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Gas phase activation and spectroscopy of mass and charge selected ions

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Gas phase spectroscopy offers the unique advantage of accessing intrinsic properties in the absence of solvent, and ultimately provides a mean to test theoretical methods. Biomolecules and large assemblies are fragile and difficult to place in the gas phase intact and studies are usually limited to building blocks and small oligomers. Modern ionization techniques, such as electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI) have demonstrated their potential to place large, complex and fragile assemblies intact in the gas phase. Direct absorption spectroscopy of ions is not trivial on such dilute matter. Action spectroscopy offers a mean to circumvent the difficulties of measuring the attenuation of photon beams through ion clouds. Hence, mass spectrometry-based action spectroscopy provides unprecedented control over the target, such as the ability to control the isotopic content and elemental composition, the charge, eventually the temperature, or the molecular shape in combination with ion mobility.
Action spectroscopy of polypeptides has been probed using synchrotron radiation in the VUV and soft X-ray ranges. The targets are produced by ESI, stored and irradiated in the photon energy range on interest in an ion trap [1]. The products of the irradiation are monitored by measuring the mass spectrum after photon excitation. This method is sensitive to any changes of the mass to charge ratio of the precursor ion of interest, thereby allowing photoionization, photodetachment and photofragmentation to be detected.
Through some applications to biomolecules we will illustrate the potential of the method for analytical and structural chemistry as well as for gaining information on the electronic structure and the photodynamic of the system.

Reference
[1] Milosavljević, A. R., Nicolas, C., Gil, J. F., Canon, F., Réfrégiers, M., Nahon, L., & Giuliani, A. VUV synchrotron radiation: A new activation technique for tandem mass spectrometry. Journal of Synchrotron Radiation, 19(2), 174–178 (2012)

Summary

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