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Conformational preference determined by inequivalent n-pairs: rotational studies on acetophenone and its monohydrate

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1. Experimental rotational transition frequencies of AP (Tables S1-S9)

Table S1. Experimental transition frequencies of the parent species of AP

Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz	Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz
J' K_a' K_c'	J'' K_a'' K_c''				J' K_a' K_c'	J'' K_a'' K_c''			
3 0 3	2 0 2	A	6306.5628	-3.0	6 1 5	5 1 4	E	13458.5263	-0.1
3 0 3	2 0 2	E	6306.5628	1.5	6 2 5	5 2 4	A	12698.4088	3.9
3 1 3	2 1 2	A	5947.2545	-3.1	6 2 5	5 2 4	E	12698.3945	-1.3
3 1 3	2 1 2	E	5947.2545	-0.7	6 2 4	5 2 3	A	13421.6468	0.0
3 1 2	2 1 1	A	6831.3333	2.7	6 2 4	5 2 3	E	13421.6319	0.0
3 1 2	2 1 1	E	6831.3177	-5.1	6 3 4	5 3 3	A	12912.7016	3.1
3 2 2	2 2 1	A	6404.8986	8.2	6 3 4	5 3 3	E	12912.7209	-3.5
3 2 2	2 2 1	E	6404.9136	-0.8	6 3 3	5 3 2	A	12983.9711	0.0
3 2 1	2 2 0	A	6503.2231	8.0	6 3 3	5 3 2	E	12983.9211	-1.4
3 2 1	2 2 0	E	6503.1806	0.6	7 0 7	6 0 6	A	13908.9084	-1.2
4 0 4	3 0 3	A	8301.1204	2.5	7 0 7	6 0 6	E	13908.9084	4.2
4 0 4	3 0 3	E	8301.1104	-2.2	7 1 7	6 1 6	A	13658.5346	-3.4
4 1 4	3 1 3	A	7903.5597	-3.1	7 1 7	6 1 6	E	13658.5346	1.0
4 1 4	3 1 3	E	7903.5597	0.0	7 1 6	6 1 5	A	15568.8961	-2.7
4 1 3	3 1 2	A	9076.2197	-3.7	7 1 6	6 1 5	E	15568.8840	0.6
4 1 3	3 1 2	E	9076.2197	6.4	7 2 6	6 2 5	A	14753.6146	-6.0
4 2 3	3 2 2	A	8520.4732	-0.3	7 2 6	6 2 5	E	14753.6126	2.6
4 2 3	3 2 2	E	8520.4732	1.6	7 2 5	6 2 4	A	15782.6180	0.2
4 2 2	3 2 1	A	8759.1427	-5.7	7 2 5	6 2 4	E	15782.5986	-1.5
4 2 2	3 2 1	E	8759.1328	-2.3	7 3 5	6 3 4	A	15077.8777	-1.8
4 3 2	3 3 1	A	8585.8817	2.2	7 3 5	6 3 4	E	15077.8777	0.0
4 3 2	3 3 1	E	8586.5708	-1.2	7 3 4	6 3 3	A	15233.2838	1.1
5 0 5	4 0 4	A	10223.1260	2.3	7 3 4	6 3 3	E	15233.2547	-2.8
5 0 5	4 0 4	E	10223.1153	-2.7	8 0 8	7 0 7	A	15719.5789	-5.3
5 1 5	4 1 4	A	9841.0775	-3.3	8 0 8	7 0 7	E	15719.5789	0.0
5 1 5	4 1 4	E	9841.0775	0.4	8 1 8	7 1 7	A	15541.8063	-2.4
5 1 4	4 1 3	A	11289.4975	0.4	8 1 8	7 1 7	E	15541.8063	2.1
5 1 4	4 1 3	E	11289.4882	3.3	8 1 7	7 1 6	A	17606.7509	-0.2
5 2 4	4 2 3	A	10619.5804	4.4	8 1 7	7 1 6	E	17606.7381	3.2
5 2 4	4 2 3	E	10619.5653	-3.8	8 2 7	7 2 6	A	16782.6125	-2.8
5 2 3	4 2 2	A	11070.7993	-0.5	8 2 7	7 2 6	E	16782.6125	9.0
5 2 3	4 2 2	E	11070.7909	3.8	8 2 6	7 2 5	A	18124.2356	2.6
5 3 3	4 3 2	A	10747.3264	2.8	8 2 6	7 2 5	E	18124.2099	-2.7
5 3 3	4 3 2	E	10747.4746	-1.6	8 3 6	7 3 5	A	17237.4560	-4.5
5 3 2	4 3 1	A	10774.5480	0.5	8 3 6	7 3 5	E	17237.4521	2.4

5 3 2	4 3 1	E	10774.3748	-1.7	8 3 5	7 3 4	A	17533.0310	1.4
6 0 6	5 0 5	A	12084.4585	-1.3	8 3 5	7 3 4	E	17533.0048	-3.7
6 0 6	5 0 5	E	12084.4520	-2.2	9 0 9	8 0 8	A	17530.7519	-3.3
6 1 6	5 1 5	A	11759.0655	-3.4	9 0 9	8 0 8	E	17530.7519	1.8
6 1 6	5 1 5	E	11759.0655	0.6	9 1 9	8 1 8	A	17411.8989	-3.9
6 1 5	5 1 4	A	13458.5341	-6.3	9 1 9	8 1 8	E	17411.8989	0.8
9 1 8	8 1 7	A	19564.0519	0.3	3 3 0	2 2 1	A	19523.8847	-11.1
9 1 8	8 1 7	E	19564.0403	5.2	3 3 0	2 2 1	E	19524.7740	-6.1
9 2 8	8 2 7	A	18783.8115	-0.1	3 2 1	2 1 2	A	14832.4387	8.4
9 2 8	8 2 7	E	18783.8062	7.2	3 2 1	2 1 2	E	14832.3951	4.2
9 3 7	8 3 6	A	19385.4129	-0.7	3 2 2	2 1 1	A	13823.8550	8.5
9 3 7	8 3 6	E	19385.4001	1.4	3 2 2	2 1 1	E	13823.8019	3.9
9 3 6	8 3 5	A	19887.7905	2.4	4 0 4	3 1 3	A	6457.7021	0.9
9 3 6	8 3 5	E	19887.7599	-6.2	4 0 4	3 1 3	E	6457.7021	-2.2
10 0 10	9 0 9	A	19347.9848	-1.7	4 1 4	3 0 3	A	9746.9899	10.4
10 0 10	9 0 9	E	19347.9848	3.3	4 1 4	3 0 3	E	9746.9658	-2.2
10 1 10	9 1 9	A	19271.9505	-1.7	4 2 2	3 1 3	A	17644.3253	4.2
10 1 10	9 1 9	E	19271.9505	3.0	4 2 2	3 1 3	E	17644.2762	5.3
2 1 2	1 0 1	A	6447.7915	7.7	4 2 3	3 1 2	A	15512.9967	7.4
2 1 2	1 0 1	E	6447.7670	-2.9	4 2 3	3 1 2	E	15512.9473	0.5
2 2 0	1 1 1	A	12304.0137	0.1	5 1 5	4 0 4	A	11286.9444	2.0
2 2 0	1 1 1	E	12304.0137	5.6	5 1 5	4 0 4	E	11286.9301	-2.4
2 2 1	1 1 0	A	11984.0140	-0.2	5 2 4	4 1 3	A	17056.3486	6.6
2 2 1	1 1 0	E	11983.9380	2.0	5 2 4	4 1 3	E	17056.3030	0.4
3 3 1	2 2 0	A	19497.6973	-13.6	6 0 6	5 1 5	A	11020.6392	-2.0
3 3 1	2 2 0	E	19496.6817	-6.9	6 0 6	5 1 5	E	11020.6392	-0.5
7 0 7	6 1 6	A	13170.4788	-3.1	6 1 6	5 0 5	A	12822.8793	-8.3
7 0 7	6 1 6	E	13170.4788	-0.3	6 1 6	5 0 5	E	12822.8793	-0.1
7 1 7	6 0 6	A	14396.9677	2.0	6 2 5	5 1 4	A	18465.2492	-0.6
7 1 7	6 0 6	E	14396.9619	3.2	6 2 5	5 1 4	E	18465.2147	1.2
8 0 8	7 1 7	A	15231.5252	-2.9	8 0 8	7 1 7	E	15231.5252	0.8

Table S2. Experimental transition frequencies of the ^{13}C1 isotopologue of AP

Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz	Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz
J' K_a' K_c'	J'' K_a'' K_c''				J' Ka' Kc'	J'' Ka'' Kc''			
3 0 3	2 0 2	A	6221.4779	0.2	5 1 4	4 1 3	A	11125.3980	-1.2
3 0 3	2 0 2	E	6221.4779	4.7	5 1 4	4 1 3	E	11125.3920	4.5
3 1 3	2 1 2	A	5869.4800	0.7	6 0 6	5 0 5	A	11939.3040	6.1
3 1 3	2 1 2	E	5869.4800	2.9	6 0 6	5 0 5	E	11939.2970	5.4
3 1 2	2 1 1	A	6729.1737	2.0	6 1 6	5 1 5	A	11610.7110	-0.8
3 1 2	2 1 1	E	6729.1557	-8.4	6 1 6	5 1 5	E	11610.7060	-1.9
4 0 4	3 0 3	A	8193.6273	-3.8	7 0 7	6 0 6	A	13744.6630	-3.7
4 0 4	3 0 3	E	8193.6273	1.4	7 0 7	6 0 6	E	13744.6630	1.7
4 1 4	3 1 3	A	7801.3363	0.1	2 2 0	1 1 1	A	12283.2980	-5.0
4 1 4	3 1 3	E	7801.3363	3.1	2 2 0	1 1 1	E	12283.2980	-1.9
4 1 3	3 1 2	A	8942.0399	-3.7	3 3 1	2 2 0	A	19483.1780	0.3
4 1 3	3 1 2	E	8942.0346	0.8	3 3 1	2 2 0	E	19482.1200	2.1
5 0 5	4 0 4	A	10096.2350	-2.6	3 3 0	2 2 1	A	19507.7550	1.4
5 0 5	4 0 4	E	10096.2350	2.9	3 3 0	2 2 1	E	19508.6770	1.1
5 1 5	4 1 4	A	9715.3541	-2.9	4 0 4	3 1 3	A	6316.9878	1.5
5 1 5	4 1 4	E	9715.3541	0.7	4 0 4	3 1 3	E	6316.9878	-1.8
5 1 5	4 0 4	A	11199.6980	-8.6	6 0 6	5 1 5	A	10835.8270	-1.2
5 1 5	4 0 4	E	11199.6980	1.3	6 0 6	5 1 5	E	10835.8270	0.0

Table S3. Experimental transition frequencies of the ^{13}C2 isotopologue of AP

Transitions J' K_a' K_c'	J'' K_a'' K_c''	state	ν_{obs}/MHz	ν_{diff}/kHz	Transitions J' K_a' K_c'	J'' K_a'' K_c''	state	ν_{obs}/MHz	ν_{diff}/kHz
3 0 3	2 0 2	A	6251.3877	-6.8	6 0 6	5 0 5	A	11975.4610	-0.3
3 0 3	2 0 2	E	6251.3877	-2.4	6 0 6	5 0 5	E	11975.4610	5.3
3 1 3	2 1 2	A	5894.7378	-5.2	6 1 6	5 1 5	A	11654.2280	-4.1
3 1 3	2 1 2	E	5894.7378	-2.9	6 1 6	5 1 5	E	11654.2280	-0.1
3 1 2	2 1 1	A	6773.4571	6.3	2 2 0	1 1 1	A	12172.3560	2.0
3 1 2	2 1 1	E	6773.4412	-2.0	2 2 0	1 1 1	E	12172.3480	-0.8
4 0 4	3 0 3	A	8227.6697	5.0	3 3 0	2 2 1	A	19312.0790	0.5
4 0 4	3 0 3	E	8227.6609	1.5	3 3 0	2 2 1	E	19312.9430	-2.5
4 1 4	3 1 3	A	7833.5622	-1.4	4 0 4	3 1 3	A	6410.2350	-0.8
4 1 4	3 1 3	E	7833.5622	1.6	4 0 4	3 1 3	E	6410.2350	-3.7
4 1 3	3 1 2	A	8999.0338	-1.3	5 1 5	4 0 4	A	11176.9580	-2.1
4 1 3	3 1 2	E	8999.0338	8.6	5 1 5	4 0 4	E	11176.9580	7.5
5 0 5	4 0 4	A	10131.6510	-5.6	6 0 6	5 1 5	A	10930.1590	1.7
5 0 5	4 0 4	E	10131.6510	0.0	6 0 6	5 1 5	E	10930.1590	3.1
5 1 5	4 1 4	A	9753.6321	-0.4	5 1 4	4 1 3	A	11192.9610	-3.5
5 1 5	4 1 4	E	9753.6272	-1.8	5 1 4	4 1 3	E	11192.9530	0.2

Table S4. Experimental transition frequencies of the ^{13}C3 isotopologue of AP

Transitions J' K_a' K_c'	J'' K_a'' K_c''	state	v_{obs}/MHz	v_{diff}/kHz	Transitions J' K_a' K_c'	J'' K_a'' K_c''	state	v_{obs}/MHz	v_{diff}/kHz
3 0 3	2 0 2	A	6293.5133	0.3	5 1 4	4 1 3	A	11273.9426	4.3
3 0 3	2 0 2	E	6293.5085	0.0	5 1 4	4 1 3	E	11273.9273	1.2
3 1 3	2 1 2	A	5933.3483	-3.1	6 0 6	5 0 5	A	12047.6760	-1.8
3 1 3	2 1 2	E	5933.3440	-5.0	6 0 6	5 0 5	E	12047.6760	3.7
3 1 2	2 1 1	A	6823.8491	-9.4	6 1 6	5 1 5	A	11727.9478	-1.1
3 1 2	2 1 1	E	6823.8491	-1.6	6 1 6	5 1 5	E	11727.9478	2.9
4 0 4	3 0 3	A	8280.9203	-0.8	2 2 0	1 1 1	A	12187.6375	0.1
4 0 4	3 0 3	E	8280.9203	4.4	2 2 0	1 1 1	E	12187.6375	6.6
4 1 3	3 1 2	A	9065.2400	-4.9	3 3 0	2 2 1	A	19328.5337	1.6
4 1 3	3 1 2	E	9065.2400	5.2	3 3 0	2 2 1	E	19329.3761	-5.8
5 0 5	4 0 4	A	10194.6375	4.0	4 0 4	3 1 3	A	6478.0022	-0.6
5 0 5	4 0 4	E	10194.6286	0.6	4 0 4	3 1 3	E	6478.0022	-3.4
5 1 5	4 1 4	A	9816.0708	-5.2	5 1 5	4 0 4	A	11222.3876	-5.5
5 1 5	4 1 4	E	9816.0708	-1.5	5 1 5	4 0 4	E	11222.3876	4.1
6 0 6	5 1 5	A	11019.9195	1.2	6 0 6	5 1 5	E	11019.9195	2.7

Table S5. Experimental transition frequencies of the ^{13}C4 isotopologue of AP

Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz	Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz
J' K_a' K_c'	J'' K_a'' K_c''				J' K_a' K_c'	J'' K_a'' K_c''			
3 0 3	2 0 2	A	6306.3510	5.1	5 1 4	4 1 3	A	11289.0400	7.2
3 0 3	2 0 2	E	6306.3510	9.7	5 1 4	4 1 3	E	11289.0300	10.3
3 1 3	2 1 2	A	5947.0650	-1.6	6 1 6	5 1 5	A	11758.7200	-0.3
3 1 3	2 1 2	E	5947.0650	0.8	6 1 6	5 1 5	E	11758.7200	3.7
4 0 4	3 0 3	A	8300.8500	-2.7	3 3 0	2 2 1	A	19524.2500	-6.6
4 0 4	3 0 3	E	8300.8500	2.6	4 0 4	3 1 3	A	6457.2250	-10.7
4 1 3	3 1 2	A	9075.8390	-1.0	4 0 4	3 1 3	E	6457.2250	-13.8
4 1 3	3 1 2	E	9075.8390	9.1	6 0 6	5 1 5	A	11020.0900	-8.2
5 0 5	4 0 4	A	10222.8300	1.4	6 0 6	5 1 5	E	11020.0900	-6.8
5 0 5	4 0 4	E	10222.8300	7.0	5 1 5	4 1 4	E	9840.7770	0.2
5 1 5	4 1 4	A	9840.7770	-3.4					

Table S6. Experimental transition frequencies of the [13]C5 isotopologue of AP

Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz	Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz
J' K_a' K_c'	J'' K_a'' K_c''				J' K_a' K_c'	J'' K_a'' K_c''			
3 0 3	2 0 2	A	6292.8337	2.5	5 1 5	4 1 4	A	9815.1349	0.8
3 0 3	2 0 2	E	6292.8337	-0.1	5 1 5	4 1 4	E	9815.1285	-5.6
3 1 3	2 1 2	A	5932.7505	2.3	5 1 4	4 1 3	A	11272.5290	0.6
3 1 3	2 1 2	E	5932.7505	4.2	5 1 4	4 1 3	E	11272.5230	0.4
3 1 2	2 1 1	A	6822.9648	-5.1	6 0 6	5 0 5	A	12046.6710	-0.6
3 1 2	2 1 1	E	6822.9477	0.7	6 0 6	5 0 5	E	12046.6640	3.4
4 0 4	3 0 3	A	8280.1053	6.0	6 1 6	5 1 5	A	11726.8540	2.1
4 0 4	3 0 3	E	8280.1053	-2.7	6 1 6	5 1 5	E	11726.8490	-2.8
4 1 4	3 1 3	A	7883.5377	0.4	2 2 0	1 1 1	A	12188.5630	3.6
4 1 4	3 1 3	E	7883.5377	-2.9	2 2 0	1 1 1	E	12188.5630	-6.0
4 1 3	3 1 2	A	9064.0753	2.0	3 3 0	2 2 1	A	19330.2640	6.7
4 1 3	3 1 2	E	9064.0702	-1.8	3 3 0	2 2 1	E	19331.1270	1.4
5 0 5	4 0 4	A	10193.7150	3.8	4 0 4	3 1 3	A	6476.4806	-1.4
5 0 5	4 0 4	E	10193.7150	3.5	4 0 4	3 1 3	E	6476.4806	-9.4
5 1 5	4 0 4	A	11222.1830	0.1	6 0 6	5 1 5	A	11018.1950	-2.5
5 1 5	4 0 4	E	11222.1830	0.1	6 0 6	5 1 5	E	11018.1910	0.0

Table S7. Experimental transition frequencies of the ^{13}C6 isotopologue of AP

Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz	Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz
J' K_a' K_c'	J'' K_a'' K_c''				J' K_a' K_c'	J'' K_a'' K_c''			
3 0 3	2 0 2	A	6249.9800	4.1	6 0 6	5 0 5	A	11974.7761	-2.2
3 0 3	2 0 2	E	6249.9758	4.4	6 0 6	5 0 5	E	11974.7761	3.3
3 1 3	2 1 2	A	5893.6866	4.7	6 1 6	5 1 5	A	11652.7578	-1.2
3 1 3	2 1 2	E	5893.6818	2.2	6 1 6	5 1 5	E	11652.7536	-1.4
3 1 2	2 1 1	A	6770.7749	9.3	2 2 0	1 1 1	A	12185.5122	-3.3
3 1 2	2 1 1	E	6770.7535	-4.5	2 2 0	1 1 1	E	12185.5082	-2.1
4 0 4	3 0 3	A	8226.3179	1.1	3 3 0	2 2 1	A	19334.8210	-3.2
4 0 4	3 0 3	E	8226.3109	-0.7	3 3 0	2 2 1	E	19335.7052	8.5
4 1 4	3 1 3	A	7832.2794	-5.3	4 0 4	3 1 3	A	6402.8935	2.3
4 1 4	3 1 3	E	7832.2794	-2.2	4 0 4	3 1 3	E	6402.8988	4.6
4 1 3	3 1 2	A	8995.6385	-9.4	5 1 5	4 0 4	A	11181.6126	-1.0
4 1 3	3 1 2	E	8995.6385	0.5	5 1 5	4 0 4	E	11181.6032	-0.7
5 0 5	4 0 4	A	10130.6173	-4.5	6 0 6	5 1 5	A	10923.7879	1.4
5 0 5	4 0 4	E	10130.6173	1.0	6 0 6	5 1 5	E	10923.7879	2.8
5 1 5	4 1 4	A	9752.2230	2.9	5 1 4	4 1 3	A	11189.0692	-9.0
5 1 5	4 1 4	E	9752.2158	-0.7	5 1 4	4 1 3	E	11189.0692	3.0

Table S8. Experimental transition frequencies of the ^{13}C7 isotopologue of AP

Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz	Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz
J' K_a' K_c'	J'' K_a'' K_c''				J' K_a' K_c'	J'' K_a'' K_c''			
3 0 3	2 0 2	A	6269.8945	4.4	5 1 4	4 1 3	A	11218.7554	-3.6
3 0 3	2 0 2	E	6269.8945	8.9	5 1 4	4 1 3	E	11218.7554	8.4
3 1 3	2 1 2	A	5913.7178	-0.8	6 0 6	5 0 5	A	12021.9098	1.2
3 1 3	2 1 2	E	5913.7178	1.5	6 0 6	5 0 5	E	12021.8999	-3.2
3 1 2	2 1 1	A	6787.2728	-3.1	6 1 6	5 1 5	A	11695.1099	-2.5
3 1 2	2 1 1	E	6787.2586	-9.6	6 1 6	5 1 5	E	11695.1099	1.6
4 0 4	3 0 3	A	8254.8057	2.1	2 2 0	1 1 1	A	12294.5996	-1.7
4 0 4	3 0 3	E	8254.7946	-3.7	2 2 0	1 1 1	E	12294.5996	2.7
4 1 4	3 1 3	A	7859.4850	-0.9	3 3 0	2 2 1	A	19516.1308	0.2
4 1 4	3 1 3	E	7859.4850	2.2	3 3 0	2 2 1	E	19517.0313	0.2
4 1 3	3 1 2	A	9018.3665	-2.1	4 0 4	3 1 3	A	6397.2388	4.5
4 1 3	3 1 2	E	9018.3567	-2.0	4 0 4	3 1 3	E	6397.2388	1.3
5 0 5	4 0 4	A	10168.4588	0.4	5 1 5	4 0 4	A	11249.1311	1.9
5 0 5	4 0 4	E	10168.4495	-3.3	5 1 5	4 0 4	E	11249.1179	-1.5
5 1 5	4 1 4	A	9786.8752	-2.5	6 0 6	5 1 5	A	10941.2392	1.3
5 1 5	4 1 4	E	9786.8752	1.1	6 0 6	5 1 5	E	10941.2353	-1.2

Table S9. Experimental transition frequencies of the ^{13}C8 isotopologue of AP

Transitions J' K_a' K_c'	J'' K_a'' K_c'	state	v_{obs}/MHz	ν_{diff}/kHz	Transitions J' K_a' K_c'	J'' K_a'' K_c'	state	v_{obs}/MHz	ν_{diff}/kHz
3 0 3	2 0 2	A	6217.2735	-4.6	5 1 4	4 1 3	A	11125.9217	-0.3
3 0 3	2 0 2	E	6217.2735	-0.2	5 1 4	4 1 3	E	11125.9111	0.9
3 1 2	2 1 1	A	6731.4138	4.1	6 0 6	5 0 5	A	11919.1447	2.5
3 1 2	2 1 1	E	6731.3963	-5.8	6 0 6	5 0 5	E	11919.1357	-1.0
4 0 4	3 0 3	A	8185.0649	3.1	6 1 6	5 1 5	A	11595.8139	-1.8
4 0 4	3 0 3	E	8185.0553	-1.3	6 1 6	5 1 5	E	11595.8139	2.2
4 1 4	3 1 3	A	7793.0177	-2.5	2 2 0	1 1 1	A	12177.8524	-7.6
4 1 4	3 1 3	E	7793.0177	0.5	2 2 0	1 1 1	E	12177.8524	-3.3
4 1 3	3 1 2	A	8943.9690	-6.9	3 3 0	2 2 1	A	19329.1830	1.2
4 1 3	3 1 2	E	8943.9690	2.8	3 3 0	2 2 1	E	19330.0759	6.8
5 0 5	4 0 4	A	10081.9702	-0.1	4 0 4	3 1 3	A	6348.7065	4.9
5 0 5	4 0 4	E	10081.9635	-1.3	4 0 4	3 1 3	E	6348.7065	1.8
5 1 5	4 1 4	A	9703.9446	-3.3	5 1 5	4 0 4	A	11148.2681	1.5
5 1 5	4 1 4	E	9703.9446	0.2	5 1 5	4 0 4	E	11148.2552	-1.7
6 0 6	5 1 5	A	10852.8467	0.8	6 0 6	5 1 5	E	10852.8467	2.1

2. Molecular structures of AP and semiexperimental rotational constants with vibrational corrections calculated at B3LYP(GD3BJ)/6-31+G(d,p) anharmonic force field (Table S10-S12)

Table S10. R_s and r_e coordinates of all carbon atoms in AP

	a/Å		b/Å	
	r_s	r_e	r_s	r_e
C1	±2.5930(6)[a]	2.601	0[b]	0.055
C2	±1.8659(8)	1.870	±1.245(1)	1.248
C3	±0.461(3)	0.471	±1.211(1)	1.214
C4	±0.13(1)	-0.207	0	-0.017
C5	±0.523(3)	0.533	±1.205(1)	-1.212
C6	±1.9216(8)	1.928	±1.171(1)	-1.175
C7	±1.6951(9)	-1.706	±0.07(2)	-0.104
C8	±2.5082(6)	-2.503	±1.175(1)	1.186

[a] Uncertainties are expressed in unit of the last digit.

[b] Imaginary values, fixed at zero.

Table S11. Semi-experimental rotational constants of nine isotopologues of AP with vibrational corrections calculated from the B3LYP(GD3BJ)/6-31+G(d,p) anharmonic force field

	Parent	C1	C2	C3	C4	C5	C6	C7	C8
A/MHz	3731.9757(5)	3688.0297(4)[b]	3690.2997(5)	3692.3966(5)	36731.879(1)	3692.3885(5)	3695.887(6)	3731.632(5)	3696.5375(5)
B/MHz	1222.6331(2)	1203.2305(2)	1212.5092(2)	1221.9894(3)	1222.5174(6)	1221.8064(2)	1211.7896(3)	1214.2255(2)	1204.3684(2)
C/MHz	926.4124(1)	915.2471(1)	918.0277(1)	923.5827(1)	926.3416(4)	923.4793(1)	917.9657(2)	921.5569(1)	913.7437(1)

Table S12. R_s, r_e and r^{SE} geometries of AP

	r_e	r_s	r^{SE}
Bond lengths/Å			
C1C2	1.399	1.441(1)[a]	1.446(1)
C2C3	1.399	1.405(3)	1.389(3)
C3C4	1.405	1.351(5)	1.43(2)
C4C5	1.405	1.374(6)	1.36(2)
C5C6	1.396	1.399(3)	1.394(2)
C6C1	1.402	1.350(1)	1.338(1)
C4C7	1.502	1.56(1)	1.501(8)
C7C8	1.516	1.49(2)	1.50(1)
Valence angles/°			
C4C7C8	118.4	120(1)	120(1)
C3C4C7	122.1	119.1(8)	120(2)
C5C4C7	118.4	115.9(8)	120(2)

[a] Errors in parenthesis are expressed in units of the last digit.

3. Experimental rotational transition frequencies of AP- H_2O (Tables S13-S17)

Table S13. Experimental transition frequencies of the normal species of AP-H_2O

Transitions J' K_a' K_c'	J'' K_a'' K_c''	state	ν_{obs}/MHz	ν_{diff}/kHz	Transitions J' K_a' K_c'	J'' K_a'' K_c''	state	ν_{obs}/MHz	ν_{diff}/kHz
5 0 5	4 0 4	A	5574.0095	-2.6	8 1 7	7 1 6	A	9288.9462	4.0
5 0 5	4 0 4	E	5574.0095	1.1	8 1 7	7 1 6	E	9288.9333	0.8
6 0 6	5 0 5	A	6667.6749	1.7	9 1 8	8 1 7	A	10434.7996	1.0
6 0 6	5 0 5	E	6667.6749	5.7	9 1 8	8 1 7	E	10434.7884	0.4
7 0 7	6 0 6	A	7750.7034	-3.8	10 1 9	9 1 8	A	11574.4590	-5.5
7 0 7	6 0 6	E	7750.7034	0.5	10 1 9	9 1 8	E	11574.4590	5.9
8 0 8	7 0 7	A	8822.4568	-4.0	11 1 10	10 1 9	A	12706.8442	0.5
8 0 8	7 0 7	E	8822.4568	0.4	11 1 10	10 1 9	E	12706.8369	5.3
9 0 9	8 0 8	A	9883.0143	-5.8	12 1 11	11 1 10	A	13830.7666	-1.1
9 0 9	8 0 8	E	9883.0143	-1.5	12 1 11	11 1 10	E	13830.7598	4.7
10 0 10	9 0 9	A	10933.2564	-4.7	13 1 12	12 1 11	A	14945.0390	-5.3
10 0 10	9 0 9	E	10933.2564	-0.5	13 1 12	12 1 11	E	14945.0349	3.6
11 0 11	10 0 10	A	11974.7378	-4.2	5 2 4	4 2 3	A	5609.0353	-1.1
11 0 11	10 0 10	E	11974.7378	-0.3	5 2 4	4 2 3	E	5609.0505	0.7
12 0 12	11 0 11	A	13009.4512	0.4	6 2 5	5 2 4	A	6727.1948	1.3
12 0 12	11 0 11	E	13009.4449	-2.2	6 2 5	5 2 4	E	6727.1948	-0.3
13 0 13	12 0 12	A	14039.4837	3.7	7 2 6	6 2 5	A	7843.3644	-1.1
13 0 13	12 0 12	E	14039.4785	2.1	7 2 6	6 2 5	E	7843.3644	1.8
5 1 5	4 1 4	A	5385.7931	-3.1	8 2 7	7 2 6	A	8957.2319	1.9
5 1 5	4 1 4	E	5385.7931	-1.1	8 2 7	7 2 6	E	8957.2247	-0.3
6 1 6	5 1 5	A	6457.9024	-2.6	9 2 8	8 2 7	A	10068.4777	5.4
6 1 6	5 1 5	E	6457.9024	-0.3	9 2 8	8 2 7	E	10068.4646	-1.4
7 1 7	6 1 6	A	7527.5102	8.4	10 2 9	9 2 8	A	11176.7979	8.9
7 1 7	6 1 6	E	7527.4978	-1.4	10 2 9	9 2 8	E	11176.7800	-1.6
8 1 8	7 1 7	A	8594.3578	-2.4	11 2 10	10 2 9	A	12281.9014	9.2
8 1 8	7 1 7	E	8594.3578	0.4	11 2 10	10 2 9	E	12281.8813	-2.8
9 1 9	8 1 8	A	9658.3260	-4.5	12 2 11	11 2 10	A	13383.5249	9.4
9 1 9	8 1 8	E	9658.3260	-1.5	12 2 11	11 2 10	E	13383.5064	-0.4
10 1 10	9 1 9	A	10719.3383	-3.0	6 2 4	5 2 3	A	6795.6581	-4.2
10 1 10	9 1 9	E	10719.3383	0.2	6 2 4	5 2 3	E	6795.6529	3.3
11 1 11	10 1 10	A	11777.3999	2.7	7 2 5	6 2 4	A	7951.4585	5.0
11 1 11	10 1 10	E	11777.3940	0.2	7 2 5	6 2 4	E	7951.4429	-0.1
12 1 12	11 1 11	A	12832.5698	-2.6	8 2 6	7 2 5	A	9116.1680	-2.7
12 1 12	11 1 11	E	12832.5658	-3.1	8 2 6	7 2 5	E	9116.1614	1.2
13 1 13	12 1 12	A	13884.9965	-5.1	9 2 7	8 2 6	A	10289.3711	0.2
13 1 13	12 1 12	E	13884.9965	-1.6	9 2 7	8 2 6	E	10289.3629	3.4

5 1 4	4 1 3	A	5823.7342	5.1	10 2 8	9 2 7	A	11469.8005	-5.1
5 1 4	4 1 3	E	5823.7211	-1.6	10 2 8	9 2 7	E	11469.7929	0.1
6 1 5	5 1 4	A	6982.5635	5.9	11 2 9	10 2 8	A	12655.5161	-4.7
6 1 5	5 1 4	E	6982.5465	-3.6	11 2 9	10 2 8	E	12655.5061	-0.5
7 1 6	6 1 5	A	8137.8998	4.1	12 2 10	11 2 9	A	13844.0984	-4.5
7 1 6	6 1 5	E	8137.8846	-2.5	12 2 10	11 2 9	E	13844.0859	-1.3
6 3 4	5 3 3	A	6746.2743	-0.7	9 4 5	8 4 4	E	10123.1818	-3.6
6 3 4	5 3 3	E	6746.6864	-1.4	10 4 6	9 4 5	A	11252.4624	2.7
7 3 5	6 3 4	A	7873.5826	-0.5	10 4 6	9 4 5	E	11252.2199	2.0
7 3 5	6 3 4	E	7873.9255	-0.1	3 2 1	2 1 2	A	12213.4886	-2.0
8 3 6	7 3 5	A	9001.8778	-1.7	3 2 1	2 1 2	E	12213.5586	6.0
8 3 6	7 3 5	E	9002.0474	0.6	4 2 3	3 1 2	A	12931.2741	-1.7
9 3 7	8 3 6	A	10131.0657	2.2	4 2 3	3 1 2	E	12931.2166	-0.1
9 3 7	8 3 6	E	10131.1336	0.2	4 2 2	3 1 3	A	13487.2297	-3.5
10 3 8	9 3 7	A	11260.9585	2.2	4 2 2	3 1 3	E	13487.2297	-1.5
10 3 8	9 3 7	E	11260.9828	-1.0	5 1 5	4 0 4	A	7873.1979	-5.6
10 3 7	9 3 6	A	11282.8504	-1.6	5 1 5	4 0 4	E	7873.1979	1.6
10 3 7	9 3 6	E	11282.8039	-1.9	5 2 3	4 1 4	A	14824.2551	5.1
11 3 9	10 3 8	A	12391.3022	-1.0	5 2 3	4 1 4	E	14824.2242	-2.7
11 3 9	10 3 8	E	12391.3156	4.1	6 1 6	5 0 5	A	8757.0895	-6.9
12 3 10	11 3 9	A	13521.7836	3.5	6 1 6	5 0 5	E	8757.0895	-1.1
12 3 10	11 3 9	E	13521.7785	-0.4	7 1 7	6 0 6	A	9616.9202	-4.8
6 3 3	5 3 2	A	6747.8503	1.1	7 1 7	6 0 6	E	9616.9202	-0.5
6 3 3	5 3 2	E	6747.4272	1.6	8 1 8	7 0 7	A	10460.5874	9.4
7 3 4	6 3 3	A	7877.1174	-0.3	8 1 8	7 0 7	E	10460.5758	0.7
7 3 4	6 3 3	E	7876.7639	1.3	9 1 9	8 0 8	A	11296.4473	-0.5
8 3 5	7 3 4	A	9008.9273	1.3	9 1 9	8 0 8	E	11296.4473	1.1
8 3 5	7 3 4	E	9008.7422	-1.8	10 1 10	9 0 9	A	12132.7730	4.0
9 3 6	8 3 5	A	10143.9215	0.2	10 1 10	9 0 9	E	12132.7730	4.4
9 3 6	8 3 5	E	10143.8370	2.2	9 4 6	8 4 5	A	10123.0570	3.1
11 3 8	10 3 7	A	12426.5596	-1.2	9 4 6	8 4 5	E	10123.1705	2.9
11 3 8	10 3 7	E	12426.5273	-4.3	10 4 7	9 4 6	A	11251.8939	-0.6
12 3 9	11 3 8	A	13575.9581	-2.1	10 4 7	9 4 6	E	11252.1159	-2.4
12 3 9	11 3 8	E	13575.9362	-1.9	11 4 8	10 4 7	A	12381.9439	0.0
7 4 4	6 4 3	A	7868.6288	-6.7	11 4 8	10 4 7	E	12382.2849	-4.0
7 4 4	6 4 3	E	7868.6515	1.8	7 4 3	6 4 2	A	7868.6712	-4.0
8 4 5	7 4 4	A	8995.3273	-7.9	7 4 3	6 4 2	E	7868.6515	2.8
8 4 5	7 4 4	E	8995.3808	-1.1	8 4 4	7 4 3	A	8995.4466	2.4
9 4 5	8 4 4	A	10123.3168	1.5	8 4 4	7 4 3	E	8995.3806	-2.7

Table S14. Experimental transition frequencies of AP-$H_2{}^{18}O$.

Transitions		state	v_{obs}/MHz	v_{diff}/kHz	Transitions		state	v_{obs}/MHz	v_{diff}/kHz
J' Ka' Kc'	J'' Ka'' Kc''				J' K_a' K_c'	J'' K_a'' K_c''			
5 0 5	4 0 4	A	5336.1960	-2.8	6 1 5	5 1 4	E	6670.2277	-1.9
5 0 5	4 0 4	E	5336.1960	0.9	7 1 6	6 1 5	A	7774.9864	4.2
6 0 6	5 0 5	A	6385.6975	-1.0	7 1 6	6 1 5	E	7774.9734	-0.1
6 0 6	5 0 5	E	6385.6975	3.1	8 1 7	7 1 6	A	8876.2092	2.4
7 0 7	6 0 6	A	7426.1526	-4.1	8 1 7	7 1 6	E	8876.1949	-2.1
7 0 7	6 0 6	E	7426.1526	0.3	9 1 8	8 1 7	A	9973.1927	2.8
8 0 8	7 0 7	A	8456.8635	-2.3	9 1 8	8 1 7	E	9973.1799	0.7
8 0 8	7 0 7	E	8456.8635	2.3	10 1 9	9 1 8	A	11065.1305	0.8
9 0 9	8 0 8	A	9477.6713	-2.6	10 1 9	9 1 8	E	11065.1135	-4.6
9 0 9	8 0 8	E	9477.6713	1.9	11 1 10	10 1 9	A	12151.1436	-1.1
10 0 10	9 0 9	A	10489.0547	-3.8	11 1 10	10 1 9	E	12151.1368	4.4
10 0 10	9 0 9	E	10489.0547	0.5	12 1 11	11 1 10	A	13230.2858	0.7
11 0 11	10 0 10	A	11492.0943	1.1	12 1 11	11 1 10	E	13230.2760	3.8
11 0 11	10 0 10	E	11492.0882	-0.8	13 1 12	12 1 11	A	14301.5564	-3.0
12 0 12	11 0 11	A	12488.2949	-3.9	13 1 12	12 1 11	E	14301.5502	4.1
12 0 12	11 0 11	E	12488.2949	0.0	5 2 4	4 2 3	A	5365.4672	9.9
13 0 13	12 0 12	A	13479.4092	-2.8	5 2 4	4 2 3	E	5365.4701	-3.6
13 0 13	12 0 12	E	13479.4043	-4.1	6 2 5	5 2 4	A	6435.5036	1.6
5 1 5	4 1 4	A	5161.1698	-1.5	6 2 5	5 2 4	E	6435.5036	-1.1
5 1 5	4 1 4	E	5161.1698	0.4	7 2 6	6 2 5	A	7503.8882	-0.8
6 1 6	5 1 5	A	6189.1576	-2.6	7 2 6	6 2 5	E	7503.8882	1.5
6 1 6	5 1 5	E	6189.1576	-0.3	8 2 7	7 2 6	A	8570.3481	0.2
7 1 7	6 1 6	A	7215.0164	-2.4	8 2 7	7 2 6	E	8570.3445	1.5
7 1 7	6 1 6	E	7215.0164	0.2	9 2 8	8 2 7	A	9634.6177	4.3
8 1 8	7 1 7	A	8238.5378	-2.1	9 2 8	8 2 7	E	9634.6070	-0.1
8 1 8	7 1 7	E	8238.5378	0.8	10 2 9	9 2 8	A	10696.4347	6.4
9 1 9	8 1 8	A	9259.5727	-3.4	10 2 9	9 2 8	E	10696.4208	-0.2
9 1 9	8 1 8	E	9259.5727	-0.3	11 2 10	10 2 9	A	11755.5547	8.4
10 1 10	9 1 9	A	10278.0390	-3.6	11 2 10	10 2 9	E	11755.5377	-0.5
10 1 10	9 1 9	E	10278.0390	-0.3	12 2 11	11 2 10	A	12811.7416	5.6
11 1 11	10 1 10	A	11293.9152	-0.5	12 2 11	11 2 10	E	12811.7296	2.5
11 1 11	10 1 10	E	11293.9152	3.0	6 2 4	5 2 3	A	6492.7725	-3.2
12 1 12	11 1 11	A	12307.2277	-2.5	6 2 4	5 2 3	E	6492.7640	2.2
12 1 12	11 1 11	E	12307.2277	1.0	7 2 5	6 2 4	A	7594.5065	2.4
13 1 13	12 1 12	A	13318.0768	3.9	7 2 5	6 2 4	E	7594.4924	-0.8
13 1 13	12 1 12	E	13318.0699	0.6	8 2 6	7 2 5	A	8704.0203	0.7
5 1 4	4 1 3	A	5562.6212	3.4	8 2 6	7 2 5	E	8704.0082	-0.7
5 1 4	4 1 3	E	5562.6097	-1.7	9 2 7	8 2 6	A	9821.1770	-2.2

6 1 5	5 1 4	A	6670.2427	5.5	9 2 7	8 2 6	E	9821.1690	1.3
10 2 8	9 2 7	A	10945.1953	-4.9	9 4 5	8 4 4	E	9680.2471	-1.9
10 2 8	9 2 7	E	10945.1876	0.2	5 1 5	4 0 4	A	7701.0734	-2.2
11 2 9	10 2 8	A	12074.6789	-8.9	5 1 5	4 0 4	E	7701.0672	-1.9
11 2 9	10 2 8	E	12074.6789	5.3	5 2 3	4 1 4	A	14591.8816	-2.0
12 2 10	11 2 9	A	13207.7719	-6.6	5 2 3	4 1 4	E	14591.8667	1.8
12 2 10	11 2 9	E	13207.7636	0.9	6 1 6	5 0 5	A	8554.0320	-5.0
6 3 4	5 3 3	A	6451.4719	-1.9	6 1 6	5 0 5	E	8554.0320	0.1
6 3 4	5 3 3	E	6451.8386	-0.3	7 1 7	6 0 6	A	9383.3561	-1.2
7 3 5	6 3 4	A	7529.2211	0.0	7 1 7	6 0 6	E	9383.3561	2.4
7 3 5	6 3 4	E	7529.5862	-0.6	8 1 8	7 0 7	A	10195.7397	-0.7
8 3 6	7 3 5	A	8607.8434	-1.1	8 1 8	7 0 7	E	10195.7397	1.3
8 3 6	7 3 5	E	8608.0494	-0.1	9 1 9	8 0 8	A	10998.4515	0.7
9 3 7	8 3 6	A	9687.2821	0.0	9 1 9	8 0 8	E	10998.4515	1.3
9 3 7	8 3 6	E	9687.3724	-0.6	10 1 10	9 0 9	A	11798.8227	3.3
10 3 8	9 3 7	A	10767.4096	-0.5	10 1 10	9 0 9	E	11798.8227	2.7
10 3 8	9 3 7	E	10767.4485	0.6	9 3 6	8 3 5	A	9697.0605	-5.4
10 3 7	9 3 6	A	10784.0884	-2.1	9 3 6	8 3 5	E	9696.9584	0.0
10 3 7	9 3 6	E	10784.0328	-1.2	11 3 8	10 3 7	A	11874.9460	-0.2
11 3 9	10 3 8	A	11848.0412	-1.7	11 3 8	10 3 7	E	11874.9077	-4.1
11 3 9	10 3 8	E	11848.0519	-4.5	12 3 9	11 3 8	A	12970.3669	-3.2
12 3 10	11 3 9	A	12928.9397	2.6	12 3 9	11 3 8	E	12970.3421	-3.2
12 3 10	11 3 9	E	12928.9397	1.1	8 4 5	7 4 4	A	8602.1347	-1.3
6 3 3	5 3 2	A	6452.6685	-1.1	8 4 5	7 4 4	E	8602.1620	-4.6
6 3 3	5 3 2	E	6452.2917	-2.0	9 4 6	8 4 5	A	9680.1653	2.4
8 3 5	7 3 4	A	8613.1987	-3.2	9 4 6	8 4 5	E	9680.2471	5.8
8 3 5	7 3 4	E	8612.9819	-0.3	7 4 3	6 4 2	A	7524.9999	9.1
8 4 4	7 4 3	A	8602.2095	-1.9	7 4 3	6 4 2	E	7524.9796	9.2
8 4 4	7 4 3	E	8602.1620	-4.6	9 4 5	8 4 4	A	9680.3430	-0.6

Table S15. Experimental transition frequencies of AP-DOH

Transitions		state	v_{obs}/MHz	ν_{diff}/kHz	Transitions		state	v_{obs}/MHz	ν_{diff}/kHz
J' K_a' K_c'	J'' K_a'' K_c''				J' K_a' K_c'	J'' K_a'' K_c''			
5 0 5	4 0 4	A	5498.0510	3.9	9 1 8	8 1 7	E	10288.3061	1.6
5 0 5	4 0 4	E	5498.0452	1.7	6 2 5	5 2 4	A	6634.2389	-4.1
6 0 6	5 0 5	A	6577.4747	-4.2	6 2 5	5 2 4	E	6634.2389	-6.1
6 0 6	5 0 5	E	6577.4747	-0.1	7 2 6	6 2 5	A	7735.1562	-2.8
7 0 7	6 0 6	A	7646.7258	-4.4	7 2 6	6 2 5	E	7735.1562	-0.2
7 0 7	6 0 6	E	7646.7258	-0.1	8 2 7	7 2 6	A	8833.8729	-2.3
8 0 8	7 0 7	A	8705.1287	-0.9	8 2 7	7 2 6	E	8833.8729	2.6
8 0 8	7 0 7	E	8705.1287	3.4	7 2 5	6 2 4	A	7838.3022	7.8
9 0 9	8 0 8	A	9752.6951	1.7	7 2 5	6 2 4	E	7838.2769	-7.1
9 0 9	8 0 8	E	9752.6899	0.8	6 1 6	5 0 5	A	8681.3920	-4.7
10 0 10	9 0 9	A	10790.1845	1.2	6 1 6	5 0 5	E	8681.3920	1.1
10 0 10	9 0 9	E	10790.1769	-2.3	7 1 7	6 0 6	A	9531.0539	-1.1
11 0 11	10 0 10	A	11819.0243	1.7	7 1 7	6 0 6	E	9531.0539	3.3
11 0 11	10 0 10	E	11819.0192	0.5	8 1 8	7 0 7	A	10364.3501	-1.3
12 0 12	11 0 11	A	12841.0762	4.1	8 1 8	7 0 7	E	10364.3501	1.6
12 0 12	11 0 11	E	12841.0710	2.6	9 1 9	8 1 8	A	9530.1378	-3.9
13 0 13	12 0 12	A	13858.3303	-1	9 1 9	8 1 8	E	9530.1378	-0.9
13 0 13	12 0 12	E	13858.3303	2.5	10 1 10	9 1 9	A	10577.4045	-2.5
5 1 5	4 1 4	A	5313.7029	-1	10 1 10	9 1 9	E	10577.4045	0.7
5 1 5	4 1 4	E	5313.7029	0.9	5 1 4	4 1 3	A	5741.0233	1.1
6 1 6	5 1 5	A	6371.6219	-0.6	5 1 4	4 1 3	E	5741.0128	-3.2
6 1 6	5 1 5	E	6371.6219	1.6	6 1 5	5 1 4	A	6883.6032	5.7
7 1 7	6 1 6	A	7427.1343	-2.8	6 1 5	5 1 4	E	6883.5863	-3.8
7 1 7	6 1 6	E	7427.1343	-0.3	7 1 6	6 1 5	A	8022.8647	6.9
8 1 8	7 1 7	A	8480.0235	-3.1	7 1 6	6 1 5	E	8022.8455	-3.8
8 1 8	7 1 7	E	8480.0235	-0.3	9 1 8	8 1 7	A	10288.3190	4.1
8 1 7	7 1 6	A	9158.0489	2.7	8 1 7	7 1 6	E	9158.0319	-4.8

Table S16. Experimental transition frequencies of AP-HOD

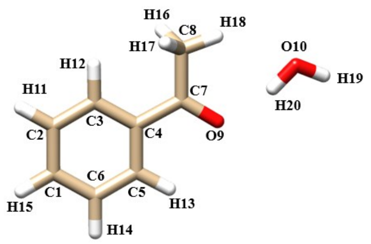
Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz	Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz
J' K_a' K_c'	J'' K_a'' K_c''				J' K_a' K_c'	J'' K_a'' K_c''			
5 0 5	4 0 4	A	5420.1298	-2.2	5 1 4	4 1 3	A	5656.1367	1.4
5 0 5	4 0 4	E	5420.1298	1.4	5 1 4	4 1 3	E	5656.1239	-5.3
6 0 6	5 0 5	A	6484.9545	-2.2	6 1 5	5 1 4	A	6782.0289	5.6
6 0 6	5 0 5	E	6484.9545	1.7	6 1 5	5 1 4	E	6782.0103	-5.8
7 0 7	6 0 6	A	7540.0510	-6.3	7 1 6	6 1 5	A	7904.7772	4.9
7 0 7	6 0 6	E	7540.0510	-2.2	7 1 6	6 1 5	E	7904.7623	-1.8
8 0 8	7 0 7	A	8584.7455	-2.8	8 1 7	7 1 6	A	9023.6707	0.7
8 0 8	7 0 7	E	8584.7455	1.5	8 1 7	7 1 6	E	9023.6585	-2.3
9 0 9	8 0 8	A	9618.9777	-2.4	9 1 8	8 1 7	A	10137.9247	5.8
9 0 9	8 0 8	E	9618.9777	1.8	9 1 8	8 1 7	E	10137.9094	0.6
10 0 10	9 0 9	A	10643.4045	0.8	6 2 5	5 2 4	A	6538.9348	1.2
10 0 10	9 0 9	E	10643.4045	4.9	6 2 5	5 2 4	E	6538.9348	-1.3
11 0 11	0 0 10	A	11659.3067	-0.1	7 2 6	6 2 5	A	7624.2001	-2.7
11 0 11	0 0 10	E	11659.3067	3.8	7 2 6	6 2 5	E	7624.2001	-0.4
12 0 12	1 0 11	A	12668.4199	0.0	8 2 7	7 2 6	A	8707.3842	3.4
12 0 12	1 0 11	E	12668.4199	3.7	8 2 7	7 2 6	E	8707.3747	-1.5
13 0 13	2 0 12	A	13672.6437	1.2	7 2 5	6 2 4	A	7722.3284	4.0
13 0 13	2 0 12	E	13672.6437	4.7	7 2 5	6 2 4	E	7722.3109	-3.2
6 1 6	5 1 5	A	6283.2384	-4.0	6 1 6	5 0 5	A	8603.1818	-5.5
6 1 6	5 1 5	E	6283.2384	-1.8	6 1 6	5 0 5	E	8603.1818	0.3
7 1 7	6 1 6	A	7324.3242	-5.3	7 1 7	6 0 6	A	9442.5623	2.2
7 1 7	6 1 6	E	7324.3242	-2.9	7 1 7	6 0 6	E	9442.5623	6.6
8 1 8	7 1 7	A	8362.9045	-2.5	8 1 8	7 0 7	A	10265.4036	-6.2
8 1 8	7 1 7	E	8362.9045	0.2	8 1 8	7 0 7	E	10265.4036	-3.2
9 1 9	8 1 8	A	9398.8230	-3.6	9 1 9	8 0 8	A	11079.4896	1.5
9 1 9	8 1 8	E	9398.8230	-0.6	9 1 9	8 0 8	E	11079.4896	3.2
10 1 10	9 1 9	A	10432.0063	-3.0	10 1 10	9 1 9	E	10432.0063	0.1

Table S17. Experimental transition frequencies of AP-D_2O

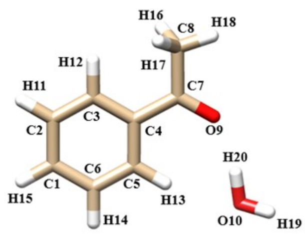
Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz	Transitions		state	ν_{obs}/MHz	ν_{diff}/kHz
J' K_a' K_c'	J'' K_a'' K_c''				J' K_a' K_c'	J'' K_a'' K_c''			
5 0 5	4 0 4	A	5498.0510	3.9	9 1 8	8 1 7	E	10288.3061	1.6
5 0 5	4 0 4	E	5498.0452	1.7	6 2 5	5 2 4	A	6634.2389	-4.1
6 0 6	5 0 5	A	6577.4747	-4.2	6 2 5	5 2 4	E	6634.2389	-6.1
6 0 6	5 0 5	E	6577.4747	-0.1	7 2 6	6 2 5	A	7735.1562	-2.8
7 0 7	6 0 6	A	7646.7258	-4.4	7 2 6	6 2 5	E	7735.1562	-0.2
7 0 7	6 0 6	E	7646.7258	-0.1	8 2 7	7 2 6	A	8833.8729	-2.3
8 0 8	7 0 7	A	8705.1287	-0.9	8 2 7	7 2 6	E	8833.8729	2.6
8 0 8	7 0 7	E	8705.1287	3.4	7 2 5	6 2 4	A	7838.3022	7.8
9 0 9	8 0 8	A	9752.6951	1.7	7 2 5	6 2 4	E	7838.2769	-7.1
9 0 9	8 0 8	E	9752.6899	0.8	6 1 6	5 0 5	A	8681.3920	-4.7
10 0 10	9 0 9	A	10790.1845	1.2	6 1 6	5 0 5	E	8681.3920	1.1
10 0 10	9 0 9	E	10790.1769	-2.3	7 1 7	6 0 6	A	9531.0539	-1.1
11 0 11	10 0 10	A	11819.0243	1.7	7 1 7	6 0 6	E	9531.0539	3.3
11 0 11	10 0 10	E	11819.0192	0.5	8 1 8	7 0 7	A	10364.3501	-1.3
12 0 12	11 0 11	A	12841.0762	4.1	8 1 8	7 0 7	E	10364.3501	1.6
12 0 12	11 0 11	E	12841.0710	2.6	9 1 9	8 1 8	A	9530.1378	-3.9
13 0 13	12 0 12	A	13858.3303	-1	9 1 9	8 1 8	E	9530.1378	-0.9
13 0 13	12 0 12	E	13858.3303	2.5	10 1 10	9 1 9	A	10577.4045	-2.5
5 1 5	4 1 4	A	5313.7029	-1	10 1 10	9 1 9	E	10577.4045	0.7
5 1 5	4 1 4	E	5313.7029	0.9	5 1 4	4 1 3	A	5741.0233	1.1
6 1 6	5 1 5	A	6371.6219	-0.6	5 1 4	4 1 3	E	5741.0128	-3.2
6 1 6	5 1 5	E	6371.6219	1.6	6 1 5	5 1 4	A	6883.6032	5.7
7 1 7	6 1 6	A	7427.1343	-2.8	6 1 5	5 1 4	E	6883.5863	-3.8
7 1 7	6 1 6	E	7427.1343	-0.3	7 1 6	6 1 5	A	8022.8647	6.9
8 1 8	7 1 7	A	8480.0235	-3.1	7 1 6	6 1 5	E	8022.8455	-3.8
8 1 8	7 1 7	E	8480.0235	-0.3	9 1 8	8 1 7	A	10288.3190	4.1
8 1 7	7 1 6	A	9158.0489	2.7	8 1 7	7 1 6	E	9158.0319	-4.8

4. Natural Bond Orbital (NBO) analysis of AP- H_2O (Tables S18 and S19)

Table S18. Second order perturbative stabilization energies for AP-H_2O obtained by Natural Bond Orbital (NBO) analysis at the B3LYP/6-311++G(2df,2pd) level of the theory. Stabilization energy contributions (≥ 0.10 kcal/mol) for AP-H_2O



Isomer I



Isomer II

Donor NBO	Acceptor NBO	E(2)/kcal mol^{-1}	Donor NBO	Acceptor NBO	E(2)/kcal mol^{-1}
From AP to H_2O			From AP to H_2O		
BD(1) C4-C7	BD*(1) O10-H20	0.14	BD(1) C5-H13	BD*(1) O10-H19	0.13
BD(1) C8-H18	BD*(1) O10-H19	0.14	BD(1) C7-C8	BD*(1) O10-H20	0.12
LP(1) O9	BD*(1) O10-H20	2.11	BD(1) C7-O9	RY(3)*H20	0.16
LP(2) O9	BD*(1) O10-H20	6.56	BD(2) C7-O9	BD*(1) O10-H20	0.14
From H_2O to AP			LP(1) O9	BD*(1) O10-H20	2.47
BD(1) O10-H19	RY*(1) H18	0.48	LP(2) O9	BD*(1) O10-H20	2.78
BD(1) O10-H20	RY*(1) H18	0.12	From H_2O to AP		
BD(1) O10-H20	BD*(1) C8-H18	0.13	BD(1) O10-H20	RY(1)*H13	0.38
LP(1) O10	BD*(1) C8-H18	0.11	BD(1) O10-H20	BD*(1) C5-H13	0.43
LP(2) O10	BD*(1) C8-H18	0.72	BD(1) O10-H20	BD*(1) C7-O9	0.10
			BD(1) O10-H19	RY(1)*H13	0.46
			LP(1) O10	BD*(1) C5-H13	0.14
			LP(2) O10	BD*(1) C5-H13	1.44

Table S19. NBO charges for isomer I of the AP-H_2O complex and AP and H_2O isolated molecules. Bold values highlight the values of the oxygen and hydrogen atoms involved in the charge transfer

	AP-H_2O complex	AP	H_2O
C	-0.17135	-0.17611	
C	-0.20278	-0.20362	
C	-0.16588	-0.17201	
C	-0.15839	-0.15464	
C	-0.14414	-0.14730	
C	-0.19928	-0.19963	
C	0.59118	0.57018	
C	-0.67683	-0.66719	
O	**-0.60361**	**-0.56783**	
O_w[a]	**-0.95856**		**-0.91803**
H	0.20661	0.20521	
H	0.20849	0.20627	
H	0.22864	0.22925	
H	0.20707	0.20603	
H	0.20613	0.20503	
H	0.22193	0.21959	
H	0.22356	0.21962	
H	0.24843	0.22716	
H_w[b]	0.45514		0.45901
H_w	**0.48366**		**0.45901**

[a] O_w represents the oxygen atom in water.

[b] H_w represents the hydrogen atom in water.

5. The AP-H_2O II to I isomerization pathway (Fig. S1).

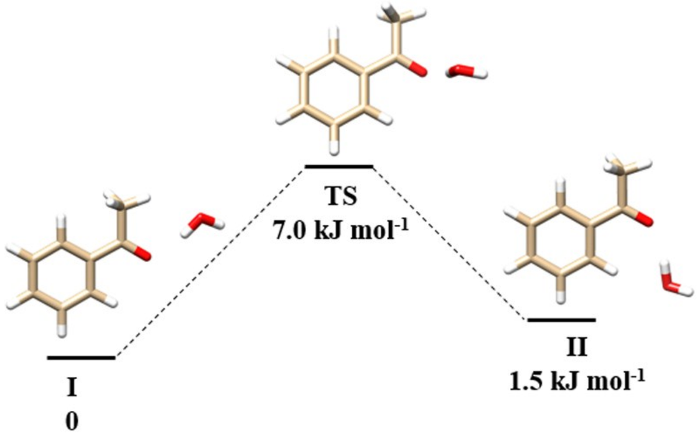


Fig. S1. The AP-H_2O II to I isomerization pathway: Barrier calculated at B3LYP/6-31+G(d,p) with zero-point energy correction.

6. Geometries of AP-H_2O (Table S20 & Fig. S2)

Table S20. MP2/6-311++G(2df,2pd) calculated geometries of AP-H_2O

Bond distance/Å		Valence and dihedral angles/°			
C2C1	1.392				
C3C2	1.392	C3C2C1	120.1		
C4C3	1.398	C4C3C2	120.1	C4C3C2C1	0.003
C5C4	1.398	C5C4C3	119.5	C5C4C3C2	-0.04
C6C5	1.388	C6C5C4	120.2	C6C5C4C3	0.05
C7C4	1.490	C7C4C3	121.9	C7C4C3C2	180.0
C8C7	1.504	C8C7C4	118.7	C8C7C4C3	-0.1
O9C7	1.226	O9C7C4	120.0	O9C7C4C3	179.8
O9O10	2.839	C7O9O10	111.9	C4C7O9O10	-175.6
H11C2	1.081	H11C2C3	119.8	H11C2C3C4	179.9
H12C3	1.080	H12C3C2	119.5	H12C3C2C1	-180.0
H13C5	1.081	H13C5C4	118.5	H13C5C4C3	-179.9
H14C6	1.081	H14C6C5	119.9	H14C6C5C4	180.0
H15C1	1.081	H15C1C2	120.0	H15C1C2C3	-180.0
H16C8	1.089	H16C8C7	110.1	H16C8C7C4	-58.2
H17C8	1.090	H17C8C7	110.0	H17C8C7C4	60.1
H18C8	1.085	H18C8C7	109.9	H18C8C7C4	-179.2
H19O10	0.958	H19O10O9	114.5	H19O10O9C7	-157.8
H20O10	0.969	H20O10H19	104.8	H20O10H19H18	68.2

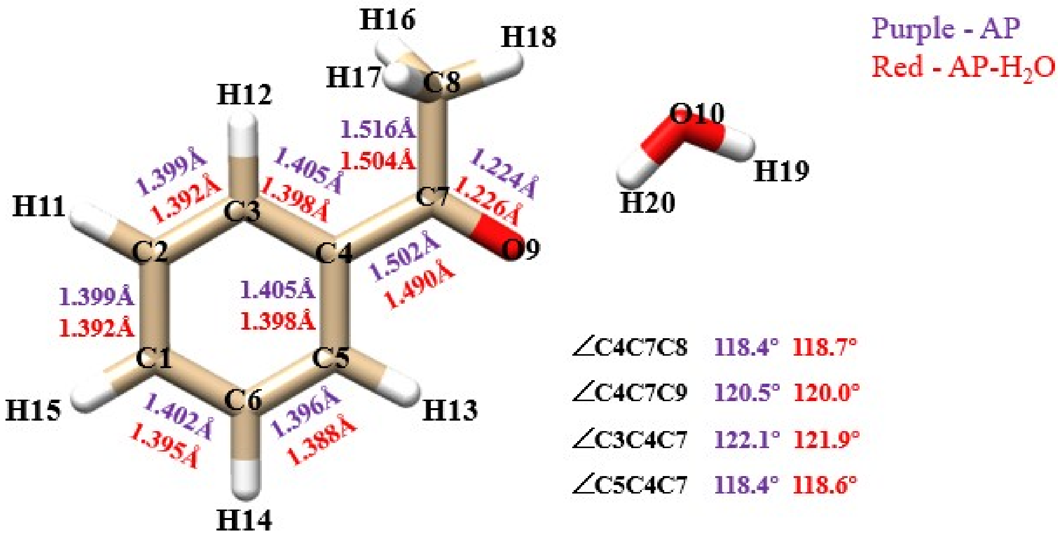


Fig. S2. Comparing the r_e structural parameters of AP in the complex to those of the monomer.