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CHEMISTRY AND BIOCHEMISTRY COLLOQUIUM

Pathways and Thermodynamics of Polyproline Helix Formation in Solution from Measurements of Ions in the Gas Phase

Abstract: It is well accepted that a measurement of an ion's mobility through an inert gas can be compared with calculated mobilities for trial geometries to obtain insight about the abundances and overall shapes of specific ions. In these studies, energy can be added to induce structural transitions and follow changes in the abundances of different conformations that are favored before and after activation. Here, we extend this idea as a means of following structural transitions in solution, examining the well-studied model systems: bradykinin and polyproline. Our approach is to vary the solution composition from which ions are electrosprayed. Overall, we conclude that in some cases it appears that the solution phase structures are more or less preserved in the gas phase; in other cases, new structures are favored in the gas phase –but, these can be mapped back in order to obtain insight about populations of states that were favored in solution. In the case of bradykinin, we find evidence for ~10 different solution phase states that vary in abundance as the solution composition is changed. These populations largely arise from variations in the cis- and trans-configurations of three proline residues in the nonapeptide sequence. The polyproline system provides a chance to study such transitions in detail. When in relatively non-polar solvents such as propanol, polyproline forms a compact type PPI helix; when placed in water the polymer undergoes a series of cis-trans interconversions to produce a type PPII helix, in which water molecules intercalate along the peptide backbone, stabilizing a much more extended structure in solution. We find that although the PPII helix collapses in the gas phase, IMS-MS techniques provide an ideal means of studying the step-by-step transitions that connect these different structures.

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