

Cosmic ion bombardment of the icy moons of Jupiter

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ABSTRACT

A large number of experiments have been performed in many laboratories in the world with the aim to investigate the physico-chemical effects induced by fast ions irradiating astrophysical relevant materials. The laboratory in Catania (Italy) has given a contribution to some experimental works. In this paper I review the results of two class of experiments performed by the Catania group, namely implantation of reactive (H^+ , C^+ , N^+ , O^+ and S^+) ions in ices and the ion irradiation induced synthesis of molecules at the interface between water ice and carbonaceous or sulfurous solid materials. The results, discussed in the light of some questions concerning the surfaces of the Galilean moons, contribute to understand whether minor molecular species (CO_2 , SO_2 , H_2SO_4 , etc.) observed on those objects are endogenic i.e. native from the satellite or are produced by exogenic processes, such as ion implantation. The results indicate that:

- C-ion implantation is not the dominant formation mechanism of CO_2 on Europa, Ganymede and Callisto.
- Implantation of sulfur ions into water ice produces hydrated sulfuric acid with high efficiency such to give a very important contribution to the sulfur cycle on the surface of Europa and other satellites.
- Implantation of protons into carbon dioxide produces some species containing the projectile (H_2CO_3 , and O–H in poly-water).
- Implantation of protons into sulfur dioxide produces SO_3 , polymers, and O_3 but not H–S bonds.
- Water ice has been deposited on refractory carbonaceous materials: a general finding is the formation of a noteworthy quantity of CO_2 . We suggest that this is the primary mechanism to explain the presence of carbon dioxide on the surfaces of the Galilean satellites.
- Water ice has been deposited on refractory sulfurous materials originating from SO_2 or H_2S irradiation. No evidence for an efficient synthesis of SO_2 has been found.

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1. Introduction

Icy surfaces are present both in the interstellar medium as mantles on interstellar and circumstellar dust [1–3] and in/on many objects in the Solar System [4]. Icy surfaces are exposed to a number of energetic processes such as UV photolysis, thermal annealing, micrometeoritic bombardment and irradiation by energetic particles. These latter belong to a number of different populations such as low energy cosmic rays, magnetospheric ions, solar flares and solar wind particles. The interaction produces a number of relevant and potentially observable (some observed) effects. Fast ions penetrating molecular solids deposit energy in the target: along the path of the incoming ion atoms of the target can be moved from their equilibrium positions and chemical bonds can be broken.

The processing of astrophysical ices starts since their formation as icy mantles on interstellar dust. However in circumstellar envi-

ronments (including the solar nebula) dust is, to some extent, “reprocessed”. The irradiation history, during accretion of planetary objects, may be at least as important as that in the interstellar medium, particularly if accretion occurs in the so called T-Tauri phase during which intense particle fluxes occur. After formation planetary objects are exposed to the fluxes of solar, heliospheric, and galactic cosmic rays.

Since the pioneer work on water ice sputtering [5] a large number of experiments have been and are performed in many laboratories in the world with the aim to investigate on the physico-chemical effects induced by fast ions irradiating astrophysical relevant materials.

Laboratory experiments have shown that ion irradiation of ices causes not only the erosion of the target (sputtering) (e.g., [6–8]) but also modification of the structure (crystalline or amorphous) of the sample [9–12] as well as a number of non-thermal, “hot” chemical reactions [13–16] that can lead the formation of a large number of molecules and also organic refractory residues. These laboratory experiments simulate relevant targets bombarded with

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fast charged particles under physical conditions as close as possible to the astrophysical ones [16,17].

The laboratory in Catania has given a contribution to some of those experimental works and applications as e.g., to understand the chemical–physical phenomena that govern the properties of the CO₂ ices in the interstellar medium (ISM) as evidenced by the profile of its infrared bands [18], the formation of an organic crust on comets and trans-Neptunian objects (TNOs) [19], and the color of TNOs [20,21] and main belt asteroids [22].

One of the most known results is the production, starting from simple ices, of species different from the initial ones, including organic refractory materials [13–16]. Reviews of the effects expected on comets and on TNOs have been presented [16,19]. As an example it has been estimated that the external (on the order of meters) layers of a comet were subjected to significant irradiation doses that allow to comets and TNOs to obtain an outer web of non-volatile material which will lead to the formation of a substantial “crust” [23,24] already formed during bombardment at low temperature during a long residence far from the Sun.

While the surfaces of comets and TNOs i.e. in the very outer part of the Solar System are dominated by colored materials (from very red to grey) probably made of organics (however some TNOs have ice-rich surfaces), observations of the surfaces of icy satellites of Jupiter and Saturn at ultraviolet, visible, and infrared wavelengths reveals that they consist mainly of water ice and hydrated materials along with minor amounts of some volatiles such as H₂O₂, SO₂, and CO₂. A still open question is whether those minor species are endogenic i.e. native from the satellite or are produced by exogenic processes. The exogenic sources might be implantation of sulfur ions coming from the Io torus, neutrals from Io, and bombardment by micrometeorites.

To give a contribution to answer those questions a series of experiments have been performed at the Laboratory for Experimental Astrophysics (LASp) in Catania, Italy. Here I review some of these experiments and outline their relevance in particular to understand the properties of the surfaces of the Galilean Jupiter’s moons. The experiments on which I concentrate in this paper are:

- implantation of reactive (H⁺, C⁺, N⁺, O⁺ and S⁺) ions in ices. In particular C⁺, N⁺ and S⁺ have been implanted in water ice and H⁺ in carbon dioxide and sulfur dioxide;
- synthesis of molecules at the interface between water ice and carbonaceous or sulfurous solid materials.

2. Experimental apparatus

Experiments have been performed in a high vacuum ($P < 10^{-7}$ mbar) chamber that has been recently up-graded to ultra-high vacuum ($P \sim 10^{-9}$ mbar), faced to an IR spectrometer (Bruker Equinox or Vertex, 1–25 μm). The spectra here shown have a resolution of 1 cm^{-1} and a sampling of 0.25 cm^{-1} . Icy films are prepared by vapor deposition on IR-transparent substrata (KBr or silicon) at 15–150 K. Ions are obtained from a 200 kV ion implanter (Danfysik). Ion currents are maintained low enough (10–100’s nA) to avoid a significant heating of the sample and are continuously measured by an opportune apparatus placed just in front of the target [15]. The ion beam is swept to obtain uniform irradiation on an area of about 3 cm^2 i.e. much larger than the area sounded by the IR beam. The geometry of our apparatus allows to obtain spectra during irradiation and without tilting the sample for details see [15]. An He–Ne laser can be used to monitor the thickness (micrometers) of the ice film during accretion; this is achieved by looking at the interference pattern (intensity versus time) given by the laser beam reflected at an angle of 45° both by the vacuum-film and film-substrate interfaces [25]. In addition the thickness of the deposited ices (molecules cm^{-2}) can be obtained by measuring the integrated band area (in cm^{-1} and in an optical depth scale) of the bands in the IR spectra and by knowing the band strength of that band (cm molecule^{-1}).

3. Ion implantation

As schematically shown in Fig. 1, we can deposit icy films having a thickness greater or smaller than the penetration depth of the incoming ions. We refer to irradiation experiments when the film

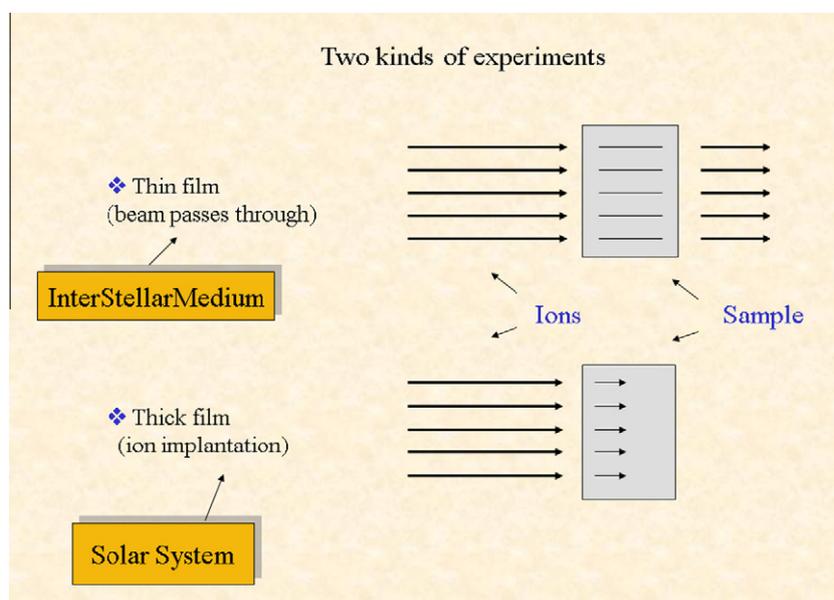


Fig. 1. Schematic view of two kinds of experiments performed in the Laboratorio di Astrofisica SPerimentale (LASp) in Catania (Italy). Ice films are deposited from the gas phase having a thickness larger or smaller than the penetration depth of the incoming ions. We refer to thin films those having a thickness smaller with respect to the ion penetration depth. In this case the ion travels through the target, deposits part of its energy and is implanted in the substrate. In the other case the ions are implanted in the target and we refer to them as thick films. The first case is more appropriate to simulate icy mantles on grains in the interstellar medium. The second better represents what happens to cosmic ion populations irradiating Solar System objects.

is thin with respect to the ion penetration depth. In this case the ion travels through the target, deposits part of its energy and is implanted in the substrate. In the other case the ions are implanted in the target and we refer to as implantation experiments. The first case is more appropriate to simulate icy mantles on grains in the interstellar medium. The second better represents what happens to cosmic ion populations irradiating Solar System objects.

Reactive ions (e.g., H^+ , C^+ , N^+ , O^+ , S^+) induce all of the effects of any other ion, but in addition have a chance, by implantation in the target, to form new species containing the projectile. Each incoming ion having energies between 10 and 200 keV, breaks 10^3 – 10^4 bonds and a large number of new molecules can be formed per single incoming ion by recombination of fragments of the irradiated species. In addition only reactive ions have a chance to form species that include the projectile with a maximum yield of one molecule per incoming ion. For several years we conducted experiments that have the aim to investigate the implantation of reactive ions in many ices of planetary relevance. The experiments conducted so far are listed in Table 1.

The results as a whole indicate that some molecular species observed on icy planetary surfaces, in particular of the Jovian moons, could not be native of that object but formed by implantation of reactive ions.

Although water ice is by far the dominant species on Europa, Callisto and Ganymede, absorption features have been reported at 3.4 ($\sim 2940\text{ cm}^{-1}$), 3.5 ($\sim 2857\text{ cm}^{-1}$), 3.88 ($\sim 2580\text{ cm}^{-1}$), 4.05 ($\sim 2470\text{ cm}^{-1}$), 4.25 ($\sim 2350\text{ cm}^{-1}$) and 4.57 ($\sim 2190\text{ cm}^{-1}$) μm [27]. The prime candidates for the five bands are: C–H, H_2O_2 , S–H, SO_2 , CO_2 , and CN respectively. It has been also suggested that H_2CO_3 is a more likely candidate for the band at 3.88 μm [28]. In addition abundant surface constituents of the Galilean moons are darker, non-ice materials [29], and, in the case of Europa, hydrated sulfuric acid [30]. Some of the darker materials could be organic compounds present at the time of the satellite formation or later delivered by cometary and meteoritic bombardment [31]. Results based on space observations have shown that most of the CO_2 detected on the surfaces of Callisto and Ganymede is contained in the non-ice materials [32,33]. The SO_2 is believed to be present on the surfaces of the icy moons as a molecule trapped in the dark material and/or the water ice [27].

To explain the origin of the SO_2 several mechanisms have been proposed. For the case of Europa, some of those mechanisms are S implantation [34,35], SO_2 volcanism [35], SO_2 from an endogenic source [36], and sulfur dioxide synthesized from a radiolytic cycling of sulfur [30]. In the case of Callisto, as the SO_2 is detected on the leading hemisphere [37] suggested an endogenic source, but others suggested an exogenic source [38].

Icy Galilean satellites orbit within Jupiter's giant magnetosphere and their surfaces are subjected to intense bombardment

by protons and ions such as H^+ , S^{n+} and O^{n+} , and by energetic electrons [39]. This motivated recent experiments of implantation of reactive ions (H, C, N, O, S) in some ices such as water, carbon dioxide and sulfur dioxide. Some of those experiments are here discussed in some detail.

3.1. Ion (C, N, S) implantation in water ice

The chemistry of irradiated water starts with the dissociation to $H + OH$ followed by the formation of many neutral, excited and ionized species: H , H_2 , O , O_2 , H_2O , HO_2 , H_2O_2 [40,41]. In mixtures with other species such as CO or CH_4 , a great variety of molecules can be formed [42,43].

In the case of implantation of C (or N and S), carbon (or nitrogen or sulfur) bearing species might be formed. In a series of experiments [44,45] we have looked, in particular, to the formation of carbon (or nitrogen or sulfur) dioxide that might be formed by direct addition of C to O_2 that is one of the products of water radiolysis or by:

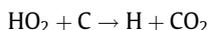


Fig. 2 shows the IR spectra (in optical depth and in two spectral regions) of H_2O (77 K) ice as prepared (thickness of about 1 μm) and after implantation of 30 keV $^{13}C^+$ ions at two different fluences (ions cm^{-2}). The use of isotopically labeled carbon is due to an unavoidable (small) contamination of carbon dioxide in the target sample and to the need to avoid the influence of gas phase CO_2 within the spectrometer. The appearance of bands in the two spectral regions testifies for the formation of H_2O_2 , and $^{13}CO_2$. Although here we are interested in the formation of species containing the projectile ($^{13}CO_2$), the formation of hydrogen peroxide is of primary relevance. Hydrogen peroxide has been in fact found on the surface of Europa [46], Ganymede and Callisto [47,48] by instruments on board of the Galileo spacecraft identifying the absorption feature at about 2850 cm^{-1} (NIMS spectrometer) and/or a feature in the UV spectrum at about 280 nm (UVS spectrometer).

Different groups have studied the formation of hydrogen peroxide by ion bombardment of water ice [49–51]: the results support the idea that ion irradiation is the primary mechanism responsible

Table 1

Summary of reactive ion implantation experiments. The major produced species that contain the projectile are indicated in bold face in column 3.

Ion (energy in keV)	Target $T = 16\text{--}80\text{ K}$	Major produced species (in bold those containing the projectile)	References
H (1.5, 30–100)	CO_2	CO , H_2CO_3 , CO_3 , O_3 O–H in poly-water	[63,64]
	SO_2	SO_3 , $polySO_3$, O_3 , elemental S	[64]
C (10, 30)	H_2O	H_2O_2 , CO_2	[44]
N (15, 30)	H_2O	H_2O_2	[44]
	$H_2O + CH_4$	C_2H_6 , CO , CO_2 , OCN^- , HCN	[56]
O (30)	CH_4	C_2H_6 , C_2H_4	[26]
	$N_2 + CH_4$	C_2H_6 , C_2H_4 , HCN	[55,56]
S (200)	H_2O	H_2SO_4 dissolved in H_2O	[45]

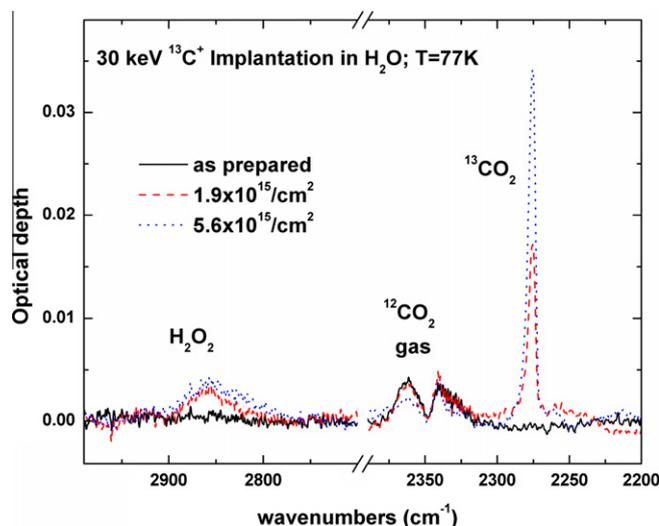


Fig. 2. IR spectra (in optical depth scale and in two spectral regions) of H_2O (77 K) ice as prepared and after implantation of 30 keV $^{13}C^+$ ions at two different fluences. The two solid state bands that appear at about 2860 and 2270 cm^{-1} testify the formation of H_2O_2 , and $^{13}CO_2$. The two bands that appear at about 2350 cm^{-1} are due to an unavoidable (small) contamination of gaseous $^{12}CO_2$ carbon dioxide along the path of the infrared beam within the spectrometer (a purged Bruker Equinox).

for the formation of hydrogen peroxide on the surfaces of the Jupiter's moons. Ion irradiation has been also suggested to be responsible for the formation of O_2 and O_3 observed on Ganymede [52,53] via the dissociation of water molecules and diffusive loss of hydrogen with retention of oxygen.

The column density (molecules cm^{-2}) of $^{13}CO_2$ synthesized after implantation of 30 keV $^{13}C^+$ ions in pure H_2O have been obtained by using an integrated absorbance of 7.6×10^{-17} cm molecule $^{-1}$ as given for $^{12}CO_2$ [54]. The production yield (CO_2 molecules produced per impinging ion) can be then easily obtained and results to be 0.42 ± 0.04 .

Experiments of nitrogen implantation in pure H_2O ice have been conducted and species such as N_2O , NO and NO_2 have been looked for. In Fig. 3 the spectrum obtained after implantation of 4.2×10^{16} 15 keV N^+ ions cm^{-2} in water ice at 16 K is shown and compared with that obtained after irradiation of a mixture $H_2O:N_2 = 1:1$ with 60 keV Ar^{++} (2.4×10^{15} ions cm^{-2}) at 16 K. The results indicate that N_2O and NO (also NO_2 not shown in the figure) are formed after irradiation of the mixture but there was no evidence of their formation after nitrogen implantation. Similarly we have no evidence of the formation of N–H and C–H bonds after implantation of N and C in water. These experiments confirms that, at present, it is not possible to predict when implantation will produce a given species but by doing the experiments. In fact oxygen implantation in frozen methane does not produce the “expected” CO and CO_2 [26]. N implantation in frozen mixtures $H_2O:CH_4$ produces an OCN^- band but implantation of O in frozen mixtures $N_2:CH_4$ does not [55,56].

In Fig. 4 we show the spectra of frozen (80 K) water before and after implantation with 200 keV S^+ ions. Once again, after implantation, the band attributed to H_2O_2 is formed along with a broad band centered at about 1100 cm^{-1} that has been attributed to hydrated sulfuric acid that is formed with a high yield (0.65 ± 0.1 molecules/ion) [45]. Such an yield has been obtained after a comparison with a theoretical spectrum (also shown in Fig. 4) calculated by using the temperature and composition dependent optical constants of H_2SO_4 in water [57]. In the computations we considered different mixtures, having different H_2SO_4 concentration, with variable thickness. The best solution was found for a layer of sulfuric acid hydrate whose thickness is of 0.1 μm constituted by 32 wt.% of sulfuric acid. We used, among the available

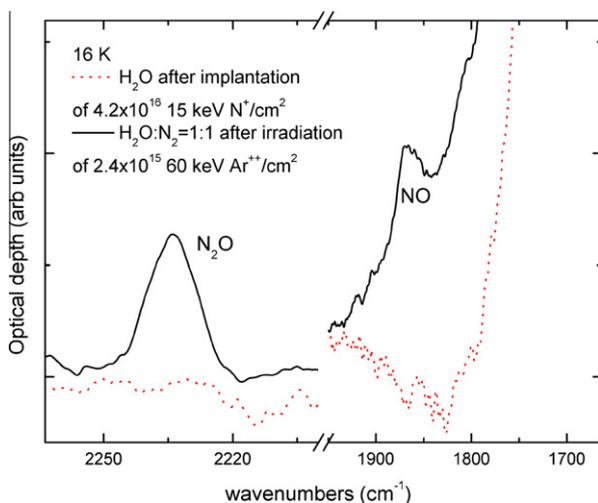


Fig. 3. Spectra (in arbitrary units and in an optical depth scale) obtained after implantation of 4.2×10^{16} 15 keV N^+ ions cm^{-2} in water ice at 16 K (full line) and after irradiation of a mixture $H_2O:N_2 = 1:1$ with 60 keV Ar^{++} (2.4×10^{15} ions cm^{-2}) at 16 K (dashed line). The results indicate that N_2O and NO (also NO_2 not shown in the figure) are formed after irradiation of the mixture but there was no evidence of their formation after nitrogen implantation.

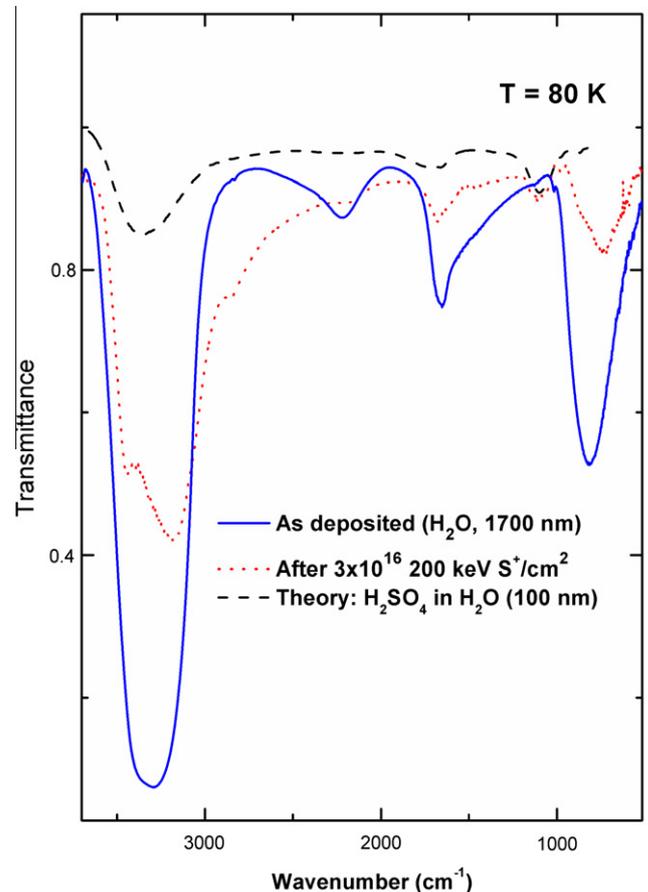


Fig. 4. Transmittance spectra (3700 – 700 cm^{-1}) of frozen (80 K) water before (full line) and after (dotted) implantation with 200 keV S^+ ions. After implantation we observe a band at about 2860 cm^{-1} that is attributed to H_2O_2 . The broad band centered at about 1100 cm^{-1} has been attributed to hydrated sulfuric acid after a comparison with a theoretical spectrum also shown in the figure (dashed).

optical constants, those corresponding to that mixture at 210 K (the lowest available temperature). Concerning the formation of SO_2 it has been possible to find only an upper limit to the production yield ($Y \leq 0.025$ SO_2 -molecules/ion).

The results described so far have some interesting implications for the so called sulfur and carbon cycles (e.g., Johnson et al. 2004) on the Jupiter's moons. The fluxes of sulphur (keV–MeV) ions at the surfaces of the Galilean moons as reported in the literature [31,39] are listed in Table 2. Although the abundance of carbon ions has not been quantified, the number ratio C/S has been considered and found to increase from about 0.2 near by Europa to about unity near Callisto [58,59]. Using C/S = 0.2 at Europa, 0.5 at Ganymede and 1 at Callisto we estimated the flux of carbon ions (Table 2); the time scales necessary to produce a column density of 3×10^{17} CO_2 -molecules cm^{-2} , 2×10^{17} SO_2 -molecules cm^{-2} , and 3×10^{19} H_2SO_4 -molecules cm^{-2} are also reported. Those abundances correspond to those evaluated to be present on the surface of one or more of the Galilean moons.

As noted by McCord et al. [27,29], CO_2 should be in a condensed phase, possibly dispersed in another material, because of the absence of vibro-rotational spectral signatures. In this case a column density as low as 3×10^{17} molecules cm^{-2} is required to produce the observed absorption. Our conclusion is that although a relevant quantity of CO_2 can be formed, however ion implantation is not the dominant formation mechanism because we would then expect more CO_2 on the polar region of Ganymede than at the equator (see Table 2) but observations indicate that the CO_2 absorption bands are clearly greatest in the equatorial region and weakest in

Table 2
Fluxes of sulphur ions [31,39], carbon ions (estimated by using C/S ratios given in [58]), and times necessary to produce the given molecules by ion implantation in the surfaces of jovian satellites.

Satellite	S-ions $\text{cm}^{-2} \text{s}^{-1}$	C-ions $\text{cm}^{-2} \text{s}^{-1}$	Time (years) to produce $3 \times 10^{17} \text{ CO}_2 \text{ molecules cm}^{-2}$	Time (years) to produce $2 \times 10^{17} \text{ SO}_2 \text{ molecules cm}^{-2}$	Time (years) to produce $3 \times 10^{19} \text{ H}_2\text{SO}_4 \text{ molecules cm}^{-2}$
Europa global	$0.2\text{--}1.4 \times 10^8$	$0.4\text{--}2.8 \times 10^7$	$0.8\text{--}5.7 \times 10^3$	$0.2\text{--}1.2 \times 10^4$	$1.0\text{--}7.3 \times 10^4$
Ganymede polar	3.2×10^6	1.6×10^6	1.5×10^4	1.5×10^4	1.5×10^4
Ganymede equator	5.8×10^4	2.9×10^4	8.2×10^5	8.2×10^5	8.2×10^5
Callisto global	3.6×10^5	3.6×10^5	6.6×10^4	6.6×10^4	6.6×10^4

the south polar region [29]. Moreover the escape rate of CO_2 from the Callisto's atmosphere has been estimated to be of about $6 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ (Carlson 1999). Such amount requires a continuous supply from the surface for which C-ion implantation followed by desorption of the formed carbon dioxide cannot be enough.

McCord et al. [27,29] have suggested that the dissociation of water molecules due to ion irradiation (not only implantation) in the presence of a C-bearing species induces the formation of bonds with oxygen-bearing fragments leading to the synthesis of carbon dioxide. In fact the formation of carbon (and sulfur) dioxide at the interface of solid carbon (or sulfur) bearing refractories has been studied and will be discussed below.

Carlson et al. [30] evaluated the amount of sulfur-bearing species present on the surface of Europa and suggest three sulfur-bearing species: polymerized sulfur, SO_2 (about $2 \times 10^{17} \text{ cm}^{-2}$) and hydrated sulfuric acid H_2SO_4 (about and $3 \times 10^{19} \text{ molecules cm}^{-2}$). The results of our calculations (Table 2) indicate that the observed quantity of hydrated sulfuric acid can be formed by implantation of sulfur on time scales of the order of 10^4 years that is of the same order estimated by Carlson et al. (1999b) for the production due to radiolysis of sulfur dioxide in water. In fact radiolysis of SO_2 forms SO_3 [45,60] that in water, rapidly produces H_2SO_4 . To discriminate between exogenic and endogenic sources it is possible to use measurements of the spatial distribution of total sulfur, which is given by the distribution of the sulfur hydrate since $[\text{H}_2\text{SO}_4] > [\text{S}_x] > [\text{SO}_2] > [\text{H}_2\text{S}]$ [31]. It has been evidenced that the global distribution of hydrate shows a trailing side enhancement that is suggestive of the plasma implantation distribution [31]. This is also true for the sulfur dioxide UV signature. Our results confirm that sulfur implantation can produce the observed amount of H_2SO_4 . It is also interesting to note the absence of H_2S in our experiments, and the fact that the polymer-like sulfur residues that are obtained after photolysis and radiolysis of sulfur-bearing species [61,62], well reproduce the Europa observed reflectance spectrum [30].

On the basis of the present results it is not possible to say if the observed sulfur dioxide is quantitatively justified by sulfur implantation, in fact we have been able to find only an upper limit to its production yield.

3.2. H^+ implantation in CO_2

Ion implantation of low energy (1.5 keV) protons in CO_2 demonstrated the formation of H_2CO_3 [63]. Recently a new series of experiments has been conducted with higher energy protons. We have deposited CO_2 frost onto a silicon substrate at 16–80 K and we have irradiated the ice with 50–100 keV H^+ (and He^+ as a check) beam at various fluencies [64]. After H^+ implantation new bands appear that have been attributed to ozone (O_3 , 1039 cm^{-1} see Fig. 5), carbon monoxide (CO , 2139 cm^{-1}) and its isotope (^{13}CO , 2093 cm^{-1}), carbon trioxide (CO_3 , 2045 cm^{-1}), and three wide bands peaked at 1302, 1500 and 1728 cm^{-1} , that can be attributed to carbonic acid H_2CO_3 . In addition O–H bonds are clearly formed testifying for the formation of water as can be seen in Fig. 6 where the spectra of CO_2 ice as deposited at 16 K and after 50 keV H^+

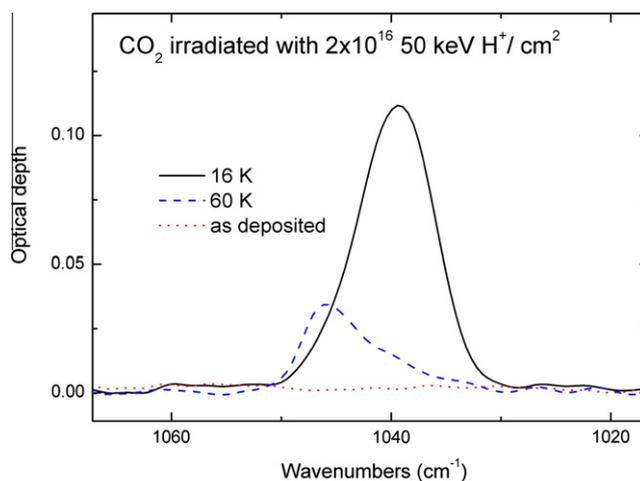


Fig. 5. Spectra, in an optical depth scale, of: pure CO_2 (about 3 micrometer thick layer) deposited on a silicon substrate (dotted line); CO_2 after implantation of $2 \times 10^{16} \text{ 50 keV H}^+$ ions cm^{-2} at 16 K (full line) and after warming up to 60 K. In the shown spectral range we can see the appearance of a band at 1039 cm^{-1} that has been attributed to ozone (O_3).

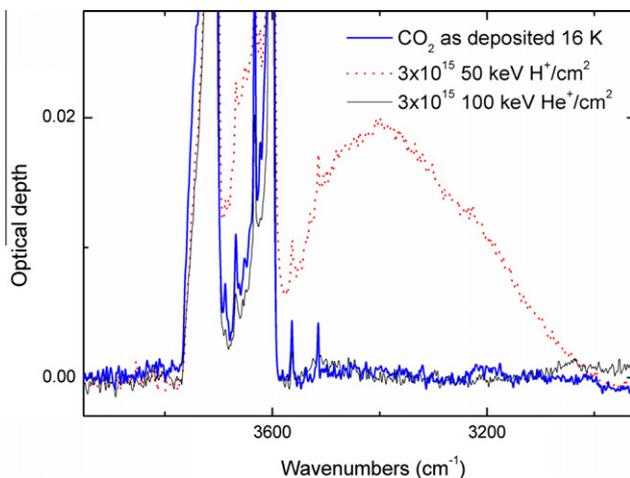


Fig. 6. Spectra ($4000\text{--}2900 \text{ cm}^{-1}$) in an optical depth scale, of: pure CO_2 (about $3 \mu\text{m}$ thick layer) deposited on a silicon substrate; CO_2 after implantation of $3 \times 10^{15} \text{ 50 keV H}^+$ ions cm^{-2} at 16 K and of a similar carbon dioxide film but implanted with $3 \times 10^{15} \text{ 100 keV He}^+$ ions cm^{-2} . Only after H^+ implantation O–H bonds are clearly formed testifying for the formation of water molecules.

implantation are shown in the spectral region $4000\text{--}2900 \text{ cm}^{-1}$. The shape of the newly formed broad band centred at about 3400 cm^{-1} is however different from that of pure water ice indicating that most probably poly-water i.e. small amount of neighbouring water molecules are embedded in the carbon dioxide matrix. Implantation of 100 keV He^+ shows clearly that the three bands attributed to H_2CO_3 as well as to O–H bonds do not appear (Fig. 6).

These results indicate that molecules such as ozone, water dispersed and carbonic acid should be searched for whenever CO₂ has been observed in the Solar System. Carbonic acid is easily formed after irradiation of water–carbon dioxide mixtures but the result of the present experiments confirm the possibility of forming carbonic acid, and its dissociation products (e.g., formaldehyde) by proton implantation in CO₂ also in the absence of water ice. This could occur in some Martian regions dominated by carbon dioxide ice [65].

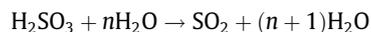
In addition to the Jovian moons, carbon dioxide is abundant in comets [66], on the surface of Triton [67], and the uranian satellite Ariel [68]. CO₂ has been also detected on Iapetus and Phoebe [69,70]. On some of these objects CO₂ could be segregated in patches. In this case the present experiments demonstrate the possibility to synthesize carbonic acid, O₃ and poly-water by implantation of cosmic protons. Those molecules would contribute to a complex chemistry on some of the above listed objects [71].

3.3. H⁺ implantation in SO₂

Among the Galilean moons Io is very peculiar: its intense volcanic activities cause a continuous deposition of sulphur rich material that produces, by rapid cooling, a variety of colours and a surface composition dominated by frozen sulphur dioxide. One question that has been discussed in recent years concerns the presence of sulfurous acid (H₂SO₃) whose formation and stability is possible only under opportune conditions. In the absence of oxidants (that would strongly favour the formation of SO₃ [72] the acid is formed by the reaction



In addition water concentration must not be greater than that of SO₂ otherwise exceeding water would destroy H₂SO₃ [73] by the reaction



H₂SO₃ 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 [72]. Io seems to satisfy all of those requirements but it remains to understand how this acid is formed in absence of water.

Some authors [74] proposed that formation of H₂SO₃ on Io may happen by H⁺ implantation in SO₂ ices analogously to what discussed above for carbonic acid (H₂CO₃). This inspired some laboratory experiments of implantation of 30 keV H⁺ (and He⁺ as check) in SO₂ ice at the temperature of 16 and 80 K [64]. The results indicate that H⁺ implantation in pure SO₂ ice does not produce, in the IR spectrum, any band attributable to H₂SO₃, H₂SO₄ or H₂S, but only SO₃, polymers, and O₃ [64]. The only molecules containing the projectile are O–H bonds and most probably H₂ molecules that are not easily noticeable with IR-spectroscopy.

4. Synthesis of molecules at the interface water ice–solids

As said above the surfaces of Jovian moons are thought to contain significant amounts of the refractory (non-ice) materials, among which sulfurous materials (e.g., elemental sulfur) [30] and organic compounds [31].

In particular results based on space observations have shown that most of the CO₂ detected on the surfaces of Callisto and Ganymede is contained in the non-ice materials [32,33].

These facts stimulated a number of experiments devoted to irradiate water ice deposited on top of solid carbonaceous (or sulfurous) materials.

A schematic view of the experimental concept is shown in Fig. 7. Water ice films were obtained by depositing H₂O vapour

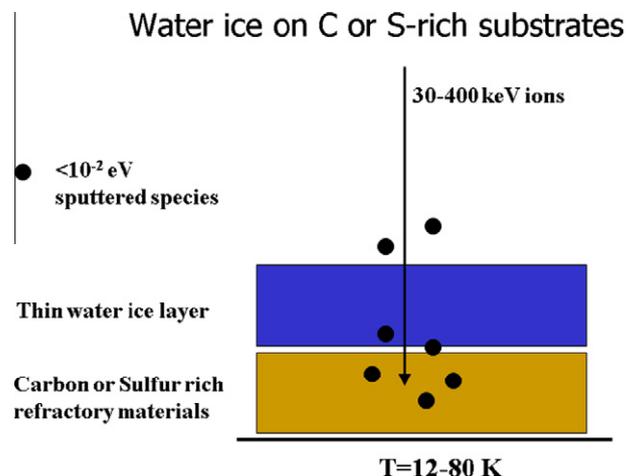


Fig. 7. Schematic depiction of the samples used to study the ion-induced interaction between solid materials (carbon or sulfur rich) and water ice layers deposited on them. Water ice films were obtained by depositing H₂O vapor onto the refractory materials. Ice thickness of about 1000 Å have been prepared and irradiated with energetic charged particles that have always a penetration depth greater than the water ice thickness in order to reach the ice–carbon (or sulfur) interface. Upon irradiation a mixing between species expelled (sputtered) at the interface and having energies on the order of 10^{–2} eV may cause the formation of molecules containing atoms of both the solid and the ice.

onto the refractory materials. Ice thicknesses of about 1000 Å have been prepared and irradiated with energetic charged particles that have always a penetration depth greater than the water ice thickness in order to reach the ice–carbon (or sulfur) interface.

The carbonaceous materials used in these experiments were:

- Organic residues obtained after bombarding frozen hydrocarbon films, e.g., benzene [75].
- Hydrogenated amorphous carbon grains [76].
- Asphaltite, a natural bitumen [77].

Frozen benzene layers were obtained by depositing benzene gas onto a Si substrate at T ~ 16 K. Subsequently, frozen benzene films were irradiated with 200 keV of He⁺ and warmed up to room temperature. It is well known that ion irradiation of simple carbon-containing ices produces complex refractory organic materials that mimic those present on icy mantles in the interstellar medium and on objects such as comets or TNOs and are eventually delivered to the satellite surfaces [78,79].

The hydrogenated carbon grains are good analogs of the interstellar aliphatic component: hydrogen free carbon grains were produced by laser ablation of carbon targets and collected on KBr substrates. Hydrogenation was then obtained by exposure to hydrogen atoms produced by microwave excited dissociation of molecular hydrogen: this simulates hydrogenation of carbon particles by H atoms, likely the key mechanism to explain the presence of C–H bonds in the interstellar medium [80].

Asphaltite, a natural complex hydrocarbon, has been considered as a template of carbonaceous materials containing both aliphatic and aromatic structures. To obtain asphaltite samples suitable for the planned experiments, some drops of asphaltite diluted in chloroform has been deposited on Si substrates at room temperature. After chloroform evaporation uniform asphaltite layers are left over the substrate. The thickness, evaluated by an optical microscope, is of the order of 1 μm [81].

Being the study of the formation of CO₂ one of the main purposes of these experiments it is important to outline that some CO₂ is unavoidably produced by accretion and photolysis and/or radiolysis of background gases, i.e. contamination, as testified by

the appearance of bands attributed to carbon dioxide in the IR spectra of ices whilst being irradiated [82,83]. We have then conducted many blank experiments and demonstrated that the amount of carbon dioxide produced by contamination is always one order of magnitude smaller [76,84].

Fig. 8 shows the spectra of water ice deposited on an asphaltite sample at 16 K (dotted line; asphaltite has no bands in this spectral range, and water ice exhibits a band at about 2200 cm^{-1}), of the sample after ion irradiation (1.5×10^{16} 30 keV He^+ cm^{-2}), dashed line; and after warming the target to 200 K, solid line. The thickness of the deposited water ice layer was about 1.8×10^{17} H_2O molecules cm^{-2} , i.e. lower than the ion penetration depth. We can see that during irradiation some bands are formed as indicated in the figure. Column one in Table 3 lists the peak positions (cm^{-1}) of the newly formed bands (including those not shown in Fig. 8). Their assignment is given in the last column. Formation of CO_2 and CO is evident from the detection of the bands at 2341 and 2135 cm^{-1} , respectively. In addition bands at about 3290 and 2110 cm^{-1} that are attributed to C–H stretch in carbynoid structures ($\text{R}-(\text{C}\equiv\text{C}_m)\text{-H}$; odd ending polyynes) and to $\text{C}\equiv\text{C}$ stretch, respectively appear [77]. Also clearly detectable are bands at 3232 cm^{-1} due to the C–H stretch in acetylenes ($\text{H}-(\text{C}\equiv\text{C}_m)\text{-H}$), 3086 cm^{-1} to the aromatic C–H stretch, and a band at 1956 cm^{-1} that could be due to cumulene ($\text{C}=\text{C}_n$) bonds [85].

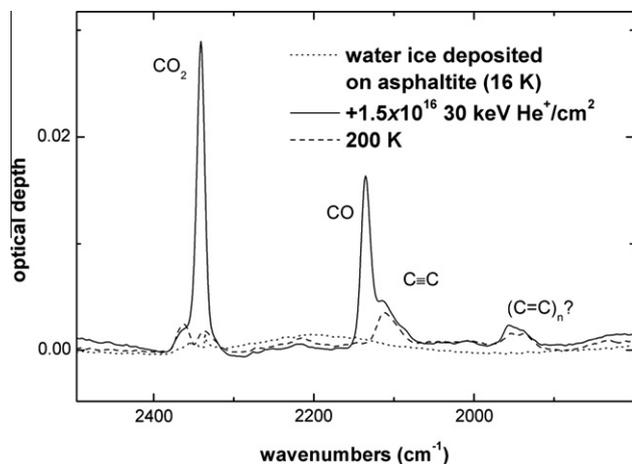


Fig. 8. Spectra ($2500\text{--}1800\text{ cm}^{-1}$) in an optical depth scale, of: a thin film (about 1.8×10^{17} H_2O molecules cm^{-2}) of water ice deposited on an asphaltite sample at 16 K (dotted line; please note that asphaltite has no bands in this spectral range, and water ice exhibits a band at about 2200 cm^{-1}), of the sample after ion irradiation (1.5×10^{16} 30 keV He^+ cm^{-2} ; dashed line) and after warming the target to 200 K (solid line). Formation of CO_2 and CO is evident from the detection of the bands at 2341 and 2135 cm^{-1} , respectively. In addition bands at 2112 and 1956 cm^{-1} that are attributed to $\text{C}\equiv\text{C}$ stretch and, tentatively, to cumulenes ($\text{C}=\text{C}_n$) appear.

Table 3

Peak positions of newly formed IR bands in the $3700\text{--}1900\text{ cm}^{-1}$ region after irradiation (30 keV He^+ ions) of water ice deposited on asphaltite.

H_2O on asphaltite 16 K cm^{-1}	Residue 200 K cm^{-1}	Assignment
3286	3297	$\text{R}-(\text{C}\equiv\text{C})_m\text{-H}$ str (carbynoids)
3232	–	C–H asym str (acetylene)
3086	3076	C–H aromatic str
2341	–	C=O str in CO_2
2135	–	C=O str in CO
2114	2112	$\text{C}\equiv\text{C}$ str
1956	1954	$\text{C}=\text{C}_n$?

At the end of irradiation the sample was warmed and the spectrum at 200 K is also shown in Fig. 8 (solid line). The spectrum does not change any further up to room temperature. The bands due to volatile species disappear because of sublimation and those of a refractory material remain. The peak positions of the latter bands are also reported in Table 3.

Fig. 9 shows the integrated intensities (band areas; cm^{-1}) of the C=O stretching band of carbon dioxide versus ion fluences for the experiments with asphaltite/ice at two different temperatures (16 and 77 K). We can see that the amount of CO_2 reaches a maximum value that using the integrated absorbance value of 7.6×10^{-17} cm/mol [54] is about 4×10^{15} CO_2 mol cm^{-2} and 5×10^{15} CO_2 mol cm^{-2} at 16 and 77 K respectively. It has been proved that the production yield of carbon dioxide does not depend on the ice thickness if this latter is lower than the ion penetration depth. Otherwise no CO_2 is produced but that due to contaminations.

In the laboratory experiments carbon dioxide is formed from a single interface ice-carbon; in a porous regolith as is a satellite surface shaped by interplanetary meteoroid impacts [31], ion irradiation of carbonaceous grains covered with water ice would produce a quantity of CO_2 high enough to explain the amount of carbon dioxide detected on the surfaces of the jovian moons [75].

The energetic charged particles impinging on the surfaces of the Galilean satellites release their energy to the target molecules as simulated in the laboratory. Some authors [31,39] calculated the time necessary to accumulate a significant dose, 100 eV/16 amu, on the surfaces of the Galilean satellites as a function of surface depth. On these basis it has been shown that ion irradiation of the top 10–1000 μm of Galilean satellites can in fact synthesize enough CO_2 to explain the detected amount of such a molecule.

In some of the experiments carbonaceous material/ice the formation of CO is observed; usually CO is detected only at low T (16–20 K) while irradiation at about 80 K does not produce a detectable CO band. However some authors [76] still detect CO after irradiation, at 77 K, of water ice on amorphous carbon. This means that there are some instances at which CO is formed and resides in the ice well above its sublimation temperature. Thus quantities of CO can be formed also at the temperatures on the Galilean satellites (greater or at most equal to 80 K), but their residence time should be very short although a small quantity could remain trapped and could be searched for.

An interesting result is that after irradiation of asphaltite samples carbon bonds characteristic of linear chains are formed (carbynoids and cumulenes) and are still evident after warming

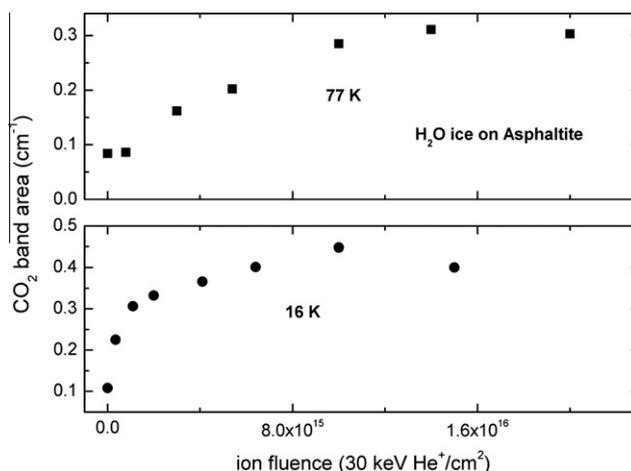


Fig. 9. Band areas (cm^{-1}) of the C=O stretching band of carbon dioxide versus ion fluences (30 keV He^+ cm^{-2}) for the experiments with asphaltite/ice at two different temperatures (16 and 77 K).

the low T samples. The band centered near 3300 cm^{-1} has also been detected after irradiation of solid acetylene, solid benzene and cluster-assembled carbon thin films [86–88]. Thus its formation seems to be a rather general result. The band centered near 2110 cm^{-1} is even more common, being produced also after irradiation of hydrogenated amorphous carbon [76]. Formation of the latter two bands in circumstellar environments, in dense and diffuse clouds is likely [77]. Species bearing the bonds causing those features could then be present on a large number of objects in the Solar System because they mimic the composition of the pre-solar nebula (e.g., comets and Trans-Neptunian Objects) or because delivered by successive meteoritic impacts.

Less investigated has been the ion-induced interaction between water ice and sulfur rich solid materials. The sulfurous materials used in those experiments were residues obtained by irradiation of frozen SO_2 at 16 K [89] or H_2S that have been used as templates of sulfur bearing solid materials. Analysis of the IR transmittance spectra of a SO_2 ice film deposited at 16 K and after irradiation with 200 keV He^+ ions evidence the formation of bands centered at about 1400 cm^{-1} (doublet) and at 1072 cm^{-1} that testify for the formation of SO_3 , along with a band at 1204 cm^{-1} characteristic of polymeric SO_3 . Those results confirm and extend the finding that SO_3 is the dominant molecule synthesized after irradiation of SO_2 with 1 MeV protons [60]. Relevant experiments have been performed on mixtures water– SO_2 [90] that evidenced the formation of H_2O^+ , HSO_3^- , HSO_4^- and SO_4^{2-} after irradiation with 800 keV protons i.e. products similar to those found after sulfur ion implantation in water ice [45] but not after H^+ implantation in SO_2 [64]. One of the effects induced by ion irradiation is however the formation of a refractory material, essentially a not well characterized sulfate that is left over after warming up the sample. Such a sulfurous material “simulates” what could be produced in space irradiating low temperature ices as it could occur for interstellar grains or cometary ices.

In alternative we have also irradiated H_2S to obtain the residue to prepare a residuum rich in S and H (instead that S and O). In fact although SO_2 [91] and OCS [92] are the only S-bearing molecules detected so far among the constituent of icy mantles of interstellar grains, the presence of H_2S has been suggested by chemical models [93] and it has been also observed in the coma of some comets such as Hale-Bopp and Hyakutake [94].

After the preparation of residues, in a typical experiment H_2O ice (80 K) was then deposited on a substrate made of a sulfurous residue and irradiated with ion beams (mainly 200 keV He^+) whose penetration depth was larger than the thickness of ice. We have not found evidences of the efficient formation of SO_2 after irradiation at the interface ice/sulfurous residue. An upper limit to the production yield of SO_2 , $Y \leq 6.3 \times 10^{-7}$ molecules cm^{-2} of interface area for each 100 eV of energy absorbed in 1 cm^3 of ice-covered residue, has been estimated.

As said above the surface of the icy Galilean satellites of Jupiter are dominated by water ice along with other components among which minor amounts of SO_2 [27,34,36,37]. In addition, forms of sulfur-rich species, have been suggested as impurities present on the surfaces of the icy moons [34–37]. Those sulfur-bearing species that could, under irradiation, produce new compounds can be exogenic or endogenic. The exogenic sources are implantation of sulfur ions as discussed above. Endogenic sources are hydrated salts such as sulfates that may be important constituents of the Galilean satellites as suggested by the models of evolution of the satellites [95,96]. All those forms of sulfur-rich species if brought to the surface are subject to radiolysis that initiates the synthesis of refractory sulfurous material as stated before. A still open question is whether those minor icy species are native from the satellite or are produced by processes such as ion irradiation. If the latter is the case then laboratory studies such as those presented here are

valuable in exploring what radiation chemistry may contribute as far as the synthesis of the icy species is concerned.

Based on the described laboratory results we conclude that ion irradiation of mixtures of H_2O ice and solid sulfurous materials likely present on the surfaces of the icy moons can not be the primary formation mechanism responsible for the SO_2 detected on the surfaces of the Galilean moons. Our experiments have also shown that SO_3 is the dominant molecule produced after irradiation of SO_2 ice at low temperature. Thus, we highlight the importance of searching for SO_3 in future observations that could be synthesized by radiolysis on the surfaces of Europa, Ganymede, and Callisto where SO_2 was detected as a minor species.

Also in the case of a residue made from H_2S we have not been able to identify any molecule produced at the interface water/residuum. Irradiation of H_2S itself produces H_2S_2 [90,97]. After warming up to 185 K spectra indicates that a fraction of H–S bonds remains that are part of a more refractory material.

5. Conclusion

Since the pioneer work on water ice sputtering [5] a large number of experiments have been and are performed in many laboratories in the world with the aim to investigate on the physico-chemical effects induced by fast ions irradiating astrophysical relevant materials. The experiments have found relevant application and contributed to understand some properties of ices in the inter-circum-stellar medium and in the Solar System.

The laboratory in Catania has given a contribution to some of those experimental works and applications as e.g., to understand the chemical–physical phenomena that govern the properties of the CO_2 ices in the ISM as evidenced by the profile of its infrared bands [18], the formation of an organic crust on comets and TNOs [19], and the color of TNOs [20,21] and main belt asteroids [22].

In this paper I have reviewed the results of two class of experiments performed by the Catania group, namely implantation of reactive (H^+ , C^+ , N^+ , O^+ , S^+) ions in ices and the synthesis of molecules at the interface between water ice and carbonaceous or sulfurous solid materials. The results have been mainly discussed in the light of some questions relative to the surfaces of the Galilean moons. In particular to contribute to understand whether the minor molecular species (CO_2 , SO_2 , H_2SO_4 , etc.) observed on those objects are endogenic i.e. native from the satellite or are produced by exogenic processes, in particular ion implantation.

The main results indicate that:

- Although a relevant quantity of CO_2 can be formed by carbon ions implantation on Europa, Ganymede and Callisto, this is not the dominant formation mechanism. In particular we would expect more CO_2 at the polar region of Ganymede than at the equator but observations indicate that this is not the case.
- Implantation of sulfur ions into water ice produces hydrated sulfuric acid with high efficiency such to give a very important contribution to the sulfur cycle on the surface of Europa and other Jovian satellites.
- Implantation of protons into carbon dioxide produces some species containing the projectile (H_2CO_3 , and O–H in poly-water) along with other species (CO , CO_3 , O_3) that are produced whatever are the incident ions. All of these species should be searched for whenever CO_2 is observed with the cautions that their relative abundance is dependent on the temperature.
- Implantation of protons into sulfur dioxide produces mainly SO_3 and polymers, and O_3 but not H–S bonds. The suggested hypothesis that H implantation could result in the formation of H_2SO_3 on Io is not confirmed by our experiments.

- Water ice has been deposited on different refractory carbonaceous materials, namely organic residues obtained after bombarding frozen hydrocarbon films, hydrogenated amorphous carbon grains and asphaltite. Although results obtained for different solid substrates have each their own peculiarities, a general finding is the formation of a noteworthy quantity of CO₂. We suggest that this is the primary mechanism to explain the presence of carbon dioxide on the surfaces of the Galilean satellites.
- Water ice has been deposited on refractory sulfurous materials originating from SO₂ or H₂S irradiation. No evidence for an efficient synthesis of SO₂ has been found.

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