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Stabilization of peptide helices by length and vibrational free energies: ***Ab initio*** **case study of polyalanine** MARIANA ROSSI, VOLKER BLUM, MATTHIAS SCHEFFLER, Fritz-Haber-Institut der MPG, Berlin — Helices are one of the most abundant secondary structure "building blocks" of polypeptides and proteins. Here, we explore helix stabilization as a function of peptide length and temperature [harmonic approximation to the vibrational free energy (FE)], for the alanine-based peptide, Ac-Ala$_n$-LysH$^+$ n=4-15, in the gas phase. For n=4-8, we predict the lowest energy structures in density-functional theory, using the van der Waals (vdW) corrected[1] PBE exchange-correlation potential. α-helices become the lowest energy structures at $n \approx$7-8 on the potential energy surface, but only barely and if including vdW interactions. At finite temperatures, the helices are further stabilized over compact conformers. While the vibrational entropy is the leading stabilizing term at 300 K, also the zero-point-energies favor the helical structures. For $n \geq$8, the α-helix should be the only accessible conformer in the FE surface at 300 K, in agreement with experiment[2] and with our own comparison[3] of calculated *ab initio* anharmonic IR spectra to experimental IR multiple photon dissociation data for n=5, 10, and 15. [1] Tkatchenko and Scheffler, PRL 102, 073055 (2009); [2] Kohtani and Jarrold, JACS 108, 8454 (2004); [3] Rossi et al., JPCL 1, 3465 (2010).

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