Supporting Information:

Temperature Dependence of Peptide

Conformational Equilibria from Simulations at

a Single Temperature

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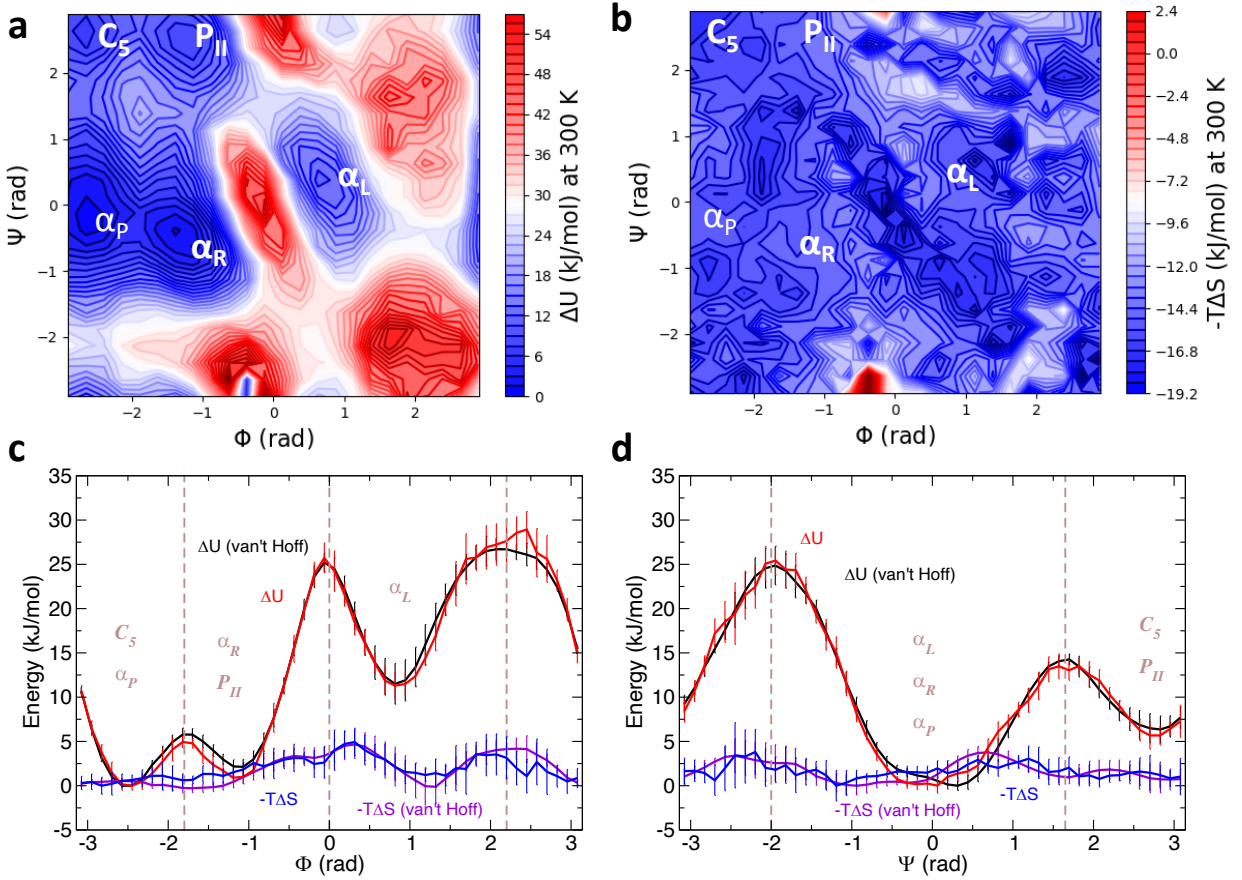
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Figure S1: Results corresponding to those shown in Fig. 3, but without using the fitting procedure described in the Appendix. Contour plots of the (a) internal energy, $\Delta U(\Psi, \Phi)$, and (b) entropic contribution, $-T\Delta S(\Psi, \Phi)$ of alanine dipeptide in water at 300 K obtained by the fluctuation method. Also shown are one-dimensional plots of the ΔU (red lines) and $-T\Delta S$ (blue lines) as a function of (c) Φ and (d) Ψ; results for ΔU (black lines) and $-T\Delta S$ (violet lines) from a van't Hoff analysis are also shown for comparison.
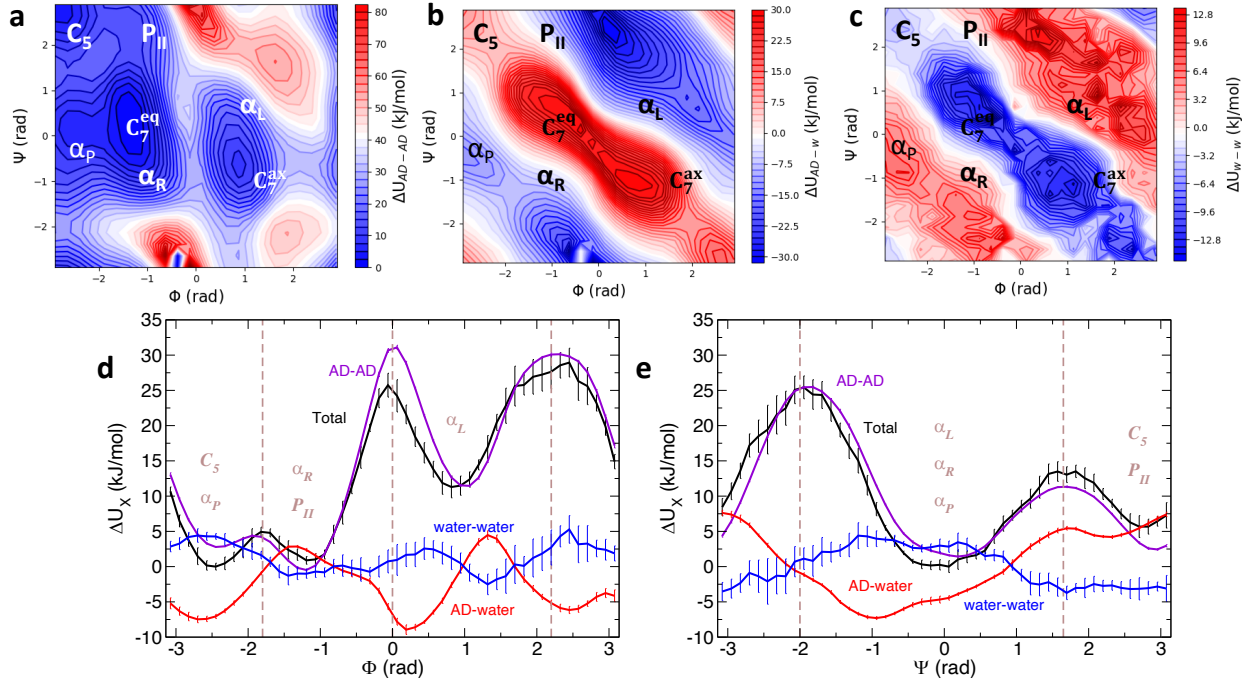
Figure S2: Results corresponding to those shown in Fig. 4, but without using the fitting procedure described in the Appendix. Contribution to the total internal energy at 300 K from (a) AD-AD, (b) AD-water, and (c) water- water interactions shown as two-dimensional contour plots. One dimensional internal energy contributions are shown as a function of (d) Φ and (e) Ψ.
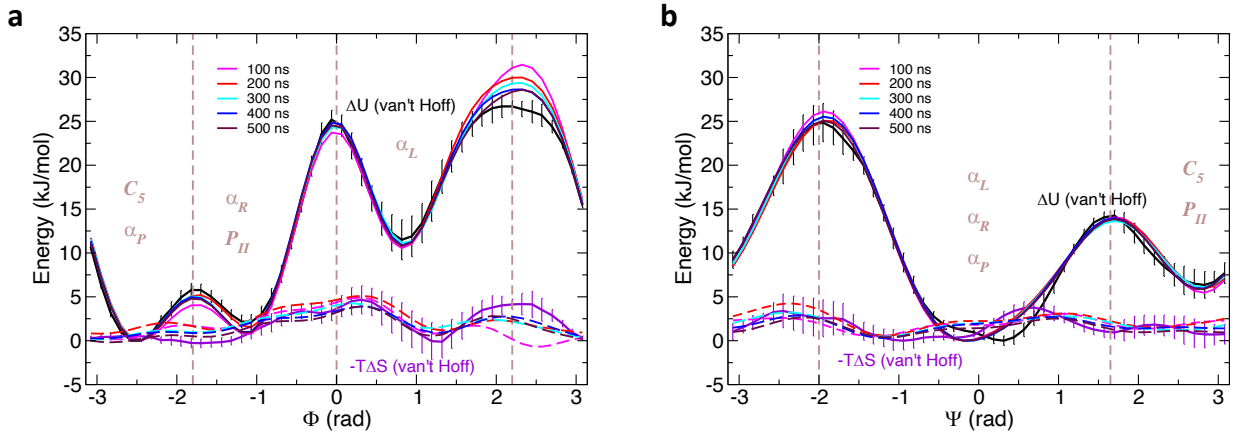

Figure S3: Convergence with simulation time of the internal energy, ΔU (solid lines), and entropic contribution, $-T\Delta S$ (dashed lines), obtained with the fluctuation method (and the fitting approach described in the Appendix). Results are shown as a function of (a) Φ and (b) Ψ; ΔU (black solid lines) and $-T\Delta S$ (violet solid lines) from a van't Hoff analysis are also shown for comparison. Note that, as described in the Computational Methods, five independent 100 ns trajectories and the results for different simulation times reflect averages from 1, 2, 3, 4, and 5 of these trajectories.