

Effect of microhydration on the conformational preferences of a capped dipeptide in the gas phase

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Studies on the structures and conformations of microsolvated peptides in the gas phase are scarce in the literature. This scarcity arises primarily from the difficulty of achieving sufficient cooling during jet expansion when laser desorption is used to vaporize peptides and generate microhydrated peptide clusters. In this work, we investigate the effect of microhydration on the secondary structure of a capped dipeptide, Boc-DPro-Gly-NHBn-OMe (Boc = tert-butyloxycarbonyl, Bn = benzyl), i.e., Pro-Gly (PG), in the presence of a single H₂O molecule using gas-phase laser spectroscopy combined with quantum chemical calculations. In the gas phase, the PG monomer adopts a C7–C7 conformation, whereas in the condensed phase, it assumes a β -turn structure.¹ IR–UV hole-burning spectroscopy of PG⋯(H₂O)₁ confirms the observation of a single conformer in the experiment. Both experimental and theoretical IR spectra demonstrate that the H₂O molecule is selectively inserted into the relatively weak C7 hydrogen bond (γ -turn) formed between the Pro C=O and NHBn N–H groups, while the other C7 hydrogen bond (γ -turn) between the Gly N–H and Boc C=O groups remains unaffected. Consequently, the single H₂O molecule in the PG⋯(H₂O)₁ complex significantly distorts the peptide backbone without appreciable alteration of the overall secondary structural motif (γ – γ) of the isolated PG monomer.² This study of the monohydrated peptide suggests that multiple water molecules may be required to switch the secondary structure of PG from the double γ -turn to the β -turn conformation that is favored in the condensed phase. Future work is in progress to study the conformations of PG with a larger number of water molecules.

References

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