Supporting Information

The Reaction between the Bromine Atom and the Water Trimer: High Level Theoretical Studies

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Figure S1. Three pathways of the water trimer reaction Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ with the MPW1K/cc-pVTZ(-PP) method.

Table S1. Harmonic vibrational frequencies and zero-point energies for the stationary points of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction obtained at the CCSD(T)/cc-pVTZ(-PP) level of theory.

Table S2. Cartesian coordinates for optimized stationary points in pathway (a) of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction at the MPW1K/cc-pVTZ(-PP) level of theory.

Table S3. Cartesian coordinates for optimized stationary points in pathway (b) of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction at the MPW1K/cc-pVTZ(-PP) level of theory.

Table S4. Cartesian coordinates for optimized stationary points in pathway (c) of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction at the MPW1K/cc-pVTZ(-PP) level of theory.

Table S5. Cartesian coordinates for optimized stationary points in pathway (a) of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction at the CCSD(T)/cc-pVDZ(-PP) level of theory.

Table S6. Cartesian coordinates for optimized stationary points in pathway (a) of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction at the CCSD(T)/cc-pVTZ(-PP) level of theory.

Complete Gaussian 16 reference.

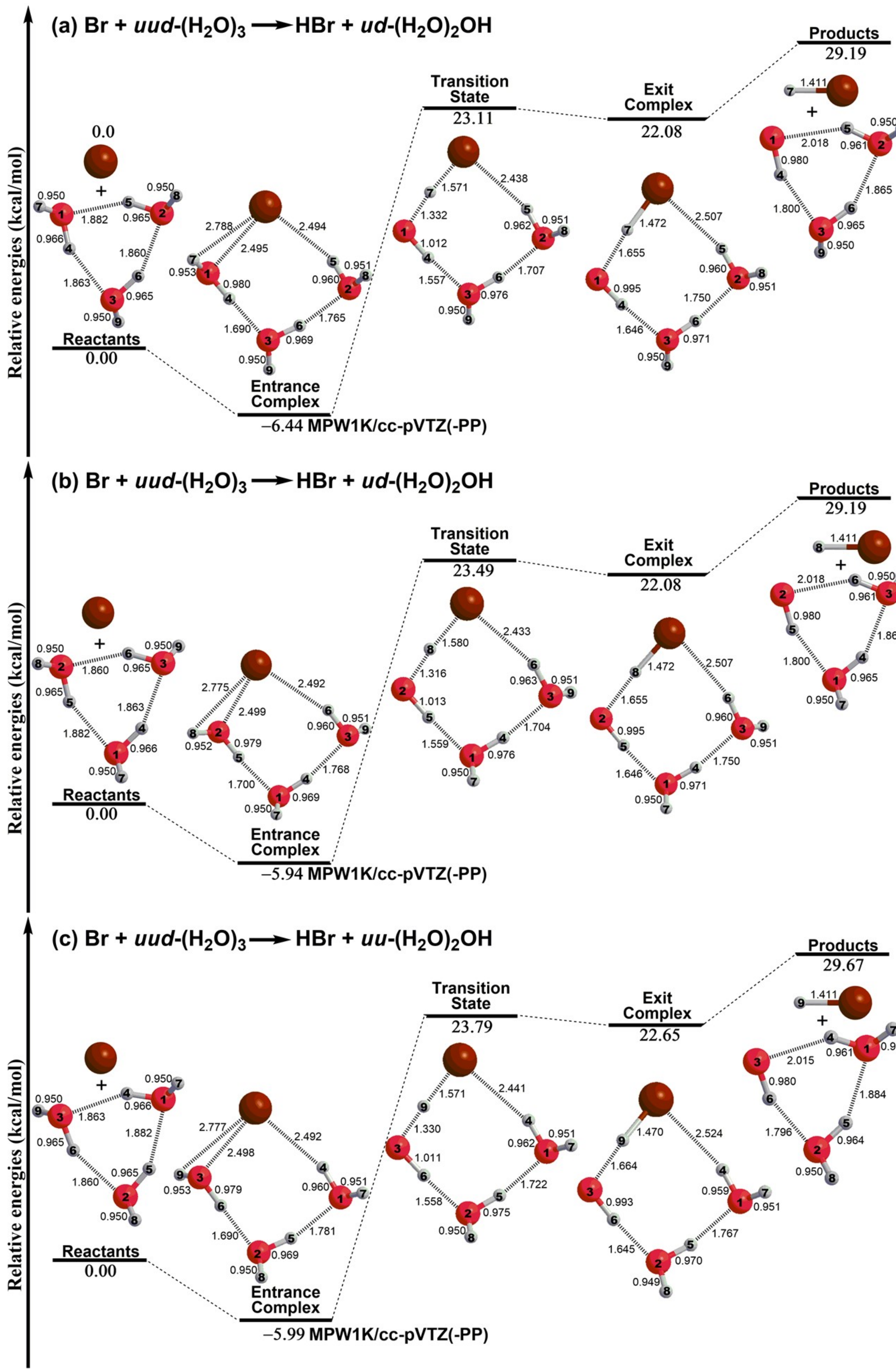

Figure S1 Three pathways of the water *trimer* reaction Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ with the MPW1K/cc-pVTZ(-PP) method. All bond distances were given in angstroms.

Table S1. Harmonic vibrational frequencies (in cm^{-1}) and zero-point energies (ZPE, in kcal/mol) for the stationary points of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction obtained at the CCSD(T)/cc-pVTZ(-PP) level of theory. Experimental results are also shown for comparison.

	ZPE	ΔZPE	Vibrational Frequencies
$(H_2O)_3$	46.46	0.00	188, 194, 202, 209, 228, 253, 360, 372, 471, 614, 689, 926, 1685, 1690, 1707, 3613, 3683, 3689, 3903, 3907, 3909
Entrance Complex	46.67	+0.21	30, 60, 114, 179, 195, 231, 249, 259, 270, 384, 403, 462, 516, 771, 933, 1672, 1687, 1704, 3473, 3620, 3760, 3866, 3900, 3901
Transition State	41.88	-4.58	650*i*, 33, 76, 122, 210, 229, 279, 298, 313, 446, 533, 595, 716, 768, 879, 1040, 1200, 1672, 1701, 3108, 3546, 3736, 3898, 3899
Exit Complex	42.90	-3.56	30, 54, 112, 145, 186, 227, 258, 278, 284, 402, 429, 491, 570, 629, 785, 954, 1673, 1699, 2275, 3357, 3602, 3766, 3901, 3906
$(H_2O)_2OH$	37.85	-4.82	163, 196, 211, 230, 252, 291, 375, 534, 557, 668, 916, 1667, 1687, 3498, 3675, 3737, 3908, 3911
HBr	3.79		2649
Experiment			
Bonded OH in $(H_2O)_3$			3533,[a] 3544/3529,[b] 3528,[c] 3531.8±1.2,[d] 3516.7±2.3[d]
Free OH in $(H_2O)_3$			3726,[a] 3717[b]
OH radical in $(H_2O)_2OH$			3365.2[c]
HBr			2649[e]

[a] In gas phase from Ref. 40. [b] In liquid He from Ref. 40. [c] In solid Ne from Ref. 41.
[d] From Ref. 42. [e] From Ref. 43.

Table S2. Cartesian coordinates (in Å) for optimized stationary points in pathway (a) of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction, as shown in Figure S1 and Figure 1, obtained at the MPW1K/cc-pVTZ(-PP) level of theory.

***uud*-$(H_2O)_3$, in Å**

0 1
O,0.2973653142,0.7447415337,-0.141269676
H,0.077234833,0.6208494016,0.7743246814
H,1.0474808588,0.162329631,-0.3158292958
O,2.1669429919,2.4961115369,-1.1813094804
H,1.3527864973,2.1637343813,-0.7840553349
H,2.4665837078,3.2024870649,-0.621560374
O,2.799396646,-0.1648077755,-0.8592898722
H,2.8681295377,0.777530389,-1.0579689104
H,2.9451677129,-0.6152350913,-1.6830653029

Enterance Complex, in Å

0 2
O,0.,0.,0.
H,0.,0.,0.95273
H,0.9420413669,0.,-0.2690898391
O,2.5612991915,2.7023031103,-1.4517156281
H,1.6240327565,2.8256357628,-1.28583154
H,3.0030011285,3.3374338231,-0.8985561049
O,2.5664811284,0.0839073585,-0.7272513288
H,2.7098127405,1.0002754046,-1.0093133002
H,2.8112325811,-0.4632228616,-1.4647412367
Br,-0.6400739007,2.3884131431,-0.3345165171

Transition State, in Å

0 2
O,-0.0079945675,0.000639368,0.0077430607
H,-0.0235312569,-0.0214881473,1.3390099644
H,0.9744428129,0.0102040335,-0.2336782595
O,3.3640106009,0.18077158,2.0800855446
H,2.5202357627,0.3344303274,2.5167958642
H,3.7433310499,-0.5750623575,2.5153651613
O,2.5172680833,-0.0004078387,-0.445786581
H,2.9423839062,0.0421824204,0.4313561352
H,2.9024138326,0.6886343865,-0.9752448215
Br,0.1063515158,0.365469899,2.855961228

Exit Complex, in Å

0 2
O,-0.0000095566,0.0000361683,-0.0000080045
H,-0.0000010887,-0.0000080782,1.6550964605
H,0.9667311645,0.0000114439,-0.2339059483
O,3.4199367259,0.0865454852,2.1834326869
H,2.5882117889,0.1856367704,2.6515566343
H,3.8285759769,-0.6880859324,2.5545280701
O,2.6046622209,-0.0111887119,-0.3990932744
H,3.0038029885,0.0211029738,0.485295672
H,3.0354091472,0.6561082071,-0.9203844877
Br,0.1287953346,0.0486221293,3.1202155551

***ud*-$(H_2O)_2OH$, in Å**

0 2
O,0.195142335,0.2083715694,-0.0484520945
H,-0.1019051642,-0.2141410142,0.7663837464
H,0.9710892866,-0.2623113864,-0.3294134349
O,-0.5553236426,-0.1081958361,2.57257675
H,-0.4169679725,0.8425889894,2.5653494144
H,-1.433486602,-0.2455128399,2.9084534231
O,0.1669055015,2.4540280054,1.4997418571
H,0.2774685537,1.8098320639,0.7689781584

HBr, in Å

0 1
H,0.,0.,0.04429631
Br,0.,0.,1.45570369

Table S3. Cartesian coordinates (in Å) for optimized stationary points in pathway (b) of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction, as shown in Figure S1 and Figure 1, obtained at the MPW1K/cc-pVTZ(-PP) level of theory.

***uud*-$(H_2O)_3$, in Å**
0 1
O,0.2973653142,0.7447415337,-0.141269676
H,0.077234833,0.6208494016,0.7743246814
H,1.0474808588,0.162329631,-0.3158292958
O,2.1669429919,2.4961115369,-1.1813094804
H,1.3527864973,2.1637343813,-0.7840553349
H,2.4665837078,3.2024870649,-0.621560374
O,2.799396646,-0.1648077755,-0.8592898722
H,2.8681295377,0.777530389,-1.0579689104
H,2.9451677129,-0.6152350913,-1.6830653029

Enterance Complex, in Å
0 2
O,0.,0.,0.
H,0.,0.,0.95249
H,0.939465273,0.,-0.2756147393
O,2.0393705943,2.3080664512,-2.4202047236
H,1.2707044413,2.5776846711,-1.9129855119
H,1.7234964373,2.1726226727,-3.3071646935
O,2.5098276792,0.088158139,-0.9209143136
H,2.4724966162,0.8470988327,-1.5229675561
H,3.264166991,0.2311249667,-0.3614210706
Br,-0.6109705486,2.4054471303,-0.2882979255

Transition State, in Å
0 2
O,-0.0168370579,-0.019497235,0.0076885358
H,-0.0344347814,-0.033424082,1.3236320501
H,0.9681890396,-0.0202068102,-0.2282032935
O,3.3478515588,0.3673868747,2.0730381011
H,2.5011144612,0.3110230149,2.5276997533
H,3.71810293,1.2057925008,2.3275265182
O,2.512932934,0.0137654187,-0.4365824712
H,2.9314250122,0.1532889926,0.4341895443
H,2.9444961645,-0.7327030024,-0.8363616762
Br,0.090176204,0.341008274,2.8535881986

Exit Complex, in Å
0 2
O,-0.0000191458,0.0001233627,-0.0000197984
H,0.0000253107,0.0000051227,1.6550791036
H,0.9667192275,0.000072593,-0.2339270247
O,3.4199854725,-0.086686389,2.1833738458
H,2.5882694352,-0.1858340464,2.6515022878
H,3.8285578398,0.687985139,2.5544606896
O,2.6046582845,0.0111010202,-0.3991405643
H,3.0038151448,-0.0212178921,0.4852400761
H,3.0353236986,-0.6562499502,-0.9204296835
Br,0.1288516163,-0.0487686229,3.1201921542

***ud*-$(H_2O)_2OH$, in Å**
0 2
O,-0.195142335,-0.2083715694,0.0484520945
H,0.1019051642,0.2141410142,-0.7663837464
H,-0.9710892866,0.2623113864,0.3294134349
O,0.5553236426,0.1081958361,-2.57257675
H,0.4169679725,-0.8425889894,-2.5653494144
H,1.433486602,0.2455128399,-2.9084534231
O,-0.1669055015,-2.4540280054,-1.4997418571
H,-0.2774685537,-1.8098320639,-0.7689781584

HBr, in Å
0 1
H,0.,0.,0.04429631
Br,0.,0.,1.45570369

Table S4. Cartesian coordinates (in Å) for optimized stationary points in pathway (c) of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction, as shown in Figure S1 and Figure 1, obtained at the MPW1K/cc-pVTZ(-PP) level of theory.

***uud*-$(H_2O)_3$, in Å**
0 1
O,0.2973653142,0.7447415337,-0.141269676
H,0.077234833,0.6208494016,0.7743246814
H,1.0474808588,0.162329631,-0.3158292958
O,2.1669429919,2.4961115369,-1.1813094804
H,1.3527864973,2.1637343813,-0.7840553349
H,2.4665837078,3.2024870649,-0.621560374
O,2.799396646,-0.1648077755,-0.8592898722
H,2.8681295377,0.777530389,-1.0579689104
H,2.9451677129,-0.6152350913,-1.6830653029

Enterance Complex, in Å
0 2
O,-0.0000048347,0.000007598,0.0000067431
H,0.0000414572,0.0000205896,-0.9528341333
H,-0.9422877026,-0.0000008979,0.2665215687
O,-2.502956267,-2.6605485834,1.614195852
H,-1.6449777833,-2.836873304,1.2216537652
H,-2.3985756566,-2.8540637794,2.5394168946
O,-2.5708069458,-0.088886083,0.7089414567
H,-2.7001301961,-0.9682584708,1.0944500084
H,-2.8914458054,0.5393240589,1.3451717992
Br,0.6269569946,-2.3998355545,0.2960995078

Transition State, in Å
0 2
O,0.0058006281,0.0410198652,-0.0065968858
H,0.0214640095,0.0367311741,-1.3369291241
H,-0.9755863068,0.0176252253,0.2348487006
O,-3.3674830018,-0.3185396919,-2.0723143964
H,-2.515915362,-0.2796618161,-2.5189137775
H,-3.7959965796,-1.0977857354,-2.4087364449
O,-2.5186257652,-0.0007170614,0.4496250137
H,-2.95910156,-0.1410031111,-0.4084231616
H,-2.8967419197,-0.6138927529,1.0689307122
Br,-0.0993567508,-0.3804010621,-2.8469206825

Exit Complex, in Å
0 2
O,-0.0000083938,0.0000134759,-0.0000029967
H,0.0000001778,-0.0000380393,-1.6644219592
H,-0.9664868283,0.0000171612,0.2284302444
O,-3.3958668721,-0.5221267957,-2.1928316405
H,-2.6000747105,-0.2731981781,-2.667202209
H,-3.586361681,-1.4097755666,-2.4762032247
O,-2.6064748057,0.0138928778,0.3534865256
H,-3.0181656127,-0.2097635264,-0.4953748026
H,-3.1107546521,-0.4072875745,1.0385966628
Br,-0.129575803,-0.033911973,-3.1278273047

***uu*-$(H_2O)_2OH$, in Å**
0 2
O,-0.0166968205,-0.1409349551,0.0723053137
H,-0.0592244187,0.262280938,-0.8021173879
H,-0.8472101174,0.0365237897,0.4973983907
O,0.2890771233,0.1159337507,-2.6477504019
H,0.5364717188,-0.8070186355,-2.5485533781
H,-0.3021017442,0.1553118022,-3.3900972282
O,0.7233299134,-2.3757716081,-1.2985360426
H,0.4734868336,-1.7309846333,-0.6038901238

HBr, in Å
0 1
H,0.,0.,0.04429631
Br,0.,0.,1.45570369

Table S5. Cartesian coordinates (in Bohr) for optimized stationary points in pathway (a) of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction, as shown in Figure 1, obtained at the CCSD(T)/cc-pVDZ(-PP) level of theory.

***uud*-$(H_2O)_3$, in Bohr**

0 1
O,-2.57756438,1.62979841,-0.11187444
H,-3.36036450,1.88148465,1.52036232
H,-2.23016354,-0.18763709,-0.10804916
O,2.70489029,1.39960166,-0.09845909
H,0.97088909,2.03720930,-0.19000541
H,3.30632743,2.08850654,1.48372189
O,-0.13029905,-3.03770681,0.12448214
H,1.26945573,-1.82835523,0.14995884
H,0.09104168,-3.85937417,-1.49346469

Enterance Complex, in Bohr

0 2
O,0.69284309,-3.55737554,-0.32962020
H,0.39028600,-4.28755878,1.32333849
H,2.40028644,-2.82937928,-0.13952655
O,3.61973610,3.54232321,-0.23746869
H,1.88677064,3.07414746,-0.62373585
H,3.43374137,4.42575893,1.35387835
O,5.33967585,-1.38597339,0.31289872
H,4.95549956,0.42300665,0.20180501
H,6.44585630,-1.65239495,-1.11803995
Br -2.20547125,0.29476458,0.03877709

Transition State, in Bohr

0 2
O,1.28192613,3.85247825,-0.16307325
H,-0.41105951,2.10144715,-0.60316335
H,2.90256388,2.81833625,-0.02067603
O,3.24071500,-3.70047061,-0.03828466
H,1.49100649,-3.21317279,0.25973093
H,3.14921288,-4.51182994,-1.67559153
O,5.31465520,1.01063117,0.06774452
H,4.74466824,-0.75941716,-0.05408348
H,6.24378299,1.04620892,1.64230616
Br -2.22519492,-0.20347837,0.03284591

Exit Complex, in Bohr

0 2
O,2.14017185,-4.02235737,-0.02190925
H,-0.51603406,-1.86233884,0.03701665
H,3.63036490,-2.85668391,0.02727305
O,3.00631890,3.90245684,-0.10709834
H,1.30395743,3.29738634,-0.43253366
H,2.82139984,4.73455924,1.51168413
O,5.84637805,-0.50017221,0.12092972
H,4.96994558,1.13278355,0.08002013
H,6.99757606,-0.39032664,-1.29387093
Br -2.47328459,0.07388520,0.00253637

***ud*-$(H_2O)_2OH$, in Bohr**

0 2
O,2.08916373,-2.41146961,-0.00624496
O,-3.04310421,-0.47601863,-0.10960786
O,1.12498437,2.72389333,0.11737253
H,2.22639939,-0.53836559,0.04356213
H,-1.66746174,-1.70040548,-0.16012168
H,-3.89854951,-0.89545470,1.45035572
H,-0.61727423,2.10478569,0.11022133
H,1.24229538,3.62581003,-1.46813654

HBr, in Bohr

0 1
H,-0.00000000,0.00000000,2.66119360
Br 0.00000000,0.00000000,-0.03398472

Table S6. Cartesian coordinates (in Bohr) for optimized stationary points in pathway (a) of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction, as shown in Figure 1, obtained at the CCSD(T)/cc-pVTZ(-PP) level of theory.

***uud*-$(H_2O)_3$, in Bohr**
0 1
O,-2.65261793,1.50032150,-0.10633497
H,-3.73963216,1.75797437,1.32120417
H,-2.24923826,-0.29155296,-0.06591336
O,2.62996378,1.52947819,-0.09357003
H,0.89232610,2.12158252,-0.04928732
H,3.43796005,2.34824833,1.30720704
O,0.02122954,-3.03590337,0.12076531
H,1.37796825,-1.79759531,0.10412966
H,0.30322555,-4.04178710,-1.36133603

Enterance Complex, in Bohr
0 2
O,0.77242142,-3.58041303,-0.15546373
H,0.48695690,-4.24733869,1.51143234
H,2.46416707,-2.82777252,-0.06567435
O,3.44574308,3.56510462,-0.12490149
H,1.70826003,3.03203793,-0.30837915
H,3.44491038,4.56381675,1.39088010
O,5.38109115,-1.27883136,0.15307129
H,4.95495272,0.51093413,0.08537282
H,6.49294888,-1.54579410,-1.25467034
Br -2.19523720,0.26885760,0.00844494

Transition State, in Bohr
0 2
O,1.38197776,3.80736748,-0.27151537
H,-0.43072483,1.98202457,-0.67552527
H,2.96897280,2.78642833,-0.04783137
O,3.14332645,-3.69212847,-0.11637107
H,1.41112340,-3.12978714,0.05549824
H,3.16635067,-4.60650174,-1.68424903
O,5.42476784,0.92092893,0.17177928
H,4.82389637,-0.82136327,0.03444264
H,6.36167376,0.98236847,1.72369660
Br -2.25036490,-0.17416261,0.05138516

Exit Complex, in Bohr
0 2
O,2.18561293,-3.97486798,0.02638329
H,-0.49051987,-1.84920807,0.06583094
H,3.64707832,-2.79701980,0.02694406
O,2.88248970,3.85719825,-0.07057802
H,1.20373716,3.16535719,-0.26330114
H,2.78873506,4.82661325,1.46138176
O,5.86092102,-0.42314941,0.06751678
H,4.97587578,1.19185081,0.01819207
H,7.09509278,-0.33189152,-1.25719329
Br -2.46050799,0.05590265,-0.00538904

***ud*-$(H_2O)_2OH$, in Bohr**
0 2
O,2.05865745,-2.44944340,-0.00663349
O,-3.03637394,-0.43704961,-0.10463192
O,1.16039085,2.70740037,0.11271341
H,2.23137593,-0.59517469,-0.00805151
H,-1.71388891,-1.69973794,-0.03697262
H,-4.16675174,-0.87392300,1.24386732
H,-0.59219356,2.16460567,0.06392521
H,1.34228361,3.84656004,-1.28574921

HBr, in Bohr
0 1
H,-0.00000000,0.00000000,2.64652073
Br 0.00000000,0.00000000,-0.03379734

Complete Gaussian 16 reference

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