ACTION IRMPD SPECTROSCOPY OF B_2 FRAGMENT IONS FROM QAXIG AND NAXIG PENTAPEPTIDES

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The N-terminal fragments of peptides in MS/MS studies, or b ions, have been the subject of controversy for many years. The result of amide bond cleavage, these ions can be generated by two main pathways, forming either a head-to-tail cyclic peptide or a 5-membered oxazolone ring structure. The b_2 ion is particularly interesting because the head-to-tail isomer, or diketopiperazine, is typically more stable than the oxazolone but requires a high energy trans-cis isomerization of the peptide bond in order to form. Although amino acid identity in the first two positions is known to influence diketopiperazine vs. oxazolone formation, the factors that influence diketopiperazine formations are still incompletely understood.

Action IRMPD (infrared multi-photon dissociation) spectroscopy was used to interrogate the gas-phase structures of the b_2 ions from QAXIG and NAXIG (X = L, D, or E) peptides. Irradiation of b_2 ions in the 1000 to 2000 cm^{-1} range interrogates the amide, amine, and carbonyl vibrational modes characteristic of diketopiperazine and oxazolone b_2 ions. Examination of the b_2 structures of QAXIG and NAXIG peptides by this strategy has yielded novel information regarding the formation pathway of the diketopiperazine structure in the gas phase. Peptides without a basic residue in one of the first two positions are shown to generate diketopiperazine b_2 ions, which suggests that a bridging side chain is critical for b_2 ion formation by this pathway. Moreover, the third residue is shown for the first time to play a role in discriminating between the oxazolone and diketopiperazine product ions.