Supplementary Material (ESI) for *Physical Chemistry Chemical Physics*

Seven Structures of Threonine in the Gas Phase: a LA-MB-FTMW Study

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Supplementary Information

Table S1. Observed frequencies and residuals (in MHz) for the nuclear quadrupole coupling hyperfine components of the conformer Ia of threonine

J´	K'_{-1}	K'_{+1}	J´´	K''_{-1}	K''_{+1}	F´	F´´	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
2	0	2	1	0	1	3	2	5560.819	0.000
						2	1	5560.813	-0.000
						1	0	5559.638	-0.002
						2	2	5559.560	0.003
						1	1	5562.775	-0.000
2	1	1	1	1	0	3	2	6038.528	0.001
						2	1	6037.220	0.003
						1	0	6039.693	0.003
						2	2	6037.670	-0.003
2	1	1	1	0	1	3	2	7699.622	0.005
						2	1	7700.018	0.002
						1	0	7698.209	0.001
2	2	0	1	1	0	3	2	9909.456	-0.002
						2	1	9910.257	-0.001
						1	0	9909.435	-0.004
3	0	3	2	0	2	4	3	8160.523	-0.001
						3	2	8160.585	0.000
						2	1	8160.245	0.001
						3	3	8159.323	0.000
						2	2	8162.208	0.001
3	1	3	2	1	2	4	3	7818.995	-0.001
						3	2	7818.650	-0.004
						3	3	7818.160	-0.003
						2	2	7819.780	0.000
3	1	2	2	1	1	4	3	9001.385	-0.003
						3	2	9001.038	-0.003
						2	1	9001.330	-0.003
4	1	4	3	1	3	5	4	10352.605	0.002
						4	3	10352.471	0.000
						3	2	10352.562	0.003

Table S2. Observed frequencies and residuals (in MHz) for the nuclear quadrupole coupling hyperfine components of the conformer IIa of threonine

J´	K'_{-1}	K'_{+1}	J´´	K''_{-1}	K''_{+1}	F´	F´´	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
2	0	2	1	0	1	3	2	5589.264	0.000
						2	1	5589.495	-0.009
						1	0	5588.986	-0.001
3	0	3	2	0	2	4	3	8143.823	-0.001
						3	2	8144.124	0.001
						2	1	8143.742	0.003
3	1	3	2	0	2	4	3	8671.162	0.000
						3	2	8671.800	-0.003
3	1	2	2	1	1	4	3	9176.274	-0.002
						3	2	9176.297	0.004
						2	1	9176.102	0.003
3	0	3	2	1	2	4	3	7252.703	-0.003
						3	2	7252.403	0.001
3	1	3	2	1	2	4	3	7780.040	0.002
						3	2	7780.075	-0.007
						2	1	7780.155	-0.001
4	0	4	3	0	3	5	4	10538.645	-0.001
						4	3	10538.901	0.001
						3	2	10538.614	0.002
4	1	4	3	1	3	5	4	10277.520	-0.001
						4	3	10277.598	0.000
						3	2	10277.561	-0.002
4	1	3	3	1	2	5	4	12065.812	-0.003
						4	3	12065.945	0.000
						3	2	12065.703	-0.004
5	0	5	4	0	4	6	5	12873.578	0.002
						5	4	12873.761	0.002

Table S3. Observed frequencies and residuals (in MHz) for the nuclear quadrupole coupling hyperfine components of the conformer $III_{\alpha}a$ of threonine

J´	K´$_{-1}$	K´$_{+1}$	J´´	K´´$_{-1}$	K´´$_{+1}$	F´	F´´	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
1	1	1	0	0	0	2	1	4131.633	-0.005
						1	1	4132.411	0.002
						0	1	4130.482	-0.000
2	0	2	1	0	1	1	0	5572.478	-0.001
						2	1	5573.601	0.001
						3	2	5573.636	-0.001
						1	1	5575.593	0.000
						2	2	5572.363	0.001
2	1	2	1	1	1	3	2	5298.052	-0.002
2	1	1	1	1	0	2	1	5957.750	0.001
						3	2	5959.053	0.004
2	1	2	1	0	1	3	2	6615.327	-0.003
2	2	1	1	1	1	1	0	10242.354	-0.002
						2	1	10242.506	0.000
						3	2	10241.945	0.004
3	0	3	2	0	2	2	1	8232.497	0.004
						3	2	8232.795	-0.004
						4	3	8232.769	0.002
3	1	3	2	1	2	3	2	7914.664	0.001
						4	3	7915.013	0.002
3	1	2	2	1	1	3	2	8900.366	-0.002
						4	3	8900.720	-0.003

Table S4. Observed frequencies and residuals (in MHz) for the nuclear quadrupole coupling hyperfine components of the conformer IIb of threonine

J´	K'_{-1}	K'_{+1}	J´´	K''_{-1}	K''_{+1}	F´	F´´	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
2	0	2	1	0	1	3	2	5574.455	0.001
						2	1	5574.390	0.003
						1	0	5573.502	0.002
						2	2	5573.340	0.001
						1	1	5576.122	-0.000
2	1	2	1	1	1	3	2	5337.580	-0.003
						2	1	5336.494	-0.002
						1	0	5338.682	0.001
2	1	1	1	1	0	3	2	5869.248	0.001
						2	1	5868.163	0.003
						1	0	5870.349	0.002
3	0	3	2	0	2	4	3	8291.726	0.000
						3	2	8291.700	0.003
						2	1	8291.509	0.002
						3	3	8290.584	0.002
						2	2	8293.245	0.003
3	1	3	2	1	2	4	3	7989.005	-0.001
						3	2	7988.697	0.001
						2	1	7988.990	-0.008
3	1	2	2	1	1	4	3	8784.532	-0.001
						3	2	8784.222	-0.003
						2	1	8784.522	-0.004
3	0	3	2	1	2	4	3	6830.094	-0.000
						3	2	6829.511	-0.001
						2	1	6830.180	-0.002
						3	3	6828.950	0.000
						2	2	6831.061	0.003
3	1	3	2	0	2	4	3	9450.637	-0.001
						3	2	9450.881	0.001
						2	1	9450.322	-0.001
						3	3	9449.767	0.002
						2	2	9452.057	-0.002
4	0	4	3	0	3	5	4	10936.504	0.001
						4	3	10936.492	0.001
						3	2	10936.401	0.001

Table S5. Observed frequencies and residuals (in MHz) for the nuclear quadrupole coupling hyperfine components of the conformer $III_{\beta}b$ of threonine

J´	K´$_{-1}$	K´$_{+1}$	J´´	K´´$_{-1}$	K´´$_{+1}$	F´	F´´	$\nu_{obs.}$	$\nu_{obs.}$-$\nu_{cal.}$
3	0	3	2	0	2	4	3	8071.626	0.001
						3	2	8071.530	-0.000
3	1	3	2	1	2	4	3	7779.043	-0.002
						3	2	7778.817	-0.002
						2	1	7778.968	0.000
3	1	2	2	1	1	4	3	8511.135	0.002
						3	2	8510.938	0.002
						2	1	8511.213	0.000
4	0	4	3	0	3	5	4	10667.426	-0.000
						4	3	10667.322	-0.002
						3	2	10667.376	0.001
4	1	4	3	1	3	5	4	10348.939	0.000
						4	3	10348.821	-0.001
						3	2	10348.882	0.004
4	1	3	3	1	2	5	4	11319.247	-0.002
						4	3	11319.143	-0.002
						3	2	11319.262	-0.000
5	0	5	4	0	4	6	5	13201.545	-0.003
						5	4	13201.444	0.002
						4	3	13201.519	0.001

Table S6. Spectroscopic constants[a] for the observed conformers of threonine.

	Ia	**I'b**	**IIa**	**IIb**	**IIc**	**III$_\alpha$a**	**III$_\beta$b**
A (MHz) [a]	2872.77049(48) [b]	3148.59247(32)	2912.6227(20)	3232.4827(12)	2670.72096(53)	2889.93352(45)	3379.841(14)
B (MHz)	1608.95699(26)	1506.27679(37)	1660.21807(34)	1533.71801(32)	1784.66894(60)	1572.32152(50)	1482.04984(21)
C (MHz)	1211.39762(38)	1316.33575(44)	1189.31443(34)	1267.88615(34)	1383.75384(51)	1241.83423(47)	1237.59121(22)
Δ_J (kHz) [a]	0.197(13)	0.409(18)	0.1393(83)	0.183(12)	0.278(15)	0.384(26)	0.1182(71)
χ_{aa} (MHz) [a]	-4.1859(25)	-0.7403(21)	-0.544(11)	-3.4971(21)	-3.7652(73)	-4.1529(32)	-2.201(14)
χ_{bb} (MHz)	2.6611(42)	2.8781(28)	2.582(16)	1.7519(27)	2.4258(75)	2.5682(46)	-0.157(50)
χ_{cc} (MHz)	1.5248(17)	-2.1378(70)	-2.038(50)	1.7452(60)	1.3394(20)	1.5846(46)	2.358(64)
N [c]	30	27	27	35	22	22	20
σ (kHz)[d]	2.4	2.1	3.0	2.4	2.6	2.4	1.6

[a] The Hamiltonian $\boldsymbol{H} = \boldsymbol{H_R}^{(A)} + \boldsymbol{H_Q}$ is constructed in the coupled basis set $I + J = F$ and diagonalized. The semirigid Watson Hamiltonian is given by

$$\boldsymbol{H}_R^{(A)} = A\,\boldsymbol{P}_a^2 + B\,\boldsymbol{P}_b^2 + C\,\boldsymbol{P}_c^2 - \Delta_J\,\boldsymbol{P}^4 - \Delta_{JK}\,\boldsymbol{P}^2\boldsymbol{P}_a^2 - \Delta_K\,\boldsymbol{P}_a^4 - 2\,\delta_J\,\boldsymbol{P}^2(\boldsymbol{P}_b^2 - \boldsymbol{P}_c^2) - \delta_K[\boldsymbol{P}_a^2(\boldsymbol{P}_b^2 - \boldsymbol{P}_c^2) + (\boldsymbol{P}_b^2 - \boldsymbol{P}_c^2)\boldsymbol{P}_a^2] \quad (2)$$

where the coefficients A, B, C represent the rotational constants and Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. Only Δ_J needed to be floated to obtain an rms deviation of the fit consistent with the estimated frequency accuracy. The term $\boldsymbol{H}_Q$ accounts for the interaction energy of the ^{14}N electric quadrupole moment (eQ) with the molecular electric field gradient ($q_{\alpha\beta}=\partial^2 V/\partial\alpha\partial\beta$; α, β = a, b, c) at the nitrogen nucleus. χ_{aa} , χ_{bb} , and χ_{cc} are the diagonal elements of the ^{14}N nuclear quadrupole coupling tensor.

[b] Standard error in parentheses in units of the last digit.

[c] Number of fitted transitions.

[d] rms of the fit.

Table S7. Observed frequencies and residuals (in MHz) for the nuclear quadrupole coupling hyperfine components of the conformer IIc of threonine

J′	K'_{-1}	K'_{+1}	J′′	K''_{-1}	K''_{+1}	F′	F′′	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal}$
2	1	2	1	0	1	3	2	6821.880	-0.001
						2	1	6822.580	0.000
						2	2	6821.449	-0.001
2	2	1	1	1	0	3	2	9395.705	-0.001
						2	1	9396.518	0.004
						1	0	9395.638	0.001
						2	2	9396.913	-0.003
3	0	3	2	1	2	4	3	8522.511	0.004
						3	2	8521.936	0.002
						2	1	8522.619	0.001
3	1	3	2	0	2	4	3	9436.649	-0.002
						3	2	9437.014	-0.001
						2	1	9436.298	-0.002
4	0	4	3	1	3	5	4	11554.619	-0.001
						4	3	11554.407	-0.001
						3	2	11554.602	-0.006
4	1	4	3	0	3	5	4	12021.630	0.004
						4	3	12021.793	0.001
						3	2	12021.492	0.002

Table S8. Observed frequencies and residuals (in MHz) for the nuclear quadrupole coupling hyperfine components of the conformer I'b of threonine

J′	K'_{-1}	K'_{+1}	J′′	K''_{-1}	K''_{+1}	F′	F′′	$\nu_{obs.}$	$\nu_{obs.}-\nu_{cal.}$
2	1	1	1	0	1	3	2	7667.578	-0.000
						2	1	7666.878	0.003
						1	0	7667.759	-0.000
						2	2	7666.650	-0.003
						1	1	7668.317	0.003
2	1	2	1	0	1	3	2	7097.395	-0.001
						2	1	7098.307	0.001
						1	0	7096.681	-0.002
2	2	0	1	1	0	3	2	10777.501	0.001
						2	1	10778.291	0.000
						1	0	10776.458	0.003
						2	2	10777.649	-0.000
						1	1	10778.057	-0.001
2	2	1	1	1	1	3	2	10952.130	-0.002
						2	1	10951.503	-0.004
						1	0	10953.297	0.002
2	2	1	1	1	0	3	2	10761.942	0.002
3	1	2	2	0	2	4	3	10780.517	0.002
						3	2	10779.676	0.002
						2	1	10780.778	-0.001
						3	3	10779.526	0.001
						2	2	10781.006	-0.005
3	2	1	2	1	1	4	3	13471.611	-0.002
						3	2	13472.313	0.001
						2	1	13471.180	0.002
3	2	2	2	1	2	4	3	13964.715	-0.001
						3	2	13964.027	-0.002
						2	1	13965.099	0.001

Table S9. Cartesian coordinates for the ab initio predicted geometry (MP2/6-311++G(d,p) level of theory) of conformer Ia of threonine

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.132624	-0.245984	0.365039
2	6	0	0.025056	0.468872	-0.435626
3	7	0	0.216200	1.906921	-0.247834
4	6	0	-1.336983	-0.007597	0.027956
5	8	0	-1.900230	0.407153	1.018742
6	8	0	-1.848654	-0.969887	-0.773881
7	1	0	-2.692909	-1.233457	-0.376162
8	1	0	0.166259	0.223498	-1.492123
9	1	0	-0.175815	2.180165	0.651360
10	1	0	-0.279311	2.433137	-0.960999
11	1	0	0.981594	0.009215	1.427114
12	6	0	1.131814	-1.752223	0.190180
13	8	0	2.385268	0.243130	-0.079421
14	1	0	2.255227	1.199336	-0.165688
15	1	0	1.999076	-2.171911	0.705497
16	1	0	0.227101	-2.201864	0.608104
17	1	0	1.199233	-2.008137	-0.871076

Rotational constants (GHZ): 2.8697326 1.6085914 1.2249382

Table S10. Cartesian coordinates for the ab initio predicted geometry (MP2/6-311++G(d,p) level of theory) of conformer I'b of threonine

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.062591	-0.597176	0.003992
2	6	0	0.005021	0.359898	-0.580941
3	7	0	0.260085	1.707558	-0.077749
4	6	0	-1.382344	-0.070829	-0.141087
5	8	0	-2.181205	0.636863	0.430985
6	8	0	-1.633266	-1.351822	-0.488128
7	1	0	-2.524178	-1.548913	-0.162988
8	1	0	0.026443	0.285811	-1.678298
9	1	0	-0.620011	2.174574	0.121842
10	1	0	0.773708	2.263578	-0.751091
11	6	0	0.802249	-1.623110	-0.266508
12	1	0	2.458105	-0.260790	-0.507093
13	8	0	0.992887	-0.531069	1.419471
14	1	0	1.007988	0.417383	1.616787
15	1	0	3.183542	-0.947987	-0.065067
16	1	0	2.507373	-0.351020	-1.598109
17	1	0	2.734709	0.758384	-0.220175

Rotational constants (GHZ): 3.1642508 1.5207517 1.3236166

Table S11. Cartesian coordinates for the ab initio predicted geometry (MP2/6-311++G(d,p) level of theory) of conformer IIa of threonine

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.101010	0.158160	0.353886
2	6	0	0.046308	-0.388736	-0.504560
3	7	0	0.173607	-1.829342	-0.255054
4	6	0	1.353303	0.302441	-0.095325
5	8	0	1.685321	1.391066	-0.503287
6	8	0	2.069209	-0.402245	0.796010
7	1	0	1.589305	-1.257767	0.860297
8	1	0	-0.158357	-0.133182	-1.551256
9	1	0	0.597959	-2.293508	-1.053652
10	1	0	-0.753998	-2.227822	-0.134716
11	6	0	-1.372687	1.635335	0.124612
12	1	0	-0.851240	-0.026045	1.409920
13	8	0	-2.236580	-0.639861	-0.005817
14	1	0	-2.991716	-0.300301	0.484557
15	1	0	-2.222711	1.953715	0.737729
16	1	0	-0.508232	2.245547	0.392695
17	1	0	-1.615351	1.809879	-0.927120

Rotational constants (GHZ): 2.9060278 1.6684835 1.2010277

Table S12. Cartesian coordinates for the ab initio predicted geometry (MP2/6-311++G(d,p) level of theory) of conformer IIb of threonine.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.130448	-0.504656	-0.195644
2	6	0	-0.036556	0.442374	-0.498585
3	7	0	-0.028076	1.693657	0.264208
4	6	0	-1.366160	-0.284650	-0.229868
5	8	0	-1.514750	-1.470039	-0.430907
6	8	0	-2.335533	0.512540	0.230735
7	1	0	-1.882589	1.375058	0.362169
8	1	0	-0.035917	0.682993	-1.569532
9	1	0	0.527637	2.407393	-0.193494
10	1	0	0.376460	1.523565	1.183733
11	6	0	2.482461	0.120481	-0.482624
12	1	0	0.994218	-1.406134	-0.802507
13	8	0	1.107673	-0.840955	1.194057
14	1	0	0.425203	-1.512031	1.310726
15	1	0	3.273656	-0.609529	-0.298809
16	1	0	2.541155	0.450340	-1.524791
17	1	0	2.656444	0.979079	0.172291

Rotational constants (GHZ): 3.2326990 1.5426801 1.2716983

Table S13. Cartesian coordinates for the ab initio predicted geometry (MP2/6-311++G(d,p) level of theory) of conformer IIc of threonine.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.282545	0.395318	-0.181712
2	6	0	-0.186787	0.480531	-0.642350
3	7	0	-0.848630	1.761221	-0.361431
4	6	0	-1.006109	-0.665371	-0.028883
5	8	0	-0.595033	-1.807803	0.010620
6	8	0	-2.196035	-0.300888	0.451319
7	1	0	-2.226227	0.667735	0.281376
8	1	0	-0.189788	0.304637	-1.723632
9	1	0	-0.839011	2.368928	-1.172700
10	1	0	-0.392965	2.258061	0.398517
11	6	0	1.425604	0.430258	1.338821
12	1	0	1.800305	1.258437	-0.615859
13	8	0	1.908131	-0.746334	-0.739129
14	1	0	1.341872	-1.495410	-0.500730
15	1	0	2.486472	0.416607	1.599006
16	1	0	0.982495	1.333014	1.775176
17	1	0	0.949235	-0.444770	1.791119

Rotational constants (GHZ): 2.6616059 1.7938537 1.3951773

Table S14. Cartesian coordinates for the ab initio predicted geometry (MP2/6-311++G(d,p) level of theory) of conformer $III_{\alpha}a$ of threonine.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.132798	-0.238866	0.350912
2	6	0	0.024571	0.455988	-0.460855
3	7	0	0.130063	1.895946	-0.211156
4	6	0	-1.331296	-0.145605	-0.151586
5	8	0	-1.971947	-0.864761	-0.884729
6	8	0	-1.749999	0.206686	1.095032
7	1	0	-2.608842	-0.223135	1.222966
8	1	0	0.223987	0.270167	-1.519908
9	1	0	-0.263713	2.121219	0.698971
10	1	0	-0.386747	2.425285	-0.906594
11	6	0	1.186080	-1.736120	0.116589
12	1	0	0.946274	-0.031606	1.416719
13	8	0	2.379671	0.310342	-0.040236
14	1	0	2.220136	1.263567	-0.100159
15	1	0	2.041201	-2.155334	0.652006
16	1	0	0.276376	-2.227713	0.473682
17	1	0	1.306156	-1.944596	-0.950485

Rotational constants (GHZ): 2.8855853 1.5785377 1.2499657

Table S15. Cartesian coordinates for the ab initio predicted geometry (MP2/6-311++G(d,p) level of theory) of conformer III$_\beta$b of threonine

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.156160	0.361043	-0.398391
2	6	0	0.043402	-0.585960	-0.273667
3	7	0	-0.131266	-1.459984	0.885714
4	6	0	1.336994	0.214178	-0.194741
5	8	0	1.428618	1.409601	0.008509
6	8	0	2.419990	-0.585925	-0.338726
7	1	0	3.196905	-0.017922	-0.223862
8	1	0	0.099843	-1.211593	-1.172630
9	1	0	-0.290430	-0.887033	1.710826
10	1	0	0.699192	-2.023335	1.039873
11	1	0	-0.973503	1.017897	-1.260377
12	6	0	-2.458314	-0.391325	-0.598078
13	8	0	-1.292138	1.145246	0.785207
14	1	0	-0.521727	1.726846	0.801211
15	1	0	-3.277267	0.323556	-0.707353
16	1	0	-2.406069	-1.011415	-1.498248
17	1	0	-2.655387	-1.036109	0.259909

Rotational constants (GHZ): 3.3822264 1.4879644 1.2394059