

Selectivity in the photofragmentation of halo-pyrimidines

P. Bolognesi^{*1}, A. Kettunen[†], A. Cartoni[&], R. Richter[#], S. Tosic[§], S. Maclot[§], P. Rousseau[§],
R. Delaunay[§], A. Domaracka[§], L. Avaldi^{*}

^{*} CNR-Istituto di Struttura della Materia, Area della Ricerca di Roma1, Monterotondo Scalo, Italy

[†] Department of Physics, University of Oulu, Finland

[&] Dipartimento di Chimica, Sapienza Università di Roma, Roma, Italy

[#] Elettra-Sincrotrone Trieste, Basovizza, Italy

[§] Institute of Physics, University of Belgrade, Belgrade, Serbia

[§] CIMAP, CEA/CNRS/ENSICAEN, Université de Caen Basse-Normandie, Caen, France

Synopsis The fragmentation of 2Br-, 2Cl- and 5Br-pyrimidine following direct valence photoionization or inner shell excitation and decay has been studied by electron-ion coincidence experiments. The results show that the fragmentation is strongly selective on the final singly charged ion state and the dominant fragmentation patterns correlate to the nearest appearance potential.

Pyrimidines are an important class of organic molecules because the pyrimidine ring forms the base structure of three nucleic acids (uracil, cytosine and thymine) and their halogenated substituted bases have found applications as radiosensitizers in radiotherapy.

In a previous work on pyrimidine [1] it has been observed that the resonant Auger spectrum shows a selective population of the final states of the cation and the site and state selected fragmentation patterns appear to depend only on these final states. In this work we have studied the fragmentation of 2Br-, 2Cl- and 5Br-pyrimidine following direct valence shell photoionization as well as inner shell excitations. In the case of valence ionization the detection of the fragment ions in coincidence with energy selected photoelectrons allows a state selected study on the different cation states involved in the process. In the case of inner shell excitation the fragment ions are detected in coincidence with the resonant Auger electrons. In this way the selectivity on the site of the initial energy deposition is added, too.

The experiments have been performed at the Gas Phase Beamline at the Elettra Synchrotron (Trieste).

In Figure 1 the electron-ion coincidence yield for several 2Br-pyrimidine fragments as a function of the binding energy of the cation state measured either in direct photoionization at 100 eV or following the inner shell excitation are shown. Regardless of the initial process the coincidence mass spectra show a very similar behavior as long as the same final ionic state is selected. This behavior of the fragmentation can

be explained by the fact that the fragmentation occurs on a time scale longer than the non-radiative relaxation of the inner shell vacancy. It is also clear that a certain ionic state preferentially correlates to the nearest fragmentation threshold, even though other fragmentation channels are energetically open.

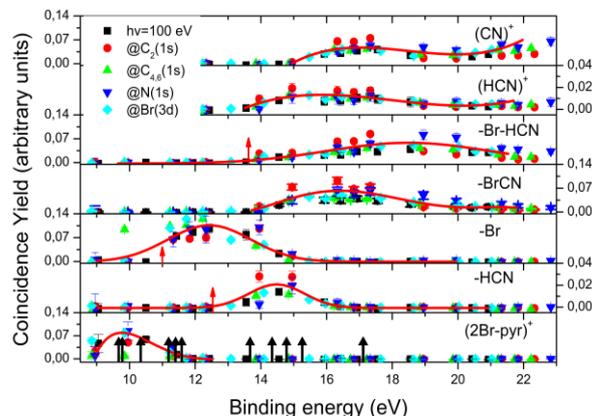


Figure 1. The PEPICO coincidence yields as a function of the binding energy of the cation state. The black arrows in the bottom panel indicate the position of the ion states, while the red ones the measured appearance energy of the fragments.

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References

[1] P. Bolognesi *et al* 2012 in “Radiation Damage in Biomolecular Systems”, G. Garcia Gomez-Tejedor and M.C. Fuss eds., Springer, 165-176

¹E-mail: Paola.Bolognesi@cnr.it

