We thank the reviewer for his/hers useful comments which we address in the following:

• As requested by also the first reviewer, CCSD(T) calculations were performed on the smallest systems. Please consult the reply to the first reviewer for a description of the results of these.

• Next, we thank the reviewer for pointing out the improper use of "tight" and "loose". We will in stead use the notation "dense" and "rare".

• Concerning the sovation effect of S_N2 reactions, we have included a sentence elaborating some more on this interesting topic.

P. 29654 l. 6. " However, the addition of more water molecules tend to increase the energy barrier, i.e. stabilise the reactant complexes more than the transition states. Although ionic S_N2 reactions generally are known to proceed slower when fully solvated than in the gas phase (Olmstead and Brauman, 1977; Chabinyc et al., 1998), this is somewhat surprising since many studies have found an increasing catalytic effect of at least a few water molecules in various gas phase systems (Larson et al., 2000; Niedner-Schatteburg and Bondybey, 2000). However, in this case the lowest barrier is found for the systems containing exactly 2 water molecules".

• The reviewer requests that the sentence on p. 29656, lines 15-16, should be clarified. We have rephrased the paragraph as: "Having determined the $SO_3^-(H_2O)_n$ structures and energies, the thermodynamics of O_2 evaporation was readily available. The strength of the $SO_3^-O_2$ bond is highly dependent of the level of hydration. The binding energy is $25\,\mathrm{kJ\,mol^{-1}}$ in the dehydrated system but only ca. $4\,\mathrm{kJ\,mol^{-1}}$ in the 5 water system. Considering the large release of internal energy due to the oxidation, the nascent O_2 molecule will have a high probability of evaporating, but given the large concentration of atmospheric O_2, this equilibrium will quickly settle. The final product distribution is discussed in detail in Sect. 3.4."

• The reviewer requests that the discussion concerning the equilibrium of SO_3^- with O_2 and H_2O should be clarified. The section has been carefully restructured and now reads:

3.4 Equilibrium with H_2O and O_2

From the previous section, the possibility of growth of $SO_2O_3^-(H_2O)_n$ via stepwise water condensation has been excluded since these clusters are too short lived for the equilibrium to settle. Even though some water molecules possibly may evaporate prior to Reaction (R4), we note that this will in no way alter the overall kinetics. Regardless of the state of hydration, once the collision complex is formed no other outcome than Reaction (R4) is probable. Consequently, the degree of hydration prior

to Reaction (R4) is not of primary interest.

After Reaction (R4), both the $SO_3^-O_2(H_2O)_n$ and $SO_3^-(H_2O)_n$ clusters will, most likely, be stable enough to reach thermal equilibrium via H_2O and O_2 evaporation and condensation. The thermodynamics of these equilibria, i.e.

$$SO_3^-(H_2O)_n + O_2 \leftrightarrow SO_3^-O_2(H_2O)_n \quad (1)$$
$$SO_3^-O_2(H_2O)_n + H_2O \leftrightarrow SO_3^-O_2(H_2O)_{n+1} \quad (2)$$
$$SO_3^-(H_2O)_n + H_2O \leftrightarrow SO_3^-(H_2O)_{n+1} \quad (3)$$

are therefore considered. The energetics associated with these reactions are all available from the previous calculations and are shown in Fig. 9 along with the critical energy of cluster growth. Here exemplified for Reaction (3), this corresponds to the value of ΔG where

$$[H_2O] \times \exp\left(-\frac{\Delta G}{RT}\right) = 1, \quad (4)$$

implying that

$$[SO_3^-(H_2O)_n] = [SO_3^-(H_2O)_{n+1}]. \quad (5)$$

A value of ΔG more positive than the critical clustering energy thus implies $[SO_3^-(H_2O)_n] > [SO_3^-(H_2O)_{n+1}]$ and vice versa. At a given set of conditions, i.e. temperature and pressure of the condensing species, the critical clustering energy thus separates the regimes of condensation and evaporation

Considering first the equilibria with water, i.e. Reactions (2) and (3), we observe that the thermodynamics of water condensation is considerably weaker than expected. Although binding energies are positive for the smallest clusters, the binding energy becomes negative for condensation of the 4th and 5th water molecule. In all cases, the binding energy of H_2O to $SO_3O_2^-$ is more positive than the critical clustering energy and for the SO_3^- species, at most a few clustering water molecules will be found at atmospheric conditions.

Some experimental data are available for Reaction (3) in the $n = 0$ and $n = 1$ case. For $n = 0$, Fehsenfeld and Ferguson (1974) and Möhler et al. (1992) determined ΔG to $-24.7\,\mathrm{kJ\,mol^{-1}}$ and $-23.5\,\mathrm{kJ\,mol^{-1}}$ respectively. Further, Möhler et al. (1992) determined ΔG for the clustering of the second water molecule to $-15.5\,\mathrm{kJ\,mol^{-1}}$. Finally, the first hydration energy of $SO_2O_3^-$ was determined to -17.2 $\mathrm{mol^{-1}}$. Considering the difficulties in describing the multireference electronic structure of the systems at hand, we conclude that the calculated energetics are in good qualitative agreement with the available experimental data although some discrepancies are found.

Considering next the equilibrium with oxygen, i.e. Reaction (1), we see that the oxygen binding energy to the dehydrated SO_3^- anion is quite strong, but also that it

quickly and smoothly converges to a value close to the critical clustering energy. To our knowledge, no direct data is available for this reaction but Möhler et al. (1992) determined the energy of the ligand exchange reaction $SO_3^-(H_2O) + O_2 \leftrightarrow SO_3^-O_2 + H_2O$ to -55 kJ mol^{-1}. This is significantly more than the ca. -20 kJ mol^{-1} found here. However, both studies agree that SO_3^- binds O_2 significantly stronger than H_2O, and that the binding energy of O_2 is significantly stronger than the critical clustering energy.

Assuming that the clusters reach thermal equilibrium, the final populations are readily determined using the law of mass action. Hereby, it is realised that the main product is dehydrated $SO_3O_2^-$. Assuming standard conditions and 50% relative humidity, this configuration constitutes ca. 80–90% of the resulting clusters, depending on altitude. The remaining 10–20% of the clusters are mainly found as $SO_3^-O_2(H_2O)_1$ with any other constitution populating less than 1%.

• The reviewer points out the mistaken use of electronegativity in stead of electron affinity. This error on p. 29656 l. 6. is corrected, as is the same error on p. 29663 l. 13.

• The reviewer mentions that the abbreviation hTST is undefined. Theis should have been stated at its first mention on p. 29658 l. 14. This is now corrected.

• Finally, the Atkins reference has been corrected to "Atkins, P. and de Paula, J.: Physical Chemistry, 8'th edition, Oxford University Press, New York, USA, 2006."

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