Formation and Alteration of Complex Organics Induced by Energetic Processing

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Abstract The frozen surface of small bodies in the outer Solar System are exposed to energetic charged particles that alter their chemical composition. Laboratory experiments allow to simulate the interaction between cosmic rays and solar particles with frozen surfaces, showing the formation of complex organic compounds. However, irradiation also determines the destruction of both simple and complex molecules. We here report about recent laboratory experiments to simulate the irradiation and heating of surfaces in the outer Solar System and the detection of complex organics. We also present experiments that will be held on the International Space Station (OREOCube and Exocube) and a new facility to study the alteration induced on such complex organics, as well as on prebiotic species and biosignatures.

Keywords Astrochemistry · Laboratory · Solar system

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1 Introduction

The surfaces of various small bodies in the outer Solar System exhibit frozen volatiles. In particular, frozen methanol is revealed on the surface of the centaur Pholus, the trans-neptunian object (TNO) 2002 VE95, and the Kuiper-belt object (KBO) Arrokoth (Stern et al. 2019, and references therein). A number of outer small bodies also show the presence of water (Barucci et al. 2011) and N-bearing compounds (Grundy et al. 2016; Lisse et al. 2020). Furthermore, Pholus, VE95, Arrokoth and other small bodies also exhibit red slopes in the visible (Vis) and near-infrared (NIR). Such red slopes might be attributed to the presence of complex organic compounds inherited from the presolar cloud or that formed in the Solar System, after the bodies accretion (Dalle Ore et al. 2011).

The study of the presence of complex organics and their survival on small, atmosphere-less bodies is fundamental to shed light on the contribution that such bodies might have had in the emergence of life on Earth by delivering organics and prebiotic species.

On the one hand, laboratory experiments show that cosmic rays and solar wind particles interacting with C-bearing molecules trigger the formation of organic compounds (Strazzulla et al. 1992) whose complexity can further increase taking into account the heating that surfaces experience during their lifetime (Mispelaer et al. 2013). Mixtures including methanol, water, and ammonia determines the formation of organic refractory residues that contain complex compounds, including species of astrobiological relevance (Meinert et al. 2016; Nuevo et al. 2018). Red slopes appear in the Vis-NIR spectra of frozen mixtures exposed to ion irradiation (Brunetto et al. 2006).

On the other hand, high extent of irradiation by energetic photons or charged particles cause the destruction of both simple and complex species (Brucato et al. 2006; Johnson et al. 2012) and can thus determine the depletion of molecules, including complex organics and prebiotic species, in primitive small bodies.

We here report about the formation of complex organics in frozen mixtures exposed to ion irradiation and on new strategies to study the alteration induced to such organics by energetic radiation or charged particles on atmosphere-less surfaces. In this regard, we present two experiments that will be held on the International Space Station (ISS) and a new setup available at the Freie Universitaet Berlin (FUB, Germany) to study the survival of complex organics exposed to radiation.

1.1 Methods

Ion irradiation of CH_3OH:H_2O:NH_3 mixtures is performed by means of the IrradiatioN de Glaces et Météorites Analysées par Réflectance Vis-IR (INGMAR) at the Laboratoire de Physique des 2 Infinis Irène Joliot-Curie (Orsay). Mixtures are deposited at temperatures close to those estimated on surfaces in the outer Solar

System and then exposed to 40 keV H^+ produced by the SIDONIE ion implanter (Chauvin et al. 2004). Samples are then warmed up to room temperature to produce organic refractory residues. Analyses are performed *in-situ* by means of MIR spectroscopy and residues are also analysed by means of Very-High Resolution Mass Spectrometry (VHRMS) at the Institut de Planétologie et d'Astrophysique de Grenoble (IPAG, France). Further details are given in Urso et al. (2020a, 2020b).

A new experimental setup available at FUB allows to study the alteration of complex organics deposited as pure or in mixtures and their exposure to various irradiation sources. At present time, in-situ analysis are performed by means of UV-Vis and MIR spectroscopy and a quadrupole mass spectrometer will be soon available to allow the analysis of the volatiles released during the processing. The interpretation of future space-based experiments on board the ISS, ORganics Exposure in Orbit cube (OREOcube Elsaesser et al. 2014) and the Exposure of organics/organisms cube (Exocube Elsaesser et al. 2018) will further deepen our understanding on the alteration of organics in space.

1.2 Results and Discussion

Figure 1 shows the spectra of a $CH_3OH{:}H_2O{:}NH_3{=}1{:}1{:}1$ frozen mixture bombarded with 40 keV H^+ at doses that are expected to be accumulated in about 10^7 years on a frozen surface in the outer Solar System (Urso et al. 2020b) and then warmed up to 300 K. The MIR spectra acquired after irradiation and warm-up show various new features attributed to several chemical functions, testifying the rich chemical diversity of processed samples.

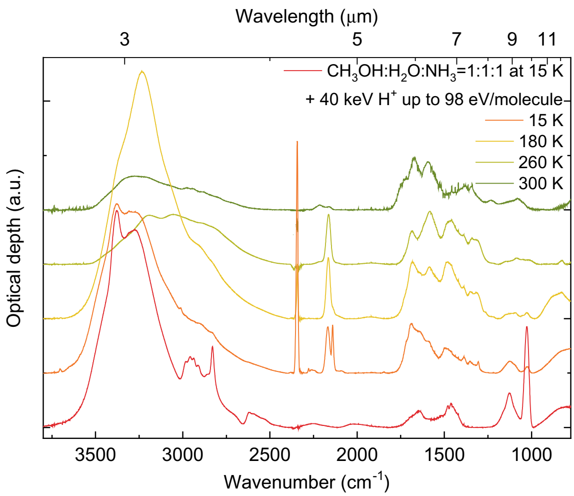

Fig. 1 MIR spectra of a $CH_3OH{:}H_2O{:}NH_3{=}1{:}1{:}1$ exposed to 40 keV H^+ and then warmed up to 300 K with a constant heating rate of 3 K min^{-1} (Color figure online)

The analysis of residues by means of VHRMS reveals thousands of molecular fragments in each sample, including CHO-, CHN-, and CHNO-bearing molecules. Complex organic molecules are also detected, including isomers of amino acids and nucleobases (Urso et al. 2020b).

Once formed, the high extent of irradiation that atmosphere-less bodies experience might determine the destruction of both simple and complex molecules on their surfaces. Exposure platforms on board the ISS are a unique tool to evaluate the effect of both particle radiation and unfiltered solar light on organics. The OREOcube and the Exocube experiments will allow the in-situ characterization of the alteration induced in complex organics, prebiotic compounds, biosignatures, and biological samples. In particular, OREOcube will allow the analysis of complex organics and biosignatures by means of in-situ UV-Vis spectroscopy. Exocube consists of two modules: ExocubeBio, for fluorescence and colorimetry of microorganisms, and ExocubeChem, to analyse organic compounds by means of IR spectroscopy. In both facilities, samples will be deposited as pure, on minerals, and at the interface between minerals and gaseous mixtures. Further activities will be carried out with a new facility at FUB, where complex organics including those formed after irradiation of simple frozen mixtures, prebiotics, and biosignatures will be exposed to various sources of radiation. The aim of these experiments is to shed light on the chemical pathways of degradation of complex organics in simulated space and planetary conditions.

1.3 Conclusions

Ion irradiation triggers the formation of organic molecules on frozen surfaces in the outer Solar System. Complex organics, including prebiotic species, are revealed in organic refractory residues which are laboratory analogues of the refractory materials on the surface of small bodies. Future experiments on board the ISS, OREOcube and Exocube, as well as experiments carried out with a new facility to simulate the temperature and irradiation conditions in atmosphere-less bodies will target the survival of complex organics. Samples will be analysed as pure and in presence of minerals and gases, allowing to understand the fate of organics on surfaces in the outer Solar System as well as on planetary surfaces.

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