

Can sulfur implantation in interstellar ice analogs lead to the formation of sulfur-bearing organics?

Alexis Bouquet¹, Alexander Ruf², Grégoire Danger², Philippe Boduch³, Philippe Schmitt-Kopplin⁴, Fabrice Duvernay², Vassilissa Vinogradoff², Olivier Mouis¹

¹Aix Marseille Université, CNRS, CNES, LAM, Marseille, France, ²Université Aix-Marseille, Laboratoire de Physique des Interactions Ioniques et Moléculaires (PIIM), Marseille, France, ³Centre de Recherche sur les Ions, les Matériaux et la Photonique (CEA/CNRS/ENSICAEN/UCBN), CIMAP, CIRIL, GANIL, ⁴Helmholtz Zentrum München, Analytical BioGeoChemistry, Neuherberg, Germany

Abstract

We present the results of the irradiation of interstellar ice analogs ($\text{H}_2\text{O}:\text{NH}_3:\text{CH}_3\text{OH}$) with argon and sulfur energetic ions. The samples were generated and irradiated at 10 K, and were thick enough to ensure the projectiles were implanted in the ice, allowing the sulfur projectiles to become part of the ensuing chemistry. The samples were measured on-site with Fourier Transform Infra-Red (FT-IR) spectroscopy, and the organic residues were analyzed off-site through Very High Resolution Mass Spectrometry (VHRMS). The IR spectra did not reveal any difference between the Ar-irradiated and S-irradiated samples, but the VHRMS allowed to investigate the potential formation of sulfur-bearing organic compounds.

1. Introduction

The irradiation of ices is a ubiquitous cause of chemical evolution in the universe, including interstellar ices or the surface of icy moons. Radiation chemistry can be induced by ions, electrons and high-energy photons. In the case of ions, in addition to the stopping power and total energy of the projectile [1], its reactivity is a possible factor in the chemistry. Sulfur is a cosmically abundant and highly reactive species, present in the solar wind [2] and Jupiter's magnetosphere [3]. Experiments with sulfur projectiles have been performed and have shown the efficient creation of sulfuric acid in water ice [4, 5]. Here, we investigate a target water ice including ammonia, shown to open new chemical pathways [6, 7], along with methanol, and for the first time conduct VHRMS analysis on the residues of sulfur-bombarded samples.

2. Experiments

We performed the experiments at the ARIBE low-energy line at the Grand Accélérateur National d'Ions Lourds (GANIL) in Caen, France. The projectiles were 105 keV and 105 keV argon. The samples were formed at 10K on a ZnSe window from a 2:1:1 $\text{H}_2\text{O}:\text{NH}_3:\text{CH}_3\text{OH}$ gas mixture and irradiated at a fluence of approximately 10^{14} ions. Multiple layers were so deposited and irradiated to ensure the products would be abundant enough to be detected. The samples were slowly warmed up to 300K to sublimate the volatiles and leave the refractory organic residue. This residue was analyzed off-site using electrospray ionization - Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS). This FT-ICR-MS technique represents the highest mass resolving power ($R > 10^6$) and highest mass accuracy (<200 ppb) among all mass spectrometric instruments [8]. This technique allows for detection and identification of species well beyond what is accessible with FT-IR.

3. Results

We show in Figure 1 the IR spectra of the samples (argon and sulfur irradiated) after irradiation of multiple layers but before warming. We see that there is no qualitative difference between the result of irradiation by argon and irradiation by sulfur.

Spectra after warming up and a visual examination of the windows confirm the creation of a refractory residue.

The results from the ESI-FT-ICR-MS analysis allow investigating the presence of sulfur-bearing compounds. We discuss whether these results indicate the presence of organic sulfur-bearing compounds and the differences between the two types of residues.

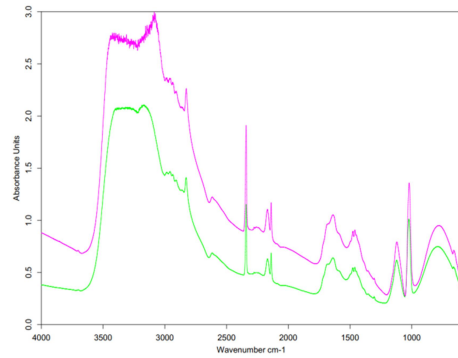


Figure 1: Spectra of the samples at 10K after argon irradiation (magenta) and sulfur irradiation (green)

Acknowledgements

A.B. and O.M. acknowledge funding by CNES. G.D. acknowledge the CNRS programs "Programme National de Planétologie" (P.N.P, INSU), "Programme de Physique et Chimie du Milieu Interstellaire" (P.C.M.I, INSU) and the "Centre National d'Etudes Spatiales" (C.N.E.S) from its exobiology program. This work was further supported by the RAHIA_SSOM grant (ANR-16-CE29-0015) of the French "Agence Nationale de la Recherche".

References

- [1] Teolis et al. *JGR: Planets* 122.10 (2017): 1996-2012.
- [2] von Steiger, R., Schwadron, N., Fisk, L., et al. 2000, *Journal of Geophysical Research: Space Physics*, 105, 27217
- [3] Paranicas, C., Cooper, J., Garrett, H., Johnson, R., & Sturmer, S. 2009, Europa. University of Arizona Press, Tucson, 529
- [4] Ding et al. *Icarus* 226.1 (2013): 860-864.
- [5] Strazzulla, et al. *Icarus* 192.2 (2007): 623-628.
- [6] Danger et al. (2013), *Geochimica & Cosmochimica Acta*, 2013, 118, 184-201
- [7] Danger et al. (2016) *Geochimica & Cosmochimica Acta*, 189, 184-196
- [8] Ruf et al.(2017) *PNAS* 114(11), 2819-2824.