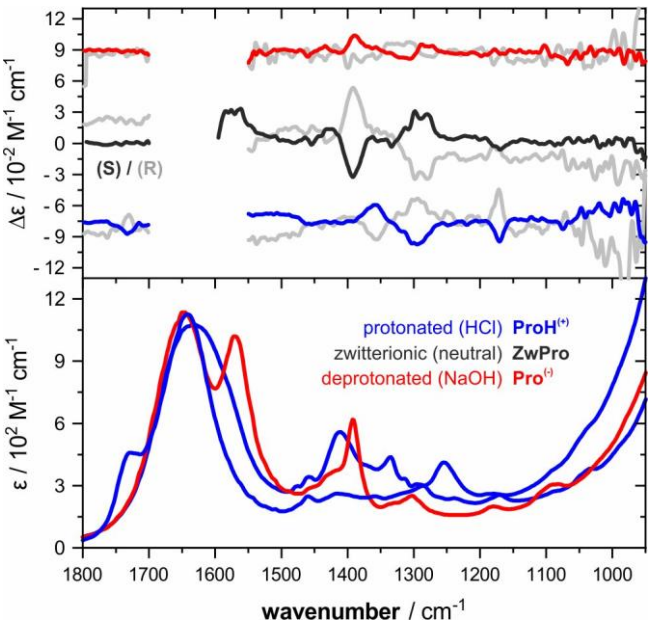

Figure S1. Experimental spectra of both enantiomers of proline at different pH values, baseline correction for VCD spectra was performed by subtracting the VCD spectra of the racemic mixture at same conditions.

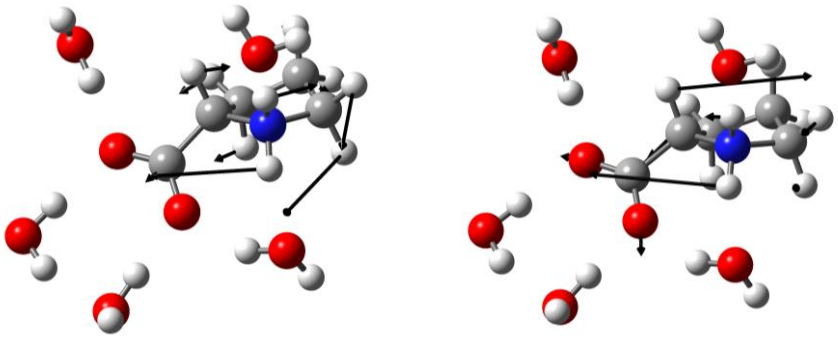

Figure S2. Displacement vectors exemplifying the vibrational modes that change the most among the solvated clusters **ZwPro**-$(H_2O)_5$. Left: Mode at ~1375 cm^{-1}; right: mode at ~1430 cm^{-1}.

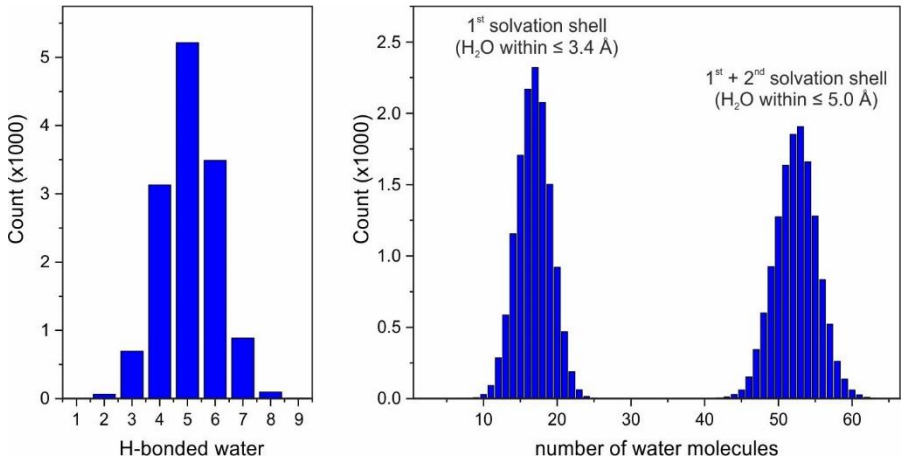

Figure S3. Statistical analysis of solute-solvent hydrogen bonds and number of solvent molecules in the first and second solvation sphere of **ZwPro**.

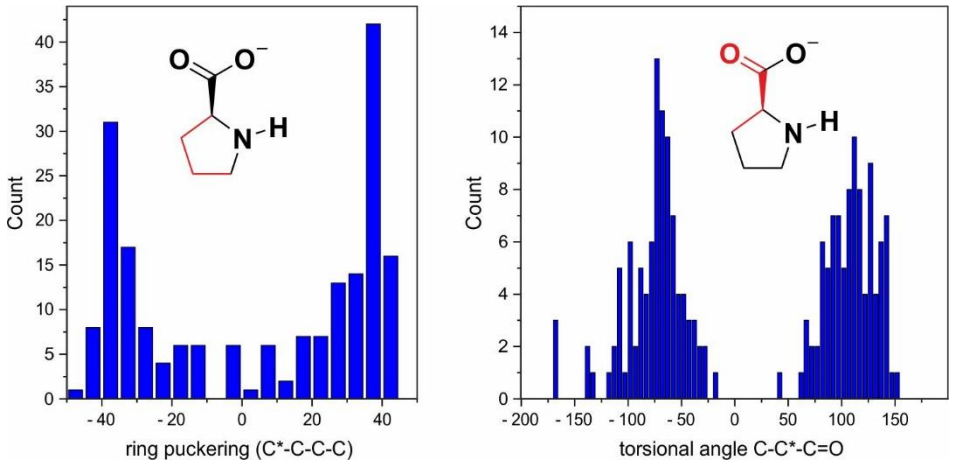

Figure S4. Conformation of **ZwPro** in DFT-optimized **ZwPro**-$(H_2O)_{30}$ clusters.

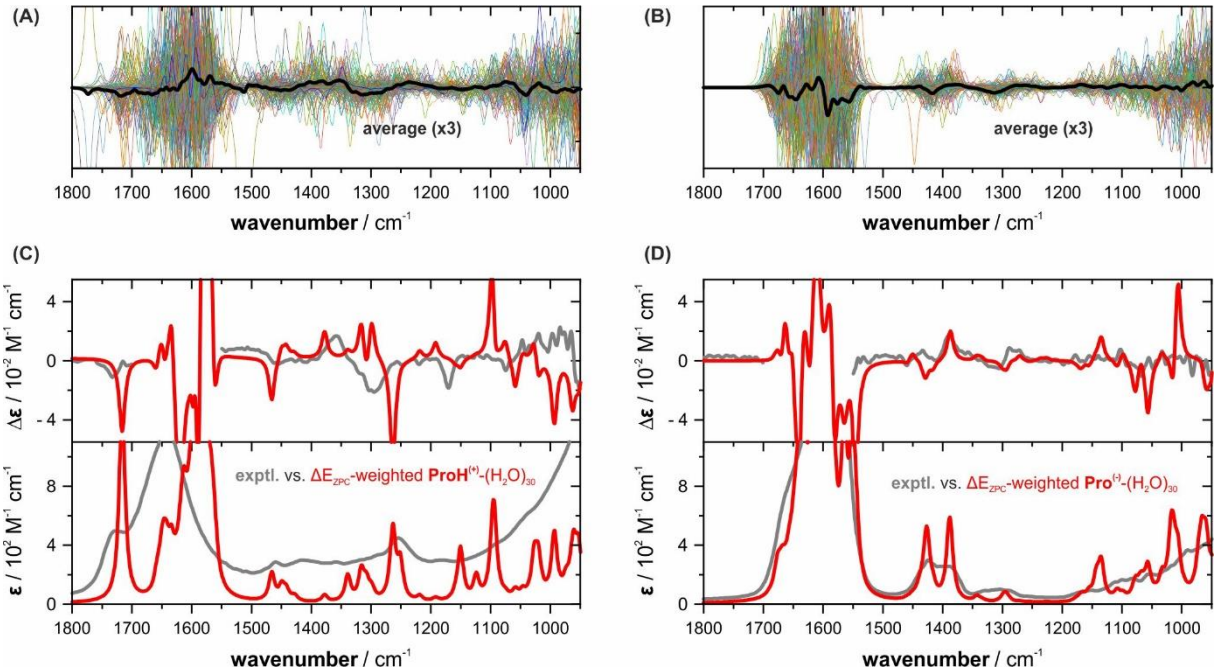

Figure S5. Overlay of all computed spectra of (A) **ProH$^{(+)}$**-$(H_2O)_{30}$ and (B) **Pro$^{(-)}$**-$(H_2O)_{30}$ and comparison of the Boltzmann-weighted spectra of (C) **ProH$^{(+)}$**-$(H_2O)_{30}$ and (D) **Pro$^{(-)}$**-$(H_2O)_{30}$ with the experimental spectra.

Table S1. Conformer energies of isolated **ZwPro**, **ProH$^{(+)}$** and **Pro$^{(-)}$**, total energies (E, E_{zpc}, G) in Hartree, energies with respect to lowest conformer energy (ΔE, ΔE_{zpc}, ΔG) in kcal/mol.

Conformer	E	E_{zpc}	G	ΔE	ΔE_{zpc}	ΔG
ZwPro_c1	-401.2207854	-401.0746245	-401.0675176	0.000	0.000	0.000
ZwPro_c2	-401.2202572	-401.0740545	-401.0668673	0.331	0.358	0.408

Conformer	E	E_{zpc}	G	ΔE	ΔE_{zpc}	ΔG
ProH+_c1	-401.6645956	-401.5051234	-401.4975282	0.000	0.000	0.000
ProH+_c2	-401.6642843	-401.5045057	-401.4970419	0.195	0.388	0.305
ProH+_c3	-401.6606887	-401.5010353	-401.4934212	2.452	2.565	2.577
ProH+_c4	-401.6599087	-401.5002016	-401.4926728	2.941	3.088	3.047

Conformer	E	E_{zpc}	G	ΔE	ΔE_{zpc}	ΔG
Pro-_c1	-400.7469547	-400.6155980	-400.6084086	0.000	0.000	0.000
Pro-_c2	-400.7465385	-400.6154400	-400.6081267	0.261	0.099	0.177
Pro-_c3	-400.7425714	-400.6117159	-400.6043151	2.751	2.436	2.569
Pro-_c4	-400.7417821	-400.6106026	-400.6032891	3.246	3.135	3.213

Energies and structures of all solvated structures are given in a separate SI file.