High-Energy Processing of Ices in Space

G. A. Baratta, M. E. Palumbo, and C. Scirè

Abstract Most of our knowledge on the physical and chemical properties of ices in space is based on the comparison between observations and laboratory experiments performed at low temperature (10–100 K). After ion bombardment 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 C-bearing species are present in the original sample a refractory residue is also formed. Here we present some laboratory experiments which show the formation of (complex) molecular species in ion irradiated simple ices and in the organic residues formed after warm up of the processed ices at room temperature. In particular it will be shown that complex organic species found in organic residues, could have contributed to provide the early Earth with the seeds from which life has initiated.

Keywords Astrochemistry · Astrobiology · International space station

1 Introduction

Solid phase molecules have been identified in a variety of environments including icy grain mantles in star forming regions, comets, and the surface of outer Solar System bodies (see Boogert et al. 2015 for a review, see also M. Rubin and G. Filacchione et al. in this volume). It is generally accepted that in these environments solid phase molecules suffer from energetic processing due to UV photons, galactic cosmic rays, solar wind, solar energetic particles or stellar ions (e.g. Prasad and Tarafdar 1983; Mennella et al. 2003; Strazzulla et al. 2003; Padovani et al. 2020, see also C. Ceccarelli in this volume). Most of our knowledge on the physical and chemical effects induced by energetic processing on ices in space is based on experimental simulations. Laboratory spectra presented here were acquired at

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V. Mennella and C. Joblin (eds.), *European Conference on Laboratory Astrophysics ECLA2020*, Astrophysics and Space Science Proceedings 59,
https://doi.org/10.1007/978-3-031-29003-9_24

INAF-Osservatorio Astrofisico di Catania. Experiments were performed in an ultra-high vacuum chamber (UHV; $P < 10^{-9}$ mbar) in which a IR transparent substrate is placed in thermal contact with the cold finger of a closed-cycle helium cryocooler (CTI) for which temperature can be varied between 15 and 300 K. Pure gas or mixtures are admitted through a needle valve and accrete on the cold substrate. The vacuum chamber is placed in the sample compartment of a FTIR spectrometer (Bruker Vertex 70) and transmission spectra of the sample are acquired in the range 7800–400 cm^{-1} (1.28–25 μm). The UHV chamber is connected to a 200 kV ion implanter by Danfysik. More details on the experimental setup and procedure can be found in Islam et al. (2014), Modica and Palumbo (2010), Baratta et al. (2015).

2 COMs Formation in Irradiated Ices

Laboratory experiments have clearly shown that complex organic molecules (COMs) are formed after energetic processing (ion irradiation and UV photolysis) of ice mixtures made of simple frozen species such as H_2O, CO, CO_2, CH_4, CH_3OH, NH_3 (e.g. Modica and Palumbo 2010; Palumbo et al. 2000; Hudson and Moore 2000; Oberg et al. 2009, see also R. Martin-Domenech et al. and R.G. Urso et al. in this volume).

As an example, Fig. 1 shows the spectrum of a CH_3OH:N_2 mixture after ion irradiation with 200 keV H^+ at 16 K (see Islam et al. 2014). The most intense features observed after ion irradiation are labeled in the figure. Among them the formation of HNCO, OCN^-, and NH_2CHO is evidenced. For comparison the spectrum of pure NH_2CHO after ion irradiation with 200 keV H^+ is also shown (see Kaňuchová et al. 2016). Comparing the flux (ions cm^{-2} s^{-1}) of energetic ions in space environments with the fluence (ions cm^{-2}) adopted in experimental simulations it has been possible to estimate the time required in space to obtain the same effects observed in the laboratory. As discussed by Strazzulla et al. (2003) and Kaňuchová et al. (2016) the effects measured in the laboratory occur in space in the time scale of ice evolution making laboratory simulations a powerful tool for our comprehension of the physical and chemical properties of ices in space.

3 Organic Residues

3.1 Organic Residues Formation

Laboratory experiments conducted over many years have shown that ion irradiation or UV photolysis of ice mixtures containing carbon atoms probably results in formation of a stable organic material. The organic material left over after the energetic processing of a simple icy mixture and the following warm-up is commonly

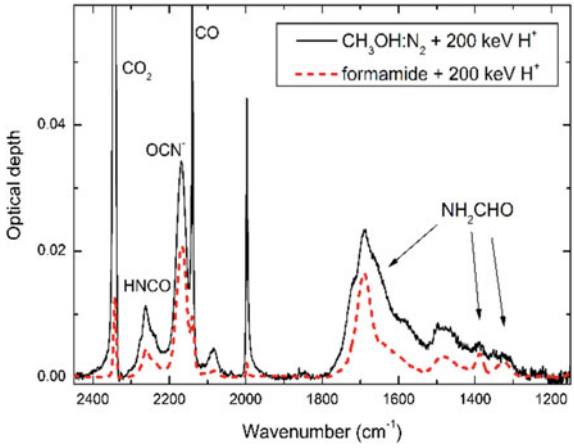

Fig. 1 Infrared spectrum of a $CH_3OH:N_2$ mixture after ion irradiation with 200 keV H^+ compared to the spectrum of irradiated formamide at 16 K

called organic residue and remains, at room temperature after the sublimation of the most volatile species, as a yellow-brownish film on the substrate where the icy sample was processed (e.g., Greenberg et al. 1972; Jenniskens et al. 1993; Accolla et al. 2018). Both ion irradiation and UV photolysis of simple ices containing H, C, N and O bearing molecules leads to the formation of organic residues containing complex organic molecules such as succinonitrile, 3-amminocrotonitrile (Hudson et al. 2008), glyceric acid, lactid acid (Materese et al. 2014) and even nucleobases (Ruf et al. 2019). It has been suggested that energetic processing (UV or fast ions) of almost any ice mixture containing C, H, N, and O atoms, probably results in formation of aminoacid precursors that, if hydrolyzed, give rise to the aminoacids themselves (Hudson et al. 2008). By means of similar mechanisms, COMs may be formed on the icy surfaces of some objects in the outer Solar System, such as Trans-Neptunian Objects (TNO) and comets. In the primitive solar system nebula, ices covered small (from sub-micrometer to mm) refractory grains in the cold part of the disk. It has been found that icy grains originating in the outer disk (T lower than 30 K), experienced ultraviolet irradiation exposures and thermal warming similar to those which have been shown to produce complex organics in laboratory experiments (Ciesla and Sandford 2012). Comets accreted in the cold outer regions of the protoplanetary disk, hence materials similar to those produced in laboratory could have been incorporated into comets. It is believed that a large fraction of Interplanetary Dust Particles (IDPs) has a cometary origin. Today, most of the extraterrestrial organic matter is brought to Earth by IDPs. According to Chyba and Sagan (1992), during the Late Heavy Bombardment, the amount of organics brought by IDPs was significantly higher than today. Hence material similar to those we produce in the laboratory could have reached the prebiotic Earth. Nevertheless, once expelled from comets, IDPs can spend in the interplanetary medium thousands of years before reaching the Earth atmosphere. Hence: how long complex organics present in IDPs can survive in the interplanetary medium? In the next section we discuss some results obtained

on the International Space Station (ISS) that give some insight on the stability of complex organics in the interplanetary medium.

3.2 Exposure on the International Space Station

Photochemistry on the Space Station (PSS, PI Hervè Cottin) was one of the experiments of the Expose-R2 mission on the ISS. Several samples, many of which were of astrobiological interest, have been exposed for sixteen months outside the ISS to the unshielded solar UV photons (Cottin and Rettberg 2019). Our contribution was to prepare 30 organic residues over three different thicknesses: 50 nm (2f), 135 nm (4f) and 180 nm (6f) (Baratta et al. 2015). For each thickness, four were aboard the ISS, in particular: two exposed and two, shielded from solar UV, were used as in-flight dark controls. The others six were in the DLR (German Aerospace Center) laboratory, in particular: two in vacuum suffered the same temperature variations as the ISS exposed ones by telemetry; two in vacuum at a constant temperature of 5 °C; two exposed by a solar simulator to electromagnetic radiation at wavelength greater than 200 nm (Baratta et al. 2019). The organic residues have been produced by 200 keV He^+ irradiation of N_2:CH_4:CO (1:1:1) ice mixtures deposited at 17 K on MgF_2 substrates furnished by ESA. Just after their formation, all the organic residues have been characterized, at room temperature, by IR, UV-Vis-NIR and VUV transmittance spectroscopy. The post-flight FTIR, UV-Vis-NIR and VUV spectra of the organic residues have been acquired by using the same conditions adopted for the pre-flight samples. The comparison between the in-flight dark controls and the DLR controls reveals that, for each thickness, no systematic differences can be found between the spectra (Baratta et al. 2019). Hence the organic residues are very stable with respect to the temperature cycles experienced in orbit. The highest and lowest temperatures experienced by Expose-R2 trays were 58 °C and −20.9 °C respectively. The infrared spectra of the organic residues are consistent with the presence of $–NH_2$ and possibly -NH- functional groups of primary and secondary amine functions respectively and with the presence of C=C aromatics and C=N heteroaromatics functional groups. The feature peaking at ~2200 cm^{-1} reveals the presence of –C≡N/–N≡C (nitrile/iso-nitrile) terminal groups (Baratta et al. 2019). The presence of the nitriles feature is relevant for astrobiology. We chose a N_2:CH_4:CO (1:1:1) mixture in order to maximize the nitriles formation, the mixture is also representative of the ices present on solid objects of the solar system beyond the nitrogen frost line such as TNOs and comets. It might be argued that water ice is the most abundant solid-phase species in cometary ices, hence a representative ice mixture should include water. On the other hand we saw in the previous section that similar COMs are present in the organic residues obtained by energetic processing of almost any ice mixture containing C, H, N, and O atoms (Hudson et al. 2008). Indeed the 2200 cm^{-1} nitriles feature is also observed in the organic residue of a H_2O:CH_3OH:NH_3 (1:1:1) ice mixture irradiated with 40 keV H^+ (see Fig. 1 of R.G. Urso et al. in this volume). It is thought that nitriles could be key intermediates to form biologically relevant

molecules (Kaiser and Balucani 2001), indeed nitriles can be hydrolyzed and react via multistep synthesis ultimately to amino acids. Noteworthy the 2200 cm^{-1} nitriles feature is observed also in the spectra of Ultra Carbonaceous Antarctic Micrometeorites (UCAMMs). UCAMMs have a very high organic matter content (50% in volume on average) and have high N/C ratio (0.05–0.12) (Dartois et al. 2013). The comparison between the PSS organic residues and the UCAMMs infrared spectra reveals that they have similar functional groups (Baratta et al. 2015). The comparison between the exposed samples and the in-flight dark controls shows that as a consequence of the solar UV exposure, the organic residue is stabilized into a C = C amorphous carbon network while losing –NH–, $–NH_2$ (amine) and –C≡N/–N≡C (nitrile/iso-nitrile) functional groups (Baratta et al. 2019). Here we focus our attention on the nitriles feature. By comparing the spectra over the three different thicknesses it was possible to derive the IR spectra at different depths in the exposed samples. In Fig. 2, the spectra of the exposed samples are compared with the spectra of the in-flight dark controls. From the reduction of intensity of the 2200 cm^{-1} feature it was possible to compute the effective absorption coefficient $\alpha(UV)_{\mathbf{eff}} = 5.1\ \mu m^{-1}$ of the organic residue and the destruction rate $\Gamma = 10.6\ yr^{-1}$ of the –C≡N units contained in the samples exposed to the unshielded solar spectrum.

Figure 3 reports the corresponding surviving fraction of CN units contained in spherical particles made 50% vol. by the organic residue, as observed in UCAMMs, and the remaining part made of silicates. From the figure it is evident that a significant fraction of CN units can survive, in the interplanetary medium, for thousands of years in IDPs larger than 20–30 μm.

This support the hypothesis that organic species found in the organic residues could have reached the early Earth contributing to the seeds from which life has initiated (Baratta et al. 2019). We want to remark that a decreasing amount of nitriles is expected when the relative amount of nitrogen atoms decreases in the irradiated ice mixture, in particular nitriles formation in the organic residues, requires a N- and C- rich environment (Dartois et al. 2013). Hence is not surprising that UCAMMs represent a few percent of the micrometeorites (Dartois et al. 2013) and hence they are probably not representative of the majority of the mass delivered to early Earth.

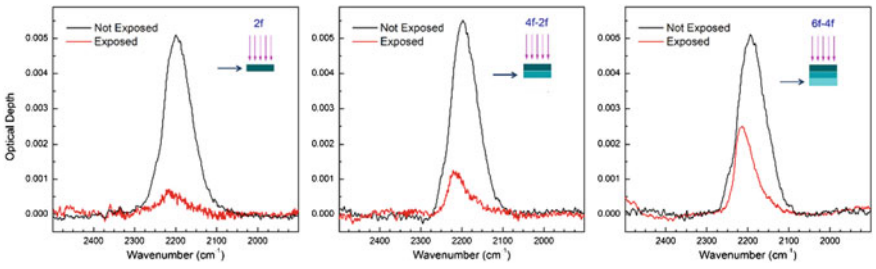

Fig. 2 Comparison of the 2200 cm^{-1} CN feature between the in-flight dark control and flight exposed samples at different depths (see text)

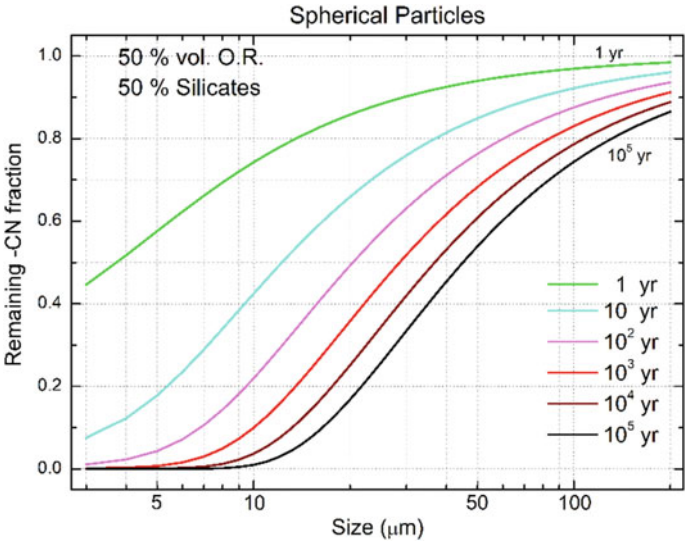

Fig. 3 Surviving fraction of the CN units in the organic material contained in spherical particles of different diameters and different exposure time to solar radiation at 1 au obtained in the hypothesis that the organic residue is diluted by a factor of 50% in volume and the remaining fraction is made of crystalline forsterite (see text)

Nevertheless, even for very low abundances (~10^{-9}), nitriles are of particular importance because they are thought to be key intermediates to form amino acids, thus providing one of the basic "ingredients" for life (Kaiser and Balucani 2001).

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