

# The morphology of interstellar water ice

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**Abstract.** We have studied, by infrared absorption spectroscopy, the effects of ion irradiation (with 200 keV protons) on the morphology/porosity of thin amorphous water ice ( $\text{H}_2\text{O}$ ) samples at 15 K. We have found that the intensity of the OH dangling bond feature decreases after ion irradiation and that the amount of carbon monoxide (CO) absorbed in water ice decreases as the fluence of impinging ions increases. These results indicate that the porosity of amorphous water ice decreases after ion irradiation. Here we present the experimental results and suggest that because of cosmic ray bombardment water ice in interstellar grain mantles is compact in structure.

## 1. Introduction

It has been shown that amorphous water ice has a porous structure (Rowland et al. 1991) characterized by micro-pores where OH dangling groups are present. Furthermore its morphology/porosity depends on experimental conditions such as temperature, deposition rate and growth angle (e.g., Hagen et al. 1983; Jenniskens & Blake 1994; Kimmel et al. 2001a, 2001b; Dohnáleck et al. 2003). The morphology of water ice also depends on the effects of ion and UV photon irradiation (e.g., Baratta et al. 1991; Moore & Hudson 1992; Leto & Baratta 2003). When amorphous ice is irradiated a modification of the profile of the  $3300\text{ cm}^{-1}$  band is also observed (Leto et al. 1996; Leto & Baratta 2003). However based only on the study of the profile of the  $3300\text{ cm}^{-1}$  band no definitive conclusions can be drawn on the morphology of amorphous water after irradiation. The infrared spectrum of pure carbon monoxide at low temperature shows an absorption feature at about  $2140\text{ cm}^{-1}$  ( $4.67\text{ }\mu\text{m}$ ) due to the fundamental vibration  $\text{C}\equiv\text{O}$ . The profile (shape, width, and peak position) of the solid CO band strongly depends on the host molecules when it is mixed in with other species (e.g., Sandford et al. 1988; Palumbo & Strazzulla 1993). In particular, the band profile of CO in a  $\text{H}_2\text{O}$  matrix is very peculiar, showing two features at about  $2138\text{ cm}^{-1}$  and  $2152\text{ cm}^{-1}$ . It has been shown that both bands are due to CO molecules in the micro-pores with the  $2152\text{ cm}^{-1}$  band due to the interaction of CO molecules with the OH dangling groups of the pore surface while the  $2138\text{ cm}^{-1}$  feature has been tentatively identified with CO molecules interacting with the oxygen atoms of the pore-surface water molecules (e.g., Devlin 1992; Palumbo 1997; Al-Halabi et al. 2004). Simple molecules, such as  $\text{H}_2$ ,  $\text{N}_2$ , CO, Ar, and  $\text{CH}_4$ , absorbed in amorphous or crystalline water ice are often used as a probe to study the properties of water ice. This can be achieved by looking at both the profile of the OH dangling bond (db) feature present in porous amorphous ice and on the surface of large crystalline ice clusters (Rowland et al. 1991; Hixon et al. 1992) and at

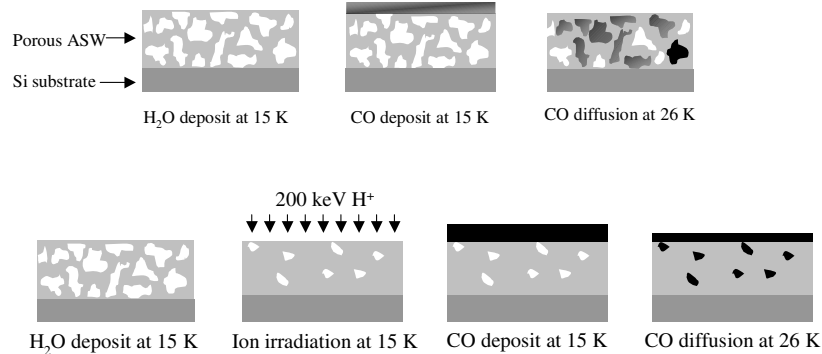
the profile of the absorbed species as in the case of carbon monoxide (Devlin 1992; Palumbo 1997; Fraser et al. 2004).

Here we present new experimental results meant to study the morphology of amorphous solid water after ion irradiation. Both the behaviour of the OH db feature and the amount of CO adsorbed in water ice after diffusion have been used to investigate the evolution of icy samples after ion irradiation.

## 2. Experimental procedure

Icy samples have been prepared in a stainless steel vacuum chamber where pressure is kept at  $10^{-7}$  mbar. A crystalline silicon substrate, is placed in thermal contact with a cold finger which temperature can be varied between 300 K and 10 K. The vacuum chamber can be placed in the sample compartment of an infrared spectrometer (Bruker Equinox 55) and transmission spectra are obtained through the KBr windows and a hole in the final tale of the cold finger which allows the infrared beam to transmit through the substrate and the sample. A leak valve is used to admit gaseous species into the chamber, where they freeze out on the substrate. The gas inlet is not directed towards the substrate, thus a “background deposition” is obtained. The vacuum chamber is interfaced to an ion implanter (200 kV; Danfysik) from which ions with energy up to 200 keV (400 keV for double ionisations) can be obtained. Results presented in this paper have been obtained using 200 keV  $H^+$  ions. In all these experiments the penetration depth of impinging ions was larger than the ice sample thickness. The ion beam produces on the target a spot larger than the area probed by the infrared beam. A current integrator on the path of the ion beam measures the charge which reaches the sample during irradiation. Ion current density ranges between  $100 \text{ nA cm}^{-2}$  and few  $\mu\text{A cm}^{-2}$  in order to avoid a macroscopic heating of the sample. The substrate holder forms an angle of  $45^\circ$  both with the infrared beam and the ion beam. This configuration offers the advantage that spectra can be taken in situ, even during irradiation, without tilting the sample. A rotatable polarizer is placed in the path of the infrared beam. This gives the opportunity to take spectra with the electric vector parallel (P polarized) and perpendicular (S polarized) to the plane of incidence. In fact at oblique incidence spectra taken in P polarization may show added features for strong transitions that are related to the strong variation of the real part of the refractive index ( $n$ ) and do not correspond to any peak of the imaginary part ( $k$ ) (Baratta & Palumbo 1998). Furthermore it has been shown (Baratta et al. 2000) that taking spectra in both polarizations it is possible to know whether laboratory spectra of thin films are representative of small particle extinction spectra. All the spectra here shown have been ratioed to a background spectrum which includes the substrate, have been taken with a resolution of  $1 \text{ cm}^{-1}$  and use S polarization which is more directly comparable with other experiments at normal incidence described in the literature. Further details on the experimental set up can be found in Baratta & Palumbo (1998) and Strazzulla et al. (2001).

The experimental procedure followed to perform diffusion experiments is schematically shown in Fig. 1. In a blank experiment (top part of Fig. 1) CO was deposited on top of the water ice sample (about  $0.25 \mu\text{m}$ ) at 15 K and then the sample was warmed-up to 26 K. At this temperature CO molecules diffuse in the porous ice underneath and a  $H_2O:CO$  mixture is obtained. Then the temperature of the sample has been raised in a stepwise fashion up to the water sublimation temperature. Transmission infrared spectra, in P and S polarizations, have been recorded at each step of this procedure. In the irradiation experiments (bottom part of Fig. 1), the water ice sample has been irradiated with 200 keV  $H^+$  ions. After irradiation, CO was deposited on top of the irradiated ice at 15 K and then the sample has been warmed up to allow diffusion of CO in the ice underneath. Again, transmission infrared spectra, in P and S polarizations, have been recorded at each step of this procedure. This experimental procedure has been repeated in order to test the diffusion of CO in water ice samples irradiated at different ion fluences.

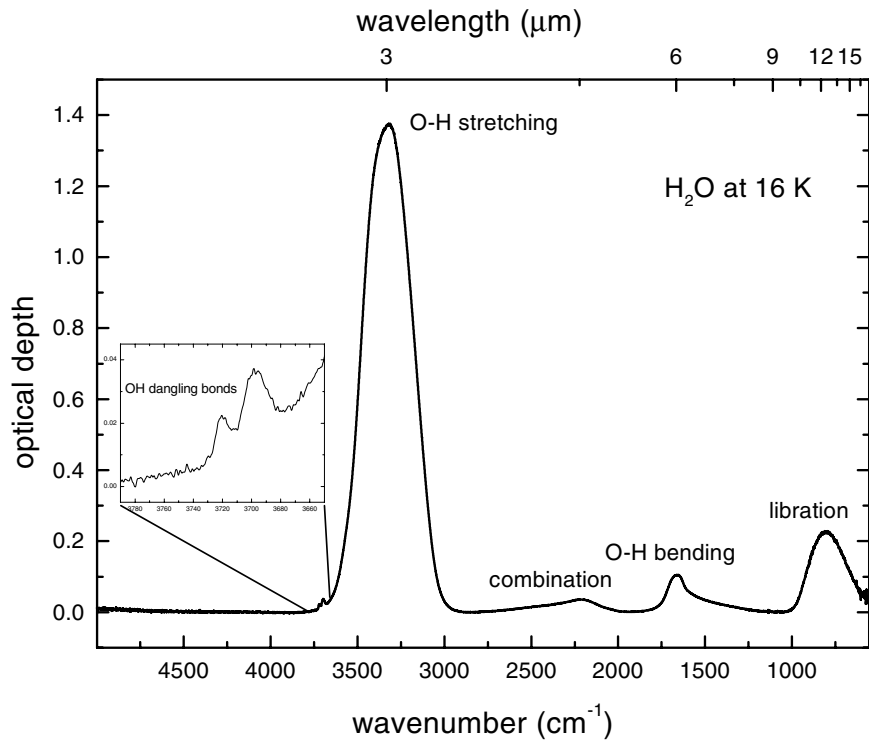


**Figure 1.** Schematic depiction of the experimental procedure.

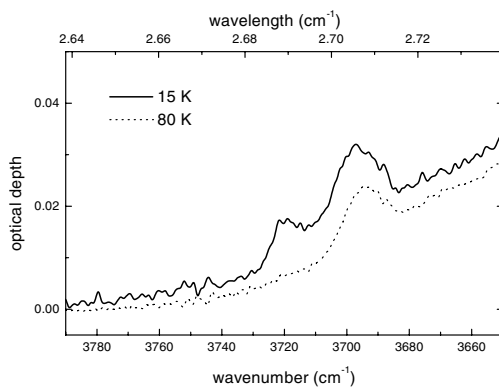
### 3. Results and discussion

The mid-infrared spectrum of amorphous solid water (ASW; see Fig. 2) shows absorption bands at about  $3300\text{ cm}^{-1}$  ( $3.03\text{ }\mu\text{m}$ ; due to the O–H symmetric and anti-symmetric stretching modes),  $2205\text{ cm}^{-1}$  ( $4.53\text{ }\mu\text{m}$ ; combination mode),  $1650\text{ cm}^{-1}$  ( $6.06\text{ }\mu\text{m}$ ; overtone of the libration mode and H–O–H bending mode),  $803\text{ cm}^{-1}$  ( $12.4\text{ }\mu\text{m}$ ; libration mode). In addition a small feature is present, on the short wavelength wing of the O–H stretching modes band, due to OH dangling bonds (db) in the micro-pores of the amorphous structure. This feature shows two peaks at  $3720\text{ cm}^{-1}$  and  $3696\text{ cm}^{-1}$  due to two-coordinate and three-coordinate water molecules respectively (e.g., Rowland et al. 1991). Figures 3 and 4 show that the profile of the OH dangling bond feature depends on the temperature of the ice samples and on the presence of other species mixed in with water ice. In particular in Fig. 3 the spectra of a pure water ice sample, in the  $3800\text{--}3650\text{ cm}^{-1}$  range, at 15 K and at 80 K are shown. Figure 4 compares the profile of the OH db feature in pure ASW with that in  $\text{H}_2\text{O}:\text{CO}$ ,  $\text{H}_2\text{O}:\text{CO}_2$  and  $\text{H}_2\text{O}:\text{N}_2$  mixtures. In the case of  $\text{H}_2\text{O}:\text{CO}_2$  mixtures the bands at about  $3700\text{ cm}^{-1}$  and  $3600\text{ cm}^{-1}$  are due to combination modes of  $\text{CO}_2$ . Figure 5 shows the decrease of the integrated intensity (area) of the OH dangling bond feature normalized to the initial value as a function of ion fluence. A similar trend has also been observed after ion irradiation of pure water ice at 80 K (Raut et al. 2004) and of  $\text{H}_2\text{O}:\text{N}_2$  ice mixtures at 16 K (Palumbo & Strazzulla 2003). Figure 6 reports the fraction of deposited CO which diffuses in water ice underneath after the ice sample has been irradiated with 200 keV protons. It is evident that this fraction decreases as the ion fluence increases. At the highest fluence investigated ( $6.2 \times 10^{15}\text{ }200\text{ keV H}^+\text{ cm}^{-2}$ ), no CO molecules diffuse in the water sample. Thus we conclude that the porosity of amorphous water ice decreases after ion irradiation. The solid lines in Figs. 5 and 6 are a fit of the experimental data with an exponential curve  $y = e^{-\sigma\Phi}$  where  $\Phi$  is the ion fluence in ions  $\text{cm}^{-2}$ . From the fit the resulting cross sections are  $\sigma = 4.13 \times 10^{-14}\text{ cm}^2$  and  $\sigma = 1.14 \times 10^{-14}\text{ cm}^2$  respectively.

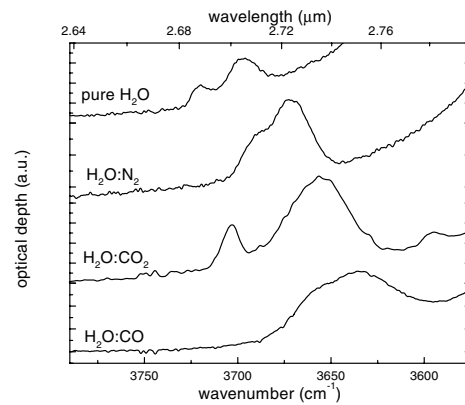
It is generally accepted that interstellar water ice forms because of surface reactions on grain mantles at low temperature (about 10 K). Thus interstellar water ice is believed to be mainly amorphous (Hagen et al. 1981). However we have a very poor knowledge of its morphology and in particular of its porosity. It has been suggested (e.g., McCoustra & Williams 1996) that the detection of the OH dangling bond feature in interstellar spectra would have given important information on the properties of water ice. This feature was predicted to have a detectable strength and should have been seen with the Infrared Space Observatory (ISO). However, so



**Figure 2.** Mid-infrared spectrum of amorphous solid water.

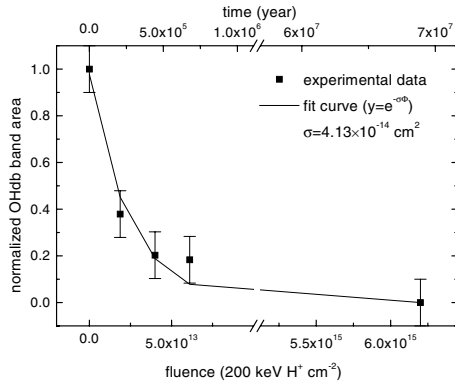


**Figure 3.** Profile of the OH db of pure water ice at 15 K and 80 K.

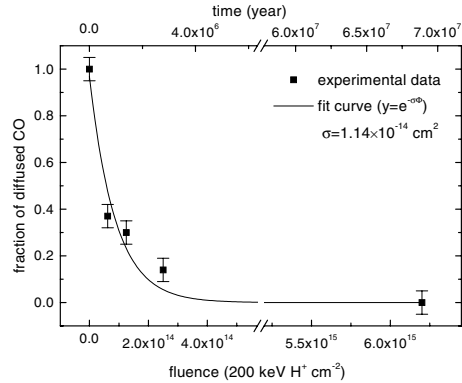


**Figure 4.** Profile of the OH db feature in different ice mixtures at 15 K.

far, no clear detection of this feature has been reported (e.g., Keane et al. 2001). A detailed study (Fraser et al. 2004) of the profile of the interstellar solid CO band based on high signal to noise ratio observations towards low-mass stars forming clouds (Pontoppidan et al. 2003) indicates that interstellar water ice is compact. Laboratory experiments have shown that when carbon monoxide is mixed in with water ice a feature appears at  $2152\text{ cm}^{-1}$  due to the interaction of CO with OH dangling bonds (e.g., Sandford et al. 1988; Devlin 1992; Palumbo 1997). This feature has been extensively searched for through the spectra of interstellar ices and never detected. The good quality of available observations leads to the conclusion that interstellar solid CO molecules



**Figure 5.** Normalized integrated intensity of the OH dangling bond feature of amorphous solid water after ion irradiation with 200 keV  $H^+$  ions.



**Figure 6.** Fraction of deposited CO which diffuses in amorphous solid water after the ice sample has been irradiated with 200 keV  $H^+$  ions as a function of ion fluence.

do not interact with the OH dangling bonds of solid water (Pontoppidan et al. 2003; Fraser et al. 2004). The compact nature of interstellar water ice and then the absence of OH dangling bond could be one possible explanation of the non detection of the  $2152\text{ cm}^{-1}$  feature. Furthermore the asymmetric profile of the interstellar CO feature presents a component at  $2136\text{ cm}^{-1}$ . This was formerly known as the broad component or polar component (e.g. Tielens et al. 1991; Chiar et al. 1995; Teixeira et al. 1998). After Pontoppidan et al. (2003) this is known as the red component. Based on laboratory spectra this component has been attributed by Fraser et al. (2004) to solid CO embedded in compact water ice. The existence of compact ice would prevent small molecules (such as CO) to diffuse into water ice. This is consistent with the hypothesis that the  $2139\text{ cm}^{-1}$  component of the observed interstellar solid CO feature is due to CO-ice layers accreted on other ice layers. This suggests that CO- $H_2O$  containing interstellar ices are best represented by a layered ice model rather than a mixed ice (Fraser et al. 2004).

It is possible that after surface reactions only compact amorphous water ice forms on interstellar grains. Alternatively, we have presented experimental results which show that after ion irradiation the porous structure of water ice collapses and the ice becomes compact. In order to estimate the time necessary to obtain the effects, observed in the laboratory, in interstellar dense clouds we consider the approximation of monoenergetic 1 MeV protons and assume that in dense interstellar regions the 1 MeV proton flux is equal to  $1\text{ proton cm}^{-2}\text{ s}^{-1}$  (see Mennella et al. 2003 for a detailed discussion). However our experimental results are obtained using 200 keV protons. Thus in order to extrapolate the laboratory results to the interstellar medium conditions we assume that they scale with the stopping power ( $S$ ) of impinging ions. In the case of protons impinging on pure water ice  $S(200\text{keV})/S(1\text{MeV})$  is 2.9. With these hypotheses in mind we have indicated in Figs. 5 and 6 timescale axes (top x-axis) which give an estimation of the time (years) necessary to obtain the effects, observed in the laboratory, on interstellar ices. As reported by Greenberg (1982) dense cloud lifetime ranges between  $3 \times 10^7$  and  $5 \times 10^8$  years. Assuming  $n_0 \sim 10^4\text{ cm}^{-3}$ , the gas takes  $10^9/n_0 \simeq 10^5$  years to condense on grains (Tielens & Allamandola 1987). Thus, icy grain mantles suffer cosmic ray irradiation for about  $10^5 - 10^8$  years. The first estimate refers to the case of icy mantles which sublime as soon as they are formed (which could be the case for volatile species such as CO), the latter estimate refers to the limit case of icy mantles which survive for all the cloud lifetime (which could be the case for less volatile species such as  $H_2O$ ). Figure 5 shows that after about  $1 \times 10^6$  years the integrated intensity of the OH dangling bond feature is reduced to 10% of the value it would have without

the effects of cosmic ray bombardment. This period is shorter than the estimated lifetime of water ice mantles in dense clouds.

Here we conclude that because of cosmic ray irradiation interstellar water ice is amorphous and non porous. This would explain why the  $2152\text{ cm}^{-1}$  band and the OH dangling bond feature have never been detected in interstellar spectra. Recently, Mennella et al. (2004) have suggested that the  $2136\text{ cm}^{-1}$  component of the observed CO profile is formed after cosmic ray bombardment of carbon grains covered with water ice mantles. In fact laboratory experiments have shown that carbon monoxide molecules form after ion irradiation when water ice is deposited on top of carbon grains. The profile of the CO band formed well resembles, in peak position and width, the observed red component. This suggestion would explain the presence of CO embedded in compact water and simultaneously the smooth profile of the  $3\text{ }\mu\text{m}$  interstellar water ice band.

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### References

- Al-Halabi A, Fraser H J, Kroes G J and van Dishoeck E F 2004 *Astron. Astrophys.* **422** 777  
 Baratta G A and Palumbo M E 1998 *J. Opt. Soc. Am A* **15** 3076  
 Baratta G A, Leto G, Spinella F, Strazzulla G and Foti G 1991 *Astron. Astrophys.* **252** 421  
 Baratta G A, Palumbo M E and Strazzulla G 2000 *Astron. Astrophys.* **357** 1045  
 Chiar J E, Adamson A J, Kerr T H and Whittet D C B 1995 *Astrophys. J.* **455** 234  
 Devlin J P 1992 *J. Phys. Chem.* **96** 6185  
 Dohnálek Z, Kimmel G A, Ayotte P, Smith R S, and Kay B D 2003 *J. Chem. Phys.* **118** 364  
 Fraser H J, Collings M P, Dever J W and McCoustra M R S 2004 *MNRAS* **353** 59  
 Greenberg M 1982, in *Comets* ed L L Wilkening (The University of Arizona Press, Tucson) p 131  
 Hagen W, Tielens A G G M and Greenberg J M 1981 *Chem. Phys.* **56** 267  
 Hagen W, Tielens A G G M and Greenberg J M 1983 *Astron. Astrophys. Suppl.* **51** 389  
 Hixson H G, Wojcik M J, Devlin M S, Devlin J P, and Buch V 1992 *J. Chem. Phys.* **97** 753  
 Jenniskens P and Blake D 1994 *Science* **265** 753  
 Keane J K, Boogert A C A, Tielens A G G M, Ehrenfreund P and Schutte W A 2001 *Astron. Astrophys.* **375** L43  
 Kimmel G A, Stevenson K P, Dohnálek Z, Smith R S and Kay B D 2001a *J. Chem. Phys.* **114** 5284  
 Kimmel G A, Dohnálek Z, Stevenson K P, Smith R S and Kay B D 2001b *J. Chem. Phys.* **114** 5295  
 Leto G and Baratta G A 2003 *Astron. Astrophys.* **397** 7  
 Leto G, Palumbo M E and Strazzulla G 1996 *Nucl. Instr. Meth. B* **116** 49  
 McCoustra M and Williams D A 1996 *MNRAS* **279** L53  
 Mennella V, Baratta G A, Esposito A, Ferini G and Pendleton Y J 2003 *Astrophys. J.* **587** 727  
 Mennella V, Palumbo M E and Baratta G A 2004 *Astrophys. J.* **615** 1073  
 Moore M H and Hudson R L 1992 *Astrophys. J.* **401** 353  
 Palumbo M E 1997 *J. Phys. Chem. A* **101** 4298  
 Palumbo M E and Strazzulla G 1993 *Astron. Astrophys.* **269** 568  
 Palumbo M E and Strazzulla G 2003 *Can. J. Phys.* **81** 217  
 Pontoppidan, K. M., Fraser, H. J., Dartois, E., et al. 2003, *Astron. Astrophys.* 408, 981  
 Raut U, Loeffler M J, Vidal R A and Baragiola R A 2004 *LPI* **35** 1922  
 Rowland B, Fisher M and Devlin J P 1991 *J. Chem. Phys.* **95** 1378  
 Sandford S A, Allamandola L J, Tielens, A G G M and Valero G J 1988 *Astrophys. J.* **329** 498  
 Strazzulla G, Baratta G A and Palumbo M E 2001 *Spectrochim. Acta A* **57** 825  
 Teixeira T C, Emerson J P and Palumbo M E 1998 *Astron. Astrophys.* bf 330 711  
 Tielens A G G M and Allamandola L J 1987, in *Physical processes in interstellar clouds* ed G E Morfill and M Scholer (Reidel, Dordrecht) p 333  
 Tielens A G G M, Tokunaga A T, Geballe T R and Baas F 1991 *Astrophys. J.* **381** 181