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Ionization and fragmentation of pyrimidine and pyridazine induced by proton and electron impact

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Synopsis The ionization and fragmentation of pyrimidine and pyridazine have been studied experimentally, by recording the time of flight mass spectra, and theoretically, by calculating the valence shell MOs ionization cross sections. The absolute total non-dissociative and dissociative cross section has been measured between 70 to 400 eV for electron impact on pyrimidine and from 250 to 2500 keV for proton impact on both molecules. The partial yields and the absolute cross sections measured as a function of the energy combined with the model calculation allows us to suggest the vacancy population of the valence MOs from which several sets of fragment ions are produced.

The study of the light and heavy particles interactions that drive the ionization and fragmentation of pyrimidine and pyridazine are of prime importance including in radiation therapy, since these biomolecules constitute key building blocks of many important natural and synthetic bio-active molecules, as the nucleobases and as core of drugs against disorders belonging to almost all therapeutic classes. Also, the large abundance of electrons and protons in regions of the interstellar space medium and the existence of nitrogen containing molecules that form subunits of hetero-aromatic molecules may produce pyrimidine.

In this context, the present work appears as one of the first combined theoretical and experimental study providing (i) measurements of the absolute total, non-dissociative and dissociative cross sections of the electron- and proton-induced ionization for pyrimidine [1] and pyridazine for energies ranging from 70 to 400 eV for electron impact and from 125 up to 2500 keV for proton impact and (ii) the percentage contribution of the valence molecular orbitals ionization in the production of the ionic parent molecule and fragments. The overlapping and velocity range of the electron and proton measurements allowed the determination of absolute cross sections for proton impact based on effusive gas target and the use of the Born Approximation to estimate the distribution of primary vacancies in the molecular orbitals.

Results, such as those shown in Figure 1, for pyrimidine losing two up to all atoms of the ring as a function of the proton impact energy will be presented and discussed for both molecules. A detailed analysis of the experimental partial dissociation cross sections as function of the impact energy shows characteristic changes in the ion production compared to the model calculations based on single vacancies: in most cases, the cross sections are well described from 200 keV upwards, but in some others, a steep increase is observed downwards in energy. This indication enables us to discriminate rather directly which process is active, a single step, where most species are dominated by a single vacancy, or a two-step process, that becomes important in multiple particle fragmentation.

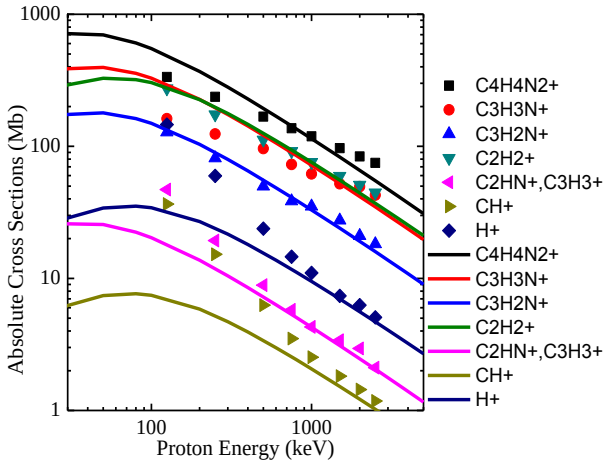

Figure 1. Absolute cross sections for the parent molecule and several fragments of pyrimidine: closed symbols and lines representing experimental results and model calculations, respectively.

This work show a simple and effective strategy to study the fragmentation of rather complex molecules in the gas phase based on standard time of flight mass spectroscopy and a simple semi-classical framework.

Reference

[1] W. Wolff *et al* 2014 *J. Chem. Phys.* **140**, 064309

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