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Supporting Information

Structure Determination, Conformational Flexibility, Internal Dynamics, and Chiral Analysis of Pulegone and Its Complex with Water

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Supplementary information for:

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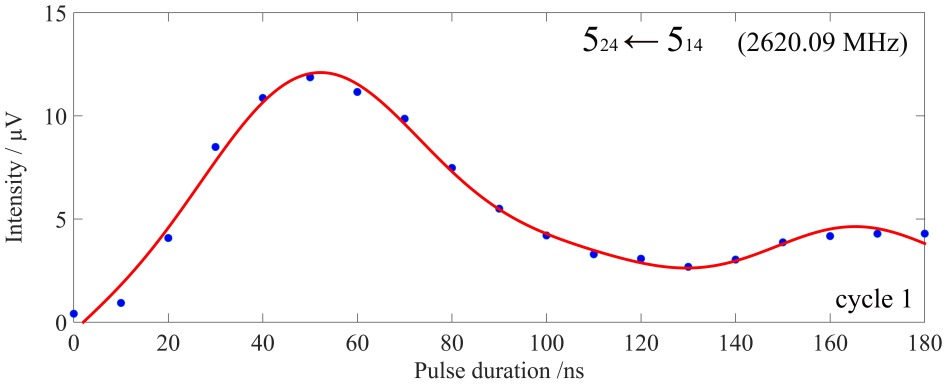
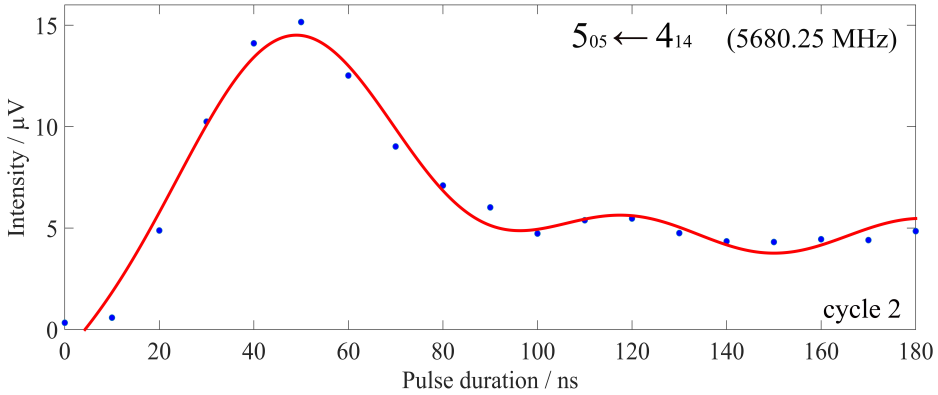


a)



b)

Figure S1: Nutation curves for the drive transitions of the two M3WM cycles to determine the optimal pulse durations ($\pi/2$ conditions) by direct excitation with increasing pulse durations of (a) the c-type transition $5_{24} \leftarrow 5_{14}$ at 2620.09 MHz (cycle 1) and (b) the b-type transition $5_{05} \leftarrow 4_{14}$ at 5680.25 MHz (cycle 2). In both cases, maximum amplitudes for the drive signal are found for pulse durations around 50 ns.

Table S1: Comparison of experimental and calculated molecular parameters (MP2/6-311++G(d,p) level of theory) for pulegone. The fits reported here include only AA states due to internal rotation.

Parameter	Experimental		MP2[a]			
	Chair 1	Chair 2	Chair 1	Chair 2	Twist-Boat 1	Twist-Boat 2
A /MHz	1909.05435(71)[b]	1820.46706(90)	1885.42	1817.17	1974.04	1966.07
B / MHz	739.06297(21)	816.91977(53)	734.76	822.31	764.90	746.45
C / MHz	578.14181(21)	635.95024(53)	584.11	640.85	606.24	588.09
Δ_J /kHz	0. 0302(24)	0.0318(35)				
Δ_{JK} /kHz	-0.273(10)	0.0597(67)				
Δ_K /kHz	1.079(48)	-0.136(30)				
κ	-0.76	-0.69	-0.75	-0.69	-0.77	-0.77
μ_a / D[c]			0.7	0.4	-0.1	0.5
μ_b / D			-2.7	-2.7	-2.8	-2.7
μ_c / D			-1.0	-1.1	0.9	0.8
ΔE /kJmol^{-1}			0	2.7	11.3	12.2
σ [d] /kHz	7.53	10.6				
N [e] /kHz	97	38				

[a] $6-311++G(d,p)$

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

[c] $D \approx 3.3356 * 10^{-30} C \cdot m$

[d] RMS deviation of the fit.

[e] Number of fitted transitions.

Table S2: Experimentally determined rotational and quartic centrifugal distortion constants for the normal and the ^{13}C substituted species of pulegone, Chair 1.

	normal	^{13}C1	^{13}C2	^{13}C3
A(MHz)	1909.05435(71)	1908.82932(75)	1894.60622(64)	1891.8428(10)
B(MHz)	739.06297(21)	733.63115(48)	736.70257(32)	738.63051(34)
C(MHz)	578.14181(21)	574.81129(34)	575.35935(30)	576.85245(33)
Δ_J /kHz	0.0302(24)	[0.0302]	[0.0302]	[0.0302]
Δ_{JK} /kHz	−0.273(10)	[−0.273]	[−0.273]	[−0.273]
Δ_K /kHz	1.079(48)	[1.079]	[1.079]	[1.079]
N_{lines}	97	32	29	24
σ(kHz)	7.5	10.3	8.4	10.1

	^{13}C4	^{13}C5	^{13}C6	^{13}C7
A(MHz)	1908.22352(64)	1900.38586(46)	1900.44453(54)	1907.22272(57)
B(MHz)	738.48520(23)	739.04968(25)	736.77871(29)	724.92918(31)
C(MHz)	577.81614(22)	577.41426(19)	576.09403(29)	569.59083(27)
Δ_J /kHz	[0.0302]	[0.0302]	[0.0302]	[0.0302]
Δ_{JK} /kHz	[−0.273]	[−0.273]	[−0.273]	[−0.273]
Δ_K /kHz	[1.079]	[1.079]	[1.079]	[1.079]
N_{lines}	30	27	25	26
σ(kHz)	8.1	5.8	7.1	7.5

	^{13}C8	^{13}C9	^{13}C10	^{18}O1
A(MHz)	1908.35143(60)	1900.95685(57)	1891.52188(76)	1842.0286(32)
B(MHz)	734.62714(32)	730.04926(30)	730.47932(41)	737.5350(22)
C(MHz)	575.38085(27)	572.35728(22)	571.30610(32)	571.93637(74)
Δ_J /kHz	[0.0302]	[0.0302]	[0.0302]	[0.0302]
Δ_{JK} /kHz	[−0.273]	[−0.273]	[−0.273]	[−0.273]
Δ_K /kHz	[1.079]	[1.079]	[1.079]	[1.079]
N_{lines}	29	26	21	5
σ(kHz)	7.8	7.2	8.2	8.3

Table S3: r_s structure, a, b and c coordinates of the isotopically substituted atoms for Chair 1 and their comparison with r_0, and r_e (MP2/6-311++G(d,p)) structures. All coordinates are in Å.

	atom	a	b	c
r_s		2.25040(67)	−0.129(12)	0.122(12)
r_0	$C1$	2.2484(27)	−0.1132(52)	0.1732(39)
r_e		2.239	−0.125	0.157
r_s		1.4820(10)	−1.4300(10)	$-0.0948i$
r_0	$C2$	1.4769(69)	−1.4300(52)	−0.057(10)
r_e		1.467	−1.429	−0.035
r_s		$0.1644i$	−1.4081(11)	0.6582(23)
r_0	$C3$	0.142(11)	−1.4152(59)	0.640(11)
r_e		0.121	−1.398	0.701
r_s		−0.6764(22)	0.1914(79)	0.2813(54)
r_0	$C4$	−0.6976(66)	−0.243(10)	0.1923(94)
r_e		−0.725	−0.227	0.250
r_s		$0.2166i$	1.0731(14)	0.2444(62)
r_0	$C5$	0.024(11)	1.0692(90)	0.203(14)
r_e		0.000	1.083	0.226
r_s		1.4195(11)	1.0495(14)	−0.3277(46)
r_0	$C6$	1.4199(70)	1.0585(92)	−0.342(11)
r_e		1.400	1.048	−0.362
r_s		3.62451(42)	−0.1528(99)	−0.4872(31)
r_0	$C7$	3.6260(26)	−0.1286(85)	−0.4733(68)
r_e		3.604	−0.164	−0.528
r_s		−2.03111(74)	−0.2874(52)	−0.127(12)
r_0	$C8$	−2.0240(51)	−0.320(14)	−0.248(15)
r_e		−2.021	−0.304	−0.151
r_s		−2.84277(53)	0.8805(17)	−0.6128(25)
r_0	$C9$	−2.8433(38)	0.887(11)	−0.603(15)
r_e		−2.808	0.877	−0.662
r_s		−2.82829(53)	−1.57903(96)	−0.124(12)
r_0	$C10$	−2.8276(39)	−1.5875(70)	−0.071(21)
r_e		−2.825	−1.580	−0.139
r_s		−0.5598(27)	2.11240(72)	0.6437(24)
r_0	$O1$	−0.563(10)	2.1152(29)	0.6313(92)
r_e		−0.492	2.124	0.645

Table S4: The r_0, r_s and r_e (MP2/6-311++G(d,p)) structures for Chair 1.

	r_0	r_s	*Ab initio* r_e
r(C1-C2) / Å	1.5434(81)	*1.515(10)*[a]	1.53
r(C2-C3) / Å	1.505(12)	*1.6217(13)*	1.53
r(C3-C4) / Å	1.511(16)	*1.4423(70)*	1.51
r(C4-C5) / Å	1.497(15)	*1.4345(71)*	1.49
r(C5-C6) / Å	[1.52][b]	*1.5306(30)*	1.52
r(C6-C1) / Å	1.524(13)	1.511(10)	1.53
r(C7-C1) / Å	1.5219(55)	1.5031(52)	1.52
r(C4-C8) / Å	1.3999(91)	1.4181(44)	1.36
r(C8-C9) / Å	1.501(17)	1.5029(58)	1.51
r(C8-C10) / Å	1.511(16)	1.5178(46)	1.51
r(C5-O1) / Å	1.2736(97)	*1.2462(28)*	1.23
∠(C1-C2-C3) / °	[111.4]	*114.78(30)*	111.4
∠(C2-C3-C4) / °	[111.3]	*109.50(18)*	111.3
∠(C3-C4-C5) / °	[114.2]	*121.95(19)*	114.2
∠(C4-C5-C6) / °	[115.7]	*115.67(24)*	115.7
∠(C5-C6-C1) / °	[113.0]	*114.26(37)*	113.0
∠(C6-C1-C2) / °	[109.5]	*111.53(28)*	109.5
∠(C7-C1-C2) / °	[111.9]	*114.70(79)*	111.9
∠(C7-C1-C6) / °	[110.9]	113.22(80)	110.9
∠(C6-C5-O1) / °	123(1)	*123.32(15)*	121.5
∠(O1-C5-C4) / °	[122.8]	*121.00(26)*	122.8
∠(C5-C4-C8) / °	[120.5]	*120.18(53)*	120.5
∠(C3-C4-C8) / °	[125.3]	*117.78(53)*	125.3
∠(C4-C8-C9) / °	123.14(79)	123.80(45)	123.6
∠(C4-C8-C10) / °	120.89(91)	123.97(53)	123.7
∠(C9-C8-C10) / °	[112.8]	112.23(28)	112.8
∠(C3-C4-C8-C9) / °	-183(1)	*-176.81(63)*	-176.7
∠(C5-C4-C8-C10) / °	[180.8]	*179.95(83)*	180.8
∠(C1-C6-C5-O1) / °	136(2)	*139.23(63)*	134.5

[a] The distances and angles which involve C2, C3 and C5 atoms (in italics) have been calculated by setting the imaginary r_s coordinates to zero.

[b] Values kept fixed to ab initio predicted structure.

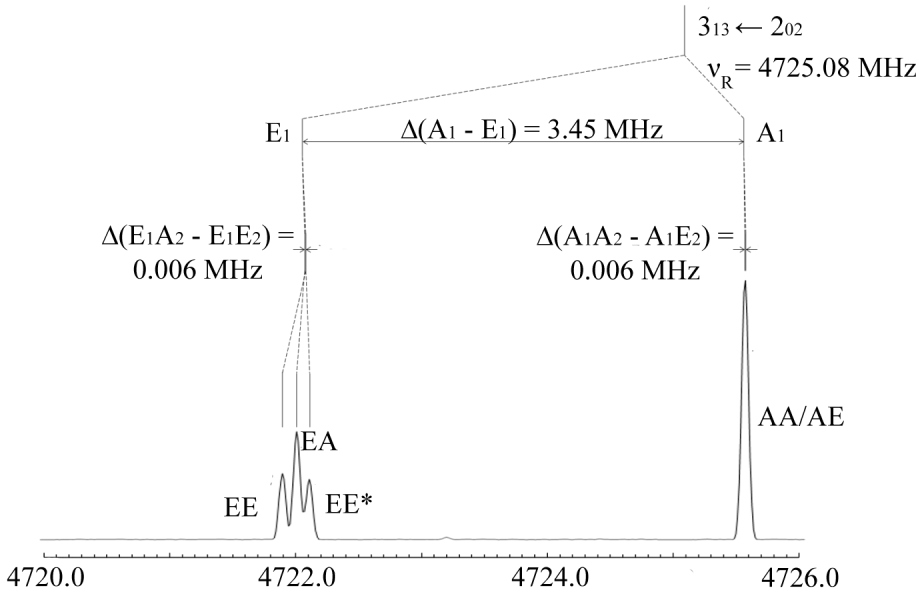


Figure S2: Coupling scheme for the $3_{13} \leftarrow 2_{02}$ rotational transition of the Chair 1. ν_R refers to the unperturbed transition. Top 1 (V_3 = 1.961911(46) kJ/mol) splits this transition into A_1 and E_1 components, which are predicted to be 3.45 MHz apart. Top 2 (V_3 = 6.3617(12) kJ/mol) further splits each of those components, resulting in four components subsequently (0.006 MHz apart). They are labeled A_1A_2 (AA), A_1E_2 (AE), E_1A_2 (EA) and E_1E_2. Note that top-top interaction splits also the E_1E_2 component into a doublet labeled EE and EE*. In summary, the interaction between top 1 and top 2 splits all rotational transitions into five components labeled AA, AE, EA, EE and EE*, but AA and AE splittings could not be resolved with our instrument.

Table S5: Measured rotational transitions (ν_{obs}) and the residuals ($\nu_{\mathrm{obs}} - \nu_{\mathrm{calc}}$) for the pulegone conformer Chair 1, as obtained after the fit with the programm XIAM.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c		$\nu_{\mathrm{obs}} - \nu_{\mathrm{calc}}$ (MHz)	ν_{obs}(GHz)
6	0	6	$\leftarrow$	5	1	4	AA	-.0106	4.6380420
7	0	7	$\leftarrow$	6	1	5	AA	-.0134	5.0167800
							EA	.0092	5.0196240
							EE	.0039	5.0196240
							EE*	-.0158	5.0196240
6	1	5	$\leftarrow$	5	2	3	AA	.0001	5.1182580
6	1	5	$\leftarrow$	5	2	4	AA	-.0003	5.6153480
							EA	.0033	5.6454730
							EE	.0031	5.6460130
							EE*	.0021	5.6449130
8	2	6	$\leftarrow$	7	3	5	AA	.0037	5.9438960
							EA	.0008	6.0909040
							EE	-.0023	6.0922710
							EE*	.0040	6.0895150
7	1	6	$\leftarrow$	6	2	4	AA	.0036	6.3764780
5	3	3	$\leftarrow$	4	3	2	AA	.0053	6.6301280
7	1	6	$\leftarrow$	6	2	5	AA	-.0016	7.3042490
							EA	.0012	7.3130830
							EE	-.0009	7.3134370
							EE*	-.0028	7.3126950
6	4	3	$\leftarrow$	5	4	2	AA	.0014	7.9553790
6	4	2	$\leftarrow$	5	4	1	AA	.0044	7.9570530
3	1	3	$\leftarrow$	2	0	2	AA	-.0003	4.7255370
							EA	-.0002	4.7220130
							EE	.0003	4.7219020
							EE*	-.0008	4.7221120
5	2	4	$\leftarrow$	4	2	3	AA	-.0018	6.5516370
							EA	-.0063	6.5830080
							EE	-.0057	6.5833050
							EE*	-.0072	6.5826920
5	2	3	$\leftarrow$	4	2	2	AA	-.0046	6.8253750
							EA	-.0033	6.7919530
							EE	-.0048	6.7916150
							EE*	-.0045	6.7922630
4	2	2	$\leftarrow$	3	2	1	AA	.0007	5.4036120
							EA	.0008	5.3613070
							EE	-.0008	5.3610950
							EE*	-.0005	5.3614990
4	2	3	$\leftarrow$	3	2	2	AA	-.0001	5.2567500
							EA	.0013	5.2974950
							EE	.0008	5.2976730
							EE*	-.0019	5.2972960
4	1	4	$\leftarrow$	3	0	3	AA	-.0108	5.7535400
							EA	-.0044	5.7536120

							EE	.0207	5.7535400
							EE*	-.0159	5.7536870
5	0	5	←	4	1	4	AA	-.0080	5.6802390
							EA	-.0062	5.6776120
							EE	-.0114	5.6777000
							EE*	.0023	5.6775120
5	1	5	←	4	0	4	AA	-.0137	6.7566780
							EA	-.0040	6.7583870
							EE	-.0035	6.7583000
							EE*	.0054	6.7584750
6	1	6	←	5	0	5	AA	.0333	7.7649750
							EA	.0022	7.7669500
							EE	-.0002	7.7668700
							EE*	-.0066	7.7670120
6	0	6	←	5	1	5	AA	-.0111	7.0260360
							EA	.0027	7.0232870
							EE	-.0025	7.0233500
							EE*	.0035	7.0232000
4	1	3	←	3	1	2	AA	-.0468	5.5566720
							EA	.0073	5.5514820
							EE	.0312	5.5514820
							EE*	.0040	5.5514820
3	2	2	←	2	1	1	AA	.0278	7.4616120
							EA	.0068	7.3347880
							EE	-.0025	7.3336910
							EE*	-.0060	7.3358290
2	1	2	←	1	0	1	AA	-.0073	3.6434750
							EA	.0094	3.6330070
							EE	.0076	3.6328430
							EE*	.0038	3.6331510
5	1	4	←	4	1	3	AA	-.0047	6.9103500
6	0	6	←	5	0	5	AA	-.0077	7.4708370
6	1	6	←	5	1	5	AA	.0059	7.3201500
4	0	4	←	3	1	3	AA	.0005	4.2869740
							EA	-.0094	4.2861130
							EE	-.0068	4.2862470
							EE*	-.0070	4.2859730
3	0	3	←	2	1	2	AA	.0138	2.8660640
							EA	.0070	2.8711580
							EE	-.0094	2.8713420
							EE*	-.0021	2.8709430
4	1	4	←	3	1	3	AA	.0045	4.9186250
5	1	5	←	4	1	4	AA	.0324	6.1250770
4	1	3	←	4	0	4	AA	.0016	2.2343330
4	1	3	←	3	2	2	AA	.0080	2.2779480
							EA	-.0163	2.3933450
							EE	-.0025	2.3943390
							EE*	-.0096	2.3923690
1	1	1	←	0	0	0	AA	-.0135	2.4871840
							EA	.0285	2.4584290

							EE	-.0178	2.4580420
							EE*	-.0181	2.4587110
7	2	6	←	6	3	4	AA	.0067	2.5908220
							EA	-.0029	2.7609020
							EE	-.0022	2.7622370
							EE*	-.0027	2.7595900
2	0	2	←	1	0	1	AA	-.0025	2.6189230
1	1	0	←	0	0	0	AA	-.0048	2.6481130
							EA	.0139	2.6766110
							EE	-.0016	2.6769070
							EE*	.0075	2.6762820 .
2	1	1	←	1	1	0	AA	.0014	2.7953320
5	1	4	←	5	0	5	AA	-.0091	2.8327830
4	2	3	←	4	1	3	AA	-.0111	2.9787990
							EA	-.0014	2.9041310
							EE	-.0118	2.9033190
							EE*	.0017	2.9049210
5	2	3	←	5	1	4	AA	-.0045	3.1171800
							EA	-.0061	3.1559720
							EE	.0008	3.1563430
							EE*	-.0025	3.1555970
6	2	4	←	6	1	5	AA	-.0039	3.1464120
							EA	.0040	3.1739020
							EE	.0050	3.1739970
							EE*	-.0013	3.1737830
4	2	2	←	4	1	3	AA	.0034	3.2021630
							EA	-.0099	3.2680790
							EE	.0014	3.2688010
							EE*	-.0035	3.2673610
4	0	4	←	3	1	2	AA	-.0063	3.3223810
7	2	5	←	7	1	6	AA	-.0144	3.3260740
							EA	.0046	3.3487230
							EE	-.0081	3.3486500 .
3	2	1	←	3	1	2	AA	.0049	3.3552720
							EA	-.0133	3.4582440
							EE	-.0076	3.4591470
							EE*	-.0080	3.4573350
3	1	3	←	2	1	2	AA	.0016	3.7009820
5	1	4	←	4	2	2	AA	.0009	3.7081960
							EA	.0098	3.6359880
							EE	-.0026	3.6352750
							EE*	-.0020	3.6366660
3	0	3	←	2	0	2	AA	.0050	3.8906120
5	1	4	←	4	2	3	AA	.0053	3.9315500
							EA	.0084	3.9999430
							EE	.0016	4.0007480
							EE*	.0008	3.9991140
5	0	5	←	4	1	3	AA	-.0086	4.0775540
9	2	7	←	9	1	8	AA	-.0151	4.2353300
7	1	6	←	7	0	7	AA	.0021	4.5060990

4	0	4	←	3	0	3	AA	.0003	5.1219040
6	2	5	←	6	1	6	AA	-.0116	5.5219210
							EA	.0010	5.5016740
							EE	-.0001	5.5013900
							EE*	.0019	5.5019000
3	1	2	←	2	0	2	AA	.0005	5.6901240
							EA	.0045	5.7002040
5	3	3	←	5	2	3	AA	.0061	5.8832890
							EA	.0116	5.6361620
							EE	-.0043	5.6342290
							EE*	-.0002	5.6380330
11	2	9	←	11	1	10	AA	.0036	5.9067320
2	2	1	←	1	1	0	AA	.0024	6.3052990
5	0	5	←	4	0	4	AA	-.0021	6.3118920
							EA	-.0068	6.3110750
							EE	.0008	6.3110750
							EE*	-.0008	6.3110750
6	2	4	←	6	1	6	AA	-.0028	6.4497060
							EA	-.0064	6.4720170
							EE	-.0100	6.4721600
							EE*	-.0072	6.4717940
2	2	1	←	1	1	1	AA	.0051	6.4662220
6	3	3	←	6	2	5	AA	.0075	6.5870710
							EA	-.0136	6.7853400
							EE	-.0059	6.7870050
							EE*	.0069	6.7836590
7	3	5	←	7	2	6	AA	-.0040	6.7070660
							EA	.0056	6.5759720
							EE	-.0014	6.5747280
							EE*	-.0103	6.5771400
7	3	4	←	7	2	6	AA	.0038	6.8914280
							EA	-.0049	7.0408600
							EE	.0092	7.0422830
							EE*	.0188	7.0394230
4	1	3	←	3	0	3	AA	-.0072	7.3562280
3	2	1	←	2	1	1	AA	-.0006	7.5380720
							EA	.0229	7.6349480
							EE	.0152	7.6357540
							EE*	-.0086	7.6340700
6	2	5	←	5	2	4	AA	-.0040	7.8339840
							EA	.0018	7.8490190
							EE	.0050	7.8492270
							EE*	.0050	7.8487970
6	2	5	←	6	1	5	AA	-.0087	2.2186310
							EA	-.0025	2.2035450
							EE	-.0041	2.2032080
							EE*	.0008	2.2038820
3	0	3	←	2	1	1	AA	-.0010	2.3832880
2	1	2	←	1	1	1	AA	.0001	2.4734900
							EE*	-.0036	2.4898120

6	2	4	←	6	1	5	AA	-.0039	3.1464120
							EA	.0030	3.1739010
							EE	.0030	3.1739950
							EE*	.0017	3.1737860
7	3	4	←	7	2	6	AA	.0048	6.8914290
7	2	6	←	7	1	7	AA	.0051	6.1189030
							EA	.0057	6.1050660
							EE	-.0012	6.1048900
							EE*	.0076	6.1051670
3	2	1	←	2	1	1	AA	-.0006	7.5380720
							EA	.0009	7.6349260
							EE	.0182	7.6357570
							EE*	-.0036	7.6340750
4	3	1	←	4	2	2	AA	.0049	6.0850650
							EA	-.0153	6.2264580
							EE	-.0076	6.2271850
							EE*	-.0075	6.2257090
5	3	3	←	5	2	4	AA	.0018	6.3803750
							EA	-.0008	6.2090480
							EE	-.0022	6.2080090
							EE*	.0013	6.2100480
8	3	5	←	8	2	6	AA	.0008	5.0693090
							EA	-.0006	5.1522820
							EE	.0081	5.1532380
							EE*	.0101	5.1513310
4	3	2	←	4	2	3	AA	.0097	6.3018990
							EA	.0007	6.1531650
							EE	-.0013	6.1524270
							EE*	.0041	6.1538670
3	3	1	←	3	2	1	AA	.0030	6.1849700
3	3	1	←	3	2	2	AA	.0036	6.2614590
							EA	-.0008	6.1513810
							EE	.0033	6.1508350
							EE*	.0013	6.1518950
6	3	4	←	6	2	5	AA	-.0116	6.5110350
							EA	.0029	6.3467640
							EE	-.0045	6.3455280
							EE*	-.0154	6.3479290
4	3	2	←	4	2	2	AA	.0053	6.0785450
7	2	6	←	6	3	3	AA	.0086	2.5148070
								RMS	9.085 kHz

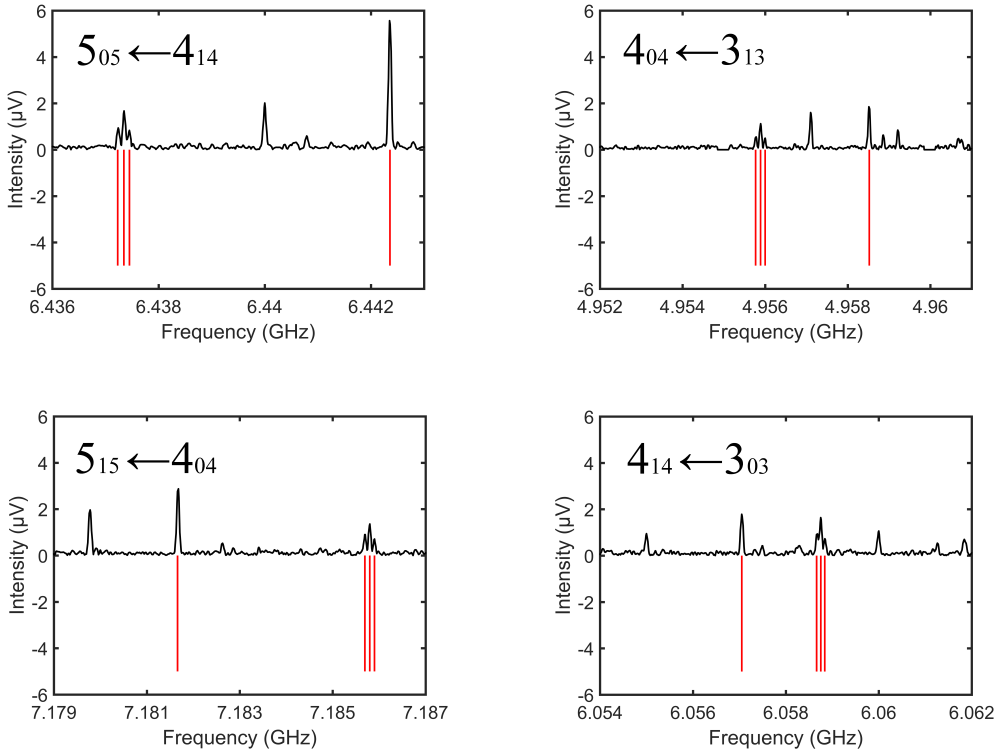


Figure S3: Parts of the broadband rotational spectrum (1.5 million acquisitions and using neon as carrier gas) of the pulegone, Chair 2. The four sections are zoom-ins of individual rotational transitions to illustrate the multiplet structure due to internal dynamics. In all parts, the upper traces (black) are the experimentally obtained spectrum. The lower (red) traces are stick spectra based on simulations using the fitted molecular constants for Chair 2 and employing the program XIAM. The labeling of the rotational transition follows the $J_{K_aK_c}$ scheme.

Table S6: Measured rotational transitions (ν_{obs}) and the residuals ($\nu_{\mathrm{obs}} - \nu_{\mathrm{calc}}$) for the pulegone conformer Chair 2, as obtained after the fit with the programm XIAM.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c		$\nu_{\mathrm{obs}} - \nu_{\mathrm{calc}}$ (MHz)	ν_{obs}(GHz)
5	0	5	$\leftarrow$	4	1	4	AA	-.0036	6.4423540
							AE	.0020	6.4373490
							EE	.0063	6.4372370
							EE*	-.0026	6.4374490
5	1	5	$\leftarrow$	4	0	4	AA	.0100	7.1816710
							AE	.0013	7.1857990
							EE	-.0003	7.1858990
							EE*	.0004	7.1856930
4	1	4	$\leftarrow$	3	0	3	AA	-.0010	6.0570500
							AE	-.0021	6.0587500
							EE	-.0001	6.0588370
							EE*	-.0001	6.0586620
4	0	4	$\leftarrow$	3	1	3	AA	-.0081	4.9585120
							AE	-.0008	4.9558870
							EE	-.0054	4.9557620
							EE*	.0018	4.9560000
3	2	1	$\leftarrow$	2	1	1	AA	.0050	7.4787750
3	2	2	$\leftarrow$	2	1	1	AA	-.0187	7.3692370
							AE	.0083	7.2550500
							EE	-.0044	7.2557750
							EE*	-.0040	7.2542750
6	4	2	$\leftarrow$	6	3	3	AA	.0015	7.4732930
3	2	1	$\leftarrow$	2	1	1	AA	.0000	7.4787700
5	4	1	$\leftarrow$	5	3	2	AA	-.0051	7.5654440
5	4	2	$\leftarrow$	5	3	3	AA	-.0109	7.6118690
7	4	4	$\leftarrow$	7	3	5	AA	.0071	7.6173530
6	0	6	$\leftarrow$	5	1	5	AA	.0095	7.8660220
							AE	-.0033	7.8578320
							EE	-.0005	7.8576750
							EE*	.0023	7.8579850
6	4	3	$\leftarrow$	6	3	3	AA	.0172	7.4683420
2	2	0	$\leftarrow$	1	1	1	AA	.0090	6.3006750
9	2	8	$\leftarrow$	8	3	6	AA	-.0069	6.2494180
6	3	4	$\leftarrow$	6	2	5	AA	-.0109	5.8303260
3	3	0	$\leftarrow$	3	2	1	AA	.0047	5.3755960
5	3	2	$\leftarrow$	5	2	3	AA	.0066	5.0130850
3	1	3	$\leftarrow$	2	0	2	AA	.0047	4.9188800
5	2	4	$\leftarrow$	5	1	5	AA	.0034	4.7068180
3	0	3	$\leftarrow$	2	1	2	AA	-.0065	3.4265040
3	1	3	$\leftarrow$	2	1	2	AA	-.0048	4.0739530
8	3	6	$\leftarrow$	7	4	3	AA	.0042	4.0870020
11	5	6	$\leftarrow$	10	6	5	AA	-.0026	4.4085380
10	4	7	$\leftarrow$	9	5	5	AA	.0010	5.0637860
4	3	1	$\leftarrow$	4	2	2	AA	.0036	5.2378960

3	3	1	←	3	2	2	AA	-.0065	5.4833600
9	4	5	←	9	3	6	AA	-.0035	6.6932890
8	5	4	←	9	2	7	AA	-.0029	7.1452000
15	5	10	←	15	4	11	AA	.0004	7.2464410
4	4	1	←	4	3	2	AA	-.0021	7.6225570
11	2	10	←	10	3	8	AA	.0009	7.8613150
								RMS	6.936 kHz

Table S7: Measured rotational transitions (ν_{obs}) and the residuals ($\nu_{\mathrm{obs}} - \nu_{\mathrm{calc}}$) for the pulegone conformer Chair 1 with one water molecule, as obtained after the fit with the programm XIAM.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c		$\nu_{\mathrm{obs}} - \nu_{\mathrm{calc}}$ (MHz)	ν_{obs}(GHz)
2	0	2	$\leftarrow$	1	0	1	A	-.0085	2.0562620
3	0	3	$\leftarrow$	2	0	2	A	-.0032	3.0616000
							E	.0054	3.0589130
3	1	2	$\leftarrow$	2	1	1	A	-.0009	3.2397000
							E	.0092	3.2375130
4	0	4	$\leftarrow$	3	1	3	A	-.0037	3.5232620
							E	.0270	3.5167190
4	1	4	$\leftarrow$	3	1	3	A	-.0037	3.9175000
							E	-.0118	3.9182080
4	0	4	$\leftarrow$	3	0	3	A	.0082	4.0425000
							E	-.0099	4.0399700
4	2	3	$\leftarrow$	3	2	2	A	-.0002	4.1239120
4	3	1	$\leftarrow$	3	3	0	A	.0097	4.1516250
4	2	2	$\leftarrow$	3	2	1	A	-.0010	4.2126000
4	1	3	$\leftarrow$	3	1	2	A	.0086	4.3073500
							E	-.0054	4.3042730
2	2	1	$\leftarrow$	1	1	0	A	-.0044	4.3370750
4	1	4	$\leftarrow$	3	0	3	A	.0072	4.4367370
2	2	0	$\leftarrow$	1	1	1	A	-.0059	4.4447000
5	0	5	$\leftarrow$	4	1	4	A	-.0102	4.6039750
5	1	5	$\leftarrow$	4	1	4	A	-.0055	4.8828120
							E	-.0018	4.8844570
5	0	5	$\leftarrow$	4	0	4	A	.0019	4.9982250
							E	-.0043	4.9952300
5	2	4	$\leftarrow$	4	2	3	A	.0063	5.1432500
5	3	2	$\leftarrow$	4	3	1	A	.0064	5.2021120
3	2	2	$\leftarrow$	2	1	1	A	.0051	5.2715870
5	1	5	$\leftarrow$	4	0	4	A	.0066	5.2770620
							E	-.0046	5.2859820
5	2	3	$\leftarrow$	4	2	2	A	-.0020	5.3088000
5	1	4	$\leftarrow$	4	1	3	A	.0018	5.3627870
							E	-.0062	5.3581800
5	4	1	$\leftarrow$	5	3	2	A	-.0017	5.3784000
3	2	1	$\leftarrow$	2	1	2	A	.0072	5.6126000
6	1	6	$\leftarrow$	5	1	5	A	.0071	5.8412500
							E	.0062	5.8454060
6	0	6	$\leftarrow$	5	0	5	A	.0058	5.9348370
							E	-.0046	5.9296700
7	1	6	$\leftarrow$	6	2	5	A	.0076	6.0338500
							E	-.0392	6.0288450
6	1	6	$\leftarrow$	5	0	5	A	.0118	6.1200870
6	2	5	$\leftarrow$	5	2	4	A	.0065	6.1550080
4	2	3	$\leftarrow$	3	1	2	E	-.0062	6.1557870

6	4	3	←	5	4	2	A	.0008	6.2281370
6	4	2	←	5	4	1	A	-.0070	6.2291120
6	3	4	←	5	3	3	A	.0032	6.2339500
6	3	3	←	5	3	2	A	.0065	6.2638870
4	2	2	←	3	1	2	A	-.0028	6.2906250
6	1	5	←	5	1	4	A	-.0027	6.4010620
							A	-.0046	6.3955550
6	2	4	←	5	2	3	E	-.0007	6.4159750
7	1	7	←	6	1	6	A	-.0229	6.7933250
							A	.0118	6.8018900
7	0	7	←	6	0	6	E	-.0019	6.8616120
							A	-.0011	6.8521500
4	2	2	←	3	1	3	E	-.0039	6.8798000
3	3	0	←	2	2	0	A	.0040	6.9629370
7	1	7	←	6	0	6	A	-.0069	6.9785850
5	2	4	←	4	1	3	A	.0045	6.9917000
7	2	6	←	6	2	5	A	.0054	7.1580120
7	4	4	←	6	4	3	A	-.0011	7.2747250
7	3	5	←	6	3	4	A	-.0091	7.2765460
7	4	3	←	6	4	2	A	-.0029	7.2779620
8	1	7	←	7	2	6	A	.0020	7.2809120
							A	.0208	7.2702230
5	2	3	←	4	1	3	E	.0115	7.2921000
7	3	4	←	6	3	3	A	-.0007	7.3412250
7	1	6	←	6	1	5	A	-.0005	7.4166890
							A	-.0062	7.4113610
7	2	5	←	6	2	4	E	.0036	7.5227250
8	0	8	←	7	1	7	A	.0019	7.6691000
8	1	8	←	7	1	7	A	-.0176	7.7401200
							A	.0244	7.7533370
6	2	5	←	5	1	4	E	.0002	7.7839120
8	0	8	←	7	0	7	A	-.0012	7.7860750
							A	.0062	7.7718680
8	1	8	←	7	0	7	E	-.0037	7.8571120
7	0	7	←	6	1	6	A	.0051	6.6763750
7	1	7	←	6	0	6	A	-.0049	6.9785870
							E	-.0056	7.0083500
5	1	5	←	4	0	4	A	.0066	5.2770620
							E	-.0116	5.2859750
3	2	2	←	2	1	1	A	-.0069	5.2715750
							E	-.0042	5.2200000
								RMS	9.829 kHz