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Astrobiology studies and extraterrestrial sample analysis at the Laboratory for Experimental Astrophysics - Catania

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Abstract. Energetic ions (galactic cosmic rays, solar wind, energetic solar ions) and UV photons are believed to significantly contribute to the evolution of solid matter in astrophysical environments. At the Laboratory for Experimental Astrophysics at INAF-Osservatorio Astrofisico di Catania samples are exposed to space conditions such as high vacuum, low temperature (15-300 K), UV irradiation (266 nm and Lyman-α at 121.6 nm) and fast ion bombardment (60-400 keV) and are analyzed in situ by Infrared and Raman spectroscopy. Ices, carbons and silicates have been processed and analyzed. In addition, extraterrestrial dust particles (e.g. IDPs, cometary dust particles, and meteorites) have been characterized by non destructive techniques such as micro-Raman and UV-Vis-IR spectroscopy. Furthermore, spectra of extraterrestrial samples have been compared to spectra of laboratory analogues. Here we present some of the most recent results relevant to Astrobiology and the ongoing upgrade of the experimental set-up.

Key words. Astrobiology – Astrochemistry – Methods: laboratory – Techniques: spectroscopic – Comets: general

1. Introduction

More than 200 molecular species have been detected in space[1]. Molecules are observed in the atmosphere of planets and satellites, on the surface of icy bodies, in comets, in the atmosphere of exo-planets and of evolved stars and in the interstellar medium. The interstellar medium is the nearly empty space between the stars. It consists of gas and dust grains and it is not an uniform environment. There are locations, known as molecular clouds, where the density is relatively high so that molecules form and are preserved. In molecular clouds, gas phase species adhere to the grain surface accreting an ice coating which is referred to as "icy grain mantle". Molecular clouds are the site of star formation and complex organic molecules formed in these regions have a chance to be incorporated in planets, satellites and comets formed around a new star.

Comets are among the most pristine objects in the Solar System. When a comet from the Oort cloud or from the Kuiper belt (i.e., the TNOs region) enters the inner Solar System, the water ice-dominated sublimation at about 3 au (astronomical units) or the sublimation of other more volatile species such as CO,

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[1] An updated list is available at http://www.astrochymist.org/astrochymist_ism.html

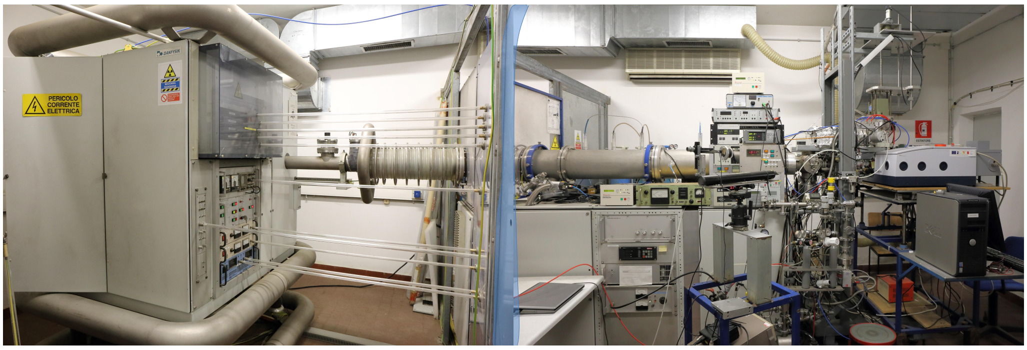

Fig. 1. Available instrumentation at the Laboratory for Experimental Astrophysics (INAF-Catania). On the left-hand side the ion source (Danfysik 1080-200). On the right-hand side the ultra high vacuum (UHV) chamber (P<10^{-9} mbar) and the cryostat (15-300 K). The UHV chamber fits the sample compartment of the IR spectrometer (Bruker-Vertex 70).

CO_2, N_2, CH_4 at much longer heliocentric distances (up to about 25 au) ejects gas and dust. Cometary dust constitutes a fraction of those interplanetary dust particles (IDPs) that have been collected in Earth's atmosphere by airborne impacting collectors flown at an altitude of 18-20 km and of those micrometeorites collected in Antarctica. The remaining fraction of IDPs and of the micrometeorites come from asteroids (e.g. Genge et al. 2008). Finally, IDPs could also have interstellar and planetary origin.

One of the key point for the synthesis of the first biomonomers is the availability of suitable precursor organics under primitive Earth conditions. Indeed extraterrestrial organics included in IDPs and micrometeorites are believed to have provided the precursor materials to early Earth (e.g. Ruiz-Mirazo et al. 2014).

It is largely accepted that solid objects in space (interstellar grains, comets, interplanetary dust particles), are continuously exposed to energetic processes such as cosmic ray irradiation and UV photolysis. The energy released to the target by fast ions (E~MeV) and UV photons (E~10 eV) induces chemical and physical modifications. As an example, complex organic molecules are formed after ion bombardment and UV photolysis of ice mixtures made of simple molecules (e.g. Öberg et al. 2009; Modica & Palumbo 2010; Kaňuchová et al. 2016; Urso et al. 2017). On the other hand, complex organic molecules trapped in IDPs and micrometeorites could be destroyed by galactic cosmic rays (GCRs), solar UV photons, and the solar ion population before reaching Earth or other objects in the Solar System.

2. Recent results

Most of the knowledge on the effects of energetic processing on astrophysical relevant analogs (ices, carbons, and silicates) is based on laboratory experiments. The Laboratory for Experimental Astrophysics at INAF-Catania (Italy) is fully equipped for these studies. Figure 1 shows part of the available instrumentations. The main constituents are the ultra high vacuum chamber (UHV; P<10^{-9} mbar), the closed-cycle He cryocooler (CTI), the ion implanter (Danfysik 1080-200), a microwave powered Lyman-alpha resonance lamp (OPTHOS) with a system for "in situ" real-time measurement of the UV photon flux, and a Nd-YAG 266 nm UV laser. Further details on the experimental set up and procedure can be found in Palumbo et al. (2004) and Urso et al. (2016).

2.1. Formation of complex molecules

Several experimental investigations have shown that "complex" molecules are formed after ion bombardment (E~keV-MeV) and UV photolysis (mainly Lyman-α) of ice mixtures at low temperature (10-30 K). In particular, Kaňuchová et al. (2016) and Urso et al. (2017) have shown that formamide (NH_2CHO) is formed after 200 keV proton bombardment of ice (10-20 K) mixtures made of simple species (i.e. H_2O:CH_4:N_2, H_2O:CH_4:NH_3, CH_3OH:N_2) along with other organic molecules (e.g. HNCO, CH_3CHO). After warm up to room temperature most volatile species sublimate while a refractory organic material stable at room temperature is left over. The thickness of the residue is about 10% of the thickness of the initial ice sample and it is able to partially trap volatile species formed at low temperature (e.g. Palumbo et al. 2000; Baratta et al. 2015; Urso et al. 2017). Kaňuchová et al. (2016) have shown that formamide formed after energetic processing of icy mixtures can account for the amount observed in the gas phase in cometary comae and in many circumstellar regions. Urso et al. (2017) speculate that formamide, tentatively detected on the surface of comet 67P/Churyumov-Gerasimenko by the Cometary Sampling and Composition (COSAC) mass spectrometer, onboard the Philae lander of the Rosetta mission (Goesmann et al. 2015), is formed after energetic ion bombardment of the cometary ice surface.

2.2. Analysis of extraterrestrial samples

Raman and infrared spectra of interplanetary dust particles (IDPs), micrometeorites, and cometary particles collected by Stardust mission clearly show the presence of organic material (Baratta et al. 2004; Sandford et al. 2006; Rotundi et al. 2008, 2014; Dartois et al. 2018). In fact Raman spectra are dominated by the D and G bands centered around 1360 and 1590 cm^{-1} respectively, while the IR spectra show the C-H stretching mode features at about 2900 cm^{-1}. The IR spectra of micrometeorites have been compared with those of an organic residue obtained after ion bombardment of ice mixtures (Baratta et al. 2015). This comparison suggests that the organic residue is a good spectral analog for ultra carbonaceous micrometeorites. The Raman features of extraterrestrial particles have been compared with that of laboratory analogs, such as graphite (HOPG), hydrogenated amorphous carbon, and the refractory residue obtained after ion bombardment of ice mixtures (Rotundi et al. 2008). It has been pointed out that the most disordered amorphous carbon detected by Raman spectroscopy in some Stardust grains could be indicative of ion irradiation of carbon containing ices or of pre-existing more ordered carbons.

2.3. Evolution in harsh environments

As discussed by Baratta et al. (2019), organic refractory material produced after ion bombardment of ice mixtures is representative of the organic material present in IDPs and micrometeorites. During their journey in the interplanetary medium ($\sim 10^5$ years), these materials are exposed to GCRs, solar UV photons, and the solar ion population before reaching Earth or other objects in the Solar System. Then it is fundamental to investigate its evolution under UV irradiation and ion bombardment. To this aim organic refractory samples formed after 200 keV He^+ irradiation at 16 K of a N_2:CH_4:CO ice mixture have been exposed to the unshielded solar photon radiation outside the International Space Station (ISS; Baratta et al. 2019) for about 16 months. Taking into account the orbit and the inclination of the ISS, this period is equivalent to 2111 hours of perpendicular solar irradiation. Samples have been analyzed before and after exposure by IR transmission spectroscopy. These samples contain, among other species, nitriles and isonitriles as evidenced by a feature at about 2200 cm^{-1} in the IR spectra. These species are particularly relevant since they are considered key intermediates to form biologically relevant molecules (Kaiser & Balucani 2001). Analysis of the samples after exposure has shown that the nitriles contained in relatively large IDPs (>20-30 μm) would have survived in the interplanetary medium; hence they could have reached prebiotic Earth.

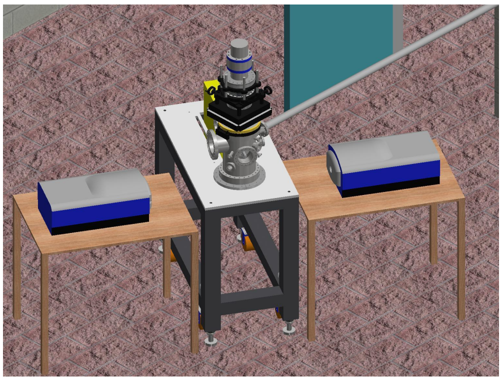

Fig. 2. New experimental setup (scale 1:12) composed by a UHV chamber interfaced with a TOF-MS, an IR laser, a UV laser and connected to the ion source line by the tube on the right-hand side. The cryostat is mounted on x, y, z translators and θ rotator. The lasers are placed on standard optical benches while the UHV chamber and the TOF-MS are mounted on a custom table.

3. Ongoing upgrade of the experimental set-up

The installation of new instrumentation is in progress at the Laboratory for Experimental Astrophysics. This will give us the unique opportunity to study "in situ" the complex chemistry induced by ion irradiation and UV photolysis in ice mixtures. In particular the new experimental set-up will detect molecules "in situ" by a combination of laser desorption, jet cooling and VUV-UV photo-ionization followed by high resolution mass-spectrometric (TOF-MS) analysis of ices after energetic processing. This will contribute to understand the origin of complex molecules which were incorporated in planets, satellites and comets at the time of the formation of the Solar System and are believed to be the seeds from which life has developed on Earth. Figure 2 shows a drawing of the set up in the laboratory. Even if the new system is optimized to analyze ice samples after energetic processing, it can also be used to analyze other samples such as meteorites or extraterrestrial particles obtained from sample return missions.

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