

Ultraviolet photodissociation of protonated peptides and proteins can proceed with H/D scrambling.

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Streszczenie

Ultraviolet photodissociation (UVPD) has recently been introduced as an ion activation method for the determination of single-residue deuterium levels in H/D exchange tandem mass spectrometry experiments. In this regard, it is crucial to know which fragment ion types can be utilized for this purpose. UVPD yields rich product ion spectra where all possible backbone fragment ion types (*a/x*, *b/y*, and *c/z*) are typically observed. Here we provide a detailed investigation of the level of H/D scrambling for all fragment ion types upon UVPD of the peptide scrambling probe P1 (HHHHHHIIKIIK) using an Orbitrap tribrid mass spectrometer equipped with a solid-state 213 nm UV laser. The most abundant UVPD-generated fragment ions (i.e., *b/y* ions) exhibit extensive H/D scrambling. Similarly, *a/x* and *c/z* ions have also undergone H/D scrambling due to UV-induced heating of the precursor ion population. Therefore, dominant *b/y* ions upon UVPD of protonated peptides are a strong indicator for the occurrence of extensive H/D scrambling of the precursor ion population. In contrast to peptide P1, UV-irradiation of ubiquitin did not induce H/D scrambling in the nonfragmented precursor ion population. However, the UVPD-generated *b*₂ and *a*₄ ions from ubiquitin exhibit extensive H/D scrambling. To minimize H/D scrambling, short UV-irradiation time and high gas pressures are recommended.

Słowa kluczowe

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