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Formation and elongation of polyglycine via unimolecular reaction in the gas phase

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Peptide chains of amino acids play a crucial role in the emergence of living organisms. Understanding the growth of peptide chains under abiotic conditions is an important question, especially considering the increasing amount of complex molecules detected in various astrophysical environments [1]. Gas-phase collisions between isolated molecules or cosmic ray-induced reactions in seeded ice and dust grains are presently the main pathways considered for polymer synthesis under astrophysical conditions. Within these two routes of polymerization, the possible role of protonated dimers existing in the gas phase remains undocumented. Recently, we found that the growth of peptide chains can occur under gas-phase conditions via a dehydration reaction in a protonated molecular amino-acid dimer ion [2]. The proton not only induces dipeptide formation but also contributes to further elongating the peptide chain. Combining experimental results and quantum chemistry calculations, we show that polymerization reaction leading to the peptide of glycine (diglycine) is taking place after excitation of a protonated glycine dimer in a single high velocity collision, and we provide evidence the further growth of the peptide chain. The formation of a protonated mixed dimer consisting of a diglycine and a glycine molecule is dominant and its further excitation can lead to the formation of a tripeptide. The various relaxation pathways of the excited protonated dimers and the unimolecular reaction dynamics is investigated by velocity measurements of the water molecules eliminated in the polymerization reactions (Figure 1). Peptide chain growth is thus demonstrated to occur via a unimolecular gas-phase reaction in an excited cluster ion without extra substrate such as dust or ice. The proton facilitates the dehydration reaction in a pure molecular dimer and chaperons the further growth of the peptide-chain via further dehydration reactions in mixed dimer and cluster ions. These results obtained with glycine, the most abundant amino acid detected in extraterrestrial objects, shows that the detected intra-dimer dehydration reaction could be a conceivable abiotic pathway towards the possible existence of peptide chains in Space.

[1] Pearce, B.et al. (2017) *Proc. Natl. Acad. Sci. U.S.A.* 114, 11327–11332.

[2] D. Comte, et al. (2023) *J. Phys. Chem. A* 127, 775–780.

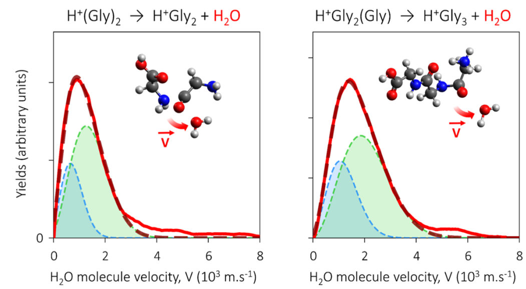

Figure 1: Measured velocity distribution (red solid line) of the water molecule eliminated by the pure or mixed protonated glycine dimer (8 keV), after a collision with an argon atom. The fit of the experimental distribution (red dashed line) consists of two Maxwell-Boltzmann distributions (blue and green dashed lines).