Fragmentation of amino acids induced by collisions with low-energy highly charged ions

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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 bio-molecules 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 fs 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 multicoincidence detection mass spectrometric techniques were used to determine the charge state of the molecule before fragmentation. The experimental data were 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, this methodological approach has been applied to study the fragmentation dynamics of amino acids in the gas phase. In the fragmentation of GABA [7], we found that the intact molecule hardly survives the collision and that many fragments are observed corresponding to numerous dissociation channels (computed and detected). In the fragmentation dynamics of excited molecular glycine dications [8], doubly-charged molecular species were observed in the mass spectrum. The existence of these species can only be explained considering a fast intramolecular H migration mechanism followed by loss of neutral moieties. These processes appear in competition with the expected Coulomb repulsion of the doubly charged glycine that leads to fission in two singly charged cations. OH migration explains the characteristic fragmentation pathways of dicationic beta-alanine.

References:
[1] P. Swiderek, Angew. Chem. Int. Ed. **45** 4056 (2006).
[2] E. Pittenauer and G. Allmaier, Comb. Chem. High T. Scr. **12** 137 (2009).
[3] M.A. Baldwin. Biol. Mass Spectrom. **402** 3 (2005).
[4] Y.H. Jiang et al., Phys. Rev. Lett. **105** 263002 (2010).
[5] M. Madjet et al., Phys. Rev. Lett. **107** 263002 (2011).
[6] R. Itakura et al., J. Chem. Phys. **127** 104306 (2007).
[7] M. Capron et al., Chem. Eur. J. **18** 9321 (2012).
[8] S. Maclot et al., submitted (2013).