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Probing micro-solvation in "numbers": The case of neutral dipeptides in water.

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Further details for eqns (2) and (5)

As it was mentioned, scalar contribution is insignificant to T_1 determination and it can be calculated by the following equation:

$$\frac{1}{T_{1,C_iN,sc}} = \frac{16\pi^2 J_{C_iN}^2 T_{2,N}}{3\left[1+\left(\omega_C-\omega_N\right)^2 T_{2,N}^2\right]}, \qquad \text{(S1)}$$

since ${}^1J_{C_iN}$ coupling constant and $T_{2,N}$ relaxation time of the nitrogen atoms are known. ${}^1J_{C_iN}$ coupling constant is approximately equal to 30 Hz, whereas $T_{2,N}$ values are determined by the width at the half height ($\Delta\nu_{1/2}$) of the ^{14}N-NMR peak. Our previous studies, concerning amino acids[1] and acetyl-amino acids[2] amino and imino groups' hydration, respectively, indicated that $T_{2,N}$ values for amino acids lie between 36 to 108 Hz and for acetyl-amino acids between 710 to 1495 Hz. Nevertheless, the scalar contribution to T_1 relaxation is very small (< 0.01 %) and the overall estimated error in the calculation of the relaxation times ratio [eqn (5)] is less than 10^{-6} %, if no subtraction of the scalar contribution takes place.

In fact, none of the terms in eqn (2) can be calculated precisely, mainly due to the variation in distance *r* between *i*-carbon and *i*- or *j*-protons for all studied molecules and it cannot be defined accurately. However, X-ray diffraction measurements showed that the mean proton-carbon (C-H) distance is approximately ~1.1 Å.[3] Moreover, our research group calculated by the means of DFT and MP2 theoretical calculations[2] the above distance for various amino acids and dipeptides resulting in 1.085-1.095 Å. This small variation in proton-carbon distance contributes quite significantly (6 % deviation) to the τ_C calculation.

Consequently, the accurate determination of the correlation time, τ_C, demands either the knowledge of the exact proton-carbon distances or an independent of them novel method for τ_C calculation.

The case of internal motion (Lipari and Szabo)

According to Lipari and Szabo,[4] in the case of internal motion the spectral density is given by the expression:

$$J_i(\omega) = \frac{2}{5}\left(\frac{S^2\tau_C}{1+\omega^2\tau_C^2} + \frac{\left(1-S^2\right)\tau}{1+\omega^2\tau} \right), \quad \text{(S2)}$$

where S is a generalized order parameter, which is the measure of motion's spatial restriction degree and τ equals to:

$$\tau^{-1} = \tau_C^{-1} + \tau_e^{-1}, \quad \text{(S3)}$$

where τ_e is an effective correlation time, which is a measure of the internal motion's rate. Thus, the longitudinal relaxation time (T_1), described by eqn (1), will be the sum of two terms. Namely, one term will be characterized by the correlation time, τ_C, and multiplied by the factor S^2, while the other term will be characterized by the correlation time $\tau_C\tau_e/\left(\tau_C+\tau_e\right)$ and multiplied by the factor $\left(1-S^2\right)$:

$$\frac{1}{T_{1,i}} = S^2 f\left(\omega,\tau_C\right) + \left(1-S^2\right) f\left(\omega, \frac{\tau_C\tau_e}{\tau_C+\tau_e}\right), \quad \text{(S4)}$$

where $f\left(\omega,\tau_C\right)$ is the second term in eqn (1).

Considering the above, someone could wonder if eqn (5) still permits the accurate calculation of τ_C. The error of using eqn (5) as is (without taking into consideration the effect of the internal motion), can be calculated by expanding eqn (5), after the inclusion of eqn (S4) in it, in a Maclaurin series (since τ_e is expected to be very small, namely few ps) around $\tau_e = 0$ s.

Inclusion of eqn (S4) to eqn (5) leads to:

$$f\left(\omega_1,\omega_2,\tau_C,\tau_e\right)=\frac{\left\{S^2\left[\frac{3}{1+\tau_C^2\omega_{1C}^2}+\frac{1}{1+\tau_C^2\left(\omega_{1C}-\omega_{1H}\right)^2}+\frac{6}{1+\tau_C^2\left(\omega_{1C}+\omega_{1H}\right)^2}\right]+\frac{\left(1-S^2\right)\tau_e}{\tau_C+\tau_e}\left[\frac{3}{1+\frac{\tau_C^2\tau_e^2\omega_{1C}^2}{\left(\tau_C+\tau_e\right)^2}}+\frac{1}{1+\frac{\tau_C^2\tau_e^2\left(\omega_{1C}-\omega_{1H}\right)^2}{\left(\tau_C+\tau_e\right)^2}}+\frac{6}{1+\frac{\tau_C^2\tau_e^2\left(\omega_{1C}+\omega_{1H}\right)^2}{\left(\tau_C+\tau_e\right)^2}}\right]\right\}}{\left\{S^2\left[\frac{3}{1+\tau_C^2\omega_{2C}^2}+\frac{1}{1+\tau_C^2\left(\omega_{2C}-\omega_{2H}\right)^2}+\frac{6}{1+\tau_C^2\left(\omega_{2C}+\omega_{2H}\right)^2}\right]+\frac{\left(1-S^2\right)\tau_e}{\tau_C+\tau_e}\left[\frac{3}{1+\frac{\tau_C^2\tau_e^2\omega_{2C}^2}{\left(\tau_C+\tau_e\right)^2}}+\frac{1}{1+\frac{\tau_C^2\tau_e^2\left(\omega_{2C}-\omega_{2H}\right)^2}{\left(\tau_C+\tau_e\right)^2}}+\frac{6}{1+\frac{\tau_C^2\tau_e^2\left(\omega_{2C}+\omega_{2H}\right)^2}{\left(\tau_C+\tau_e\right)^2}}\right]\right\}} \quad \text{(S5)}$$

Expansion of the above equation in a Maclaurin series results in:

$$f\left(\omega_1,\omega_2,\tau_C,\tau_e\right)=f\left(\omega_1,\omega_2,\tau_C,0\right)+\sum_{n=1}^{\infty}\frac{1}{n!}f^n\left(\omega_1,\omega_2,\tau_C,0\right)\tau_e^n, \quad \text{(S6)}$$

where f^n is the n-th derivative of equation f. The term $f\left(\omega_1,\omega_2,\tau_C,0\right)$ represents the T_1 ratio at two different magnetic fields when no internal motion is taken into consideration [named eqn (5)] therefore, the term $\sum_{n=1}^{\infty}\frac{1}{n!}f^n\left(\omega_1,\omega_2,\tau_C,0\right)\tau_e^n$ represents the error of the approximation.

Assuming that $S=0.8$, since slower motion dominates in relaxation processes (according to Lipari S value is expected to be almost one), $\tau_C=10^{-10}$ s, $\tau_e=10^{-11}$ s, ω_1 are the proton and carbon resonances at 250.13 and 62.895 MHz and ω_2 are the resonances at 500.13 and 125.758 MHz respectively, the calculated error is -0.07 %. As a result, the estimated error in eqn (5) is much less than 0.1 %, proving that eqn (5) still leads to the accurate calculation of the correlation time, τ_C.

From eqns (5) and (6) to the calculation of the weighted correlation times

The inclusion of eqn (1) to eqns (5) and (6) results in two equations whose expansion in a Maclaurin series until the 3rd term leads to:

$$\frac{\frac{1}{\left(T_{1,O,i}\right)_1}}{\frac{1}{\left(T_{1,O,i}\right)_2}} = 1 - \frac{1}{10}\left(10\omega_{1C}^2 - 10\omega_{2C}^2 + 10\omega_{1C}\omega_{1H} + 7\omega_{1H}^2 - 10\omega_{2C}\omega_{2H} - 7\omega_{2H}^2\right)\tau_C^2 \qquad \text{(S7)}$$

and

$$\frac{\frac{1}{\left(T_{1,O,i}\right)_1}}{\frac{1}{\left(T_{1,O,i}\right)_2}} = 1 - \frac{1}{10}\left(10\omega_{1C}^2 - 10\omega_{2C}^2 + 10\omega_{1C}\omega_{1H} + 7\omega_{1H}^2 - 10\omega_{2C}\omega_{2H} - 7\omega_{2H}^2\right)\times \left[P_b\left(1+2P_\alpha\right)\tau_{C,b}^2 - 4P_bP_\alpha\tau_{C,b}\tau_{C,\alpha} + \left(1+2P_b\right)P_\alpha\tau_{C,\alpha}^2\right] \qquad \text{(S8)}$$

Furthermore, taking into consideration that the 1st terms of eqn (S7) and eqn (S8) are equal, lead to their 2nd terms equality and a 2nd degree polynomial whose solution around τ_C results in the weighted average calculation of the correlation times through eqn (S9):

$$\tau_C = \sqrt{P_b\left(1+2P_a\right)\tau_{C,b}^2 - 4P_bP_a\tau_{C,b}\tau_{C,\alpha} + \left(1+2P_b\right)P_a\tau_{C,\alpha}^2} \qquad \text{(S9)}$$

Full expression of eqn (11)

$$\frac{\dfrac{1}{\left(T_{1,O,i}\right)_1}}{\dfrac{1}{\left(T_{1,O,i}\right)_2}} = f\left(\omega_1,\omega_2,M_W\right) =$$

$$\frac{\left\{\begin{array}{l} P_\alpha\, c\, M_W\left[\dfrac{1}{1+\left(\omega_{1C}-\omega_{1H}\right)^2\left(cM_W\right)^2}+\dfrac{3}{1+\omega_{1C}^2\left(cM_W\right)^2}+\dfrac{6}{1+\left(\omega_{1C}+\omega_{1H}\right)^2\left(cM_W\right)^2}\right]+ \\ P_b\left(cM_W+18N_w\right)\left[\dfrac{1}{1+\left(\omega_{1C}-\omega_{1H}\right)^2\left(cM_W+18N_w\right)^2}+\dfrac{3}{1+\omega_{1C}^2\left(cM_W+18N_w\right)^2}+\dfrac{6}{1+\left(\omega_{1C}+\omega_{1H}\right)^2\left(cM_W+18N_w\right)^2}\right] \end{array}\right\}}{\left\{\begin{array}{l} P_\alpha\, c\, M_W\left[\dfrac{1}{1+\left(\omega_{2C}-\omega_{2H}\right)^2\left(cM_W\right)^2}+\dfrac{3}{1+\omega_{2C}^2\left(cM_W\right)^2}+\dfrac{6}{1+\left(\omega_{2C}+\omega_{2H}\right)^2\left(cM_W\right)^2}\right]+ \\ P_b\left(cM_W+18N_w\right)\left[\dfrac{1}{1+\left(\omega_{2C}-\omega_{2H}\right)^2\left(cM_W+18N_w\right)^2}+\dfrac{3}{1+\omega_{2C}^2\left(cM_W+18N_w\right)^2}+\dfrac{6}{1+\left(\omega_{2C}+\omega_{2H}\right)^2\left(cM_W+18N_w\right)^2}\right] \end{array}\right\}}$$

The measured relaxation times (T_1) for $^{13}C_\alpha$ and $^{13}C_\beta$ nuclei at three magnetic fields

Table S1. The $^{13}C_\alpha$ nuclei measured T_1 values (at 298 K) of each dipeptide at three magnetic fields (± indicates the StdDev with n = 20).

Dipeptides (-NH_2 → -COOH)	M_W[a]	pH = 6.0		
		500 MHz	400 MHz	250 MHz
		T_1 (s) for $^{13}C_\alpha$		
Ala−Gly	146.14	1.713 ± 0.036 − 0.846 ± 0.011	1.660 ± 0.032 − 0.819 ± 0.014	1.600 ± 0.031 − 0.788 ± 0.012
Gly−Ala	146.14	0.834 ± 0.021 − 1.681 ± 0.036	0.806 ± 0.018 − 1.623 ± 0.032	0.776 ± 0.013 − 1.565 ± 0.023
Ala−Ala	160.17	1.291 ± 0.019 − 1.292 ± 0.021	1.247 ± 0.024 − 1.250 ± 0.022	1.198 ± 0.026 − 1.202 ± 0.025
Gly−Ser	162.14	0.738 ± 0.013 − 1.450 ± 0.024	0.712 ± 0.012 − 1.398 ± 0.033	0.687 ± 0.016 − 1.347 ± 0.032
Gly−Leu	188.23	0.583 ± 0.010 − 1.116 ± 0.034	0.559 ± 0.008 − 1.080 ± 0.029	0.536 ± 0.010 − 1.035 ± 0.026
Val−Ser	204.20	1.186 ± 0.028 − 1.111 ± 0.031	1.138 ± 0.031 − 1.074 ± 0.026	1.090 ± 0.028 − 1.025 ± 0.027
Val−Thr	218.30	1.008 ± 0.029 − 0.885 ± 0.021	0.965 ± 0.024 − 0.845 ± 0.018	0.911 ± 0.028 − 0.803 ± 0.018
Thr−Leu	232.30	0.890 ± 0.023 − 0.824 ± 0.025	0.845 ± 0.018 − 0.783 ± 0.016	0.801 ± 0.021 − 0.743 ± 0.018
Ala−Phe	236.30	0.908 ± 0.027 − 0.907 ± 0.024	0.863 ± 0.022 − 0.860 ± 0.020	0.815 ± 0.020 − 0.815 ± 0.016
Phe−Ala	236.30	0.957 ± 0.030 − 0.966 ± 0.035	0.917 ± 0.026 − 0.919 ± 0.021	0.862 ± 0.018 − 0.869 ± 0.014
Val−Met	248.30	0.827 ± 0.024 − 0.905 ± 0.033	0.784 ± 0.020 − 0.856 ± 0.016	0.738 ± 0.017 − 0.809 ± 0.019
Tyr−Ala	252.30	0.892 ± 0.031 − 0.883 ± 0.028	0.845 ± 0.021 − 0.834 ± 0.017	0.795 ± 0.019 − 0.784 ± 0.011
Met−Leu	262.40	0.787 ± 0.015 − 0.803 ± 0.023	0.742 ± 0.017 − 0.760 ± 0.014	0.698 ± 0.014 − 0.712 ± 0.016
Phe−Val	264.30	0.817 ± 0.022 − 0.776 ± 0.018	0.775 ± 0.020 − 0.733 ± 0.018	0.724 ± 0.021 − 0.687 ± 0.017

[a] M_W is the molecular weight of dipeptides' zwitterionic form.

Table S2. The $^{13}C_{\beta}$ nuclei measured T_1 values (at 298 K) of each dipeptide at three magnetic fields (± indicates the StdDev with n = 20).

Dipeptides (-NH_2 → -COOH)	M_W[a]	pH = 6.0		
		500 MHz	400 MHz	250 MHz
		T_1 (s) for $^{13}C_{\beta}$		
Ala−Gly	146.14	0.565± 0.008 − //	0.548 ± 0.010 − //	0.527 ± 0.010 − //
Gly−Ala	146.14	// − 0.559 ± 0.008	// − 0.540 ± 0.012	// − 0.520 ± 0.010
Ala−Ala	160.17	0.427 ± 0.007 − 0.428 ± 0.011	0.412 ± 0.012 − 0.451 ± 0.012	0.396 ± 0.011 − 0.398 ± 0.010
Gly−Ser	162.14	// − 0.729 ± 0.016	// − 0.704 ± 0.015	// − 0.678 ± 0.013
Gly−Leu	188.23	// − 0.563 ± 0.014	// − 0.543 ± 0.011	// − 0.520 ± 0.014
Val−Ser	204.20	1.179 ± 0.028 – 0.591 ± 0.015	1.131 ± 0.028 − 0.566 ± 0.014	1.076 ± 0.025 − 0.540 ± 0.014
Val−Thr	218.30	0.995 ± 0.021 − 0.924 ± 0.020	0.948 ± 0.024 − 0.882 ± 0.018	0.902 ± 0.018 − 0.838 ± 0.018
Thr−Leu	232.30	0.892 ± 0.019 − 0.405 ± 0.015	0.854 ± 0.018 − 0.388 ± 0.016	0.808 ± 0.018 − 0.368 ± 0.011
Ala−Phe	236.30	0.300 ± 0.010 − 0.448 ± 0.015	0.285 ± 0.012 − 0.427 ± 0.010	0.269 ± 0.010 − 0.402 ± 0.011
Phe−Ala	236.30	0.478 ± 0.014 − 0.318 ± 0.010	0.456 ± 0.016 − 0.302 ± 0.011	0.433 ± 0.011 − 0.284 ± 0.008
Val−Met	248.30	0.822 ± 0.019 − 0.445 ± 0.011	0.778 ± 0.017 − 0.422 ± 0.012	0.731 ± 0.015 − 0.398 ± 0.011
Tyr−Ala	252.30	0.441 ± 0.022 − 0.291 ± 0.018	0.418 ± 0.017 − 0.276 ± 0.013	0.394 ± 0.012 − 0.260 ± 0.011
Met−Leu	262.40	0.389 ± 0.013 − 0.396 ± 0.011	0.368 ± 0.014 − 0.375 ± 0.014	0.344 ± 0.014 − 0.350 ± 0.011
Phe−Val	264.30	0.400 ± 0.012 − 0.772 ± 0.018	0.380 ± 0.010 − 0.729 ± 0.016	0.354 ± 0.011 − 0.685 ± 0.016

[a] M_W is the molecular weight of dipeptides' zwitterionic form.

Comparison between relaxation rates for $^{13}C_{\alpha}$ and $^{13}C_{\beta}$ nuclei

The relaxation rate of ^{13}C nucleus is equal to $1/(NT_1)$, where N is the number of the attached protons to the carbon. The following Tables S3-S5 describe the corresponding relaxation rates of $^{13}C_{\alpha}$ and $^{13}C_{\beta}$ nuclei and their differences $\left(1/(NT_1)_{^{13}C_a} - 1/(NT_1)_{^{13}C_\beta}\right)$ for each studied dipeptide's component at three magnetic fields:

Table S3. The $^{13}C_{\alpha}$ and $^{13}C_{\beta}$ nuclei measured relaxation rates $\left[1/(NT_1)\right]$ values (at 298 K) of each dipeptide at 500 MHz (± indicates the StdDev with n = 20).

Dipeptides (-NH_2 → -COOH)	M_W [a]	pH = 6.0		
		500 MHz		
		$1/(NT_1)$ (s^{-1}) for $^{13}C_{\alpha}$	$1/(NT_1)$ (s^{-1}) for $^{13}C_{\beta}$	$1/(NT_1)_{^{13}C_a} - 1/(NT_1)_{^{13}C_\beta}$ [b] (s^{-1})
Ala−Gly	146.14	0.584 ± 0.012 − 0.591 ± 0.008	0.590± 0.008 − //	-0.006 − //
Gly−Ala	146.14	0.600 ± 0.015 − 0.591 ± 0.013	// − 0.596 ± 0.007	// − -0.005
Ala−Ala	160.17	0.775 ± 0.012 – 0.774 ± 0.013	0.780 ± 0.012 − 0.779 ± 0.020	-0.005 − -0.005
Gly−Ser	162.14	0.678 ± 0.013 – 0.690 ± 0.012	// − 0.686 ± 0.015	// − 0.004
Gly−Leu	188.23	0.858 ± 0.015 – 0.869 ± 0.023	// − 0.888 ± 0.022	// − -0.019
Val−Ser	204.20	0.843 ± 0.019 – 0.900 ± 0.024	0.848 ± 0.020 – 0.846 ± 0.021	-0.005 − 0.054
Val−Thr	218.30	0.992 ± 0.028 – 1.130 ± 0.026	1.005 ± 0.021 – 1.082 ± 0.023	-0.013 − 0.048
Thr−Leu	232.30	1.124 ± 0.029 – 1.214 ± 0.036	1.121 ± 0.023 – 1.235 ± 0.045	0.003 − -0.021
Ala−Phe	236.30	1.101 ± 0.031 − 1.103 ± 0.029	1.111 ± 0.032 – 1.116 ± 0.036	-0.010 − -0.013
Phe−Ala	236.30	1.045 ± 0.032 – 1.035 ± 0.036	1.046 ± 0.030 – 1.048 ± 0.032	-0.001 − -0.013
Val−Met	248.30	1.209 ± 0.034 – 1.105 ± 0.039	1.217 ± 0.028 – 1.124 ± 0.028	-0.008 − -0.019
Tyr−Ala	252.30	1.121 ± 0.038 – 1.133 ± 0.035	1.134 ± 0.054 – 1.145 ± 0.066	-0.013 − -0.012
Met−Leu	262.40	1.271 ± 0.024 – 1.245 ± 0.034	1.285 ± 0.040 – 1.263 ± 0.034	-0.014 − -0.018
Phe−Val	264.30	1.224 ± 0.030 – 1.289 ± 0.030	1.250 ± 0.036 – 1.295 ± 0.029	-0.026 − -0.006

[a] M_W is the molecular weight of dipeptides' zwitterionic form. [b] $1/(NT_1)_{^{13}C_a} - 1/(NT_1)_{^{13}C_\beta}$ values correspond to each dipeptide's component.

Table S4. The $^{13}C_{\alpha}$ and $^{13}C_{\beta}$ nuclei measured relaxation rates $\left[1/\left(NT_1\right)\right]$ values (at 298 K) of each dipeptide at 400 MHz (± indicates the StdDev with n = 20).

Dipeptides (-NH_2 → -COOH)	M_W [a]	pH = 6.0		
		400 MHz		
		$1/\left(NT_1\right)$ (s^{-1}) for $^{13}C_{\alpha}$	$1/\left(NT_1\right)$ (s^{-1}) for $^{13}C_{\beta}$	$1/\left(NT_1\right)_{^{13}C_{\alpha}} - 1/\left(NT_1\right)_{^{13}C_{\beta}}$ [b] (s^{-1})
Ala−Gly	146.14	0.602 ± 0.011 – 0.611 ± 0.011	0.608 ± 0.011 − //	-0.006 – //
Gly−Ala	146.14	0.607 ± 0.013 – 0.616 ± 0.014	// − 0.618 ± 0.014	// − -0.002
Ala−Ala	160.17	0.802 ± 0.016 – 0.800 ± 0.011	0.809 ± 0.021 − 0.807 ± 0.023	-0.007 − -0.007
Gly−Ser	162.14	0.702 ± 0.012 – 0.715 ± 0.016	// − 0.710 ± 0.015	// − 0.005
Gly−Leu	188.23	0.894 ± 0.012 – 0.902 ± 0.024	// − 0.921 ± 0.018	// − -0.019
Val−Ser	204.20	0.879 ± 0.024 – 0.931 ± 0.022	0.884 ± 0.021 − 0.883 ± 0.021	-0.005 − 0.048
Val−Thr	218.30	1.036 ± 0.025 – 1.183 ± 0.024	1.055 ± 0.026 – 1.134 ± 0.023	-0.019 − 0.049
Thr−Leu	232.30	1.183 ± 0.024 – 1.277 ± 0.026	1.171 ± 0.024 – 1.289 ± 0.049	0.012 − -0.012
Ala−Phe	236.30	1.159 ± 0.029 – 1.163 ± 0.027	1.170 ± 0.048 – 1.171 ± 0.027	-0.011 − -0.008
Phe−Ala	236.30	1.091 ± 0.031 – 1.088 ± 0.024	1.096 ± 0.037 – 1.104 ± 0.039	-0.005 − -0.024
Val−Met	248.30	1.276 ± 0.032 − 1.168 ± 0.021	1.285 ± 0.026 – 1.152 ± 0.033	-0.009 − 0.016
Tyr−Ala	252.30	1.183 ± 0.028 − 1.175 ± 0.024	1.196 ± 0.047 – 1.208 ± 0.055	-0.013 − -0.033
Met−Leu	262.40	1.348 ± 0.030 – 1.316 ± 0.024	1.359 ± 0.050 – 1.333 ± 0.048	-0.011 − -0.017
Phe−Val	264.30	1.290 ± 0.032 – 1.364 ± 0.033	1.316 ± 0.034 – 1.372 ± 0.030	-0.026 − -0.008

[a] M_W is the molecular weight of dipeptides' zwitterionic form. [b] $1/\left(NT_1\right)_{^{13}C_{\alpha}} - 1/\left(NT_1\right)_{^{13}C_{\beta}}$ values correspond to each dipeptide's component.

Table S5. The $^{13}C_\alpha$ and $^{13}C_\beta$ nuclei measured relaxation rates $\left[1/\left(NT_1\right)\right]$ values (at 298 K) of each dipeptide at 250 MHz (± indicates the StdDev with n = 20).

Dipeptides (-NH_2 → -COOH)	M_W [a]	pH = 6.0		
		250 MHz		
		$1/\left(NT_1\right)$ (s^{-1}) for $^{13}C_\alpha$	$1/\left(NT_1\right)$ (s^{-1}) for $^{13}C_\beta$	$1/\left(NT_1\right)_{^{13}C_\alpha} - 1/\left(NT_1\right)_{^{13}C_\beta}$ [b] (s^{-1})
Ala−Gly	146.14	0.625 ± 0.012 – 0.634 ± 0.010	0.633 ± 0.012 − //	-0.008 − //
Gly−Ala	146.14	0.644 ± 0.010 – 0.639 ± 0.009	// − 0.641 ± 0.011	// − -0.002
Ala−Ala	160.17	0.835 ± 0.018 – 0.832 ± 0.017	0.842 ± 0.035 − 0.838 ± 0.021	-0.007 − -0.006
Gly−Ser	162.14	0.728 ± 0.017 – 0.742 ± 0.017	// − 0.737 ± 0.013	// − 0.005
Gly−Leu	188.23	0.933 ± 0.017 – 0.966 ± 0.023	// − 0.962 ± 0.026	// − 0.004
Val−Ser	204.20	0.917 ± 0.023 – 0.976 ± 0.025	0.929 ± 0.021 − 0.926 ± 0.023	-0.012 − 0.050
Val−Thr	218.30	1.098 ± 0.033 – 1.245 ± 0.027	1.109 ± 0.022 – 1.193 ± 0.025	-0.011 − 0.052
Thr−Leu	232.30	1.248 ± 0.031 – 1.346 ± 0.032	1.238 ± 0.027 – 1.359 ± 0.041	0.010 − -0.013
Ala−Phe	236.30	1.227 ± 0.029 – 1.227 ± 0.024	1.239 ± 0.044 – 1.244 ± 0.033	-0.012 − -0.017
Phe−Ala	236.30	1.160 ± 0.024 – 1.151 ± 0.018	1.155 ± 0.029 – 1.174 ± 0.032	0.005 − -0.023
Val−Met	248.30	1.355 ± 0.030 – 1.236 ± 0.028	1.368 ± 0.028 – 1.256 ± 0.033	-0.013 − -0.020
Tyr−Ala	252.30	1.258 ± 0.029 – 1.276 ± 0.018	1.269 ± 0.037 – 1.230 ± 0.052	-0.011 − 0.046
Met−Leu	262.40	1.433 ± 0.029 – 1.404 ± 0.030	1.453 ± 0.056 – 1.429 ± 0.044	-0.010 − -0.025
Phe−Val	264.30	1.381 ± 0.039 – 1.456 ± 0.036	1.412 ± 0.042 – 1.460 ± 0.033	-0.031 − -0.004

[a] M_W is the molecular weight of dipeptides' zwitterionic form. [b] $1/\left(NT_1\right)_{^{13}C_\alpha} - 1/\left(NT_1\right)_{^{13}C_\beta}$ values correspond to each dipeptide's component.

Obviously, ^{13}C relaxation rates depend on the magnetic field [eqn (1)], however their differences, namely in our case $1/\left(NT_1\right)_{^{13}C_\alpha} - 1/\left(NT_1\right)_{^{13}C_\beta}$, for the three magnetic fields, are independent of the magnetic field. Therefore, as indicated in Fig. S1 (see below), almost all $1/\left(NT_1\right)_{^{13}C_\alpha} - 1/\left(NT_1\right)_{^{13}C_\beta}$ values lie between the [2 × (StdDev)] = 0.042 around their mean value,[5] demonstrating $1/\left(NT_1\right)$ values coincidence for both $^{13}C_\alpha$ and $^{13}C_\beta$ nuclei.

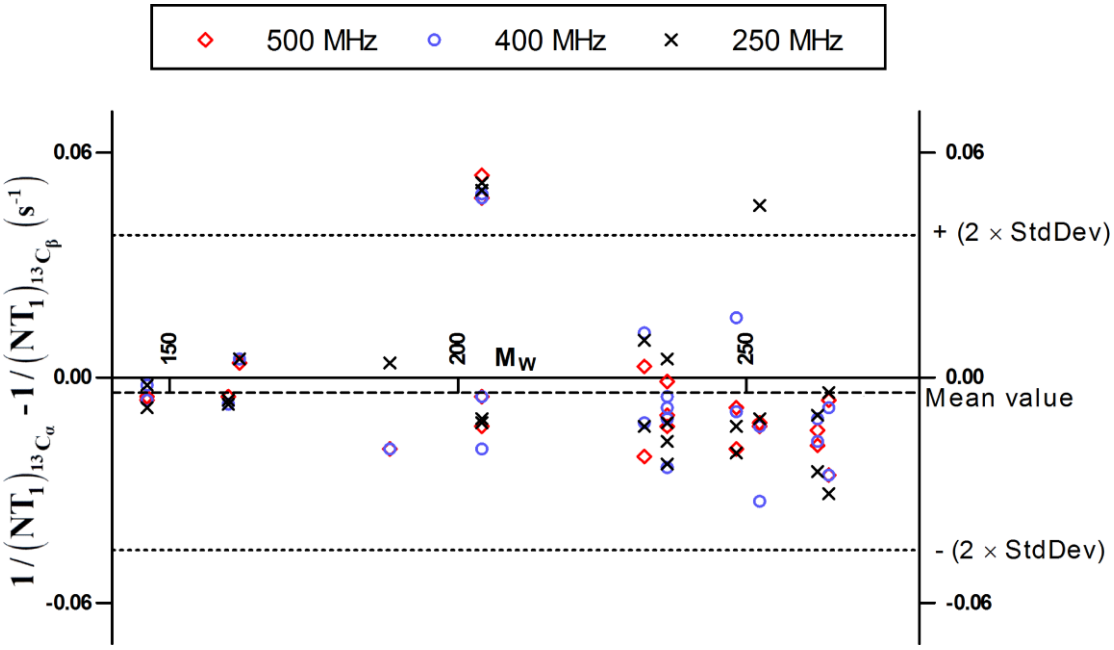

Fig. S1. Comparison between $^{13}C_{\alpha}$ and $^{13}C_{\beta}$ nuclei relaxation rates. Since, the $1/\left(NT_1\right)_{^{13}C_a} - 1/\left(NT_1\right)_{^{13}C_\beta}$ values for the three magnetic fields are independent of the magnetic field, they are plotted vs. dipeptides' M_W. Almost all values (except of 7, n = 72) lie between the calculated $\pm (2 \times \text{StdDev})$ around their mean value $\left(\overline{1/\left(NT_1\right)_{^{13}C_a} - 1/\left(NT_1\right)_{^{13}C_\beta}} = -0.004\, s^{-1}\right)$. Obviously, $1/\left(NT_1\right)_{^{13}C_a}$ and $1/\left(NT_1\right)_{^{13}C_\beta}$ values coincide.

Dipeptides' correlation times (τ_c) from $^{13}C_\alpha$ and $^{13}C_\beta$ relaxation data

Table S6. The calculated τ_C values from $^{13}C_\alpha$ and $^{13}C_\beta$ T_1 values of each dipeptide by eqn (5).

Dipeptides (-NH_2 → -COOH)	M_W [a]	$^{13}C_\alpha$ τ_C [b] (s)	$^{13}C_\beta$ τ_C [b] (s)
Ala-Gly	146.14	1.006 ± 0.038	0.990 ± 0.071
Ala-Gly	146.14	1.010 ± 0.010	1.021 ± 0.038
Ala-Gly	146.14	1.013 ± 0.021	1.046 ± 0.031
Ala-**Gly**	146.14	1.025 ± 0.071	–
Ala-**Gly**	146.14	1.033 ± 0.018	–
Ala-**Gly**	146.14	1.039 ± 0.025	–
Gly-Ala	146.14	1.029 ± 0.088	–
Gly-Ala	146.14	1.042 ± 0.068	–
Gly-Ala	146.14	1.057 ± 0.057	–
Gly-**Ala**	146.14	1.006 ± 0.070	1.026 ± 0.036
Gly-**Ala**	146.14	1.037 ± 0.051	1.043 ± 0.038
Gly-**Ala**	146.14	1.074 ± 0.040	1.065 ± 0.134
Ala-Ala	160.17	1.047 ± 0.043	1.054 ± 0.008
Ala-Ala	160.17	1.063 ± 0.055	1.068 ± 0.013
Ala-Ala	160.17	1.066 ± 0.082	1.086 ± 0.174
Ala-**Ala**	160.17	1.037 ± 0.024	1.015 ± 0.061
Ala-**Ala**	160.17	1.043 ± 0.038	1.046 ± 0.005
Ala-**Ala**	160.17	1.061 ± 0.039	1.085 ± 0.046
Gly-Ser	162.14	1.040 ± 0.050	–
Gly-Ser	162.14	1.061 ± 0.049	–
Gly-Ser	162.14	1.088 ± 0.026	–
Gly-**Ser**	162.14	1.018 ± 0.031	1.025 ± 0.023
Gly-**Ser**	162.14	1.055 ± 0.044	1.045 ± 0.021
Gly-**Ser**	162.14	1.100 ± 0.116	1.070 ± 0.026
Gly-Leu	188.23	1.089 ± 0.068	–
Gly-Leu	188.23	1.137 ± 0.017	–
Gly-Leu	188.23	1.198 ± 0.052	–
Gly-**Leu**	188.23	1.032 ± 0.064	1.093 ± 0.089
Gly-**Leu**	188.23	1.068 ± 0.042	1.101 ± 0.017
Gly-**Leu**	188.23	1.096 ± 0.061	1.107 ± 0.056
Val-Ser	204.20	1.065 ± 0.025	1.190 ± 0.009
Val-Ser	204.20	1.118 ± 0.036	1.194 ± 0.010
Val-Ser	204.20	1.185 ± 0.065	1.197 ± 0.012
Val-**Ser**	204.20	1.052 ± 0.062	1.159 ± 0.011
Val-**Ser**	204.20	1.110 ± 0.015	1.185 ± 0.004
Val-**Ser**	204.20	1.154 ± 0.029	1.219 ± 0.014
Val-Thr	218.30	1.226 ± 0.074	1.196 ± 0.076
Val-Thr	218.30	1.268 ± 0.010	1.245 ± 0.006
Val-Thr	218.30	1.300 ± 0.068	1.309 ± 0.073
Val-**Thr**	218.30	1.213 ± 0.008	1.215 ± 0.019
Val-**Thr**	218.30	1.238 ± 0.006	1.242 ± 0.010

Val-**Thr**	218.30	1.272 ± 0.044	1.277 ± 0.023
Thr-Leu	232.30	1.246 ± 0.062	1.224 ± 0.009
Thr-Leu	232.30	1.299 ± 0.006	1.251 ± 0.007
Thr-Leu	232.30	1.370 ± 0.078	1.271 ± 0.025
Thr-**Leu**	232.30	1.232 ± 0.052	1.213 ± 0.053
Thr-**Leu**	232.30	1.285 ± 0.046	1.227 ± 0.058
Thr-**Leu**	232.30	1.355 ± 0.142	1.238 ± 0.142
Ala-Phe	236.30	1.295 ± 0.013	1.302 ± 0.055
Ala-Phe	236.30	1.319 ± 0.039	1.327 ± 0.024
Ala-Phe	236.30	1.352 ± 0.063	1.360 ± 0.154
Ala-**Phe**	236.30	1.249 ± 0.047	1.303 ± 0.179
Ala-**Phe**	236.30	1.311 ± 0.047	1.321 ± 0.043
Ala-**Phe**	236.30	1.393 ± 0.055	1.335 ± 0.095
Phe-Ala	236.30	1.210 ± 0.023	1.223 ± 0.011
Phe-Ala	236.30	1.278 ± 0.055	1.251 ± 0.027
Phe-Ala	236.30	1.293 ± 0.071	1.287 ± 0.095
Phe-**Ala**	236.30	1.303 ± 0.029	1.349 ± 0.101
Phe-**Ala**	236.30	1.335 ± 0.228	1.356 ± 0.028
Phe-**Ala**	236.30	1.354 ± 0.014	1.365 ± 0.083
Val-Met	248.30	1.337 ± 0.031	1.360 ± 0.020
Val-Met	248.30	1.362 ± 0.048	1.387 ± 0.016
Val-Met	248.30	1.397 ± 0.067	1.424 ± 0.040
Val-**Met**	248.30	1.285 ± 0.060	1.312 ± 0.010
Val-**Met**	248.30	1.333 ± 0.136	1.345 ± 0.019
Val-**Met**	248.30	1.396 ± 0.046	1.390 ± 0.074
Tyr-Ala	252.30	1.343 ± 0.013	1.319 ± 0.130
Tyr-Ala	252.30	1.371 ± 0.077	1.353 ± 0.140
Tyr-Ala	252.30	1.409 ± 0.171	1.399 ± 0.164
Tyr-**Ala**	252.30	1.354 ± 0.085	1.327 ± 0.065
Tyr-**Ala**	252.30	1.399 ± 0.125	1.353 ± 0.014
Tyr-**Ala**	252.30	1.460 ± 0.020	1.388 ± 0.181
Met-Leu	262.40	1.345 ± 0.035	1.424 ± 0.038
Met-Leu	262.40	1.407 ± 0.010	1.428 ± 0.052
Met-Leu	262.40	1.491 ± 0.072	1.433 ± 0.081
Met-**Leu**	262.40	1.397 ± 0.042	1.415 ± 0.165
Met-**Leu**	262.40	1.409 ± 0.046	1.432 ± 0.023
Met-**Leu**	262.40	1.425 ± 0.178	1.444 ± 0.063
Phe-Val	264.30	1.385 ± 0.014	1.360 ± 0.071
Phe-Val	264.30	1.413 ± 0.010	1.422 ± 0.013
Phe-Val	264.30	1.432 ± 0.030	1.467 ± 0.052
Phe-**Val**	264.30	1.392 ± 0.012	1.359 ± 0.021
Phe-**Val**	264.30	1.420 ± 0.015	1.403 ± 0.007
Phe-**Val**	264.30	1.459 ± 0.022	1.464 ± 0.033

[a] M_W is the molecular weight of dipeptides' zwitterionic form. [b] The correlation times (τ_C) are multiplied by 10^{10}. They were calculated by eqn (5) for three magnetic fields as follows: 400 MHz / 500 MHz, 250 MHz / 500 MHz and 250 MHz / 400 MHz, corresponding to each dipeptide's component (in bold for each case) $^{13}C_\alpha$ and $^{13}C_\beta$ nuclei, respectively.

Dipeptides correlation times (τ_c) from $^{13}C_\alpha$ and $^{13}C_\beta$ relaxation data *vs.* their M_W

1st order data fitting

Table S7. Statistics for a least-squares linear (1st degree polynomial) regression analysis of dipeptides correlation times (τ_C) from $^{13}C_\alpha$ and $^{13}C_\beta$ T_1 values *vs.* their M_W (*see* Fig. 1).

	α_0	α_1	R^2	S.S.
		$^{13}C_\alpha$ (Fig. 1a)		
Dipeptides (pH = 6.0)	0.5041 ± 0.0273	0.0034 ± 0.0001	0.90	0.0484
		$^{13}C_\beta$ (Fig. 1b)		
Dipeptides (pH = 6.0)	0.5065 ± 0.0270	0.0034 ± 0.0002	0.92	0.0395

2nd order data fitting

Table S8. Statistics for a least-squares nonlinear (2nd degree polynomial) regression analysis of dipeptides correlation times (τ_C) from $^{13}C_\alpha$ and $^{13}C_\beta$ T_1 values *vs.* their M_W (*see below* Fig. S2).

	α_0	α_1	α_2	R^2	S.S.
			$^{13}C_\alpha$ (Fig. S2a)		
Dipeptides (pH = 6.0)	1.1730 ± 0.1553	-0.0035 ± 0.0016	$1.687\times10^{-5} \pm 3.867\times10^{-6}$	0.91	0.044
			$^{13}C_\beta$ (Fig. S2b)		
Dipeptides (pH = 6.0)	1.0070 ± 0.1484	-0.0017 ± 0.0015	$1.229\times10^{-5} \pm 3.588\times10^{-6}$	0.93	0.0368

$^{13}C_{\alpha}$ & $^{13}C_{\beta}$–NMR
(2^{nd} order)

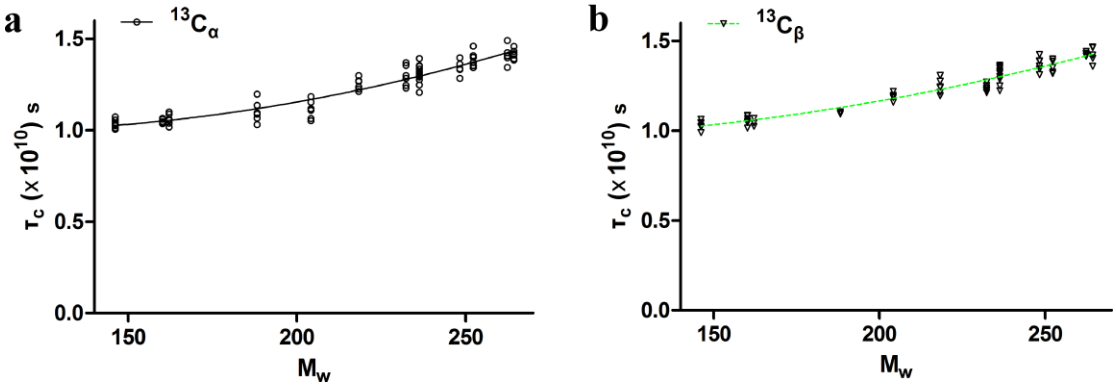

Fig. S2. Statistics for a least-squares nonlinear regression (2^{nd} degree polynomial) analysis of dipeptides correlation times (τ_C) from $^{13}C_{\alpha}$ and $^{13}C_{\beta}$ T_1 values. (a) The correlation times τ_C derived from $^{13}C_{\alpha}$ T_1 relaxation data *vs* dipeptides M_W. (b) The correlation times, τ_C , derived from $^{13}C_{\beta}$ T_1 relaxation data *vs* dipeptides M_W.

Alanine Dipeptide–Fully optimized structure by DFT

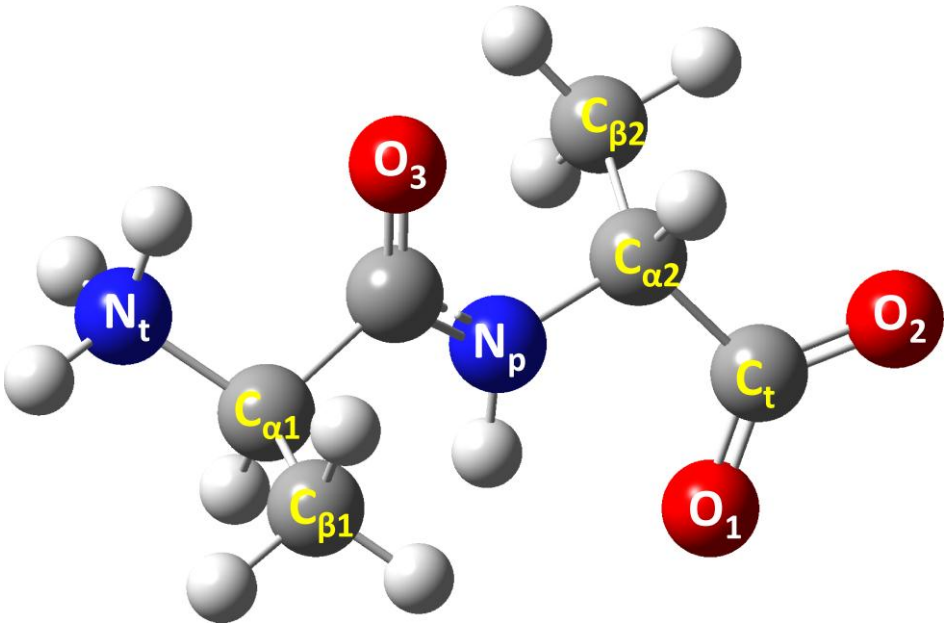

Fig. S3. The fully optimized neutral pH structure of alanine dipeptide in aqueous solution. The unconstraint optimization performed at the X3LYP/cc-pVTZ level of theory using the IEF-PCM model for bulk water and characterized by vibrational analysis at the same level of theory, resulting in the most stable AD structure. Geometrical details and energetics of the above fully optimized structure are reported at the end of ESI.

H-bonds interaction energies (E_{int}) calculation

The H-bond interaction energy is the energy of interaction of all the separated molecules in the solvated complexes and it can be calculated through the following equation:

$$E_{int} = E_{AB}(AB) - \left[E_A(AB) + E_B(AB)\right], \quad \text{(S10)}$$

where $E_{AB}(AB)$ is the energy of the AD/H_2Os supermolecule, and $E_A(AB)$ and $E_B(AB)$ are the single-point energies of monomers A (energy calculation of the AD structure at the same intermolecular configuration as in the fully optimized supermolecule in the absence of the H-bonded H_2Os cluster counterpart) and B (energy calculation of the H-bonded H_2Os cluster structure at the same intermolecular configuration as in the fully optimized supermolecule in the absence of the AD counterpart), respectively. Namely, comparison between the interaction energies (E_{int}) for the AD/$(H_2Os)_n$ (n = 7-9) supermolecules indicates the most favorably stabilized complex. All energy calculations performed at the X3LYP/cc-PVTZ level of theory and the IEF-PCM model was applied to mimic aqueous solution.

The following Supplementary Table S9 collects the electronic and interaction energies for the hydrated AD/$(H_2Os)_n$ (n = 7-9) and Supplementary Fig. S4 presents their interaction energies evolution.

Table S9. Total energy, E_{tot}, (in Hartree) and interaction energy, E_{int}, (in kcal mol^{-1}) for the hydrated AD/$(H_2Os)_n$ (n = 7–9) supermolecules calculated at X3LYP/cc-PVTZ level of theory, applying the IEF-PCM model for bulk water.

	AD/7 H_2Os	AD/8 H_2Os	AD/9 H_2Os
$-E_{tot}$	1106.225	1182.681	1259.143
$-E_{int}$	55.04	59.28	56.10

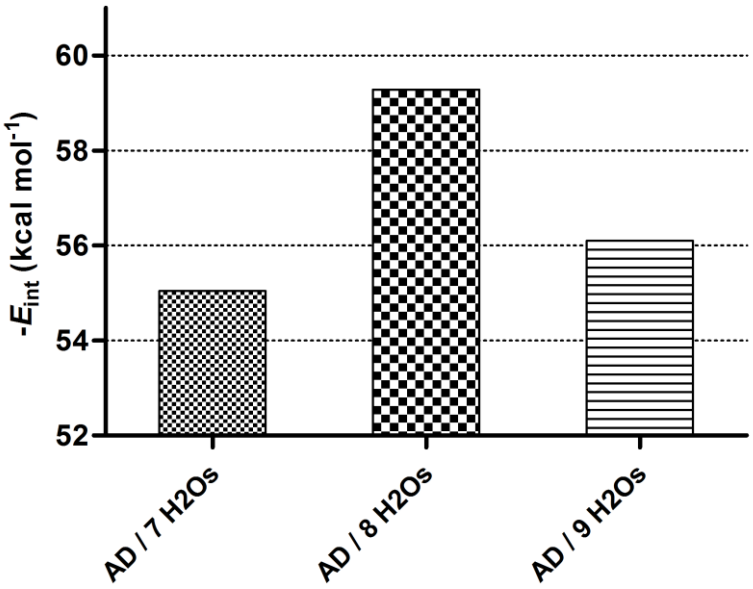

Fig. S4. Comparison between E_{int} for the three AD/H_2Os supermolecules. The AD/8 H_2Os supermolecule exhibits the highest interaction energy among the ones studied, implying its extra stabilization and providing further support to our spectroscopic results.

Alanine Dipeptide/10 H_2Os complex

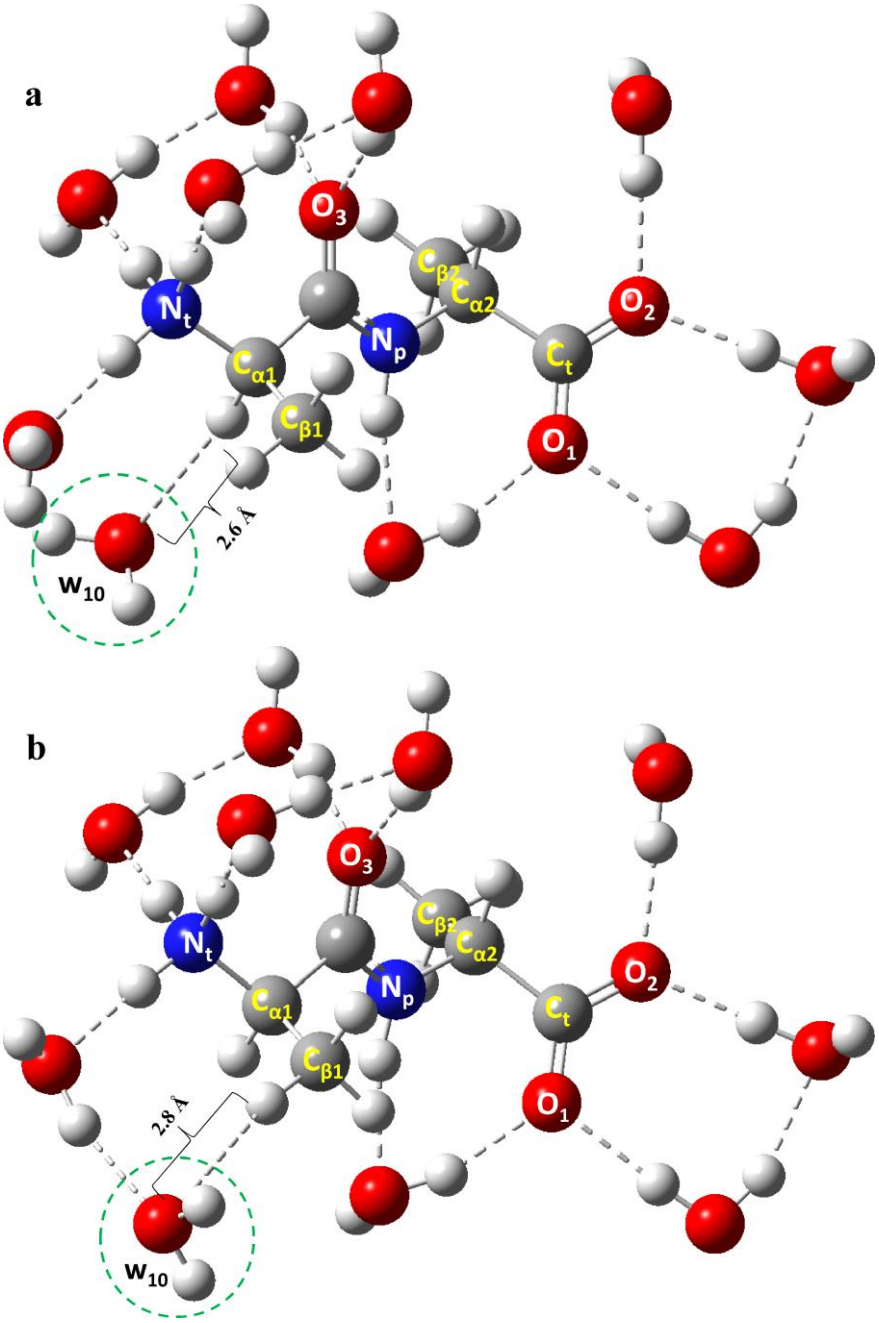

Fig. S5. DFT calculations of alanine dipeptide/10 H_2Os supermolecule. DFT calculations demonstrated that the tenth H_2O (w_{10}) directly interacts either with (a) C_α or (b) CH_3 of AD. Both H-bond lengths vary between 2.6-2.8 Å. Comparison between these H-bond lengths and those of all other bound H_2Os with the polar sides of AD (<1.9 Å) indicates the weakness of the w_{10} H-bonds, as expected from similar studies,[6,7] implying their insignificant contribution to the AD τ_C values.

Supplementary References

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Geometrical details and energetics of fully optimized AD/$(H_2O)_n$ (n=0, 7-9) supermolecules

AD/$(H_2O)_0$ (Fig. S3)

(Charge = 0)
23 Atoms
E = -571.319175 Hartrees

	X	Y	Z
N	-3.363505	0.501270	-0.539515
H	-3.223236	1.099927	-1.365991
C	-2.233749	-0.475329	-0.373587
C	-1.039501	0.347815	0.132543
O	-1.257258	1.305006	0.881926
H	-3.393056	1.121809	0.284604
H	-4.273866	0.034174	-0.646646
N	0.157781	-0.081908	-0.247650
H	0.252456	-0.880221	-0.874850
C	1.423646	0.463992	0.237745
C	1.777342	1.781061	-0.460973
H	1.004763	2.529077	-0.287003
H	2.723579	2.156035	-0.074378
H	1.877566	1.627849	-1.537039
H	1.326736	0.644551	1.310613
C	2.546695	-0.585860	0.027078
O	2.287479	-1.561270	-0.721414
O	3.624811	-0.345058	0.614735

C	-2.625978	-1.547365	0.636995
H	-1.807873	-2.257129	0.747358
H	-2.833833	-1.104975	1.611957
H	-3.506445	-2.094167	0.297737
H	-2.037712	-0.907769	-1.357009

AD/$(H_2O)_7$ (Fig. 4a)

(Charge = 0)
44 Atoms
E = -1106.225237 Hartrees

	X	Y	Z
N	-3.673901	0.000577	0.178751
H	-3.811490	0.759198	-0.510630
C	-2.379877	-0.707925	-0.046288
C	-1.246826	0.323213	-0.132493
O	-1.376587	1.457456	0.354653
H	-3.683423	0.450929	1.111931
H	-4.457398	-0.674529	0.110743
H	-2.368847	1.710363	2.012404
O	-3.087333	1.394518	2.586378
H	-3.592716	2.176458	2.832510
H	-6.120146	-2.281001	0.701678
O	-5.719616	-1.927333	-0.100112
H	-5.535906	-2.696687	-0.650514
H	-2.716507	2.562320	-0.847700
O	-3.583279	2.443005	-1.262457
H	-3.438754	2.559266	-2.207439
N	-0.148386	-0.113853	-0.738600
H	-0.132066	-1.068175	-1.095101
C	1.088796	0.650918	-0.831747
C	1.472550	0.882483	-2.297545
H	0.694997	1.451260	-2.805222

H	2.406273	1.438455	-2.356381
H	1.603817	-0.066661	-2.818298
H	0.909026	1.606934	-0.349579
C	2.258696	-0.035354	-0.093259
O	2.225905	-1.277460	0.086959
O	3.201632	0.727039	0.244658
O	4.646675	-2.583728	0.641263
H	3.784708	-2.145572	0.504867
H	5.239623	-1.823661	0.760560
O	5.734319	0.031421	1.023822
H	4.822238	0.285166	0.754201
H	5.734553	0.108228	1.983275
O	0.473151	-2.902402	-1.204534
H	0.846640	-3.207000	-2.037409
H	1.205615	-2.449168	-0.730631
O	2.929379	3.466601	0.244993
H	3.168633	3.766024	-0.636868
H	3.037398	2.492541	0.217899
C	-2.140190	-1.720702	1.071575
H	-2.030289	-1.220717	2.033420
H	-2.977487	-2.414635	1.130457
H	-1.238825	-2.292347	0.865391
H	-2.466511	-1.222794	-1.001062

AD/$(H_2O)_8$ (Fig. 4b)

(Charge = 0)
47 Atoms
E = -1182.680546 Hartrees

	X	Y	Z
N	3.434416	-0.128901	-0.285361
H	3.756841	0.458711	0.503587
C	2.285391	-0.996160	0.106950
C	1.161818	-0.104155	0.658111
O	1.359312	1.111479	0.833016
H	3.161189	0.506266	-1.063911
H	4.221527	-0.723322	-0.600738
H	2.267143	1.259833	-3.188875
O	2.563242	1.606225	-2.341138
H	1.836212	2.169895	-2.009320
H	5.591027	-2.061822	-2.085229
O	5.526028	-1.843717	-1.148972
H	5.656246	-2.678922	-0.686574
H	2.961728	1.756299	1.839858
O	3.929524	1.700989	1.852084
H	4.161594	1.388118	2.732841
N	0.017596	-0.718041	0.927748
H	-0.060622	-1.723531	0.782704
C	-1.174700	-0.035272	1.430844
C	-1.543266	-0.539335	2.828405
H	-0.728345	-0.348775	3.525554

H	-2.433973	-0.024949	3.187347
H	-1.746455	-1.609745	2.811202
H	-0.943687	1.023381	1.473640
C	-2.371376	-0.233094	0.472307
O	-2.571893	-1.381849	0.004950
O	-3.091702	0.776380	0.268103
O	-4.893984	-1.883527	-1.508438
H	-4.074266	-1.768043	-0.991794
H	-5.213348	-0.968897	-1.586611
O	-5.264368	0.938206	-1.377326
H	-4.480971	0.877032	-0.782862
H	-4.918978	1.285200	-2.205898
O	-0.870899	-3.443041	0.373978
H	-1.122363	-4.010713	1.109128
H	-1.616497	-2.812882	0.247598
O	-2.062264	3.368806	0.240887
H	-1.250559	3.295631	-0.281715
H	-2.428606	2.464309	0.265865
C	1.866012	-1.854824	-1.083047
H	1.477172	-1.234666	-1.890280
H	2.724208	-2.413646	-1.452571
H	1.100512	-2.569896	-0.793990
H	2.634052	-1.633278	0.919731
O	0.637903	3.075571	-0.930931
H	1.032891	3.924239	-0.700662
H	0.841791	2.475630	-0.185854

AD/$(H_2O)_9$ (Fig. 4c)

(Charge = 0)
50 Atoms
E = -1259.143155 Hartrees

	X	Y	Z
N	3.357274	0.593994	-0.009983
H	3.460086	0.050831	-0.896344
C	1.981153	1.150250	0.122246
C	0.958941	0.028393	-0.064830
O	1.231417	-1.134524	0.283619
H	3.608248	-0.023611	0.793264
H	4.034096	1.381358	-0.025611
H	4.492554	-0.439896	2.934714
O	4.201584	-0.957258	2.165838
H	3.452703	-1.510185	2.480923
H	5.519032	3.071433	0.786766
O	5.104382	2.794691	-0.049018
H	4.773340	3.616997	-0.450799
H	2.939250	-1.643159	-2.297109
O	3.571107	-0.893304	-2.359020
H	3.341084	-0.422364	-3.177055
N	-0.200452	0.406058	-0.583218
H	-0.310469	1.381208	-0.867761
C	-1.348435	-0.480680	-0.740622
C	-1.534613	-0.882665	-2.209094
H	-0.651362	-1.410598	-2.566329

H	-2.397392	-1.539558	-2.306784
H	-1.696443	-0.002477	-2.833066
H	-1.151662	-1.372949	-0.152481
C	-2.647083	0.157508	-0.200873
O	-2.726538	1.406775	-0.110643
O	-3.564559	-0.657490	0.075487
O	-5.189716	2.546848	0.701655
H	-4.320852	2.180504	0.453932
H	-5.703882	1.740344	0.873136
O	-6.086478	-0.136768	1.047387
H	-5.191008	-0.326967	0.690285
H	-6.017032	-0.328865	1.995660
O	-0.879165	3.170384	-1.051268
H	-1.095044	3.429446	-1.961628
H	-1.666329	2.686964	-0.722336
O	-3.010987	-3.362417	0.377545
H	-3.145674	-3.767294	-0.491534
H	-3.230266	-2.417982	0.249648
C	1.812802	1.827300	1.481049
H	1.913734	1.106205	2.291894
H	2.567196	2.603412	1.607263
H	0.830785	2.291685	1.543914
H	1.860316	1.885636	-0.676348
O	1.909502	-2.319585	2.723401
H	1.948251	-3.286639	2.635873
H	1.537323	-1.996991	1.883892

O	1.639892	-2.782278	-1.943045
H	1.391555	-2.423620	-1.072964
H	1.869993	-3.714441	-1.793358