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Exploring in the Laboratory the Impact of Low Energy Oxygen Ions on Titan's Aerosols

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1. Introduction

The Saturn system has been explored for 13 years (2004-2017) by the Cassini-Huygens mission that revealed the extraordinary chemical diversity of Titan and Enceladus. In particular, O^+ ions (1 - 100 keV), originating from Enceladus' geysers, precipitate in Titan's upper atmosphere where molecules reaching mass-on-charge (m/z) of several thousand atomic mass units have been detected. These aerosol embryos have been attributed to polycyclic aromatic (nitrogen bearing) hydrocarbons (PANHs) that most likely result from the ionization and dissociation of the major atmospheric compounds, N_2 and CH_4 by solar photons [Hörst, 2017]. It is to be expected that the small fraction of energetic O^+ ions, implanting themselves in organic aerosols, would modify their optical properties and chemical composition. If complex oxygenated molecules are formed, the aerosols, by sedimenting towards the surface, can then provide it with prebiotic material, adding a dimension with strong exobiological implications to the carbon / nitrogen / hydrogen chemistry endogenous to Titan [Hörst et al., 2012]. The objective of this project is thus to study the impact of oxygen ions from 1 to 100 keV on Titan aerosol analogues (tholins) and model materials by characterizing their effect on the chemical, structural and optical properties of the targets.

2. Experimental Methodology

Preliminary experiments were performed with adenine samples. Adenine was chosen because (i) it is a PANH, (ii) it has been identified in Titan's tholins [Hörst et al. 2012; Sebree et al., 2018], (iii) there is some existing literature on its irradiation by

UV photons and ions over a wide energy range showing that it does form a solid residue probably of macromolecular nature [Gerakines et al. 2012; Vignoli Muniz et al. 2017; Poch et al. 2014], (iv) some protocols to deposit it as a thin film on windows were available at LISA [Poch et al. 2014; Saïagh et al. 2014]. The samples consist of a thin (150 – 500 nm) adenine deposit on a MgF_2 or $ZnSe$ window. 8 samples were irradiated in the IGLIAS set-up at the ARIBE beam line at GANIL (Caen, France) with 35 or 70 keV $^{17}O^{4+}$, $^{18}O^{5+}$, or $^{20}Ne^{3,4+}$ at a total fluence ranging from 9×10^{14} to 5×10^{15} ions cm^{-2} . Samples were kept at 300 or 150 K and under ultra-high vacuum. Using the Stopping and Ranges of Ions in Matter (SRIM) software, we calculated that ions stop at a depth of 100 and 200 nm, for 35 and 70 keV incident ions, respectively, ensuring that they are implanted well within the sample. IR absorption spectra were obtained *in situ* during the irradiation with a Brüker V70 FTIR spectrometer.

3. Results and Conclusions

During energetic ion irradiation of the adenine films, their overall IR absorption intensity decreases (Fig. 1). The adenine molecule disappearance is caused by both destruction and sputtering. The projected stopping range being lower than the sample thickness, a part of the sample is not irradiated and the evolution of a given peak area A as a function of the ion fluence F can be written as

$$A(F) = a \cdot \exp(-bF) - Y \cdot F + c,$$

where a is the initial absorption of the peak area, b is the destruction cross section, Y characterizes the sputtering yield and c gives the number of molecules

in the non-irradiated layer at the end of the experiment.

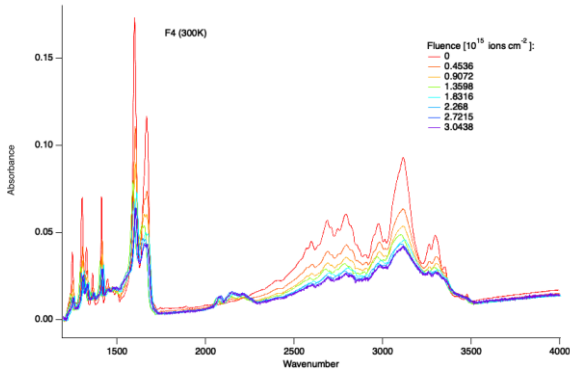


Figure 1: Infrared absorption spectra of adenine at 300 K under irradiation of 35 keV $^{18}\text{O}^{5+}$ at different fluences.

Table 1 displays the destruction cross section and sputtering yield ($v7$, 1609 cm^{-1}) for different projectiles and temperatures. Our destruction cross sections are similar to that obtained for 1 keV and 0.8 MeV H^+ [Gerakines et al. 2012; Vignoli Muniz et al. 2017]. The sputtering yield often has a large error but a rough approximation is that 15% to 35% of the sample is sputtered away. Further experiments with *in situ* mass spectrometry measurements of the gas phase could determine whether the sputtered material is intact adenine or some other molecules. Samples irradiated at 150 K have the largest destruction cross section and sputtering yield. This behavior has also been observed in previous experiments performed in the MeV range where the decay rate increased with decreasing temperature [Gerakines et al. 2012; Vignoli Muniz et al. 2017].

Projectile	T	b	Y
35 keV $^{18}\text{O}^{5+}$	300	$(1.71 \pm 0.08)e^{-15}$	6 ± 1
35 keV $^{18}\text{O}^{5+}$	150	$(3.6 \pm 0.9)e^{-15}$	11 ± 26
35 keV $^{20}\text{Ne}^{3+}$	300	$(2.5 \pm 0.1)e^{-15}$	13 ± 1

Table 1: Destruction cross section (cm^2) and sputtering yield (molecules/ion) for different projectiles and temperatures (K).

Beyond adenine destruction, a new broad IR absorption band clearly arises between 2050 and

2250 cm^{-1} that may be attributed to nitriles or isonitriles. However, we could not find any evidence for absorption bands from oxygen-bearing molecules. More sensitive *ex situ* analysis of the irradiated samples by mass spectrometry are ongoing to characterize the macromolecular residue.

Acknowledgements

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