

IR/UV investigations on hydrated and aluminum containing peptides

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Secondary structures play an important role to explain the function of proteins and the interplay with metal ions is of high interest to obtain information on e.g. ion transport or induction of diseases. To investigate the interactions of proteins with metal ions and water molecules on a molecular level the analysis of isolated model systems in a molecular beam experiment is an ideal starting point. The influence of water or metal ions on secondary structures of isolated peptides is analyzed by mass selective IR or IR/UV spectroscopy.

In order to figure out different binding motifs in metal/peptide clusters the attachment of Al^+ and Al^{3+} cations to the backbone of different protected amino acids and dipeptide models is investigated by means of mass selective IR photodissociation spectroscopy. In case of clusters with very strong bonds between the aluminum cation and a peptide containing an aromatic chromophore a combined IR/UV technique is applied in order to yield the vibrational spectra in the NH stretching region. The comparison with extensive ab initio and DFT calculations lead to suggestions for structural arrangements. The aluminum cations are attached to the carbonyl groups and lead to strong changes of the backbone conformation. The structures are discussed with respect to their stability, spin state and the influence of the aromatic chromophore.

Furthermore the influence of a successive back-bone hydration is investigated by attaching one to three water molecules to the backbone of the neutral protected amino acid Ac-Phe-OMe. The structures of the resulting species are investigated by the mass- and isomer selective IR/Resonant 2-photon ionisation technique which is applied in the region of the OH and NH stretching vibrations as well as in the region of the amide I and II modes. Two isomers are observed both for the mono- and dihydrated cluster. For all isomers the β_L backbone conformation of the monomer is almost conserved. In case of the trihydrated cluster only one isomer is obtained with a strong change of the backbone conformation compared to the monomer. This change is driven by the possibility to form a hydrogen-bonded network (a first solvation shell) including all water molecules as well as the CO and NH groups of the backbone.