

## THE ROLE OF ENERGETIC PROCESSING ON SOLID-PHASE CHEMISTRY IN STAR FORMING REGIONS

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**Abstract.** It is generally accepted that complex molecules observed in star forming regions are formed in the solid phase on icy grain mantles and are released to the gas-phase after desorption of icy mantles. Most of our knowledge on the physical and chemical properties of ices in star forming regions is based on the comparison between observations and laboratory experiments performed at low temperature (10-100 K). Here we present some recent laboratory experiments which show the formation of (complex) molecular species after ion bombardment of simple ices.

### 1 Introduction

Solid-phase molecules exist as icy grain mantles in dense molecular clouds where  $T \sim 10$  K and gas density  $n \geq 10^4$  cm<sup>-3</sup>. Water (H<sub>2</sub>O), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methanol (CH<sub>3</sub>OH), methane (CH<sub>4</sub>) and ammonia (NH<sub>3</sub>) have been firmly identified and are the most abundant species detected. Other species, such as cyanate ion (OCN<sup>-</sup>), carbonyl sulfide (OCS), sulfur dioxide (SO<sub>2</sub>), and formaldehyde (H<sub>2</sub>CO), are likely identified species (see Boogert *et al.* 2015 for a recent review). Furthermore it is largely accepted that many other (also complex) species are present in icy grain mantles which cannot be easily detected due to the intrinsic limits of infrared absorption spectroscopy. In dense molecular clouds, icy grain mantles suffer from continuous processing by low-energy cosmic rays and UV photons (e.g. Jenniskens *et al.* 1993; Shen *et al.* 2004). Most of our knowledge on the effects of energetic processing on ices is based on laboratory experiments. Energetic ions (keV-MeV) passing through molecular solids release energy to the target along the ion track. As a consequence molecular bonds are broken and

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in a very short time (one picosecond or less), radicals and molecular fragments recombine giving rise to molecular species not present in the original sample, furthermore the structure of the target is modified. In the case of UV photolysis the energy is released to the target material through single photo-dissociation or ionization events per incoming photon. Thus after ion bombardment and UV photolysis the chemical composition and the structure of the sample is modified (e.g. Palumbo & Strazzulla 1993; Gerakines *et al.* 1996; Cottin *et al.* 2003; Palumbo 2006; Öberg *et al.* 2009). Both more volatile and less volatile species are formed and if C-bearing species are present in the original sample a refractory residue is also formed (e.g. Moore *et al.* 1983; Foti *et al.* 1984; Strazzulla & Baratta 1992; Palumbo *et al.* 2004).

More than 170 molecules have been detected in the gas-phase in space<sup>1</sup>. As known, this number keeps increasing with time, thanks to the advent of large radio and millimeter telescopes, like IRAM, ALMA or GBT, and an ever increasing sensitivity of the receivers. Notably, the complexity of the detected molecules is also steadily increasing, and the number of sources where these complex molecules are detected is also increasing. As concerns the origin of gas-phase molecules, three different mechanisms have been invoked in the literature: 1) gas phase reactions taking place once the icy mantles sublime in the warm regions (e.g. Charnley *et al.* 1995); 2) reactions taking place on the grain surfaces during the period of grain mantles formation (e.g. Tielens & Hagen 1982) and existence (e.g. Garrod & Herbst 2006); 3) energetic processing (i.e. ion bombardment and UV photolysis) of the mantles (e.g. Palumbo & Strazzulla 1993; Palumbo *et al.* 2008).

Here we present some recent laboratory experiments which show the formation of (complex) molecular species after ion bombardment of simple ices.

## 2 Experimental procedure

Laboratory experiments here described have been performed in the Laboratory for Experimental Astrophysics at INAF - Osservatorio Astrofisico di Catania, Italy. Experiments were carried out in a stainless steel high-vacuum chamber with a base pressure lower than  $10^{-7}$  mbar. Inside the vacuum chamber an infrared transparent substrate (KBr or crystalline Si) is placed in thermal contact with a cold finger whose temperature can be varied between 10 K and 300 K. Pure gases or gas mixtures were prepared in a pre-chamber connected to the vacuum chamber by a gas inlet and were then admitted into the chamber where they freeze on the substrate. During accretion the thickness of the ice film was monitored by a He-Ne laser (543 nm) looking at the interference pattern (intensity versus time) given by the laser beam reflected at near normal incidence by the vacuum-film and film-substrate interfaces (see Baratta & Palumbo 1998 and Fulvio *et al.* 2009 for more details on the technique used to measure the thickness). Infrared (IR) transmission spectra of solid samples were taken with a Fourier Transform

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<sup>1</sup>[http://www.astrochymist.org/astrochymist\\_ism.html](http://www.astrochymist.org/astrochymist_ism.html)

Infrared (FTIR) spectrometer (Bruker Vertex 70) in the range 7800-400  $\text{cm}^{-1}$  (1.3-25  $\mu\text{m}$ ) at a resolution of 1  $\text{cm}^{-1}$ . The vacuum chamber was connected to an ion implanter (Danfysik) from which ions with energy up to 200 keV (400 keV for double ionizations) are obtained. To avoid a macroscopic heating of the target, we used an ion current density between 100  $\text{nA cm}^{-2}$  and a few  $\mu\text{A cm}^{-2}$ . The ion beam is scanned electrostatically to ensure a uniform fluence on the target. The irradiated area is larger than that probed by the IR beam. The vacuum chamber was also interfaced with an UV lamp (Ophos Instruments) from which mainly 10.2 eV photons (Lyman- $\alpha$ ) are obtained. The substrate holder formed an angle of 45° with both the ion beam and the IR beam while the UV flux was perpendicular to the sample. With this set-up icy samples can be analyzed before and after energetic processing without rotation of the sample. The samples can be processed by ions and UV photons in separate experiments or simultaneously. A more detailed description of the experimental set-up can be found in Strazzulla *et al.* (2001); Baratta *et al.* (2002); Palumbo *et al.* (2004); Islam *et al.* (2014).

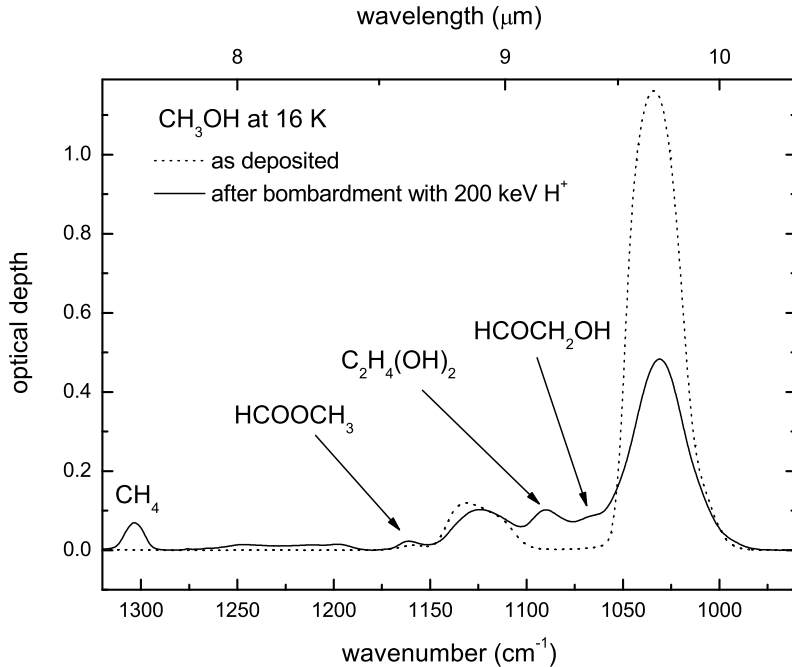
### 3 Results

Laboratory experiments show that after energetic processing the column density of pristine molecules decreases and new absorption features appear in the IR spectra indicating the formation of molecules not present before processing. As an example, after ion bombardment of  $\text{CH}_3\text{OH}$ -rich mixtures new molecules are identified such as carbon monoxide ( $\text{CO}$ ), carbon dioxide ( $\text{CO}_2$ ), formyl radical ( $\text{HCO}$ ), formaldehyde ( $\text{H}_2\text{CO}$ ), methane ( $\text{CH}_4$ ), ethylene glycol ( $\text{C}_2\text{H}_4(\text{OH})_2$ ), methyl formate ( $\text{HCOOCH}_3$ ), and glycolaldehyde ( $\text{HCOCH}_2\text{OH}$ ) (e.g. Moore *et al.* 1996; Palumbo *et al.* 1999; Hudson & Moore 2000; Modica & Palumbo 2010). Figure 1 shows the infrared transmission spectra (in optical depth scale) of pure methanol as deposited at 16 K and after ion bombardment with 200 keV protons. The features assigned to methane, methyl formate, ethylene glycol and glycolaldehyde are labeled.

Recently, Kaňuchová *et al.* (2015) have investigated the formation of formamide ( $\text{NH}_2\text{CHO}$ ) after ion bombardment of ice mixtures containing C-, O-, and N-bearing species, namely  $\text{H}_2\text{O}:\text{CH}_4:\text{NH}_3$ ,  $\text{H}_2\text{O}:\text{CH}_4:\text{N}_2$ , and  $\text{CH}_3\text{OH}:\text{N}_2$  mixtures at 10-20 K. After a quantitative analysis of the experimental data they have shown that the amount of formamide observed in the gas-phase in star-forming regions (e.g. Mendoza *et al.* 2014; López-Sepulcre *et al.* 2015) can be accounted for by cosmic-ray bombardment of icy grain mantles. In fact species formed in the solid-phase are released to the gas-phase after desorption of icy mantles.

#### 3.1 Reaction rates

Fitting the experimental data to an exponential curve it is possible to obtain formation rates of new molecules formed after energetic processing. As an example, Occhiogrosso *et al.* (2011) have obtained the formation rate of methyl formate after cosmic ion bombardment of a  $\text{CO}:\text{CH}_3\text{OH}$  mixture at 16 K,  $R(\zeta_0) = 6.2 \times 10^{-18}$



**Fig. 1.** Infrared transmission spectra, in optical depth scale, in the  $1320\text{--}960\text{ cm}^{-1}$  ( $7.57\text{--}10.42\text{ }\mu\text{m}$ ) range, of pure methanol before (dotted line) and after (solid line) ion bombardment with 200 keV protons at 16 K. Features assigned to molecules formed after ion bombardment are labeled.

$\text{s}^{-1}$ . In their calculation they assumed a standard ionization rate  $\zeta_0$  equal to  $3 \times 10^{-17}\text{ s}^{-1}$ . If a different ionization rate ( $\zeta$ ) is used then  $R(\zeta)$  is given by

$$R(\zeta) = \frac{R(\zeta_0) \times \zeta}{\zeta_0} \quad (3.1)$$

In a different work Woods *et al.* (2015) have obtained the formation rates of S-bearing molecules after ion bombardment of CO:H<sub>2</sub>S ice mixture at 20 K. In particular they have studied the formation of H<sub>2</sub>S<sub>2</sub>, OCS, SO<sub>2</sub>, CS<sub>2</sub> and a S-rich residue. These values have been added to chemical models to investigate the chemical evolution of protostellar objects. Occhiogrosso *et al.* (2011) have found that low-energy cosmic rays interaction with icy grain mantles could explain the abundance of methyl formate in dark clouds, such as B1-b core (Öberg *et al.* 2010).

## 4 Future prospects

The results here presented support the experimental effort (e.g. Gudipati & Yang 2012; Jones & Kaiser 2013; Allodi *et al.* 2013; Paardekooper *et al.* 2014) to use more sensitive techniques to evidence the formation of complex molecules and/or fragments that could be of primary relevance also to understand which species should be searched for, by ground-based or space-borne facilities, in protostellar environments and protoplanetary disks. Jones & Kaiser (2013) present a novel application of reflectron time-of-flight (ReTOF) mass spectrometry coupled to soft photoionization to probe the molecules formed upon interaction of ionizing radiation (5 keV electrons) with simple ices on line and in situ. Paardekooper *et al.* (2014) describe a new ultra-high vacuum experiment that allows studying photo-induced chemical processes in interstellar ice analogues by combining laser desorption and time-of-flight mass spectrometry with the ultimate goal to characterize in situ and in real time the solid state evolution of organic compounds upon UV photolysis for astronomically relevant ice mixtures and temperatures.

Thanks to the financial support received within the project *iALMA* (MIUR - *Progetti Premiali 2012*) the installation of a new and innovative experimental set-up is in progress in the Laboratory for Experimental Astrophysics at INAF - Osservatorio Astrofisico di Catania. The new set-up will allow the detection of complex molecules formed on ice samples after bombardment with fast ions (100-400 keV). This will be obtained by a combination of laser desorption, jet cooling, laser ionization followed by high resolution time of flight mass-spectrometric analysis.

All these experimental setups have a sensitivity higher than traditional techniques mainly based on infrared spectroscopy.

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