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Quantum chemical studies on peroxodisulfuric acid–sulfuric acid–water clusters

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ABSTRACT

We have applied a multistep quantum chemistry method to study the formation energetics and binding patterns of sulfuric acid–peroxodisulfuric acid–water clusters, with special focus on the O–O bridge. The length of the O–O bridge correlates linearly with the average length of S–O bonds next to it. The clustering of peroxodisulfuric acid with sulfuric acid and water is thermodynamically favorable, as is the replacement by peroxodisulfuric acid of one (but only one) of the sulfuric acid molecules in a sulfuric acid–water cluster. However, the presence of $H_2S_2O_8$ does not enhance the addition of sulfuric acid to the clusters.

1. Introduction

The sulfur cycle is one of the most important geochemical processes in the Earth's atmosphere. In addition to affecting human and ecosystem health, sulfur compounds have a central role in the formation of both primary and secondary aerosol particles, some of which act as cloud condensation nuclei, modifying the Earth's radiative balance. The effect of the increase in atmospheric aerosol particles is estimated to be the single greatest source of uncertainty in the global estimates of anthropogenic radiative forcing [1].

The most important sulfur-containing aerosol precursor gas is sulfur dioxide, SO_2, which is produced from combustion processes, volcanoes and the oxidation of organic (mostly biogenic) sulfur compounds. In the gas phase, SO_2 is oxidized to sulfuric acid, H_2SO_4, via a series of reactions initiated by the OH radical [2]:

$$SO_2 + OH + M \rightarrow HSO_3 + M \quad (a)$$

$$HSO_3 + O_2 \rightarrow HSO_5 \quad (b)$$

$$HSO_5 \rightarrow SO_3 + HO_2 \quad (c)$$

$$SO_3 + 2H_2O \rightarrow H_2SO_4 + H_2O \quad (d)$$

where M is a catalyst. In the liquid phase (e.g. inside cloud droplets), several other oxidation pathways exist [2]. Alternative oxidation pathways have been proposed also for the gas phase, but so far their atmospheric relevance is unknown. Sulfuric acid formed in reaction (d) is thought to be the single most important molecule for new-particle formation in the Earth's atmosphere (e.g. Kulmala et al. [3] or Faloona [4]), though other compounds such as water and base molecules are also believed to play a role [5–7]

A few years ago, experimental measurements [8,9] on new-particle formation from H_2SO_4 vapor produced in different ways gave reason to expect that other sulfur-containing compounds are also involved in the nucleation process. Specifically, the threshold concentration of H_2SO_4 required for nucleation was measured to be 1–3 orders of magnitude lower if H_2SO_4 was produced in situ via SO_2 oxidation, compared to the case where H_2SO_4 was taken from liquid sample. This observation motivated a number of studies [10–13] on alternative nucleation pathways in the sulfur–oxygen–hydrogen system. These included both alternative oxidation mechanisms for SO_2, as well as the co-nucleation of sulfuric acid with other sulfur–oxygen–hydrogen compounds. In our previous study [11], we were able to rule out any direct enhancement of sulfuric acid nucleation by several sulfur–oxygen–hydrogen compounds such as H_2SO_5 or HSO_3. The only sulfur–oxygen–hydrogen compound able to bind more strongly to H_2SO_4 than another H_2SO_4 molecule was peroxodisulfuric acid, $H_2S_2O_8$. As the lifetime of HSO_3 is very short due to the high rate of reaction (b), and the high concentration of molecular oxygen,

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the formation of this peroxo acid would most likely involve reactions of HSO_5. For example, self-reaction of HSO_5 would produce $H_2S_2O_8$ plus an oxygen molecule:

$$HSO_5 + HSO_5 \rightarrow H_2S_2O_8 + O_2 \quad \text{(e)}$$

Though these types of reactions have been proposed already in the 1980s by Friend et al. [14], experimental, or even computational data, on their rates or yields are nonexistent. Partial support for the possible existence of alternative HSO_5 reaction products was given by Kurtén et al. [15], who found, based on computational results, that the lifetime of HSO_5 with respect to dissociation into SO_3 and HO_2 (Reaction (c)) is significantly increased by hydration.

Unfortunately for this line of study, recent reanalysis of the experimental data [16] has resolved the previous experimental discrepancy between experiments with different H_2SO_4 production mechanism without need to invoke the participation of either alternative H_2SO_4 formation pathways, or alternative sulfur-containing compounds. The earlier laboratory experiments have been affected the by size–sensitivity of the counting efficiency of particle detectors and the dependence of H_2SO_4 production and loss mechanisms on the SO_2 and H_2SO_4 concentration profiles. Although sulfur–oxygen–hydrogen compounds other than H_2SO_4 are thus no longer needed to explain the experimental data, kinetic modeling [15] still indicates that they may be formed in at least moderate amounts. Also, very recent ambient ion concentration measurements by Ehn et al. [17] demonstrate the presence in the atmosphere of a large variety of sulfur–oxygen–hydrogen species in addition to H_2SO_4 and its clusters. For example, the SO_5^- ion, possibly formed by proton loss from HSO_5, was detected at concentrations around one-fifth of the dominant ion HSO_4^-. This implies that bimolecular reactions involving HSO_5 may have non-negligible yields in the atmosphere. $HS_2O_8^-$ ions, with an integer mass of 193 a.m.u., were not identified in the study by Ehn et al. [17]. This may be due to a lower proton affinity (relative to HSO_4^-.), low concentrations, or a combination of both. On the other hand, the region of the mass spectrum just below 200 a.m.u contained several as yet unidentified low-intensity peaks, so the presence of low to moderate concentrations of $H_2S_2O_8$ cannot be ruled out by their data.

In addition to their possible – albeit likely minor - role in sulfuric acid – dominated nucleation, $H_2S_2O_8$ and its clusters are also an interesting study object in their own right. The nature and behavior or S–O–O bonds are of central interest in understanding the atmospheric sulfur cycle. S–O–O bonds are found in reaction intermediates of the SO_2 + OH oxidation chain shown above, as well as in other, more hypothetical, SO_2 oxidation pathways. These include the reactions of SO_2 with peroxo radicals [2,18] or Criegee intermediates [2,19]. Recently, experimental evidence of the existence of a peroxo isomer of the sulfate radical anion (SO_4^-) has been presented by Zama et al. [20]. In addition to understand the characteristics of S–O–O bonds in isolated molecules, the effect of clustering on the bond properties is also likely to be important for atmospheric chemistry, as indicated e.g. by the recent evidence for the catalytic effect of water clustering on atmospheric reactions of sulfur-containing compounds (see e.g. Jørgensen and Kjaergaard [21]).

Peroxodisulfuric acid, a peroxo acid containing a S–O–O–S bridge structure, presents a unique opportunity to study S–O–O bonds as it is, compared to the abovementioned reaction intermediates, fairly stable and long-lived. In this study, we have investigated H_2SO_4–$H_2S_2O_8$–H_2O clusters computationally, with specific focus on the properties of the S–O–O bonds, and the effect of clustering on the S–O–O–S bridge. We hope that our computational data will eventually be complemented by experimental data to increase our understanding of sulfur–oxygen bonding in the atmosphere.

2. Methods

Calculations on clusters have been performed using a systematic multi-step approach recently developed by our group. This method is described elsewhere [22,23] so only the relevant details are given here.

The initial molecule and cluster geometries were taken from earlier computational studies [22,11] when possible, or generated with the DL_POLY_2 [24] molecular dynamics (MD) program. We used both intact sulfuric acid molecules and the bisulfate - hydronium ion pair in our simple MD annealing. The details of the force-field construction and annealing procedure used to generate input structures are identical to those used by Loukonen et al. [5] and force field parameters for $H_2S_2O_8$ are given in the supplementary material.

The set of reasonable cluster structures obtained from the MD annealing were optimized using the SIESTA program [25]. The gradient-corrected BLYP functional [26] and the double-ζ polarized (DZP) functions were used.

Finally, we calculated single point energies using the Turbomole program suite [27]. Energies were computed at the RI-MP2/aug-cc-pV(T + d)Z level. Single-point calculations on the $(H_2SO_4)\cdot(H_2O)$ cluster in an earlier study [28] shows that second order Møller–Plesset perturbation theory [29] MP2 calculations reproduce well the higher level (CCSD(T)) energies, which are computationally too demanding to calculate for our fairly large clusters. The resolution of identity (RI) approximation Møller–Plesset perturbation theory (RI-MP2) produces binding energies that are essentially identical to normal MP2 [30,31]. The aug-cc-pV(T + d)Z basis set is identical to aug-cc-pVTZ for hydrogen, oxygen and nitrogen atoms, and contains one extra set of d-orbitals for the sulfur atoms [32]. The choice of basis set was based on previous results [33] which indicate that basis-set effects beyond the aug-cc-pV(T + d)Z level are, at least with the MP2 method, too small (under 0.5 kcal/mol in terms of binding energy per molecule) to justify the computational effort of using e.g. a quadruple-zeta-basis.

To obtain a more realistic picture of the stability of clusters in the atmosphere, we also need to consider the free energies. Thermal contributions to enthalpies and entropies and the free energies were computed using ideal gas, rigid rotor and harmonic oscillator approximations. Vibrational harmonic frequencies were calculated using SIESTA (BLYP/DZP). Gibbs formation free energy ΔG is calculated at standard conditions: reference pressure $p = 1$ atm and $T = 298$ K.

We used Quantum Theory – Atoms-in-Molecules (QTAIM) based methods to study the O–O-bridge in the peroxodisulfuric acid molecules. The analyzed electron density distribution provides information about the bonds between atoms. The variables used to describe the bond strength are the bond length, and the electron density at the bond critical point (BCP). The bond path is the line of maximum electron density between nuclei and the BCP corresponds to the minimum value of the density along this line [34]. We carried out the QTAIM-analysis using the AIM2000 program [35].

The level of the wave function calculations used for the QTAIM analysis was B3LYP/6-31+g(d) [36–38], and the wave functions were generated using the Gausian 03 program suite [39]. The same computational level was used to calculate atomic charges from electrostatic potentials using a grid-based method by Breneman and Wiberg [40]. This method is commonly used to create input charges for molecular mechanics calculations. The cluster structures studied are shown in Figs. 1–3. The clusters have been drawn using the MOLEKEL 4.3.linux visualization package [41]. Bonds are depicted as single or double in Figs. 1–3 based on the default values of the bond lengths in the MOLEKEL program. The sulfur atoms are depicted in yellow, oxygen atoms in red and hydrogen atoms in white. The hydrogen bonds are indicated with dotted lines.

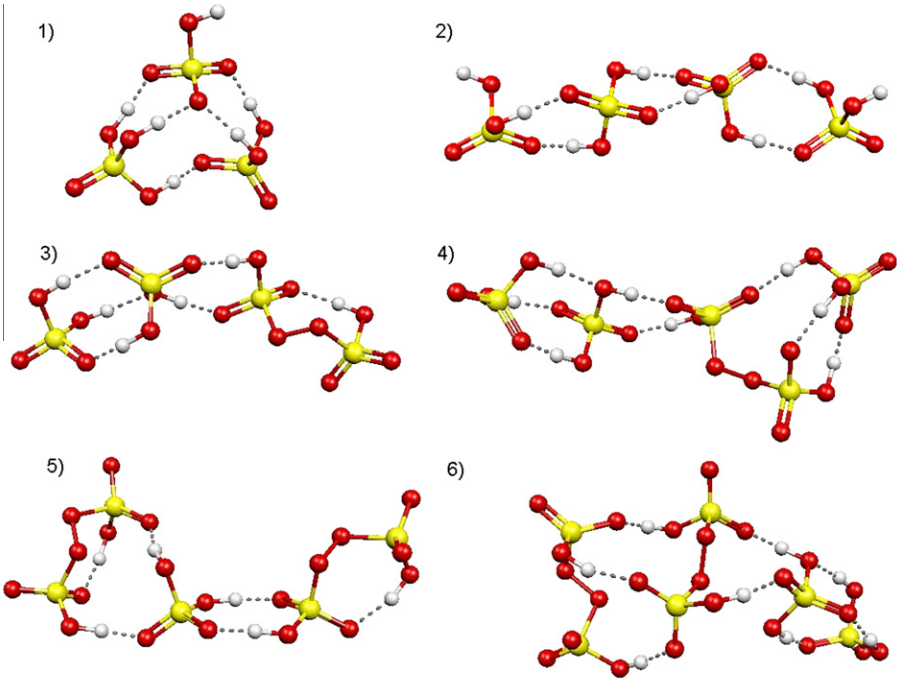

Fig. 1. BLYP/DZP optimized minimum energy (RI-MP2/aug-cc-pV(T + d)Z) geometries of the studied unhydrated clusters: (1) $(H_2SO_4)_3$, (2) $(H_2SO_4)_4$, (3) $H_2S_2O_8{\cdot}(H_2SO_4)_2$, (4) $H_2S_2O_8{\cdot}(H_2SO_4)_3$, (5) $(H_2S_2O_8)_2{\cdot}H_2SO_4$ and (6) $(H_2S_2O_8)_2{\cdot}(H_2SO_4)_2$.

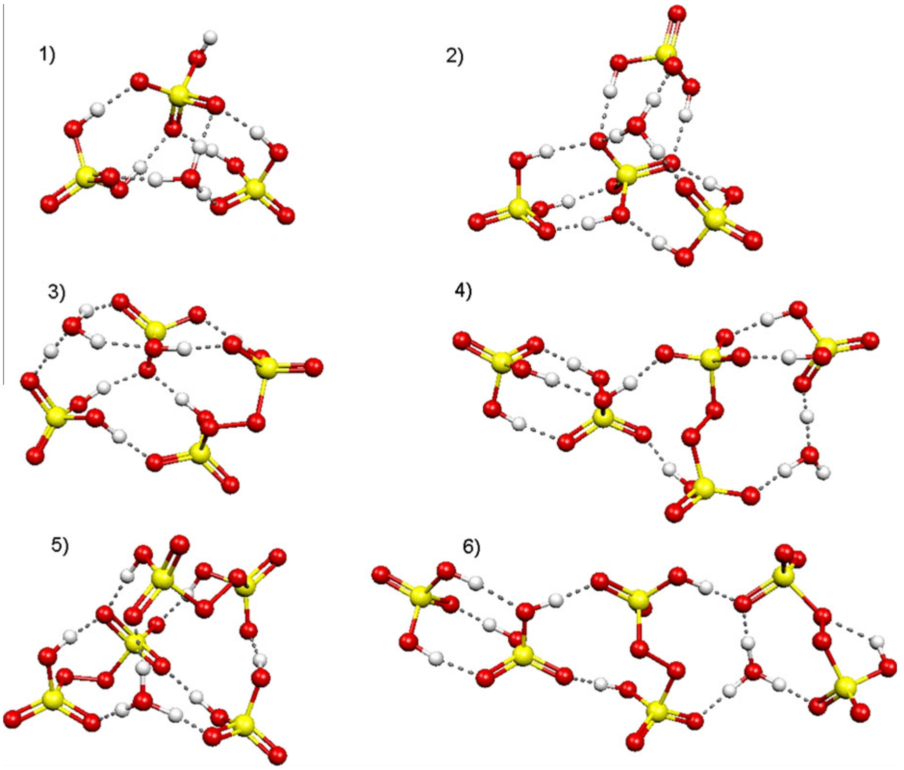

Fig. 2. BLYP/DZP optimized minimum energy (RI-MP2/aug-cc-pV(T + d)Z) geometries of the studied monohydrated clusters: (1) $(H_2SO_4)_3{\cdot}(H_2O)$, (2) $(H_2SO_4)_4{\cdot}(H_2O)$, (3) $H_2S_2O_8{\cdot}(H_2SO_4)_2{\cdot}(H_2O)$, (4) $H_2S_2O_8{\cdot}(H_2SO_4)_3{\cdot}(H_2O)$, (5) $(H_2S_2O_8)_2{\cdot}H_2SO_4{\cdot}(H_2O)$ and (6) $(H_2S_2O_8)_2{\cdot}(H_2SO_4)_2{\cdot}(H_2O)$.

3. Results and discussion

We have studied the following clusters: $(H_2SO_4)_3{\cdot}(H_2O)_n$, $(H_2SO_4)_4{\cdot}(H_2O)_n$, $H_2S_2O_8{\cdot}(H_2SO_4)_2{\cdot}(H_2O)_n$, $H_2S_2O_8{\cdot}(H_2SO_4)_3{\cdot}(H_2O)_n$, $(H_2S_2O_8)_2{\cdot}H_2SO_4{\cdot}(H_2O)_n$, $(H_2S_2O_8)_2{\cdot}H_2SO_4)_2{\cdot}(H_2O)_n$, where the number of water molecules is $n = 0–2$. First we calculated the binding energies and formation free energies at standard conditions ($p = 1$ atm, $T = 298.15$ K). Then we studied more carefully the O–O bridges in the peroxodisulfuric acid molecules using the QTAIM approach.

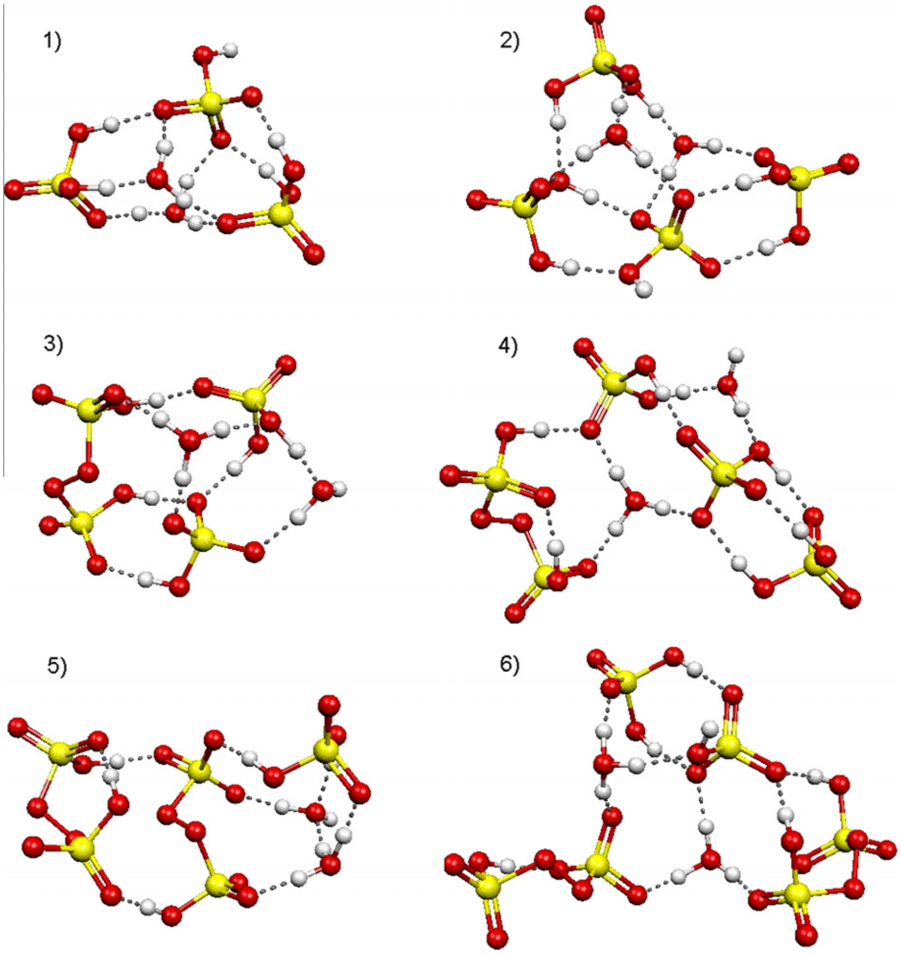

Fig. 3. BLYP/DZP optimized minimum energy (RI-MP2/aug-cc-pV(T + d)Z) geometries of the studied dihydrated clusters: (1) $(H_2SO_4)_3{\cdot}(H_2O)_2$, (2) $(H_2SO_4)_4{\cdot}(H_2O)_2$, (3) $H_2S_2O_8{\cdot}(H_2SO_4)_2{\cdot}(H_2O)_2$, (4) $H_2S_2O_8{\cdot}(H_2SO_4)_3{\cdot}(H_2O)_2$, (5) $(H_2S_2O_8)_2{\cdot}H_2SO_4{\cdot}(H_2O)_2$ and (6) $(H_2S_2O_8)_2{\cdot}(H_2SO_4)_2{\cdot}(H_2O)_2$.

The most stable cluster geometries with respect to the electronic energies are shown in Figs. 1–3. All the geometries are characterized by several hydrogen bonds, and almost all hydrogen atoms participate in hydrogen bonding. The hydrogen atoms in the $H_2S_2O_8$ molecule always participate in either inter- or intramolecular hydrogen bonds. Computed formation energies of these clusters are summarized in the supplementary material.

Most of the clusters without water are chain-like: the molecules are organized more or less in a linear structure. If two sulfuric acid molecules are present, they form a tight pair with three intermolecular hydrogen bonds (Fig. 1). The unhydrated sulfuric acid trimer is exceptional, as all the three molecules are bonded to each other. The proton transfer ($H_2SO_4{\cdot}H_3SO_4{\cdot}HSO_4$) found in the most stable trimer may be an artefact of the geometry optimization method, because the earlier studies have shown that the DFT method overestimates the acidity of H_2SO_4 [42]. We have calculated the free energy difference (using RI-MP2/aug-cc-pV(T + d)Z) energies and BLYP/DZP frequencies) between the minimum-energy trimer structure found here and that given in an earlier study [22], and found it to be only 0.3 kcal/mol. The possibly erroneous prediction of sulfuric autodissociation in the unhydrated trimer does thus not affect the computed energetics significantly. The unhydrated sulfuric acid trimer has previously been found to be a very stable cluster [43].

Ding et al. [44] predict that proton transfer occurs in the cluster containing two H_2SO_4 and one water molecule, though more recent studies including dynamic effects [45–47] have contested this prediction. A similar pattern is shown in the clusters we calculated (Figs. 2 and 3). The hydronium ion formed by the proton transfer always forms several hydrogen bonds with the sulfur-containing molecules around it. The geometries of the hydrated clusters are more cage-like and compact than the unhydrated clusters. Water does not seem to prefer one of the sulfur-containing molecules (H_2SO_4, $H_2S_2O_8$) over the other.

Next, we have calculated the energetics for the reactions where one H_2SO_4 molecule in a cluster is replaced by a $H_2S_2O_8$ molecule. The reaction energies are given in Table 1. The values correspond to the minimum electric energy geometries shown in Figs. 1–3. If some other structural isomer has a lower Gibbs free energy of formation, the corresponding replacement energy has been written in parentheses. The results in Table 1 shows that if $H_2S_2O_8$ is present, sulfuric acid–water clusters will prefer to take up one, and precisely one, $H_2S_2O_8$ molecule. Due to the stable structure of the pure sulfuric acid clusters $(H_2SO_4)_3$ and $(H_2SO_4)_4$, the replacement is not favorable, but the addition of water loosens the structure and the replacement becomes exothermic.

From an atmospheric nucleation point of view, the sulfuric acid addition reaction is perhaps the most interesting. According to our calculations, it is slightly more favorable to add a sulfuric acid molecule to the unhydrated $H_2S_2O_8{\cdot}(H_2SO_4)_2$ and $(H_2S_2O_8)_2{\cdot}H_2SO_4$ clusters than to the pure sulfuric acid trimer $(H_2SO_4)_3$. This is likely due to the stability of the unhydrated pure trimer, and very likely is not indicative of any general nucleation enhancement by $H_2S_2O_8$. Contrary to our earlier preliminary results [11], the presence of

Table 1
Replacement energies in kcal/mol. *n* is the number of water molecules.

Reaction	$n = 0$		$n = 1$		$n = 2$	
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
$(H_2SO_4)_3 \cdot (H_2O)_n + H_2S_2O_8 \rightarrow (H_2SO_4)_2 \cdot (H_2S_2O_8) \cdot (H_2O)_n + H_2SO_4$	1.2 (1.4)	1.7 (−0.5)	−2.5 (1.7)	−1.2 (−6.1)	−6.7	−5.2
$(H_2SO_4)_4 \cdot (H_2O)_n + H_2S_2O_8 \rightarrow (H_2SO_4)_3 \cdot (H_2S_2O_8) \cdot (H_2O)_n + H_2SO_4$	0.3 (1.9)	5.0 (4.7)	−0.4	−1.9	−6.5	−7.1
$(H_2SO_4)_2 \cdot (H_2S_2O_8) \cdot (H_2O)_n + H_2S_2O_8 \rightarrow (H_2SO_4) \cdot (H_2S_2O_8)_2 \cdot (H_2O)_n + H_2SO_4$	0.3	1.7	2.9	8.8	1.5	2.1
$(H_2SO_4)_3 \cdot (H_2S_2O_8) \cdot (H_2O)_n + H_2S_2O_8 \rightarrow (H_2SO_4)_2 \cdot (H_2S_2O_8)_2 \cdot (H_2O)_n + H_2SO_4$	−1.1	−1.9	5.0	6.8	5.1 (6.9)	9.4 (6.7)

water molecules does not increase the relative capability of $H_2S_2O_8$-containing clusters to attract sulfuric acid. A table of sulfuric acid addition energies is given in the supplementary material.

The bond length depends usually on the strength of the bond and therefore on the electron density at the bond critical point and on the atomic charges. According to our knowledge, the bond properties of O–O bridges have not been studied together with bond dissociation energies. Gibbs et al. [48] have studied the correlation between the bond strength and electron density at the bond critical point of Si–O bonds at silicates, and found a linear correlation between the two. Also, a linear correlation between bond length and charge density at the BCP has been reported in earlier studies (see e.g. Gillespie and Popelier [49], Love [50]). The O–O bridge is not an exception to this rule, and the electron density at the bond critical point of the O–O bond and bond length have a very good linear relationship (Fig. 4). The energy required to break the O–O bond in a free $H_2S_2O_8$ molecule (forming two HSO_4 radicals) is 32.2 kcal/mol at the highly accurate CBS-QB3 level. The O–O bcp electron density in the clusters (see the supplementary material) varies from about 4% above the value for free $H_2S_2O_8$ to about 11% below it. Assuming a linear relationship between the bond dissociation energy and the bcp density, this would correspond to a variation of about 5 kcal/mol in the bond strength; from 28.9 kcal/mol to 33.7 kcal/mol. Clustering may thus either increase or decrease the O–O bond strength compared to the free $H_2S_2O_8$ molecule, depending on the precise H-bonding pattern in the cluster.

Both oxygen atoms of the O–O bridge are bonded to an adjacent sulfur atom. Bonding of an oxygen to a sulfur atom in different molecules has been studied by several groups (see e.g. Love [50]). The BCP at the S–O bond next to an O–O bridge is on average 0.16 Å closer to the sulfur than the oxygen atom. In other words, the S–O bond is a moderately polar bond. The average (over all studied $H_2S_2O_8$ molecules) atomic charge of O–O bridge oxygens is −0.2e, and the corresponding value for sulfur atoms in $H_2S_2O_8$ molecules is +1.1e. Sulfur atoms are also bonded to the three other oxygen atoms. The atomic charges of these oxygen are −0.5e or −0.4e depending if they are bonded to a hydrogen or not. According to our calculations, the length of a S–O bond next to the O–O bridge correlates linearly with the electron density at the bond critical point (ρ_{BCP}) of this bond, as expected. However, the quality of the least square fitting of a straight line is not as good as for the O–O bridge bond ($R^2 = 0.964$). This implies that the S–O-bonds are more affected by their different environments.

The distance between the O–O bridge oxygen and sulfur atom next to it (d(S–O)) and the bond length of the O–O bridge (d(O–O)) at $H_2S_2O_8$ do not correlate with each other ($R^2 = 0.176$). The lengths of the S–O bonds in the same O–O bridge can vary substantially from each other. However, if we plot the average distance between the O–O bridge oxygen and the sulfur atom next to it (d(S–O)) against the bond length of the O–O bridge (d(O–O)) (Fig. 5), we can see a correlation between these bond lengths. The O–O bond is clearly affected by both the S–O bonds. The length of O–O bridge decreases with increasing d(S–O). Similar reasoning has been applied in earlier studies where the enthalpy for homolysis of related peroxides such as ZO–OY has been derived from the mean bond dissocation energies for ZO–OZ and YO–OY [51]. From Fig. 5 we can see how one of the d(S–O)–d(O–O)-points deviate from the trend of the others, which lie more or less on the same line. This point (1.76; 1.52) belongs to the $(H_2S_2O_8)_2 \cdot (H_2SO_4)_2 \cdot (H_2O)$ cluster. In this cluster, one peroxodisulfuric acid molecule forms an intramolecular hydrogen bond from the O–O bridge oxygen to an OH group. This O–O bond is longer than the other O–O bonds with a similar average S–O bond length. This mean that the formation of the hydrogen bond to the O–O bridge makes the O–O-bond weaker. Closer look at the S–O bonds reveals that one of the S–O bond is the shortest and the other one is longest one of all the studied S–O bonds. The additional H-bond to the hydrogen is from the oxygen belonging to the longest S–O bond

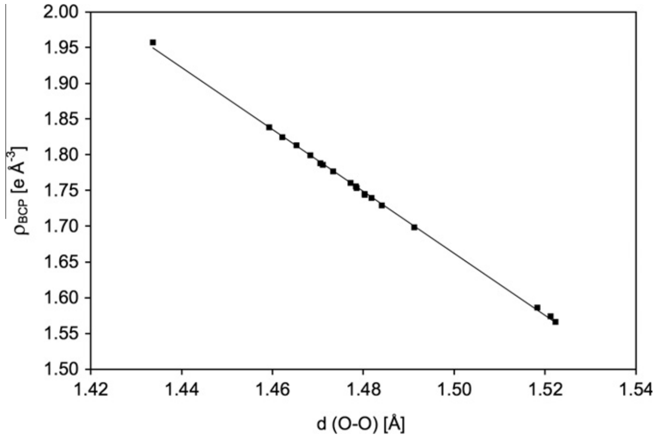

Fig. 4. Electron density at the bond critical point of the O–O-bridge. The straight line is a least-square fit to the calculated points. Correlation coefficient R^2 is 0.999.

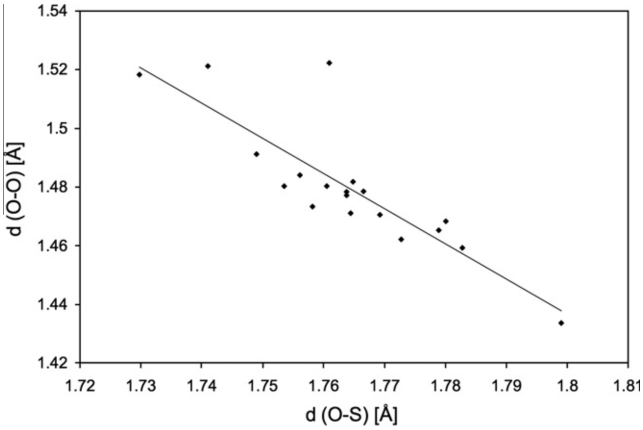

Fig. 5. Bond lengths (d(O–O)) of the O–O bridge in the peroxodisulfuric acid molecule correlate with the average of the bond lengths between the bridge oxygens and the sulfur atoms next to them (d(S–O)). The straight line is a least-square fit to the calculated points ($R^2 = 0.725$).

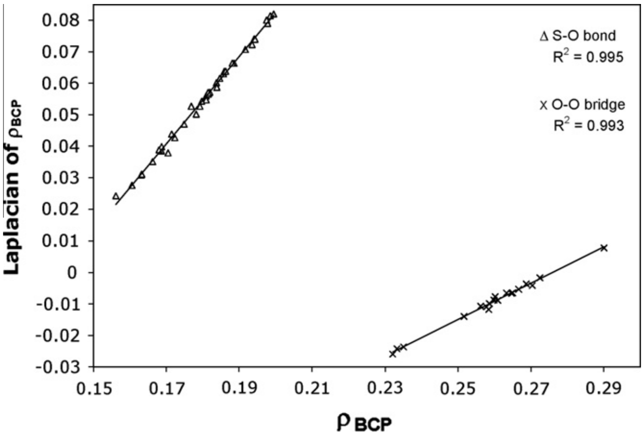

Fig. 6. Variation of the Laplacian at the bond critical point (atomic units) with electron density at the bond critical point (atomic units). The crosses correspond the BCP values at O–O bridges and square points correspond S–O bonds next to the O–O bridge.

The second derivative of the electron density $\nabla^2\rho$ (also called the Laplacian) shows where the electron density is locally concentrated or depleted. Generally the Laplacian for a polar covalent bond is positive, and the magnitude of Laplacian increases with electron density at the bond critical point. This applies also to S–O bonds next to O–O bridges in $H_2S_2O_8$ molecules (Fig. 6). The Laplacian at the BCP of the O–O bridge is negative for all the bonds except for the shortest one (highest ρ_{BCP}). The square points in Fig. 6 represent the Laplacian values for the S–O bonds next to the O–O bridge. The crosses in Fig. 6 shows the ρ_{BCP}(O–O) dependence of the Laplacian at the O–O-bridges. Due to the linear correlation between the Laplacian values and $\rho_{BCP,}$ and ρ_{BCP} and the bond length, no linear correlation can be expected between $\nabla^2\rho$(S–O) and $\nabla^2\rho$(O–O).

Numerical values for the electronic density and the Laplacian at bond critical points, as well as the bond lengths, are summarized in the supplementary material.

4. Conclusion

We studied clusters of sulfuric acid, peroxodisulfuric acid and water molecules. If $H_2S_2O_8$ is available, replacement of one sulfuric acid in a sulfuric acid–water cluster by $H_2S_2O_8$ is thermodynamically favorable. However, a second replacement reaction is unfavorable. $H_2S_2O_8$ likely does not enhance sulfuric acid addition to the clusters in the atmospheric conditions. The length of the O–O bridge correlates linearly with the average length of S–O bonds next to it. The O–O bridge at $H_2S_2O_8$ molecule seems to be affected by the cluster formation. The bond between the oxygen atoms can become both weaker or stronger compared to the free molecule. However, among the studied clusters, the weakest O–O bridge forms an extra bond with a hydrogen. This implies that cluster formation can weaken the SO–OS bond, and make dissociation of $H_2S_2O_8$ more probable. This may lead to the situation where $H_2S_2O_8$ molecules are not detected in experiments even if they might be present in the clusters. However, intra- and intermolecular hydrogen bonding in the clusters may in some cases also strengthen the O–O bond.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.comptc.2011.04.023.

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