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Ion irradiation of ices relevant to astrophysics

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Abstract. Ices, silicates, and carbonaceous materials have been observed in different astrophysical environments such as the interstellar medium, circumstellar regions, comets, and solid surfaces of Solar System objects. In space these materials suffer from processing caused by cosmic rays, photons and thermal annealing. Our knowledge of the effects of processing on the evolution of solids in different astrophysical environments in mainly based on laboratory experiments. The Laboratory of Experimental Astrophysics in Catania (Italy) is equipped to study the effects of processing on astrophysical relevant materials. Here we briefly describe the experimental set up and discuss some recent results.

Key words. laboratory experiments – processing – solid materials

1. Introduction

Solid objects in space (interstellar grains, comets, interplanetary dust particles), are continuously exposed to energetic processes such as cosmic ray irradiation, UV photolysis, and thermal annealing. Fast ions passing through a molecular solid release energy to the target material. As a consequence many molecular bonds are broken along the ion-track and, in a very short time (one picosec or less), the molecular fragments recombine giving rise to a rearrangement of the chemical structure. Hence, in addition to the alteration of the chemical and lattice structure of the target material, new molecular species (not present before irradiation) are formed. In the case of UV photolysis, the energy is released to the target material through single photo-dissociations, photo-excitations or ionization events per incoming photon. Also in this case new molecular species are formed. Thermal annealing causes segregation and crystallization.

Our knowledge of these processes and of their effect in different astrophysical environments is based on laboratory experiments. In fact the effects induced by fast ions and UV photons on solids of astrophysical interest have been studied in different laboratories for many years (e.g., Hagen et al. 1979; Moore et al. 1983; Strazzulla et al. 1983; Allamamdola et al. 1988; Westley et al. 1995; Leto & Baratta 2003; Gomis et al. 2004). Laboratory experiments have shown that both processes induce chemical and structural modifications of the ice samples.

Infrared and Raman spectroscopies 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

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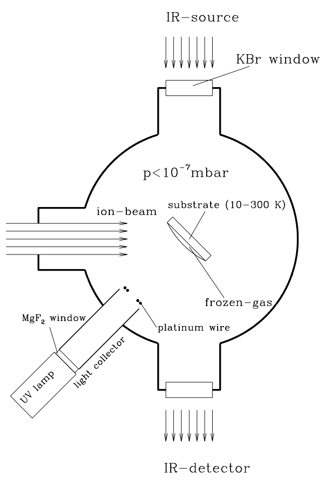

Fig. 1. Schematic view of the vacuum chamber.

to study the effects of ion induced lattice damage in carbonaceous solids (e.g., Elman et al. 1982; Strazzulla et al. 2001 and references therein).

Here we briefly present the experimental apparatus available in the Laboratory of Experimental Astrophysics in Catania and discuss a few recent results.

2. Experimental

The in situ analyses are performed in a stainless steel high vacuum chamber (Figure 1). Inside the chamber, in which pressure is kept below 10^{-7} mbar, a substrate (crystalline silicon) is placed in thermal contact with a cold finger whose temperature can be varied between 10 K and 300 K. Silicates and carbonaceous materials are firmly placed on the substrate. In order to study frozen ices, a needle valve is used to admit pre-prepared gases (or mixtures) into the chamber, where they freeze on the substrate.

The vacuum chamber is interfaced with an ion implanter (200 kV; Danfysik) from which ions with energy up to 200 keV (400 keV for double ionizations) can be obtained. The ion beam produces a 2×2 cm^2 spot on the target and current density in the range of 100 nA cm^{-2} to a few μA cm^{-2}, in order to avoid a macroscopic heating of the target. A current integrator on the path of the ion beam, measures the charge which reaches the sample during irradiation.

A hydrogen microwave discharge resonance lamp (Opthos Instruments) is interfaced with the vacuum chamber through an MgF_2 window; from this lamp mainly 10.2 eV photons are obtained. An aluminium light collector is placed at the end of the lamp in order to increase the number of UV photons that reaches the sample. A light detector, placed at the end of the aluminium light collector, is used to measure the UV flux during photolysis. The detector is a platinum wire which gives a current, by the photoelectric effect, proportional to the UV flux. The calibration procedure of the system is described in Baratta et al. (2002).

Infrared spectra are taken with a Fourier Transform Infrared (FTIR) spectrometer (Bruker Equinox 55). The sample holder has a hole, with a diameter of 4.5 mm, which allows the infrared beam to transmit through the substrate and the sample. The infrared beam forms an angle of 45^o with both the ion beam and the substrate holder.

In order to obain Raman spectra, a continuous multiline Ar-ion laser beam (λ=514 nm) enters a confocal illuminator perpendicularly to its optical axis, into which it is deflected by a microprism. The confocal optical system is arranged in such a way that any parallel beam incident along the optical axis in the opposite direction of the laser is focused onto the entrance slit of the spectrometer (Triplemate SPEX). By means of two flat mirrors, the laser beam is reflected towards the vacuum chamber, where it is focused on a 40 μm spot on the sample. The same objective which focuses the laser beam on the sample collects the Raman-scattered light, which reaches the confocal illuminator going back along the same path of the laser beam. This confocal system makes it possible to obtain Raman spectra of samples located several meters away from the spectrometer with negligible performance losses. The substrate holder is mounted at an angle of 45^o both with the ion beam and the Ar-ion laser beam. This configuration offers the advantage that both IR and Raman spectra can be easily taken in situ, even during processing, without tilting the sample. Futher details on the experimental apparatus and calibration procedures can be found in Baratta & Palumbo (1998); Strazzulla et al. (2001); Baratta et al. (2002) and Palumbo et al. (2004).

3. Results and discussion

Using infrared and Raman spectroscopies, we have studied the effects induced by ion irradiation on icy mixtures at low temperature (T=12 K) and after warm up to room temperature. In particular, we have considered mixtures made of H_2O, CO, CH_4, and N_2. These mixtures have been irradiated with 30 keV He^+ and 60 keV Ar^{++} ions. After ion irradiation at low temperature, several new absorption features appear in the infrared spectra, some of which are due to N-bearing molecular species. A refractory organic residue is left over after warm-up to room temperature. After further irradiation of the residue at room temperature, the intensity of all infrared absorption features decreases. Raman spectroscopy of similar mixtures has shown that ion irradiation causes a modification of the structure of the samples which evolve towards an amorphous carbon (Palumbo et al. 2004).

Figure 2 shows the infrared transmission spectra of a mixture $H_2O:CH_4:N_2$=1:1:1 after irradiation with 60 keV Ar^{++} ions at 12 K. Because of processing new absorption features appear, indicating that different molecular species, not present in the original sample, are formed. In particular, 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_2O, OCN^-, CO, HCN and/or CN^- respectively (e.g., Grim & Greenberg 1987; Elsila et al. 1997; Demyk et al. 1998; Hudson et al. 2001). Also an absorption feature at about 2328 cm^{-1} is present. This is attributed to solid N_2. Actually N_2, being a homonuclear molecule has no infrared active bands. However, in the solid phase, due to the interaction with neighbouring molecules, the symmetry is broken and a weak band appears. After warm-up all volatile species sublime and a refractory organic residue, stable at room temperature, is left over.

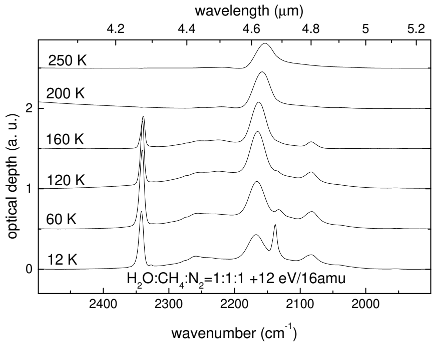

Fig. 2. Infrared transmission spectra, in optical depth scale, in the 2500-2000 cm^{-1} range, of the mixture $H_2O:CH_4:N_2$=1:1:1 after ion irradiation with 60 keV Ar^{++} at 12 K and after warm-up to different temperatures. Thickness of the irradiated sample is 6 μm. Spectra have been shifted in the vertical scale for clarity.

Figure 3 shows a comparison between a laboratory spectrum and the feature at 2165 cm^{-1} (4.62 μm) observed towards the infrared source W33A. This is a protostellar object still embedded in its placental cloud. In the outer part of this cloud icy grain mantles are present which give rise to the absorption features observed in its infrared spectrum (e.g., Gibb et al. 2000). Such a comparison gives the possibility to identify the carrier of this feature as a N-bearing molecule. In particular, on the basis of several laboratory experiments this feature has been attributed to the C≡N stretching mode of the cyanate anion OCN^- (e.g., Grim & Greenberg 1987; Demyk et al. 1998; Hudson et al. 2001).

Finally, laboratory experiments have shown that different nitrogen-bearing molecules as well as complex species are formed after ion irradiation of simple icy mixtures, consistent with observations of ice in the interstellar medium (Pendleton et al. 1999; Palumbo et al. 2000). These molecules could have a fundamental role in the devel-

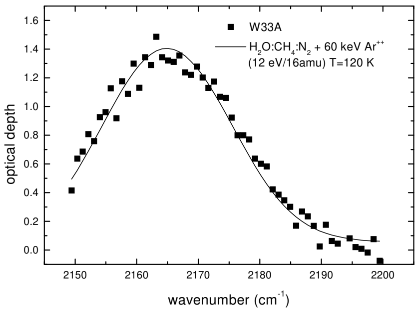

Fig. 3. Comparison, in the 2100-2200 cm^{-1} range, between the spectrum observed towards the embedded source W33A (points) and the laboratory spectrum obtained after ion irradiation at 12 K of a mixture $H_2O:CH_4:N_2$=1:1:1 and warm-up to 120 K (solid line).

opment of a very complex chemistry. In fact, these molecules could have been delivered by comets on the primitive Earth during the early heavy bombardment. Here, they could have contributed to the development of more complex biogenic compounds.

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