

Implantation of multiply charged sulfur ions in water ice



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ABSTRACT

Sulfuric acid has been suggested to be present on the surface of the jovian moon Europa where it is mixed with the dominant water ice. The formation mechanism of sulfuric acid is still under discussion.

We present new experimental results on the implantation of S^{q+} ($q = 7, 9, 11$) ions at an energy range between 35 and 176 keV in water ice at 80 K. Previous results on 200 keV S^+ implantation in H_2O at 80 K have also been included in the data analysis. Experiments with multiply-charged ions at different energies are particularly relevant to simulate the complexity of the irradiation environment to which the surface of Europa is exposed being embedded in the jovian magnetosphere.

The experiments were performed at the low energy ion beam facility ARIBE of GANIL in Caen (France). 35–176 keV S^{q+} ($q = 7, 9, 11$) ions were implanted in solid H_2O layers which were frozen at 80 K. Fourier Transform Infrared Spectrometry (FTIR) was used to analyze the sample in the 5000–600 cm^{-1} (2–16.7 μm) region with a spectral resolution of 1 cm^{-1} .

The results of our experiments indicate that implantation produces hydrated sulfuric acid with yields that increase with ion energy, from 0.12 molecules ion^{-1} for 35 keV ions to 0.64 molecules ion^{-1} for 200 keV ions. We have also searched for the production of SO_2 and H_2S , but we were not able to find any evidence for their synthesis.

We conclude that sulfur ion implantation is the dominant formation mechanism of hydrated sulfuric acid at Europa. The suggestion that the observed distribution of sulfuric acid on the surface is well correlated with the local flux of sulfur ions find a full explanation by present experimental data.

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1. Introduction

The surface of Europa is rich in water ice, which is the dominant species, along with abundant hydrated materials (particularly sulfuric acid) and minor amounts of some volatile molecules such as H_2O_2 , SO_2 , and CO_2 (Carlson et al., 1997, 1999a; Carlson, 2001; Noll et al., 1995, 1997). There is a general consensus that the formation mechanism of H_2O_2 is radiolysis of water ice by plasma ions and energetic particles, which are abundant in the jovian magnetosphere. The origin of the other observed species is still an open question. A possible way to form CO_2 or SO_2 is via exogenic processes such as implantation of carbon or sulfur ions present in the jovian magnetosphere, as suggested since several years on the basis of numerous experimental results, for a review see Strazzulla (2011).

As an example, results on C^{n+} ($n = 1, 2, 3$) implantation into water ice have shown that although a relevant quantity of carbon dioxide can be synthesized by carbon ion implantation into water

ice on the Galilean moons, this is not the dominant formation mechanism (Lv et al., 2012; Strazzulla et al., 2003). The dominant mechanism would be the efficient formation of CO_2 after irradiation of water ice deposited on top of carbonaceous materials. The latter is continuously delivered by impact of cometary debris on the icy moons (Gomis and Strazzulla, 2005).

Implanted ions deposit energy in the icy target, for a detailed description of the interaction phenomenology between fast ions and target species see Johnson (1990). As an example, each incoming 35–200 keV S^{n+} ion breaks 10^3 – 10^5 water molecules, producing fragments that can then react to synthesize new molecules. In fact the synthesis of H_2O_2 has been observed in many experiments and its presence on Europa has been attributed to radiolytic processes occurring on the icy surface of the satellite (Carlson et al., 1999a; Moore and Hudson, 2000; Gomis et al., 2004; Loeffler et al., 2006). In addition to the radiolytic effects induced by un-reactive ions, reactive ions could possibly synthesize species that contain the projectile with a maximum yield of one molecule per incoming ion (Strazzulla, 2011).

This paper reports some results of an ongoing research program on the study of the implantation of reactive ions (S in the present

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case) to verify if and when new molecules that contain the projectile can be synthesized and how the respective formation yields depend on parameters such as ion energy and charge state. In particular we present the results of new experiments in which sulfur ions, S^{q+} ($q = 7, 9, 11$) ions are implanted into thick films (i.e. thicker than the penetration depth of the ions) of water ice at 80 K. Previous results on 200 keV S^+ implantation in H_2O at 80 K have also been included in the data analysis.

In spite of the fact that S implantation has been thought to produce SO_2 (Lane et al., 1981; Noll et al., 1995, 1997; McCord et al., 1997) and/or hydrated sulfuric acid (Carlson et al., 1999b, 2002) trapped in the icy surfaces of satellites in the outer Solar System, to the best of our knowledge the only previous experiment concerning sulfur implantation concerns 200 keV singly ionized ions implanted in water ice at 80 K (Strazzulla et al., 2007). The result of that experiment showed the formation of hydrated sulfuric acid, but not of SO_2 . The present results confirm that implantation produces hydrated sulfuric acid and show for the first time that production yields depend on the ion energy, from $Y = 0.12$ molecules/ions for 35 keV ions to $Y = 0.64$ molecules/ions for 200 keV ions and do not depend on the charge of the incoming ions. The results are discussed in the light of the relevance they have to the chemico-physical evolution of Europa and other icy moons in the outer Solar System.

2. Experiments

The experimental apparatus has been described elsewhere (Lv et al., 2012). In brief, ion beams are produced in a 14.5 GHz electron cyclotron resonance (ECR) ion source at the low energy facility ARIBE of GANIL in Caen (France). For the present experiments we used S^{q+} ($q = 7, 9, 11$) ion beams with fluxes of 10^{11} – 10^{12} ions $cm^{-2} s^{-1}$. Ion beams were scanned to assure a uniform bombardment of the target. A Faraday-Cup was inserted into the beam in order to measure the beam current. For more details see (Lv et al., 2012).

The ice layers were prepared by condensing water vapor on a CsI window at 80 K. About $1 cm^3$ pure H_2O , which was produced by a Milli-Q Integral Water Purification System, was stored in a cuvette. The H_2O was frozen to solid phase, then after pumping the cuvette for a few minutes, the H_2O was warmed up to liquid phase. This procedure was repeated 2 or 3 times in order to obtain H_2O vapor of high purity. H_2O vapor was introduced in a pre-chamber. A fine valve allowed controlling the deposition rate. A nozzle was used to transmit the gas into the high vacuum chamber and onto the cold CsI substrate. The pressure in the high vacuum chamber was below 10^{-7} mbar during the measurements. The CsI window was installed in the center of the chamber on a cold finger connected to a closed cycle helium cryostat. The temperature of the substrate was controlled by a carbon resistance and a compound linear thermal sensor (CLTS) situated on the holder, providing a precision of 0.1 K. The cold head with the CsI window could be rotated from 0° to 180° and fixed in three positions allowing bombardment (0°), FTIR analysis (90°) and deposition (180°). A Nicolet Magna 550 Fourier Transform Infrared Spectrometer (FTIR) was used to analyze the sample in the 5000 – $600 cm^{-1}$ (2 – $16.7 \mu m$) region with a spectral resolution of $1 cm^{-1}$. The spectra are taken in transmittance, at normal incidence and were corrected by a background recorded before deposition.

The thickness of the sample (estimated from their column density assuming an ice density of $1 g cm^{-3}$, details of calculation can be found in Pilling et al., 2011) was always much larger than the range (i.e. penetration depth) of 35–200 keV sulfur ions in water ice that ranges between $83 \pm 22 nm$ and $484 \pm 91 nm$ (Ziegler et al., 2008). Ions were then implanted in the target.

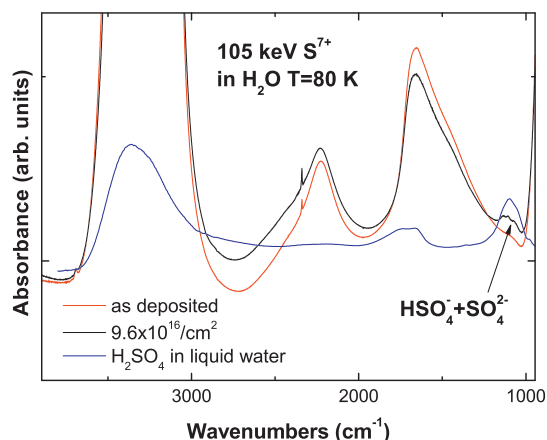


Fig. 1. The spectrum of as deposited water ice at 80 K is shown along with the spectrum obtained after implantation of 9.6×10^{16} 105 keV S^{7+}/cm^2 . For comparison the synthetic spectrum of sulfuric acid hydrate (32 wt%, 210 K; Niedziela et al., 1999) is also shown.

3. Results

Fig. 1 shows spectra measured before and after implantation of 9.6×10^{16} 105 keV S^{7+}/cm^2 in H_2O ice deposited at 80 K. For comparison, the synthetic spectrum of sulfuric acid hydrate (32 wt%, 210 K; Niedziela et al., 1999) is also shown. The appearance of a band that exhibits three peaks at 1135, 1106, $1065 cm^{-1}$ easily attributed to hydrated sulfuric acid is clearly observed (see e.g. Loeffler et al., 2011; Loeffler and Hudson, 2012).

In Fig. 2 some spectra obtained after different ion fluences are shown in the spectral region 1250 – $1000 cm^{-1}$. Also shown is the spectrum of the refractory residue left over after warm up of the target to 190 K. We can see the increase of the band intensity with increasing ion fluence. Furthermore, a change of the structure of the material at 190 K produces a band having a single peak as already observed after thermal processing of mono and tetra sulfuric acid hydrates (Loeffler and Hudson, 2012). As outlined by those authors, it is relevant to say that H_2SO_4 is a strong acid that in mixtures with H_2O , it is easily dissociated into ions. Crystallographic studies have shown, as examples, that the monohydrate is actually $(H_3O^+)(HSO_4^-)$, and $(H_5O_2^+)_2(SO_4^{2-})$ is the tetrahydrate's composition (see e.g. Loeffler and Hudson, 2012) and references therein.

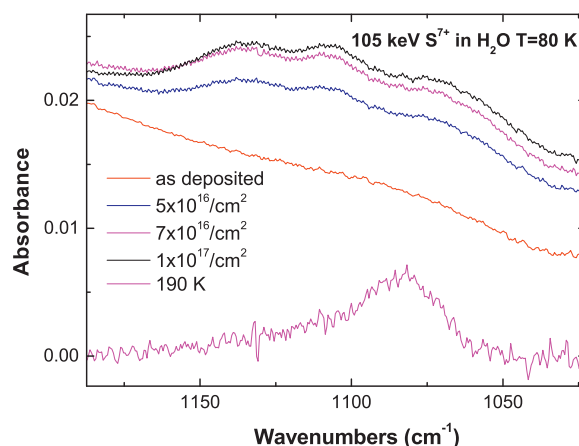


Fig. 2. The spectrum of as deposited water ice at 80 K is shown in the spectral region of the most intense band of hydrated sulfuric acid. Also shown are the spectra obtained after implantation of different fluences of 105 keV S^{7+}/cm^2 and the spectrum obtained after warm up of the sample at 190 K.

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