Supporting Information (22 pages)

Electronic Structures and Spin Density Distributions of BrO_2 and $(HO)_2BrO$ Radicals. Mechanisms for Avoidance of Hypervalency and for Spin Delocalization and Spin Polarization

Rainer Glaser* and Cory Camasta

Department of Chemistry, University of Missouri, Columbia, Missouri 65211

glaserr@missouri.edu

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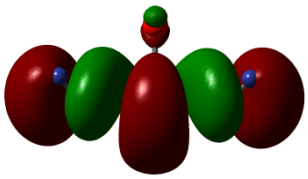
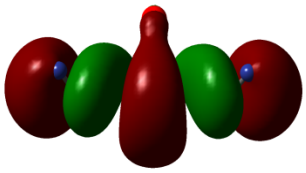
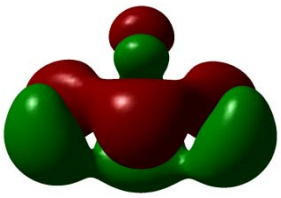
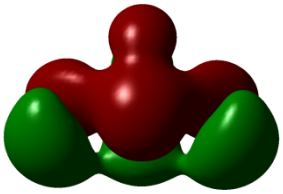
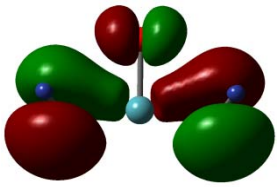
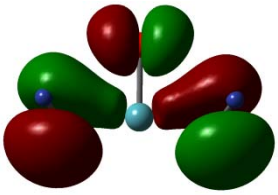
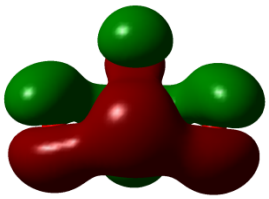
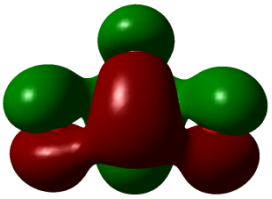
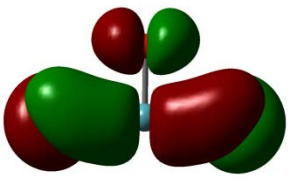
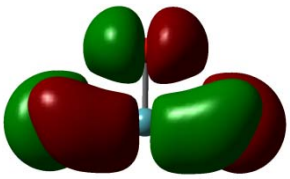
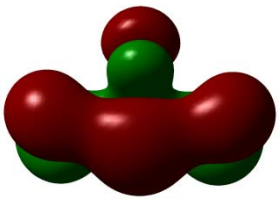
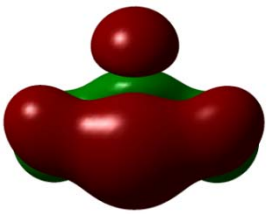
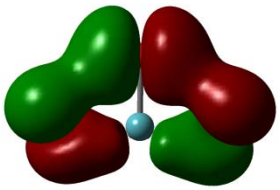
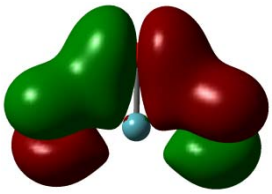
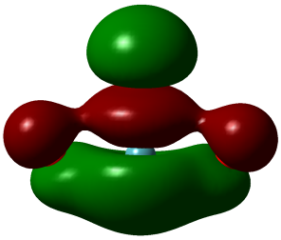
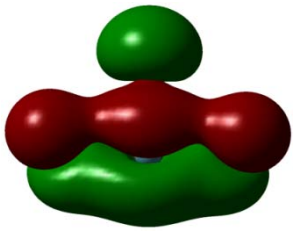
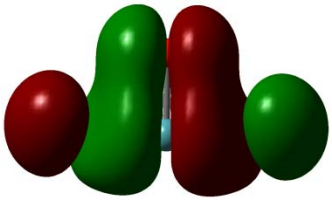
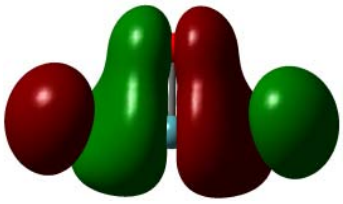
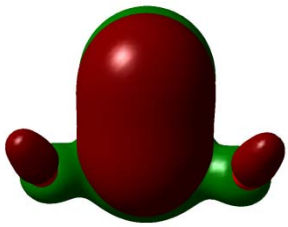
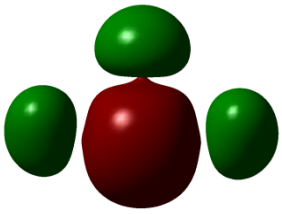
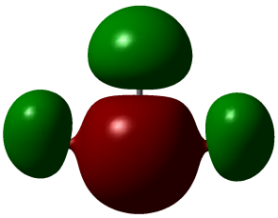
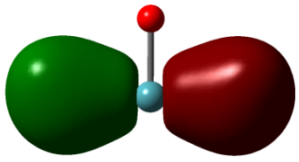
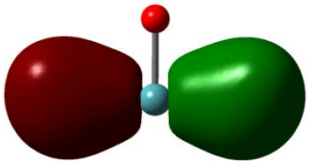
ASMO31 σ*			BSMO30 σ*
ASMO30 “$\alpha\pi_4$”			BSMO29 “$\beta\pi_3$”
ASMO29			BSMO28
ASMO28			BSMO27
ASMO27 “$\alpha\pi_3$”			BSMO26 “$\beta\pi_2$”
ASMO26 “$\alpha\pi_2$”			<u>BSMO24</u> “$\beta\pi_1$”

ASMO25			BSMO25
ASMO24			BSMO23
ASMO23			BSMO22
ASMO22 “$\alpha\pi_1$”			
ASMO21			BSMO21
ASMO20			BSMO19

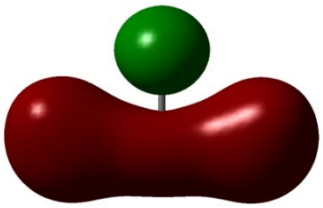
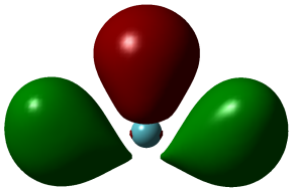
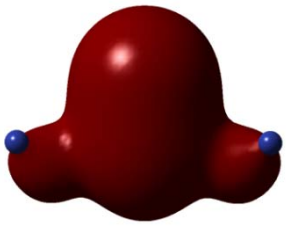
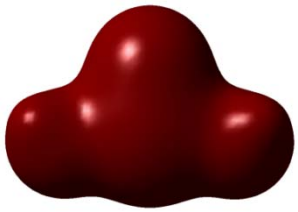
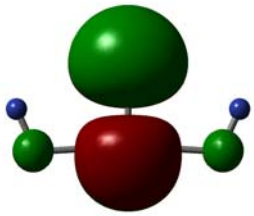
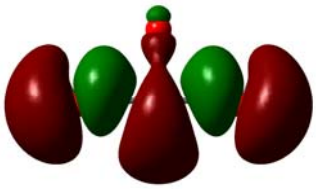
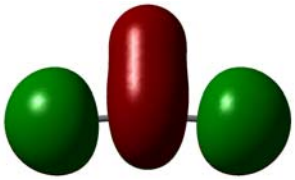
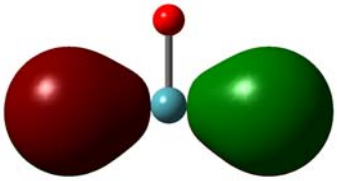
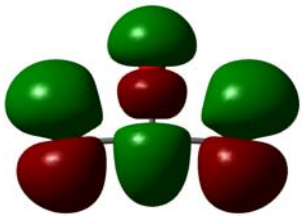
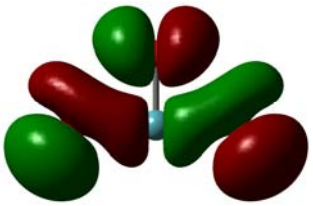
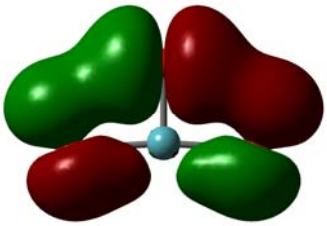
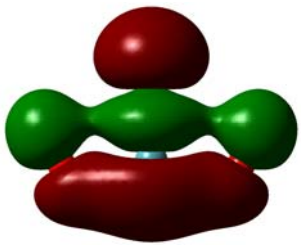
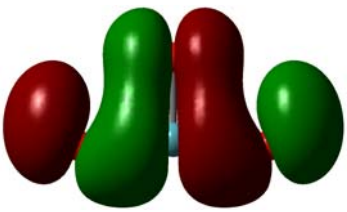
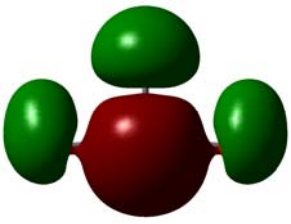
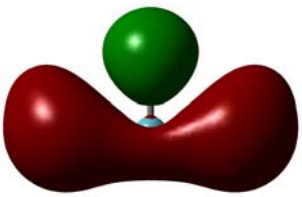
ASMO19			BSMO20
ASMO18			BSMO18

Figure S9b. Molecular spin orbitals of C_2-symmetric radical **2a**.

MO31 π_4			MO30 σ^*
MO29 π_3			MO28 π_2
MO26			MO27
MO25 π_1			MO24
MO23			MO22
MO21			MO20

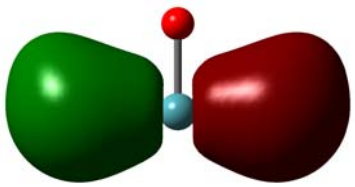
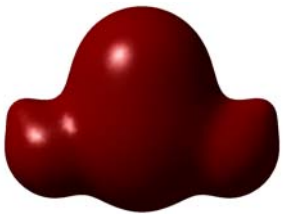
MO19			MO18

Figure S9b. ROHF valence-MOs of C_{2v}-symmetric radical **2c**.

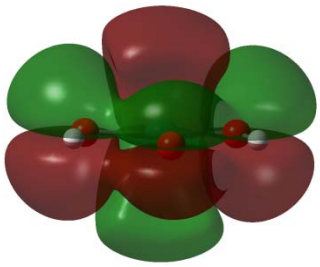
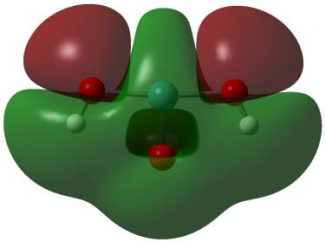
ASMO30 $\alpha\pi_4$			ASMO26

Figure S10. Selected α-spin molecular orbitals of C_{2v}-symmetric radical **2c** drawn with density value 0.002 e Å^3.

Table S1. Total Energies and Thermochemical Parameters Computed at the MP2 Level and QCISD Level Energies

Parameter	*E*(MP2)	*VZPE*	*TE*	*S*	ν_1	ν_2	*E*(Q1)	*E*(Q2)	*E*(Q3)
1, C_{2v}	-2722.849310	2.92	5.03	65.95	319	850	-2722.816577	-2722.996148	-2723.035496
H_2O, C_{2v}	-76.253654	13.72	15.50	45.03	1738	3861	-76.262196	-76.347474	-76.355187
HO, $C_{\infty v}$	-75.576720	5.43	6.91	42.55	3796		-75.568071	-75.652176	-75.657319
2a, C_s	-2799.044895	18.04	21.69	77.34	195	225	-2799.044321	-2799.302914	-2799.346003
2b, C_2	-2799.044680	18.03	21.68	75.99	197	208	-2799.042776		
2c, C_{2v}	-2799.044274	17.84	21.62	77.00	163	197	-2799.047673	-2799.310062	-2799.353146
2d, C_{2v}	-2799.028945	17.34	20.39	72.59	-264	-255	-2799.031087		
2e, C_s	-2799.036393	17.41	20.44	73.83	-236	-142	-2799.040939		
3a, C_1	-2799.044510	19.00	22.35	75.52	189	255	-2799.040711		
3b, C_1	-2799.043760	19.08	22.47	75.75	204	216	-2799.040426		
3c, C_s	-2799.043066	18.69	21.79	74.07	-216	203	-2799.041063		
3d, C_s	-2799.040882	18.55	21.65	73.97	-297	201	-2799.039635		
3e, C_s	-2799.032175	18.84	21.90	73.83	-291	201	-2799.030969		
4, C_1	-2723.463590	10.01	12.47	67.05	245	401	-2723.447632	-2723.636685	-2723.672410
5, C_s	-2798.476742	12.08	15.27	74.75	47	315	-2798.447649	-2798.704555	-2798.754137
6a, C_s	-2798.805023	18.90	23.09	82.42	76	97	-2798.755629	-2798.997388	-2799.054638
6b, C_s	-2798.804348	18.69	22.47	79.59	-92	70	-2798.754688		
6c, C_1	-2798.807232	18.85	22.92	80.71	92	112	-2798.750512		
7a, C_1	-2798.757572	19.23	22.50	73.38	230	269	-2798.735320	-2798.994632	-2799.042373
7b, C_s	-2798.758096	19.04	22.42	74.45	133	254	-2798.736361	-2798.995002	-2799.042724
7c, C_1	-2798.759293	19.28	22.58	73.56	209	269	-2798.736850	-2798.994216	-2799.042399
7e, C_s	-2798.754604	19.08	22.55	75.76	69	274	-2798.732346		
8a, C_s	-2798.633489	18.58	21.55	71.51	236	334	-2798.606356		
8b, C_s	-2798.620477	18.00	20.68	69.81	-421	318	-2798.594518		
H_3O^+, C_{3v}	-76.536732	22.27	24.10	48.39	761	1790	-76.546294	-76.623050	-76.629886
1,[b] C_{2v}	-2722.867058	2.89	5.00	64.21	315	843	-2722.833765	-2722.996226	-2723.035611
5,[b] C_s	-2798.513746	12.05	15.18	73.09	124	308	-2798.482682	-2798.703876	-2798.753953
HO^-,[b] $C_{\infty v}$	-75.659033	5.48	6.67	41.16	3836		-75.659272	-75.705020	-75.714417
9,[b] C_1	-2798.589649	10.10	13.72	78.04	109	219	-2798.555543	-2798.762445	-2798.814159

(a) Unless otherwise indicated, MP2 data are computed at MP2(full)/6-311G* (all neutral molecules and cations), Q1 := QCISD(full)/6-311G*//MP2, Q2 := QCISD(full)/6-311++G(2df,2pd)//MP2, and Q3 := QCISD(full,T)/6-311++G(2df,2pd)//MP2.
(b) MP2 data computed at MP2(full)/6-311++G** (for all anions and selected neutral species). In these cases, Q1 refers to QCISD(full)/6-311++G**//MP2.

Table S2. Total Energies and Thermochemical Parameters Computed at the SMD(MP2) Level

Parameter	*E*(SMD)	*VZPE*	*TE*	*S*	ν_1	ν_2
1, C_{2v}	-2722.855204	2.87	4.98	64.62	318	839
H_2O, C_{2v}	-76.270007	13.61	15.39	45.06	1707	3853
HO, $C_{\infty v}$	-75.587227	5.43	6.91	42.55	3796	
2a, C_s	-2799.060254	18.03	21.69	77.42	179	217
2c, C_{2v}	-2799.056463	17.04	20.20	73.34	-275	-227
4, C_1	-2723.475671	10.08	12.49	66.79	253	454
5, C_s	-2798.487046	11.99	15.18	74.66	49	317
6a, C_s	-2798.896667	19.57	23.30	77.62	144	167
6b, C_s	-2798.894285	18.79	22.47	78.02	-399	110
6c, C_1	-2798.895705	18.85	22.87	79.61	119	153
7a, C_1	-2798.858446	19.08	22.40	73.75	191	260
7b, C_s	-2798.859690	19.35	22.47	72.30	273	290
7c, C_1	-2798.858459	19.15	22.41	73.24	249	274
7e, C_s	-2798.855918	19.52	22.68	72.51	277	284
H_3O^+, C_{3v}	-76.692168	22.81	24.60	48.21	1096	1794
1,[b] C_{2v}	-2722.873414	2.83	4.95	64.68	315	826
5,[b] C_s	-2798.523234	11.97	15.08	72.78	142	315
HO^-,[b] $C_{\infty v}$	-75.809344	5.55	7.03	41.15	3884	
9,[b] C_1	-2798.690780	9.91	13.63	79.13	147	157

(a) Unless otherwise indicated, SMD(MP2) data are computed at SMD(MP2(full)/6-311G* level (all neutral molecules and cations).

(b) SMD(MP2) data computed at SMD(MP2(full)/6-311++G**) level (for all anions and selected neutral species).

Cartesian Coordinates of Protonated Bromic Acid Isomers 6 – 8, MP2 Level

H_3O^+

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.061760	0.000000
2	1	0	0.472740	-0.164696	0.818808
3	1	0	0.472740	-0.164696	-0.818808
4	1	0	-0.945480	-0.164687	0.000000

$HBrO_3$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.132814	0.000070	-0.266328
2	8	0	-1.693731	-0.002210	0.122457
3	8	0	0.665479	1.326413	0.452915
4	8	0	0.669352	-1.324475	0.453286
5	1	0	-1.777290	-0.000253	1.092233

6a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.363592	0.000018	-0.265999
2	1	0	-2.712216	0.776234	0.138670
3	8	0	0.619237	-1.378263	0.531779
4	8	0	0.618672	1.378457	0.531671
5	8	0	-2.150566	-0.000213	0.065745
6	1	0	-2.712240	-0.776729	0.137739

6b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.338423	0.000001	-0.260358
2	1	0	-2.876668	-0.000422	-0.581639
3	8	0	0.702118	-1.378037	0.498594
4	8	0	0.701870	1.378145	0.498515
5	8	0	-2.195473	-0.000095	0.095903
6	1	0	-2.636247	0.000290	0.950065

6c

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-0.259791	-0.108833	-0.000004
2	1	0	2.902070	0.331604	-0.000016
3	8	0	-1.872792	-0.519215	0.000008
4	8	0	0.042883	1.487524	0.000006
5	8	0	2.259668	-0.382724	0.000001
6	1	0	2.752532	-1.207127	0.000037

7a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-0.045585	-0.123377	-0.297086
2	1	0	-0.552464	2.155326	-0.092462
3	8	0	-0.810549	1.330255	0.369282
4	8	0	-0.742153	-1.236297	0.551916
5	8	0	1.606773	0.162472	0.238450
6	1	0	1.715364	0.111448	1.213306

7b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.000038	0.108945	-0.292402
2	1	0	1.634570	-0.708330	1.161224
3	8	0	1.358653	-0.876952	0.234567
4	8	0	-0.000749	1.455449	0.519966
5	8	0	-1.358183	-0.877781	0.234404
6	1	0	-1.633659	-0.710473	1.161358

7c

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-0.165105	-0.051472	-0.289420
2	8	0	-1.446183	-0.101727	0.615662
3	8	0	1.082070	-1.153447	0.236603
4	8	0	0.854254	1.319872	0.247368
5	1	0	0.372704	2.172363	0.240108
6	1	0	1.484847	-0.888434	1.092531

7e

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-0.164131	-0.000314	-0.289685
2	8	0	-1.462783	-0.001526	0.594305
3	8	0	1.007156	-1.179017	0.313211
4	8	0	1.004248	1.181712	0.312339
5	1	0	0.674225	2.096935	0.191323
6	1	0	0.681380	-2.095306	0.188815

8a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.101758	0.000030	0.139549
2	1	0	-0.143441	-0.000181	1.613069
3	8	0	0.727421	1.369379	-0.295978
4	8	0	0.728847	-1.368650	-0.296030
5	8	0	-1.643129	-0.000747	-0.091168
6	1	0	-1.923194	-0.000734	-1.031855

8b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.107540	0.000002	0.144977
2	1	0	0.003654	-0.000042	1.643084
3	8	0	0.701002	1.376493	-0.298895
4	8	0	0.701080	-1.376450	-0.298905
5	8	0	-1.594881	-0.000036	-0.298367
6	1	0	-2.225168	-0.000072	0.452056

Cartesian Coordinates of 1, 2a & 2c, 4, 5 and 6 & 7, SMD(MP2) Level

BrO_2, 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.000000	0.000000	0.275739
2	8	0	0.000000	1.404957	-0.603179
3	8	0	0.000000	-1.404957	-0.603179

H_2O

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.116030
2	1	0	0.000000	0.762476	-0.464118
3	1	0	0.000000	-0.762476	-0.464118

H_3O^+

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.087644	0.000000
2	1	0	0.458289	-0.235191	0.792507
3	1	0	0.458289	-0.235191	-0.792507
4	1	0	-0.916577	-0.230772	0.000000

HO

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.107470
2	1	0	0.000000	0.000000	-0.859762

$(HO)_2BrO$, 2a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.930714	-0.264306	-0.083338
2	1	0	-2.297516	0.051499	0.755105
3	35	0	-0.000003	-0.223550	0.002766
4	8	0	-1.930716	-0.264281	-0.083344
5	8	0	0.000015	1.493732	-0.034193
6	1	0	2.297510	0.051572	0.755074

$(HO)_2BrO$, 2c

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.000000	0.000000	0.223834
2	8	0	0.000000	0.000000	-1.433428
3	8	0	0.000000	1.923657	0.300720
4	8	0	0.000000	-1.923657	0.300720
5	1	0	0.000000	2.304887	-0.589146
6	1	0	0.000000	-2.304887	-0.589146

$HBrO_2$, 4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.565960	0.475199	-0.118283
2	1	0	-1.817424	0.782547	0.768738
3	35	0	0.107275	-0.315742	0.007509
4	8	0	1.323811	0.808353	-0.010659

$HBrO_3$, 5

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.124434	0.000023	-0.268452
2	8	0	-1.674555	-0.000840	0.131538
3	8	0	0.676196	1.321675	0.452561
4	8	0	0.677672	-1.320923	0.452705
5	1	0	-1.789697	-0.000094	1.101384

6a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.323202	0.000122	-0.269629
2	1	0	-2.516860	0.776195	-0.102555
3	8	0	0.611229	-1.363206	0.522779
4	8	0	0.608184	1.364261	0.522461
5	8	0	-2.004145	-0.001382	0.160318
6	1	0	-2.517340	-0.777848	-0.104883

6b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.296483	0.000000	-0.260221
2	1	0	-2.726897	-0.000042	-0.568250
3	8	0	0.699765	-1.360693	0.486412
4	8	0	0.699753	1.360699	0.486404
5	8	0	-2.046164	-0.000004	0.114532
6	1	0	-2.476827	0.000039	0.977201

6c

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.236176	-0.111362	-0.000052
2	1	0	-2.834185	0.307074	0.001190
3	8	0	1.865800	-0.497992	0.000152
4	8	0	-0.053281	1.483545	0.000045
5	8	0	-2.163287	-0.383325	-0.000244
6	1	0	-2.625816	-1.227229	0.001016

7a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-0.038334	-0.117225	-0.293446
2	1	0	-0.533479	2.159095	-0.038265
3	8	0	-0.833626	1.307231	0.355265
4	8	0	-0.747852	-1.241053	0.540351
5	8	0	1.599629	0.152795	0.240676
6	1	0	1.729954	0.192017	1.218545

7b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.000001	0.106471	-0.288253
2	1	0	1.582383	-0.797441	1.182723
3	8	0	1.357895	-0.863679	0.223752
4	8	0	0.000096	1.460740	0.517906
5	8	0	-1.357994	-0.863523	0.223764
6	1	0	-1.582400	-0.797357	1.182759

7c

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-0.150460	-0.051727	-0.288700
2	8	0	-1.440994	-0.201632	0.598388
3	8	0	1.134872	-1.098681	0.226286
4	8	0	0.751155	1.364134	0.265777
5	1	0	0.230850	2.199618	0.249561
6	1	0	1.474985	-0.899738	1.131328

7e

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-0.155188	-0.014296	-0.289445
2	8	0	-1.459925	-0.084003	0.586349
3	8	0	1.055942	-1.115381	0.341474
4	8	0	0.904539	1.249242	0.310585
5	1	0	0.535127	2.149176	0.154756
6	1	0	0.892004	-2.047659	0.068551

Cartesian Coordinates of 1, 5, 9 and OH^- with 6-311++G, MP2 Level**

Bromine Dioxide **1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.000000	0.000000	0.273370
2	8	0	0.000000	1.410912	-0.597998
3	8	0	0.000000	-1.410912	-0.597998

Bromic Acid **5**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.134094	0.000018	-0.267905
2	8	0	-1.710506	-0.000587	0.124634
3	8	0	0.671294	1.325837	0.455093
4	8	0	0.672343	-1.325313	0.455191
5	1	0	-1.758344	-0.000108	1.097345

Radical Anion **9**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-0.147628	-0.142420	-0.000068
2	8	0	0.033251	1.546785	-0.000002
3	8	0	-1.844710	-0.452544	0.000193
4	8	0	2.115261	-0.500742	-0.000031
5	1	0	2.736568	0.236707	0.001104

HO^-

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.107175
2	1	0	0.000000	0.000000	-0.857398

Cartesian Coordinates of 1, 5, 9 and OH^- with 6-311++G, SMD(MP2) Level**

Bromine Dioxide **1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.000000	0.000000	0.279907
2	8	0	0.000000	1.399712	-0.612297
3	8	0	0.000000	-1.399712	-0.612297

Bromic Acid **5**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-0.124874	0.000012	-0.271109
2	8	0	1.685174	-0.000530	0.134844
3	8	0	-0.680257	-1.320717	0.456316
4	8	0	-0.679336	1.321192	0.456213
5	1	0	1.765937	0.000032	1.109824

Radical Anion **9**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-0.183113	-0.150232	0.000003
2	8	0	0.096436	1.504322	-0.000007
3	8	0	-1.868623	-0.393253	-0.000004
4	8	0	2.244673	-0.501607	-0.000014
5	1	0	2.629084	0.382421	0.000082

HO^-

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.106844
2	1	0	0.000000	0.000000	-0.854755

Results of QCISD(full,T)/6-311++G(2df,2pd)//MP2(full)/6-311G* Computations

Bromine Dioxide **1**

```
 1\1\GINC-D17B-10\SP\UQCISD(T)-Full\6-311++G(2df,2pd)\Br1O2(2)\RGLASER\
 03-Apr-2013\0\\# QCISD(full,T)/6-311++G(2df,2pd) 5d 7f\\single point e
 nergy of BrO2 @ QCISD(full,T)/6-311++G(2df,2pd)//MP2(full)/6-311G*\\0,
 2\O,0,0.038236268,0.,0.0796702733\Br,0,-0.0074308498,0.,1.734839071\O,
 0,1.4414377682,0.,2.5379467957\\Version=EM64L-G09RevB.01\State=2-A"\HF
 =-2721.9024634\MP2=-2723.0308713\MP3=-2722.9626856\MP4D=-2722.9969108\
 MP4DQ=-2722.978219\PUHF=-2721.9112376\PMP2-0=-2723.0366546\PMP3-0=-272
 2.9653066\MP4SDQ=-2723.0002445\QCISD=-2722.9961484\QCISD(T)=-2723.0354
 961\S2=0.791722\S2-1=0.762815\S2A=0.751143\RMSD=8.094e-09\PG=CS [SG(Br
 1O2)]\\@

 S**2, projected HF & approx projected MPn energies after annihilation of
 unwanted spin states (see manual for definitions):
 spins       (S**2,0) (S**2,1)    PUHF        PMP2        PMP3        PMP4
 annihilated
 s+1         0.74932  0.75026-2721.911238-2723.036655-2722.965307
 s+1,s+2     0.75000  0.75000-2721.911122-2723.036549-2722.965216
 s+1 to s+3  0.75000  0.75000-2721.911123-2723.036549-2722.965215
 s+1 to s+4  0.75000  0.75000-2721.911123-2723.036549-2722.965215
 s+1 to s+5  0.75000  0.75000-2721.911123
 s+1 to s+6  0.75000  0.75000-2721.911123
```

$(HO)_2BrO$-Radical **2a**

```
 N-N= 3.044381546883D+02 E-N=-1.092966537355D+04  KE= 4.194650187978D+03
 1\1\GINC-C24-37\SP\UQCISD(T)-Full\6-311++G(2df,2pd)\Br1H2O3(2)\RGLASER
 \07-Apr-2013\0\\# QCISD(full,T,maxcyc=200)/6-311++G(2df,2pd) 5d 7f\\si
 ngle point energy of Rad2a @ QCISD(full,T)/6-311++G(2df,2pd)//MP2(full
 )/6-311G*\\0,2\O,0,0.0519762341,0.152367508,0.0657120629\H,0,0.2022217
 975,-0.2531623172,4.363593305\Br,0,0.3733554992,0.11522859,1.961476752
 4\O,0,0.8932497616,0.1375798177,3.8128610843\O,0,0.1352573659,-1.58310
 45276,2.0080822166\H,0,-0.8090294983,-0.2349170609,-0.1397391813\\Vers
 ion=EM64L-G09RevB.01\State=2-A\HF=-2797.9289839\MP2=-2799.3090505\MP3=
 -2799.2657132\MP4D=-2799.297898\MP4DQ=-2799.2779256\PUHF=-2797.934471\
 PMP2-0=-2799.3130131\PMP3-0=-2799.2684573\MP4SDQ=-2799.297334\QCISD=
-2799.302914\QCISD(T)=-2799.346003\S2=0.773983\S2-1=0.760517\S2A=0.75042
 3\RMSD=9.094e-09\PG=C01 [X(Br1H2O3)]\\@

 S**2, projected HF & approx projected MPn energies after annihilation of
 unwanted spin states (see manual for definitions):

 spins       (S**2,0) (S**2,1)    PUHF        PMP2        PMP3        PMP4
 annihilated
 s+1         0.74975  0.75004-2797.934471-2799.313013-2799.268457
 s+1,s+2     0.75000  0.75000-2797.934423-2799.312969-2799.268417
 s+1 to s+3  0.75000  0.75000-2797.934424-2799.312969-2799.268417
 s+1 to s+4  0.75000  0.75000-2797.934424-2799.312970-2799.268418
 s+1 to s+5  0.75000  0.75000-2797.934424
 s+1 to s+6  0.75000  0.75000-2797.934424
```

$(HO)_2BrO$-Radical **2c**

```
 1\1\GINC-D19-02\SP\UQCISD(T)-Full\6-311++G(2df,2pd)\Br1H2O3(2)\RGLASER
 \03-Apr-2013\0\\# QCISD(full,T)/6-311++G(2df,2pd) 5d 7f\\single point
```

```
energy of Rad2c @ QCISD(full,T)/6-311++G(2df,2pd)//MP2(full)/6-311G*\\
0,2\Br,0,0.,0.,0.1140092855\O,0,0.,0.,1.743176778\O,0,1.9014227205,0.,
-0.0030260602\O,0,-1.9014227205,0.,-0.0030260602\H,0,2.3067531727,0.,0
.8741256492\H,0,-2.3067531727,0.,0.8741256492\\Version=EM64L-G09RevB.0
1\State=2-B1\HF=-2797.9255567\MP2=-2799.3136996\MP3=-2799.2673334\MP4D
=-2799.2993212\MP4DQ=-2799.2798347\PUHF=-2797.9321071\PMP2-0=-2799.318
0798\PMP3-0=-2799.2700949\MP4SDQ=-2799.3005363\QCISD=-2799.3100622\QCI
SD(T)=-2799.3531463\S2=0.776303\S2-1=0.758695\S2A=0.750453\RMSD=5.262e
-09\PG=C02V [C2(O1Br1),SGV(H2O2)]\\@

S**2, projected HF & approx projected MPn energies after annihilation of
unwanted spin states (see manual for definitions):
spins       (S**2,0) (S**2,1)    PUHF        PMP2        PMP3        PMP4
annihilated
s+1         0.74973  0.75008-2797.932107-2799.318080-2799.270095
s+1,s+2     0.75000  0.75000-2797.932053-2799.318029-2799.270050
s+1 to s+3  0.75000  0.75000-2797.932053-2799.318029-2799.270050
s+1 to s+4  0.75000  0.75000-2797.932053-2799.318029-2799.270048
s+1 to s+5  0.75000  0.75000-2797.932053
s+1 to s+6  0.75000  0.75000-2797.932053
```

Bromous Acid **4**

```
1\1\GINC-C24-24\SP\RQCISD(T)-Full\6-311++G(2df,2pd)\Br1H1O2\RGLASER\03
-Apr-2013\0\\# QCISD(full,T)/6-311++G(2df,2pd) 5d 7f\\single point ene
rgy of HBrO2 @ QCISD(full,T)/6-311++G(2df,2pd)//MP2(full)/6-311G*\\0,1
\O,0,0.0585350585,-0.2811161574,0.0474112794\H,0,0.0644453111,0.331870
5027,0.7980871951\Br,0,1.7125983122,-0.0580811456,-0.8224858136\O,0,1.
8110147836,1.338575123,-1.6855874602\\Version=EM64L-G09RevB.01\State=1
-A\HF=-2722.5274499\MP2=-2723.6616051\MP3=-2723.6094151\MP4D=-2723.639
4876\MP4DQ=-2723.6240979\MP4SDQ=-2723.6406993\QCISD=-2723.6366851\QCIS
D(T)=-2723.67241\RMSD=6.924e-09\PG=C01 [X(Br1H1O2)]\\@
```

Bromic Acid **5**

```
1\1\GINC-C24-12\SP\RQCISD(T)-Full\6-311++G(2df,2pd)\Br1H1O3\RGLASER\03
-Apr-2013\0\\# QCISD(full,T)/6-311++G(2df,2pd) 5d 7f\\single point ene
rgy of HBrO3 @ QCISD(T,full)/large-basis//MP2ful/6-311G*\\0,1\Br,0,0.2
293338542,0.225667036,-0.0241824123\O,0,-1.1031303539,-1.0779966351,-0
.1356431087\O,0,1.4560841185,-0.4261667128,-0.8181760816\O,0,-0.397680
556,1.4687601838,-0.8126682491\H,0,-1.2657997227,-1.237100432,-1.08204
51582\\Version=EM64L-G09RevB.01\State=1-A\HF=-2797.326033\MP2=-2798.74
04413\MP3=-2798.6691838\MP4D=-2798.7068706\MP4DQ=-2798.6840971\MP4SDQ=
-2798.7086944\QCISD=-2798.704555\QCISD(T)=-2798.754137\RMSD=9.907e-09\
PG=C01 [X(Br1H1O3)]\\@
```

H_2OBrO_2-Cation **6a**

```
1\1\GINC-D19-40\SP\RQCISD(T)-Full\6-311++G(2df,2pd)\Br1H2O3(1+)\RGLASE
R\02-Apr-2013\0\\# QCISD(full,T)/6-311++G(2df,2pd) 5d 7f\\cation 6a @
QCID(full,T)/6-311++G(2df,2dp)//MP2(full)/6-311G*\\1,1\Br,0,0.08684663
61,-0.3887566247,-0.4270456908\H,0,-0.5547183699,0.8446941889,2.452859
7228\O,0,1.2652047174,0.4999198762,-1.0775771515\O,0,-1.433463022,0.04
83393921,-0.7417556622\O,0,0.1836008448,0.7243574568,1.8494999934\H,0,
0.9657559296,1.0982703083,2.2643019842\\Version=EM64L-G09RevB.01\State
=1-A\HF=-2797.5920765\MP2=-2799.0510407\MP3=-2798.9519062\MP4D=-2799.0
059897\MP4DQ=-2798.9728643\MP4SDQ=-2799.0053394\QCISD=-2798.9973878\QC
ISD(T)=-2799.0546379\RMSD=3.382e-09\PG=C01 [X(Br1H2O3)]\\@
```

$(HO)_2BrO$-Cation **7c**

```
1\1\GINC-D19-37\SP\RQCISD(T)-Full\6-311++G(2df,2pd)\Br1H2O3(1+)\RGLASE
R\02-Apr-2013\0\\# QCISD(full,T)/6-311++G(2df,2pd) 5d 7f\\cation 7c @
QCID(full,T)/6-311++G(2df,2dp)//MP2(full)/6-311G*\\1,1\Br,0,-0.2499766
554,1.220657173,-0.0673604042\O,0,-0.4748490777,2.45828345,-1.00574894
51\O,0,0.8472634998,0.0445790596,-0.7451502841\O,0,-1.5990097593,0.069
0127296,-0.3156434263\H,0,-2.4759426301,0.4791915824,-0.1692682012\H,0
,0.4713113227,-0.4176768347,-1.5262094991\\Version=EM64L-G09RevB.01\St
ate=1-A\HF=-2797.6164638\MP2=-2799.0226476\MP3=-2798.9605475\MP4D=-279
8.9968763\MP4DQ=-2798.9746285\MP4SDQ=-2798.9978673\QCISD=-2798.9942161
\QCISD(T)=-2799.0423993\RMSD=2.587e-09\PG=C01 [X(Br1H2O3)]\\@
```

Results for H_2O

```
1\1\GINC-C24-18\SP\RQCISD(T)-Full\6-311++G(2df,2pd)\H2O1\RGLASER\03-Ap
r-2013\0\\# QCISD(full,T)/6-311++G(2df,2pd) 5d 7f\\HO @ QCISD(full,T)/
6-311++G(2df,2pd)//MP2(full)/6-311G*\\0,1\O,0,-0.0087400775,0.,-0.0068
284969\H,0,-0.0313311693,0.,0.9491097109\H,0,0.9133374004,0.,-0.260010
92\\Version=EM64L-G09RevB.01\State=1-A1\HF=-76.0578805\MP2=-76.3414181
\MP3=-76.344988\MP4D=-76.3495602\MP4DQ=-76.3456465\MP4SDQ=-76.3474373\
QCISD=-76.3474742\QCISD(T)=-76.3551868\RMSD=5.467e-09\PG=C02V [C2(O1),
SGV(H2)]\\@
```

Results for H_3O^+

```
1\1\GINC-C24-37\SP\RQCISD(T)-Full\6-311++G(2df,2pd)\H3O1(1+)\RGLASER\0
3-Apr-2013\0\\# QCISD(full,T)/6-311++G(2df,2pd) 5d 7f\\single point en
ergy of hydronium @ QCISD(fu,T)/6-311++G(2df,2pd) from MP2 opt\\1,1\O,
0,-0.4707423373,-0.2671818192,0.1698392975\H,0,0.4707754871,-0.3536851
751,-0.056594857\H,0,-0.8665691064,0.5914565291,-0.056594857\H,0,-1.01
64157247,-1.0392918121,-0.0566495817\\Version=EM64L-G09RevB.01\State=1
-A\HF=-76.3368539\MP2=-76.6140589\MP3=-76.6213306\MP4D=-76.625394\MP4D
Q=-76.6217067\MP4SDQ=-76.6229065\QCISD=-76.6230495\QCISD(T)=-76.629886
2\RMSD=5.195e-09\PG=C01 [X(H3O1)]\\@
```

Results of QCISD(full,T)/6-311++G(2df,2pd)//MP2(full)/6-311++G Computations**

Bromine Dioxide **1**

```
1\1\GINC-D19-06\SP\UQCISD(T)-Full\6-311++G(2df,2pd)\Br1O2(2)\RGLASER\0
5-Apr-2013\0\\# QCISD(full,T)/6-311++G(2df,2pd) 5d 7f\\radical BrO2 @
QCISD/6-311++G(2df,2pd)//MP2(full)/6-311++G**\\0,2\Br,0,0.0879601234,0
.,0.0615903415\O,0,-0.0075224061,0.,1.7171379011\O,0,1.6110090001,0.,-
0.5943645006\\Version=EM64L-G09RevB.01\State=2-B1\HF=-2721.9023929\MP2
=-2723.0308649\MP3=-2722.9627302\MP4D=-2722.9969593\MP4DQ=-2722.978217
1\PUHF=-2721.9111787\PMP2-0=-2723.0366595\PMP3-0=-2722.9653571\MP4SDQ=
-2723.0002632\QCISD=-2722.9962264\QCISD(T)=-2723.0356107\S2=0.791859\S
2-1=0.762891\S2A=0.75115\RMSD=7.323e-09\PG=C02V [C2(Br1),SGV(O2)]\\@

S**2, projected HF & approx projected MPn energies after annihilation of
unwanted spin states (see manual for definitions):
spins       (S**2,0) (S**2,1)    PUHF        PMP2        PMP3        PMP4
annihilated
s+1         0.74932  0.75026-2721.911179-2723.036660-2722.965357
s+1,s+2     0.75000  0.75000-2721.911063-2723.036553-2722.965266
s+1 to s+3  0.75000  0.75000-2721.911064-2723.036553-2722.965265
s+1 to s+4  0.75000  0.75000-2721.911064-2723.036553-2722.965265
s+1 to s+5  0.75000  0.75000-2721.911064
s+1 to s+6  0.75000  0.75000-2721.911064
```

Bromic Acid **5**

```
1\1\GINC-D19-07\SP\RQCISD(T)-Full\6-311++G(2df,2pd)\Br1H1O3\RGLASER\05
-Apr-2013\0\\# QCISD(full,T)/6-311++G(2df,2pd) 5d 7f\\HBrO3 @ QCISD/6-
311++G(2df,2pd)//MP2/6-311++G**\\0,1\Br,0,0.2310648014,0.2257056853,-0
.0226478925\O,0,-1.1165218042,-1.0893635048,-0.1286693536\O,0,1.456935
7297,-0.4276999177,-0.8222774821\O,0,-0.3947966893,1.469574951,-0.8164
787691\H,0,-1.2578746976,-1.2250537739,-1.0826415126\\Version=EM64L-G0
9RevB.01\State=1-A\HF=-2797.3237419\MP2=-2798.7400535\MP3=-2798.668069
2\MP4D=-2798.7062015\MP4DQ=-2798.682991\MP4SDQ=-2798.7079743\QCISD=-27
98.7038757\QCISD(T)=-2798.7539526\RMSD=3.379e-09\PG=C01 [X(Br1H1O3)]\\
@
```

Radical Anion **9**

```
1\1\GINC-D17B-10\SP\UQCISD(T)-Full\6-311++G(2df,2pd)\Br1H1O3(1-,2)\RGL
ASER\04-Apr-2013\0\\# QCISD(full,T)/6-311++G(2df,2pd) scf=(maxcycle=30
0) 5d 7f\\radical anion at QCISD/6-311++G(2df,2pd)//MP2(full)/6-311++G
** 5d 7f\\-1,2\Br,0,-0.1340793727,0.186951224,-0.5149144813\O,0,-0.265
3324476,-1.476724005,-0.1969743021\O,0,1.4346313986,0.6649521212,0.020
7413975\O,0,-2.242708534,0.301277631,-1.4035507776\H,0,-2.8039212204,-
0.481031827,-1.4572898039\\Version=EM64L-G09RevB.01\State=2-A\HF=-2797
.3593022\MP2=-2798.8003518\MP3=-2798.721229\MP4D=-2798.7634937\MP4DQ=-
2798.7384056\PUHF=-2797.3680766\PMP2-0=-2798.8063817\PMP3-0=-2798.7242
904\MP4SDQ=-2798.7658982\QCISD=-2798.7624452\QCISD(T)=-2798.8141591\S2
=0.796421\S2-1=0.766811\S2A=0.751536\RMSD=7.796e-09\PG=C01 [X(Br1H1O3)
]\\@

S**2, projected HF & approx projected MPn energies after annihilation of
unwanted spin states (see manual for definitions):
spins       (S**2,0) (S**2,1)    PUHF        PMP2        PMP3        PMP4
annihilated
s+1         0.74909  0.75024-2797.368077-2798.806382-2798.724290
```

```
s+1,s+2     0.75001  0.74999-2797.367942-2798.806256-2798.724178
s+1 to s+3  0.75000  0.75000-2797.367943-2798.806256-2798.724178
s+1 to s+4  0.75000  0.75000-2797.367943-2798.806256-2798.724178
s+1 to s+5  0.75000  0.75000-2797.367943
s+1 to s+6  0.75000  0.75000-2797.367943
```

HO^-

```
1\1\GINC-D19-39\SP\RQCISD(T)-Full\6-311++G(2df,2pd)\H1O1(1-)\RGLASER\0
4-Apr-2013\0\\# QCISD(full,T)/6-311++G(2df,2pd) 5d 7f\\hydroxide at QC
ISD/6-311++G(2df,2pd)//MP2(full)/6-311++G** 5d 7f\\-1,1\O,0,0.,0.,0.01
77137172\H,0,0.,0.,0.9822862828\\Version=EM64L-G09RevB.01\State=1-SG\H
F=-75.4082137\MP2=-75.7066529\MP3=-75.6986655\MP4D=-75.7057921\MP4DQ=-
75.7018767\MP4SDQ=-75.7057606\QCISD=-75.7050204\QCISD(T)=-75.7144166\R
MSD=2.402e-09\PG=C*V [C*(H1O1)]\\@
```