Triplet State Promoted Reaction of SO_2 with H_2O by Competition Between Proton Coupled Electron Transfer (*pcet*) and Hydrogen Atom Transfer (*hat*) Processes.

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(Supplementary Information)

Theoretical Methods

We have employed the density functional methods B3LYP,[1] along with the aug-cc-pVTZ basis set[2, 3] to optimize the stationary points investigated. At this level of theory, we have performed harmonic vibrational frequency calculations to confirm the nature (minima or saddle points) of the stationary points, and to calculate the zero-point energy and the thermal contributions to enthalpy and Gibbs energy as well. In addition, we have carried out intrinsic reaction coordinate (IRC) calculations[4-6] in order to confirm the connectivity between a given transition state structure (TS) and the corresponding reactant and product. For some stationary points of interest, additional geometry optimizations have carried out at CCSD(T) level of theory[7] with the 6-311+G(2df,2p) basis set.[8, 9]

The final energies have been obtained by carrying out single point energy calculations at the CCSD(T) level of theory employing the aug-cc-pVTZ and aug-cc-pVQZ basis sets, and considering the extrapolation to the complete basis set (CBS) limit, according to the extrapolation scheme by Helgaker et al. [10] We have also looked at the reliability of these results, in regards to the possible multi-reference character of the corresponding wave function, by checking the T1 diagnostic (T1d) value of the CCSD wave function.[11] In all cases the T1d values (up to 0.045) lie among the standards reported in reference[11], with the exception of the transition state ATS2, ATS3, and ATS4, for which we got T1D values

of 0.060. In order to check the reliability of these results, for ACR1, ATS1 and ATS2, we have also calculated the corresponding relative energies between the pre-reactive complex and the transition state by performing large scale MRCI+Q/aug-cc-pVTZ level of theory (multireference CI calculations including the Davidson extrapolation to quadruple excitations), and the calculated MRCI+Q/aug-cc-pVTZ values differ in 0.25 and 1.39 kcal·mol^{-1} for ACR1 – ATS1 and ACR1 – ATS2, respectively, relative to the values computed at CCSD(T)/aug-cc-pVTZ. ATS3 and ATS4 have the same electronic features as ATS2 and therefore their description presents the same technical problems. A similar issue has been found in the study of the *cis*-HONO and ClO where the MRCI+Q energy barrier compares very well with the CCSD(T) barrier, having the CCSD expansion a T1d value of 0.06.[12] The analysis of the charge distribution has been carried out in the context of the Natural bonds orbital (NBO) approach by Weinhold and co-workers.[13] For some selected stationary points we have also analyzed the bonding interactions within the framework of the topological theory of Atoms in Molecules (AIM).[14] For some elementary reactions, transition state theory (TST) was used to estimate the reaction rate constants employing the one-dimensional Eckart tunneling correction.

The quantum chemical calculations carried out in this work were performed by using Gaussian[15] and ORCA program packages. [16] The Molden[17] and VMD[18] programs were employed to visualize and plot the geometric and electronic features. The EXTREM program[19] has been employed for the AIM analysis and the Polyrate program for the kinetic calculations.[20]

The ground and low lying electronic states of SO_2.

The ground and lowest lying electronic states of SO_2 have been extensively investigated [21-25] and we refer the reader to these articles for a more detailed discussion on the ground and excited states of sulfur dioxide. For the purposes of this investigation, we have considered the ground X^1A_1 and the $^3B_1$, $^3A_2$, and $^3B_2$ electronic states. Our computed adiabatic excitation energies, along with the electronic characterization and the corresponding optimized geometrical parameters, are contained in Table S1; they are in very good agreement with previous theoretical work from the literature[21-25] and with experimental measurements[26-29].

Table S1: Adiabatic excitation energies (in eV, including ZPE), and optimized geometrical parameters for the ground electronic state and low lying triplet states of SO_2. Distances are in angstroms and angles in degrees.[a]

State	Electronic characterization	r(SO)	a(OSO)	ΔE(eV)
$\mathbf{X^1A_1}$	$.....8a_1^2 2b_1^2 5b_2^2 1a_2^2$	1.451	118.2	0.00
$\mathbf{^3B_1}$	$.....7a_1^2 2b_1^2 5b_2^2 1a_2^2 8a_1^1 3b_1^1$	1.515	124.8	3.15
$\mathbf{^3A_2}$	$.....8a_1^2 2b_1^2 4b_2^2 1a_2^2 3b_1^1 5b_2^1$	1.550	93.6	3.19
$\mathbf{^3B_2}$	$.....8a_1^2 2b_1^2 5b_2^2 1a_2^1 3b_1^1$	1.576	104.7	3.39

a) Geometries optimized at B3LYP/aug-cc-pVTZ. Relative energies computed at CCSD(T)/CBS//B3LYP/aug-cc-pVTZ

The reaction of $^3SO_2$ with H_2O.

In the main text we have discussed the elementary reactions of $^3SO_2$ with H_2O through the ATS1 transition state, which involves a proton coupled electron transfer mechanism, and also via ATS2 which corresponds to a conventional hydrogen atom transfer process. We have pointed out that the last one is stabilized by a hydrogen bond between the hydrogen atom of the water moiety and the oxygen atom of the SO_2 moiety that does not participate in the reaction. Beyond these reaction paths we have found two additional elementary reactions (via ATS3 and ATS4), whose transition states lie higher in energy (12.44 and 12.77 kcal·mol^{-1}, respectively above the energy of the separate reactants). In Figure S1 we have plotted a schematic potential energy surface which contains all elementary processes we have found. The structure and electronic features of ATS3 and ATS4 indicated that they correspond to a conventional hydrogen transfer mechanism (*hat*), and both are conformers of ATS2. Comparing the relative energy of these conformers, our results displayed in Figure S2 and Table S2 indicate that the stabilization of ATS2 originated by the hydrogen bond is 4.5 kcal·mol^{-1}.

The reaction between $^3SO_2$ and H_2O starts with the formation of a pre-reactive complex and, along with the reaction paths, we have also carried out an exhaustive investigation of it. Indeed, we have found up to five complexes involving the interaction of a triplet

electronic state of sulfur dioxide with water (ACR1 to ACR5), and their main geometric parameters are displayed in Figure S2. Their geometric and electronic structure suggest that they connect with different triplet electronic states of SO_2. If we compare, for instance, the geometrical parameters of the SO_2 moiety in the complexes with the optimized structure of the three triplet excited state of sulfur dioxide (see Table S1 and Figure S2), we can infer that ACR3 and ACR4, with an OSO angle close to 93°, correlate with the $^3A_2$ electronic state of SO_2, the ACR5 complex, with an OSO angle of 124°, correlates with the $^3B_1$ electronic state of SO_2, and ACR2, with an OSO angle of 100°, correlates with the $^3B_2$ electronic state of SO_2. ACR1 has different features, as it maintains the O-O interaction involved in the electron transfer via ATS1. This kind of interaction in the pre-reactive complex has been also found in previous works associated to *pcet* reaction mechanisms.[30] The results of Table S2 indicate that the relative energies of these pre-reactive complexes range between -2.21 and 1.46 kcal·mol^{-1} relative to the SO_2 (a^3B_1) + H_2O energy. We have also found transition states connecting all these pre-reactive complexes. Their corresponding structures are drawn in Figure S2 and their relative energies are contained in Table S2.

Table S2. Relative energies, energies plus ZPE (Zero Point Energy), (in kcal·mol^{-1}), enthalpies, and free energies (in kcal·mol^{-1}, at 298 K) calculated for the different stationary points of the $^3SO_2 + H_2O$ reaction investigated in this work.[a] The values of the T1d of the CCSD expansion are also given.

State	ΔE	Δ (E+ZPE)	ΔH	ΔG	T1d
SO_2 ($^3B_1$) + H_2O	0.00	0.00	0.00	0.00	
	(0.00)	(0.00)	(0.00)	(0.00)	
SO_2 ($^3A_2$) + H_2O	1.29	0.94	1.00	0.81	
SO_2 ($^3B_2$) + H_2O	6.19	5.54	5.66	5.34	
HOSO + OH	5.53	4.52	4.75	3.81	
ACR1	-0.83	1.46	0.65	9.74	0.033
ACR2	-0.66	0.51	0.57	7.27	0.030
ACR3	-2.85	-2.04	-1.80	4.03	0.028
ACR4	-1.54	-0.77	-0.50	4.30	0.028
ACR5	-3.44	-2.21	-2.07	3.65	0.030

TS-ACR2-ACR3	-1.01	-0.26	-0.53	6.76	0.037
TS-ACR3-ACR4	-1.49	-0.81	-1.07	5.55	0.028
TS-ACR1-ACR4	0.65	1.31	1.11	7.79	0.028
TS-ACR3-ACR5	-0.06	0.59	0.37	7.55	0.027
ATS1	6.94	6.53	5.13	15.39	0.036
	(6.90)	(6.49)	(5.09)	(15.34)	
ATS2	9.64	8.01	6.88	16.44	0.060
	(9.81)	(8.18)	(7.05)	(16.61)	
ATS3	14.78	12.77	11.99	20.21	0.060
ATS4	14.61	12.44	11.67	20.05	0.056
ACP1	-1.90	-0.90	-1.44	6.67	0.023
ACP2	1.00	1.86	1.33	9.09	0.020

a) Energies computed at CCSD(T)/CBS//B3LYP/aug-cc-pVTZ level of theory. The ZPE, enthalpic and entropic corrections correspond to B3LYP/aug-cc-pVTZ values. Values in parenthesis are computed at CCSD(T)/CBS//CCSD(T)/6-311+G(2df,2p) level of theory.

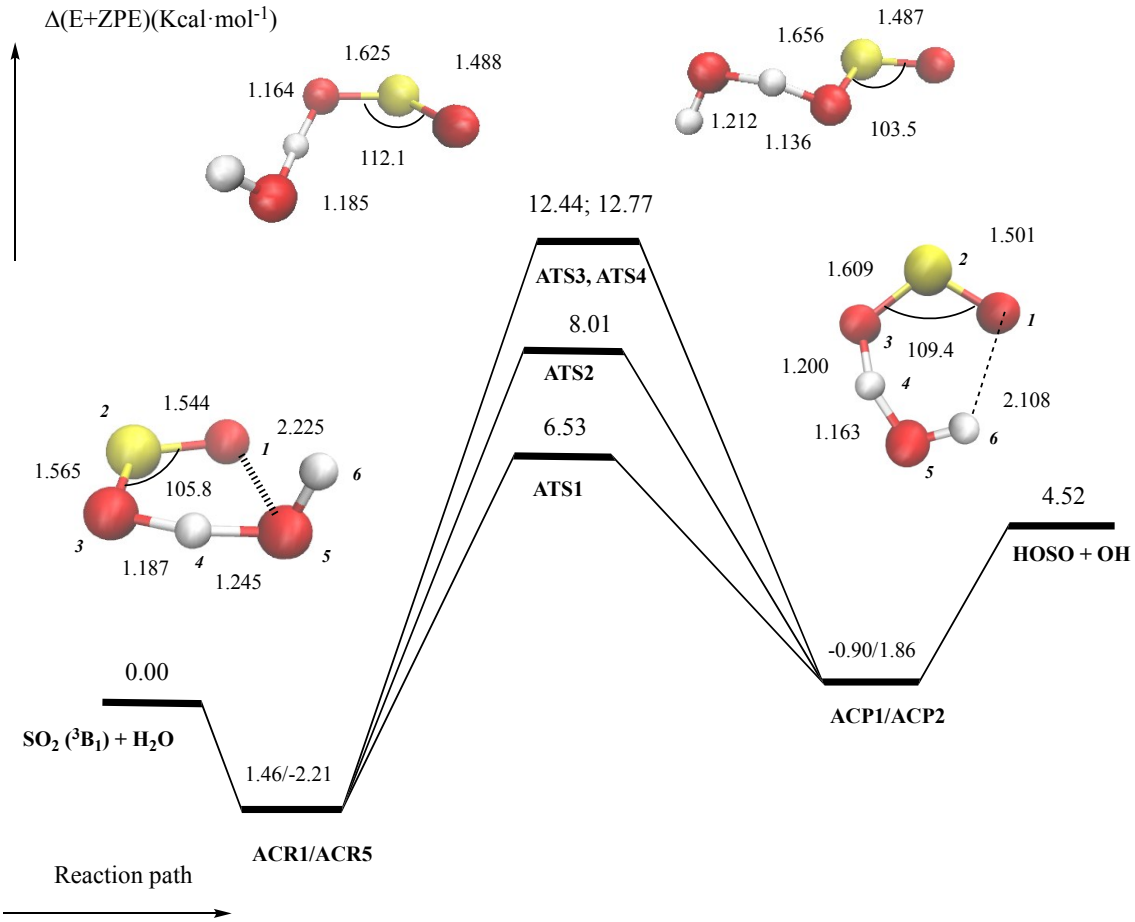

Figure S1. Schematic potential energy surface (CCSDT/CBS//B3LYP/aug-cc-pVTZ) for the $^3SO_2 + H_2O$ reaction. Energies (kcal·mol^{-1}) include zero-point energies. Interatomic distances are in Å and OSO angle in degrees.

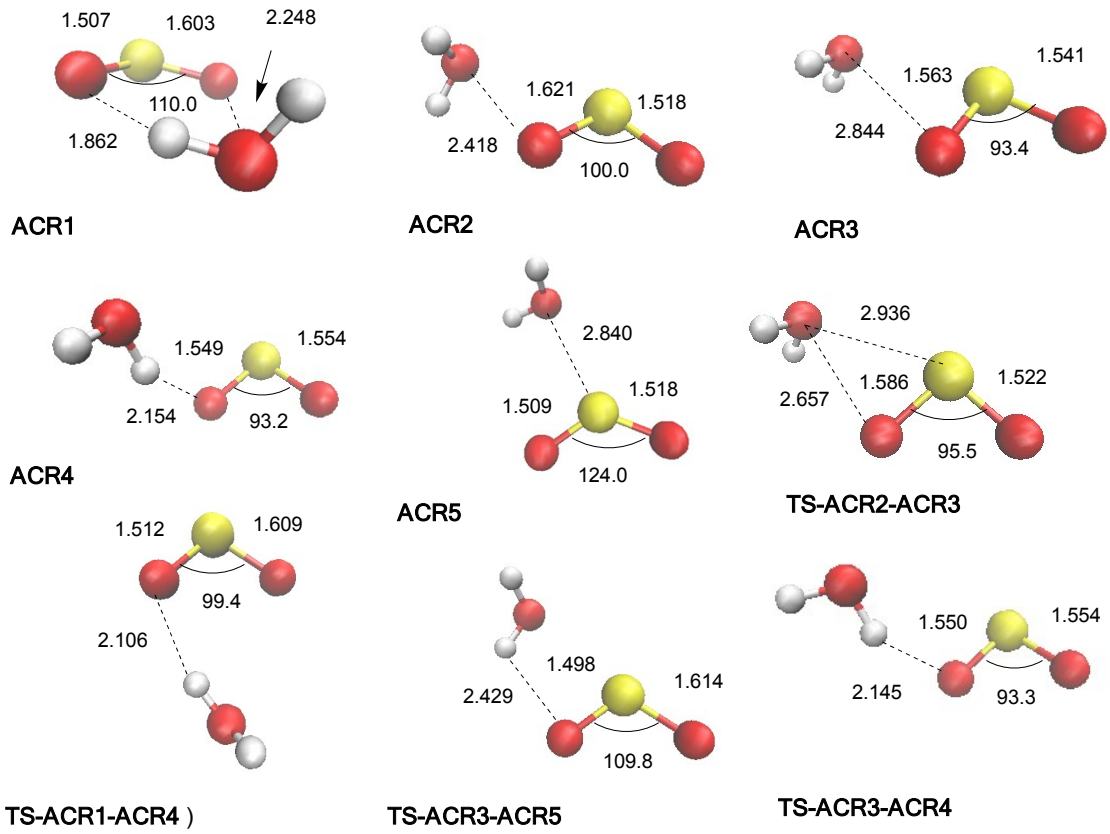

Figure S2. Main geometrical parameters of the ACR1 – ACR5 pre-reactive complexes of the $^3SO_2 + H_2O$ interaction and the transition states connecting them. Interatomic distances are in Å and OSO angle in degrees.

In Table S3 We have collected the results of the AIM analysis. For the purpose of the present work, what is relevant for **ATS1** is the existence of a bond critical point between O5 and O1 where the values of the density and the Laplacian of the density indicates the existence of a weak interaction between both atoms where the electron transfer takes place. For **ATS2**, this analysis shows the existence of a stabilizing hydrogen bond interaction between H6 and O1. In both cases there is a ring critical point indicating a stabilizing effect. Similar results were described for the same kind of interactions in the literature.[31]

Table S3. Electronic characterization of chemical bonds according to the AIM theory. Atom numbering according Figure S1

Bond	**ρ(e·bohr^{-3})**	**∇^2ρ(e·bohr^{-5})**	**ε**	**H(hartreee·bohr^{-3})**
		ATS1		
S2 – O1	.251931	.338748	.264694	-.318355
Ring	.026003	.135119	-1.480919	.004577

O2 – S2	.243112	.208396	.278226	-.306651
O5 – O1	.042401	.161478	.069305	.002323
H4 – O3	.184099	-.496828	.004129	-.211022
H4 - O5	.158062	-.255368	.010472	-.146792
H6 – O5	.364118	-2.674983	.016276	-.738209
		ATS2		
S2 – O1	.268939	.612777	.185008	-.338231
Ring	.014653	.068453	-1.572842	.002603
O3 – S2	.222584	.025509	.303495	-.274202
H4 – O3	.174452	-.294685	.035892	-.166389
H6 – O1	.019790	.073456	.259770	.002559
O5 – H4	.193553	-.488304	.025250	-.216153
H6 – O5	.352028	-2.612469	.021238	-.718110

The reaction of $^3SO_2$ with water dimer.

Figure S3 shows a schematic potential energy surface of the reaction of triplet sulfur dioxide with water dimer. Table S3 contains the corresponding relative energies and Figure S4 shows the most relevant geometrical parameters. As we discussed for the reaction with a single water molecule, in the study of the reaction of $^3SO_2$ with $(H_2O)_2$ we have found additional reaction paths than those described in the main text and that are commented in this section. Thus, along with BTS1 (*pcet*) and BTS2 (*hat*), we have found BTS4 (*pcet*) and BTS5 (*hat*), which display very similar configurations. They differentiate from each other in the relative orientation of the dangling hydrogen atom of the water moiety and, consequently, they have the same kind of interactions and almost the same relative energies (BTS1 and BTS4 differ in 0.22 kcal·mol^{-1} and BTS2 and BTS5 differ in 0.19 kcal·mol^{-1}).

Table S4. Relative energies, energies plus ZPE (Zero Point Energy), (in kcal·mol^{-1}), enthalpies, and free energies (in kcal·mol^{-1}, at 298 K) calculated for the different stationary points of the $^3SO_2 + (H_2O)_2$ reaction investigated in this work.[a] The values of the T1d of the CCSD expansion are also given.

State	ΔE	Δ (E+ZPE)	ΔH	ΔG	T1d
SO_2 ($^3B_1$) + $(H_2O)_2$	0.00	0.00	0.00	0.00	
HOSO + H_2O··OH	4.80	3.72	3.74	2.94	
HOSO + H_2O + OH	10.55	7.42	8.13	1.07	
BCR1	-3.95	-1.56	-2.43	9.30	0.034
BTS1	1.18	0.62	-0.78	12.10	0.028
BTS4	1.47	0.84	-0.51	12.24	0.027
BCR2	0.15	1.49	1.38	9.45	0.028
BTS3	8.71	7.58	6.75	16.86	0.034
BCR3	-4.04	-1.54	-2.53	9.37	0.033
BTS2	2.96	1.60	0.14	12.87	0.032
BTS5	3.20	1.79	0.35	13.02	0.032
BCR4	-4.93	-3.73	-3.79	5.47	0.037
BTS6	16.62	13.98	13.62	23.09	0.044
BCP1	-3.17	-1.84	-2.82	8.69	0.13

a) Energies computed at CCSD(T)/CBS//B3LYP/aug-cc-pVTZ level of theory. The ZPE, enthalpic and entropic corrections correspond to B3LYP/aug-cc-pVTZ values.

In addition to these reaction paths, we have found two additional elementary reactions via BTS3 involving a *pcet* mechanism and via BTS6 with a *hat* mechanism. In BTS3, the interaction of the *pcet* structure with the solvating water molecule takes place in a very different way as occurs in BTS1 and BTS4 (see main text). Figure S3 shows that in this case, there is a single hydrogen bond interaction between the oxygen of the water molecule taking place in the reaction and one hydrogen atom of the solvating H_2O molecule. This hydrogen bond originates a charge transfer from the reactive moiety to the solvating water molecule of 0.007 a.u., which hinders the electron transfer process of the reaction and consequently produces a destabilization effect. Our results predict BTS3 to lie 7.58 kcal·mol^{-1} above the energy of the separate reactants, compared with the 0.62

or 0.84 kcal·mol^{-1} of BTS1 and BTS4. Comparing the relative energy of BTS3 with that of ATS1 (see Figures 1 and S1 and Table S2), this kind of interaction with the solvating water produces a destabilization of 1.2 kcal·mol^{-1}. The BTS6 transition state is a conformer of BTS2 involving a *hat* mechanism, in which there is a single hydrogen bond interaction that corresponds to the water dimer moiety. Consequently, there is not a cooperative hydrogen-bond network, as described in the main text for BTS2, and our calculations predict BTS6 to lie 13.98 kcal·mol^{-1} above the energy of the separate reactants, that is, more than 11 kcal·mol^{-1} above the energy of BTS2 and BTS5.

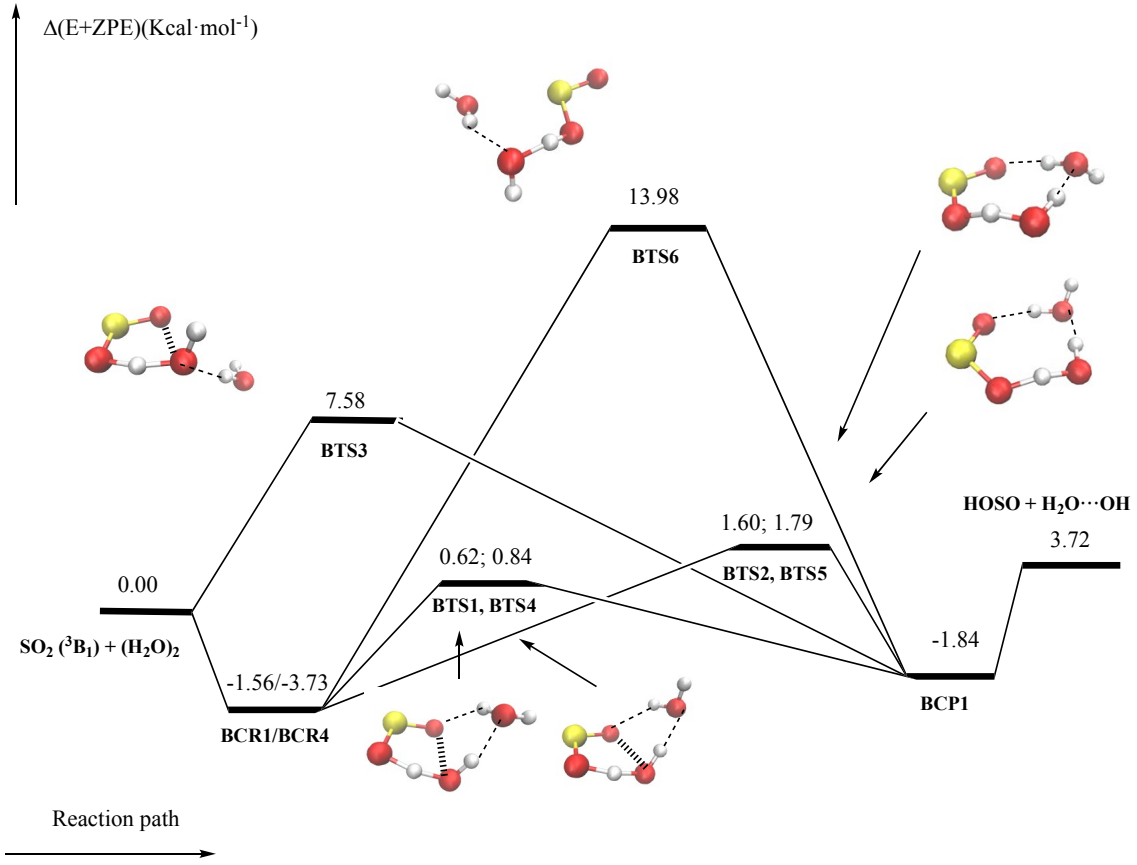

Figure S3. Schematic potential energy surface (CCSDT/CBS//B3LYP/aug-cc-pVTZ) for the $^3SO_2 + (H_2O)_2$ reaction. Energies (kcal·mol^{-1}) include zero-point energies.

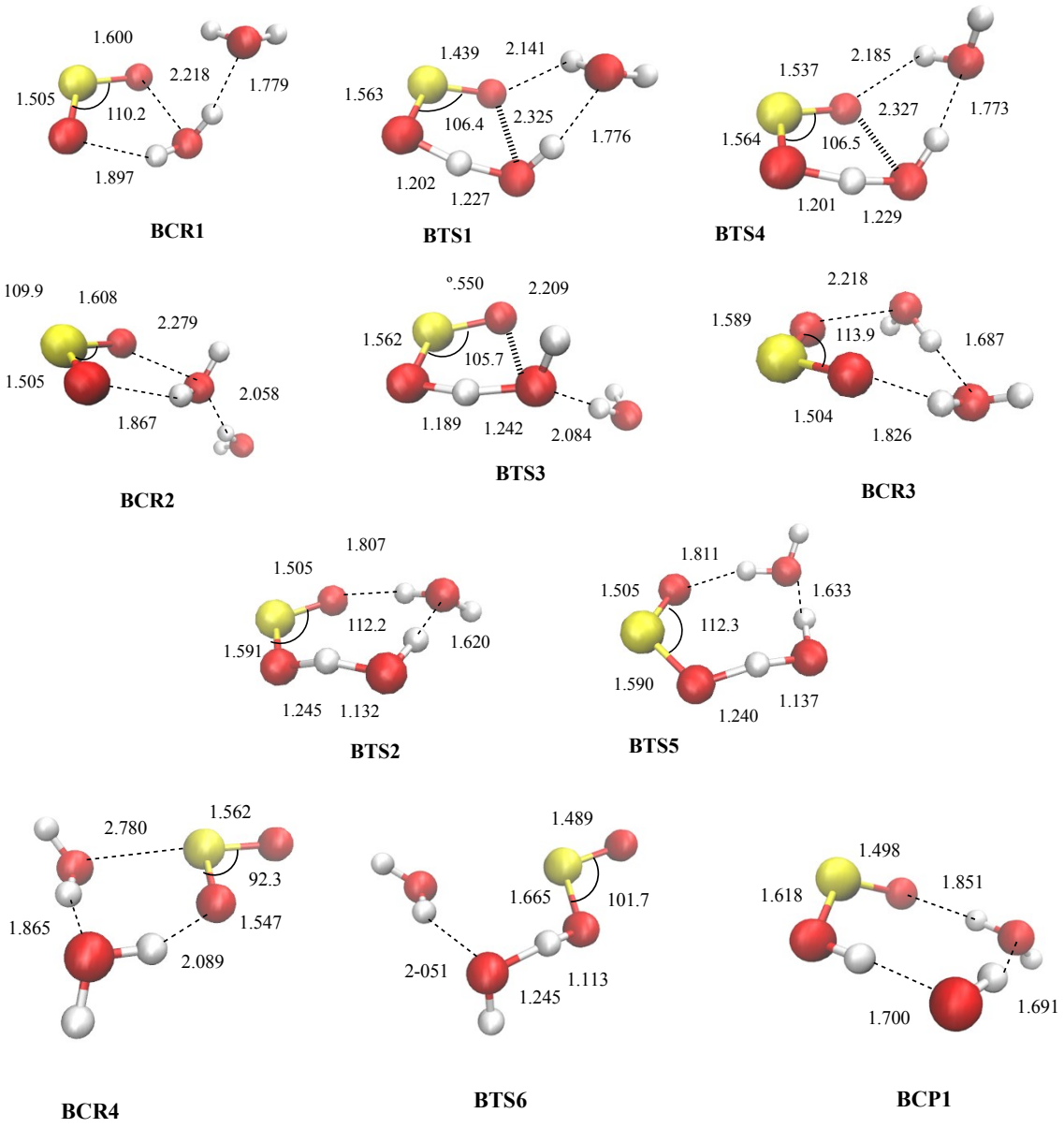

Figure S4. Main geometrical parameters of the stationary points of the $^3SO_2 + (H_2O)_2$ reaction. Interatomic distances are in Å and OSO angle in degrees.

Effect of further water molecules in the reaction.

In order to analyze the effect of additional solvating molecules on these *pcet* and *hat* reaction mechanisms in the $^3SO_2 + H_2O$ reaction, we have considered the reaction with water trimer and water tetramer. For both water clusters we have taken as the reactants the most stable conformations,[32] and the results are contained in Tables S4 and S5 and in Figures S5, S6, and S7.

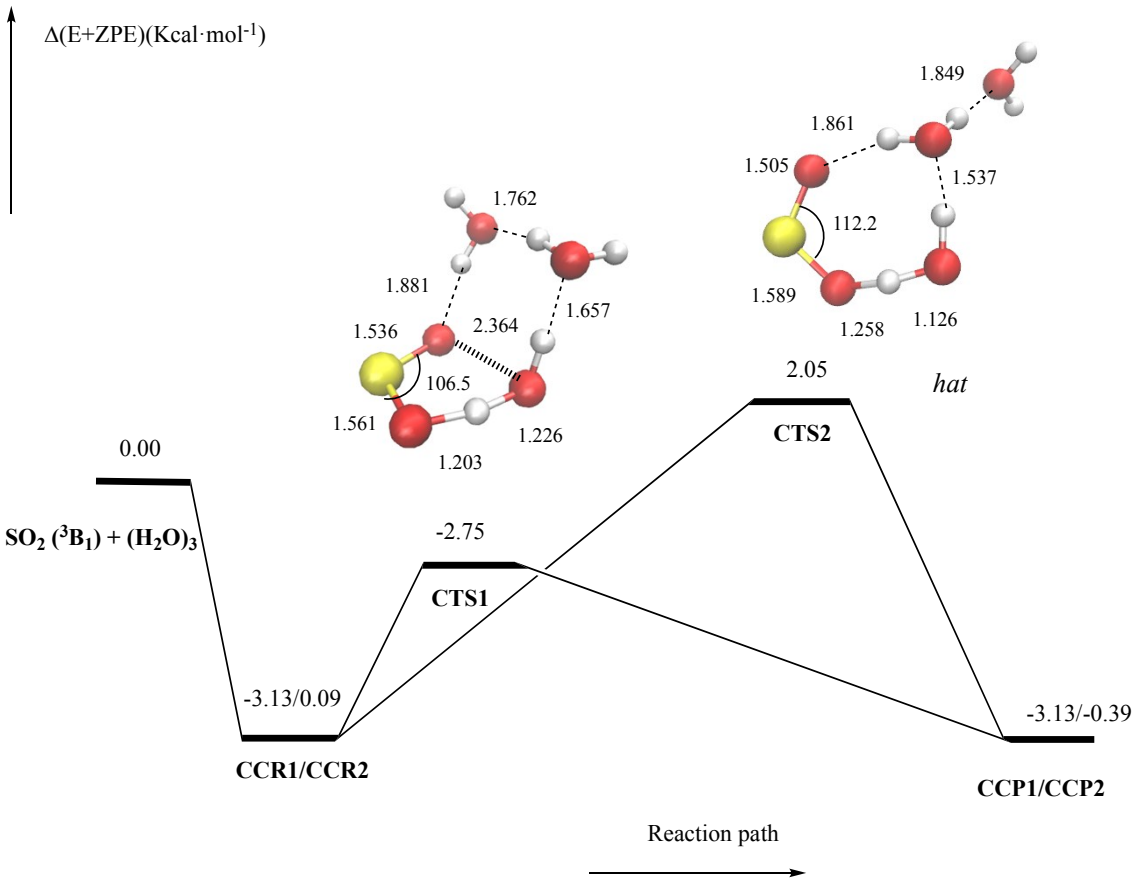

Figure S5. Schematic potential energy surface (CCSDT/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ) for the $^3SO_2 + (H_2O)_3$ reaction. Energies (kcal·mol^{-1}) include zero-point energies.

Table S5. Relative energies, energies plus ZPE (Zero Point Energy), (in kcal·mol^{-1}), enthalpies, and free energies (in kcal·mol^{-1}, at 298 K) calculated for the different stationary points of the $^3SO_2 + (H_2O)_3$ reaction investigated in this work.[a] The values of the T1d of the CCSD expansion are also given.

	ΔE	**Δ (E+ZPE)**	**ΔH**	**ΔG**	**T1d**
SO_2 ($^3B_1$) + $(H_2O)_3$	0.00	0.00	0.00	0.00	
CCR1	-4.81	-3.13	-3.59	7.38	0.0340
CTS1	-1.22	-2.75	-3.59	8.17	0.0230
CCP1	-3.48	-3.13	-3.39	6.36	0.0170
CCR2	-0.53	0.09	0.52	7.82	0.0310

CTS2	5.28	2.05	1.91	10.88	0.0270
CCP2	-0.08	-0.39	-0.12	7.76	0.0170
HOSO + $2H_2O$ + OH	20.18	13.71	15.77	-1.77	

a) Energies computed at CCSD(T)/CBS//B3LYP/aug-cc-pVTZ level of theory. The ZPE, enthalpic and entropic corrections correspond to B3LYP/aug-cc-pVTZ values.

For the reaction with water trimer, we have found a reaction path involving a *pcet* mechanism (via CTS1) and a reaction path with a *hat* mechanism (via CTS2). Our results predict CTS1 to lie 2.75 kcal·mol^{-1} below the energy of the separate reactants (see Table S4 and Figure S5). That is, there is an additional stabilization of about 3.4 kcal·mol^{-1} with respect to the reaction with the water dimer. Figures S5 and S6 show that the two solvating molecules have the same kind of interactions as in BTS1, but in CTS1 the geometry of the transition state is less strained,, which results in a more effective interaction with the solvent. Our calculations predict CTS2 to be slightly less stable.

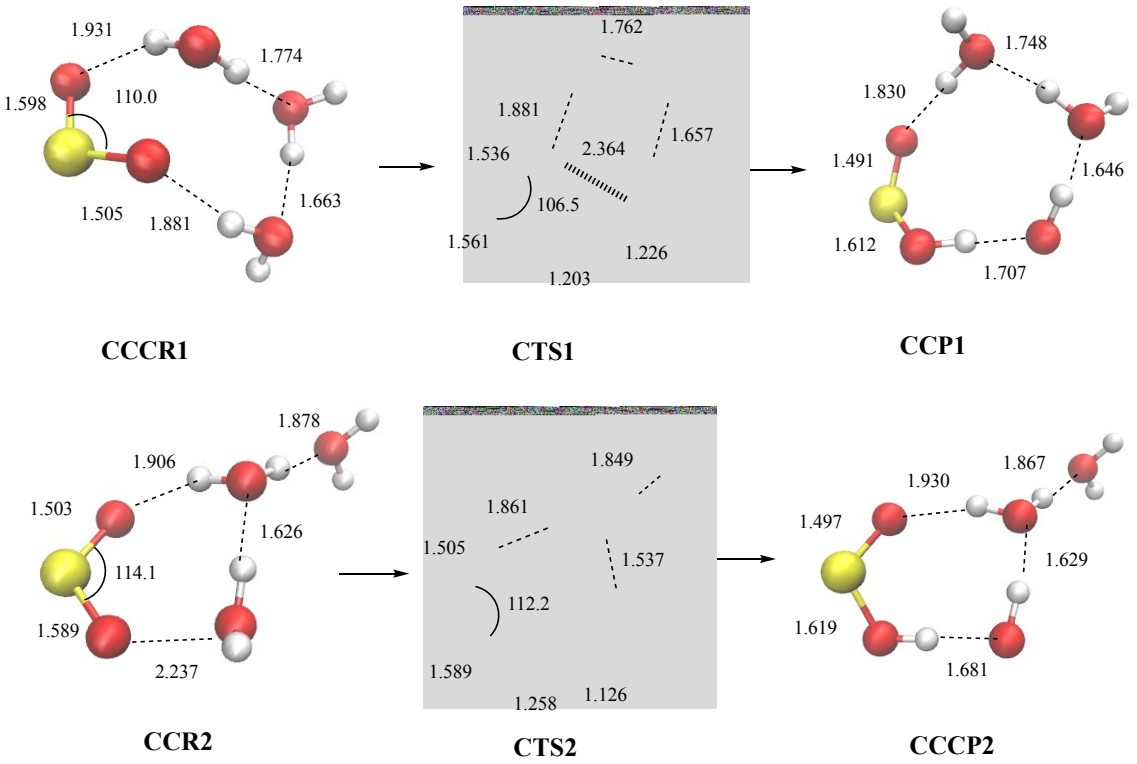

Figure S6. Main geometrical parameters of the stationary points of the $^3SO_2$ + $(H_2O)_3$ reaction. Interatomic distances are in Å and OSO angle in degrees.

Table S5 and Figure S7 show that for the reaction with water tetramer, two elementary reactions via a *pcet* mechanism (DTS1 and DTS3) and one elementary reaction going through a *hat* mechanism (DTS2) take place. Figure S7 shows that DTS1 has the same kind of interaction as in BTS1, BTS4, and CTS1, and our calculations predict it to lie below the energy of the separate reactants by 1.14 kcal·mol^{-1}. DTS3 is less stable than DTS1 by 3 kcal·mol^{-1}, because the two hydrogen bonds formed between the solvating waters and the reactant water display a competitive donor-acceptor character.

Table S6. Relative energies, energies plus ZPE (Zero Point Energy), (in kcal·mol^{-1}), enthalpies, and free energies (in kcal·mol^{-1}, at 298 K) calculated for the different stationary points of the $^3SO_2 + (H_2O)_4$ reaction investigated in this work.[a] The values of the T1d of the CCSD expansion are also given.

	ΔE	**Δ (E+ZPE)**	**ΔH**	**ΔG**	**T1d**
SO_2 ($^3B_1$) + $(H_2O)_4$	0.00	0.00	0.00	0.00	
DCR1	-2.37	-1.35	-1.32	8.14	0.0310
DTS1	1.05	-1.14	-1.51	8.84	0.0210
DCP1	0.46	-0.03	0.30	8.19	0.0160
DCR2	-1.92	-1.15	-0.96	8.25	0.0260
DTS2	6.92	3.65	3.34	13.74	0.0320
DCP2	-5.68	-5.91	-5.80	3.46	0.0160
DCR3	-2.39	-1.37	-1.35	8.05	0.0180
DTS3	3.82	1.88	1.56	11.78	0.0260
DCP3	-2.36	-2.41	-2.14	6.35	0.0320
HOSO + $3H_2O$ + OH	32.30	22.97	26.05	-1.29	

a) Energies computed at CCSD(T)/CBS//B3LYP/aug-cc-pVTZ level of theory. The ZPE, enthalpic and entropic corrections correspond to B3LYP/aug-cc-pVTZ values.

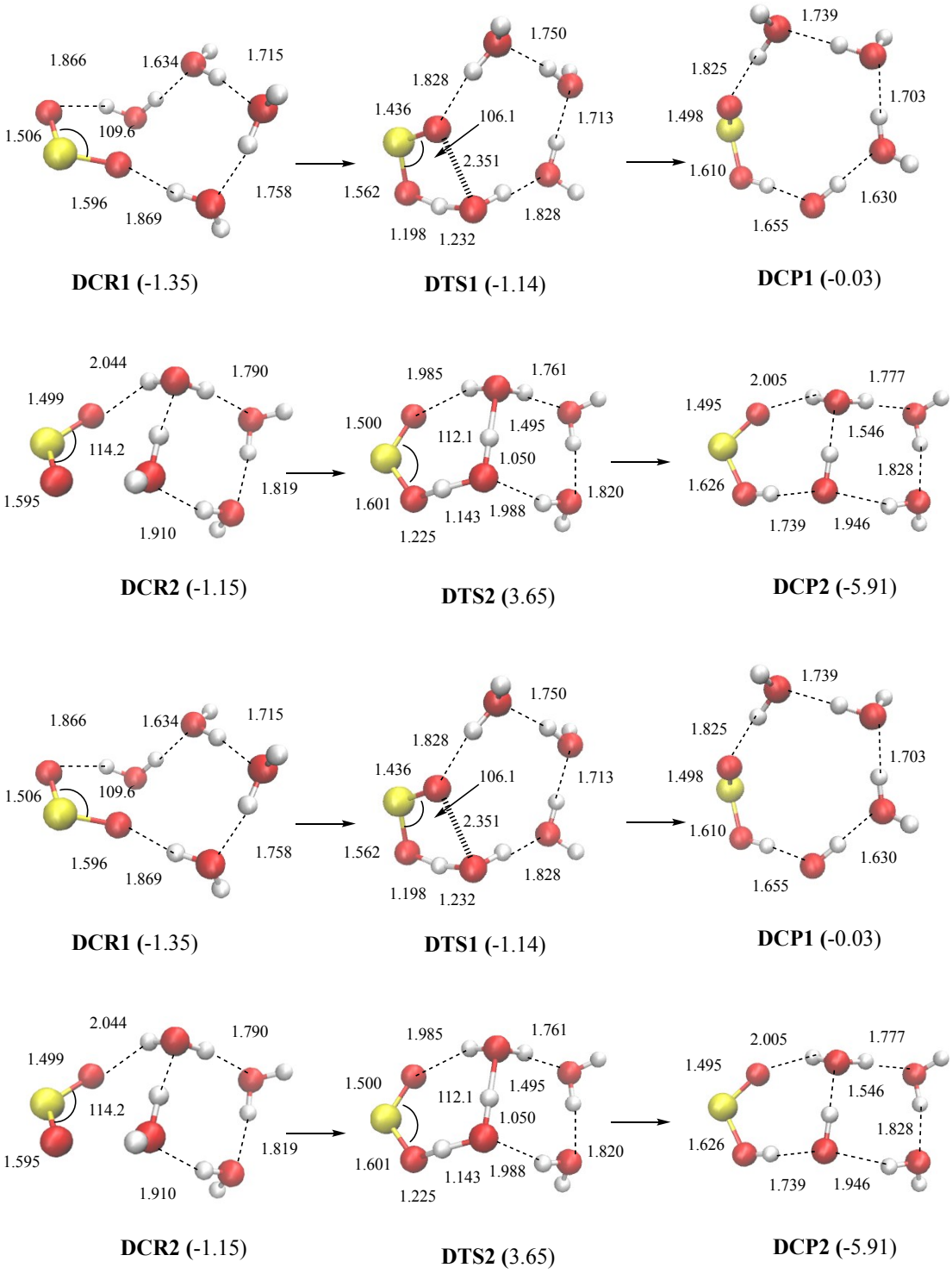

Figure S7. Main geometrical parameters of the stationary points of the $^3SO_2 + (H_2O)_4$ reaction. Interatomic distances are in Å and OSO angle in degrees. Values in parenthesis correspond to relative energies including zero point energies (in Kcal·mol^{-1}) relative to reactants (see Table S5)

Table S7. Cartesian coordinates of the stationary points investigated in this work optimized at B3LYP/aug-cc-pVTZ level of theory.

$^3SO_2 + H_2O$

ACR1

O	-.7389170000	.0166900000	-.9539150000
S	-.7742540000	.0187060000	.6486400000
O	.6305070000	.0301820000	1.1941430000
O	1.4608760000	-.1301900000	-1.3910060000
H	1.5591340000	-.0395900000	-.4185270000
H	1.3963060000	.7686010000	-1.7384180000

ACR2

O	1.9374250000	.2127250000	.0512030000
S	.5733650000	-.4107370000	-.0304710000
O	-.3498010000	.9192850000	.0640260000
O	-2.4264580000	-.3095590000	-.0989050000
H	-2.6006330000	.2971530000	-.8280420000
H	-2.6441750000	.1872500000	.6985150000

ACR3

O	.0600570000	-.0123250000	-.0358530000
O	.1250100000	-.2377830000	2.7985650000
S	1.6033420000	.0934770000	2.4143840000
O	2.0946920000	.0271130000	3.8736590000
H	-.4361510000	.7994220000	-.1844930000
H	-.6001490000	-.6663580000	.2178980000

ACR4

S	.3075910000	-.5634600000	.1422210000
O	-.3187550000	.2741930000	1.2920510000
O	1.5086070000	.4006220000	-.0242750000
H	3.2612870000	-.2229880000	1.0634560000
O	3.8185100000	-.9252310000	1.4193810000
H	4.4810410000	-.4799380000	1.9549760000

ACR5

O	.0026680000	-.4391060000	.0555780000
S	1.0421330000	-.0942910000	1.1073190000
O	.7195570000	.5588000000	2.4292350000
O	3.8530880000	-.3970230000	1.3753190000
H	3.9972740000	.1454030000	2.1588260000
H	4.0796460000	-1.2947140000	1.6412870000

TS-ACR2-ACR3

O	.0127860000	.0019300000	-.0004920000
O	.1073460000	-.0015600000	2.6556930000
S	1.6756310000	-.0005310000	2.4190850000
O	2.0450300000	-.0025130000	3.8954410000
H	-.5627070000	.7664260000	.1124630000
H	-.5632850000	-.7622050000	.1119690000

TS-ACR3-ACR4

S	-.0262440000	.0565680000	.0209960000
O	.0170790000	-.0005260000	1.5731690000

O	1.5161160000	-.0083680000	-.1135740000
H	2.1863190000	-1.8062430000	-1.0721220000
O	1.9554790000	-2.4721160000	-1.7306940000
H	2.7902110000	-2.7505150000	-2.1181360000

TS-ACR1-ACR4

S	.2095180000	.4402000000	.1324250000
O	-.0719300000	-.4634290000	1.4339190000
O	1.2847330000	-.3973180000	-.5219460000
H	2.0866500000	-1.9279690000	.6823150000
O	2.2734650000	-2.4993680000	1.4383760000
H	1.7512120000	-3.2932660000	1.2892350000

TS-ACR3-ACR5

S	-.0371700000	-.0065480000	.0327070000
O	.0724820000	.0228830000	1.6422950000
O	1.3345460000	-.0071700000	-.5705280000
H	.3027610000	-.0378560000	-2.7692890000
O	-.6615110000	-.0225120000	-2.7437830000
H	-.9446660000	-.8311390000	-3.1823920000

ATS1

O	.0007350000	-.0015300000	-.0058620000
S	-.0029040000	.0013370000	1.5384900000
O	1.5016640000	-.0004310000	1.9693200000
O	2.1993080000	-.1420660000	-.3179320000
H	2.0407980000	-.0314340000	.9117650000

H	2.0665740000	.7168380000	-.7484680000

ATS2

O	-.6797980000	.3007660000	-1.1301230000
S	-.9090380000	.2602020000	.3532000000
O	.4006880000	-.3256870000	1.0815840000
H	1.3677790000	-.2259670000	.3784220000
O	1.9373000000	-.4755200000	-.6049220000
H	1.3856700000	-.0827540000	-1.3131680000

ATS3

O	-.2481560000	.0631570000	.0099970000
S	.0000180000	-.0067280000	1.4757950000
O	1.5857740000	-.0035430000	1.8293150000
H	2.2871320000	-.6284830000	1.1427120000
O	2.8957540000	-.8277110000	.1453740000
H	3.4998440000	-.0752060000	.0339830000

ATS4

O	1.9865480000	.2833040000	-.1404290000
S	.7100460000	-.4499850000	.0661380000
O	-.4260160000	.7549000000	.1041000000
O	-2.4517950000	-.2178150000	-.1735050000
H	-1.4321230000	.4234340000	-.3072070000
H	-2.9088040000	.1632470000	.5941850000

ACP1

O	-.8310770000	.0366990000	-.8764210000
S	-.8263220000	.0292020000	.6242740000
O	.7215050000	.0091790000	1.1302880000
O	1.6179070000	-.1170830000	-1.4003490000
H	1.2934030000	.0177880000	.3175560000
H	1.1664840000	.5656130000	-1.9280690000

ACP2

O	.0521850000	.4466860000	-1.2438880000
S	.8836530000	.2713460000	-.0109960000
O	-.1016730000	.0639960000	1.2790800000
O	-2.5261460000	.1115750000	-.1377190000
H	-1.0429050000	.0362150000	.9787880000
H	-1.8953450000	.2588450000	-.8819430000

$^3SO_2 + (H_2O)_2$

CRBTS1

S	-.8861470000	-.1544080000	-1.1351590000
O	-.4909340000	.8927180000	.0079210000
O	.2593900000	-1.0956150000	-1.3968920000
H	1.4997640000	-.3640410000	-.1614120000
O	1.6360440000	.4141640000	.4186180000
H	1.2923160000	.1787250000	1.3116520000
H	-.5043660000	.4962130000	2.2544210000
O	.2154740000	.0512060000	2.7214330000

H	.3590000000	.5446630000	3.5347150000

BTS1

S	.2193060000	-.0492550000	-.1490120000
O	.5320470000	.9721650000	.9588250000
O	1.5199020000	-.8903240000	-.3551060000
H	2.2738750000	-.4050300000	.4455620000
O	2.7582450000	.3736590000	1.2615490000
H	2.3994140000	.2012290000	2.1701000000
H	.6424720000	.6126390000	3.0660360000
O	1.3239340000	.1585030000	3.5827290000
H	1.4866230000	.7037030000	4.3584110000

CPBTS

S	-1.0444410000	-.3310030000	-1.0685910000
O	-1.3477000000	.3504800000	.2309470000
O	.5337870000	-.2272690000	-1.4103480000
H	1.1255990000	-.3518190000	-.6121590000
O	2.1599370000	-.4331230000	.7349250000
H	1.5786240000	-.1514150000	1.5021180000
H	-.4199750000	.4631850000	1.8291880000
O	.2924020000	.3386380000	2.4844730000
H	.2840520000	1.1048140000	3.0646420000

BTS4

S	-.0012680000	.0861100000	-.0229730000
O	-.0071750000	.0113850000	1.5126680000
O	1.4994980000	.0676680000	-.4624270000
H	2.0777850000	.0311330000	.5892260000
O	2.3015210000	.0831630000	1.7964040000

H	2.1032720000	-.7868240000	2.2286850000
H	.3846340000	-1.7271100000	2.7772600000
O	1.2358280000	-2.0942620000	3.0550840000
H	1.2233050000	-3.0262910000	2.8180560000

CRBTS3

S	-1.8123650000	-.2888540000	-.7680420000
O	-1.2360090000	.1691110000	.6614660000
O	-.7639780000	-1.0665420000	-1.5180650000
H	.6434310000	-.9567970000	-.2968980000
O	.9181440000	-.5667700000	.5597340000
H	.7204230000	-1.2237290000	1.2390640000
H	2.5110890000	.6410830000	1.0488200000
O	3.3083810000	1.0371170000	1.4230030000
H	3.1054450000	1.9715450000	1.5201010000

BTS3

S	.2231380000	.6764920000	.3302200000
O	.9780620000	1.0067440000	1.6428820000
O	1.0314310000	-.4787150000	-.3422790000
H	1.9254200000	-.6108990000	.4299020000
O	2.6751760000	-.3852290000	1.3946320000
H	2.3364190000	-.8159810000	2.1949090000
H	4.0288190000	1.1104040000	1.9175940000
O	4.7120200000	1.6955010000	2.2692110000
H	4.2578850000	2.5200480000	2.4634580000

CRBTS2

O	-.5913520000	.5276790000	-1.1559750000
S	-1.4301680000	.0263080000	-.0121800000
O	-.5960390000	-.7049240000	1.1261120000
H	1.5849140000	-.8262440000	1.7028490000
O	1.5681520000	-1.0212010000	.7576290000
H	1.8147130000	-.1778070000	.2875380000
H	2.6239830000	1.2118580000	-1.3687780000
O	2.0104510000	1.2248020000	-.6284180000
H	1.1113250000	1.1703660000	-1.0078320000

BTS2

O	.9975290000	1.5340600000	-.3889620000
S	.1754400000	.7388310000	.5893090000
O	1.0485940000	-.3347720000	1.3740050000
H	2.2254340000	-.0855530000	1.6937810000
O	3.3496200000	-.1142520000	1.5578980000
H	3.6006310000	.6470250000	.9371170000
H	4.2319210000	1.7608960000	-.9273010000
O	3.7069790000	1.8628850000	-.1280120000
H	2.7679540000	1.8966470000	-.4036890000

BTS5

S	.0333540000	.1674000000	-.0668280000
O	.0071090000	-.0650590000	1.4198290000
O	1.4830760000	-.0472640000	-.6856700000
H	2.2442810000	-.9050630000	-.2147460000

O	3.1064650000	-1.2719200000	.4288180000
H	2.7464010000	-1.4083680000	1.3645880000
O	1.9744900000	-1.3845390000	2.8029680000
H	1.1580090000	-.9223960000	2.5250520000
H	1.7070530000	-2.1767550000	3.2775260000

CRBTS6

O	-.4530540000	.0466920000	-2.3619710000
S	-.7663770000	-.1507580000	-.8440820000
O	.7245230000	-.0180570000	-.4535530000
O	1.6596870000	.6067070000	2.2267320000
H	1.7365660000	.6091380000	1.2625340000
H	2.3877270000	.0649640000	2.5461220000
H	-.0786690000	-.0694980000	2.2168920000
O	-.9522940000	-.3868470000	1.9195980000
H	-1.5991800000	.1646590000	2.3692200000

BTS6

O	-.0300110000	.1409950000	.0281740000
S	-.0549350000	-.0684630000	1.5022070000
O	1.5591010000	.0645380000	1.8897430000
O	1.9063220000	.5684140000	4.0851030000
H	1.7648930000	.5913560000	2.8478880000
H	2.6032420000	-.0857600000	4.2560710000
H	.0676660000	.0264200000	4.8143450000
O	-.7989910000	-.3928180000	4.7291860000
H	-1.3708860000	.0528560000	5.3601640000

$^3SO_2 + (H_2O)_3$

CRCTS1

O	-2.0648660000	-1.5074590000	-1.0364580000
H	-2.2254900000	-1.4220020000	-.0712060000
O	-1.9446830000	-1.1021980000	1.6509810000
H	-1.0481870000	-.7337130000	1.5645620000
O	.5566540000	-1.0803190000	-1.2150980000
H	-.4348900000	-1.2153620000	-1.1867340000
H	-2.3757340000	-2.3799400000	-1.2942690000
H	-2.4550280000	-.4603450000	2.1528120000
H	.7260640000	-.1778430000	-1.5609540000
O	1.2012750000	1.5580250000	-1.0120930000
S	1.1160380000	1.3303230000	.4733530000
O	.6158120000	-.1580370000	.7714060000

CTS1

O	.2997660000	-.1748110000	.1351130000
H	.1498200000	-.1090940000	1.1049970000
O	.3833690000	.1501880000	2.8322820000
H	1.2651580000	.5614210000	2.7776430000
O	2.9090520000	.2784680000	-.1552730000
H	1.9169630000	.1278000000	-.0579930000
H	-.0038760000	-1.0472990000	-.1313700000
H	-.1632150000	.7454750000	3.3526530000
H	3.1791140000	1.4716570000	-.2355800000

O	3.4801000000	2.5985040000	.0580260000
S	3.3479430000	2.6068210000	1.6138450000
O	2.8608170000	1.2068250000	2.0180200000

CPCTS1

O	-1.9924350000	-1.8398110000	-1.0076240000
H	-2.0364080000	-1.5268520000	-.0728280000
O	-1.8824840000	-.8772860000	1.5121650000
H	-1.0178060000	-.4327440000	1.5941100000
O	.1992550000	-.8738710000	-2.1272770000
H	-.6494340000	-1.2691940000	-1.7491770000
H	-2.1765110000	-2.7829270000	-.9988680000
H	-2.5360400000	-.2532870000	1.8398440000
H	.6921140000	.4609400000	-1.2459150000
O	.9910330000	1.2894270000	-.7644620000
S	1.6457670000	.9982700000	.6811040000
O	.6564530000	.3180220000	1.5774480000

CRCTS2

O	-1.2146840000	-.4767030000	-1.1871920000
H	-1.0160420000	-.7911250000	-.2884800000
H	-.0213090000	.6264110000	-1.2358220000
O	.7535220000	1.2668440000	-1.1801400000
H	.3803840000	2.1558310000	-1.2217560000
O	.7121880000	1.8147150000	.9645270000
S	.3276300000	.6705230000	1.9977200000
O	-.0639130000	-.6306650000	1.3547960000

H	-1.1351730000	-1.2420470000	-1.7816240000
O	-.9739730000	-2.6722790000	-2.9875880000
H	-1.6324580000	-2.7930770000	-3.6785930000
H	-.1219590000	-2.8448300000	-3.4001870000

CTS2

O	.6513150000	-.5246660000	.1977180000
H	.7772350000	-.7677690000	1.1341940000
H	1.6788030000	.6111820000	.0667460000
O	2.4116800000	1.3349930000	.1289620000
H	2.5887050000	1.5360370000	1.2221460000
O	3.0916050000	1.3228020000	2.3558250000
S	2.2828740000	.5152270000	3.4592240000
O	1.4461370000	-.5838800000	2.8613230000
H	.7751650000	-1.3290820000	-.3369540000
O	.9817130000	-2.8111230000	-1.4230800000
H	.2853590000	-3.0378870000	-2.0471730000
H	1.8124380000	-2.9747210000	-1.8802830000

CPCTS2

O	-1.0368630000	-.5378280000	-1.3452870000
H	-.8805180000	-.7825390000	-.4180910000
H	-.0963040000	.7767720000	-1.5483100000
O	.5306730000	1.5667640000	-1.4696020000
H	.9571840000	1.5660160000	.1566180000
O	1.2632250000	1.5197260000	1.1119040000
S	.2374360000	.7243750000	2.0792700000

O	-.2899780000	-.4996250000	1.3970550000
H	-.9843900000	-1.3465480000	-1.8825000000
O	-.9625560000	-2.8434030000	-2.9975810000
H	-1.7593430000	-3.0134100000	-3.5097440000
H	-.2258020000	-2.9905570000	-3.5988040000

$^3SO_2 + (H_2O)_4$

CRDTS1

O	1.5894870000	-.3818030000	-.8235690000
H	1.6571870000	-.2411590000	.1698450000
O	1.8820140000	-.0613020000	1.7779310000
H	2.7142460000	-.3989460000	2.1203990000
H	1.1705560000	-.4426740000	2.3478610000
O	-.1186510000	-1.1837260000	3.2029360000
H	-.7723570000	-1.4653740000	2.5250060000
H	-.6046550000	-.6598090000	3.8456340000
H	1.5945400000	.5066630000	-1.2428880000
O	.4983640000	1.8380150000	-1.9555250000
S	-.8235900000	1.1940560000	-1.6317740000
O	-.5747800000	-.1914910000	-.8790210000
O	-1.7772520000	-1.8031930000	1.1223600000
H	-1.8672350000	-2.7044150000	.7998590000
H	-1.4132920000	-1.2870350000	.3816190000

DTS1

O	-.0201680000	-.0583740000	-.0081180000

H	-.0209190000	-.0251420000	1.0025240000
O	.1516900000	.0466020000	2.6267320000
H	.9579180000	-.3452600000	2.9737680000
H	-.5898720000	-.3305420000	3.1607660000
O	-1.8946150000	-1.0472840000	4.0088570000
H	-2.5714970000	-1.3293110000	3.3527010000
H	-2.3575690000	-.5143140000	4.6609940000
H	-.4685830000	.9893980000	-.4767930000
O	-1.2203470000	1.8109290000	-.9181590000
S	-2.6254190000	1.1775220000	-.6641240000
O	-2.3681990000	-.1674700000	.0320210000
O	-3.6417280000	-1.6737580000	2.0118000000
H	-3.7549050000	-2.5816050000	1.7168210000
H	-3.2725160000	-1.1854830000	1.2520420000

CPDTS1

O	2.4660600000	.3663930000	-.5722000000
H	2.3330300000	.1055500000	.3939630000
O	2.2128850000	-.3099680000	1.9655930000
H	2.9095860000	-.8694210000	2.3190310000
H	1.3658630000	-.6261860000	2.3654350000
O	-.0860810000	-1.1989900000	3.0465030000
H	-.7962550000	-1.3988810000	2.3947540000
H	-.4962130000	-.6692280000	3.7354090000
H	1.1984080000	.8985030000	-1.4937980000
O	.5117150000	1.2654650000	-2.1290890000
S	-1.0047890000	1.0833570000	-1.6184740000

O	-1.2197060000	-.3229210000	-1.1483150000
O	-2.0115500000	-1.6593830000	1.1782650000
H	-2.2451380000	-2.5593190000	.9345040000
H	-1.7885660000	-1.2043940000	.3450540000

CRDTS2

O	-1.6347640000	-1.0978850000	.0708010000
H	-1.7083760000	-1.2577160000	1.0372960000
O	-1.3698320000	-1.5383990000	2.7722980000
H	-.3919520000	-1.5067070000	2.8217000000
O	1.3901810000	-1.3585320000	2.4906930000
H	1.4454970000	-1.2500760000	1.5250290000
O	.9228570000	-1.1212410000	-.3073020000
H	-.0929750000	-1.1515110000	-.2423200000
H	-1.7824450000	-.1508240000	-.0678820000
H	-1.6408220000	-2.3444850000	3.2195410000
H	1.8671720000	-.6144230000	2.8691990000
H	1.1885330000	-1.6597600000	-1.0613340000
O	1.2871770000	.5425760000	-1.7745040000
S	.2405860000	1.7454410000	-1.7051760000
O	-.8461770000	1.5570290000	-.6897880000

DTS2

O	.1338570000	.0108050000	.0417380000
H	.0494980000	-.0380500000	1.0218120000
O	.3641100000	-.1876760000	2.7476050000
H	1.3385980000	-.2713230000	2.7938410000

O	3.1157020000	-.3746850000	2.4160360000
H	3.1917280000	-.2847680000	1.4518880000
O	2.6150700000	-.0883280000	-.4406800000
H	1.5760150000	-.1099740000	-.2908530000
H	-.0588430000	.9236620000	-.2266270000
H	.0012380000	-.9210430000	3.2516700000
H	3.7476370000	.2440050000	2.7934810000
H	2.8718300000	.8170010000	-1.0899100000
O	3.0882440000	2.0095690000	-1.2707770000
S	1.8894760000	2.9581780000	-1.7469930000
O	.5835310000	2.5781810000	-1.1152870000

CPDTS2

O	-1.4430510000	-1.0681470000	.1953980000
H	-1.5974850000	-1.1136890000	1.1652510000
O	-1.3668350000	-1.3657630000	2.9094760000
H	-.4204530000	-1.6083380000	2.9683190000
O	1.3358340000	-1.9789030000	2.6223610000
H	1.4837840000	-1.7868410000	1.6799750000
O	1.0979570000	-1.0962900000	-.0978800000
H	.0729620000	-1.2042240000	-.0515060000
H	-1.6590440000	-.1737380000	-.1111920000
H	-1.8545510000	-2.0618580000	3.3580920000
H	2.0583810000	-1.5608100000	3.0993250000
H	1.2855640000	.3020230000	-1.1149990000
O	1.3642660000	1.1723580000	-1.5912110000
S	-.0569200000	1.7011520000	-2.1794170000

O	-1.1584710000	1.4303350000	-1.2057060000

CRDTS3

O	-2.0968110000	1.4585830000	.0407430000
H	-2.0368290000	1.3695160000	1.0230610000
O	-1.7688310000	1.2424040000	2.7124240000
H	-.8156730000	1.0311180000	2.8268190000
O	.8889800000	.6090220000	2.7319190000
H	1.0692000000	.3697770000	1.8056520000
O	.1796890000	1.3607870000	-1.2854310000
H	-.6766000000	1.3566860000	-.7579630000
H	-2.6102980000	2.2533330000	-.1284430000
H	-2.2546520000	.5786000000	3.2094740000
H	1.5585140000	1.2547230000	2.9749880000
H	.1256730000	.6233770000	-1.9322600000
O	.6479530000	-1.1428390000	-2.2438950000
S	1.3022220000	-1.3891230000	-.9104030000
O	1.1792150000	-.0812350000	-.0036030000

DTS3

O	.0333810000	.0412270000	-.0081550000
H	.0172540000	-.0042630000	.9777000000
O	.3527080000	-.0885470000	2.6844510000
H	1.3334000000	-.1347450000	2.7046280000
O	3.0839510000	-.2250340000	2.3579630000
H	3.1341130000	-.3515900000	1.3944670000
O	2.6238960000	-.3087440000	-.5107470000

H	1.6293440000	-.2087120000	-.4086020000
H	-.4062690000	.8599390000	-.2531640000
H	.0396300000	-.8692260000	3.1499520000
H	3.6680930000	.5110670000	2.5602730000
H	2.9069270000	-.9025540000	-1.5754710000
O	3.1399920000	-1.7772840000	-2.3327200000
S	2.8516510000	-3.0360920000	-1.4435950000
O	2.4196740000	-2.4975560000	-.0681080000

CPDTS3

O	-2.1527570000	1.3069360000	.1201820000
H	-2.1650570000	1.3284840000	1.1060900000
O	-1.8120240000	1.3446360000	2.8175980000
H	-.8321980000	1.2816940000	2.8259490000
O	.9025000000	1.1253040000	2.4343400000
H	.9302450000	1.0358900000	1.4630830000
O	.4599830000	1.0223640000	-.3923520000
H	-.5386630000	1.0653340000	-.2935750000
H	-2.6388850000	2.0795330000	-.1800100000
H	-2.1314860000	.5997220000	3.3344850000
H	1.5558400000	1.7915560000	2.6640080000
H	.9898190000	.2947000000	-1.8453880000
O	1.2226930000	-.4602030000	-2.4567660000
S	.8131150000	-1.8234170000	-1.6675490000
O	.2439190000	-1.4358800000	-.3337580000

Table S8. Cartesian coordinates of the stationary points investigated in this work optimized at CCSD(T)/6-311+G(2df,2p) level of theory.

SO_2 ($^3B_1$)

S	0.000000	0.000000	0.328190
O	0.000000	1.348764	-0.328190
O	0.000000	-1.348764	-0.328190

H_2O

H	0.756886	-0.470922	0.000000
O	-0.000000	0.117738	0.000000
H	-0.756886	-0.470922	0.000000

ATS1

O	0.061468	-0.003025	-0.022862
S	0.019520	0.013283	1.518200
O	1.501895	0.007046	1.978517
O	2.166279	-0.152597	-0.302817
H	2.035861	-0.039124	0.881729
H	2.021153	0.717132	-0.705453

ATS2

O	-0.620385	0.323853	-1.154054
S	-0.882978	0.242028	0.314434
O	0.409137	-0.365183	1.055911
H	1.447305	-0.163806	0.375854
O	1.891020	-0.479005	-0.586728
H	1.258503	-0.106847	-1.240424

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