SECONDARY STRUCTURES OF SHORT PEPTIDE CHAINS IN THE GAS PHASE AS REVEALED BY IR/UV DOUBLE RESONANCE SPECTROSCOPY

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The flexibility of peptide chains and their sensitivity to environment are key properties for the biological function of these molecules. Chemically protected peptides are short chains mimicking protein segments and are therefore suitable models, whose complicated conformational landscape have been studied so far only theoretically. The coupling of a laser-desorption device to a supersonic expansion provides a unique opportunity to perform a cooling-assisted folding of these peptides in the gas phase and then to characterise by IR-UV double resonance spectroscopy the H-bonding network of their most stable conformations.

A bottom-up approach, based on the investigation of species of increasing size, has allowed us to characterize the local conformational preferences of these species and to address the issue of the emergence of secondary structures. In particular, with the help of quantum chemistry energetic and IR calculations, gas phase IR signatures in the amide A region (NH stretches around 3μm) of the C5, C7 and C10 interactions between NH and CO groups along the chain have been determined. These are responsible for the β-strand, γ-turn[a] and β-turn[b] secondary structures of proteins, respectively.

Two main issues will be discussed:

- The spontaneous formation under environment-free conditions of the secondary structures of proteins (in particular β- and γ-turns), which are therefore intrinsic folding properties of these biomolecules.
- The extreme sensitivity of the nature of the most stable conformations to the presence of backbone/side-chain or side-chain/side-chain interactions.

[a] W. Chin, M. Mons, J.-P. Dognon, F. Piuzzi, B. Tardivel and I. Dimicoli, *Phys. Chem. Chem. Phys.* **6**, 2700 (2004).
[b] W. Chin, J.-P. Dognon, F. Piuzzi, B. Tardivel, I. Dimicoli and M. Mons, *J. Am. Chem. Soc.* **127**, 707 (2005).