Irradiation of Water Ices by 2 keV Carbon Ions

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Abstract. In this paper, we report on the results of experimental studies of the irradiation of pure water ices using 2 keV ¹³C⁺ and ¹³C²⁺ ions. Studies have been carried out at two temperatures (30 and 90 K) and the influence of the different morphologies at these temperatures has also been studied. With singly charged ions, the formation of ¹³CO₂ was observed to be strongly dependent upon morphology and showed a weaker dependence upon temperature. With doubly charged ions, the dependence upon temperature was significantly stronger. This is explained by enhanced production of reactive species resulting from the additional potential energy contained within the doubly charged ions. Increased temperature provides mobility to these species which may then yield additional ¹³CO₂.

1. Introduction

Ion processing plays an important role in the chemical and physical modification of ice surfaces in astrophysical environments. Magnetospheric ions surrounding the Gas Giants in the outer Solar System impinge upon and modify the icy satellite surfaces creating new chemical species [1], incorporating elements not originally present in the local ice composition [2]. These may be formed via ion induced dissociative or reactive processes. Carbon is the fourth most abundant element in the interstellar medium (ISM) and plays an important role in many chemical networks, both in the ISM and in our own Solar System. Most of the carbon ions present in planetary magnetospheres, in our solar system, are thought to originate from the slow component of the solar wind [2] with charge states ranging from 4⁺ to 6⁺ [3] and energies in the low keV range [4]. However, surface sputtering and ionization of the atmospheres of local satellites can give rise to carbon ions with different charge state contributions. For example, the extraction of carbon bearing species (e.g. CH₄ from the atmosphere of Titan), may lead to the enrichment of the Saturnian magnetospheric plasma with carbon ions and carbon containing molecular ions. Similarly, the detection of CO₂ on the surface of the Galilean moons (Io, Europa, Ganymede and Callisto) and
the surface of the Uranian satellite Ariel, suggests the presence of CO$_2^+$, CO$^+$ and C$^+$ ions in the local planetary magnetospheres [5]. Results from Cassini’s Cosmic Dust analyser, on the Jovian and Saturnian stream particles, have revealed C$^+$ as a dominant component in the mass spectra [6]. The Cassini instruments will be the first to measure the charge states of low energy ions (2 – 30 keV/q) and fill the gap in the ion energy spectrum between 4 and 50 keV [7].

The majority of experiments have been carried out using ions with energies greater than 30 keV where electronic stopping (due to inelastic collisions) dominates the energy loss process. However, on a satellite surface where ice crusts are thick, an energetic ion will progressively lose energy via electronic processes until it reaches energies where nuclear stopping (due to elastic collisions) dominates and dissociative [8] and chemical processes may occur. Above about 30 keV, electronic stopping becomes increasingly larger than nuclear stopping. Thus it is expected that secondary processes involving secondary electrons and excited species will dominate reaction schemes.

In the present work we have investigated the interaction of low energy (2 keV) singly and doubly charged carbon ions with amorphous ice films at 30 K and 90 K. We also explore the role of the potential energy carried by doubly charged projectiles in the regime where nuclear stopping dominates.

2. Experimental Approach
Detailed descriptions of the irradiation chamber and ion beam arrangement have been given in previous publications [9,10] so that only a brief summary will be given here. Water ice samples were prepared in situ in an ultra-high vacuum chamber by directed vapour deposition onto a 20 mm diameter transmitting zinc selenide (ZnSe) substrate which was in thermal contact with a continuous flow open cycle cryostat. Beams of $^{13}$C$q^+$ (q = 1 or 2) ions were extracted from a 9.0 -10.5 GHz Electron Cyclotron Resonance (ECR) ion source.

Analysis of the irradiated water ice was carried out using in situ infrared spectroscopy derived from a purged Thermo-Nicolet Nexus 670 FTIR spectrometer. Changes in the infrared absorption spectrum of the ice were monitored as a function of ion fluence (ions cm$^{-2}$).

3. Results

![Graph 1](image1.png)

Figure 1 CO$_2$ yield, induced by 2 keV $\bullet$ C$^+$ (fit shown by solid line) and $\circ$ C$^{2+}$ (fit shown by dashed line), in H$_2$O ice (a) deposited and irradiated at 30 K (30 30) and (b) deposited at 90 K and irradiated at 30 K (90 30).

Figure 1(a) shows the yield of $^{13}$CO$_2$ in a water ice formed and irradiated at 30 K (denoted 30 30) as a function of the total ion fluence (for both C$^+$ and C$^{2+}$). At low fluences, the CO$_2$ yield increased rapidly before beginning to saturate at fluences above several $10^{15}$ ions cm$^{-2}$. Beyond a fluence of $\sim 10^{16}$ ions cm$^{-2}$, little or no increase was observed in the CO$_2$ yield. This effect had been observed previously with both CO$_2$ [10,11] and H$_2$O$_2$ [12].
4. Discussion

4.1. Morphological effects
Comparing the C+ results in figures 1(a) and 1(b), it can be seen that CO2 yield was significantly greater with 3030 (30 K morphology) than 90 30 (90 K morphology). The enhanced yield with the 30 K morphology was a result of the increased porosity of this ice and thus larger surface area on which reactions may take place – a result which agrees with previous experiments [10,12].

4.2. Temperature and Potential Energy Effects
Ions approaching and entering the icy surface will capture electrons and deposit their potential energy close to the ice surface beyond which the projectile is likely to be neutralized. As a result of the initial kinetic energy of the projectile, it will continue to travel through the ice after it has been neutralized, progressively losing energy until it comes to rest. As a result of this, two spatially separated regions exist within the ice. In the absence of migration between these regions, the yield of CO2 would be independent of the ion charge state since CO2 would be formed in the chemical region whilst any effects due to the potential energy of the initial ion would be isolated in the capture region.

Considering the experiments carried out on the 3030 ice, it is clear that the CO2 yield is independent of the ion charge state (figure 1(a)). Experiments performed on the 9030 ice (figure 1(b) - irradiation temperature again 30 K) demonstrate a similar trend with little difference observed between C+ and C2+ irradiations.

In contrast to irradiations carried out at 30K, when the irradiation was carried out at 90 K, (9030 ice – 2), a notable difference was observed in the CO2 yield for C+ and C2+ irradiation. Since little difference was observed between the different ions when this ice morphology was irradiated at 30 K, it is likely that the result at 90 K was a consequence of increased mobility of reactive species at the higher irradiation temperature. This additionally implies an enhanced yield of reactive species in the capture region when the ice is irradiated with a C2+ ion. This is as would be expected when considering the potential energy released by the C+ and C2+ ions upon single electron capture. Such events would release 11.26 eV and 24.38 eV for C+ and C2+ respectively. Considering the energetics of ice phase water [13], it is clear that C2+ deposits sufficient energy into the H2O molecules to exothermically access a dissociative ionization channel whereas the energy deposited by C+ is insufficient to do so. It is therefore expected that C2+ irradiation will result in more dissociation and fragmentation within the ‘capture’ region than will be the case with C+ [14]. At 30 K, these products are isolated from the ‘chemical region’ and thus do not modify the CO2 yield. At 90 K, the products of the capture processes (and products formed in the chemical region) are able to migrate and subsequently react yielding additional CO2.
5. Conclusion
The results presented in this article have demonstrated several important effects which determine molecular formation within water ices.

- Higher charge state ions result in more CO$_2$ formation at irradiation temperatures of 90 K due to more fragmentation in the ‘capture region’.
- At 90 K, the mobility of species which may subsequently yield CO$_2$ is higher than it is at 30 K.
- The more porous structure of 30 K ices results in a larger CO$_2$ yield which is thought to result from the enhancement of surface reactions.

However, several important questions remain to be answered. The chemical reactions leading to the formation (or destruction) of CO$_2$ were not able to be confirmed. This was further complicated by the absence of species such as CO - expected either as precursors in the formation, or products from the destruction. Whilst the work demonstrated that some species, present or formed in the ice, are immobile at the lowest temperatures (30 K), not all species will be confined and thus may escape the ice as rapidly as they are formed or they may simply not be visible to the IR spectroscopic technique.

Acknowledgements
This experiment has been performed at the QU-LEIF facility, part of the distributed LEIF infrastructure. The support received by the European Project ITS LEIF (RII3/026015) is gratefully acknowledged.

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