Molecular Hydrogen Formation on Porous Dust Grains

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20 March 2022

ABSTRACT

Recent laboratory experiments on interstellar dust analogues have shown that H₂ formation on dust grain surfaces is efficient in a range of grain temperatures below 20 K. These results indicate that surface processes may account for the observed H₂ abundance in cold diffuse and dense clouds. However, high abundances of H₂ have also been observed in warmer clouds, including photon-dominated regions (PDRs), where grain temperatures may reach 50 K, making the surface processes extremely inefficient. It was suggested that this apparent discrepancy can be resolved by chemisorption sites. However, recent experiments indicate that chemisorption processes may not be efficient at PDR temperatures. Here we consider the effect of grain porosity on H₂ formation, and analyze it using a rate equation model. It is found that porosity extends the efficiency of the recombination process to higher temperatures. This is because H atoms that desorb from the internal surfaces of the pores may re-adsorb many times and thus stay longer on the surface. However, this porosity-driven extension may enable efficient H₂ formation in PDRs only if porosity also contributes to significant cooling of the grains, compared to non-porous grains.

Key words: ISM: molecules - molecular processes

1 INTRODUCTION

H₂ is the most abundant molecule in the Universe. It plays a key role in interstellar chemistry and serves as a coolant during gravitational collapse and star formation. Therefore, the processes of formation and dissociation of molecular hydrogen strongly affect the evo-
olution of interstellar clouds (Duley & Williams 1984; Williams 1998). Already in the 1960’s it was found that $H_2$ cannot form efficiently enough in the gas phase to account for its observed abundances, and it was suggested that dust grains serve as catalysts for this process (Gould & Salpeter 1963). The formation of molecular hydrogen on dust grain surfaces was studied, assuming that H atoms that collide with a grain are physically adsorbed (physisorbed). These atoms diffuse on the surface and form $H_2$ molecules when they encounter each other (Hollenbach & Salpeter 1970; Hollenbach & Salpeter 1971; Hollenbach et al. 1971).

The formation rate $R_{H_2}$ ($cm^{-3}s^{-1}$) of $H_2$ molecules can be expressed by

$$R_{H_2} = n_H v_H \sigma n_{\text{grain}} \xi \eta / 2$$

(1)

where $n_H$ ($cm^{-3}$) is the number density of hydrogen atoms in the gas, $v_H = \sqrt{8k_BT_g/(\pi m_H)}$ ($cm s^{-1}$) is their typical velocity (where $m_H = 1.67 \cdot 10^{-24}$ gram is the mass of an H atom and $T_g$ is the gas temperature), $n_{\text{grain}}$ ($cm^{-3}$) is the number density of dust grains and $\sigma$ ($cm^2$) is the average grain cross section (Hollenbach et al. 1971). Assuming spherical grains, $\sigma = \pi r^2$ where $r$ (cm) is the grain radius. The parameter $0 \leq \xi \leq 1$ is the sticking coefficient and the parameter $0 \leq \eta \leq 1$ is the recombination efficiency, namely, the fraction of adsorbed atoms 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 $n_{\text{grain}} \approx 10^{-12} n$ where $n = n_H + 2n_{H_2}$ ($cm^{-3}$) is the total density of hydrogen atoms in both atomic and molecular ($n_{H_2}$) forms (Hollenbach et al. 1971). Assuming compact grains with mass density of $\rho_g = 2$ (gram $cm^{-3}$), these parameters lead to a typical grain diameter of about 0.2$\mu m$. Assuming gas temperature of 100 K as well as $\xi \approx 1$ and $\eta \approx 1$, one obtains

$$R_{H_2} \approx R n_{\text{HN}},$$

(2)

where the rate constant is $R \approx 10^{-17}$ ($cm^3s^{-1}$), in agreement with observations for diffuse clouds (Jura 1975). More recent observations in photon dominated regions, indicate that in these regions the rate coefficient should be $R \approx 10^{-16}$ ($cm^3s^{-1}$), in order to account for the observed $H_2$ abundance (Habart et al. 2003).

Recent laboratory experiments indicate that a model based on physisorbed atoms may account for the $H_2$ formation rate in cold interstellar clouds, where the grain temperature does not exceed 20 K. However, molecular hydrogen has also been observed in large abundances in photon-dominated regions (PDRs), which are exposed to high fluxes of untra-violet radiation (Tielens & Charnley 1997). In these regions, typical grain temperatures are in the
range of 30 - 50 K. In order to explain the formation of H\textsubscript{2} in PDRs it was suggested that some of the H atoms are chemically adsorbed (chemisorbed), and thus may remain on the surface long enough to form molecules even at higher grain temperatures. However, recent experimental and theoretical results indicate that such chemisorption processes are likely to contribute to H\textsubscript{2} formation only at grain temperatures above 450 K. Such high grain temperatures can be achieved by ultra-small grains with diameters of the order of 1 nm, which may exhibit large temperature fluctuations (Draine & Anderson; Guhathakurta & Draine). However, the efficiency of H\textsubscript{2} production on such extremely small grains is expected to be low. This is due to the very small population of H atoms on each grain, where the recombination rate is dominated by the discreteness and fluctuations in the population of adsorbed H atoms (Lipshtat & Biham 2005). Thus, chemisorption processes may be irrelevant to the range of grain temperatures observed in PDRs.

In this paper we consider the effect of porosity on the rate of H\textsubscript{2} formation on interstellar dust grains. We present a model in which H atoms can be adsorbed either on the external surface of the grains or inside the pores. The model shows that H atoms can be retained in pores for longer times, and recombine there to form H\textsubscript{2} molecules at higher temperatures than on non-porous grains.

The paper is organized as follows. In Sec. 2 we consider the formation of H\textsubscript{2} molecules on compact grains, which is efficient only within a narrow temperature range below 20 K. In Sec. 3 we describe the high H\textsubscript{2} abundance in PDRs, which cannot be explained by the processes considered in Sec. 2. In Sec. 4 we review some of the evidence that interstellar dust grains are porous. A model for H\textsubscript{2} formation on porous grains is presented in Sec. 5. It is shown that porosity extends the efficiency range of H\textsubscript{2} formation toward higher grain temperatures. The results are discussed in Sec. 6 and summarized in Sec. 7.

2 \textbf{H\textsubscript{2} FORMATION ON DUST GRAINS WITH COMPACT SHAPE}

During the past decade, the formation of molecular hydrogen on analogues of interstellar dust materials has been studied by laboratory experiments. In particular, carbonaceous samples (Pirronello et al. 1997a,b; Vidali et al. 1998a,b; Pirronello et al. 1999; Zecho et al. 2002a,b; Perry & Price 2003; Guttler et al. 2004; Zecho et al. 2004), silicates such as olivine (Pirronello et al. 1997a,b; Vidali et al. 1998a) and a variety of amorphous ice samples (Manicò et al. 2001; Roser et al. 2001, 2002; Hornekaer et al. 2003, 2005; Perets et al. 2003) have been stud-
ied. The results of some of these experiments were analyzed using rate equation models. The relevant parameters, namely the energy barriers for the atomic diffusion and desorption and for molecular desorption, have been found. These parameters were used in order to calculate the efficiency of molecular recombination under conditions relevant to the interstellar clouds. It was found that the recombination of H atoms physisorbed on these surfaces is efficient within a narrow temperature range, below 20 K (Katz et al. 1999; Cazaux & Tielens 2004; Perets et al. 2005).

Consider an interstellar dust grain exposed to a flux of H atoms. The formation of molecular hydrogen on the grain surface is described by

$$\frac{dN}{dt} = F - WN - 2AN^2,$$

where $N$ is the number of H atoms on the grain. The first term in Eq. (3) describes the effective flux, $F$ ($s^{-1}$), of H atoms sticking to the surface, given by $F = n_H v_H \sigma \xi$. The Langmuir-Hinshelwood (LH) rejection of atoms deposited on top of already adsorbed hydrogen atoms (or molecules) is neglected here, since the coverage is assumed to be low. The second term describes the thermal desorption of H atoms from the surface where

$$W = \nu \exp(-E_1/k_B T)$$

is the desorption rate, $\nu$ is the attempt rate [standardly taken as $10^{12}$ ($s^{-1}$)], $E_1$ is the activation energy barrier for desorption and $T$ (K) is the grain temperature. The third term in Eq. (3) accounts for the depletion of adsorbed H atoms due to formation of H$_2$ molecules. The parameter $A = a/S$ is the rate at which H atoms scan the entire surface of the grain, where

$$a = \nu \exp(-E_0/k_B T)$$

is the hopping rate between adjacent adsorption sites and $E_0$ is the energy barrier for hopping. For a spherical grain the number of adsorption sites on the surface is $S = 4\pi r^2 s$ where $s$ (cm$^{-2}$) is their density. The formation rate, $R_{\text{grain}}$, of H$_2$ on a single grain is given by $R_{\text{grain}} = AN^2$. Here we assume, for simplicity, that all H$_2$ molecules desorb from the surface upon formation. 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). The recombination efficiency

$$\eta = \frac{2R_{\text{grain}}}{F}$$

turns out to exhibit strong temperature dependence. Taking into account the Langmuir
rejection term, it is found that $H_2$ recombination is efficient at grain temperatures in the range $T_0 \leq T \leq T_1$ where (Biham & Lipshtat 2002)

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

(7)

and

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

(8)

The simulations presented in this paper are based on the parameters obtained experimentally for amorphous carbon, namely the activation energies are $E_0 = 44.0$ meV and $E_1 = 56.7$ meV (Katz et al. 1999), and the density of adsorption sites on the surface is $s \simeq 5 \times 10^{15}$ (cm$^{-2}$) (Biham et al. 2001). For simplicity, the sticking coefficient is assumed to be $\xi = 1$. The gas phase density is $n_H = 100$ (cm$^{-3}$) and its temperature is $T_g = 500$ K, thus $v_H = 3.24 \times 10^5$ (cm s$^{-1}$). Under these conditions one obtains that for amorphous carbon the range of grain temperatures in which $H_2$ formation is efficient is $12 \leq T \leq 16$ K.

3 THE ABUNDANCE OF $H_2$ IN PHOTON DOMINATED REGIONS

The temperatures of both the gas and dust grains in PDRs are significantly higher than in other H I regions. This is due to far ultraviolet radiation which penetrates the clouds, heats the gas through photon adsorption and the dust through photoelectric heating (Hollenbach & Tielens 1997). The temperatures of interstellar grains in several PDR environments, such as Chamaeleon, Oph W, S140, IC63, NGC2023 and the Orion Bar, were recently calculated (Habart et al. 2004). An analytic expression for the temperatures of large grains (Hollenbach et al. 1991) was used, and the median temperature of small grains was evaluated. It was found that in most of these regions the *average* temperatures of small grains are in the range of 10 - 30 K (though temperature fluctuations may heat them to temperatures higher than 100 K for very short durations), while the temperatures of large grains are between 30 - 50 K. Observations show that in all these PDRs, the rate constant of $H_2$ formation is $3 \cdot 10^{-17} \leq R \leq 1.5 \cdot 10^{-16}$ (cm$^3$ s$^{-1}$). This is a rather high formation rate, which is comparable with that obtained in colder, diffuse clouds. In order to achieve such rate, the recombination efficiency must be very high, namely $\eta \simeq 1$.

The process of $H_2$ formation on compact grains described above is not efficient at these high grain temperatures and cannot account for the observed abundance. This is because at these temperatures the residence time of H atoms on the grain is too short to enable them to
encounter each other and recombine. In order to explain the formation efficiency at higher temperatures it was suggested (Hollenbach & Salpeter 1971) that the grain surface contains enhanced adsorption sites with “semi-chemical binding” sites where atoms can stick much stronger to the surface. As a result they retain on the surface for a longer period, that enables more efficient recombination. It was suggested that these enhanced binding sites are chemical adsorption (chemisorption) sites. Their binding energies were calculated, mainly for carbonaceous dust materials (Bennet et al. 1971; Dovesi et al. 1976, 1981; Aronowitz & Chang 1985). However, recent theoretical and experimental results indicate that chemisorption sites play an important role only at much higher surface temperatures. Theoretical studies have shown that H atoms on graphite need to penetrate an energy barrier of $\approx 0.2$ eV in order to reach a chemisorption site on basal planes (Jeloaica & Sidis 1999; Sha & Jackson 2002; Sha et al. 2002). This result was confirmed experimentally when an activation energy barrier of 0.18 eV was found experimentally for hydrogen on C(0001) (Zecho, private communication). The gas temperatures prevalent in PDRs may enable H atoms from the gas phase to enter chemisorption sites upon collision with a grain. However, it is unlikely for atoms already adsorbed in physisorption sites (and thus equilibrated with the surface) to penetrate this barrier and hop into chemisorption sites.

Chemisorbed H atoms may reside in defect sites, in step edges (for which the energy barrier for penetration is negligible) or in basal plane sites. The recombination of these atoms takes place through two possible processes. In the LH process, a desorbing H atom picks another H atom from an adjacent site to form a molecule. In the Eley-Rideal (ER) mechanism, an atom from the gas phase abstracts an adsorbed atom to from a molecule. However, the ER mechanism is relevant only at high surface coverage, which is not likely to exist under interstellar conditions. The LH process occurs only at surface temperatures higher than 440 K for basal plane sites, and at even higher temperatures around 850 K for step edge and defect sites (Zecho et al. 2002a,b; Guttler et al. 2004; Zecho et al. 2004).

The relevance of these results to interstellar dust materials is thus not yet clear. If interstellar dust materials exhibit these features, it may indicate that in PDRs (where typical grain temperatures are between 30-50 K), chemisorption processes do not contribute significantly to $\text{H}_2$ formation on dust grain surfaces (Cazaux & Tielens 2004; Habart et al. 2004).
4 EVIDENCE FOR POROSITY IN INTERSTELLAR DUST GRAINS

The formation and evolution of interstellar dust grains are complex processes which involve accretion and chemical reactions of impinging atoms and molecules, grain-grain collision and coagulation, photolysis and alteration by UV starlight, X-rays and cosmic rays, erosion by sputtering and vaporization (Draine 2003). Due to the complexity of these processes, there is no complete model that accounts for all the relevant properties of interstellar dust grains. The known properties are based on a combination of astronomical observations, theoretical studies and analysis of meteorites and solar-system dust. Useful insight about the porosity of interstellar dust grains can be obtained from its effect on the observed extinction curves (Wright 1987; Jones 1988; Mathis 1996; Snow & Witt 1996; Fogel & Leung 1998; Wolff et al. 1998; Schnaiter et al. 1999; Vadia & Gupta 1999; Krivova & Il’in 2000; Wurm & Blum 2000; Iati et al. 2001). Interplanetary dust particles and meteorites, collected in the upper atmosphere of Earth (Brownlee 1985), were found to be fluffy and porous (Fig. 1). Although these particles are larger than the typical interstellar dust grains, it is likely that similar processes are responsible for their formation. Theoretical and experimental simulations of cosmic dust formation, through aggregation of molecular clusters, produce fluffy and porous structures with amorphous surface morphology.

In most calculations of grain temperatures in PDRs, it was assumed that grains are compact and can be considered as spherical. However, several studies considered the temperatures of non-spherical as well as porous grains (Greenberg & Sha 1971; Blanco & Bussoletti 1980; Voshchinnikov et al. 1999; Voshchinnikov et al. 2005). It was found that porous grains are significantly colder, in most cases, than predicted by models which use compact spherical grains. While models of spherical grains predict grain temperatures in the range of 30 – 50 K, the actual temperatures of porous interstellar grains may thus be significantly lower. In most favorable cases, the grain temperatures may go down to the range of 15 – 30 K for large grains and to 10 – 20 K for small grains (Blanco & Bussoletti 1980).

It was suggested long ago that micro-pores in interstellar dust grains may trap gas particles and affect the formation of molecules (Abadi et al. 1976). Recent experiment on ice surfaces at low temperatures (10–25 K) have shown that the porous morphology increases the desorption energy barriers of adsorbed hydrogen atoms and molecules (Pirronello et al. 1999; Manicò et al. 2001; Roser et al. 2002; Hornekaer et al. 2003, 2005; Perets et al. 2005; Viti et al. 2004; Collings et al. 2004). Analysis of some of these experiments shows that
on such surfaces H\textsubscript{2} would form efficiently only at low surface temperatures of up to 20 K (Perets et al. 2005), resembling the results obtained for olivine and carbon (Katz et al. 1999; Cazaux & Tielens 2004). In PDRs, the relevant grain surfaces are expected to consist of bare silicate and carbon, not covered by ice mantles. Below we examine the role of grain porosity in extending the efficiency range of H\textsubscript{2} formation toward higher temperatures.

5 H\textsubscript{2} FORMATION ON POROUS DUST GRAINS

To evaluate the formation of H\textsubscript{2} on porous grains we introduce a suitable rate equation model. In this model we make a distinction between the external surface of the grain and the internal surfaces within the pores. Atoms adsorbed on the external surface behave as in the previous models. They may hop between adjacent sites or desorb. In addition, they may enter the pores and slits in the surface. In the internal surfaces, similar diffusion and desorption processes apply. However, an atom which desorb from an internal surface, may re-adsorb inside the pore, rather than leave the grain. Such an atom may leave the grain only after it reaches the external surface, through a series of diffusion and desorption moves (Fig. 2). Detailed modeling of these processes requires knowledge on the exact geometry of the grains and their surface morphology. However, the most important effects of grain porosity can be analyzed by a simple rate equation model. The model, described below, assumes high connectivity of the pores, namely, that most of the internal surface of the grain is connected (Kimmel et al. 2001) and is treated as a single surface. The model thus consists of two coupled rate equations

\begin{align}
\dot{N}_{\text{ext}} &= F - \left( \frac{S_{\text{edge}}}{S_{\text{ext}}} \right) aN_{\text{ext}} + \left( \frac{S_{\text{edge}}}{S_{\text{in}}} \right) aN_{\text{in}} - 2 \left( \frac{a}{S_{\text{ext}}} \right) N_{\text{ext}}^2 - WN_{\text{ext}} \quad (9a) \\
\dot{N}_{\text{in}} &= \left( \frac{S_{\text{edge}}}{S_{\text{ext}}} \right) aN_{\text{ext}} - \left( \frac{S_{\text{edge}}}{S_{\text{in}}} \right) aN_{\text{in}} - 2 \left( \frac{a}{S_{\text{in}}} \right) N_{\text{in}}^2, \quad (9b)
\end{align}

where \(N_{\text{ext}}\) and \(N_{\text{in}}\) are the populations of H atoms on the external and internal surfaces, respectively. The first term in Eq. (9a) describes the incoming flux of H atoms. The second and third terms in Eq. (9a) [and the corresponding first and second terms in Eq. (5)] describe the diffusion of atoms between the external surface and the pores, where \(a\) is the hopping rate given by Eq. (5). The numbers of adsorption sites on the external and the internal surfaces of the grain are \(S_{\text{ext}}\) and \(S_{\text{in}}\), respectively. In addition, there is a small number, \(S_{\text{edge}}\), of sites, located at the edges of the pores, thus connecting the internal and
the external surfaces of the grain. An adsorbed atom moving between the internal and the external surfaces must pass through one of these edge sites. The fourth term in Eq. (9a) corresponds to recombination of atoms on the external surface. Similarly, the third term in Eq. (9a) corresponds to the recombination of atoms on the internal surface, inside the pores. The last term in Eq. (9a) describes the desorption of atoms into the gas phase, where \( W \) is the desorption rate given by Eq. (4).

To examine the effect of porosity on molecular hydrogen formation, we performed numerical integration of Eqs. (9) under steady state conditions for grains of diameter \( d = 10^{-5} \) (cm). The porosity was characterized by the ratio between the internal and external surfaces, \( S_{in}/S_{ext} \). The formation rate of molecular hydrogen per grain is given by

\[
R_{\text{grain}} = \left( \frac{a}{S_{ext}} \right) N_{ext}^2 + \left( \frac{a}{S_{in}} \right) N_{in}^2.
\] (10)

In Fig. 3 we show the recombination efficiency of molecular hydrogen on porous grains, vs. grain temperature, in the range between \( 10 - 35 \) K. Different levels of porosity are used, namely \( S_{in}/S_{ext} = 10, 100 \) and 1000. The results show that porosity in interstellar grains extends the temperature range of high efficiency toward higher temperatures. The extension of the temperature range is logarithmic with the level of porosity (Fig. 3).

The number of edge sites in the grain is given by \( S_{\text{edge}}/S_{ext} = 5 \cdot 10^{-2} \). We found that although the edge sites control the flow between the external and internal surfaces, the recombination efficiency is only weakly dependent on \( S_{\text{edge}} \). In particular, we performed simulation with \( S_{\text{edge}} \) values 10 times larger and smaller than the value reported above. In both cases, the edges of the high-efficiency window were only slightly shifted (not shown).

In Fig. 4 we show the number of H atoms on the internal and external surfaces (solid and dashed lines, respectively) vs. temperature, for a grain of diameter \( d = 10^{-5} \) (cm) where \( S_{in}/S_{ext} = 100 \). It is found that for the relevant temperatures there is a large population of H atoms in the pores, thus the rate equations are suitable for the calculations presented here. The inset in Fig. 4 shows the coverages of H atoms on the internal and on the external surfaces. Both coverages are very small. Since the desorption barrier of hydrogen molecules on the amorphous carbon surface is lower than the desorption barrier of atoms, the coverage of molecules is also expected to be small. This justifies the approximation made in this paper, ignoring the population of molecules on the surface and neglecting the LH rejection term.
6 DISCUSSION

The results presented above show that porosity extends the range of efficient hydrogen recombination to higher temperatures. This extension does not reach the grain temperatures of 30 - 50 K expected in PDRs and thus cannot, by itself, explain the high abundance of H$_2$ in these regions. However, porous grains, particularly small ones, are expected to be colder and thus may be within the extended temperature range of high efficiency.

The roughness of interstellar grain surfaces may broaden the distribution of binding energies compared to the experimental samples. Thus, some of the adsorbed H atoms may be more strongly bound, further extending the range of high efficiency towards higher temperatures (Cuppen & Herbst 2005). Composite grains, which consist of both silicates and carbon also exhibit a broader temperature window of high efficiency (Chang & Herbst 2005). Grains of diameters smaller than 10$^{-5}$ (cm) account for most of the surface area of grains in interstellar clouds and may thus contribute significantly to H$_2$ formation (Lipshtat & Biham 2005). Temperature fluctuations may also reduce the average temperature of small grains compared to large ones.

In addition to molecular hydrogen, dozens of other molecular species have been observed in interstellar clouds. Many of these molecules are formed through gas phase processes not involving dust grains. Others are formed on dust-grain surfaces. For example, certain organic molecules are believed to be formed on dust grains covered by ice mantles (Tielens & Charnley 1997). The effect of dust morphology on H$_2$ formation may indicate that it plays a role in other gas-grain processes. Moreover, our results may have implications on the formation of molecules which have been previously thought to be formed mainly by gas phase reactions. For example, recent observations of interstellar N$_2$ have indicated much higher abundances than predicted before (Knauth 2004). It was suggested that these abundances may be explained by gas-grain reactions that had not been considered earlier. An analysis of these processes on porous grains may help to understand this new puzzle.

7 SUMMARY

We have considered the effect of porosity on the formation of molecular hydrogen on interstellar dust grains. The analysis was done using a rate equation model, which takes into account both the internal and external surfaces of the grain. It was found that porosity gives rise to enhanced H$_2$ formation rates. It extends the range of high recombination effi-
ciency toward higher temperatures. This may contribute to the understanding of molecular hydrogen formation in PDRs, which cannot be explained by models of compact dust grains.

8 ACKNOWLEDGMENTS

We thank E. Herbst, G. Vidali and V. Pirronello for helpful discussions. This work was supported by the Israel Science Foundation and the Adler Foundation for Space Research.
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Figure 1. Interplanetary dust grain found in the stratosphere, which exhibits the typical porous structure, but at a much larger scale. The sizes of interplanetary dust grains range from several \( \mu m \) to 100 \( \mu m \). Acknowledgement is made to NASA for allowing reproduction of this picture from web site [http://stardust.jpl.nasa.gov](http://stardust.jpl.nasa.gov).
Figure 2. Schematic description of H diffusion and desorption in the internal and external surfaces of a porous dust grain.

Figure 3. H$_2$ recombination efficiency for non-porous grains (dashed line) and for porous grains (solid lines) with $S_{int}/S_{ext} = 10$, 100 and 1000. The more porous grains exhibit higher bounds for efficient recombination.
Figure 4. The number of H atoms on the internal (solid line) and the external (dashed line) surfaces of a porous grain with $S_{in}/S_{ext} = 100$ as a function of the grain temperature. Most of the H$_2$ molecules form on the internal surface. The inset shows the coverages of H atoms on the internal (solid line) and the external (dashed line) surfaces. These coverages turn out to be nearly identical.