

**Supplementary online material for the article “Hydration increases the lifetime of HSO<sub>5</sub> and enhances its ability to act as a nucleation precursor” by Theo Kurtén, Torsten Berndt and Frank Stratmann**

Table 1-3 contain the energetics, and Tables 4-7 the structures of all molecules and clusters in the study. Tables 8-9 contains the vibrational temperatures of all studied structures.

**Table 1.** G3B3 electronic energies ( $E_{\text{elec}}$ ), enthalpies (H), Gibbs free energies (G) and entropies (S) of all studied structures.  $E_{\text{elec}}$ , H and G given in hartree, S given in  $\text{cal K}^{-1} \text{mol}^{-1}$ . H, G and S values correspond to 298 K and 1 atm.

Molecule	$E_{\text{elec}}$ /hartree	H /hartree	G /hartree	S /cal K <sup>-1</sup> mol <sup>-1</sup>
H <sub>2</sub> O	-76.404044	-76.379946	-76.401393	45.162
SO <sub>2</sub>	-548.434248	-548.423679	-548.451964	59.561
OH	-75.704340	-75.693062	-75.713308	42.633
HSO <sub>3</sub>	-624.181697	-624.155821	-624.189025	69.919
O <sub>2</sub>	-150.256364	-150.249426	-150.272713	49.036
HSO <sub>5</sub> (R)	-774.461589	-774.426642	-774.465985	82.846
HSO <sub>5</sub> (TS)	-774.454858	-774.423558	-774.460525	77.843
HSO <sub>5</sub> (P)	-774.462534	-774.426877	-774.465853	82.073
SO <sub>3</sub>	-623.598905	-623.582989	-623.612401	61.934
HO <sub>2</sub>	-150.843423	-150.826148	-150.852147	54.747
SO <sub>2</sub> •H <sub>2</sub> O	-624.845546	-624.808495	-624.846288	79.582
OH•H <sub>2</sub> O	-152.117291	-152.079591	-152.111297	66.764
HSO <sub>3</sub> •H <sub>2</sub> O	-700.605332	-700.552509	-700.592111	83.391
HSO <sub>5</sub> (R)•H <sub>2</sub> O	-850.893167	-850.830931	-850.875157	93.128
HSO <sub>5</sub> (P)•H <sub>2</sub> O	-850.885200	-850.822812	-850.867709	94.541
SO <sub>3</sub> •H <sub>2</sub> O	-700.019397	-699.976489	-700.014403	79.837
HO <sub>2</sub> •H <sub>2</sub> O	-227.261618	-227.216883	-227.249830	69.378
OH•(H <sub>2</sub> O) <sub>2</sub>	-228.535332	-228.469884	-228.506083	76.225
HSO <sub>3</sub> •(H <sub>2</sub> O) <sub>2</sub>	-777.028190	-776.948801	-776.995478	98.289
HSO <sub>5</sub> (R)•(H <sub>2</sub> O) <sub>2</sub>	-927.3160277	-927.228142	-927.278437	105.908
HSO <sub>5</sub> (P)•(H <sub>2</sub> O) <sub>2</sub>	-927.314788	-927.225969	-927.274178	101.515
SO <sub>3</sub> •(H <sub>2</sub> O) <sub>2</sub>	-776.442471	-776.372243	-776.415238	90.536
HO <sub>2</sub> •(H <sub>2</sub> O) <sub>2</sub>	-303.683916	-303.612234	-303.651219	82.092

**Table 2.** UB3LYP/6-311++G(3df,3pd) electronic energies ( $E_{\text{elec}}$ ), enthalpies (H), Gibbs free energies (G) and entropies (S) of all studied structures.  $E_{\text{elec}}$ , H and G given in hartree, S given in  $\text{cal K}^{-1} \text{mol}^{-1}$ . H, G and S values correspond to 298 K and 1 atm, and have been computed using a vibrational scaling factor of 0.967.

Molecule	$E_{\text{elec}}$ /hartree	H /hartree	G /hartree	S /cal $\text{K}^{-1} \text{mol}^{-1}$
H <sub>2</sub> O	-76.464512	-76.440124	-76.461544	45.083
SO <sub>2</sub>	-548.715953	-548.705149	-548.733350	59.353
OH	-75.766245	-75.754756	-75.774986	42.577
HSO <sub>3</sub>	-624.528551	-624.502010	-624.534861	69.142
O <sub>2</sub>	-150.379489	-150.372556	-150.395826	48.975
HSO <sub>5</sub> (R)	-774.924401	-774.888244	-774.926283	80.061
HSO <sub>5</sub> (TS)	-774.916831	-774.884767	-774.921355	77.005
HSO <sub>5</sub> (P)	-774.923021	-774.886629	-774.925368	81.534
SO <sub>3</sub>	-623.936315	-623.919872	-623.949082	61.479
HO <sub>2</sub>	-150.968332	-150.950846	-150.976824	54.676
SO <sub>2</sub> •H <sub>2</sub> O	-625.186453	-625.149150	-625.188537	82.898
OH•H <sub>2</sub> O	-152.239925	-152.201883	-152.233617	66.789
HSO <sub>3</sub> •H <sub>2</sub> O	-701.010827	-700.957327	-700.997229	83.981
HSO <sub>5</sub> (R)•H <sub>2</sub> O	-851.409991	-851.347141	-851.392051	94.522
HSO <sub>5</sub> (P)•H <sub>2</sub> O	-851.403972	-851.340951	-851.386209	95.254
SO <sub>3</sub> •H <sub>2</sub> O	-700.414151	-700.370705	-700.409334	81.301
HO <sub>2</sub> •H <sub>2</sub> O	-227.446932	-227.402198	-227.436650	72.51
HSO <sub>3</sub> •(H <sub>2</sub> O) <sub>2</sub>	-777.493510	-777.413260	-777.459704	97.749
SO <sub>3</sub> •(H <sub>2</sub> O) <sub>2</sub>	-776.896654	-776.825811	-776.869630	92.224
HO <sub>2</sub> •(H <sub>2</sub> O) <sub>2</sub>	-303.929834	-303.857944	-303.897740	83.758

**Table 3.** UCCSD/6-311++G(3df,3pd), UCCSD(T)/6-311++G(3df,3pd), UCCSD/aug-cc-pV(T+d)Z and UCCSD(T)/aug-cc-pV(T+d)Z electronic energies for all studied structures, in hartree. All values computed at the UB3LYP/6-311++G(3df,3pd) geometries.

Molecule	UCCSD /Pople <sup>a</sup>	UCCSD(T) /Pople <sup>a</sup>	UCCSD /ATZ <sup>b</sup>	UCCSD(T) /ATZ <sup>b</sup>
H <sub>2</sub> O	-76.329114	-76.337427	-76.333649	-76.342308
SO <sub>2</sub>	-547.944848	-547.979170	-547.970302	-548.006177
OH	-75.634137	-75.639794	-75.639579	-75.645546
HSO <sub>3</sub>	-623.618912	-623.661497	-623.652299	-623.696874
O <sub>2</sub>	-150.108567	-150.128194	-150.120459	-150.140835
HSO <sub>5</sub> (R)	-773.753469	-773.815199	-773.800806	-773.865330
HSO <sub>5</sub> (TS)	-773.736797	-773.804861	-773.783715	-773.854605
HSO <sub>5</sub> (P)	-773.745879	-773.810984	-773.791524	-773.859457
SO <sub>3</sub>	-623.034224	-623.078294	-623.066180	-623.112153
HO <sub>2</sub>	-150.695370	-150.713373	-150.707761	-150.726523
SO <sub>2</sub> •H <sub>2</sub> O	-624.280885	-624.323740	-624.310870	-624.355677
OH•H <sub>2</sub> O	-151.972417	-151.986776	-151.982199	-151.997223
HSO <sub>3</sub> •H <sub>2</sub> O	-699.967480	-700.019175	-700.005138	-700.059194
HSO <sub>5</sub> (R)•H <sub>2</sub> O	-850.104220	-850.175964	-850.155605	-850.230510
HSO <sub>5</sub> (P)•H <sub>2</sub> O	-850.091599	-850.166314	-850.141563	-850.219494
SO <sub>3</sub> •H <sub>2</sub> O	-699.377681	-699.430460	-699.414897	-699.470014
HO <sub>2</sub> •H <sub>2</sub> O	-227.038566	-227.066042	-227.055307	-227.083931
HSO <sub>3</sub> •(H <sub>2</sub> O) <sub>2</sub>	-776.314762	-776.375833	-776.356695	-776.420458
SO <sub>3</sub> •(H <sub>2</sub> O) <sub>2</sub>	-775.724864	-775.787112	-775.767348	-775.832329
HO <sub>2</sub> •(H <sub>2</sub> O) <sub>2</sub>	-303.384956	-303.422332	-303.405915	-303.444796

a)6-311++G(3df,3pd) basis set

b)aug-cc-pV(T+d)Z basis set

**Table 4.** Minimum-energy Cartesian co-ordinates at the G3B3 (BLYP/6-31G(d)) level for all cluster structures and monomers, in Ångström.

H<sub>2</sub>O

O	0.0	0.0	0.119743
H	0.0	0.761545	-0.478972
H	0.0	-0.761545	-0.478972

SO<sub>2</sub>

S	0.0	0.0	0.370768
O	0.0	1.261823	-0.370768
O	0.0	-1.261823	-0.370768

OH

O	0.0	0.0	0.109207
H	0.0	0.0	-0.873653

HSO<sub>3</sub>

S	0.135514	0.082866	0.265579
O	-0.258936	1.432049	-0.194674
O	1.349193	-0.600155	-0.209055
O	-1.12019	-0.947481	-0.1065
H	-1.928763	-0.401154	-0.167433

O<sub>2</sub>

O	-0.607262	0.0	0.0
O	0.607262	0.0	0.0

HSO<sub>5</sub>(R)

S	-0.542843	-0.012355	0.0
O	-1.145764	-0.344034	1.271753
O	-1.145764	-0.344033	-1.271753
O	1.1	-0.881171	0.0
O	2.09362	-0.041837	0.0
O	0.052338	1.46591	0.0
H	1.050054	1.358999	0.0

HSO<sub>5</sub>(TS)

S	0.094127	0.590995	0.0
O	-1.374812	0.176801	0.0
H	-1.258318	-1.047273	0.0
O	0.615183	1.056049	1.26936
O	0.615183	1.056049	-1.26936
O	0.615183	-1.334334	0.0
O	-0.5017	-2.005646	0.0

HSO<sub>5</sub>(P)

S	-0.68658	0.096958	0.0
O	-1.170331	-0.426532	1.263671
O	-1.170332	-0.426532	-1.26367
O	0.008138	1.399841	0.0
O	1.297711	-0.903032	0.0
O	2.20183	0.049811	-0.000001
H	1.649165	0.900229	0.0

SO<sub>3</sub>

S	0.0	0.0	0.0
O	0.0	1.453255	0.0
O	1.258556	-0.726628	0.0
O	-1.258556	-0.726628	0.0

HO<sub>2</sub>

O	0.055885	-0.611741	0.0
O	0.055885	0.720187	0.0
H	-0.894157	-0.867570	0.0

SO<sub>2</sub>•H<sub>2</sub>O

S	-0.590533	0.000005	-0.381624
O	-0.702108	1.256043	0.367415
O	-0.702235	-1.256004	0.367446
O	2.057265	0.000001	-0.095911
H	2.112478	0.766816	0.497467
H	2.112685	-0.767224	0.496915

OH•H<sub>2</sub>O

O	0.050316	1.580766	0.0
H	0.163132	0.595169	0.0
O	0.050316	-1.272783	0.0
H	-0.484098	-1.529517	0.767319
H	-0.484098	-1.529517	-0.767319

HSO<sub>3</sub>•H<sub>2</sub>O

S	-0.765187	0.085564	-0.266149
O	0.052658	1.289691	0.058409
O	-2.030059	-0.180093	0.441736
O	0.183250	-1.225735	-0.076350
H	1.148227	-0.916737	-0.100296
O	2.551326	-0.028345	0.006255
H	2.082716	0.828535	0.034766
H	2.954651	-0.124969	0.883523

HSO<sub>5</sub>(R)•H<sub>2</sub>O

S	-0.756404	-0.235303	0.080234
O	-2.159657	-0.269032	-0.244256
O	-0.204551	-0.589553	1.377830
O	0.093949	-0.870493	-1.083759
H	1.071694	-0.962815	-0.764850
O	-0.344929	1.513406	-0.153207
O	0.935157	1.741632	-0.024038
O	2.464785	-0.803135	-0.054887
H	2.349982	-1.210704	0.820755
H	2.402755	0.155766	0.118892

HSO<sub>5</sub>(P)•H<sub>2</sub>O

S	-0.892129	-0.273663	0.017030
O	-2.172373	0.401271	-0.036257
O	-0.356377	-0.731162	1.300516
O	-0.343157	-0.896408	-1.189783
O	0.226523	1.550855	-0.094664
O	1.539838	1.482196	-0.087443
H	1.822817	0.468628	-0.028414

O	2.229296	-0.984689	0.055285
H	1.711731	-1.377389	-0.674511
H	1.749507	-1.289131	0.849218

SO<sub>3</sub>•H<sub>2</sub>O

S	-0.430272	0.000002	-0.046199
O	-0.347511	1.255976	-0.777792
O	-0.347111	-1.254967	-0.779481
O	-0.853925	-0.001005	1.340928
O	1.866484	-0.000018	0.34765
H	2.170455	0.7746	-0.15552
H	2.170404	-0.774512	-0.15574

HO<sub>2</sub>•H<sub>2</sub>O

O	0.954998	-0.655413	0.006544
O	1.044234	0.672583	0.01506
H	-0.036865	-0.807229	-0.036445
O	-1.608976	-0.015491	-0.098557
H	-1.049344	0.786169	-0.11987
H	-2.035846	0.007625	0.771934

OH•(H<sub>2</sub>O)<sub>2</sub>

O	0.669379	1.549545	0.003097
H	1.05035	0.619735	-0.045815
O	0.991989	-1.149861	-0.111847
H	1.268122	-1.573863	0.714837
H	0.005852	-1.114913	-0.061227
O	-1.561351	-0.199348	0.108333
H	-2.077414	-0.171821	-0.711671
H	-1.047051	0.638169	0.107215

HSO<sub>3</sub>•(H<sub>2</sub>O)<sub>2</sub>

S	1.213563	-0.088286	-0.280148
O	0.240020	-1.210172	-0.135474
O	2.545021	-0.189841	0.343273
O	0.540288	1.274986	0.254824
H	-0.469643	1.313198	0.026661
O	-1.993255	1.395082	-0.217000
H	-2.342479	0.474094	-0.053326
H	-2.397051	1.951283	0.467201
O	-2.545188	-1.178332	0.284326
H	-2.910168	-1.652355	-0.478823
H	-1.592751	-1.407436	0.281072

HSO<sub>5</sub>(R)•(H<sub>2</sub>O)<sub>2</sub>

S	1.042946	-0.196851	0.251534
O	0.162901	0.099245	1.373167
O	2.474752	-0.324400	0.375036
O	0.458216	-1.302707	-0.671597
H	-0.619257	-1.420295	-0.589124
O	0.902613	1.245786	-0.852735
O	-0.293791	1.765395	-0.867968
O	-2.005930	-1.561036	-0.521836
H	-2.359085	-0.738475	-0.056478
H	-2.403371	-1.569556	-1.407119
O	-2.593509	0.715530	0.682204
H	-2.301849	0.556399	1.595199
H	-1.845581	1.219056	0.302809

HSO<sub>5</sub>(P)•(H<sub>2</sub>O)<sub>2</sub>

S	0.977624	-0.430764	0.087001
O	2.380776	-0.780157	0.021966
O	0.030757	-1.113648	-0.819777
O	0.409002	-0.126512	1.431511
O	1.056105	1.271097	-0.693740
O	-0.061428	1.947146	-0.667839
H	-1.382310	1.402069	0.281708
O	-1.904829	0.851490	0.948336
H	-1.107489	0.399526	1.409136
H	-2.357612	0.076068	0.390252
O	-2.654720	-1.129040	-0.415818
H	-3.110518	-0.962160	-1.256181
H	-1.729348	-1.386297	-0.654032

SO<sub>3</sub>•(H<sub>2</sub>O)<sub>2</sub>

S	0.799174	-0.203285	0.036191
O	-0.185051	-1.288239	0.103951
O	1.585517	-0.062388	-1.173577
O	1.270607	0.375828	1.28617
O	-0.618668	1.341975	-0.349928
H	-0.488004	1.968753	0.383327
H	-1.522112	0.911025	-0.211106
O	-2.736192	-0.157239	0.09496
H	-3.189097	-0.414351	-0.723824
H	-2.117278	-0.892365	0.279928

HO<sub>2</sub>•(H<sub>2</sub>O)<sub>2</sub>

O	-1.600834	0.333263	-0.055782
O	-1.242016	-0.939778	0.059382
H	-0.728227	0.86469	-0.069342
O	0.75603	1.516556	-0.084952
H	1.293254	0.679338	-0.06258
H	0.948149	1.962547	0.754315
O	1.586038	-1.020365	0.081801
H	0.619361	-1.204928	0.127804
H	1.87372	-1.419063	-0.753785

**Table 5.** Minimum-energy Cartesian co-ordinates at the U3BLYP/6-311++G(3df,3pd) level for all cluster structures and monomers, in Ångström.

H<sub>2</sub>O

O	0.0	0.0	0.116967
H	0.0	0.762631	-0.467868
H	0.0	-0.762631	-0.467868

SO<sub>2</sub>

S	0.0	0.0	0.363387
O	0.0	1.239317	-0.363387
O	0.0	-1.239317	-0.363387

OH

O	0.0	0.0	0.108235
H	0.0	0.0	-0.865879

HSO<sub>3</sub>

S	0.134107	0.068449	0.251264
O	-0.110877	1.427482	-0.185946
O	1.263975	-0.706853	-0.19286
O	-1.176936	-0.826546	-0.110678
H	-1.955009	-0.247854	-0.104348

O<sub>2</sub>

O	0.0	0.0	0.601629
O	0.0	0.0	-0.601629

HSO<sub>5</sub>(R)

S	-0.468747	-0.039063	0.087117
O	-0.335258	1.176023	-0.90388
H	0.199632	1.877225	-0.498669
O	-0.466238	0.416760	1.430567
O	-1.396151	-0.95358	-0.458183
O	1.056791	-0.810476	-0.189461
O	2.053396	0.014745	0.009056

HSO<sub>5</sub>(TS)

S	0.093009	0.576197	0.0
O	-1.353564	0.188519	0.0
H	-1.254577	-1.01408	0.0
O	0.606463	1.03536	1.242314
O	0.606463	1.03536	-1.242314
O	0.606463	-1.300486	0.0
O	-0.49502	-1.984387	0.0

HSO<sub>5</sub>(P)

S	-0.679574	0.094582	0.000000
O	-1.146800	-0.429071	1.237825
O	-1.146800	-0.42907	-1.237825
O	-0.022595	1.383673	0.000000
O	1.283913	-0.885885	0.000000
O	2.185803	0.05823	-0.000001
H	1.645006	0.903666	0.000000

SO<sub>3</sub>

S	0.0	0.0	0.0
O	0.0	1.425288	0.0
O	1.234335	-0.712644	0.0
O	-1.234335	-0.712644	0.0

HO<sub>2</sub>

O	0.055294	-0.607811	0.0
O	0.055294	0.716364	0.0
H	-0.884697	-0.868421	0.0

SO<sub>2</sub>•H<sub>2</sub>O

S	0.612369	0.000006	-0.367789
O	0.775997	-1.235311	0.351751
O	0.775728	1.235395	0.351687
O	-2.176743	-0.000027	-0.082045
H	-2.399087	-0.76625	0.456307
H	-2.398678	0.765708	0.45717

OH•H<sub>2</sub>O

O	0.0371	1.612035	0.0
H	0.064879	0.629977	0.0
O	0.0371	-1.262812	0.0
H	-0.329236	-1.711879	0.767402
H	-0.329236	-1.711879	-0.767402

HSO<sub>3</sub>•H<sub>2</sub>O

S	-0.755593	0.081342	-0.255616
O	-0.016299	1.287286	0.09817
O	-2.049952	-0.20138	0.314761
O	0.177346	-1.184266	0.018228
H	1.13285	-0.888561	-0.009117
O	2.578442	-0.036885	-0.018425
H	2.206626	0.844337	0.125209
H	3.233709	-0.175283	0.671904

HSO<sub>5</sub>(R)•H<sub>2</sub>O

S	-0.74812	-0.289535	0.079694
O	-2.089252	-0.472501	-0.329655
O	-0.275178	-0.551214	1.396444
O	0.213391	-0.854931	-0.984257
H	1.177927	-0.830675	-0.656819
O	-0.519589	1.433857	-0.172624
O	0.717916	1.805268	0.009392
O	2.627442	-0.575712	-0.107529
H	2.867718	-1.133143	0.640473
H	2.526433	0.318247	0.247068

HSO<sub>5</sub>(P)•H<sub>2</sub>O

S	-0.961244	-0.251185	0.021066
O	-2.177275	0.445100	-0.216786
O	-0.591538	-0.638529	1.347216
O	-0.321643	-0.935756	-1.072259
O	0.219132	1.540708	-0.041365
O	1.521493	1.452873	0.003243
H	1.806439	0.4546800	0.011828

O	2.289679	-0.991519	-0.074609
H	1.535195	-1.402372	-0.530001
H	2.352429	-1.429557	0.781365

SO<sub>3</sub>•H<sub>2</sub>O

S	0.446688	0.000081	-0.031132
O	0.412241	-1.230992	-0.75279
O	0.412003	1.234086	-0.747745
O	0.74737	-0.002761	1.359544
O	-1.907609	-0.000354	0.258745
H	-2.229617	-0.772122	-0.221562
H	-2.229427	0.770993	-0.222367

HO<sub>2</sub>•H<sub>2</sub>O

O	0.951285	-0.658906	0.003666
O	1.145657	0.64999	0.01601
H	-0.035917	-0.7467	-0.011082
O	-1.652438	-0.001297	-0.092482
H	-1.249502	0.875656	-0.04888
H	-2.270617	-0.047256	0.642414

HSO<sub>3</sub>•(H<sub>2</sub>O)<sub>2</sub>

S	-1.189586	-0.124801	0.253488
O	-0.253788	-1.195627	-0.084074
O	-2.550882	-0.181383	-0.220525
O	-0.591385	1.270638	-0.176272
H	0.422165	1.322998	-0.044998
O	1.962575	1.43549	0.134327
H	2.354826	0.535121	0.044776
H	2.408513	2.002207	-0.501298
O	2.580968	-1.169588	-0.145566
H	3.023369	-1.710893	0.513604
H	1.644588	-1.428859	-0.131018

SO<sub>3</sub>•(H<sub>2</sub>O)<sub>2</sub>

S	-0.817864	-0.209297	-0.025866
O	0.138826	-1.215268	-0.394538
O	-1.342202	-0.222256	1.29678
O	-1.514271	0.479305	-1.064542
O	0.625087	1.34942	0.2867
H	0.505455	1.959151	-0.451732
H	1.515132	0.918548	0.182543
O	2.776717	-0.164545	-0.086305
H	3.381149	-0.407371	0.621093
H	2.210833	-0.934823	-0.242811

HO<sub>2</sub>•(H<sub>2</sub>O)<sub>2</sub>

O	-1.621699	0.295633	-0.037224
O	-1.227422	-0.961593	0.043319
H	-0.779698	0.84917	-0.04154
O	0.714406	1.544216	-0.087228
H	1.286445	0.747637	-0.040672
H	0.975146	2.117358	0.63874
O	1.613768	-1.001491	0.081603
H	0.661304	-1.214636	0.059595
H	2.024377	-1.513644	-0.61989

**Table 6.** Cartesian co-ordinates for local minima identified for the HSO<sub>5</sub> dihydrates at the G3B3 (BLYP/6-31G(d)) level, in Ångström.

HSO<sub>5</sub>(R)•(H<sub>2</sub>O)<sub>2</sub> alternative isomer

H	3.269069	0.773603	-1.482164
O	2.77789	1.026786	-0.685287
H	1.849668	1.120502	-0.979933
H	2.581847	-0.239985	0.381811
O	2.245761	-0.965619	0.988262
H	2.269638	-0.597849	1.885903
S	-0.845036	-0.335384	-0.358655
O	0.041275	0.50101	-1.165697
O	-2.137613	-0.748529	-0.851214
O	-0.09938	-1.532471	0.304036
H	0.898733	-1.289773	0.595684
O	-1.098416	0.583244	1.160546
O	-1.398065	1.835534	0.916501

Difference in E<sub>elec</sub> to the best minimum-energy structure: 0.9987 kcal mol<sup>-1</sup>

Difference in G(298 K) to the best minimum-energy structure: -0.2105 kcal mol<sup>-1</sup>

HSO<sub>5</sub>(P)•(H<sub>2</sub>O)<sub>2</sub> alternative isomer

S	-0.69329	-0.26988	-0.054563
O	-1.160395	-1.399014	-0.826194
O	-0.259891	0.949722	-0.748094
O	-0.694459	-0.275004	1.398402
O	1.513767	-1.345177	-0.057087
O	2.677373	-0.768472	0.192072
H	2.514762	0.239303	0.192329
O	-2.990949	0.728394	0.072093
H	-3.157787	0.673638	1.027004
H	-2.826461	1.669284	-0.099871
O	2.240208	1.830688	0.052787
H	2.672632	2.149967	-0.755211
H	1.28426	1.81679	-0.163065

Difference in E<sub>elec</sub> to the best minimum-energy structure: 11.9288 kcal mol<sup>-1</sup>

Difference in G(298 K) to the best minimum-energy structure: 7.5425 kcal mol<sup>-1</sup>

**Table 7.** Cartesian co-ordinates for the minimum-energy structure of  $\text{HSO}_5(\text{P})\bullet(\text{H}_2\text{O})_2$  obtained at different levels of theory, starting from the G3B3 minimum, in Ångström. For the structures differing qualitatively from the G3B3 structure, single-point energies have been computed at the G3B3 level. Frequency calculations have been carried out on the UMP2/6-311++G(2d,2p) structure to verify that it is a minimum-energy geometry.

UB3LYP/6-311++G(3df,3pd)

S	0.949675	-0.448343	0.114862
O	2.310310	-0.854945	0.119126
O	0.020158	-1.120241	-0.768209
O	0.366378	-0.073972	1.407710
O	1.127439	1.179007	-0.705471
O	0.052021	1.909445	-0.731665
H	-1.358365	1.475541	0.195719
O	-1.861203	0.946491	0.877001
H	-1.045013	0.473475	1.306060
H	-2.352374	0.204069	0.356682
O	-2.688386	-1.060693	-0.421998
H	-3.265740	-1.074341	-1.190451
H	-1.787038	-1.305998	-0.717749

UMP2/6-311++G(2d,2p)

S	1.02294	-0.483442	0.137755
O	2.404409	-0.723322	-0.159147
O	0.004265	-1.187953	-0.620801
O	0.647122	-0.054424	1.474937
O	0.93218	1.250644	-0.809967
O	-0.206215	1.930644	-0.669625
H	-0.985171	1.397382	0.079757
O	-1.808567	0.963178	0.857062
H	-1.234617	0.520563	1.505642
H	-2.304476	0.231883	0.404213
O	-2.790935	-1.150221	-0.37102
H	-3.376685	-1.190081	-1.128786
H	-1.924169	-1.453057	-0.676425

Difference in single-point G3B3 electronic energy to G3B3 minimum-energy structure: 0.5556 kcal mol<sup>-1</sup>

RI-MP2/aug-cc-pV(T+d)Z

S	0.959420343	-0.45766118	0.137002993
O	2.343828417	-0.664334159	-0.135151508
O	-0.019223043	-1.162190325	-0.658038149
O	0.552773637	-0.066477439	1.466145428
O	0.849595666	1.25737525	-0.755531331
O	-0.295131569	1.913740605	-0.622553948
H	-1.060242008	1.362555834	0.08765984
O	-1.92860481	0.907681329	0.849981921
H	-1.374322448	0.473356571	1.522898511
H	-2.396406536	0.164231254	0.378222805
O	-2.790281402	-1.220563337	-0.42423561
H	-3.361568983	-1.293706237	-1.194181834
H	-1.897975053	-1.469043	-0.718109385

Difference in single-point G3B3 electronic energy to G3B3 minimum-energy structure: -0.3120 kcal mol<sup>-1</sup>

**Table 8.** Vibrational temperatures (in Kelvin) of the minimum – energy isomers of all studied structures, at the B3LYP/6-31G(d) level (without scaling). Vibrational temperatures are defined as  $h\nu/k_B$ , where  $h$  is the Planck constant,  $\nu$  is the vibrational frequency (in  $\text{s}^{-1}$ ) and  $k_B$  is the Boltzmann constant.

H<sub>2</sub>O

2464.68 5363.35 5538.95

SO<sub>2</sub>

722.36 1640.91 1924.38

OH

5245.46

HSO<sub>3</sub>

357.67 561.88 575.20 722.44 1042.55  
1514.72 1619.18 1800.16 5296.21

O<sub>2</sub>

2387.30

HSO<sub>5</sub>(R)

35.12 363.38 421.30 526.75 631.68  
640.06 761.04 778.18 861.18 1184.97  
1697.61 1755.39 1900.39 2013.86 4624.16

HSO<sub>5</sub>(TS)

188.97 355.33 397.62 664.83 695.76  
841.69 858.91 1039.66 1454.67 1473.37  
1789.69 1830.48 1989.22 2700.76

(Imaginary frequency: 977.64i  $\text{cm}^{-1}$ )

HSO<sub>5</sub>(P)

133.99 254.50 279.93 379.24 588.10  
717.54 728.65 750.71 1027.77 1434.59  
1795.39 1840.42 1968.02 2267.25 4404.10

SO<sub>3</sub>

654.11 715.97 715.98 1471.68 1944.62  
1944.65

HO<sub>2</sub>

1693.94 2094.84 5071.99

### SO<sub>2</sub>•H<sub>2</sub>O

104.98	201.27	228.48	254.89	557.00
561.28	739.34	1641.36	1902.03	2448.45
5337.95	5507.99			

### OH•H<sub>2</sub>O

183.35	279.94	362.41	746.55	980.48
2445.87	5019.21	5363.23	5532.37	

### HSO<sub>3</sub>•H<sub>2</sub>O

76.51	236.88	341.55	361.36	539.46
588.92	622.14	734.23	890.83	1124.38
1244.36	1492.87	1722.49	2066.39	2455.65
4355.77	5261.96	5473.31		

### HSO<sub>5</sub>(R)•H<sub>2</sub>O

113.55	146.57	189.89	310.59	354.41
378.02	458.64	484.62	629.85	673.99
684.81	798.98	876.61	914.62	1279.30
1596.11	1696.60	1712.50	1967.35	2129.57
2464.62	3897.31	5281.48	5444.62	

### HSO<sub>5</sub>(P)•H<sub>2</sub>O

99.68	151.65	192.14	266.15	297.54
340.24	381.84	443.44	612.15	713.13
714.05	751.92	763.26	1046.58	1453.97
1641.96	1802.15	1867.09	1957.73	2314.11
2497.42	3491.34	5269.53	5375.01	

### SO<sub>3</sub>•H<sub>2</sub>O

146.00	237.70	244.91	311.66	675.87
695.99	699.74	809.98	854.53	1474.14
1933.54	1958.49	2417.28	5327.51	5495.60

### HO<sub>2</sub>•H<sub>2</sub>O

307.62	401.83	451.07	506.47	956.64
1118.26	1740.90	2326.86	2465.31	4601.51
5233.31	5474.05			

### OH•(H<sub>2</sub>O)<sub>2</sub>

300.45	348.63	363.03	402.46	449.40
460.89	657.25	930.13	987.45	1137.33
1583.59	2455.54	2493.60	4665.24	4966.80
5111.14	5462.61	5466.81		

### HSO<sub>3</sub>•(H<sub>2</sub>O)<sub>2</sub>

39.28	72.76	150.72	255.12	367.36
375.02	436.81	446.76	583.97	611.49
627.56	735.56	799.92	954.61	1177.57
1243.81	1492.67	1540.55	1730.30	2119.79
2468.75	2499.31	3799.22	4717.39	5202.18
5456.07	5469.83			

HSO<sub>5</sub>(R)•(H<sub>2</sub>O)<sub>2</sub>

59.56	100.98	159.87	164.70	202.75
310.73	368.87	400.34	431.79	462.23
493.65	515.64	628.68	688.53	731.61
798.54	903.70	942.25	986.26	1347.52
1439.83	1618.72	1690.87	1734.17	1997.20
2248.96	2474.10	2495.10	2756.91	4472.60
5239.74	5447.03	5449.56		

HSO<sub>5</sub>(P)•(H<sub>2</sub>O)<sub>2</sub>

75.71	139.37	164.72	214.16	274.24
357.74	403.49	442.81	460.73	492.17
554.79	680.35	726.62	760.38	769.51
836.89	924.66	1003.04	1102.61	1409.14
1433.25	1729.27	1770.79	1936.72	2187.49
2461.43	2535.78	2595.83	3375.18	4097.86
4531.44	4971.97	5455.53		

SO<sub>3</sub>•(H<sub>2</sub>O)<sub>2</sub>

31.88	245.84	309.55	323.55	369.92
384.01	457.41	505.80	713.51	728.21
736.55	792.41	919.84	1094.42	1466.30
1665.46	1903.52	1961.49	2434.99	2468.38

HO<sub>2</sub>•(H<sub>2</sub>O)<sub>2</sub>

124.67	246.09	352.07	387.21	419.40
491.89	532.01	575.86	755.22	1049.15
1304.33	1495.23	1777.93	2375.03	2479.89
2503.09	4182.10	4795.13	5052.94	5456.30
5462.38				

**Table 9.** Vibrational temperatures (in Kelvin) of the minimum – energy isomers of all studied structures, at the UB3LYP/6-311++G(3df,3pd) level (without scaling). Vibrational temperatures are defined as  $h\nu/k_B$ , where  $h$  is the Planck constant,  $\nu$  is the vibrational frequency (in  $s^{-1}$ ) and  $k_B$  is the Boltzmann constant.

H<sub>2</sub>O

2340.07 5488.19 5630.67

SO<sub>2</sub>

746.81 1695.55 1981.07

OH

5345.18

HSO<sub>3</sub>

416.18 602.20 613.82 758.88 1071.10  
1586.92 1597.85 1890.22 5390.81

O<sub>2</sub>

2367.19

HSO<sub>5</sub>(R)

144.82 309.02 469.02 491.60 552.93  
653.40 720.50 821.96 934.68 1241.46  
1649.46 1656.06 1775.94 2133.30 5376.70

HSO<sub>5</sub>(TS)

194.24 395.12 422.22 694.42 730.40  
851.09 895.49 1094.81 1509.52 1548.91  
1798.24 1865.79 2059.55 2714.19

(Imaginary frequency: 941.01i  $cm^{-1}$ )

HSO<sub>5</sub>(P)

132.49 253.32 312.60 361.39 592.77  
752.47 760.68 779.59 1058.61 1511.92  
1783.89 1907.19 2034.45 2217.13 4527.48

SO<sub>3</sub>

712.39 754.43 754.45 1548.58 2013.72  
2013.73

HO<sub>2</sub>

1684.85 2065.43 5183.86

SO<sub>2</sub>•H<sub>2</sub>O

87.82	137.58	155.04	214.39	375.47
409.98	755.95	1694.60	1962.08	2335.97
5462.81	5604.56			

OH•H<sub>2</sub>O

246.13	267.45	279.01	643.05	941.84
2338.71	5111.07	5481.44	5622.49	

HSO<sub>3</sub>•H<sub>2</sub>O

92.93	163.45	320.29	326.74	508.35
606.69	637.11	732.74	773.15	1157.92
1199.61	1568.11	1816.86	2000.22	2332.85
4513.48	5397.99	5577.72		

HSO<sub>5</sub>(R)•H<sub>2</sub>O

90.80	129.75	156.34	238.92	358.51
362.09	489.23	523.55	566.37	678.31
721.68	728.21	832.40	922.94	1340.08
1521.70	1689.21	1768.84	1948.35	2123.42
2343.54	4041.38	5403.91	5554.25	

HSO<sub>5</sub>(P)•H<sub>2</sub>O

76.31	143.42	191.62	241.95	292.35
364.98	387.22	432.26	605.23	657.71
734.69	754.20	778.75	952.27	1519.10
1531.25	1799.52	1931.55	2025.25	2286.20
2388.30	3669.34	5273.36	5529.19	

SO<sub>3</sub>•H<sub>2</sub>O

79.69	238.96	251.33	252.83	659.94
698.68	706.33	774.70	802.46	1549.94
1999.68	2022.32	2326.64	5430.77	5571.61

HO<sub>2</sub>•H<sub>2</sub>O

135.05	306.86	370.25	438.59	682.89
997.98	1723.47	2248.43	2339.00	4781.03
5420.77	5588.90			

HSO<sub>3</sub>•(H<sub>2</sub>O)<sub>2</sub>

52.45	86.96	154.98	222.61	328.80
365.27	406.80	469.41	521.71	628.20
649.48	753.44	778.25	884.90	1217.93
1262.96	1413.30	1570.52	1821.01	2059.19
2346.03	2392.44	3919.67	4858.28	5272.85
5561.09	5578.07			

SO<sub>3</sub>•(H<sub>2</sub>O)<sub>2</sub>

24.67	192.49	275.22	337.56	353.07
360.30	433.72	467.95	663.54	747.52
749.04	755.65	769.83	1023.33	1508.46
1550.54	1962.42	2020.50	2330.47	2360.92
4642.41	5368.75	5488.76	5574.87	

HO<sub>2</sub>•(H<sub>2</sub>O)<sub>2</sub>

119.56	213.45	305.51	345.75	362.91
446.25	485.82	542.94	678.33	963.78
1220.20	1287.31	1758.69	2324.48	2353.84
2398.28	4351.27	4974.23	5143.32	5566.68
5574.58				