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Insights in the fragmentation of biomolecules by PEPICO and time-resolved experiments

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The knowledge of the aminoacids and peptide structure and reactivity is crucial to understand the role of transient species involved in protein radical catalysis as well as the effects of oxidative damage in proteins. To the purpose the combination of "static"techniques like the spectroscopic ones performed with synchrotron radiation and "time-resolved"ones, like ultrafast pump-probe experiments, is needed. In this work we show how this combination can provide deep insights in glycine fragmentation. Glycine (NH2CH2COOH) is the simplest amino acid, with a single hydrogen atom as side chain attached to the α-carbon and it is often used as a prototype for several physical processes occurring in more complex amino acids.
Photoelectron-photoion coincidence, PEPICO, experiments have been used to characterize the fate of the glycine cation following its interaction with UV photons and an ultrafast pump-probe experiment has been done to investigate the intra-molecular H migration. The PEPICO experiments have been performed at the GAPH beamline at Elettra (Trieste, Italy), while the ultrafast XUV pump-NIR probe experiments have been done at the Department of Physics, Politecnico Milano (Milan, Italy).
In Fig. 1 (left panel) [1] the photoelectron spectrum and the PEPICO yields of the two main fragments, H2NCH2+ (m/z 30) and COOH+ (m/z 45), are shown. Glycine fragments at its ionization threshold, with the charge localized on the H2NCH2+ moiety, due to ionization of the N lone pair of the HOMO. The formation of the complementary cation COOH+ needs 3 eV more. The flexibility with respect to rotation about the C-C, C-N and C-O bonds makes glycine existing in the gas phase in several conformers. Ionization can lead to stabilization of some conformations, rearrangements and, last but not the least, H migration between the two moieties. The sensitivity of PEPICO to pin point the latter process, despite its very low intensity, is shown in Fig. 1, where the C(OH)2+ ion (m/z 46), due to H migration to form the diol conformer, is observed in a well-defined binding energy range. The dynamics of the H migration has been investigated by measuring the yields of m/z 45 and 46 fragments versus the delay between a XUV pump and a NIR probe pulse [2]. The fits to the ion yields (see Fig.1 right panel) resulted in a decay time τ_decay= 49.5 ± 2.7 fs and a rise time τ_rise= 47.9 ±1.7 fs, respectively.

Images are in the material section of the talk.

Acknowledgment
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References

[1] Jacopo Chiarinelli et al., Insights in the fragmentation of glycine by PEPICO experiments, Phys. Chem. Chem. Phys. 20, 22841 (2018).
[2] Mattea C. Castrovilli et al., Ultrafast hydrogen migration in photoionized glycine, J. Phys. Chem. Lett. 9, 6012 (2018).

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