Slow ion interaction with N-methylglycine and N-acetylglycine

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Slow ion interaction with N-methylglycine and N-acetylglycine

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Synopsis N-acetyl glycine and N-methyl glycine molecules in the gas phase are ionized by electron exchange with slow O^{6+} ions at an energy of 48 keV. After ionization, the methyl and acetyl substituted glycines dissociate into fragments analogous to that resulting from ionization and fragmentation of amino acids and peptides, respectively. N-acetylglycine which contains a peptide bond also effectively tautomerizes to the diol form. Such tautomerization is typical for amino acids, however, we show that the tautomerization mechanism of the N-acetylglycine is different.

We studied two N- substituted amino acids N-methylglycine and N-acetylglycine by means of the COLIMACON [1] experimental setup based at the ARIBE facility of the GANIL accelerator (Caen, France). The molecules were ionized in collisions with slow 48 keV O^{6+} ions. The ionization products were analyzed by coincidence mass spectrometry. The studied molecules together with the glycine molecule are sketched in Fig. 1. The figure demonstrates also the main differences observed in the present study.

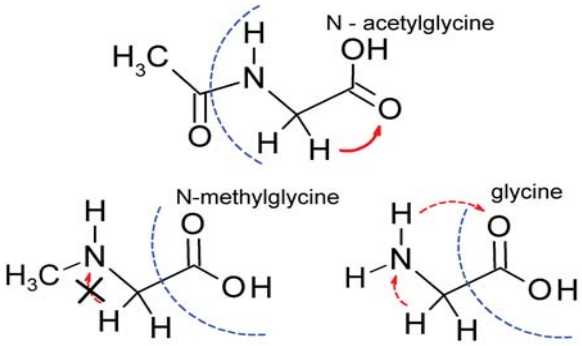

Figure 1. Fragmentation (blue) and tautomerization (red) of the studied N substituted glycine molecules in comparison with the glycine [2].

In the case of N-methylglycine, single ionization results in charge localization on the nitrogen atom and the molecule primarily decomposes by neutral carboxyl group loss in the process analogous to that of glycine molecule [2]. In the case of N-acetylglycine, charge delocalizes on the peptide bond. Therefore, fragmentation via COOH loss competes with the peptide bond dissociation and the acetyl cation dominates the mass specrum.

For N-acetylglycine molecule, we detect metastable parent ions which dissociate exclusively by neutral water release. Quantum chemical calculations indicate that the stabilization of the parent ion occurs via tautomerization to the diol form. Due to the charge delocalization within the molecule, the barrier towards direct hydrogen transfer between C_α and the carboxyl group lowers and direct hydrogen transfer becomes possible.

We show that the substitution which mimics the peptide bond significantly changes the behavior of the ion. The main difference lies in the charge distribution which is delocalized over the whole peptide bond in contrast to localization on the nitrogen atom which is typical for amino acids. We show also that the reactions typical for amino acids can be caused by different mechanism in peptide bonded systems.

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References

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