Ultrafast hydrogen migration in ionized biomolecules in the gas phase: unusual fragmentation mechanisms

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Radiation damage of biological tissues starts at the femtosecond timescale, where ionization processes lead to the production of numerous secondary particles (electrons, ions, radicals). An important research activity focuses on the understanding of these processes at the molecular level [1]. In this context, ion-biomolecule collisions have become a fundamental technique to study radiation damage at the physical stage [2,3]. The knowledge of ionized biomolecules properties, in particular their structures and stability against dissociation is thus of prime importance. Moreover, it is also essential to understand the fragmentation mechanisms taking place after ionization-excitation with highly-charged ions.

The dynamics of multiply charged (excited) molecular cations could be finely probe using physical techniques giving insight into ultrafast chemical processes at the femtosecond timescale [4-6]. We have recently implemented a strategy based on the combination of experimental and theoretical studies to successfully disentangle the complicated fragmentation dynamics of complex molecular systems after ionization and excitation in collisions with energetic multiply charged ions [7]. We obtain the experimental data in the gas phase for neutral molecules in collisions with low-energy highly-charged ions. State-of-the-art multi-coincidence detection mass spectrometry techniques are used to determine the charge state of the molecule before fragmentation. The experimental data are analyzed by means of quantum chemistry calculations (density functional theory and *ab-initio* molecular dynamics). The calculated fragmentation pathways leading to the most abundant fragments observed in the mass spectra allow us to discern the structure of these ions and how they are produced.

In this communication I will present our results obtained by applying this methodological approach to study the fragmentation dynamics of excited doubly charged amino acids [7-9] and DNA basis in the gas phase [10]. In competition with the expected Coulomb repulsion of the doubly charged excited molecules, other fast mechanisms have been identified, in particular intramolecular H migration. I will also show recent results for ionized ethanol molecules with strong infrared fields, in which the time of intramolecular single and double hydrogen migration has been measured with pump-probe techniques, and the corresponding mechanisms have been elucidated with molecular dynamics simulations.

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