

## AN INTERNAL AFFAIR: THE INFLUENCE OF INTRAMOLECULAR HYDROGEN BONDING ON THE STRUCTURE OF METAL-ION-PEPTIDE COMPLEXES

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Understanding the interplay of the various non-covalent interactions present in biomolecular systems is important as these are the driving forces of the structure of these systems. In the condensed phase, however, it is difficult to disentangle the individual contributions of these interactions due to the plethora of structures present, which ultimately limits any systematic studies. One popular way of bypassing this is to study relevant model complexes in the gas phase where these can be mass-isolated and spectroscopically interrogated. In this way, one can obtain an in-depth understanding of the competing non-covalent interactions on a molecular level and correlate structural changes systematically, for example by increasing the system size or changing interaction partners. Due to their structural flexibility, popular model systems for such studies are small amino acids or peptides and their complexes with water or metal ions. In this contribution, we will study the complexes of three alkali metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) with di- and tripeptides with cryogenic ion vibrational spectroscopy illustrating how the interaction strength changes with the size of the cation and peptide chain length by analyzing their OH, NH, and C=O stretching as well as NH bending vibrations. Of particular interest is the interplay of metal ion peptide interaction with internal  $\text{NH} \cdots \text{NH}_2$  hydrogen bonding of the neutral peptide itself, whose strength is modulated by the metal cation interaction.