Supplementary Information

for

Fourier Transform Microwave Spectroscopy of Ac-Ser-NH_2: The Role of the Side Chain Interactions in Peptide Folding

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Table S1. Calculated spectroscopic parameters for the five lowest energy conformers of Ac-Ser-NH_2 at the B3LYP/6-311++G(d,p) level of theory.

	C_7^{eq}-I	C_5-I	C_7^{eq}-II	C_5-II	C_5-III
A[a]	1854	1953	2110	1960	1838
B	992	888	862	853	952
C	741	651	693	734	666
$\|\mu_a\|$	1.9	1.3	3.5	1.5	2.5
$\|\mu_b\|$	0.4	0.5	0.8	0.3	1.9
$\|\mu_c\|$	0.1	0.4	2.2	0.5	0.6
N_c/χ_{aa}	2.16	2.58	2.33	2.45	2.38
N_c/χ_{bb}	-0.48	0.85	-2.25	-1.45	1.31
N_c/χ_{cc}	-1.68	-3.43	0.08	-1.00	-3.69
N_t/χ_{aa}	0.63	2.38	0.22	1.88	2.18
N_t/χ_{bb}	1.65	1.58	2.33	-0.28	1.02
N_t/χ_{cc}	-2.28	-3.96	-2.55	-1.60	-3.20
ΔE[b]	0	938	1069	2013	1176
ΔG[c]	0	561	848	1310	767

[a] A, B, and C represent the rotational constants (in MHz); Δ_J is the quartic centrifugal distortion constant (in kHz), χ_{aa}, χ_{bb} and χ_{cc} are the diagonal elements of the ^{14}N nuclear quadrupole coupling tensor (in MHz); N_c and N_t correspond to the central and terminal ^{14}N nuclei respectively; μ_a, μ_b and μ_c are the electric dipole moment components (in D). [b] Relative energies (in cm^{-1}) with respect to the global minimum calculated at MP2/6-311++G(d,p) level of theory. [c] Gibbs energies (in cm^{-1}) calculated at 298 K at B3LYP/6-311++G(d,p) level of theory.

Table S2. Measured frequencies and residuals (in MHz) for the nuclear quadrupole coupling hyperfine components of the C_7^{eq}-I conformer of Ac-Ser-NH_2.

J′	K′$_{-1}$	K′$_{+1}$	J′′	K′′$_{-1}$	K′′$_{+1}$	I′	F′	I′′	F′′	$\nu_{obs.}$	$\nu_{obs.}$-$\nu_{cal.}$
2	1	2	1	1	1	2	4	2	3	3253.2947	-0.0016
2			1			2	3	2	2	3253.6556	-0.0033
2			1			1	3	1	2	3253.7713	0.0013
2			1			2	3	2	3	3254.0502	0.0004
2	0	2	1	0	1	1	2	1	1	3457.7848	0.0004
2			1			2	4	2	3	3457.8059	0.0009
2			1			1	3	1	2	3457.9453	0.0020
2			1			0	2	2	1	3458.3416	0.0000
2			1			2	1	2	1	3458.4543	0.0003
2	1	1	1	1	0	2	4	2	3	3755.1759	0.0004
2			1			1	1	1	0	3755.7180	0.0044
3	1	3	2	1	2	2	5	2	4	4853.3402	-0.0009
3			2			0	3	0	2	4853.4209	-0.0034
3			2			2	4	2	3	4853.4689	-0.0003
3			2			1	4	1	3	4853.5106	0.0010
3			2			2	3	2	2	4853.6782	-0.0011
3	0	3	2	0	2	2	5	2	4	5080.1787	-0.0002
3			2			2	4	2	3	5080.2553	0.0001
3			2			0	3	0	2	5080.2829	-0.0003
3			2			1	4	1	3	5080.3450	0.0002
3			2			2	3	2	2	5080.4511	0.0007
3	1	3	2	0	2	2	5	2	4	5527.1869	-0.0015
3			2			2	4	2	3	5527.3630	0.0023
3			2			1	4	1	3	5527.4459	-0.0021
3			2			2	3	2	2	5527.6396	0.0002
3	1	2	2	1	1	1	3	1	2	5600.4904	0.0014
3			2			2	5	2	4	5600.5726	0.0021
3			2			0	3	0	2	5600.5994	0.0016
3			2			2	4	2	3	5600.6513	0.0019
3			2			1	4	1	3	5600.7512	0.0012
4	0	4	3	1	3	2	5	2	4	6169.1921	0.0018
4			3			2	6	2	5	6169.2007	0.0005
4			3			1	4	1	3	6169.2270	-0.0016
4			3			1	5	1	4	6169.2591	0.0027
4	1	4	3	1	3	2	6	2	5	6428.1234	-0.0002
4			3			1	4	1	3	6428.1421	0.0019
4			3			2	5	2	4	6428.1947	-0.0002
4			3			1	5	1	4	6428.2288	-0.0003
4			3			2	4	2	3	6428.3229	-0.0002
4	0	4	3	0	3	1	4	1	3	6616.1990	-0.0041
4			3			2	6	2	5	6616.2096	-0.0002
4			3			0	4	0	3	6616.2521	0.0001
4			3			2	2	2	1	6616.2614	0.0000
4			3			1	3	1	2	6616.2826	-0.0008
4			3			2	5	2	4	6616.2973	0.0014
4			3			1	5	1	4	6616.3584	-0.0011
4			3			2	3	2	2	6616.4228	-0.0010
4			3			2	4	2	3	6616.4596	-0.0021
4	1	4	3	0	3	2	6	2	5	6875.1312	-0.0019
4			3			0	4	0	3	6875.1638	0.0065
4			3			1	3	1	2	6875.2791	0.0005
4			3			2	5	2	4	6875.2996	-0.0009
4			3			1	5	1	4	6875.3341	0.0019
4			3			2	3	2	2	6875.3713	-0.0010
4			3			2	4	2	3	6875.5089	-0.0031

4	2	3	3	2	2	2	2	2	1	6972.0959	0.0009
4			3			0	4	2	4	6972.1293	0.0015
4			3			2	6	2	5	6972.1939	-0.0001
4			3			2	3	2	2	6972.2219	-0.0005
4			3			1	5	1	4	6972.2989	-0.0004
4			3			1	3	1	2	6972.4522	0.0011
4			3			2	5	2	4	6972.4712	-0.0022
4			3			2	4	2	3	6972.5680	-0.0018
4	2	2	3	2	1	1	3	1	2	7364.0801	-0.0030
4			3			2	2	2	1	7364.1195	0.0003
4			3			2	5	2	4	7364.1366	-0.0019
4			3			0	4	1	3	7364.1564	-0.0001
4			3			2	6	2	5	7364.1938	-0.0028
4			3			1	4	0	3	7364.2049	0.0013
4			3			2	4	2	3	7364.3187	-0.0026
4			3			2	3	2	2	7364.4030	0.0013
4			3			1	5	1	4	7364.4225	-0.0011
4	1	3	3	1	2	2	6	2	5	7399.5038	0.0009
4			3			2	5	1	4	7399.5964	0.0004
5	1	5	4	1	4	2	7	2	6	7978.6505	-0.0002
5			4			1	5	1	4	7978.6678	0.0009
5			4			0	5	0	4	7978.6802	0.0007
5			4			2	6	2	5	7978.7055	0.0013
5			4			1	6	1	5	7978.7263	-0.0008
5			4			2	4	2	3	7978.7830	0.0003
5			4			2	5	2	4	7978.7943	0.0009
5	0	5	4	0	4	2	7	2	6	8102.7330	-0.0004
5			4			1	5	1	4	8102.7413	0.0009
5			4			2	3	2	2	8102.7745	0.0027
5			4			1	4	1	3	8102.8155	0.0003
5			4			2	6	2	5	8102.8184	0.0005
5			4			1	6	1	5	8102.8389	-0.0008
5			4			2	4	2	3	8102.8784	-0.0024
5			4			2	5	2	4	8102.9351	0.0005

Table S3. Observed splittings and residuals (in MHz) for the A-E internal rotation components of conformer of Ac-Ser-NH_2.

J′	K'_{-1}	K'_{+1}	J′′	K''_{-1}	K''_{+1}	$\nu_A - \nu_{E\ obs.}$	$(\nu_A-\nu_E)_{obs}-(\nu_A-\nu_E)_{cal.}$
4	1	4	3	1	3	-133.667	-0.025
4	0	4	3	0	3	125.073	-0.042
4	3	2	3	3	1	-24.529	0.031
4	2	3	3	2	2	-165.277	-0.014
4	3	1	3	3	0	24.177	0.031
4	2	2	3	2	1	146.979	0.063
4	1	3	3	1	2	64.338	-0.016
5	1	5	4	1	4	-134.729	-0.037
5	0	5	4	0	4	136.462	-0.042
6	1	6	5	1	5	-116.850	-0.074
6	0	6	5	0	5	123.951	0.110
6	1	5	5	1	4	97.913	-0.113
7	1	7	6	1	6	-100.275	-0.061
7	0	7	6	0	6	110.650	-0.064
5	1	4	4	1	3	72.986	0.054
5	2	4	4	2	3	-167.577	0.092

5	3	3	4	3	2	-70.178	0.081
5	3	2	4	3	1	65.861	0.073
5	2	3	4	2	2	145.176	-0.099
6	2	5	5	2	4	-147.712	0.053
6	3	4	5	3	3	-145.442	0.113
6	4	3	5	4	2	-18.007	0.075
6	4	2	5	4	1	21.677	-0.101
6	3	3	5	3	2	133.416	0.097
6	2	4	5	2	3	114.593	0.126

Table S4. Cartesian coordinates for the observed conformer C_7^{eq}-I of Ac-Ser-NH_2. The geometries have been optimized *ab initio* at the MP2/6-311++G(d,p) level of theory.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.479284	-0.126350	0.674310
2	6	1.055048	1.063997	-0.109246
3	8	2.115418	0.977364	-0.728395
4	7	-0.633231	-0.715006	-0.055524
5	6	-1.892558	-0.204305	0.002065
6	8	-2.157398	0.808884	0.654990
7	7	0.303976	2.190820	-0.038313
8	1	-0.410814	-1.491390	-0.665654
9	1	0.546643	2.949994	-0.659323
10	1	0.100795	0.226145	1.640869
11	6	1.543959	-1.197376	0.884613
12	1	1.133150	-1.995914	1.507231
13	1	2.405935	-0.754173	1.396132
14	8	1.919293	-1.790216	-0.349246
15	1	2.340579	-1.069608	-0.839718
16	6	-2.949630	-0.964363	-0.766858
17	1	-3.448726	-0.274054	-1.450278
18	1	-2.544413	-1.808066	-1.329358
19	1	-3.694440	-1.330039	-0.055869
20	1	-0.645836	2.112288	0.312787