Pyridine under Electron-Impact and Multiphoton Ionisation: Estimation of Appearance Energies and Identification of Dissociation Pathways

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Investigating the fragmentation dynamics of nitrogen-containing aromatic molecules provides insights into sequential hydrogen loss, thereby strengthening our understanding of their chemistry in astrochemical environments. Pyridine, a nitrogen-containing aromatic heterocycle relevant to both biological chemistry and astrochemistry, provides a useful model system for investigating ionisation-induced fragmentation [1]. In this work, the fragmentation dynamics of pyridine are investigated using electron-impact ionisation (EI) and multiphoton ionisation (MPI), focusing on appearance energies, sequential hydrogen loss, and competing dissociation pathways.

Mass spectra obtained under EI and MPI reveal sequential hydrogen loss from the pyridine molecular ion (m/z 79), producing fragments spanning m/z 78−74. Electron-energy-dependence measurements are used to determine the appearance energies of prominent fragments and examine their energy-dependent formation [2]. Notably, the m/z 77 and 76 signals exhibit similar onset regions, although the latter increases more rapidly with electron energy. These observations indicate sequential hydrogen loss, with the m/z 77 ion undergoing further dehydrogenation to form the m/z 76 ion. Density functional theory (DFT) calculations will be used to evaluate the structural stability of both ions and the energetic feasibility of this fragmentation pathway. Comparing the calculated energy requirements with experimental appearance energies will help assess the feasibility of this process. Previous studies have also demonstrated the complexity of pyridine fragmentation, including HCN and HNC loss, highlighting the importance of theoretical investigations in understanding its dissociation mechanisms [2].

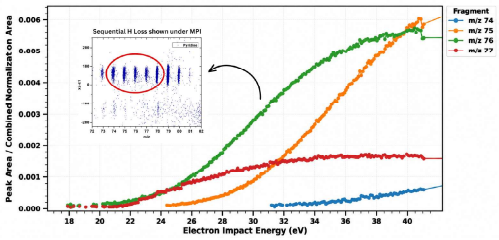

Figure 1. Electron Energy Dependence plot of pyridine showing the sequential H loss under EI along with the 2D Energy Correlation plot under MPI

The combined experimental and theoretical investigation provides insights into the sequential hydrogen-loss series from the pyridine parent ion (m/z 79) to the fragments at m/z 78−74, as well as the energy-dependent fragmentation of pyridine under EI and MPI. This study contributes to a better understanding of fragmentation processes in nitrogen-containing aromatic molecules relevant to astrochemical environments.

References

[1] Mondal S, Wouterlood B, Garcia G A, Nahon L, Stienkemeier F and Hartweg S 2026 *Phys. Chem. Chem. Phys.* **28** 17361–17370

[2] Jurkowski M K, Wasowicz T J 2023 *Rom. J. Phys.* **68** 205

[3] Rap D B, Simon A, Steenbakkers K, Schrauwen J G M, Redlich B and Brünken S 2023 *Faraday Discuss.* **245** 221–244

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