Electronic Supplementary Information

Fluorination Effects Probed in 4-fluoroacetophenone and Its Monohydrate

Xiujuan Wang,[a] Jiayi Li,[a] Juncheng Lei,[a] Xuefang Xu,*[a] Yang Zheng,[a] Junhua Chen,*[b] Xiao Tian,[a] and Qian Gou*[a,c]

[a] *School of Chemistry and Chemical Engineering, Chongqing University, Daxuecheng South Rd. 55, 401331, Chongqing, China.*

[b] *School of Pharmacy, Guizhou Medical University, Guiyang 550025, Guizhou, China*

[c] *Chongqing Key Laboratory of Theoretical and Computational Chemistry, Daxuecheng South Rd. 55, 401331, Chongqing, China.*

Corresponding Author

*Qian Gou, E-mail: qian.gou@cqu.edu.cn;
*Xuefang Xu, E-mail: xuefang_xu@cqu.edu.cm;
*Junhua Chen, E-mail: chenjh@gmc.edu.cn.

Contents:

Isomer II of 4FAP-DOH.

Table S23: Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs-calc}$, kHz) of the Isomer II of 4FAP-D_2O.

Fig. S2: The structural comparison of 4FAP and isomer II of 4FAP-H_2O in the distance (Å) between the H atoms of -CH_3 and the O atoms of -C=O.

Table S24: Transition frequencies and intensities of isomer I and isomer II of the 4FAP-H_2O complex for the population ratio.

Table S25: The r_s and r_e coordinates of the oxygen atom of water in 4FAP-H_2O.

Table S26: Theoretical, experimental and semi-experimental rotational constants of $H_2{}^{18}O$, DOH (with D participating in the HB), HOD, and D_2O isotopologues of isomers I of the 4FAP-H_2O.

Table S27: Theoretical, experimental and semi-experimental rotational constants of $H_2{}^{18}O$, DOH (with D participating in the HB), HOD, and D_2O isotopologues of isomers II of the 4FAP-H_2O.

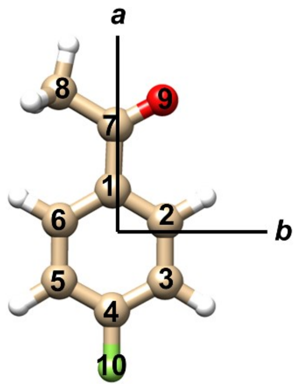

Fig. S1. Structure, principal axes of inertia and heavy atomic labels of the 4FAP monomer optimized at the MP2/6-311++G(d,p) level of theory.

Table S1 Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs-calc}$, kHz) of 4FAP.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs-calc}$/kHz
4	0	4	3	0	3	A	5613.2017	-2.1
4	0	4	3	0	3	E	5613.2017	1.5
4	1	4	3	1	3	A	5385.3023	-0.8
4	1	4	3	1	3	E	5385.3023	1.1
4	1	3	3	1	2	A	5910.3442	3.0
4	1	3	3	1	2	E	5910.3376	2.6
4	2	3	3	2	2	A	5653.1607	-0.3
4	2	3	3	2	2	E	5653.1888	1.1
4	2	2	3	2	1	A	5696.5106	-1.1
4	2	2	3	2	1	E	5696.4782	1.8
4	3	2	3	3	1	A	5665.0171	-1.3
4	3	2	3	3	1	E	5665.2578	3.6
4	3	1	3	3	0	A	5665.5620	0.1
4	3	1	3	3	0	E	5665.3187	1.0
5	0	5	4	0	4	A	6984.8343	-0.5
5	0	5	4	0	4	E	6984.8343	3.7
5	1	5	4	1	4	A	6724.0404	-1.4
5	1	5	4	1	4	E	6724.0404	0.9
5	1	4	4	1	3	A	7379.1204	1.8
5	1	4	4	1	3	E	7379.1099	-1.2
5	2	4	4	2	3	A	7060.9999	3.6
5	2	4	4	2	3	E	7060.9999	-0.2
5	2	3	4	2	2	A	7146.8426	0.5
5	2	3	4	2	2	E	7146.8264	-0.8
5	3	3	4	3	2	A	7084.7637	0.7
5	3	3	4	3	2	E	7085.2789	-0.6
5	3	2	4	3	1	A	7086.6609	-1.5
5	3	2	4	3	1	E	7086.1363	1.0
5	4	2	4	4	1	A	7080.3892	-0.7
5	4	2	4	4	1	E	7080.3892	-2.3
5	4	1	4	4	0	A	7080.4067	4.3
5	4	1	4	4	0	E	7080.3892	-1.1
6	0	6	5	0	5	A	8337.1386	-2.8
6	0	6	5	0	5	E	8337.1386	1.7
6	1	6	5	1	5	A	8058.1936	-1.2
6	1	6	5	1	5	E	8058.1936	1.5
6	1	5	5	1	4	A	8841.5153	1.7
6	1	5	5	1	4	E	8841.5037	-1.0
6	2	5	5	2	4	A	8465.2047	-1.3
6	2	5	5	2	4	E	8465.2047	1.3
6	2	4	5	2	3	A	8612.8391	1.9
6	2	4	5	2	3	E	8612.8234	-2.8

6	3	4	5	3	3	A	8506.3617	-0.2
6	3	4	5	3	3	E	8506.7696	0.4
6	3	3	5	3	2	A	8511.4134	0.3
6	3	3	5	3	2	E	8510.9934	0.5
6	4	3	5	4	2	A	8499.6479	-0.6
6	4	3	5	4	2	E	8499.6698	-1.1
6	4	2	5	4	1	A	8499.7000	-4.7
6	4	2	5	4	1	E	8499.6698	0.1
7	0	7	6	0	6	A	9668.9394	-2.1
7	0	7	6	0	6	E	9668.9394	2.5
7	1	7	6	1	6	A	9387.2896	-1.3
7	1	7	6	1	6	E	9387.2896	1.7
7	1	6	6	1	5	A	10295.7410	1.8
7	1	6	6	1	5	E	10295.7280	-1.2
7	2	6	6	2	5	A	9865.0829	-2.6
7	2	6	6	2	5	E	9865.0829	2.8
7	2	5	6	2	4	A	10094.9213	1.7
7	2	5	6	2	4	E	10094.9070	-1.8
7	3	5	6	3	4	A	9929.7397	0.1
7	3	5	6	3	4	E	9929.9015	0.5
7	3	4	6	3	3	A	9941.0518	-1.7
7	3	4	6	3	3	E	9940.8768	-0.2
7	4	4	6	4	3	A	9920.6127	-1.6
7	4	4	6	4	3	E	9920.7027	4.9
7	4	3	6	4	2	A	9920.7964	-4.8
7	4	3	6	4	2	E	9920.7011	-1.8
8	0	8	7	0	7	A	10981.0574	-2.3
8	0	8	7	0	7	E	10981.0574	2.3
8	1	8	7	1	7	A	10711.0634	-1.5
8	1	8	7	1	7	E	10711.0634	1.8
8	1	7	7	1	6	A	11739.7484	2.4
8	1	7	7	1	6	E	11739.7337	-1.1
8	2	7	7	2	6	A	11259.9534	1.1
8	2	7	7	2	6	E	11259.9451	-0.4
8	2	6	7	2	5	A	11591.4755	1.4
8	2	6	7	2	5	E	11591.4610	-1.2
8	3	6	7	3	5	A	11354.6138	-0.9
8	3	6	7	3	5	E	11354.6713	0.8
8	3	5	7	3	4	A	11377.0823	-2.0
8	3	5	7	3	4	E	11377.0113	0.4
8	4	5	7	4	4	A	11343.5304	-1.6
8	4	5	7	4	4	E	11343.7481	-1.0
8	4	4	7	4	3	A	11344.0440	-1.0
8	4	4	7	4	3	E	11343.8110	0.2

9	0	9	8	0	8	A	12276.3025	-1.4
9	0	9	8	0	8	E	12276.3025	3.0
9	1	9	8	1	8	A	12029.4564	-1.5
9	1	9	8	1	8	E	12029.4564	2.0
9	1	8	8	1	7	A	13171.2218	3.0
9	1	8	8	1	7	E	13171.2059	-0.8
9	2	8	8	2	7	A	12649.1609	1.4
9	2	8	8	2	7	E	12649.1511	-0.4
9	2	7	8	2	6	A	13098.8534	1.1
9	2	7	8	2	6	E	13098.8371	-1.7
9	3	7	8	3	6	A	12780.4986	-0.5
9	3	7	8	3	6	E	12780.5156	-0.8
9	3	6	8	3	5	A	12821.2669	-1.7
9	3	6	8	3	5	E	12821.2320	0.9
9	4	6	8	4	5	A	12768.6088	-2.1
9	4	6	8	4	5	E	12769.0180	-0.4
9	4	5	8	4	4	A	12769.8361	-2.1
9	4	5	8	4	4	E	12769.4113	0.0
10	0	10	9	0	9	A	13558.8483	-1.8
10	0	10	9	0	9	E	13558.8483	2.5
10	1	10	9	1	9	A	13342.6007	-1.8
10	1	10	9	1	9	E	13342.6007	1.8
10	1	9	9	1	8	A	14587.6299	2.3
10	1	9	9	1	8	E	14587.6150	0.3
10	2	9	9	2	8	A	14032.1130	2.1
10	2	9	9	2	8	E	14032.1022	0.1
10	2	8	9	2	7	A	14611.9661	2.2
10	2	8	9	2	7	E	14611.9454	-3.4
10	3	8	9	3	7	A	14206.7152	0.9
10	3	8	9	3	7	E	14206.7152	-0.7
10	3	7	9	3	6	A	14275.5758	-3.2
10	3	7	9	3	6	E	14275.5556	1.0
10	4	7	9	4	6	A	14196.0069	-1.4
10	4	7	9	4	6	E	14196.4945	0.4
10	4	6	9	4	5	A	14198.6548	-1.4
10	4	6	9	4	5	E	14198.1478	-0.8
11	0	11	10	0	10	A	14833.2527	-2.7
11	0	11	10	0	10	E	14833.2527	1.4
11	1	11	10	1	10	A	14650.7948	-0.4
11	1	11	10	1	10	E	14650.7948	3.3
11	1	10	10	1	9	A	15986.3686	3.0
11	1	10	10	1	9	E	15986.3511	-1.1
11	2	10	10	2	9	A	15408.2811	0.5
11	2	10	10	2	9	E	15408.2709	-0.2

11	2	9	10	2	8	A	16125.2343	-0.4
11	2	9	10	2	8	E	16125.2173	-0.5
11	3	9	10	3	8	A	15632.4158	-4.1
11	3	9	10	3	8	E	15632.4158	1.6
12	0	12	11	0	11	A	16103.5377	-2.4
12	0	12	11	0	11	E	16103.5377	1.6
12	1	12	11	1	11	A	15954.4557	-1.6
12	1	12	11	1	11	E	15954.4557	2.2
13	0	13	12	0	12	A	17372.6703	-0.9
13	0	13	12	0	12	E	17372.6703	3.0
13	1	13	12	1	12	A	17254.0910	-1.3
13	1	13	12	1	12	E	17254.0910	2.6
2	1	2	1	0	1	A	5597.2451	8.7
2	1	2	1	0	1	E	5597.2233	-0.1
2	2	1	1	1	0	A	11660.7282	-1.8
2	2	1	1	1	0	E	11660.4725	2.3
2	2	0	1	1	1	A	11796.4911	1.4
2	2	0	1	1	1	E	11796.6746	0.6
3	2	2	2	1	1	A	12943.4694	-3.9
3	2	2	2	1	1	E	12943.3915	2.3
3	3	1	2	2	0	A	19070.9753	1.7
3	3	1	2	2	0	E	19069.2255	-1.9
3	3	0	2	2	1	A	19075.4295	1.2
3	3	0	2	2	1	E	19077.0482	-1.3
4	1	4	3	0	3	A	7976.2784	7.0
4	1	4	3	0	3	E	7976.2590	-1.2
4	2	3	3	1	2	A	14159.8986	1.5
4	2	3	3	1	2	E	14159.8447	0.1
5	1	5	4	0	4	A	9087.1155	6.2
5	1	5	4	0	4	E	9087.0984	-1.1
5	2	4	4	1	3	A	15310.5570	4.8
5	2	4	4	1	3	E	15310.5099	0.2
6	0	6	5	1	5	A	6234.8685	1.7
6	0	6	5	1	5	E	6234.8685	0.5
6	1	6	5	0	5	A	10160.4731	3.8
6	1	6	5	0	5	E	10160.4601	-0.9
6	2	5	5	1	4	A	16396.6409	1.3
6	2	5	5	1	4	E	16396.6027	0.7
6	2	4	5	1	5	A	18663.6460	-7.3
6	2	4	5	1	5	E	18663.6046	0.8
7	0	7	6	1	6	A	7845.6136	0.1
7	0	7	6	1	6	E	7845.6136	0.8
7	1	7	6	0	6	A	11210.6113	-7.6
7	1	7	6	0	6	E	11210.6113	-0.7

7	2	6	6	1	5	A	17420.2085	-2.9
7	2	6	6	1	5	E	17420.1791	1.8
8	0	8	7	1	7	A	9439.3813	-1.1
8	0	8	7	1	7	E	9439.3813	1.3
8	1	8	7	0	7	A	12252.7369	-5.4
8	1	8	7	0	7	E	12252.7369	0.1
8	2	7	7	1	6	A	18384.4197	-4.8
8	2	7	7	1	6	E	18384.3965	2.9
9	0	9	8	1	8	A	11004.6198	-1.6
9	0	9	8	1	8	E	11004.6198	2.0
9	1	9	8	0	8	A	13301.1370	-3.4
9	1	9	8	0	8	E	13301.1370	1.0
9	2	8	8	1	7	A	19293.8340	-4.0
9	2	8	8	1	7	E	19293.8141	3.7
10	0	10	9	1	9	A	12534.0116	-2.1
10	0	10	9	1	9	E	12534.0116	2.3
10	1	10	9	0	9	A	14367.4369	-2.1
10	1	10	9	0	9	E	14367.4369	1.4
11	0	11	10	1	10	A	14024.6647	-1.8
11	0	11	10	1	10	E	14024.6647	3.1
11	1	11	10	0	10	A	15459.3825	-1.5
11	1	11	10	0	10	E	15459.3825	1.4
12	0	12	11	1	11	A	15477.4096	-1.8
12	0	12	11	1	11	E	15477.4096	3.3
12	1	12	11	0	11	A	16580.5847	-1.3
12	1	12	11	0	11	E	16580.5847	1.4
13	0	13	12	1	12	A	16895.6244	-0.9
13	0	13	12	1	12	E	16895.6244	4.2
13	1	13	12	0	12	A	17731.1353	-2.9
13	1	13	12	0	12	E	17731.1353	-0.3
14	0	14	13	1	13	A	18284.0214	-2.1
14	0	14	13	1	13	E	18284.0214	2.9
14	1	14	13	0	13	A	18908.7079	-1.9
14	1	14	13	0	13	E	18908.7079	0.7

Table S2 Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs\text{-}calc}$, kHz) of ^{13}C1 isotopologue of 4FAP.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs\text{-}calc}$/kHz
6	0	6	5	0	5	A	8331.8457	-1.3
6	0	6	5	0	5	E	8331.8457	3.2
7	0	7	6	0	6	A	9662.9171	6.3
7	0	7	6	0	6	E	9662.9062	0.0
8	0	8	7	0	7	A	10974.3156	-9.1
8	0	8	7	0	7	E	10974.3156	-4.5
2	1	2	1	0	1	A	5596.1890	8.4
2	1	2	1	0	1	E	5596.1663	-1.2
3	1	3	2	0	2	A	6814.2294	9.8
3	1	3	2	0	2	E	6814.2033	-4.1
3	2	2	2	1	1	A	12942.6186	-2.5
3	2	2	2	1	1	E	12942.5312	-5.6
4	1	4	3	0	3	A	7973.9204	0.1
4	1	4	3	0	3	E	7973.8975	-1.6
4	2	3	3	1	2	A	14158.3650	0.4
4	2	3	3	1	2	E	14158.3059	-6.1
5	1	5	4	0	4	A	9084.1780	5.9
5	1	5	4	0	4	E	9084.1602	-2.0
5	2	4	4	1	3	A	15308.4429	3.8
5	2	4	4	1	3	E	15308.3808	-5.8
6	1	6	5	0	5	A	10156.9667	2.3
6	1	6	5	0	5	E	10156.9549	-1.1
7	1	7	6	0	6	A	11206.5151	-2.7
7	1	7	6	0	6	E	11206.5036	-7.3
7	0	7	6	1	6	A	7837.7944	1.0
7	0	7	6	1	6	E	7837.7944	1.7
8	1	8	7	0	7	A	12247.9898	5.9
8	1	8	7	0	7	E	12247.9780	-0.4
8	0	8	7	1	7	A	9430.7164	-1.4
8	0	8	7	1	7	E	9430.7164	0.9
9	1	9	8	0	8	A	13295.6400	-3.2
9	1	9	8	0	8	E	13295.6400	1.1
9	0	9	8	1	8	A	10995.2172	-1.8
9	0	9	8	1	8	E	10995.2172	1.7

Table S3 Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs\text{-}calc}$, kHz) of ^{13}C2 isotopologue of 4FAP.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs\text{-}calc}$/kHz
6	0	6	5	0	5	A	8325.6816	-4.0
6	0	6	5	0	5	E	8325.6816	0.5
7	0	7	6	0	6	A	9654.0914	-4.2
7	0	7	6	0	6	E	9654.0914	0.4
8	0	8	7	0	7	A	10962.5766	-3.6
8	0	8	7	0	7	E	10962.5766	0.9
2	2	1	1	1	0	A	11542.9670	-4.1
2	2	1	1	1	0	E	11542.7218	-1.1
3	1	3	2	0	2	A	6770.6325	-8.2
3	1	3	2	0	2	E	6770.6325	3.7
4	1	4	3	0	3	A	7927.6802	9.0
4	1	4	3	0	3	E	7927.6593	-1.0
4	2	3	3	1	2	A	14036.7893	4.0
4	2	3	3	1	2	E	14036.7347	0.3
5	1	5	4	0	4	A	9035.1562	8.8
5	1	5	4	0	4	E	9035.1366	-1.2
6	1	6	5	0	5	A	10105.4248	3.3
6	1	6	5	0	5	E	10105.4115	-1.9
6	0	6	5	1	5	A	6266.8847	1.7
6	0	6	5	1	5	E	6266.8847	0.7
7	1	7	6	0	6	A	11153.1304	-6.9
7	1	7	6	0	6	E	11153.1304	-0.2
7	0	7	6	1	6	A	7874.3583	-1.4
7	0	7	6	1	6	E	7874.3583	-0.4
8	1	8	7	0	7	A	12193.7779	-4.3
8	1	8	7	0	7	E	12193.7779	1.1
8	0	8	7	1	7	A	9463.5386	0.1
8	0	8	7	1	7	E	9463.5386	2.6
9	1	9	8	0	8	A	13241.7946	0.1
9	1	9	8	0	8	E	13241.7946	4.3
9	0	9	8	1	8	A	11022.9799	-1.4
9	0	9	8	1	8	E	11022.9799	2.3

Table S4 Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs\text{-}calc}$, kHz) of ^{13}C3 isotopologue of 4FAP.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs\text{-}calc}$/kHz
5	0	5	4	0	4	A	6957.9828	-3.1
5	0	5	4	0	4	E	6957.9828	1.0
6	0	6	5	0	5	A	8304.1677	-3.1
6	0	6	5	0	5	E	8304.1677	1.4
7	0	7	6	0	6	A	9629.6122	-0.7
7	0	7	6	0	6	E	9629.6122	3.9
8	0	8	7	0	7	A	10935.2570	-2.5
8	0	8	7	0	7	E	10935.2570	2.0
2	2	1	1	1	0	A	11543.6703	-8.3
2	2	1	1	1	0	E	11543.4249	-3.1
3	1	3	2	0	2	A	6763.9295	2.7
3	1	3	2	0	2	E	6763.9035	-1.3
4	1	4	3	0	3	A	7918.4551	6.7
4	1	4	3	0	3	E	7918.4352	-2.3
4	2	3	3	1	2	A	14031.6096	2.9
4	2	3	3	1	2	E	14031.5584	2.8
5	1	5	4	0	4	A	9023.6008	5.1
5	1	5	4	0	4	E	9023.5845	-1.6
6	1	6	5	0	5	A	10091.5709	4.5
6	1	6	5	0	5	E	10091.5555	-2.8
6	0	6	5	1	5	A	6238.5575	-3.5
6	0	6	5	1	5	E	6238.5525	-9.6
7	1	7	6	0	6	A	11136.8496	1.0
7	1	7	6	0	6	E	11136.8386	-3.3
7	0	7	6	1	6	A	7842.2178	0.6
7	0	7	6	1	6	E	7842.2178	1.4
8	1	8	7	0	7	A	12174.7931	-0.9
8	1	8	7	0	7	E	12174.7875	-1.2
8	0	8	7	1	7	A	9428.0252	1.4
8	0	8	7	1	7	E	9428.0252	3.8
9	1	9	8	0	8	A	13219.7541	-4.6
9	1	9	8	0	8	E	13219.7541	-0.4
9	0	9	8	1	8	A	10984.5396	-0.5
9	0	9	8	1	8	E	10984.5396	3.1

Table S5 Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs-calc}$, kHz) of ^{13}C4 isotopologue of 4FAP.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs-calc}$/kHz
5	0	5	4	0	4	A	6945.4437	-4.1
5	0	5	4	0	4	E	6945.4437	0.1
6	0	6	5	0	5	A	8290.8953	3.2
6	0	6	5	0	5	E	8290.8857	-1.9
7	0	7	6	0	6	A	9616.2071	-2.3
7	0	7	6	0	6	E	9616.2022	-2.6
7	1	7	6	1	6	A	9335.7978	-3.1
7	1	7	6	1	6	E	9335.7978	-0.1
8	0	8	7	0	7	A	10922.1147	-2.7
8	0	8	7	0	7	E	10922.1147	1.8
2	2	1	1	1	0	A	11657.6625	-5.5
2	2	1	1	1	0	E	11657.4016	-1.6
3	1	3	2	0	2	A	6799.8878	6.3
3	1	3	2	0	2	E	6799.8675	-1.8
4	1	4	3	0	3	A	7954.7389	7.0
4	1	4	3	0	3	E	7954.7190	-1.8
4	2	3	3	1	2	A	14144.0868	1.5
4	2	3	3	1	2	E	14144.0360	3.5
5	1	5	4	0	4	A	9060.4781	2.5
5	1	5	4	0	4	E	9060.4621	-3.6
6	1	6	5	0	5	A	10128.8247	2.3
6	1	6	5	0	5	E	10128.8119	-2.1
7	1	7	6	0	6	A	11173.7370	5.8
7	1	7	6	0	6	E	11173.7211	-3.2
7	0	7	6	1	6	A	7778.2802	1.1
7	0	7	6	1	6	E	7778.2802	1.8
8	1	8	7	0	7	A	12210.1145	3.5
8	1	8	7	0	7	E	12210.1040	-1.5
8	0	8	7	1	7	A	9364.5935	-2.1
8	0	8	7	1	7	E	9364.5935	0.1
9	1	9	8	0	8	A	13252.0857	-0.5
9	1	9	8	0	8	E	13252.0788	-3.0
9	0	9	8	1	8	A	10923.2778	0.1
9	0	9	8	1	8	E	10923.2778	3.5

Table S6 Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs-calc}$, kHz) of ^{13}C5 isotopologue of 4FAP.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs-calc}$/kHz
6	0	6	5	0	5	A	8304.6475	-1.4
6	0	6	5	0	5	E	8304.6475	3.0
7	0	7	6	0	6	A	9630.0855	-2.1
7	0	7	6	0	6	E	9630.0855	2.4
8	0	8	7	0	7	A	10935.7136	-2.6
8	0	8	7	0	7	E	10935.7136	1.9
2	2	1	1	1	0	A	11539.1724	-8.3
2	2	1	1	1	0	E	11538.9301	-0.5
3	1	3	2	0	2	A	6762.4884	6.8
3	1	3	2	0	2	E	6762.4679	-1.8
3	2	2	2	1	1	A	12816.4727	7.2
3	2	2	2	1	1	E	12816.3849	0.8
4	1	4	3	0	3	A	7916.9988	4.6
4	1	4	3	0	3	E	7916.9808	-2.5
4	2	3	3	1	2	A	14027.1574	2.8
4	2	3	3	1	2	E	14027.1032	-0.4
5	1	5	4	0	4	A	9022.1178	5.9
5	1	5	4	0	4	E	9022.1013	-1.0
5	2	4	4	1	3	A	15171.8093	-4.1
5	2	4	4	1	3	E	15171.7712	-0.8
6	1	6	5	0	5	A	10090.0686	5.9
6	1	6	5	0	5	E	10090.0542	-0.3
7	1	7	6	0	6	A	11135.3485	-6.9
7	1	7	6	0	6	E	11135.3485	-0.3
7	0	7	6	1	6	A	7844.6730	-0.9
7	0	7	6	1	6	E	7844.6730	0.0
8	1	8	7	0	7	A	12173.3551	-4.2
8	1	8	7	0	7	E	12173.3551	1.1
8	0	8	7	1	7	A	9430.4471	-1.3
8	0	8	7	1	7	E	9430.4471	1.2
9	1	9	8	0	8	A	13218.4371	-2.0
9	1	9	8	0	8	E	13218.4378	2.9
9	0	9	8	1	8	A	10986.8655	-2.1
9	0	9	8	1	8	E	10986.8655	1.5

Table S7 Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs-calc}$, kHz) of ^{13}C6 isotopologue of 4FAP.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs-calc}$/kHz
5	0	5	4	0	4	A	6976.5462	-4.9
5	0	5	4	0	4	E	6976.5462	-0.7
6	0	6	5	0	5	A	8325.9600	-2.5
6	0	6	5	0	5	E	8325.9600	2.0
7	0	7	6	0	6	A	9654.4510	-1.8
7	0	7	6	0	6	E	9654.4510	2.8
8	0	8	7	0	7	A	10963.0203	-2.9
8	0	8	7	0	7	E	10963.0203	1.6
2	2	1	1	1	0	A	11545.6704	-2.2
2	2	1	1	1	0	E	11545.4239	-0.2
3	1	3	2	0	2	A	6771.6983	2.9
3	1	3	2	0	2	E	6771.6705	-2.9
4	1	4	3	0	3	A	7928.8027	9.7
4	1	4	3	0	3	E	7928.7806	-1.5
4	2	3	3	1	2	A	14039.6077	-6.1
4	2	3	3	1	2	E	14039.5650	2.1
5	1	5	4	0	4	A	9036.3567	8.5
5	1	5	4	0	4	E	9036.3377	-0.9
6	1	6	5	0	5	A	10106.6997	5.1
6	1	6	5	0	5	E	10106.6862	-0.3
6	0	6	5	1	5	A	6266.1670	1.6
6	0	6	5	1	5	E	6266.1670	0.6
7	1	7	6	0	6	A	11154.4695	2.0
7	1	7	6	0	6	E	11154.4602	-0.6
7	0	7	6	1	6	A	7873.7212	0.5
7	0	7	6	1	6	E	7873.7212	1.5
8	1	8	7	0	7	A	12195.1408	-6.4
8	1	8	7	0	7	E	12195.1408	-1.1
8	0	8	7	1	7	A	9463.0082	-0.3
8	0	8	7	1	7	E	9463.0082	2.1
9	1	9	8	0	8	A	13243.1653	-3.8
9	1	9	8	0	8	E	13243.1653	0.4
9	0	9	8	1	8	A	11022.5842	-3.7
9	0	9	8	1	8	E	11022.5842	-0.1

Table S8 Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs-calc}$, kHz) of ^{13}C7 isotopologue of 4FAP.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs-calc}$/kHz
6	0	6	5	0	5	A	8283.6182	-2.8
6	0	6	5	0	5	E	8283.6182	1.7
7	0	7	6	0	6	A	9607.9046	-3.1
7	0	7	6	0	6	E	9607.9046	1.5
8	0	8	7	0	7	A	10912.8247	-1.7
8	0	8	7	0	7	E	10912.8247	2.9
2	1	2	1	0	1	A	5585.3990	5.8
2	1	2	1	0	1	E	5585.3759	-4.3
2	2	1	1	1	0	A	11656.5188	-6.1
2	2	1	1	1	0	E	11656.2577	-1.7
3	1	3	2	0	2	A	6797.1339	4.9
3	1	3	2	0	2	E	6797.1050	-1.7
3	2	2	2	1	1	A	12931.4387	2.0
3	2	2	2	1	1	E	12931.3487	-2.6
4	1	4	3	0	3	A	7951.1062	6.5
4	1	4	3	0	3	E	7951.0863	-2.2
4	2	3	3	1	2	A	14140.9297	4.9
4	2	3	3	1	2	E	14140.8688	-3.0
5	1	5	4	0	4	A	9056.0371	7.0
5	1	5	4	0	4	E	9056.0179	-2.3
6	1	6	5	0	5	A	10123.5834	5.0
6	1	6	5	0	5	E	10123.5682	-1.8
7	1	7	6	0	6	A	11167.6589	1.1
7	1	7	6	0	6	E	11167.6488	-2.1
7	0	7	6	1	6	A	7767.9496	-0.6
7	0	7	6	1	6	E	7767.9496	0.0
8	1	8	7	0	7	A	12203.1363	0.0
8	1	8	7	0	7	E	12203.1280	-2.8
8	0	8	7	1	7	A	9353.0749	-1.4
8	0	8	7	1	7	E	9353.0749	0.9
9	1	9	8	0	8	A	13244.1063	-4.9
9	1	9	8	0	8	E	13244.1063	-0.5
9	0	9	8	1	8	A	10910.6985	-1.7
9	0	9	8	1	8	E	10910.6985	1.8

Table S9 Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs-calc}$, kHz) of ^{13}C8 isotopologue of 4FAP.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs-calc}$/kHz
6	0	6	5	0	5	A	8227.2873	-1.6
6	0	6	5	0	5	E	8227.2873	2.7
7	0	7	6	0	6	A	9542.0276	-1.3
7	0	7	6	0	6	E	9542.0276	3.3
8	0	8	7	0	7	A	10837.4289	-3.4
8	0	8	7	0	7	E	10837.4289	1.1
2	1	2	1	0	1	A	5535.3323	-0.3
2	1	2	1	0	1	E	5535.3105	-9.4
2	2	1	1	1	0	A	11541.9182	2.5
2	2	1	1	1	0	E	11541.6568	0.2
3	1	3	2	0	2	A	6738.3659	-3.8
3	1	3	2	0	2	E	6738.3659	8.2
4	1	4	3	0	3	A	7883.9029	9.7
4	1	4	3	0	3	E	7883.8794	-2.8
4	2	3	3	1	2	A	14008.7181	-5.0
4	2	3	3	1	2	E	14008.6734	2.0
5	1	5	4	0	4	A	8980.6451	5.8
5	1	5	4	0	4	E	8980.6260	-3.6
6	1	6	5	0	5	A	10040.3291	3.1
6	1	6	5	0	5	E	10040.3155	-2.3
6	0	6	5	1	5	A	6139.1076	2.7
6	0	6	5	1	5	E	6139.1076	1.5
7	1	7	6	0	6	A	11076.9113	2.2
7	1	7	6	0	6	E	11076.8992	-3.1
7	0	7	6	1	6	A	7728.9913	-0.5
7	0	7	6	1	6	E	7728.9913	0.2
8	1	8	7	0	7	A	12105.2742	3.8
8	1	8	7	0	7	E	12105.2631	-1.9
8	0	8	7	1	7	A	9302.5505	-1.6
8	0	8	7	1	7	E	9302.5505	0.7
9	1	9	8	0	8	A	13139.4677	-4.0
9	1	9	8	0	8	E	13139.4677	0.2
9	0	9	8	1	8	A	10848.3542	-3.0
9	0	9	8	1	8	E	10848.3542	0.4

Table S10 Comparison of the *ab* initio (r_e), the substituted (r_s) and the semi-experimental equilibrium ($r_{s\rightarrow e}^{SE}$) coordinates of carbon atoms in 4FAP. (See Fig. S1 for the atomic labels).

	a/Å			*b*/Å		
	r_e	r_s	$r_{s\rightarrow e}^{SE}$	r_e	r_s	$r_{s\rightarrow e}^{SE}$
C1	-0.718	±-0.693(2)	±0.706(2)	-0.0191	0[a]	0.04(3)
C2	0.0102	0[a]	0[a]	-1.221	±1.215(1)[b]	±1.215(1)
C3	1.404	±1.398(1)	±1.395(1)	-1.209	±1.205(1)	±1.204(1)
C4	2.060	±2.049(7)	±2.0437(7)	0.0210	0[a]	0[c]
C5	1.372	±1.367(1)	±1.357(1)	1.230	±1.229(1)	±1.226(1)
C6	-0.0253	0[a]	0[a]	1.203	±1.201(1)	±1.197(1)
C7	-2.217	±2.203(6)	±2.2038(7)	-0.0922	0.06(2)	±0.09(1)
C8	-3.000	±3.0047(5)	±2.9851(5)	1.204	1.192(1)	±1.195(1)

[a] Imaginary values, fixed at zero.

[b] Errors in parenthesis are given in units of the last digit.

[c] The coordinate value is too small to determine, fixed at zero.

Table S11 Theoretical, experimental and semi-experimental rotational constants of all nine isotopologues of 4FAP.

		B_e^{theo}	B_0^{theo}	ΔB_{vib}	B_0^{exp}	B_e^{SE}
Normal	*A*/MHz	3652.515	3629.056	23.459	3673.1127(4)[a]	3696.5717(4)
	B/MHz	768.889	763.336	5.553	772.76796(6)	778.32096(6)
	C/MHz	637.956	633.648	4.308	641.37113(4)	645.67913(4)
C1	*A*/MHz	3652.500	3629.192	23.308	3673.2148(8)	3696.5228(8)
	B/MHz	768.288	762.763	5.525	772.2018(2)	777.7268(2)
	C/MHz	637.543	633.258	4.285	640.98518(9)	645.27018(9)
C2	*A*/MHz	3613.728	3590.751	22.977	3634.2544(6)	3657.2314(6)
	B/MHz	768.888	763.342	5.546	772.7838(1)	778.3298(1)
	C/MHz	636.763	632.477	4.286	640.18763(6)	644.37363(6)
C3	*A*/MHz	3614.613	3591.567	23.046	3635.0126(8)	3658.0586(8)
	B/MHz	766.591	761.060	5.531	770.4674(1)	775.9984(1)
	C/MHz	635.213	630.935	4.278	638.62055(7)	642.89855(7)
C4	*A*/MHz	3652.503	3629.18	23.323	3673.2194(6)	3696.5424(6)
	B/MHz	763.977	758.470	5.507	767.8587(1)	773.3657(1)
	C/MHz	634.570	630.295	4.275	637.98926(6)	642.26426(6)
C5	*A*/MHz	3614.303	3591.149	23.154	3633.5063(5)	3656.6603(5)
	B/MHz	766.154	760.600	5.554	770.5668(1)	776.1208(1)
	C/MHz	634.905	630.605	4.300	638.64200(6)	642.94200(6)
C6	*A*/MHz	3614.812	3591.591	23.221	3635.1455(7)	3658.3665(7)
	B/MHz	768.888	763.337	5.551	772.7845(1)	778.3355(1)
	C/MHz	636.796	632.500	4.296	640.21584(8)	644.51184(8)
C7	*A*/MHz	3652.293	3628.976	23.317	3673.0162(6)	3696.3332(6)
	B/MHz	763.201	757.731	5.470	767.0947(1)	772.5647(1)
	C/MHz	634.029	629.778	4.251	637.45558(8)	641.70658(8)
C8	*A*/MHz	3615.338	3592.508	22.83	3636.2955(6)	3659.1255(6)
	B/MHz	758.510	752.969	5.541	762.2555(1)	767.7965(1)
	C/MHz	629.682	625.395	4.287	633.00903(7)	637.29603(7)

[a] Values of centrifugal distortion constants were fixed at those of the parent species.

Table S12. Theoretical, experimental and semi-experimental rotational constants of all nine isotopologues of AP.

		B_e^{theo}	B_0^{theo}	ΔB_{vib}	B_0^{exp}	B_e^{SE}
Normal	*A*/MHz	3663.006	3640.200	22.806	3688.0267(5)[a]	3710.8327(5)
	B/MHz	1210.575	1200.512	10.063	1215.0491(2)	1225.1121(2)
	C/MHz	917.072	910.402	6.670	919.9144(1)	926.5844(1)
C1	*A*/MHz	3662.995	3640.273	22.722	3688.109(1)	3710.831(1)
	B/MHz	1210.451	1200.475	9.976	1214.9904(6)	1224.9664(6)
	C/MHz	917.001	910.381	6.620	919.8906(4)	926.5106(4)
C2	*A*/MHz	3624.670	3602.210	22.460	3649.1986(5)	3671.6586(5)
	B/MHz	1209.747	1199.752	9.995	1214.4274(3)	1224.4224(3)
	C/MHz	914.188	907.569	6.619	917.1257(1)	923.7447(1)
C3	*A*/MHz	3627.280	3604.716	22.564	3647.5047(5)	3670.0687(5)
	B/MHz	1199.895	1189.995	9.900	1204.9562(2)	1214.8562(2)
	C/MHz	908.715	902.126	6.589	911.6077(1)	918.1967(1)
C4	*A*/MHz	3662.930	3640.166	22.764	3688.0297(4)	3710.7937(4)
	B/MHz	1191.365	1181.526	9.839	1195.8145(2)	1205.6535(2)
	C/MHz	906.001	899.429	6.572	908.8471(1)	915.4191(1)
C5	*A*/MHz	3622.901	3600.361	22.540	3652.138(6)	3674.678(6)
	B/MHz	1200.495	1190.548	9.947	1204.3566(3)	1214.3036(3)
	C/MHz	908.783	902.172	6.611	911.5537(2)	918.1647(2)
C6	*A*/MHz	3624.457	3601.821	22.636	3649.5745(5)	3672.2105(5)
	B/MHz	1209.919	1199.896	10.023	1214.2504(2)	1224.2734(2)
	C/MHz	914.273	907.640	6.633	917.0483(1)	923.6813(1)
C7	*A*/MHz	3662.726	3640.051	22.675	3687.869(5)	3710.544(5)
	B/MHz	1202.229	1192.277	9.952	1206.7535(2)	1216.7055(2)
	C/MHz	912.258	905.680	6.578	915.1419(1)	921.7199(1)
C8	*A*/MHz	3626.912	3604.647	22.265	3652.2545(5)	3674.5195(5)
	B/MHz	1192.675	1182.691	9.984	1196.9384(2)	1206.9224(2)
	C/MHz	904.577	897.960	6.617	907.3087(1)	913.9257(1)

[a] Values of centrifugal distortion constants were fixed at those of the parent species.

Table S13. Geometries of the carbon skeletons of the 4FAP and AP. (r_e, r_s and $r_{s\rightarrow e}^{SE}$ structure)

	4FAP			AP		
	r_e	r_s	$r_{s\rightarrow e}^{SE}$	r_e	r_s	$r_{s\rightarrow e}^{SE}$
Bond lengths/Å						
C1C2	1.406	1.400(3)	1.405(1)	1.405	1.350(5)	1.399(4)
C2C3	1.387	1.398(1)[a]	1.395(1)	1.396	1.405(3)	1.384(3)
C3C4	1.388	1.370(1)	1.368(1)	1.402	1.441(1)	1.435(1)
C4C5	1.386	1.405(1)	1.405(1)	1.399	1.350(1)	1.345(1)
C5C6	1.391	1.368(1)	1.357(1)	1.399	1.399(3)	1.386(3)
C6C1	1.400	1.387(1)	1.390(2)	1.405	1.374(5)	1.417(4)
C1C7	1.497	1.511(2)	1.501(1)	1.502	1.56(1)	1.474(7)
C7C8	1.516	1.49(2)	1.50(1)	1.516	1.49(2)	1.51(1)
Valence angles/°						
C2C3C4	118.53	118.7(1)	118.7(1)	120.18	118.9(9)	118.85(9)
C3C4C5	122.34	122.65(8)	122.47(8)	119.81	119.88(5)	119.98(7)
C4C5C6	118.50	117.8(1)	118.0(1)	120.14	121.2(1)	121.2(1)
C5C6C1	120.6	121.2(1)	121.7(1)	120.18	117.3(4)	120.8(3)
C6C1C7	122.6	122.3(9)	123.9(6)	122.2	121.5(8)	126.1(6)
C1C7C8	118.6	120(1)	117.8(9)	118.3	120(1)	118.0(8)
C2C1C7	118.4	117.5(9)	116.6(6)	118.4	113.5(8)	116.2(6)

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

Table S14. Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs-calc}$, kHz) of the isomer I of 4FAP-H_2O.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs-calc}$/kHz
6	0	6	5	0	5	A	4900.7910	-0.9
6	0	6	5	0	5	E	4900.7910	0.8
6	1	6	5	1	5	A	4773.6264	1.1
6	1	6	5	1	5	E	4773.6264	1.6
6	1	5	5	1	4	A	5058.0187	-2.3
6	1	5	5	1	4	E	5058.0187	0.8
6	2	5	5	2	4	A	4917.7793	-0.7
6	2	5	5	2	4	E	4917.8081	0.9
6	2	4	5	2	3	A	4937.2960	3.2
6	2	4	5	2	3	E	4937.2618	0.2
6	3	4	5	3	3	A	4923.2568	-0.8
6	3	4	5	3	3	E	4923.3574	-5.9
6	3	3	5	3	2	A	4923.4931	4.2
6	3	3	5	3	2	E	4923.3816	2.2
7	0	7	6	0	6	A	5709.2457	-0.6
7	0	7	6	0	6	E	5709.2457	1.2
7	1	7	6	1	6	A	5567.2255	-0.2
7	1	7	6	1	6	E	5567.2255	0.4
7	1	6	6	1	5	A	5898.7687	-1.1
7	1	6	6	1	5	E	5898.7687	2.5
7	2	6	6	2	5	A	5735.9898	-1.1
7	2	6	6	2	5	E	5736.0027	1.0
7	2	5	6	2	4	A	5767.0956	1.8
7	2	5	6	2	4	E	5767.0743	-4.0
7	3	5	6	3	4	A	5744.7346	0.2
7	3	5	6	3	4	E	5744.9595	5.2
7	3	4	6	3	3	A	5745.2550	0.6
7	3	4	6	3	3	E	5745.0375	-2.4
8	0	8	7	0	7	A	6513.9990	-1.6
8	0	8	7	0	7	E	6513.9990	0.4
8	1	8	7	1	7	A	6359.9553	-1.8
8	1	8	7	1	7	E	6359.9553	-1.0
8	1	7	7	1	6	A	6738.4198	1.0
8	1	7	7	1	6	E	6738.4141	-0.7
8	2	7	7	2	6	A	6553.5494	1.5
8	2	7	7	2	6	E	6553.5494	-2.5
8	2	6	7	2	5	A	6599.9373	1.5
8	2	6	7	2	5	E	6599.9234	-2.9
8	3	6	7	3	5	A	6566.5870	0.7
8	3	6	7	3	5	E	6566.8981	-1.5
8	3	5	7	3	4	A	6567.6264	0.9

8	3	5	7	3	4	E	6567.3055	-1.5
8	4	5	7	4	4	A	6564.2962	1.7
8	4	5	7	4	4	E	6564.2962	-0.2
8	4	4	7	4	3	A	6564.3055	2.7
8	4	4	7	4	3	E	6564.2962	0.4
9	0	9	8	0	8	A	7314.6913	-0.5
9	0	9	8	0	8	E	7314.6913	1.6
9	1	9	8	1	8	A	7151.7342	0.4
9	1	9	8	1	8	E	7151.7342	1.2
9	1	8	8	1	7	A	7576.7624	-6.0
9	1	8	8	1	7	E	7576.7699	5.9
9	2	8	8	2	7	A	7370.3594	0.8
9	2	8	8	2	7	E	7370.3594	0.0
9	2	7	8	2	6	A	7436.0878	1.7
9	2	7	8	2	6	E	7436.0761	-2.9
9	3	7	8	3	6	A	7388.8295	1.0
9	3	7	8	3	6	E	7389.1508	-2.4
9	3	6	8	3	5	A	7390.7324	1.3
9	3	6	8	3	5	E	7390.4005	0.1
9	4	6	8	4	5	A	7385.7758	4.3
9	4	6	8	4	5	E	7385.7758	-3.2
9	4	5	8	4	4	A	7385.7984	6.9
9	4	5	8	4	4	E	7385.7758	-2.5
10	0	10	9	0	9	A	8111.0648	-2.3
10	0	10	9	0	9	E	8111.0648	-0.1
10	1	10	9	1	9	A	7942.4842	-0.5
10	1	10	9	1	9	E	7942.4842	0.4
10	1	9	9	1	8	A	8413.6027	0.9
10	1	9	9	1	8	E	8413.5947	-2.3
10	2	9	9	2	8	A	8186.3319	0.3
10	2	9	9	2	8	E	8186.3319	1.2
10	2	8	9	2	7	A	8275.7017	1.4
10	2	8	9	2	7	E	8275.6914	-2.8
10	3	8	9	3	7	A	8211.4616	0.2
10	3	8	9	3	7	E	8211.6939	-2.8
10	3	7	9	3	6	A	8214.7187	1.3
10	3	7	9	3	6	E	8214.4745	-0.9
10	4	7	9	4	6	A	8207.5702	-6.8
10	4	7	9	4	6	E	8207.5937	-2.0
10	4	6	9	4	5	A	8207.6244	4.0
10	4	6	9	4	5	E	8207.5937	-1.5
11	0	11	10	0	10	A	8903.0099	-1.3
11	0	11	10	0	10	E	8903.0099	0.9
11	1	11	10	1	10	A	8732.1534	-0.2

11	1	11	10	1	10	E	8732.1534	0.7
11	1	10	10	1	9	A	9248.6849	1.3
11	1	10	10	1	9	E	9248.6762	-2.1
11	2	10	10	2	9	A	9001.3773	0.4
11	2	10	10	2	9	E	9001.3773	2.4
11	2	9	10	2	8	A	9118.7971	1.8
11	2	9	10	2	8	E	9118.7851	-4.3
11	3	9	10	3	8	A	9034.4707	0.0
11	3	9	10	3	8	E	9034.6069	-2.3
12	0	12	11	0	11	A	9690.5647	-0.8
12	0	12	11	0	11	E	9690.5647	1.3
12	1	12	11	1	11	A	9520.7005	0.3
12	1	12	11	1	11	E	9520.7005	1.2
12	1	11	11	1	10	A	10081.7601	2.3
12	1	11	11	1	10	E	10081.7496	-2.6
12	2	11	11	2	10	A	9815.4062	0.2
12	2	11	11	2	10	E	9815.4062	2.9
13	0	13	12	0	12	A	10473.9339	-1.5
13	0	13	12	0	12	E	10473.9339	0.6
13	1	13	12	1	12	A	10308.0969	-3.1
13	1	13	12	1	12	E	10308.0969	-2.2
13	1	12	12	1	11	A	10912.5519	4.1
13	1	12	12	1	11	E	10912.5368	-5.1
13	2	12	12	2	11	A	10628.3343	1.6
13	2	12	12	2	11	E	10628.3289	-0.6
13	2	11	12	2	10	A	10814.6877	-2.1
13	2	11	12	2	10	E	10814.6772	-6.1
14	0	14	13	0	13	A	11253.4776	-1.1
14	0	14	13	0	13	E	11253.4776	1.0
14	1	14	13	1	13	A	11094.3459	1.7
14	1	14	13	1	13	E	11094.3459	2.5
14	1	13	13	1	12	A	11740.7566	-0.1
14	1	13	13	1	12	E	11740.7566	6.1
15	0	15	14	0	14	A	12029.6743	-2.9
15	0	15	14	0	14	E	12029.6743	-0.9
15	1	15	14	1	14	A	11879.4411	1.9
15	1	15	14	1	14	E	11879.4411	2.7
15	1	14	14	1	13	A	12566.0685	-0.5
15	1	14	14	1	13	E	12566.0586	-3.9
16	0	16	15	0	15	A	12803.0932	-1.2
16	0	16	15	0	15	E	12803.0932	0.7
16	1	16	15	1	15	A	12663.4052	0.1
16	1	16	15	1	15	E	12663.4052	0.8
17	0	17	16	0	16	A	13574.3235	-2.4

17	0	17	16	0	16	E	13574.3235	-0.5
18	0	18	17	0	17	A	14343.9513	-0.7
18	0	18	17	0	17	E	14343.9513	1.2
19	0	19	18	0	18	A	15112.4990	-0.9
19	0	19	18	0	18	E	15112.4990	1.2
20	0	20	19	0	19	A	15880.4170	-1.3
20	0	20	19	0	19	E	15880.4170	0.9
2	2	1	1	1	0	A	10657.7521	3.5
2	2	1	1	1	0	E	10656.8824	1.7
2	2	0	1	1	1	A	10705.7469	0.3
2	2	0	1	1	1	E	10706.5457	1.5
3	2	2	2	1	1	A	11430.3586	-1.2
3	2	2	2	1	1	E	11429.9610	0.7
4	1	4	3	0	3	A	6058.1634	5.5
4	1	4	3	0	3	E	6058.1453	-1.2
4	2	3	3	1	2	A	12179.1654	-1.6
4	2	3	3	1	2	E	12178.9969	-0.1
5	1	5	4	0	4	A	6762.8056	5.6
5	1	5	4	0	4	E	6762.7884	-1.0
5	2	4	4	1	3	A	12904.2288	3.9
5	2	4	4	1	3	E	12904.1307	-1.1
6	1	6	5	0	5	A	7447.3485	4.2
6	1	6	5	0	5	E	7447.3347	0.1
6	2	5	5	1	4	A	13605.6462	-1.6
6	2	5	5	1	4	E	13605.5860	1.3
6	2	4	5	1	5	A	14356.1739	-1.3
6	2	4	5	1	5	E	14356.1739	-1.1
7	1	7	6	0	6	A	8113.7831	4.9
7	1	7	6	0	6	E	8113.7643	-5.2
7	2	6	6	1	5	A	14283.6208	3.1
7	2	6	6	1	5	E	14283.5708	2.3
8	1	8	7	0	7	A	8764.4814	-7.5
8	1	8	7	0	7	E	8764.4814	0.1
8	2	7	7	1	6	A	14938.3949	-0.9
8	2	7	7	1	6	E	14938.3569	2.7
9	0	9	8	1	8	A	5064.2068	3.4
9	0	9	8	1	8	E	5064.2068	-0.1
9	1	9	8	0	8	A	9402.2156	-6.6
9	1	9	8	0	8	E	9402.2156	-0.1
9	2	8	8	1	7	A	15570.3371	1.5
9	2	8	8	1	7	E	15570.2978	-1.0
10	0	10	9	1	9	A	6023.5374	0.7
10	0	10	9	1	9	E	6023.5374	-1.5
10	1	10	9	0	9	A	10030.0086	-6.5

10	1	10	9	0	9	E	10030.0086	-1.3
10	2	9	9	1	8	A	16179.9014	2.6
10	2	9	9	1	8	E	16179.8668	1.3
11	0	11	10	1	10	A	6984.0642	1.0
11	0	11	10	1	10	E	6984.0642	0.2
11	1	11	10	0	10	A	10651.0994	-2.2
11	1	11	10	0	10	E	10651.0994	1.8
12	0	12	11	1	11	A	7942.4719	-3.2
12	0	12	11	1	11	E	7942.4719	-2.8
12	1	12	11	0	11	A	11268.7924	1.7
12	1	12	11	0	11	E	11268.7872	-0.7
13	0	13	12	1	12	A	8895.7097	-0.5
13	0	13	12	1	12	E	8895.7097	1.0
13	1	13	12	0	12	A	11886.3248	-0.4
13	1	13	12	0	12	E	11886.3248	1.2
14	0	14	13	1	13	A	9841.0891	0.2
14	0	14	13	1	13	E	9841.0891	2.8
14	1	14	13	0	13	A	12506.7340	0.0
14	1	14	13	0	13	E	12506.7340	0.3
15	0	15	14	1	14	A	10776.4193	-2.6
15	0	15	14	1	14	E	10776.4284	0.2
15	1	15	14	0	14	A	13132.6999	5.4
15	1	15	14	0	14	E	13132.6910	-4.4
3	3	0	2	2	0	A	17528.7682	-5.6
3	3	0	2	2	0	E	17529.4935	1.6
3	3	1	2	2	1	A	17529.3344	4.7
3	3	1	2	2	1	E	17528.4926	-2.1

Table S15. Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs-calc}$, kHz) of the Isomer I of 4FAP-$H_2{}^{18}O$.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs-calc}$/kHz
7	0	7	6	0	6	A	5486.9787	-0.3
7	0	7	6	0	6	E	5486.9787	1.4
7	1	7	6	1	6	A	5353.9426	-0.8
7	1	7	6	1	6	E	5353.9426	-0.3
7	1	6	6	1	5	A	5660.5619	-4.2
7	1	6	6	1	5	E	5660.5619	-0.7
7	2	6	6	2	5	A	5509.8027	-1.8
7	2	6	6	2	5	E	5509.8185	0.8
7	2	5	6	2	4	A	5536.3495	3.2
7	2	5	6	2	4	E	5536.3266	-2.1
8	0	8	7	0	7	A	6261.5388	0.2
8	0	8	7	0	7	E	6261.5388	2.0
8	1	8	7	1	7	A	6116.5724	-0.4
8	1	8	7	1	7	E	6116.5724	0.1
8	1	7	7	1	6	A	6466.6471	-1.1
8	1	7	7	1	6	E	6466.6471	2.8
8	2	7	7	2	6	A	6295.3265	2.2
8	2	7	7	2	6	E	6295.3265	-3.1
8	2	6	7	2	5	A	6334.9453	2.3
8	2	6	7	2	5	E	6334.9299	-2.7
9	0	9	8	0	8	A	7032.5841	0.1
9	0	9	8	0	8	E	7032.5841	1.9
9	1	9	8	1	8	A	6878.3792	1.6
9	1	9	8	1	8	E	6878.3792	2.1
9	1	8	8	1	7	A	7271.6321	-2.2
9	1	8	8	1	7	E	7271.6321	2.1
9	2	8	8	2	7	A	7080.2084	1.0
9	2	8	8	2	7	E	7080.2084	-0.6
9	2	7	8	2	6	A	7136.4121	1.7
9	2	7	8	2	6	E	7136.4002	-2.7
10	0	10	9	0	9	A	7799.8647	-0.2
10	0	10	9	0	9	E	7799.8647	1.7
10	1	10	9	1	9	A	7639.2927	-0.1
10	1	10	9	1	9	E	7639.2927	0.5
10	1	9	9	1	8	A	8075.3397	-5.2
10	1	9	9	1	8	E	8075.3397	-0.5
10	2	9	9	2	8	A	7864.3773	1.8
10	2	9	9	2	8	E	7864.3773	2.2
10	2	8	9	2	7	A	7940.9113	-5.1
10	2	8	9	2	7	E	7940.9113	1.2
11	0	11	10	0	10	A	8563.2358	-0.1

11	0	11	10	0	10	E	8563.2358	1.7
11	1	11	10	1	10	A	8399.2659	0.4
11	1	11	10	1	10	E	8399.2659	1.0
11	1	10	10	1	9	A	8877.5871	1.9
11	1	10	10	1	9	E	8877.5794	-0.8
11	2	10	10	2	9	A	8647.7519	0.5
11	2	10	10	2	9	E	8647.7519	2.0
11	2	9	10	2	8	A	8748.5225	-0.2
11	2	9	10	2	8	E	8748.5135	-3.3
12	0	12	11	0	11	A	9322.6729	-2.1
12	0	12	11	0	11	E	9322.6729	-0.3
12	1	12	11	1	11	A	9158.2553	-0.4
12	1	12	11	1	11	E	9158.2553	0.2
12	1	11	11	1	10	A	9678.1470	2.4
12	1	11	11	1	10	E	9678.1371	-2.1
13	0	13	12	0	12	A	10078.2919	-1.3
13	0	13	12	0	12	E	10078.2919	0.4
13	1	13	12	1	12	A	9916.2375	1.2
13	1	13	12	1	12	E	9916.2375	1.7
13	1	12	12	1	11	A	10476.7963	0.9
13	1	12	12	1	11	E	10476.7876	-2.0
14	0	14	13	0	13	A	10830.3344	1.3
14	0	14	13	0	13	E	10830.3344	2.9
15	0	15	14	0	14	A	11579.1527	0.0
15	0	15	14	0	14	E	11579.1527	1.4
16	0	16	15	0	15	A	12325.1960	-1.5
16	0	16	15	0	15	E	12325.1960	-0.1
2	2	1	1	1	0	A	10622.4206	2.7
2	2	1	1	1	0	E	10621.5264	5.5
2	2	0	1	1	1	A	10666.7643	7.1
2	2	0	1	1	1	E	10667.5838	-0.5
3	2	2	2	1	1	A	11366.1978	-3.3
3	2	2	2	1	1	E	11365.7597	3.7
6	1	6	5	0	5	A	7298.0198	4.6
6	1	6	5	0	5	E	7298.0061	0.2
7	1	7	6	0	6	A	7942.7259	5.1
7	1	7	6	0	6	E	7942.7135	0.9
8	1	8	7	0	7	A	8572.3088	-5.8
8	1	8	7	0	7	E	8572.3088	1.2
9	1	9	8	0	8	A	9189.1488	-4.8
9	1	9	8	0	8	E	9189.1488	0.9
10	1	10	9	0	9	A	9795.8581	-4.2
10	1	10	9	0	9	E	9795.8581	0.2
11	0	11	10	1	10	A	6567.2386	0.1

11	0	11	10	1	10	E	6567.2386	-0.6
11	1	11	10	0	10	A	10395.2612	-1.7
11	1	11	10	0	10	E	10395.2612	1.4
12	0	12	11	1	11	A	7490.6457	-2.3
12	0	12	11	1	11	E	7490.6457	-1.7
12	1	12	11	0	11	A	10990.2806	-2.0
12	1	12	11	0	11	E	10990.2806	-0.3
13	0	13	12	1	12	A	8410.6849	-0.6
13	0	13	12	1	12	E	8410.6849	1.1
13	1	13	12	0	12	A	11583.8432	-0.7
13	1	13	12	0	12	E	11583.8432	-0.3
14	0	14	13	1	13	A	9324.7817	-0.7
14	0	14	13	1	13	E	9324.7817	2.2
14	1	14	13	0	13	A	12178.7447	0.9
14	1	14	13	0	13	E	12178.7447	0.0
3	3	0	2	2	0	A	17477.7382	-3.1
3	3	0	2	2	0	E	17478.4181	-9.0
3	3	1	2	2	1	A	17478.2199	4.5
3	3	1	2	2	1	E	17477.4120	-1.3

Table S16. Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs-calc}$, kHz) of the Isomer I of 4FAP-HOD.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs-calc}$/kHz
7	0	7	6	0	6	A	5568.8083	-1.1
7	0	7	6	0	6	E	5568.8083	0.6
7	1	7	6	1	6	A	5431.9612	-3.9
7	1	7	6	1	6	E	5431.9612	-3.3
7	1	6	6	1	5	A	5749.4620	-1.2
7	1	6	6	1	5	E	5749.4562	-3.5
8	0	8	7	0	7	A	6354.3276	-1.4
8	0	8	7	0	7	E	6354.3276	0.4
8	1	8	7	1	7	A	6205.5672	-1.4
8	1	8	7	1	7	E	6205.5672	-0.8
8	1	7	7	1	6	A	6568.0298	1.7
8	1	7	7	1	6	E	6568.0197	-4.4
9	0	9	8	0	8	A	7136.0705	-6.9
9	0	9	8	0	8	E	7136.0705	-4.9
9	1	9	8	1	8	A	6978.2834	-3.4
9	1	9	8	1	8	E	6978.2834	-2.7
9	1	8	8	1	7	A	7385.4028	1.3
9	1	8	8	1	7	E	7385.3949	-2.3
10	0	10	9	0	9	A	7913.8013	-1.9
10	0	10	9	0	9	E	7913.8013	0.1
10	1	10	9	1	9	A	7750.0485	-3.1
10	1	10	9	1	9	E	7750.0485	-2.4
10	1	9	9	1	8	A	8201.3876	1.2
10	1	9	9	1	8	E	8201.3806	-1.1
11	0	11	10	0	10	A	8687.3762	0.7
11	0	11	10	0	10	E	8687.3866	3.0
11	1	11	10	1	10	A	8520.8045	-4.4
11	1	11	10	1	10	E	8520.8045	-3.7
11	1	10	10	1	9	A	9015.7760	7.1
11	1	10	10	1	9	E	9015.7648	1.0
12	0	12	11	0	11	A	9456.8008	-2.2
12	0	12	11	0	11	E	9456.8008	-0.3
12	1	12	11	1	11	A	9290.5184	-0.1
12	1	12	11	1	11	E	9290.5184	0.6
12	1	11	11	1	10	A	9828.3225	5.5
12	1	11	11	1	10	E	9828.3086	-2.9
13	0	13	12	0	12	A	10222.2392	-2.9
13	0	13	12	0	12	E	10222.2392	-1.1
13	1	13	12	1	12	A	10059.1571	2.4
13	1	13	12	1	12	E	10059.1496	-4.4
13	1	12	12	1	11	A	10638.7781	-1.8

13	1	12	12	1	11	E	10638.7781	4.1
14	0	14	13	0	13	A	10983.9934	2.2
14	0	14	13	0	13	E	10983.9934	4.0
15	0	15	14	0	14	A	11742.4739	5.3
15	0	15	14	0	14	E	11742.4739	6.9
16	0	16	15	0	15	A	12498.1760	-1.5
16	0	16	15	0	15	E	12498.1760	0.1
7	1	7	6	0	6	A	7981.9676	-3.9
7	1	7	6	0	6	E	7981.9600	-3.3
8	1	8	7	0	7	A	8618.7272	-3.5
8	1	8	7	0	7	E	8618.7272	3.5
9	1	9	8	0	8	A	9242.6851	-3.3
9	1	9	8	0	8	E	9242.6851	2.5
10	1	10	9	0	9	A	9856.6640	1.3
10	1	10	9	0	9	E	9856.6640	5.9

Table S17. Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs\text{-}calc}$, kHz) of the Isomer I of 4FAP-DOH.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs\text{-}calc}$/kHz
7	0	7	6	0	6	A	5634.5191	-1.5
7	0	7	6	0	6	E	5634.5191	0.3
7	1	7	6	1	6	A	5495.2194	0.8
7	1	7	6	1	6	E	5495.2194	1.4
7	1	6	6	1	5	A	5819.3471	-2.7
7	1	6	6	1	5	E	5819.3471	0.8
8	0	8	7	0	7	A	6429.0403	-2.0
8	0	8	7	0	7	E	6429.0403	0.0
8	1	8	7	1	7	A	6277.7664	-1.1
8	1	8	7	1	7	E	6277.7664	-0.4
8	1	7	7	1	6	A	6647.7779	-6.7
8	1	7	7	1	6	E	6647.7664	-4.2
9	0	9	8	0	8	A	7219.6542	-2.2
9	0	9	8	0	8	E	7219.6542	-0.1
9	1	9	8	1	8	A	7059.3988	0.1
9	1	9	8	1	8	E	7059.3988	0.8
9	1	8	8	1	7	A	7474.9801	2.3
9	1	8	8	1	7	E	7474.9739	0.4
10	0	10	9	0	9	A	8006.1086	-2.0
10	0	10	9	0	9	E	8006.1086	0.1
10	1	10	9	1	9	A	7840.0420	-0.8
10	1	10	9	1	9	E	7840.0420	0.0
10	1	9	9	1	8	A	8300.7334	0.0
10	1	9	9	1	8	E	8300.7201	1.5
11	0	11	10	0	10	A	8788.2801	-0.6
11	0	11	10	0	10	E	8788.2801	1.4
11	1	11	10	1	10	A	8619.6452	0.7
11	1	11	10	1	10	E	8619.6452	1.5
11	1	10	10	1	9	A	9124.8056	8.2
11	1	10	10	1	9	E	9124.7902	-2.0

Table S18. Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs\text{-}calc}$, kHz) of the Isomer I of 4FAP-D_2O.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs\text{-}calc}$/kHz
7	0	7	6	0	6	A	5498.7964	-2.6
7	0	7	6	0	6	E	5498.7964	-0.9
7	1	7	6	1	6	A	5364.4852	-6.9
7	1	7	6	1	6	E	5364.4852	-6.5
7	1	6	6	1	5	A	5675.1614	-2.3
7	1	6	6	1	5	E	5675.1614	1.2
7	2	6	6	2	5	A	5522.4724	-1.5
7	2	6	6	2	5	E	5522.4854	-0.9
7	2	5	6	2	4	A	5550.0045	0.1
7	2	5	6	2	4	E	5549.9817	-5.9
8	0	8	7	0	7	A	6274.7086	-1.9
8	0	8	7	0	7	E	6274.7086	-0.1
8	1	8	7	1	7	A	6128.5482	-1.2
8	1	8	7	1	7	E	6128.5482	-0.7
8	1	7	7	1	6	A	6483.2265	-3.8
8	1	7	7	1	6	E	6483.2265	0.1
8	2	7	7	2	6	A	6309.7464	2.5
8	2	7	7	2	6	E	6309.7464	-2.4
8	2	6	7	2	5	A	6350.8297	0.8
8	2	6	7	2	5	E	6350.8129	-6.0
9	0	9	8	0	8	A	7046.9885	-1.9
9	0	9	8	0	8	E	7046.9885	-0.1
9	1	9	8	1	8	A	6891.7526	-1.7
9	1	9	8	1	8	E	6891.7526	-1.2
9	1	8	8	1	7	A	7290.1555	-0.8
9	1	8	8	1	7	E	7290.1555	3.5
9	2	8	8	2	7	A	7096.3535	0.1
9	2	8	8	2	7	E	7096.3535	-1.3
9	2	7	8	2	6	A	7154.6209	3.6
9	2	7	8	2	6	E	7154.6077	-2.4
10	0	10	9	0	9	A	7815.3887	-0.4
10	0	10	9	0	9	E	7815.3887	1.5
10	1	10	9	1	9	A	7654.0383	-2.4
10	1	10	9	1	9	E	7654.0383	-1.8
10	1	9	9	1	8	A	8095.7547	0.8
10	1	9	9	1	8	E	8095.7471	-2.1
10	2	9	9	2	8	A	7882.2231	1.7
10	2	9	9	2	8	E	7882.2231	2.2
10	2	8	9	2	7	A	7961.5333	-0.5
10	2	8	9	2	7	E	7961.5228	-4.8
11	0	11	10	0	10	A	8579.7684	-0.9

11	0	11	10	0	10	E	8579.7684	1.0
11	1	11	10	1	10	A	8415.3542	-0.9
11	1	11	10	1	10	E	8415.3542	-0.3
11	1	10	10	1	9	A	8899.8214	2.1
11	1	10	10	1	9	E	8899.8099	-4.3
11	2	10	10	2	9	A	8667.2675	-0.3
11	2	10	10	2	9	E	8667.2675	1.3
11	2	9	10	2	8	A	8771.6334	4.9
11	2	9	10	2	8	E	8771.6226	-0.1
12	0	12	11	0	11	A	9340.1242	-0.9
12	0	12	11	0	11	E	9340.1242	0.8
12	1	12	11	1	11	A	9175.6570	-0.7
12	1	12	11	1	11	E	9175.6570	-0.1
12	1	11	11	1	10	A	9702.1366	5.0
12	1	11	11	1	10	E	9702.1261	0.0
13	0	13	12	0	12	A	10096.5892	-2.0
13	0	13	12	0	12	E	10096.5892	-0.3
13	1	13	12	1	12	A	9934.9215	-0.7
13	1	13	12	1	12	E	9934.9215	-0.2
13	1	12	12	1	11	A	10502.4580	5.8
13	1	12	12	1	11	E	10502.4460	-0.4
14	0	14	13	0	13	A	10849.4381	0.0
14	0	14	13	0	13	E	10849.4381	1.6
15	0	15	14	0	14	A	11599.0557	1.4
15	0	15	14	0	14	E	11599.0557	2.9
16	0	16	15	0	15	A	12345.9231	9.6
16	0	16	15	0	15	E	12345.9139	1.7
7	1	7	6	0	6	A	7916.4344	2.3
7	1	7	6	0	6	E	7916.4250	0.9
8	1	8	7	0	7	A	8546.1813	-1.2
8	1	8	7	0	7	E	8546.1691	-6.6
9	1	9	8	0	8	A	9163.2302	3.9
9	1	9	8	0	8	E	9163.2214	0.6
10	1	10	9	0	9	A	9770.2781	1.6
10	1	10	9	0	9	E	9770.2708	-1.5
11	1	11	10	0	10	A	10370.2405	-2.0
11	1	11	10	0	10	E	10370.2405	0.9

Table S19. Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs-calc}$, kHz) of the Isomer II of 4FAP-H_2O.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs-calc}$/kHz
8	0	8	7	0	7	A	7745.9608	-1.8
8	0	8	7	0	7	E	7745.9608	-1.4
9	0	9	8	0	8	A	8649.5044	0.4
9	0	9	8	0	8	E	8649.5044	0.8
10	0	10	9	0	9	A	9556.0990	3.9
10	0	10	9	0	9	E	9556.0990	4.3
3	3	0	2	2	1	A	7992.7803	-4.7
3	3	0	2	2	1	E	7992.8067	3.3
3	3	1	2	2	0	A	7958.3561	-0.5
3	3	1	2	2	0	E	7958.3241	1.7
4	2	3	3	1	2	A	6623.7213	-1.8
4	2	3	3	1	2	E	6623.7101	-8.2
4	3	2	3	2	1	A	9000.1484	-2.4
4	3	2	3	2	1	E	9000.1414	2.4
4	4	1	3	3	0	A	10941.4972	-4.3
4	4	1	3	3	0	E	10941.2008	3.2
4	4	0	3	3	1	A	10944.8977	-5.6
4	4	0	3	3	1	E	10945.1885	3.4
5	2	4	4	1	3	A	7339.4563	-0.2
5	2	4	4	1	3	E	7339.4563	4.5
5	3	3	4	2	2	A	9936.5805	-2.2
5	3	3	4	2	2	E	9936.5805	7.0
5	3	2	4	2	3	A	10446.8840	5.4
5	3	2	4	2	3	E	10446.8740	1.8
5	4	2	4	3	1	A	12045.9039	-1.5
5	4	2	4	3	1	E	12045.8330	1.2
5	4	1	4	3	2	A	12069.8944	-4.4
5	4	1	4	3	2	E	12069.9522	1.8
6	1	6	5	0	5	A	6043.1318	-1.7
6	1	6	5	0	5	E	6043.1318	-0.7
6	0	6	5	1	5	A	5787.3999	2.0
6	0	6	5	1	5	E	5787.3999	1.7
6	2	5	5	1	4	A	7985.3855	1.4
6	2	5	5	1	4	E	7985.3855	6.0
6	3	4	5	2	3	A	10739.4476	2.0
6	3	4	5	2	3	E	10739.4391	2.4
6	3	3	5	2	4	A	11878.2297	1.7
6	3	3	5	2	4	E	11878.2186	-3.0
6	4	3	5	3	2	A	13116.0986	-1.8
6	4	3	5	3	2	E	13116.0768	0.7
6	4	2	5	3	3	A	13211.6770	-3.1

6	4	2	5	3	3	E	13211.6870	4.7
7	1	7	6	0	6	A	6891.6196	-2.0
7	1	7	6	0	6	E	6891.6196	-1.3
7	0	7	6	1	6	A	6759.0436	-1.4
7	0	7	6	1	6	E	6759.0436	-1.5
7	2	6	6	1	5	A	8599.8724	-0.6
7	2	6	6	1	5	E	8599.8724	3.7
7	3	5	6	2	4	A	11409.9552	-2.3
7	3	5	6	2	4	E	11409.9443	-4.3
7	3	4	6	2	5	A	13541.0507	-9.9
7	3	4	6	2	5	E	13541.0602	5.1
7	4	4	6	3	3	A	14114.6110	0.5
7	4	4	6	3	3	E	14114.5945	-0.9
7	4	3	6	3	4	A	14394.7176	5.1
7	4	3	6	3	4	E	14394.7040	-1.6
8	1	8	7	0	7	A	7767.3334	-0.5
8	1	8	7	0	7	E	7767.3334	0.1
8	0	8	7	1	7	A	7701.7111	0.3
8	0	8	7	1	7	E	7701.7111	0.4
8	2	7	7	1	6	A	9230.8354	-2.2
8	2	7	7	1	6	E	9230.8279	-6.0
8	3	6	7	2	5	A	11969.7600	1.1
8	3	6	7	2	5	E	11969.7508	0.7
8	4	5	7	3	4	A	14995.5521	-2.3
8	4	5	7	3	4	E	14995.5450	3.9
9	1	9	8	0	8	A	8659.5479	-1.1
9	1	9	8	0	8	E	8659.5479	-0.6
9	0	9	8	1	8	A	8628.1339	1.2
9	0	9	8	1	8	E	8628.1339	1.4
9	2	8	8	1	7	A	9917.1573	-2.9
9	2	8	8	1	7	E	9917.1573	0.1
9	3	7	8	2	6	A	12452.5144	4.0
9	3	7	8	2	6	E	12452.4949	-6.8
10	1	10	9	0	9	A	9560.7183	-0.7
10	1	10	9	0	9	E	9560.7183	-0.3
10	0	10	9	1	9	A	9546.0485	-1.6
10	0	10	9	1	9	E	9546.0485	-1.3
10	2	9	9	1	8	A	10672.1745	-0.9
10	2	9	9	1	8	E	10672.1745	1.5
11	1	11	10	0	10	A	10466.4474	-0.8
11	1	11	10	0	10	E	10466.4474	-0.4
11	0	11	10	1	10	A	10459.7319	1.3
11	0	11	10	1	10	E	10459.7319	1.6
11	2	10	10	1	9	A	11486.2573	-1.6

11	2	10	10	1	9	E	11486.2573	0.3
12	1	12	11	0	11	A	11374.4099	0.2
12	1	12	11	0	11	E	11374.4099	0.5
12	0	12	11	1	11	A	11371.3811	0.1
12	0	12	11	1	11	E	11371.3811	0.5
12	2	11	11	1	10	A	12341.3331	-0.3
12	2	11	11	1	10	E	12341.3331	1.2
13	1	13	12	0	12	A	12283.4365	-1.4
13	1	13	12	0	12	E	12283.4365	-1.1
13	0	13	12	1	12	A	12282.0890	-0.6
13	0	13	12	1	12	E	12282.0890	-0.2
13	2	12	12	1	11	A	13221.3833	4.2
13	2	12	12	1	11	E	13221.3833	5.5
14	1	14	13	0	13	A	13192.9649	-3.2
14	1	14	13	0	13	E	13192.9696	1.7
14	0	14	13	1	13	A	13192.3794	5.1
14	0	14	13	1	13	E	13192.3700	-3.8
14	2	13	13	1	12	A	14115.4749	-1.4
14	2	13	13	1	12	E	14115.4749	-0.2
15	1	15	14	0	14	A	14102.7320	-0.6
15	1	15	14	0	14	E	14102.7320	-0.7
15	0	15	14	1	14	A	14102.4740	0.6
15	0	15	14	1	14	E	14102.4740	1.3
15	2	14	14	1	13	A	15017.1008	-2.5
15	2	14	14	1	13	E	15017.1008	-1.3

Table S20. Experimental transition frequencies (v_{obs}, MHz) and fit deviations ($v_{obs\text{-}calc}$, kHz) of the Isomer II of 4FAP-$H_2{}^{18}O$.

J′	K_a′	K_c′	*J*″	K_a″	K_c″	State	v_{obs}/MHz	$v_{obs\text{-}calc}$/kHz
6	1	6	5	0	5	A	5868.3006	1.8
6	1	6	5	0	5	E	5868.3006	2.7
6	0	6	5	1	5	A	5643.8162	-2.0
6	0	6	5	1	5	E	5643.8162	-2.2
7	1	7	6	0	6	A	6698.2908	1.9
7	1	7	6	0	6	E	6698.2908	2.6
7	0	7	6	1	6	A	6584.4163	-1.1
7	0	7	6	1	6	E	6584.4163	-1.1
7	2	6	6	1	5	A	8307.4272	-4.6
7	2	6	6	1	5	E	8307.4272	-0.7
8	1	8	7	0	7	A	7553.6028	2.5
8	1	8	7	0	7	E	7553.6028	3.0
8	0	8	7	1	7	A	7498.4381	0.3
8	0	8	7	1	7	E	7498.4381	0.5
8	2	7	7	1	6	A	8929.3356	-1.9

8	2	7	7	1	6	E	8929.3356	1.5
9	1	9	8	0	8	A	8423.7875	3.2
9	1	9	8	0	8	E	8423.7875	3.7
9	0	9	8	1	8	A	8397.9346	0.6
9	0	9	8	1	8	E	8397.9346	0.8
9	2	8	8	1	7	A	9609.5519	0.5
9	2	8	8	1	7	E	9609.5519	3.3
10	1	10	9	0	9	A	9301.8275	2.4
10	1	10	9	0	9	E	9301.8275	2.8
10	0	10	9	1	9	A	9290.0093	0.7
10	0	10	9	1	9	E	9290.0093	1.0
11	1	11	10	0	10	A	10183.7717	0.2
11	1	11	10	0	10	E	10183.7717	0.5
11	0	11	10	1	10	A	10178.4745	1.0
11	0	11	10	1	10	E	10178.4745	1.3
12	1	12	11	0	11	A	11067.5869	-1.8
12	1	12	11	0	11	E	11067.5869	-1.5
12	0	12	11	1	11	A	11065.2498	-0.1
12	0	12	11	1	11	E	11065.2498	0.2
13	1	13	12	0	12	A	11952.2797	-2.1
13	1	13	12	0	12	E	11952.2797	-1.8
13	0	13	12	1	12	A	11951.2597	-2.7
13	0	13	12	1	12	E	11951.2597	-2.3
14	1	14	13	0	13	A	12837.3780	-1.3
14	1	14	13	0	13	E	12837.3780	-1.2
14	0	14	13	1	13	A	12836.9376	-2.1
14	0	14	13	1	13	E	12836.9376	-1.6

Table S21. Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs-calc}$, kHz) of the Isomer II of 4FAP-HOD.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs-calc}$/kHz
6	1	6	5	0	5	A	5918.5375	-0.9
6	1	6	5	0	5	E	5918.5375	0.0
6	0	6	5	1	5	A	5680.5805	1.1
6	0	6	5	1	5	E	5680.5805	0.9
7	1	7	6	0	6	A	6752.7006	1.7
7	1	7	6	0	6	E	6752.7006	2.3
7	0	7	6	1	6	A	6630.6855	-0.8
7	0	7	6	1	6	E	6630.6855	-0.9
8	1	8	7	0	7	A	7612.9537	-0.9
8	1	8	7	0	7	E	7612.9537	-0.3
8	0	8	7	1	7	A	7553.2154	0.2
8	0	8	7	1	7	E	7553.2154	0.3
9	1	9	8	0	8	A	8488.7769	0.4

9	1	9	8	0	8	E	8488.7769	0.8
9	0	9	8	1	8	A	8460.4834	-0.9
9	0	9	8	1	8	E	8460.4834	-0.7
10	1	10	9	0	9	A	9372.9289	-2.0
10	1	10	9	0	9	E	9372.9289	-1.6
10	0	10	9	1	9	A	9359.8603	-1.4
10	0	10	9	1	9	E	9359.8603	-1.1
11	1	11	10	0	10	A	10261.2751	-1.2
11	1	11	10	0	10	E	10261.2751	-0.8
11	0	11	10	1	10	A	10255.3591	4.1
11	0	11	10	1	10	E	10255.3591	4.4
12	1	12	11	0	11	A	11151.6503	-0.7
12	1	12	11	0	11	E	11151.6503	-0.4
12	0	12	11	1	11	A	11149.0080	-1.6
12	0	12	11	1	11	E	11149.0080	-1.3
13	1	13	12	0	12	A	12042.9840	-1.4
13	1	13	12	0	12	E	12042.9840	-1.1
13	0	13	12	1	12	A	12041.8208	-1.2
13	0	13	12	1	12	E	12041.8208	-0.8
14	1	14	13	0	13	A	12934.7677	0.7
14	1	14	13	0	13	E	12934.7677	0.9
14	0	14	13	1	13	A	12934.2619	1.9
14	0	14	13	1	13	E	12934.2619	2.4

Table S22. Experimental transition frequencies (v_{obs}, MHz) and fit deviations ($v_{obs-calc}$, kHz) of the Isomer II of 4FAP-DOH.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	v_{obs}/MHz	$v_{obs-calc}$/kHz
6	1	6	5	0	5	A	5984.8251	0.0
6	1	6	5	0	5	E	5984.8251	1.0
6	0	6	5	1	5	A	5726.4561	0.9
6	0	6	5	1	5	E	5726.4561	0.6
7	1	7	6	0	6	A	6823.8493	0.2
7	1	7	6	0	6	E	6823.8493	0.9
7	0	7	6	1	6	A	6689.3310	-0.3
7	0	7	6	1	6	E	6689.3310	-0.3
8	1	8	7	0	7	A	7690.0535	-0.9
8	1	8	7	0	7	E	7690.0535	-0.4
8	0	8	7	1	7	A	7623.1852	-1.4
8	0	8	7	1	7	E	7623.1852	-1.3
9	1	9	8	0	8	A	8572.8404	-0.8
9	1	9	8	0	8	E	8572.8404	-0.4
9	0	9	8	1	8	A	8540.6936	-0.2
9	0	9	8	1	8	E	8540.6936	0.0
10	1	10	9	0	9	A	9464.6712	-2.7

10	1	10	9	0	9	E	9464.6712	-2.3
10	0	10	9	1	9	A	9449.6001	-0.4
10	0	10	9	1	9	E	9449.6001	-0.1
11	1	11	10	0	10	A	10361.1356	1.7
11	1	11	10	0	10	E	10361.1356	2.1
11	0	11	10	1	10	A	10354.2053	3.0
11	0	11	10	1	10	E	10354.2053	3.3
12	1	12	11	0	11	A	11259.8684	-1.2
12	1	12	11	0	11	E	11259.8684	-0.9
12	0	12	11	1	11	A	11256.7326	1.2
12	0	12	11	1	11	E	11256.7326	1.6
13	1	13	12	0	12	A	12159.6967	-0.4
13	1	13	12	0	12	E	12159.6967	-0.1
13	0	13	12	1	12	A	12158.2929	-1.4
13	0	13	12	1	12	E	12158.2929	-1.0

Table S23. Experimental transition frequencies (ν_{obs}, MHz) and fit deviations ($\nu_{obs-calc}$, kHz) of the Isomer II of 4FAP-D_2O.

J'	K_a'	K_c'	J''	K_a''	K_c''	State	ν_{obs}/MHz	$\nu_{obs-calc}$/kHz
6	1	6	5	0	5	A	5864.0282	-3.3
6	1	6	5	0	5	E	5864.0282	-2.4
6	0	6	5	1	5	A	5621.9033	-1.1
6	0	6	5	1	5	E	5621.9033	-1.3
7	1	7	6	0	6	A	6688.8948	-0.3
7	1	7	6	0	6	E	6688.8948	0.4
7	0	7	6	1	6	A	6564.0331	-0.8
7	0	7	6	1	6	E	6564.0331	-0.9
8	1	8	7	0	7	A	7539.9088	1.8
8	1	8	7	0	7	E	7539.9088	2.4
8	0	8	7	1	7	A	7478.4270	1.5
8	0	8	7	1	7	E	7478.4270	1.6
9	1	9	8	0	8	A	8406.6501	2.9
9	1	9	8	0	8	E	8406.6501	3.3
9	0	9	8	1	8	A	8377.3661	0.1
9	0	9	8	1	8	E	8377.3661	0.3
10	1	10	9	0	9	A	9281.8677	1.4
10	1	10	9	0	9	E	9281.8677	1.8
10	0	10	9	1	9	A	9268.2646	0.1
10	0	10	9	1	9	E	9268.2646	0.4
11	1	11	10	0	10	A	10161.3775	0.7
11	1	11	10	0	10	E	10161.3775	1.0
11	0	11	10	1	10	A	10155.1787	-1.2
11	0	11	10	1	10	E	10155.1787	-0.9
12	1	12	11	0	11	A	11042.9763	-1.2

12	1	12	11	0	11	E	11042.9763	-0.9
12	0	12	11	1	11	A	11040.1967	-1.1
12	0	12	11	1	11	E	11040.1967	-0.7
13	1	13	12	0	12	A	11925.5718	0.1
13	1	13	12	0	12	E	11925.5718	0.4
13	0	13	12	1	12	A	11924.3399	-0.7
13	0	13	12	1	12	E	11924.3399	-0.3
14	1	14	13	0	13	A	12808.6305	-0.8
14	1	14	13	0	13	E	12808.6305	-0.6
14	0	14	13	1	13	A	12808.0911	-0.8
14	0	14	13	1	13	E	12808.0911	-0.3

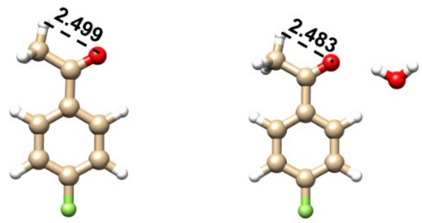

Fig. S2. The structural comparison of 4FAP and isomer II of 4FAP-H_2O in the distance (Å) between the H atoms of -CH_3 and the O atoms of -C=O.

Table S24. Transition frequencies and intensities of isomer I and isomer II of the 4FAP-H_2O complex for the population ratio.

	Isomer I		Isomer II	
	Frequency	Intensity	Frequency	Intensity
$6_{16}\leftarrow5_{05}$	7447.3343	0.0265	6043.1324	0.0157
$7_{17}\leftarrow6_{06}$	8113.7691	0.0179	6891.6204	0.0114
$8_{18}\leftarrow7_{07}$	8764.4813	0.0103	7767.33209	0.0103
$10_{110}\leftarrow9_{09}$	10030.0104	0.0071	9560.7178	0.0062

Table S25. The r_s and r_e coordinates of the oxygen atom of water in 4FAP-H_2O.

	Atom	*a*/Å		*b*/Å		*c*/Å	
		r_s	r_e	r_s	r_e	r_s	r_e
Isomer I	O18	±2.8638(5)[a]	2.802	±2.7105(6)	2.729	0[b]	0.113
Isomer II	O18	5.0465(3)	5.049	0.395(4)	0.379	0.06(2)	-0.0491

a Errors in parenthesis are given in units of the last digit.

b Imaginary values, fixed at zero.

Table S26. Theoretical, experimental and semi-experimental rotational constants of $H_2{}^{18}O$, DOH (with D participating in the HB), HOD, and D_2O isotopologues of isomers I of the 4FAP-H_2O.

		B_e^{theo}	B_0^{theo}	ΔB_{vib}	B_0^{exp}	B_e^{SE}
	A/MHz	3432.542	3439.695	-7.153	3423.8204(4)[a]	3416.6674(4)
Normal	*B*/MHz	432.584	427.517	5.067	433.74560(5)	438.812600(5)
	C/MHz	385.761	381.795	3.966	386.30681(3)	390.27281(3)
	A/MHz	3426.133	3453.576	-27.443	3416.8482(2)	3389.4052(2)
$H_2{}^{18}O$	*B*/MHz	414.671	410.068	4.603	415.75543(2)	420.35843(2)
	C/MHz	371.379	367.933	3.446	371.89280(1)	375.3388(1)
	A/MHz	3403.385	3433.798	-30.413	3398.33(2)	3367.92(2)
HOD	*B*/MHz	421.296	416.426	4.870	422.53377(8)	420.35843(2)
	C/MHz	376.444	372.849	3.595	377.10998(5)	375.3388(1)
	A/MHz	3419.975	3450.777	-30.802	3411.030(9)	3380.228(9)
DOH	*B*/MHz	426.293	422.148	4.145	427.7837(1)	431.9287(1)
	C/MHz	380.598	377.681	2.917	381.4084(1)	384.3254(1)
	A/MHz	3432.542	3439.694	-7.152	3386.049(1)	3378.897(1)
D_2O	*B*/MHz	432.584	427.517	5.067	416.96138(5)	422.02838(5)
	C/MHz	385.761	381.795	3.966	372.51670(3)	376.4827(3)

[a] Values of centrifugal distortion constants were fixed at those of the parent species.

Table S27. Theoretical, experimental and semi-experimental rotational constants of $H_2{}^{18}O$, DOH (with D participating in the HB), HOD, and D_2O isotopologues of isomers II of the 4FAP-H_2O.

		B_e^{theo}	B_0^{theo}	ΔB_{vib}	B_0^{exp}	B_e^{SE}
	A/MHz	1481.942	1460.179	21.763	1483.5073(5)[a]	1505.2703(5)
Normal	*B*/MHz	655.023	646.366	8.657	652.7972(4)	661.4542(4)
	C/MHz	456.402	450.180	6.222	455.0442(6)	461.2662(6)
	A/MHz	1422.587	1403.450	19.137	1425.0036(5)	1444.1406(5)
$H_2{}^{18}O$	*B*/MHz	641.637	631.644	9.993	638.9646(6)	648.9576(6)
	C/MHz	444.255	437.603	6.652	442.77824(5)	461.2662(6)
	A/MHz	1440.164	1419.317	20.847	1444.69(2)	1465.537(2)
HOD	*B*/MHz	644.435	633.764	10.671	641.897(5)	652.568(5)
	C/MHz	447.393	440.154	7.239	446.14194(5)	453.38094(5)
	A/MHz	1468.448	1449.610	18.838	1472.49(2)	1491.328(2)
DOH	*B*/MHz	647.577	637.257	10.320	645.481(5)	655.801(5)
	C/MHz	451.508	444.659	6.849	450.45796(5)	457.30696(5)
	A/MHz	1428.745	1409.118	19.627	1435.580(2)	1455.207(2)
D_2O	*B*/MHz	637.127	627.636	9.491	634.667(5)	644.158(5)
	C/MHz	442.768	436.214	6.554	441.7902(4)	448.3442(4)

[a] Values of centrifugal distortion constants were fixed at those of the parent species.