



# Ion implantation in ices of interest for planetology

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**Abstract.** Frozen surfaces 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  $\mu\text{m}$ ) 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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**Table 1.** Ices in the Solar System

<b>Planet</b> Satellite ( <i>Ref.</i> )	Observed Species
<b>Jupiter</b>	
Io	SO <sub>2</sub> , H <sub>2</sub> S, H <sub>2</sub> O
Europa	H <sub>2</sub> O, SO <sub>2</sub> , CO <sub>2</sub> , H <sub>2</sub> O <sub>2</sub>
Ganymede	H <sub>2</sub> O, O <sub>2</sub> , O <sub>3</sub> , CO <sub>2</sub>
Callisto ( <i>Calvin et al. 1995; Nash &amp; Betts 1995</i> )	H <sub>2</sub> O, SO <sub>2</sub> , CO <sub>2</sub>
<b>Saturn</b>	
Mimas	H <sub>2</sub> O
Enceladus	H <sub>2</sub> O
Tetis	H <sub>2</sub> O
Dione	H <sub>2</sub> O, O <sub>3</sub>
Rhea	H <sub>2</sub> O, O <sub>3</sub>
Hyperion	H <sub>2</sub> O
Iapetus ( <i>Morrison et al. 1984; Cruikshank et al. 1984; Thomas et al. 1986</i> )	H <sub>2</sub> O
<b>Uran</b>	
Miranda	H <sub>2</sub> O
Ariel	H <sub>2</sub> O
Umbriel	H <sub>2</sub> O
Titania	H <sub>2</sub> O
Oberon ( <i>Cruikshank et al. 1995</i> )	H <sub>2</sub> O
<b>Neptune</b>	
Triton ( <i>Brown et al. 1995</i> )	N <sub>2</sub> , CH <sub>4</sub> , CO, CO <sub>2</sub> , H <sub>2</sub> O
Pluto *	N <sub>2</sub> , CH <sub>4</sub> , CO, H <sub>2</sub> O
Charon ( <i>Cruikshank et al. 1995</i> )	H <sub>2</sub> O

\* 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 physico-chemical modifications can occur, including the formation of species originally not present in the target. Implantation experiments are particu-

larly 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 <sup>-2</sup> s <sup>-1</sup> )
Solar Photons	2 eV	Visible (50%)	2.0×10 <sup>17</sup>
	4 eV	NUV (10%)	1.5×10 <sup>16</sup>
	6 eV	FUV (0.02%)	3.0×10 <sup>13</sup>
Solar Wind (1 AU)	1 keV	H <sup>+</sup> (95%)	3.0×10 <sup>8</sup>
	4 keV	He <sup>2+</sup> (5%)	
Solar Flares (1 AU)	> 1 MeV	H <sup>+</sup> (95%)	10 <sup>10</sup> (cm <sup>-2</sup> yr <sup>-1</sup> )
	> 1 MeV	He <sup>2+</sup> (5%)	
GCRs	> 1 MeV	H <sup>+</sup> (87%)	≤ 10
	> 1 MeV	He <sup>2+</sup> (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<sub>2</sub>) on the surface of Europa and Callisto is due to S<sup>n+</sup> 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<sub>2</sub>. 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<sub>2</sub>. 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<sub>2</sub> molecule. In a subsequent work, Gomis & Strazzulla (2005) presented laboratory results on experiments of irradiation of water ice deposited on top of carbonaceous mate-

rials. Those authors found that CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>CO<sub>3</sub>) by H<sup>+</sup> implantation in pure carbon dioxide (CO<sub>2</sub>) ices (Brucato et al., 1997). This result is relevant in view of the presence of CO<sub>2</sub> 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<sub>2</sub>SO<sub>3</sub>)

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.

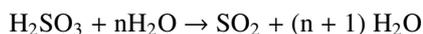
Io is permeated by an intense volcanic activity connected to the gravitational resonance forces played by other Galilean satellites, especially Europa and Ganymede. These forces induce vibrational motions able to generate the heat required so that Io's mantle is composed primarily by molten silicate rocks. During its

extensive volcanism these materials are ejected together with a number of sulfur compounds so that frozen sulfur dioxide (SO<sub>2</sub>) 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<sub>2</sub>SO<sub>3</sub> on Io surface. In fact, formation and stability of H<sub>2</sub>SO<sub>3</sub> is possible only under three opportune conditions. This acid is formed by the reaction:



but if there are oxidants for SO<sub>2</sub> it is energetically convenient to oxidize into SO<sub>3</sub>. Water concentration shouldn't be greater than that of SO<sub>2</sub> otherwise exceeding water would destroy H<sub>2</sub>SO<sub>3</sub> by the reaction:



this process becomes dominant with an increasing number of water molecules (Li & McKee, 1997). H<sub>2</sub>SO<sub>3</sub> 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<sup>+</sup>, S<sup>n+</sup> and O<sup>n+</sup> so Voegele et al. (2004) suggested that formation of H<sub>2</sub>SO<sub>3</sub> on Io may happen by H<sup>+</sup> implantation in SO<sub>2</sub> ices, proposing a possible analogy with the results discussed in Brucato et al. (1997) where authors synthesized carbonic acid (H<sub>2</sub>CO<sub>3</sub>) by 1.5 keV H<sup>+</sup> implantation on pure carbon dioxide (CO<sub>2</sub>) ice. H<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>CO<sub>3</sub>, 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<sup>+</sup> and He<sup>+</sup> in SO<sub>2</sub> ice at 16

K and 50 keV H<sup>+</sup> in SO<sub>2</sub> 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<sup>-7</sup> 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<sup>-2</sup> to avoid a macroscopic heating of the sample. The integrated ion flux (fluence in ions cm<sup>-2</sup>) 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° 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° 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  $1\text{ cm}^{-1}$  and a sampling of  $0.25\text{ cm}^{-1}$ .

#### 4. Experiments and results

In this section we show results obtained by implanting  $30\text{ keV H}^+$  and  $\text{He}^+$  in  $\text{SO}_2$  ice at  $16\text{ K}$  and  $50\text{ keV H}^+$  in  $\text{SO}_2$  ice at  $80\text{ K}$ . The deposited  $\text{SO}_2$  ice film in the two temperatures ( $16$  and  $80\text{ K}$ ) had a thickness of about  $1.5$  and  $2.1\text{ }\mu\text{m}$  respectively, larger than the penetration depth of the incoming ions calculated by SRIM 2000 software by Ziegler et al. (1996) ( $0.5\text{ }\mu\text{m}$  for  $30\text{ keV H}^+$ ,  $0.26\text{ }\mu\text{m}$  for  $30\text{ keV He}^+$  and  $0.7\text{ }\mu\text{m}$  for  $50\text{ keV H}^+$ ).

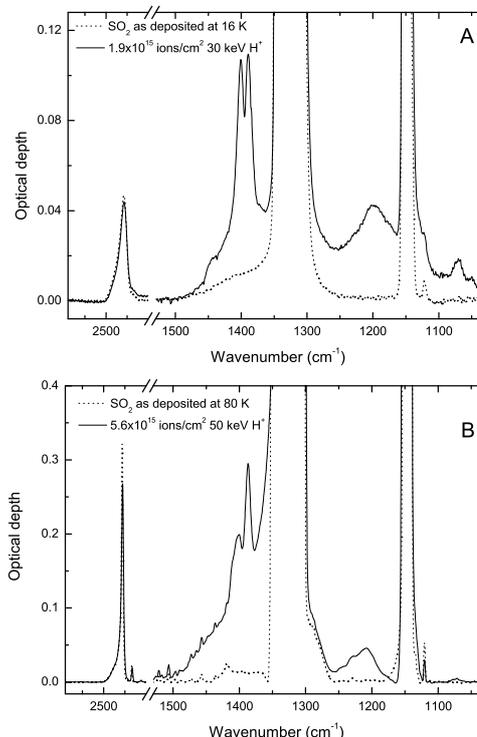
In Fig. 1 we show the spectra of  $\text{SO}_2$  ice as deposited (see Table 3 for identification of the main absorption bands; Moore, 1984; Nash & Betts, 1995) at  $16$  and  $80\text{ K}$  and after implantation with  $30$  and  $50\text{ keV H}^+$  ions respectively.

**Table 3.** Peak position of the IR bands of unirradiated  $\text{SO}_2$  ice and their assignment.

wavenumber ( $\text{cm}^{-1}$ )	mode	species
1122	$\nu_1$	$\text{S}^{16}\text{O}^{18}\text{O}$
1149	$\nu_1$	$\text{SO}_2$
1335	$\nu_3$	$\text{SO}_2$
2457	$\nu_1 + \nu_3$	$\text{SO}_2$

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  $\text{SO}_2$  samples and they are easily identified (Table 4) and attributed to sulfur trioxide ( $\text{SO}_3$ ), its polymers (Moore 1984) and ozone ( $\text{O}_3$ ; Moore and Khanna 1991).

To confirm and complete these results we made a third implantation experiment on  $\text{SO}_2$  ice at  $16\text{ K}$ , using  $\text{He}^+$  projectiles. In fact being

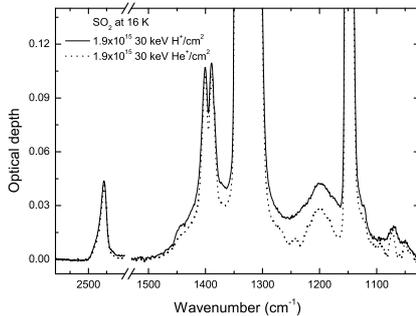


**Fig. 1.** A) IR spectra of  $\text{SO}_2$  ice as deposited at  $16\text{ K}$  and after  $30\text{ keV H}^+$  implantation. B) IR spectra of  $\text{SO}_2$  ice as deposited at  $80\text{ K}$  and after  $50\text{ keV H}^+$  implantation.

**Table 4.** Peak position, mode and responsible species of bands formed after  $30$  and  $50\text{ keV H}^+$  implantation in  $\text{SO}_2$  ice at  $16$  and  $80\text{ K}$ .

wavenumber ( $\text{cm}^{-1}$ )	mode	species
1050	$\nu_3$	$\text{O}_3$
1070	$\nu_1$	$\text{SO}_3$
1205		Poly $\text{SO}_3$
1389 - 1400	$\nu_3$	$\text{SO}_3$

$\text{He}^+$  a non-reactive ion it can't form molecular bonds with  $\text{SO}_2$  fragments. In Fig. 2 the spectrum of  $\text{SO}_2$  after  $\text{H}^+$  implantation at  $16\text{ K}$  is compared with that obtained after implantation of  $30\text{ keV He}^+$  ions at the same temperature.



**Fig. 2.** Comparison between IR spectra of SO<sub>2</sub> ice (16 K) after 30 keV H<sup>+</sup> and He<sup>+</sup> implantation

These spectra show the formation of the same new bands and this tests the efficiency of SO<sub>2</sub> in SO<sub>3</sub> oxidation and the ability of SO<sub>3</sub> to form polymeric chains.

From these results we can assert that H<sup>+</sup> implantation in pure SO<sub>2</sub> ice doesn't produce, in the IR spectrum, any band attributable to H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> or H<sub>2</sub>S, but only SO<sub>3</sub>, polymers, and O<sub>3</sub>. Also spectra after H implantation do not show any band which is not present in the spectra obtained after He implantation.

We cited Voegelé et al. (2004) suggestion (see Introduction) about the possible presence of H<sub>2</sub>SO<sub>3</sub> on Io, theoretically induced by implantation of protons on its SO<sub>2</sub>-rich surface. Io is an ideal candidate to accommodate H<sub>2</sub>SO<sub>3</sub>, 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  $1 \times 10^9$  keV cm<sup>-2</sup> s<sup>-1</sup>. If we suppose that all energy is due to 30 keV protons the total fluence used in our experiments  $1.6 \times 10^{16}$  ions/cm<sup>2</sup> 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<sub>2</sub>SO<sub>3</sub> 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<sub>3</sub> and its polymers that however have not been detected so far.

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