Computational investigation of the possible role of some intermediate products of SO$_2$ oxidation in sulfuric acid–water nucleation

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A B S T R A C T

We used quantum chemical calculations to attempt to explain why sulfuric acid produced *in situ* via the reaction of OH radicals with SO$_2$ in the presence of water vapor nucleates much more effectively than sulfuric acid evaporated from a liquid reservoir. We investigated whether or not selected SO$_2$ oxidation intermediates or alternative reaction products could take part in nucleation. We have calculated binding energies and formation free energies for H$_2$SO$_4$·H$_2$SO$_4$, HSO$_3$·H$_2$SO$_4$, HSO$_5$·H$_2$SO$_4$, H$_2$SO$_5$·H$_2$SO$_4$, H$_2$S$_2$O$_8$·H$_2$SO$_4$, H$_2$SO$_4$·H$_2$SO$_4$·H$_2$O, HSO$_3$·H$_2$SO$_4$·H$_2$O, HSO$_5$·H$_2$SO$_4$·H$_2$O, H$_2$SO$_5$·H$_2$SO$_4$·H$_2$O, and H$_2$S$_2$O$_8$·H$_2$SO$_4$·H$_2$O clusters at the RI-MP2/QZVPP level. Our calculations indicate that the only dimer cluster that is more strongly bound than H$_2$SO$_4$·H$_2$SO$_4$ is H$_2$S$_2$O$_8$·H$_2$SO$_4$. Hydration as modeled by the addition of one water molecule to the cluster does not change the situation. The binding of these intermediates, with the exception of H$_2$S$_2$O$_8$ (peroxo-disulfuric acid), to sulfuric acid is therefore not likely to explain the observations.

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1. Introduction

One of the main atmospheric aerosol particle formation mechanisms proposed in the literature is homogeneous nucleation involving a binary mixture of water and sulfuric acid (Kulmala, 2003 and his references; Kulmala et al., 2006). Water–sulfuric acid nucleation has been studied experimentally (see e. g. Hanson and Lovejoy, 2006; Viisanen et al., 1997) and computationally (Kathmann and Hale, 2001; Kusaka et al., 1998; Ianni and Bandy, 2000; Ding et al., 2003) by several groups.

Laboratory investigations by Berndt et al. (2005, 2006, 2007) give reason to expect that other sulfur-containing molecules than H$_2$SO$_4$ could be involved in particle formation from SO$_2$ oxidation. They found that the threshold H$_2$SO$_4$ concentration for particle formation was 10^7 molecules cm^{-3} if H$_2$SO$_4$ was produced *in situ* via the reaction of OH radicals with SO$_2$ in the presence of water vapor, and 10^{10} molecules cm^{-3} if the H$_2$SO$_4$ was taken from a liquid reservoir or produced *in situ* via the reaction of SO$_3$ with

water vapor. These results have been critically discussed by Sorokin and Arnold (2007). Other experimental findings confirm a H$_2$SO$_4$ threshold concentration of about 10^7 molecules cm^{-3} (Burkholder et al., 2007; Young et al., 2008).

The hypothesis that other sulfur-containing compounds could take part of the nucleation is not new. Friend et al. (1980) suggested a mechanism involving the formation and recombination of hydrated forms of HSO$_3$ and HSO$_5$ radicals to explain nucleation in certain conditions. Laaksonen et al. (submitted for publication) suggested that HSO$_5$ radicals nucleate much more efficiently than sulfuric acid if the temperature is above 250 K. We have studied possible reaction intermediates of sulfuric acid formation that could participate in particle formation and explain the results obtained by Berndt et al.

Ion-induced nucleation of H$_2$SO$_4$ and H$_2$O has been studied extensively (see e. g. Sorokin and Arnold, 2007; Lovejoy et al., 2004). However, recent experimental evidence (Kulmala et al., 2007) indicates that tropospheric nucleation proceeds predominantly via a neutral mechanism. Also, the energy of the UV radiation used in the experiments of Berndt et al. is insufficient to cause ionization, so the only possible

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source of ions in their experimental setup is background radiation. Since the rate of ionization by background radiation is the same regardless of whether sulfuric acid is produced by SO_2 oxidation or taken from a liquid solution, ion-induced nucleation of sulfuric acid itself cannot explain the observed differences. In principle, nucleation involving other SO_2 oxidation products may contain an ion-induced component, but given the high particle formation rates observed in the experiments of Berndt et al. (2005, 2006, 2007) and Young et al. (2008) this contribution is unlikely to be very large.

The nucleation rate, number of new particles formed per unit time and volume, depends exponentially on the free energy of formation of the so-called critical cluster. We cannot calculate the formation energies for critical clusters in atmospheric conditions because we do not know their composition. If the critical clusters were composed only of sulfuric acid and water, they would be too large to be studied with high level quantum chemistry methods. However, the Gibbs free energies of formation for smaller clusters give a strong indication of the relative abilites of different substances to nucleate.

In this study, we calculated binding energies and thermochemical properties for clusters containing one sulfuric acid and one other sulfur-containing compound formed in SO_2 oxidation, using a high-level *ab initio* molecular orbital method. In atmospheric and laboratory conditions, water is always present at least at some concentrations. We added one water molecule to the dimers to see if the presence of water molecules changes the relative binding energies. A necessary but not sufficient condition for some molecule to enhance H_2SO_4 nucleation by complexation is that it is bound to H_2SO_4 more strongly than another H_2SO_4 molecule.

2. Formation of sulfur-containing compounds

A major part of atmospheric sulfur originates from anthropogenic sources (Seinfeld and Pandis, 1998) and most of this is emitted in the form of sulfur dioxide (SO_2). In the atmosphere, SO_2 is oxidized to sulfuric acid (H_2SO_4). In the gas phase, the hydroxyl radical initiates the most probable oxidation route by addition to SO_2, assisted by a collision partner (here denoted M). The initially formed hydroxysulfonyl radical HSO_3 is further oxidized to H_2SO_4 (Wayne, 2000):

$$SO_2 + OH + M \rightarrow HSO_3 + M \tag{1}$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \tag{2}$$

$$SO_3 + 2H_2O \rightarrow H_2SO_4 + H_2O \tag{3}$$

HSO_5 is formed via an alternative oxidation reaction of HSO_3, where HSO_3 reacts with O_2, assisted by a collision partner:

$$HSO_3 + O_2 + M \rightarrow HSO_5 + M. \tag{4}$$

Experimental observations at 300 K by Stockwell and Calvert (1983) proposed that less than 20% of the HSO_3 formed in reaction (1) reacts by reaction (4), while 80% forms SO_3 directly. Based on experimental measurements of the rate coefficient, Cleason and Howard (1988) proposed that reaction (4) has little atmospheric significance. Majumdar et al.

(1999) showed that reaction (4) could have role also in the formation of HO_2 and SO_3 molecules.

Friend et al. (1980) suggested that HSO_3 radicals could recombine, forming $H_2S_2O_6$, or alternatively react with HSO_5 to form peroxo-disulfuric acid, $H_2S_2O_8$. However, reactions (2) and (4) are so fast that a more probable reaction route is the recombination of HSO_5 radicals that also leads to $H_2S_2O_8$:

$$HSO_5 + HSO_5 \rightarrow H_2S_2O_8 + O_2. \tag{5}$$
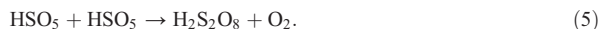
HSO_5 can also react with HO_2 to yield peroxo-sulfuric acid:

$$HSO_5 + HO_2 \rightarrow H_2SO_5 + O_2. \tag{6}$$

Both $H_2S_2O_8$ and H_2SO_5 are highly hygroscopic solids at room temperature. Wayne (2000) has also proposed that HSO_5 could react directly with SO_2. This and other similar reactions of sulfur-containing radicals with SO_2 might possibly also lead to formation of stable or metastable molecules containing more than one sulfur atom.

3. Computational details

Calculations have been performed using the TURBOMOL v.5.8. program suite (Ahlrichs et al., 1989; Häser and Ahlrichs, 1989). For structure optimizations and vibrational frequency calculations, we used the resolution of identity approximation (Weigend and Häser, 1997) with second-order Moller–Plessent perturbation theory, RI-MP2, (Weigend et al., 1998) and the def2-QZVPP basis set (Weigend and Ahlrichs, 2005) hereafter denoted simply "QZVPP". We performed a preliminary structure optimization for all molecules and clusters using a smaller def2-SVP basis set (Weigend and Ahlrichs, 2005). The auxiliary basis sets needed for the RI expansion are given by Hättig (2005). In a recent high-level study on small neutral and charged sulfuric acid–water clusters (Kurtén et al., 2007a,b), we have shown that at the RI-MP2 level, increasing the basis set size beyond aug-cc-pV(T+d)Z has only a small effect on the intermolecular binding (complexation) energies. As basis sets containing multiple diffuse functions led to serious convergence problems in the geometry optimizations, we used instead the def2-QZVPP basis set, which lacks diffuse functions but contains four basis functions per valence electron (instead of two or three as in most basis sets used in previous cluster studies). The very large size of the basis set should compensate for the lack of diffuse functions in this study (Fliegl et al., 2006).

The convergence with respect to the electronic energy in the self-consistent field (SCF) step was 10^{-7} a.u. (atomic units), and the convergence with respect to the gradient was 10^{-4} a.u. For the numerical frequency calculations, a step size of 0.01 a.u. and a SCF convergence limit of 10^{-8} a.u. were used. Thermal contributions to the free energies, enthalpies and entropies were computed using the ideal gas, rigid rotor and harmonic oscillator approximations. We noted that quantitatively highly accurate formation free energies would require (Kurtén et al., 2007a,b) the computation of anharmonic vibrational frequencies, which would be prohibitively expensive for the larger cluster types studied here. However, as this study focused on comparing formation free energies of different clusters to each other, the errors due to anharmonicity are mostly cancelled out.

Some initial molecule and cluster geometries were taken from earlier computational studies. We used data from Ding

et al. (2003) as initial configurations for H_2SO_4 dimers with and without water. The input geometries for the HSO_3 and HSO_5 radicals were taken from calculations of Majumdar et al. (1999). Steudel and Otto (2000) have studied computationally structures of free and crystalline peroxo-sulfuric acid H_2SO_5, and our input structures are based on their results.

For the other systems studied here, no previous results exist (to our knowledge), and we applied a semi-empirical molecular orbital model to find a set of initial configurations. The semi-empirical calculations were performed using the Spartan (Wavefunction, 2002) software and the RM1 (Recife Model 1) parametrization (Rocha et al., 2006).

4. Results and discussion

We studied the following dimers: $H_2SO_4 \cdot H_2SO_4$, $HSO_3 \cdot H_2SO_4$, $HSO_5 \cdot H_2SO_4$, $H_2SO_5 \cdot H_2SO_4$, and $H_2S_2O_8 \cdot H_2SO_4$ and trimers: $H_2SO_4 \cdot H_2SO_4 \cdot H_2O$, $HSO_3 \cdot H_2SO_4 \cdot H_2O$, $HSO_5 \cdot H_2SO_4 \cdot H_2O$, $H_2SO_5 \cdot H_2SO_4 \cdot H_2O$, and $H_2S_2O_8 \cdot H_2SO_4 \cdot H_2O$.

The optimized, most stable minimum-energy cluster structures are shown in Fig. 1. If the minimum-energy geometries with respect to the binding energy (electronic energy) and Gibbs free energy are different for some cluster stoichiometry, then both structures are presented in Fig. 1, and roman numerals are used to identify them. The minimum-energy configurations are
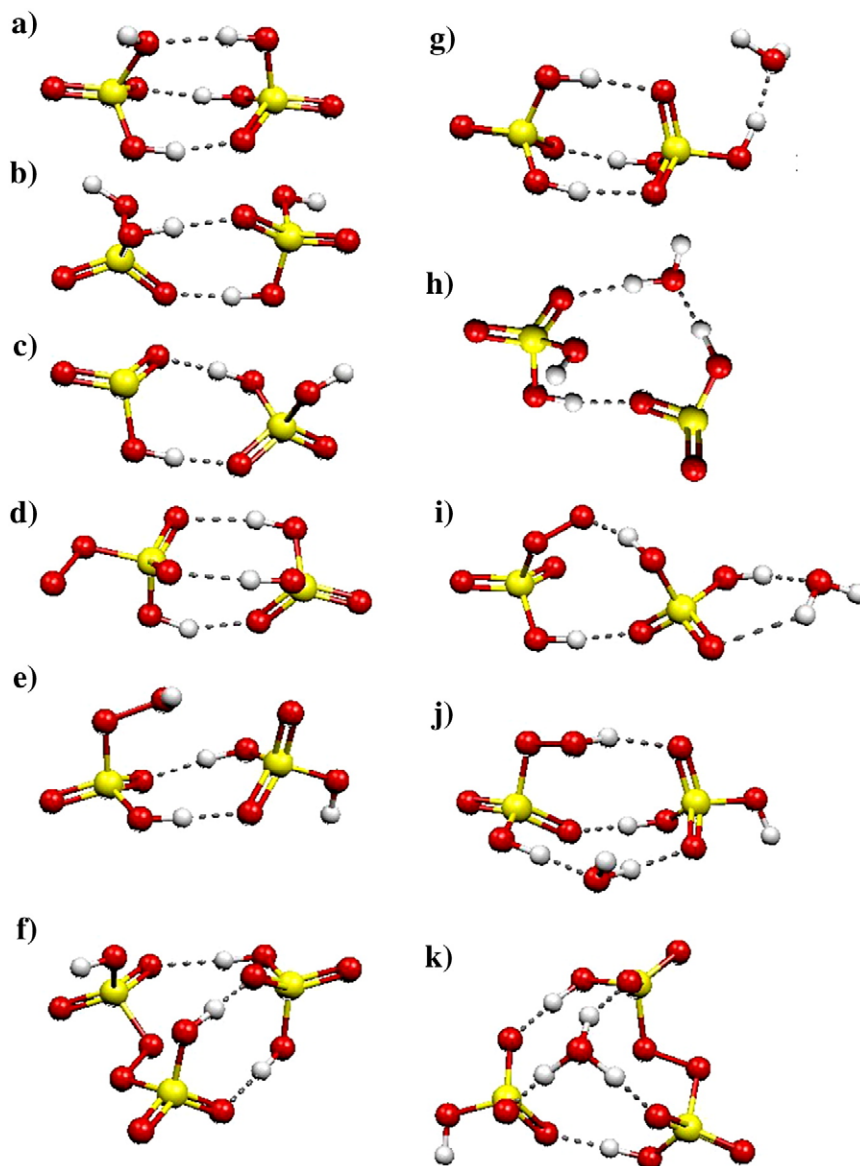

Fig. 1. Structures of hydrogen-bonded clusters containing sulfuric acid and various other sulfur-containing molecules: a) $H_2SO_4 \cdot H_2SO_4$ (I), b) $H_2SO_4 \cdot H_2SO_4$ (II), c) $H_2SO_4 \cdot HSO_3$, d) $H_2SO_4 \cdot HSO_5$, e) $H_2SO_4 \cdot H_2SO_5$, f) $H_2SO_4 \cdot H_2S_2O_8$, g) $H_2SO_4 \cdot H_2SO_4 \cdot H_2O$, h) $H_2SO_4 \cdot HSO_3 \cdot H_2O$, i) $H_2SO_4 \cdot HSO_5 \cdot H_2O$, j) $H_2SO_4 \cdot H_2SO_5 \cdot H_2O$, k) $H_2SO_4 \cdot H_2S_2O_8 \cdot H_2O$. Clusters correspond to the minimum-energy structures optimized at the RI-MP2/QZVPP level. Color coding: yellow = sulfur atom, red = oxygen and white = hydrogen. Dashed lines indicate hydrogen bonds.

characterized by multiple intermolecular hydrogen bonds. The Cartesian coordinates of all studied clusters are given in the auxiliary material.

It should be noted that the $HSO_5 \cdot H_2SO_4 \cdot H_2O$ cluster converged slowly at the RI-MP/QZVPP level even after the structures were initially optimized at the RI-MP/SVP level. For this cluster, we have found only one minimum-energy geometry at the higher level even when several were found at the lower level.

Binding energies calculated at the RI-MP2/QZVPP level are presented in Table 1. The energies correspond to most stable cluster configurations (energies for all clusters are given in the auxiliary material). The binding energy of cluster is defined as

$$\Delta E_0 = E_0(\text{cluster}) - \Sigma_{\text{reactants}} E_0(\text{reactant}), \qquad (1)$$

where $E_0(\text{cluster})$ and $E_0(\text{reactant})$ are the electronic energies of the cluster and reactants (e.g. H_2SO_4, H_2O). The corresponding thermochemical parameters (computed at 298 K and 1 atm reference pressure for all reactants), computed analogously to Eq. (1), are presented in Table 2.

Table 1 shows that $H_2S_2O_8 \cdot H_2SO_4$ is more stable than $H_2SO_4 \cdot H_2SO_4$ with respect to the electronic energy, while all other complexes between sulfuric acid and some other sulfur-containing molecule are less stable than $H_2SO_4 \cdot H_2SO_4$. However, with respect to the Gibbs free energies, $H_2SO_4 \cdot H_2SO_4$ is more stable than any other dimer including $H_2S_2O_8 \cdot H_2SO_4$. Addition of a water molecule changes this situation, as hydration increases the binding energy difference between $H_2S_2O_8 \cdot H_2SO_4$ and $H_2SO_4 \cdot H_2SO_4$ complexes (Table 1). The $H_2S_2O_8 \cdot H_2SO_4 \cdot H_2O$ cluster is the most stable trimer species studied with respect to both electronic and free energies.

From Fig. 1 we can see that a proton transfer occurs in the $H_2S_2O_8 \cdot H_2SO_4 \cdot H_2O$ cluster, and that this cluster contains more hydrogen bonds than any other cluster studied. The reason for the high stability of the $H_2S_2O_8 \cdot H_2SO_4 \cdot H_2O$ cluster is probably that the $H_2S_2O_8$ molecule, unlike any other of the sulfur-containing compounds in the studied trimers, is able to stabilize the $HSO_4^- \cdot H_3O^+$ ion pair by forming two hydrogen bonds to both of the ions. In figurative terms, the $H_2S_2O_8$ molecule forms a claw-like structure, with the ion pair held tightly in its grasp.

Simulations of larger sulfuric acid clusters $(H_2SO_4)_n$ and $H_2SO_4(H_2O)_n$ ($n \geq 3$) have been performed by several groups, see e.g. Kurtén et al. (2007a,b), Nadykto and Yu (2007) and Ortega et al. (2008). According to these studies, the formation

Table 1
Binding energies (with respect to free molecules) for sulfuric acid-containing dimers and trimers

Binding energies ΔE_0	
Cluster	ΔE kcal/mol
$H_2SO_4 \cdot H_2SO_4$ (I)	−18.22
$H_2SO_4 \cdot H_2SO_4$ (II)	−18.03
$HSO_5 \cdot H_2SO_4$	−13.94
$HSO_3 \cdot H_2SO_4$	−16.51
$H_2SO_5 \cdot H_2SO_4$	−17.33
$H_2S_2O_8 \cdot H_2SO_4$	−20.15
$H_2SO_4 \cdot H_2SO_4 \cdot H_2O$	−33.04
$HSO_3 \cdot H_2SO_4 \cdot H_2O$	−27.94
$HSO_5 \cdot H_2SO_4 \cdot H_2O$	−21.64
$H_2SO_5 \cdot H_2SO_4 \cdot H_2O$	−31.98
$H_2S_2O_8 \cdot H_2SO_4 \cdot H_2O$	−37.38

Roman numerals denote different cluster configurations (Fig. 1).

Table 2
Gibbs free energies (ΔG), entalphies (ΔH), and entropies (ΔS) for the formation of the studied clusters

Thermochemical parameters			
Cluster	ΔG kcal/mol	ΔH kcal/mol	ΔS cal K^{-1} mol^{-1}
$H_2SO_4 \cdot H_2SO_4$ (I)	−4.25	−16.89	−42.40
$H_2SO_4 \cdot H_2SO_4$ (II)	−6.13	−16.85	−35.96
$HSO_5 \cdot H_2SO_4$	−1.35	−17.18	−43.23
$HSO_3 \cdot H_2SO_4$	−2.98	−15.08	−40.58
$H_2SO_5 \cdot H_2SO_4$	−3.16	−16.33	−44.17
$H_2S_2O_8 \cdot H_2SO_4$	−5.07	−18.59	−45.35
$H_2SO_4 \cdot H_2SO_4 \cdot H_2O$	−7.29	−30.25	−76.99
$HSO_3 \cdot H_2SO_4 \cdot H_2O$	−2.28	−25.14	−76.67
$HSO_5 \cdot H_2SO_4 \cdot H_2O$	−0.98	−22,95	−73,67
$H_2SO_5 \cdot H_2SO_4 \cdot H_2O$	−5.49	−29.26	−79.73
$H_2S_2O_8 \cdot H_2SO_4 \cdot H_2O$	−9.48	−35.09	−88.64

All thermochemical parameters correspond to 1 atm and 298 K.
Roman numerals denote different cluster configurtion (Fig. 1).

free energy of the sulfuric acid trimer is relatively high, indicating that the binding of a third sulfuric acid molecule to the rather stable dimer is thermodynamically unfavourable. Hydration does not change the situation. The formation of "mixed" clusters such as $H_2S_2O_8 \cdot H_2SO_4$ would thus lower the nucleation barrier by avoiding the need to form pure sulfuric acid trimers. To investigate this further, studies on larger clusters of $H_2S_2O_8$, H_2SO_4 and H_2O are needed.

Due to lack of kinetic data for the elementary steps describing the formation and atmospheric loss processes of (e.g.) $H_2S_2O_8$ molecules, reliable estimates of the atmospheric (or even laboratory) concentration of $H_2S_2O_8$ are unavailable. Some highly uncertain order-of-magnitude estimates can be made using the assumption that up to 20% of HSO_3 radicals could react to form HSO_5 instead of SO_3. In the hypothetical situation that each HSO_5 radical formed in reaction 4 would go on to form $H_2S_2O_8$ or some other similar "efficiently nucleating" molecule with more than one sulfur atom, the concentration of these molecules could be on the order of 10% of the sulfuric acid concentration. From the law of mass balance, the free energy of formation (at 298 K) of the mixed dimers would then need to be at around 1.3–1.4 kcal/mol lower than that of the pure sulfuric acid dimers for their concentration to be equal. This condition is met by the hydrated $H_2S_2O_8 \cdot H_2SO_4$ cluster. For the $H_2S_2O_8$–H_2SO_4–H_2O mixture to nucleate more efficiently than the H_2SO_4–H_2O system alone, the differences in formation free energy for the larger clusters would still need to be somewhat (though not necessarily much) larger. However, it should be noted that the difference in binding energies and enthalpies between the hydrated $H_2S_2O_8 \cdot H_2S_2O_8 \cdot H_2SO_4$ and $H_2SO_4 \cdot H_2SO_4$ clusters is much larger (almost 5 kcal/mol) than the difference in free energies. As the entropy term is by far the least reliable component of the calculated free energy, it is possible that the real free energy difference is larger than computed here. E.g. a difference of 5 kcal/mol would already correspond (assuming a monomer concentration ratio of 1:10) to a dimer concentration ratio of the order of 500:1 in favour of $H_2S_2O_8 \cdot H_2SO_4$. More reliable estimates of the complexation entropy of $H_2S_2O_8$–H_2SO_4 clusters e.g. using a custom-built force field might thus be warranted.

5. Conclusions

Atmospheric secondary aerosol particles have a significant role as condensation nuclei in remote continental regions

(Spracklen et al., 2006). According to results by Weber et al. (1995, 1997), Sihto et al. (2006), and Riipinen et al. (2007), the formation of secondary particles is a function of the gaseous sulfuric acid concentration raised to a power between one and two in a wide variety of locations. Thus, sulfuric acid and related compounds are considered as the most prominent candidates for particle-forming vapors.

Recent experimental results give reason to expect that other sulfur-containing molecules than H_2SO_4 could be involved in particle formation from SO_2 oxidation. In this study, we compared binding energies and formation free energies of sulfuric acid dimers $H_2SO_4 \cdot H_2SO_4$ and $H_2SO_4 \cdot H_2SO_4 \cdot H_2O$ with dimers and trimers where one of the sulfuric acid molecules is substituted with another sulfur-containing compound.

According to our calculations, the binding between H_2SO_4 and most reaction intermediates of SO_2 oxidation is weaker than that between two sulfuric acid molecules, implying that these intermediates are unlikely to be responsible for the experimental observation that sulfuric acid produced via the $SO_2 + OH$ reaction nucleates more efficiently than sulfuric acid taken from a liquid reservoir. The only studied dimer that was more strongly bound than $H_2SO_4 \cdot H_2SO_4$ was $H_2S_2O_8 \cdot H_2SO_4$, indicating that $H_2S_2O_8$ (peroxo-disulfuric acid) might possibly play a role in sulfuric acid–water nucleation. The difference in binding energies between these two dimers was relatively small but seems to increase with hydration.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.atmosres.2008.05.008.

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