

## THE ROLE OF TYROSINE IN STABILIZING GAS PHASE ZWITTERIONIC CONFIGURATIONS OF PEPTIDE IONS REVEALED BY IR-UV DOUBLE RESONANCE SPECTROSCOPY

CHRISTOPHER P HARRILAL, *Department of Chemistry, Purdue University, West Lafayette, IN, USA*; ANTHONY PITTS-MCCOY, *Chemistry, Purdue University, West Lafayette, IN, USA*; SCOTT A McLUCKEY, TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN, USA*.

Growing experimental evidence suggests that zwitterionic structures are more prevalent in isolated gas phase environments than previously thought. These strong electrostatic interactions can govern the conformational landscape, alter fragmentation pathways, and promote unique chemistry upon UV irradiation. It is therefore crucial to develop methods that specifically probe for zwitterionic interactions and provide a deeper understanding of the structural factors which promote their stability. In this study we probe a series of arginine containing peptides cooled to 10 K using IR-UV double resonance spectroscopy. The main peptide sequences interrogated were YGRAR and FGRAR. Using the IR signatures of the hydride stretch as well as in the amide I/II regions it was possible to identify conformers which were zwitterionic. IR signatures reveal that YGRAR mainly adopts a zwitterionic configuration. The assigned structure for singly protonated YGRAR shows that the tyrosine OH and the middle protonated arginine residue work in tandem to solvate the carboxylate anion, while the C-terminal arginine plays a seemingly minor role in stabilizing the structure. As a consequence of the tyrosine OH engaging in a strong hydrogen bond with a highly basic site, the electronic origin transition of the zwitterionic species is shifted by  $400\text{ cm}^{-1}$  to lower energy compared to non-zwitterionic structures. The magnitude of this shift is somewhat lessened by the C-terminal protonated arginine which acts as a hydrogen bond donor to the tyrosine hydroxyl oxygen. A further consequence of this hydrogen bond is the presence of an underlying broad component to the UV spectrum. It is postulated that this broad absorption is caused by an excited state hydrogen transfer between the tyrosine chromophore and carboxylate group. Similar UV induced reactions have been observed in neutral clusters of phenol and ammonia. The importance of the hydrogen bond between the carboxylate and tyrosine OH is showcased by FGRAR, which does not form a zwitterion. These results show that neutral sidechains can play a large role in promoting zwitterionic structure in addition to the presence of highly basic residues.