19th International Mass Spectrometry Conference

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Oral Session

Thursday, 20th September

Room A

09:00 – 11:00

Session 32: Formation and Dissociation of Peptide Radical Ions

Chair: Dominic T W Chan (The Chinese University of Hong Kong, Hong Kong SAR)

S32-1020

10:20 – 10:40

Ionization energy of gas phase proteins and its dependence on charge state and structure

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Keywords:
photon activation, tandem mass spectrometry, gas phase structure, EID, photoionization

Novel aspects:
We report for the first time the relationship between the ionization energy of a protein and its charge state and structure.

Abstract:
Mass spectrometry (MS) offers the unique ability to manipulate ions in the gas phase. In particular, the potential of mass spectrometry to perform mass-selected spectroscopy on biomolecules isolated in the gas phase is very appreciable. First, electrospray ionization is a unique method to bring into the gas phase large and fragile biological species intact. Furthermore, MS is the only technique to provide additional control on the charge state of the targeted molecule. Indeed, Hirsch et al. [1] have reported spectroscopic studies on mass selected clusters of ions, while Thissen et al. [2] took profit from the storage of the ions to produce relaxed targets in their electronic ground states We report on a systemic study of the dependence of the ionization energy as a function of the protein charge states for cytochrome C, bovine pancreatic trypsin inhibitor (BPTI) and ubiquitin.

A linear ion trap (Thermo Scientific LTQ XL) has been coupled to an ultra-violet beam line at the SOLEIL synchrotron radiation facility [3] .Water acetonitrile solutions of 5 µM cytochrome C, BPTI and ubiquitin were electrosprayed at 3 µL/min. Each charge state has been selected and submitted to 100 ms irradiation between 8 and 16 eV photon energy. At each photon energy, the abundance of the photoionization product has been measured and normalized to the total ionic current and to the photon flux. From these ion yields, the ionization energy threshold has been determined.

The ionization energies for cytochrome C, BPTI and ubiquitin have been measured for charge states ranging from 4 to 15, 4 to 8 and 4 to 9, respectively. For BPTI a linear dependency of the ionization energy with the charge state is observed. This result is in line with the outcome of previous work, in which the ionization energy of peptide smaller than 3.5 kDa had been measured by electron impact [4] . The linear dependence of the ionization energies with the charge state was interpreted as the result of the increase of the attractive Coulomb potential of the ion. For ubiquitin and cytochrome C, this model is not adequate anymore, since the dependency ceased to be monotonic and he IEs appeared to plateau for particular range of charge states. The correspondence between these features in the IE vs charge state appear similar to those observed in the collision cross section obtained from ion mobility experiments.
Our molecular dynamic simulation supports this interpretation. The ionization energy of protein is thus dependent on the gas phase conformation. We propose a model which links the ionization energy, the charge state and the radius of gyration of the protein.

[1] K. Hirsch et al. J. Phys. B 42,154029 (2009)
[2] R.Thissen et al. Phys. Rev. Lett. 100,223001 (2008)
[3] A.R. Milosavljevic et al. J. Synchrotron Rad., 19, 174 (2012) .
[4] B.A. Budnik et al. J Mass Spectrom 37, 1141 (2002) .