We thank the reviewer for the many constructive comments which we have addressed as follows:

• We fully agree that the known multireference character of the systems is a potential problem. As requested by both reviewers we have calculated CCSD(T)-F12 single point energies with the VDZ-F12 basis set for the reactants and transition states. We have performed these on systems containing up to 2 water molecules. Although distinct discrepancies were found, the results did not lead us to alter any main conclusions. To describe these calculations, the following has been appended to the manuscript:

In Section 2, Computational details:

"The CAM-B3LYP functional is a modification to the well known B3LYP functional, including increasing Hartree-Fock exchange at increasing distances. Of further interest with respect to this study, it has been shown that CAM-B3LYP is superior to B3LYP with respect to evaluating classical activation barriers (Peach et al., 2006; Yanai et al., 2004). We have previously demonstrated excellent agreement between CAM-B3LYP/aug-cc-pVDZ and benchmark UCCSD(T)-F12/VDZ-F12 calculations (Bork et al., 2011b; Adler et al., 2007; Peterson et al., 2008). Also here, we use this method for testing the multireference character and energetics of the systems by single point calculations on CAM-B3LYP ground state structures. These calculations were performed using the MOLPRO 2010.1 package (http://molpro.net/)."

Further, the following subsection has been appended to section 3.1 "Structures and thermodynamics", p. 29657 after line. 4:

"3.1.1 CCSD(T) calculations

Finally, CCSD(T)-F12 calculations on the isolated reactants, reactant complexes, and transition states were performed including up to two water molecules. All T1 and D1 diagnostics as well as energies are reported in the supplement. As expected, we found rather high T1 and D1 diagnostics of ca. 0.031 and 0.16 respectively, clearly indicating partial multireference character of all reactant complexes and transition states.

Considering the energetics, distinct differences between the CAM-B3LYP and CCSD(T) energies were found. In brief, CCSD(T) predicted slightly weaker binding between the reactants in the reactant cluster, signifying a shorter lifetime towards re-evaporation of SO₂. The differences were on the order of $5-10 \text{ kJ mol}^{-1}$ and thus within the expected range of agreement. However, the agreement concerning the height of the electronic energy barrier was significantly poorer. The CCSD(T) barriers were on the order of $4-10 \text{ kJ mol}^{-1}$ compared with the 18-24 kJ mol⁻¹ from CAM-B3LYP.

A better agreement between the CAM-B3LYP and CCSD(T) energies might be obtained by optimising the structures at the CCSD(T) level or increasing the basis sets for either method. However, as shall be accounted for in the following section, these seemingly significant discrepancies will not influence the main conclusions of this study, since it will be argued that the overall reaction is diffusion limited. It should however be stressed that all of the reported energetics are to be considered qualitative rather than quantitative, both due to the mentioned discrepancies as well as the high T1 and D1 diagnostics."

• The reviewer stresses that IRC calculations must be performed to ensure that the transition states in deed connect the desired reactants and products. These calculations have been performed, which is clarified as:

On p. 29.653 l. 19 :

" Due to the O_2-O-SO_2 configuration of the reactant structures, a series of transition states were readily found and are illustrated in Fig. 4. By following the reaction coordinate in both directions it was ensured that the transition states connected the desired reactants and products." "These are shown in Fig. 6 and are denoted "rare" due to the rare structure of the water molecules. Again, by following the reaction coordinate it was ensured that also these transition states connected the desired reactants and products."

• The reviewer requests that the charge analysis is extended to the $SO_3^-O_2(H_2O)_n$ complexes. However, these species are already included in both the text of Section 3.5 and Figure 10 and are in fact the primary complexes of this investigation.

• The reviewer notices that some references to data given in the supplement are missing. We thank the reviewer for pointing out this inaccuracy. In all places where supplementary information is given, this is now explicitly pointed out. We also note that all binding energies, energy barriers and reaction energies will be available from the supplement. As further requested, the values of the rate constants and lifetimes will be given as well. The revised supplement is attched to this reply.

- The typo on on page 29.655, line 17 has been corrected (O_3S-O_2 to $[O_3S-O_2]^-$)
- Concerning the collision rates:

Collision cross section in general, but those involving ions and dipoles in particular, are difficult to asses accurately and it is beyond the scope of this study to investigate this matter. We have therefore used a simple geometric measure of the reactant diameters. We have clarified this point as follows:

On p. 29659 l. 25: "In this case, considering d = 5.5 Å obtained as a simple geometric mean of the reactants, we obtain a rate constant of $1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. It is very plausible that the one order of magnitude difference reflects a net attractive potential between the O_3^- ion and the dipolar SO₂ increasing the collision rates. One ion-dipole collision rate has been described by Su and Bowers (1973) and implemented by Kupiainen et al. (2011). However, these considerations are beyond the scope of this study."

• Finally, as requested, the distances of the forming and breaking bonds are now shown in Figures 4 and 6.

References in this reply:

Adler, T. B., Knizia, G., and Werner, H. J.: A simple and efficient CCSD (T)-F12 approximation, J. Chem. Phys., 127, 221106, doi:10.1063/1.2817618, 2007.

Bork, N., Kurten, T., Enghoff, M. B., Pedersen, J. O. P., Mikkelsen, K. V., and Svensmark, H.: Ab initio studies of $O_2(H_2O)_n$ and $O_3(H_2O)_n$ anionic molecular clusters, $n \leq 12$, Atmos. Chem. Phys., 11, 7133-7142, doi:10.5194/acp-11-7133-2011, 2011b.

Kupiainen, O., Ortega, I. K., Kurtén, T., and Vehkamäki, H.: Amine substitution into sulfuric acid - ammonia clusters, Atmos. Chem. Phys. Discuss., 11, 30853-30875, doi:10.5194/acpd-11-30853-2011, 2011.

Peterson, K. A., Adler, T. B., and Werner, H. J.: Systematically convergent basis sets for explicitly correlated wavefunctions: The atoms H, He, B-Ne, and Al-Ar, J. Chem. Phys., 128, 084102, doi:10.1063/1.2831537, 2008.

Su, T. and Bowers, M. T.: Theory of ion-polar molecule collisions. Comparison with experimental charge transfer reactions of rare gas ions to geometric isomers of diffuorobenzene and dichloroethylene, J. Chem. Phys., 58, 3027, 1973. 30857, 30858.

Structures and reaction rates of the gaseous oxidation of SO_2 by an $O_3^-(H_2O)_{0-5}$ cluster - an ab initio study

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Table SI-1: Entropies and Gibbs free energies of the most important configurations, relative to $O_3^-(H_2O)_n$ and SO₂ at T = 298.15 K. Units are J/mol·K and kJ/mol. See also Fig. 3 in the main article.

\overline{n}	$O_3^-SO_2W_n$		TS_{dense}		TS_{rare}		$SO_3^-O_2W_n$		$SO_3^-W_n + O_2$	
	ΔS	ΔG	ΔS	ΔG	ΔS	ΔG	ΔS	ΔG	ΔS	ΔG
0	-144.0	-86.8	-139.7	-59.3	-139.7	-59.3	-169.7	-241.6	-15.4	-216.7
1	-159.0	-59.9	-157.5	-37.8	-164.2	-31.0	-179.1	-211.5	-26.2	-196.5
2	-152.5	-50.1	-143.9	-33.6	-146.0	-30.0	-167.8	-200.2	-5.3	-194.0
3	-175.0	-42.1	-169.3	-17.6	-105.0	-25.7	-110.9	-192.2	33.3	-191.0
4	-211.0	-40.5	-200.8	-14.2	-112.6	-18.8	-220.1	-183.9	-68.3	-182.6
5	-156.5	-34.2	-146.7	-8.6	-72.1	-7.9	-160.3	-175.3	58.7	-173.7



Figure SI-1: Structures of the most stable $SO_3^-(H_2O)_n$ clusters. Structurally, these are similar to the $O_2SO_3^-(H_2O)_n$ complexes shown in Fig. 7 in the main article. Sulfur (yellow), oxygen (red), hydrogen (white).

System	Config.	Τ1	D1	$E - (E_{O_3^- W_n} - E_{SO_2})$
$SO_2O_3^-$	RC	0.0345	0.163	-126.50 (-135.60)
	TS	0.0348	0.132	-116.67(-102.40)
$SO_2O_3^-H_2O$	RC	0.0325	0.171	-105.27 (-113.63)
	TS _{dense}	0.0325	0.141	-101.16(-86.73)
	TSrare	0.0327	0.140	-97.10 (-81.43)
$\operatorname{SO}_2O_3^-(H_2O)_2$	RC	0.0302	0.170	-97.35 (-102.37)
	TS _{dense}	0.0299	0.139	-91.46(-77.97)
	TSrare	0.0299	0.138	-91.04(-74.47)

Table SI-2: T1 and D1 diagnostics and free electronic energies of the single point CCSD(T)-F12 calculations in kJ/mol. RC denotes reactant complexes and TS denotes transition states. CAM-B3LYP free energies are included in paranthesis for comparison.

Table SI-3: Harmonic prefactors, entropy and Gibbs free energies of the "loose" and "tight" transition states at standard conditions. There seems to be no apparent reason for the large prefactor for the "loose" n=4 complex. Units are cm⁻¹ and kJ/mol.

	Le	oose TS	Tight TS			
n	$\log_{10}(A)$	Δ S $\cdot T$	$\Delta \mathrm{G}$	$\log_{10}(A)$	Δ S $\cdot T$	$\Delta \mathrm{G}$
0	13.6	1.3	27.6	13.6	1.3	27.6
1	13.4	-1.5	28.9	13.4	0.5	22.1
2	13.5	1.9	20.1	13.8	2.6	16.6
3	13.9	20.9	16.5	13.7	1.7	24.5
4	15.0	29.3	21.7	14.0	3.0	26.3
5	13.8	25.2	26.3	13.9	2.9	25.6

Table SI-4: Total reaction rate constants and half lives of the $SO_2O_3^-(H_2O)_n$ clusters.

\overline{n}	Rate constant (s^{-1})	Half life (ps)
0	5.83×10^{8}	1189
1	3.74×10^{9}	186
2	8.47×10^{10}	8,2
3	1.15×10^{11}	$_{6,0}$
4	1.45×10^{11}	4,8
5	4.27×10^{9}	162

n=0n=2n=1n=3n=4n=5

Table SI-5: Frequencies (cm⁻¹) for the most stable $SO_2O_3^-(H_2O)_n$ clusters, shown in Fig. 2 in the main article.

n=0n=2n=1n=3n=4n=5i831 i776 i753 i555 i569 i557

Table SI-6: Frequencies (cm^{-1}) for the most stable "tight" transition states, shown in Fig. 4 in the main article.

n=0n=2n=1n=3n=4n=5i831 i765 i731 i816 i713 i705

Table SI-7: Frequencies (cm^{-1}) for the most stable "loose" transition states, shown in Fig. 6 in the main article.

n=0n=2n=3n=1n=4n=5

Table SI-8: Frequencies (cm^{-1}) for the configurations into which the "loose" transition states relax on the reactant side.