

Photo-induced fragmentation of biomolecules in the gas-phase

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Influence of radiations on biological tissues is of major concern in cancer therapy development. It is known that the primary ionizing photons and the secondary particles (electrons, ions, radicals, excited atoms and molecules) may induce important damages to DNA, with single- and double- strand breaks [1]. At the microscopic scale these lesions are related to the bond cleavages of the DNA building units. To determine the most sensitive part of the DNA molecular chains to the photon-induced bond rupture, it is important to explore the possible mechanisms leading to fragmentation of components of the DNA helix. In this perspective, investigations of the excitation, relaxation and fragmentation processes of the cyclic hydrocarbons containing oxygen and nitrogen heteroatoms (i.e. furan, tetrahydrofuran, isoxazole, pyridine and pyrimidine etc.) are of particular pertinence, because they are often considered to be simple prototypes of the structure units of the DNA. For instance, the molecules, tetrahydrofuran and furan, are built on furanose ring which may be discerned in the deoxyribose sugar of DNA. Pyrimidine molecule, on the other hand, is often considered to be an important precursor of the three nucleic bases of DNA and RNA, cytosine, thymine, and uracil, respectively. Thus, these molecules seem to be ideal candidates to characterize the mechanisms by which radiation produces their fragmentation, especially in the context of the DNA helix damage by the ionizing radiation.

In the present presentation I would like to discuss the results of recent projects performed at the Gas Phase beamline with collaboration with the Gas Phase research team at Elettra. In particular, I will show the results of the photon-induced fragmentation of the five and six-membered heterocyclic molecules (see Figure 1) in the inner-valence photon energy range of 13-70 eV [2-5]. These studies revealed molecular processes leading to formation of a number of the excited atomic H(*n*) and diatomic CH(A²Δ), CN(B²Σ⁺), C₂(d³Π_g) and NH(A³Π) fragments. In general, fragmentation mechanism involves initial excitation of these molecules into the superexcited

states, which are inner-valence or high-Rydberg excited states, lying at higher energies above the first ionization threshold. These super-excited molecules, before they dissociate into the neutral atomic and molecular excited fragments, are further a subject of molecular isomerization and hydrogen atoms migration.

Moreover, the multifragmentation mechanisms of pyridine molecules by performing double or even triple coincidence measurements have been investigated (in these measurements the fluorescence of selected excited fragmentation products was detected in coincidence).

A new class of the mechanisms of the photon-induced fragmentation, namely recapture processes to Rydberg states by detection of the neutral high-Rydberg fragments field ionized and TOF mass analyzed after inner-shell C1s, N1s and O1s core excitations and ionization of the isoxazole and pyridine molecules will be also described. Up to now these processes have not been observed in the complex systems such as the heterocyclic molecules.

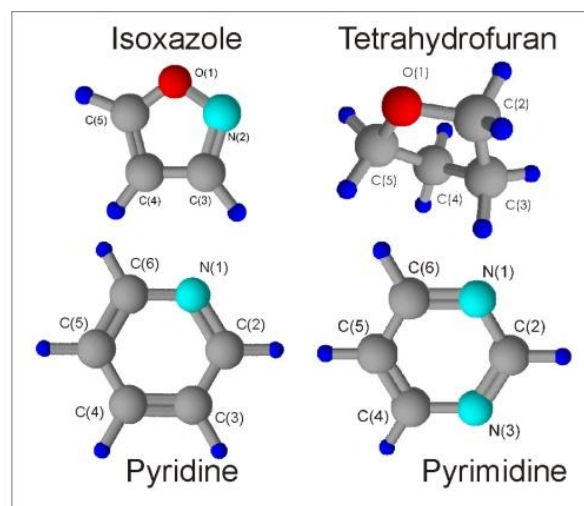


Figure 1. The five and six-membered heterocyclic molecules of interest.

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- [1] M. A. Huels, B. Boudaïffa, P. Cloutier, D. Hunting, L. Sanche, *J. Am. Chem. Soc.*, **125** (2003) 4467.
- [2] T.J. Wasowicz, A. Kivimäki, M. Coreno, M. Zubek, *J. Phys. B* **47** (2014) 055103.
- [3] M. Zubek, T.J. Wasowicz, I. Dabkowska, A. Kivimäki, M. Coreno, *J. Chem. Phys.* **141** (2014) 064301.
- [4] T.J. Wasowicz, A. Kivimäki, M. Coreno, M. Zubek, *J. Phys. B* **45** (2012) 205103.
- [5] T.J. Wasowicz, A. Kivimäki, M. Dampc, M. Coreno, M. de Simone, M. Zubek, *Phys. Rev. A* **83** (2011) 033411.