

Electron Photodetachment of Peptides and Protein Polyanions. Fundamental and Analytical Aspects

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We have recently shown that UV excitation of polypeptides and DNA polyanions induces a resonant electronic excitation of the ions followed by an efficient electron detachment. The electron detachment yield can then be used to monitor the excited electronic spectrum of the precursor ions. The spectra show bathochromic shifts and provide a direct determination of the ionization state of the chromophores in gas phase peptides or proteins.

Electron loss upon UV irradiation leads to the formation of radical biomolecular ions. Action spectroscopy in ion traps also allows to probe optical properties of radical ions in particular tryptophan radicals.

In parallel, photoelectron spectroscopy measurements will be presented. Adiabatic electron affinities (AEA) and Coulomb interaction energies were measured for these different charge states of cytochrome C from their photoelectron spectra. Comparison of experimental results with simulations shows a structural transition from a folded to an unfolded conformational state of the protein as the number of charges increases.

From analytical point of view, photogenerated radical species can be further fragmented by CID and give rise to new fragmentation pathways, and are interesting for analytical purposes, as recently shown for DNA oligomers and polypeptides.

Finally, we will present a new experimental approach, recently developed, aiming at characterizing megadalton molecular ions by mass spectrometry based method.

L. Joly, R. Antoine, A. R. Allouche, et al., *J. Am. Chem. Soc.* 129, 8428 (2007)

L. Joly, R. Antoine, A. R. Allouche and P. Dugourd, *J. Am. Chem. Soc.* 130, 13832 (2008)

K. Matheis, L. Joly, R. Antoine, et al., *J. Am. Chem. Soc.* 130, 15903-15906 (2008)

V. Gabellica, F. Rosu, T. Tabarin, et al., *J. Am. Chem. Soc.* 129, 4706 (2007)

V. Larraillet, R. Antoine, P. Dugourd, et al., *Anal. Chem.* 81, 8410 (2009).