Determining the structure of Ac-Ala$_n$LysH$^+$ *in vacuo*: computational spectroscopy using DFT MARIANA ROSSI, VOLKER BLUM, PETER KUPSER, GERT VON HELDEN, FRAUKE BIERAU, GERARD MEIJER, MATTHIAS SCHEFFLER — Well defined secondary structure motifs (e.g., helices) in polypeptides can be systematically studied *in vacuo*, offering a unique "clean room" condition to quantify the stabilizing intramolecular interactions. Here we address theoretically the structure of alanine polypeptides Ac-Ala$_n$-LysH$^+$ (n=5,10,15), for which gas-phase helical structure was indicated in experiment [1]. Using van der Waals (vdW) corrected [2] Density Functional Theory (DFT), we present vibrational spectra and compare to room temperature multiple photon IR spectroscopy data obtained at the FELIX free electron laser. For the longer molecules (n=10,15) α-helical models provide good qualitative agreement (theory vs. experiment) already in the harmonic approximation. For Ac-Ala$_5$LysH$^+$, the predicted lowest energy conformer ("g-1") in vdW corrected DFT (PBE, B3LYP, revPBE) is not a simple helix. However, the harmonic free energy suggests that g-1 and the lowest-energy α-helical conformers are energetically close at 300 K, and thus might all coexist in experiment. Consistently, their calculated vibrational spectra agree with experiment, but only if anharmonic effects are included by explicit molecular dynamics simulations. [1] R. Hudgins *et al.*, JACS **120**, 12974 (1998) [2] A. Tkatchenko, M. Scheffler, PRL **102**, 073005 (2009)

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