Sulphur Dioxide Cooperation in Hydrolysis Reactions by Vanadium Oxide and Hydroxide Cluster Dianions.

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SUPPLEMENTARY INFORMATION

Electrospray Ionization Mass Spectra

The negative electrospray ionization of sodium metavanadate solution generates a variety of singly-, doubly- and triply-charged ions. Multiply-charged ions are observed when low-voltage potentials are applied to the capillary voltage and to the tube lens (typically, -5 V). To increase the intensity of singly-charged ions, the voltage potentials need to be raised to medium or higher values.

When operating at higher voltage, the main peaks observed correspond to VO_3^- (m/z = 99), $H_2VO_4^-$ (m/z = 117), $[CH_3CN{\cdot}VO_3]^-$ (m/z = 140), $V_2O_5^-$ (m/z = 182), $H_2V_2O_6^-$ (m/z = 200), $V_3O_8^-$ (m/z = 281). In addition, two main series of singly charged ions are observed that can be attributed to ions having the general formulas $Na_yV_{y+1}O_{3y+3}^-$ and $Na_yV_{y+3}O_{3y+8}^-$ (y =1-5). Minor series correspond to $H_xV_{x+1}O_{3x+3}^-$ (x = 1,2), $H_xV_{x+3}O_{3x+8}^-$ (x = 1) and to the mixed cluster ions $H_xNa_yV_{x+y+1}O_{3x+3y+3}^-$ (x = 1, 2; y = 1, 2) and $H_xNa_yV_{x+y+3}O_{3x+3y+8}^-$ (x = 1; y =1,2). These ions were generally unreactive towards SO_2, with a few exceptions giving association complexes.

Passing to the multiply-charged species, the most abundant ions observed were: $H_2V_2O_7^{2-}$ (m/z = 108), $CH_3CN{\cdot}H_2V_2O_7^{2-}$ (m/z = 128.5), $V_2O_{11}^{2-}$ (m/z = 190), and the series $H_xV_{x+2}O_{3x+6}^{2-}$

(x = 1, 2), $Na_yV_{y+2}O_{3y+6}^{2-}$ (y = 1 to at least 8), $H_xNa_yV_{x+y+2}O_{3x+3y+6}^{2-}$ (x = 1, 2; y = 1, 2). The most intense triply-charged ions were: $V_5O_{14}^{3-}$ (m/z = 159.6), $HNaV_5O_{15}^{3-}$ (m/z = 173), and few ions from the series $Na_yV_{y+3}O_{3y+9}^{3-}$ (y = 2, 7).

For all the ions probed, an isolation width of 1 m/z was generally used. An isolation width of 4 m/z was used instead for the investigated cluster ions $[V_2O_6\text{-}(SO_2)_2]^{2-}$ (m/z = 163) and $[HV_3O_9\text{-}SO_2]^{2-}$ (m/z = 181). This wide mass window does not affect the isolation, because the ions come from precursor ions in turn isolated with a 1 m/z window, and specifically $[V_2O_6\cdot(SO_2)_2]^{2-}$ (m/z = 163) comes from isolated $[V_2O_6\cdot SO_2]^{2-}$ (m/z = 131), coming in turn from isolated $V_2O_6^{2-}$ (m/z = 99). Likewise, $[HV_3O_9\cdot SO_2]^{2-}$ (m/z = 181) comes from isolated $[HV_3O_9]^{2-}$ (m/z = 149).

Kinetic measurements

Mass discrimination effects are operative in kinetic experiments that leads to the observation of smaller abundance of the lighter singly-charged fragments with respect to the higher mass fragment. It is well documented that the kinetic energy release in charge-separation reactions of doubly-charged anions is partitioned into translational energy of the singly-charged product ions and it is proportionally greater for the lighter ion. [1-3]

In the following table the mass and intensity ratios of the heavier (M1) and lighter (M2) product ions are reported, showing that the higher the m/z ratio the greater the intensity ratio, which is the consequence of the mass discrimination towards the lighter ion.

Parent m/z	M1	M2	R M1/M2	R I1/I2
163^{2-}	263^{-}	81^{-}	3,25	2,15
181^{2-}	299^{-}	81^{-}	3,69	4,17

Accordingly, the rate constants of the investigated reactions were evaluated i- considering the sum of the intensities of the two monoanions produced, ii- attributing to the lighter ion the same intensity of the heavier one. The first procedure thus gives a lower rate constant than the second one, however the difference between the two values is below 15%, which is within the reported experimental uncertainty.

[1] J. Roithová, D. Schröder, *Phys. Chem. Chem. Phys.,* **2007**, 9, 2341–2349.
[2] J. Roithová, P. Milko, C. L. Ricketts, D. Schröder, T. Besson, V. Dekoj, M. Belohradsky, *J. Am. Chem. Soc*. **2007**, 129, 10141-10148.
[3] J. Marçalo, M. Santos, A. Pires de Matos, J. K. Gibson, R. G. Haire, *J. Phys. Chem. A*,. **2008**, 49, 12647–12656.

Mass spectra

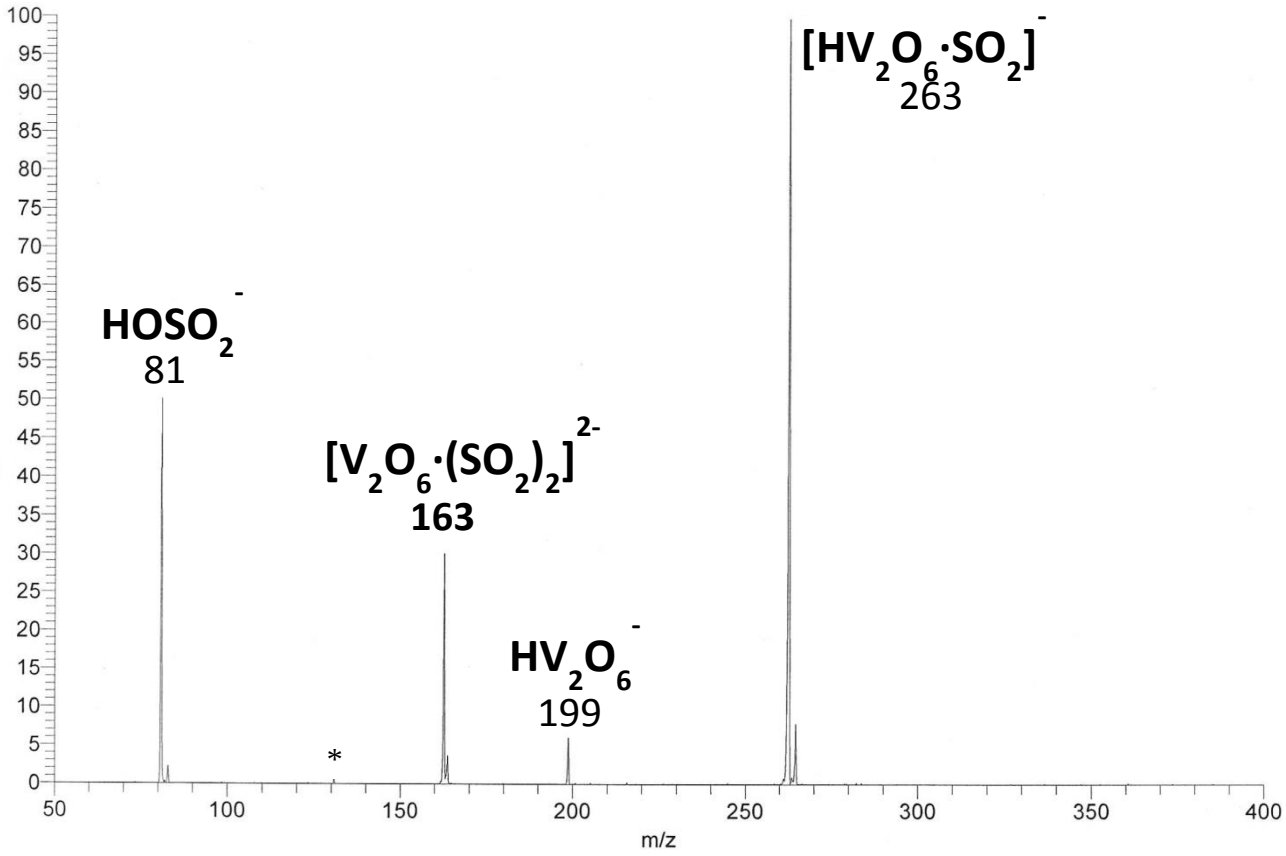

Fig. 1S

ITMS mass spectrum of the reaction of isolated $[V_2O_6{\cdot}(SO_2)_2]^{2-}$ ions (m/z 163) with H_2O at a reaction time of 2.5 seconds. *P* $H_2O = 6.2 \bullet 10^{-7}$ Torr.

$[V_2O_6{\cdot}(SO_2)_2]^{2-}$ ions were generated by multistage mass spectrometry (MS^n) experiments. Mass selected $V_2O_6^{2-}$ ions (m/z 99) were reacted with SO_2 (*P* = $1.6 \bullet 10^{-7}$ Torr). They gave $[V_2O_6{\cdot}SO_2]^{2-}$ ions (m/z 131) that were isolated after 100 ms and reacted again with SO_2 for 500 ms. The so formed $[V_2O_6{\cdot}(SO_2)_2]^{2-}$ ions (m/z 163) were isolated and eventually reacted with H_2O.

The very small signal at m/z 131 (*) is formed upon isolation of $[V_2O_6{\cdot}(SO_2)_2]^{2-}$ ions (m/z 163) by loss of SO_2.

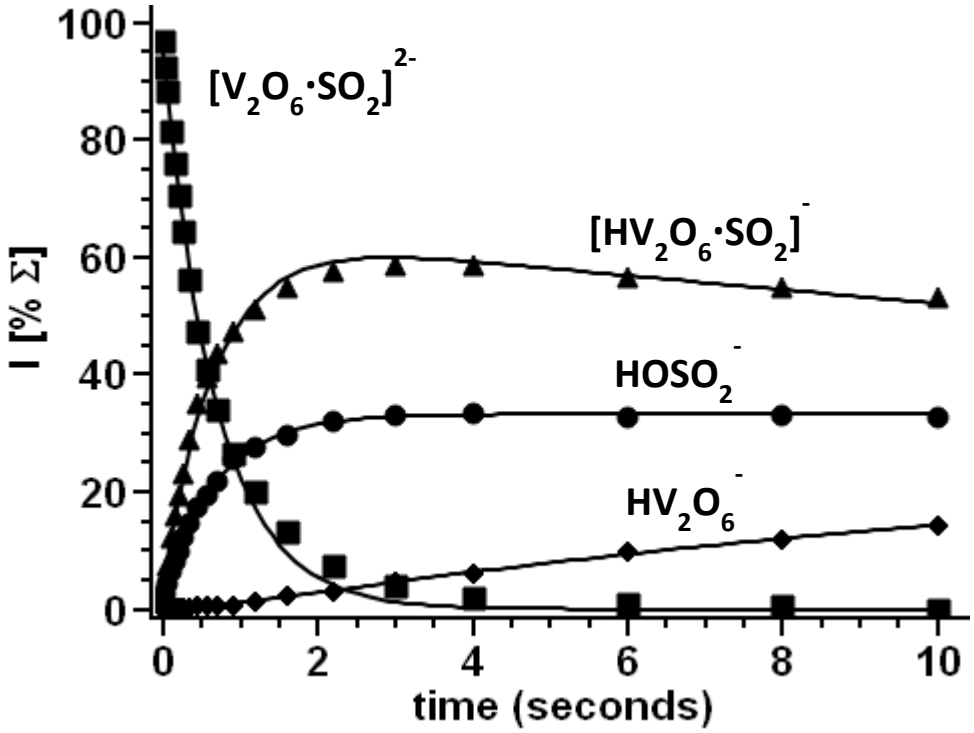

Fig. 2S

Kinetic plot and best fit lines of the reaction of thermal $[V_2O_6{\cdot}(SO_2)_2]^{2-}$ ions (■) with H_2O, showing the separate profiles of the $HOSO_2^-$ (●) and $[HV_2O_6{\cdot}SO_2]^-$ (▲) products, that are summed in Fig. 1A. Note the clear origin of the $HV_2O_6^-$ ions from $[HV_2O_6{\cdot}SO_2]^-$.
$[V_2O_6{\cdot}(SO_2)_2]^{2-}$ (■) (R^2 = 0.9970), $HV_2O_6{\cdot}SO_2^-$ (▲) (R^2 = 0.9951); $HOSO_2^-$ (●) (R^2 = 0.9985); $HV_2O_6^-$ (♦) (R^2 = 0.9944). *P* H_2O = 8.3 • 10^{-7} Torr, *P* SO_2 = 1.5 • 10^{-7} Torr.

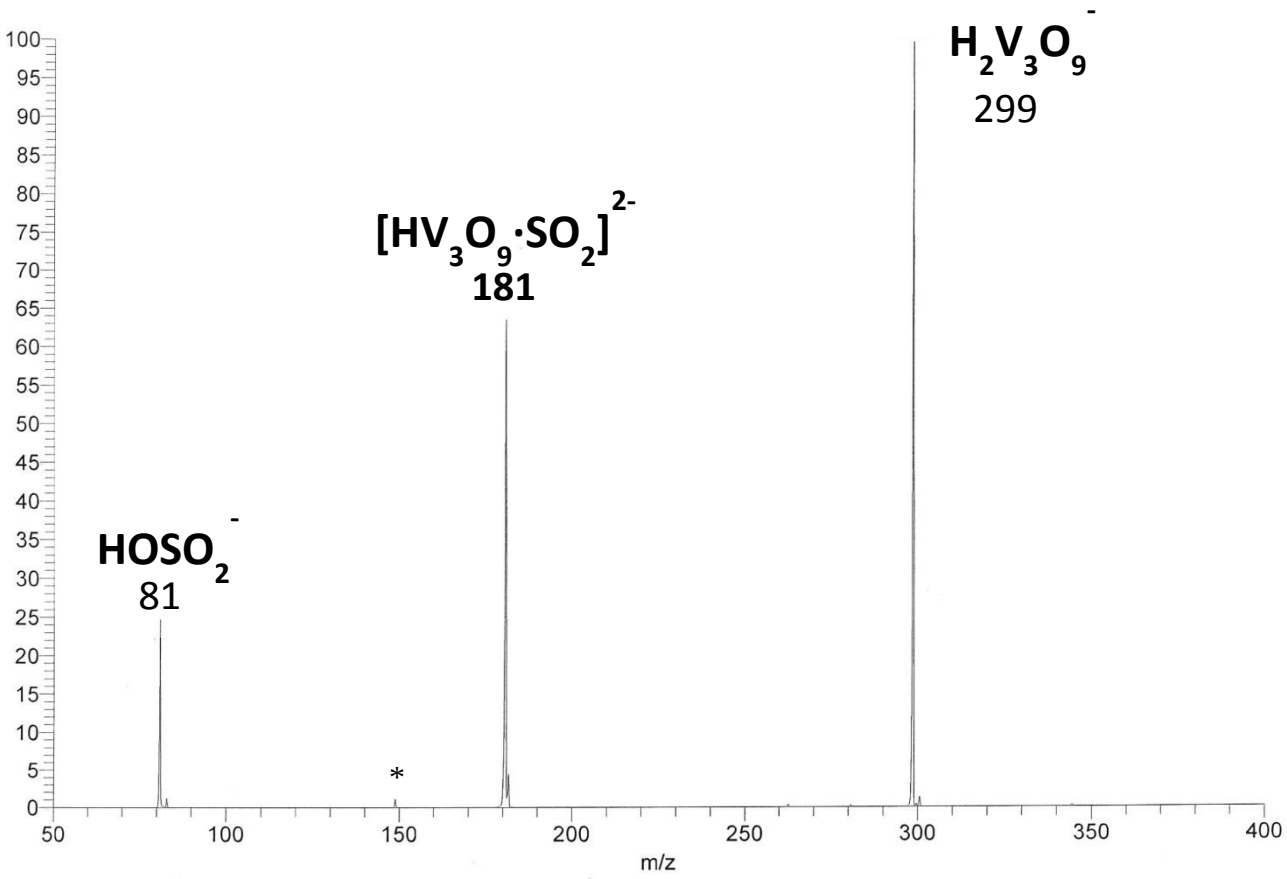

Fig. 3S

ITMS mass spectrum of the reaction of isolated $[HV_3O_9 \cdot SO_2]^{2-}$ ions (m/z 181) with H_2O at a reaction time of 2.5 seconds. *P* $H_2O = 6.2 \bullet 10^{-7}$ Torr.

$[HV_3O_9 \cdot SO_2]^{2-}$ ions were generated by reaction of mass selected $HV_3O_9^{2-}$ ions (m/z 149) with SO_2 (*P* = $1.6 \bullet 10^{-7}$ Torr) for 100 ms. $[HV_3O_9 \cdot SO_2]^{2-}$ ions were then isolated and reacted with H_2O.

The very small signal at m/z 149 (*) is formed upon isolation of $[HV_3O_9 \cdot SO_2]^{2-}$ ions (m/z 181) by loss of SO_2

Cartesian coordinates of the investigated species

H_2O

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	0.000000	0.000000	0.121307
2	1	0.000000	0.764291	-0.485227
3	1	0.000000	-0.764291	-0.485227

$[OH]^-$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	0.000000	0.000000	0.110635
2	1	0.000000	0.000000	-0.885080

SO_2

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	16	0.000000	0.000000	0.364112
2	8	0.000000	1.270523	-0.364112
3	8	0.000000	-1.270523	-0.364112

$[V_2O_6]^{2-}$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	-1.346584	0.000032	0.000001
2	8	-2.284392	-1.368016	-0.000011
3	8	-2.285692	1.367532	0.000001
4	8	0.000036	-0.000368	-1.264542
5	8	0.000017	-0.000323	1.264547
6	23	1.346284	-0.000095	0.000000
7	8	2.286153	-1.366593	0.000028
8	8	2.284741	1.367949	-0.000026

$[V_2O_6(SO_2)_2]^{2-}$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	-1.335321	0.637379	-0.011229
2	8	-2.378877	-0.712833	-0.025804
3	8	-2.210624	2.007997	-0.022940
4	8	0.010181	0.618042	-1.250256
5	8	-0.010512	0.617280	1.250034
6	23	1.335104	0.636663	0.011029
7	8	2.378024	-0.713941	0.024869
8	8	2.211030	2.006881	0.023706
9	16	-4.478792	-0.574782	-0.046955
10	8	-4.798640	-1.114913	1.300194
11	8	-4.789503	-1.479591	-1.184947
12	16	4.478835	-0.574449	0.047061
13	8	4.799780	-1.114514	-1.299833
14	8	4.789677	-1.478816	1.185338

$[HV_2O_6SO_2]^-$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	0.072933	0.348929	-0.046412
2	8	1.347736	-0.710363	0.003814
3	8	0.605902	1.872130	-0.154582
4	8	-1.278338	0.084763	1.237312
5	8	-1.308059	-0.078471	-1.251783
6	23	-2.521822	-0.245232	0.023929
7	8	-3.153763	-1.725278	0.128244
8	8	-3.866185	0.981162	-0.042459
9	16	3.581301	0.095719	-0.025537
10	8	4.126538	-0.700267	-1.142198
11	8	3.997666	-0.283399	1.338078
12	1	-4.748345	0.561267	-0.005700

$[HV_2O_6]^-$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	1.402593	0.030801	-0.000050
2	8	2.407400	-1.251128	-0.000087
3	8	2.225790	1.436491	-0.000143
4	8	-0.031618	-0.062200	1.253640
5	8	-0.031720	-0.062343	-1.253435
6	23	-1.266820	-0.083994	0.000201
7	8	-2.177686	-1.422947	-0.000155
8	8	-2.369279	1.377795	0.000165
9	1	-3.305888	1.098105	-0.003371

$[HOSO_2]^-$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	16	-0.199424	0.039872	-0.380974
2	8	-1.160601	-0.864839	0.336415
3	8	-0.071375	1.405012	0.258464
4	8	1.430590	-0.615833	0.062351
5	1	1.601868	-0.032676	0.837731

1^{2}

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	-1.541854	0.549847	-0.210090
2	8	-2.640852	-0.653674	0.265582
3	8	-2.345950	1.906519	-0.598996
4	8	-0.282125	0.050828	-1.453165
5	8	-0.116591	0.828997	0.913500
6	23	1.114991	0.364004	-0.337216
7	8	2.075228	-1.008991	0.021734
8	8	2.074267	1.591301	-0.830605
9	16	-4.765873	-0.351139	0.296776
10	8	-5.078077	-0.828880	1.667490
11	8	-5.180985	-1.253441	-0.806386
12	16	4.116114	-1.077268	-0.135276
13	8	4.308674	-2.522953	-0.412513
14	8	4.499641	-0.652008	1.245254
15	8	4.228377	2.319084	1.037338
16	1	4.359844	1.368314	1.254907
17	1	3.521297	2.253390	0.355257

3^{2-}

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	-1.910412	-0.386716	-0.115786
2	8	-3.271381	0.587849	0.148817
3	8	-2.367359	-1.824935	-0.712862
4	8	-0.715928	-0.499020	1.279986
5	8	-0.524909	0.400498	-1.039655
6	23	0.637798	0.255276	0.340942
7	8	1.117114	1.680512	0.937449
8	8	2.004904	-0.778864	0.060199
9	16	-5.290517	-0.068948	-0.255030
10	8	-5.753092	1.036738	-1.129926
11	8	-5.845325	-0.076082	1.120871
12	16	5.787667	-0.213911	-0.564425
13	8	5.959445	1.243292	-0.853045
14	8	6.856312	-0.824251	0.273796
15	8	4.301044	-0.056952	0.766785
16	1	4.202209	0.920052	0.777770
17	1	3.026912	-0.481458	0.335586

2^{2-}

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	-1.871934	-0.524588	-0.165565
2	8	-3.054638	0.653164	0.200813
3	8	-2.575964	-1.815879	-0.859867
4	8	-0.727827	-0.951353	1.193140
5	8	-0.400632	0.081850	-1.065145
6	23	0.753747	-0.356217	0.289852
7	8	1.548359	0.919924	0.996369
8	8	1.876857	-1.526888	-0.076506
9	16	-5.100215	0.446195	-0.202824
10	8	-5.328632	1.660086	-1.030555
11	8	-5.652210	0.505403	1.176487
12	16	5.369437	0.624409	-0.576962
13	8	5.933041	1.734593	0.220834
14	8	6.236168	-0.557399	-0.774707
15	8	3.988861	-0.248793	1.012225
16	1	3.246769	0.427991	1.137577
17	1	3.416944	-0.936813	0.535699

TS [$3^{2-} \rightarrow 4^{2-}$]

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	1.812329	0.427777	-0.006746
2	8	3.089841	-0.670337	-0.073719
3	8	2.385978	1.942495	0.062140
4	8	0.476144	0.064364	1.222568
5	8	0.477502	0.186199	-1.263417
6	23	-0.795807	-0.123173	-0.031466
7	8	-1.392984	-1.617131	-0.100812
8	8	-2.075141	1.104278	0.050283
9	16	5.195762	-0.006069	-0.009160
10	8	5.751835	-0.791106	-1.136757
11	8	5.572790	-0.463172	1.348595
12	16	-5.229176	0.189053	0.231967
13	8	-6.429491	0.675202	-0.514392
14	8	-5.488888	-0.900441	1.231818
15	8	-4.362722	-0.700920	-1.083251
16	1	-3.851903	-1.385925	-0.596176
17	1	-3.032382	0.816842	-0.034296

4^{2-}

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	1.751264	0.457561	-0.039892
2	8	3.004079	-0.671036	0.048332
3	8	2.360566	1.952898	-0.192952
4	8	0.433303	0.306674	1.246614
5	8	0.394350	0.073956	-1.233504
6	23	-0.868875	-0.026336	0.047688
7	8	-1.531217	-1.497937	0.202232
8	8	-2.125176	1.194128	-0.039751
9	16	5.115173	-0.076063	-0.030903
10	8	5.572654	-0.886758	-1.184741
11	8	5.566993	-0.536189	1.303800
12	16	-4.912164	0.100721	0.049986
13	8	-6.007036	0.550820	-0.856400
14	8	-5.343457	-0.311260	1.420628
15	8	-4.428713	-1.374174	-0.737437
16	1	-3.578569	-1.615594	-0.294454
17	1	-3.135289	0.893903	-0.004777

$[V_2O_6\text{-}SO_2]^{2-}$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	0.051945	0.472204	-0.025704
2	8	1.444113	-0.563235	0.007260
3	8	0.530716	2.029903	-0.092649
4	8	-1.187478	0.155678	1.248936
5	8	-1.196571	0.053279	-1.261371
6	23	-2.523524	-0.271419	0.013915
7	8	-3.052259	-1.828541	0.078194
8	8	-3.785176	0.786280	-0.024405
9	16	3.346687	0.018384	-0.020549
10	8	3.851474	-0.763110	-1.188005
11	8	3.807595	-0.484279	1.307031

$1a^{2-}$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	0.120896	0.307308	0.161984
2	8	-1.179990	-0.796251	-0.161376
3	8	-0.462989	1.770318	0.625589
4	8	1.338161	0.416501	-1.151783
5	8	1.405858	-0.321168	1.244291
6	23	2.733078	-0.228507	-0.078462
7	8	3.350970	-1.677344	-0.543217
8	8	3.927175	0.858933	0.224327
9	16	-3.121806	-0.607300	-0.026930
10	8	-3.364062	-1.052028	1.373303
11	8	-3.545547	-1.574672	-1.077719
12	8	-2.797862	2.797902	-0.622587
13	1	-3.134283	1.876855	-0.611357
14	1	-1.931920	2.650007	-0.165409

$2a^{2-}$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	-3.149153	0.000373	-0.197566
2	8	-4.066460	1.360304	-0.353228
3	8	-4.064851	-1.360102	-0.357395
4	8	-2.007402	-0.001856	1.277619
5	8	-1.576088	0.002113	-1.203747
6	23	-0.507063	-0.000504	0.258916
7	8	0.470619	1.348501	0.437692
8	8	0.471018	-1.350090	0.433507
9	16	4.176520	0.000268	-0.588760
10	8	4.872908	1.259971	-0.236523
11	8	4.879671	-1.255566	-0.236104
12	8	2.676762	-0.002985	1.032656
13	1	2.010824	0.749239	0.828207
14	1	2.008415	-0.752846	0.825105

$3a^{2-}$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	3.291278	-0.247947	0.126854
2	8	4.511513	0.849206	0.118947
3	8	3.859465	-1.771082	0.344769
4	8	2.053769	-0.058331	-1.273967
5	8	1.823374	0.212425	1.207106
6	23	0.701417	0.360780	-0.178430
7	8	0.151016	1.870100	-0.398498
8	8	-0.632689	-0.798588	-0.178498
9	16	-4.589727	-0.431549	0.373599
10	8	-4.809219	0.889278	1.053359
11	8	-5.605388	-0.770957	-0.668615
12	8	-3.076115	0.052767	-0.702254
13	1	-2.994424	1.000785	-0.457432
14	1	-1.607736	-0.489689	-0.352699

$4a^{2-}$

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	-3.063191	-0.105983	-0.017472
2	8	-4.115175	1.151501	-0.019657
3	8	-3.850432	-1.543219	-0.052379
4	8	-1.690081	0.014629	1.264431
5	8	-1.640522	0.049638	-1.239457
6	23	-0.398212	0.132993	0.039509
7	8	0.404024	1.548078	0.081461
8	8	0.750901	-1.217744	0.048723
9	16	3.685485	-0.301660	0.064314
10	8	4.747720	-0.860765	-0.827132
11	8	4.174371	0.169677	1.400090
12	8	3.277494	1.157415	-0.805823
13	1	2.420944	1.444484	-0.401666
14	1	1.757170	-0.992837	0.063725

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
TS [$3a^{2-} \rightarrow 4a^{2-}$]				
1	23	3.141183	0.137592	0.036824
2	8	4.236063	-1.076849	-0.069890
3	8	3.877206	1.592110	0.198672
4	8	1.727041	-0.174481	1.242030
5	8	1.765116	0.079383	-1.247411
6	23	0.485861	-0.188957	-0.035169
7	8	-0.247413	-1.623775	-0.189225
8	8	-0.705745	1.140229	0.100720
9	16	-3.974217	0.331948	0.234269
10	8	-5.138075	0.902348	-0.515476
11	8	-4.315675	-0.772866	1.193735
12	8	-3.149077	-0.546754	-1.105673
13	1	-2.560492	-1.189050	-0.646274
14	1	-1.669573	0.904527	0.000068
TS [$4a^{2-} \rightarrow HV_2O_6^- + HOSO_2^-$]				
1	23	-3.553364	-0.321229	0.008991
2	8	-4.838352	0.691540	0.021564
3	8	-4.028421	-1.885830	0.012096
4	8	-2.190800	0.104529	1.247812
5	8	-2.214178	0.106911	-1.254673
6	23	-0.996663	0.468860	-0.014409
7	8	-0.545246	2.019088	-0.016210
8	8	0.435159	-0.630269	-0.028607
9	16	4.764978	-0.380530	0.032795
10	8	5.548439	-1.258902	-0.897824
11	8	5.381736	-0.257513	1.408287
12	8	5.113074	1.288629	-0.555167
13	1	5.772814	1.530435	0.134351
14	1	1.346866	-0.262928	-0.032698

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
$[HV_3O_9]^{2-}$				
1	8	3.798725	-1.485922	-0.659899
2	23	2.883225	-0.305965	0.013570
3	8	3.081128	1.247391	-0.970781
4	8	3.306404	-0.059204	1.579729
5	8	1.032107	-0.701831	-0.058397
6	23	-0.319843	0.414262	0.037116
7	8	0.212221	1.953317	0.149234
8	8	-1.562017	0.010078	1.258472
9	8	-1.556469	0.193097	-1.239204
10	23	-2.913180	-0.254931	-0.021045
11	8	-4.149942	0.821979	0.055262
12	8	-3.469211	-1.794073	-0.136389
13	1	2.501767	1.893928	-0.505953
$[HV_3O_9SO_2]^{2-}$				
1	23	-1.713086	0.729529	0.470777
2	8	-2.459357	0.906226	1.894945
3	8	-1.450962	2.386454	-0.247310
4	8	-2.668386	-0.251083	-0.527899
5	8	-0.023778	-0.002881	0.663009
6	23	1.405267	0.326368	-0.342546
7	8	0.979190	1.264032	-1.609043
8	8	2.813299	0.951727	0.543558
9	8	2.350307	-1.097247	-0.814587
10	23	3.896434	-0.534967	0.119512
11	8	5.187154	-0.196544	-0.828101
12	8	4.320690	-1.470132	1.392365
13	1	-0.865614	2.241427	-1.030884
14	16	-4.607273	-0.961822	0.058337
15	8	-4.561997	-2.337437	-0.497655
16	8	-5.480682	-0.007325	-0.669354
$[H_2V_3O_9]^-$				
1	23	2.758951	-0.275204	-0.074983
2	8	3.743593	-1.271755	-0.847344
3	8	2.948034	1.361313	-0.770802
4	8	3.216937	-0.280600	1.674264
5	8	1.065742	-0.776409	-0.247536
6	23	-0.329606	0.393450	0.008116
7	8	0.335537	1.872284	0.221033
8	8	-1.560359	0.339743	-1.226630
9	8	-1.473141	-0.050431	1.244773
10	23	-2.925569	-0.240465	-0.004257
11	8	-4.158977	0.793887	0.204507
12	8	-3.453825	-1.759399	-0.226022
13	1	2.157162	1.880179	-0.450344
14	1	3.947637	-0.898195	1.876235

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
$1b^{2-}$				
1	23	-1.486226	0.351002	0.683798
2	8	-2.254049	0.297381	2.102670
3	8	-1.461750	2.098969	0.125433
4	8	-2.335935	-0.612973	-0.426565
5	8	0.258531	-0.208029	0.824179
6	23	1.592003	0.311280	-0.245810
7	8	0.999706	1.319358	-1.383823
8	8	3.002163	0.971184	0.600585
9	8	2.599413	-0.982804	-0.907861
10	23	4.164555	-0.387192	-0.019716
11	8	5.362315	0.128153	-1.005693
12	8	4.735102	-1.391179	1.136186
13	1	-0.879833	2.104290	-0.674870
14	16	-4.257052	-1.375894	-0.041399
15	8	-4.187348	-2.692536	-0.719368
16	8	-5.058705	-0.343062	-0.756317
17	1	-3.364266	2.527793	-0.287949
18	8	-4.320829	2.591521	-0.511231
19	1	-4.569639	1.647304	-0.620614
$2b^{2-}$				
1	23	-1.168770	0.241895	-0.436803
2	8	-1.841610	0.044298	1.062587
3	8	-1.014564	2.009340	-0.878905
4	8	-2.157147	-0.501329	-1.528272
5	8	0.561230	-0.432914	-0.445986
6	23	2.007051	0.439193	0.106684
7	8	1.582394	1.930780	0.618013
8	8	3.027173	-0.434874	1.265794
9	8	3.356386	0.455027	-1.049823
10	23	4.513672	-0.497497	0.099098
11	8	5.822726	0.342978	0.607725
12	8	4.929202	-1.992285	-0.418555
13	1	-0.353975	2.373496	-0.240190
14	16	-5.872125	0.061110	0.217957
15	8	-6.344400	-0.171136	1.598824
16	8	-6.618893	-0.614350	-0.864167
17	8	-4.035834	-1.329204	0.262211
18	1	-3.356821	-0.857249	0.842656
19	1	-3.563415	-1.167221	-0.611862

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
TS [$2b^{2-} \rightarrow 4b^{2-}$]				
1	23	-1.173585	0.690470	-0.220981
2	8	-1.660311	0.849543	1.297684
3	8	-0.759939	2.314698	-0.894481
4	8	-2.414263	-0.019768	-1.242269
5	8	0.382417	-0.229312	-0.242872
6	23	2.009758	0.477056	0.110855
7	8	1.836302	2.049040	0.502274
8	8	2.997171	-0.410309	1.267769
9	8	3.222863	0.215159	-1.142062
10	23	4.366694	-0.782819	0.000991
11	8	5.804703	-0.079765	0.318271
12	8	4.547645	-2.354104	-0.394618
13	1	-0.061367	2.712557	-0.320233
14	16	-5.588466	-0.574424	-0.185218
15	8	-6.482801	-1.760328	-0.347536
16	8	-6.091308	0.487977	0.752351
17	8	-4.226314	-1.264483	0.782629
18	1	-4.086246	-0.573171	1.466652
19	1	-3.352207	-0.183671	-0.929930
$4b^{2-}$				
1	23	-1.285597	0.635408	-0.245229
2	8	-1.878328	0.586436	1.261042
3	8	-0.915186	2.337447	-0.736263
4	8	-2.457031	-0.029835	-1.328417
5	8	0.306033	-0.240999	-0.290381
6	23	1.900166	0.473883	0.145147
7	8	1.677367	2.002245	0.666989
8	8	2.899431	-0.486645	1.235862
9	8	3.137615	0.348528	-1.108990
10	23	4.289034	-0.715060	-0.039311
11	8	5.706998	-0.008381	0.355710
12	8	4.512046	-2.243394	-0.564809
13	1	-0.213930	2.674983	-0.127098
14	16	-5.052437	-0.645905	-0.119031
15	8	-5.812527	0.609536	0.146346
16	8	-5.870275	-1.841380	-0.456583
17	8	-4.383772	-1.114528	1.398935
18	1	-3.664269	-0.455622	1.562885
19	1	-3.444646	-0.304444	-0.960795

TS [$4b^{2-} \rightarrow H_2V_3O_9^- + HOSO_2^-$]

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	23	-0.411501	1.009675	0.504171
2	8	-1.119261	1.350867	1.894506
3	8	-0.004730	2.564766	-0.291362
4	8	-1.524950	0.037715	-0.512421
5	8	1.129011	0.135167	0.745813
6	23	2.600204	0.267802	-0.324894
7	8	2.225571	1.281590	-1.549834
8	8	4.084285	0.700020	0.504933
9	8	3.299930	-1.244182	-0.861034
10	23	4.961742	-0.930891	0.038275
11	8	6.255761	-0.763655	-0.935234
12	8	5.279047	-1.928988	1.283594
13	1	0.675383	2.354981	-0.988827
14	16	-7.922336	-0.868118	-0.506182
15	8	-8.493377	0.532016	-0.511919
16	8	-8.537356	-1.746781	0.546759
17	8	-6.275314	-0.499451	0.139369
18	1	-6.490482	0.320937	0.641209
19	1	-2.436691	-0.110165	-0.182554