Supporting Information on

Atmospherically relevant acrolein–water complexes: spectroscopic evidence of aldehyde hydration and oxygen atom exchange

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Abstract

Direct spectroscopic evidence of a reaction occurring between acrolein and water and involving the exchange of an oxygen atom has been obtained by characterizing the non-covalently bound water complexes and their isotopic forms, via rotational spectroscopy. The experimental geometries of the binary and ternary water complexes have been determined, and other stationary points on the reaction path have been characterized using ab initio quantum chemical methods at the MP2/6-311++G(d,p) level. These results can enhance the understanding of the water-mediated atmospherically important reactions involving acrolein.

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Table S1. *Ab initio* energy values (Hartree, MP2/6-311++G(d,p)) of acrolein···H_2O complexes and the two most stable conformers of prop-1-ene-3,3-diol: electronic energy (E_e), zero-point corrected energy (E_0), Gibbs free energy (G, 298.15 K, 1 Atm), Enthalpy (H), and basis set superposition error (*BSSE*).

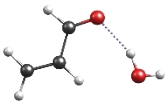
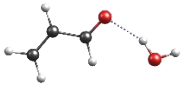
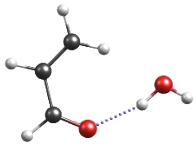
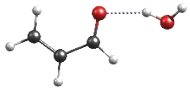
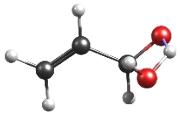
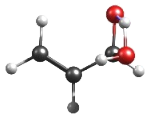
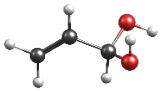
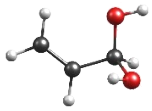
		E_e	E_0	G	H	*BSSE*
AW1-T1		-267.712631	-267.626583	-267.658314	-267.617915	0.002314
AW1-T2		-267.711551	-267.625752	-267.658408	-267.616849	0.001995
AW1-C1		-267.708843	-267.623023	-267.655248	-267.614157	0.002391
AW1-C2		-267.707922	-267.622333	-267.655465	-267.613276	0.002043
AW1-TS1		-267.637125	-267.553222	-267.581957	-267.546623	
AW1-TS2		-267.638231	-267.553907	-267.582378	-267.547455	
Diol 1		-267.710169	-267.619463	-267.648313	-267.612716	
Diol 2		-267.711127	-267.620257	-267.649138	-267.613537	
ACR *s-trans* + W		-267.702237	-267.619282	-267.663303	-267.610133	
ACR *s-cis* +W		-267.698716	-267.615965	-267.660415	-267.606698	

Table S2. *Ab initio* energy values (Hartree, MP2/6-311++G(d,p)) of acrolein···$(H_2O)_2$ and prop-1-ene-3,3-diol···H_2O complexes: electronic energy (E_e), zero-point corrected energy (E_0), Gibbs free energy (G, 298.15 K, 1 Atm), Enthalpy (H), and basis set superposition error (*BSSE*).

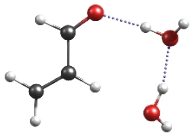
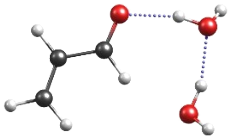
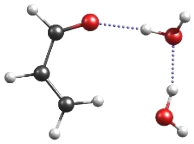
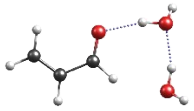
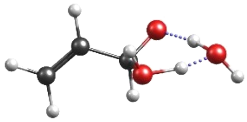
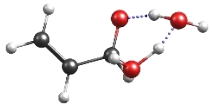
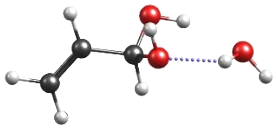
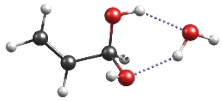
		E_e	E_0	G	H	*BSSE*
AW2-T1		-344.002946	-343.891089	-343.927452	-343.879596	0.006485
AW2-T2		-344.002475	-343.890608	-343.927231	-343.879041	0.006159
AW2-C1		-343.997346	-343.886235	-343.924369	-343.874231	0.005889
AW2-C2		-343.998485	-343.886929	-343.924244	-343.875173	0.006100
AW2-TS1		-343.950347	-343.841159	-343.872435	-343.833023	
AW2-TS2		-343.951636	-343.841927	-343.872825	-343.833960	
Diol 1-W		-343.999782	-343.883673	-343.916753	-343.873983	0.003808
Diol 2-W		-344.001201	-343.884781	-343.917662	-343.875219	0.003900
ACR *s-trans* + W + W		-343.977158	-343.872525	-343.934187	-343.859596	
ACR *s-cis* +W + W		-343.973637	-343.869208	-343.931299	-343.856161	

Table S3. *Ab initio* (MP2/6-311++G(d, p)) equilibrium structures of acrolein···$(H_2O)_{1,2}$ complexes

AW1-T1	***a*/Å**	***b*/Å**	***c*/Å**	**AW1-T2**	***a*/Å**	***b*/Å**	***c*/Å**
C1	-2.2052	-0.8599	0.0060	C1	2.4813	0.7987	0.0052
C2	-0.9123	-0.4886	-0.0276	C2	1.6899	-0.2884	-0.0297
C3	-0.5716	0.9439	0.0124	C3	0.2271	-0.1367	0.0369
O4	0.5693	1.3858	-0.0103	O4	-0.5553	-1.0776	0.0087
O5	2.3169	-0.9266	0.0388	O5	-2.8437	0.6492	-0.0420
H	-0.0941	-1.2015	-0.0825	H	2.0857	-1.2973	-0.1067
H	-2.5016	-1.9031	-0.0205	H	3.5624	0.7233	-0.0423
H	-2.9969	-0.1159	0.0619	H	2.0507	1.7943	0.0816
H	-1.4363	1.6359	0.0654	H	-0.1480	0.9024	0.1137
H	1.9676	-0.0254	0.0056	H	-2.2998	-0.1497	-0.0142
H	3.1812	-0.8596	-0.3717	H	-3.6757	0.3768	0.3490
AW2-T1	***a*/Å**	***b*/Å**	***c*/Å**	**AW2-T2**	***a*/Å**	***b*/Å**	***c*/Å**
C1	-2.4322	1.1860	-0.0229	C1	-2.7723	0.9141	0.0176
C2	-1.2787	0.4917	-0.0014	C2	-2.1884	-0.2982	0.0029
C3	-1.3366	-0.9771	0.0121	C3	-0.7207	-0.3955	-0.0169
O4	-0.3611	-1.7181	0.0234	O4	-0.1171	-1.4654	-0.0190
O5	2.3651	-0.8718	0.0163	O5	2.6220	-0.7831	-0.0243
O6	1.7660	1.8641	-0.0247	O6	1.7326	1.8819	0.0325
H	-0.3078	0.9824	0.0051	H	-2.7576	-1.2238	0.0078
H	-2.4418	2.2706	-0.0371	H	-0.1709	0.5623	-0.0297
H	-3.3931	0.6755	-0.0281	H	-3.8507	1.0318	0.0350
H	-2.3565	-1.4116	0.0093	H	-2.1658	1.8167	0.0141
H	1.4681	-1.2425	0.0380	H	1.7421	-1.1971	-0.0360
H	2.8290	-1.4070	-0.6310	H	3.1168	-1.2873	0.6248
H	2.3297	2.3434	0.5857	H	2.2164	1.0400	0.0391
H	2.1404	0.9681	-0.0350	H	2.2652	2.4504	-0.5269
AW1-C1	***a*/Å**	***b*/Å**	***c*/Å**	**AW1-C2**	***a*/Å**	***b*/Å**	***c*/Å**
C1	1.5414	0.5080	0.0402	C1	-2.5280	0.3261	-0.0799
C2	1.1169	-0.9122	0.0151	C2	-1.6198	-0.6604	0.0145
C3	0.6680	1.5280	-0.0495	C3	-0.1653	-0.3718	0.0724
O4	-0.0409	-1.3014	-0.0382	O4	0.3056	0.7580	0.0667
O5	-2.4638	0.3028	0.0555	O5	3.0090	-0.1810	-0.0864
H	1.9377	-1.6534	0.0472	H	0.5081	-1.2462	0.1202
H	2.6099	0.6906	0.1249	H	-1.9191	-1.7047	0.0473
H	1.0182	2.5551	-0.0306	H	-3.5910	0.1150	-0.1235
H	-0.4007	1.3567	-0.1376	H	-2.2054	1.3626	-0.1150
H	-1.7922	-0.3911	0.0258	H	2.2403	0.4016	-0.0207
H	-3.2263	-0.0900	-0.3738	H	3.7159	0.3210	0.3229
AW2-C1	***a*/Å**	***b*/Å**	***c*/Å**	**AW2-C2**	***a*/Å**	***b*/Å**	***c*/Å**
C1	1.0745	1.5740	-0.0276	C1	-0.6772	0.2073	0.0060
C2	2.0808	0.6803	-0.0251	C2	-2.0678	0.7252	0.0155
C3	1.8537	-0.7808	0.0256	C3	-3.1281	-0.1002	-0.0286
O4	0.7596	-1.3267	0.0274	O4	2.4025	-1.2569	-0.0571
O5	-2.1164	-1.3591	-0.0853	O5	-0.4078	-0.9908	0.0239
O6	-2.2927	1.4350	0.0806	O6	2.3737	1.5492	0.0387
H	3.1186	1.0040	-0.0481	H	1.4342	-1.3424	-0.0418
H	1.2889	2.6380	-0.0577	H	0.1326	0.9541	-0.0185
H	0.0291	1.2805	-0.0004	H	-2.1915	1.8044	0.0496
H	2.7684	-1.4024	0.0669	H	-2.9803	-1.1755	-0.0691
H	-1.1508	-1.4231	-0.0864	H	2.7109	-1.8959	0.5888
H	-2.3960	-2.0275	0.5439	H	-4.1436	0.2811	-0.0251
H	-2.9782	1.7635	-0.5042	H	2.5870	0.6022	0.0251
H	-2.4013	0.4713	0.0467	H	3.0497	1.9478	-0.5126

Table S4. Experimental spectroscopic parameters of observed conformers of acrolein···$(H_2O)_{1,2}$ and their isotopologues.

AW1-T1	**parent**	**^{18}O4**	**^{18}O5**	**^{13}C1**	**^{13}C2**	**^{13}C3**
A/MHz	6808.50**1**(4)[a]	6490.925(4)	6675.058(4)	6743.62(6)	6786.58(6)	6730.48(5)
B/MHz	2533.24**6**(2)	2525.733(1)	2402.261(1)	2473.073(1)	2522.578(1)	2528.961(1)
C/MHz	1845.926(1)	1817.763(1)	1766.122(1)	1809.096(1)	1838.672(1)	1837.881(1)
D_J/kHz	4.93(2)	4.76(2)	4.56(2)	4.64(3)	4.85(3)	4.88(3)
D_{JK}/kHz	-23.84(6)	-22.69(7)	-22.28(6)	[-23.84][b]	[-23.84]	[-23.84]
d_1/kHz	-1.7**3**(3)	-1.72(3)	-1.59(3)	[-1.73]	[-1.73]	[-1.73]
σ[c]/kHz	5.7	4.5	4.5	6.0	1.9	1.4
N[d]	21	19	20	9	9	9
AW1-T2	**parent**	**^{18}O4**	**^{18}O5**	**^{13}C1**	**^{13}C2**	**^{13}C3**
A/MHz	12678.377(3)	12017.350(2)	12438.042(2)	12495.2(1.2)	12656.9(1.2)	12670.8(1.2)
B/MHz	1762.7183(8)	1759.4661(7)	1669.8732(8)	1725.9274(8)	1745.5278(5)	1762.6052(4)
C/MHz	1546.7680(6)	1533.8399(7)	1471.4639(7)	1515.5428(8)	1533.1452(8)	1546.5836(8)
D_J/kHz	3.35(1)	3.257(6)	3.113(6)	3.25(1)	3.30(1)	3.34(1)
D_{JK}/kHz	-102.48(7)	-95.97(5)	-97.12(5)	[-102.48]	[-102.48]	[-102.48]
d_1/kHz	-0.794(8)	-0.833(8)	-0.736(8)	[-0.794]	[-0.794]	[-0.794]
σ/kHz	3.7	2.3	2.8	3.9	2.8	2
N	25	20	20	9	10	11
AW2-T1	**parent**	**^{18}O4**	**^{18}O5**	**^{18}O6**		
A/MHz	2984.8037(8)	2886.379(3)	2956.248(7)	2878.63(2)		
B/MHz	1705.4107(5)	1703.1938(5)	1646.9354(7)	1665.797(3)		
C/MHz	1086.8334(2)	1072.5966(3)	1059.1473(2)	1056.599(1)		
D_J/kHz	1.214(3)	1.171(3)	[1.214]	0.96(5)		
D_{JK}/kHz	8.17(4)	[8.17]	[8.17]	[8.17]		
d_1/kHz	-0.754(2)	[-0.754]	[-0.754]	-0.61(4)		
d_2/kHz	-0.318(2)	[-0.318]	[-0.318]	[-0.318]		
σ/kHz	3.29	2.42	3.05	3.91		
N	42	13	11	10		
AW2-T2	**parent**	**^{18}O4**	**^{18}O5**	**^{18}O6**		
A/MHz	3827.600(3)	3711.134(2)	3793.176(6)	3640.24(1)		
B/MHz	1378.5856(5)	1378.5491(1)	1329.6131(2)	1356.0129(4)		
C/MHz	1014.5870(3)	1006.1608(1)	985.5152(1)	988.9298(4)		
D_J/kHz	1.489(3)	1.458(1)	1.379(3)	1.473(3)		
D_{JK}/kHz	-6.88(6)	[-6.88]	[-6.88]	[-6.88]		
D_K/kHz	40.3(7)	[40.3]	[40.3]	[40.3]		
d_1/kHz	-0.584(3)	[-0.584]	-0.532(2)	[-0.584]		
d_2/kHz	-0.061(2)	[-0.061]	[-0.061]	[-0.061]		
σ/kHz	5.45	1.87	0.72	3.09		
N	45	22	12	13		

[a]Standard error in parentheses in units of the last digit. [b]Data in brackets fixed to the corresponding values of the parent species. [c]RMS error of the fit. [d]Number of fitted lines.

Table S5. Experimental Kraitchman's substitution coordinates of the heavy atoms of acrolein···$(H_2O)_{1,2}$ complexes in the principal axes system of parent species.

AW1-T1	$\|a_s\|$/Å	$\|b_s\|$/Å	$\|c_s\|$/Å	**AW1-T2**	$\|a_s\|$/Å	$\|b_s\|$/Å	$\|c_s\|$/Å
C1	2.2086(7)[a]	0.867(2)	0[b]	C1	2.4850(7)[a]	0.791(2)	0[b]
C2	0.921(2)	0.492(3)	0.04(3)	C2	1.690(1)	0.274(7)	0[b]
C3	0.583(3)	0.933(2)	0.02(7)	C3	0.13(1)	0.15(1)	0.04(5)
O4	0.547(3)	1.369(1)	0[b]	O4	0.526(3)	1.065(1)	0[b]
O5	2.3475(6)	0.911(2)	0[b]	O5	2.8541(5)	0.650(2)	0[b]
AW2-T1	$\|a_s\|$/Å	$\|b_s\|$/Å	$\|c_s\|$/Å	**AW2-T2**	$\|a_s\|$/Å	$\|b_s\|$/Å	$\|c_s\|$/Å
O4	0.437(3)[a]	1.7193(9)	0[b]	O4	0.10(1)[a]	1.455(1)	0[b]
O5	2.3010(7)	0.950(2)	0.02(6)	O5	2.6166(6)	0.803(2)	0.02(6)
O6	1.8491(8)	1.8343(8)	0[b]	O6	1.7398(9)	1.8873(8)	0[b]

[a]Errors in parenthesis are expressed in units of the last digit. [b] Imaginary values were obtained which were set to 0.

Table S6. Experimental transition frequencies (ν/MHz), observed minus calculated values ($\Delta\nu$/MHz) and additional observed components (ν'/MHz) of AW1-T1 and AW1-T2.

						AW1-T1			AW1-T2		
J'	K_a'	K_c'	J''	K_a''	K_c''	ν	$\Delta\nu$	ν'	ν	$\Delta\nu$	ν'
1	1	1	0	0	0	8654.4594	-0.0029	8654.4421			
1	1	0	1	0	1				11131.8030	-0.0078	11131.8305
2	0	2	1	0	1	8681.8021	-0.0024		6615.6941	0.0007	
2	1	2	1	1	1	8071.0137	-0.0018	8070.9986			
2	1	1	1	1	0	9445.5558	0.0110	9445.5406	6835.2047	0.0047	
2	1	2	1	0	1	12346.3223	-0.0040	12346.3060	17319.2143	-0.0030	17319.2323
2	1	1	2	0	2				11351.3154	-0.0020	11351.3398
3	0	3	2	0	2	12837.5794	-0.0027		9915.4188	0.0013	
3	1	3	2	1	2	12060.9904	0.0011		9602.9028	-0.0015	
3	1	2	2	1	1	14117.2275	-0.0034		10250.5544	0.0001	10250.5626
3	2	2	2	2	1	13137.5591	0.0056	13137.5428	9930.5518	-0.0043	9930.5327
3	2	1	2	2	0	13436.9483	-0.0044	13436.9265	9943.2307	-0.0045	9943.2145
3	0	3	2	1	2	9173.0578	-0.0026				
3	1	3	2	0	2	15725.5095	-0.0016				
3	1	2	3	0	3				11686.4556	0.0014	11686.4831
4	0	4	3	0	3	16802.6978	0.0011		13205.4338	0.0025	
4	1	4	3	1	3	16003.4590	0.0024		12799.9583	0.0025	
4	1	3	3	1	2	18720.0640	0.0048		13663.1752	-0.0004	13663.1881
4	2	3	3	2	2	17456.6364	0.0180		13237.8961	-0.0038	
4	2	2	3	2	1	18169.0283	-0.0065		13269.5521	-0.0027	
4	3	2	3	3	1	17655.0954	-0.0054	17655.0704			
4	3	1	3	3	0	17686.8872	-0.0019				
4	0	4	3	1	3	13914.7647	-0.0030				
4	1	3	4	0	4				12144.1990	0.0004	12144.2270
5	0	5	4	0	4				16482.6035	0.0029	
5	1	5	4	1	4				15993.7509	0.0090	
5	1	4	4	1	3				17072.0914	0.0028	17072.1030
5	2	4	4	2	3				16542.8146	0.0023	
5	2	3	4	2	2				16605.9603	-0.0038	
5	0	5	4	1	4	18499.0334	-0.0032				
5	1	4	5	0	5				12733.6893	0.0027	12733.7274
6	0	6	5	1	5				10247.2759	-0.0060	
6	1	5	6	0	6				13465.9933	0.0024	13466.0425

Table S7. Experimental transition frequencies (ν/MHz) and observed minus calculated values ($\Delta\nu$/kHz) of ^{13}C and ^{18}O species of AW1-T1.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
						C1		C2		C3	
2	0	2	1	0	1	8492.6395	0.7	8646.5078	-0.2	8655.1045	0.2
2	1	2	1	1	1	7900.3702	5.1	8038.5925	-0.1	8042.6020	0.2
2	1	1	1	1	0	9228.1973	-7.2	9406.2861	-1	9424.6446	-0.3
3	0	3	2	0	2	12565.2129	2.7	12785.9344	2.3	12792.8449	-0.1
3	1	3	2	1	2	11807.8381	2.7	12012.6739	-2.3	12017.2007	-2.2
3	1	2	2	1	1	13794.5341	-3.9	14058.7209	1.5	14084.4610	2.3
4	0	4	3	0	3	16457.2802	-2.1	16735.9061	-1	16736.2992	0.2
4	1	4	3	1	3	15670.5386	-4.6	15939.5747	1.5	15943.2370	1.4
4	1	3	3	1	2	18296.6961	6.3	18642.8122	-0.9	18673.3369	-1.6
						O4		O5			
1	1	1	0	0	0	8308.7215	0.2	8441.2126	-0.8		
2	0	2	1	0	1	8600.2534	0.0	8270.7579	0.3		
2	1	2	1	1	1	7979.0176	0.5	7700.6240	1.0		
2	1	1	1	1	0	9394.8468	1.0	8972.7996	0.3		
2	1	2	1	0	1	11944.2598	-1.0	11973.4684	-2.2		
3	0	3	2	0	2	12691.9514	-4.8	12245.8091	-2.0		
3	1	3	2	1	2	11917.1836	0.3	11511.5293	0.0		
3	1	2	2	1	1	14034.0403	-1.7	13415.3142	0.3		
3	2	2	2	2	1	13030.5263	6.1	12505.2017	7.7		
3	2	1	2	2	0	13368.5385	-0.9	12764.0412	-1.0		
3	1	3	2	0	2	15261.1914	0.6	15214.2404	-2.0		
3	0	3	2	1	2	9347.9486	-0.2	8543.0961	-1.8		
4	0	4	3	0	3	16575.3966	-5.9	16052.5342	-3.2		
4	1	4	3	1	3	15802.5889	0.3	15280.9042	1.4		
4	1	3	3	1	2	18593.9329	1.0	17799.1038	2.0		
4	2	3	3	2	2	17305.9380	15.4	16621.7506	15.3		
4	2	2	3	2	1	18102.8582	-3.5	17241.3297	-5.2		
4	3	2	3	3	1	17529.2630	-1.8	16793.7402	-4.8		
4	3	1	3	3	0	17568.9120	-5.3	16819.2855	-2.5		
4	0	4	3	1	3			13084.1027	-3.3		

Table S8. Experimental transition frequencies (ν/MHz) and observed minus calculated values ($\Delta\nu$/kHz) of ^{13}C and ^{18}O species of AW1-T2.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
						C1		C2		C3	
2	0	2	1	0	1			6554.1769	4.4	6615.0963	-0.3
2	1	1	1	1	0					6834.6747	-2.9
3	0	3	2	0	2	9711.8661	5.5	9823.3971	2.9	9914.5125	0.1
3	1	3	2	1	2	9407.2862	-4.3	9515.8840	-2.6	9601.9027	-3.4
3	1	2	2	1	1	10038.2397	-3.0	10152.8346	-0.2	10249.7739	4.2
4	0	4	3	0	3	12934.5968	5.7	13083.2146	1.1	13204.2082	2.2
4	1	4	3	1	3	12539.2820	-2.4	12684.0499	-2.9	12798.6195	-1.0
4	1	3	3	1	2	13380.2490	-0.7	13533.0089	-3.6	13662.1283	1.2
5	0	5	4	0	4	16144.9542	-4.1	16330.5913	-1.5	16481.0381	-1.1
5	1	5	4	1	4	15668.1371	2.7	15849.0553	2.4	15992.0684	2.5
5	1	4	4	1	3	16718.6870	0.5	16909.5986	1.5	17070.7713	-2.7
						O4		O5			
1	1	1	0	0	0	13551.3716	-0.9	13909.6894	-1.7		
2	0	2	1	0	1	6582.8288	1.3				
2	1	2	1	1	1	6361.2936	1.3				
2	1	1	1	1	0	6812.4934	2.2				
2	1	2	1	0	1	16619.3727	0.9	16852.9418	-2.0		
3	0	3	2	0	2	9864.8552	-0.3	9412.8185	0.8		
3	1	3	2	1	2	9539.5116	0.0	9125.0360	-1.7		
3	1	2	2	1	1	10216.1738	1.2	9720.0855	2.0		
3	2	1	2	2	0	9896.5771	-3.1	9436.8607	-2.8		
3	2	2	2	2	1	9881.8649	-4.6	9426.0050	-1.0		
4	0	4	3	0	3	13135.6710	-0.1	12537.4413	0.3		
4	1	4	3	1	3	12714.8751	0.9	12163.3389	0.0		
4	1	3	3	1	2	13616.7266	-0.7	12956.4638	4.0		
4	2	2	3	2	1	13209.3202	1.2	12592.6537	-4.7		
4	2	3	3	2	2	13172.6019	1.7	12565.5470	-0.9		
5	0	5	4	0	4	16391.6732	-5.2	15651.0265	-1.7		
5	1	5	4	1	4	15886.5205	2.0	15198.8211	3.2		
5	1	4	4	1	3	17013.0321	2.2	16189.6480	7.0		
5	2	3	4	2	2	16533.7887	-2.6	15757.0832	-1.2		
5	2	4	4	2	3	16460.5738	3.1	15702.9867	1.8		
6	0	6	5	0	5			18751.0034	-2.2		
6	1	6	5	1	5			18230.8611	1.4		
6	0	6	5	1	5			9292.0089	-3.7		

Table S9. Experimental transition frequencies (ν/MHz) and observed minus calculated values ($\Delta\nu$/kHz) of AW2-T1 and AW2-T2.

						AW2-T1		AW2-T2	
J'	K_a'	K_c'	J''	K_a''	K_c''	ν	$\Delta\nu$	ν	$\Delta\nu$
2	1	2	1	0	1			6871.3308	-4.9
2	2	1	1	1	0	10041.0350	-1.4	12496.8868	-4.7
2	2	0	1	1	1	10835.3663	1.4	12898.5140	-1.9
3	0	3	2	0	2	7750.4314	0.7	7031.4372	-2.2
3	1	3	2	1	2	7350.9087	-1.9		0
3	1	2	2	1	1	9173.7131	-6.3	7700.4650	-2.8
3	2	1	2	2	0	9002.56	12.6	7327.45	17.6
3	2	2	2	2	1	8376.44	2.3	7179.53	-1.7
3	0	3	2	1	2	6913.863	-1.2		0
3	1	3	2	0	2	8187.48	4	8733.7252	8.5
3	2	1	2	1	2			15803.6251	20.4
3	2	2	3	1	3			9007.0098	-13.3
4	0	4	3	0	3	9902.5835	1.4	9218.0343	-1.7
4	1	4	3	1	3	9656.9137	-1.2	8776.0517	-2.4
4	1	3	3	1	2	11945.8408	-4.8	10217.1710	-3.7
4	2	2	3	2	1	12289.93	4.8	9897.3032	-4.3
4	2	3	3	2	2	11029.0198	4.3	9543.1942	-1.3
4	3	2	3	3	1	11442.7963	-4.5		
4	3	1	3	3	0	11627.7872	-5.7		
4	0	4	3	1	3	9465.5336	-2.1	7515.7598	0.9
4	1	4	3	0	3	10093.96	-0.2	10478.3402	8.7
4	2	3	3	1	2			16368.8405	-1.6
5	0	5	4	0	4	12017.5371	2.7	11309.8682	-1.8
5	1	5	4	1	4	11900.9526	0.1	10914.4335	-2.5
5	1	4	4	1	3	14426.5122	0.5	12683.6028	-3.5
5	2	3	4	2	2	15476.6889	-5.1	12536.0216	-4.4
5	2	4	4	2	3	13572.6360	-2.2	11881.8839	-1.8
5	3	2	4	3	1	14868.5782	1.3		
5	0	5	4	1	4	11826.1551	-0.1	10049.5767	1.9
5	1	5	4	0	4	12092.3318	0.2	12174.7325	1.1
5	2	4	4	1	3			18033.5540	0.8
6	0	6	5	0	5	14154.3621	-0.3	13335.2305	-2.9
6	1	6	5	1	5	14106.7953	-1	13026.4029	-1.3
6	1	5	5	1	4	16623.9765	0.1	15079.1591	-1.7
6	2	4	5	2	3	18437.8646	-2.2	15207.8413	-3.3
6	2	5	5	2	4	16002.4370	-2.5	14190.1124	-1.3
6	3	4	5	3	3	17088.4882	0.1		
6	3	3	5	3	2	18274.7151	3.6		
6	0	6	5	1	5			12470.3738	1.6
6	1	6	5	0	5			13891.2612	-4.3
7	0	7	6	0	6	16311.0456	0.8	15331.2419	-1.5
7	1	7	6	1	6	16293.2726	2.1	15114.7675	-2.2
7	1	6	6	1	5	18689.0613	2	17382.0064	1.1
7	2	6	6	2	5	18332.1607	1.9	16463.4053	0

7	2	5	6	2	4			17866.7765	2.8
7	0	7	6	1	6	16283.8144	0.8	14775.2128	1.4
7	1	7	6	0	6	16320.5010	-0.6	15670.8013	-0.5
8	0	8	7	0	7	18477.5739	0.8	17323.9779	-0.4
8	1	8	7	1	7	18471.2914	-0.1	17183.8970	-0.4
8	2	7	7	2	6			18698.8496	2.4
8	0	8	7	1	7			16984.4260	6
8	1	8	7	0	7	18480.7450	-3.4	17523.4544	-1.4

Table S10. Experimental transition frequencies (ν/MHz) and observed minus calculated values ($\Delta\nu$/kHz) of ^{18}O species of AW2-T1.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
						O4		O5		O6	
3	0	3	2	0	2	7650.9866	-1.6	7549.9452	-1.6	7536.0561	7.0
3	1	3	2	1	2	7274.7655	2.4	7148.1979	2.4	7154.3563	-3.1
3	1	2	2	1	1	9127.4202	-2.7	8883.7805	3.4	8947.5344	-1.4
4	0	4	3	0	3	9762.2362	-2.0	9658.0363	0.0	9623.1993	-0.6
4	1	4	3	1	3	9545.4886	0.5	9398.9199	1.1	9394.3379	0.7
4	1	3	3	1	2	11849.8420	1.3	11592.5745	-2.3	11637.9907	0.2
5	0	5	4	0	4	11850.2888	-1.9	11719.5647	4.7	11679.4393	-5.4
5	1	5	4	1	4	11754.0581	3.9			11573.6169	1.3
5	1	4	4	1	3			14039.6732	-0.8		
6	0	6	5	0	5	13963.3717	-4.1	13798.8558	3.5	13758.4495	-4.3
6	1	6	5	1	5	13926.5069	2.9	13743.5800	-5.1	13716.3271	6.3
6	1	5	5	1	4	16382.4222	1.5	13743.5787	-5.1		
7	0	7	6	0	6	16094.7771	-2.0				
7	1	7	6	1	6	16081.8081	1.3				

Table S11. Experimental transition frequencies (ν/MHz) and observed minus calculated values ($\Delta\nu$/kHz) of ^{18}O species of AW2-T2.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
						O4		O5		O6	
3	0	3	2	0	2	6992.7300	1.2	6812.9826	-0.7	6874.7944	3.4
3	1	3	2	1	2	6571.0725	1.7	6409.1323	1.4	6459.9317	-2.0
3	1	2	2	1	1	7685.2534	2.6	7439.2505	0.9	7558.1985	-5.8
3	1	3	2	0	2	8572.4123	-0.2				
4	0	4	3	0	3	9154.3649	0.5	8942.0420	0.0	8998.7562	1.5
4	1	4	3	1	3	8719.5480	-2.1	8510.7407	0.0	8571.7421	-3.2
4	1	3	3	1	2	10191.7946	0.0	9874.5787	-1.1	10022.8056	-1.6
4	2	2	3	2	1	9890.5272	0.4				
4	2	3	3	2	2	9506.6219	3.0				
5	0	5	4	0	4	11218.4836	-0.5	10982.4570	0.0	11026.5690	0.6
5	1	5	4	1	4	10839.6652	-2.2	10588.0883	-0.9	10655.4950	0.0
5	1	4	4	1	3	12642.5235	0.6	12265.6466	0.4	12431.9727	4.2
5	2	3	4	2	2	12534.8178	-2.1				
5	2	4	4	2	3	11831.8540	1.6				
6	0	6	5	0	5	13218.8984	-2.3	12957.1231	0.2	12992.0075	-1.6
6	1	6	5	1	5	12932.1402	-0.2	12641.0238	0.1	12711.9438	5.5