Analysis of the Fragmentation of Collision Induced Dissociation of Negatively Charged Dipeptides.

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Mass spectrometry (MS) is a very useful analytical tool that exploits the response of charged particles with distinct mass-to-charge ratio to electromagnetic fields to determine their molecular composition. There are many different types of MS, particularly negative electrospray ion tandem MS which was developed by Bowie *et al* [1] (Bowie, Brinkworth et al. 2002). In negative electrospray ion tandem MS, multiple quadrupoles are used to select the desired ion, causing it to undergo fragmentation, then using collision-induced fragmentation to get results. Collision-induced fragmentation results in a fragmentation of the ion through collision of the parent molecular ion through a controlled concentration of a non-reactive gas, such as argon. We investigated a proposed fragmentation mechanism for the fragmentations of two dipeptides -- glycine-serine (GLY-SER) and alanine-glycine (ALA-SER) -- as they undergo collision induced dissociation (CID) at different collision energies and gas densities.

Using HF/6-31G*//AM1 and MP2/6-31+G*//B3LYP/6-31+G* computational methods, we analyzed the dipeptide in an attempt to verify the mechanism provided by Professor Swan. Our high-level methods like MP2/6-31+G*//B3LYP/6-31+G* suggest that seemingly simple proton transfer steps proceed through multiple transition states requiring a significant reorientation whereas simpler methods like HF/6-31G*//AM1 allow for simpler proton transfers. This is also analogous for the loss of water which also occurs in a multistep transition state researched by Kanawati et al. Interestingly, comparing our results between the AM1 level of theory, used by Bowie et al, and the MP2 level of theory, AM1 seemed to be give different results of the same fragment.

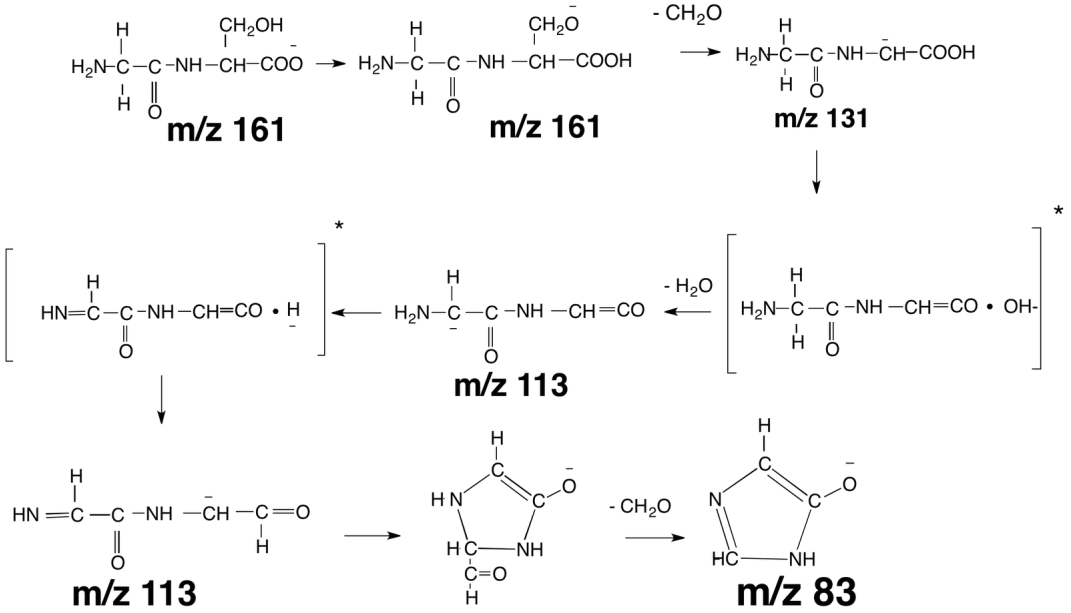

Figure 1. Proposed fragmentation mechanism for the Gly-Ser system

[1]Bowie, J. H., C. S. Brinkworth, et al. (2002). Mass Spectrometry Reviews **21**(2): 87-107.