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Ion implantation in ices of interest for planetology

G. A. Baratta[1], D. Fulvio[1,2], M. Garozzo[1], O. Gomis[3], G. Leto[1], M. E. Palumbo[1],
F. Spinella[1], and G. Strazzulla[1]

[1] INAF-Osservatorio Astrofisico di Catania, via S. Sofia 78, I-95123 Catania, Italy
e-mail: `gbaratta@oact.inaf.it`
[2] Dipartimento di Fisica e Astronomia, Università di Catania, via S. Sofia 78, I-95123 Catania, Italy
[3] Departamento de Fisica Aplicada Escuela Politecnica Superior Alcoy, Univ Politecnica de Valencia, Spain

Abstract. Frozen sufaces of planetary moons and minor planets in Solar System are continuously irradiated by energetic ions (keV-MeV). These ions deposit their energy into the target via elastic and anelastic collisions which induce a break of molecular bonds. Because of their small penetration depth (0.1 - 2.0 μm) impinging ions are implanted into the ices at the end of their path. Across the ion's path reconnection of molecular fragments can form new species and if the projectile is a reactive species it can be included into the newly formed molecules. In the Laboratory of Experimental Astrophysics (LASp) of Catania we are investigating the effects of reactive ion implantation in ices of interest for planetology. Results show that some molecules observed on frozen surfaces of minor bodies of the outer Solar System could be formed after implantation of reactive ions. After a short review of relevant experiments performed in our Laboratory we will show results of our latest experiments and their application to the moon of Jupiter Io.

Key words. Solar System: Minor planets – Planets and satellites: Jupiter, Io – Methods: laboratory – Molecular processes

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 in the Solar System are present on a variety of bodies, such as comets, trans-Neptunian objects (such as Pluto) and the surfaces of moons of outer planets (Jupiter and beyond). Table 1 reports those objects where ices have been detected along with the species detected. In these environments ices suffer from energetic processing due to solar wind ions, cosmic rays (GCRs) and solar photons. Furthermore, regarding satellites of external planets, because of their movement in the magnetosphere of their own planet they suffer from the effects of magnetospheric ions (e.g., Johnson 1990; Strazzulla and Johnson 1991). Table 2 reports

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Send offprint requests to: G. A. Baratta

Table 1. Ices in the Solar System

Planet Satellite (*Ref.*)	Observed Species
Jupiter	
Io	SO_2, H_2S, H_2O
Europa	H_2O, SO_2, CO_2, H_2O_2
Ganimede	H_2O, O_2, O_3, CO_2
Callisto	H_2O, SO_2, CO_2
(*Calvin et al. 1995; Nash & Betts 1995)*	
Saturn	
Mimas	H_2O
Enceladus	H_2O
Tetis	H_2O
Dione	H_2O, O_3
Rhea	H_2O, O_3
Hyperion	H_2O
Iapetus	H_2O
(*Morrison et al. 1984; Cruikshank et al. 1984; Thomas et al. 1986)*	
Uran	
Miranda	H_2O
Ariel	H_2O
Umbriel	H_2O
Titania	H_2O
Oberon	H_2O
(*Cruikshank et al. 1995)*	
Neptune	
Triton	N_2, CH_4, CO, CO_2, H_2O
(*Brown et al. 1995)*	
Pluto *	N_2, CH_4, CO, H_2O
Charon	H_2O
(*Cruikshank et al. 1995)*	

* After IAU resolution, in 2006, Pluto is a dwarf planet and is recognized as the prototype of trans-Neptunian objects.

the photon and ion fluxes impinging on Solar System objects.

Fast ions penetrating molecular solids deposit energy in the target by elastic interactions with target nuclei and by inelastic collisions causing ionizations and excitations. Thus chemical bonds are broken along the path of the incoming ion and physic-chemical modifications can occur, including the formation of species originally not present in the target. Implantation experiments are particularly relevant for application to objects in the Solar System where ices on planetary surfaces, comets, etc., are much thicker than the penetration depth of the impinging ions. In particular if the impinging ion is a reactive species (e.g., H, C, N, O, S, ...) it can be included into the newly formed molecules.

Effects of ion irradiation can be studied by laboratory simulations where relevant targets are bombarded with fast charged particles under physical conditions as close as possible to

Table 2. Ionizing radiation in the Solar System

	Energy	input (%)	Fluxes ($cm^{-2}s^{-1}$)
Solar Photons	2 eV	Visible (50%)	2.0×10^{17}
	4 eV	NUV (10%)	1.5×10^{16}
	6 eV	FUV (0.02%)	3.0×10^{13}
Solar Wind (1 AU)	1 keV	H^+ (95%)	3.0×10^{8}
	4 keV	He^{2+} (5%)	
Solar Flares (1 AU)	> 1 MeV	H^+ (95%)	10^{10} ($cm^{-2}yr^{-1}$)
	> 1 MeV	He^{2+} (5%)	
GCRs	> 1 MeV	H^+ (87%)	$\leq$ 10
	> 1 MeV	He^{2+} (12%)	

the astrophysical ones. Ion bombardment experiments have demonstrated that cosmic particles are able to erode the target (sputtering; e.g., Johnson 1990) and modify the structure (crystalline or amorphous) of the sample (e.g., Baratta et al. 1991; Moore & Hudson 1992; Leto & Baratta 2003) as well as its chemical composition (e.g., Strazzulla et al., 1991).

For example, it has been suggested that sulfur dioxide (SO_2) on the surface of Europa and Callisto is due to S^{n+} implantation coming from Jupiter's magnetosphere on the water ice on their surfaces (Lane et al., 1981; Sack et al., 1992). Recently such a suggestion has been challenged on the basis of new experiments (Strazzulla et al., 2007) of sulfur implantation in water ice. The experiments demonstrated the efficient formation of hydrate sulfuric acid but only an upper limit has been found for the formation of SO_2. Another example (Strazzulla et al., 2003; Dawes et al., 2007) concerns the results on C implantation into water ice to study the production of CO_2. It has been shown that, although a relevant quantity of carbon dioxide can be synthesized by C implantation into water ice on the Galilean moons, this is not the dominant formation mechanism of the CO_2 molecule. In a subsequent work, Gomis & Strazzulla (2005) presented laboratory results on experiments of irradiation of water ice deposited on top of carbonaceous materials. Those authors found that CO_2 is produced efficiently after irradiation. Their results show that radiolysis of mixtures of frost water and carbonaceous compounds could account for the quantity of CO_2 ice present on the surfaces of the Galilean satellites. The last example we want to point out here concerns the synthesis of carbonic acid (H_2CO_3) by H^+ implantation in pure carbon dioxide (CO_2) ices (Brucato et al., 1997). This result is relevant in view of the presence of CO_2 ices in many objects of the Solar System such as planets (e.g., Mars), satellites (e.g., Triton) and comets, as suggested by Strazzulla et al. (1996).

2. Io, the Jovian's magnetosphere and the sulfurous acid (H_2SO_3)

The Galileo spacecraft, during its mission around Jupiter and its moons, has allowed a better understanding of the Jovian' system but it also raised new questions. One of them concerns Io, the innermost of Jupiter's Galilean satellites.

Io is permeated by an intense volcanic activity connected to the gravitational resonance forces played by other Galilean satellites, expecially Europa and Ganymede. These forces induce vibrational motions able to generate the heat required so that Io's mantle is composed primarily by molten silicate rocks. During its extensive volcanism these materials are ejected together with a number of sulfur compounds so that frozen sulfur dioxide (SO_2) turns out to be among the main constituents. Moreover Io surface has a temperature around 100 K and a low water content.

This unique world induced Voegele et al. (2004) to ask about the possibility to observe H_2SO_3 on Io surface. In fact, formation and stability of H_2SO_3 is possible only under three opportune conditions. This acid is formed by the reaction:

$$SO_2 + H_2O \rightarrow H_2SO_3$$

but if there are oxidants for SO_2 it is energetically convenient to oxide into SO_3. Water concentration shouldn't be greater than that of SO_2 otherwise exceeding water would destroy H_2SO_3 by the reaction:

$$H_2SO_3 + nH_2O \rightarrow SO_2 + (n + 1)\,H_2O$$

this process becomes dominant with an increasing number of water molecules (Li & McKee, 1997). H_2SO_3 must stay in a low temperature environment yet. In fact its half-life is 1 day at 300 K and almost 3 billion years at 100 K (Voegele et al., 2004).

We already said that Io satisfies such conditions but it is to understand how this acid could be formed in absence of water. Since during its orbiting Io is dipped into Jupiter's magnetosphere, its surface is continuously bombarded by energetic ions accelerated by Jupiter's magnetic field (Cooper et al., 2001), mainly H^+, S^{n+} and O^{n+} so Voegele et al. (2004) suggested that formation of H_2SO_3 on Io may happen by H^+ implantation in SO_2 ices, proposing a possible analogy with the results discussed in Brucato et al. (1997) where authors synthesized carbonic acid (H_2CO_3) by 1.5 keV H^+ implantation on pure carbon dioxide (CO_2) ice. H_2SO_3 and H_2CO_3, in fact, show several common characteristics like the high half-life at low temperatures and low humidity environments. This hypothesis is an interesting cue for a laboratory experiment.

In this article we show results obtained by implanting 30 keV H^+ and He^+ in SO_2 ice at 16 K and 50 keV H^+ in SO_2 ice at 80 K. Possible application of the results to Io are also presented and a more detailed discussion can be found in Garozzo et al. (2008).

3. Experimental setup

In this section a brief description of the experimental set-up available at the Laboratory for Experimental Astrophysics (LASp) in Catania (Italy) is given. Further details can be found in Strazzulla et al. (2001), Baratta et al. (2002) and Palumbo et al. (2004).

In situ IR spectroscopy is performed in a stainless steel vacuum chamber facing an FTIR spectrometer (Bruker Equinox 55). Inside the vacuum chamber we can reach pressures below 10^{-7} mbar, an IR transparent substrate (e.g., crystalline silicon) is placed in thermal contact with a cold finger which temperature can be varied by the user between 10 K and 300 K. The vacuum chamber is interfaced with an ion implanter (200 kV; Danfysik 1080-200) from which ions with energy up to 200 keV (400 keV for doubly ionized ions) can be obtained. The ion beam produces a spot on the target larger than the area probed by the IR beam and ion current is kept under a few μA cm^{-2} to avoid a macroscopic heating of the sample. The integrated ion flux (fluence in ions cm^{-2}) is directly related to the ion current continuously measured during irradiation.

A valve is used to admit a pre-prepared pure gas (or mixture) into the chamber, where it freezes on the substrate. A 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 vs time) given by the laser beam reflected at an angle of 45^o both by the vacuum-film and film-substrate interfaces (see Baratta & Palumbo (1998) for further details on the technique used to measure the thickness). The substrate holder is mounted at an angle of 45^o with respect to both the ion beam and the IR beam, so that spectra can be taken in situ, even during irradiation, without tilting or removing the sample. For this purpose the IR spectrometer is positioned (by a moveable optical bench) such that the IR beam is transmitted, through a hole in the sample holder, by the substrate. All the spectra shown in the following have been taken with a resolution of 1 cm^{-1} and a sampling of 0.25 cm^{-1}.

4. Experiments and results

In this section we show results obtained by implanting 30 keV H^+ and He^+ in SO_2 ice at 16 K and 50 keV H^+ in SO_2 ice at 80 K. The deposited SO_2 ice film in the two temperatures (16 and 80 K) had a thickness of about 1.5 and 2.1 μm respectively, larger than the penetration depth of the incoming ions calculated by SRIM 2000 software by Ziegler et al. (1996) (0.5 μm for 30 keV H^+, 0.26 μm for 30 keV He^+ and 0.7 μm for 50 keV H^+).

In Fig. 1 we show the spectra of SO_2 ice as deposited (see Table 3 for identification of the main absorption bands; Moore, 1984; Nash & Betts, 1995) at 16 and 80 K and after implantation with 30 and 50 keV H^+ ions respectively.

Table 3. Peak position of the IR bands of unirradiated SO_2 ice and their assignment.

wavenumber (cm^{-1})	mode	species
1122	ν_1	$S^{16}O^{18}O$
1149	ν_1	SO_2
1335	ν_3	SO_2
2457	$\nu_1 + \nu_3$	SO_2

In this figure we can see the appearance, after irradiation, of new bands arising because of the formation of species not originally present in the sample. These new bands are observed in both the SO_2 samples and they are easily identified (Table 4) and attributed to sulfur trioxide (SO_3), its polymers (Moore 1984) and ozone (O_3; Moore and Khanna 1991).

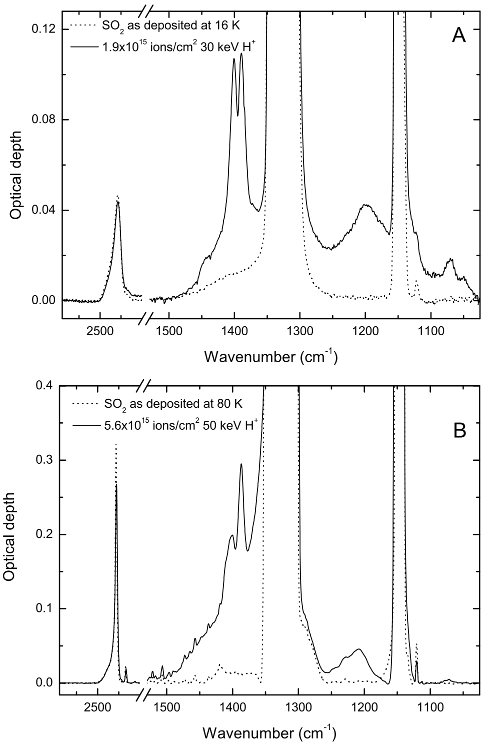

Fig. 1. A) IR spectra of SO_2 ice as deposited at 16 K and after 30 keV H^+ implantation. B) IR spectra of SO_2 ice as deposited at 80 K and after 50 keV H^+ implantation.

Table 4. Peak position, mode and responsible species of bands formed after 30 and 50 keV H^+ implantation in SO_2 ice at 16 and 80 K.

wavenumber (cm^{-1})	mode	species
1050	ν_3	O_3
1070	ν_1	SO_3
1205		Poly SO_3
1389 - 1400	ν_3	SO_3

To confirm and complete these results we made a third implantation experiment on SO_2 ice at 16 K, using He^+ projectiles. In fact being He^+ a non-reactive ion it can't form molecular bonds with SO_2 fragments. In Fig. 2 the spectrum of SO_2 after H^+ implantation at 16 K is compared with that obtained after implantation of 30 keV He^+ ions at the same temperature.

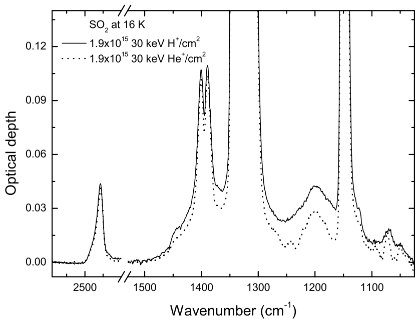

Fig. 2. Comparison between IR spectra of SO_2 ice (16 K) after 30 keV H^+ and He^+ implantation

These spectra show the formation of the same new bands and this tests the efficiency of SO_2 in SO_3 oxidation and the ability of SO_3 to form polymeric chains.

From these results we can assert that H^+ implantation in pure SO_2 ice doesn't produce, in the IR spectrum, any band attributable to H_2SO_3, H_2SO_4 or H_2S, but only SO_3, polymers, and O_3. Also spectra after H implantation do not show any band which is not present in the spectra obtained after He implantation.

We cited Voegele et al. (2004) suggestion (see Introduction) about the possible presence of H_2SO_3 on Io, theoretically induced by implantation of protons on its SO_2-rich surface. Io is an ideal candidate to accommodate H_2SO_3, in fact on this satellite the restrictive conditions occurs under which the acid is stable, having an average temperature of about 100 K and lack of water. The results described above clearly indicate that after proton implantation new molecules are formed but none of these contain the impinging ions, although hydrogen is a reactive element which could form molecular bonds with other chemical elements.

From the data collected by Galileo probe we know that cosmic ions deposit on Io surface an integrated energy flux of 1 x 10^9 keV cm^{-2} s^{-1}. If we suppose that all energy is due to 30 keV protons the total fluence used in our experiments 1.6 x 10^{16} ions/cm^2 on Io surface is reached in about 20 years. This time is much shorter than the age of the satellite, however, resurfacing effects, due to the high level of activity on Io, cannot be neglected and we expect that the ion irradiation effects do not cumulate on the surface but are easily removed.

Thus experimental results obtained allow us to say that on Io, H_2SO_3 cannot be produced in relevant quantities by proton implantation on the satellite surface. On the other hand it should be possible and reasonable to produce SO_3 and its polymers that however have not been detected so far.

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