$ production at even higher temperatures where $\eta$ is still significant.

2.3.2 Master equation method

It is convenient to use the master equation method (Biham et al. 2001) to study the formation process when the number of species in the grain is ‘small’. This process accounts for both the discrete nature of the hydrogen and the fluctuations, and solves the problem probabilistically. For instance, its dynamical variables are the probability $P_{H_2}(N_{H_2})$ that there are $N_{H_2}$ atoms on a grain at a given time. One needs to study the time evolution of the probabilities through the same type of equations as in equations (2a–d), except that the expectation values $(N_{H_2})$ and $(N_{H_2})$ are to be used instead of the average number. The equations are:

$$ \frac{d(N_{H_2})}{dt} = F_{H_2} - W_{H_2} (N_{H_2}) - 2(A_{H}/S)(N_{H_2}(N_{H_2} - 1))$$  (4a)

and

$$ \frac{d(N_{H_2})}{dt} = \mu(A_{H}/S)(N_{H_2}(N_{H_2} - 1)) - W_{H_2} (N_{H_2}).$$  (4b)

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Because \( P_H(N_H) \) represents the probability that there are \( N_H \) hydrogen atoms on the grain, by sum rule on probabilities:

\[
\Sigma_{N_H=0}^{\infty} P_H(N_H) = 1. \tag{5}
\]

The time derivatives of these probabilities, \( P_H(N_H) \), are given by (Biham et al. 2001)

\[
P_H(N_H) = F_H[P_H(N_H - 1) - P_H(N_H)]
+ W_H(N_H + 1) P_H(N_H - 1)
+ (A_H/S)[(N_H + 2)(N_H + 1)P_H(N_H + 2)
- N_H(N_H - 1)] P_H(N_H).
\tag{6a}
\]

Similarly, the probability that there are \( N_{H2} \) hydrogen molecules on the grain is given by \( P_{H2}(N_{H2}) \). The time evolution of these probabilities is given by

\[
P_{H2}(N_{H2}) = W_{H2}(N_{H2} + 1) P_{H2}(N_{H2} + 1)
- N_{H2} P_{H2}(N_{H2})
+ \mu (A_H/S)[(N_H - 1)] P_{H2}(N_{H2} - 1)
- P_{H2}(N_{H2}).
\tag{6b}
\]

Note that the last term in equation (6b), does not exactly correspond to the last term in equation (13) of Biham et al. (2001). Perhaps there was a typographical error in the latter equation.

From these probabilities, one gets the expectation value of \( H \) atoms on the grain as

\[
\langle N_H \rangle = \Sigma_{N_H=0}^{\infty} N_H P_H(N_H) \tag{7a}
\]

and the expectation value of hydrogen molecules on the surface is

\[
\langle N_{H2} \rangle = \Sigma_{N_{H2}=0}^{\infty} N_{H2} P_{H2}(N_{H2}) \tag{7b}
\]

The rate of formation of \( H_2 \) molecules on the surface is given by

\[
R_{H2} = (1 - \mu)(A_H/S)[(N_H - 1)] P_H(N_H) + W_{H2}(N_{H2}). \tag{8}
\]

Note that we kept the same symbol \( R_{H2} \) for the recombination rate both for the rate equation (equation 3) and the master equation (equation 8).

2.4 Regime of interest for self-consistent study

Before we study the molecular hydrogen formation in a collapsing cloud, we like to enquire if the rate equation or the master equation is to be used for time evolution. For these, we require the accretion rate of \( H \) falling on a given grain. We compute three accretion rates for three different sizes of the grains.

As in the kinetic theory, the accretion rate is computed from the number of \( H \) that a grain ‘sees’ per unit time. This is given by

\[
r_H = \alpha \pi r^2 V n_H, \tag{9}
\]

where \( \alpha \) is the probability that a \( H \) atom will stick to a grain, \( V \) is the root-mean-square velocity of the hydrogen, which is given by

\[
V = \sqrt{8k_b T / \pi m_H}, \tag{10}
\]

\( n_H \) is the number density of hydrogen, \( r \) is the mean radius of a grain \( r_{grain}. \) More accurately, it is the sum of the radius of the grain and the hydrogen atom. So we use, \( r = r_{grain} + r_H \) \( (r_H \sim 10^{-4} \) cm is the radius of a hydrogen atom). \( \alpha \) may vary from 0.1 to 1. We use \( \alpha = 0.5 \) throughout the paper. \( m_H \) is the mass of a hydrogen atom. (van Dishoeck et al. 1993).

Fig. 3 gives the time evolution of the variation of the number of \( H \) and \( H_2 \) on a grain surface at a given accretion rate of \( H \) for the small grains (Type 1) using both the rate equation (long dashed) and the master equation (solid curve). We choose the gas/grain temperature to be 10 K. The accretion rate has been chosen to be \( 1.5 \times 10^{-4} \). Note that, within about \( 10^4 \) s, both \( H \) and \( H_2 \) saturate. This time is negligible compared with the infall time. Thus, in our computation in future, we assume that \( H \) and \( H_2 \) saturate instantaneously.

In Figs 4(a) and (b), we plot the saturation values for all three types of grains as functions of the accretion rate of \( H \) when the gas/grain temperature is 10 K. In Fig. 4(a), we compare the number of \( H \) for all three types of grains (marked) obtained from the rate (long dashed) and from the master (solid curves) equations. Note that for an extremely low value of the accretion rate, these two methods are close to each other. For a sufficiently high rate, these two values merge. For a lower rate, the results from the master equation are independent of the grain size. In Fig. 4(b), we draw similar curves for the saturated values of \( H_2 \). The rate equation gives different saturation values for different types of grains (marked) while the master equation gives virtually similar values. Because in both Figs 4(a) and (b) the rate and master equations roughly merge...
3 CLOUD COLLAPSE AND H₂ FORMATION

In our first exercise, we assume an interstellar cloud that is static. We start with a spherical molecular cloud having the outer radius at \( R_{\text{out}} = 1 \) pc. The outer region of the cloud is assumed to be isothermal at \( T_{\text{out}} \) where the gas is optically thin. \( T_{\text{out}} \) is assumed to be a parameter. In this phase, we assume \( \rho \sim r^{-2} \) (Shu, Adams & Adams 1987), where \( r \) is the radial distance. The accretion rate of H on the grain surface will automatically increase as the density rises. In presence of rotation, a centrifugal barrier is formed at \( r = r_\text{c} \), where the centrifugal force balances gravity. At this stage, the cloud is expected to be disc-like and the opacity becomes high enough to trap radiations. Inside this region, \( \rho \propto 1/r \). As a test of our code, we evolve the cloud for 10 million years to judge how far inside the cloud the production rate of H is significant.

Biham et al. (2001) pointed out and we have also verified it to be true that there is indeed a narrow temperature range in which the recombination efficiency is the highest. In the case of olivine, the peak is at around 7–9 K and for amorphous carbon the peak is at around 12–16 K. We chose temperatures at higher side of this peak. In our model calculation, we have taken two generic molecular clouds with \( R_{\text{out}} = 1 \) pc, and \( M = 10 \) and 100 M⊙. We assume the angular velocity of the outer edge of the cloud to be \( 10^{-16} \) rad s\(^{-1}\) so that \( r_\text{c} = 6.8 \times 10^{14} \) and \( 6.8 \times 10^{15} \) cm respectively in these two cases. With these masses, the densities of the gas at the outer edge are \( \rho_{\text{out}} = 0.162 \times 10^{-21} \) and \( 0.162 \times 10^{-20} \) gm cm\(^{-3}\), respectively. Densities of the gas at \( r_\text{c} \) are found out to be \( \rho_\text{c} = 0.324 \times 10^{-14} \) and \( 0.262 \times 10^{-11} \) gm cm\(^{-3}\), respectively. This density is the initial density of the collapsing shell. A notional inflow velocity is provided [which gives an indication of the evolution time to be \( t_{\text{ev}} \sim r/c \) by assuming a subsonic flow where the sound velocity is given by \( a_s \sim (4kT/3m_H)^{1/2} \)]. In our runs, the velocity is always assumed to be less than this value. We choose \( 10^4 \) cm s\(^{-1}\) for concreteness. The activation barrier energies are chosen to be as those of olivine.

The computational procedure involves dividing the entire cloud into 10\(^5\) shells. We compute the number density in each shell and the mean thermal velocity for temperature \( T = T_{\text{out}} \) K. These enable us to get the accretion rate of H on the grain surface. The rate of desorption of H\(_2\) that controls how much goes back into the gas at each radius is computed. These are normalized by the number density of grains at each radius. We continue our procedure for each shell.

The results presented in this Section are for olivine grains. In Fig. 5(a), we present the mass fraction of H and H\(_2\) in the gas...
phase as a function of the radius of the cloud when $T_{\text{out}} = 10$ K when the mass of the cloud is $M = 10$ (dotted) and 100 $M_\odot$ (solid), respectively. Higher mass clouds produce significant $H_2$ at a much early stage of the evolution because the density is higher. In Fig. 5(b), we present the number densities of $H$ and $H_2$ on the grain surfaces. We remind here that the $H_2$ values are actually the saturation expectation values at corresponding radii and $H$ values are the corresponding equilibrium values. $H_2$ goes back to the gas at the rate of $R_{H_2}$ (equation 3).

In Figs 6(a) and (b), we present similar results at $T_{\text{out}} = 11$ K. The notations and styles are the same as before. Generally speaking, the saturation values of $H$, $H_2$ on the grain surfaces increase with decreasing radius as before. Understandably, the production rate is higher when the cloud mass is higher because the accretion rate itself is high. With the rise in temperature, $H$ is not significantly affected, but the production of $H_2$ in grains and therefore the desorption of $H_2$ into the gas are dropped. However, as one goes inside, the conversion of $H_2$ is higher because more $H$ was left over in the gas to increase the accretion rate on grains. As a result, the mass fraction of $H_2$ crossed the 0.5 mark at a larger radius.

### 3.2 Collapsing shell

We now compute the variation of $H$ and $H_2$ with a somewhat different initial condition. We start with a hollow spherical shell that is collapsing. Masses of the shell for two model runs are chosen to be 1 and 10 $M_\odot$, respectively. The initial densities are $1.1 \times 10^{-19}$ gm cc$^{-1}$, respectively. The shell thickness is given by $\Delta R = 0.0005$ pc. In order to understand the effect of grain types and the effect of temperature, we choose two sets of activation energy barriers as presented in Section 2.3 above. For each grain type, we choose two temperatures for each of which we run two models with the mass of the shell taken to be 1 and 10 $M_\odot$, respectively. Our strategy is to compute the expectation of $H_2$ in each shell and let the shell collapse into the next shell subsonically with a velocity $v = 10^4$ cm s$^{-1}$ as written in Section 3.1. The smallest time-step after which the expectation value of $H_2$ was updated was 25 yr (this is much larger compared with the saturation time, see Fig. 3 above). The output of each shell is carried forwards into the next shell as the initial condition. The evolution proceeds from then on in that shell. The density increases in the same way discussed above while the mass of the shell remains fixed. For clarity, we find it convenient to plot the quantities with time of the collapse. The accretion rate of $H$ on the grains is very high in this model. The resulting number densities of $H$ and $H_2$ are also large. As a result, $H$ to $H_2$ conversion is very rapid at early phases of the cloud collapse.

#### 3.2.1 Olivine shell

First, we choose the activation energy barriers to be those of olivine (see Section 2.3). Fig. 7(a) shows the evolution of $H$ and $H_2$ in the gas phase when the cloud is of mass $M = 1$ (dotted) and 10 $M_\odot$ (solid), respectively. The temperature of the cloud has been chosen to be $T = 10$ K. The mass fraction of $H_2$ crosses 0.9 at $t \sim 7.81 \times 10^6$ yr and...
Figure 7. Variation of (a) mass fractions of H and H$_2$ in the gas phase, and (b) number densities of H and H$_2$ on grains with time during the chemical evolution of a collapsing shell. Dotted curves are for $M = 1 M_\odot$ and the solid curves are for $M = 10 M_\odot$, respectively. Mass fraction of H$_2$ reaches $\sim 0.9$ in a matter of $7.8 \times 10^6$ and $4.7 \times 10^5$ yr for low and high mass shells, respectively.

$t = 4.7 \times 10^3$ yr, respectively. In Fig. 7(b), the number densities on the grain surfaces are plotted. Note that as the conversion to H$_2$ is rapid (Fig. 7a), the number density of H decreases rapidly in the gas phase. At some point (around $T \sim 10^{5-6}$ yr) the formation H$_2$ on grains is at a slower rate compared with the desorption rate) and hence the reserve of H$_2$ on grains goes down. On the other hand, the density of cloud itself increases as the collapse progresses, which started increasing the accretion rate towards the end. This increases the number density of the H and H$_2$. Thus, in the collapsing shell model the number densities on the grains are lower at the intermediate times.

In Figs 8(a) and (b), we repeat the same model (i.e. with the activation barrier energies as those of olivine) but chose the cloud temperature to be slightly higher at $T = 12$ K. The motivation is to show the sensitivity of the final outcome on temperature. The behaviour is similar as in Figs 7(a) and (b) except that the mass fraction of H$_2$ became $\sim 0.9$ at $t = 9.4 \times 10^6$ and $8.1 \times 10^6$ yr for $M = 1$ and $10 M_\odot$, respectively. This is expected as the recombination efficiency is smaller (see Fig. 2).

3.2.2 Amorphous carbon shell

We now assume the activation barrier energies chosen to be those of amorphous carbon grains. In this case, it is possible to go to higher temperatures. We run at two temperatures, $T = 20$ and 25 K respectively for the shells of $M = 1$ and $10 M_\odot$ respectively. In Figs 9(a) and (b), we plot the results for $T = 20$ K. Here, the plot characteristics remained the same as before. The mass fraction of H$_2$ reaches 0.9 at $t = 9.1 \times 10^6$ and $6.4 \times 10^6$ yr for $M = 1 M_\odot$ and $M = 10 M_\odot$, respectively. In Fig. 9(b), we show the number densities of H and H$_2$ on grains. Here too, there is a minimum at an intermediate time. Similar figures as above for $T = 25$ K are plotted in Figs 10(a) and (b), and the mass fraction of H$_2$ reached 0.9 at $t = 9.5 \times 10^6$ and $9.36 \times 10^6$ yr, respectively. Thus, in the case of higher activation energy, the sensitivity of the final result on the shell mass is weaker.

In this context, we wish to mention that while computing the formation of H$_2$ using a constant surface reaction rate supplied by the University of Manchester Institute of Science and Technology (UMIST) data base (Millar et al. 1997), it was observed that most of the H is converted to H$_2$ at a somewhat later stage (Chakrabarti & Chakrabarti 2000), at least after $10^7$ yr of the beginning of the collapse. Our work with computation with up-to-date grain surface chemical processes indicates that the conversion is perhaps faster. In future, we shall compute more complex molecules and will compare them with the observed tabulated value (e.g. Herbst 1992; van Dishoeck et al. 1993).

4 DISCUSSION AND CONCLUDING REMARKS

In this paper, we studied the evolution of molecular hydrogen in the gas phase and on the grain surface in two toy models, namely, in (i) a static interstellar cloud and (ii) the collapsing phase of a spherical shell. In the later case, we chose two different types of activation barrier energies, which correspond to olivine and amorphous carbon grains. Instead of using the complete grain size distribution, we assumed three major grain sizes where there are humps in the WD distribution. We compared the results from the rate and the master equation for each type of grain and determined the applicability of
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Figure 9. Same as in Figs 7(a) and (b) but the activation barrier energies of the cloud are assumed to be those of amorphous carbon. The temperature is chosen to be $T = 20$ K. Mass fraction of $\sim 0.9$ is achieved by $\text{H}_2$ in a matter of $9.1 \times 10^6$ and $6.4 \times 10^4$ yr for low ($M = 1 \text{ M}_\odot$) and high ($M = 10 \text{ M}_\odot$) mass shells, respectively.

Figure 10. Same as in Figs 8(a) and (b) but the temperature of the cloud is assumed to be 25 K. Mass fraction of $\sim 0.9$ is achieved by $\text{H}_2$ in a matter of $9.5 \times 10^6$ and $9.36 \times 10^6$ yr for low ($M = 1 \text{ M}_\odot$) and high ($M = 10 \text{ M}_\odot$) mass shells, respectively. Amorphous carbon grains are used.

these equations as a function of the accretion rate of H on grains. Using static and collapsing shell models with prescribed density, temperature and velocity distributions, we showed how gradually $\text{H}_2$ builds up in the grain and the gas. Earlier, using a constant and representative surface reaction rate given in the UMIST data base for H to $\text{H}_2$ conversion, it was shown that the conversion process is slower (e.g. reaching a mass fraction of $\sim 0.5$ after $t \sim 10^7$ yr). However, here we find that 90 per cent conversion to $\text{H}_2$ is achieved in a matter of $10^7$–$10^8$ yr depending on cloud parameters such as activation energy and temperature of the grains, and the mass of the cloud. In terms of spatial distribution, we find that most of the conversion takes place for a radial distance $r > 0.1$ pc, i.e. at the outer shell of the molecular cloud.

In our work, we chose simple power-law density distribution inside an isothermal cloud. Li & Draine (2001) considered the effect of radiations on the grains in diffused interstellar clouds and computed the grain temperature as functions of grain size distribution. They also computed the resulting infrared spectra. Recent numerical solutions of several workers, such as Zucconi, Walmsley & Galli (2001) and Galli, Walmsley & Goncalves (2002), have shown that dust temperature inside the dense cloud could be as low as 6 K, and the temperatures of the gas and grain become roughly identical when the gas density $n \gtrsim \text{ few } \times 10^4 \text{ cm}^{-3}$. Thus, our assumption of the equality of the grain and the dust temperatures may be justified because our number densities are of this order or higher. On the other hand, the Cosmic Background Explorer Diffuse Infrared Background Experiment (COBE/DIRBE) results (e.g. Lagache et al. 1998) do not seem to support the existence of very cold dusts. We therefore chose the cloud temperature at 10 K and above. Indeed, laboratory experiments also seem to indicate that $\text{H}_2$ formation is significant only in the very narrow range of temperature which we chose in this paper.

Our work concentrated on the gravitational collapse of a dense cloud induced by Jean's instability. In a different context, Bergin et al. (2004) studied the evolution of the molecular hydrogen inside an extremely diffused cloud the formation of which is induced by the passage of a shock wave. The temperatures used were very high (reaching several thousand), which is appropriate for such a cloud of very low extinction. In their work, though the gas–grain interaction was simplified by using a production rate of $\text{H}_2$ as given in Millar et al. (1997), they used destruction of $\text{H}_2$ through cosmic rays and UV radiation. They also studied the formation rate of the CO molecule.

In our paper, we have thoroughly dealt with the most basic surface chemistry, namely the $\text{H}_2$ formation deep inside a cold, dense cloud. In future, we shall apply our procedure to include diffused clouds at high temperatures following the above work and explore the possibility of formation of more complex molecules and especially the formation of biomolecules during the collapse phase.

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