Mem. S.A.It. Suppl. Vol. 19, 85

Memorie della
Supplementi

Changes in the Morphology of Interstellar Ice Analogues after Hydrogen Atom Exposure

M. Accolla[1], E. Congiu[2], F. Dulieu[2], V. Pirronello[3] and J. L. Lemaire[2]

[1] INAF – Osservatorio Astronomico di Capodimonte, Salita Moiariello 16, 80131 Napoli, Italy
[2] Université de Cergy-Pontoise & Observatoire de Paris, LERMA, UMR 8112 du CNRS, 95000 Cergy-Pontoise, France
[3] Universitá di Catania, DMFCI, Viale Doria 6, 95125 Catania, Italy
e-mail: mario.accolla@gmail.com

Abstract. The morphology of water ice in the interstellar medium is still an open question. It is known that in the dark clouds H_2 formation occurs on the icy surface of dust grains and that part of the energy (4.48 eV) released when adsorbed atoms react to form H_2 is deposited in the ice. The experimental work described in the present work focuses on how relevant changes of the ice morphology result from atomic hydrogen exposure and subsequent recombination. Using the temperature-programmed desorption (TPD) technique and a method of inversion analysis of TPD spectra, we show that there is an exponential decrease in the porosity of the amorphous water ice sample following D-atom irradiation. Under interstellar conditions, this effect is likely to be efficient and, together with other compaction processes, provides a good argument to believe that interstellar ice is amorphous and non-porous.

Key words. Interstellar Ices – Hydrogen Exposure – Morphology of Ices – Laboratory Simulations – Molecular Clouds – TPD Experiments

1. Introduction

Spectroscopic observations of cold and dense clouds show the presence of "dirty ice" mantles on dust grains, mainly composed by water molecules. These ices are enriched by the presence of other simple species that are either formed by surface reactions or accreted from the gas phase. While there is quite a general consensus that interstellar water ice is mainly amorphous, its morphology (porous or compact) still remains poorly known. Morphology is important due to its influence both on the catalytic efficiency of grain surfaces and on the release to the grain of the fraction of the formation energy of species, as shown by laboratory simulations of molecular hydrogen formation (Hornekar et al. 2003).

Ice porosity may be identified through the weak infrared absorption features (≈ 2.7 μm) showing the presence of dangling bonds on the pore surface. To our knowledge, there has been to date no detection of such absorptions in the infrared spectra of interstellar ices, perhaps suggesting that they may have a compact nature (Keane et al. 2001). It has been already investigated that interstellar porous ice may be compacted by the transient heating of

Send offprint requests to: M. Accolla

stellar radiation (Chakarov & Kasemo 1998) and cosmic ray bombardment (Palumbo 2006).

In this paper we report on our experimental work: it is shown that a thin highly porous ice film is gradually changed into a more compact structure following atomic hydrogen exposure. This is probably due to the transient heating caused by the energy released to the ice during H_2 formation. Such a process may also produce in the interstellar space compact amorphous ice mantles concurrently with the other envisaged processes.

2. Experimental procedures

The experiments described in this paper are performed using the set-up FORMOLISM (FORmation of MOLecules in the InterStellar Medium) located at the astrophysical laboratory of the University of Cergy-Pontoise (France). The main tool of analysis is the quadrupole mass spectrometer (QMS) able to monitor the desorbing species during TPD experiments. Details of this tecnique and of the set-up FORMOLISM can be founded elsewhere (Amiaud et al. 2006).

The thermal desorption of a molecule previously deposited on it is a powerful method to characterize the morphology of an ice. In our experiments, D_2 molecules serve as probe molecule to characterize the ice morphology (Fillion et al. 2009). Fig. 1 shows a comparison between several TPD spectra of D_2 from a compact ASW, i.e. from a compact amophous solid water (curve a) and from different thickness of highly porous ices grown over compact ice (curves b, c, d and e). These TPD spectra show obviously a high sensitivity to the ice surface roughness: their peaks shift towards higher temperatures as the porous ice network is progressively formed. D_2 molecules have completely desorbed by 21 K in the case of the compact non-porous substrate. When a layer of porous ice is deposited on the surface, D_2 is more bound to the ice surface and the desorption occurs at higher temperatures. In other words, increasing the porous ice thickness favours the formation of more energetic binding sites.

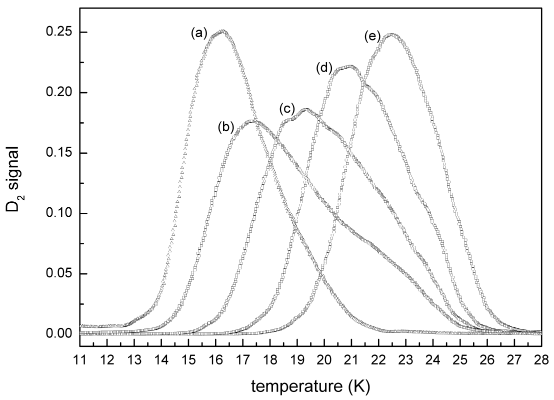

Fig. 1. Comparison of TPD spectra obtained after equivalent D_2 exposure (~ 0.15 ML) from compact ice (**a**) and from different thickness of highly porous ices grown over a compact ice: compact + 1ML porous ASW (**b**), compact + 2ML porous ASW (**c**), compact + 4ML porous ASW (**d**) and compact + 8ML porous ASW (**e**).

3. Experimental results

TPD spectra of a fraction of a monolayer of D_2 molecules are performed before and after D-atoms exposure of the porous ASW film to probe its morphology and the possible loss of porosity as a function of D-atom fluence. Fig. 2 shows the effects of D-atom exposure on the morphology of a 4-ML porous ASW film. The solid line represents a D_2 desorption spectrum from compact ice, while the open squares show the thermal D_2 desorption from a non-irradiated 4-ML porous ASW ice. The other TPD spectra of Fig. 2 show D_2 desorption after subsequent D-atom bombardment of the porous ice sample kept at 10 K. Increasing the D-atom fluence, a progressive shift of the desorption peaks appears towards lower temperatures, as the arrows indicate in the figure. Our set of experiments demonstrates that this effect is strictly due to D-atom irradiation of the ice. In fact, no changes of the ice morphology (namely, no changes of the TPD spectra) are observed in a porous ice film even after long exposures to molecular deuterium.

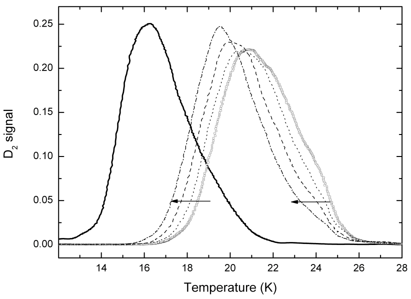

Fig. 2. Normalized TPD spectra of 0.11 ML of D_2 from compact ASW (solid line) and of 0.17 ML of D_2 from a 4-ML porous ASW film as deposited (open squares), after 64 min (dotted line), after 224 min (dashed line) and 288 min (dash-dot line) of D-atom irradiation. The arrows are meant to emphasize the shift of the TPD curves towards lower temperatures following D-atom irradiation.

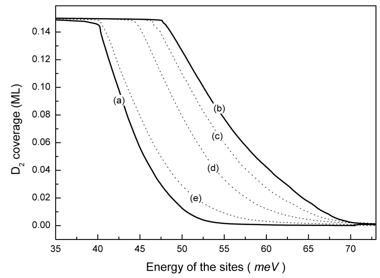

Fig. 3. D_2 coverage vs desorption energy. It is evaluated the distribution of the adsorption sites for a compact ASW (**a**), for 1 ML of porous ice, before D-atoms exposure (**b**) after 64 min (**c**), 160 min (**d**) and 224 min (**e**) of D-atoms exposure.

3.1. Analysis by direct inversion of TPD curves

It is known that each TPD spectrum follows the *Polanyi-Wigner equation* (Redhead 1962). By inverting this equation, the desorption energy can be evaluated as a function of the coverage, namely the number of molecules still adsorbed on the surface (Zubkov et al. 2007):

$$E_\vartheta = -kT\ ln(r/A\vartheta) \qquad (1)$$

where r is is the rate of desorption, A is the pre-exponential factor, ϑ is the number of molecules adsorbed, E_ϑ is the energy barrier for desorption, k is the Boltzmann constant and T is the absolute temperature of the surface.

Fig. 3 displays the D_2 coverage on a 1-ML porous ASW film as calculated using Eq. (1) vs. the desorption energy E_ϑ. These curves give us the number of D_2 molecules still bound to the ice sample as a function of their binding energy. Growing an overlayer of porous ice increases not only the number of adsorption sites but also the energy distribution of binding sites associated to the ASW ice surface. This analysis emphasizes the existence of a small fraction of more energetic adsorption sites that are not present on compact ASW. We can see that binding sites with energy greater than 53 *meV* are certainly to be assigned to porous water ice. On the other hand, binding sites with lower energy may belong to either a compact or a porous water substrate. The binding sites below this energy range are those from which D_2 molecules desorb at a temperature below 21 K (see Fig. 1).

Moreover, Fig. 3 shows that for 1 ML the number of the most energetic binding sites decreases gradually with the increase of the D atom fluence on the ice sample. This confirms the progressive destruction of the porous binding sites, namely the compaction of the water ice sample after D-atoms exposure.

Therefore, this experimental technique allows us to derive the binding-energy distribution of each porous ASW sample before and after irradiation, enabling to follow their evolution as the surface roughness becomes smoother.

3.2. Influence of the thickness of the ice

The compaction of porous ASW ice due to D-atom irradiation was investigated for various thickness of the ice film. Fig. 4 summarizes all the experiments performed in the present study, i.e., for porous ice thickness of 1 ML, 2 ML, 4 ML, 6.5 ML and 8 ML. In Fig. 4, we show the normalized fraction of D_2 molecules with adsorption energy greater than 66 meV (corresponding adsorption energy of

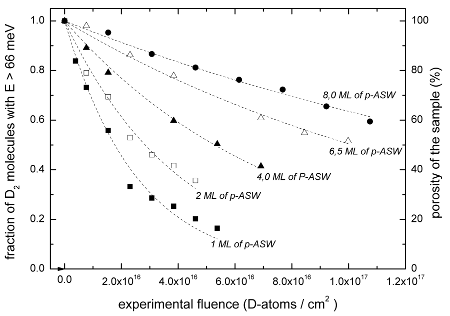

Fig. 4. Fraction of D_2 molecules remaining on the ice surface in sites of depth larger than 66 meV vs D-atoms fluence, for different thicknesses of ice: 1 ML plain squares; 2 ML empty squares; 4 ML plain triangles; 6.5 ML empty triangles; plain circles 8 ML.

molecules coming off at a surface temperature greater than 22.5 K). We quantified the porosity of each ASW ice sample as the surface area subtended by the TPD trace for temperatures greater than 22.5 K, since in this range the desorbing molecules were almost certainly adsorbed on porous binding sites. In fact, the trailing edges of the TPD curves give information on the distribution of adsorption sites available in the ice, providing thus a signature of the water ice surface roughness.

We can see in Fig. 4 that, for each ice thickness, the number of molecules that can adsorb on the surface with an energy larger than 66 *meV* decreases gradually as the D-atoms fluence is increased on the porous ice sample.

4. Astrophysical implication

In this last section, we want to assess the time necessary to achieve a considerable destruction of porosity as it applies to an interstellar dense cloud. Actually, we want to know whether or not the decrease of the ice porosity by atomic hydrogen exposure is astrophysically relevant.

We have evaluated that, in the case of very thin ice films ($\leq$ 10 ML), the ice compaction is completed in a lapse of time shorter than the estimated lifetime of a molecular cloud, 3×10^7 - 5×10^8 years (Palumbo 2006). For thicker ices, the time of compaction is, however, at least comparable to the time icy mantles suffer H-irradiation, being $\approx 2\times10^7$ years.

To conclude, we can say that the compaction of porous water ice in consequence of H-atoms recombination should be a very efficient process whenever H-atoms are far more abundant than O-atoms. Hence, on the basis of our and other laboratory results, interstellar water ice undergoes a compaction process that is the result of H-atom irradiation, cosmic ray and UV bombardment. These experimental evidences lead us to suggest that water ice in space is almost certainly amorphous and compact (non-porous).

References

Amiaud, L. et al., 2006 J. Chem. Phys., 124, 094702

Chakarov, D. & Kasemo, B. 1998, Phys. Rev. Lett, 81, 5181

Fillion, J. H. et al., 2009,Phys. Chem. Chem. Phys.,11, 4396

Hornekar, L. et al. 2003, Science, 302, 1943;

Jenniskens, P. & Blake, D. F. 1994, Science, 265, 753

Keane, J. V. et al. 2001, A&A, 375, L43

Palumbo, 2006, Astron.Astrophys., 453, 903

Redhead, P. A. 1962, Vacuum, 12, 203

Zubkov, T. et al. 2007, J. Chem. Phys., 127, 184707