SUPPLEMENTARY MATERIAL FOR MANUSCRIPT: Secondary Structure of Ac-Ala$_n$-LysH$^+$ Polyalanine Peptides (n=5,10,15) in Vacuo: Helical or Not?

Detailed development of the H-bond network of Ac-Ala$_{15}$-LysH$^+$ during our AIMD simulation.

In this supplementary material, we illustrate how the H-bond network of Ac-Ala$_{15}$-LysH$^+$ evolves through the *ab initio* NVE molecular dynamics simulation (Density Functional Theory, PBE exchange-correlation potential with van der Waals corrections[1], using the FHI-aims code package[2]) used to compute the anharmonic IR spectrum shown in Figure 1(c) of our manuscript. What is shown in Figure 1(a) is the H-bond connection for each oxygen of the molecule starting from the Ac termination (O(Ac)) and finishing at the Lysine termination against the time of simulation. We consider a H-bond every (C-)O - NH pair that is closer than 2.5Å, which is a conservative definition, in the sense that e.g. a 3_{10} bond might be counted even though not really there, but for us it is more important that we don't miss any possible bond. Each color represents a different kind of H-bond, labeled on the figure, and the respective ratios of each type computed for the whole trajectory are shown on the right of the plot. These ratios can exceed 100% because when a bond is bifurcated we count it twice, once for each kind of H-bond. In Figure 1(b) a schematic picture of the molecule is shown for illustration.

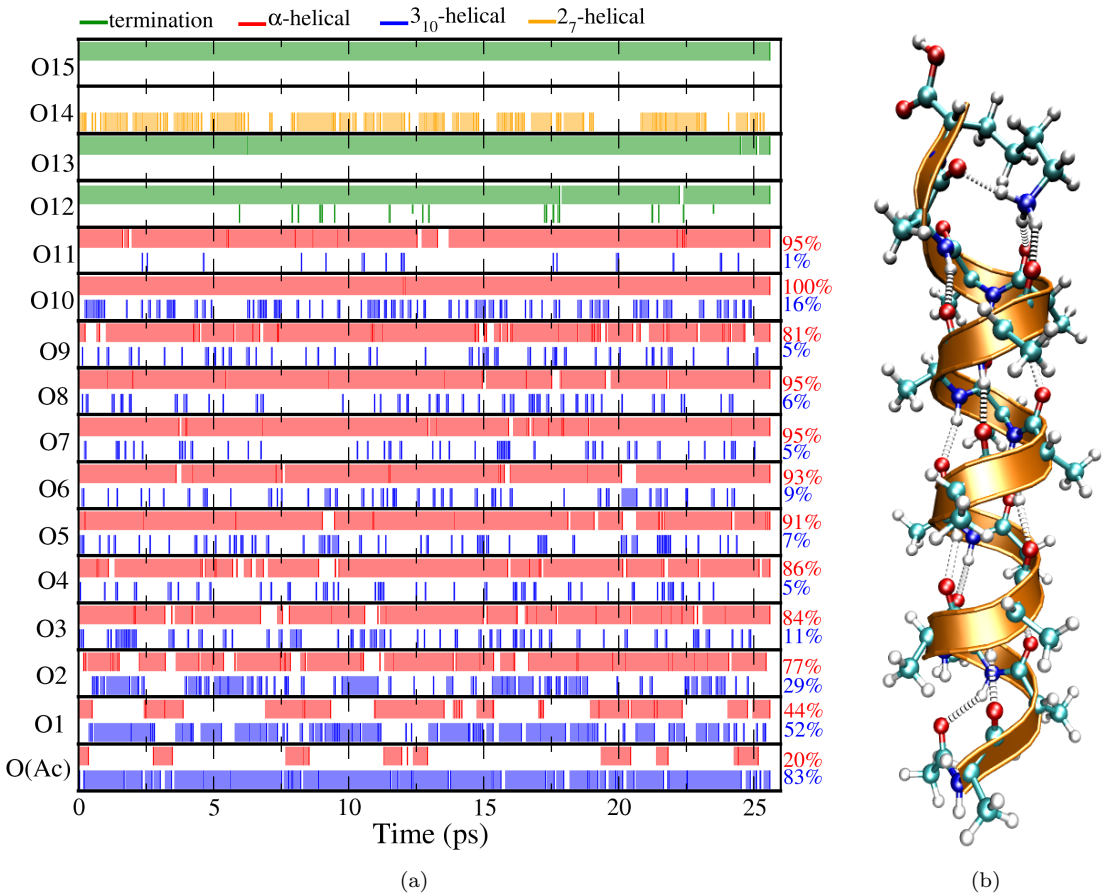

FIG. 1: (a) Evolution of the H-bond pattern of Ac-Ala$_{15}$-LysH$^+$ with time, withing a NVE *ab initio* molecular dynamics simulation: red corresponds to an α-helical H-bond, blue to 3_{10}, yellow to 2_7, and green corresponds to H-bonds to the NH_3^+ group of the Lysine termination. (b) Schematic picture of Ac-Ala$_{15}$-LysH$^+$.

The NVE trajectory starts after a few picoseconds of NVT equilibration, therefore already at t=0 the molecule is not a perfect α-helix. Here, it is clear that the H-bond associated with the Ac termination is predominantly 3_{10} helical, the next one is predominantly bifurcated, and a bifurcation can happen with less probability for one H-bond further up. Yet, the next nine H-bonds in the structure (all those remaining up to the LysH+ termination) are "purely" alpha helical more than 84% of the time. We therefore label this molecule as clearly α-helical in character, even in a dynamic situation. We note also that for Ac-Ala$_{10}$-LysH$^+$ the situation is similar.

[1] A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. **102**, 073005 (2009)
[2] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler, Comp. Phys. Comm. **180**, 2175 (2009).