Fragmentation Dynamics of Doubly Charged Methionine in the Gas Phase

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In this contribution we report electronic state selective fragmentation studies of methionine using Auger electron Photo-ion Photo-ion Coincidence (AEPIPICO) spectroscopy technique and first-principles molecular dynamics (MD) calculations. Methionine ($C_5H_{11}NO_2S$) is an essential amino acid as it is a building block of proteins, and is of particular importance as starting marker during protein assembly.

The AEPIPICO technique was used to record the sulfur (S) LMM Auger electron spectra in coincidence with time-of-flight (TOF) mass spectra of cationic fragments from the dissociation of doubly charged methionine (M^{2+}) molecules produced by absorption of synchrotron radiation. The dicationic states of the parent molecules were created as the result of initial inner-shell (S 2p) ionization followed by normal Auger decay of the shell vacancy. The measurement instrument consists of a modified Scienta SES-100 hemispherical electron analyzer [1] and a Wiley-McLaren type ion TOF spectrometer [2]. The experiments were carried out at the undulator beamline I411 at the MAX-II storage ring.

To complement the experiments we performed *ab initio* calculations. All-electron calculations are applied to assign doubly charged final states of sulphur 2p core ionized methionine. In addition, Car-Parrinello molecular dynamics (with the help of the CPMD code [3]) is used for a thermal equilibration process and for modelling fragmentation of doubly charged methionine molecules with selected initial temperatures. The simulations starting from M^{2+} molecules with the double vacancy in HOMO orbital in several temperatures show bond scissions leading to fragments COOH, $(CH_2\text{-}CH\text{-}NH_2)^+$ and $(CH_3\text{-}S\text{-}CH_2)^+$ that were observed in the AEPIPICO experiments.

References:
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