On the gas-phase reaction between SO_2 and $O_2^-(H_2O)_n$ clusters, $n = 0 - 3$ – an ab initio study

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Electronic Supplementary Information

Table S1: Gibbs free energy (ΔG at 298.15 K) and enthalpy (ΔH) (in kcal/mol) of the most stable configurations relative to separated reactants. The dehydrated reaction catalysed by SO_2 is shown at the end of the table. All Gibbs free energies are shown in Figure 2 in the main article. "TS" is shorthand for a transition state structure.

n	$O_2SO_2^-(H_2O)_n$		$O_2 + SO_2^-(H_2O)_n$		TS		$SO_4^-(H_2O)_n$	
	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH
0	-31.22	-40.02	-16.33	-15.61	-0.86	-11.45	-85.87	-96.78
1	-21.46	-31.67	-10.46	-10.82	4.75	-7.81	-75.90	-87.82
2	-15.34	-26.06	-4.99	-6.15	8.47	-4.06	-70.18	-81.75
3	-11.83	-25.03	-3.89	-5.79	13.79	-0.26	-67.23	-77.47

$O_2SO_2^- + SO_2$		$SO_2SO_2O_2^-$		TS_{cat}		$SO_4^- + SO_2$	
ΔG	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	ΔH
-31.22	-40.02	-36.96	-54.34	-15.75	-38.48	-67.23	-77.47

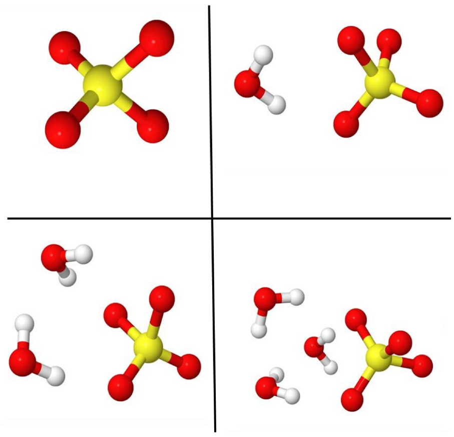

Figure S1: Ground state structures of $SO_4^-(H_2O)_n$, n= 0–3. Colour coding: yellow = sulphur, red = oxygen, and white = hydrogen

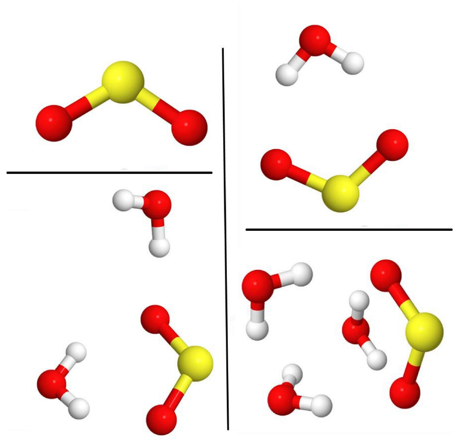

Figure S2: Ground state structures of $SO_2^-(H_2O)_n$, n= 0–3, formed when O_2 evaporates from $O_2SO_2^-(H_2O)_n$. Colour coding: yellow = sulphur, red = oxygen, and white = hydrogen

Table S2: Evaporation rate constant of $O_2SO_2^-(H_2O)_n$ to $SO_2^-(H_2O)_n$ and O_2 (k_{evap}). Isomerization rate constant of $O_2SO_2^-(H_2O)_n$ to $SO_4^-(H_2O)_n$, k_{isom}. The fraction of reactive collisions, r_{ox}/Z_{coll}. The model is presented in detail in Bork et al, Atmos. Chem. Phys., 12, 3639-3652, 2012.

n	k_{evap}(s^{-1})	k_{isom} (s^{-1})	r_{isom}/Z_{coll}
0	1.79×10^{-1}	5.83×10^{-11}	3.26×10^{-10}
1	1.25×10^{2}	1.88×10^{-8}	1.51×10^{-10}
2	3.61×10^{2}	7.84×10^{-6}	2.17×10^{-8}
3	2.09×10^{4}	7.44×10^{-7}	3.56×10^{-11}

Table S3: Energy (in kcal/mol) of the decomposition of $O_2SO_2^-(H_2O)_n$ into O_2 and $SO_2^-(H_2O)_n$.

n	ΔG	ΔH
0	14.89	24.41
1	11.00	20.85
2	10.35	19.91
3	7.94	19.24

Table S4: Energy (in kcal/mol) of the growth of $O_2SO_2^-(H_2O)_n$ and $SO_2^-(H_2O)_n$ by H_2O condensation.

	$O_2SO_2^-(H_2O)_n$		$SO_2^-(H_2O)_n$	
n	ΔG	ΔH	ΔG	ΔH
0	-2.90	-12.00	-6.80	-15.57
1	-1.60	-10.72	-2.25	-11.66
2	-0.17	-12.38	-2.58	-13.04

Table S5: Frequencies (in cm^{-1}) for the most stable $O_2SO_2^-(H_2O)_n$ clusters, shown in Figure 1 in the main article.

$n=0$	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$
50	32	34	36	36	23
193	56	43	56	58	29
241	99	54	72	70	43
299	166	76	75	76	57
478	200	132	108	79	70
571	266	181	148	89	75
1072	319	193	160	109	75
1168	325	208	181	131	89
1275	386	263	198	164	110
	496	308	207	194	118
	583	332	209	207	132
	674	391	262	222	151
	1061	456	318	228	193
	1142	492	461	245	207
	1271	553	470	270	211
	1695	580	474	322	226
	3735	688	526	405	230
	3761	763	557	450	273
		1061	584	464	291
		1149	584	487	325
		1267	651	522	388
		1675	732	551	404
		1696	750	587	447
		3530	957	616	474
		3691	1067	638	476
		3738	1149	686	529
		3863	1268	732	562
			1670	798	589
			1677	805	622
			1700	991	636
			3546	1063	693
			3598	1140	755
			3618	1266	782
			3669	1688	826
			3693	1692	838
			3777	1696	996
				1705	1062
				3427	1136
				3529	1263
				3578	1662
				3620	1683
				3640	1687
				3724	1699
				3761	1712
				3792	3451
					3512
					3529
					3553
					3595
					3613
					3714
					3763
					3786
					3907

Table S6: Frequencies (in cm^{-1}) for the most stable transition states, shown in Figure 3 in the main article.

$n=0$	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$
301i	172i	217i	237i	148i	83i
154	61	21	18	37	22
364	74	50	25	47	29
409	176	61	43	65	52
467	280	76	47	70	54
791	326	147	69	82	68
846	373	173	72	105	87
1019	419	268	132	117	98
1115	471	277	141	143	106
	487	301	172	177	114
	804	321	253	194	132
	858	373	261	215	142
	930	422	275	242	176
	1028	462	288	327	177
	1133	483	303	370	210
	1700	568	308	378	219
	3214	781	381	415	264
	3877	852	423	437	314
		911	453	462	374
		1021	477	486	389
		1116	523	498	402
		1672	540	526	425
		1695	779	563	456
		3253	852	587	478
		3767	889	638	485
		3839	1015	656	502
		3884	1120	816	552
			1660	861	598
			1670	867	638
			1690	976	697
			3295	1027	772
			3772	1078	780
			3787	1130	809
			3850	1661	830
			3866	1674	869
			3889	1684	904
				1706	1030
				2993	1042
				3424	1137
				3521	1662
				3600	1677
				3722	1693
				3782	1699
				3795	1720
				3874	3243
					3352
					3531
					3540
					3614
					3695
					3720
					3760
					3815
					3908

Table S7: Frequencies (in cm^{-1}) for the most stable $SO_4^-(H_2O)_n$ clusters

$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
332	37	34	23	46	25
360	77	37	48	60	30
373	172	62	54	69	49
505	305	127	81	74	63
517	322	169	95	86	71
676	337	179	134	107	76
906	356	248	181	118	87
1131	398	298	185	150	90
1203	511	343	193	195	112
	521	360	234	219	122
	651	405	332	230	148
	680	461	355	242	177
	909	510	376	322	213
	1128	529	392	337	220
	1208	556	425	400	242
	1688	665	444	418	276
	3672	669	481	440	322
	3845	700	518	472	340
		906	525	487	396
		1135	552	511	397
		1228	669	531	420
		1669	711	576	442
		1693	761	619	476
		3687	816	634	493
		3696	921	668	513
		3756	1134	696	530
		3849	1176	705	582
			1659	788	625
			1681	804	632
			1691	924	678
			3518	992	699
			3641	1136	719
			3683	1189	778
			3712	1684	820
			3807	1692	840
			3895	1694	926
				1703	999
				3462	1138
				3520	1185
				3557	1660
				3588	1684
				3688	1687
				3740	1698
				3770	1702
				3790	3433
					3497
					3537
					3555
					3607
					3645
					3727
					3774
					3787
					3909