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Helical secondary structure of polyalanine peptides in vacuo: Ac-Ala$_n$-LysH$^+$ (n=5,10,15), experiment and theory MARIANA ROSSI, VOLKER BLUM, PETER KUPSER, GERT VON HELDEN, FRAUKE BIERAU, GERARD MEIJER, MATTHIAS SCHEFFLER, Fritz Haber Institute, D-14195 Berlin, Germany — The presence of a solvent is often viewed as indispensable to explain the structure of peptides and proteins. However, well defined *secondary* structure motifs (helices, sheets, ...) also exist *in vacuo*, offering a unique "clean room" condition to quantify the stabilizing interactions. 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 van der Waals-corrected all-electron density-functional theory (DFT) in the generalized gradient approximation in the FHI-aims code [1]. Earlier ion mobility studies of these molecules indicate helical structure [2], which we here demonstrate quantitatively. For n=5, we find a close energetic competition of different helix motifs (α, 3_{10}), with similar and good agreement between measured and calculated vibrational spectra. We show how the LysH$^+$ termination acts to induce helices also for longer peptides, and how vibrational modes develop with helix length (n=10,15), yielding, e.g., a softening of collective modes towards the infinite helix limit. [1] V. Blum *et al*, Comp. Phys. Comm. (2008), accepted. [2] M. Kohtani *et al.*, JACS 120, 12975 (1998).

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