The effect of grain size distribution on H$_2$ formation rate in the interstellar medium

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ABSTRACT

The formation of molecular hydrogen in the interstellar medium takes place on the surfaces of dust grains. Hydrogen molecules play a role in gas-phase reactions that produce other molecules, some of which serve as coolants during gravitational collapse and star formation. Thus, the evaluation of the production rate of hydrogen molecules and its dependence on the physical conditions in the cloud are of great importance. Interstellar dust grains exhibit a broad size distribution in which the small grains capture most of the surface area. Recent studies have shown that the production efficiency strongly depends on the grain composition and temperature as well as on its size. In this paper we present a formula which provides the total production rate of H$_2$ per unit volume in the cloud, taking into account the grain composition and temperature as well as the grain size distribution. The formula agrees very well with the master equation results. It shows that for a physically relevant range of grain temperatures, the production rate of H$_2$ is significantly enhanced due to their broad size distribution.

Key words: ISM: molecules - molecular processes

1 INTRODUCTION

The chemistry of interstellar clouds consists of reactions taking place in the gas phase as well as on the surfaces of dust grains (Hartquist and Williams 1995). In particular, the formation of H$_2$ takes place on grain surfaces while all competing gas phase processes are orders of
magnitude less efficient (Gould & Salpeter 1963). Hydrogen molecules are necessary for the initiation of gas-phase reaction networks that give rise to the chemical complexity observed in interstellar clouds. Molecules serve as coolants during gravitational collapse, enabling the formation of stars.

In diffuse clouds the H$_2$ formation process takes place on bare grains that consist of amorphous silicates and carbon. In dense molecular clouds the grains are coated by ice mantles. Upon collision with a grain, an H atom has a probability $\xi$ to become adsorbed on the surface. The adsorbed H atom (adatom) resides on the surface for an average time $t_H$ (residence time) before it desorbs. In the Langmuir-Hinshelwood mechanism, the adsorbed H atoms diffuse on the surface of the grain either by thermal hopping or by tunneling. When two H atoms encounter each other on the surface, an H$_2$ molecule may form (Williams 1968; Hollenbach & Salpeter 1970, 1971; Hollenbach et al. 1971; Smoluchowski 1981, 1983; Aronowitz & Chang 1985; Dulev & Williams 1986; Pirronello & Avera 1988; Sandford & Allamandola 1993). The formation rate $R_{\text{total}}$ (cm$^{-3}$s$^{-1}$) of molecular hydrogen on dust-grain surfaces is commonly evaluated using the Hollenbach-Werner-Salpeter formula

$$R_{\text{total}} = \frac{1}{2} n_H \langle v_H \rangle n_{\text{grain}} \langle \sigma_g \rangle \gamma,$$

(1)

where $n_H$ (cm$^{-3}$) is the number density of hydrogen atoms in the gas, $\langle v_H \rangle$ (cm s$^{-1}$) is the average velocity of hydrogen atoms, $n_{\text{grain}}$ (cm$^{-3}$) is the number density of dust grains and $\langle \sigma_g \rangle$ (cm$^2$) is the average grain cross section (Hollenbach et al. 1971). Assuming spherical grains, $\langle \sigma_g \rangle = \pi \langle r^2 \rangle$ where $r$ (cm) is the grain radius. The parameter $0 \leq \gamma \leq 1$ is the recombination efficiency, namely, the fraction of atoms hitting the grain which come out in molecular form.

The total grain mass amounts to about 1% of the hydrogen mass in the cloud. The number density of dust grains is about $10^{-13}$ to $10^{-12}$ smaller than the total number density of hydrogen atoms. In previous studies, a typical grain radius of 0.17$\mu$m was used, assuming a mass density of $\rho_g = 2$ (gram cm$^{-3}$) (Hollenbach et al. 1971). Under these assumptions, for gas temperature of 100 K and $\gamma = 0.3$, Eq. (1) can be simplified to

$$R_{\text{total}} = R \cdot n_H n,$$

(2)

where $R \simeq 10^{-17}$ (cm$^3$ s$^{-1}$) is the rate coefficient and $n = n_H + 2n_{H_2}$ (cm$^{-3}$) is the total density of hydrogen atoms in both atomic and molecular ($n_{H_2}$) form (Hollenbach et al. 1971). Eq. (2) is commonly used for the evaluation of the hydrogen recombination rate in models...
of interstellar chemistry. In this paper we present a direct calculation of $R_{\text{total}}$, without using rate coefficients.

The grain size distribution $n_g(r) \text{ (cm}^{-4}\text{)}$ in interstellar clouds is broad with many small grains and few large grains. The surface area is dominated by the small grains. This distribution can be approximated by a power law of the form (Mathis et al. 1977, Weingartner 2001)

$$n_g(r) = cr^{-\alpha}$$

(3)

where $n_g(r) dr \text{ (cm}^{-3}\text{)}$ is the density of grains with radii in the range $(r, r + dr)$ in the cloud. This distribution is bounded between the upper cutoff $r_{\text{max}} = 0.25\mu\text{m}$ and the lower cutoff $r_{\text{min}} = 5\text{nm}$. The exponent is $\alpha \simeq 3.5$ (Draine & Lee 1984). In general, the normalization constant is given by

$$c = \frac{3M_g(4 - \alpha)}{4\pi \rho_g (r_{\text{max}}^{4 - \alpha} - r_{\text{min}}^{4 - \alpha})},$$

(4)

where $M_g \text{ (gram cm}^{-3}\text{)}$ is the mass density of grain material in the cloud. The total number density, $n_{\text{grain}} \text{ (cm}^{-3}\text{)}$, of grains is given by

$$n_{\text{grain}} = \frac{c(r_{\text{min}}^{1 - \alpha} - r_{\text{max}}^{1 - \alpha})}{\alpha - 1}.$$  

(5)

Recent experiments have shown that the mobility of H atoms on dust analogues under interstellar conditions is dominated by thermal hopping rather than tunneling (Pirronello et al. 1997a,b, 1999; Katz et al. 1999; Roser et al. 2002). As a result, the production efficiency of H$_2$ molecules is highly dependent on the grain temperature. The efficiency is very high within a narrow window along the temperature axis, with exponential decay on both sides. Theoretical studies have shown that for sufficiently small grains, the production efficiency is strongly dependent on the grain size, namely it decreases as the grain size is reduced (Biham et al. 2001, Green et al. 2001). The Hollenbach-Werner-Salpeter formula, in which all the surface processes are captured in the parameter $\gamma$ cannot account for the temperature and grain-size dependence of the production efficiency.

In this paper we present a formula for the production rate of H$_2$ in interstellar clouds, which takes into account explicitly the dependence of the recombination efficiency on the grain temperature and size, integrating the size dependence over the entire distribution of grain sizes. This formula is in very good agreement with the results obtained from the master equation. It applies for a broad range of steady-state and quasi steady-state conditions and
enables the evaluation of the production rate of \( \text{H}_2 \) in a closed form without the need for any simulation or numerical integration.

The paper is organized as follows. In Sec. 2 we present the different approaches to the calculation of reaction rates on surfaces. The dependence of these rates on the grain size and temperature is considered in Sec. 3. In Sec. 4 we introduce a formula that accounts for the formation rate of molecular hydrogen per unit volume of the clouds, integrated over the entire distribution of grain sizes. The results are discussed in Sec. 5 and summarized in Sec. 6.

## 2 RECOMBINATION RATES ON SINGLE GRAINS

Calculations of reaction rates of \( \text{H}_2 \) formation and other chemical reactions on dust grains are typically done using rate equation models (Pickles & Williams 1977; d’Hendecourt et al. 1985; Brown & Charnley 1990; Hasegawa et al. 1992; Caselli et al. 1993; Willacy & Williams 1993). These models consist of coupled ordinary differential equations that provide the time derivatives of the populations of the species involved. The reaction rates are obtained by numerical integration of these equations. The production of molecular hydrogen on a single grain of radius \( r \) is described by

\[
\frac{dN}{dt} = F - WN - 2AN^2, \tag{6}
\]

where \( N \) is the number of \( \text{H} \) atoms on the grain. The first term on the right hand side is the flux \( F \) (sec\(^{-1}\)) of hydrogen atoms onto the grain surface. The second term describes the thermal desorption of \( \text{H} \) atoms from the surface where

\[
W = \nu \exp(-E_1/k_BT) \tag{7}
\]

is the desorption rate, \( \nu \) is the attempt rate (standardly taken as \( 10^{12} \text{sec}^{-1} \)), \( E_1 \) is the activation energy barrier for desorption and \( T \) (K) is the grain temperature. The third term in Eq. (6) accounts for the depletion in the number of adsorbed atoms due to formation of molecules. The parameter \( A = a/S \) is the rate at which \( \text{H} \) atoms scan the entire surface of the grain, where

\[
a = \nu \exp(-E_0/k_BT) \tag{8}
\]

is the hopping rate between adjacent adsorption sites on the grain, \( E_0 \) is the energy barrier for hopping, \( S = 4\pi r^2 s \) is the number of adsorption sites on the grain surface and \( s \) (cm\(^{-2}\)) is their density. The formation rate, \( R_{\text{grain}} \) of \( \text{H}_2 \) on a single grain is given by \( R_{\text{grain}} = AN^2 \).
Under steady state conditions one can obtain an exact solution for $R_{\text{grain}}$ in terms of $F$, $W$ and $A$ (Biham et al. 1998).

Following the experimental results reported by Katz et al. (1999) for the amorphous carbon sample, we use the parameters: $s = 5 \cdot 10^{13} \, \text{(cm}^{-2})$, $E_0 = 44.0 \, \text{(meV)}$ and $E_1 = 56.7 \, \text{(meV)}$. It is found (Biham & Lipshtat 2002) that the process of molecular hydrogen formation is efficient only within a narrow window of grain temperatures, $T_0 < T < T_1$, where

$$T_0 = \frac{E_0}{k_B \ln(\nu S/F)}$$

and

$$T_1 = \frac{2E_1 - E_0}{k_B \ln(\nu S/F)}.$$

At temperatures below $T_0$ the mobility of H atoms on the surface is very low, sharply reducing the production rate. At temperatures above $T_1$ most atoms quickly desorb before they encounter each other and form molecules.

Rate equations are an ideal tool for the simulation of surface reactions, due to their simplicity and high computational efficiency. In particular, they account correctly for the temperature dependence of the reaction rates. However, in the limit of small grains under low flux they become unsuitable. This is because they ignore the fluctuations as well as the discrete nature of the populations of atoms on the grain (Charnley et al. 1997; Caselli et al. 1998; Shalabiea et al. 1998; Stantcheva et al. 2001). For example, as the number of H atoms on a grain fluctuates in the range of 0, 1 or 2, the $H_2$ formation rate cannot be obtained from the average number alone. This can be easily understood, since the recombination process requires at least two H atoms simultaneously on the surface.

Recently, a master equation approach was proposed, that takes into account both the discrete nature of the population of H atoms as well as the fluctuations, and is thus suitable for the simulation of $H_2$ formation on interstellar dust grains (Biham et al. 2001; Green et al. 2001). Its dynamical variables are the probabilities $P(N)$ that there are $N$ atoms on the grain. The time derivatives $\dot{P}(N)$, $N = 0, 1, 2, \ldots$, are expressed in terms of the adsorption, reaction and desorption terms according to

$$\dot{P}(N) = F \left[ P(N-1) - P(N) \right] + W \left[ ((N+1)P(N+1) - NP(N) \right]$$
where \( N = 0, 1, 2, \ldots \). Note that the equations for \( \dot{P}(0) \) and \( \dot{P}(1) \) do not include all the terms, because at least one H atom is required for desorption to occur and at least two for recombination. Direct integration of the master equation provides the time evolution of the probabilities \( P(N) \). The recombination rate per grain

\[
R_{\text{grain}} = A \left( \langle N^2 \rangle - \langle N \rangle \right)
\]

(12)
can then be calculated, where \( \langle N^k \rangle, \ k = 1, 2, \ldots, \) is the \( k \)’th moment of the distribution \( P(N) \). Under steady state conditions the recombination rate is given by (Green et al. 2001; Biham & Lipshtat 2002)

\[
R_{\text{grain}} = \frac{F I_W/A + 1}{2 I_W/A - 1} \left( \frac{2 \sqrt{2F/A}}{2 \sqrt{2F/A}} \right).
\]

(13)

where \( I_x(y) \) is the modified Bessel function.

Using suitable summations over the master equation, one obtains the moment equations, namely a set of coupled differential equations for the time derivatives of the moments \( \langle N^k \rangle, \ k = 1, 2, \ldots, \) of the distribution \( P(N) \) (Lipshtat & Biham 2003). The recombination rate on grains of a given size depends only on the first two moments, \( \langle N \rangle \) and \( \langle N^2 \rangle \). The time derivatives of these moments are given by

\[
\frac{d\langle N \rangle}{dt} = F + (-W + 2A) \langle N \rangle - 2A \langle N^2 \rangle
\]

\[
\frac{d\langle N^2 \rangle}{dt} = F + (2F + W - 4A) \langle N \rangle + (8A - 2W) \langle N^2 \rangle - 4A \langle N^3 \rangle.
\]

(14)

Using suitable cutoffs in the master equation one can replace the third moment \( \langle N^3 \rangle \) by \( \langle N^3 \rangle = 3\langle N^2 \rangle - 2\langle N \rangle \), and obtain a closed set of two coupled differential equations for the first two moments. Under steady state conditions Eq. (14) takes the form of two coupled linear algebraic equations for \( \langle N \rangle \) and \( \langle N^2 \rangle \). The solution of these equations is given by \( \langle N \rangle = F(A + W)/(2AF + WA + W^2) \) and \( \langle N^2 \rangle = F(F + A + W)/(2AF + WA + W^2) \). Inserting these moments into Eq. (12) we obtain

\[
R_{\text{grain}} = \frac{AF^2}{2AF + WA + W^2}.
\]

(15)
3 THE LIMITS OF SMALL AND LARGE GRAINS

Expressing the production rate $R_{\text{grain}}$ of Eq. (15) in terms of the size-independent hopping rate $a = AS$ (sec$^{-1}$) and the incoming flux $f = F/S$ (monolayer sec$^{-1}$) we obtain

$$R_{\text{grain}} = \frac{fS^2}{\left(\frac{W}{a}\right) \left[1 + S\left(\frac{W}{a} + \frac{2f}{W}\right)\right]}.$$ (16)

The ratio $a/W$ is the number (up to a logarithmic correction) of sites that the atom visits before it desorbs (Montroll & Weiss 1965). The ratio $W/f$ is roughly the average number of vacant sites in the vicinity of an H atom. Using these parameters we can identify two regimes of grain sizes. For grains that are sufficiently large such that $S > \min(a/W, W/f)$, the size dependence of the production rate is given by $R_{\text{grain}} \sim S \sim r^2$ and the production efficiency is independent of the grain size. This is the range in which rate equations apply. In the limit of small grains, namely when $S < \min(a/W, W/f)$, the production efficiency depends linearly on $S$, and $R_{\text{grain}} \sim S^2 \sim r^4$. This is the regime in which the grain size becomes the smallest relevant length-scale in the system and rate equations fail (Biham & Lipshtat 2002).

To illustrate the implications of these results, consider a given mass $M$ of dust matter. Dividing the mass $M$ to spherical grains of radius $r$, the number of grains is given by $n_{\text{grain}} \sim r^{-3}$. In an interstellar cloud, the $r$ dependence of the production rate of H$_2$ due to such ensemble differs in the two limits discussed above. For large grains the total production rate is $R_M = n_{\text{grain}}R_{\text{grain}} \sim r^{-1}$. Reducing the grain size increases their total surface area, and as a result the production rate goes up. In the limit of small grains the efficiency decreases as the grain size is reduced and thus $R_M \sim r$. This indicates that there is an intermediate grain size for which the production rate is maximal. In Fig. 1 we present the total production rate $R_M$ (sec$^{-1}$) for a total dust mass of $M = 1$ (gram) which is divided into spherical grains of dradius $r$. Clearly, there is an optimal grain size for which the production rate is maximal. This optimal radius depends on the grain composition and temperature and is given by

$$r_{\text{opt}} = \sqrt{S_{\text{opt}}/4\pi s}$$ (17)

where $S_{\text{opt}} = (W/a + 2f/W)^{-1}$. For typical interstellar conditions this optimal grain radius is of the order of tens of nm, with several thousand adsorption sites.
4 THE OVERALL PRODUCTION RATE OF MOLECULAR HYDROGEN

As discussed above, interstellar grains exhibit a broad size distribution of the form \( n_g(r) \sim r^{-\alpha} \). For \( \alpha > 2 \) the surface area is dominated by the small grains, while for \( \alpha > 3 \) even the grain mass is dominated by the small grains. Therefore, these small grains are expected to contribute significantly to \( \text{H}_2 \) formation. Taking this size distribution into account we find that the production rate on grains with radii in the range \((r, r + dr)\) is given by

\[
n_g(r)R_{\text{grain}}(r)dr = \begin{cases} c_1 r^{4-\alpha}dr : & \text{small grains} \\ c_2 r^{2-\alpha}dr : & \text{large grains} \end{cases}
\]

(18)

where

\[
c_1 = \frac{(4\pi sf)^2c}{W} \quad (19)
\]

and

\[
c_2 = \frac{4\pi sW^2c}{16a}\left(-1 + \sqrt{1 + 8\frac{af}{W^2}}\right)^2 \quad (20)
\]

are obtained directly from Eq. (16) in the limits of \( S \ll S_{\text{opt}} \) and \( S \gg S_{\text{opt}} \), respectively. Eq. (16) is expected to be highly accurate in the limit of small grains. For large grains its accuracy may be limited because its derivation requires to impose a cutoff on the master equation. For large grains the rate equations apply, and therefore one can use

\[
c_2 = \frac{4\pi sW^2c}{16a}\left(-1 + \sqrt{1 + 8\frac{af}{W^2}}\right)^2 ,
\]

(21)

which is obtained directly from the exact solution of the rate equation (6) under steady state conditions (Biham et al. 1998).

To evaluate the total production rate of molecular hydrogen per unit volume in an interstellar cloud, one should take into account the size distribution of dust grains, and the dependence of the production efficiency on the grain size and temperature. The total production rate is given by

\[
R_{\text{total}} = \int_{r_{\text{min}}}^{r_{\text{max}}} n_g(r)R_{\text{grain}}(r)dr
\]

(22)

where \( n_g(r)dr \) is the density of grains with radii in the range \((r, r + dr)\), and \( R_{\text{grain}}(r) \) can be taken either from the exact result of Eq. (13) or from the approximate result of Eq. (16). Assuming a power law distribution of grain sizes, given by Eq. (3), and the result of of Eq. (16) one can divide the range of integration into two parts, namely the domain of small grains, \( r_{\text{min}} < r < r_{\text{opt}} \), and the domain of large grains, \( r_{\text{opt}} < r < r_{\text{max}} \). Integrating each one of them separately, for \( \alpha \neq 3 \), we obtain
\[ R_{\text{total}} = \frac{c_1}{5-\alpha} \left( r_{\text{opt}}^{5-\alpha} - r_{\text{min}}^{5-\alpha} \right) + \frac{c_2}{3-\alpha} \left( r_{\text{max}}^{3-\alpha} - r_{\text{opt}}^{3-\alpha} \right), \] (23)

In the special case of \( \alpha = 3 \), the total production rate is

\[ R_{\text{total}} = \frac{c_1}{2} \left( r_{\text{opt}}^2 - r_{\text{min}}^2 \right) + c_2 \ln \left( \frac{r_{\text{max}}}{r_{\text{opt}}} \right). \] (24)

In Fig. 2 we present the total production rate obtained from Eq. (23) for flux \( f = 6.88 \times 10^{-9} \) (ML sec\(^{-1}\)), which corresponds to gas temperature of 90 K and hydrogen density \( n_H = 10 \) (cm\(^{-3}\)). The results of this formula are shown for the case in which the parameter \( c_2 \) is taken from Eq. (21) (○) and for the case in which it is taken from Eq. (22) (+). Both results are in very good agreement with those obtained from the master equation (solid line). The rate equation results (dashed line) are found to significantly over-estimate the total production for most of the temperature range. The results obtained (using the master equation) under the assumption that the same total grain mass is divided into grains of identical size (0.17 \( \mu m \)) are also shown (dotted line). For the range of grain temperatures in which the \( \text{H}_2 \) production is efficient, this assumption leads to an under-estimate of the total production rate by about an order of magnitude. This indicates that within this temperature range the broad size distribution of the grains tends to enhance the production rate due to the increase in grain-surface area.

5 DISCUSSION

The formula introduced in this paper [Eq. (23)] enables us to calculate the formation rate of molecular hydrogen in interstellar clouds for a broad range of conditions without the need to perform computer simulations or numerical integration. It applies both in the case of diffuse clouds in which the \( \text{H}_2 \) formation takes place on bare silicate and carbon grains and for molecular clouds in which the grains are coated by ice mantles. The formula applies directly for grain size distributions that can be approximated by a power-law of the form of Eq. (3). For other distribution functions for which the integration cannot be done analytically one can solve Eq. (22) by numerical integration.

The relaxation time for \( \text{H}_2 \) formation processes on dust grains can be obtained from Eq. (6). It is given by \( \tau = (W^2 + 8AF)^{-1/2} \). Under typical conditions, this time is extremely short compared to the time scales of interstellar clouds. Therefore, the formula can be used even in the context of evolving clouds. The time dependence can be taken into account by updating the input parameters to the formula as the physical conditions in the cloud vary.
At very low grain temperatures below $T_0$, the mobility of H atoms on the surface is suppressed and the rate of $H_2$ formation is sharply reduced. In this limit, H atoms keep accumulating on the surface, the relaxation time $\tau$ increases and the behavior may no longer be well described by steady state calculations. In this limit the coverage is relatively high and thus the rate equations are valid. However, the Langmuir rejection of atoms that hit the grain in the vicinity of already adsorbed atoms should be included. This is done by replacing the flux term $F$ by $F(1 - N/S)$. The formula introduced in this paper, Eq. (23), is valid only for grain temperatures higher than $T_0$. To extend its validity below $T_0$ one should incorporate the Langmuir rejection term into it, by replacing all the appearances of $W$ in Eqs. (19) - (21) by $W + f$.

In Eq. (23) it is assumed that all the grains are at the same temperature. This assumption does not apply in photon dominated regions (PDR’s), where small grains exhibit large temperature fluctuations. In general, the formation of molecular hydrogen in PDR’s is not well understood. The typical grain temperatures in these regions is significantly higher than the temperature range in which the formation of H$_2$ on olivine, carbon and ice is found to be efficient. Several approaches have been considered in attempt to explain this puzzle. One approach is based on the assumption that chemisorbed H atoms play a role in the formation of H$_2$ ([Cazaux & Tielens 2002, 2004]). Other explanations may involve porous grains that capture H atoms more strongly within pores or with the temperature fluctuations of small grains.

6 SUMMARY

We have presented a formula for the evaluation of the formation rate of molecular hydrogen in interstellar clouds, taking into account the composition and temperature of the grains as well as their size distribution. The formula is found to be in excellent agreement with the results of the master equation. It enables us to obtain reliable results for the production rates without the need to perform computer simulations or numerical integrations. It is found that for an astrophysically relevant range of grain temperatures the broad size distribution of the grains provides an enhancement of the H$_2$ formation rate compared to previous calculations.
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Figure 1. The total production rate $R_M$ (sec$^{-1}$) vs. grain radius $r$ for an ensemble of identical, spherical grains, with total grain mass of $M = 1$ (gram). The density of the grain material is $\rho = 2$ (gram cm$^{-3}$). The grain temperature is $T = 16$ (solid line) and $T = 19$ (dashed). The flux is $3.44 \times 10^{-9}$ (ML s$^{-1}$). The optimal radius is $r_{\text{opt}} = 5.6 \times 10^{-7}$ (cm) for $T = 16$K and $r_{\text{opt}} = 1.9 \times 10^{-6}$ (cm) for $T = 19$K.
Figure 2. The total production rate $R_{\text{total}}$ (cm$^{-3}$sec$^{-1}$) of H$_2$ vs. grain temperature as calculated by the formula (Eq. 23) introduced in this paper, where $c_2$ is given by Eq. (19) ($\circ$) or by Eq. (20) (+). Both results are in very good agreement with the master equation (solid line), although the latter one is slightly better. The rate equation (dashed line) is found to overestimate the production rate. These results are compared to those obtained if the same mass of grains is divided into identical, spherical grains of 'typical' radium ($r = 0.17$ µm) (dotted line). It is found that for an astrophysically relevant range of high recombination efficiency, the broad size distribution significantly enhances the production rate.