

Possible observation of glycine during processing of $\text{NH}_3:\text{H}_2\text{O}:\text{CO}$ ice by heavy cosmic ray analog. S. Pilling^{1,2}, E. Seperuelo Duarte^{1,3,4}, E. F. da Silveira¹, E. Balanzat³, H. Rothard³, A. Domaracka³, and P. Boduch³, ¹Pontifícia Universidade Católica do Rio de Janeiro (PUC-Rio), RJ, Brazil, ²Universidade do Vale do Paraíba (UNIVAP/IP&D), SP, Brazil (sergiopilling@yahoo.com.br), ³Centre de Recherche sur les Ions, les Matériaux et la Photonique (CEA /CNRS /ENSICAEN /Université de Caen-Basse Normandie), CIMAP - CIRIL - GANIL, Caen, France, ⁴Grupo de Física e Astronomia, CEFET/Química de Nilópolis, RJ, Brazil.

Introduction

Deep inside dense molecular clouds and protostellar disks, interstellar ices are protected from stellar energetic UV photons. However, X-rays and energetic cosmic rays can penetrate inside these regions triggering chemical reactions, molecular dissociation, and evaporation processes such as sputtering. Laboratory studies and astronomical observations indicate that photolysis and radiolysis of such ices can lead to the formation of complex organic compounds, and even prebiotic molecules such as amino acids and nucleobases [1-6].

Inside these dense regions the dust grains can reach a size of the order of a micron, as a coagulation of sub-micron grains occurs with ice-rich mantles of tens of nanometers [7-9]. In those sites X-rays (despite some degree of attenuation) and cosmic rays are the main drivers of the gas-phase and grain-surface chemistry. Figure 1a illustrates, as a schematic view, the interaction between heavy-ion cosmic rays and a typical interstellar grain inside dense clouds.

Although the flux of heavy ions (e.g., Fe, Ni, Mg, ...) is about 3-4 orders of magnitude lower than that of protons [10,11], their effects play an important role on interstellar grains since they can deposit about 100 times more energy than the light ions (He^+ and protons) inside the grains. Consequently, the number of species released per impact to gas phase due to heavy ions could be 4-5 orders of magnitude higher than for protons [12,13].

In this work, we present infrared measurements of ammonia-containing astrophysical ice analog $\text{H}_2\text{O}:\text{NH}_3:\text{CO}$ (1:0.6:0.4) irradiated by 46 MeV $^{58}\text{Ni}^{13+}$ to simulate the modification induced by heavy cosmic rays inside dense astrophysical environments.

Experimental methodology and results

The measurements were performed inside a high vacuum chamber coupled to the IRRSUD beamline at the heavy-ion accelerator GANIL (Grand Accélérateur National d'Ions Lourds) in Caen, France. The gas samples were deposited onto a polished CsI substrate previously cooled to 13 K. *In-situ* analysis were performed by

a) Typical dense cloud grain

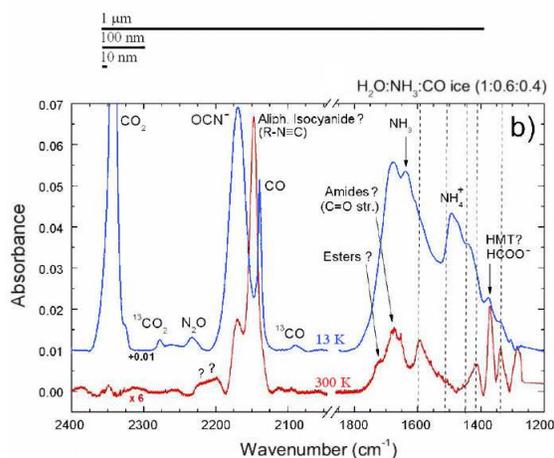
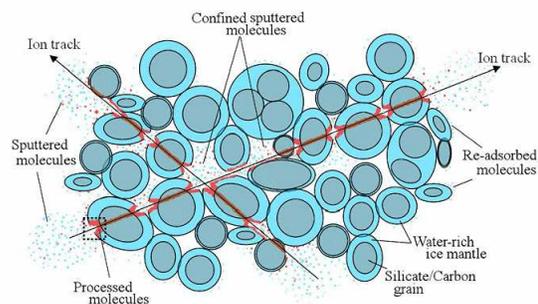


Figure 1: a) Schematic view showing the interaction between a heavy-ion cosmic ray and a typical interstellar grain inside dense clouds. b) Comparison between the irradiated ice at 13 K (top spectrum) and the 300 K residue (bottom spectrum). Vertical dashed lines indicate the frequencies of some vibration modes of zwitterionic glycine ($\text{NH}_3^+\text{CH}_2\text{COO}^-$).

a Fourier transform infrared spectrometer (FTIR) at different fluences. Experimental details is given elsewhere [13,14].

The measured value for the dissociation cross-section of water, ammonia, and carbon monoxide due to heavy cosmic ray analogs were $\sim 2 \times 10^{-13}$, 1.4×10^{-13} , and

$1.9 \times 10^{-13} \text{ cm}^2$, respectively. In the presence of a typical heavy-ion cosmic ray field [11,14], the estimated half-lives of the studied species is about $2 - 3 \times 10^6$ years. This value is in a good agreement with the half-lives of typical molecular clouds and protostellar clouds.

The infrared (IR) spectra of the irradiated ice samples exhibit lines of several new species including HNCO, N_2O , OCN^- , and NH_4^+ (see Fig. 1b). The IR spectra at room temperature contain five bands that are tentatively assigned to vibration modes of the zwitterionic glycine ($\text{NH}_3^+\text{CH}_2\text{COO}^-$). The IR peak centered around 1370 cm^{-1} observed in both 13 K and 300 K spectra was tentatively assigned to hexamethylenetetramine - HMT ($(\text{CH}_2)_6\text{N}_4$), since a similar feature was also observed in the UV photolysis of $\text{H}_2\text{O}:\text{NH}_3:\text{CH}_3\text{OH}:\text{CO}:\text{CO}_2$ ice [15]. The observation of NH_4^+ in the same organic residue reinforces the evidence for HMT, since the ammonium is an essential component of its formation. The complete list of IR absorption features and its tentative assignments is given elsewhere [14].

Summary

We present experimental studies of the interaction of heavy, highly charged, and energetic ions (46 MeV Ni) with $\text{H}_2\text{O}:\text{NH}_3:\text{CO}$ (1:0.6:0.4) ice in an attempt to simulate the physical chemistry induced by heavy-ion cosmic rays inside dense astrophysical environments. Dissociation cross sections, sputtering yields and half-lives of the studied species have been determined. The IR spectra of the irradiated ice sample exhibit lines of several new species including HNCO, N_2O , OCN^- , NH_4^+ , HMT and five bands that are tentatively assigned to vibration modes of the zwitterionic glycine ($\text{NH}_3^+\text{CH}_2\text{COO}^-$).

Although they represent only a small fraction ($\sim 1\%$) of the cosmic-ray flux, some effects (e.g., molecular sputtering and ice compaction) caused by heavy ions on interstellar ice grains are more intense than those caused by protons. This should be taken into consideration in future chemical models of inner regions of molecular clouds since heavy ions will contribute molecules to the gas phase and trigger chemical surface and bulk reactions.

The presence of complex molecules (e.g. glycine and HMT) in the organic residue produced by the bombardment of interstellar ice analogs by energetic and heavy ions has to be confirmed. However, the result of this experiment suggests that even deep inside molecular cores or other dense regions such as protoplanetary disks, the interstellar grains are being transformed significantly. The organic molecules produced, trapped into and onto

dust grains, meteoroids, and comets, could be delivered into the planets/moons possibly allowing prebiotic chemistry to take place in these environments where water is also found in liquid state.

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