Combining first principles and replica exchange for the structure of two large peptides: Ac-Ala\textsubscript{19}-LysH\textsuperscript{+} vs. Ac-LysH\textsuperscript{+}-Ala\textsubscript{19}\textsuperscript{↓} FRANZISKA SCHUBERT, MARIANA ROSSI, CARSTEN BALDAUF, VOLKER BLUM, MATTHIAS SCHEFFLER, Fritz-Haber-Institut der MPG, D-14195 Berlin — Predicting the structure of peptides requires a high accuracy for “weak” interactions. We here focus on the predominant structure types of two alanine-based peptides \textit{in vacuo} from first principles and in comparison to experimental IR spectroscopy\textsuperscript{1}: Ac-Ala\textsubscript{19}-LysH\textsuperscript{+}, which is expected to be $\alpha$-helical [1,2], and Ac-LysH\textsuperscript{+}-Ala\textsubscript{19}, where globular monomers, helical dimers, and helices with non-standard protonation sites are expected [2]. Despite supposedly very different conformers, Ac-LysH\textsuperscript{+}-Ala\textsubscript{19} and Ac-Ala\textsubscript{19}-LysH\textsuperscript{+} yield very similar experimental IR spectra in the $\approx$1000-2000 cm\textsuperscript{-1} wavenumber range. We utilize a two-stage structure search approach: we begin by a force-field based replica exchange molecular dynamics (REMD) scan followed by further REMD scans based on density functional theory with the van der Waals corrected [3] PBE functional. We suggest plausible candidates for all likely structure prototypes. Helix-turn-helix motifs emerge as the most likely candidates and explain a subtle peak shift in experiment. [1] M. Rossi \textit{et al.}, JPCL 1, 3465 (2010); [2] M. Jarrold, PCCP 9, 1659 (2007); [3] A. Tkatchenko, M. Scheffler, PRL 102, 073005 (2009).

\textsuperscript{1}IRMPD experiments: G. von Helden, P. Kupser, K. Pagel, F. Filsinger, G. Meijer, Department of Molecular Physics, Fritz-Haber-Institut der MPG, D-14195 Berlin