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MOLECULAR HYDROGEN FORMATION ON AMORPHOUS SILICATES UNDER INTERSTELLAR CONDITIONS

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ABSTRACT

Experimental results on the formation of molecular hydrogen on amorphous silicate surfaces are presented for the first time and analyzed using a rate equation model. The energy barriers for the relevant diffusion and desorption processes are obtained. They turn out to be significantly higher than those obtained earlier for polycrystalline silicates, demonstrating the importance of grain morphology. Using these barriers we evaluate the efficiency of molecular hydrogen formation on amorphous silicate grains under interstellar conditions. It is found that unlike polycrystalline silicates, amorphous silicate grains are efficient catalysts of H_2 formation within a temperature range which is relevant to diffuse interstellar clouds. The results also indicate that the hydrogen molecules are thermalized with the surface and desorb with low kinetic energy. Thus, they are unlikely to occupy highly excited states.

Subject headings: dust — ISM: molecules — molecular processes

1. INTRODUCTION

H_2 is the most abundant molecule in the interstellar medium (ISM). It plays a crucial role in the initial cooling of clouds during gravitational collapse and is involved in most reaction schemes that produce other molecules (Duley & Williams 1984). It is widely accepted that H_2 formation in the ISM takes place on dust grains (Gould & Salpeter 1963). In this process, H atoms that collide with a grain and adsorb on its surface quickly equilibrate and diffuse either by thermal activation or tunneling. They may encounter each other and form H_2 molecules (Williams 1968; Hollenbach & Salpeter 1970), or desorb thermally in atomic form.

In recent years, we have conducted a series of experiments on the formation of molecular hydrogen on dust grain analogues such as polycrystalline silicates (Pirronello et al. 1997a; Pirronello et al. 1997b), amorphous carbon (Pirronello et al. 1999) and amorphous water ice (Manico et al. 2001; Roser et al. 2002; Roser et al. 2003; Perets et al. 2005), under astrophysically relevant conditions. In these experiments, the surface was irradiated by beams of H and D atoms. The production of HD molecules was measured during the irradiation and during a subsequent temperature programmed desorption (TPD) experiment. To disentangle the process of diffusion from the one of desorption, separate experiments were carried out in which molecular species were irradiated on the sample and were later induced to desorb. Related studies were done on amorphous ice surfaces (Hornekaer et al. 2003; Hornekaer et al. 2005; Dulieu et al 2005; Perets et al. 2005; Amiaud et al. 2006; Williams et al. 2007).

The results were analyzed using rate equation models and the energy barriers for the relevant diffusion and desorption processes were obtained (Katz et al. 1999; Cazaux & Tielens 2004; Perets et al. 2005). Using these parameters, the conditions for efficient H_2 formation on different astrophysically relevant surfaces were found. In particular, the formation of H_2 on polycrystalline silicates was found to be efficient only in a narrow temperature window below 10K. Since the typical dust grain temperature in diffuse interstellar clouds is higher than 10K, these results indicated that polycrystalline silicate grains cannot be efficient catalysts for H_2 formation in most diffuse clouds.

In this *Letter* we present, for the first time, experiments on molecular hydrogen formation on *amorphous* silicates and analyze the results using a suitable rate equation model (Perets et al. 2005). Using the parameters that best fit the experimental results, the efficiency of hydrogen recombination on grains is obtained for a range of conditions pertinent to diffuse interstellar clouds. It is found that unlike the polycrystalline silicate grains, amorphous silicate grains, which are the main silicate component in interstellar clouds (Tielens 2005), are efficient catalysts for H_2 formation within a broad temperature window that extends at least up to about 14K.

2. EXPERIMENTAL METHODS AND RESULTS

The apparatus consists of an ultra-high vacuum chamber housing the sample holder and a detector. The sample can be cooled by liquid helium to ∼5K, as measured by a calibrated silicon diode and thermocouple placed in the back of the sample. A heater in the back of the sample is used to maintain a set temperature between 5 and 30K during the irradiation phase of the experiment. The sample and detector can rotate around the vertical axis. Prior to a series of measurements, the sample is heated to 380-400K. During a series of measurements, the sample is taken periodically to 200-250K to desorb condens-

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ables. Hydrogen and deuterium gases are dissociated in two radio-frequency dissociation sources, with dissociation efficiency of 80-90%, and are sent into the sample chamber via two triple differentially pumped beam lines (Vidali et al. 2004).

In the experiments reported here, we used beams of low fluxes and short dosing times. Using the standard Langmuir-Hinshelwood analysis, plotting the total yield of HD vs. the exposure time (Biham et al. 2001), we estimated the coverage to be a small fraction (a few percent) of a monolayer (ML). This is still far from interstellar values but is within the regime in which results can be safely extrapolated to diffuse cloud conditions (Katz et al. 1999; Perets et al. 2005). The interstellar dust analogues we used are amorphous silicate samples, $(\mathrm{Fe}_x, \mathrm{Mg}_{1-x})_2\mathrm{SiO}_4$, prepared by one of us (J.R.B.) by laser ablation (wavelength 266 nm) of a mixed MgO, FeO and SiO_2 target in an oxygen atmosphere (10 mbar). The optical and stochiometric characterization of samples produced with this technique is given elsewhere (Brucato et al. 2002). The results reported here are for a sample with $x = 0.5$.

The experiment consists of adsorbing hydrogen atoms onto the surface while monitoring the amount of hydrogen molecules that are formed. To increase the signal to noise ratio, hydrogen and deuterium atoms are used and the formation of HD is monitored. The measurement of HD formation is done in two steps. First, we record the amount of HD that forms and comes off the surface while the sample is being dosed with H and D atoms (the *irradiation phase*). Next, after dosing is completed, in a TPD experiment, the surface temperature is raised rapidly and the rate of HD desorption is measured (the *TPD phase*). By far, the main contribution comes from the TPD phase.

Irradiations with beams of H and D ("H+D" thereafter) were done on an amorphous silicate surface in order to explore the formation processes of HD molecules. The H+D irradiation runs were performed with different irradiation times (15, 30, 60, 120 and 240 s), at a surface temperature of $T_0 \simeq 5.6$K. In a separate set of experiments, beams of HD molecules were irradiated on the same surface. During the TPD runs, the sample temperature was monitored as a function of time. The temperature ramps $T(t)$ deviate from linearity but are highly reproducible (see inset in Fig. 2).

The desorption rates of HD molecules vs. surface temperature during the TPD runs are shown in Fig. 1, for H+D irradiation on polycrystalline silicate (*circles*) and amorphous silicate (*squares*) surfaces, with irradiation times of 120 s. The TPD curve following irradiation of HD molecules on an amorphous silicate surface is also shown (*crosses*). The results of current experiments of H+D irradiation on amorphous silicates, clearly differ from those of earlier experiments on polycrystalline silicates. The desorption curves from amorphous silicates contain two wide peaks, located at a significantly higher temperatures than the single narrow peak obtained for the polycrystalline silicate. The higher peak temperatures indicate that the relevant energy barriers are larger, while their large width reflects a broader distribution of the energy barriers of the HD desorption sites. The TPD curve of HD desorption from amorphous silicates, after irradiation with HD molecules (crosses in Fig. 1), is qualitatively similar to the curve obtained for H+D irradiation. In particular, the peak temperatures are the same. The relative weights of the high temperature peaks vs. the low temperature peaks are somewhat different. Also, in similar experiments with higher values of T_0, a third peak was observed at higher temperatures. We attribute this behavior to diffusion of HD molecules, which gradually migrate from shallow into deep adsorption sites (Perets et al. 2005; Dulieu et al 2005; Amiaud et al. 2006).

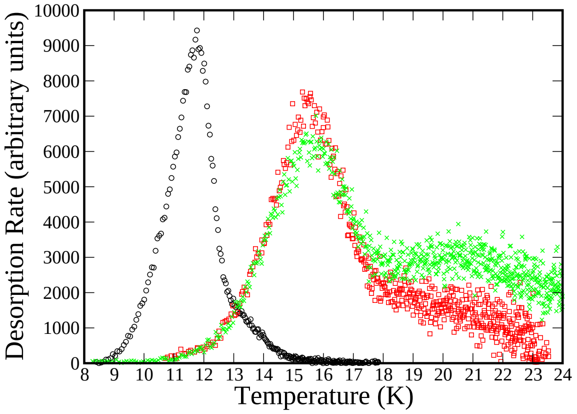

FIG. 1.— TPD curves of HD desorption after irradiation of HD molecules (×) and H+D atoms (□) on amorphous silicate. Also shown, for comparison, is HD desorption after irradiation with H+D atoms on polycrystalline silicate (○).

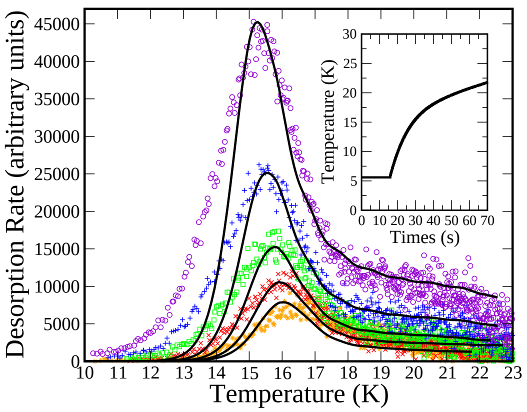

FIG. 2.— TPD curves of HD desorption after irradiation with H+D atoms on amorphous silicate with irradiation times of 15 (*), 30 (×), 60 (□) 120 (+) and 240 (○) s. The solid lines are fits obtained using the rate equation model. The temperature ramps (shown in the inset) are identical for all the runs.

In Fig. 2 we present a series of TPD curves for HD desorption after irradiation with H+D atoms on an amorphous silicate surface with different irradiation times. Each curve exhibits a large peak at a lower temperature and a broader peak (or a shoulder) at a higher temperature. The position of the high temperature peak is found to be independent of the irradiation time, indicating that this peak exhibits first order kinetics. The low temperature peak shifts to the right as the irradiation time is reduced. Since in the low-coverage regime studied here, the activation energies and the pre-exponential factor are not expected to depend on the coverage, these results indicate that the low temperature peak exhibits second order kinetics. This is unlike the case of irradiation with HD molecules, where the lower-temperature peak does not shift, showing first order kinetics.

3. ANALYSIS OF THE EXPERIMENTAL RESULTS

In the model used here, there is no distinction between the H and D atoms, namely the same diffusion and desorption barriers are used for both isotopes. Hydrogen atoms that stick to the surface hop as random walkers and may either encounter each other and form molecules, or desorb from the surface. As the sample temperature is raised, both the diffusion and desorption rates quickly increase. If a large fraction of the energy released when two H atoms recombine is transformed into kinetic energy of the formed molecule, it would immediately desorb from the grain surface in a high ro-vibrational state, and with large translational energy. However, both our experiments on ice (Perets et al. 2005) and the current experiments indicate that such prompt desorption does not occur on amorphous surfaces [but see Perry and Price (2003), Tine et al. (2003) and Creighan et al. (2006) for other, more ordered, surfaces]. Instead, the newly formed molecules dissipate their energy, probably through multiple collisions with the rough surface or internal pores. These molecules thermalize with the surface and become trapped in adsorption sites before they thermally desorb. Consequently, the desorbed molecules are not highly excited, and desorb only with a thermal energy comparable with the grain surface temperature. Therefore, in our model it is assumed that the newly formed molecules do not promptly desorb, but are trapped in adsorption sites with a range of potential barriers.

The experimental results were fitted using the rate equation model described in Perets et al. (2005). The parameters for the diffusion and desorption of hydrogen atoms and molecules on the amorphous silicate surface were obtained. These include the energy barrier $E_{\rm H}^{\rm diff}$ for the diffusion of H atoms and the barrier $E_{\rm H}^{\rm des}$ for their desorption. The value obtained for the desorption barrier should be considered only as a lower bound, because the TPD results are insensitive to variations in $E_{\rm H}^{\rm des}$, as long as it is higher than the reported value. The desorption barriers of HD molecules adsorbed in shallow (lower temperature peak) and deep (higher temperature peak) sites, are given by $E_{\rm H_2}^{\rm des}(j)$, where $j = 1, 2$, respectively.

The rate equation model is integrated using a Runge-Kutta stepper. For any given choice of the parameters, one obtains a set of TPD curves for the different irradiation times used in the experiments. The actual temperature curve of the sample, recorded during the experiment, is used in the analysis (see inset in Fig. 2). In the first step, the barriers $E_{\rm H_2}^{\rm des}(j)$, $j = 1, 2$, for the desorption of molecules are obtained using the results of the experiments in which HD molecules are irradiated on the surface. To obtain better fits, we incorporate suitable Gaussian distributions of energy barriers around these two values. In the second step, the barriers for diffusion and desorption of H atoms are obtained, using the model to fit the results of H+D irradiation experiments (Table 1).

TABLE 1
ENERGY BARRIERS FOR DIFFUSION AND DESORPTION.

Material	$E_{\rm H}^{\rm diff}$(meV)	$E_{\rm H}^{\rm des}$(meV)	$E_{\rm HD}^{\rm des}$(meV)
Polycrystalline Silicate	25	32	27
Amorphous Silicate	35	44	35, 53

The second order behavior of the low temperature peak in the H+D irradiation experiments can be explained as follows. Most HD molecules are formed only when the surface temperature is sufficiently high to enable significant mobility of H and D atoms. At this temperature, the shallow adsorption sites cannot retain the newly formed molecules adsorbed in these sites, which quickly desorb from the surface by thermal activation. However, those newly formed molecules which are trapped in deeper sites do not desorb yet, and remain on the surface until its temperature increases further. Thus, the high temperature peak exhibits first order kinetics and is located at the same temperatures in both HD and H+D irradiation experiments. Note that we cannot exclude the possibility that some fraction of the molecules desorbed in the high temperature peak are formed during irradiation and remain trapped in deep adsorption sites until the temperature becomes sufficiently high for them to desorb.

At longer H+D irradiation times, more atoms are adsorbed on the surface, and they find each other more easily. The low temperature peak (corresponding to HD desorption from shallower sites) shifts to lower temperatures with longer irradation times, thus showing second order behavior. This behavior must saturate with even longer irradiation times, when the temperature needed for HD formation becomes lower than the temperature needed for thermal desorption from the shallower HD adsorption sites. The HD molecules then form at low temperatures, but are trapped in the shallow sites. They then await until the temperature is further increased, much like the adsorbed HD molecules in the HD irradiation experiments. Therfore, at longer irradiation times the low temperature peak should saturate into first-order like behavior and the TPD curves of the H+D and HD irradiation experiments should become more similar. This behavior is confirmed by the TPD curves for H+D and HD irradiation shown in Fig. 1.

Using the parameters obtained from the experiments we now calculate the recombination efficiency of hydrogen on amorphous silicate surfaces under interstellar conditions. The recombination efficiency is defined as the fraction of hydrogen atoms adsorbed on the surface which come out as molecules. In Fig. 3 we present the recombination efficiency vs. surface temperature for the amorphous silicate sample under flux of 5.2×10^{-10} (ML s^{-1}). This flux is within the typical range for diffuse interstellar clouds, where bare amorphous silicate grains are expected to play a crucial role in H_2 formation. This flux corresponds to gas density of 10 (atoms cm^{-3}), gas temperature of 100K and density of 7×10^{14} adsorption sites per cm^2 on the surface, obtained using the procedure described in Biham et al. (2001).

A window of high recombination efficiency is found

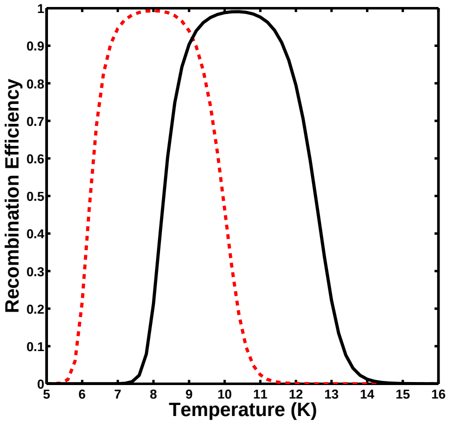

FIG. 3.— Calculated recombination efficiency of Hydrogen at steady state on amorphous silicate (solid line) and polycrystalline silicate (dashed line) vs. temperature, using the parameters obtained from the TPD experiments.

between 8-13K, compared to 6-10K for polycrystalline silicate under similar conditions. For gas density of 100 (atoms cm^{-2}), the high efficiency window for the amorphous silicates surface shifts to 9-14K. At higher temperatures atoms desorb from the surface before they have sufficient time to encounter each other. At lower temperatures diffusion is suppressed and the Langmuir-Hinshelwood mechanism is no longer efficient. Saturation of the surface with immobile H atoms might render the Eley-Rideal mechanism more efficient in producing some recombination (Katz et al. 1999; Perets et al. 2005). Our results thus indicate that recombination efficiency of hydrogen on amorphous silicates is high in this temperature range, which is relevant to interstellar clouds. Therefore, amorphous silicates seem to be good candidates for interstellar grain components on which hydrogen recombines with high efficiency.

4. DISCUSSION AND SUMMARY

The analysis of the TPD curves from amorphous silicate surfaces shows that the relevant energy barriers on these surfaces are significantly higher than on polycrystalline silicates (Katz et al. 1999; Cazaux & Tielens 2004). A similar trend was observed in amorphous and porous ice surfaces (Williams et al. 2007). These results confirm the effect of surface morphology on the distribution of energy barriers. This effect can be parameterized using a model that provides a quantitative connection between the roughness and the energy barriers (Cuppen & Herbst 2005). Our results are consistent with this model and can be used to quantitatively constrain its parameters. More specifically, we find a 1.4-1.5 times increase in the energy barriers of the amorphous silicate vs. the polycrystalline silicate surface. This gives rise to shifting and broadening of the temperature window in which H_2 formation is efficient, by a similar factor. Scanning electron microscope images show that the morphology of the amorphous silicate samples is very rough (H. Cuppen, private communication). These samples are made of a broad (log-normal like) distribution of spheres and agglomerates, from several nanometers up to a micron size. It is safe to conclude that our present results, together with those on amorphous carbon (Pirronello et al. 1999; Katz et al. 1999), show that amorphous silicate and carbon grains are efficient catalysts for the formation of molecular hydrogen in diffuse clouds. However, the results indicate that surface roughness is unlikely to extend the window of efficient recombination to temperatures of the order of 30-50K observed in photo-dissociation regions (PDRs). We thus conclude that surface roughness, by itself, does not explain the high abundance of H_2 in PDRs.

In the model used here, it is assumed that H_2 molecules do not desorb immediately upon formation. Instead, they stay trapped in the adsorption sites or hop between them until thermal desorption takes place. Consequently, one needs to consider mechanisms for the dissipation of the excess energy acquired from the recombination process in order to prevent prompt desorption. For amorphous, porous ice surfaces it was shown, using time of flight (TOF) measurements, that the kinetic energy of the desorbed molecules is small ($\simeq$3 meV), namely the excess energy is absorbed by the surface (Roser et al. 2003; Hornekaer et al. 2003; Hornekaer et al. 2005). Although we do not have direct measurements of the TOF of the HD molecules desorped from the amorphous silicate surface, the similarity between the TPD curves obtained after HD and H+D irradiations indicates that newly formed HD molecules reside and then desorb from the same adsorption sites as HD molecules irradiated on the surface. In light of the results on both ice and amorphous silicates, it is likely than H_2 molecules formed on realistic interstellar dust would have low kinetic energy and would probably not occupy excited vibrational or rotational states.

In summary, we have analyzed a set of TPD experiments on molecular hydrogen formation and desorption from amorphous silicate surfaces under conditions relevant to interstellar clouds. Fitting the TPD curves by rate equation models, the essential parameters of H_2 formation on amorphous silicate surfaces were obtained. These parameters include the energy barrier for diffusion of H atoms as well as their barrier for desorption (considered as a lower bound). The distribution of barriers for desorption of H_2 molecules is also obtained. Interestingly, a single type of adsorption site for hydrogen atoms is identified, vs. two types of sites for molecules. The fraction of the adsorption sites, which belong to each of the two types is also evaluated. The rate equation model provides a unified description of several first and second order processes. It enables us to extrapolate the production rate of H_2 molecules from laboratory conditions to astrophysical conditions. It thus provides a quantitative evaluation of the efficiency of amorphous silicate surfaces as catalysts in the formation of H_2 molecules in interstellar clouds. We find that the recombination efficiency strongly depends on the surface temperature. In particular, the amorphous silicate sample studied here exhibits high efficiency within a range of surface temperatures which is relevant to diffuse interstellar clouds. The comparison of the current results with earlier ones on polycrystalline silicate surfaces shows the importance of surface morphology in molecular hydrogen formation. The results are in agreement with theoretical predictions on the effects of surface roughness (Cuppen & Herbst 2005). The results also indicate that on amorphous surfaces, newly formed H_2 molecules are thermalized on the surface and do not promptly desorb. Consequently, H_2 molecules formed on and desorbed from realistic *amorphous* interstellar dust are expected to have very low kinetic energy and would probably not occupy excited vibrational or rotational states.

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