Structure, stability and spectroscopic properties of H-bonded complexes of HOSO and CH_3SO with H_2O

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Figure SI-5 TD-B3LYP/6-311++G(2df,2pd) computed electronic spectrum of CH_3SO-water complexes.

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

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

$H_2O\cdots H_2O$

	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	1.392028	-0.001638	0.108819	1.403409	-0.001708	0.110427
H	1.757241	-0.759690	-0.356887	1.772313	-0.756356	-0.364451
H	1.751633	0.771800	-0.335571	1.767468	0.768810	-0.342202
H	-0.563990	-0.002020	0.035241-	0.576984	-0.002103	0.038025
O	-1.520021	0.001848	-0.120604-	1.533273	0.001915	-0.121712
H	-1.920937	-0.011776	0.751498-	1.923885	-0.012008	0.758908

HOSO

	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	1.332422	0.258730	-0.052524	-1.356396	0.274634	-0.000096
H	1.261945	1.157305	0.304210	-1.170871	1.229652	0.000576
S	-0.144042	-0.478340	0.018631	0.145104	-0.502072	0.000035
O	-1.202081	0.553287	-0.022764	1.212546	0.575804	-0.000046

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

Table SI-1. Continued.

HOSO$\cdots$H$_2$O

	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	0.137320	1.279248	0.040486	0.157778	1.314265	0.097500
H	-0.802151	0.952862	0.001119	-0.772935	0.988426	0.021679
S	1.162750	0.021075	-0.022785	1.177415	0.006449	-0.066868
O	0.391607	-1.252949	0.041943	0.365673	-1.274979	0.102298
H	-1.661340	-0.875534	-0.018458	-1.676466	-0.857044	0.012269
O	-2.187445	-0.065218	-0.105651	-2.207604	-0.057154	-0.135055
H	-2.872366	-0.103183	0.567680	-2.916021	-0.091631	0.517994

syn-**HOSO$\cdots$2H$_2$O**

	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	0.957866	1.212929	0.336319	0.943901	1.193784	0.508599
H	-0.022598	1.329865	0.114276	0.008206	1.329539	0.193895
S	1.578452	-0.178822	-0.164075	1.593052	-0.152553	-0.196078
O	0.626589	-1.301633	0.086862	0.649609	-1.338512	-0.000027
H	-1.971451	0.573071	-0.124984	-2.003584	0.608167	-0.171006
O	-1.582110	1.470735	-0.240798	-1.590099	1.479522	-0.341818
H	-2.085962	2.069641	0.316685	-2.135746	2.122510	0.124745
H	-2.587541	-1.713195	-0.496023	-2.605542	-1.780330	-0.367331
O	-2.172138	-1.134018	0.147976	-2.191764	-1.143109	0.225382
H	-1.229343	-1.382339	0.172383	-1.245342	-1.372516	0.219861

anti-**HOSO$\cdots$2H$_2$O**

	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	-0.133090	-0.489412	-0.681298	-0.176420	-0.675568	-0.905852
H	0.378980	0.368556	-0.607343	0.325139	0.187384	-0.915602
S	-1.698179	-0.304201	-0.255287	-1.589740	-0.410638	-0.045701
O	-1.787005	0.434687	1.026298	-1.344055	0.726903	0.935688
O	1.570344	1.515546	-0.335036	1.278172	1.549788	-0.496128
H	1.361158	2.125714	0.378661	0.728321	1.898935	0.220357
H	2.204980	0.871174	0.029531	1.965068	1.033833	-0.040834
H	1.769854	-1.311323	0.236825	1.683795	-1.286879	0.167012
O	2.619969	-0.924414	0.485565	2.437099	-0.828483	0.566291
H	3.294152	-1.478167	0.082683	3.175157	-1.444180	0.500281

Table SI-1. Continued.

cyc-$\mathbf{CH_3SO\cdots H_2O}$

	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	0.049119	-1.212009	0.183938	-0.113694	-1.269655	0.000244
S	1.209325	-0.290486	-0.116090	-1.259227	-0.215926	-0.000157
C	0.595488	1.402607	0.090602	-0.422122	1.406329	0.000154
H	1.389779	2.074830	-0.233088	-1.213374	2.174214	-0.000386
H	0.359042	1.576435	1.139260	0.205152	1.491511	-0.899700
H	-0.299695	1.536026	-0.514334	0.204192	1.491766	0.900645
H	-1.765543	-0.463978	0.089857	1.700913	-0.518718	0.000115
O	-2.467241	0.189980	-0.049650	2.432901	0.119596	-0.000123
H	-3.260732	-0.314941	-0.242173	3.229834	-0.421461	-0.000049

acyc-$\mathbf{CH_3SO\cdots H_2O}$

	B3LYP/6-311++G(2df,2pd)		
O	-1.677871	0.348414	0.232391
S	-0.423140	-0.364666	-0.197962
C	0.920886	0.853572	-0.093185
H	1.842104	0.357839	-0.399299
H	1.007451	1.206614	0.933357
H	0.703692	1.687312	-0.759238
O	1.028544	-0.457932	0.167981
H	1.921197	-0.207204	0.542554
H	0.965108	-1.455188	0.206145

$\mathbf{CH_3SO\text{-}2H_2O}$

	B3LYP/6-311++G(2df,2pd)		
O	0.801317	-1.267698	-0.000591
S	1.712162	-0.095440	-0.289977
C	1.003473	1.342269	0.546208
H	1.643408	2.192306	0.308517
H	1.002966	1.164941	1.621149
H	-0.013377	1.513143	0.188226
H	-1.045590	-1.418977	0.272563
O	-2.015783	-1.355701	0.318236
H	-2.348630	-2.057135	-0.247330
O	-2.208094	1.357681	-0.392691
H	-2.979734	1.790506	-0.020415
H	-2.293997	0.414386	-0.159957

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 H_2O molecule, H_2O dimer, and HOSO radical and CH_3SO radical.

H_2O				HOSO			CH_3SO			
H	A	I	Exp [a,b]	H	A	I	H	A	I	Exp [c]
3818	3647	8	3660.6	3744	3555	101	3131	2981	2	2995 vw
1630	1575	72	1595.6	1168	1157	111	3130	2979	4	
3921	3736	64	3750.7	1067	1044	14	3037	2917	3	2919 vw
				753	740	194	1460	1419	8	1417 w
				395	367	30	1446	1404	10	1405 w
				109	405	110	1323	1299	1	1289 w
							1061	1047	47	1068 vs
							947	921	11	927 m
							887	869	1	868 vw
$H_2O\cdots H_2O$							662	646	14	670 w
							332	333	7	341 w
H	A	I	Exp [a]				137	93	0	n.o.
3911	3715	87	3730							
3892	3691	89								
3811	3625	14								
3705	3547	330	∼3530							
1650	1591	37								
1630	1577	94								
638	499	121								
367	253	64								
190	78	206								
160	9	45								
158	87	82								
135	-25	135								

[a] Forney, D.; Jacox, M. E.; Thompson, W. E. *J. Mol. Spectrosc.* **1993**, **157**, 479-493.
[b] Tsuge, M.; Tsuji, K.; Kawai, A.; Shibuya, K. *J. Phys. Chem. A* **2007**, *111*, 3540-3547.
[c] Reisenauer, H. P.; Romańska, J.; Mlostoń, G.; Schreiner, P. R. *ChemComm* **2013**, *49*, 9467-9469.

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 HOSO-water complexes.

$HOSO\cdots H_2O$			syn-$HOSO\cdots 2H_2O$			*anti*-$HOSO\cdots 2H_2O$		
H	A	I	H	A	I	H	A	I
3785	3579	109	3881	3698	105	3891	3700	135
3682	3492	152	3873	3694	87	3864	3664	96
3233	2999	961	3599	3403	641	3757	3590	122
1637	1586	80	3398	3173	696	3603	3445	379
1316	1237	70	2911	2610	1673	3102	2850	1407
1114	1096	82	1668	160	22	1643	1601	23
816	802	169	1640	1600	78	1632	1586	105
736	640	143	1374	1445	65	1349	1275	96
574	493	153	1114	1098	131	1139	1120	87
451	413	7	946	829	135	900	838	99
433	409	67	859	844	157	801	786	180
387	333	128	811	741	65	673	585	193
221	199	20	659	613	133	467	390	89
158	130	10	514	464	79	441	342	161
45	189	10	431	416	30	402	377	43
			381	360	25	340	193	90
			319	312	132	259	213	45
			283	259	28	245	211	73
			251	229	131	202	172	10
			232	206	25	183	-18	126
			178	164	4	118	77	4
			110	106	7	67	19	5
			79	38	4	40	49	6
			41	31	2	24	10	2

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-water complexes.

cyc-$CH_3SO\cdots H_2O$			*acyc*-$CH_3SO\cdots H_2O$			$CH_3SO\cdots 2H_2O$		
H	A	I	H	A	I	H	A	I
3891	3713	101	3915	3733	73	3887	3682	66
3692	3532	281	3814	3646	13	3882	3685	109
3138	2986	1	3143	3000	0	3633	3456	582
3129	2981	3	3126	2978	3	3569	3411	410
3037	2918	3	3038	2923	6	3124	2975	3
1646	1599	73	1634	1593	79	3112	2967	28
1458	1414	13	1460	1413	9	3016	2935	34
1443	1396	11	1456	1420	5	1668	1610	31
1333	1289	1	1320	1288	2	1648	1599	77
1055	1044	61	1055	1043	54	1470	1440	10
958	929	11	957	934	11	1447	1405	9
893	869	2	891	875	1	1343	1310	1
667	655	10	663	663	14	1061	1044	73
527	444	99	334	360	9	965	940	12
368	350	54	173	178	23	905	877	2
337	330	85	141	185	103	744	606	102
157	143	14	128	77	164	672	635	10
145	79	26	90	90	27	636	579	145
121	130	97	43	14	10	394	338	114
84	51	18	29	-102	1	370	332	33
41	-17	3	20	-370	6	334	314	25
						227	134	85
						207	163	3
						186	156	7
						172	148	20
						163	-127	116
						122	93	11
						77	64	1
						51	23	4
						32	14	5

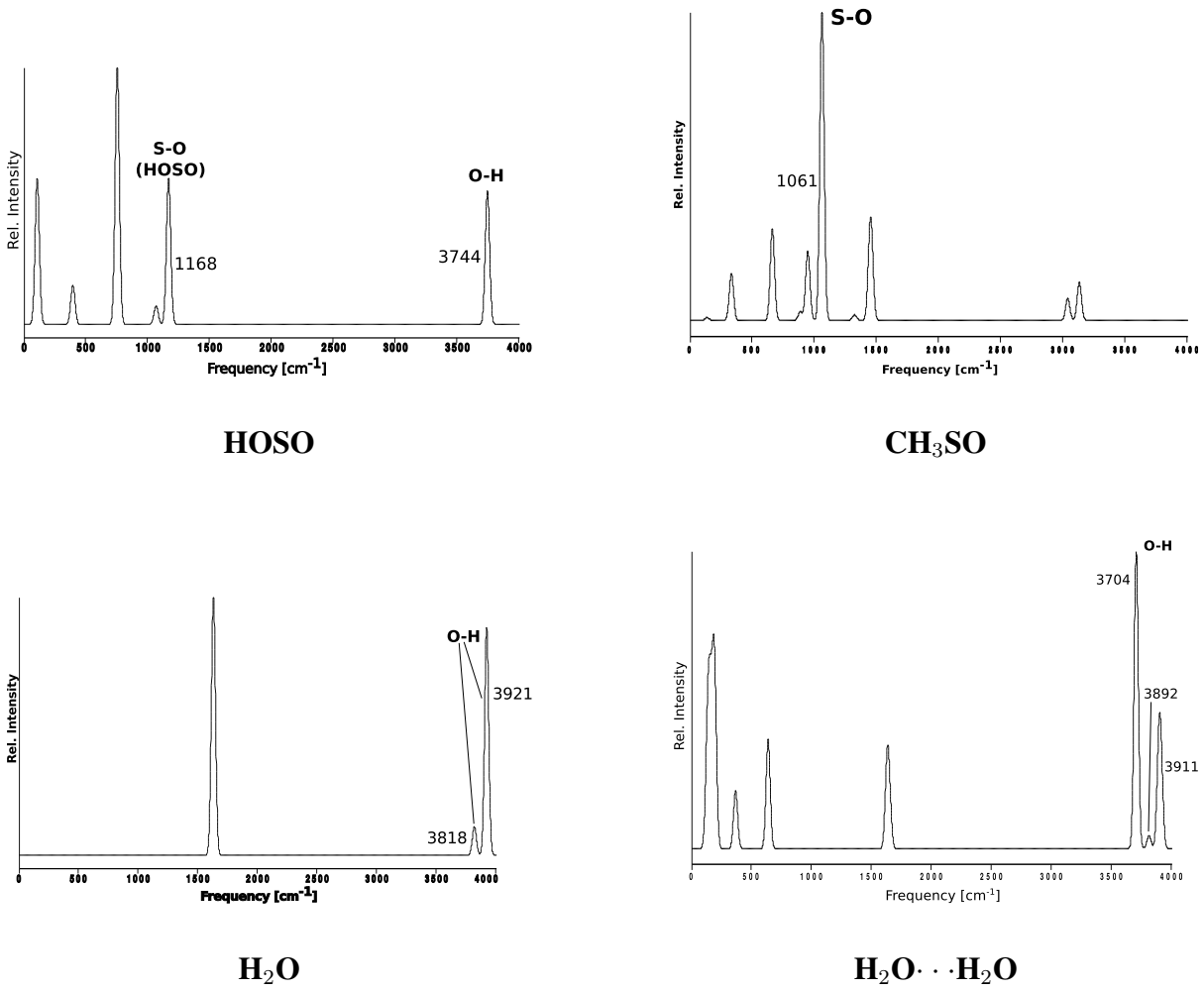
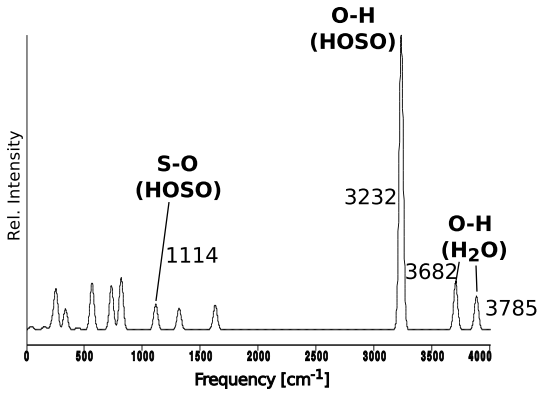
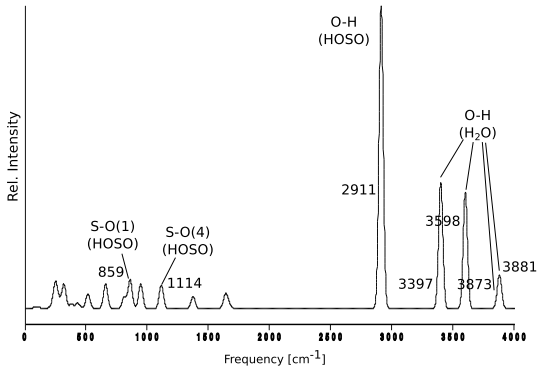


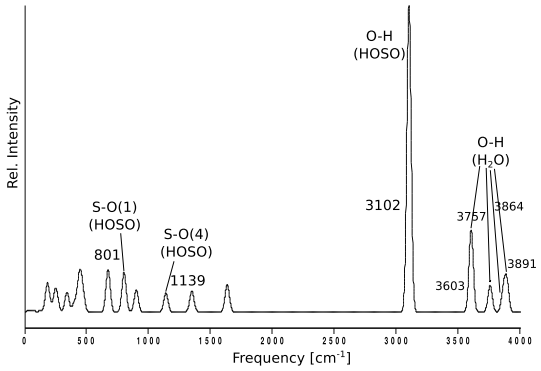
Figure SI-1: B3LYP/6-311++G(2df,2pd) computed IR spectrum of HOSO radical, CH_3SO radical, H_2O molecule and H_2O dimer.



HOSO· · ·H_2O

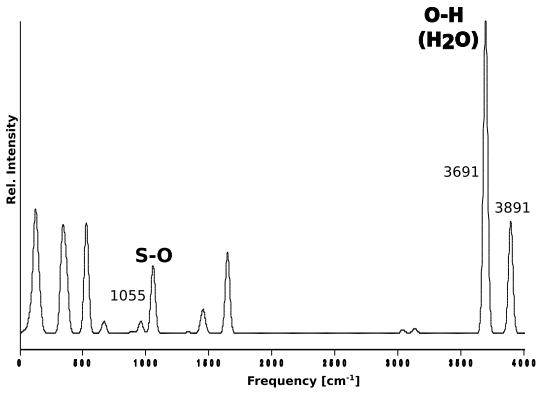


syn-**HOSO· · ·2H_2O**

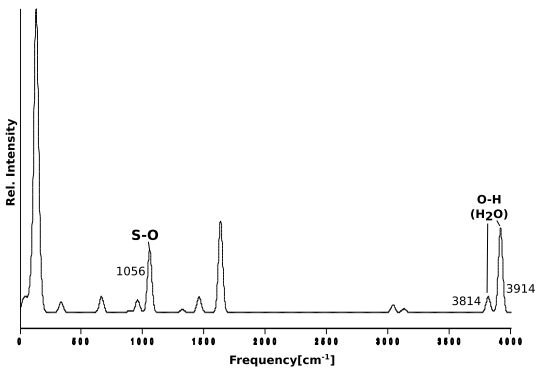


anti-**HOSO· · ·2H_2O**

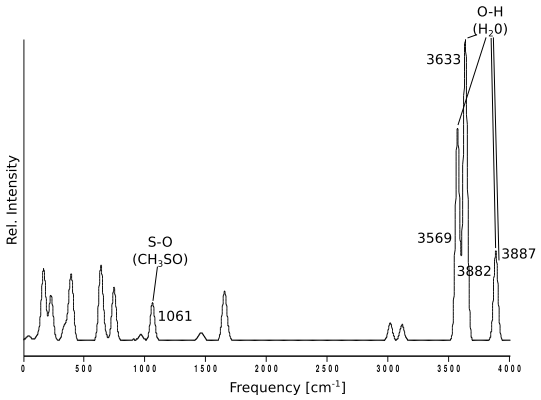
Figure SI-2: B3LYP/6-311++G(2df,2pd) computed IR spectrum of HOSO-water complexes.



cyc-$\mathbf{CH_3SO\cdots H_2O}$



acyc-$\mathbf{CH_3SO\cdots H_2O}$



$\mathbf{CH_3SO\cdots 2H_2O}$

Figure SI-3: B3LYP/6-311++G(2df,2pd) computed IR spectrum of CH_3SO-water complexes.

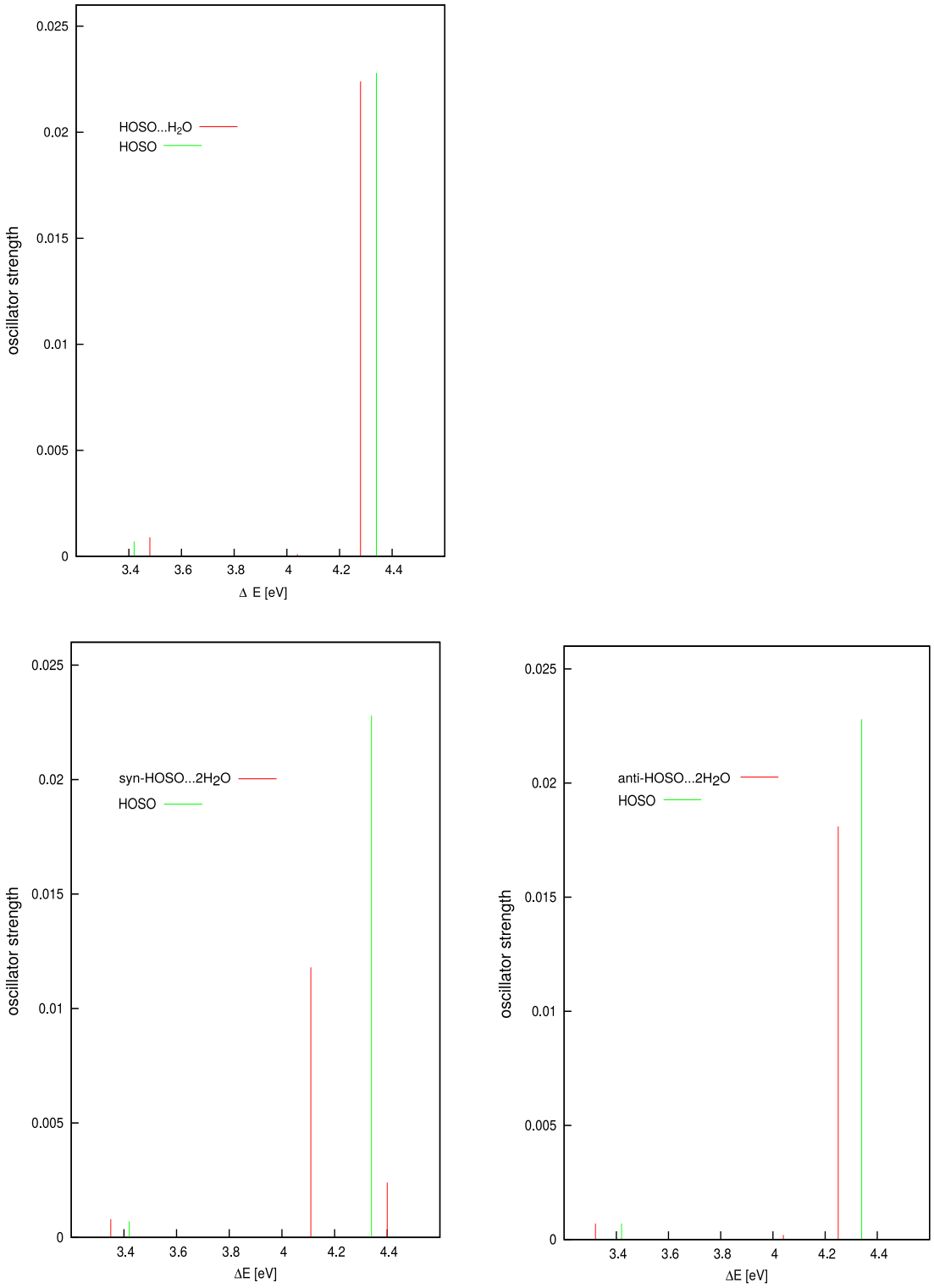


Figure SI-4: TD-B3LYP/6-311++G(2df,2pd) computed electronic spectrum of HOSO-water complexes.

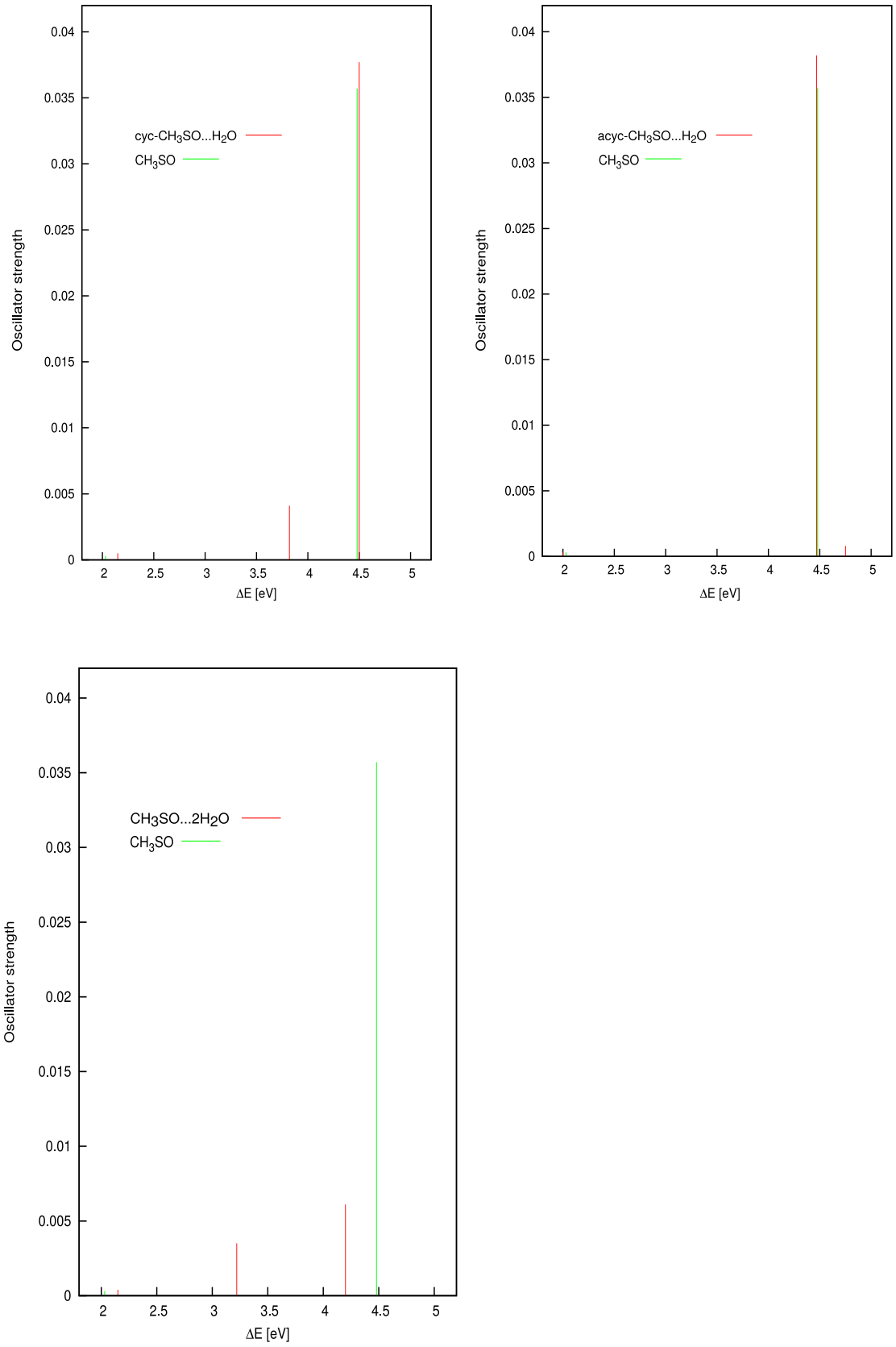


Figure SI-5:TD-B3LYP/6-311++G(2df,2pd) computed electronic spectrum of CH_3SO-water complexes.