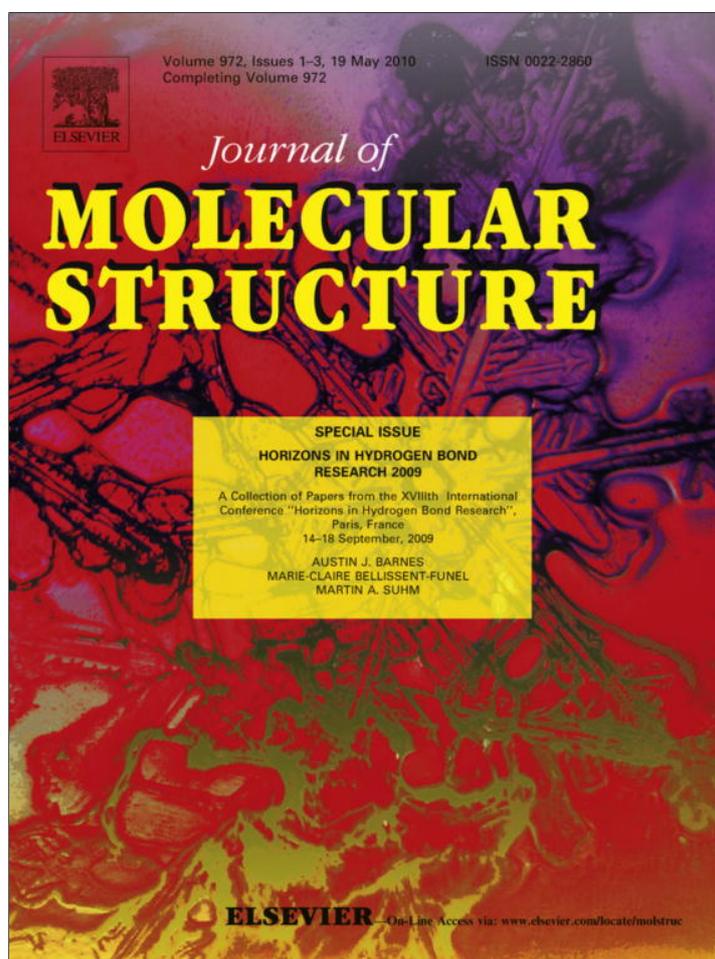


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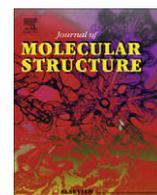
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H bonds in astrophysical ices

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ABSTRACT

We have studied, by infrared absorption spectroscopy, the profile (shape and peak position) of the OH dangling bond feature in pure porous amorphous solid water (ASW) and in mixtures of water with other species (CO, CO₂, O₂, N₂, H₂O₂, CH₄, SO₂, and CH₃OH) at 12–16 K. Furthermore, we have investigated the effects of ion and UV irradiation on the morphology/porosity of amorphous water ice. Thin films (about 0.25–1 μm) of porous amorphous water ice were irradiated with 200 keV H⁺, 30 keV He⁺, and 10.2 eV Lyman alpha photons at 12–16 K. We have found that the profile of the OH dangling bond feature depends on the mixture considered and that the intensity of the OH dangling bond feature decreases after irradiation. This latter result indicates that the porosity of amorphous water ice decreases after both ion and UV irradiation.

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1. Introduction

In astrophysics the word *ice* refers to any volatile species which can be frozen out from the gas phase at $T < 273$ K. Ices are present in different environments in both the Solar System and the interstellar medium. In the Solar System, ices are present in the surface of satellites of outer planets, in trans-Neptunian objects (such as Pluto) and in comets. In the interstellar medium, inside dense molecular clouds, where the temperature of the gas and dust is about 10 K, gas species freeze out on dust grains forming the so-called icy grain mantles. In these environments, ices suffer from energetic processing due to cosmic ions and UV photons.

Most of the information astronomers have on the physico-chemical properties of ices in the Universe is obtained by analyzing electromagnetic radiation absorbed or reflected by those objects in which ices are present. The comparison with laboratory spectra is essential to identify the molecular species responsible for the observed spectral features. In the laboratory, ices (pure species and mixtures) are analyzed at low temperature (10–100 K) before and after processing with fast ions (keV–MeV) and UV photons. Infrared absorption spectroscopy is a powerful tool to study the physical and chemical properties of icy samples. In particular it gives the possibility to identify molecular groups and specific molecules and to study the profile of the bands which depends on the structure of the sample.

Fast ions, passing through a molecular solid, release energy to the target material. As a consequence many molecular bonds are broken along the ion-track and, in a very short time (1 ps or less),

the molecular fragments recombine giving rise to the rearrangement of the chemical and lattice structure. In the case of UV photolysis, energy is released to the target material through a single photo-dissociation or photoexcitation event. Laboratory experiments have shown that after ion and UV irradiation the chemical composition and the structure of the sample are modified. Both more volatile and less volatile species are formed and, if a C-bearing species is present in the original sample, a refractory residue is left over after warm-up to room temperature. In the case of irradiation of solid water, hydrogen peroxide (H₂O₂), along with other species, is formed [1–3]. Furthermore, crystalline ice is transformed into amorphous ice if it is irradiated at low temperature ($T < 100$ K) with fast ions or Lyman alpha photons [4–6].

In recent papers [7–9], on the basis of laboratory experiments, it has been suggested that cosmic ion irradiation causes the compaction of amorphous solid water (ASW) on interstellar grains. In this work, we present new data concerning UV photolysis of ASW and we compare these results with those obtained after ion irradiation [7]. We show that energetic processing (both radiolysis and photolysis) of astrophysical water ice causes its compaction. In particular, we find that after irradiation the intensity of the bands due to the OH dangling bonds decreases and the bands eventually disappear.

2. Experimental

The experiments described here have been carried out in the Laboratory for Experimental Astrophysics, Catania (Italy). Samples are prepared in a vacuum chamber, in which pressure is kept below 10^{-7} mbar and analyzed in situ by infrared spectroscopy using an FTIR spectrometer (Bruker Equinox 55). A schematic depiction of the vacuum chamber is shown in Fig. 1.

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An IR transparent substrate (crystalline silicon or KBr pellet) is placed in thermal contact with a cold finger whose temperature can be varied from 12 K to 300 K. A needle valve is used to admit the chosen gas (or mixtures) into the chamber, where it freezes out on the substrate. An He–Ne laser can be used to monitor the thickness of the ice film during accretion; this is achieved by looking at the interference pattern (intensity versus time) given by the laser beam reflected by both the vacuum-film and the film-substrate interfaces (see [10,11] for further details on the technique used to measure thickness). As discussed [10,11], the interference curve is a function of phase which in turn depends on both the refractive index and the thickness of the film. The refractive index is derived, by numerical methods, from the amplitude of the interference curve. Once it is known, the thickness can be obtained. Several experiments (e.g. [9]) have shown that the refractive index of ice changes after irradiation. Then any variation of the intensity of the reflected light after irradiation cannot be used to obtain the thickness of the film unless the refractive index is known. In principle the refractive index could be derived following the interference curve, during irradiation, in order to get the amplitude. However, in our experimental conditions the phase does not vary enough to obtain the amplitude.

The vacuum chamber is interfaced with an ion implanter (Danfysik) from which ions with energy up to 200 keV (400 keV for double ionizations) can be obtained. The ion beam produces a spot on the target larger than the area probed by the IR beam. In order to avoid macroscopic heating of the sample, current densities in the range from 100 nA cm^{-2} to few $\mu\text{A cm}^{-2}$ are used.

A hydrogen microwave discharge resonance lamp (Ophos Instruments) is interfaced with the vacuum chamber through an MgF_2 window; from this lamp 10.2 eV photons are mainly obtained. A cylindrical aluminium light collimator is placed at the end of the lamp in order to increase the number of UV photons that reaches the sample. A light detector, placed at the end of the aluminium collimator, is used to measure the UV flux during the experiment. The detector is a platinum wire which gives a current, produced by the photoelectric effect, proportional to the UV flux. The wire detector has been calibrated using the same procedure described elsewhere [12].

The mounting surface of the sample holder is placed at an angle of 45° with the IR beam of the spectrometer and the ion beam and

it is perpendicular to the UV flux so that spectra can be taken in situ, even during irradiation, without tilting the sample. For this purpose the IR spectrometer is positioned (with a moveable optical bench) in such a way that the IR beam is transmitted, through a hole in the sample holder, by the substrate. Spectra have been taken with a resolution of 1 cm^{-1} .

3. Results

Fig. 2 shows the mid-infrared spectrum, in optical depth scale, of vapor-deposited porous amorphous solid water at 16 K. It presents absorption bands at 3300 cm^{-1} ($3.03 \mu\text{m}$; O–H symmetric and anti-symmetric stretching modes), 2205 cm^{-1} ($4.53 \mu\text{m}$; combination mode), 1650 cm^{-1} ($6.06 \mu\text{m}$; overtone of the libration mode and H–O–H bending mode). In addition, a small feature is present (see figure's inset), on the high wavenumber wing of the O–H stretching modes band, due to OH dangling bonds (db) in the micropores of the amorphous structure. This feature shows two peaks at 3720 cm^{-1} and 3695 cm^{-1} due to two-coordinate and three-coordinate water molecules, respectively [13]. For comparison, in the same figure, we have plotted the rotovibrational bands due to stretching and bending modes in water vapor at room temperature.

The profile of the OH dangling bond feature (peak position and shape) depends on the temperature of the sample and on the presence of other species mixed in with water ice. In polycrystalline water ice O–H dangling bonds are present at the surface of large ice clusters [13] and the intensity of the related spectral features is too weak to be detected by infrared transmission spectroscopy of thin films [14]. Table 1 reports the position of the OH db feature in different $\text{H}_2\text{O}:\text{X}$ mixtures. In a few instances, the two- and three-coordinate peaks merge into one broad feature.

We have studied the profile of the OH db feature after ion and UV irradiation of porous ASW at 15 K. In order to compare the effects induced by fast ions and UV photons, the irradiation dose (energy released to target molecules i.e. eV molecule^{-1}) has been derived. In the case of ion irradiation, the dose has been obtained from the knowledge of the ion fluence (ions cm^{-2}), measured during irradiation, and the value of the stopping power for 200 keV protons in solid water ($22.5 \times 10^{-15} \text{ eV cm}^2 \text{ molecule}^{-1}$), obtained using the SRIM software [16]; in the case of UV irradiation, the

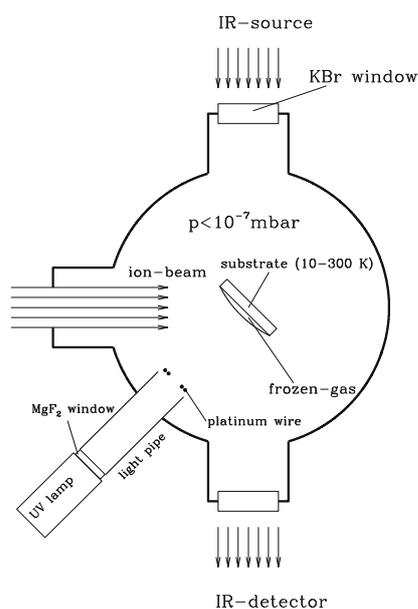


Fig. 1. Schematic view of the experimental apparatus used for in situ IR spectroscopy of ion and UV irradiated frozen gases.

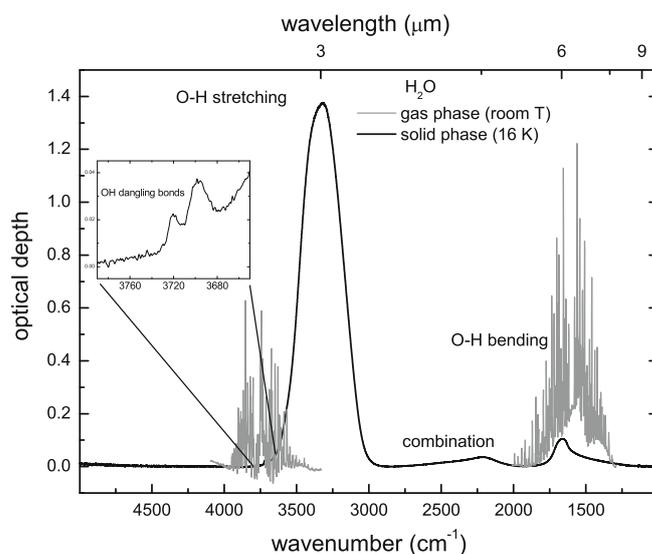


Fig. 2. Mid-IR transmittance spectrum, in optical depth scale, of an amorphous water ice (ASW) film deposited at 16 K. The OH dangling bond feature observed in ASW is expanded in the inset. For comparison the rotovibrational spectrum of water vapor is also shown.

Table 1

Peak position of the OH dangling bond feature in different H₂O:X mixtures. In a few instances the two- and three-coordinate peaks merge into one broad feature.

Sample	OH db peak positions (cm ⁻¹)	Reference
Pure H ₂ O	3695, 3720	[13,7]
H ₂ O:N ₂	3672, 3694	[13,15]
H ₂ O:O ₂	3669, 3694	[7]
H ₂ O:CH ₄	3669, 3684	[7]
H ₂ O:H ₂ O ₂	3664	[7]
H ₂ O:CO ₂	3657	[7]
H ₂ O:CO	3636	[7]
H ₂ O:SO ₂	3606	[7]
H ₂ O:CH ₃ OH	3710	This work

dose has been obtained from the knowledge of the absorption coefficient of solid H₂O for Lyman alpha photons ($\alpha = 28 \mu\text{m}^{-1}$; [12]) and the knowledge of the UV fluence (photons cm⁻²) measured during the experiments. In order to compare the results obtained after irradiation of different targets, the dose is usually given in units of eV per 16 u, where u is the unified atomic mass unit.

Fig. 3 shows the integrated intensity (band area) of the OH db feature, normalized to the initial value, as a function of dose (eV/16 u) after ion and UV irradiation. In these experiments, porous amorphous solid water has been irradiated at 15 K with 200 keV protons or with 10.2 eV Lyman alpha photons. It is evident that the intensity of the OH db feature decreases as the dose increases after both ion and UV irradiation at comparable doses. This is attributed to the loss of OH dangling groups in the micropores, which in turn means a modification of the structure of the icy sample.

We have obtained similar results after ion irradiation of pure ASW and of all of the mixtures reported in Table 1. As an example, Fig. 4 shows the OH db feature in an H₂O:CH₄ mixture deposited at 12 K. In the same figure, it is possible to see that after ion irradiation (30 keV He⁺ in this particular case) the OH dangling bond feature progressively decreases in intensity and eventually disappears. The dose values have been calculated using the stopping power for 30 keV He⁺ ($67.8 \times 10^{-15} \text{ eV cm}^2 \text{ molecule}^{-1}$) obtained using the SRIM software [16].

The disappearance of the OH dangling bond feature has been connected with the compaction of the ice accomplished by a decrease of the number and/or the dimension of micropores. In fact, simple molecules, such as H₂, N₂, CO, CH₄, and Ar, adsorbed in amorphous ice, are often used as a probe to study the properties of the ice. This can be achieved by looking at both the profile of the OH db feature present in porous amorphous ice [13,17,18]

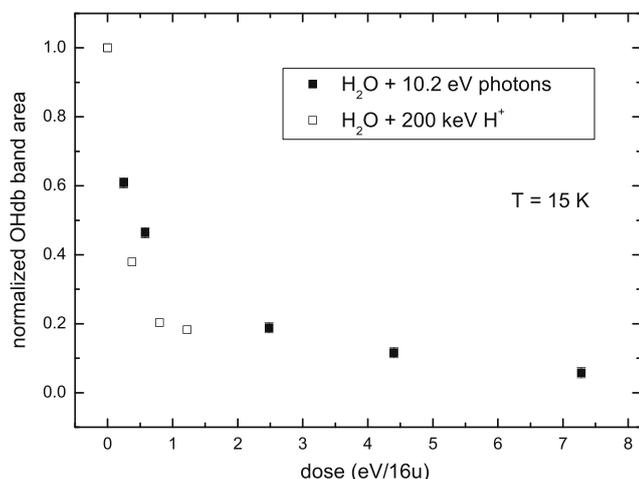


Fig. 3. Normalized integrated intensity (area) of the OH db feature of pure H₂O after irradiation with 200 keV protons and 10.2 eV Lyman alpha photons at 15 K.

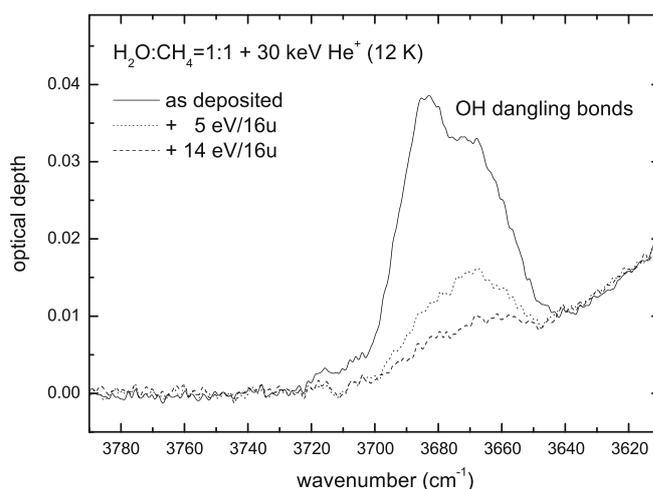


Fig. 4. IR transmittance spectra in optical depth scale of a H₂O:CH₄ (1:1) mixture as deposited at 12 K and after ion irradiation (30 keV He⁺) at two different doses. We can see that the OH dangling bond feature progressively decreases in intensity and eventually disappears.

and at the profile of the infrared bands of absorbed species, as in the case of carbon monoxide [7,19]. Recently, independent experiments [7,9] have shown that the amount of adsorbed species decreases if the ice sample is irradiated. On the basis of these experimental results, it is possible to conclude that simple molecules do not diffuse into amorphous solid water after ion irradiation because compaction of amorphous water ice is induced by ion irradiation itself. The experimental data presented here suggest that compaction is obtained after UV irradiation of ASW.

4. Discussion

As shown in Fig. 2, the mid-infrared spectrum of amorphous solid water shows a number of absorption bands, one of which is at about 3300 cm⁻¹, due to the O–H symmetric and anti-symmetric stretching modes. The peak position of the band due to the stretching modes is sensitively different from the one observed in gas phase water molecules. In the solid (or liquid) phase, the H-bond occurring between the H atom of a molecule and the O atom of a different molecule causes a shift of the O–H stretching band. This simple fact permitted, since the 70s of last century, to observe the O–H stretching band in the spectra of many astrophysical objects [20] with ground-based IR telescopes otherwise inhibited by the presence of abundant water vapor in the Earth atmosphere. Those observations opened the era for a new chapter of astrophysical research, that on the frozen gases (ices) present in several astrophysical environments such as icy mantles on interstellar and circumstellar dust grains and large solid objects in the Solar System.

In the spectrum of ASW (Fig. 2), a small feature is present on the high wavenumber wing of the OH stretching modes band, due to OH dangling bonds in the micropores of the amorphous structure. This db feature can be considered as due to a “lacking H-bond”. The profile of the OH dangling bond feature (peak position and shape) depends on the temperature of the sample and on the presence of other species mixed in with water ice.

Water ice is expected to be amorphous and porous in different astronomical environments [21,22]. Evidence of a porous structure would be given by the detection of the OH db feature on the high wavenumber wing of the OH stretching modes band. However, the frequency region of the OH db feature is saturated by water absorption in the atmosphere (see Fig. 2) and then this feature cannot be observed with ground-based telescopes. After the launch of

the Infrared Space Observatory (ISO) by the European Space Agency (ESA), the OH db feature has been searched towards the line of sight of different star forming regions where the main OH stretching modes band had been already observed. So far, no clear detection of this feature has been reported [23]. On the basis of the experimental results obtained, it has been suggested that the compact structure of interstellar water ice is caused by cosmic ion irradiation of icy grain mantles [7,9]. In fact it has been estimated that porous icy grain mantles in dense molecular clouds are compacted by cosmic ions in $1-5 \times 10^7$ years. This time is comparable or shorter than the estimated ice mantles lifetime ($3 \times 10^7-5 \times 10^8$ years) [24]. The experimental results presented here suggest that UV irradiation also contributes to the compaction of icy mantles.

Acknowledgements

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References

- [1] M.H. Moore, R.E. Hudson, *Icarus* 145 (2000) 282.
- [2] O. Gomis, G. Leto, G. Strazzulla, *Astron. Astrophys.* 420 (2004) 405.
- [3] P.A. Gerakines, W.A. Schutte, P. Ehrenfreund, *Astron. Astrophys.* 312 (1996) 289.
- [4] G.A. Baratta, G. Leto, F. Spinella, G. Strazzulla, G. Foti, *Astron. Astrophys.* 252 (1991) 421.
- [5] M.H. Moore, R.L. Hudson, *Astrophys. J.* 401 (1992) 353.
- [6] G. Leto, G.A. Baratta, *Astron. Astrophys.* 397 (2003) 7.
- [7] M.E. Palumbo, *Astron. Astrophys.* 453 (2006) 903.
- [8] U. Raut, B.D. Teolis, M.J. Loeffler, R.A. Vidal, M. Famá, R.A. Baragiola, *J. Chem. Phys.* 126 (2007) 244511.
- [9] U. Raut, M. Famá, M.J. Loeffler, R.A. Baragiola, *Astrophys. J.* 687 (2008) 1070.
- [10] G.A. Baratta, M.E. Palumbo, *J. Opt. Soc. Am. A* 15 (1998) 3076.
- [11] D. Fulvio, B. Sivaraman, G.A. Baratta, M.E. Palumbo, N.J. Mason, *Spectrochim. Acta A* 72 (2009) 1007.
- [12] G.A. Baratta, G. Leto, M.E. Palumbo, *Astron. Astrophys.* 384 (2002) 343.
- [13] B. Rowland, M. Fisher, J.P. Devlin, *J. Chem. Phys.* 95 (1991) 1378.
- [14] M.E. Palumbo, *J. Phys. Chem. A* 101 (1997) 4298.
- [15] M.E. Palumbo, G. Strazzulla, *Can. J. Phys.* 81 (2003) 217.
- [16] J.F. Ziegler, J.P. Biersack, U. Littmark, *The Stopping and Range of Ions in Solids*, Pergamon Press, New York, 1996. Available from: <<http://www.srim.org>>.
- [17] U. Raut, M. Famá, B.D. Teolis, R.A. Baragiola, *J. Chem. Phys.* 127 (2007) 204713.
- [18] H.G. Hixson, M.J. Wojcik, M.S. Devlin, J.P. Devlin, V. Buch, *J. Chem. Phys.* 97 (1992) 753.
- [19] J.P. Devlin, *J. Phys. Chem.* 96 (1992) 6185.
- [20] K.M. Merrill, B.T. Soifer, *Astrophys. J. Lett.* 189 (1974) L27.
- [21] W. Hagen, A.G.G.M. Tielens, J.M. Greenberg, *Chem. Phys.* 56 (1981) 267.
- [22] M. McCoustra, D.A. Williams, *Mon. Not. R. Astron. Soc.* 279 (1996) L53.
- [23] J.K. Keane, A.C.A. Boogert, A.G.G.M. Tielens, P. Ehrenfreund, W.A. Schutte, *Astron. Astrophys.* 375 (2001) L43.
- [24] M. Greenberg, in: L.L. Wilkening (Ed.), *Comets*, The University of Arizona Press, Tucson, 1982, p. 131.