Ion irradiation of astrophysical ices

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Abstract. Ices, silicates and carbonaceous materials have been detected in several astrophysical environments such as interstellar molecular clouds, comets, and planetary surfaces. These solids are continuously exposed to ion irradiation and UV photolysis. Our knowledge on the properties of solids and molecules and on the modification induced by fast ions (keV-MeV) and UV photons is mainly based on laboratory experiments and on the comparison of experimental results with observations. Here we will give a few examples of the role of laboratory experiments to our understanding of the physical and chemical properties of ices in space.

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 are present on a variety of places in the Solar System, such as the surfaces of satellites of outer planets, the trans-Neptunian objects (such as Pluto), and the comets. In the interstellar medium, inside dense molecular clouds, where the temperature of the gas and dust is about 10 K gas species freeze out on dust grains forming the so called icy grain mantles. In these environments ices suffer from energetic processing due to cosmic ions and UV photons. 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 physical-chemical modifications occur, including the formation of molecules originally not present in the target. These molecules include species that can be both more volatile than the parent ones and less volatile. When carbon is an important constituent of the irradiated target it gives rise to a refractory residue which is left over after warming up to room temperature. That residue has a complex structure, and after prolonged irradiation evolves to form hydrogenated amorphous carbon. Furthermore laboratory experiments have shown that ion irradiation of ices causes the erosion of the target (sputtering; e.g., Johnson 1990) and modification of the structure (crystalline or amorphous) of the sample (e.g., Baratta et al. 1991; Moore and Hudson 1992; Leto and Baratta 2003; Leto et al. 2005). Infrared and Raman spectroscopy are two powerful and complementary tools to study the physical and chemical properties of icy samples. In particular, it is possible to identify molecular groups and specific molecules by infrared (IR) spectroscopy. Raman spectroscopy gives further information on the structural properties of the sample and is often used to study the effects of ion induced lattice damage in carbonaceous
Table 1. Ices in the Solar System.

| Planet   | Satellite | Observed Species                          |
|----------|-----------|-------------------------------------------|
| Jupiter  | Io        | SO₂, H₂S, H₂O                            |
|          | Europa    | H₂O, SO₂, CO₂, H₂O₂                      |
|          | Ganymede  | H₂O, O₂, O₃, CO₂                         |
|          | Callisto  | H₂O, SO₂, CO₂                            |
|          |           | (Calvin et al. 1995; Nash and Betts 1995) |
| Saturn   | Mimas     | H₂O                                       |
|          | Enceladus | H₂O                                       |
|          | Tetis     | H₂O                                       |
|          | Dione     | H₂O, O₃                                   |
|          | Rhea      | H₂O, O₃                                   |
|          | Hyperion  | H₂O                                       |
|          | Iapetus   | H₂O                                       |
|          |           | (Morrison et al. 1984; Cruikshank et al. 1984; Thomas et al. 1986) |
| Uran     | Miranda   | H₂O                                       |
|          | Ariel     | H₂O                                       |
|          | Umbriel   | H₂O                                       |
|          | Titania   | H₂O                                       |
|          | Oberon    | H₂O                                       |
|          |           | (Cruikshank et al. 1995)                  |
| Neptune  | Triton    | N₂, CH₄, CO, CO₂, H₂O                    |
|          |           | (Brown et al. 1995)                      |
|          | Pluto*    | N₂, CH₄, CO, H₂O                         |
|          | Charon    | H₂O                                       |
|          |           | (Cruikshank et al. 1995)                  |

* After IAU resolution, in 2006, Pluto is a dwarf planet and is recognized as the prototype of trans-Neptunian objects.

solids (e.g., Elman et al. 1982; Strazzulla and Baratta 1992; Baratta et al. 1996; Kalish et al. 1999; Strazzulla et al. 2001; Costantini et al. 2002; Ferini et al. 2004).

2. Experimental methods
Several laboratories worldwide are involved in the study of astrophysical relevant ices and of the modifications induced by ion irradiation, UV photolysis and thermal annealing. Here a brief
Table 2. Ionizing radiation in the Solar System.

| Energy   | Input (%) | Flux (cm⁻²s⁻¹) |
|----------|-----------|----------------|
| Solar Photons |           |                |
| 2 eV     | Visible (50%) | 2.0×10¹⁷       |
| 4 eV     | NUV (10%)   | 1.5×10¹⁶       |
| 6 eV     | FUV (0.02%) | 3.0×10¹³       |
| Solar Wind (1 AU) |     |                |
| 1 keV    | H⁺ (95%)   | 3.0×10⁸        |
| 4 keV    | He²⁺ (5%)  |                |
| Solar Flares (1 AU) | |          |
| > 1 MeV  | H⁺ (95%)   | 10¹⁰ (cm⁻²yr⁻¹) |
| > 1 MeV  | He²⁺ (5%)  |                |
| Galactic cosmic rays | |          |
| > 1 MeV  | H⁺ (87%)   | ≤ 10           |
| > 1 MeV  | He²⁺ (12%) |                |

description of the experimental set-up available at the Laboratory of Experimental Astrophysics in Catania (Italy) is given. Further details can be found elsewhere (e.g., Baratta and Palumbo 1998; Baratta et al. 2002; Leto and Baratta 2003; Palumbo et al. 2004)

In situ IR spectroscopy is performed in a stainless steel vacuum chamber facing an FTIR spectrometer. Inside the vacuum chamber, in which pressure is kept below 10⁻⁷ mbar, an IR transparent substrate (e.g., crystalline silicon) is placed in thermal contact with a cold finger which temperature can be varied between 10 K and 300 K. The vacuum chamber is interfaced with an ion implanter (200 kV; Danfysik) from which ions with energy up to 200 kV (400 kV for doubly ionized species) can be obtained. The ion beam produces a 2×2 cm² spot on the target and current in the range of 100 nA cm⁻² to a few µA cm⁻². The amount of energy released to the sample (dose) is often expressed in eV per small molecule (16 a.m.u.) because this is a convenient way to characterize the chemical changes and to compare the effects induced on icy mixtures with different chemical composition (Strazzulla and Johnson 1991). In the case of ion irradiation the dose is calculated from the knowledge of the ion fluence (ions cm⁻²), the stopping power (eV cm² molecules⁻¹) of the projectile, and its penetration depth or range in the target (molecules cm⁻²). The first is given by a current integrator on the path of the ion beam, which measures the charge which reaches the sample during irradiation; the other parameters are well known and can be provided by a software such as TRIM simulation program (Ziegler et al. 1985). A needle 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 versus time) given by the laser beam reflected at an angle of 45° both by the vacuum-film and film-substrate interfaces (see Baratta and 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 easily taken in situ, even during irradiation, without tilting 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.
Table 3. Composition of icy grain mantles (with respect to H$_2$O = 100).

| Species | Abundance | References                                      |
|---------|-----------|------------------------------------------------|
| H$_2$O  | 100       | Chiar et al. 1994;                              |
| CO      | 0 - 40    | Allamandola et al. 1992; Boogert et al. 1997;   |
| CH$_3$OH| 3 - 30    | Palumbo et al. 1997;                            |
| OCS     | 0.04 - 0.1| Lacy et al. 1991; Boogert et al. 1997;          |
| CH$_4$  | 0.3 - 4   | Schutte et al. 1996;                            |
| H$_2$CO | 3 - 7     | Lacy et al. 1998;                               |
| NH$_3$  | 5 - 10    | Gerakines et al. 1999;                          |
| CO$_2$  | 10 - 25   | Tegler et al. 1995;                             |

3. Solar System ices

Ices are present on many objects in the Solar System such as the satellites of the external planets (Jupiter and beyond), Pluto and the so-called trans-Neptunian objects (a class of numerous small objects not yet well investigated), and comets. In these cases, the study of the composition of the ices is based on the study of the electromagnetic radiation coming from the Sun and reflected by the surface to the observer. Table 1 reports those objects where ices have been detected along with the species detected. Icy surfaces in the Solar System suffer from processing due to solar photons, to solar wind and solar flares ions, and galactic cosmic rays. Table 2 reports the photon and ion fluxes impinging on Solar System objects. These are exposed to the continuous expansion of the solar corona, referred to as solar wind. Superimposed on this flux are higher energy particles associated with very energetic particles produced in solar flares, and the galactic cosmic-ray particles. Assuming one solar flare event per year the flux of such particles is much lower than the solar wind flux but with a very different energy spectrum (see Johnson 1990 for a detailed discussion). Furthermore, those satellites moving in the magnetosphere of their planet suffer from the effects of magnetospheric ions (e.g., Johnson 1990; Strazzulla and Johnson 1991).

On Europa, among others, hydrogen peroxide (H$_2$O$_2$), has been detected. The identification of this species is based both on an absorption feature at 3.5 µm (2857 cm$^{-1}$) in the Galileo NIMS spectra and looking at the UV spectrum taken by the Galileo Ultraviolet Spectrometer (UVS) (Carlson et al. 1999). Comparison with laboratory spectra indicates a surface concentration of about 0.13 percent, by number of molecules, relative to water ice. Europa, as well as the other Galilean satellites, is immersed into a highly energetic plasma environment originating in the Jupiter magnetosphere. The plasma is mainly constituted by energetic electrons, protons, and ions. It has been estimated that the total average energy flux received by Europa is about 7.8×10$^{10}$ keV cm$^{-2}$ s$^{-1}$ (Cooper et al. 2001). Thus radiolysis is supposed to be the dominant formation mechanism of hydrogen peroxide on Europa. This hypothesis has been recently confirmed on the base of laboratory results (Gomis et al. 2004; Moore and Hudson 2000). Water ice has been irradiated at 16 and 80 K with different types of ions (H, C, N, O, and Ar) with energy of 30 keV. It has been found that hydrogen peroxide is produced by all the different ions at both temperatures and it has been estimated that H$_2$O$_2$ can in fact be produced on Europa by radiolysis of water ice. Laboratory experiments also suggest a patchy distribution of H$_2$O$_2$ on Europa. This result could be useful to support the hypothesis of a radiation-driven ecosystem on Europa based on the availability of organic molecules and oxidants such as hydrogen peroxide (Chyba 2000).
Table 4. Cosmic ion and UV fluxes in quiescent interstellar regions.

| region     | proton (1 MeV) flux (cm\(^{-2}\)s\(^{-1}\)) | UV flux (cm\(^{-2}\)s\(^{-1}\)) |
|------------|---------------------------------------------|----------------------------------|
| diffuse    | 1.8                                         | 8×10\(^7\)                       |
| dense      | 1.0                                         | 1.4 - 4.8×10\(^3\)               |

Mathis et al. 1983; Prasad and Tarafdar 1983; Mennella et al. 2003

4. Ices in dense interstellar clouds

The presence of ices along the line of sight of dense interstellar molecular clouds is clearly evidenced by infrared observations (e.g., Willner et al. 1982; Whittet et al. 1988; Smith et al. 1989; Tielens et al. 1991; Gerakines et al. 1999; Gibb et al. 2000; Boogert et al. 2004; Bergin et al. 2005). In fact absorption features are superposed to the spectrum of a field star or of the embedded object in star forming regions. Most of these features are attributed to icy grain mantles. It is generally accepted that grain mantles form after direct freeze out of gas phase species and after surface reactions of atoms and radicals on grains. Thus the chemical composition of icy mantles differs from that of the gas phase. As an example observed spectra show that water is the most abundant species in icy grain mantles towards all lines of sight while it is not an abundant species in the gas phase. Table 3 reports the most abundant species detected in the solid phase in icy grain mantles. Since solid water is the most abundant species detected the amount of other species is given with respect to that of water ice.

In dense molecular clouds icy mantles suffer from ion bombardment, UV photolysis and thermal annealing. Table 4 reports the flux of cosmic ion and UV photons which interact with icy grain mantles. The ion flux has been estimated following the approximation of effective monoenergetic 1 MeV protons. In dense regions the UV flux is due to cosmic ray induced fluorescence of molecular hydrogen (Prasad and Tarafdar 1983). As reported by Greenberg (1982), dense cloud lifetime has been estimated at 3×10\(^7\) - 5×10\(^8\) years. Assuming that the gas density values \(n \approx 10^4\) cm\(^{-3}\), the gas takes 10\(^9\)/\(n\) \(\approx 10^5\) years to condense on grains (Tielens and Allamandola 1987). Thus icy grain mantles suffer ion irradiation for about 10\(^5\) - 5×10\(^8\) years. The former estimate refers to the case of grain mantles which sublimate immediately after formation while the latter refers to the limit case of icy grain mantles (or at least part of them) which survive for all the cloud lifetime. The specific energy loss (stopping power) of 1 MeV protons in a typical grain containing heavy atoms (C, N, O, Si) is \(S \approx 5×10^{-15}\) eV cm\(^2\) atom\(^{-1}\). Thus the energy deposited on a grain (dose), given by the product of the stopping power times the flux times the mantle lifetimes (3×10\(^{12}\) - 1.5×10\(^{16}\) s), values 0.015 - 75 eV/atom(C, N, O, Si). In star forming regions the flux of ions and then the doses absorbed by icy mantles can be higher than the values reported above.

Among the absorption features detected in the spectra of protostellar objects, there is a band at 4.62 \(\mu\)m (2165 cm\(^{-1}\); e.g., Pendleton et al. 1999). This feature is generally assigned to the C≡N group in a molecular species not well identified often referred to as XCN (e.g., Demyk et al. 1998; Hudson and Moore 2000; Palumbo et al. 2000; Bernstein et al. 2000). In laboratory this feature is readily formed after ion irradiation and UV photolysis of ice mixtures containing O-C- and N-bearing species and is attributed to OCN\(^-\). The presence of this band in observed spectra of icy grain mantles is often pointed out as evidence of energetic processing of interstellar ices. Figure 1 shows the infrared transmission spectra of a H\(_2\)O:CH\(_4\):N\(_2\)=1:1:1 ice mixture irradiated...
Figure 1. Infrared transmission spectra, in optical depth scale, of a H$_2$O:CH$_4$:N$_2$ ice mixture after ion irradiation with 60 keV Ar$^{++}$ ions (dose equal to 12 eV/16amu). Spectra taken at different temperatures have been shifted in y-axis for clarity.

Figure 2. Comparison between the profile of the band at 4.62 µm (2165 cm$^{-1}$) observed towards the protostellar object W33A and the laboratory spectrum of a H$_2$O:CH$_4$:N$_2$ ice mixture irradiated at 12 K and warmed up to 120 K.
at 12 K. A spectrum has been taken at low temperature after irradiation and spectra have also been taken after warm up at selected temperatures. In the 2500-2000 cm\(^{-1}\) spectral region, new features appear at about 2340, 2262, 2235, 2165, 2139, 2080 cm\(^{-1}\). These are attributed to CO\(_2\), HNCO, N\(_2\)O, OCN\(^-\), CO, HCN and/or CN\(^-\) respectively (e.g., Grim and Greenberg 1987; Sandford and Allamandola 1990; Elsila et al. 1997; Demyk et al. 1998; Novozamsky et al. 2001; Hudson et al. 2001; Moore and Hudson 2003). A recent study has shown that formamide is also formed after ion irradiation of a H\(_2\)O:CH\(_4\):N\(_2\)=1:1:1 ice mixture (Brucato et al. 2006; Strazzulla et al. in preparation). After warm up the intensity of some absorption bands decreases indicating that volatile species sublimate while the band at about 2165 cm\(^{-1}\) is still present in the spectrum taken at 250 K suggesting that the C≡N bearing species remain trapped in the refractory residue also formed after ion irradiation at low temperature.

Figure 2 shows a comparison between the profile of the 2165 cm\(^{-1}\) band observed towards the high mass protostellar object W33A and the band formed after ion irradiation of a H\(_2\)O:CH\(_4\):N\(_2\) ice mixture. The goodness of the comparison supports the hypothesis that energetic processing plays a very important role in the evolution of icy grain mantles and that the chemical composition of icy mantles can be strongly influenced by the interaction with cosmic ions (see e.g., Palumbo and Strazzulla 1993; Palumbo et al. 1999, 2000; Mennella et al. 2004).

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