

MOLECULAR HYDROGEN FORMATION IN THE INTERSTELLAR MEDIUM

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ABSTRACT

We have developed a model for molecular hydrogen formation under astrophysically relevant conditions. This model takes fully into account the presence of both physisorbed and chemisorbed sites on the surface, allows quantum mechanical diffusion as well as thermal hopping for absorbed H atoms, and has been benchmarked versus recent laboratory experiments on H₂ formation on silicate surfaces. The results show that H₂ formation on grain surfaces is efficient in the interstellar medium up to some 300 K. At low temperatures (≤ 100 K), H₂ formation is governed by the reaction of a physisorbed H with a chemisorbed H. At higher temperatures, H₂ formation proceeds through a reaction between two chemisorbed H atoms. We present simple analytical expressions for H₂ formation that can be adopted to a wide variety of surfaces once their surface characteristics have been determined experimentally.

Subject headings: dust, extinction — ISM: molecules — molecular processes

1. INTRODUCTION

Molecular hydrogen is the most abundant molecule in the universe and dominates the mass budget of gas in regions of star formation. H₂ is also an important chemical intermediate in the formation of larger species and can be an important gas coolant in some conditions, particularly in the early universe. Yet, despite its importance, the H₂ formation process is still not well understood. Observationally, it has been shown that H₂ can be efficiently formed over a wide range of temperatures (Jura 1974; Tielens & Hollenbach 1985a, 1985b; Hollenbach & McKee 1979). Theoretically, Gould & Salpeter (1963) showed the inefficiency of H₂ formation in the gas phase and concluded that the recombination of physisorbed H on “dirty” ice surfaces is efficient between 10 and 20 K. Hollenbach & Salpeter (1970, 1971), recognizing that this small temperature range presents a problem, considered reactions involving H atoms bound to dislocations and impurities, with energies exceeding normal physisorbed energies, and obtained a recombination efficiency of ≈ 1 up to a critical temperature between 25 and 50 K. Goodman (1978) calculated the quantum and thermal mobility of the atoms on graphite grains assuming that these atoms could only be physisorbed. Many studies focused for various reasons on icy surfaces where H is physisorbed (Buch & Zhang 1991; Takahashi, Masuda, & Nagaoka 1999). However, most astrophysically relevant material (e.g., silicates, graphite) can also bind H in chemisorbed sites (Barlow & Silk 1976; Aronowitz & Chang 1980; Leitch-Devlin & Williams 1984; Klose 1992; Fromherz, Mendoza, & Ruetten 1993). On these surfaces, binding can occur in a physisorption layer ($E \sim 500$ K) at a distance of some $Z \sim 3$ Å as well as in a chemisorption layer ($E \sim 10,000$ K) deeper into the surface ($Z \sim 0.5$ Å; Barlow & Silk 1976; Zangwill 1988). Recently, Katz et al. (1999) developed a model for H₂ formation benchmarked by two sets of experiments. This model considers the atoms bound only in physisorbed sites and diffusing only thermally on the surface, colliding and recombining to form molecules. As for the ice models studied earlier, this model allows molecule formation only below 15 K for olivine grains and only below 20 K for carbon grains, which contradicts the interstellar medium (ISM) observations. Perusing these models, it is clear that the process of H₂ formation is governed by the binding of atomic H to the surface and the concomitant mobility

of these atoms (Leitch-Devlin & Williams 1984; Tielens & Allamandola 1987). Surface diffusion can occur through quantum mechanical tunneling (at low temperatures) and through thermal hopping (at high temperatures). For a proper description of molecular hydrogen formation in the ISM, both types of binding diffusion processes have to be taken into account (Cazaux & Tielens 2002).

2. MODEL

Recently, we have developed a model for H₂ formation on grain surfaces based on Langmuir kinetics in which species accrete, migrate, and react and in which the product species, possibly assisted by thermal energy, evaporate. This model is based on two main points: (1) The atomic mobilities are due to a combination of quantum tunneling and thermal diffusion, and this is controlled by the temperature of the grain and the mass of the species; and (2) atoms can bind to the surface in two energetically different sites, a chemisorption site and a physisorption site. These interaction energies set the migration between the different sites and the reactions among the species. We have compared the results of our model with laboratory experiments on molecular hydrogen formation on olivine surfaces (Pirronello et al. 1999; Katz et al. 1999) to determine the relevant parameters. Here we extrapolate this model to study H₂ formation under astrophysically relevant conditions (e.g., low accretion rates and long timescales). We consider three different populations: physisorbed H, chemisorbed H, and physisorbed H₂. The surface concentrations of these species are described by three rate equations. Using the surface concentration of these species, the H₂ desorption rate, which contains two contributions, can be determined. First-order desorption occurs when the grain temperature is high enough to allow evaporation of previously formed molecules. Second-order desorption occurs when two atoms come together, and the newly formed molecule is directly released into the gas phase. We define H_p , H_c and H_2 as the physisorbed H, chemisorbed H, and molecular hydrogen concentrations, respectively; their evaporation rates are written as β_{H_p} , β_{H_c} , and β_{H_2} . The different mobilities that go from a site i to a site j are given by α_{ij} , where i and j are either a physisorbed site (P) or a chemisorbed site (C) and where the barrier between two sites is assumed to be square. However, the shape of the barrier is found to be

TABLE 1
MODEL PARAMETERS FOR SILICATE SURFACE

| Parameter | Value |
|--------------------------------------|----------------------|
| E_{H_2} (K) | 320 |
| μ | 0.005 |
| E_S (K) | 200 |
| E_{H_p} (K) | 600 |
| E_{H_c} (K) | 10000 |
| ν_{H_2} (s ⁻¹) | 3×10^{12} |
| ν_{H_c} (s ⁻¹) | 1.3×10^{13} |

NOTE.— E_{H_2} , E_{H_p} , and E_{H_c} are the desorption energies of H_2 , physisorbed H (H_p), and chemisorbed H (H_c), and E_S is the energy of the saddle point between a physisorbed and a chemisorbed site; μ is the fraction of the newly formed H_2 that stays on the surface, and ν_{H_2} and ν_{H_c} are the vibrational frequencies of H_2 and H in their surface sites. For more details about the determination and calculation of these parameters, see Cazaux & Tielens 2002.

unimportant (see below); μ is the fraction of H_2 that stays on the surface upon formation. The rate equation can then be written as (for details, see Cazaux & Tielens 2002)

$$\dot{H}_p = F(1 - H_p - H_2) - \alpha_{pc}H_p - 2\alpha_{pp}H_p^2 + \alpha_{cp}H_c(1 - H_p) - \beta_{H_p}H_p, \quad (1)$$

$$\dot{H}_c = \alpha_{pc}H_p(1 - H_c) - \alpha_{pc}H_pH_c - \alpha_{cp}H_c - 2\alpha_{cc}H_c^2\beta_{H_c}H_c, \quad (2)$$

$$\dot{H}_2 = \mu(2\alpha_{pp}H_p^2 + \alpha_{pc}H_pH_c + \alpha_{cp}H_cH_p + \alpha_{cc}H_c^2) - \beta_{H_2}H_2, \quad (3)$$

where F is the accretion rate in units of monolayers per second. The first-order H_2 desorption rate is given by

$$k_1 = \beta_{H_2}H_2. \quad (4)$$

For second-order desorption, several processes contribute, depending on whether physisorbed atoms, chemisorbed atoms, or both are involved:

$$k_2 = (1 - \mu)(\alpha_{pc}H_pH_c + \alpha_{cp}H_cH_p + \alpha_{pp}H_p^2 + \alpha_{cc}H_c^2); \quad (5)$$

β_i , the desorption rate for a population i , is written as $\beta_i = \nu_i \exp(-E_i/kT)$, where ν_i is the frequency factor of species i , perpendicular to the surface, and E_i is the desorption energy of species i . The total H_2 formation rate R is the sum of the first- and second-order terms, and the H_2 recombination efficiency—the fraction of the accreted hydrogen that desorbs as H_2 —is defined by $\epsilon = 2R/F$. The parameters in this model are summarized in Table 1. They have been discussed extensively elsewhere (see Cazaux & Tielens 2002). We have integrated this set of time-dependent equations using a Runge-Kutta method with adaptive step size control (“odeint,” a subroutine package from Press et al. 1992) until steady state was achieved. Under astrophysically relevant conditions, steady state is generally achieved. These steady state results are shown as a function of temperature T in Figure 1 for three different

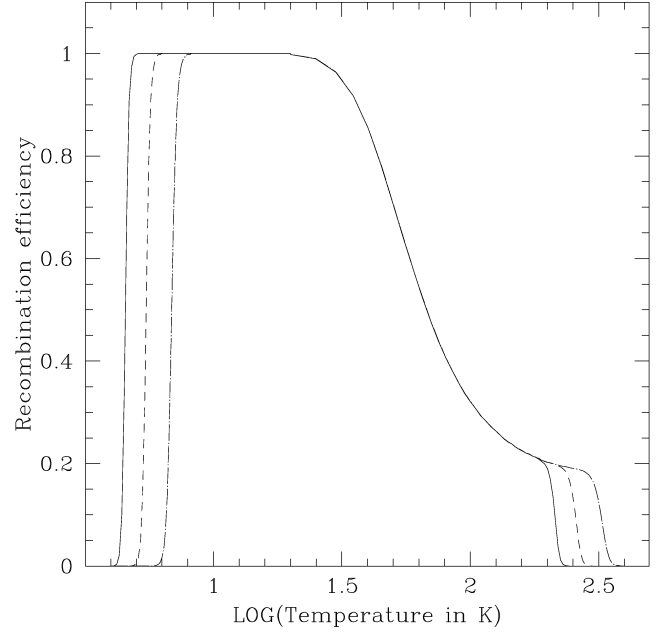


FIG. 1.— H_2 recombination efficiency for three different flux: 10^{-15} monolayers per second (solid curve), 10^{-10} monolayers per second (dashed curve), and 10^{-5} monolayers per second (dot-dashed curve).

H fluxes. All curves are characterized by a very low efficiency at low temperatures, a steep rise around ~ 5 K (whose location depends on the actual H flux), an efficiency of unity until some 25 K, followed by a gradual decline to ~ 0.2 at ~ 100 K, and a final drop to very low efficiency around 300 K (whose location again depends on the actual H accretion rate). In steady state, the system of equations (1)–(3) can be simplified by setting the time derivatives equal to zero. We can now discern two different temperatures regimes, low temperatures ($T \leq 100$ K) and high temperatures ($T \geq 100$ K), where different processes dominate H_2 formation. In these limits, the set of steady state equations can be further simplified, and this yields much insight in the numerical results.

2.1. Physisorbed H

By far, at low temperatures, the most efficient way to form H_2 is when a physisorbed atom reacts with a chemisorbed atom. Other routes toward H_2 formation as well as the evaporation of chemisorbed atoms are negligible. Realizing that H_p is always small compared with 1 (physisorbed H quickly migrate to a chemisorbed well), the steady state equations can be simplified to

$$F(1 - H_2) - \alpha_{pc}H_p - \beta_{H_p}H_p = 0, \quad (6)$$

$$\alpha_{pc}H_p(1 - 2H_c) = 0, \quad (7)$$

$$\mu(\alpha_{pc}H_pH_c) - \beta_{H_2}H_2 = 0. \quad (8)$$

The different populations can easily be determined in this system [e.g., $H_c = \frac{1}{2}$, $H_p = (\mu\alpha_{pc}/2\beta_{H_2} + \alpha_{pc}/F + \beta_{H_2}/F)^{-1}$ and $H_2 = (\mu\alpha_{pc}/2\beta_{H_2})H_p$]; the H_2 desorption rate is calculated,

and we deduce the recombination efficiency:

$$\epsilon_{\text{H}_2} = \left(\frac{\mu F}{2\beta_{\text{H}_2}} + 1 + \frac{\beta_{\text{H}_p}}{\alpha_{pc}} \right)^{-1}. \quad (9)$$

We can recognize three different regimes in this temperature range. At really low temperatures, below some 10 K, the high mobility of H atoms due to tunneling permits the recombination of incoming H atoms. The H_2 formed stays on the surface, since the temperature is not high enough to allow evaporation and blocks further H-atom accretion. Then, the recombination efficiency is $\epsilon_{\text{H}_2} = (\mu F / 2\beta_{\text{H}_2})^{-1}$. At higher temperatures (6–25 K), the desorption rate depends only on the flux because all the incoming H atoms adsorb, recombine, and desorb as H_2 . In this temperature regime, hydrogen accretes into a physisorbed site but quickly drops into a chemisorbed well. If this chemisorbed site is empty, the H atom will be trapped. If an H atom is already present, reaction will occur, and the product will evaporate quickly either upon formation or thermally assisted; thus, $\text{H}_c = \frac{1}{2}$ and $\epsilon_{\text{H}_2} = 1$. Between ~ 25 and ~ 100 K, evaporation of physisorbed atoms competes with recombination, and the desorption rate decreases considerably.

2.2. Chemisorbed H

With increasing temperature, the physisorbed (at $T \sim 100$ K) and then the chemisorbed atoms (at $T \sim 300$ K) will start to evaporate. The most efficient reaction to form H_2 is then the “collision” of two chemisorbed atoms. The system of equations reduces to

$$F - \alpha_{pc} \text{H}_p - \beta_{\text{H}_p} \text{H}_p = 0, \quad (10)$$

$$\alpha_{pc} \text{H}_p - 2\alpha_{cc} \text{H}_c^2 - \beta_{\text{H}_c} \text{H}_c = 0, \quad (11)$$

$$\mu(\alpha_{cc} \text{H}_c^2) - \beta_{\text{H}_2} \text{H}_2 = 0, \quad (12)$$

and the H_2 recombination efficiency can be written as

$$\epsilon = \left(1 + \frac{\beta_{\text{H}_p}}{\alpha_{pc}} \right)^{-1} \xi, \quad (13)$$

where ξ is the correction factor at high temperatures,

$$\xi = \left(1 + \frac{\beta_{\text{H}_c}^2 \beta_{\text{H}_p}}{2F\alpha_{pc}\alpha_{cc}} \right)^{-1}, \quad (14)$$

which reflects the evaporation of chemisorbed H. This factor is flux-dependent.

2.3. General Expression for the Recombination Efficiency

The above expression for the H_2 recombination efficiency can be combined into one general expression that is valid at any temperature:

$$\epsilon_{\text{H}_2} = \left(1 + \frac{\mu F}{2\beta_{\text{H}_2}} + \frac{\beta_{\text{H}_p}}{\alpha_{pc}} \right)^{-1} \xi. \quad (15)$$

The mobilities, α_{pc} and α_{cc} , are due to a combination of quantum mechanical tunneling and thermal hopping, but considering the

temperatures at which these parameters play a role, these mobilities are dominated by thermal hopping. Therefore, the H_2 recombination efficiency is independent of the width of the considered barriers, and we can approximate ξ and $\beta_{\text{H}_p}/\alpha_{pc}$ by the following expressions:

$$\xi = \left\{ 1 + \left[\nu_{\text{H}_c} \exp \left(\frac{1.5E_{\text{H}_c}}{kT} \right) \left(1 + \sqrt{\frac{E_{\text{H}_c} - E_s}{E_{\text{H}_p} - E_s}} \right)^2 \right] / (2F)^{-1} \right\}, \quad (16)$$

$$\frac{\beta_{\text{H}_p}}{\alpha_{pc}} = \frac{1}{4} \left(1 + \sqrt{\frac{E_{\text{H}_c} - E_s}{E_{\text{H}_p} - E_s}} \right)^2 \exp \left(-\frac{E_s}{kT} \right). \quad (17)$$

The parameters in these expressions have been determined from experimental data (Table 1; Cazaux & Tielens 2002). The H_2 recombination efficiency for the three different fluxes is reported in Figure 1. In astrophysical environments, the recombination rate is written as

$$R_{\text{H}_2} = \frac{1}{2} n_{\text{H}} v_{\text{H}} n_d \sigma_d \epsilon_{\text{H}_2} S_{\text{H}}(T), \quad (18)$$

where n_{H} and v_{H} are the number density and the thermal velocity of H atoms in the gas phase, respectively, $n_d \sigma_d$ is the total cross section of the interstellar grains, and $S_{\text{H}}(T)$ is the sticking coefficient of the H atoms, which can depend on temperature.

3. DISCUSSION

Our study reveals the presence of two distinct regimes of H_2 formation, which reflect directly the presence of two types of atomic H-binding sites. At low temperature ($T \leq 100$ K), H_2 formation involves the migration of physisorbed H atoms. At higher temperatures ($T \geq 100$ K), H_2 formation results from chemisorbed H recombination. The presence of these two types of binding sites allows H_2 formation to proceed relatively efficiently even at elevated temperatures. The study of Hollenbach & Salpeter (1971) focused on icy surfaces on which H can only physisorb. As a result, H_2 formation ceased at temperatures in excess of ~ 20 K. Recognizing this problem, Hollenbach & Salpeter added the presence of enhanced binding sites on the ice with ill-determined parameters. These sites allowed H_2 formation to proceed up to some 75 K. Since their study, it has become abundantly clear that interstellar grains are not covered by ice in the diffuse ISM (Whittet et al. 1983, 1988). Silicate and graphitic surfaces are now widely accepted as astrophysically relevant grain surfaces (Mathis & Lee 1991), and those surfaces intrinsically possess enhanced binding sites (e.g., chemisorbed sites). The parameters of these chemisorbed sites have not yet been well determined because experiments have focused on low-temperature H_2 formation (Pirronello et al. 1997a, 1997b; Katz et al. 1999). The values adopted in this study, however, are quite reasonable and illustrate well the efficiency of H_2 formation at elevated temperatures. When future experiments determine the values of the parameters involved (E_{H_c} , E_{H_p} , and μ), the results can be directly adjusted. Inside dense clouds, interstellar grains are covered by ice. Of course, in such environments, almost all hydrogen is already in molecular form, and H_2 formation is perhaps only of academic interest. Nevertheless, we note that in such environ-

ments, molecular hydrogen formation may proceed mainly through H abstraction from molecules such as H_2S and N_2H_2 (Tielens & Hagen 1982). In a sense, these species act as “chemisorption” sites for hydrogen. Migrating atomic H may tunnel through the reaction barriers involved and form H_2 . Eventually, these ice-covered grains are transported back into the diffuse ISM, when the molecular cloud is disrupted. Photodesorption and sputtering in strong shocks quickly remove their ice on a timescale of some 10^6 yr (Tielens & Hagen 1982; Jones et al. 1994; Draine & Salpeter 1979; Barlow 1978). At that point, molecular hydrogen formation is again governed by the properties of bare grain surfaces. Similarly, any (thin) layer accreted in the diffuse ISM will be quickly sputtered in even a modest velocity ($\sim 30 \text{ km s}^{-1}$) shock (Jones et al. 1994). Finally, the formation efficiency of molecular hydrogen will also depend on the sticking coefficient of H atoms colliding with the grain. In our model and the formulae derived, the sticking coefficient is subsumed in the incident flux, F . Astrophysical studies of the sticking of H on grain surfaces have concentrated on physisorbed interactions, and the sticking coefficient is ~ 1 at low temperatures and decreases with increasing temperature to about 0.3 at $T = 300 \text{ K}$ (Hollenbach & Salpeter 1970; Hollenbach & McKee 1979; Burke & Hollenbach 1983; Leitch-Devlin & Williams 1985). However, if the interaction occurs through much stronger chemisorption, then the sticking coefficient might be large even at high temperatures (Tielens & Allamandola 1987; Duley & Williams 1984).

3.1. Summary and Conclusions

Recently, we have modeled molecular hydrogen formation on grain surfaces. This model considers hydrogen atoms bound to the surface at two energy levels (i.e., chemisorption and physisorption). The H mobility from one site to another is a combination of tunneling effect and thermal diffusion. This model has been experimentally benchmarked (Pirronello et al. 1997a, 1997b, 1999), and the relevant surface characteristics have been determined. These characteristics allow us to extend our model for H_2 formation under astrophysically relevant conditions. The results show efficient H_2 formation from ~ 6 to $\sim 300 \text{ K}$. The different processes involved in H_2 formation at different temperatures have been discussed. Until about 100 K , H_2 forms by recombination of a physisorbed H with a chemisorbed H and is highly efficient. At higher temperatures, when physisorbed atoms evaporate quickly, the recombination of two chemisorbed atoms is required to form H_2 . H_2 formation is then less efficient, $\epsilon_{\text{H}_2} \sim 0.2$. The parameters involved in H chemisorption and H_2 formation at high temperatures are presently not well known. The adopted values are very reasonable, and the gross characteristic— H_2 formation at high temperatures—is undoubtedly correct. Nevertheless, future experiments are very important to determine the maximum temperature to which H_2 formation in the ISM can occur.

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