# Structure and Fragmentation Behavior of Metal-Cationized Phosphopeptides

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**Abstract:** In this study the metal-binding tendency and fragmentation patterns of phosphoserine and a series of model phosphopeptides was investigated. The goal was to elucidate the fragmentation patterns for the phosphopeptides, and whether the dissociation reactions are sensitive or dependent on the choice of cation. To gain a better picture of gas-phase conformation, infrared multiple photon dissociation (IRMPD) was used to determine the most probable structures for potassium and sodium-cationized phosphoserine. Structure assignment was made by comparing experimental IRMPD spectra to those predicted by density functional theory (DFT) calculations. ESI, tandem MS with CID was performed using a ThermoFinnigan LCQDeca quadrupole ion trap mass spectrometer with helium as the bath/collision gas. DFT calculations to support IRMPD experiments were performed at the B3LYP/6-311++G(3df,2pd) level of theory (scaled by a factor of 0.98) to generate probable conformations of potassium and sodium cationized phosphoserine. For CID studies, phosphoserine, alanine-phosphoserine-glycine, phosphoserine-valine-alanine-leucine, alaninephosphoserine-valine-leucine and leucine-alanine-phosphoserine-valine were examined. The metal cations used included lithium, sodium, potassium, calcium, zinc and silver. For the IMRPD study, several minima for K and Na-cationized phosphoserine were identified. The experimental IRMPD spectra for the Na and Kcationized phosphoserine were similar, exhibiting peak characteristic both of amino acids and phosphates. The best agreement between experimental and theoretical spectra is achieved by combining the absorptions predicted for the two lowest energy minima, both of which feature coordination of the metal cation by the carbonyl C=O and phosphate P=O groups and the C-O-P ester group.

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