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Activation and spectroscopy of mass and charge selected ions

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Gas phase spectroscopy provides unique advantages by allowing access to intrinsic properties of matter in the absence of solvents, making it an excellent means to test theoretical methods. However, this approach requires placing the sample in the gas phase, which can be challenging for large or fragile species such as biomolecules. Modern ionization techniques, such as electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI), have demonstrated potential for bringing large, complex, and fragile assemblies intact into the gas phase, albeit in ionic form (protonated or deprotonated). Confining ions is difficult, but ion trapping devices spatially confine the ions, though they remain highly dilute.
Direct absorption spectroscopy of dilute ionic targets is challenging. Action spectroscopy offers a means to circumvent this difficulty by observing the effects of photon absorption by mass spectrometry. Mass spectrometry-based action spectroscopy offers unprecedented control over the target, including the isotopic content, elemental composition, charge, temperature, and molecular shape/conformation, in combination with ion mobility. However, such experiments require highly brilliant photon sources found in accelerator-based facilities.
Action spectroscopy of bioorganic ions has been performed using synchrotron radiation at the SOLEIL facility in the VUV using the DESIRS beamline [1]. Targets are produced by ESI, stored, and irradiated in the photon energy range of interest in an ion trap [2]. The products of irradiation are monitored by measuring the mass spectrum after photon excitation, which is sensitive to changes in the mass-to-charge ratio of the product compared to the precursor ion of interest, allowing the study of photoionization, photodetachment, and photofragmentation dynamics.
We will illustrate the potential of this method for analytical and structural chemistry, as well as for gaining information on the electronic structure and VUV photodynamics of a broad array of biomolecular targets.

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Affiliation de l'auteur principal

Synchrotron SOLEIL

Auteur principal: GIULIANI, Alexandre (Synchrotron SOLEIL)

Co-auteur: NAHON, Laurent (Synchrotron SOLEIL)

Orateur: GIULIANI, Alexandre (Synchrotron SOLEIL)

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