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Oxidants produced after ion bombardment of water/carbon dioxide icy mixtures

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Abstract.
Hydrogen peroxide, ozone, carbon monoxide and carbonic acid, have been formed by ion irradiation, at low temperatures, of icy species such as water, carbon dioxide, and their mixtures. The technique used to identify and quantify the synthesized species has been infrared spectroscopy. Irradiation of pure water ice produces H_2O_2 and no O_3 (within the detection limit). Irradiation of pure CO_2 causes the formation of CO, CO_3 and O_3. For the mixtures we find that the H_2O_2 production increases with increasing CO_2 abundance both at 16 and 80 K. The CO and H_2CO_3 production increases with increasing CO_2 abundance at 16 K. At 80 K the synthesis is less efficient. O_3 is detected only after ion irradiation of CO_2 rich mixtures. The experimental results are discussed with a view to the relevance they could have in planetary environments such as icy moons in the external solar system.

Key words. Astrobiology - methods: laboratory - Planets and satellites: Mars, Europa - techniques: spectroscopic

1. Introduction

Water is the dominant ice in a number of objects in the Solar System (surfaces of some planets, satellites, and comets; see e.g., Schmitt et al 1998). Frozen carbon dioxide is abundant in comets (Huebner 2002), on the surface of Triton (Cruikshank et al. 1993) and has been also observed as a minor component on the surfaces of the Galilean satellites Europa, Ganymede, and Callisto (McCord et al. 1997, 1998), and of the Uranian satellite Ariel (Grundy et al. 2003).

Frozen water and carbon dioxide in the martian polar caps have been revealed since from early mapping (for a recent view see Birbring et al. 2004).

Solid matter in the Solar System is subjected to chemical and structural alterations driven by energy released from energetic charged particles irradiation and/or UV photolysis. These processes have been "simulated" in the laboratory with the aim to explain some observational facts (e.g., Johnson 2001, Moore et al. 2001, Strazzulla et al. 2001, Baragiola et al. 2003).

In this paper we present the results of recent studies on the formation of some

Send offprint requests to: G. Strazzulla molecules (carbon monoxide, hydrogen peroxide, ozone, and carbonic acid) due to ion irradiation of frozen water, carbon dioxide and their mixtures at different temperatures (10-150 K). The experimental results are discussed in the light of the relevance they could have to predict the presence of those molecules, in particular oxidants, on some objects of the Solar System.

2. Experimental apparatus

The experimental apparatus used in our laboratory has been described many times (see e.g. Strazzulla et al. 2001). A high-vacuum chamber ($P \leq 10^{-7}$ mbar) faces, through IR-transparent windows, a FTIR spectrophotometer (Bruker Equinox 55). An IR-transparent silicon substrate is put in thermal contact with a closed-cycle helium cryostat (10-300 K). Gases (or mixtures) are admitted into the chamber by a needle valve and accrete as ices on the substrate. Energetic ion beams (up to 200 keV for single ionization) are obtained by an implanter (Danfysik 1080-200) and, impinging on the target, produce a spot greater than the area probed by the infrared beam. Current densities are maintained low enough to avoid thermal annealing of the target. Being the substrate plane placed at an angle of 45 degrees with the IR beam and the ion beam, the spectra can be obtained, even during irradiation, without tilting the sample. The spectra shown in the following have been taken with a resolution of 1 cm^{-1} and a sampling of 0.25 cm^{-1}.

3. Results

3.1. Pure water ice

In recent years a number of works have been done by different groups on the study of the formation of hydrogen peroxide by ion bombardment of pure water ice (Moore & Hudson 2000, Strazzulla et al. 2003, Gomis et al. 2004 a,b; Baragiola et al. 2004). As an example we show, in Fig. 1, the transmittance IR spectra (4000-2400 cm^{-1}) obtained for pure water ice (77 K) before and after implantation of 30 keV protons. The top spectrum refers to the as prepared ice. The other spectra, from the top to the bottom, to implants at increasing fluences, up to $1x10^{16}$ 30 keV H^+ cm^{-2}. The appearance, upon irradiation, of a band at about 2850 cm^{-1} demonstrates the synthesis of hydrogen peroxide. The experiments, have been carried out by using different ions (30-800 keV H^+, He^+, C^+, N^+, O^+, Ar^{++}) and have demonstrated that hydrogen peroxide is easily produced by all of the different ions in a wide range of temperatures. The quantity of H_2O_2 produced is on the order of a few percent into respect to water. Ion irradiation is the primary candidate to explain the presence of H_2O_2 on the Galilean moons detected by space observations (Carlson et al. 1999).

3.2. Mixtures

Table 1 summarizes the experiments we have done concerning irradiation of pure ices and different mixtures H_2O/CO_2.

In Fig. 2 we show, as an example, the spectra (4000-1200 cm^{-1}) of a 1:0.4 mixture of water and carbon dioxide as deposited at 80 K (dotted line) and after irradiation with 3×10^{14} 200 keV He^+ cm^{-2} (solid line). Because of irradiation the intensities of the bands of the original species (water and carbon dioxide) decrease and new features appear due to the synthesis of other species. These features indicate the synthesis of CO, H_2O_2, and H_2CO_3. After warm up the volatile species are lost and a refractory residue, made essentially of carbonic acid, is left over as already demonstrated in previous studies (Moore and Khanna 1991; Strazzulla et al. 1996; Brucato et al. 1997). To better evidence the formation of solid carbonic acid we present, in Fig. 3, the IR spectra (1850-920 cm^{-1}) of a 1:1 mixture of water and carbon dioxide at 10 K, after ion irradiation (($9x10^{16}$ 1.5 keV H^+ cm^{-2}); solid line), and after warming up the irradiated sample from 10 to 217 K. It is evident the formation of H_2CO_3 and O_3 at low temperature. After the warm-up the volatile ozone is lost and a refractory residue made of solid carbonic acid is left over.

Upon irradiation of mixtures, CO_2 is destroyed at a rate larger than that of H_2O. Thus the molecular number ratio CO_2/H_2O decreases, more rapidly at 80 K, and reaches an asymp-

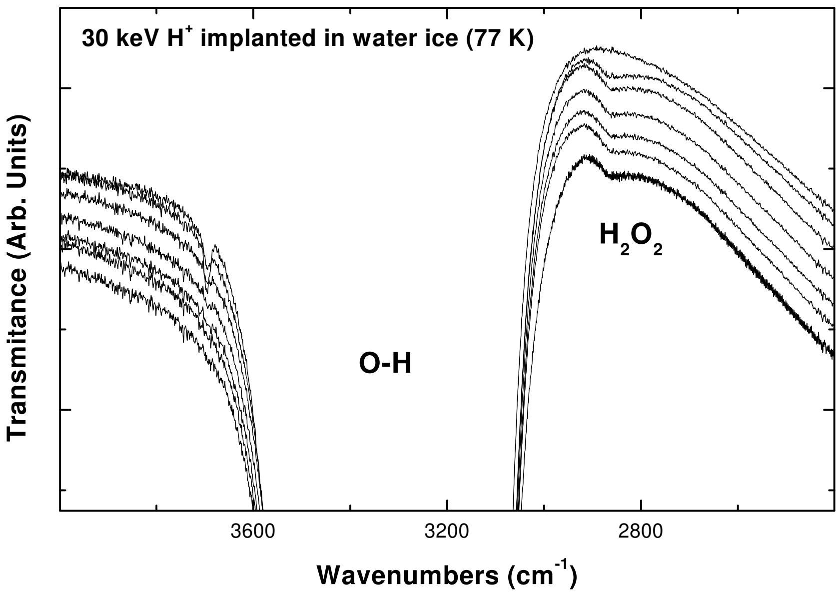

Fig. 1. Transmittance IR spectra (4000-2400 cm^{-1}) of pure water ice (77 K) before and after implantation of 30 keV protons. The top spectrum refers to the as prepared ice. The other spectra, from the top to the bottom, to implants at increasing fluences, up to 1x10^{16} 30 keV H$^+$ cm^{-2}.

Table 1. Species synthesized after ion irradiation (1.5-200 keV ions) of the given icy mixtures at the indicated temperature ranges

H_2O:CO_2	Temperature (K)	Synthesized species
0:1	16, 80	CO, CO_3, O_3
1:1	10-16	H_2O_2, CO, H_2CO_3, O_3
1:0.4	80	H_2O_2, CO, H_2CO_3, CO_3
1:0.2	16	H_2O_2, CO, H_2CO_3
1:0	16-150	H_2O_2

totic value of about 10% (Strazzulla et al. 2005).

The obtained results are summarized in Table 1 where we report the species that have been synthesized from the different targets. The only molecule that appears after ion irradiation of pure water is hydrogen peroxide. The amount of synthesized hydrogen peroxide increases as the quantity of CO_2 in the mixture increases as already demonstrated by Moore and Hudson (2000).

CO is formed from pure CO_2 and whatever is the mixture. Interesting is the case of O_3 and CO_3: O_3 is detected only for pure CO_2 and the mixture 1:1 i.e. with the largest amount of CO_2. It is significant to outline that the syn-

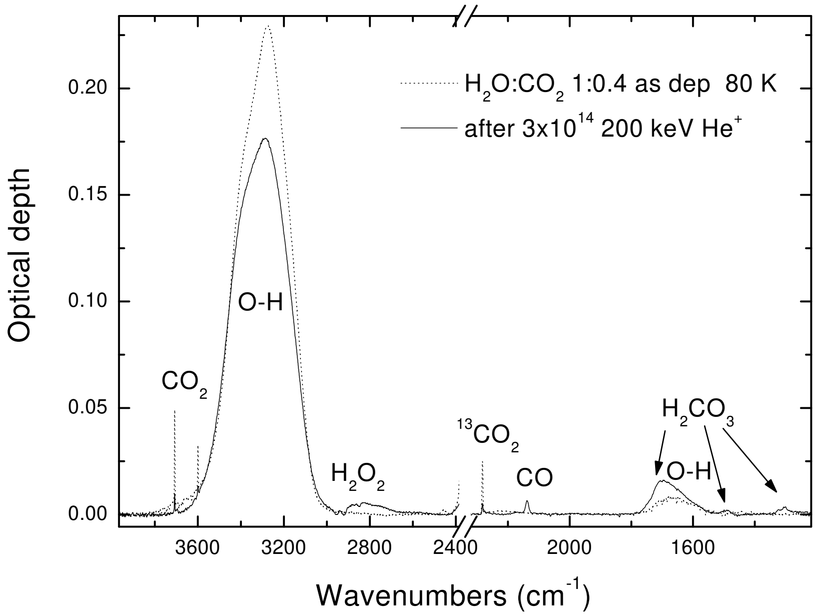

Fig. 2. IR spectra (4000-1200 cm^{-1}) of a 1:0.4 mixture of water and carbon dioxide as deposited at 80 K (dotted line) and after ion irradiation (3 x 10^{14} 200 keV He^+ cm^{-2}).

thesis of ozone is connected to the significant (more than 30%) presence of carbon dioxide in the mixture. CO_3 has been detected only for the mixture prepared and irradiated at 80 K, for which we have noticed a lower efficiency in the production of carbonic acid. This is due to the high mobility of H_2 that easily escape from the target at 80 K instead to react with CO_3 as it occurs at 16 K.

4. Conclusion

We have presented some experimental results obtained after ion irradiation of different icy species at low T (10-150 K): water, carbon dioxide, and their mixtures.

The results are relevant for applications to several objects in the Solar System. The production of oxidants could help in sustaining a carbon-based biochemistry e.g in the case of Europa, the Jovian satellite, for which the existence of a subsurface ocean has been suggested as a possible carrier of aerobic life that should however be maintained by the transport of oxidants formed at the surface (Chyba 2000, Cooper et al., 2001). Europa and the other Galilean moons are continuously bombarded by relevant fluxes of energetic charged particles of the Jovian magnetosphere. Recently the production of oxidants in Europa's surface has been discussed and modeled using available experimental data on ion irradiation of pure water ice (Johnson et al., 2003). Carbon dioxide has been also observed as minor component on the surfaces of the Galilean satellites (McCord et al. 1997, 1998), and of Ariel (Grundy et al. 2003). Recent data from the Galileo spacecraft indicate that most of the CO_2 detected on the surfaces of Callisto and Ganymede is contained in the non-ice materials (Hibbitts et al., 2002a,b, 2003). Thus carbon dioxide is likely concentrated in patches and locally its abundance could be high. On the basis of the results here presented we confirm that hydrogen peroxide is more abun-

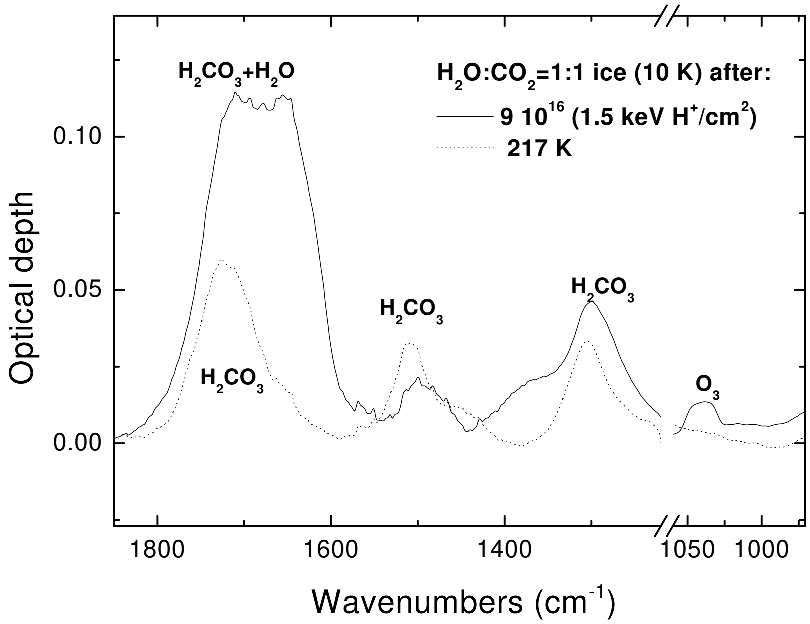

Fig. 3. IR spectra (1850-920 cm^{-1}) of a 1:1 mixture of water and carbon dioxide at 10 K, after ion irradiation ($9x10^{16}$ 1.5 keV H^+ cm^{-2}); solid line), and after warming up the irradiated sample from 10 to 217 K.

dant where CO_2 is concentrated (Moore and Hudson 2000). Ozone could be formed where fresh CO_2 rich layers are exposed to radiation. Ozone has been observed on Ganymede (Noll et al. 1996) and on the Saturn's satellites Rhea and Dione (Noll et al. 1997). We suggest that the spatial distribution of ozone and carbon dioxide on Ganymede should be correlated. CO_2 has not (yet?) been observed on the Saturn's satellites: the observations of ozone suggest its presence on Rhea and Dione. Carbonic acid and CO_3 should also be likely formed where water and carbon dioxide are present, and possibly initiate a complex organic chemistry via, as an example, the decomposition of H_2CO_3 in H_2CO+O_2.

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