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Formation and fragmentation of protonated molecules after ionization of molecular clusters with multiply charged ions

V. Vizcaino^{*1}, J.-C. Pouilly*, L. Schwob*, R. Delaunay*, J. Kočíšek*, S. Eden†, J.-Y. Chesnel*, A. Méry*, J. Rangama*, L. Adoui* and B. Huber*

* CIMAP (UMR 6252) - CEA, CNRS, ENSICAEN, UCBN, Bd Henri Becquerel, BP 5133, 14070 Caen, France

† Dept. of Physical Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom.

Synopsis Collisions between neutral clusters of biomolecules (amino-acids and lactic acid) and keV ions in the gas-phase lead, in very large majority, to protonated species. We found that the target proton affinity and the nature of the projectile ion influence the protonation of monomers within these clusters. New fragment ion channels were also observed and have been assigned to the statistical dissociation of these protonated molecules formed upon ionization of the clusters. These new dissociation channels exhibit strong delayed fragmentation in the μ s time scale.

Ionizing radiation-induced physical and chemical phenomena in biological matter are important, not only from a fundamental point of view, but also for a deeper understanding of radio- and hadron therapy mechanisms. Gas-phase investigations allow extracting the intrinsic properties of molecular systems, because all solvent effects are removed. In this contribution, we present our results on irradiation of gas phase amino acid and lactic acid clusters by ion beams at keV kinetic energy.

Experiments have been performed with a crossed-beam apparatus where the collimated molecular clusters beam formed in a gas aggregation chamber crossed the pulsed ion beam delivered by an Electron Cyclotron Resonance ion source. The cationic products were extracted from the interaction region orthogonally to both beams and mass-over-charge analyzed in a linear Wiley-McLaren time-of-flight mass spectrometer.

After ionization with O^{3+} at 30 keV, monomers and dimers are found protonated to a very large extent for all amino acids studied however, in the case of lactic acid, which has a lower proton affinity, the radical cation corresponds to around 12% of the protonated specie (Figure 1).

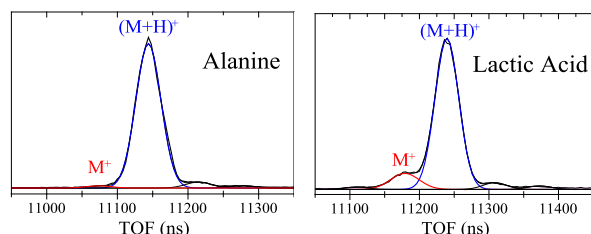


Figure 1. Radical cations M^+ vs. protonated monomers $(M+H)^+$ in alanine and lactic acid.

This ratio decreases to 8% after interaction with a beam of He^+ at 6 keV where the ioniza-

tion occurs at smaller mean impact parameter and therefore higher excitation energy is transferred during the collision. This would indicate that proton transfer involves a potential energy barrier in ionized lactic acid clusters.

New fragments specific to the ionization/fragmentation of clusters have been found and are assigned to statistical fragmentation from the protonated molecule (Figure 2). Indeed, following multi-ionization, the clusters undergo a succession of evaporation and fission processes to accommodate the excess of charges and energy transferred in the collision. After these relaxation mechanisms, protonated monomers can still have a high internal energy and fragment in similar pathways (loss of CO) than in CID experiments.

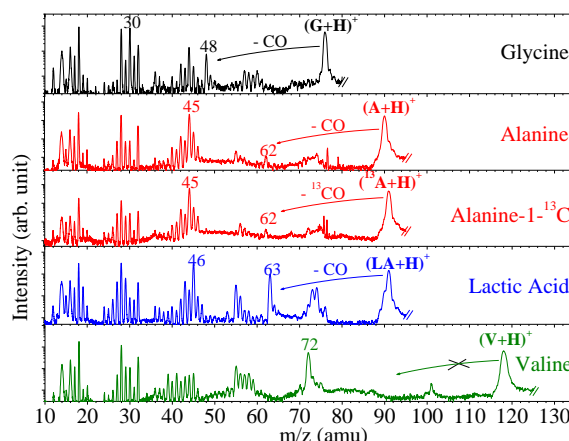


Figure 2. Cationic products (below the monomer) of the interaction between molecular clusters and O^{3+} ions at 30 keV.

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¹ E-mail: vizcaino@ganil.fr