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FORMATION OF MOLECULAR HYDROGEN ON AMORPHOUS SILICATE SURFACES

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Abstract.

Experimental results on the formation of molecular hydrogen on amorphous silicate surfaces are presented 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 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 H₂ formation in diffuse interstellar clouds.

H₂ 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. It is widely accepted that H₂ formation in the ISM takes place on the surfaces of dust grains (Gould & Salpeter 1963). In this process, H atoms that collide with a grain quickly equilibrate and stick on its surface. The adsorbed atoms diffuse on the surface. They may encounter each other and form H₂ molecules (Williams 1968, Hollenbach & Salpeter 1971, Hollenbach et al. 1971), or desorb thermally in atomic form.

In recent years, we have conducted a series of experiments on molecular hydrogen formation on dust grain analogues such as polycrystalline silicates (Pirronello et al. 1997), amorphous carbon (Pirronello et al. 1999) and amorphous water ice (Manico et al. 2001, Roser et al. 2002, 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. Related studies were done on amorphous ice and other surfaces (Hornekaer et al. 2003, Perets et al. 2005, Dulieu et al. 2005, Hornekaer et al. 2005, Amiaud et al. 2006, Creighan et al. 2006, Williams et al. 2007).

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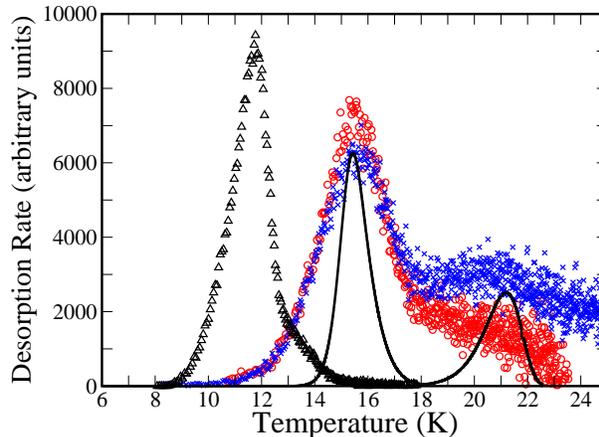


Fig. 1. TPD curves of HD desorption after irradiation of HD molecules (\times) and H+D atoms (\circ) on amorphous silicate. The H+D results are fitted using the rate equation model (solid line). Also shown, for comparison, is HD desorption after irradiation with H+D atoms on polycrystalline silicate (Δ).

The results were analyzed using rate equation models. The energy barriers for the 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.

Here we present 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, are efficient catalysts for H_2 formation within a broad temperature window that extends at least up to about 14K (Perets et al. 2007).

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 (Perets et al. 2007) 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, $(Fe_{0.5}, Mg_{0.5})_2SiO_4$, prepared by laser ablation (Brucato et al. 2002).

The experiment consists of adsorbing hydrogen atoms onto the surface while monitoring the amount of hydrogen molecules that are formed. To increase the signal

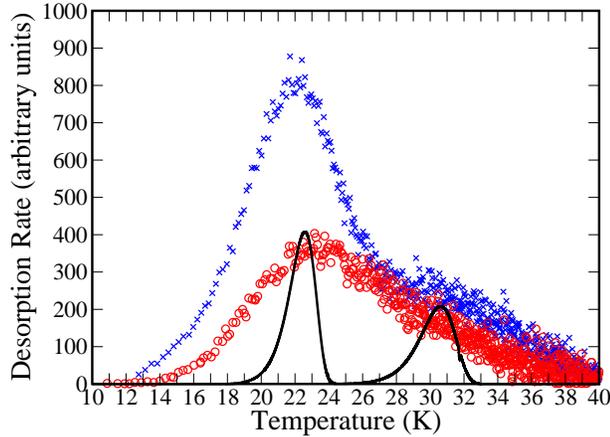


Fig. 2. TPD curves of HD desorption after irradiation of H+D atoms (\circ) and HD molecules (\times) on the amorphous silicate sample at surface temperature of 10K. The H+D data was fitted using the rate equation model (solid line).

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, at a surface temperature of $T_0 \simeq 5.6\text{K}$, and the formation of HD molecules was measured. In a separate experiment, a beam of HD molecules was irradiated on the same surface. During the TPD runs, the sample temperature was monitored as a function of time. 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 (Δ) and amorphous silicate (\circ) surfaces, with irradiation times of 120 s. The TPD curve following irradiation of HD molecules on an amorphous silicate surface is also shown (\times). 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 (Vidali et al. 2007), a third peak was

Table 1. Parameters for molecular hydrogen formation: the diffusion and desorption barriers of H atoms, the desorption barrier of HD molecules and the density of adsorption sites.

Material	$E_{\text{H}}^{\text{diff}}$ (meV)	$E_{\text{H}}^{\text{des}}$ (meV)	$E_{\text{HD}}^{\text{des}}$ (meV)	s (cm^{-2})
Polycrystalline Silicate	25	32	27	2×10^{14}
Amorphous Silicate	35	44	35, 53, 75	7×10^{14}

observed at higher temperatures (Fig. 2). We attribute this behavior to diffusion of HD molecules, which gradually migrate from shallow into deep adsorption sites (Perets et al. 2005, Amiaud et al. 2006). An analysis of experimental data for irradiation at higher temperature and from amorphous silicates with other Mg/Fe ratios will be given elsewhere.

The experimental results were fitted using the rate equation model described in Perets et al. (2005). The fits are shown as solid lines in Figs. 1 and 2. When a Gaussian distribution of activation energies is introduced around the reported barrier for each process, the solid lines follow the experimental traces much more closely (Perets et al. 2007). The parameters for the diffusion and desorption of hydrogen atoms and molecules on the amorphous silicate surface were obtained. These include the energy barrier $E_{\text{H}}^{\text{diff}}$ for the diffusion of H atoms and the barrier $E_{\text{H}}^{\text{des}}$ for their desorption. The value obtained for the desorption barrier of H atoms should be considered only as a lower bound, because the TPD results are insensitive to variations in $E_{\text{H}}^{\text{des}}$, as long as it is higher than the reported value. A justification for not considering explicitly the two isotopes (H and D) is given in Vidali et al. (2007). The desorption barriers of HD molecules adsorbed in shallow (lower temperature peak) and deep (higher temperature peaks) sites, are given by $E_{\text{HD}}^{\text{des}}(j)$, where $j = 1, 2$ and 3 , respectively. The density of adsorption sites, $s = 7 \times 10^{14}$ (cm^{-2}) on the amorphous silicate sample, was also obtained (Perets et al. 2007).

The recombination efficiency is defined as the fraction of hydrogen atoms adsorbed on the surface which come out as molecules. Using the parameters obtained from the experiments, we evaluated the recombination efficiency on amorphous silicate surfaces under interstellar conditions as a function of the grain temperature. The incoming flux was taken as 5.2×10^{-10} (ML s^{-1}). This flux corresponds to gas density of 10 (atoms cm^{-3}) and gas temperature of 100K. A window of high recombination efficiency is found 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 the recombination efficiency of hydrogen on amorphous silicates is high in this temperature range, which is relevant to diffuse interstellar clouds. Therefore, amorphous silicates seem to be good candidates for interstellar grain components on which hydrogen recombines with high efficiency. These results are in agreement with theoretical predictions on the effects of surface roughness (Cuppen & Herbst 2005). They also indicate that on amorphous surfaces, newly formed H_2 molecules are thermalized on the surface

and do not promptly desorb. Consequently, H₂ molecules formed on and desorbed from realistic *amorphous* interstellar dust are expected to have low kinetic energy and would probably not occupy excited vibrational or rotational states.

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