

Ionic Desorption from Astrophysical Ice Analogs by Energetic Electrons: Implications for the Detectability of Interstellar N-Heterocycles

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Synopsis Unsuccessful radio-astronomical searches have been attempted for pyrimidine and pyridine towards star-forming regions. However, molecules can condensate onto cold dust grains forming ice mantles exposed to ionization agents. Electron-stimulated ion desorption of positive charged desorbed fragments from pure pyridine and pyrimidine by high-energy are measured. Also electronic structure calculations were done at DFT level to obtain thermodynamic properties.

Uracil has been identified in the Murchison meteorite [1]. On the other hand, unsuccessful radio-astronomical searches have been attempted for pyrimidine [2] and pyridine [3] towards star-forming regions. Condensation onto cold dust grains may lead to gas-phase molecular depletion and formation of ice mantles [4]. Both interstellar and planetary icy surfaces are exposed to several ionization agents [5] from the radiation field, stellar winds and cosmic-rays. Once confined within ice mantles, N-heterocycles participate in a complex surface chemistry.

In the present work, we measured the electron-stimulated ion desorption (ESID) of positively charged desorbed fragments from a pure pyrimidine and pyridine ice bombarded by high-energy electrons. Electronic structure calculations were done at DFT level, with Gaussian09 package. In the search of minimum energy structure of chemical systems, were applied the hybrid functional B3LYP and Def2SVP basis set. Thermodynamic properties and final geometries were obtained with hybrid functional M06-2X and Def2TZVP basis set. Many atomic and molecular cations desorbs, including the pyridine molecule ($C_5H_5NH^+$ and $C_4H_4NH^+$) and ionic clusters (like $(C_5H_5N)_2H^+$).

The highest yield ion desorption of $C_5H_5N^+$ and $C_5H_5NH^+$ compared to the ions $C_4H_4N^+$ and $C_4H_4NH^+$ indicates that the heteroatoms included in the aromatic ring increases the probability of molecular fragmentation, decreasing the pyrimidine stability with respect to pyridine in radiation exposure.

A typical mass-converted ESID spectrum for

vapour deposited C_5H_5N is shown in Figure 1. Light fragments such as those of the H_n^+ ($n = 1-3$) ion series are the predominant ions to desorb, since their low mass and high initial kinetic energy prevents neutralization on surface after they are formed. It is possible to clearly distinguish six groups of ions in the ESID mass spectrum up to $m/z = 90$, in which each group is composed by desorbed fragments bearing one to six members of the original pyridine ring, respectively. These groups are labelled from A to F in Figure 1.

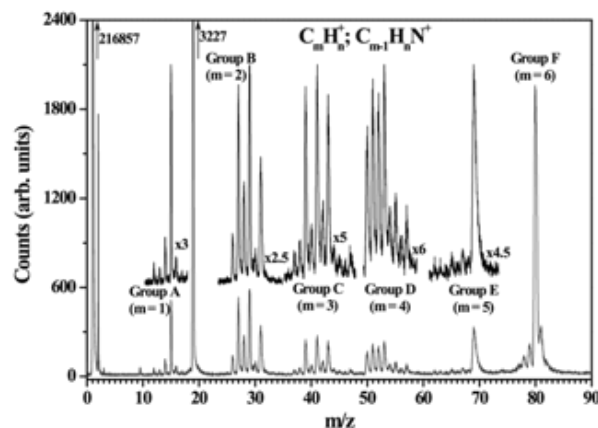


Figure 1. Pyridine ESID spectrum at 2.1 keV.

References

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