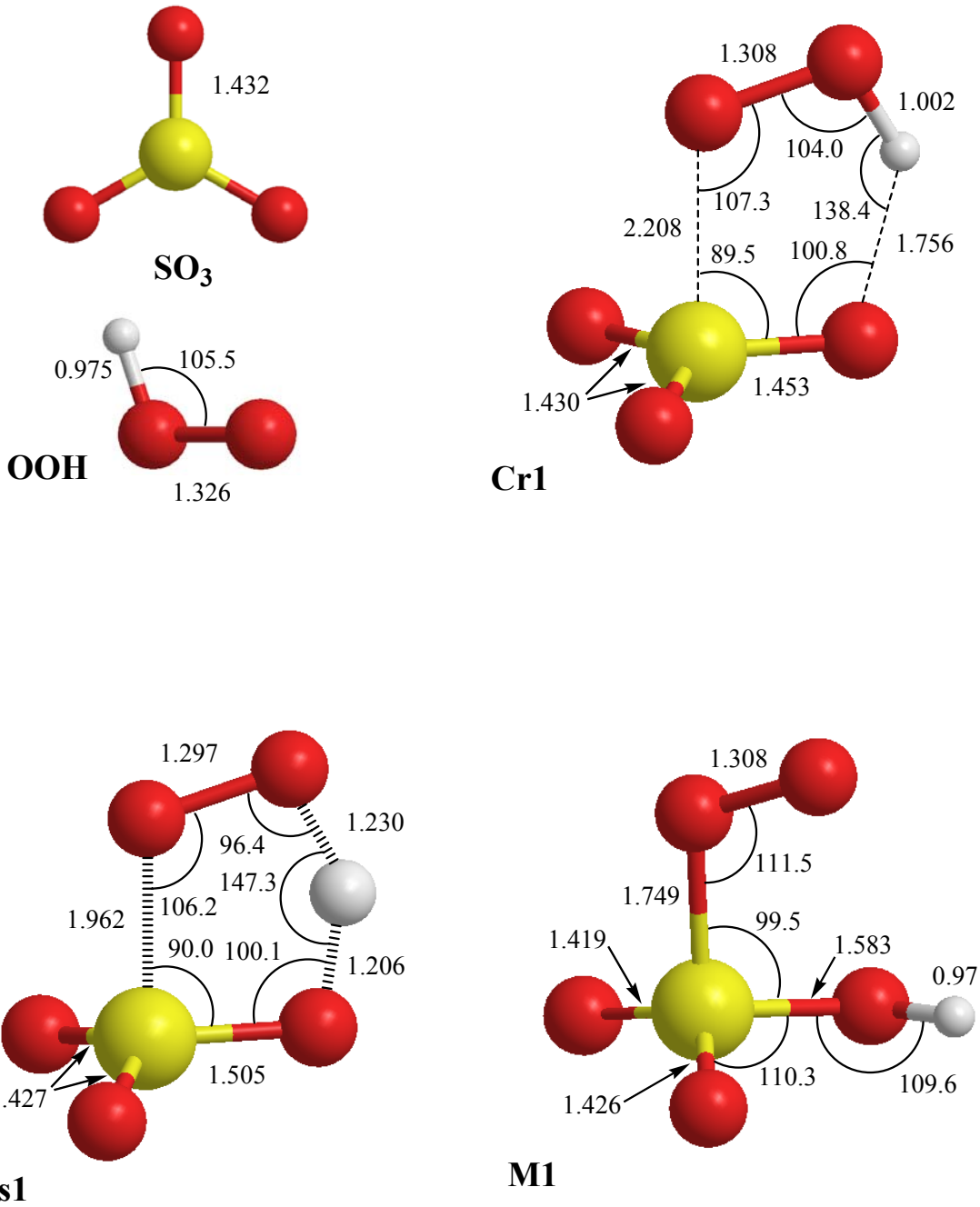
The reactions of SO_3 with HO_2 radical and $H_2O\cdots HO_2$ radical complex. Atmospheric formation of HSO_5 and H_2SO_4.

Javier Gonzalez, Miquel Torrent-Sucarrat, and Josep M. Anglada *

Departament de Química Biològica i Modelització Molecular. IQAC – CSIC. c/ Jordi Girona 18, E-08034 Barcelona, Spain.

(Supporting information)

* Corresponding author. e-mail: anglada@iqac.csic.es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100.8
1.756
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1.453
Cr1
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106.2
90.0
100.1
1.206
1.505
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Ts1
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1.583
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110.3
109.6
1.426
M1

Figure S1

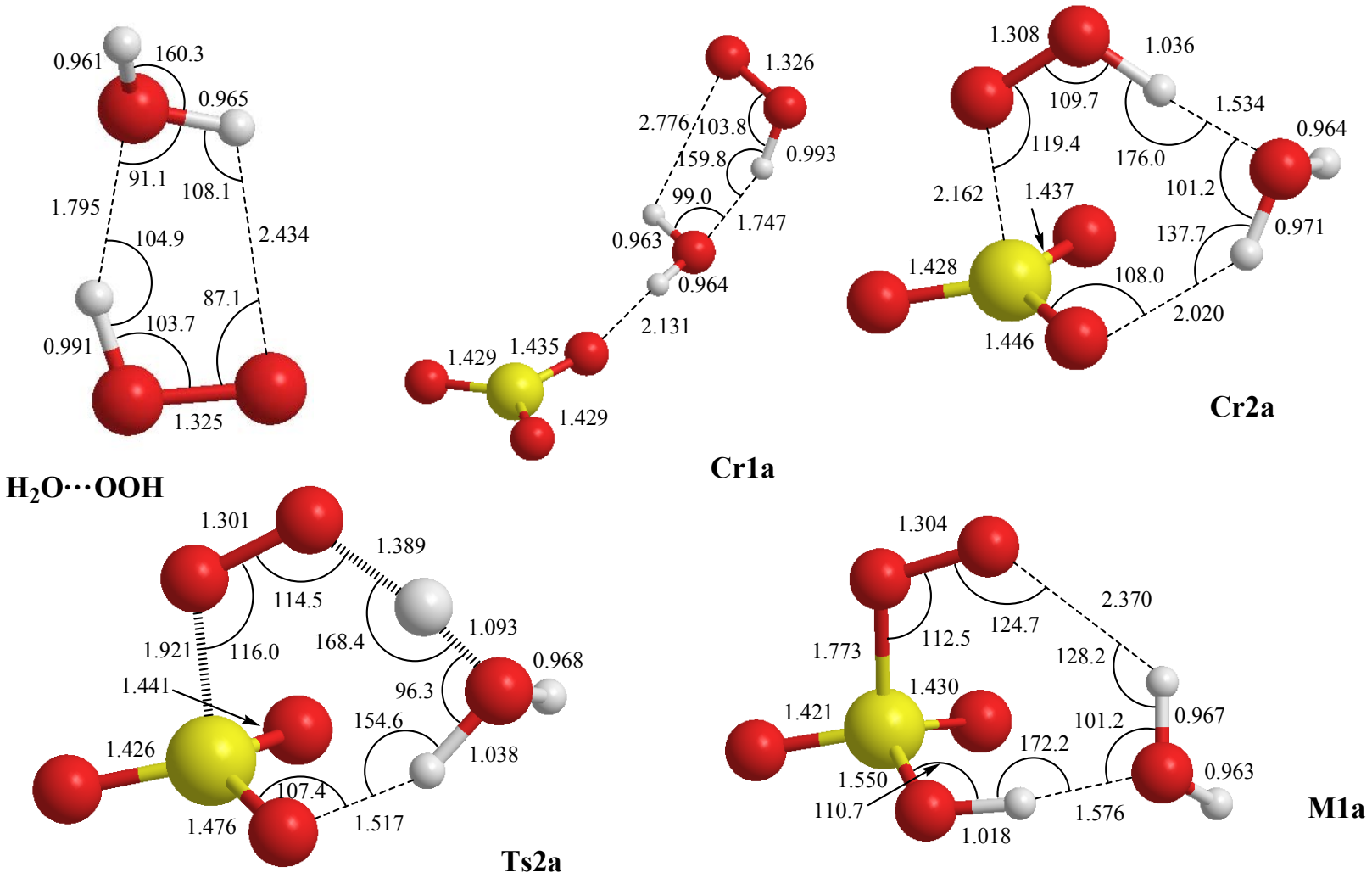
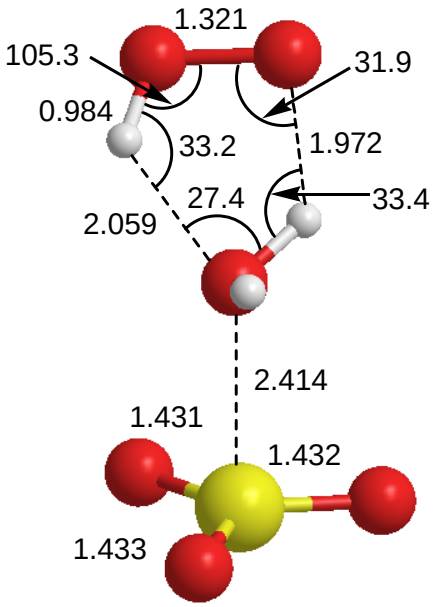
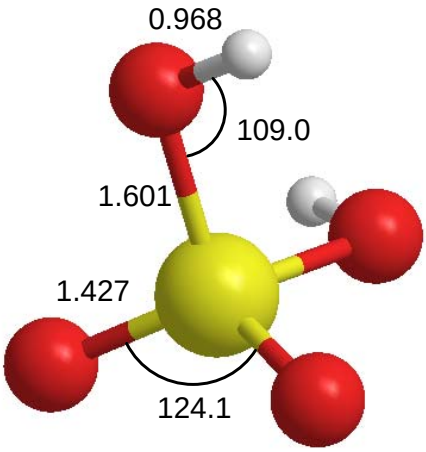


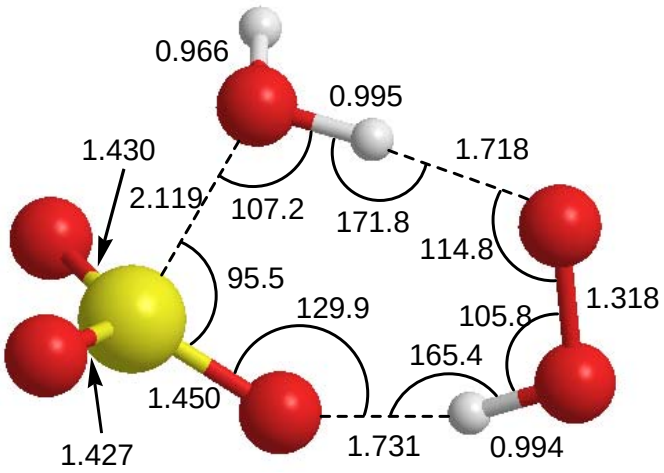
Figure S2



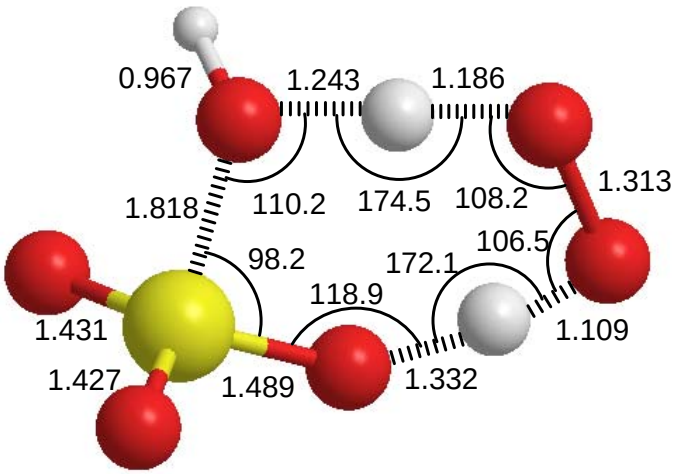
Cr1b



H_2SO4

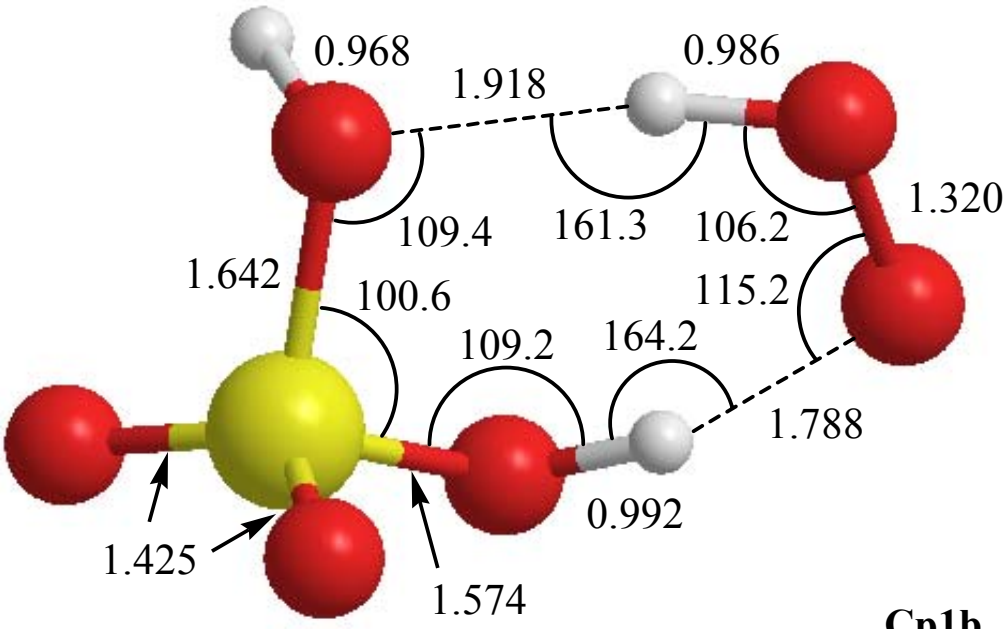


Cr2b

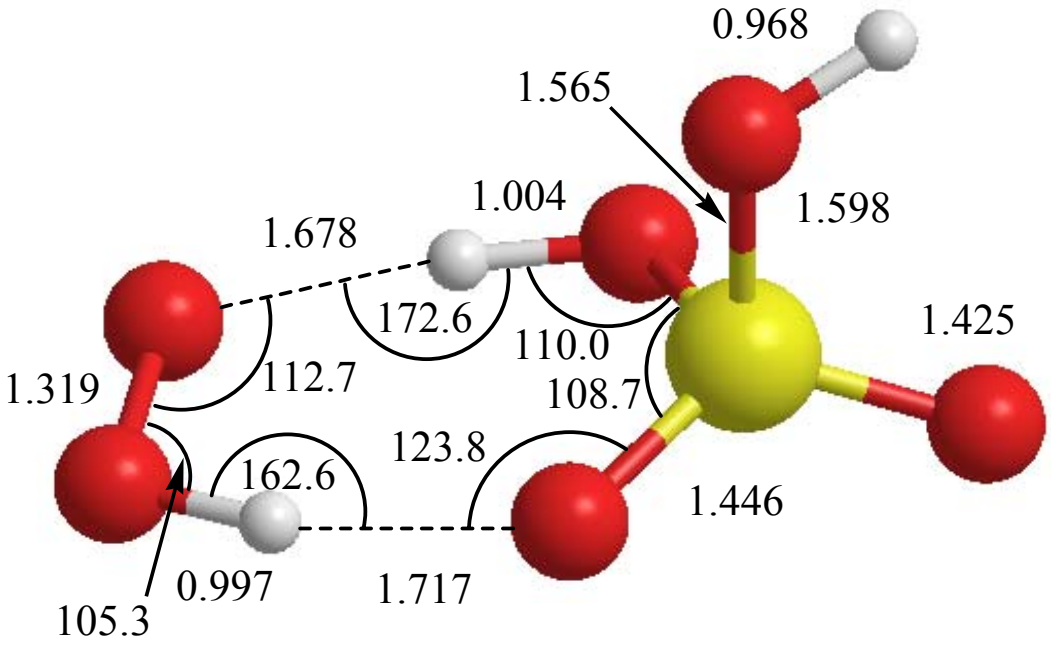


Ts2b

Figure S3



Cp1b



Cp2b

Figure S4

Table S1: Experimental and calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2df,2p) level for the ·OOH and H_2O systems.

Molecule	**Mode**		**I(har)**	**ν(har)**	**ν(anhar)**	**ν(exp)**[a]
·OOH	O-H st	A'	29.4	3616.9	3410.8	3436.2
	O-O-H bend	A'	38.3	1441.5	1399.9	1391.8
	O-O st	A'	28.7	1166.5	1142.9	1097.6
H_2O	O-H st asy	A_1	62.8	3922.4	3736.7	3755.8
	O-H st asy	A_1	8.1	3818.8	3646.7	3656.7
	H-O-H bend	B_1	71.0	1630.7	1574.6	1594.6

[a] The ·OOH and H_2O experimental vibrational frequencies are from Refs. 1-3 and 4, respectively.

Table S2: Experimental and calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2df,2p) level for the H_2SO_4 systems.

Mode		I(har)	ν(har)	ν(anhar)	ν(exp)[a]
O-H st sy	A	49.3	3773.2	3593.6	3563
O-H st asy	B	207.1	3768.9	3589.3	3566.7
S=O_2 st asy	B	303.6	1448.8	1418.3	1452.4
S=O_2 st sy	A	167.1	1201.2	1179.1	1216.1
S-O-H bend asy	B	84.2	1165.3	1135.4	1156.9
S-O-H bend sy	A	77.7	1150.9	1126.8	1135.9
S-O_2 st asy	B	342.4	851.3	831.5	881.7
S-O_2 st sy	A	113.2	798.6	780.8	834.1
S=O_2 wagg	B	24.2	540.0	531.0	558.0
S=O_2 bend	A	38.2	530.6	524.4	548.1
O-S=O rock	B	41.5	485.3	474.6	506
O-S=O bend	A	16.0	428.3	388.3	421.7
O-S=O twist	A	2.2	364.0	341.9	378.5
H(O) out asy	B	59.6	322.6	264.0	287.7
H(O) out sy	A	100.5	245.4	208.8	224

[a] The H_2SO_4 experimental vibrational frequencies are from Refs. 5, 6.

Table S3: Experimental and calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2df,2p) level for the **M1** system.

Mode		**I(har)**	**ν(har)**	**ν(anhar)**
O-H st sy	A	141.6	3742.8	3540.2
$S=O_2$ st asy	A	243.4	1460.7	1430.1
$S=O_2$ st sy	A	154.3	1213.5	1192.4
S-O-H bend	A	101.8	1154.0	1124.8
O-O st	A	15.6	1146.8	1127.6
S-OH st	A	196.3	847.5	825.0
S-OO st	A	83.6	639.3	621.9
$S=O_2$ wagg	A	82.1	564.5	556.6
$S=O_2$ bend	A	20.0	490.4	482.7
O-S=O bend	A	26.7	445.0	433.8
O-S=O rock	A	28.8	371.6	323.3
O-S-O bend	A	3.1	334.8	325.0
H(O), O(O) out asy	A	24.5	317.6	267.4
O-S=O twist	A	23.7	209.1	191.8
H(O), O(O) out sy	A	3.7	96.7	83.0

Table S4: Calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2df,2p) level for the **M1a**.

Mode		*I(har)*	*ν(har)*	*ν(anhar)*
O-H st asy (H_2O)	A	127.8	3870.2	3699.6
O-H st sy (H_2O)	A	44.4	3764.5	3590.3
SO-H st sy	A	1683.4	2837.3	2760.7
H-O-H bend	A	62.8	1638.3	1598.6
S=O_2 st asy	A	243.1	1460.3	1426.0
S-O-H bend	A	79.0	1352.8	1304.9
S=O_2 st sy	A	225.7	1209.1	1189.1
O-O st	A	9.1	1173.6	1154.5
unique mode H(O)-O out wag	A	83.6	1059.0	963.7
S-OH st	A	148.2	914.3	894.7
S-OO st	A	63.2	634.2	616.1
S=O_2 wagg	A	88.9	570.9	563.7
S=O_2 bend	A	29.7	496.8	476.8
O-S=O bend	A	209.0	491.9	452.2
O-S=O rock	A	85.2	462.9	449.0
H(O)-S out asy	A	18.6	392.2	415.4
O-S-O bend	A	14.6	350.7	339.1
O-S=O twist	A	4.4	333.2	321.0
unique mode	A	30.7	244.8	222.4
H(O)-S out sy	A	9.4	242.2	248.1
unique mode	A	43.6	157.2	315.0
unique mode	A	8.8	103.9	126.7
unique mode	A	23.8	88.6	97.8
unique mode	A	1.7	60.2	161.2

Table S5: Calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2df,2p) level for the **Cp1b**.

Mode		*I(har)*	*v(har)*	*v(anhar)*
SO-H st[a]	A	124.2	3764.0	3573.3
OO-H st	A	633.7	3451.8	3236.8
SO-H st[b]	A	640.5	3307.2	3030.6
H-O-O bend	A	42.3	1533.9	1480.7
S-O-H bend asy	A	317.0	1456.4	1423.2
$S=O_2$ st asy	A	52.2	1317.7	1253.5
O-O st	A	20.7	1213.1	1190.2
$S=O_2$ st sy	A	218.2	1206.8	1178.8
S-O-H bend sy	A	66.7	1155.3	1120.6
$S-O_2$ st asy	A	183.8	873.4	850.6
$S-O_2$ st sy	A	290.4	759.7	726.2
H(O)-S out asy	A	0.2	721.5	653.0
unique mode H(O)-O out wag	A	96.0	560.3	481.5
$S=O_2$ wagg	A	49.5	536.3	526.8
$S=O_2$ bend	A	26.8	528.6	517.6
O-S=O rock	A	17.3	487.3	469.8
O-S=O bend	A	28.6	413.9	373.9
O-S=O twist	A	8.2	370.7	353.4
H(O)-S out sy	A	38.4	318.6	263.1
unique mode	A	53.6	248.2	226.6
unique mode	A	0.2	153.4	134.7
unique mode	A	5.3	125.3	113.7
unique mode	A	1.8	89.6	89.2
unique mode	A	1.8	54.3	51.0

[a] OH group of the H_2SO_4, which makes a hydrogen bond with the hydrogen of the hydroperoxide moiety.

[b] OH group of the H_2SO_4, which makes a hydrogen bond with the terminal oxygen of the

hydroperoxide moiety.

Table S6: Calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2df,2p) level for the **Cp2b**.

Mode		*I(har)*	*v(har)*	*v(anhar)*
SO-H st	A	136.9	3769.6	3595.9
OO-H st	A	1322.7	3265.0	3037.6
SO-H st	A	787.4	3053.4	2695.0
H-O-O bend	A	28.4	1575.1	1536.7
S-O-H bend asy	A	333.0	1441.3	1394.2
$S=O_2$ st asy	A	139.4	1344.1	1299.2
O-O st	A	8.8	1224.9	1202.2
S-O-H bend sy	A	76.2	1177.2	1149.0
$S=O_2$ st sy	A	174.3	1144.9	1112.5
$S-O_2$ st asy	A	299.4	911.9	894.9
H(O)-S out asy	A	129.6	825.4	787.1
$S-O_2$ st sy	A	29.7	816.1	776.7
unique mode H(O)-O out wag	A	145.7	671.2	625.4
$S=O_2$ wagg	A	49.5	557.9	549.6
$S=O_2$ bend	A	19.8	538.3	533.5
O-S=O rock	A	3.9	511.0	505.5
O-S=O bend	A	27.0	425.1	398.8
O-S=O twist	A	2.7	367.9	349.8
unique mode	A	77.4	293.8	285.7
H(O)-S out sy	A	78.0	251.7	189.7
unique mode	A	6.0	191.0	182.4
unique mode	A	10.0	168.3	157.7
unique mode	A	1.8	90.5	91.6
unique mode	A	1.4	45.3	46.3

[a] OH group of the H_2SO_4, which doesn't participate in the hydrogen bond.

[b] OH group of the H_2SO_4, which participates in the hydrogen bond.

Table S7: Calculated harmonic and anharmonic rotational constants (in cm^{-1}) at B3LYP/6-311+G(2df,2p) level for some selected molecules.

	Harmonic			***Anharmonic***		
Molecule	***A***	***B***	***C***	***A***	***B***	***C***
·OOH	20.7303	1.1229	1.0652	20.5775	1.1190	1.0575
H_2O	27.6499	14.3617	9.4455	28.1208	14.2742	9.2169
H_2SO_4	0.1680	0.1648	0.1587	0.1672	0.1630	0.1584
$\mathbf{M_1}$	0.1608	0.0931	0.0912	0.1598	0.0921	0.0902
$\mathbf{M_{1a}}$	0.1008	0.0601	0.0487	0.0990	0.0593	0.0478
$\mathbf{Cp_{1b}}$	0.1425	0.0442	0.0424	0.1419	0.0436	0.0419
$\mathbf{Cp_{2b}}$	0.1464	0.0431	0.0417	0.1459	0.0428	0.0415

References

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2. D. D. Nelson and M. S. Zahniser, *J. Mol. Spectrosc.*, 1991, **150**, 527-534.
3. C. Yamada, Y. Endo and E. Hirota, *J. Chem. Phys.*, 1983, **78**, 4379-4384.
4. T. Shimanouchi, *Tables of Molecular Vibrational Frequencies Consolidated Volume I*, 1972.
5. J. Demaison, M. Herman, J. Lievin and H. D. Rudolph, *J. Phys. Chem. A*, 2007, **111**, 2602-2609.
6. A. Givan, L. A. Larsen, A. Loewenschuss and C. J. Nielsen, *J. Mol. Struct.*, 1999, **509**, 35-47.

Cartesian coordinates in Ångstroms for all structures studied in this work

OOH ^{2}A" B3LYP/6-311+G(2df,2p)

O	0.055279	-0.608518	0.000000
H	-0.884464	-0.869983	0.000000
O	0.055279	0.717266	0.000000

OOH ^{2}A" QCISD/6-311+G(2df,2p)

O	0.055179	-0.611966	0.000000
O	0.055179	0.718768	0.000000
H	-0.882859	-0.854409	0.000000

SO_3 ^{2}A" B3LYP/6-311+G(2df,2p)

S	0.000000	0.000000	0.000000
O	0.000000	1.431664	0.000000
O	1.239857	-0.715832	0.000000
O	-1.239857	-0.715832	0.000000

SO_3 ^{2}A" B3LYP/6-311+G(2df,2p)

S	0.000000	0.000000	0.000000
O	0.000000	1.422015	0.000000
O	1.231501	-0.711007	0.000000
O	-1.231501	-0.711007	0.000000

Cr1 ^{2}A" B3LYP/6-311+G(2df,2p)

S	0.031208	0.690206	0.000000
O	-1.362699	0.280910	0.000000
O	0.635945	-1.433752	0.000000
O	-0.458406	-2.148978	0.000000
H	-1.193173	-1.467250	0.000000
O	0.635945	1.052407	1.243667
O	0.635945	1.052407	-1.243667

Cr1 ^{2}A" QCISD/6-311+G(2df,2p)

S	0.019730	0.710230	0.000000
O	-1.357553	0.303071	0.000000
O	0.637049	1.036903	1.234359
O	0.637049	1.036903	-1.234359
H	-1.182966	-1.523842	0.000000
O	0.637049	-1.429411	0.000000
O	-0.445183	-2.177445	0.000000

Ts1 ^{2}A" B3LYP/6-311+G(2df,2p)

S	-0.094368	0.580049	0.000000
O	-0.608357	-1.313669	0.000000
O	0.499185	-1.988820	0.000000
O	1.358133	0.185379	0.000000
H	1.251903	-1.015966	0.000000
O	-0.608357	1.042004	1.248610
O	-0.608357	1.042004	-1.248610

Ts1 ^{2}A" QCISD/6-311+G(2df,2p)

S	0.085412	0.564417	0.000000
O	-1.353201	0.187259	0.000000
O	0.606325	1.014269	1.238902
O	0.606325	1.014269	-1.238902
H	-1.225992	-1.044409	0.000000
O	0.606325	-1.253020	0.000000
O	-0.483347	-1.961061	0.000000

M1 ^{2}A B3LYP/6-311+G(2df,2p)

S	0.473767	-0.039663	0.087392
O	0.332683	1.175261	-0.917412
O	0.479997	0.429374	1.433748
O	1.400222	-0.963405	-0.461360
H	-0.199689	1.876307	-0.508500

O	-1.072248	-0.814270	-0.176982
O	-2.063227	0.017830	0.010784

M1 ^{2}A QCISD/6-311+G(2df,2p)

O	0.322374	1.129432	-0.950513
S	0.452643	-0.031594	0.090663
O	-1.001148	-0.833835	-0.185409
O	-2.021219	-0.007545	0.001029
O	0.404295	0.491779	1.406089
O	1.414251	-0.947709	-0.382547
H	-0.190708	1.848523	-0.559811

$HOSO_2$ ^{2}A B3LYP/6-311+G(2df,2p)

S	-0.135992	0.067114	0.256012
O	0.091329	1.434318	-0.189689
O	-1.259204	-0.726355	-0.196330
O	1.194620	-0.814470	-0.113313
H	1.961906	-0.221775	-0.101529

$HOSO_2$ ^{2}A QCISD/6-311+G(2df,2p)

S	-0.124144	0.079858	0.248617
O	0.281854	1.398046	-0.182353
O	-1.335964	-0.554727	-0.192084
O	1.065970	-0.947180	-0.107537
H	1.891424	-0.446841	-0.122072

O_2 $^3\Sigma_g$ B3LYP/6-311+G(2df,2p)

O	0.000000	0.000000	0.602321
O	0.000000	0.000000	-0.602321

O_2 $^3\Sigma_g$ QCISD/6-311+G(2df,2p)

O	0.000000	0.000000	0.600671
O	0.000000	0.000000	-0.600671

Cr1a ^{2}A B3LYP/6-311+G(2df,2p)

O	-4.320885	0.418778	-0.785023
O	-4.021569	-0.769565	-0.278917
H	-3.250693	-0.583547	0.318565
O	-2.041025	0.360407	1.163438
H	-1.113594	0.232594	0.934861
H	-2.288536	1.220956	0.807626
O	0.896214	-0.198005	0.376488
S	2.247346	-0.023088	-0.072958
O	3.113205	-1.156220	-0.160862
O	2.710971	1.282031	-0.426840

Ts1a ^{2}A B3LYP/6-311+G(2df,2p)

S	-2.005422	-0.070517	-0.014010
O	-0.942923	0.870475	-0.230537
O	-2.023814	-0.850846	1.183640
O	-3.033483	-0.209964	-0.995958
H	1.043952	1.349371	0.368570
O	1.990813	1.419940	0.537265
H	2.138229	1.000317	1.391449
H	2.988477	0.425307	-0.491353
O	3.566708	-0.307634	-0.830415
O	3.682209	-1.127811	0.205442

Cr2a ^{2}A B3LYP/6-311+G(2df,2p)

S	0.930276	-0.272323	0.013495
O	0.288303	-0.940620	-1.096312
O	0.544450	-0.670226	1.339031
O	2.157209	0.422904	-0.208417
H	-1.597076	-1.404196	-0.538042
O	-2.330339	-0.981045	-0.061579
H	-2.372014	-1.413805	0.798265
H	-1.839734	0.470305	0.013898

O	-1.549385	1.464917	0.005990
O	-0.244685	1.542178	-0.039969

Ts2a ^{2}A B3LYP/6-311+G(2df,2p)

S	0.818314	-0.228456	0.033647
O	2.142381	0.195789	-0.282264
O	-0.056390	1.475050	-0.123466
O	-1.350057	1.468187	0.017417
O	0.441108	-0.576910	1.380291
O	0.096254	-0.987089	-1.006628
H	-1.335399	-1.155664	-0.534323
O	-2.218881	-0.841104	-0.088949
H	-1.920877	0.201905	0.043675
H	-2.272068	-1.262315	0.781094

M1a ^{2}A B3LYP/6-311+G(2df,2p)

S	0.751981	-0.291107	0.080259
O	2.100072	-0.468591	-0.331660
O	0.512904	1.448778	-0.165857
O	-0.726616	1.811833	0.011903
O	0.273786	-0.563124	1.400531
O	-0.212534	-0.854138	-0.995055
H	-1.174253	-0.830562	-0.662663
H	-2.628811	-0.585973	-0.107565
H	-2.550903	0.315689	0.231939
H	-2.856949	-1.137698	0.648201

H_2O $^1A_1$ B3LYP/6-311+G(2df,2p)

O	0.000000	0.116717	0.000000
H	0.763265	-0.466869	0.000000
H	-0.763265	-0.466868	0.000000

$H_2O\cdots OOH$ ^{2}A B3LYP/6-311+G(2df,2p)

O	1.149042	0.651942	0.016216
O	0.957611	-0.659061	0.003456
H	-0.028543	-0.751720	-0.011817
O	-1.657423	-0.002166	-0.090912

H	-2.292293	-0.056346	0.628642
H	-1.273000	0.882339	-0.046908

Cr2b ^{2}A B3LYP/6-311+G(2df,2p)

S	-1.085941	-0.243072	0.002658
O	-1.396835	-0.347526	1.390970
O	-2.038225	0.276813	-0.929184
O	-0.018085	-1.072349	-0.522005
H	1.683113	-1.020685	-0.209039
O	2.628842	-0.743993	-0.076829
O	2.599506	0.561898	0.099902
O	0.072890	1.526122	0.128604
H	1.029046	1.254210	0.095058
H	-0.121853	2.047909	-0.660203

Ts2b ^{2}A B3LYP/6-311+G(2df,2p)

S	-0.967961	-0.145283	0.029889
O	-1.199859	-0.330626	1.426064
O	-2.017284	0.255225	-0.856610
O	0.005282	-1.097909	-0.572297
H	1.299340	-0.960322	-0.288487
O	2.361934	-0.701504	-0.103134
O	2.395246	0.590649	0.127495
O	0.088007	1.335142	0.037429
H	1.286390	1.006808	0.066543
H	-0.164969	1.870227	-0.727846

Cr1b ^{2}A B3LYP/6-311+G(2df,2p)

S	1.41121	0.16954	0.0821
O	1.37669	-0.25171	1.44993
O	2.12368	-0.61244	-0.88388
O	0.90678	1.45932	-0.27785
H	-2.22087	0.3554	-0.90217
O	-3.0584	0.53746	-0.41942
O	-3.01701	-0.23405	0.65261
O	-0.66111	-0.92579	-0.49648

H	-1.27138	-1.05907	0.25254
H	-0.45227	-1.79143	-0.86328

Ts1b ^{2}A B3LYP/6-311+G(2df,2p)

S	1.437372	-0.143380	-0.114233
O	0.797529	-0.834730	-1.191561
O	2.002866	1.154088	-0.336754
O	1.678337	-0.816758	1.124957
H	-2.298591	-0.479635	0.858345
O	-3.126918	-0.573657	0.335846
O	-3.036046	0.334578	-0.620093
O	-0.681272	0.761614	0.670002
H	-1.263779	1.012573	-0.071358
H	-0.511545	1.560055	1.181565

Cp1b ^{2}A B3LYP/6-311+G(2df,2p)

S	-0.975221	-0.038547	0.107054
O	-0.694435	-0.088160	1.503488
O	-2.289997	0.041463	-0.436295
O	-0.227355	-1.194076	-0.656557
H	0.730245	-1.189071	-0.398816
O	2.420167	-0.708845	-0.068128
O	2.618963	0.588520	0.070692
O	-0.127010	1.267917	-0.413733
H	1.735245	1.014685	-0.029012
H	-0.464606	1.536587	-1.280772

Cp2b ^{2}A B3LYP/6-311+G(2df,2p)

H	-0.464606	1.536587	-1.280772
S	0.888157	-0.072606	-0.120622
O	-0.048635	-1.156316	-0.316663
O	0.117085	1.284470	-0.232244
O	2.085289	0.025554	-0.887237
O	1.266764	-0.158532	1.428996
H	-0.862349	1.136330	-0.070581
H	2.088952	0.328619	1.584582
O	-2.471283	0.694491	0.105427

O	-2.660092	-0.603864	-0.026553
H	-1.750134	-0.989664	-0.157859

H_2SO_4 ^{1}A B3LYP/6-311+G(2d,2p)

S	0.000000	0.000000	0.163255
O	0.598714	-1.114699	0.827048
O	1.076426	0.632890	-0.850721
O	-0.598715	1.114703	0.827040
O	-1.076424	-0.632894	-0.850720
H	1.691723	-0.065609	-1.116636
H	-1.691728	0.065600	-1.116629