

INVESTIGATING ELECTRONIC AND STRUCTURAL CHANGES IMPOSED BY ZWITTERIONIC PAIRING IN MODEL PEPTIDE SYSTEMS USING IR-UV-IR TRIPLE RESONANCE SPECTROSCOPY

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Strong electrostatic interactions such as zwitterionic pairing between oppositely charged amino acids are common in the condensed phase at neutral pH and can play a large role in determining the conformational landscape of peptides and proteins. Whether such interactions are possible in the absence of solvent however, has been previously debated. Growing experimental evidence suggests that these interactions are indeed possible in isolated gas phase ions and may give rise to unique fragmentation upon UV irradiation. In this study we use a series IR-UV-IR triple resonance techniques performed at 10 K to investigate the influences of these electrostatic interactions on the electronic and structural properties of model YGRXR (X = gly, asp) pentapeptide systems and their methyl ester counterparts. The initial electronic spectra, under single UV photon conditions, of model systems which may possess zwitterionic pairing hardly show discrete electronic transitions, rather a broad absorption which mainly gives rise to tyrosine side chain cleavage is observed. Upon methylation of the carboxylate functional groups, which prevents zwitterionic interactions, the cold action spectra become well resolved such that sharp electronic transitions due to the $\pi\pi^*$ transition of the tyrosine aromatic ring are observed. Using an UV-IR double resonance scheme it is possible to enhance the tyrosine side chain cleavage after an initial UV excitation, provided that the IR laser is fixed on a vibrational. Under these conditions the Franck Condon progressions for the non-methyl esterified systems become clearly observable. These initial results suggest that local excitation of the chromophore may couple to the autoionizing state responsible for electron detachment, similar to the mechanism postulated for photoinduced electron detachment from gas phase anions. Using IR-UV-IR triple resonance, conformer specific IR spectra can be taken for zwitterionic systems despite the large "off-resonance" absorption. A comparison of the IR spectra reveal that the +1 charge states are more prone to form zwitterionic interactions than the +2. Harmonic-level vibrational frequency calculations will be performed on candidate structures and compared to experimental spectra such that the influences of zwitterionic ionic pairing on the 3-dimensional structure can be directly compared to conformations without such pairings.