

Experimental Study of H₂ Formation on Ices

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Abstract. We present new experimental data and review previous experimental results on molecular hydrogen formation from atomic recombination on porous amorphous solid water (ASW) surfaces at temperatures from 10 K to 30 K, i.e. under conditions of relevance to cold dense interstellar clouds. We show that the desorption of molecular hydrogen formed on porous ASW surfaces is well described by a model, in which the molecules are assumed to be completely thermalized to the surface temperature and to be evenly distributed throughout the porous network of the ASW films. These results emphasize that, not only the chemical properties, but also the physical morphology of dust grain surfaces must be considered to obtain a full understanding of molecular hydrogen formation on interstellar dust grain surfaces.

1. Introduction

Molecular hydrogen is the most abundant molecule in the interstellar medium (ISM) and plays a pivotal role in the thermal and chemical development of interstellar dust and molecular clouds. There is no known effective gas-phase route for H₂ formation at the low number densities in interstellar clouds and it is the generally accepted view that H₂ is formed on the surface of interstellar dust grains. Observations indicate that H₂ formation must be a very efficient process under conditions ranging from those found in cold interstellar clouds to those found in photodissociation regions (PDRs). This entails that efficient H₂ formation mechanisms must exist on both ice-covered and bare dust grain surfaces and that these mechanisms must be efficient under grain temperatures ranging from 10 K to 30 K, or even higher (smaller dust grains might experience thermal spikes to much higher temperatures due to e.g. absorption of individual UV photons) and gas temperatures ranging from 10 K to several hundred Kelvin. In recent years several groups have embarked on experimental studies of molecular hydrogen formation under conditions of interstellar relevance. The studies include molecular hydrogen formation from weakly bound (physisorbed) states on carbonaceous and silicate surfaces (Katz *et al.* 1999), from strongly bound (chemisorbed) states on graphite (Zecho *et al.* 2002), and from physisorbed states on amorphous solid water (ASW) surfaces (Manicó *et al.* 2001; Roser *et al.* 2002; and Hornekær *et al.* 2003). In spite of all of these activities, the mechanisms behind molecular hydrogen formation in the ISM are not yet fully uncovered.

In the present paper we present new experimental data and review previous experimental results reported on in Hornekær *et al.* (2003) pertaining to molecular hydrogen formation under conditions of relevance to cold, dense interstellar clouds; e.g., molecular hydrogen formation on amorphous solid water (ASW) surfaces at temperatures from

10 K to 30 K. We show that the desorption of molecular hydrogen formed on porous ASW surfaces is well described by a model, in which the molecules are assumed to be completely thermalized to the surface temperature and to be evenly distributed throughout the porous network of the ASW films. These results emphasize that, not only the chemical properties, but also the physical morphology of dust grain surfaces must be considered to obtain a full understanding of molecular hydrogen formation on interstellar dust grain surfaces.

2. Amorphous Solid Water

Amorphous Solid Water (ASW) ice films furnish an ideal system for studying the influence of surface morphology on molecular hydrogen formation in the ISM. First, ASW ice is a well characterized porous system, which makes it possible to study molecular hydrogen formation on surfaces of controlled and varying porosity. Second, according to present models, the icy mantles on interstellar dust grains are composed predominantly of water ice with other molecular species, such as CO, CH₃OH, CO₂, NH₃, CH₄, O₂ and N₂, added in varying amounts (Tielens & Hagen 1982; D'Hendecourt *et al.* 1985). The majority of the water ice is formed in situ, by recombination of hydrogen and oxygen atoms to H₂O molecules on the grain surface, rather than by condensation of H₂O molecules from the gas phase (Jones *et al.* 1984). However, the absorption features of interstellar ice are well reproduced by the absorption features of ASW ice formed by vapor deposition of H₂O and kept at a temperature below 30 K (Hagen *et al.* 1981). Hence, we believe that ASW ice films formed by low-temperature vapour deposition constitute the best simple one-component model for icy mantles on interstellar grains.

The morphology of ASW films grown by vapor deposition on low-temperature substrates under vacuum at low deposition rates (a few ML s⁻¹ or lower) is known to depend on deposition temperature, deposition rate, angular distribution of the incoming water molecules and the thermal history of the ASW film after formation (Narten *et al.* 1976; Mayer & Pletzer 1986; Jenniskens & Blake 1994; Stevenson *et al.* 1999; Kimmel *et al.* 2001a,b; Parent *et al.* 2002). For deposition on low-temperature substrates (< 90 K), normal incidence water molecules produce non-porous ASW films, while off-normal incidence (or background dosing) produces porous films consisting of open networks of nanometer sized pores (Stevenson *et al.* 1999; Kimmel *et al.* 2001a,b). The ASW film porosity for non-normal or background dosing also depends on the growth temperature or subsequent annealing temperature of the film (Mayer & Pletzer 1986; Jenniskens & Blake 1994; Stevenson *et al.* 1999; Parent *et al.* 2002; Hornekær *et al.* 2005). For example, dosing or annealing at substrate temperatures above 90 K reduces the porosity strongly (Stevenson *et al.* 1999) and at temperatures above 120 K, fully non-porous ASW structures result (Rowland & Devlin 1991; Horimoto *et al.* 2002). At temperatures above ~136 K, crystallization into a cubic crystalline structure sets in and at even higher temperatures, the normal hexagonal crystalline ice structure is produced (Jenniskens & Blake 1994; Dohnalek *et al.* 2000). The porosity of ASW films can also be influenced by co-deposition of other gases (Bar-Nun *et al.* 1987).

Apart from changes in ASW film porosity with growth temperature, X-ray (Narten *et al.* 1976) and electron diffraction (Jenniskens & Blake 1994) experiments imply that ASW films grown at temperatures below 30 K arrange in a "local" chemical structure of higher density than ASW films grown at higher temperatures. This high-density state is referred to as the high-density amorphous (HDA) phase, while the low-density state obtained at temperatures above 30 K is referred to as the low-density amorphous (LDA) phase (Jenniskens & Blake 1994). Annealing ASW films in the HDA phase to

temperatures above 30 K results in a slow and irreversible phase transition to the LDA phase (Jenniskens & Blake 1994). It is important to distinguish between the high-density (HDA) and low-density (LDA) nomenclature introduced by Jenniskens *et al.* and the actual physical density of the ice. The physical density of the ice is determined both by its local chemical structure (HDA or LDA) and, even more importantly, by its morphology/porosity. Hence a porous HDA ice film can easily have a lower physical density than a non-porous LDA ice film.

In the following, we will restrict our characterization of the ices to their porosity, since experiments indicate that porosity, rather than local chemical bulk structure, is the most important factor for understanding chemical reactions and molecular desorption from ice surfaces (see e.g. Bar-Nun *et al.* 1985; Mayer & Pletzer 1986; Rowland *et al.* 1991; Takahashi *et al.* 1999; Watanabe *et al.* 2000; Sadtchenko *et al.* 2000; Ayotte *et al.* 2001; Horimoto *et al.* 2002; Hornekær *et al.* 2003; Collings *et al.* 2003; Hornekær *et al.* 2005).

3. Experimental Setup and Results

The experimental setup has been described in detail in Hornekær *et al.* (2005). All experiments are performed under ultrahigh vacuum (UHV) with a base operating pressure below 1×10^{-10} Torr. Porous amorphous solid water (ASW) films are grown by depositing deionized H₂O, purified by a series of freeze-thaw cycles, onto a 10 K Cu substrate. H₂O deposition is done from a capillary array doser positioned 5 mm from the sample surface with a $\sim 45^\circ$ HWHM angular spread. Typical dose rates are 0.3–3 monolayers sec^{-1} (ML s^{-1}). Under these H₂O deposition conditions and a surface temperature of $T_s \leq 10$ K, modestly porous ASW films are grown. Based on the angular distribution and the temperature of the sample we estimate a porosity of $\xi_{por} \simeq 0.1$ (where ξ_{por} is defined as the percentage increase in internal surface area per monolayer of ASW relative to the external surface area of the film; Kimmel *et al.* 2001), however, this estimate is somewhat uncertain. Although we have not made any independent studies of the nature of the porous distribution, we certainly anticipate that this forms a 3D interconnected network, as reported on previously in Stevenson *et al.* (1999) and predicted by ballistic growth models (Kimmel *et al.* 2001a,b).

H and D atomic beams are produced in separate microwave discharges and thermalized to 300 K by passing through phosphoric acid coated glass tubes. The beam dissociation probabilities range from 65–80 %. The beams pass through three differential pump stages before being admitted into the UHV chamber. The H beam has a diameter of 3.5 mm and is directed onto the center of the ASW film at normal incidence. The D beam has an incidence angle of 4° off normal and a diameter of 1.5 mm at the sample where it is overlapped with the H beam. The typical flux employed is $10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ or $\simeq 0.01 \text{ ML s}^{-1}$.

Temperature programmed desorption (TPD) measurements are performed by heating the sample with a 0.5 K s^{-1} linear ramp and detecting the desorbing species in a differentially pumped movable quadrupole mass spectrometer (QMS) fitted with a cone cap with a 3 mm aperture. During the TPD measurement the opening in the cone is moved to within 2 mm of the sample surface. Desorption of H₂, HD and D₂ can be monitored simultaneously. Molecular hydrogen formation is detected by monitoring the production of HD, which is not present in the atomic beams and can only be produced via surface reactions.

4. Model for TPD Spectra from Molecular Hydrogen Formation on Porous ASW Surfaces

Based on previous experimental results reported on in Hornekær *et al.* (2003), molecular hydrogen formation on ASW films is expected to be well described by a Langmuir-Hinshelwood, or hot-atom mechanism, in which H and D atoms are mobile at temperatures as low as 8 K, move into the pore-structure and recombine in the pores. The majority of the formed molecules are retained in the porous ASW film and thermalized to the ASW surface temperature. Subsequent desorption of the formed H₂ molecules during TPD experiments is therefore expected to follow the normal desorption kinetics for molecular hydrogen on ASW surfaces.

The desorption rate for hydrogen molecules adsorbed on a non-porous surface with binding energy E_b is:

$$\frac{d\Theta}{dt} = -k_0 e^{-E_b/k_B T_s} \Theta \quad (4.1)$$

where k_0 is the pre-exponential factor (typically of the order 10^{12} – 10^{13} s⁻¹), k_B is Boltzmann's constant, T_s is the surface temperature and Θ is the H₂ coverage on the surface.

To take the effect of porosity into account, the desorption rate can be modified by considering that only molecules in the top layer of the porous film can desorb directly into the gas phase. Molecules adsorbed in the porous structure might desorb locally, but will subsequently collide with the pore walls resulting in a high probability for re-adsorption. The net result is a series of desorption-re-adsorption events, in which the molecules perform a random walk in the porous structure until they finally reach the upper layers and are able to desorb directly into the gas phase. In this picture, the measured desorption from the sample is not proportional to the total H₂ coverage, but instead to the H₂ coverage in only the top layer at the vacuum interface. If we assume that the molecules diffuse sufficiently fast to be evenly distributed throughout the ASW film, then the coverage in the top layer, Θ_s , for a N_l monolayer thick ASW film with porosity ξ_{por} is given by: $\Theta/(1 + N_l \xi_{por})$, where Θ is the total H₂ dose adsorbed on the surface. The coverage in the pores is in turn given by: $\Theta N_l \xi_{por}/(1 + N_l \xi_{por})$. Assuming fast diffusion and a uniform H₂ distribution throughout the film then leads to the following modification of the expression for the H₂ desorption rate for a single fixed binding energy E_b of H₂ on the surface:

$$\frac{d\Theta}{dt} = -k_0 e^{-E_b/k_B T_s} \Theta_s = -k_0 e^{-E_b/k_B T_s} \frac{1}{1 + N_l \xi_{por}} \Theta \quad (4.2)$$

This simple model predicts an upwards shift in the TPD peak with increasing ASW film thickness, since the pre-factor scales as $\propto 1/(1 + N_l \xi_{por})$.

One limitation of the model is the assumption of a single binding energy for H₂ on the ASW surface. Experiments show that in reality a wide distribution of binding energies exists (Hornekær *et al.* 2005). However, in the low-coverage limit the molecules preferentially occupy the high energy binding sites and the assumption of a single binding energy is more realistic.

5. Experimental Results and Comparison with Model TPD Spectra

Figure 1(a) shows background subtracted HD TPD spectra from a 1500 ML porous ASW film, after deposition of H and D atoms at a surface temperature of 10 K. Deposition times vary from 1 to 10 min. At a flux of 0.01 ML s⁻¹ and a porosity of $\xi_{por} = 0.1$, a

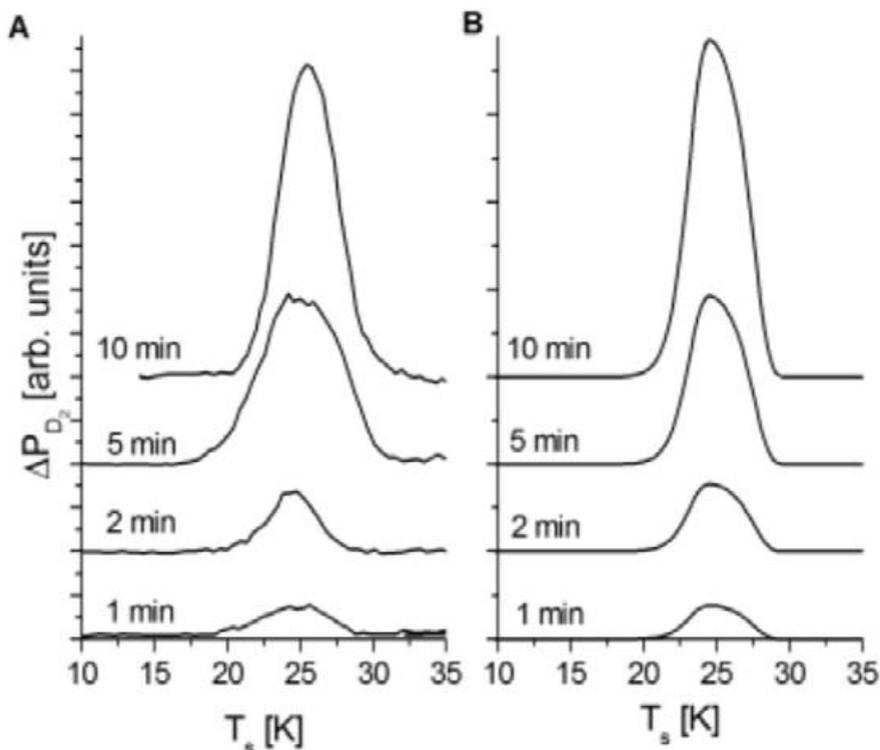


Figure 1. (a) TPD spectra after increasing doses of H and D atoms on a 1500 ML porous amorphous solid water film cooled to 10 K. The employed ramp rate is 0.5 K s^{-1} . The TPD traces have been offset for clarity. (b) Modelled TPD spectra assuming molecular desorption as described in eq. 4.2. The TPD traces have been offset for clarity.

10 min dose on a 1500 ML ASW film corresponds to a coverage of 0.04. Hence, even at the longest dose time employed we are in the low-coverage limit. A single peak at 25 K is visible in all the spectra. The fact that the peak temperature is independent of coverage indicates that the desorption is a first-order process; i.e., that the recombination of H and D atoms takes place prior to molecular desorption and that the formed molecules have been thermalized to the surface temperature before desorbing. As discussed in § 3 the desorption kinetics of HD molecules formed on the surface should therefore be well described by the same desorption kinetics as H₂ molecules deposited onto the ASW surface as molecules, i.e. the desorption kinetics described in § 3.

The binding energy for a D₂ molecule on a porous ASW surface in the low coverage limit is around 59 meV (Hørnekær *et al.* 2005). A zero-point corrected binding energy for an HD molecule on a porous ASW film is then approximately 56 meV.

Figure 1(b) shows simulated TPD spectra based on the model described in Eq. 4.2. The molecules are assumed to distribute evenly between sites with binding energies ranging from 52–60 meV. The only free parameter is the detection efficiency. This has been normalized to obtain the same total peak area in theory and experiment for the 10 min. dose. As can be seen the simple model provides a reasonably good fit to the experimental data.

The fact that desorption of HD molecules formed on the ASW surface is a first-order process and can be described by the same kinetics as desorption of H₂ molecules deposited onto the surface as molecules (adjusting for the difference in zero-point energy) rebuts

earlier models of molecular hydrogen formation on porous ASW surfaces, according to which HD desorption was described as a second-order process with thermally activated atomic diffusion as the rate limiting step (Manicó *et al.* 2001).

6. Conclusion

We have presented new experimental data on molecular hydrogen formation on porous amorphous solid water films at low temperature. The data show that the desorption of HD molecules formed on the ASW surface is a first-order process, which is well described by molecular desorption kinetics from porous ASW films. This indicates that the recombination of H and D atoms takes place prior to molecular desorption and that the formed HD molecules have been thermalized to the surface temperature before desorbing. Additional experimental data reported on in Hornekær *et al.* (2003) indicate that H and D atoms are mobile and recombine on ASW surfaces at temperatures as low as 8 K. After recombination, the molecules are retained in the porous structure and thermalize to the surface temperature. The rate limiting step in desorption of the formed HD molecules is therefore not atomic diffusion and recombination, but molecular desorption. The porosity of the ASW film plays a double role, by both facilitating the retainment of newly formed molecules and by reducing the desorption rate of the molecules. Even though the experiments have only been performed on porous ASW surfaces, we expect that the reported results can be extended to other materials exhibiting nanometer scale porosity, and that they therefore are potentially relevant for molecular hydrogen formation and desorption in diffuse clouds, where molecular hydrogen is formed on bare carbonaceous and silicate grains. Laboratory experiments on interstellar carbon dust grain analogues indicate that these could very well exhibit porosity on the nanometer scale (Schnaiter *et al.* 1999). Hence, to correctly describe both dust grain chemistry and desorption from dust grain surfaces, further knowledge of interstellar dust grain morphology is needed.

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Discussion

KROES: Have you performed, or will you perform, experiments on non-porous ice to see if H₂ then desorbs immediately upon its formation?

HORNEKÆR: We have performed experiments showing that if any HD molecules form on non-porous ASW surfaces, then they are not retained on the surface after formation. However, with our experimental setup we cannot detect HD molecules, which form during atom deposition and immediately desorb. Hence, we cannot say for sure whether any HD forms on these surfaces. Fortunately this question will probably be answered in the coming years by the group of Stephen Price at UCL.



Photo: E. Herbst