Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Table S1.

Species	GA (MP2/6-311++G(3df,3pd))	GA (CCSD/6-311++G(d,p))
H_2SO	346.5022	350.6437
H_2SO_2	327.8653	350.3300
H_2SO_3	311.9895	331.9441
H_2SO_4	303.2045	306.6557
H_2SO_5	295.1724	300.1366
H_2S_2O	329.8733	337.0268
$H_2S_2O_3$	298.4982	304.7462
$H_2S_2O_4$	305.0869	308.3500
$H_2S_2O_6$	282.2459	278.9828
$H_2S_2O_7$	279.9868	280.1123

Table S2.

Species	Total Energy			Free Energy		
	Neutral	Monoanion	Dianion	Neutral	Monoanion	Dianion
H_2SO	-473.9925	-473.4209	-472.6219	-473.9936	-473.4314	-472.6417
H_2SO_2	-549.1145	-548.5675	-547.7710	-549.1106	-548.5781	-547.7916
H_2SO_3	-624.2623	-623.7474	-622.9855	-624.2582	-623.7510	-623.0021
H_2SO_4	-699.4014	-698.8952	-698.1698	-699.3902	-698.8970	-698.1828
H_2SO_5	-774.4134	-773.9216	-773.1755	-774.4012	-773.9208	-773.1875
H_2S_2O	-871.7156	-871.1698	-870.3892	-871.7181	-871.1824	-870.4122
$H_2S_2O_3$	-1021.9719	-1021.4744	-1020.7723	-1021.9676	-1021.4819	-1020.7874
$H_2S_2O_4$	-1097.0858	-1096.5800	-1095.8687	-1097.0792	-1096.5830	-1095.8867
$H_2S_2O_6$	-1247.3267	-1246.8546	-1246.1999	-1247.3107	-1246.8509	-1246.2064
$H_2S_2O_7$	-1322.4761	-1322.0070	-1321.3516	-1322.4547	-1321.9985	-1321.3546

Table S3.

Species	Total Energy			Free Energy		
	Neutral	Monoanion	Dianion	Neutral	Monoanion	Dianion
H_2SO	-473.9117	-473.3333	-472.5169	-473.9126	-473.3438	-472.5366
H_2SO_2	-548.9784	-548.3954	-547.6041	-548.9741	-548.4058	-547.6246
H_2SO_3	-624.0467	-623.4988	-622.7473	-624.0412	-623.5022	-622.7636
H_2SO_4	-699.1052	-698.5935	-697.8644	-699.0933	-698.5946	-697.8772
H_2SO_5	-774.0762	-773.5762	-772.8336	-774.0634	-773.5751	-772.8458
H_2S_2O	-871.5900	-871.0330	-870.2518	-871.5921	-871.0450	-870.2746
$H_2S_2O_3$	-1021.6927	-1021.1848	-1020.4807	-1021.6879	-1021.1923	-1020.4956
$H_2S_2O_4$	-1096.7503	-1096.2388	-1095.5161	-1096.7428	-1096.2414	-1095.5342
$H_2S_2O_6$	-1246.8368	-1246.3708	-1245.7007	-1246.8201	-1246.3655	-1245.7072
$H_2S_2O_7$	-1321.9176	-1321.4596	-1320.7762	-1321.8967	-1321.4403	-1320.7779

Table S4.

Species	$\Delta G_{sol.}$		
	Neutral	Monoanion	Dianion
H_2SO	-4.40	-64.52	-241.48
H_2SO_2	-7.46	-65.13	-240.58
H_2SO_3	-9.46	-62.68	-235.56
H_2SO_4	-12.10	-64.91	-231.53
H_2SO_5	-11.02	-62.54	-226.33
H_2S_2O	-4.70	-57.68	-203.28
$H_2S_2O_3$	-7.77	-57.01	-209.81
$H_2S_2O_4$	-3.79	-60.52	-202.14
$H_2S_2O_6$	-12.15	-55.77	-197.67
$H_2S_2O_7$	-11.69	-50.85	-192.46

Table S5.

Species	$\Delta G_{sol.}$		
	Neutral	Monoanion	Dianion
H_2SO	-5.09	-64.88	-243.38
H_2SO_2	-8.45	-70.19	-246.32
H_2SO_3	-11.57	-65.59	-241.44
H_2SO_4	-14.07	-67.16	-234.38
H_2SO_5	-12.94	-64.71	-227.15
H_2S_2O	-5.30	-58.06	-203.71
$H_2S_2O_3$	-9.94	-60.43	-212.27
$H_2S_2O_4$	-7.28	-63.79	-208.65
$H_2S_2O_6$	-14.62	-57.90	-199.95
$H_2S_2O_7$	-13.62	-52.83	-195.27

Electronic Supplementary Material (ESI) for Dalton Transactions

Molecular Cartesian Coordinates

B3LYP/6-311++G(d,p) Gas and Aqueous Phases

H_2SO (Gas Phase)

S	0.589182	-0.090312	0.006843
H	0.867145	1.236078	0.047958
O	-1.103734	0.029614	-0.116734
H	-1.464184	-0.027995	0.776433

H_2SO_2 (Gas Phase)

S	0.000000	0.000000	0.567082
O	0.000000	1.313899	-0.472841
O	0.000000	-1.313899	-0.472841
H	0.908641	1.490424	-0.753928
H	-0.908641	-1.490424	-0.753928

H_2SO_3 (Gas Phase)

S	0.296309	0.345267	0.000000
O	0.296309	-0.718162	1.280815
O	0.296309	-0.718162	-1.280815
H	-0.617950	-0.961756	1.504598
H	-0.617950	-0.961756	-1.504598
O	-1.030748	0.986229	0.000000

H_2SO_4 (Gas Phase)

S	0.000000	0.000000	0.169103
O	0.000000	1.259716	-0.859347
O	0.000000	-1.259716	-0.859347
H	0.901927	1.413628	-1.181762
H	-0.901927	-1.413628	-1.181762
O	1.273099	-0.056150	0.837964
O	-1.273099	0.056150	0.837964

H_2SO_5 (Gas Phase)

S	0.463972	-0.128367	0.064095
O	0.268817	-0.668960	1.380268
O	1.454550	-0.587056	-0.876010
O	0.577051	1.470174	0.254247
O	-0.952172	-0.279996	-0.815980
O	-2.083983	0.169308	-0.044727
H	0.832595	1.883289	-0.586449
H	-2.370251	-0.657181	0.378553

H_2S_2O (Gas Phase)

S	0.542243	0.629804	0.001570
S	-1.362645	-0.205646	-0.086920
O	1.613706	-0.677762	0.113456
H	1.803101	-0.992033	-0.780926
H	-1.586322	-0.372392	1.238881

$H_2S_2O_3$ (Gas Phase)

S	-0.437507	0.055805	-0.145956
O	-0.837639	1.431807	-0.312762
O	-0.949086	-0.336654	1.358511
O	-0.825271	-1.007852	-1.051102
S	1.689716	-0.080285	0.005284
H	1.772824	0.992891	0.821966
H	-0.912213	-1.299624	1.471615

$H_2S_2O_4$ (Gas Phase)

S	0.531242	1.165200	0.459734
S	-0.531242	-1.165200	0.459734
O	-0.531242	1.683631	-0.476830
O	1.751832	0.516796	-0.358901
O	-1.751832	-0.516796	-0.358901
O	0.531242	-1.683631	-0.476830
H	-1.510150	0.425955	-0.669900
H	1.510150	-0.425955	-0.669900

$H_2S_2O_6$ (Gas Phase)

S	-0.187774	1.116474	0.124370
O	1.072847	1.761770	-0.163610
O	-1.072847	1.245574	-1.231434
O	-1.006555	1.413291	1.280735
H	-1.984275	0.944773	-1.075449
S	0.187774	-1.116474	0.124370
O	-1.072847	-1.761770	-0.163610
O	1.072847	-1.245574	-1.231434
O	1.006555	-1.413291	1.280735
H	1.984275	-0.944773	-1.075449

$H_2S_2O_7$ (Gas Phase)

S	0.000000	1.450103	0.069732
O	0.101960	2.480908	1.050217
O	-1.484800	1.475872	-0.511561
O	0.959805	1.265228	-1.005234
H	-1.635094	0.689269	-1.076522
S	0.000000	-1.450103	0.069732
O	-0.101960	-2.480908	1.050217
O	1.484800	-1.475872	-0.511561
O	-0.959805	-1.265228	-1.005234
H	1.635094	-0.689269	-1.076522
O	0.000000	0.000000	0.923360

HSO^- (Gas Phase)

S	0.037547	-0.663782	0.000000
O	0.037547	1.157686	0.000000
H	-0.901130	1.359019	0.000000

HSO_2^- (Gas Phase)

S	0.000092	0.367016	-0.132215
O	1.286562	-0.439693	0.065649
O	-1.286729	-0.439599	0.065608
H	-0.000133	1.162075	1.065381

HSO_3^- (Gas Phase)

S	0.000000	0.000000	0.172821
O	0.000000	1.442425	-0.180031
O	-1.249177	-0.721213	-0.180031
O	1.249177	-0.721213	-0.180031
H	0.000000	0.000000	1.55560

HSO_4^- (Gas Phase)

S	-0.155904	-0.023194	-0.008759
O	1.487716	0.452330	0.102587
O	-0.415224	-0.732323	1.262624
H	1.987603	-0.372978	0.081835
O	-0.827520	1.275480	-0.157873
O	-0.181614	-0.902477	-1.200051

HSO_5^- (Gas Phase)

S	-0.502159	-0.062792	-0.016679
O	-0.761625	-0.818571	1.215901
O	-1.440785	1.025535	-0.314139
O	-0.077218	-0.897946	-1.171159
O	0.946786	0.875219	0.252286
O	2.106145	0.005749	0.132306
H	1.848126	-0.515210	-0.654704

HS_2O^- (Gas Phase)

S	0.461907	0.650897	0.020685
S	-1.396630	-0.254006	-0.010121
O	1.677195	-0.646377	-0.106940
H	1.538022	-1.179240	0.686493

$HS_2O_3^-$ (Gas Phase)

S	0.538510	0.002948	-0.000042
O	0.862448	1.442425	-0.003272
O	0.874529	-0.726989	-1.239618
O	0.875304	-0.721359	1.242584
S	-1.728684	0.079016	0.000139
H	-1.855469	-1.264054	0.000897

$HS_2O_4^-$ (Gas Phase)

S	-0.788276	0.066294	-0.002128
S	1.267699	-0.811549	0.063679
O	2.111976	0.678616	0.067420
O	-0.478346	1.285708	-0.803442
O	-1.227864	0.348616	1.377303
O	-1.559431	-0.979403	-0.702683
H	1.558554	1.255784	-0.493597

$HS_2O_6^-$ (Gas Phase)

S	-1.114792	-0.168985	0.018432
O	-1.734229	-0.637469	1.259935
O	-1.382542	1.481137	-0.004021
O	-1.598543	-0.716876	-1.254517
H	-0.608120	1.857137	-0.466189
S	1.234738	-0.035526	0.014957
O	1.309604	1.219520	-0.776081
O	1.581557	0.090381	1.434606
O	1.660276	-1.259812	-0.668427

$HS_2O_7^-$ (Gas Phase)

S	1.574220	0.015127	0.009503
O	2.327434	-0.553833	1.117168
O	1.879055	1.381229	-0.387233
O	1.233384	-0.918313	-1.090763
S	-1.478603	0.113630	0.080178
O	-2.520472	-0.048687	1.073926
O	-1.389610	-1.298951	-0.713108
O	-1.577194	1.192545	-0.888278
H	-0.479520	-1.350674	-1.099103
O	-0.083889	0.157330	0.846314

SO^{2-} (Gas Phase)

S	0.000000	0.000000	0.565111
O	0.000000	0.000000	-1.130223

SO_2^{2-} (Gas Phase)

S	0.000000	0.000000	0.461717
0	0.000000	1.335948	-0.461717
0	0.000000	-1.335948	-0.461717

SO_3^{2-} (Gas Phase)

S	0.000000	0.000000	0.338982
O	0.000000	1.460817	-0.225988
O	-1.265105	-0.730409	-0.225988
O	1.265105	-0.730409	-0.225988

SO_4^{2-} (Gas Phase)

S	-0.000012	-0.000013	0.000010
O	1.060225	0.174550	1.084622
O	-1.287733	-0.528370	0.627336
O	0.500972	-0.992629	-1.046248
O	-0.273442	1.346474	-0.665732

SO_5^{2-} (Gas Phase)

S	-0.401912	0.127274	0.000000
O	-0.827704	-0.589038	1.241466
O	-0.827704	1.567725	0.000000
O	-0.827704	-0.589038	-1.241466
O	1.241362	0.305479	0.000000
O	2.045574	-0.949677	0.000000

S_2O^{2-} (Gas Phase)

S	0.000000	1.551392	-0.175060
S	0.000000	-1.551392	-0.175060
O	0.000000	0.000000	0.700240

$S_2O_3^{2-}$ (Gas Phase)

S	0.000000	0.000000	-0.416236
O	0.000000	1.435296	-0.879786
O	-1.243003	-0.717648	-0.879786
O	1.243003	-0.717648	-0.879786
S	0.000000	0.000000	1.735915

$S_2O_4^{2-}$ (Gas Phase)

S	0.336115	1.255763	0.000000
S	-0.336115	-1.255763	0.000000
O	-0.336115	1.806566	1.273307
O	-0.336115	1.806566	-1.273307
O	0.336115	-1.806566	-1.273307
O	0.336115	-1.806566	1.273307

$S_2O_6^{2-}$ (Gas Phase)

S	0.000000	0.000000	1.163203
O	0.000000	1.440666	1.558569
O	1.247654	-0.720333	1.558569
O	-1.247654	-0.720333	1.558569
S	0.000000	0.000000	-1.163203
O	0.000000	-1.440666	-1.558569
O	1.247654	0.720333	-1.558569
O	-1.247654	0.720333	-1.558569

$S_2O_7^{2-}$ (Gas Phase)

S	0.000000	1.560901	-0.000647
O	0.000000	2.380871	1.234876
O	1.241734	1.672557	-0.793628
O	-1.241734	1.672557	-0.793628
S	0.000000	-1.560901	-0.000647
O	0.000000	-2.380871	1.234876
O	-1.241734	-1.672557	-0.793628
O	1.241734	-1.672557	-0.793628
O	0.000000	0.000000	0.707351

H_2SO (Aqueous Phase)

S	0.591090	-0.089081	0.011926
H	0.867242	1.238996	-0.019240
O	-1.106220	0.014492	-0.118375
H	-1.474921	0.070362	0.775424

H_2SO_2 (Aqueous Phase)

S	0.000000	0.000000	0.565296
O	0.000000	1.314775	-0.473924
O	0.000000	-1.314775	-0.473924
H	0.911806	1.526577	-0.730973
H	-0.911806	-1.526577	-0.730973

H_2SO_3 (Aqueous Phase)

S	0.293115	0.344476	0.000000
O	0.293115	-0.708785	1.272603
O	0.293115	-0.708785	-1.272603
H	-0.574297	-1.143157	1.390597
H	-0.574297	-1.143157	-1.390597
O	-1.028885	1.014408	0.000000

H_2SO_4 (Aqueous Phase)

S	0.000000	0.000000	0.150254
O	0.000000	1.259348	-0.842548
O	0.000000	-1.259348	-0.842548
H	0.845217	1.346760	-1.324275
H	-0.845217	-1.346760	-1.324275
O	1.259076	-0.086523	0.857829
O	-1.259076	0.086523	0.857829

H_2SO_5 (Aqueous Phase)

S	0.460939	-0.094517	0.082370
O	0.327164	-0.267250	1.507720
O	1.435898	-0.816762	-0.703763
O	0.571445	1.477774	-0.150367
O	-0.957652	-0.493269	-0.685544
O	-2.082797	0.149353	-0.052990
H	0.746165	1.704149	-1.085808
H	-2.473655	-0.590645	0.447445

H_2S_2O (Aqueous Phase)

S	0.540272	0.629918	-0.001649
S	-1.362907	-0.210066	-0.086828
O	1.618006	-0.674901	0.118497
H	1.826828	-0.992871	-0.774457
H	-1.608716	-0.325546	1.242112

$H_2S_2O_3$ (Aqueous Phase)

S	0.426001	-0.115681	0.072456
O	0.869668	0.031080	1.448084
O	0.961603	1.224255	-0.651335
O	0.807362	-1.282708	-0.710456
S	-1.685492	-0.013151	-0.061420
H	-1.764359	1.071761	0.748950
H	0.807161	1.208529	-1.615864

$H_2S_2O_4$ (Aqueous Phase)

S	-0.514586	1.153325	-0.465699
S	0.514586	-1.153325	-0.465699
O	0.514586	1.694187	0.495299
O	-1.766375	0.539686	0.349261
O	1.766375	-0.539686	0.349261
O	-0.514586	-1.694187	0.495299
H	1.558826	0.389132	0.694700
H	-1.558826	-0.389132	0.694700

$H_2S_2O_6$ (Aqueous Phase)

S	0.511856	1.012619	-0.111741
O	-0.511856	2.013856	0.110263
O	1.355720	0.933586	1.244744
O	1.379095	1.032815	-1.276310
H	2.177675	0.407820	1.158282
S	-0.511856	-1.012619	-0.111741
O	0.511856	-2.013856	0.110263
O	-1.355720	-0.933586	1.244744
O	-1.379095	-1.032815	-1.276310
H	-2.177675	-0.407820	1.158282

$H_2S_2O_7$ (Aqueous Phase)

S	0.000000	1.482556	0.047367
O	0.239739	2.413957	1.112917
O	-1.519228	1.647100	-0.365556
O	0.857214	1.364641	-1.109798
H	-1.753934	1.159447	-1.181889
S	0.000000	-1.482556	0.047367
O	-0.239739	-2.413957	1.112917
O	1.519228	-1.647100	-0.365556
O	-0.857214	-1.364641	-1.109798
H	1.753934	-1.159447	-1.181889
O	0.000000	0.000000	0.830879

HSO^- (Aqueous Phase)

S	0.037279	-0.663954	0.000000
O	0.037279	1.153036	0.000000
H	-0.894689	1.398972	0.000000

HSO_2^- (Aqueous Phase)

S	0.000007	0.396366	-0.122573
O	1.277572	-0.464576	0.054748
O	-1.277586	-0.464567	0.054746
H	-0.000001	1.091287	1.085214

HSO_3^- (Aqueous Phase)

S	-0.000148	-0.000122	0.194714
O	0.501514	1.346785	-0.194754
O	-1.417493	-0.239269	-0.194795
O	0.916276	-1.107302	-0.194873
H	0.000002	0.000234	1.559959

HSO_4^- (Aqueous Phase)

S	0.133021	-0.010590	-0.000037
O	-1.500808	0.292452	-0.000408
O	0.399622	-0.782094	-1.236035
H	-1.990012	-0.547058	0.000681
O	0.684359	1.357960	-0.001709
O	0.399536	-0.778755	1.238142

HSO_5^- (Aqueous Phase)

S	-0.497371	-0.062555	-0.003376
O	-0.540374	-0.779196	1.283386
O	-1.433608	1.068129	-0.127531
O	-0.398507	-0.939801	-1.185434
O	0.968127	0.839940	0.013431
O	2.103592	-0.044215	0.123695
H	2.364096	-0.157966	-0.806355

HS_2O^- (Aqueous Phase)

S	0.466054	0.642457	0.015704
S	-1.404820	-0.252093	-0.004602
O	1.658160	-0.651010	-0.117759
H	1.754978	-1.037744	0.764436

$HS_2O_3^-$ (Aqueous Phase)

S	0.491498	0.001943	-0.000029
O	0.843243	1.443499	-0.001679
O	0.888024	-0.716436	-1.236899
O	0.888333	-0.713497	1.238454
S	-1.687418	0.070944	0.000048
H	-1.822083	-1.274716	0.000685

$HS_2O_4^-$ (Aqueous Phase)

S	0.777167	-0.070425	0.000617
S	-1.246894	0.740241	-0.009800
O	-2.180678	-0.658127	0.118538
O	0.910121	-0.931967	-1.203063
O	0.953923	-0.821854	1.268763
O	1.548580	1.198823	-0.069538
H	-2.339926	-1.012065	-0.770660

$HS_2O_6^-$ (Aqueous Phase)

S	-1.078863	-0.148075	-0.027900
O	-1.561142	-0.992406	1.066866
O	-1.556544	1.358078	0.399816
O	-1.540464	-0.421763	-1.394575
H	-1.405452	2.001009	-0.318497
S	1.220555	0.008288	0.004156
O	1.447922	1.127400	-0.924785
O	1.495646	0.283459	1.421768
O	1.606878	-1.325321	-0.481789

$HS_2O_7^-$ (Aqueous Phase)

S	-1.566859	-0.001523	0.000424
O	-2.345561	0.380595	1.171336
O	-1.813628	-1.327591	-0.555949
O	-1.255536	1.062592	-0.965619
S	1.457348	-0.124376	0.060071
O	2.508699	-0.241673	1.049120
O	1.517379	1.399275	-0.448114
O	1.444241	-1.018447	-1.087493
H	0.724445	1.608064	-0.988358
O	0.072873	-0.203963	0.839275

SO^{2-} (Aqueous Phase)

S	0.000000	0.000000	0.596614
O	0.000000	0.000000	-1.193228

SO_2^{2-} (Aqueous Phase)

S	0.000000	0.000000	0.497571
O	0.000000	1.325122	-0.497571
O	0.000000	-1.325122	-0.497571

SO_3^{2-} (Aqueous Phase)

S	0.000768	-0.000462	0.371769
O	-1.105439	-0.925895	-0.247679
O	1.354343	-0.493156	-0.248350
O	-0.250440	1.419974	-0.247509

SO_4^{2-} (Aqueous Phase)

S	-0.000349	0.000341	-0.000477
O	0.409426	-0.902252	1.148161
O	1.194518	0.238075	-0.904368
O	-0.491401	1.326024	0.548314
O	-1.111846	-0.662530	-0.791152

SO_5^{2-} (Aqueous Phase)

S	-0.398721	0.151744	0.000000
O	-0.790625	-0.572522	1.236918
O	-0.790625	1.585412	0.000000
O	-0.790625	-0.572522	-1.236918
O	1.245419	0.286216	0.000000
O	1.923899	-1.030071	0.000000

S_2O^{2-} (Aqueous Phase)

S	0.000000	1.537181	-0.181535
S	0.000000	-1.537181	-0.181535
O	0.000000	0.000000	0.726139

$S_2O_3^{2-}$ (Aqueous Phase)

S	0.376324	0.000087	-0.000267
O	0.874135	-0.421695	1.365936
O	0.877303	1.393365	-0.317506
O	0.875983	-0.972831	-1.046853
S	-1.690034	0.000493	-0.000521

$S_2O_4^{2-}$ (Aqueous Phase)

S	0.354905	1.156614	0.000000
S	-0.354905	-1.156614	0.000000
O	-0.354905	1.678749	1.267361
O	-0.354905	1.678749	-1.267361
O	0.354905	-1.678749	-1.267361
O	0.354905	-1.678749	1.26736

$S_2O_6^{2-}$ (Aqueous Phase)

S		0.000000	0.000384	1.126669
O		0.000000	1.439192	1.508448
O		1.246159	-0.719060	1.506996
O		-1.246159	-0.719060	1.506996
S		0.000000	-0.000384	-1.126669
O		0.000000	-1.439192	-1.508448
O		1.246159	0.719060	-1.506996
O		-1.246159	0.719060	-1.506996

$S_2O_7^{2-}$ (Aqueous Phase)

S	0	0.000000	1.523346	0.004383
O		0.000000	2.391028	1.196334
O		1.238738	1.576758	-0.794665
O		-1.238738	1.576758	-0.794665
S		0.000000	-1.523346	0.004383
O		0.000000	-2.391028	1.196334
O		-1.238738	-1.576758	-0.794665
O		1.238738	-1.576758	-0.794665
O		0.000000	0.000000	0.768457