

**GAS PHASE CHEMISTRY OF 2-OXO-HISTIDINE AND ITS DERIVATIVES**

Adrian Lam,<sup>1,2</sup> Francis Separovic<sup>1,2</sup> and Richard A. J. O'Hair<sup>1,2</sup>

<sup>1</sup>*School of Chemistry, University of Melbourne, Victoria 3010, Australia,* <sup>2</sup>*Bio21 Institute of Molecular Science and Biotechnology, University of Melbourne, Victoria 3010, Australia*

Post translational modification, which includes methylation, alkylation and oxidation can extend functionality of proteins, peptides and amino acids, resulting in a double edged sword: whilst some modifications may be beneficial as in the case of protein activation/deactivation via phosphorylation, others may yield less desirable attributes. One of these may be the oxidation of histidine, which can result in formation of 2-oxo-histidine. Despite its association with His-His crosslinking, there have been few studies on its gas phase chemistry.

Previous work in our group has examined the sites of fragmentation of protonated tryptophan and its oxidised derivatives<sup>3</sup> and more recently the proton affinities of methionine, methionine sulfoxide, including the effects of N- and C- terminal derivatives<sup>4</sup>. Building upon this, we report on the fragmentation reactions of protonated 2-oxo-histidine and the proton affinities and relative stabilities of the neutral and protonated species of 2-oxo-Histidine, using a combination of mass spectrometry and molecular orbital calculations at the MP2/6-31G(d,p)//B3LYP/6-31G(d,p) level of theory. In addition, the gas phase chemistry of N- and C- terminal derivatives of 2-oxo-histidine will also be discussed.

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<sup>3</sup>H. Lioe; R. A. J. O'Hair; G. E. Reid, *Journal of the American Society for Mass Spectrometry* (2004), 15(1), 65-76.

<sup>4</sup>H. Lioe; R. A. J. O'Hair; S. Gronert; A. Austin; G. E. Reid, Submitted to *Int. J. Mass Spectrom.*