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Mapping the electronic transitions of protonation sites in peptides using soft X-ray radiation

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Proton transfer is a fundamental charge transfer process in Chemistry, and it is particularly important for biological molecules, since they usually contain basic groups. Therefore, in order to study charge dynamics in isolated biomolecules, it is crucial to determine the initial location of protons. Although it is now well established that protonation occurs primarily at nitrogen atoms of the most basic side chains (arginine, histidine, lysine) of protonated peptides, in the absence of such group or in the case of multi-fold protonated species, the N-terminus and the peptide backbone oxygens can compete for the proton(s). IR multiphoton dissociation (IRMPD) has been extensively used for the determination of protonation sites but also geometrical structure of biomolecules in the gas phase [1]. However, the fragmentation yield falls rapidly with the number of atoms in the molecule, since IRMPD is a statistical process. Thus, there is a need for other methods able to determine the protonation sites of large systems.

In this context, near-edge X-ray absorption mass spectrometry (NEXAMS) is a promising technique as it provides a local probe into the atomic environment. NEXAMS is based on the electronic excitations of core electrons to unoccupied molecular orbitals and thus captures the electronic and geometric structure of a system under investigation. For instance, through photoabsorption around the nitrogen K-edge, it is possible to distinguish between the secondary and primary amine groups of proline and glycine, respectively.[2] In order to map the electronic transitions of the different protonation sites in peptides, we studied, experimentally and theoretically, the following tailored glycine-based peptides: G4X where X is the basic residue Arginine, Histidine or Lysine (i.e. the singly-protonated peptides contain a protonated side chain and a non-protonated N-terminus), PG4 where P stands for Proline, G5 (protonation on N-terminus), and G3 (controversial protonation site)[3],[4].
The NEXAMS experiments have been carried out at the P04 soft X-ray beamline of the PETRA III synchrotron (DESY, Hamburg, Germany) using our home-built tandem mass spectrometer and at the UE52_PGM Ion trap endstation of the BESSY II synchrotron (HZB, Berlin, Germany). The analysis was supported by calculations of the electronic transitions of the most stable conformers obtained with a REMD (Replica Exchange Molecular Dynamics) method. Results obtained on the custom-made peptides at the nitrogen K-edge will be presented.

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