

**Helical secondary structure and vibrations of polyalanine peptides
Ac-Ala_n-LysH⁺ (*n*=5,10,15) *in vacuo***

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The native structure of peptides and proteins involves the presence of a solvent, but studies *in vacuo* offer a unique “clean-room” condition to separate and quantify the intramolecular interactions that are critical to stabilize secondary structure. We here unravel the structure of LysineH⁺ capped polyalanine peptides Ac-Ala_n-LysH⁺ (*n*=5, 10, 15), by combining experimental multi-photon IR spectra obtained using the FELIX free-electron laser at room-temperature with all-electron density-functional theory (DFT) in the generalized gradient approximation and van der Waals corrections (GGA+vdW) in the FHI-aims code [1]. For these molecules, earlier ion mobility studies indicate helical secondary structure [2], which we here demonstrate quantitatively. We use a force field (OPLS) to screen roughly the conformational energetics of as many structure candidates as possible (>10⁴ in practice), following up with GGA+vdW for a wide range of low-energy conformers. For *n*=5, we find a close energetic competition between α - and 3_{10} -like conformers. We show how the LysH⁺ termination induces helices also for longer peptides, and that the inclusion of vdW contributions is critical to decide the detailed energy hierarchy. We also show how the vibrational modes develop with helix length (*n*=10, 15), and discuss the question of systematic frequency deviations between experiment and DFT, including the role of anharmonic contributions through extensive *ab initio* molecular dynamics simulations.

[1] V. Blum *et al*, *Comp. Phys. Comm.*(2008), accepted.

[2] M. Kohtani *et al.*, *JACS* **120**, 12975 (1998).