



<b>Publication Year</b>	2015
<b>Acceptance in OA @INAF</b>	2020-03-14T16:22:46Z
<b>Title</b>	Solid-phase chemistry driven by energetic processing
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<b>Handle</b>	<a href="http://hdl.handle.net/20.500.12386/23250">http://hdl.handle.net/20.500.12386/23250</a>
<b>Journal</b>	BULLETIN DE LA SOCIÉTÉ ROYALE DES SCIENCES DE LIÈGE
<b>Number</b>	84

# Solid-phase chemistry driven by energetic processing

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**Abstract:** Molecules in the solid phase have been detected in the line of sight of quiescent molecular clouds and star forming regions as icy mantles on dust grains. Although about 10 molecular species have been firmly identified in icy grain mantles, it is believed that many, also complex, species are present in the solid phase which are not detected due to the detection limits of infrared spectroscopy. It is generally accepted that some of the observed species (such as CO) freeze out from the gas phase while others (such as water and methanol) are formed on grains after surface reactions. Other species (such as CO<sub>2</sub> and OCS), are not expected to freeze out in significant amount from the gas phase and grain surface models do not account for their observed abundance. It has been suggested that these molecules, along with other more complex species, are formed after energetic processing (i.e. cosmic ion and UV irradiation) of icy grain mantles. All these species are released to the gas-phase after desorption of icy mantles. Here we will present some recent laboratory experiments which show the formation of (complex) molecular species after energetic processing of simple ices. Icy targets have been processed by ion bombardment and UV photolysis both in separate experiments and recently, for the first time, simultaneously. When C-rich species are present in the initial ice, an organic refractory material is also formed.

## 1 Introduction

More than 170 molecular species have been detected in space.<sup>1</sup> Molecules are observed in the atmosphere of planets and satellites, on the surface of icy bodies (e.g. Merlin et al. 2010), in comets (e.g. Bockelée-Morvan et al. 2000; Schneider et al. 2012), in the atmosphere of exo-planets (e.g. Swain et al. 2009) and of evolved stars (e.g. Cernicharo et al. 2001, 2008) and in the interstellar medium (e.g. Caselli and Ceccarelli 2012). In interstellar dense molecular clouds, due to the high density, the visible and ultraviolet electromagnetic radiation emitted by nearby stars cannot penetrate and the temperature can drop as low as 10 K. This creates a special environment where molecules form and are preserved. Owing to the high density and low temperature, gas phase species adhere to the grain surface accreting an ice coating which is often referred to as icy grain mantle. The presence of icy grain mantles is indirectly deduced from depletion of gas phase species (e.g. Caselli et al. 1999; Tafalla et al. 2004, 2006; Brady Ford and Shirley 2011) and is observed in the infrared from absorption features attributed to vibrational modes of solid phase molecules superposed to the background stellar spectrum (e.g. Willner et al. 1982; Tielens et al. 1991; Gibb et al. 2000; Pontoppidan et al. 2008). Molecular clouds are the site of star formation and complex organic molecules formed in these regions are expected to be incorporated in planets, satellites and comets also formed with a new

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

star. Ices have been observed in star forming regions (both low- and high-mass young stellar objects) as well as in quiescent dense clouds. It is widely accepted that icy grain mantles are continuously processed by low-energy cosmic rays, electrons, and UV photons (e.g. Jenniskens et al. 1993; Shen et al. 2004). In fact, while the external visible and ultraviolet electromagnetic radiation is absorbed in the outer layers of a molecular cloud, cosmic rays can penetrate and pass through dense clouds (e.g. Prasad and Tarafdar 1983; Mennella et al. 2003). The interaction of cosmic rays with hydrogen causes the production of low-energy cosmic rays, electrons and UV photons.

Water (H<sub>2</sub>O), carbon monoxide (CO), methanol (CH<sub>3</sub>OH), methane (CH<sub>4</sub>), carbonyl sulfide (OCS), and carbon dioxide (CO<sub>2</sub>) are some of the most abundant molecular species detected in the interstellar medium in solid phase (e.g. Gibb et al. 2004; Öberg et al. 2011). Some of the observed molecules freeze out from the gas phase (such as CO and N<sub>2</sub>), others (such as H<sub>2</sub>O, CH<sub>3</sub>OH, CO<sub>2</sub> and OCS) form on grains. Among these H<sub>2</sub>O and CH<sub>3</sub>OH form after grain surface reactions (Ioppolo et al. 2008; Fuchs et al. 2009). Others (such as CO<sub>2</sub> and OCS) form after irradiation of icy mantles (Ioppolo et al. 2009, 2013; Garozzo et al. 2010) and/or after surface reactions (e.g. Ioppolo et al. 2011; Noble et al. 2011).

Most of our knowledge on the effects of energetic processing (i.e. UV photolysis and ion and electron bombardment) on ices is based on laboratory experiments. Experimental results clearly indicate that after energetic processing the chemical composition (e.g. Sandford et al. 1988; Palumbo and Strazzulla 1993; Gerakines et al. 1996; Cottin et al. 2003; Bennett et al. 2007; Öberg et al. 2009; Boduch et al. 2012) and the structure (e.g. Palumbo 2006; Raut et al. 2007; Palumbo et al. 2010; Dartois et al. 2013) of the ice is modified. Both more volatile and less volatile species are formed and if C-bearing species are present in the original mantle a refractory residue is left over after warm-up to the sublimation temperature of volatile species (e.g. Moore et al. 1983; Foti et al. 1984; Strazzulla and Baratta 1992; Palumbo et al. 2004). Due to the active role of dust grains in the formation of molecules, the chemical composition of icy mantles is significantly different from the composition of the gas during the contraction phase of dense molecular clouds. When the newly born central object warms up the surrounding dust, volatile icy mantles sublimate and the gas phase is enriched of complex molecules (e.g. Miao et al. 1995; Horn et al. 2004; Palumbo et al. 2008; Modica & Palumbo 2010). Eventually these species could be incorporated in planets, satellites and comets formed with the star. However the abundance of complex molecules is too low to be detected by infrared spectroscopy in the solid phase and they are only detected in the gas phase, after sublimation, thank to their rotational emission at radio wavelength.

Here we will present some recent laboratory experiments which show the formation of (complex) molecular species after energetic processing (ion bombardment and UV photolysis) of simple ices. Icy targets have been processed by ion bombardment (30-200 keV) and UV photolysis (10.2 eV) both in separate experiments and recently, for the first time, simultaneously. Furthermore we will discuss the formation of a stable, refractory organic residue left over after processing of C-rich ice mixtures.

## **2 Experimental procedures**

Experimental results here described have been obtained in the Laboratory for Experimental Astrophysics at INAF - Osservatorio Astrofisico di Catania, Italy.

Icy samples were prepared in a stainless steel vacuum chamber (pressure better than 10<sup>-7</sup> mbar), schematically depicted in Fig. 1. An infrared (IR) transparent substrate (KBr or crystalline silicon) was placed in thermal contact with a cold finger whose temperature can be varied between 300 K and 10 K. A leak valve was used to admit gaseous species into the chamber, where they froze out on the substrate. The gas inlet was intentionally not directed towards the substrate, thus a “background deposition” was obtained. During accretion the thickness of the ice sample was monitored by the

laser interference method as described by Baratta & Palumbo (1998); Fulvio et al. (2009); Modica & Palumbo (2010).

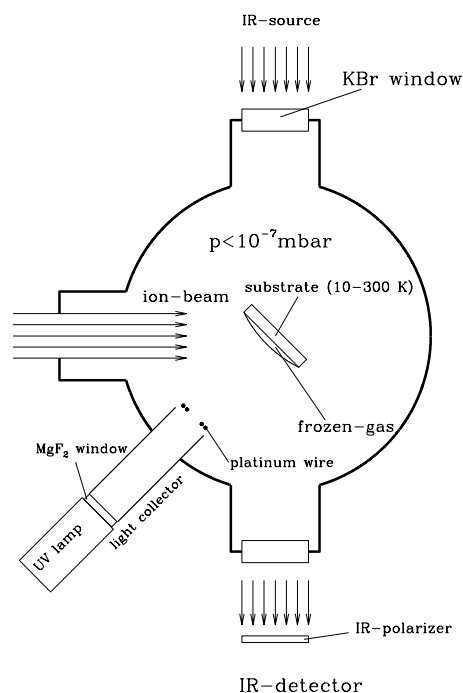


Figure 1: Schematic depiction of the experimental set-up.

The vacuum chamber was interfaced with an ion implanter (Danfysik) from which ions with energy up to 200 keV (400 keV for double ionization) can be obtained and with an UV lamp (Ophos Instruments) from which mainly 10.2 eV photons (Lyman- $\alpha$ ) are obtained. The ice samples can be analyzed before and after energetic processing by infrared transmission spectroscopy and Raman spectroscopy (e.g. Palumbo et al. 2004). The substrate holder formed an angle of 45 degrees both with the infrared beam and the ion beam while the UV flux was perpendicular to the sample. This configuration offered the advantage that spectra can be taken in situ, even during irradiation, without tilting the sample. More details on the UV lamp and on the calibration procedure of the UV flux can be found in Baratta et al. (2002) and Islam et al. (2014).

A rotatable polarizer was placed in the path of the infrared beam in front of the detector. This gave the opportunity of recording spectra with the electric vector parallel (P polarized) and perpendicular (S polarized) to the plane of incidence. The plane of incidence is the plane of the paper in Fig. 1; this plane contains P polarized light, while the plane of S polarization is perpendicular to the paper. As shown by Baratta et al. (2000) spectra recorded at oblique incidence in S polarization are equivalent to spectra at normal incidence.

All IR spectra were divided by the corresponding spectrum of the background acquired before deposition and were taken at a resolution of 1 or 2  $\text{cm}^{-1}$ . After normalization to the continuum, each spectrum was plotted on an optical depth ( $\tau$ ) scale using the relation  $I = I_0 e^{-\tau}$  (Beer-Lambert law), where  $\tau = \alpha x$  ( $\alpha$  = absorption coefficient;  $x$  = pathlength through the material). The column density  $N$  (molecules  $\text{cm}^{-2}$ ) of a given species was calculated by the equation

$$N = \frac{\int \tau_\nu d\nu}{A} \quad (1)$$

where  $\int \tau_\nu d\nu$  ( $\text{cm}^{-1}$ ) is the band area (in optical depth scale) and  $A$  ( $\text{cm molecule}^{-1}$ ) is the band strength value.

To compare the effects that are induced by fast ions and UV photons, the irradiation dose was derived (energy released onto the target molecules, i.e.,  $\text{eV molecule}^{-1}$ ). As suggested by Strazzulla & Johnson (1991), the dose given in units of eV per small molecule (16u) is a convenient way to characterize chemical changes and to compare the results obtained after processing of different samples. The energy released into the sample by impinging ions or photons (dose) is then given in  $\text{eV}/16\text{u}$ , where u is the unified atomic mass unit defined as 1/12 of the mass of an isolated atom of carbon-12. For the ion bombardment, the dose ( $\text{eV}/16\text{u}$ ) was obtained from the ion fluence values ( $\text{ions cm}^{-2}$ ) measured during the experiment and the stopping power  $S$  ( $\text{eV cm}^2 \text{ molecule}^{-1}$ ) calculated using the SRIM code (Ziegler et al. 2008). For the UV photolysis, the dose ( $\text{eV}/16\text{u}$ ) was obtained from the UV fluence ( $\text{photons cm}^{-2}$ ) measured during the experiment and the absorption cross-section of UV photons in the ice estimated as described by Baratta et al (2002).

### 3 Results

Figure 2 shows the column density of  $\text{CH}_4$  as a function of the dose ( $\text{eV}/16\text{u}$ ) after ion bombardment (with  $30 \text{ keV He}^+$ ) and UV photolysis of a sample of pure  $\text{CH}_4$  at  $12.5 \text{ K}$ . The column density values are normalized to the initial value.

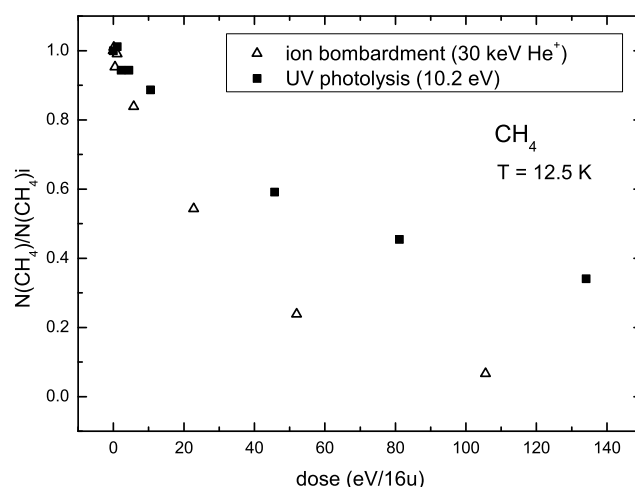


Figure 2: Normalized column density of  $\text{CH}_4$  as a function of the dose ( $\text{eV}/16\text{u}$ ) after ion bombardment (with  $30 \text{ keV He}^+$ ) and UV photolysis of a sample of pure  $\text{CH}_4$  at  $12.5 \text{ K}$ .

Figure 3 shows the column density of  $\text{CH}_3\text{OH}$  as a function of the dose ( $\text{eV}/16\text{u}$ ) after ion bombardment (with  $30 \text{ keV He}^+$ ) and UV photolysis of a sample of pure  $\text{CH}_3\text{OH}$  at  $12.5 \text{ K}$ . Again the column density values are normalized to the initial value.

In Fig. 2, it is evident that in the case of ion bombardment the column density decreases faster than in the case of UV photolysis. As discussed in Baratta et al. (2002), and in Islam et al. (2014) this behaviour is ascribed to the modification of the optical constants of the sample during processing. In fact due to processing in both cases the optical constants of the sample change. It is well known that hydrocarbons evolve towards a polymer-like material and eventually to a refractory residue (e.g.

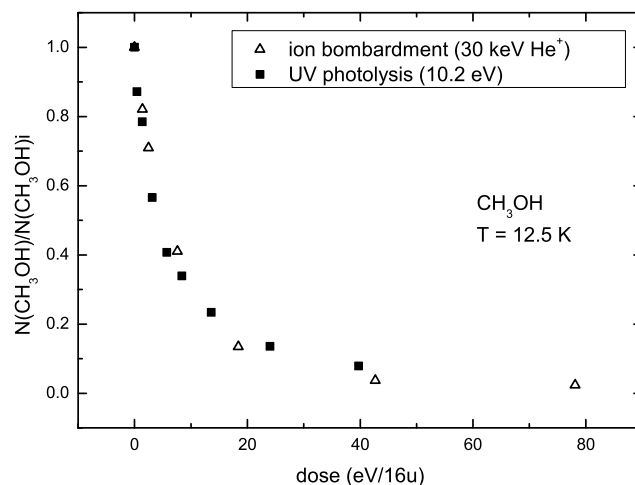


Figure 3: Normalized column density of CH<sub>3</sub>OH as a function of the dose (eV/16u) after ion bombardment (with 30 keV He<sup>+</sup>) and UV photolysis of a sample of pure CH<sub>3</sub>OH at 12.5 K.

Moore et al. 1983; Strazzulla et al. 1983; Strazzulla & Johnson 1991; Jenniskens et al. 1993; Palumbo et al. 2004). Also the experiments of UV photolysis show that a refractory residue is eventually formed. However while the energy released by ions is independent of the optical constants of the sample, the refractory residue is opaque to UV photons. Thus at higher doses impinging ions continue to release energy to the sample which is further modified while UV photons are strongly absorbed at increasing smaller depths as photolysis proceeds and cause negligible additional modifications.

Along with the destruction of original species, laboratory infrared spectra clearly show the appearance of new absorption bands that indicate the formation of new species both more volatile and less volatile than the original ones. After processing of methane new absorption bands are observed in the infrared spectra which indicate the formation of additional volatile species such as ethane (C<sub>2</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>) and acetylene (C<sub>2</sub>H<sub>2</sub>). When CH<sub>4</sub> is mixed with H<sub>2</sub>O and/or N<sub>2</sub> other and more complex species, such as CO<sub>2</sub>, HNC, N<sub>2</sub>O, OCN<sup>-</sup>, CO, and HCN, are formed (e.g. Grim and Greenberg 1987; Moore and Hudson 1998, 2003; Baratta et al. 2002, 2003). In any case after further bombardment a refractory residue is formed as demonstrated by the appearance of the amorphous carbon feature in the Raman spectra (e.g. Ferini et al 2004; Palumbo et al. 2004). Similarly after processing of methanol several new volatile species are formed. Among these the formation of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), formyl radical (HCO), formaldehyde (H<sub>2</sub>CO), ethylene glycol (C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub>), methyl formate (HCOOCH<sub>3</sub>), and glycolaldehyde (HCOCH<sub>2</sub>OH) has been reported (e.g. Moore et al. 1996; Palumbo et al. 1999; Hudson and Moore 2000; Modica and Palumbo 2010). As an example, Fig. 4 shows the spectrum of pure methanol in the 1900-900 cm<sup>-1</sup> (5.26-11 μm) range before and after ion bombardment with 200 keV H<sup>+</sup> at 16 K. In the figure the peak position of the bands assigned to H<sub>2</sub>CO (1720 cm<sup>-1</sup>), CH<sub>4</sub> (1303 cm<sup>-1</sup>), HCOOCH<sub>3</sub> (1160 cm<sup>-1</sup>), and C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub> (1090 cm<sup>-1</sup>) are indicated. It is interesting to point out that Raman spectra of methanol-rich ice mixtures do not show the amorphous carbon feature after ion bombardment at 12 K (Ferini et al., 2004).

Other recent experiments (Compagnini et al. 2009; Puglisi et al. 2014) have shown, by infrared and Raman spectroscopy, that polyynes (-(C≡C)<sub>n</sub>-) and polycumulenes (=C=C)<sub>n</sub>= are formed after ion bombardment of acetylene (C<sub>2</sub>H<sub>2</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), and benzene (C<sub>6</sub>H<sub>6</sub>).

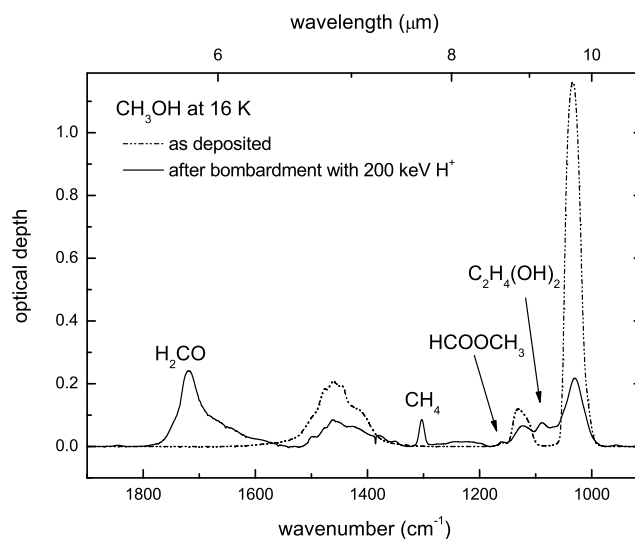


Figure 4: Infrared spectra in the  $1900\text{-}900\text{ cm}^{-1}$  ( $5.26\text{-}11\text{ }\mu\text{m}$ ) range of pure methanol at 16 K before and after ion bombardment with  $200\text{ keV H}^+$ . Main molecular species formed after processing are labeled.

Islam et al. (2014) have studied, for the first time, the effects of simultaneous ion bombardment and UV photolysis on ice mixtures. Among all possible astrophysically relevant mixtures they have considered a  $\text{CH}_3\text{OH:N}_2$  mixture at 16 K. The un-combined processes of UV irradiation and ion bombardment of  $\text{CH}_3\text{OH:N}_2$  ice were also studied. The aim was to investigate the effects of simultaneous processing on the destruction of the original species (i.e.  $\text{CH}_3\text{OH}$ ), on the formation of new species (i.e.  $\text{CH}_4$ ) and to search for synergistic effects, if any. Their results confirm that when UV photolysis and ion bombardment act separately, their effects are very similar from a qualitative point of view but significant quantitative differences may exist (Baratta et al. 2002; Loeffler et al. 2005). In particular they have found that at low doses the trend of methanol column density is very similar in all cases, while at high doses the destruction of methanol is slightly slower in the case of UV photolysis. After ion bombardment, species such as  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{HNCO}$ , and  $\text{OCN}^-$  are formed in the ice mixture while after UV photolysis, species such as  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{CO}$ , and  $\text{CH}_4$  are formed, but no N-bearing species are detected. The initial formation rate of  $\text{CH}_4$ , within the experimental uncertainties, is the same in all cases studied, while the saturation value of  $\text{CH}_4$  is higher for UV photolysis than for ion bombardment when they act separately. In the case of simultaneous processing, when the dose ( $\text{eV}/16\text{u}$ ) given by UV photons is similar to the dose given during ion bombardment, the saturation value of  $\text{CH}_4$  reaches a value intermediate between the value obtained after UV photolysis and ion bombardment separately. No synergistic effects have been detected in their study.

Several experiments have shown that energetic processing of C-rich ices eventually form a refractory residue often referred to as IPHAC (Ion Produced Hydrogenated Amorphous Carbon). IPHAC formation is a general process, it has been observed for a large number of carbon containing targets both frozen ( $\text{CH}_4$ ,  $\text{C}_4\text{H}_{10}$ ,  $\text{C}_6\text{H}_6$ , etc. and their mixtures with  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ; Strazzulla and Baratta 1992; Ferini et al. 2004) and refractory (polystyrene, polypropylene, graphite, diamond, PAHs, fullerenes, etc.; Compagnini and Baratta 1992; Cannia et al. 1994; Cataldo et al. 2002, 2003; Brunetto et al. 2004; Baratta et al. 2008).

## 4 Future work

Refractory organic residues, similar to those described above, have been prepared (Baratta et al. 2014, 2015) in order to be exposed to solar radiation on the International Space Station (ISS). These samples are part of the experiment “Photochemistry on the Space Station (PSS)” and have reached the ISS on 24 July 2014. The exposure to solar radiation is expected to last for about one year starting on 22 October 2014. The ice mixture ( $N_2:CH_4:CO$ ) used to prepare the residues is well representative of ices present on the surfaces of Trans Neptunian Objects (TNO) and of comets in the Oort cloud. Once expelled from comets these materials are exposed to solar radiation during their interplanetary journey before they eventually land on Earth and other planetary objects where they might give a contribution to the chemical and pre-biogenic evolution. The samples have been analysed by UV-Vis-IR spectroscopy soon after their preparation and will be analysed by the same technique when they return on Earth. This will allow analysis of their destruction or modification and evaluation of their lifetime in the interplanetary medium.

Finally, the results presented above support the experimental effort (e.g. Gudipati and Yang 2012; Jones and Kaiser 2013; Allodi et al. 2013) to use more sensitive techniques to evidence the formation of complex molecules and/or fragments that could be of primary relevance for Astrobiology also to understand which species should be searched for, by ground-based or space-borne facilities, in protostellar environments, protoplanetary disks and in the atmospheres of extrasolar planets and moons.

## Acknowledgements

This work was partly supported by the Italian Ministero dell’Istruzione, Università e Ricerca (MIUR) through the grant *Progetti Premiali 2012 - iALMA*.

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