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# Master Equation for Hydrogen Recombination on Grain Surfaces

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## ABSTRACT

Recent experimental results on the formation of molecular hydrogen on astrophysically relevant surfaces under conditions similar to those encountered in the interstellar medium provided useful quantitative information about these processes. Rate equation analysis of experiments on olivine and amorphous carbon surfaces provided the activation energy barriers for the diffusion and desorption processes relevant to hydrogen recombination on these surfaces. However, the suitability of rate equations for the simulation of hydrogen recombination on interstellar grains, where there might be very few atoms on a grain at any given time, has been questioned. To resolve this problem, we introduce a master equation that takes into account both the discrete nature of the H atoms and the fluctuations in the number of atoms on a grain. The hydrogen recombination rate on microscopic grains, as a function of grain size and temperature, is then calculated using the master equation. The results are compared to those obtained from the rate equations and the conditions under which the master equation is required are identified.

*Subject headings:* dust—ISM; abundances — ISM; molecules — molecular processes

## 1. Introduction

The formation of molecular hydrogen in the interstellar medium (ISM) is a process of fundamental importance (Duley & Williams 1984; Williams 1998). It was recognized long ago (Gould & Salpeter 1963) that  $H_2$  cannot form in the gas phase efficiently enough to account for its abundance. It was thus proposed that dust grains act as catalysts, where an H atom approaching the surface of a grain has a probability  $\xi$  to become adsorbed. The adsorbed H atom (adatom) spends an average time  $t_H$  (residence time) before leaving the surface. If during the residence time the H adatom encounters another H adatom, an  $H_2$  molecule will form with a certain probability. Various aspects of this process were addressed in extensive theoretical studies (Gould & Salpeter

1963; Williams 1968; Hollenbach & Salpeter 1970, 1971; Hollenbach et al. 1971; Smoluchowski 1981, 1983; Aronowitz & Chang 1985; Duley & Williams 1986; Pirronello & Aversa 1988; Sandford & Allamandola 1993; Takahashi et al. 1999; Farebrother et al. 1999). In particular, Hollenbach et al. calculated the sticking and mobility of H atoms on grain surfaces. They concluded that tunneling between adsorption sites, even at temperature as low as  $T = 10\text{K}$ , provides the required mobility. The steady state production rate of molecular hydrogen per unit volume was expressed according to (Hollenbach et al. 1971)

$$\mathcal{R}_{\text{H}_2} = \frac{1}{2}\rho_{\text{H}}v_{\text{H}}\sigma\gamma\rho_{\text{g}}, \quad (1)$$

where  $\rho_{\text{H}}$  and  $v_{\text{H}}$  are the number density and the speed of H atoms in the gas phase, respectively,  $\sigma$  is the average cross-sectional area of a grain and  $\rho_{\text{g}}$  is the number density of dust grains. The parameter  $\gamma$  is the fraction of H atoms striking the grain that eventually form a molecule, namely  $\gamma = \xi\eta$ , where  $\eta$  is the probability that an H adatom on the surface will recombine with another H atom to form  $\text{H}_2$ .

Recently, a series of experiments were conducted to measure hydrogen recombination in an ultra high-vacuum (UHV) chamber by irradiating the sample with two beams of H and D atoms and monitoring the HD production rate (Pirronello et al. 1997a,b, 1999). Two different substrates have been used: a natural olivine (a polycrystalline silicate containing  $\text{Mg}_2\text{SiO}_4$  and  $\text{Fe}_2\text{SiO}_4$ ) slab and an amorphous carbon sample. The substrate temperatures during hydrogen irradiation were in the range between 5 K and 15 K. The HD formation rate was measured using a quadrupole mass spectrometer both during irradiation and in a subsequent temperature programmed desorption (TPD) experiment in which the sample temperature was quickly ramped to over 30 K to desorb all weakly adsorbed species. It was found that H and D atoms adsorbed on the surface at the lowest irradiation temperature of 5 K form molecules during TPD only above 9 K in the case of olivine and above 14 K in the case of amorphous carbon. This indicates that tunneling alone does not provide enough mobility to H adatoms to enable recombination, and thermal activation is required. The experimental results were analyzed using a rate equation model (Katz et al. 1999). In this analysis the parameters of the rate equations were fitted to the experimental TPD curves. These parameters are the activation energy barriers for atomic hydrogen diffusion and desorption, the barrier for molecular hydrogen desorption and the probability of spontaneous desorption of a hydrogen molecule upon recombination. Using the values of the parameters that fit best the experimental results, the efficiency of hydrogen recombination on the olivine and amorphous carbon surfaces was calculated for interstellar conditions using the same rate equation model. It was found that for both samples the recombination efficiency is strongly dependent on temperature and exhibits a narrow window of high recombination efficiency along the temperature axis.

It was recently pointed out that since hydrogen recombination in the interstellar space takes place on small grains, rate equations have a limited range of validity (Tielens 1995; Charnley et al. 1997; Caselli et al. 1998; Shalabiea et al. 1998). This is due to the fact that these equations take into account only average concentrations and ignore fluctuations as well as the discrete nature of the H atoms. These properties become significant in the limit of very small grains and low incoming flux of H atoms, exactly the conditions encountered in diffuse interstellar clouds where hydrogen recombination on silicate and carbon surfaces is expected to be relevant. As the number of H atoms on a grain fluctuates in the range of 0, 1 or 2, the recombination 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. Comparisons with Monte Carlo simulations have shown that the rate equations tend to over-estimate the recombination rate. A modified set of rate equations which exhibits better agreement with Monte Carlo simulations was introduced by Caselli et al. (1998) and applied by Shalabiea et al. (1998) to a variety of chemical reactions. In these equations the rate coefficients are modified in a semi-empirical way to take into account the effect of the finite grain size on the recombination process.

In this paper we introduce a master equation that is particularly suitable for the simulation of chemical reactions on microscopic grains. It takes into account both the discrete nature of the H atoms as well as the fluctuations. Its dynamical variables are the probabilities  $P_{\text{H}}(N_{\text{H}})$  that there are  $N_{\text{H}}$  atoms on the grain at time  $t$ . The time derivatives  $\dot{P}_{\text{H}}(N_{\text{H}})$ ,  $N_{\text{H}} = 0, 1, 2, \dots$  are expressed in terms of the adsorption, reaction and desorption terms. The master equation provides the time evolution of  $P_{\text{H}}(N_{\text{H}})$ ,  $N_{\text{H}} = 0, 1, 2, \dots$ , from which the recombination rate can be calculated. We use it in conjunction with the surface parameters obtained experimentally, to explore the hydrogen recombination process on microscopic grains for grain sizes, flux and surface temperatures pertinent to the conditions in the interstellar medium.

The paper is organized as follows. The rate equation model is described in Sec. 2. The master equation is introduced in Sec. 3. Computer simulations and results for hydrogen recombination on microscopic grains under interstellar conditions are presented in Sec. 4. The case of more complex reactions involving multiple species is considered in Sec. 5 and a summary in Sec. 6.

## 2. Rate Equations for H<sub>2</sub> Formation on Macroscopic Surfaces

Consider an experiment in which a flux of H atoms is irradiated on the surface. If the temperature is not too low H atoms that stick to the surface perform hops as random walkers and recombine when they encounter one another. Let  $n_{\text{H}}(t)$  (in monolayers [ML]) be the coverage of H atoms on the surface and  $n_{\text{H}_2}(t)$  (also in ML) the coverage of H<sub>2</sub> molecules at time  $t$ . We obtain the following set of rate equations:

$$\frac{dn_{\text{H}}}{dt} = f_{\text{H}} \cdot (1 - n_{\text{H}} - n_{\text{H}_2}) - W_{\text{H}}n_{\text{H}} - 2a_{\text{H}}n_{\text{H}}^2 \quad (2a)$$

$$\frac{dn_{\text{H}_2}}{dt} = \mu a_{\text{H}}n_{\text{H}}^2 - W_{\text{H}_2}n_{\text{H}_2}. \quad (2b)$$

The first term on the right hand side of Eq. (2a) represents the flux of H atoms multiplied by the Langmuir-Hinshelwood rejection term. In this scheme H atoms deposited on top of H atoms or H<sub>2</sub> molecules already on the surface are rejected. The parameter  $f_{\text{H}}$  represents the *effective* flux of atoms (in units of  $MLs^{-1}$ ), namely, the (temperature dependent) sticking coefficient  $\xi(T)$  of the bare surface is absorbed into  $f_{\text{H}}$ . The second term in Eq. (2a) represents the desorption of H atoms from the surface. The desorption coefficient is

$$W_{\text{H}} = \nu \cdot \exp(-E_1/k_B T) \quad (3)$$

where  $\nu$  is the attempt rate (standardly taken to be  $10^{12} \text{ s}^{-1}$ ),  $E_1$  is the activation energy barrier for desorption of an H atom and  $T$  is the temperature. The third term in Eq. (2a) accounts for the depletion of the H population on the surface due to recombination into H<sub>2</sub> molecules, where

$$a_{\text{H}} = \nu \cdot \exp(-E_0/k_B T) \quad (4)$$

is the hopping rate of H atoms on the surface and  $E_0$  is the activation energy barrier for H diffusion. Here we assume that diffusion occurs only by thermal hopping, in agreement with recent experimental results (Katz et al. 1999). We also assume that there is no barrier for recombination. The first term on the right hand side of Eq. (2b) represents the creation of  $H_2$  molecules. The factor 2 in the third term of Eq. (2a) does not appear here since it takes two H atoms to form one molecule. The parameter  $\mu$  represents the fraction of  $H_2$  molecules that remains on the surface upon formation, while a fraction of  $(1 - \mu)$  is spontaneously desorbed due to the excess energy released in the recombination process. The second term in Eq. (2b) describes the desorption of  $H_2$  molecules. The desorption coefficient is

$$W_{H_2} = \nu \cdot \exp(-E_2/k_B T), \quad (5)$$

where  $E_2$  is the activation energy barrier for  $H_2$  desorption. The  $H_2$  production rate  $r_{H_2}$  ( $ML\ s^{-1}$ ) is given by:

$$r_{H_2} = (1 - \mu) \cdot a_H n_H^2 + W_{H_2} n_{H_2}. \quad (6)$$

This model can be considered as a generalization of the Polanyi-Wigner equation [see e.g. Chan et al. (1978)]. It provides a description of both first order and second order desorption kinetics for different regimes of temperature and flux.

The model described by Eqs. (2) was used by Katz et al. (1999) to analyze the results of the TPD experiments (Pirronello et al. 1997a,b, 1999). The values of the parameters  $E_0$ ,  $E_1$ ,  $E_2$ , and  $\mu$ , that best fit the experimental results were obtained. For the olivine sample it was found that  $E_0 = 24.7$  meV,  $E_1 = 32.1$  meV,  $E_2 = 27.1$  meV and  $\mu = 0.33$ , while for the amorphous carbon sample  $E_0 = 44.0$  meV,  $E_1 = 56.7$  meV,  $E_2 = 46.7$  meV and  $\mu = 0.413$ .

The model [Eqs. (2)] was then used in order to describe the steady state conditions that are reached when both the flux and the temperature are fixed. The steady state solution is then easily obtained by setting  $dn_H/dt = 0$  and  $dn_{H_2}/dt = 0$  and solving the quadratic equation for  $n_H$  (Biham et al. 1998; Katz et al. 1999). In case that the Langmuir-Hinshelwood rejection term can be neglected, the steady-state coverages are

$$n_H = \frac{-W_H + \sqrt{W_H^2 + 8a_H f_H}}{4a_H} \quad (7a)$$

$$n_{H_2} = \frac{\mu}{8a_H W_{H_2}} \left( W_H^2 + 4a_H f_H - W_H \sqrt{W_H^2 + 8a_H f_H} \right). \quad (7b)$$

More complicated expressions are obtained when the rejection term is taken into account (Katz et al. 1999). The recombination efficiency  $\eta$  is defined as the fraction of the adsorbed H atoms that desorb in the form of  $H_2$  molecules, namely

$$\eta = \frac{r_{H_2}}{f_H/2}. \quad (8)$$

Note that under steady state conditions  $\eta$  is limited to the range  $0 \leq \eta \leq 1$ .

By varying the temperature and flux over the astrophysically relevant range the domain in which there is non-negligible recombination efficiency was identified. It was found that the recombination efficiency is highly temperature dependent. For each of the two samples there is a narrow window of high efficiency along the temperature axis, which shifts to higher temperatures as the

flux is increased. For the astrophysically relevant flux range the high efficiency temperature range for olivine was found to be between 7 – 9K, while for amorphous carbon it is between 12 – 16 K.

Note that in steady state the dependence of the production rate  $r_{\text{H}_2}$  on  $\mu$  and  $W_{\text{H}_2}$  is only through the Langmuir-Hinshelwood rejection term. This is easy to understand since the parameter  $\mu$  only determines what fraction of the  $\text{H}_2$  will desorb upon formation and what fraction will desorb thermally at a later time. The desorption rate  $W_{\text{H}_2}$  determines the coverage of  $\text{H}_2$  molecules at steady state. As long as the coverage of H and  $\text{H}_2$  is low, the Langmuir-Hinshelwood rejection term is small and  $\mu$  and  $W_{\text{H}_2}$  have little effect on the production rate  $r_{\text{H}_2}$ . Under interstellar conditions the coverage is expected to be low. Therefore, the master equation presented below, that is required only when the number of atoms on the grain is small, does not include the rejection term. Note, however, that at lower temperatures in which H atoms are immobile (thus recombination and desorption are suppressed) they may accumulate on the surface and reach a high coverage.

### 3. Master Equation for $\text{H}_2$ Formation on Small Grains

We will now consider the formation of  $\text{H}_2$  molecules on small dust grains in interstellar clouds. In this case it is more convenient to rescale our parameters such that instead of using quantities per unit area - the total amount per grain will be used. The number of H atoms on the grain is denoted by  $N_{\text{H}}$ . Its expectation value is given by  $\langle N_{\text{H}} \rangle = S \cdot n_{\text{H}}$  where  $S$  is the number of adsorption sites on the grain. Similarly, the number of  $\text{H}_2$  molecules on the grain is  $N_{\text{H}_2}$  and its expectation value is  $\langle N_{\text{H}_2} \rangle = S \cdot n_{\text{H}_2}$  (we assume that each adsorption site can adsorb either an H atoms or an  $\text{H}_2$  molecule). The incoming flux of H atoms onto the grain surface is given by  $F_{\text{H}} = S \cdot f_{\text{H}}$  (atoms  $\text{s}^{-1}$ ). The desorption rates  $W_{\text{H}}$  and  $W_{\text{H}_2}$  remain unchanged. The hopping rate  $a_{\text{H}}$  (hops  $\text{s}^{-1}$ ) is replaced by  $A_{\text{H}} = a_{\text{H}}/S$  which is approximately the inverse of the time  $t_{\text{s}}$  required for an atom to visit nearly all the adsorption sites on the grain surface. This is due to the fact that in two dimensions the number of distinct sites visited by a random walker is linearly proportional to the number of steps, up to a logarithmic correction (Montroll & Weiss 1965). The  $\text{H}_2$  production rate of the single grain is given by  $R_{\text{H}_2} = S \cdot r_{\text{H}_2}$  (molecules  $\text{s}^{-1}$ ). The rate equations (neglecting the Langmuir-Hinshelwood rejection term) will thus take the form

$$\frac{d\langle N_{\text{H}} \rangle}{dt} = F_{\text{H}} - W_{\text{H}}\langle N_{\text{H}} \rangle - 2A_{\text{H}}\langle N_{\text{H}} \rangle^2 \quad (9a)$$

$$\frac{d\langle N_{\text{H}_2} \rangle}{dt} = F_{\text{H}_2} + \mu A_{\text{H}}\langle N_{\text{H}} \rangle^2 - W_{\text{H}_2}\langle N_{\text{H}_2} \rangle, \quad (9b)$$

where the first term in (9b) accounts for the flux of hydrogen molecules from the gas phase that are adsorbed on the grain surface. While for large grains Eqs. (9) provide a good description of the recombination processes, in the limit in which the number of atoms on the grain becomes small they are not suitable anymore.

In order to resolve this problem we will now introduce a different approach based on a master equation that is suitable for the study of  $\text{H}_2$  formation on small grains. Each grain is exposed to a flux  $F_{\text{H}}$  of H atoms. At any given time the number of H atoms adsorbed on the grain may be  $N_{\text{H}} = 0, 1, 2, \dots$ . The probability that there are  $N_{\text{H}}$  hydrogen atoms on the grain is given

by  $P_{\text{H}}(N_{\text{H}})$ , where

$$\sum_{N_{\text{H}}=0}^{\infty} P_{\text{H}}(N_{\text{H}}) = 1. \quad (10)$$

The time derivatives of these probabilities,  $\dot{P}_{\text{H}}(N_{\text{H}})$ , are given by

$$\begin{aligned} \dot{P}_{\text{H}}(0) &= -F_{\text{H}}P_{\text{H}}(0) + W_{\text{H}}P_{\text{H}}(1) + 2 \cdot 1 \cdot A_{\text{H}}P_{\text{H}}(2) \\ \dot{P}_{\text{H}}(1) &= F_{\text{H}}[P_{\text{H}}(0) - P_{\text{H}}(1)] + W_{\text{H}}[2P_{\text{H}}(2) - P_{\text{H}}(1)] + 3 \cdot 2 \cdot A_{\text{H}}P_{\text{H}}(3) \\ \dot{P}_{\text{H}}(2) &= F_{\text{H}}[P_{\text{H}}(1) - P_{\text{H}}(2)] + W_{\text{H}}[3P_{\text{H}}(3) - 2P_{\text{H}}(2)] \\ &\quad + A_{\text{H}}[4 \cdot 3 \cdot P_{\text{H}}(4) - 2 \cdot 1 \cdot P_{\text{H}}(2)] \\ &\quad \vdots \\ \dot{P}_{\text{H}}(N_{\text{H}}) &= F_{\text{H}}[P_{\text{H}}(N_{\text{H}} - 1) - P_{\text{H}}(N_{\text{H}})] + W_{\text{H}}[(N_{\text{H}} + 1)P_{\text{H}}(N_{\text{H}} + 1) - N_{\text{H}}P_{\text{H}}(N_{\text{H}})] \\ &\quad + A_{\text{H}}[(N_{\text{H}} + 2)(N_{\text{H}} + 1)P_{\text{H}}(N_{\text{H}} + 2) - N_{\text{H}}(N_{\text{H}} - 1)P_{\text{H}}(N_{\text{H}})]. \quad (11) \\ &\quad \vdots \end{aligned}$$

Each of these equations includes three terms. The first term describes the effect of the incoming flux  $F_{\text{H}}$  on the probabilities. The probability  $P_{\text{H}}(N_{\text{H}})$  increases when an H atom is adsorbed on a grain that already has  $N_{\text{H}} - 1$  adsorbed atoms [at a rate of  $F_{\text{H}}P_{\text{H}}(N_{\text{H}} - 1)$ ], and decreases when a new atom is adsorbed on a grain with  $N_{\text{H}}$  atoms on it [at a rate of  $F_{\text{H}}P_{\text{H}}(N_{\text{H}})$ ]. The second term includes the effect of desorption. An H atom desorbed from a grain with  $N_{\text{H}}$  adsorbed atoms decreases the probability  $P_{\text{H}}(N_{\text{H}})$  [at a rate of  $N_{\text{H}}W_{\text{H}}P_{\text{H}}(N_{\text{H}})$ , where the factor  $N_{\text{H}}$  is due to the fact that each of the  $N_{\text{H}}$  atoms can desorb] and increases the probability  $P_{\text{H}}(N_{\text{H}} - 1)$  at the same rate. The third term describes the effect of recombination on the number of adsorbed H atoms. The production of one molecule reduces this number from  $N_{\text{H}}$  to  $N_{\text{H}} - 2$ . For one pair of H atoms the recombination rate is proportional to the sweeping rate  $A_{\text{H}}$  multiplied by 2 since both atoms are mobile simultaneously. This rate is multiplied by the number of possible pairs of atoms, namely  $N_{\text{H}}(N_{\text{H}} - 1)/2$ . Note that the equations for  $\dot{P}_{\text{H}}(0)$  and  $\dot{P}_{\text{H}}(1)$  do not include all the terms, because at least one H atom is required for desorption to occur and at least two for recombination. The rate of formation of  $\text{H}_2$  molecules,  $R_{\text{H}_2}$  (molecules  $\text{s}^{-1}$ ), is thus given by

$$R_{\text{H}_2} = A_{\text{H}} \sum_{N_{\text{H}}=2}^{\infty} N_{\text{H}}(N_{\text{H}} - 1)P_{\text{H}}(N_{\text{H}}). \quad (12)$$

Note that the sum could start from  $N_{\text{H}} = 0$  since the first two terms vanish. The recombination efficiency is given by

$$\eta = \frac{R_{\text{H}_2}}{(F_{\text{H}}/2)}. \quad (13)$$

The probability that there are  $N_{\text{H}_2}$  hydrogen molecules on the grain is given by  $P_{\text{H}_2}(N_{\text{H}_2})$ . The time evolution of these probabilities is given by

$$\begin{aligned} \dot{P}_{\text{H}_2}(0) &= -F_{\text{H}_2}P_{\text{H}_2}(0) + W_{\text{H}_2}P_{\text{H}_2}(1) - \mu R_{\text{H}_2}P_{\text{H}_2}(0) \\ \dot{P}_{\text{H}_2}(1) &= F_{\text{H}_2}[P_{\text{H}_2}(0) - P_{\text{H}_2}(1)] + W_{\text{H}_2}[2P_{\text{H}_2}(2) - P_{\text{H}_2}(1)] + \mu R_{\text{H}_2}[P_{\text{H}_2}(0) - P_{\text{H}_2}(1)] \\ \dot{P}_{\text{H}_2}(2) &= F_{\text{H}_2}[P_{\text{H}_2}(1) - P_{\text{H}_2}(2)] + W_{\text{H}_2}[3P_{\text{H}_2}(3) - 2P_{\text{H}_2}(2)] + \mu R_{\text{H}_2}[P_{\text{H}_2}(1) - P_{\text{H}_2}(2)] \\ &\quad \vdots \end{aligned}$$

$$\begin{aligned}
 \dot{P}_{\text{H}_2}(N_{\text{H}_2}) &= F_{\text{H}_2} [P_{\text{H}_2}(N_{\text{H}_2} - 1) - P_{\text{H}_2}(N_{\text{H}_2})] + W_{\text{H}_2} [(N_{\text{H}_2} + 1)P_{\text{H}_2}(N_{\text{H}_2} + 1) - N_{\text{H}_2}P_{\text{H}_2}(N_{\text{H}_2})] \\
 &+ \mu R_{\text{H}_2} [P_{\text{H}_2}(N_{\text{H}_2} - 1) - P_{\text{H}_2}(N_{\text{H}_2})] \\
 &\vdots
 \end{aligned} \tag{14}$$

where  $F_{\text{H}_2}$  (molecules  $\text{s}^{-1}$ ) is the flux of  $\text{H}_2$  molecules that stick on the grain surface,  $W_{\text{H}_2}$  is the desorption rate of molecules from the surface (which is inversely proportional to their residence time, namely  $t_{\text{H}_2} = 1/W_{\text{H}_2}$ ). Each of these equations includes three terms, describing the effects of an incoming  $\text{H}_2$  flux, desorption and recombination, respectively.

Note that the fact that we ignored the Langmuir-Hinshelwood rejection term allowed us to split the master equation into two parts: Eq. (11) for the H atoms and Eq. (14) for the  $\text{H}_2$  molecules. Moreover, Eq. (11) does not depend on the distribution of  $N_{\text{H}_2}$ , while Eq. (14) depends only on the first and second moments of the distribution of  $N_{\text{H}}$ . The most general case, in which the rejection term is included, would require to use a master equation for the joint probability distribution  $P_{\text{H}\&\text{H}_2}(N_{\text{H}}, N_{\text{H}_2})$ , which is clearly much more complicated.

The expectation value for the number of H atoms on the grain is

$$\langle N_{\text{H}} \rangle = \sum_{N_{\text{H}}=0}^{\infty} N_{\text{H}} P_{\text{H}}(N_{\text{H}}) \tag{15}$$

and the expectation value for the number of molecules is

$$\langle N_{\text{H}_2} \rangle = \sum_{N_{\text{H}_2}=0}^{\infty} N_{\text{H}_2} P_{\text{H}_2}(N_{\text{H}_2}). \tag{16}$$

The time dependence of these expectation values, obtained from Eqs. (11) and (14), is given by

$$\frac{d\langle N_{\text{H}} \rangle}{dt} = F_{\text{H}} - W_{\text{H}} \langle N_{\text{H}} \rangle - 2A_{\text{H}} \langle N_{\text{H}}(N_{\text{H}} - 1) \rangle \tag{17}$$

$$\frac{d\langle N_{\text{H}_2} \rangle}{dt} = F_{\text{H}_2} + \mu A_{\text{H}} \langle N_{\text{H}}(N_{\text{H}} - 1) \rangle - W_{\text{H}_2} \langle N_{\text{H}_2} \rangle, \tag{18}$$

and the recombination rate  $R_{\text{H}_2}$  (molecules  $\text{s}^{-1}$ ) for the grain is

$$R_{\text{H}_2} = (1 - \mu) A_{\text{H}} \langle N_{\text{H}}(N_{\text{H}} - 1) \rangle + W_{\text{H}_2} \langle N_{\text{H}_2} \rangle. \tag{19}$$

These equations resemble the rate equations (9) apart from one important difference: the recombination term  $\langle N_{\text{H}}^2 \rangle$  is replaced by  $\langle N_{\text{H}}^2 \rangle - \langle N_{\text{H}} \rangle$ . On a macroscopically large grain it is expected that the difference between these two terms will be small and Eqs. (9) would provide a good description of the system. However, on a small grain, where  $\langle N_{\text{H}} \rangle$  is small these two terms are significantly different and it is necessary to use the master equation rather than the rate equations.

In principle the master equation consists of infinitely many equations for each atomic or molecular specie. In practice, for each specie such as atomic hydrogen we simulate a finite number of equations for  $P_{\text{H}}(N_{\text{H}})$ ,  $N_{\text{H}} = 1, \dots, N_{\text{max}}$ , where  $P_{\text{H}}(N_{\text{H}}) = 0$  for  $N_{\text{H}} > N_{\text{max}}$ . Obviously,  $N_{\text{max}}$  cannot exceed the number of adsorption sites,  $S$ , on the grain. In the equations for  $P_{\text{H}}(N_{\text{max}} - 1)$  and for  $P_{\text{H}}(N_{\text{max}})$ , the terms that couple them to  $P_{\text{H}}(N_{\text{max}} + 1)$  and  $P_{\text{H}}(N_{\text{max}} + 2)$  are removed (these terms describe the flow of probability from  $P_{\text{H}}(N_{\text{H}})$ ,  $N_{\text{H}} > N_{\text{max}}$  to  $P_{\text{H}}(N_{\text{H}})$ ,  $N_{\text{H}} \leq N_{\text{max}}$ ). Terms



such as  $F_{\text{H}}P_{\text{H}}(N_{\text{H}})$  that describe probability flow in the opposite direction are also removed. The latter terms are evaluated separately and frequently during the integration of the master equation in order to examine whether  $N_{\text{max}}$  should be increased. The condition for adding more equations is typically  $\dot{P}_{\text{H}}(N_{\text{max}} + 1) > \epsilon$  at a certain time  $t$ , where  $\epsilon$  is a small parameter, suitably chosen according to the desired precision.

Note that the master equation is typically needed when  $\langle N_{\text{H}} \rangle$  is of order unity. Under such conditions most of the probability  $P_{\text{H}}(N_{\text{H}})$  is concentrated at small values of  $N_{\text{H}}$  and therefore  $N_{\text{max}}$  is expected to be small. In a time dependent simulation, when  $\langle N_{\text{H}} \rangle$  increases reaching the limit  $\langle N_{\text{H}} \rangle \gg 1$  (thus requiring  $N_{\text{max}} \gg 1$ ) the master equation can be easily replaced by the rate equations, during the run. One simply has to evaluate  $\langle N_{\text{H}} \rangle$  at a certain time  $t$  and from that point to continue the run using the rate equations. The opposite move of switching from the rate equations to the master equation (when  $\langle N_{\text{H}} \rangle$  decreases towards  $\langle N_{\text{H}} \rangle \approx 1$ ) is nearly as simple. One has to pick as an initial condition for the master equation a narrow distribution  $P_{\text{H}}(N_{\text{H}})$  that satisfies the average  $\langle N_{\text{H}} \rangle$  given by the rate equations, and after some relaxation time it will converge to the proper distribution. In simulations of more complex reactions involving multiple species, the coupling between different species typically involves only averages such as  $\langle N_{\text{H}} \rangle$  (this is an approximation that will be discussed below). Therefore, one can simultaneously use the rate equations for some species and the master equation for others, according to the criteria mentioned above.

To couple the master equation, consisting of Eqs. (11) and (14), to the densities in the gas phase we will consider the densities  $\rho_{\text{H}}$  (atoms  $\text{cm}^{-3}$ ) of H atoms and  $\rho_{\text{H}_2}$  (molecules  $\text{cm}^{-3}$ ) of  $\text{H}_2$  molecules in the gas phase. The incoming fluxes onto the surface of a single grain can be expressed as  $F_{\text{H}} = \rho_{\text{H}}v_{\text{H}}\sigma$  and  $F_{\text{H}_2} = \rho_{\text{H}_2}v_{\text{H}_2}\sigma$  where  $v_{\text{H}_2}$  is the average speed of an  $\text{H}_2$  molecule in the gas phase. The time derivatives of the densities are given by

$$\dot{\rho}_{\text{H}} = [-F_{\text{H}} + W_{\text{H}}\langle N_{\text{H}} \rangle] \rho_{\text{g}} \quad (20)$$

$$\dot{\rho}_{\text{H}_2} = [-F_{\text{H}_2} + (1 - \mu)A_{\text{H}}\langle N_{\text{H}}(N_{\text{H}} - 1) \rangle + W_{\text{H}_2}\langle N_{\text{H}_2} \rangle] \rho_{\text{g}}. \quad (21)$$

#### 4. Simulations and Results

To examine the effect of the finite grain size on the recombination rate of hydrogen in the interstellar medium we performed simulations of the recombination process using the master equation [that consists of Eqs. (11) and (14)] and compared the results to those obtained from the rate equations (9). Since we focus here on steady state conditions, only the part of the master equation included in Eq. (11) needs to be integrated, and the recombination rate is given by Eq. (12). For non-steady state conditions, Eq. (14) would be essential in order to evaluate the time dependent recombination rate. The parameters we have used are given below. Assuming, for simplicity, a spherical grain of diameter  $d$  we obtain a cross section of  $\sigma = \pi d^2/4$ . The estimate of the number of adsorption sites on the grain was based on the experimental data for the olivine and amorphous carbon surfaces (Pirronello et al. 1997a, 1997b, 1999) using the following procedure. The flux of the H and D beams was estimated as  $b \cong 10^{12}$  (atoms  $\text{cm}^{-2} \text{s}^{-1}$ ). The beams passed through a chopper that reduced their flux by a factor of  $c = 20$ . A measurement of the flux in units of ML per second was done using the data for the total HD yield vs. exposure time [Fig. 3 in Pirronello

et al. (1997a)]. The theoretical Langmuir-Hinshelwood mechanism provides a prediction for the coverage of adsorbed atoms after irradiation time  $t$ , which is

$$n_{\text{H}}(t) = 1 - \exp(-f_{\text{H}} \cdot t). \quad (22)$$

Fitting the total HD yield to this expression we obtained good fits that provide the flux values  $f_{\text{H}} = 2.7 \cdot 10^{-4}$  (in  $\text{ML s}^{-1}$ ) for the olivine experiment and  $f_{\text{H}} = 9.87 \cdot 10^{-4}$  for the amorphous carbon experiment. From these two measurements we obtain the density of adsorption sites (sites  $\text{cm}^{-2}$ )

$$s = \frac{b}{c \cdot f_{\text{H}}}. \quad (23)$$

For the olivine surface it is found that  $s \cong 2 \cdot 10^{14}$  and for the amorphous carbon surface  $s \cong 5 \cdot 10^{13}$  (sites  $\text{cm}^{-2}$ ).

Observations indicate that there is a broad distribution of grain sizes, that roughly resembles power-law behavior, in the range of  $10^{-6}\text{cm} < d < 10^{-4}\text{cm}$  (Mathis et al. 1977, 1996; O’Donnell & Mathis 1997). The number of adsorption sites on a (spherical) grain is given by  $S = \pi d^2 s$ . In the simulations we focus on diffuse clouds and use as a typical value for the density of H atoms  $\rho_{\text{H}} = 10$  (atoms  $\text{cm}^{-3}$ ). The temperature of the H gas is taken as  $T = 100\text{K}$ . The typical velocity of H atoms in the gas phase is given by (see e.g. Landau & Lifshitz 1980)

$$v_{\text{H}} = \sqrt{\frac{8}{\pi} \cdot \frac{k_{\text{B}}T}{m}} \quad (24)$$

where  $m = 1.67 \cdot 10^{-24}$  (gram) is the mass of an H atom. We thus obtain  $v_{\text{H}} = 1.45 \cdot 10^5$  ( $\text{cm s}^{-1}$ ). The density of grains is typically taken as  $\rho_{\text{g}} = 10^{-12} \rho_{\text{H}}$  and hence in our case  $\rho_{\text{g}} = 10^{-11}$  (grains  $\text{cm}^{-3}$ ). The sticking probability of H atoms onto the grain surface is taken as  $\xi = 1$ . Experimental results indicate that the sticking probability is close to 1 for temperatures below about 10K and possibly somewhat lower at higher temperatures. Since there is no high quality experimental data for the temperature dependence  $\xi(T)$ , and in order to simplify the analysis we chose  $\xi = 1$ .

We will now analyze the processes that take place on a single grain using numerical integration of the master equation and comparison to the rate equations. The flux of H atoms onto the grain surface is given by  $f_{\text{H}} = \rho_{\text{H}} v_{\text{H}} / (4s)$  ( $\text{ML s}^{-1}$ ), where the factor of 4 in the denominator is the ratio between the surface area and the cross section for a spherical grain. Using the parameters above we obtain that  $f_{\text{H}} = 0.18 \cdot 10^{-8}$  for olivine and  $f_{\text{H}} = 0.73 \cdot 10^{-8}$  for amorphous carbon. The total flux on a grain of diameter  $d$  is given by  $F_{\text{H}} = f_{\text{H}} \cdot S$  (atoms  $\text{s}^{-1}$ ).

In Fig 1 we present the recombination efficiency  $\eta$  for an olivine grain, under steady state conditions, as a function of the grain temperature. The solid line shows the results obtained from the rate equations, showing a range of very high efficiency between 7 – 9 K and a tail of decreasing efficiency between 9 – 10 K. The results of the master equation are shown for grains of diameters  $d = 10^{-5}\text{cm}$  ( $\circ$ ) and  $d = 10^{-6}\text{cm}$  ( $\times$ ). In this case the total flux on a grain amounts to  $F_{\text{H}} = 10^{-3}$  and  $10^{-5}$  (atoms  $\text{s}^{-1}$ ) for the larger and smaller grain sizes, respectively. It is found that for the larger grain there is good agreement between the master equation and rate equation results. However, for the smaller grain the master equation predicts significantly lower recombination efficiency for temperatures higher than 8 K. Note that in order to produce the rate equation results for the entire temperature range of 5 - 15 K we had to include in these equations

the Langmuir-Hinshelwood rejection term (Katz et al. 1999). In the low temperature limit, where atoms are immobile (and the recombination rate decreases to zero), this is necessary in order to make sure that the coverage does not exceed 1 ML. For higher temperatures, where the comparison with the master equation results is made, the coverage is low and the rejection term makes no difference. From the results for the recombination efficiency one obtains the production rate of  $\text{H}_2$  molecules  $\mathcal{R}_{\text{H}_2} = \frac{1}{2}F_{\text{H}}\rho_{\text{g}}\eta$  (molecules  $\text{cm}^{-3} \text{s}^{-1}$ ) released to the gas phase by a density  $\rho_{\text{g}}$  of grains.

In Fig. 2 we present the expectation value for the number  $\langle N_{\text{H}} \rangle$  of H atoms on an olivine grain as a function of the grain diameter  $d$ . The results ( $\circ$ ) are obtained from the master equation under steady state conditions at  $T = 10\text{K}$ . The solid line is simply a guide to the eye. As may be expected,  $\langle N_{\text{H}} \rangle \sim d^2$ , namely, it is proportional to the surface area of the grain. It is observed that for a grain diameter smaller than about  $10^{-5}$  (cm) the expectation value  $\langle N_{\text{H}} \rangle$  decreases below one H atom on the grain. Under these conditions significant deviations are expected between the recombination efficiency predicted by the rate equations and the correct results obtained from the master equation.

The recombination efficiency  $\eta$  for an olivine grain as a function of the grain size ( $\bullet$ ) is shown in Fig. 3. The temperature and the flux are identical to those used in Fig. 2. The dashed line shows the recombination efficiency obtained from the rate equations under similar conditions, which is independent of the grain size. It is observed that for grain diameter smaller than about  $10^{-5}$  (cm) the recombination efficiency sharply drops below the rate-equation value. This is due to the fact that in this range  $\langle N_{\text{H}} \rangle < 2$ , hence most often an H atom resides alone on the grain and no recombination is possible.

In Fig. 4 we present the distribution  $P_{\text{H}}(N_{\text{H}})$  on olivine grains of diameters  $d = 10^{-5}$  cm ( $\circ$ ) and  $d = 10^{-6}$  cm ( $\times$ ). The results were obtained from the master equation under steady state conditions at  $T = 9$  K. For the larger grain the distribution exhibits a peak around  $\langle N_{\text{H}} \rangle \cong 14$  and the rate equations are expected to apply. However, for the smaller grain the highest probability is for having no H atoms at all on the grain and  $\langle N_{\text{H}} \rangle < 1$ . Under these conditions the rate equations are expected to highly over-estimate the recombination efficiency. Indeed, this can be observed in Fig. 1, in which the recombination efficiency for the smaller grain size at 9 K is much lower than the rate equation result.

The results for the recombination efficiency on amorphous carbon grains are qualitatively similar to those shown here for olivine. The temperature range of very high efficiency is between 12 – 16 K and the tail of decreasing efficiency is between 16 – 18 K [see Figs. 6 and 7 in Katz et al. (1999)]. This high efficiency window is within the relevant temperature range for diffuse cloud environments. It is observed that for temperatures higher than about 15 K and grain sizes smaller than  $10^{-5}$  (cm) the master equation predicts lower recombination efficiency than the rate equations.

## 5. More Complex Reactions of Multiple Species

The master equation introduced above can be extended to describe more complex situations that involve chemical reactions with multiple species. We chose to demonstrate this procedure for the reactions involving oxygen and hydrogen on dust grains, previously studied by Caselli et al.

(1998). The rate equations that describe these reactions are

$$\begin{aligned} \frac{d\langle N_{\text{H}} \rangle}{dt} &= F_{\text{H}} - W_{\text{H}}\langle N_{\text{H}} \rangle - 2A_{\text{H}}\langle N_{\text{H}} \rangle^2 \\ &\quad - (A_{\text{H}} + A_{\text{O}})\langle N_{\text{H}} \rangle\langle N_{\text{O}} \rangle - A_{\text{H}}\langle N_{\text{H}} \rangle\langle N_{\text{OH}} \rangle \end{aligned} \quad (25\text{a})$$

$$\frac{d\langle N_{\text{O}} \rangle}{dt} = F_{\text{O}} - (A_{\text{H}} + A_{\text{O}})\langle N_{\text{H}} \rangle\langle N_{\text{O}} \rangle - 2A_{\text{O}}\langle N_{\text{O}} \rangle^2 \quad (25\text{b})$$

$$\frac{d\langle N_{\text{H}_2} \rangle}{dt} = \mu A_{\text{H}}\langle N_{\text{H}} \rangle^2 - W_{\text{H}_2}\langle N_{\text{H}_2} \rangle. \quad (25\text{c})$$

$$\frac{d\langle N_{\text{OH}} \rangle}{dt} = (A_{\text{H}} + A_{\text{O}})\langle N_{\text{H}} \rangle\langle N_{\text{O}} \rangle - A_{\text{H}}\langle N_{\text{H}} \rangle\langle N_{\text{OH}} \rangle \quad (25\text{d})$$

$$\frac{d\langle N_{\text{O}_2} \rangle}{dt} = A_{\text{O}}\langle N_{\text{O}} \rangle^2 \quad (25\text{e})$$

$$\frac{d\langle N_{\text{H}_2\text{O}} \rangle}{dt} = A_{\text{H}}\langle N_{\text{OH}} \rangle\langle N_{\text{H}} \rangle \quad (25\text{f})$$

where  $N_{\text{O}}$  is the number of oxygen atoms on the grain and  $A_{\text{O}}$  is their sweeping rate. The numbers of  $\text{H}_2$ , OH,  $\text{O}_2$  and  $\text{H}_2\text{O}$  molecules on the grain are given by  $N_{\text{H}_2}$ ,  $N_{\text{OH}}$ ,  $N_{\text{O}_2}$  and  $N_{\text{H}_2\text{O}}$ , respectively. The flux of O atoms adsorbed on the grain surface is given by  $F_{\text{O}}$  (atoms  $\text{s}^{-1}$ ) while, for simplicity, the adsorption of the four molecular species from the gas phase is neglected. Since the oxygen atoms and the molecules they form are chemisorbed on the surface they are unlikely to desorb for the surface temperatures considered here. Their desorption coefficients are thus neglected. It is also assumed that the diffusion of the four molecular species is negligible. Except for the OH molecule, this assumption is inconsequential since the three other molecular species do not participate in any subsequent reactions. Furthermore, it is typically assumed that the diffusion rate of oxygen atoms is much slower than of hydrogen, namely  $A_{\text{O}} \ll A_{\text{H}}$ . In the analysis below we will assume that  $A_{\text{O}} = 0$ , namely the reaction between H and O is driven only by the diffusion rate of the hydrogen atoms. Under this assumption and for low coverage of O atoms on the grain, the production of oxygen molecules is suppressed and Eq. (25e) can be ignored. The assumption that H atoms are much more mobile than heavier atomic species such as C, O and N implies that the diffusion of H atoms is dominant in other reactions that take place on grain surfaces besides hydrogen recombination. Thus, the activation energies obtained by Katz et al. (1999) may be used not only for the hydrogen recombination process but for a large number of other reactions on dust grain surfaces. However, one should carefully examine the possibility that some of these reactions involve an additional activation energy associated with the reaction itself.

For simplicity we will now neglect the reaction between H atoms and OH molecules which generates  $\text{H}_2\text{O}$  molecules. We will also assume, for simplicity, that  $\text{H}_2$  molecules desorb into the gas phase immediately upon formation, namely that  $\mu = 0$ . Under these conditions the rate equations will simplify into

$$\frac{d\langle N_{\text{H}} \rangle}{dt} = F_{\text{H}} - W_{\text{H}}\langle N_{\text{H}} \rangle - 2A_{\text{H}}\langle N_{\text{H}} \rangle^2 - A_{\text{H}}\langle N_{\text{H}} \rangle\langle N_{\text{O}} \rangle \quad (26\text{a})$$

$$\frac{d\langle N_{\text{O}} \rangle}{dt} = F_{\text{O}} - A_{\text{H}}\langle N_{\text{H}} \rangle\langle N_{\text{O}} \rangle \quad (26\text{b})$$

$$\frac{d\langle N_{\text{OH}} \rangle}{dt} = A_{\text{H}}\langle N_{\text{H}} \rangle\langle N_{\text{O}} \rangle. \quad (26\text{c})$$

The part of the master equation describing the time evolution of the population of H atoms on the

grain surface takes the form

$$\begin{aligned}
\dot{P}_H(0) &= -F_H P_H(0) + W_H P_H(1) + 2 \cdot 1 \cdot A_H P_H(2) + A_H P_H(1) \langle N_O \rangle \\
\dot{P}_H(1) &= F_H [P_H(0) - P_H(1)] + W_H [2P_H(2) - P_H(1)] \\
&\quad + 3 \cdot 2 \cdot A_H P_H(3) + A_H [2P_H(2) - P_H(1)] \langle N_O \rangle \\
\dot{P}_H(2) &= F_H [P_H(1) - P_H(2)] + W_H [3P_H(3) - 2P_H(2)] \\
&\quad + A_H [4 \cdot 3 \cdot P_H(4) - 2 \cdot 1 \cdot P_H(2)] + A_H [3P_H(3) - 2P_H(2)] \langle N_O \rangle \\
&\quad \vdots \\
\dot{P}_H(N_H) &= F_H [P_H(N_H - 1) - P_H(N_H)] + W_H [(N_H + 1)P_H(N_H + 1) - N_H P_H(N_H)] \\
&\quad + A_H [(N_H + 2)(N_H + 1)P_H(N_H + 2) - N_H(N_H - 1)P_H(N_H)] \\
&\quad + A_H [(N_H + 1)P_H(N_H + 1) - N_H P_H(N_H)] \langle N_O \rangle \\
&\quad \vdots
\end{aligned} \tag{27}$$

where

$$\langle N_O \rangle = \sum_{N_O=1}^{\infty} N_O P_O(N_O). \tag{28}$$

The equations for oxygen atoms are

$$\begin{aligned}
\dot{P}_O(0) &= -F_O P_O(0) + A_H P_O(1) \langle N_H \rangle \\
\dot{P}_O(1) &= F_O [P_O(0) - P_O(1)] + A_H [2P_O(2) - P_O(1)] \langle N_H \rangle \\
\dot{P}_O(2) &= F_O [P_O(1) - P_O(2)] + A_H [3P_O(3) - 2P_O(2)] \langle N_H \rangle \\
&\quad \vdots \\
\dot{P}_O(N_O) &= F_O [P_O(N_O - 1) - P_O(N_O)] + A_H [(N_O + 1)P_O(N_O + 1) - N_O P_O(N_O)] \langle N_H \rangle. \\
&\quad \vdots
\end{aligned} \tag{29}$$

where

$$\langle N_H \rangle = \sum_{N_H=1}^{\infty} N_H P_H(N_H). \tag{30}$$

The equations describing the distribution of the number of OH molecules are

$$\begin{aligned}
\dot{P}_{OH}(0) &= -A_H P_{OH}(0) \langle N_O \rangle \langle N_H \rangle \\
\dot{P}_{OH}(1) &= +A_H [P_{OH}(0) - P_{OH}(1)] \langle N_O \rangle \langle N_H \rangle \\
\dot{P}_{OH}(2) &= +A_H [P_{OH}(1) - P_{OH}(2)] \langle N_O \rangle \langle N_H \rangle \\
&\quad \vdots \\
\dot{P}_{OH}(N_{OH}) &= +A_H [P_{OH}(N_{OH} - 1) - P_{OH}(N_{OH})] \langle N_O \rangle \langle N_H \rangle. \\
&\quad \vdots
\end{aligned} \tag{31}$$

The rate of formation of H<sub>2</sub> molecules is given by Eq. (12). The rate of formation of OH molecules is given by  $R_{OH} = A_H \langle N_O \rangle \langle N_H \rangle$ . Unlike the H<sub>2</sub> molecules that desorb, the OH as well as H<sub>2</sub>O molecules (not included in the master equation above) are believed to stick to the grain and form an ice mantle. The parameters of the bare surface, used in this paper, are suitable only in the early

stages before the first monolayer of ice is formed. Beyond this stage one needs the activation energies for H diffusion on ice, which can be obtained from TPD experiments of hydrogen recombination on ice mantles.

Note that in the equations above the coupling between different species is only through the expectation values  $\langle N_O \rangle$  and  $\langle N_H \rangle$ . Therefore, one can simultaneously use the rate equations for some of the species and the master equation others according to the criteria discussed above. This is, in fact, an approximation in which the correlation between the probability distributions of different species such as  $P_O(N_O)$  and  $P_H(N_H)$  is neglected. In cases where significant correlation is expected one can use a set of master equation for the joint probability distribution  $P_{H\&O}(N_O, N_H)$ . However, in this case the number of equations that are needed is  $N_{\max}(O) \cdot N_{\max}(H)$ , which may become impractical for systems with a larger number of species. In principle, such correlations could be significant in cases in which there are two species that react only with each other and thus the density of one specie would be strongly dependent on the availability of the other. However, in the interstellar medium such correlations are not expected to be strong since the reactive species (particularly atomic hydrogen) react with a large number of species.

## 6. Summary

We have introduced a new approach for the simulation of hydrogen recombination on microscopic dust grains in the interstellar medium. This approach is based on a set of master equation for the probabilities  $P_H(N_H)$ ,  $N_H = 0, 1, 2 \dots$  that there are  $N_H$  hydrogen atoms on the grain surface. Unlike the rate equations that provide a mean-field analysis, suitable for macroscopic surfaces, these rate equations provide an exact description of the recombination process on small grains taking into account the discrete nature of  $N_H$  as well as the fluctuations. The approach can be extended to more complex chemical reactions with multiple species and coupled to the densities of the reactants in the gas phase.

## 7. Acknowledgments

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### Figure Captions

Fig. 1.— The recombination efficiency  $\eta$ , obtained from the master equation, for olivine grains of diameters  $d = 0.1\mu\text{m}$  and  $d = 0.01\mu\text{m}$  ( $\times$ ) under steady state conditions at a constant flux, as a function of the grain temperature. The flux is  $f = 0.18 \times 10^{-8} \text{ MLs}^{-1}$ , which amounts to  $F_{\text{H}} = 10^{-3}$  and  $10^{-5}$  (atoms  $\text{s}^{-1}$ ) for the larger and smaller grain sizes, respectively. The recombination efficiency, obtained from the rate equations under similar conditions is also shown (solid line) showing a window of high efficiency between 7 - 9 K and a tail of decreasing efficiency above 9 K. We observe that in the center of the high efficiency peak there is good agreement between the master equation and rate equation results. However, for the smaller grain at higher temperatures, the master equation predicts significantly lower recombination efficiencies than the rate equations. These deviations persist at temperatures as high as 11 and 12 K but cannot be seen in the Figure due to the limited resolution.

Fig. 2.— The expectation value for the number  $\langle N_{\text{H}} \rangle$  of H atoms on an olivine grain as a function of the grain diameter under steady state conditions at  $T = 10\text{K}$ , as obtained from the master equation ( $\circ$ ). The solid line is simply a guide to the eye.

Fig. 3.— The recombination efficiency  $\eta$  for an olivine grain as a function of the grain size ( $\bullet$ ). at  $T = 10\text{K}$  and  $f = 0.18 \times 10^{-8} \text{ MLs}^{-1}$ . The results predicted by the rate equations under similar conditions, which are independent of the grain size, are also shown (dashed line). It is observed that as the grain size decreases below  $d = 0.1\mu\text{m}$  the recombination efficiency quickly decreases.

Fig. 4.— The distributions  $P_{\text{H}}(N_{\text{H}})$  on olivine grains of diameters  $d = 0.1 \mu\text{m}$  ( $\circ$ ) and  $d = 0.01 \mu\text{m}$  ( $\times$ ), obtained from the master equation at  $T = 9\text{K}$  and  $f = 0.18 \times 10^{-8} \text{ MLs}^{-1}$ .

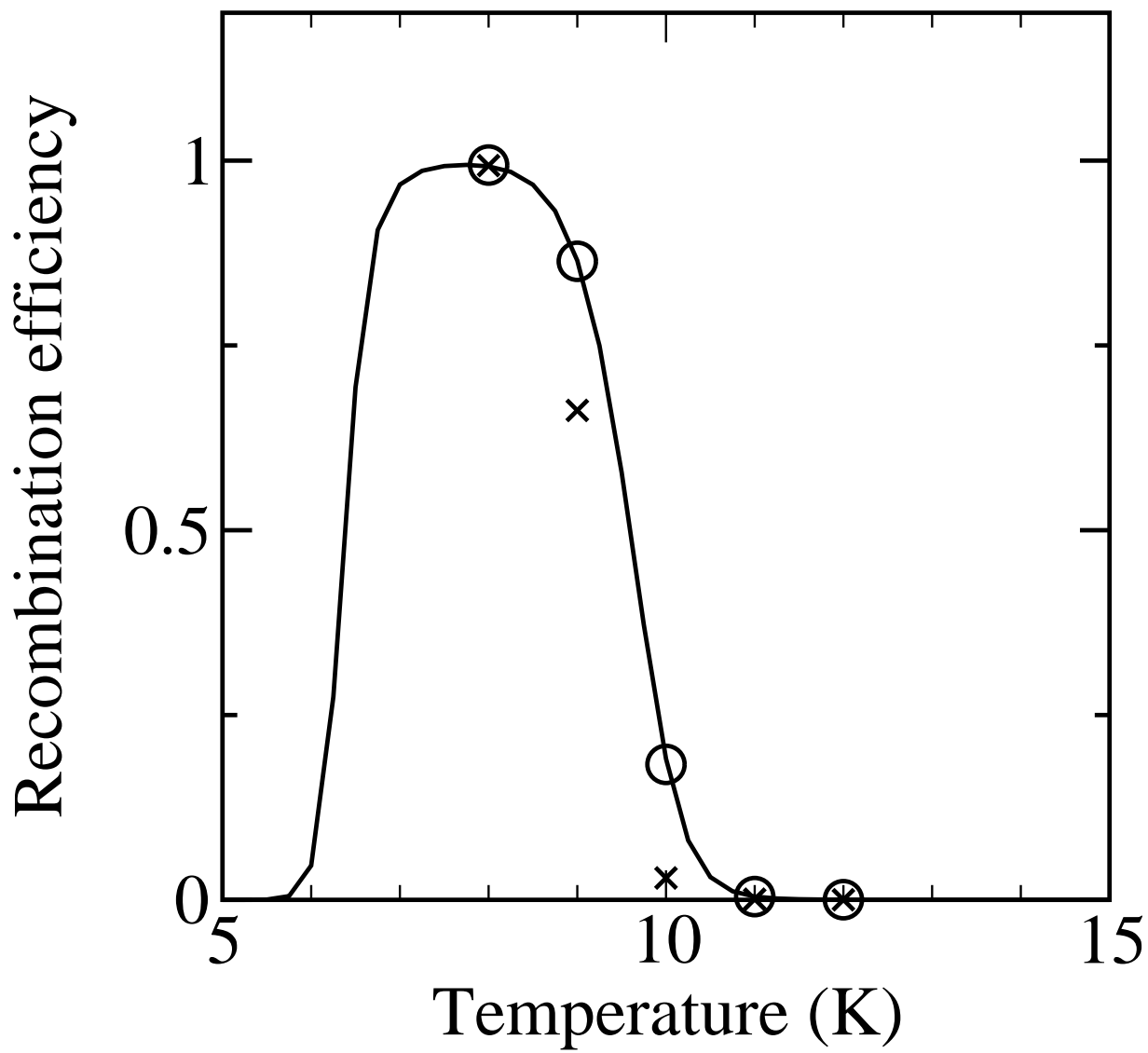


Fig. 1



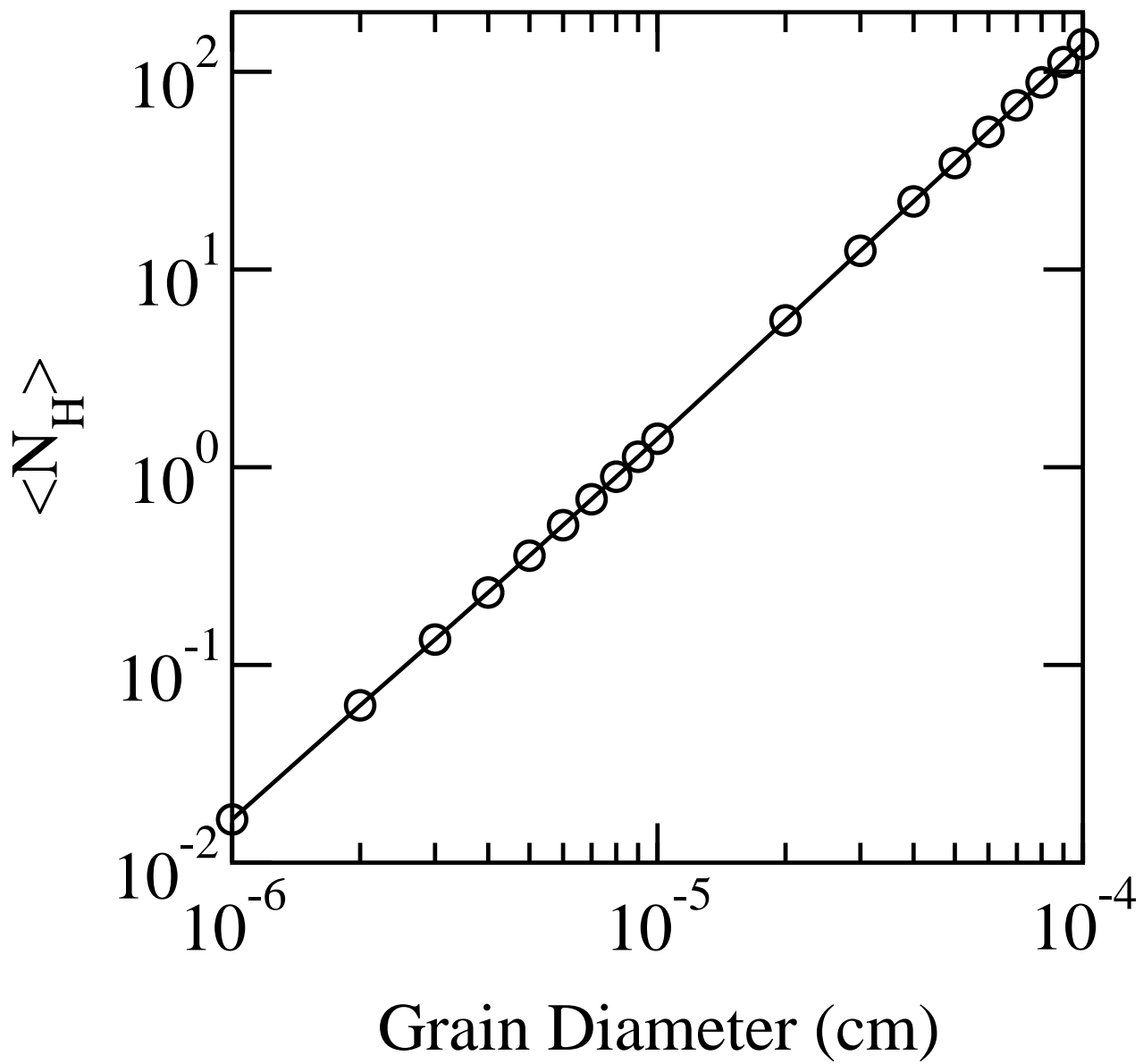


Fig. 2

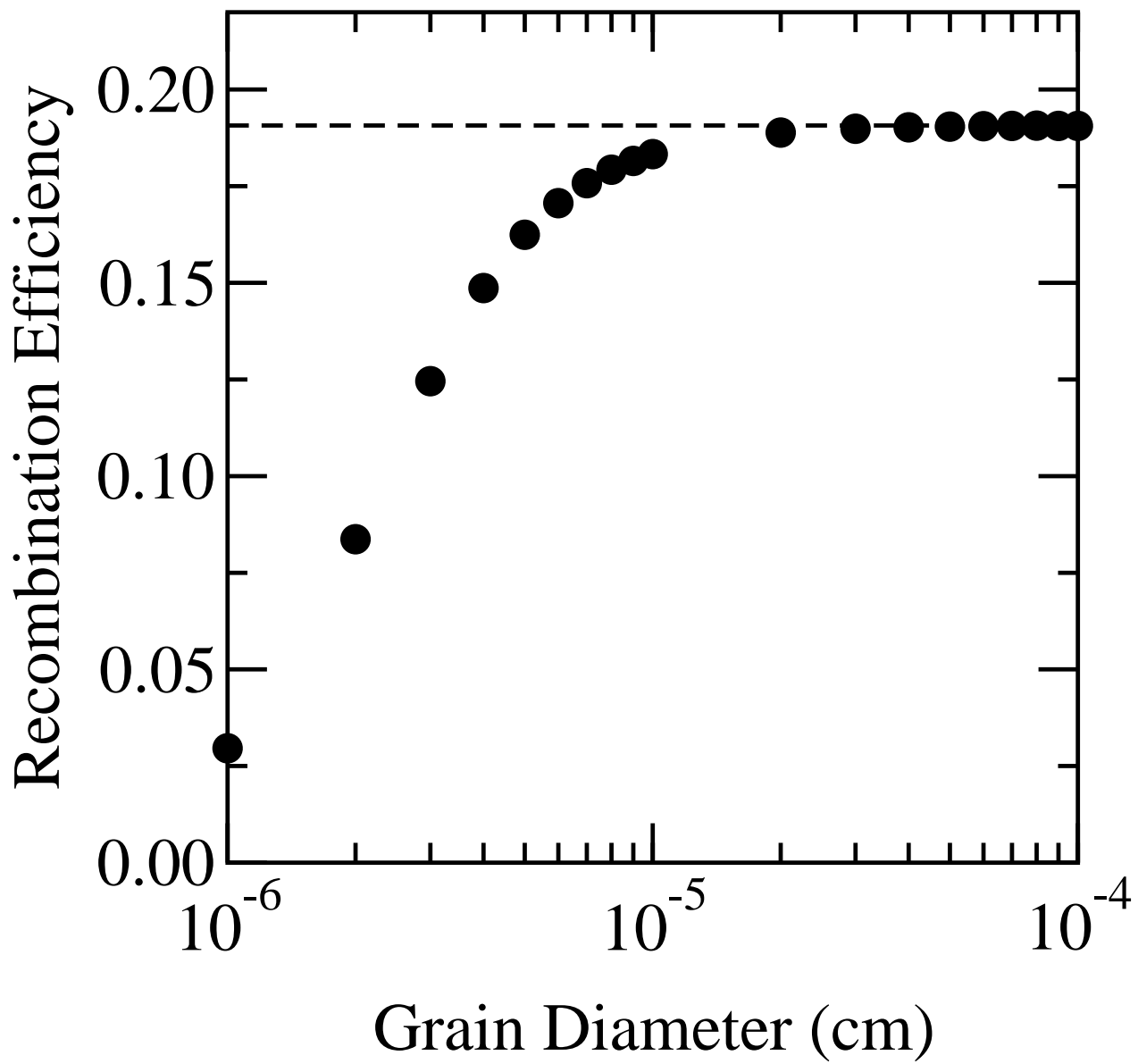


Fig. 3

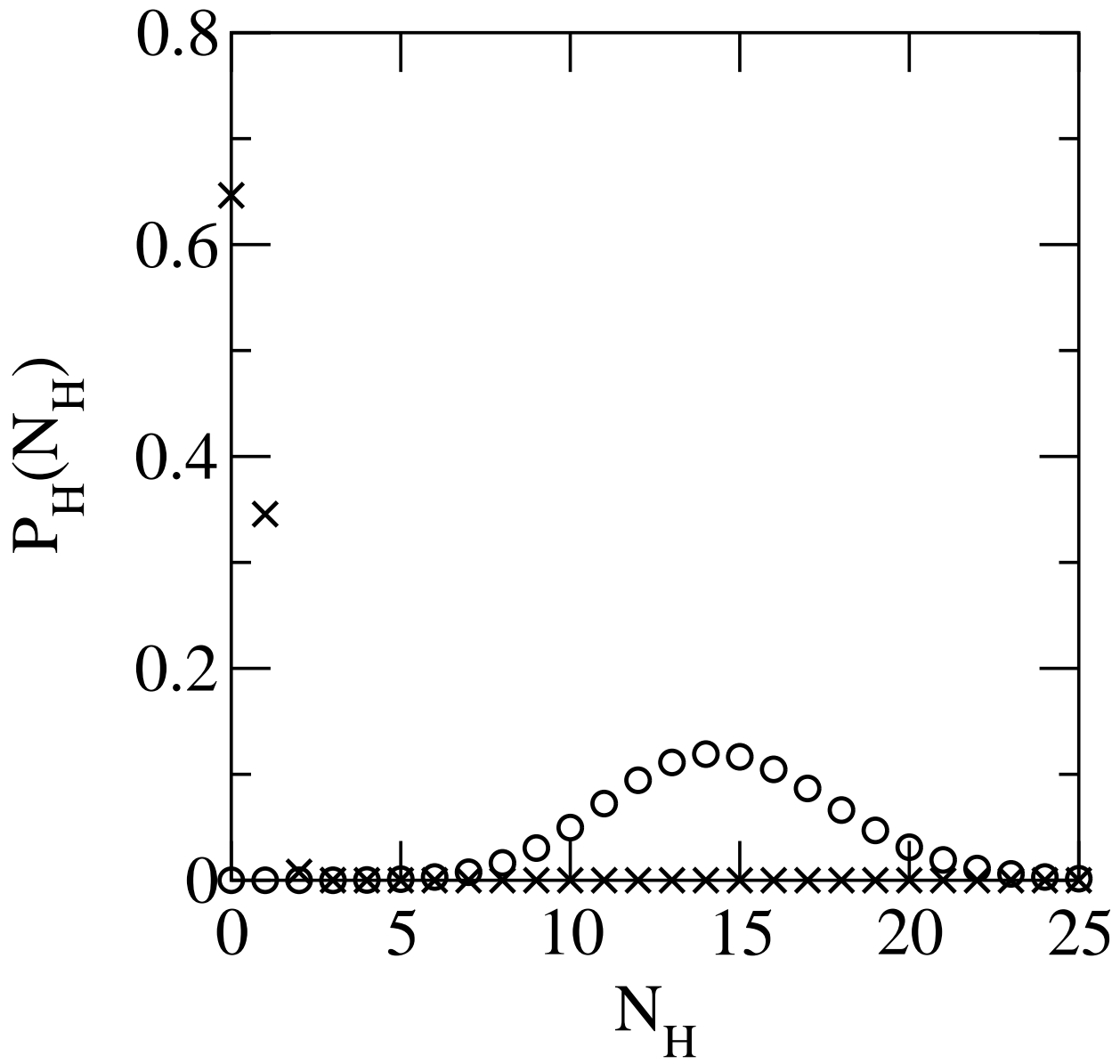


Fig. 4