The Role of Proton Mobility in Peptide Fragmentation Dynamics and Complex Formation

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Abstract: Surface-induced dissociation (SID) is a process in which the collision of a gas-phase ion with a surface results in fragmentation of the ion. It is a well-known mass spectrometry technique that can provide a "fingerprint" of the ion's structure and hence has been the focus of several experimental and theoretical studies. Experimentalists have determined that the fragmentation efficiency depends strongly on the collision energy. They have also developed the empirical "mobile" proton model that links proton motion to peptide fragmentation. The mobile proton model is a statistical model based on the relative stability of protonation sites within a peptide. Here we present quantum mechanical/molecular mechanical direct dynamics simulations employing the semi-empirical RM1 method to explore the role of proton mobility during SID for the gly_8-H^+ + FSAM system. We classify each fragmentation event as non-statistical or statistical based on the absence or presence of a relevant proton hop within the peptide. Preliminary results also show a good correlation between proton mobility and statistical fragmentation. We observed that peptide fragments would often form stable complexes for several picoseconds following peptide dissociation. These complexes could play an important role in additional fragmentation events later in time.

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