Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Theory Meets Experiment for Elucidating the Structure and Stability of Non-covalent Complexes: Water-Amine Interaction as a Proof of Concept

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Table S1. Spectroscopic parameters of the PA-W and IPA-W adducts[a] (main isotopic species).

		PA-W					IPA-W	
		TGW	GG'W	TTW	GTW	GGW	TW	GW
A_0/MHz	theo.	5378.9	4963.8	9895.1	11290.1	4818.3	4805.5	7239.2
	exp.	5466.2596(9)[b]	5003.9028(9)	9977.1499(8)	11477.9594(7)	_	4880.478(2)	7271.1043(1)
B_0/MHz	theo.	2180. 5	2450.3	1452.8	1471.6	2608.0	2520.2	2101.3
	exp.	2172.6407(3)	2411.8257(3)	1467.3249(3)	1478.4918(2)	_	2496.0733(8)	2102.8262(3)
C_0/MHz	theo.	1686.2	1995.4	1307.6	1418.1	1835.9	2425.5	1799.2
	exp.	1688.9887(2)	1979.0333(3)	1319.2830(2)	1427.6159(2)	_	2401.5471(7)	1805.9597(3)
χ_{aa}/MHz	theo.	-0.40	-1.68	-3.38	-4.22	-1.03	-2.99	-4.07
	exp.	-0.400(3)	-1.626(2)	-3.195(5)	-3.963(5)	_	-2.730(3)	-3.825(8)
$(\chi_{bb}-\chi_{cc})$/MHz	theo.	-3.71	-2.76	-0.48	0.53	-3.24	0.86	-0.14
	exp.	-3.232(4)	-2.387(3)	-0.198(6)	0.627(6)	_	0.731(7)	-0.131(9)
D_J/kHz	theo	5.41	14.57	2.47	2.08	5.47	5.02	2.82
	exp	6.185(7)[b]	17.884(7)	3.123(2)	2.465(2)	-	5.56(1)	3.551(4)
D_{JK}/kHz	theo	-23.76	-56.11	-66.34	-46.12	-2.35	13.46	-2.49
	exp	-28.52(3)	-49.20(4)	-86.06(3)	-56.62(2)	-	16.16(5)	-7.83(3)
D_K/kHz	theo	56.69	141.07	626.28	1126.02	5.31	-14.65	55.22
	exp	70.4(2)	167.1(2)	-	-	-	-	-
d_1/kHz	theo	-1.73	-5.42	-0.55	0.21	-1.59	0.19	-0.19
	exp	-1.953(5)	-7.060(6)	-0.713(2)	0.230(2)	-	0.22(1)	-0.152(4)
d_2/kHz	theo	-0.08	-0.18	-0.01	-0.03	-0.18	0.00	-0.05
	exp	-0.076(1)	-0.357(4)	-	-0.030(1)	-	-0.012(5)	-0.042(2)
μ_a/D	theo	0.51	1.32	2.01	-2.62	1.62	-1.70	-2.20
μ_b/D	theo	2.95	2.40	2.71	1.71	-2.94	0.0	-1.86
μ_c/D	theo	0.57	-1.38	0.00	1.25	-0.87	2.57	1.12
N[c]	exp	103	86	95	99	-	52	52
σ[d]/kHz	exp	3.3	2.5	3.7	3.2	-	3.1	2.3

[a] Ground-state rotational constants (A_0, B_0, C_0) from B2-CP equilibrium rotational constants augmented by vibrational corrections at the B3LYP-D3(BJ)/SNSD level (for details, see the SI). Nitrogen quadrupole coupling constants (χ_{ii}, with $i=a,b,c$) at the B2 level. Quartic centrifugal distortion constants and dipole moment at the B2 level of theory. [b] Standard errors within parentheses are expressed in units of the last digit. [c] Number of lines in the fit. [d] Standard deviation of the fit.

Table S2. Experimental spectroscopic parameters (in MHz) of the four observed PA-$H_2{}^{18}O$ and PA-DOH isomeric adducts.

	TG-$H_2{}^{18}O$	GG'-$H_2{}^{18}O$	TT-$H_2{}^{18}O$	GT-$H_2{}^{18}O$	TG-DOH	GG'-DOH	TT-DOH	GT-DOH
A_0	5338.1010(8)[a]	4955.846(2)	9813.336(1)	11435.1612(9)	5468.724(4)	5003.060(4)	9924(3)	11459[b]
B_0	2074.9414(8)	2284.9576(6)	1391.6193(3)	1397.5066(3)	2137.700(1)	2375.832(2)	1442.989(2)	1456.1568(4)
C_0	1617.8078(4)	1885.8242(5)	1255.0786(2)	1352.3556(3)	1668.0121(8)	1955.428(1)	1299.911(2)	1406.4744(4)
χ_a	-0.649(7)	-1.797(3)	-3.2639(1)	[-3.963]	[-0.400]	[-1.626]	[-3.195]	[-3.963]
$(\chi_{bb}-\chi_{cc})$	-3.02(1)	-2.232(6)	-0.143(8)	[0.627]	[-3.232]	[-2.387]	[-0.198]	[0.627]
$D_J\times10^3$	5.98(1)	15.631(9)	2.940(2)	2.293(3)	5.96(2)	16.94(2)	2.39(2)	2.360(6)
$D_{JK}\times10^3$	-29.31(6)	-34.22(5)	-83.30(6)	-56.00(4)	[-28.52]	[-49.20]	-59.7(9)	-54.7(2)
$D_K\times10^3$	[70.4][c]	146.0(4)	-	-	[70.4]	[167.1]	-	-
$d_1\times10^3$	-1.86(1)	-6.00(1)	-0.647(2)	0.202(3)	[-1.953]	-6.60(3)	-1.13(2)	[0.229]
$d_2\times10^3$	[-0.076]	[-0.357]	-	[-0.030]	[-0.076]	[-0.357]	-	[-0.030]
N[c]	55	63	53	81	26	27	25	24
σ[d]/kHz	3.7	3.0	2.9	4.0	4.6	4.8	4.8	3.6

[a] Standard errors within parentheses are expressed in units of the last digit. [b] Scaled parameter using the experimental/theoretical ratio of the parent species. The value is fixed in the fit procedure. [c] Values within square brackets are fixed at the values of the main isotopic species.

Table S3. Experimental spectroscopic parameters (in MHz) of three isotopologues of the IPA-W isomeric adducts.

	T-$H_2{}^{18}O$	T-DOH	T-HOD	G-$H_2{}^{18}O$	G-DOH	G-HOD
A_0	4869.612(1)[a]	4876.914(3)	4870.199(4)	7258.808(1)	7257.832(2)	7229.068(1)
B_0	2360.8805(7)	2463.525(1)	2384.165(1)	1982.1054(3)	2072.5464(4)	2010.6607(3)
C_0	2278.5259(6)	2372.066(1)	2298.261(1)	1716.8403(3)	1782.3212(4)	1737.4055(3)
χ_a	-2.799(5)	-2.705(9)	-2.74(1)	-3.84(2)	-3.803(2)	-3.784(1)
$(\chi_{bb}-\chi_{cc})$	0.636(7)	0.67(1)	0.57(1)	-0.136(1)	-0.14(2)	-0.37(1)
$D_J\times10^3$	5.191(9)	5.41(1)	4.84(1)	3.333(5)	3.410(5)	3.110(4)
$D_{JK}\times10^3$	15.68(5)	15.08(6)	14.60(6)	-7.99(4)	-7.77(4)	-6.90(3)
$d_1\times10^3$	0.20(1)	0.20(1)	0.19(2)	-0.139(4)	-0.146(4)	-0.125(3)
$d_2\times10^3$	-0.010(5)	-	-	-0.035(2)	-0.042(3)	-0.034(2)
N[c]	45	37	30	44	44	35
σ[d]/kHz	2.6	3.6	2.9	2.4	2.8	1.9

[a] Standard errors within parentheses are expressed in units of the last digit.

Table S4. Experimental transition frequencies ν and obs.–calc. residuals $\Delta\nu$ for TGW: H_2O and $H_2{}^{18}O$.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F	TGW		TGW ($H_2{}^{18}O$)	
								ν_{obs}(MHz)	$\Delta\nu_{obs-calc}$(MHz)	ν_{obs}(MHz)	$\Delta\nu_{obs-calc}$(MHz)
3	0	3	4	2	0	2	3	11389.8858	0.0019	10901.5288	0.0030
3	0	3	3	2	0	2	2	11389.7745	0.0015	10901.4166	-0.0070
3	0	3	2	2	0	2	1	11389.8858	0.0038	10901.5054	-0.0005
3	1	3	4	2	1	2	3	10829.6961	0.0008	10365.6126	0.0030
3	1	3	3	2	1	2	2	10829.6155	-0.0037	10365.5068	-0.0081
3	1	3	2	2	1	2	1	10829.6033	0.0013	10365.5161	-0.0054
3	1	2	4	2	1	1	3	12277.0162	0.0021	11733.8083	-0.0133
3	1	2	3	2	1	1	2	12276.9754	0.0023	11733.7546	-0.0054
3	1	2	2	2	1	1	1	12277.1197	-0.0022	11733.9254	0.0039
3	2	2	4	2	2	1	3	11584.9390	-0.0011		
3	2	2	3	2	2	1	2	11584.8127	0.0012		
3	2	2	2	2	2	1	1	11585.0126	0.0008		
4	0	4	5	3	0	3	4	14979.1502	-0.0030	14346.0836	-0.0001
4	0	4	4	3	0	3	3	14979.0228	0.0021	14345.9680	0.0054
4	0	4	3	3	0	3	2	14979.1548	-0.0040	14346.0836	0.0027
4	1	4	5	3	1	3	4	14388.3804	0.0001	13774.1868	-0.0001
4	1	4	4	3	1	3	3	14388.3217	0.0001	13774.1263	0.0037
4	1	4	3	3	1	3	2	14388.3314	-0.0027	13774.1443	0.0043
4	1	3	5	3	1	2	4	16303.0457	0.0027		
4	1	3	4	3	1	2	3	16302.9987	0.0008		
4	1	3	3	3	1	2	2	16303.0950	0.0019		
4	2	3	5	3	2	2	4	15407.3327	-0.0063	14735.5798	-0.0033
4	2	3	4	3	2	2	3	15407.2631	-0.0040	14735.4794	0.0001
4	2	3	3	3	2	2	2	15407.3576	0.0001	14735.6124	0.0028
4	2	2	5	3	2	1	4	15872.9166	-0.0004	15158.7916	-0.0022
4	2	2	4	3	2	1	3	15872.9748	0.0002	15158.8122	0.0058
4	2	2	3	3	2	1	2	15872.9166	-0.0019	15158.8122	0.0070
5	0	5	6	4	0	4	5	18442.5688	0.0028	17672.6506	-0.0033
5	0	5	5	4	0	4	4	18442.4311	0.0003	17672.5293	0.0003
5	0	5	4	4	0	4	3	18442.5688	-0.0009	17672.6506	-0.0019
5	1	5	6	4	1	4	5	17911.7145	0.0012	17150.2595	0.0017
5	1	5	5	4	1	4	4	17911.6646	0.0040	17150.2077	0.0039
5	1	5	4	4	1	4	3	17911.6866	0.0010	17150.2293	0.0005
2	2	1	3	1	1	0	2	18087.2158	0.0035	17631.5685	0.0059
2	2	1	2	1	1	0	1	18086.7931	-0.0031	17631.2218	0.0006
2	2	1	1	1	1	0	0	18087.9555	-0.0025	17632.271	-0.0006
2	2	1	2	1	1	0	2			17631.7689	-0.0022
2	2	0	3	1	1	1	2	18620.1145	0.0044		
2	2	0	2	1	1	1	1	18620.7313	-0.0017		
2	2	0	1	1	1	1	0	18619.3587	-0.0041		
2	1	2	3	1	0	1	2	10533.3100	0.0016	10191.6040	0.0001
2	1	2	2	1	0	1	1	10532.8441	-0.0006	10191.2101	0.0006
2	1	2	1	1	0	1	0	10533.4551	0.0025	10191.6383	-0.0011
2	2	0	1	2	1	1	2	9929.3150	-0.0010		
2	2	0	3	2	1	1	2	9929.4250	-0.0012		
2	2	0	2	2	1	1	2	9929.6246	0.0001	9833.6644	0.0001

2	2	0	3	2	1	1	3	9929.8833	0.0020	9833.7772	0.0023
2	2	0	1	2	1	1	1	9930.0238	0.0001	9833.8341	-0.0020
2	2	0	2	2	1	1	3	9930.0735	-0.0060		
2	2	0	2	2	1	1	1	9930.3307	-0.0016		
2	2	1	1	2	1	2	1	11330.6452	-0.0019		
2	2	1	3	2	1	2	3	11331.0455	0.0026		
2	2	1	1	2	1	2	2	11331.5553	0.0002		
2	2	1	3	2	1	2	2	11331.6298	0.0032		
2	2	1	2	2	1	2	2	11331.7541	-0.0011		
3	0	3	4	2	1	2	3	8530.2163	-0.0019	8050.5191	-0.0023
3	0	3	3	2	1	2	2	8530.4962	0.0034	8050.7431	0.0049
3	0	3	2	2	1	2	1	8530.0026	0.0004	8050.3269	0.0024
3	1	3	4	2	0	2	3	13689.3637	0.0027	13216.6142	0.0003
3	1	3	3	2	0	2	2	13688.8993	-0.0002	13216.2026	0.0022
3	1	3	2	2	0	2	1	13689.4827	0.0010	13216.7019	-0.0011
3	2	1	3	3	1	2	3	94318967	0.0011		
3	2	1	4	3	1	2	4	9432.1363	0.0025		
3	2	1	2	3	1	2	2	9432.2149	-0.0022		
3	2	2	2	3	1	3	2	12086.0510	-0.0059		
3	2	2	4	3	1	3	4	12086.2888	0.0010		
3	2	2	3	3	1	3	3	12086.9465	-0.0008		
4	0	4	5	3	1	3	4	12679.6731	-0.0031	12031.0010	0.0053
4	0	4	4	3	1	3	3	12679.8952	0.0011	12031.1908	0.0049
4	0	4	3	3	1	3	2	12679.5596	0.0005	12030.8818	-0.0019
4	1	4	5	3	0	3	4	16687.8587	0.0013	16089.2735	-0.0015
4	1	4	4	3	0	3	3	16687.4497	0.0013	16088.8996	0.0003
4	1	4	3	3	0	3	2	16687.9274	-0.0065	16089.3378	0.0007
4	2	3	5	4	1	4	5	13105.2550	0.0086		
4	2	3	4	4	1	4	4	13105.8919	-0.0008		
4	2	3	3	4	1	4	3	13105.0716	-0.0086		
4	2	2	3	4	1	3	4	9001.5858	0.0065		
4	2	2	5	4	1	3	4	9001.6417	0.0024		
4	2	2	4	4	1	3	4	9001.8764	0.0037		
4	2	2	5	4	1	3	5	9002.0033	-0.0045		
4	2	2	3	4	1	3	3	9002.0455	0.0029		
4	2	2	4	4	1	3	5	9002.2427	0.0014		
4	2	2	4	4	1	3	3	9002.3364	0.0004		
5	0	5	6	4	1	4	5	16733.8632	0.0013	15929.4610	-0.0016
5	0	5	5	4	1	4	4	16734.0050	0.0019	15929.5926	0.0002
5	0	5	4	4	1	4	3	16733.7933	-0.0014	15929.3916	-0.0047
5	1	5	6	4	0	4	5	19620.4202	0.0028	18893.4468	-0.0022
5	1	5	5	4	0	4	4	19620.0871	-0.0011	18893.1406	0.0001
5	1	5	4	4	0	4	3	19620.4556	-0.0050	18893.4826	-0.0023
5	2	4	4	5	1	5	4	14389.9725	0.0081		
5	2	4	6	5	1	5	6	14390.0901	-0.0052		
5	2	4	5	5	1	5	5	14390.7384	0.0001		
6	2	4	5	6	1	5	5	8954.5288	-0.114		
6	2	4	7	6	1	5	7	8954.5731	0.0085		
6	2	4	6	6	1	5	6	8954.7089	0.0002		
1	1	0	2	0	0	0	1	7638.7676	0.0041		
1	1	0	1	0	0	0	1	7639.3078	-0.0004		

1	1	0	0	0	0	0	1	7637.9454	-0.0009
2	1	1	3	1	0	1	2	11983.8947	0.0018
2	1	1	2	1	0	1	1	11984.4663	-0.0017
2	1	1	1	1	0	1	0	11983.4590	-0.0010
3	1	2	4	2	0	2	3	16587.2677	0.0034
3	1	2	3	2	0	2	2	16587.8748	-0.0017
3	1	2	2	2	0	2	1	16587.0072	-0.0019

Table S5. Experimental transition frequencies ν and obs.–calc. residuals $\Delta\nu$ for GG'W: H_2O and $H_2{}^{18}O$.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F	GG'W		GG'W ($H_2{}^{18}O$)	
								ν_{obs}(MHz)	$\Delta\nu_{obs-calc}$(MHz)	ν_{obs}(MHz)	$\Delta\nu_{obs-calc}$(MHz)
2	0	2	3	1	0	1	2	8731.4234	-0.0014	8299.6609	0.0001
2	0	2	2	1	0	1	1	8731.3373	0.0013	8299.5774	0.0003
2	0	2	1	1	0	1	0	8731.0148	0.0012	8299.2019	0.0035
2	0	2	2	1	0	1	2	8730.8482	0.0001		
2	1	2	3	1	1	1	2	8348.9028	0.0024	7942.3985	-0.0013
2	1	2	2	1	1	1	1	8348.3703	0.0006	7941.8086	-0.0020
2	1	2	1	1	1	1	0	8349.0849	-0.0024	7942.6573	0.0045
2	1	2	2	1	1	1	2	8348.2567	0.0013		
2	1	2	1	1	1	1	1	8349.3712	-0.0017		
2	1	1	3	1	1	0	2	9213.9873	0.0051	8740.2312	0.0051
2	1	1	2	1	1	0	1	9213.5052	0.0025	8739.6947	0.0031
2	1	1	1	1	1	0	0	9214.8198	0.0026	8741.0958	0.0016
2	1	1	2	1	1	0	2	9214.1026	-0.0019		
2	1	1	1	1	1	0	1	9213.3170	0.0046		
3	0	3	4	2	0	2	3	12976.0509	-0.0017		
3	0	3	3	2	0	2	2	12975.9492	0.0046		
3	0	3	2	2	0	2	1	12975.9732	-0.0046		
3	1	3	4	2	1	2	3	12493.0862	-0.0037		
3	1	3	3	2	1	2	2	12492.9147	0.0003	11888.0115	0.0009
3	1	3	2	2	1	2	1	12493.0203	0.0015	11888.1277	-0.0028
3	1	2	4	2	1	1	3	13786.3134	-0.0016	13081.5739	0.0010
3	1	2	3	2	1	1	2	13786.1645	-0.0003	13081.4084	-0.0012
3	1	2	2	2	1	1	1	13786.3916	0.0010	13081.6424	-0.0018
3	2	2	4	2	2	1	3	13171.9741	-0.0027	12511.6466	0.0064
3	2	2	3	2	2	1	2	13171.4530	-0.0012	12511.0630	0.0005
3	2	2	2	2	2	1	1	13172.2688	0.0016	12511.9592	-0.0019
3	2	1	4	2	2	0	3	13366.5243	0.0029	12674.3070	0.0016
3	2	1	3	2	2	0	2	13366.0772	-0.0031	12673.7921	-0.0046
3	2	1	2	2	2	0	1	13366.7909	-0.0033	12674.6113	-0.0001
4	0	4	5	3	0	3	4	17097.5517	-0.0011	16289.9470	-0.0023
4	0	4	4	3	0	3	3	17097.4426	-0.0005	16289.8503	-0.0008
4	0	4	3	3	0	3	2	17097.5200	0.0018	16289.9070	-0.0013
4	1	4	5	3	1	3	4	16606.0620	0.0004	15807.4521	0.0001
4	1	4	4	3	1	3	3	16605.9655	0.0008	15807.3536	0.0012
4	1	4	3	3	1	3	2	16606.0093	-0.0009	15807.4020	0.0017
4	1	3	5	3	1	2	4	18312.2401	0.0008	17384.8258	0.0001
4	1	3	4	3	1	2	3	18312.1538	0.0029	17384.7354	0.0001
4	1	3	3	3	1	2	2			17384.8471	0.0069
4	2	3	5	3	2	2	4	17521.7869	-0.0021	16648.0845	0.0019
4	2	3	4	3	2	2	3	17521.5556	0.0017	16647.8289	0.0027
4	2	3	3	3	2	2	2	17521.8530	0.0035	16648.1477	-0.0007
4	2	2	5	3	2	1	4	17982.7157	-0.0036	17036.9508	-0.0037
4	2	2	4	3	2	1	3	17982.5822	0.0008	17036.7814	-0.0012
4	2	2	3	3	2	1	2	17982.7700	0.0026	17037.0060	-0.0034
2	1	2	1	1	0	1	0	10940.4997	-0.0017	10612.6945	-0.0041
2	1	2	2	1	0	1	2	10940.2252	-0.0045		

2	1	2	3	1	0	1	2	10940.8751	0.0004	10613.1450	-0.0025
2	1	2	2	1	0	1	1	10940.7198	0.0023	10613.0363	-0.0027
2	1	2	1	1	0	1	1	10941.7202	-0.0005		
2	2	1	1	1	1	0	0	16989.3770	-0.0017	16752.0094	-0.0067
2	2	1	2	1	1	0	2	16989.2887	0.0001	16752.0094	0.0014
2	2	1	3	1	1	0	2	16988.7687	0.0026	16751.4342	0.0039
2	2	1	2	1	1	0	1	16988.6819	-0.0048		
2	2	1	1	1	1	0	1	16987.8725	-0.0014		
2	2	0	1	1	1	1	0	17470.6321	0.0024	17191.3848	0.0018
2	2	0	2	1	1	1	2	17471.7026	0.0047	17192.4502	-0.0001
2	2	0	3	1	1	1	2	17471.1217	0.0003	17191.8278	0.0005
2	2	0	2	1	1	1	1	17471.8104	-0.0017	17192.5135	-0.0022
2	2	0	1	1	1	1	1	17470.9188	0.0035		
2	2	1	1	2	1	2	1	9071.8328	-0.0009		
2	2	1	3	2	1	2	3	9072.4761	-0.0062		
2	2	1	2	2	1	2	2	9073.6515	0.0016		
3	0	3	4	2	1	2	3	10766.6002	-0.0016	10034.4596	0.0023
3	0	3	3	2	1	2	2	10766.5698	0.0003	10034.3910	-0.0003
3	0	3	2	2	1	2	1	10766.4765	-0.0041	10034.3412	-0.0060
3	0	3	3	2	1	2	3	10765.9221	-0.0023	10033.7412	-0.0024
3	0	3	2	2	1	2	2	10767.4859	0.0020	10035.3538	-0.0011
3	1	3	4	2	0	2	3	14702.5393	-0.0004	14201.6897	0.0050
3	1	3	3	2	0	2	2	14702.2935	-0.0023	14201.4730	0.0005
3	1	3	2	2	0	2	1	14703.4004	-0.0031	14201.6377	0.0069
3	1	3	2	2	0	2	2			14202.5958	-0.0043
3	2	2	2	3	1	3	2	9751.0772	-0.0049	9831.1620	-0.0012
3	2	2	4	3	1	3	4	9751.3689	-0.0003	9831.4560	0.0004
3	2	2	3	3	1	3	3	9752.1906	0.0008	9832.2899	-0.0008
4	0	4	4	3	1	3	3	15371.0968	-0.0014	14436.2361	0.0041
4	0	4	3	3	1	3	2	15370.9778	-0.0022	14436.1249	-0.0001
4	0	4	5	3	1	3	4	15371.0641	-0.0007	14436.2063	-0.0022
4	1	4	4	3	0	3	3	18332.3109	0.0013	17660.9682	-0.0033
4	1	4	3	3	0	3	2	18332.5509	0.0025	17661.1833	-0.0002
4	1	4	5	3	0	3	4	18332.5509	0.0013	17661.1951	0.0021
2	1	1	1	1	0	1	0	12237.7748	0.0011		
2	1	1	3	1	0	1	2	12238.5732	0.0001		
2	1	1	2	1	0	1	2	12238.6979	0.0024		
2	1	1	1	1	0	1	1	12238.9906	-0.0023		
2	1	1	2	1	0	1	1	12239.1792	-0.0040		
2	2	0	3	1	1	0	2	17038.5075	0.0027		
2	2	1	3	1	1	1	2	17421.3880	0.0053		
2	2	1	2	1	1	1	1	17422.0174	-0.0020		

Table S6. Experimental transition frequencies v and obs.–calc. residuals Δv for TTW: H_2O and $H_2{}^{18}O$.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F	TTW		TTW ($H_2{}^{18}O$)	
								v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)	v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)
2	0	2	3	1	0	1	2	5571.2714	0.0013		
2	0	2	2	1	0	1	1	5571.2092	0.008		
2	0	2	1	1	0	1	0	5570.4047	0.0015		
3	0	3	4	2	0	2	3	8351.8732	0.0007	7933.2312	-0.0035
3	0	3	3	2	0	2	2	8351.8316	-0.002	7933.1981	0.0026
3	0	3	2	2	0	2	1	8351.6725	-0.0021		
3	1	3	4	2	1	2	3	8136.9162	0.001	7734.6032	0.0075
3	1	3	3	2	1	2	2			7734.3126	0.0043
3	1	3	2	2	1	2	1	8136.9162	0.0013	7734.6086	0.0125
3	1	2	4	2	1	1	3	8580.8681	-0.0009	8144.0716	0.0013
3	1	2	3	2	1	1	2	8580.5853	0.0005	8143.7816	0.0024
3	1	2	2	2	1	1	1	8580.8695	-0.0001		
4	0	4	5	3	0	3	4	11126.5501	0.0002	10569.6293	-0.0004
4	0	4	4	3	0	3	3	11126.5235	-0.0012	10569.6050	0.0006
4	0	4	3	3	0	3	2	11126.4597	0.0023	10569.5330	-0.0019
4	1	4	5	3	1	3	4	10846.6902	0.0025	10310.5849	-0.0005
4	1	4	4	3	1	3	3	10846.5590	-0.0006	10310.4539	-0.0009
4	1	4	3	3	1	3	2	10846.6480	-0.0046	10310.5448	0.0038
4	1	3	5	3	1	2	4	11438.3955	-0.0004	10856.3418	-0.0006
4	1	3	4	3	1	2	3	11438.2699	0.0005	10856.2148	0.0019
4	1	3	3	3	1	2	2	11438.3583	0.0009	10856.2945	-0.0074
4	2	3	5	3	2	2	4	11147.0154	0.0011		
4	2	3	4	3	2	2	3	11146.5792	0.0007		
4	2	3	3	3	2	2	2	11147.1252	-0.0010		
4	2	2	5	3	2	1	4	11166.1218	0.0014		
4	2	2	4	3	2	1	3	11165.6795	-0.0059		
4	2	2	3	3	2	1	2	11166.2320	-0.0002		
5	0	5	6	4	0	4	5	13893.3638	-0.0010	13199.2296	-0.0020
5	0	5	5	4	0	4	4	13893.3495	0.0026	13199.2121	-0.0016
5	0	5	4	4	0	4	3	13893.3082	-0.0019	13199.1720	-0.0036
5	1	5	6	4	1	4	5	13554.4197	0.0012	12884.7874	-0.0041
5	1	5	5	4	1	4	4	13554.3495	0.0014	12884.7183	-0.0015
5	1	5	4	4	1	4	3	13554.3809	-0.0005	12884.7539	-0.0002
5	1	4	6	4	1	3	5	14293.5910	0.0013	13566.5871	-0.0004
5	1	4	5	4	1	3	4	14293.5165	-0.0037	13566.5160	-0.0005
5	1	4	4	4	1	3	3	14293.5567	0.0007	13566.5533	0.0006
5	2	4	6	4	2	3	5	13930.7403	0.0000	13231.7659	-0.0058
5	2	4	5	4	2	3	4	13930.5122	-0.0000	13231.5301	-0.0025
5	2	4	4	4	2	3	3	13930.7627	-0.0007	13231.7903	0.0007
5	2	3	6	4	2	2	5	13968.8632	-0.0059		
5	2	3	5	4	2	2	4	13968.6355	-0.0067		
5	2	3	4	4	2	2	3	13968.8879	-0.0042		
6	0	6	7	5	0	5	6	16650.4650	-0.0041	15820.4267	-0.0042
6	0	6	6	5	0	5	5	16650.4519	-0.0035	15820.4124	-0.0050
6	0	6	5	5	0	5	4	16650.4299	0.0028	15820.3905	-0.0031
6	1	6	7	5	1	5	6	16259.6439	0.0033	15456.8070	0.0012

6	1	6	6	5	1	5	5	16259.5999	0.0030	15456.7619	0.0005
6	1	6	5	5	1	5	4	16259.6130	0.0010	15456.7752	-0.0017
6	1	5	7	5	1	4	6	17145.8000	0.0042	16274.2416	0.0032
6	1	5	6	5	1	4	5	17145.7554	0.0026	16274.1994	0.0050
6	1	5	5	5	1	4	4	17145.7681	-0.0013	16274.2148	0.0037
6	2	5	7	5	2	4	6	16712.5347	0.0056		
6	2	5	6	5	2	4	5	16712.3949	0.0012		
6	2	5	5	5	2	4	4	16712.5347	0.0059		
6	2	4	7	5	2	3	6	16779.0179	0.0006		
6	2	4	6	5	2	3	5	16778.8763	-0.0069		
6	2	4	5	5	2	3	4	16779.0179	0.0011		
7	0	7	8	6	0	6	7	19396.1584	-0.0054	18431.7285	-0.0037
7	0	7	7	6	0	6	6	19396.1460	-0.0068	18431.7285	0.0069
7	0	7	6	6	0	6	5	19396.1311	-0.0067	18431.7021	-0.0034
7	1	7	8	6	1	6	7	18961.9388	0.0037	18026.2583	0.0025
7	1	7	7	6	1	6	6	18961.9062	0.0007	18026.2285	0.0029
7	1	7	6	6	1	6	5	18961.9181	0.0052	18026.2363	0.0031
7	1	6	8	6	1	5	7	19994.3358	0.0030		
7	1	6	7	6	1	5	6	19994.3045	0.0008		
7	1	6	6	6	1	5	5	19994.3167	0.0045		
1	1	0	2	1	0	1	2	8657.7965	0.0049		
1	1	0	1	1	0	1	2	8658.3001	-0.0003		
1	1	0	2	1	0	1	1	8658.7464	-0.0037		
1	1	0	0	1	0	1	1	8657.9927	0.0056		
2	1	1	2	2	0	1	3	8807.7125	0.0016		
2	1	1	3	2	0	1	3	8808.1937	0.0011		
2	1	1	2	2	0	1	2	8808.7416	0.0033		
2	1	1	1	2	0	1	1	8807.8843	-0.0051		
3	1	2	2	3	0	3	2	9037.0819	-0.0022		
3	1	2	4	3	0	3	4	9037.1885	-0.0006		
3	1	2	3	3	0	3	3	9037.4882	-0.0012		
4	1	3	5	4	0	4	5	9349.0337	-0.0015		
4	1	3	4	4	0	4	4	9349.2375	0.0034		
5	1	4	6	5	0	5	6	9749.2690	0.0089		
5	1	4	5	5	0	5	5	9749.4036	-0.0038		
5	1	4	4	5	0	5	4	9749.2261	-0.0039		
1	1	1	2	0	0	0	1	11296.5167	-0.0037	11068.4913	-0.0019
1	1	1	1	0	0	0	1	11296.9694	-0.0005	11068.9649	0.0025
1	1	1	0	0	0	0	1	11295.8484	0.0023	11067.7927	0.0031
2	1	2	1	1	0	1	0	13934.2726	0.005	13577.7979	0.0057
2	1	2	3	1	0	1	2	13935.4007	-0.0016		
2	1	2	2	1	0	1	1	13935.8416	-0.0009	13579.3887	-0.0023
2	1	2	1	1	0	1	1	13936.6660	0.0018	13580.2441	0.0005
3	1	3	4	2	0	2	3	16501.0451	-0.0022	16021.8294	-0.0035
3	1	3	3	2	0	2	2	16501.2466	0.0036	16022.0518	0.0085
3	1	3	2	2	0	2	1	16501.7586	-0.009		
3	1	2	4	3	0	3	4	9037.1980	0.0088	8907.6333	-0.0009
3	1	2	3	3	0	3	3	9037.4880	-0.0014	8907.9342	0.0036
3	1	2	2	3	0	3	2	9037.0766	-0.0075	8907.5277	-0.0028

Table S7. Experimental transition frequencies v and obs.–calc. residuals Δv for GTW: H_2O and $H_2{}^{18}O$.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F	GTW		GTW ($H_2{}^{18}O$)	
								v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)	v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)
2	0	2	3	1	0	1	2	5812.0269	-0.0006		
2	0	2	2	1	0	1	1	5811.9459	0.0027		
2	0	2	1	1	0	1	0	5810.9466	-0.0051		
3	0	3	4	2	0	2	3	8717.3294	0.0006	8248.7769	-0.0007
3	0	3	3	2	0	2	2	8717.2860	0.0035	8248.7245	-0.0066
3	0	3	2	2	0	2	1	8717.0829	-0.0002		
3	1	3	4	2	1	2	3	8642.0396	0.0002	8181.9363	0.0022
3	1	3	3	2	1	2	2	8641.6932	0.0038	8181.5829	-0.0011
3	1	3	2	2	1	2	1	8642.0404	-0.0109	8181.9433	-0.0027
3	1	2	4	2	1	1	3	8794.7258	0.0022	8317.4402	0.0023
3	1	2	3	2	1	1	2	9794.3642	-0.0019	8317.0776	-0.0028
3	1	2	2	2	1	1	1	8794.6980	0.0011	8317.4049	-0.0062
4	0	4	5	3	0	3	4	11621.8912	-0.0003	10997.3730	0.0025
4	0	4	4	3	0	3	3	11621.8602	-0.0024	10997.3416	0.0001
4	0	4	3	3	0	3	2	11621.7766	-0.0002	10997.2567	0.0013
4	1	4	5	3	1	3	4	11522.1131	0.00013	10908.7132	0.0045
4	1	4	4	3	1	3	3	11521.9573	0.0005	10908.5589	0.0052
4	1	4	3	3	1	3	2	11522.0768	0.0075	10908.6621	-0.0040
4	1	3	5	3	1	2	4	11725.7367	0.0017	11089.4204	0.0012
4	1	3	4	3	1	2	3	11725.5752	0.0001	11089.2595	0.0001
4	1	3	3	3	1	2	2	11725.6744	0.0001	11089.3617	0.0032
4	2	3	5	3	2	2	4	11625.6156	0.0036	11000.6807	-0.0061
4	2	3	4	3	2	2	3	11625.0734	0.0017	11000.1449	-0.0016
4	2	3	3	3	2	2	2	11625.7528	0.0019	11000.8226	-0.0030
4	2	2	5	3	2	1	4	11627.5379	0.0024	11002.2005	0.0071
4	2	2	4	3	2	1	3	11626.9904	-0.0035	11001.6531	0.0010
4	2	2	3	3	2	1	2	11627.6752	0.0007	11002.3291	-0.0032
5	0	5	6	4	0	4	5	14525.4486	-0.0010	13745.1418	-0.0002
5	0	5	5	4	0	4	4	14525.4341	0.0038	13745.1262	0.0037
5	0	5	4	4	0	4	3	14525.3769	-0.0045	13745.0740	0.0001
5	1	5	6	4	1	4	5	14401.7603	0.0013	13635.1187	0.0006
5	1	5	5	4	1	4	4	14401.6776	0.0029	13635.0402	0.0064
5	1	5	4	4	1	4	3	14401.7185	-0.0019	13635.0775	-0.0020
5	1	4	6	4	1	3	5	14656.3623	0.0004	13861.0720	-0.0003
5	1	4	5	4	1	3	4	14656.2772	0.0029	13860.9848	0.0001
5	1	4	4	4	1	3	3	14656.3135	0.0009	13861.0232	0.0001
5	2	4	6	4	2	3	5	14531.2399	0.0011	13750.1678	0.0025
5	2	4	5	4	2	3	4	14530.9550	-0.0012	13749.8850	0.0022
5	2	4	4	4	2	3	3	14531.2663	-0.0010	13750.1960	0.0020
5	2	3	6	4	2	2	5	14535.0854	-0.0010		
5	2	3	5	4	2	2	4	14534.8011	-0.0014		
5	2	3	4	4	2	2	3	14535.1126	-0.0026		
5	3	3	6	4	3	2	5	14535.2150	-0.0124		
6	0	6	7	5	0	5	6	17427.7431	-0.0021	16491.8800	-0.0001
6	0	6	6	5	0	5	5	17427.7334	0.0016	16491.8672	0.0007
6	0	6	5	5	0	5	4	17427.6982	-0.0015	16491.8333	-0.0014

6	1	6	7	5	1	5	6	17280.8556	0.0015	16361.0509	0.0007
6	1	6	6	5	1	5	5	17280.8053	0.0029	16361.0032	0.0047
6	1	6	5	5	1	5	4	17280.8249	0.0013	16361.0121	-0.0075
6	1	5	7	5	1	4	6	17586.4846	0.0011	16632.2901	-0.0011
6	1	5	6	5	1	4	5	17586.4300	0.0006	16632.2369	-0.0001
6	1	5	5	5	1	4	4	17586.4419	-0.0038	16632.2533	-0.0002
6	2	5	7	5	2	4	6	17436.4429	0.0019	16499.2663	-0.0083
6	2	5	6	5	2	4	5	17436.2722	-0.0013		
6	2	5	5	5	2	4	4	17436.4429	0.0024	16499.2663	-0.0079
6	2	4	7	5	2	3	6	17443.1793	0.0032		
6	2	4	6	5	2	3	5	17443.0074	0.0005		
6	2	4	5	5	2	3	4	17443.1793	0.0035		
7	0	7	8	6	0	6	7	20328.5207	-0.0027	19237.3787	0.0031
7	0	7	7	6	0	6	6	20328.5115	-0.0023	19237.3656	-0.0001
7	0	7	6	6	0	6	5	20328.4888	-0.0020	19237.3418	-0.0011
7	1	7	8	6	1	6	7	20159.2825	0.0008		
7	1	7	7	6	1	6	6	20159.2480	0.0007		
2	1	1	1	2	0	2	1	10101.3428	-0.0017	10128.0269	-0.0084
2	1	1	3	2	0	2	3	10101.6436	0.0016	10128.3383	0.0054
2	1	1	2	2	0	2	2	10102.1788	0.0011	10128.8688	0.0003
2	1	1	3	2	0	2	2	10102.9133	-0.0019	10129.6058	-0.0003
2	1	1	1	2	0	2	2	10103.3219	-0.0036	10130.0205	0.0040
2	1	1	2	2	0	2	3			10127.5882	-0.0069
2	1	1	2	2	0	2	1			10126.8810	-0.0063
3	1	2	4	3	0	3	4	10179.0380	0.0011	10196.9944	0.0013
3	1	2	3	3	0	3	3	10179.2661	0.0047	10197.2219	0.0041
3	1	2	2	3	0	3	2	10178.9589	0.0006	10196.9168	0.0023
4	1	3	5	4	0	4	5	10282.8862	0.0059	10289.0451	0.0033
4	1	3	4	4	0	4	4	10282.9727	-0.0012	10289.1388	0.0031
4	1	3	3	4	0	4	3	10282.8476	-0.0085	10289.0113	-0.0062
5	1	4	4	5	0	5	4	10413.7882	0.0009	10404.9667	0.0001
5	1	4	6	5	0	5	6	10413.7882	-0.0042	10404.9667	-0.0053
5	1	4	5	5	0	5	5	10413.8232	0.0052	10405.0051	0.0071
6	1	5	7	6	0	6	7	10572.5374	0.0066		
6	1	5	5	6	0	6	5	10572.5374	0.0041		
1	1	1	2	0	0	0	1	12905.5602	-0.0027		
1	1	1	1	0	0	0	1	12906.2548	0.0034		
1	1	1	0	0	0	0	1	12904.5295	-0.0008		
1	1	0	0	1	0	1	1			10083.0820	0.0068
1	1	0	1	1	0	1	2			10083.1386	0.0016
1	1	0	2	1	0	1	1			10083.8260	0.0004
2	1	2	3	1	0	1	2	15760.9803	-0.0002		
2	1	2	2	1	0	1	1	15761.6328	-0.0005		
5	1	5	6	5	0	5	6	9650.1932	0.0001		
5	1	5	5	5	0	5	5	9650.4367	0.0010		
4	1	4	5	4	0	4	5	9773.8885	0.0046	9837.3169	0.0019
4	1	4	4	4	0	4	4	9774.1938	0.0025	9837.6240	0.0012
4	1	4	3	4	0	4	3	9773.8072	0.0024	9837.2363	0.0004
3	1	3	2	3	0	3	2	9873.5088	-0.0030	9925.8250	-0.0001
3	1	3	4	3	0	3	4	9873.6634	-0.0001	9925.9781	0.0012
3	1	3	3	3	0	3	3	9874.0962	-0.0009	9926.4118	0.0012

2	1	2	3	2	0	2	3	9947.9548	0.0018	9992.8216	0.0011
2	1	2	2	2	0	2	2	9949.6919	0.0017	9993.5592	0.0014
2	1	2	1	2	0	2	1	9948.5431	-0.0005	9992.4122	0.0010
1	1	0	2	0	0	0	1	12956.4650	-0.0070	12832.6878	-0.0002
1	1	0	1	0	0	0	1	12956.9657	-0.0065	12833.1860	-0.0021
1	1	1	2	1	0	1	2			10037.4424	-0.0104
1	1	1	0	1	0	1	1			10037.5959	-0.0131
1	1	1	1	1	0	1	2			10038.1482	0.0070
2	1	1	3	1	0	1	2	15913.6711	0.0015		
2	1	1	2	1	0	1	1	15914.1170	-0.0037		

Table S8. Experimental transition frequencies v and obs.–calc. residuals Δv for TGW and GG'W: DOH isotopologue.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F	TGW (DOH)		GG'W (DOH)	
								v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)	v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)
2	0	2	3	1	0	1	2			8615.5318	0.0039
2	0	2	2	1	0	1	1			8615.4454	0.0045
2	0	2	1	1	0	1	0			8615.1247	0.0091
3	0	3	4	2	0	2	3	11234.5126	-0.0057	12809.8644	0.0072
3	0	3	3	2	0	2	2	11234.4101	-0.0008	12809.7583	-0.0005
3	0	3	2	2	0	2	1	11234.5126	-0.0030	12809.7654	-0.0080
3	1	3	4	2	1	2	3	10684.7786	0.0018	12334.8118	-0.0030
3	1	3	3	2	1	2	2	10684.7124	0.0109	12334.6366	-0.0031
3	1	3	2	2	1	2	1			12334.7332	-0.0103
3	1	2	4	2	1	1	3			13591.3384	-0.0014
3	1	2	3	2	1	1	2			13591.1860	-0.0044
3	1	2	2	2	1	1	1			13591.4175	0.0002
4	0	4	5	3	0	3	4	14783.9512	0.0006	16887.4992	0.0087
4	0	4	4	3	0	3	3	14783.8217	0.0003	16887.3883	0.0053
4	0	4	3	3	0	3	2	14783.9512	-0.0047	16887.4587	0.0030
4	1	4	5	3	1	3	4	14198.2414	0.0009	16398.1098	-0.0047
4	1	4	4	3	1	3	3	14198.1811	-0.0017	16398.0143	-0.0040
4	1	4	3	3	1	3	2	14198.1958	0.0017	16398.0630	-0.0001
4	1	3	5	3	1	2	4			18057.1359	-0.0018
4	1	3	4	3	1	2	3			18057.0524	0.0017
4	1	3	3	3	1	2	2			18057.1555	-0.0020
2	1	2	3	1	0	1	2	10472.8438	-0.0065	10869.2275	-0.0029
2	1	2	2	1	0	1	1	10472.3802	-0.0065	10869.0756	0.0023
2	1	2	1	1	0	1	0	10473.0041	0.0095		
3	0	3	4	2	1	2	3			10556.1518	-0.0027
3	0	3	3	2	1	2	2			10556.1321	0.0055
3	1	3	4	2	0	2	3	13592.6117	0.0004	14588.5204	0.0029
3	1	3	3	2	0	2	2	13592.1541	0.0060	14588.2704	-0.0017
3	1	3	2	2	0	2	1	13592.7384	0.0052		
4	0	4	5	3	1	3	4	12425.8560	-0.0015		
4	0	4	4	3	1	3	3	12426.0834	-0.0008		
4	0	4	3	3	1	3	2	12425.7313	-0.0071		
4	1	4	5	3	0	3	4	16556.3300	-0.0034		
4	1	4	4	3	0	3	3	16555.9147	-0.0052		
4	1	4	3	3	0	3	2	16556.4096	-0.0020		
5	0	5	6	4	1	4	5	16439.6356	0.0016		
5	0	5	5	4	1	4	4	16439.7876	0.0028		
5	0	5	4	4	1	4	3	16439.5682	0.0032		

Table S9. Experimental transition frequencies v and obs.–calc. residuals Δv for TTW and GTW: DOH isotopologue.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F	TTW (DOH)		GTW (DOH)	
								v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)	v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)
2	0	2	3	1	0	1	2			5725.0942	0.0064
3	0	3	4	2	0	2	3	8221.3044	-0.0064	8586.9451	-0.0026
3	0	3	3	2	0	2	2	8221.2708	-0.0013	8586.9036	0.0022
3	0	3	2	2	0	2	1	8221.1086	-0.0045		
3	1	2	4	2	1	1	3	8442.2481	-0.0089		
3	1	2	3	2	1	1	2	8441.9818	0.0090		
3	1	2	2	2	1	1	1	8442.2481	-0.0092		
4	0	4	5	3	0	3	4	10953.1121	0.0002	11448.1029	-0.0006
4	0	4	4	3	0	3	3	10953.0859	-0.0007	11448.0715	-0.0031
4	0	4	3	3	0	3	2	10953.0209	0.0016	11447.9844	-0.0040
4	1	4	5	3	1	3	4	10682.1101	0.0016	11350.6129	0.0054
4	1	4	4	3	1	3	3	10681.9773	-0.0030	11350.4715	0.0061
4	1	4	3	3	1	3	2			11350.5846	0.0042
4	1	3	5	3	1	2	4	11253.7506	0.0040	11549.4747	0.0042
4	1	3	4	3	1	2	3	11253.6217	0.0017	11549.3055	-0.0051
4	1	3	3	3	1	2	2	11253.7157	0.0077	11549.4102	0.0004
5	0	5	6	4	0	4	5	13677.6065	0.0028	14308.3005	0.0001
5	0	5	5	4	0	4	4	13677.5945	0.0088	14308.2834	0.0025
5	0	5	4	4	0	4	3	13677.5537	0.0047	14308.2325	0.0002
5	1	5	6	4	1	4	5	13349.1210	0.0004	14187.4333	-0.0013
5	1	5	5	4	1	4	4	13349.0486	-0.0015	14187.3477	-0.0026
5	1	5	4	4	1	4	3	13349.0858	0.0022	14187.3974	0.0012
5	1	4	4	4	1	3	3	14063.0488	-0.0030	14436.0681	-0.0026
5	1	4	5	4	1	3	4			14435.9838	0.0005
5	1	4	4	4	1	3	3			14436.0240	0.0024
6	0	6	7	5	0	5	6	16393.0714	-0.0015	17167.2934	0.0013
6	0	6	6	5	0	5	5	16393.0570	-0.0022	17167.2783	-0.0001
6	0	6	5	5	0	5	4	16393.0319	-0.0046	17167.2465	0.0001

Table S10. Experimental transition frequencies ν and obs.–calc. residuals $\Delta\nu$ for TW: H_2O and $H_2{}^{18}O$.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F	TW		TW ($H_2{}^{18}O$)	
								ν_{obs}(MHz)	$\Delta\nu_{obs-calc}$(MHz)	ν_{obs}(MHz)	$\Delta\nu_{obs-calc}$(MHz)
2	0	2	3	1	0	1	2	9792.3660	0.0012	9276.7124	0.0014
2	0	2	2	1	0	1	1	9792.3168	0.0054		
2	0	2	1	1	0	1	0	9791.6251	0.0040		
2	1	2	3	1	1	1	2	9700.6277	0.0046	9196.3882	0.0023
2	1	2	2	1	1	1	1	9699.7806	-0.0022	9195.5232	0.0001
2	1	2	1	1	1	1	0	9701.5785	-0.0021		
3	0	3	4	2	0	2	3	14681.2840	0.0011	13909.7177	0.0004
3	0	3	3	2	0	2	2	14681.2649	0.0065	13909.6915	0.0017
3	0	3	2	2	0	2	1	14681.1141	0.0020	13909.5441	0.0014
3	0	3	2	2	0	2	2	14682.4699	0.0006		
3	1	3	4	2	1	2	3	14548.7229	0.0011	13792.8432	-0.0060
3	1	3	3	2	1	2	2	14548.4856	0.0016	13792.6045	0.0002
3	1	3	2	2	1	2	1	14548.7378	-0.0012	13792.8625	-0.0009
3	1	3	3	2	1	2	3	14548.1616	-0.0013		
3	1	2	4	2	1	1	3	14832.3051	-0.0004	14039.9349	0.0007
3	1	2	3	2	1	1	2	14832.0588	-0.0003	14039.6822	0.0005
3	1	2	2	2	1	1	1	14832.2786	0.0013	14039.9138	0.0048
3	1	2	3	2	1	1	3	14831.5022	-0.0006	14039.1302	0.0005
3	2	2	4	2	2	1	3	14692.0676	-0.0017	13917.4846	0.0017
3	2	2	3	2	2	1	2	14691.1951	0.0033		
3	2	2	2	2	2	1	1	14692.5590	0.0021		
3	2	1	4	2	2	0	3	14703.0767	-0.0010	13925.4545	-0.0009
3	2	1	3	2	2	0	2	14702.1939	0.0017		
3	2	1	2	2	2	0	1	14703.5690	0.0020		
3	2	1	2	2	2	0	2	14702.2066	-0.0034		
4	0	4	5	3	0	3	4	19561.6557	0.0062	18536.4285	-0.0003
4	0	4	4	3	0	3	3	19561.6449	0.0052	18536.4173	0.0019
4	0	4	3	3	0	3	2	19561.5644	-0.0043	18536.3468	0.0004
4	1	4	5	3	1	3	4	19394.4929	-0.0005	18387.5458	-0.0004
4	1	4	4	3	1	3	3	19394.3899	-0.0002	18387.4391	0.0000
4	1	4	3	3	1	3	2	19394.4674	-0.0007	18387.5186	-0.0001
4	1	3	5	3	1	2	4	19772.4119	-0.0011	18716.8914	-0.0007
4	1	3	4	3	1	2	3	19772.3035	-0.0009	18716.7797	-0.0006
4	1	3	3	3	1	2	2	19772.3697	0.0033	18716.8462	0.0001
4	2	3	5	3	2	2	4	19586.5005	0.0012	18554.3445	-0.0019
4	2	3	4	3	2	2	3	19586.1275	-0.0008	18553.9650	-0.0006
4	2	3	3	3	2	2	2	19586.5925	-0.0022	18554.4471	0.0028
4	2	2	5	3	2	1	4	19613.9236	0.0005	18574.2300	0.0000
4	2	2	4	3	2	1	3	19613.5411	-0.0001	18573.8406	-0.0008
4	2	2	3	3	2	1	2	19614.0197	-0.0004	18574.3311	0.0020
1	1	0	2	0	0	0	1	7376.4451	-0.0025	7230.3872	-0.0002
1	1	0	1	0	0	0	1	7376.7462	-0.0011	7230.7117	-0.0001
1	1	0	0	0	0	0	1	7375.9955	-0.0025	7229.9011	0.0004
2	1	1	3	1	0	1	2			11951.9812	-0.0023
2	1	1	2	1	0	1	1			11952.2763	0.0051
2	1	1	1	1	0	1	0			11951.0324	0.0017

3	0	3	4	2	1	1	3	12105.2246	-0.0052	11234.4428	-0.0020
3	0	3	3	2	1	1	2	12104.8919	0.0027	11234.0751	0.0019
3	0	3	2	2	1	1	1	12105.2246	-0.0100	11234.4561	-0.0052
3	1	2	4	2	0	2	3	17408.3544	-0.0042	16715.2047	-0.0020
3	1	2	3	2	0	2	2	17408.4271	-0.0012	16715.2948	-0.0035
3	1	2	2	2	0	2	1	17408.1510	-0.0038	16714.9875	-0.0030
4	0	4	5	3	1	2	4	16834.5787	0.0049	15730.9482	0.0089
4	0	4	4	3	1	2	3	16834.4656	-0.0042	15730.8033	-0.0036
4	0	4	3	3	1	2	2	16834.5225	-0.0035	15730.8948	-0.0039

Table S11. Experimental transition frequencies v and obs.–calc. residuals Δv for TW: DOH and HOD isotopologues.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F	TW (DOH)		TW (HOD)	
								v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)	v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)
2	0	2	3	1	0	1	2	9668.5135	-0.0014	9362.5668	-0.0016
3	0	3	4	2	0	2	3	14496.0271	0.0001	14038.0460	0.0024
3	0	3	3	2	0	2	2	14496.0024	0.0006	14038.0158	-0.0007
3	0	3	2	2	0	2	1	14495.8559	-0.0021	14037.8735	0.0009
3	1	3	4	2	1	2	3	14367.3820	-0.0015	13916.5109	-0.0014
3	1	3	3	2	1	2	2	14367.1485	0.0011	13916.2727	0.0007
3	1	3	2	2	1	2	1	14367.3997	0.0008	13916.5195	-0.0051
3	1	2	4	2	1	1	3	14641.7618	-0.0049	14174.2393	0.0016
3	1	2	3	2	1	1	2	14641.5245	0.0018	14173.9895	-0.0012
3	1	2	2	2	1	1	1			14174.2098	-0.0050
3	2	2	4	2	2	1	3	14506.0246	0.0048	14046.6094	0.0062
3	2	2	3	2	2	1	2	14505.1530	0.0025	14045.7236	0.0017
3	2	2	2	2	2	1	1	14506.5045	0.0016	14047.0940	0.0010
4	0	4	5	3	0	3	4	19315.6024	0.0058	18706.6810	0.0010
4	0	4	4	3	0	3	3	19315.5924	0.0067	18706.6749	0.0082
4	0	4	3	3	0	3	2	19315.5125	-0.0043	18706.5959	-0.0034
4	1	4	5	3	1	3	4	19152.9509	-0.0026	18552.2561	-0.0006
4	1	4	4	3	1	3	3	19152.8505	-0.0001	18552.1509	-0.0006
4	1	4	3	3	1	3	2	19152.9261	-0.0015		
4	1	3	5	3	1	2	4	19518.6314	0.0017	18895.7672	0.0006
4	1	3	4	3	1	2	3	19518.5204	-0.0016	18895.6562	-0.0011
4	1	3	3	3	1	2	2	19518.5835	-0.0009	18895.7226	0.0002
4	2	3	5	3	2	2	4	19338.6083	-0.0012	18726.3980	0.0000
4	2	3	4	3	2	2	3	19338.2428	0.0011	18726.0231	-0.0019
4	2	3	3	3	2	2	2	19338.7052	0.0012	18726.4941	0.0002
4	2	2	5	3	2	1	4	19364.0075	-0.0043	18748.2003	-0.0066
4	2	2	4	3	2	1	3	19363.6289	-0.0056	18747.8287	0.0024
4	2	2	3	3	2	1	2	19364.1107	0.0030	18748.3053	0.0014
1	1	0	2	0	0	0	1	7340.3352	-0.0014		
1	1	0	1	0	0	0	1	7340.6393	-0.0025		
3	0	3	4	2	1	1	3	11897.3183	-0.0066	11378.1713	0.0006
3	0	3	3	2	1	1	2	11896.9840	0.0069		
3	0	3	2	2	1	1	1	11897.3321	-0.0030	11378.1917	-0.0001
3	1	2	4	2	0	2	3	17240.4653	-0.0035		
3	1	2	3	2	0	2	2	17240.5571	0.0096		
3	1	2	2	2	0	2	1	17240.2596	-0.0039		
4	0	4	4	3	1	2	3	16571.0396	-0.0005	15910.4734	-0.0004
4	0	4	3	3	1	2	2	16571.1128	0.0015		

Table S12. Experimental transition frequencies v and obs.–calc. residuals Δv for GW: H_2O and $H_2{}^{18}O$.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F	GW		GW ($H_2{}^{18}O$)	
								v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)	v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)
2	0	2	3	1	0	1	2	7805.1158	0.0001	7388.1136	-0.0021
3	0	3	4	2	0	2	3	11676.4675	-0.0011	11057.6041	-0.0023
3	0	3	3	2	0	2	2	11676.4247	0.0012	11057.5586	-0.0021
3	0	3	2	2	0	2	1	11676.2312	-0.0006	11057.3679	-0.0004
3	1	3	4	2	1	2	3	11273.2387	0.0072	10692.7665	0.0067
3	1	3	3	2	1	2	2	11272.8885	-0.0011	10692.4163	0.0005
3	1	3	2	2	1	2	1	11273.2303	0.0098	10692.7575	0.0090
3	1	2	4	2	1	1	3	12163.4706	-0.0019	11488.3017	0.0022
3	1	2	3	2	1	1	2	12163.1309	-0.0012	11487.9577	0.0005
3	1	2	2	2	1	1	1	12163.4672	-0.0023	11488.2970	0.0003
4	0	4	5	3	0	3	4	15511.3228	-0.0012	14698.2371	-0.0026
4	0	4	4	3	0	3	3	15511.2936	-0.0020	14698.2081	-0.0025
4	0	4	3	3	0	3	2	15511.2123	-0.0007	14698.1264	-0.0018
4	1	4	5	3	1	3	4	15016.7585	-0.0017	14245.7073	-0.0029
4	1	4	4	3	1	3	3	15016.6061	-0.0017	14245.5559	-0.0009
4	1	4	3	3	1	3	2	15016.7080	-0.0006	14245.6602	0.0020
4	1	3	5	3	1	2	4	16202.1995	-0.0004	15305.3538	-0.0017
4	1	3	4	3	1	2	3	16202.0480	-0.0005	15305.2015	-0.0017
4	1	3	3	3	1	2	2	16202.1531	0.0011	15305.3053	-0.0022
4	2	3	5	3	2	2	4	15624.9674	0.0002	14787.7450	-0.0022
4	2	3	4	3	2	2	3	15624.4433	-0.0028		
4	2	3	3	3	2	2	2	15625.0988	-0.0023		
4	2	2	5	3	2	1	4	15747.8778	-0.0016		
4	2	2	4	3	2	1	3	15747.3561	-0.0017		
4	2	2	3	3	2	1	2	15748.0123	-0.0012		
5	0	5	6	4	0	4	5	19300.0543	-0.0015	18301.9542	-0.0010
5	0	5	5	4	0	4	4	19300.0368	0.0005	18301.9354	0.0004
5	0	5	4	4	0	4	3	19299.9899	-0.0002	18301.8889	-0.0003
5	1	5	6	4	1	4	5	18749.1388	-0.0006	17789.7191	-0.0004
5	1	5	5	4	1	4	4	18749.0564	0.0004	17789.6367	0.0012
5	1	5	4	4	1	4	3	18749.0970	0.0010	17789.6777	0.0019
5	1	4	6	4	1	3	5	20226.5199	0.0025	19111.2141	0.0004
5	1	4	5	4	1	3	4	20226.4344	-0.0003	19111.1328	0.0023
5	1	4	4	4	1	3	3	20226.4747	-0.0015	19111.1750	0.0026
5	2	4	6	4	2	3	5	19514.9669	-0.0005	18471.8154	-0.0015
5	2	4	5	4	2	3	4	19514.6946	-0.0003	18471.5446	0.0018
5	2	4	4	4	2	3	3	19514.9985	0.0035	18471.8441	-0.0005
5	2	3	6	4	2	2	5	19756.9881	-0.0008	18662.8750	-0.0008
5	2	3	5	4	2	2	4	19756.7177	0.0019	18662.6031	0.0015
5	2	3	4	4	2	2	3	19757.0181	0.0015	18662.9017	-0.0018
1	1	1	2	0	0	0	1	9076.9730	-0.0013		
1	1	1	1	0	0	0	1	9077.5231	-0.0051		
2	1	2	3	1	0	1	2	12688.8734	0.0011	12409.2272	0.0017
2	1	2	2	1	0	1	1	12689.3836	-0.0004		
3	1	3	4	2	0	2	3	16156.9893	0.0011	15713.8704	0.0008
3	1	3	3	2	0	2	2	16157.2383	-0.0012	15714.1199	-0.0016

3	1	3	2	2	0	2	1	16156.6457	-0.0020	15713.5242	-0.0033
4	1	4	5	3	0	3	4	19497.2812	0.0014	18901.9746	0.0012
4	1	4	4	3	0	3	3	19497.4244	0.0006	18902.1156	-0.0020
4	1	4	3	3	0	3	2	19497.1237	-0.0009	18901.8181	0.0007
2	1	1	3	1	0	1	2	13579.4580	0.0050	13205.0025	0.0012
2	1	1	2	1	0	1	1	13580.0049	-0.0011		
3	1	2	4	2	0	2	3	17937.8125	0.0027	17305.1866	0.0015
3	1	2	3	2	0	2	2	17938.1045	0.0004		

Table S13. Experimental transition frequencies v and obs.–calc. residuals Δv for GW: DOH and HOD isotopologues.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F	GW (DOH)		GW (HOD)	
								v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)	v_{obs}(MHz)	$\Delta v_{obs-calc}$(MHz)
2	0	2	3	1	0	1	2	7697.8572	-0.0059	7485.6635	0.0013
3	0	3	4	2	0	2	3	11517.0330	-0.0017	11202.2024	-0.0003
3	0	3	3	2	0	2	2	11516.9879	-0.0017	11202.1543	-0.0004
3	0	3	2	2	0	2	1	11516.7935	-0.0056		
3	1	3	4	2	1	2	3	11121.8083	0.0037	10827.7263	-0.0004
3	1	3	3	2	1	2	2	11121.4625	-0.0017	10827.3850	-0.0010
3	1	3	2	2	1	2	1	11121.7994	0.0061		
3	1	2	4	2	1	1	3	11992.1449	0.0003	11647.2103	-0.0006
3	1	2	3	2	1	1	2	11991.8064	0.0004		
3	1	2	2	2	1	1	1	11992.1449	0.0029		
4	0	4	5	3	0	3	4	15301.3652	0.0003	14887.8945	-0.0010
4	0	4	4	3	0	3	3	15301.3389	0.0026	14887.8643	0.0015
4	0	4	3	3	0	3	2	15301.2548	0.0003		
4	1	4	5	3	1	3	4	14815.4945	-0.0031	14424.9309	0.0004
4	1	4	4	3	1	3	3	14815.3429	-0.0030	14424.7774	-0.0002
4	1	4	3	3	1	3	2	14815.4451	-0.0010		
4	1	3	5	3	1	2	4	15974.5112	-0.0001	15516.3883	0.0020
4	1	3	4	3	1	2	3	15974.3708	0.0101	15516.2350	-0.0012
4	1	3	3	3	1	2	2	15974.4648	0.0009		
4	2	3	5	3	2	2	4	15409.7765	-0.0026	14983.7024	-0.0012
4	2	3	4	3	2	2	3			14983.1888	0.0017
4	2	3	3	3	2	2	2	15409.9144	0.0020	14983.8363	-0.0001
4	2	2	3	3	2	1	2	15527.1446	-0.0027		
5	0	5	6	4	0	4	5	19041.5476	-0.0018	18534.2562	-0.0039
5	0	5	5	4	0	4	4	19041.5278	-0.0019	18534.2367	0.0015
5	0	5	4	4	0	4	3	19041.4839	-0.0003	18534.1942	-0.0015
5	1	5	6	4	1	4	5	18498.5242	0.0001	18012.6358	-0.0001
5	1	5	5	4	1	4	4	18498.4427	0.0017	18012.5527	0.0013
5	1	5	4	4	1	4	3	18498.4836	0.0028	18012.5927	0.0017
5	1	4	6	4	1	3	5	19943.1756	-0.0036	19373.5546	0.0021
5	1	4	5	4	1	3	4	19943.0975	0.0006	19373.4716	0.0019
5	1	4	4	4	1	3	3	19943.1386	0.0003	19373.5119	-0.0022
5	2	4	6	4	2	3	5	19246.7303	-0.0016	18715.9285	0.0002
5	2	4	5	4	2	3	4	19246.4611	0.0005	18715.6582	0.0006
5	2	4	4	4	2	3	3	19246.7596	0.0002	18715.9538	-0.0020
5	2	3	6	4	2	2	5	19477.7439	-0.0002	18920.3940	0.0014
5	2	3	5	4	2	2	4	19477.4734	0.0008	18920.1223	-0.0046
5	2	3	4	4	2	2	3	19477.7709	-0.0007	18920.4218	0.0023
3	1	3	4	2	0	2	3	16028.6331	0.0022		
3	1	3	3	2	0	2	2	16028.8773	-0.0019		
4	1	4	5	3	0	3	4	19327.0946	0.0007	19005.9798	-0.0029
4	1	4	4	3	0	3	3	19327.2378	0.0023	19006.0872	0.0001
4	1	4	3	3	0	3	2	19326.9388	-0.0010	19005.8421	0.0039
2	1	1	3	1	0	1	2	13475.3426	-0.0018	13260.9170	-0.0033
3	1	2	4	2	0	2	3	17769.6256	-0.0004	17422.4712	0.0023

Table S14. Calculated equilibrium structure of TGW at the B2 and B2-CP levels of theory.

Atom	B2			B2-CP		
	x	*y*	*z*	*x*	*y*	*z*
C	1.017366	-0.237713	0.456399	1.022046	-0.243867	0.454767
H	1.203653	0.160285	1.457944	1.207152	0.148545	1.458698
H	0.284447	-1.036671	0.564817	0.285620	-1.040389	0.557694
C	0.420163	0.861365	-0.408810	0.431858	0.861709	-0.406911
H	0.200202	0.462917	-1.399741	0.213879	0.469051	-1.400601
H	1.154089	1.664632	-0.537023	1.169909	1.662308	-0.528829
N	-0.847990	1.344139	0.164266	-0.836077	1.346694	0.164124
H	-0.690700	1.715552	1.093971	-0.680424	1.713754	1.095751
H	-1.226151	2.100976	-0.392221	-1.209785	2.106809	-0.390760
C	2.315350	-0.785194	-0.126675	2.319372	-0.794174	-0.127151
H	3.067187	-0.001982	-0.228785	3.074714	-0.013626	-0.223543
H	2.732675	-1.565453	0.507203	2.731675	-1.579034	0.504320
H	2.147156	-1.215750	-1.113771	2.152253	-1.219485	-1.116701
O	-2.305164	-1.118786	-0.092048	-2.332867	-1.109798	-0.090769
H	-1.947080	-0.222100	0.067226	-1.958771	-0.219572	0.064598
H	-3.243471	-1.058942	0.100542	-3.272931	-1.026946	0.083687

Table S15. Calculated equilibrium structure of GG'W at the B2 and B2-CP levels of theory.

Atom	B2			B2-CP		
	x	*y*	*z*	*x*	*y*	*z*
C	0.99792	-0.462929	0.652903	1.005485	-0.44962	0.663479
H	0.118226	-1.086388	0.811082	0.113992	-1.03651	0.883596
H	1.627634	-0.564041	1.538478	1.669364	-0.53706	1.525267
C	0.562616	0.993546	0.55422	0.613504	1.015763	0.523676
H	1.448681	1.633175	0.469055	1.515974	1.620882	0.378431
H	0.043337	1.277785	1.468562	0.141965	1.352944	1.445938
N	-0.378505	1.198276	-0.562095	-0.36514	1.209092	-0.56157
H	-0.706094	2.156268	-0.572986	-0.66399	2.175794	-0.59565
H	0.086395	1.043723	-1.448278	0.058937	1.008025	-1.45882
C	1.765939	-0.949114	-0.573191	1.703117	-1.0096	-0.57313
H	2.633071	-0.317283	-0.773398	2.579572	-0.41486	-0.83652
H	2.123779	-1.967132	-0.429988	2.03542	-2.03208	-0.40297
H	1.138294	-0.956708	-1.464108	1.036141	-1.03299	-1.43458
O	-2.386399	-0.765701	0.083656	-2.38871	-0.75935	0.090564
H	-1.793091	-0.057364	-0.238747	-1.79957	-0.03717	-0.20611
H	-3.195038	-0.676109	-0.425529	-3.25971	-0.53488	-0.24426

Table S16. Calculated equilibrium structure of TTW at the B2 and B2-CP levels of theory.

Atom	B2			B2-CP		
	x	*y*	*z*	*x*	*y*	*z*
C	1.689696	0.417977	0	1.694381	0.417197	0
H	1.866324	1.047571	0.875705	1.870688	1.046966	0.875659
H	1.866324	1.047571	-0.875705	1.870688	1.046966	-0.875659
C	0.234407	-0.038758	0	0.239207	-0.04027	0
H	0.042204	-0.664467	0.872292	0.047625	-0.666132	0.872337
H	0.042204	-0.664467	-0.872292	0.047625	-0.666132	-0.872337
N	-0.76567	1.03789	0	-0.761266	1.035744	0
H	-0.643914	1.630934	0.812529	-0.639542	1.628649	0.812543
H	-0.643914	1.630934	-0.812529	-0.639542	1.628649	-0.812543
C	2.664422	-0.755475	0	2.670012	-0.755489	0
H	2.52078	-1.38293	-0.879665	2.526885	-1.383047	-0.879677
H	3.698145	-0.414227	0	3.703477	-0.413442	0
H	2.52078	-1.38293	0.879665	2.526885	-1.383047	0.879677
O	-3.084219	-0.668946	0	-3.100759	-0.665318	0
H	-3.920329	-0.197826	0	-3.932969	-0.187403	0
H	-2.396101	0.025701	0	-2.407499	0.023523	0

Table S17. Calculated equilibrium structure of GTW at the B2 and B2-CP levels of theory.

Atom	B2			B2-CP		
	x	*y*	*z*	*x*	*y*	*z*
C	1.687915	-0.615642	-0.26801	-1.690986	-0.617556	0.267725
H	1.87414	-0.540282	-1.342596	-1.86906	-0.54744	1.344042
H	2.040873	-1.603152	0.036681	-2.045285	-1.604006	-0.038847
C	0.182379	-0.549574	-0.016375	-0.187398	-0.548429	0.004876
H	-0.018014	-0.640185	1.052018	0.004598	-0.633752	-1.065509
H	-0.309567	-1.395563	-0.494988	0.308958	-1.396281	0.475601
N	-0.49371	0.66891	-0.484746	0.490778	0.668409	0.473924
H	-0.11903	1.488363	-0.023554	0.111206	1.489433	0.019776
H	-0.34294	0.796457	-1.478727	0.347539	0.790473	1.469642
C	2.479788	0.457352	0.472599	-2.489853	0.458001	-0.461558
H	2.315103	0.389284	1.548547	-2.334417	0.394524	-1.539166
H	3.54851	0.354016	0.292971	-3.55693	0.353316	-0.273171
H	2.195868	1.46069	0.154889	-2.20375	1.46019	-0.142178
O	-3.149088	-0.123841	0.295329	3.167434	-0.124823	-0.282325
H	-2.312339	0.272992	-0.018493	2.325228	0.272675	0.014071
H	-3.830201	0.517183	0.080358	3.835251	0.544632	-0.118549

Table S18. Calculated equilibrium structure of GGW at the B2 and B2-CP levels of theory.

Atom	B2			B2-CP		
	x	*y*	*z*	*x*	*y*	*z*
C	-1.610685	0.336643	0.143446	1.616547	0.335842	-0.142518
H	-1.872506	0.144753	1.188387	1.879516	0.144072	-1.187177
H	-2.554894	0.511325	-0.375452	2.560276	0.509563	0.377583
C	-0.985469	-0.922029	-0.444044	0.989227	-0.922299	0.443891
H	-0.673565	-0.72984	-1.471514	0.677464	-0.73018	1.471423
H	-1.740008	-1.714254	-0.47568	1.743022	-1.715365	0.47551
N	0.211811	-1.333623	0.311543	-0.208382	-1.331192	-0.312093
H	-0.031007	-1.474802	1.285999	0.034617	-1.474986	-1.286012
H	0.54785	-2.225869	-0.031331	-0.548336	-2.221192	0.032468
C	-0.731733	1.579483	0.044743	0.738617	1.579406	-0.044571
H	-0.475661	1.789896	-0.993566	0.481288	1.789798	0.993429
H	-1.251112	2.449869	0.443481	1.25899	2.449568	-0.442469
H	0.201491	1.464793	0.589436	-0.193806	1.46531	-0.590803
O	2.489154	0.423225	-0.105721	-2.505741	0.422286	0.104793
H	3.279612	-0.051853	0.160402	-3.292408	-0.063494	-0.152878
H	1.746726	-0.187637	0.075438	-1.758447	-0.181922	-0.075578

Table S19. Calculated equilibrium structures of the isomerization transition states involving the TGW isomer at the B2 level of theory.

9	TGW-GG'W			TGW-GGW			TGW-TTW		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
C	-0.934272	-0.590539	0.056728	1.249693	0.018123	0.494628	-1.446306	0.160984	-0.459291
H	-0.401903	-0.860606	-0.855624	2.20308	0.412519	0.84774	-1.892757	1.134356	-0.676479
H	-0.70163	-1.378348	0.771202	0.622405	-0.117627	1.376755	-1.054885	-0.225736	-1.403534
C	-0.382582	0.752552	0.564801	0.574235	1.044596	-0.430693	-0.286028	0.345283	0.507935
H	0.089782	0.627173	1.53733	1.238661	1.896277	-0.600806	0.130866	-0.63236	0.755373
H	-1.208037	1.459178	0.697225	0.381291	0.5918	-1.402746	-0.652208	0.778061	1.440075
N	0.650701	1.278866	-0.34781	-0.732943	1.46533	0.110695	0.792922	1.191742	-0.04638
H	0.258458	1.420785	-1.271639	-1.161424	2.156375	-0.493954	0.560994	1.49805	-0.982454
H	0.97844	2.18309	-0.029159	-0.608236	1.90735	1.014043	0.931798	2.024065	0.508863
C	-2.43684	-0.559751	-0.207528	1.464734	-1.337873	-0.171733	-2.507104	-0.790897	0.082189
H	-2.691897	0.203807	-0.943863	0.510531	-1.765321	-0.474581	-2.928993	-0.417859	1.015608
H	-2.791961	-1.517405	-0.585395	1.949595	-2.037735	0.507674	-3.324707	-0.915695	-0.625525
H	-2.992543	-0.336132	0.703244	2.096528	-1.241743	-1.055473	-2.083015	-1.77503	0.279188
O	2.504479	-0.883221	0.026353	-1.990096	-1.107915	-0.018491	2.765313	-0.880119	-0.054414
H	1.985387	-0.087392	-0.206416	-1.702503	-0.179565	0.099635	2.22785	-0.063231	-0.088368
H	3.381541	-0.730007	-0.331997	-2.919433	-1.122519	0.220691	3.65867	-0.605917	-0.272546

Table S20. Calculated equilibrium structures of the isomerization transition states involving the GTW isomer at the B2 level of theory.

Atom	GTW-GG'W			GTW-GGW			GTW-TTW		
	x	*y*	*z*	*x*	*y*	*Z*	*x*	*y*	*z*
C	1.331735	-0.767478	-0.095415	-1.712348	-0.11289	-0.259225	-1.709175	0.334688	0.383354
H	0.917635	-1.091479	-1.053702	-2.302191	-0.706745	0.443765	-1.83896	1.321037	-0.066102
H	1.646946	-1.675684	0.420029	-2.292424	-0.056057	-1.181932	-2.035246	0.430092	1.419854
C	0.220232	-0.11883	0.720372	-0.408128	-0.83978	-0.563834	-0.211531	-0.039188	0.33531
H	0.630964	0.256565	1.659502	0.1632	-0.253822	-1.286344	-0.084195	-0.985974	-0.189166
H	-0.523825	-0.873439	0.975206	-0.624789	-1.799471	-1.032512	0.176496	-0.197113	1.339974
N	-0.459878	0.979325	-0.002832	0.437249	-1.05961	0.631613	0.679752	0.931659	-0.318218
H	-0.402371	1.850689	0.504682	0.007552	-0.663952	1.457572	0.385613	1.09156	-1.27461
H	-0.031001	1.137891	-0.904992	0.564314	-2.045403	0.810796	0.63197	1.826877	0.153598
C	2.540628	0.136103	-0.320992	-1.500471	1.296739	0.288663	-2.601142	-0.67264	-0.337616
H	2.988432	0.427847	0.629409	-0.917844	1.898077	-0.408249	-2.512777	-1.661975	0.110912
H	3.30519	-0.368905	-0.908941	-2.452444	1.797391	0.457347	-3.649695	-0.381246	-0.296418
H	2.273699	1.049852	-0.85188	-0.964095	1.293393	1.23751	-2.319787	-0.76153	-1.387526
O	-2.976449	-0.364692	-0.208609	2.552098	0.668964	-0.209365	3.111293	-0.569067	0.03531
H	-2.202668	0.234238	-0.199612	3.40027	0.538493	0.220141	2.373064	0.04372	-0.153578
H	-3.704708	0.165821	-0.538837	1.953503	0.006975	0.191802	3.891201	-0.148184	-0.332971

Table S21. Calculated equilibrium structure of the GG'W-GGW isomerization transition state at the B2 level of theory.

Atom	*x*	*y*	*z*
C	-1.323591	0.42988	0.564566
H	-0.721993	0.511173	1.472483
H	-2.364107	0.569308	0.866236
C	-1.168921	-0.979891	0.003094
H	-1.721029	-1.052263	-0.93547
H	-1.623462	-1.696792	0.688011
N	0.248558	-1.329863	-0.230732
H	0.537184	-2.091672	0.367475
H	0.402917	-1.635322	-1.181473
C	-0.924344	1.514306	-0.430189
H	-1.560518	1.478498	-1.315676
H	-1.022706	2.507032	0.006666
H	0.107451	1.392697	-0.75431
O	2.585315	0.380982	0.099565
H	1.745482	-0.114352	0.039705
H	2.420325	1.081123	0.735229

Table S22. Calculated equilibrium structure of GW at the B2 and B2-CP levels of theory.

Atom	B2			B2-CP		
	x	*y*	*z*	*x*	*y*	*z*
C	0.455366	1.3931	-0.292177	0.460597	1.393375	-0.28688
H	1.007923	2.146902	0.266083	1.017666	2.146129	0.268297
H	-0.603533	1.637515	-0.25541	-0.59767	1.639492	-0.24338
C	0.786574	1.44153	-1.331987	0.784946	1.442287	-1.3288
H	0.712065	0.006557	0.28071	0.719522	0.006097	0.283167
H	0.345082	-0.014706	1.308547	0.359991	-0.01539	1.313643
N	2.199592	-0.336499	0.283419	2.206892	-0.33802	0.27549
H	2.765197	0.377008	0.882755	2.777224	0.374749	0.871241
H	2.373537	-1.331455	0.693814	2.383061	-1.3333	0.684164
C	2.598937	-0.314046	-0.732138	2.599256	-0.31544	-0.74278
H	-0.106174	-0.971101	-0.463506	-0.10462	-0.97016	-0.45589
H	0.144945	-0.950034	-1.446625	0.138174	-0.94697	-1.441
H	0.085352	-1.911425	-0.136652	0.090329	-1.91092	-0.13253
O	-2.69604	0.041712	0.256044	-2.7142	0.044417	0.246183
H	-1.895279	-0.413917	-0.074248	-1.90789	-0.41139	-0.06845
H	-3.435965	-0.495379	-0.035713	-3.44365	-0.53302	0.010734

Table S23. Calculated equilibrium structure of TW at the B2 and B2-CP levels of theory.

Atom	B2			B2-CP		
	x	*y*	*z*	*x*	*y*	*z*
C	0.919357	-1.259992	0.609795	0.928587	-1.259966	0.608619
H	1.69078	-1.295915	1.377556	1.70377	-1.295807	1.37259
H	1.018879	-2.155922	-0.004387	1.025124	-2.155896	-0.006008
C	-0.056573	-1.282799	1.09232	-0.044871	-1.283145	1.09615
H	1.065005	0	-0.231461	1.069739	0	-0.233344
H	2.062252	0	-0.686801	2.065065	0	-0.693087
N	0.919357	1.259992	0.609795	0.928587	1.259966	0.608619
H	1.69078	1.295915	1.377556	1.70377	1.295807	1.37259
H	1.018879	2.155922	-0.004387	1.025124	2.155896	-0.006008
C	-0.056573	1.282799	1.09232	-0.044871	1.283145	1.09615
H	0.014682	0	-1.271183	0.0145	0	-1.26769
H	0.11089	0.813912	-1.867582	0.107928	0.813937	-1.864402
H	0.11089	-0.813912	-1.867582	0.107928	-0.813937	-1.864402
O	-2.364692	0	0.366769	-2.383814	0	0.367229
H	-1.65228	0	-0.304221	-1.666447	0	-0.297612
H	-3.186607	0	-0.128914	-3.201375	0	-0.135481

Table S24. Calculated equilibrium structure of the GW-TW isomerization transition state at the B2 level of theory.

Atom	*x*	*y*	*z*
C	-0.314634	1.37811	-0.170007
H	-1.048577	2.175788	-0.285097
H	0.501161	1.55286	-0.867962
H	0.099126	1.429978	0.836713
C	-0.957136	0.016842	-0.411525
H	-1.365471	0.005054	-1.424192
C	-2.094957	-0.239881	0.568741
H	-2.837787	0.554784	0.521894
H	-2.594085	-1.185674	0.358543
H	-1.710151	-0.272912	1.589796
N	0.070366	-1.053995	-0.318272
H	-0.170909	-1.715732	0.408687
H	0.123089	-1.580028	-1.180169
O	2.704349	0.060067	0.266414
H	1.849142	-0.372018	0.071971
H	3.343837	-0.654051	0.316113

SAPT Analysis

The nature of the intermolecular interactions has been investigated using the Symmetry-Adapted Perturbation Theory (SAPT) [1], which allows for evaluating the different contributions (electrostatic, induction, dispersion and exchange-repulsion terms) to the stabilization energy. The results, obtained at the SAPT2+3(CCD)/aug-cc-pVDZ-RI level using the PSI4 program [2], are summarized in Table S25. The B2 structures have been used.

Table S25. SAPT analysis for alkyl amine-water adducts as well as B2-CP and ChS interaction energies.[a]

Adduct	Electrost.	Induct.	Dispers.	Exch.	Total	Total B2-CP	ChS-CP
$(H_2O)_2$[b]	-34.1	-10.4	-9.4	34.8	-19.0	-21.0	
MAW	-55.1	-20.7	-16.3	63.1	-29.1	-31.2	
ETW	-55.3	-20.9	-16.7	63.4	-29.5	-31.5	
EGW	-58.7	-22.0	-19.2	68.8	-31.0	-32.9	
TGW	-59.0	-22.2	-19.7	69.5	-31.4	-33.2	-33.51
TTW	-55.4	-21.0	-16.9	63.5	-29.7	-31.6	-31.45
GTW	-55.4	-21.0	-16.9	63.7	-29.6	-31.6	-31.46
GG'W	-59.4	-22.5	-19.9	70.4	-31.3	-33.1	-33.32
GGW	-56.8	-21.6	-19.8	68.8	-29.4	-31.2	-31.52
TW	-60.4	-22.6	-21.4	72.3	-32.1	-33.5	-34.12
GW	-59.4	-22.4	-19.7	69.8	-31.7	-33.4	-33.72

[a] Values in kJ mol^{-1}. [b] The water dimer has been reported for comparison purposes.

NBO Analysis

The Natural Bond Orbital (NBO) analysis [3] has been performed at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level using the Gaussian16 package [4], in order to obtain the second-order perturbative stabilization energies and NBO atomic charges (see tables below) for all PA-W and IPA-W isomers as well as for MAW, EGW and ETW. NBO atomic charges are also compared to the values of the isolated monomers, evaluated at the same level of theory.

Figure S1. MAW, EGW, ETW, PA-W and IPA-W: atom labelling for Tables S26-S45.

Table S26. NBO charges at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level for isolated methylamine, water and MAW complex.

	MAW	Methylamine	Water
O1	-0.967		-0.922
H2	0.450		0.461
H3	0.483		0.461
N4	-0.857	-0.840	
C5	-0.382	-0.378	
H6	0.166	0.156	
H7	0.195	0.184	
H8	0.195	0.184	
H9	0.358	0.347	
H10	0.358	0.347	

Table S27. NBO stabilization energy contributions in the MAW complex at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level.

Donor NBO	Acceptor NBO	$E(2)$/kcal·mol^{-1}
From water to methylamine		
BD (1) O1 - H3	RY*(1) N4	0.07
LP (2) O1	RY*(2) N4	0.10
From methylamine to water		
BD (1) N4 - C5	RY*(1) H3	0.11
LP (1) N4	RY*(2) O1	0.07
LP (1) N4	RY*(7) O1	0.15
LP (1) N4	RY*(10) O1	0.07
LP (1) N4	RY*(4) H3	0.31
LP (1) N4	RY*(5) H3	0.15
LP (1) N4	RY*(7) H3	0.09
LP (1) N4	BD*(1) O1 - H3	12.58

Table S28. NBO charges at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level for isolated G ethylamine, water and EGW complex.

	EGW	G ethylamine	Water
N1	-0.861	-0.844	
H2	0.356	0.345	
H3	0.362	0.352	
C4	-0.191	-0.188	
H5	0.188	0.178	
H6	0.160	0.151	
C7	-0.596	-0.587	
H8	0.223	0.204	
H9	0.205	0.201	
H10	0.189	0.190	
O11	-0.971		-0.922
H12	0.484		0.461
H13	0.452		0.461

Table S29. NBO stabilization energy contributions in the EGW complex at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level.

Donor NBO	Acceptor NBO	$E(2)$/kcal·mol^{-1}
From G ethylamine to water		
BD (1) C7 - H8	RY*(2) O11	0.18
LP (1) N1	RY*(3) O11	0.06
LP (1) N1	RY*(7) O11	0.07
LP (1) N1	RY*(10) O11	0.07
LP (1) N1	RY*(4) H12	0.31
LP (1) N1	RY*(5) H12	0.16
LP (1) N1	RY*(7) H12	0.07
LP (1) N1	BD*(1) O11 - H12	13.08
From water to G ethylamine		
BD (1) O11 - H13	RY*(1) H8	0.14
LP (1) O11	BD*(1) C7 - H8	0.08
LP (2) O11	BD*(1) C7 - H8	0.17

Table S30. NBO charges at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level for isolated T ethylamine, water and ETW complex.

	ETW	T ethylamine	Water
N1	-0.854	-0.836	
H2	0.356	0.345	
H3	0.356	0.345	
C4	-0.198	-0.194	
H5	0.190	0.178	
H6	0.190	0.178	
C7	-0.598	-0.599	
H8	0.193	0.191	
H9	0.206	0.200	
H10	0.193	0.191	
O11	-0.968		-0.922
H12	0.484		0.461
H13	0.450		0.461

Table S31. NBO stabilization energy contributions in the ETW complex at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level.

Donor NBO	Acceptor NBO	$E(2)$/kcal·mol^{-1}
From T ethylamine to water		
LP (1) N1	RY*(4) O11	0.14
LP (1) N1	RY*(7) O11	0.07
LP (1) N1	RY*(4) H12	0.33
LP (1) N1	RY*(5) H12	0.13
LP (1) N1	RY*(6) H12	0.09
LP (1) N1	BD*(1) O11 - H12	12.77
From water to T ethylamine		
BD (1) O11 - H12	RY*(1) N1	0.08
BD (1) O11 - H12	RY*(1) C4	0.05
BD (1) O11 - H13	RY*(1) C4	0.07
LP (2) O11	RY*(2) N1	0.12

Table S32. NBO charges at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level for isolated G isopropylamine, water and GW complex.

	GW	G isopropylamine	Water
C1	-0.591	-0.583	
H2	0.204	0.200	
H3	0.228	0.211	
H4	0.188	0.189	
C5	-0.036	-0.035	
H6	0.182	0.171	
C7	-0.592	-0.594	
H8	0.205	0.200	
H9	0.197	0.196	
H10	0.193	0.191	
N11	-0.857	-0.839	
H12	0.354	0.343	
H13	0.359	0.349	
O14	-0.971		-0.922
H15	0.485		0.461
H16	0.452		0.461

Table S33. NBO stabilization energy contributions in the GW complex at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level.

Donor NBO	Acceptor NBO	$E(2)$/kcal·mol^{-1}
From G isopropylamine to water		
BD (1) C1 - H3	RY*(2) O14	0.11
LP (1) N11	RY*(4) O14	0.07
LP (1) N11	RY*(7) O14	0.05
LP (1) N11	RY*(4) H15	0.29
LP (1) N11	RY*(5) H15	0.10
LP (1) N11	RY*(7) H15	0.13
LP (1) N11	BD*(1) O14 - H15	13.55
From water to G isopropylamine		
BD (1) O14 - H15	RY*(1) H3	0.06
BD (1) O14 - H15	RY*(1) C5	0.05
BD (1) O14 - H15	RY*(1) N11	0.09
BD (1) O14 - H16	RY*(1) H3	0.14
LP (1) O14	BD*(1) C1 - H3	0.06
LP (2) O14	RY*(2) N11	0.09
LP (2) O14	BD*(1) C1 - H3	0.18

Table S34. NBO charges at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level for isolated T isopropylamine, water and TW complex.

	TW	T isopropylamine	Water
C1	-0.593	-0.583	
H2	0.204	0.200	
H3	0.194	0.195	
H4	0.221	0.203	
C5	-0.029	-0.030	
H6	0.158	0.147	
C7	-0.593	-0.583	
H8	0.204	0.200	
H9	0.194	0.195	
H10	0.221	0.203	
N11	-0.865	-0.849	
H12	0.360	0.350	
H13	0.360	0.350	
O14	-0.973		-0.922
H15	0.484		0.461
H16	0.452		0.461

Table S35. NBO stabilization energy contributions in the TW complex at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level.

Donor NBO	Acceptor NBO	$E(2)$/kcal·mol^{-1}
From T isopropylamine to water		
BD (1) C1 - H4	RY*(2) O14	0.07
BD (1) C1 - H4	RY*(3) O14	0.05
BD (1) C5 - H6	BD*(1) O14 - H15	0.09
BD (1) C7 - H10	RY*(2) O14	0.07
BD (1) C7 - H10	RY*(3) O14	0.05
LP (1) N11	RY*(7) O14	0.14
LP (1) N11	RY*(10) O14	0.06
LP (1) N11	RY*(4) H15	0.27
LP (1) N11	RY*(5) H15	0.19
LP (1) N11	RY*(7) H15	0.06
LP (1) N11	BD*(1) O14 - H15	13.28
From water to T isopropylamine		
BD (1) O14 - H15	RY*(1) N11	0.07
BD (1) O14 - H16	RY*(1) H4	0.12
BD (1) O14 - H16	RY*(1) H10	0.12
LP (1) O14	BD*(1) C1 - H4	0.10
LP (1) O14	BD*(1) C7 - H10	0.10
LP (2) O14	RY*(2) N11	0.09
LP (2) O14	BD*(1) C1 - H4	0.11
LP (2) O14	BD*(1) C7 - H10	0.11

Table S36. NBO charges at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level for isolated TT propylamine, water and TTW complex.

	TTW	TT propylamine	Water
C1	-0.394	-0.396	
H2	0.185	0.184	
H3	0.185	0.184	
C4	-0.194	-0.190	
H5	0.189	0.177	
H6	0.189	0.177	
N7	-0.853	-0.835	
H8	0.356	0.345	
H9	0.356	0.345	
C10	-0.582	-0.583	
H11	0.197	0.194	
H12	0.203	0.202	
H13	0.197	0.194	
O14	-0.968		-0.922
H15	0.450		0.461
H16	0.484		0.461

Table S37. NBO stabilization energy contributions in the TTW complex at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level.

Donor NBO	Acceptor NBO	$E(2)$/kcal·mol^{-1}
From TT propylamine to water		
LP (1) N7	RY*(2) O14	0.05
LP (1) N7	RY*(4) O14	0.11
LP (1) N7	RY*(7) O14	0.07
LP (1) N7	RY*(4) H16	0.33
LP (1) N7	RY*(5) H16	0.14
LP (1) N7	RY*(6) H16	0.09
LP (1) N7	BD*(1) O14 - H16	12.83
From water to TT propylamine		
BD (1) O14 - H15	RY*(2) C4	0.06
BD (1) O14 - H16	RY*(1) N7	0.09
BD (1) O14 - H16	RY*(8) N7	0.05
LP (2) O14	RY*(2) N7	0.13

Table S38. NBO charges at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level for isolated TG propylamine, water and TGW complex.

	TGW	TG propylamine	Water
C1	-0.396	-0.388	
H2	0.181	0.182	
H3	0.217	0.199	
C4	-0.187	-0.185	
H5	0.187	0.177	
H6	0.160	0.151	
N7	-0.858	-0.842	
H8	0.356	0.345	
H9	0.361	0.352	
C10	-0.578	-0.579	
H11	0.191	0.193	
H12	0.204	0.202	
H13	0.197	0.194	
O14	-0.972		-0.922
H15	0.484		0.461
H16	0.452		0.461

Table S39. NBO stabilization energy in the TGW complex at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level.

Donor NBO	Acceptor NBO	$E(2)$/kcal·mol^{-1}
From TG propylamine to water		
BD (1) C1 - H3	RY*(1) O14	0.29
BD (1) C4 - N7	RY*(1) H15	0.05
LP (1) N7	RY*(3) O14	0.08
LP (1) N7	RY*(4) O14	0.06
LP (1) N7	RY*(7) O14	0.05
LP (1) N7	RY*(8) O14	0.07
LP (1) N7	RY*(4) H15	0.28
LP (1) N7	RY*(5) H15	0.19
LP (1) N7	RY*(6) H15	0.06
LP (1) N7	BD*(1) O14 - H15	13.19
From water to TG propylamine		
BD (1) O14 - H16	RY*(1) H3	0.12
LP (1) O14	BD*(1) C1 - H3	0.12
LP (2) O14	RY*(2) N7	0.06
LP (2) O14	BD*(1) C1 - H3	0.19

Table S40. NBO charges at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level for isolated GT propylamine, water and GTW complex.

	GTW	GT propylamine	Water
C1	-0.397	-0.397	
H2	0.185	0.184	
H3	0.198	0.193	
C4	-0.195	-0.191	
H5	0.188	0.177	
H6	0.194	0.182	
N7	-0.856	-0.838	
H8	0.358	0.347	
H9	0.356	0.345	
C10	-0.587	-0.587	
H11	0.196	0.194	
H12	0.206	0.203	
H13	0.188	0.190	
O14	-0.968		-0.922
H15	0.484		0.461
H16	0.450		0.461

Table S41. NBO stabilization energy contributions in the GTW complex at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level.

Donor NBO	Acceptor NBO	$E(2)$/kcal·mol^{-1}
From GT propylamine to water		
LP (1) N7	RY*(2) O14	0.06
LP (1) N7	RY*(4) O14	0.14
LP (1) N7	RY*(7) O14	0.08
LP (1) N7	RY*(4) H15	0.34
LP (1) N7	RY*(5) H15	0.12
LP (1) N7	RY*(6) H15	0.09
LP (1) N7	BD*(1) O14 - H15	12.85
From water to GT propylamine		
BD (1) O14 - H15	RY*(1) N7	0.08
BD (1) O14 - H16	RY*(2) C4	0.07
LP (2) O14	RY*(2) N7	0.13

Table S42. NBO charges at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level for isolated GG' propylamine, water and GG'W complex.

	GG'W	GG' propylamine	Water
C1	-0.398	-0.388	
H2	0.217	0.197	
H3	0.194	0.191	
C4	-0.186	-0.186	
H5	0.159	0.150	
H6	0.189	0.183	
N7	-0.863	-0.847	
H8	0.361	0.353	
H9	0.359	0.347	
C10	-0.587	-0.586	
H11	0.189	0.191	
H12	0.208	0.203	
H13	0.194	0.193	
O14	-0.972		-0.922
H15	0.484		0.461
H16	0.451		0.461

Table S43. NBO stabilization energy contributions in the GG'W complex at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level.

Donor NBO	Acceptor NBO	$E(2)$/kcal·mol^{-1}
From GG' propylamine to water		
BD (1) C1 - H2	RY*(1) O14	0.28
BD (1) C1 - H2	BD*(1) O14 - H16	0.09
BD (1) C4 - H5	BD*(1) O14 - H15	0.07
LP (1) N7	RY*(3) O14	0.17
LP (1) N7	RY*(4) O14	0.06
LP (1) N7	RY*(7) O14	0.06
LP (1) N7	RY*(4) H15	0.29
LP (1) N7	RY*(5) H15	0.19
LP (1) N7	BD*(1) O14 - H15	13.39
From water to GG' propylamine		
BD (1) O14 - H15	RY*(1) N7	0.06
BD (1) O14 - H16	RY*(1) C1	0.05
BD (1) O14 - H16	RY*(1) H2	0.23
LP (1) O14	BD*(1) C1 - H2	0.23
LP (2) O14	BD*(1) C1 - H2	0.08

Table S44. NBO charges at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level for isolated GG propylamine, water and GGW complex.

	GGW	GG propylamine	Water
C1	-0.388	-0.386	
H2	0.183	0.183	
H3	0.197	0.193	
C4	-0.185	-0.186	
H5	0.185	0.177	
H6	0.164	0.156	
N7	-0.862	-0.848	
H8	0.355	0.345	
H9	0.361	0.353	
C10	-0.588	-0.584	
H11	0.198	0.191	
H12	0.197	0.196	
H13	0.217	0.212	
O14	-0.968		-0.922
H15	0.450		0.461
H16	0.484		0.461

Table S45. NBO stabilization energy contributions in the GGW complex at the B3LYP-D3(BJ)/maug-cc-pVTZ-*d*H level.

Donor NBO	Acceptor NBO	$E(2)$/kcal·mol^{-1}
From GG propylamine to water		
BD (1) C4 - H6	BD*(1) O14 - H16	0.09
BD (1) N7 - H9	BD*(1) O14 - H16	0.11
BD (1) C10 - H13	RY*(2) O14	0.14
BD (1) C10 - H13	BD*(1) O14 - H15	0.06
LP (1) N7	RY*(3) O14	0.06
LP (1) N7	RY*(4) O14	0.12
LP (1) N7	RY*(5) O14	0.06
LP (1) N7	RY*(10) O14	0.06
LP (1) N7	RY*(4) H16	0.27
LP (1) N7	RY*(5) H16	0.19
LP (1) N7	RY*(7) H16	0.05
LP (1) N7	BD*(1) O14 - H16	13.30
From water to GG propylamine		
BD (1) O14 - H15	RY*(1) C10	0.10
BD (1) O14 - H15	RY*(1) H13	0.10
BD (1) O14 - H16	RY*(2) N7	0.06
BD (1) O14 - H16	RY*(1) H13	0.09
BD (1) O14 - H16	BD*(1) C4 - N7	0.07
LP (1) O14	BD*(1) C4 - N7	0.06
LP (2) O14	BD*(1) C10 - H13	0.35

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