

# Cosmic ion irradiation and UV photolysis of solids in star forming regions

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**Abstract.** The presence of icy grain mantles along the line of sight of star forming regions is clearly evidenced by infrared observations. Due to the presence of the protostar and of cosmic radiation, ices suffer from ion bombardment, UV photolysis and thermal annealing. Most of our knowledge on the physical and chemical properties of ices is based on the comparison between observations and laboratory experiments performed at low temperature (10-80 K). Experimental results show that after ion irradiation and UV photolysis the chemical composition and the structure of the sample is modified. Both more volatile and less volatile species are formed and if a C-bearing species is present in the original sample a refractory residue is formed. Eventually thermal annealing causes the sublimation of icy mantles. Thus molecules are released to the gas phase which could be enriched by species formed in the solid phase. Here we will discuss some recent laboratory experiments relevant to the knowledge of the physico-chemical properties of ices in star forming regions.

**Key words.** Astrochemistry – molecular processes – methods: laboratory – techniques: spectroscopic – stars: formation – ISM: molecules

## 1. Introduction

In dense molecular clouds ( $n_H > 10^4 \text{ cm}^{-3}$ ) gas phase species condense on silicatic and carbonaceous grains giving rise to icy mantles. These mantles are made of molecules which directly freeze out from the gas phase (such as CO) and molecules which are formed after grain surface reactions (such as H<sub>2</sub>O). The presence of icy grain mantles is indirectly deduced from depletion of gas phase species and observed in the infrared from absorption features attributed to vibrational modes of solid phase molecules superposed to the background stellar spectrum. Ices have been observed in

star forming regions (both low- and high-mass) as well as in quiescent dense clouds. In particular, solid water (H<sub>2</sub>O), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methanol (CH<sub>3</sub>OH) and methane (CH<sub>4</sub>) have been securely identified. Other species such as carbonyl sulphide (OCS), formaldehyde (H<sub>2</sub>CO), formic acid (HCOOH), cyanate ion (OCN<sup>-</sup>) and ammonia (NH<sub>3</sub>) have been likely identified. Some features, observed in the astronomical spectra, still remain unidentified (see Gibb et al. 2004, for a recent review).

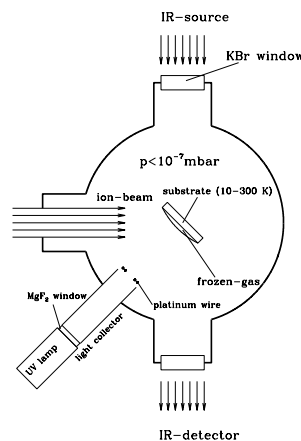
Solid objects in space (e.g., interstellar grains, comets, interplanetary dust particles), are continuously exposed to energetic processes such as cosmic ion irradiation and UV photolysis. Fast ions passing through a molec-

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ular 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. 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 a single photo-dissociation or photo-excitation event. Also in this case new molecular species are formed. Our knowledge on the effects of ion irradiation and UV photolysis on astrophysical relevant materials is mainly based on laboratory experiments.

Following the approximation of monoenergetic 1 MeV protons it has been estimated that the proton flux values  $1.8 \text{ protons cm}^{-2}\text{s}^{-1}$  in diffuse quiescent regions and  $1 \text{ proton cm}^{-2}\text{s}^{-1}$  in dense quiescent regions (Mennella et al. 2003). Estimates of the UV flux under diffuse medium conditions give a value of  $8 \times 10^7 \text{ photons cm}^{-2}\text{s}^{-1}$  (Mathis et al. 1983). In dense regions the internal UV flux due to cosmic-ray induced fluorescence of molecular hydrogen values  $1.4 \div 4.8 \times 10^3 \text{ photons cm}^{-2}\text{s}^{-1}$  (Prasad & Tarafdar 1983; Mennella et al. 2003). Taking into account the amount of energy released by ions and photons passing through an ice mantle, the effects of UV photons dominate in diffuse regions while the effects of ions and UV photons are comparable in dense regions (Moore 1999). As reported by Greenberg (1982), dense cloud lifetime has been estimated at  $3 \times 10^7 - 5 \times 10^8$  years. Assuming  $n_H \sim 10^4 \text{ cm}^{-3}$ , the gas takes  $10^9/n_H \approx 10^5$  years to condense on grains (Tielens & Allamandola 1987). Thus icy grain mantles suffer ion irradiation for about  $10^5 - 5 \times 10^8$  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  $S \approx 5 \times 10^{-15} \text{ eV cm}^2 \text{ atom}^{-1}$ . Thus the energy deposited on a



**Fig. 1.** Schematic view of the experimental apparatus used for in situ IR spectroscopy of ion irradiated and UV photolyzed frozen gases and solids.

grain (dose), given by the product of the stopping power times the flux times the mantle lifetimes ( $3 \times 10^{12} - 1.5 \times 10^{16} \text{ s}$ ), values  $0.015 - 75 \text{ eV/atom(C, N, O, Si)}$ . Of course in star forming regions the flux of ions and then the doses absorbed by icy mantles can be very different from the values reported above.

## 2. Experimental methods

A schematic view of the experimental apparatus available at the Laboratory of Experimental Astrophysics (L.A.SP.) in Catania (Italy) is reported in Fig. 1.

In situ IR spectroscopy is performed in a stainless steel vacuum chamber facing an FTIR spectrometer (Bruker Equinox 55). Inside the vacuum chamber, in which pressure is kept below  $10^{-7} \text{ mbar}$ , 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 keV (400 keV for double ionizations) can be obtained. The ion beam produce a spot on the targets greater than the area sampled by the IR beam and the cur-

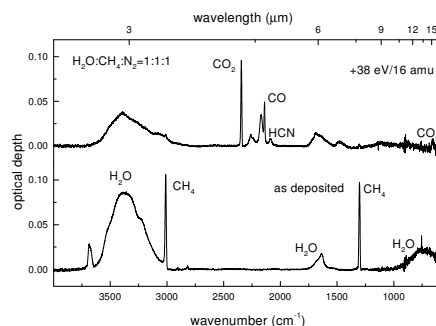
rent is kept in the range of  $100 \text{ nA cm}^{-2}$  to a few  $\mu\text{A cm}^{-2}$  in order to avoid a macroscopic heating of the sample.

A hydrogen microwave discharge resonance lamp (Ophos Instruments) is interfaced with the vacuum chamber through an  $\text{MgF}_2$  window; from this lamp mainly  $10.2 \text{ eV}$  (Lyman- $\alpha$ ) photons are obtained.

A needle valve is used to admit pre-prepared gas (or mixtures) into the chamber, where they freeze on the substrate. The substrate holder is mounted at an angle of  $45^\circ$  with respect to both the ion beam and the IR beam and it is orthogonal to the UV beam, so that spectra can be easily taken in situ, even during irradiation with ions and UV photons, without tilting the sample.

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 & Johnson 1991). In the case of ion irradiation the dose is calculated from the knowledge of the ion fluence ( $\text{ions cm}^{-2}$ ), the stopping power ( $\text{eV cm}^2 \text{ molecules}^{-1}$ ) of the chosen projectile, and its penetration depth or range in the target ( $\text{molecules cm}^{-2}$ ). 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 two parameters are well known and can be provided by a software such as the TRIM Montecarlo simulation program (Ziegler et al. 1985). In the case of UV photolysis the dose can be calculated from the knowledge of the UV fluence ( $\text{photons cm}^{-2}$ ) and the absorption coefficient of UV photons in ices which can be measured experimentally as described by Baratta et al. (2002).

Further information on the experimental apparatus and calibration procedures can be found in Baratta & Palumbo (1998); Strazzulla et al. (2001); Baratta et al. (2002); Palumbo et al. (2004).

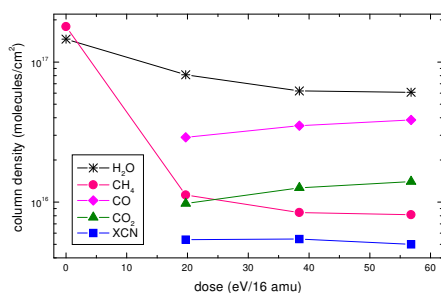


**Fig. 2.** Infrared spectra of an ice mixture  $\text{H}_2\text{O}:\text{CH}_4:\text{N}_2$  before (bottom curve) and after (top curve) ion irradiation with  $30 \text{ keV He}^+$  ions at  $12 \text{ K}$ .

### 3. Results and discussion

Figure 2 shows the infrared transmission spectra, in optical depth scale, of an ice mixture  $\text{H}_2\text{O}:\text{CH}_4:\text{N}_2$  at  $12 \text{ K}$  before and after ion irradiation with  $30 \text{ keV He}^+$  ions (dose about  $38 \text{ eV}/16 \text{ amu}$ ). The absorption bands due to water ice and methane are clearly evident in the spectra while  $\text{N}_2$  being a homonuclear molecule has no active infrared bands. After ion irradiation other absorption bands appear indicating the formation of other molecular species not present in the original sample. In particular carbon monoxide ( $\text{CO}$ ) and carbon dioxide ( $\text{CO}_2$ ) are abundantly formed. Furthermore several N-bearing species, such as  $\text{HNC}$ ,  $\text{OCN}^-$ ,  $\text{N}_2\text{O}$ , and  $\text{HCN}$ , are formed. This is a general result. In fact several laboratory experiments have shown that molecular species not present in the original sample are formed after ion irradiation and UV photolysis of simple ices (e.g., Allamandola et al. 1988; Gerakines et al. 1996; Strazzulla et al. 2001; Moore et al. 2001).

Figure 3 shows the behaviour of the column density of the most abundant species present in the mixture during irradiation. It is evident that at the beginning the abundance of water and methane is comparable while after ion irradiation the abundance of methane rapidly decreases and at the end of irradiation carbon monoxide is the most abundant species after water ice indicating that the chemical composition of the ice sample has been deeply modified.



**Fig. 3.** Column density of the most abundant species in an ice mixture  $\text{H}_2\text{O}:\text{CH}_4:\text{N}_2$  during ion irradiation with 30 keV  $\text{He}^+$  ions at 12 K.

It is interesting to note that because of grain surface reactions, cosmic ion irradiation and UV photolysis, the chemical composition of interstellar ices is different from that of the gas phase from which they freeze out. Thus, when, owing to the formation of a new star, icy mantles sublimate several molecular species are released in the gas phase. In fact it has been suggested that energetic processing of ices could cause the formation of molecules present in the gas phase which cannot be formed, in the observed abundances, after gas phase reactions.

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