H-Bonded $CH_3SO/H_2SO_4/H_2O$ Complexes: Quantum Chemical Study

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Dedicated to Prof. Dr. Joe Koller on the occasion of his 70th birthday

Supplementary Data

Table SI-1: Cartesian coordinate in Å for all structures studied in this work.

Table SI-2: B3LYP/6-311++G(2df,2pd) harmonic and anharmonic (cm^{-1}) frequencies together with IR intensities (I, in km mol^{-1}) of CH_3SO radical, H_2SO_4 and H_2O molecule.

Table SI-3: B3LYP/6-311++G(2df,2pd) harmonic and anharmonic (cm^{-1}) frequencies together with IR intensities (I, in km mol^{-1}) for CH_3SO-H_2SO_4 complexes.

Table SI-4: B3LYP/6-311++G(2df,2pd) harmonic and anharmonic (cm^{-1}) frequencies together with IR intensities (I, in km mol^{-1}) for CH_3SO-H_2SO_4-H_2O complexes.

Table SI-5: B3LYP/6-311++G(2df,2pd) harmonic and anharmonic (cm^{-1}) frequencies together with IR intensities (I, in km mol^{-1}) for CH_3SO-H_2SO_4-$2H_2O$ complexes.

Table SI-1. Cartesian coordinate in Å for all structures studied in this work.

CH_3SO

	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	1.245682	0.607973	0.000015	1.259622	0.628078	-0.000006
S	0.226446	-0.501169	0.000008	0.218014	-0.523920	-0.000010
C	-1.404128	0.300882	-0.000030	-1.402817	0.320911	-0.000002
H	-2.160317	-0.483992	-0.001712	-2.186249	-0.455515	0.000091
H	-1.500815	0.918097	-0.891509	-1.481282	0.944148	-0.904076
H	-1.502681	0.915529	0.893153	-1.480759	0.943995	0.904210

H_2SO_4

	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	-0.515762	0.496061	0.657449	-0.002745	0.003610	-0.039658
S	0.194842	-0.332201	1.576467	0.008355	0.000037	1.422287
O	1.600978	-0.567132	1.520097	1.212291	-0.003655	2.251710
O	-0.096703	0.184158	3.063908	-0.880159	1.265122	1.953102
H	-0.960199	0.621629	3.081825	-1.535727	1.463274	1.263661
S	-0.562314	-1.742955	1.559748	-0.929696	-1.264900	1.860041
H	0.021913	-2.418467	1.933516	-0.726983	-1.462902	2.789592

H_2O

	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	0.000000	0.000000	0.116800	0.000000	0.000000	0.118740
H	0.000000	0.763077	-0.467198	0.000000	0.760299	-0.474961
H	0.000000	-0.763077	-0.467198	0.000000	-0.760299	-0.474961

Table SI-1. Continued.

MS-SA$_A$

	B3LYP/6-311++G(2df,2pd)		
O	0.332699	0.804917	-0.125607
S	0.029616	0.757528	1.356394
C	1.459144	0.008029	2.167803
H	1.209643	-0.083978	3.224687
H	2.325662	0.656003	2.041851
H	1.653942	-0.967579	1.725753
H	1.196162	-0.058090	-1.268840
O	1.644165	-0.534379	-2.019223
S	2.660546	-1.609410	-1.494595
O	2.197937	-2.160583	-0.255399
O	3.017024	-2.422941	-2.613467
O	3.938397	-0.717330	-1.086710
H	4.443219	-0.515773	-1.887212

MS-SA$_B$

	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	0.060500	-0.218138	0.858442	-0.077942	-0.147128	0.038226
S	0.994610	0.689066	1.637853	0.009682	0.339633	1.518190
C	2.445695	-0.337641	1.967804	1.741673	-0.016586	1.954052
H	3.153597	0.268155	2.532568	1.891748	0.294286	3.001146
H	2.885647	-0.650355	1.022369	2.401869	0.555450	1.284175
H	2.145576	-1.208349	2.548298	1.922574	-1.096795	1.843231
H	-1.336863	0.358737	0.130478	-1.453108	0.294367	-0.855073
O	-2.143641	0.683760	-0.352847	-2.244873	0.581695	-1.382314
S	-2.749385	1.944700	0.366691	-3.515369	0.580224	-0.397403
O	-1.797077	2.424353	1.337118	-3.031041	0.664083	0.996700
O	-3.994503	1.324733	1.170627	-4.120360	-0.930388	-0.602612
H	-3.689522	1.026664	2.038094	-3.723255	-1.484818	0.087744
O	-3.322807	2.785732	-0.627063	-4.507043	1.486569	-0.960210

MS-SA$_C$

	B3LYP/6-311++G(2df,2pd)		
O	1.078258	2.019338	0.735267
S	0.587920	0.928130	1.648910
C	1.833292	-0.387384	1.640158
H	1.490050	-1.159140	2.326950
H	2.785322	0.022533	1.972639
H	1.925216	-0.780177	0.629314
O	-0.212680	-0.847080	4.394369
S	-0.506117	0.085014	5.452599
O	-0.123019	1.543755	4.943306
H	0.035761	1.520920	3.980504
O	0.003832	-0.047048	6.770887
O	-2.094355	0.182343	5.602769
H	-2.513425	-0.080402	4.771370

Table SI-1. Continued.

MS-SA-W$_A$

	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	1.555753	-1.344575	0.394866	-0.178659	-0.032691	0.007460
S	1.614859	-0.815221	1.810859	-0.042652	0.050075	1.555042
C	0.694456	0.739386	1.833657	1.748858	0.034504	1.881440
H	0.766708	1.133205	2.847503	1.877289	0.059593	2.976182
H	-0.347751	0.555902	1.573705	2.215085	0.918947	1.422955
H	1.148552	1.434945	1.129122	2.172146	-0.894918	1.468693
H	-1.103516	-0.147747	-1.698770	3.029102	1.121014	-1.510682
O	-1.858475	0.515273	-1.517526	3.922584	1.452200	-1.174488
S	-2.897915	-0.112963	-0.528105	3.661362	2.910761	-0.553407
O	-3.233735	-1.442860	-0.961941	2.862184	3.703144	-1.504675
O	-4.133990	0.861801	-0.790436	5.190876	3.460546	-0.524521
H	-4.561755	0.615462	-1.622533	5.421282	3.720672	-1.431746
O	-2.510884	0.125734	0.831158	3.259828	2.809987	0.854458
H	0.626524	-1.216734	-1.121415	0.974268	0.337260	-1.340200
O	0.060868	-1.147403	-1.917239	1.617754	0.601847	-2.027205
H	-0.268617	-2.034697	-2.091341	1.174891	1.296146	-2.531437

MS-SA-W$_B$

	B3LYP/6-311++G(2df,2pd)		
O	0.193683	-0.305100	-0.131485
S	-0.308718	0.007102	1.263951
C	1.193514	0.210378	2.253955
H	0.885454	0.433584	3.275049
H	1.782051	1.032525	1.850088
H	1.770604	-0.712470	2.227127
H	-2.728931	0.056651	-2.316272
O	-3.616016	0.539529	-2.266886
S	-4.326991	0.278464	-0.899159
O	-3.338425	-0.083129	0.088043
O	-5.207730	-1.036774	-1.191593
H	-4.672567	-1.816678	-0.992191
O	-5.265494	1.327302	-0.684583
H	-0.812934	-0.561681	-1.578763
O	-1.339532	-0.699856	-2.393762
H	-0.761614	-0.495936	-3.133740

MS-SA-W$_C$

	B3LYP/6-311++G(2df,2pd)		
O	0.434094	-0.071181	0.044610
S	0.109631	-0.689251	1.391578
O	1.662267	-0.805452	2.303244
H	1.415653	-1.177083	3.296931
H	2.109604	0.182554	2.377883
H	2.328942	-1.498723	1.792031
H	1.647926	0.820135	-0.483299
O	2.409579	1.368340	-0.851270
S	2.520111	2.759087	-0.142660
O	1.628997	3.713204	-0.735317
O	4.014041	3.128791	-0.556216
H	3.991441	3.631851	-1.382340
O	2.535996	2.576862	1.285134
H	1.078342	2.478267	2.644517
O	0.436223	2.070015	3.241874
H	-0.224795	2.745896	3.410334

Table SI-1. Continued.

MS-SA-2W$_A$

B3LYP/6-311++G(2df,2pd)

O	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.512599
C	1.727805	0.000000	2.042981
H	1.722605	-0.042617	3.132266
H	2.219258	0.911227	1.703035
H	2.227882	-0.878301	1.637022
H	2.960402	0.934273	-1.548180
O	3.899895	1.265529	-1.126314
S	3.845341	2.710122	-0.590571
O	3.379670	3.612599	-1.625915
O	5.396519	2.995509	-0.347697
H	5.832504	3.137963	-1.199589
O	3.236160	2.776112	0.705809
H	1.117837	0.294114	-1.391764
O	1.762140	0.509897	-2.093735
H	1.397434	1.262137	-2.611901
H	1.927359	3.338375	-2.838720
O	1.248385	2.867407	-3.351660
H	0.453494	3.405167	-3.311901

MS-SA-2W$_B$

B3LYP/6-311++G(2df,2pd)

O	0.258473	-0.909281	0.022669
S	0.347507	-1.054643	1.526146
C	2.020196	-0.567594	2.003404
H	2.087729	-0.685666	3.084909
H	2.187438	0.471959	1.722781
H	2.738365	-1.221298	1.510071
H	2.569010	1.533828	-1.549507
O	3.278554	2.199821	-1.262837
S	2.696004	3.249516	-0.258426
O	1.853168	4.191563	-0.966833
O	4.021164	3.972504	0.169360
H	4.133597	4.802682	-0.371482
O	2.156506	2.580126	0.892528
H	1.093741	-0.041262	-1.287030
O	1.519190	0.457744	-2.013899
H	0.806506	0.794253	-2.564377
H	2.952918	5.849934	-1.558907
O	3.869938	6.124035	-1.398909
H	3.830293	7.010426	-1.028811

Table SI-1. Continued.

MS-SA-2W$_C$

B3LYP/6-311++G(2df,2pd)

O	0.228145	0.026523	-0.030226
S	0.228233	0.209150	1.473832
C	1.965731	0.478786	1.906043
H	2.017218	0.616212	2.985745
H	2.328364	1.369306	1.395424
H	2.550574	-0.389586	1.607424
H	-3.162762	0.844126	-0.810372
O	-3.803052	1.418233	-0.284354
S	-4.227418	0.737666	1.058387
O	-3.154930	-0.141502	1.499153
O	-5.451775	-0.172001	0.640074
H	-5.174034	-1.126115	0.631380
O	-4.714984	1.765130	1.917995
H	-1.249013	-0.053393	-1.064443
O	-2.070242	-0.020827	-1.594535
H	-1.819155	0.260625	-2.478180
H	-3.597365	-2.124092	1.225552
O	-4.345712	-2.611839	0.846391
H	-4.667280	-3.196686	1.538433

Table SI-2. Harmonic and anharmonic frequencies (cm^{-1}) with IR int. (km mol^{-1}) for CH_3SO, H_2SO_4 and H_2O molecules.

CH_3SO				H_2SO_4				H_2O			
H	A	IR int.	Exp[a]	H	A	IR int.	Exp[b]	H	A	IR int.	Exp[c,d]
3131	2981	2	2995 vw	3774	3578	50	3609	3818	3647	8	3661
3130	2979	4		3770	3574	210		1630	1575	72	1596
3037	2917	3	2919 vw	1449	1418	304	1465	3921	3736	64	3751
1460	1419	8	1417 w	1201	1180	165	1220				
1446	1404	10	1405 w	1166	1124	84	1157				
1323	1299	1	1289 w	1152	1116	79	1138				
1061	1408	47	1068 vs	851	831	342	891				
947	921	11	927 m	799	781	113	834				
887	869	1	868 vw	540	532	24	568				
662	646	14	670 w	531	525	39	550				
332	333	7	341 w	485	476	42					
137	93	0	n.o.	429	397	17					
				365	346	2	281				
				327	265	59					
				251	219	98	216				

[a] Reisenauer, H.P.; Romanski, J.; Mloston, G.; Schreiner, P.R. *ChemComm* **2013**, *49*, 9467-9469.

[b] Miller, Y.; Chaban, G. M.; Gerber, R.B. *J. Phys. Chem. A* **2005**, *109*, 6565-6574.

[c] Forney, D.; Jacox, M.E.; Thompson, W.E. *Mol. Spectrosc.* **1993**, *157*, 479-493.

[d] Tsuge, M.; Tsuji, K.; Kawai, A.; Shibuya, K. *J. Phys. Chem. A* **2007**, *111*, 3540-3547.

Table SI-3. Harmonic and anharmonic frequencies (cm^{-1}) with IR int. (km mol^{-1}) for MS-SA complexes.

MS-SA$_A$			MS-SA$_B$			MS-SA$_C$		
H	A	IR int.	H	A	IR int.	H	A	IR int.
3778	3583	119	3791	3593	100	3781	3613	115
3230	2929	1733	3226	2941	2028	3588	3366	719
3139	2990	2	3136	2983	2	3147	2999	0
3128	2983	3	3134	2983	0	3136	2988	1
3036	2920	4	3040	2918	1	3043	2926	2
1462	1423	2	1457	1413	6	1457	1417	17
1443	1408	51	1445	1405	13	1451	1409	4
1428	1398	286	1437	1404	304	1439	1408	338
1336	1289	4	1331	1284	1	1326	1295	2
1288	1249	62	1301	1263	97	1205	1170	160
1194	1172	185	1183	1162	196	1173	1152	60
1157	1122	96	1150	1105	57	1146	1115	66
1066	1049	106	1046	1033	95	1058	1045	41
961	938	18	959	933	12	958	937	11
897	878	161	892	873	193	897	887	2
893	877	81	891	873	140	864	843	370
802	783	191	807	785	182	806	788	94
764	705	23	771	701	23	667	673	8
673	659	9	676	653	16	544	535	27
544	538	33	546	537	38	532	525	26
538	530	40	535	528	31	503	503	7
510	503	10	509	501	23	450	443	66
421	381	31	419	394	14	403	399	39
379	358	2	376	363	39	356	308	4
346	351	8	362	344	2	333	335	5
270	170	61	219	130	78	192	129	63
180	175	40	156	136	12	141	117	0
157	204	3	141	78	1	93	93	2
107	108	0	120	106	5	69	95	9
93	94	5	52	24	3	62	51	2
59	75	1	45	29	3	47	51	9
36	48	2	35	-10	1	29	66	3
20	106	3	24	-31	2	19	-7	3

Table SI-4. Harmonic and anharmonic frequencies (cm^{-1}) with IR int. (km mol^{-1}) for MS-SA-W complexes.

MS-SA-W$_A$			MS-SA-W$_B$			MS-SA-W$_C$		
H	A	IR int.	H	A	IR int.	H	A	IR int.
3857	3683	118	3877	3682	116	3892	3683	116
3780	3591	120	3790	3603	99	3782	3573	132
3527	3274	839	3500	3324	1048	3737	3549	254
3129	2978	29	3133	2985	2	3152	3000	5
3128	2982	2	3132	2987	1	3133	2988	1
3031	2931	22	3038	2923	2	3043	2920	8
2775	2342	1981	2936	2489	1903	2990	2624	2253
1663	1618	38	1661	1633	43	1645	1582	58
1467	1427	7	1467	1418	189	1452	1387	7
1446	1400	10	1457	1413	9	1442	1385	10
1406	1149	180	1446	1405	11	1383	1372	301
1371	1371	241	1369	1354	236	1334	1285	15
1339	1297	2	1328	1282	0	1322	1254	91
1186	1163	147	1183	1162	249	1186	1171	169
1158	1126	123	1150	1107	55	1159	1132	105
1074	1004	22	1050	1039	92	1062	1044	91
1062	1032	138	955	932	13	960	940	19
960	938	11	938	862	203	907	887	322
910	892	283	910	888	188	896	876	1
897	879	3	888	873	1	832	782	123
822	803	143	801	783	148	811	707	101
704	694	129	711	673	52	677	653	8
673	661	8	672	650	17	547	535	19
549	539	38	554	543	23	543	540	58
543	534	22	540	526	27	518	514	8
517	513	32	536	527	34	477	470	102
463	485	34	476	468	51	407	396	30
413	363	30	419	391	4	391	365	40
405	403	17	367	348	1	351	357	15
343	345	15	363	359	29	321	369	92
330	241	102	297	202	134	225	226	62
279	244	22	270	244	35	202	200	58
248	114	74	209	139	48	151	37	18
183	104	3	162	148	15	140	68	23
175	165	35	142	124	0	118	55	12
99	93	14	101	85	6	113	-183	62
77	101	8	65	42	2	89	142	5
67	74	14	52	24	6	60	79	2
47	78	3	43	20	2	46	65	3
30	42	3	34	-14	1	31	98	4
26	31	1	29	26	2	26	99	2
23	22	3	21	-45	4	20	51	3

Table SI-5. Harmonic and anharmonic frequencies (cm^{-1}) with IR int. (km mol^{-1}) for MS-SA-2W complexes.

MS-SA-2W$_A$			MS-SA-2W$_B$			MS-SA-2W$_C$		
H	A	IR int.	H	A	IR int.	H	A	IR int.
3885	n/a	112	3879	3685	120	3878	3618	101
3780		120	3870	3694	116	3877	3683	139
3651		474	3702	3507	176	3700	3505	201
3563		913	3520	3311	867	3538	3326	923
3436		607	3194	2964	1121	3250	3051	1087
3129		19	3130	2987	56	3134	2982	2
3128		5	3128	2974	4	3133	2977	1
3031		17	3030	2914	41	3039	2913	1
1871		2666	2882	2697	2158	2988	2579	1634
1676		79	1665	1615	38	1657	1601	40
1643		56	1633	1578	62	1633	1580	53
1468		52	1469	1410	6	1457	1411	11
1464		69	1445	1387	16	1452	1393	224
1446		22	1428	1381	202	1446	1398	9
1355		377	1361	1296	122	1375	1314	79
1339		8	1337	1292	1	1329	1280	2
1300		68	1305	1265	256	1321	1277	212
1158		206	1166	1147	178	1149	1133	212
1156		112	1063	1047	78	1051	1037	76
1063		73	1033	901	80	957	903	49
962		204	961	936	12	953	898	165
960		77	931	905	355	924	896	278
897		3	901	882	2	889	857	1
874		114	859	841	76	843	825	86
829		195	804	748	86	778	626	69
730		45	697	623	102	675	628	68
673		9	674	661	9	670	630	39
626		176	584	513	183	587	516	135
590		16	554	540	18	558	540	41
554		25	551	545	40	548	507	68
535		87	526	502	43	542	533	33
522		34	454	509	24	467	384	14
420		60	414	409	11	411	376	28
413		109	387	371	46	367	357	11
388		29	352	258	109	361	340	27
344		2	344	338	13	328	192	93
321		97	285	367	97	285	20	141
244		160	270	260	11	261	231	57
238		43	256	135	113	247	209	28
227		26	217	194	17	208	183	22
180		1	182	87	0	161	126	18
161		31	172	153	35	153	85	17
148		3	152	117	46	139	137	0
115		18	113	85	8	102	14	1
91		2	90	94	2	65	-23	2
76		4	72	27	1	49	-45	7
54		2	48	55	8	36	-21	2
47		1	42	39	2	32	-101	3
38		6	28	-7	3	27	-180	1
29		3	15	5	2	20	-131	2
26		1	14	-52	1	8	-340	1