

# MASS SPECTROMETRY

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## Unusual peptide fragment ions in low-energy CID process by charge-remote fragmentation pathways

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Several unusual peptide fragment ions including bn-44, cn and bn+H<sub>2</sub>O ions are initially observed in the MS/MS spectrum of a singly charged deuterohemine N-terminated peptide (DhHP-6, deuterohemine-βAHTVEK-NH<sub>2</sub>). A detailed investigation on formation pathways of these characteristic ions are performed by using high resolution mass determination, H/D exchange, isotope labeling and density functional theory (DFT). Results indicate that the production of these ions is related to the presence of threonine (Thr) residue in the peptide. Also the N-terminal fixed charge carried by deuterohemine group may play a critical role for the activation of the hydrogen connecting with carbon, and McLafferty-type rearrangement reactions are proposed as the potential mechanism for explaining the generation of the bn-CH<sub>3</sub>CHO and cn ions. In this study, we also propose a rearrangement fragmentation pathway for the production of bn+H<sub>2</sub>O ions from the Thr/Ser residue. In that case, the N→O acyl shift occurs to generate an ester intermediate which is the first and the most critical step, following that a further fragmentation of the ester isomer leads to the formation of bn+H<sub>2</sub>O ions. Detections of these diagnostic ions from the MS/MS spectra of sodiated Thr containing peptides further support the proposed charge-remote fragmentation pathways. Present work provides mechanism insights into the production of special ions, such as cn and bn+H<sub>2</sub>O ions, in the low energy collision-induced dissociation (CID) process.

### Biography

Xinhua Guo completed her PhD in 2004 at University of the Sciences, US. Currently, she is a Full Professor at College of Chemistry, Jilin University, China. Her research interests include "The development of various methods for structural studies and assemblies of DNA strands, new matrixes and materials for sensitive MALDI-MS analysis and studies of peptide fragmentation mechanism". She has published more than 30 scientific articles. She was a member of council of Chinese Mass Spectrometry Society (CMSS) from 2008-2016.

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