

## Electronic Supplementary Information

### **Stepwise Hydrations of Anhydride Tuned by Hydrogen Bonds:**

#### **Rotational Study on Maleic Anhydride-(H<sub>2</sub>O)<sub>1-3</sub>**

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**Figure S2.** Plausible isomers of the MAH-(H<sub>2</sub>O)<sub>2</sub> complex and their relative zero-point energies inclusive of BSSE corrections optimized at the MP2/6-311++G(d,p) level within 6.5 kJ mol<sup>-1</sup>. The isomers have been labeled 2w-I, II, etc., in order of increasing energy.

**Figure S3.** Plausible isomers of the MAH-(H<sub>2</sub>O)<sub>3</sub> complex and their relative zero-point energies inclusive of BSSE corrections optimized at the MP2/6-311++G(d,p) level within 6.5 kJ mol<sup>-1</sup>. The isomers have been labeled 3w-I, II, etc., in order of increasing energy.

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**Table S1.** Spectroscopic parameters of plausible isomers of MAH-H<sub>2</sub>O calculated at the MP2/6-311++G(d,p) level of theory within 6.5 kJ mol<sup>-1</sup>.

**Table S2.** Spectroscopic parameters of plausible isomers of MAH-(H<sub>2</sub>O)<sub>2</sub> calculated at the MP2/6-311++G(d,p) level of theory within 6.5 kJ mol<sup>-1</sup>.

**Table S3.** Spectroscopic parameters of plausible isomers of MAH-(H<sub>2</sub>O)<sub>3</sub> calculated at the MP2/6-311++G(d,p) level of theory within 6.5 kJ mol<sup>-1</sup>.

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**Table S11.** Experimental transition frequencies ( $\nu_{\text{obs}}$ /MHz) together with the corresponding observed – calculated

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**Table S12.** Experimental transition frequencies ( $\nu_{\text{obs}}$ /MHz) together with the corresponding observed – calculated differences ( $\nu_{\text{diff}}$ /MHz) for the observed isotopologue of MAH-H<sub>2</sub><sup>18</sup>O<sub>9</sub>-H<sub>2</sub>O.

**Table S13.** Experimental transition frequencies ( $\nu_{\text{obs}}$ /MHz) together with the corresponding observed – calculated differences ( $\nu_{\text{diff}}$ /MHz) for the observed isotopologue of MAH-H<sub>2</sub><sup>18</sup>O<sub>8</sub>-H<sub>2</sub><sup>18</sup>O<sub>9</sub>.

**Table S14.** Experimental values of spectroscopic parameters of the minor isotopologues of MAH-H<sub>2</sub>O.

**Table S15.** Experimental values of spectroscopic parameters of the minor isotopologues of MAH-(H<sub>2</sub>O)<sub>2</sub>.

**Table S16.** Comparison between  $r_s$  and  $r_e$  coordinates of the MAH-(H<sub>2</sub>O)<sub>1-2</sub> complexes.

**Table S17.** Comparison between  $r_s$  and  $r_e$  structural parameters of the MAH-(H<sub>2</sub>O)<sub>1-2</sub> complexes.

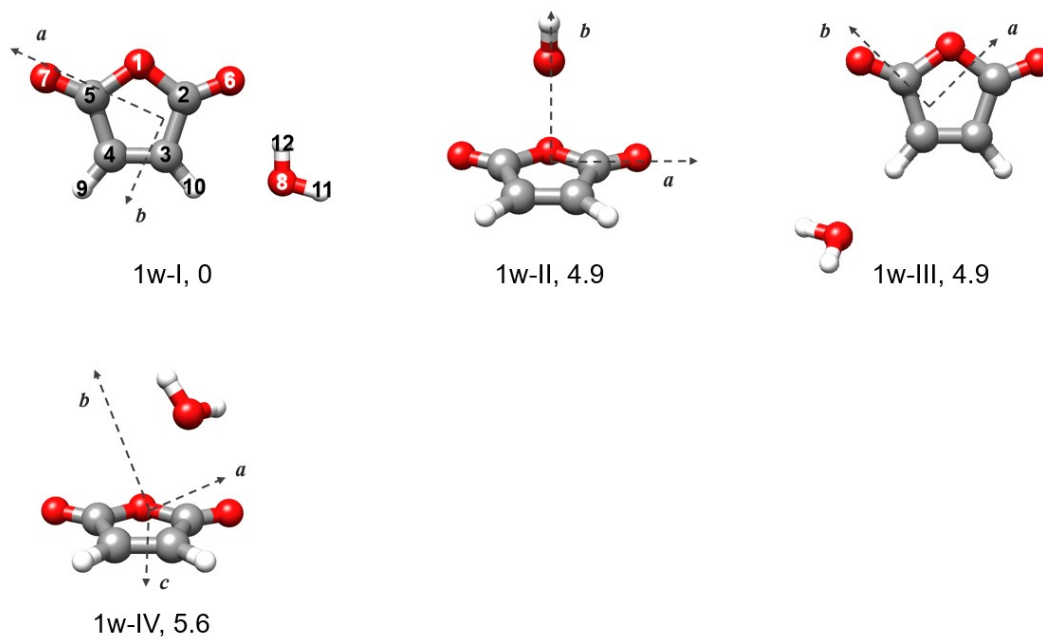
**Table S18.** MP2/6-311++G(d,p) geometry of the observed isomer of MAH-H<sub>2</sub>O.

**Table S19.** MP2/6-311++G(d,p) geometry of the observed isomer of MAH-(H<sub>2</sub>O)<sub>2</sub>.

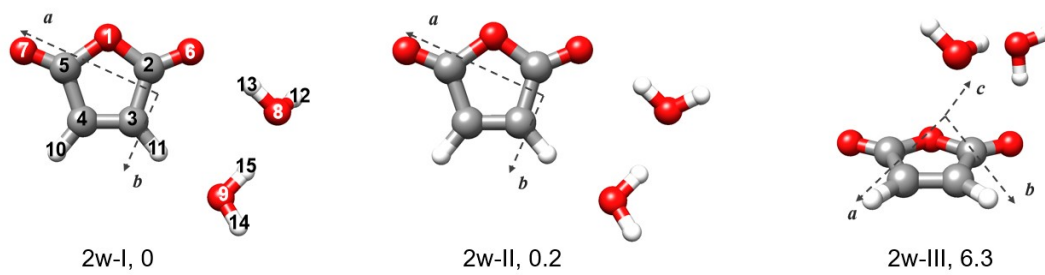
**Table S20.** MP2/6-311++G(d,p) geometry of the observed isomer of MAH-(H<sub>2</sub>O)<sub>3</sub>.

## References

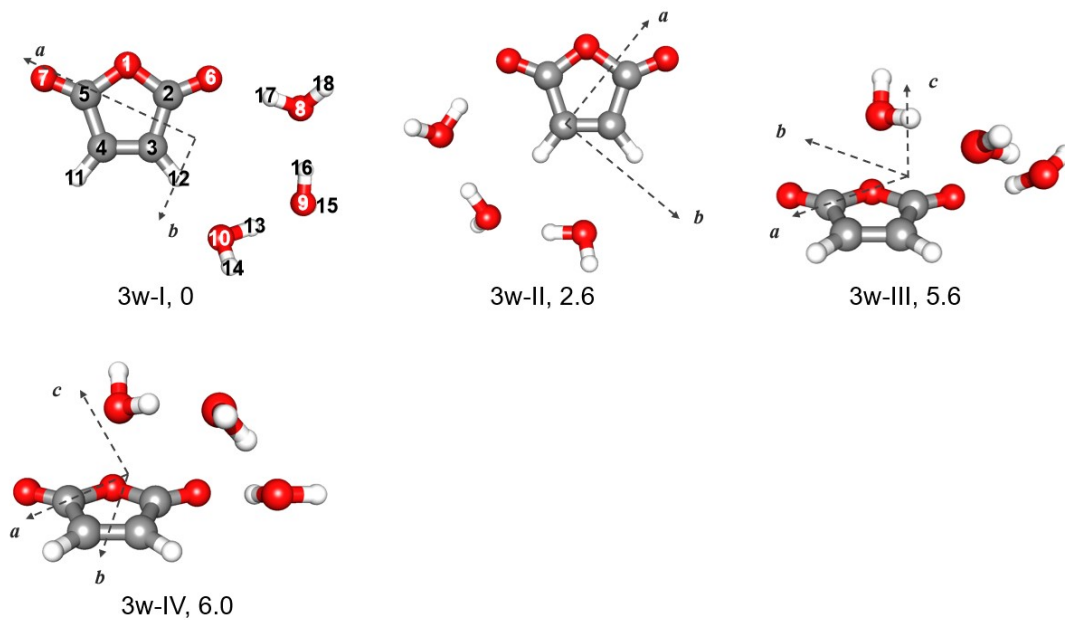
**Figure S1.** Plausible isomers of the MAH-H<sub>2</sub>O complex and their relative zero-point energies inclusive of BSSE corrections ( $\Delta E_{ZPE,BSSE}$ , in unit of kJ mol<sup>-1</sup>) optimized at the MP2/6-311++G(d,p) level<sup>[1]</sup> within 6.5 kJ mol<sup>-1</sup>. The isomers have been labeled 1w-I, II, etc., in order of increasing energy. The principal axes are also given. The absolute energy for the global minimum is  $E(1w-I)=-530.918239 E_h$ .



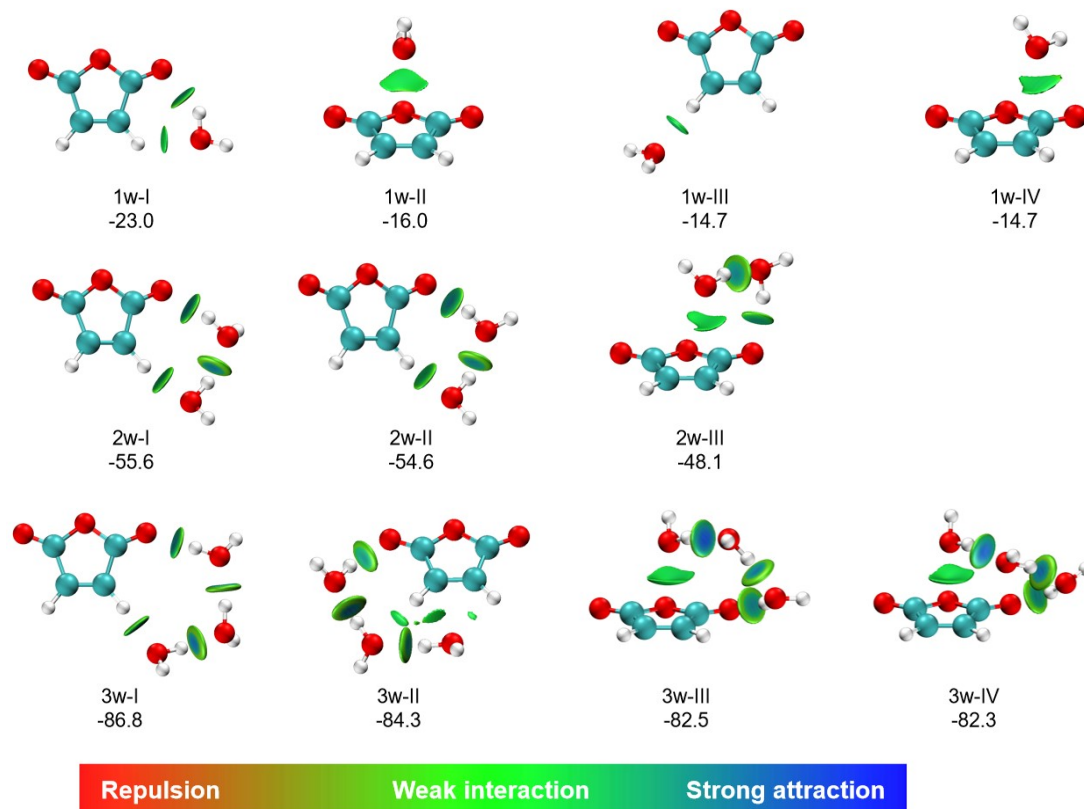
**Figure S2.** Plausible isomers of the MAH-(H<sub>2</sub>O)<sub>2</sub> complex and their relative zero-point energies inclusive of BSSE corrections ( $\Delta E_{ZPE,BSSE}$ , in unit of kJ mol<sup>-1</sup>) optimized at the MP2/6-311++G(d,p) level within 6.5 kJ mol<sup>-1</sup>. The isomers have been labeled 2w-I, II, etc., in order of increasing energy. The principal axes are also given. The absolute energy for the global minimum is  $E(2w-I)=-607.288752 E_h$ .



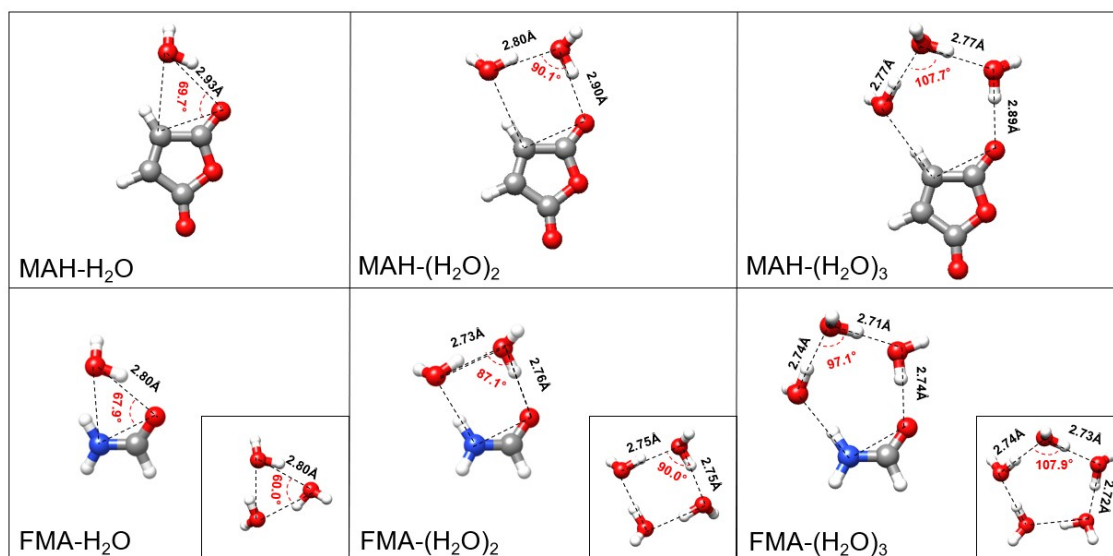
**Figure S3.** Plausible isomers of the MAH-(H<sub>2</sub>O)<sub>3</sub> complex and their relative zero-point energies inclusive of BSSE corrections ( $\Delta E_{ZPE,BSSE}$ , in unit of kJ mol<sup>-1</sup>) optimized at the MP2/6-311++G(d,p) level within 6.5 kJ mol<sup>-1</sup>. The isomers have been labeled 3w-I, II, etc., in order of increasing energy. The principal axes are also given. The absolute energy for the global minimum is  $E(3w-I)=-683.579757 E_h$ .



**Figure S4.** Results of the independent gradient model based on Hirshfeld partition (IGMH)<sup>[2]</sup> analysis of plausible isomers of the MAH-(H<sub>2</sub>O)<sub>1-3</sub> complexes. The  $\text{sign}(\lambda_2) \rho(r)$  function mapped on the  $\delta g_{\text{inter}}$  isosurface for all interactions ( $\delta g_{\text{inter}} = 0.005$  au and blue-red color scale  $-0.05 < \text{sign}(\lambda_2)\rho(r) < 0.05$ ) for the structures. Binding energies with BSSE corrections ( $B_{\text{BSSE}}$ , in unit of  $\text{kJ mol}^{-1}$ ) of MAH-(H<sub>2</sub>O)<sub>1-3</sub> calculated at the MP2/6-311++G(d,p) level within  $6.5 \text{ kJ mol}^{-1}$  are also given with the labeling shown in Figures S1-S3.



**Figure S5.** Comparison of the hydrogen bonding structures in MAH-(H<sub>2</sub>O)<sub>1-3</sub>, FMA-(H<sub>2</sub>O)<sub>1-3</sub>,<sup>[3]</sup> and (H<sub>2</sub>O)<sub>3-5</sub><sup>[4]</sup> calculated at the MP2/6-311++G(d,p) level. The dotted lines connect the heavy atoms forming a hydrogen bond loop in each hydrate.



The highly structural similarity of MAH-(H<sub>2</sub>O)<sub>1-3</sub> to FMA-(H<sub>2</sub>O)<sub>1-3</sub> and (H<sub>2</sub>O)<sub>3-5</sub> indicates that MAH can act as a replacement for a (H<sub>2</sub>O)<sub>2</sub> moiety of a pure water cluster with little effect on the overall structure.



**Table S1.** Spectroscopic parameters of plausible isomers of MAH-H<sub>2</sub>O calculated at the MP2/6-311++G(d,p) level of theory within 6.5 kJ mol<sup>-1</sup>. The isomers have been labeled 1w-I, II, etc., shown in Figure S1.

Parameters <sup>a</sup>	1w-I	1w-II	1w-III	1w-IV
A [MHz]	5328.4	2593.8	3398.6	2812.9
B [MHz]	1106.7	1822.1	1048.4	1608.5
C [MHz]	917.1	1533.6	803.1	1461.8
$ \mu_a ,  \mu_b ,  \mu_c $ [D]	2.1, 2.5, 0.7	0.0, 0.8, 3.3	5.4, 2.5, 0.5	0.9, 1.1, 2.9

<sup>a</sup> A, B and C are the asymmetric top determinable rotational constants.  $\mu_a$ ,  $\mu_b$  and  $\mu_c$  are the electric dipole moment components (in Debye).

**Table S2.** Spectroscopic parameters of plausible isomers of MAH-(H<sub>2</sub>O)<sub>2</sub> calculated at the MP2/6-311++G(d,p) level of theory within 6.5 kJ mol<sup>-1</sup>. The isomers have been labeled 2w-I, II, etc., shown in Figure S2.

Parameters <sup>a</sup>	2w-I	2w-II	2w-III
A [MHz]	2929.9	2925.5	2207.8
B [MHz]	713.8	713.9	970.8
C [MHz]	575.0	575.1	911.6
$ \mu_a ,  \mu_b ,  \mu_c $ [D]	2.6, 1.1, 0.3	2.9, 0.9, 1.8	0.3, 1.9, 2.4

<sup>a</sup> A, B and C are the asymmetric top determinable rotational constants.  $\mu_a$ ,  $\mu_b$  and  $\mu_c$  are the electric dipole moment components (in Debye).

**Table S3.** Spectroscopic parameters of plausible isomers of MAH-(H<sub>2</sub>O)<sub>3</sub> calculated at the MP2/6-311++G(d,p) level of theory within 6.5 kJ mol<sup>-1</sup>. The isomers have been labeled 3w-I, II, etc., shown in Figure S3.

Parameters <sup>a</sup>	3w-I	3w-II	3w-III	3w-IV
A [MHz]	1816.6	1344.9	1813.9	1720.8
B [MHz]	485.7	681.0	724.1	736.5
C [MHz]	387.9	456.6	625.3	625.9
$ \mu_a ,  \mu_b ,  \mu_c $ [D]	2.4, 1.3, 0.6	4.2, 0.1, 0.8	4.2, 1.1, 1.7	4.2, 0.4, 3.1

<sup>a</sup> A, B and C are the asymmetric top determinable rotational constants.  $\mu_a$ ,  $\mu_b$  and  $\mu_c$  are the electric dipole moment components (in Debye).

**Table S4.** Experimental transition frequencies ( $\nu_{\text{obs}}$ /MHz) together with the corresponding observed – calculated differences ( $\nu_{\text{diff}}$ /MHz) for the observed isomer of MAH-H<sub>2</sub>O.

Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz	Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz
$J' K_a' K_c'$	$J'' K_a'' K_c''$			$J' K_a' K_c'$	$J'' K_a'' K_c''$		
3 0 3	2 0 2	6026.0374	-0.0001	8 3 5	7 3 4	16219.6850	0.0000
3 1 3	2 1 2	5766.5067	0.0002	9 0 9	8 0 8	17526.6346	-0.0004
3 1 2	2 1 1	6325.7921	0.0000	9 1 9	8 1 8	17163.5609	-0.0008
3 2 2	2 2 1	6049.8921	0.0013	9 1 8	8 1 7	18787.6773	0.0015
3 2 1	2 2 0	6073.7353	0.0023	9 2 8	8 2 7	18042.3169	-0.0002
4 0 4	3 0 3	8007.1429	0.0000	9 2 7	8 2 6	18663.2179	0.0011
4 1 4	3 1 3	7681.9646	-0.0003	10 0 10	9 0 9	19358.9851	-0.0016
4 1 3	3 1 2	8427.1119	-0.0003	10 1 10	9 1 9	19037.9625	-0.0013
4 2 3	3 2 2	8061.8540	0.0005	1 1 1	0 0 0	6289.4469	0.0022
4 2 2	3 2 1	8121.1923	0.0007	2 1 2	1 0 1	8119.6052	0.0004
4 3 2	3 3 1	8078.1074	0.0020	2 2 1	1 1 0	17038.0546	-0.0013
4 3 1	3 3 0	8078.8235	0.0013	2 2 0	1 1 1	17230.4914	-0.0064
5 0 5	4 0 4	9965.4678	0.0002	2 2 0	2 1 1	12824.2946	0.0013
5 1 5	4 1 4	9592.0209	0.0001	2 2 1	2 1 2	13377.7350	0.0013
5 1 4	4 1 3	10521.8301	-0.0003	3 1 3	2 0 2	9858.8203	-0.0001
5 2 4	4 2 3	10069.8205	0.0002	3 2 1	2 1 2	19457.4397	0.0022
5 2 3	4 2 2	10187.4034	0.0007	3 2 2	2 1 1	18868.2109	-0.0022
5 3 3	4 3 2	10102.4012	0.0000	3 2 2	3 1 3	13661.1218	0.0038
5 3 2	4 3 1	10104.9070	0.0003	3 2 1	3 1 2	12572.2342	0.0000
5 4 2	4 4 1	10096.4092	0.0064	4 0 4	3 1 3	4174.3593	-0.0006
5 4 1	4 4 0	10096.4168	-0.0018	4 1 4	3 0 3	11514.7500	0.0022
6 0 6	5 0 5	11897.1120	0.0001	4 2 3	4 1 4	14041.0083	0.0018
6 1 6	5 1 5	11495.7452	0.0004	4 2 2	4 1 3	12266.3130	-0.0004
6 1 5	5 1 4	12607.8301	-0.0065	5 0 5	4 1 4	6457.8628	0.0002
6 2 5	5 2 4	12072.8038	-0.0002	5 1 5	4 0 4	13099.6244	-0.0012
6 2 4	5 2 3	12275.2440	-0.0004	5 2 4	5 1 5	14518.8069	0.0009
6 3 4	5 3 3	12129.2533	0.0011	5 2 3	5 1 4	11931.8849	-0.0008
6 3 3	5 3 2	12135.9160	0.0000	6 0 6	5 1 5	8762.9536	-0.0001
6 4 3	5 4 2	12119.9908	0.0044	6 1 6	5 0 5	14629.9035	0.0005
6 4 2	5 4 1	12120.0574	-0.0003	6 2 5	6 1 6	15095.8650	-0.0003
6 5 2	5 5 1	12114.6857	-0.0020	6 2 4	6 1 5	11599.2918	-0.0017
6 5 1	5 5 0	12114.6857	-0.0023	7 0 7	6 1 6	11067.4162	-0.0006
7 0 7	6 0 6	13800.2078	0.0000	7 1 7	6 0 6	16125.2541	0.0005
7 1 7	6 1 6	13392.4624	0.0000	8 0 8	7 1 7	13350.5001	-0.0001
7 1 6	6 1 5	14682.7152	-0.0003	8 1 8	7 0 7	17606.8219	0.0012
7 2 6	6 2 5	14069.8345	-0.0003	8 1 7	7 2 6	6166.4631	-0.0008
7 2 5	6 2 4	14385.5414	0.0008	9 0 9	8 1 8	15595.3596	-0.0007

7 3 5	6 3 4	14158.5767	-0.0003	9 1 9	8 0 8	19094.8361	-0.0004
7 3 4	6 3 3	14173.5070	-0.0004	9 1 8	8 2 7	8894.1692	0.0006
7 4 4	6 4 3	14145.8817	0.0002	10 0 10	9 1 9	17790.7851	-0.0002
7 4 3	6 4 2	14146.1188	-0.0003	11 0 11	10 1 10	19931.6718	0.0014
7 1 6	7 0 7	7521.0450	0.0005	11 1 10	11 0 11	12934.3409	-0.0011
8 0 8	7 0 7	15675.5459	0.0000	11 1 10	10 2 9	14457.7466	0.0017
8 1 8	7 1 7	15281.7749	-0.0001	5 3 3	6 2 4	9400.1958	0.0009
8 1 7	7 1 6	16743.7014	-0.0014	5 3 2	6 2 5	9812.7023	-0.0084
8 2 7	7 2 6	16059.9717	0.0005	4 3 2	5 2 3	11573.0421	0.0040
8 2 6	7 2 5	16516.4153	-0.0012	4 3 1	5 2 4	11780.6123	0.0041
8 3 6	7 3 5	16190.0180	-0.0015				

**Table S5.** Experimental transition frequencies ( $\nu_{\text{obs}}$ /MHz) together with the corresponding observed – calculated differences ( $\nu_{\text{diff}}$ /MHz) for the observed isomer of MAH-(H<sub>2</sub>O)<sub>2</sub>.

Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz	Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz
$J' K_a' K_c'$	$J'' K_a'' K_c''$			$J' K_a' K_c'$	$J'' K_a'' K_c''$		
4 0 4	3 0 3	5100.4966	-0.0006	9 2 8	8 2 7	11505.0418	-0.0007
4 1 4	3 1 3	4871.1526	-0.0009	9 2 7	8 2 6	12110.1753	0.0032
4 1 3	3 1 2	5433.3884	-0.0006	10 0 10	9 0 9	12151.2115	-0.0001
4 2 3	3 2 2	5160.3176	0.0016	10 1 10	9 1 9	12012.3035	0.0001
4 2 2	3 2 1	5225.2682	0.0010	11 0 11	10 0 10	13287.1497	-0.0002
4 3 2	3 3 1	5178.0201	0.0059	11 1 11	10 1 10	13181.1371	0.0002
4 3 1	3 3 0	5179.1708	0.0039	12 0 12	11 0 11	14423.9778	0.0006
5 0 5	4 0 4	6329.3253	-0.0008	12 1 12	11 1 11	14345.5436	-0.0001
5 1 5	4 1 4	6077.8446	-0.0007	13 0 13	12 0 12	15562.9653	0.0017
5 1 4	4 1 3	6778.0484	-0.0008	13 1 13	12 1 12	15506.3407	-0.0015
5 2 4	4 2 3	6442.1597	-0.0014	3 1 3	2 0 2	5713.4022	0.0009
5 2 3	4 2 2	6569.5970	0.0000	3 2 1	2 1 2	10895.9859	0.0014
5 3 3	4 3 2	6477.4144	0.0015	3 2 2	2 1 1	10440.6294	0.0016
5 3 2	4 3 1	6481.4342	-0.0011	3 3 1	2 2 0	15167.6590	0.0005
6 0 6	5 0 5	7532.1632	-0.0011	3 3 0	2 2 1	15174.4330	0.0015
6 1 6	5 1 5	7278.1127	-0.0012	2 2 1	1 1 0	9290.1242	-0.0019
6 1 5	5 1 4	8112.5017	-0.0018	2 2 0	1 1 1	9437.5556	-0.0011
6 2 5	5 2 4	7718.5495	-0.0011	2 2 0	2 1 1	6573.1164	-0.0074
6 2 4	5 2 3	7934.3514	-0.0016	3 2 1	3 1 2	6392.2808	-0.0004
6 3 4	5 3 3	7779.0989	-0.0016	3 2 2	3 1 3	7204.3778	0.0025
6 3 3	5 3 2	7789.7674	-0.0012	4 1 4	3 0 3	6736.6844	0.0002
6 4 3	5 4 2	7770.3488	0.0035	4 2 3	4 1 4	7493.5363	-0.0013
6 4 2	5 4 1	7770.5120	-0.0007	4 2 2	4 1 3	6184.1597	0.0002
6 5 2	5 5 1	7764.4251	0.0002	4 3 2	3 2 1	16445.3573	-0.0036
6 5 1	5 5 0	7764.4327	0.0068	5 0 5	4 1 4	4693.1473	0.0080
7 0 7	6 0 6	8710.3142	-0.0003	5 1 5	4 0 4	7714.0329	0.0006
7 1 7	6 1 6	8471.5627	-0.0010	5 2 4	5 1 5	7857.8544	0.0009

7 1 6	6 1 5	9433.6577	0.0008	5 2 3	5 1 4	5975.7073	0.0000
7 2 6	6 2 5	8988.4527	-0.0011	6 0 6	5 1 5	6147.4573	-0.0009
7 2 5	6 2 4	9317.0370	-0.0007	6 1 6	5 0 5	8662.8200	0.0000
7 3 5	6 3 4	9082.6439	-0.0017	6 2 5	6 1 6	8298.2839	-0.0063
7 3 4	6 3 3	9106.4299	-0.0011	6 2 4	6 1 5	5797.5572	0.0005
7 4 4	6 4 3	9071.8735	-0.0014	7 0 7	6 1 6	7579.6582	-0.0006
7 4 3	6 4 2	9072.4309	-0.0008	7 1 7	6 0 6	9602.2175	-0.0018
7 5 3	6 5 2	9062.6319	0.0037	7 2 6	7 1 7	8815.1805	0.0000
7 5 2	6 5 1	9062.6319	-0.0019	7 2 5	7 1 6	5680.9350	-0.0026
8 0 8	7 0 7	9868.4756	-0.0020	8 0 8	7 1 7	8976.5754	0.0026
8 1 8	7 1 7	9658.1674	0.0005	8 1 8	7 0 7	10550.0691	-0.0025
8 1 7	7 1 6	10737.9495	0.0006	8 1 7	7 2 6	5826.5888	-0.0035
8 2 7	7 2 6	10250.9066	0.0008	9 0 9	8 1 8	10331.6862	0.0001
8 2 6	7 2 5	10711.6646	0.0009	9 1 9	8 0 8	11519.8218	0.0022
8 3 6	7 3 5	10387.2481	-0.0011	9 1 8	8 2 7	7597.1858	0.0001
8 3 5	7 3 4	10434.1445	-0.0013	10 0 10	9 1 9	11644.6745	0.0023
8 4 5	7 4 4	10376.2152	-0.0015	11 0 11	10 1 10	12919.5213	0.0025
8 4 4	7 4 3	10377.7398	-0.0017	11 1 11	10 0 10	13548.7635	-0.0045
9 0 9	8 0 8	11013.2815	0.0013	12 0 12	11 1 11	14162.3594	0.0003
9 1 9	8 1 8	10838.2260	0.0004	12 1 12	11 0 11	14607.1612	-0.0006
9 1 8	8 1 7	12021.5007	0.0016				

**Table S6.** Experimental transition frequencies ( $\nu_{\text{obs}}$ /MHz) together with the corresponding observed – calculated differences ( $\nu_{\text{diff}}$ /MHz) for the observed isomer of MAH-(H<sub>2</sub>O)<sub>3</sub>.

Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz	Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz
$J' K_a' K_c'$	$J'' K_a'' K_c''$			$J' K_a' K_c'$	$J'' K_a'' K_c''$		
5 0 5	4 0 4	4269.2796	-0.0094	14 0 14	13 0 13	11248.4457	0.0021
5 1 5	4 1 4	4103.4108	-0.0014	14 1 14	13 1 13	11229.7793	-0.0008
5 1 4	4 1 3	4589.2501	-0.0025	3 3 1	2 2 0	9528.2441	0.0006
6 0 6	5 0 5	5075.1346	-0.0007	4 4 1	3 3 0	13178.3536	-0.0002
6 1 6	5 1 5	4912.2658	-0.0024	5 1 5	4 0 4	5058.1557	-0.0011
6 1 5	5 1 4	5489.9725	0.0020	6 0 6	5 1 5	4286.2660	-0.0015
7 0 7	6 0 6	5863.8245	0.0040	6 1 6	5 0 5	5701.1363	0.0002
7 1 7	6 1 6	5716.0140	-0.0008	7 0 7	6 1 6	5237.8216	0.0018
7 1 6	6 1 5	6379.7984	-0.0006	7 1 7	6 0 6	6342.0189	0.0033
8 0 8	7 0 7	6639.8854	0.0025	8 0 8	7 1 7	6161.6905	0.0026
8 1 8	7 1 7	6514.7478	0.0000	8 1 8	7 0 7	6992.9453	0.0025
9 0 9	8 0 8	7408.6748	0.0019	9 0 9	8 1 8	7055.6183	0.0052
9 1 9	8 1 8	7308.8171	0.0004	9 1 9	8 0 8	7661.8734	-0.0030
10 0 10	9 0 9	8174.6767	-0.0015	10 0 10	9 1 9	7921.4774	0.0027
10 1 10	9 1 9	8098.7539	0.0006	10 1 10	9 0 9	8351.9533	-0.0035
11 0 11	10 0 10	8940.7503	-0.0012	11 0 11	10 1 10	8763.4716	-0.0014

11 1 11	10 1 10	8885.1880	-0.0004	11 1 11	10 0 10	9062.4667	-0.0002
12 0 12	11 0 11	9708.2393	-0.0032	12 0 12	11 1 11	9586.5245	-0.0027
12 1 12	11 1 11	9668.7764	0.0016	12 1 12	11 0 11	9790.4915	0.0013
13 0 13	12 0 12	10477.5162	-0.0006	13 0 13	12 1 12	10395.2642	-0.0050
13 1 13	12 1 12	10450.1256	-0.0007	13 1 13	12 0 12	10532.3804	0.0065

**Table S7.** Experimental transition frequencies ( $\nu_{\text{obs}}$ /MHz) together with the corresponding observed – calculated differences ( $\nu_{\text{diff}}$ /MHz) for the observed isotopologue of MAH-H<sub>2</sub><sup>18</sup>O.

Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz	Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz
$J' K_a' K_c'$	$J'' K_a'' K_c''$			$J' K_a' K_c'$	$J'' K_a'' K_c''$		
3 0 3	2 0 2	5746.7855	-0.0014	7 1 7	6 1 6	12798.3015	-0.0004
3 1 3	2 1 2	5507.6622	-0.0009	7 1 6	6 1 5	13981.3587	0.0050
3 1 2	2 1 1	6019.5176	-0.0013	1 1 1	0 0 0	6215.2272	0.0015
4 0 4	3 0 3	7639.3044	-0.0009	2 1 2	1 0 1	7966.8150	0.0011
4 1 4	3 1 3	7337.9217	-0.0019	2 2 1	1 1 0	16893.9720	0.0013
4 1 3	3 1 2	8019.9632	-0.0005	2 2 0	1 1 1	17069.6114	0.0021
4 2 3	3 2 2	7685.0539	-0.0002	3 1 3	2 0 2	9634.9856	0.0007
4 2 2	3 2 1	7734.6649	-0.0004	3 2 1	2 1 2	19182.4092	-0.0060
5 0 5	4 0 4	9512.6407	-0.0013	3 2 2	2 1 1	18645.5560	-0.0001
5 1 5	4 1 4	9163.6260	-0.0017	4 1 4	3 0 3	11226.1227	0.0010
5 1 4	4 1 3	10014.9372	0.0016	5 0 5	4 1 4	5925.8229	-0.0028
5 2 4	4 2 3	9600.0479	-0.0022	5 1 5	4 0 4	12750.4466	0.0025
5 2 3	4 2 2	9698.5073	0.0005	6 0 6	5 1 5	8125.4707	-0.0001
6 0 6	5 0 5	11363.2706	-0.0022	6 1 6	5 0 5	14221.7622	0.0003
6 1 6	5 1 5	10983.9580	-0.0018	7 0 7	6 1 6	10330.6689	0.0024
6 1 5	5 1 4	12002.7183	0.0020	7 1 7	6 0 6	15656.7911	0.0002
7 0 7	6 0 6	13189.1562	0.0008				

**Table S8.** Experimental transition frequencies ( $\nu_{\text{obs}}$ /MHz) together with the corresponding observed – calculated differences ( $\nu_{\text{diff}}$ /MHz) for the observed isotopologue of MAH-DOH.

Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz	Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz
$J' K_a' K_c'$	$J'' K_a'' K_c''$			$J' K_a' K_c'$	$J'' K_a'' K_c''$		
3 0 3	2 0 2	5919.4985	-0.0011	7 1 7	6 1 6	12798.3015	0.0041
3 1 3	2 1 2	5668.4697	-0.0025	7 1 6	6 1 5	13981.3587	0.0020
3 1 2	2 1 1	6207.7519	0.0000	1 1 1	0 0 0	6215.2272	-0.0064
4 0 4	3 0 3	7867.1245	-0.0037	2 1 2	1 0 1	7966.8150	-0.0072
4 1 4	3 1 3	7551.7420	-0.0006	2 2 1	1 1 0	16893.9720	0.0048
4 1 3	3 1 2	8270.2744	-0.0033	2 2 0	1 1 1	17069.6114	0.0060
4 2 3	3 2 2	7917.7800	0.0011	3 1 3	2 0 2	9634.9856	-0.0077
4 2 2	3 2 1	7972.7125	0.0024	3 2 1	2 1 2	19182.4092	-0.0048
5 0 5	4 0 4	9793.5949	-0.0026	3 2 2	2 1 1	18645.5560	0.0033
5 1 5	4 1 4	9429.9931	0.0014	4 1 4	3 0 3	11226.1227	-0.0061

5 1 4	4 1 3	10326.7133	-0.0029	5 0 5	4 1 4	5925.8229	0.0004
5 2 4	4 2 3	9890.2822	-0.0020	5 1 5	4 0 4	12750.4466	-0.0022
5 2 3	4 2 2	9999.2132	0.0013	6 0 6	5 1 5	8125.4707	0.0013
6 0 6	5 0 5	11695.1586	-0.0017	6 1 6	5 0 5	14221.7622	0.0005
6 1 6	5 1 5	11302.3419	0.0023	7 0 7	6 1 6	10330.6689	0.0016
6 1 5	5 1 4	12375.1371	-0.0005	7 1 7	6 0 6	15656.7911	0.0043
7 0 7	6 0 6	13569.8418	0.0023				

**Table S9.** Experimental transition frequencies ( $\nu_{\text{obs}}$ /MHz) together with the corresponding observed – calculated differences ( $\nu_{\text{diff}}$ /MHz) for the observed isotopologue of MAH-HOD.

Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz	Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz
$J' K_a' K_c'$	$J'' K_a'' K_c''$			$J' K_a' K_c'$	$J'' K_a'' K_c''$		
3 0 3	2 0 2	5808.6479	-0.0054	7 1 7	6 1 6	12932.0932	0.0043
3 1 3	2 1 2	5565.6832	-0.0100	7 1 6	6 1 5	14135.0429	0.0097
3 1 2	2 1 1	6086.2904	-0.0105	1 1 1	0 0 0	6244.4451	0.0041
4 0 4	3 0 3	7721.0548	-0.0040	2 1 2	1 0 1	8013.9462	0.0003
4 1 4	3 1 3	7415.1136	-0.0062	2 2 1	1 1 0	16963.7028	0.0030
4 1 3	3 1 2	8108.8028	-0.0060	2 2 0	1 1 1	17142.4198	0.0022
4 2 3	3 2 2	7768.2765	0.0053	3 1 3	2 0 2	9698.6357	-0.0008
4 2 2	3 2 1	7819.4725	0.0017	3 2 1	2 1 2	19279.6135	-0.0041
5 0 5	4 0 4	9613.6884	-0.0011	3 2 2	2 1 1	18733.2002	-0.0017
5 1 5	4 1 4	9259.8484	-0.0020	4 1 4	3 0 3	11305.1016	-0.0013
5 1 4	4 1 3	10125.6614	0.0000	5 0 5	4 1 4	6029.6404	-0.0049
5 2 4	4 2 3	9703.8617	-0.0092	5 1 5	4 0 4	12843.8940	-0.0006
5 2 3	4 2 2	9805.4484	-0.0084	6 0 6	5 1 5	8252.7448	0.0005
6 0 6	5 0 5	11482.9514	0.0019	6 1 6	5 0 5	14329.2558	0.0008
6 1 6	5 1 5	11099.0509	0.0010	7 0 7	6 1 6	10480.5085	0.0075
6 1 5	5 1 4	12135.0822	0.0043	7 1 7	6 0 6	15778.3956	0.0011
7 0 7	6 0 6	13326.8131	0.0065				

**Table S10.** Experimental transition frequencies ( $\nu_{\text{obs}}$ /MHz) together with the corresponding observed – calculated differences ( $\nu_{\text{diff}}$ /MHz) for the observed isotopologue of MAH-DOD.

Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz	Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz
$J' K_a' K_c'$	$J'' K_a'' K_c''$			$J' K_a' K_c'$	$J'' K_a'' K_c''$		
3 0 3	2 0 2	5711.7705	-0.0086	7 1 7	6 1 6	12727.3062	0.0104
3 1 3	2 1 2	5476.3665	-0.0062	7 1 6	6 1 5	13890.5545	0.0053
3 1 2	2 1 1	5979.4429	-0.0009	1 1 1	0 0 0	6233.1410	-0.0014
4 0 4	3 0 3	7593.5409	-0.0060	2 1 2	1 0 1	7975.7191	-0.0055
4 1 4	3 1 3	7296.4187	-0.0055	2 2 1	1 1 0	16956.7340	0.0070
4 1 3	3 1 2	7966.7750	-0.0031	2 2 0	1 1 1	17129.2360	0.0013
4 2 3	3 2 2	7637.4670	0.0011	3 1 3	2 0 2	11220.9182	-0.0035

4 2 2	3 2 1	7685.0953	0.0040	3 2 1	2 1 2	5829.5010	0.0055
5 0 5	4 0 4	9456.8681	-0.0022	3 2 2	2 1 1	12739.4626	-0.0046
5 1 5	4 1 4	9112.0920	-0.0003	4 1 4	3 0 3	8015.7141	0.0042
5 1 4	4 1 3	9948.8596	-0.0098	5 0 5	4 1 4	14205.1861	0.0043
5 2 4	4 2 3	9540.8043	-0.0113	5 1 5	4 0 4	10208.9146	0.0053
5 2 3	4 2 2	9635.3540	-0.0102	6 0 6	5 1 5	15634.1698	-0.0009
6 0 6	5 0 5	11298.3077	0.0009	6 1 6	5 0 5	17129.2360	0.0013
6 1 6	5 1 5	10922.5893	0.0044	7 0 7	6 1 6	11220.9182	-0.0035
6 1 5	5 1 4	11924.0757	-0.0034	7 1 7	6 0 6	5829.5010	0.0055
7 0 7	6 0 6	13115.7926	0.0083				

**Table S11.** Experimental transition frequencies ( $\nu_{\text{obs}}$ /MHz) together with the corresponding observed – calculated differences ( $\nu_{\text{diff}}$ /MHz) for the observed isotopologue of MAH-H<sub>2</sub><sup>18</sup>O8-H<sub>2</sub>O. (see Figure S2 for atom labeling)

Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /kHz	Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /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	6142.3249	-0.0037	7 1 6	6 1 5	9140.6650	-0.0005
5 1 5	4 1 4	5899.3360	-0.0013	8 0 8	7 0 7	9588.2762	-0.0041
5 1 4	4 1 3	6564.7867	-0.0011	8 1 8	7 1 7	9378.0325	-0.0013
5 2 4	4 2 3	6244.9419	-0.0007	9 0 9	8 0 8	10702.6496	0.0012
5 2 3	4 2 2	6360.7993	0.0004	9 1 9	8 1 8	10525.1121	-0.0007
6 0 6	5 0 5	7312.9774	-0.0024	10 0 10	9 0 9	11809.4933	-0.0019
6 1 6	5 1 5	7065.2219	-0.0004	10 1 10	9 1 9	11666.5216	0.0019
6 1 5	5 1 4	7858.6908	0.0018	11 0 11	10 0 10	12913.6306	0.0032
6 2 5	5 2 4	7483.0089	0.0011	11 1 11	10 1 10	12802.8976	0.0027
6 2 4	5 2 3	7679.7255	0.0022	3 1 3	2 0 2	5604.5175	-0.0001
7 0 7	6 0 6	8460.3407	-0.0006	4 1 4	3 0 3	6600.9146	0.0001
7 1 7	6 1 6	8224.8119	-0.0004	5 1 5	4 0 4	7552.6232	0.0005

**Table S12.** Experimental transition frequencies ( $\nu_{\text{obs}}$ /MHz) together with the corresponding observed – calculated differences ( $\nu_{\text{diff}}$ /MHz) for the observed isotopologue of MAH-H<sub>2</sub><sup>18</sup>O9-H<sub>2</sub>O. (see Figure S2 for atom labeling)

Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz	Transitions		$\nu_{\text{obs}}$ /MHz	$\nu_{\text{diff}}$ /MHz
$J' K_a' K_c'$	$J'' K_a'' K_c''$			$J' K_a' K_c'$	$J'' K_a'' K_c''$		
5 0 5	4 0 4	6166.4022	0.0001	7 1 6	6 1 5	9197.0803	0.0072
5 1 5	4 1 4	5920.9673	-0.0045	8 0 8	7 0 7	9609.5482	-0.0021
5 1 4	4 1 3	6609.3045	0.0000	8 1 8	7 1 7	9407.3218	-0.0032
5 2 4	4 2 3	6279.3877	-0.0064	9 0 9	8 0 8	10723.4760	0.0020
5 2 3	4 2 2	6407.0218	-0.0043	9 1 9	8 1 8	10556.1901	-0.0005
6 0 6	5 0 5	7336.8070	-0.0019	10 0 10	9 0 9	11831.0772	0.0000
6 1 6	5 1 5	7089.8710	-0.0045	10 1 10	9 1 9	11699.1780	0.0027
6 1 5	5 1 4	7909.8938	0.0034	11 0 11	10 0 10	12937.0691	0.0043
6 2 5	5 2 4	7523.1941	-0.0043	11 1 11	10 1 10	12837.0350	0.0062
6 2 4	5 2 3	7739.0774	0.0001	3 1 3	2 0 2	5541.7590	0.0030

7 0 7	6 0 6	8482.8948	-0.0003	4 1 4	3 0 3	6537.2501	-0.0005
7 1 7	6 1 6	8251.9907	-0.0043	5 1 5	4 0 4	7488.0500	-0.0039

**Table S13.** Experimental transition frequencies ( $\nu_{\text{obs}}/\text{MHz}$ ) together with the corresponding observed – calculated differences ( $\nu_{\text{diff}}/\text{MHz}$ ) for the observed isotopologue of MAH-H<sub>2</sub><sup>18</sup>O8-H<sub>2</sub><sup>18</sup>O9. (see Figure S2 for atom labeling)

Transitions		$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{diff}}/\text{MHz}$	Transitions		$\nu_{\text{obs}}/\text{MHz}$	$\nu_{\text{diff}}/\text{MHz}$
$J' K_a' K_c'$	$J'' K_a'' K_c''$			$J' K_a' K_c'$	$J'' K_a'' K_c''$		
5 0 5	4 0 4	5993.0343	-0.0031	7 1 6	6 1 5	8926.6273	0.0053
5 1 5	4 1 4	5755.2775	-0.0051	8 0 8	7 0 7	9348.7806	-0.0011
5 1 4	4 1 3	6412.6001	-0.0006	8 1 8	7 1 7	9147.0398	-0.0030
5 2 4	4 2 3	6097.0163	-0.0033	9 0 9	8 0 8	10434.1081	-0.0010
5 2 3	4 2 2	6214.4399	-0.0021	9 1 9	8 1 8	10265.1612	0.0002
6 0 6	5 0 5	7133.3426	-0.0029	10 0 10	9 0 9	11512.5756	0.0028
6 1 6	5 1 5	6892.2045	-0.0047	10 1 10	9 1 9	11377.6704	0.0027
6 1 5	5 1 4	7675.7057	0.0024	11 0 11	10 0 10	12588.8349	0.0058
6 2 5	5 2 4	7305.3349	-0.0023	11 1 11	10 1 10	12485.2339	0.0046
6 2 4	5 2 3	7504.4114	0.0015	3 1 3	2 0 2	5434.5833	0.0017
7 0 7	6 0 6	8250.5383	-0.0018	4 1 4	3 0 3	6404.8225	0.0001
7 1 7	6 1 6	8022.8062	-0.0052	5 1 5	4 0 4	7331.5040	-0.0028



**Table S14.** Experimental values of spectroscopic parameters of the minor isotopologues of MAH-H<sub>2</sub>O. (see Figure S1 for atom labeling)

Parameters <sup>a</sup>	MAH-H <sub>2</sub> <sup>18</sup> O	MAH-D12OH	MAH-HOD11	MAH-DOD
<i>A</i> [MHz]	5339.4398(8) <sup>b</sup>	5377.3038(6)	5359.6967(8)	5361.859(1)
<i>B</i> [MHz]	1046.4474(2)	1080.1635(1)	1058.3245(2)	1039.0143(2)
<i>C</i> [MHz]	875.7954(1)	900.3652(1)	884.7538(1)	871.2924(1)
<i>D<sub>J</sub></i> [kHz]	[-0.2022] <sup>c</sup>	[-0.2022]	[-0.2022]	[-0.2022]
<i>D<sub>JK</sub></i> [kHz]	[0.411]	[0.411]	[0.411]	[0.411]
<i>D<sub>K</sub></i> [kHz]	[-9.80]	[-9.80]	[-9.80]	[-9.80]
<i>d<sub>1</sub></i> [kHz]	[-0.0418]	[-0.0418]	[-0.0418]	[-0.0418]
<i>d<sub>2</sub></i> [kHz]	[-0.0037]	[-0.0037]	[-0.0037]	[-0.0037]
<i>N<sub>line</sub></i>	33	33	33	33
<i>P<sub>cc</sub></i> [uÅ <sup>2</sup> ]	0.273(1)	0.275(9)	0.305(6)	0.311(5)
<i>σ</i> [kHz]	2.8	3.5	5.1	5.8

<sup>a</sup> *A*, *B* and *C* are the asymmetric top determinable rotational constants. *D<sub>J</sub>*, *D<sub>JK</sub>*, *D<sub>K</sub>*, *d<sub>1</sub>*, *d<sub>2</sub>* are centrifugal distortion constants. *N<sub>line</sub>* is the number of lines observed. *P<sub>cc</sub>* is the planar moments calculated from rotational constants through  $P_{cc} = h/(16\pi^2) (-1/C + 1/A + 1/B)$ . *σ* is the rms deviation of the fit. <sup>b</sup> Standard errors are given in parenthesis in units of the last digit. <sup>c</sup> Values in square brackets fixed to the parent species values. The *P<sub>cc</sub>* value of parent species is 0.272(5) uÅ<sup>2</sup>.

**Table S15.** Experimental values of spectroscopic parameters of the minor isotopologues of MAH-(H<sub>2</sub>O)<sub>2</sub>. (see Figure S2 for atom labeling)

Parameters <sup>a</sup>	MAH-H <sub>2</sub> <sup>18</sup> O8-H <sub>2</sub> O	MAH-H <sub>2</sub> <sup>18</sup> O9-H <sub>2</sub> O	MAH-H <sub>2</sub> <sup>18</sup> O8-H <sub>2</sub> <sup>18</sup> O9
<i>A</i> [MHz]	2874.461(3) <sup>b</sup>	2807.627(3)	2773.559(3)
<i>B</i> [MHz]	692.7219(3)	698.6590(3)	677.1513(3)
<i>C</i> [MHz]	558.9306(1)	560.1649(1)	544.9566(1)
<i>D<sub>J</sub></i> [kHz]	[0.083] <sup>c</sup>	[0.083]	[0.083]
<i>D<sub>JK</sub></i> [kHz]	[0.627]	[0.627]	[0.627]
<i>D<sub>K</sub></i> [kHz]	[5.23]	[5.23]	[5.23]
<i>d<sub>1</sub></i> [kHz]	[-0.0245]	[-0.0245]	[-0.0245]
<i>d<sub>2</sub></i> [kHz]	[-0.0059]	[-0.0059]	[-0.0059]
<i>N<sub>line</sub></i>	24	24	24
<i>P<sub>cc</sub></i> [uÅ <sup>2</sup> ]	0.591(6)	0.580(5)	0.584(7)
<i>σ</i> [kHz]	1.8	3.6	3.2

<sup>a</sup> *A*, *B* and *C* are the asymmetric top determinable rotational constants. *D<sub>J</sub>*, *D<sub>JK</sub>*, *D<sub>K</sub>*, *d<sub>1</sub>*, *d<sub>2</sub>* are centrifugal distortion constants. *N<sub>line</sub>* is the number of lines observed. *P<sub>cc</sub>* is the planar moments calculated from rotational constants through  $P_{cc} = h/(16\pi^2) (-1/C + 1/A + 1/B)$ . *σ* is the rms deviation of the fit. <sup>b</sup> Standard errors are given in parenthesis in units of the last digit. <sup>c</sup> Values in square brackets fixed to the parent species values. The *P<sub>cc</sub>* value of parent species is 0.587(2) uÅ<sup>2</sup>.

**Table S16.** Comparison between  $r_s$  and  $r_e$  coordinates of the MAH-(H<sub>2</sub>O)<sub>1-2</sub> complexes. (see Figures S1-S2 for atom labeling)

species		a /Å		b /Å		c /Å	
		$r_e^a$	$r_s$	$r_e$	$r_s$	$r_e$	$r_s$
MAH-H <sub>2</sub> O	O8	-3.486	-3.4988(4) <sup>b</sup>	0.587	0.577(3)	-0.067	-0.02(9)
	H11	-4.385	-4.3288(4)	0.489	0.486(3)	0.254	0.186(8)
MAH-(H <sub>2</sub> O) <sub>2</sub>	O8	-3.457	-3.4672(4) <sup>b</sup>	-0.956	-0.988(2)	0.014	0.05(3)
	O9	-2.919	-2.9713(5)	1.755	1.7776(8)	-0.035	[0] <sup>c</sup>

<sup>a</sup> The  $r_e$  coordinates were calculated at MP2/6-311++G(d,p) level of theory. <sup>b</sup> Errors in parentheses are 1 $\sigma$  uncertainties expressed in units of the last digit. <sup>c</sup> Slightly imaginary value: fixed at zero.

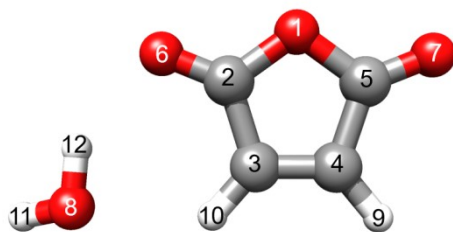
**Table S17.** Comparison between  $r_s$  and  $r_e$  structural parameters of the MAH-(H<sub>2</sub>O)<sub>1-2</sub> complexes. (see Figures S1-S2 for atom labeling)

species	parameters	$r_e^a$	$r_s$
MAH-H <sub>2</sub> O	$r_{O8H11}/\text{Å}$	0.959	0.86(2) <sup>b</sup>
MAH-(H <sub>2</sub> O) <sub>2</sub>	$r_{O8O9}/\text{Å}$	2.796	2.809(2) <sup>b</sup>

<sup>a</sup> The  $r_e$  structural parameter was calculated at MP2/6-311++G(d,p) level of theory. <sup>b</sup> Errors in parentheses are 1 $\sigma$  uncertainties expressed in units of the last digit.

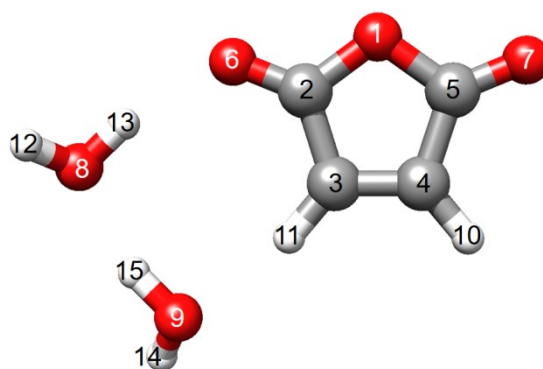
**Table S18.** MP2/6-311++G(d,p) geometry of the observed isomer of MAH-H<sub>2</sub>O.

Bond lengths (Å)		Valence angles (°)		Dihedral angles (°)	
O1C5	1.40				
C5C4	1.48	O1C5C4	107.7		
C4C3	1.34	C5C4C3	108.2	O1C5C4C3	0.0
C3C2	1.49	C4C3C2	107.4	C5C4C3C2	-0.0
C5O7	1.20	C4C5O7	130.0	O7C5C4C3	-179.9
C2O6	1.20	C3C2O6	129.2	C4C3C2O6	178.0
O6O8	2.93	C2O6O8	98.0	C3C2O6O8	3.4
C3H10	1.08	C4C3H10	131.0	C5C4C3H10	-178.0
C4H9	1.08	C5C4H9	122.1	O7C5C4H9	0.1
O8H11	0.96	O6O8H11	128.5	C2O6O8H11	-153.6
O8H12	0.96	O6O8H12	25.7	C2O6O8H12	-177.4



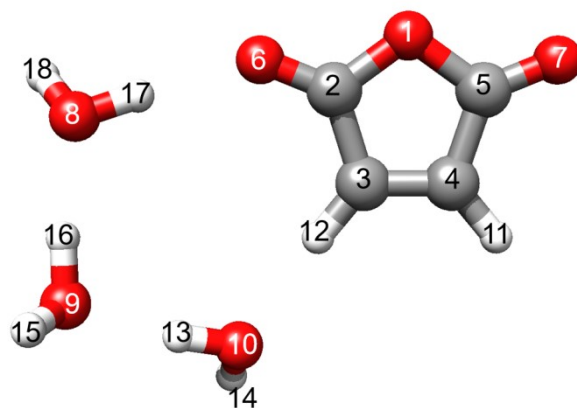
**Table S19.** MP2/6-311++G(d,p) geometry of the observed isomer of MAH-(H<sub>2</sub>O)<sub>2</sub>.

Bond lengths (Å)		Valence angles (°)		Dihedral angles (°)	
O1C2	1.38				
C2C3	1.49	O1C2C3	108.9		
C3C4	1.34	C2C3C4	107.1	O1C2C3C4	0.2
C4C5	1.49	C3C4C5	108.4	C2C3C4C5	-0.2
C2O6	1.20	C3C2O6	129.4	C4C3C2O6	-179.7
C5O7	1.20	C4C5O7	130.4	C3C4C5O7	-179.9
O6O8	2.90	C2O6O8	124.0	C3C2O6O8	1.2
O8O9	2.80	O6O8O9	90.1	C2O6O8O9	0.0
C4H10	1.08	C3C4H10	129.4	C2O3C4H10	179.9
C3H11	1.09	C2C3H11	122.6	C6C2C3H11	0.1
O8H12	0.96	O6O8H12	110.9	C2O6O8H12	135.2
O8H13	0.97	O6O8H13	9.7	C2O6O8H13	-174.2
O9H14	0.96	O8O9H14	112.4	O6O8O9H14	-140.8
O8H15	0.97	O8O9H15	11.4	O6O8O9H15	172.9



**Table S20.** MP2/6-311++G(d,p) geometry of the observed isomer of MAH-(H<sub>2</sub>O)<sub>3</sub>.

Bond lengths (Å)		Valence angles (°)		Dihedral angles (°)	
O1C2	1.38				
C2C3	1.49	O1C2C3	109.0		
C3C4	1.34	C2C3C4	107.0	O1C2C3C4	0.3
C4C5	1.49	C3C4C5	108.5	C2C3C4C5	-0.2
C2O6	1.20	C3C2O6	129.4	C4C3C2O6	-179.8
C5O7	1.20	C4C5O7	130.5	C3C4C5O7	-179.8
O6O8	2.89	C2O6O8	139.4	C3C2O6O8	20.2
O8O9	2.77	O6O8O9	110.3	C2O6O8O9	-15.1
O9O10	2.77	O8O9O10	103.0	O6O8O9O10	-8.1
C4H11	1.08	C3C4H11	129.3	C2C3C4H11	178.0
C3O12	1.09	C2C3H12	123.4	O6C2C3H12	0.6
O10H13	0.97	O9O10H13	4.6	O8O9O10H13	169.4
O10H14	0.96	O9O10H14	106.0	O8O9O10H14	-127.8
O9H15	0.95	O8O9H15	106.3	O6O8O9H15	124.1
O9H16	0.97	O8O9H16	5.0	O6O8O9H16	-166.1
O8H17	0.97	O6O8H17	1.2	C2O6O8H17	159.2
O8H18	0.96	O6O8H18	105.2	C2O6O8H18	-154.7



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