

AN ELECTRIC AFFAIR: THE IMPACT OF SOLVATION ON THE STRUCTURE OF METAL ION-PEPTIDE COMPLEXES

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The impact of electric fields on the structure and function of biomolecules is a well-known, yet not well understood phenomenon. One prominent example are enzymes, where electrostatic preorganization around the active site is thought to be vital for their catalytic function. [1] To shed light on the unique catalytic ability of enzymes, we need a better understanding of the impact of such (local) electric fields. This requires a systematic study of the interplay of the various non-covalent interactions present in biomolecular systems such as electrostatic interactions as well as inter- and intramolecular hydrogen bonding. Due to the structural complexity, however, this is difficult to obtain from studies of the condensed phase. A popular approach is therefore to prepare model complexes in the gas phase, where the individual contributions of different types of interactions can be studied in much greater detail.

In this contribution, we will study the solvation of diglycine complexes with three alkali metal ions (Li^+ , Na^+ , K^+) with cryogenic ion vibrational spectroscopy scrutinising the interplay of the electrostatic metal ion-peptide and metal ion-water interaction with intra- and intermolecular hydrogen bonding. We observe interesting structural differences in the singly hydrated complexes, which can be related to the potassium selectivity of potassium ion channels. [2] In larger solvated clusters, the competition between intramolecular hydrogen bonding in the peptide backbone and intermolecular hydrogen bonding between water and the peptide increases in favour of the latter, leading to a change in peptide structure as the number of water molecules increases, whereas switching point occurs earlier for the Li^+ compared to the Na^+ and K^+ complexes. Differences in internal hydrogen bond strength between the complexes of the three metal ions decrease in the larger solvated clusters, which is important to consider for comparisons between environments where partial solvation dominates versus the bulk phase.

References: [1] N. G. Léonard, R. Dhaoui, T. Chantarojsiri, J. Y. Yang, *ACS Catal.* 2021, 11, 10923–10932. [2] Y. Suzuki, K. Hirata, J. M. Lisy, S. Ishiuchi, M. Fujii, *Phys. Chem. Chem. Phys.* 2022, 24, 20803–20812.