Relating vibrational spectra and conformational structures of small model peptides: From gas phase to microclusters

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Biopolymers such as peptides and proteins are known to exist in a huge number of conformational structures for a given sequence of amino acid residues. In addition to our insufficient knowledge of molecular interaction, a microscopic understanding for the driving force of biomolecular conformations is further hampered by the coexistence of intra- and intermolecular forces: In particular, we often do not know whether a certain spatial structure is an intrinsic property of the biopolymer itself or whether it is mainly stabilized by the presence of solvents.

In recent years, the advent of gas phase experiments of small peptides with a controllable number of attached solvent molecules opens the way to separate inter- from intra-molecular effects on biomolecular conformations. Under favorable circumstances, UV/IR double resonance techniques can be used to measure vibrational spectra for individual conformations of a peptide with fixed number of solvent molecules. By comparison with simulated spectra, molecular conformers can be assigned to the experimental spectra. Repeating this procedure for an increasing number of solvent molecules, the evolution of molecular conformation from the gas phase toward the gaseous solution can be monitored.

In our present work, the tripeptide Z-Aib-Pro-NHMe is chosen as a model system. In a first step, quantum-chemical DFT and MP2 methods have been used to locate a large number of minimum energy structures exhibiting different H-bonding patterns. Alternatively, trajectories based on empirical force fields are used to extract information on molecular conformations. Second, vibrational spectra are calculated for all conformers to set up a structure-spectrum relation by carefully analyzing the effects of all possible H-bonding sites on various parts of the infrared spectrum. Comparison with experiments carried out in project B7 reveals competing β and γ turn structures, depending on the details of microsolvation environment.

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