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Reliable potential for small sulfuric acid–water clusters

Chang-Geng Ding^a, Tuulia Taskila^a, Kari Laasonen^{a,*}, Ari Laaksonen^b

^a Department of Chemistry, University of Oulu, P.O. Box 3000, 90014 Oulu, Finland

^b Department of Applied Physics, University of Kuopio, P.O. Box 1627, 70211 Kuopio, Finland

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Abstract

We have constructed a reliable potential model for clusters of sulfuric acid and water. Such model requires potentials for sulfuric acid (H_2SO_4), protonated sulfuric acid (HSO_4^-), hydronium ion (H_3O^+) and water (H_2O). To develop this model, we have used the available ab initio data for small clusters containing one sulfuric acid. The ab initio data are well reproduced with our model. We computed the number of waters around a sulfuric acid at atmospheric conditions (300 K and 50% relative humidity) to be ca. 1.3. This is in good agreement with experiments which predict 1.3 waters around the acid. We have also tested our model with small clusters containing two sulfuric acids and find the results to be in good agreement with ab initio calculations. Larger systems with up to 50 water molecules were studied as well. Here, the hydronium ions were found to be on the surface of the cluster and the bisulfate ions inside the cluster. The clusters are very flexible and large fluctuations were observed in the sulfur–sulfur and sulfur–hydronium distance. © 2002 Elsevier Science B.V. All rights reserved.

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Keywords: Sulfuric acid; Model potentials; Sulfuric acid–water clusters

1. Introduction

Sulfuric acid plays an important role in atmospheric chemistry and physics [1–4]. Acid rain, formation of atmospheric particulate matter, aerosol forcing of climate, as well as stratospheric ozone depletion are all processes influenced by sulfuric acid. Because of its low vapor pressure and affinity to water, atmospheric H_2SO_4 is mostly found in the condensed phase, i.e., in aerosols and

cloud drops. It is also known to be an effective nucleation agent, and extremely low concentrations of sulfuric acid will enhance the homogeneous nucleation rate of water significantly [5]. The microscopic mechanism of this process is not known, but very likely the protonated form of sulfuric acid HSO_4^- and hydronium ion H_3O^+ are responsible for the enhancement of the nucleation [6]. The sulfuric acid molecule dissociates very easily in the presence of water to form HSO_4^- and H_3O^+ . Ab initio calculations indicate that already three water molecules are enough to facilitate the dissociation process [7,8]. Thus, even small clusters contain two ions, and may therefore have a large

* Corresponding author. Tel.: +358-85-531-640; fax: +358-85-531-603.

E-mail address: kari.laasonen@oulu.fi (K. Laasonen).

dipole moment making them very attractive for the water molecules in the gas. Also the binding energies of clusters containing HSO_4^- and H_3O^+ ions are larger than those of similar water clusters.

Sulfuric acid–water nucleation has mostly been studied using the classical nucleation theory (CNT), which describes the nucleating cluster as a liquid drop. The shortcoming of CNT is that molecular clusters are described in terms of macroscopic variables such as surface tension and liquid density. Furthermore, the dissociation state of the acids is likely to be cluster size dependent, a feature not captured by the CNT. Therefore, more useful information of the nucleation process would be gained through molecular simulations. Ideally this could be done by using ab initio methods but such simulations are computationally very expensive and cannot be used for nucleation studies. We need to use more effective empirical methods, for which the interactions depend only on the atomic positions. Such potentials are very useful for molecular dynamics (MD) or Monte-Carlo (MC) simulations [9,10]. The key problem is to find potentials that are both simple and able to reliably mimic the true interactions.

The main focus of this work was to develop a reliable potential model for sulfuric acid, protonated sulfuric acid, hydronium ion and water. We used the ab initio data of Re et al. [7] when building our model. Cluster simulations were carried out with the new potential and comparisons with the available experimental and ab initio data was made. Unfortunately, very little molecular level data of sulfuric acid clusters exist, and thus our experimental comparisons are limited to only few experiments [12,13]. In some instances, where no ab initio data are available, we have also carried out ab initio calculations using the DMol³ package [11]. We also apply our model to large sulfuric acid–water clusters including up to two sulfuric acids, and last we compare the results of our model with some recent sulfuric acid–water potential models [9,10].

2. Model

In this work, we study a molecular system of sulfuric acid and few water molecules. The inter-

molecular interaction takes place between two atoms, i and j , of different molecules according to the following formula:

$$u(r_{ij}) = A \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (1)$$

where q_i , q_j are effective atomic charges, r_{ij} is the distance between sites i and j , $A = 331.05$ kcal/mol Å/e² and ϵ_{ij} , σ_{ij} are the intermolecular parameters of the Lennard–Jones (L–J) potential. Standard mixing rules [14] have been used to obtain these parameters from the atomic L–J parameters (ϵ_i , σ_i),

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}, \quad \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j).$$

For the intramolecular potentials we used simple harmonic potential, $V(r) = 0.5k(r - r_0)^2$, with $k = 1000$ kcal/mol, together with the ab initio distances. For H_2SO_4 the minimum bond distances are the following: SO, 1.43 Å, SO_H, 1.61 Å, OH, 0.97 Å. The SH distance is fixed to 2.17 Å and the OO distances to OO, 2.53 Å, OO_H, 2.44 Å, O_HO_H, 2.50 Å, these distances will fix the SOH and OSO angles. The OH groups of H_2SO_4 will repel each other. This is modelled by a soft harmonic H...H potential ($k = 10$ kcal/mol) with HH distance of 3.4 Å. The internal HSO_4^- potential is similar: the bond distances are SO, 1.45 Å, SO_H, 1.69 Å, OH, 0.96 Å, and the angle “distances”: SH, 2.12 Å, OO, 2.46 Å, OO_H, 2.48 Å. There is no OH...OH repulsion in this cluster. In water molecule, the distances are 0.98 Å (OH) and 1.57 Å (HH) and in hydronium the same distances are 0.97 Å (OH) and 1.68 Å (HH). Due to the very stiff harmonic potentials we apply the multiple timestep method RESPA [15] to integrate the equations of motions using 0.125 and 1.0 fs timesteps for the internal potentials and for the intermolecular forces, respectively. No cut-off or Ewald method [14] for the intermolecular interactions are used.

The geometries of the sulfuric acid, bisulfate ion, water and hydronium ion are shown in Fig. 1.

We use the following constraints for the atomic charges (O1 corresponds to the oxygen at OH groups):

$$\begin{aligned} q_S + 2(q_{O1} + q_{O2}) + 2q_H &= 0 & \text{for sulfuric acid,} \\ q_S + q_{O1} + 3q_{O2} + q_H &= -1 & \text{for bisulfate ion,} \end{aligned}$$

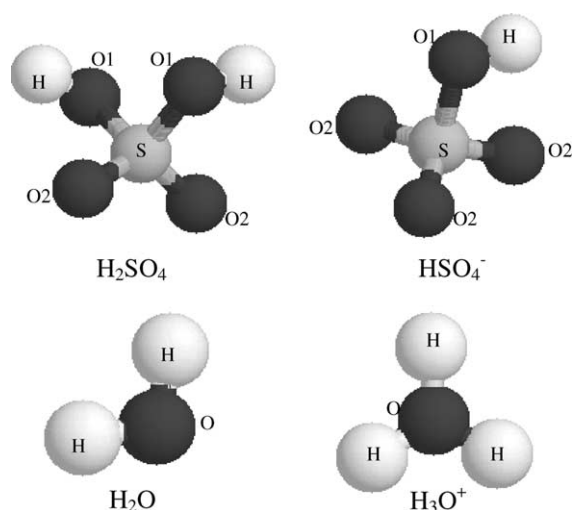


Fig. 1. Models of the sulfuric acid, bisulfate ion, water and hydronium ion.

$$q_O^w + 2q_H^w = 0 \quad \text{for water,}$$

$$q_O^h + 3q_H^h = 1 \quad \text{for hydronium ion.}$$

Here, we have ignored the fully protonated SO_4^{2-} ions. Are they important in small clusters? First, the OH bond is stronger in HSO_4^- than in sulfuric acid and when the cluster is very small the dissociated proton increase the acidity of the cluster considerably. Both these facts suppress the probability of the second proton dissociation. In bulk liquid (25 °C) at rather low concentration (ca. 1 M) the SO_4^{2-} concentration is roughly half of $[\text{HSO}_4^-]$ (or 1/3 of the total acid concentration) but in more concentrated solutions (ca. 7 M, which corresponds to the $\text{H}_2\text{SO}_4 + (\text{H}_2\text{O})_6$ cluster) the $[\text{SO}_4^{2-}]$ is only 20% of the total acid concentration [16]. However, it is rather dangerous to apply bulk data for clusters containing only few molecules. Therefore, we did some calculations using DMol³ [11] with the BLYP gradient corrections [17] to obtain the total energies of $\text{SO}_4^{2-}(\text{H}_3\text{O}^+)_2(\text{H}_2\text{O})_{n-2}$ and $\text{HSO}_4^-(\text{H}_3\text{O}^+)(\text{H}_2\text{O})_{n-1}$ clusters with $n = 6$ and 7. The total energy always favors the singly protonated forms, by 5–8 kcal/mol. One reason for this is geometrical as the second OH group is not well solvated in clusters of these sizes. This suggests that the SO_4^{2-} is not important in the small clusters and we have not build a potential for it.

A potential for SO_4^{2-} in bulk water environment can be found in [18]

The Lennard-Jones parameters of water and hydronium ion are assigned only for the oxygen sites and are selected as the SPC/E values for water [19] to simplify the computation,

$$\varepsilon_O^w = 0.1554 \text{ kcal/mol}, \quad \sigma_O^w = 3.166 \text{ \AA}.$$

In the neutral case, which includes sulfuric acid and water molecules, the intermolecular interaction (1) can be determined using 10 parameters $\lambda = \{q_S, q_{O1}, q_{O2}, q_O^w, \varepsilon_S, \varepsilon_{O1}, \varepsilon_{O2}, \sigma_S, \sigma_{O1}, \sigma_{O2}\}$. However, the ionic clusters are more complex and 13 parameters are needed to build the potentials: $\lambda = \{q_S, q_{O1}, q_{O2}, q_O^w, q_O^h, \varepsilon_S, \varepsilon_{O1}, \varepsilon_{O2}, \varepsilon_O^h, \sigma_S, \sigma_{O1}, \sigma_{O2}, \sigma_O^h\}$. We have taken the liberty to change the charges of water molecules, because we believe that the bonding environment is different than that in bulk water for which the SPC/E model has been designed. It would be better to use polarizable water model but we wanted to have as simple model as possible because the nucleation applications will be computationally very demanding.

2.1. Fitting the model

In order to determine the values of the above adjustable parameters, we fitted the energies and geometries of $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_n$ ($n = 1$ to 5) to ab initio results of Re et al. [7] (see Figs. 2 and 3).

We cannot use all the data in [7] but we need to choose the energies and distances used in the fit. For energy we have chose the zero-point corrected total ab initio energies obtained by using the larger basis set, D95++(d,p), in [7]. Our empirical model does not include the zero-point corrections but the finite temperature molecular dynamics simulations will account for the intramolecular entropy effects. Thus using the zero-point corrected energies as reference we should obtain results that are consistent with the real free energies. Our empirical method does not contain molecular bond energies. The binding energies of neutral clusters can be compared directly to ab initio data, but in the protonated clusters, the bond energies need to be taken into account. From ab initio calculation the proton affinity to H_2O is 172.12 kcal/mol, while 316.16 kcal/mol is needed to form HSO_4^-

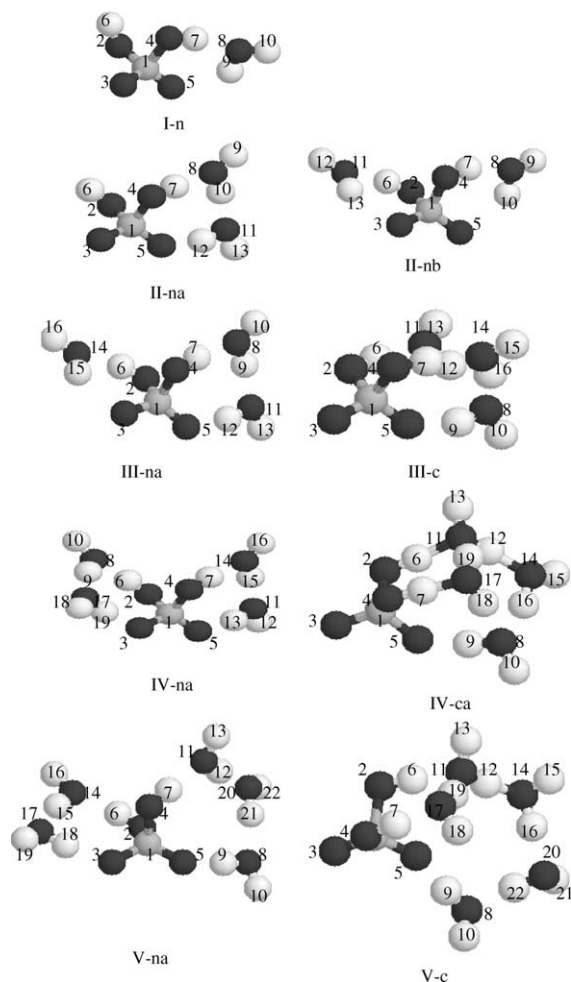


Fig. 2. Favorable structures of $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_n$ ($n = 1$ to 5) for the neutral clusters. White spheres refer to oxygen atoms, black spheres hydrogen atoms and gray spheres sulfuric atoms.

from H_2SO_4 [7]. Thus in ionic clusters the comparisons with *ab initio* energies have been made with $E(\text{ionic, empirical}) + 144.0$ kcal/mol.

The bond lengths for the fitting were chosen as the hydrogen bonds between the sulfuric acid and water. Also some hydrogen bonds between the waters were included. The water–water bonds were chosen to determine the shape of the clusters.

We also found that two of the most stable isomers need to be included in the fitting procedure. At first, we fitted the parameters by using only the most stable isomers. The resulting energy order of the lowest energy isomers was, however, different than

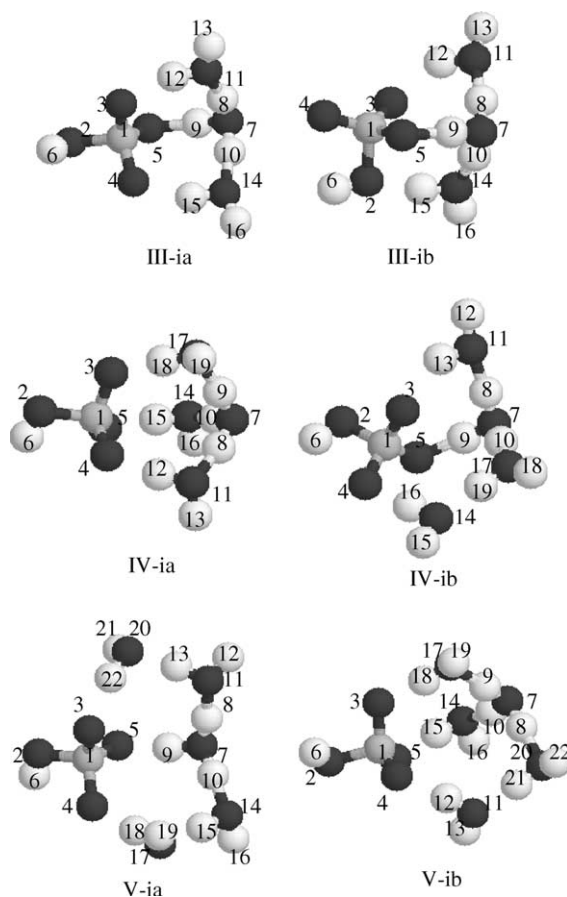


Fig. 3. Favorable structures of $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_n$ ($n = 3$ to 5) for the ionic clusters.

that from the *ab initio* data. Using the two most stable structures in the fitting produced a potential that agrees much better with the *ab initio* results. Also several kinds of interactions between the acid and the water need to be included to the fit. For instance, both III-ia and III-ib have similar interactions between bisulfate ion and water, but the OH group is not hydrogen bonded in III-ia (see Fig. 3). We therefore need to include III-ib type interactions to the fitting procedure, otherwise the parameters of the OH group ($q_{\text{O1}}, \epsilon_{\text{O1}}, \sigma_{\text{O1}}$) will be unreliable. Totally we used nine structures for the neutral isomers and six structures for the ionic ones.

The actual fitting was done by minimizing the following objective function:

$$X = \sum_i [e_i(\lambda) - E_i]^2 + \sum_j [l_j(\lambda) - L_j]^2 w_j, \quad (2)$$

Table 1
Interaction parameters of the neutral structures

| | Sulfuric acid | | | Water, O ^w |
|--------------------------|---------------|-----------|-----------|-----------------------|
| | S | O1 | O2 | |
| ε (kcal/mol) | 0.249465 | 0.241462 | 0.142482 | 0.155400 |
| σ (Å) | 3.046670 | 3.154935 | 2.878607 | 3.166000 |
| Charge (e) | 0.867761 | −0.479915 | −0.396635 | −0.765683 |

Note that the hydrogens has been omitted. Their L–J parameters are = 0 and the charges are $q_H = -q_S/2 - q_{O1} - q_{O2}$ for the acid and $q_H^w = -q_O^w/2$ for water.

Table 2
Interaction parameters of the ionic structures

| | Bisulfate ion | | | Water, O ^w | Hydronium ion, O ^h |
|--------------------------|---------------|-----------|-----------|-----------------------|-------------------------------|
| | S | O1 | O2 | | |
| ε (kcal/mol) | 0.051744 | 0.333951 | 0.247479 | 0.155400 | 0.230404 |
| σ (Å) | 3.292173 | 2.911465 | 3.196117 | 3.166000 | 2.905709 |
| Charge (e) | 1.061914 | −0.597995 | −0.641901 | −0.752190 | −0.683471 |

The hydrogens has been omitted. Their L–J parameters are = 0 and the charges are $q_H = -1 - q_S - q_{O1} - 3q_{O2}$ for the acid, $q_H^h = (1 - q_O^h)/3$ for hydronium ion and $q_H^w = -q_O^w/2$ for water.

where $e_i(\lambda)$ and $l_j(\lambda)$ are the minimum potential energies and the bond lengths by the molecular model, respectively, which depend on the set of parameters λ , and E_i and L_j are the corresponding values supplied by the ab initio calculations [7]. The weights w_j were chosen at convenience: very good parameters were be obtained by setting $w_j = 10$ for all data. The Powell direction set method [20] was used to carry out the optimization. Tables 1 and 2 give the best set of parameters from our fitting procedure.

Unfortunately there is very little experimental data available for the binding energies. The only experiment we are aware of, the free energies of $n = 1$ and $n = 2$ were estimated to be 3.6 ± 1 and 2.3 ± 0.3 kcal/mol, respectively [13]. These are in good agreement with the theoretical free energies in [7], 2.4 and 2.0 kcal/mol. No experimental–structural data are available.

3. Results

3.1. Energies of $H_2SO_4(H_2O)_n$ clusters

The calculated potential energies and bond lengths of $H_2SO_4(H_2O)_n$ ($n = 1$ to 5) are shown

in Tables 3 and 4. From these, one can see that the energies and bond lengths obtained from our potentials compare very well with the ab initio results [7]. However, the order of the energies between III-na and III-c is different from the ab initio one. It is interesting to note that without the zero-point vibration corrections III-c is more stable than III-na [7]. The case with V-na and V-c is the same. Owing the very small energy difference between the isomers, we think that our potentials are suitable for studying the clusters of hydrated sulfuric acid.

The total energy of the $HSO_4^-H_3O^+H_2O$ cluster produced by our parameters is only 9.7 kcal/mol, which is much less than 21 kcal/mol of the neutral isomer. This indicates that two waters are unable to induce the proton transfer reaction whereas in the larger clusters ($n = 3, 4, 5$) the ionic forms are more stable. We also calculated the energy of clusters with $n = 10$ and 20. The potential energies (E/n) as a function of n are shown in Fig. 4. It clearly indicates that the ionic clusters are more stable than the neutral structures when n is greater than 4, which is in agreement with the previous ab initio results. Note that Fig. 4 shows an average of several low energy structures, and thus at $n = 3$ the results are not in contradiction with Tables 2

Table 3

Potential energies and bond lengths obtained from this work and ab initio for neutral clusters

| <i>n</i> | Structure | Potential energy (kcal/mol) | | | Bond length (Å) | | |
|----------|-----------|-----------------------------|-----------|--------|-----------------|-----------|---------------|
| | | This work | Ab initio | Kusaka | Bond | This work | Ab initio [7] |
| 1 | I-n | −10.6 | −10.4 | −15.76 | 7–8 | 1.779 | 1.651 |
| | | | | | 5–9 | 2.247 | 2.230 |
| 2 | II-na | −21.1 | −20.9 | −32.4 | 7–8 | 1.736 | 1.524 |
| | | | | | 5–12 | 1.738 | 1.873 |
| | II-nb | −20.7 | −20.2 | −31.1 | 7–8 | 1.811 | 1.665 |
| | | | | | 5–10 | 2.222 | 2.181 |
| 3 | III-na | −31.4 | −31.1 | −47.8 | 7–8 | 1.742 | 1.535 |
| | | | | | 5–12 | 1.737 | 1.859 |
| | | | | | 6–14 | 1.807 | 1.675 |
| | | | | | 9–11 | 1.747 | 1.692 |
| | III-c | −32.4 | −30.8 | −49.9 | 6–11 | 1.757 | 1.658 |
| | | | | | 7–14 | 1.755 | 1.627 |
| | | | | | 8–16 | 1.846 | 1.855 |
| | | | | | 8–12 | 1.856 | 1.838 |
| 4 | IV-na | −42.0 | −42.2 | −64.4 | 6–8 | 1.739 | 1.545 |
| | | | | | 3–19 | 1.740 | 1.854 |
| | IV-ca | −41.6 | −40.0 | −62.8 | 6–11 | 1.792 | 1.711 |
| | | | | | 7–17 | 1.790 | 1.586 |
| | | | | | 5–9 | 1.707 | 1.707 |
| | | | | | 8–16 | 1.771 | 1.800 |
| 5 | V-na | −50.6 | −50.3 | −76.8 | 7–11 | 1.721 | 1.495 |
| | | | | | 5–9 | 1.696 | 1.814 |
| | | | | | 8–21 | 1.732 | 1.703 |
| | | | | | 6–14 | 1.739 | 1.545 |
| | | | | | 3–18 | 1.739 | 1.847 |
| | V-c | −50.8 | −49.5 | −75.1 | 6–11 | 1.738 | 1.677 |
| | | | | | 7–17 | 1.739 | 1.569 |
| | | | | | 5–9 | 1.682 | 1.711 |
| | | | | | 12–14 | 1.793 | 1.610 |
| | | | | | 8–22 | 1.717 | 1.782 |

In the table is also shown energies of the same structures using a model by Kusaka et al. [9].

and 4, where only two of the lowest energies are shown.

3.2. Larger cluster

To get some new information of the sulfuric acid clusters we turned our attention to larger clusters. Our purpose was not to study nucleation or evaporation at this point, but to study the ion–ion binding in cluster environment.

First, we studied the structure of ionic cluster with $n = 50$ using molecular dynamics. We performed a long MD run of 3 ns at 260 K, with 1.2 fs

timestep. The intermolecular motion were integrated using the RESPA method with 0.15 fs timestep [15]. The cluster was placed on a periodic simulation box with side length of 50 Å. Not cut-offs or Ewald method [14] were used for the long range Coulomb interactions. The molecules were allowed to evaporate but we saw only 1–2 short evaporation events in which the water molecule returned back to the cluster. To obtain the canonical distribution the temperature was controlled by using a Nosé–Hoover thermostat chain [21]. The key finding was that the hydronium ion is mostly on the surface and the bisulfate ion is well inside the

Table 4

Potential energies and bond lengths obtained from this work and ab initio for ionic clusters

| <i>n</i> | Structure | Potential energy (kcal/mol) | | | Bond length (Å) | | |
|----------|-----------|-----------------------------|-----------|--------------|-----------------|-----------|---------------|
| | | This work | Ab initio | Kusaka model | Bond | This work | Ab initio [7] |
| 3 | III-ia | −30.0 | −30.2 | −37.8 | 3–12 | 1.831 | 1.740 |
| | | | | | 5–9 | 1.495 | 1.526 |
| | | | | | 4–15 | 1.831 | 1.758 |
| | | | | | 8–11 | 1.431 | 1.543 |
| | III-ib | −28.9 | −29.2 | −41.2 | 3–12 | 1.912 | 1.728 |
| | | | | | 5–9 | 1.499 | 1.449 |
| | | | | | 2–15 | 1.824 | 1.844 |
| 4 | IV-ia | −42.2 | −42.8 | −50.5 | 10–14 | 1.433 | 1.602 |
| | | | | | 3–18 | 1.767 | 1.661 |
| | | | | | 5–15 | 1.873 | 1.673 |
| | | | | | 4–12 | 1.767 | 1.667 |
| | | | | | 10–14 | 1.427 | 1.506 |
| | IV-ib | −41.8 | −41.4 | −53.9.5 | 8–11 | 1.454 | 1.506 |
| | | | | | 3–13 | 1.883 | 1.724 |
| | | | | | 5–9 | 1.485 | 1.500 |
| | | | | | 4–16 | 1.818 | 1.739 |
| | | | | | 14–19 | 1.687 | 1.626 |
| 5 | V-ia | −53.4 | −52.7 | −71.2 | 13–20 | 1.697 | 1.627 |
| | | | | | 3–18 | 1.743 | 1.646 |
| | | | | | 5–15 | 1.934 | 1.644 |
| | | | | | 4–12 | 1.842 | 1.714 |
| | | | | | 11–21 | 1.722 | 1.612 |
| | V-ib | −51.5 | −51.8 | −65.6 | 9–17 | 1.422 | 1.491 |
| | | | | | 3–22 | 1.877 | 1.731 |
| | | | | | 5–9 | 1.501 | 1.503 |
| | | | | | 4–18 | 1.837 | 1.725 |
| | | | | | 15–17 | 1.707 | 1.627 |

In the table is also shown energies of the same structures using a model by Kusaka et al. [9].

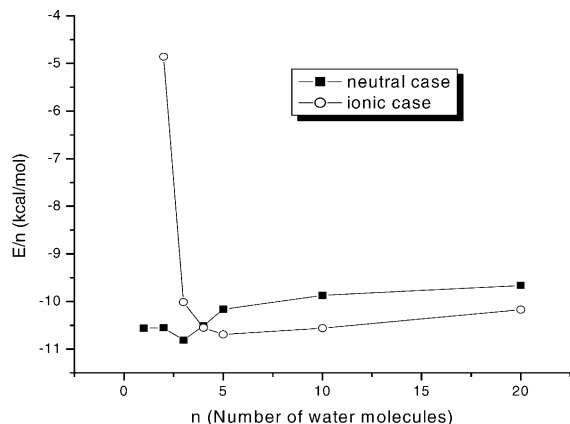


Fig. 4. Potential energies (E/n) of $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_n$ ($n=1$ to 20) from our model for both neutral and ionic structures.

cluster. This is in agreement with a very recent study of $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ clusters, in which the SO_4^{2-} was found to be inside the cluster [22]. The sulfur–hydronium oxygen distance varied considerably during the simulation, between 3.2 and 11 Å with an average of 6.1 ± 0.1 Å. We see all possible forms of ion pairs [23,24], including contact ion pairs in which the hydronium ion is hydrogen bonded to the bisulfate. The contact ion pair has a very short S–O distance of <4 Å. The other solvent separated ions had one or more water layers between the ions. We estimated the probability of the contact ion pair using the 4 Å S–O cut-off. This gave a probability of ca. 7%. Also the overall shape of the cluster varies significantly and the hydronium ion is in random positions on the surface.

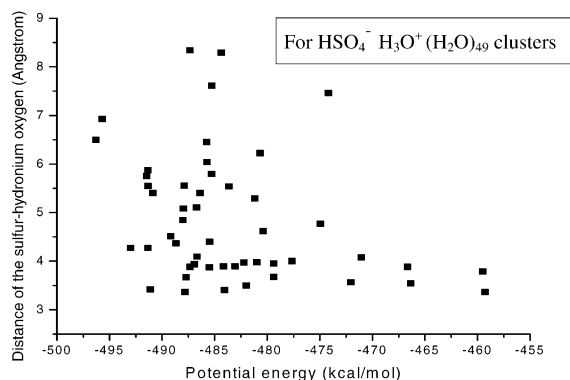


Fig. 5. Distances of the sulfur and hydronium oxygen atoms as a function of the potential energies for $\text{HSO}_4^- \text{H}_3\text{O}^+ (\text{H}_2\text{O})_{49}$.

The behavior of the contact ion pairs can be compared with the work of Kusaka et al. [9], who found only contact ion pairs in clusters of 96 water molecules and smaller. The first solvent separated ion pairs were cluster with 243 waters. This difference is due to rather different potential models used, and because there are no experiments of the subject available we cannot decide which model is more correct.

We also investigated the low temperature structures of clusters with $n = 50$. The initial screening of the structures were done by minimizing random water configurations. The lowest energy structure was used as a starting point of a series of 200 simulated annealing runs. Fig. 5 gives the relation between the potential energies and the distances of the sulfur atom and hydronium oxygen of the final structures. Once again the S–O distances vary quite much. The final structures confirm the previous findings: the hydronium is often on the surface and the bisulfate ion inside the cluster (see Fig. 6).

3.3. Two sulfuric acids and water

We expanded our study to two sulfuric acids and a few waters. There are three kinds of isomeric forms which include the neutral clusters $(\text{H}_2\text{SO}_4)_2 (\text{H}_2\text{O})_n$, clusters with one ionic pair $\text{H}_2\text{SO}_4 \text{HSO}_4^- \text{H}_3\text{O}^+ (\text{H}_2\text{O})_{n-1}$, and clusters with two ionic pairs $(\text{HSO}_4^-)_2 (\text{H}_3\text{O}^+)_2 (\text{H}_2\text{O})_{n-2}$. As mentioned earlier only small fractions of the HSO_4^- are expected to

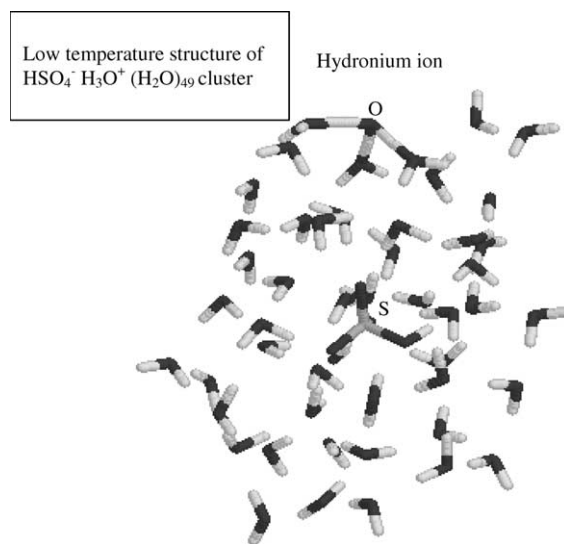


Fig. 6. Low temperature structure of $\text{HSO}_4^- \text{H}_3\text{O}^+ (\text{H}_2\text{O})_{49}$.

protonate, and thus we have not considered the SO_4^{2-} ions here. Our results show that the system favors the $(\text{HSO}_4^-)_2 (\text{H}_3\text{O}^+)_2 (\text{H}_2\text{O})_{n-2}$ isomers when $n > 4$ (see Fig. 7). Although this is not an ab initio result, it indicates that the protonation of the sulfuric acid is very easy even when there are several acid molecules in the cluster.

As an example let us examine the case of two sulfuric acids and four waters. The $(\text{HSO}_4^-)_2 (\text{H}_3\text{O}^+)_2 (\text{H}_2\text{O})_2$ is more stable than both the $(\text{H}_2\text{SO}_4)_2 (\text{H}_2\text{O})_4$ and the $\text{H}_2\text{SO}_4 \text{HSO}_4^- \text{H}_3\text{O}^+ (\text{H}_2\text{O})_3$ by 9.2 and 1.2 kcal/mol, respectively.

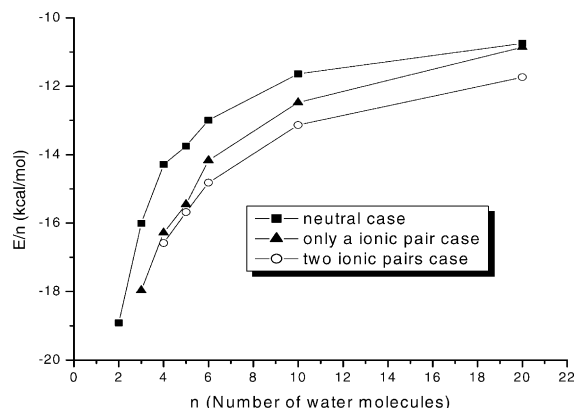


Fig. 7. Mean potential energies (E/n) of $(\text{H}_2\text{SO}_4)_2 (\text{H}_2\text{O})_n$ ($n = 2$ to 20) for all three kinds of isomers with our model.

To test this we optimized these isomers using the DMol³ package [11,25] with the Perdew-Wang gradient-corrected functionals for exchange and

Table 5

Relative energies (in kcal/mol) of the systems of two sulfuric acids with four and six waters

| | This model | DMol ³ |
|---|------------|-------------------|
| $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_4$ | 9.2 | 6.2 |
| $\text{H}_2\text{SO}_4 \text{HSO}_4^- \text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ | 1.2 | 3.3 |
| $(\text{HSO}_4^-)_2(\text{H}_3\text{O}^+)_2(\text{H}_2\text{O})_2$ | 0.0 | 0.0 |
| $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_6$ | 10.9 | 9.6 |
| $\text{H}_2\text{SO}_4 \text{HSO}_4^- \text{H}_3\text{O}^+(\text{H}_2\text{O})_5$ | 3.9 | 7.0 |
| $(\text{HSO}_4^-)_2(\text{H}_3\text{O}^+)_2(\text{H}_2\text{O})_4$ | 0.0 | 0.0 |
| $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_6$ (Bandy and Ianni [27]) | 15.5 | 13.6 |

correlation [26]. Table 5 shows the relative energies of these isomers from our empirical potential model and the DMol³ result. Both sets of energies indicate that the $(\text{HSO}_4^-)_2(\text{H}_3\text{O}^+)_2(\text{H}_2\text{O})_2$ is the most stable of the three isomers. Similarly, for the six waters case shown in Fig. 8, we found that the $(\text{HSO}_4^-)_2(\text{H}_3\text{O}^+)_2(\text{H}_2\text{O})_4$ is more stable than the $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_6$ and $\text{H}_2\text{SO}_4 \text{HSO}_4^- \text{H}_3\text{O}^+(\text{H}_2\text{O})_5$ by 10.9 and 3.9 kcal/mol from our model and by 9.6 and 7.0 kcal/mol from DMol³ result, respectively. On the whole, there are 12 hydrogen bonds for these isomers, which some are very strong. The hydrogen atoms of the H_3O^+ form very short hydrogen bonds (1.30–1.66 Å). Fig. 8 and Table 5 also show the structure and energy given by Bandy

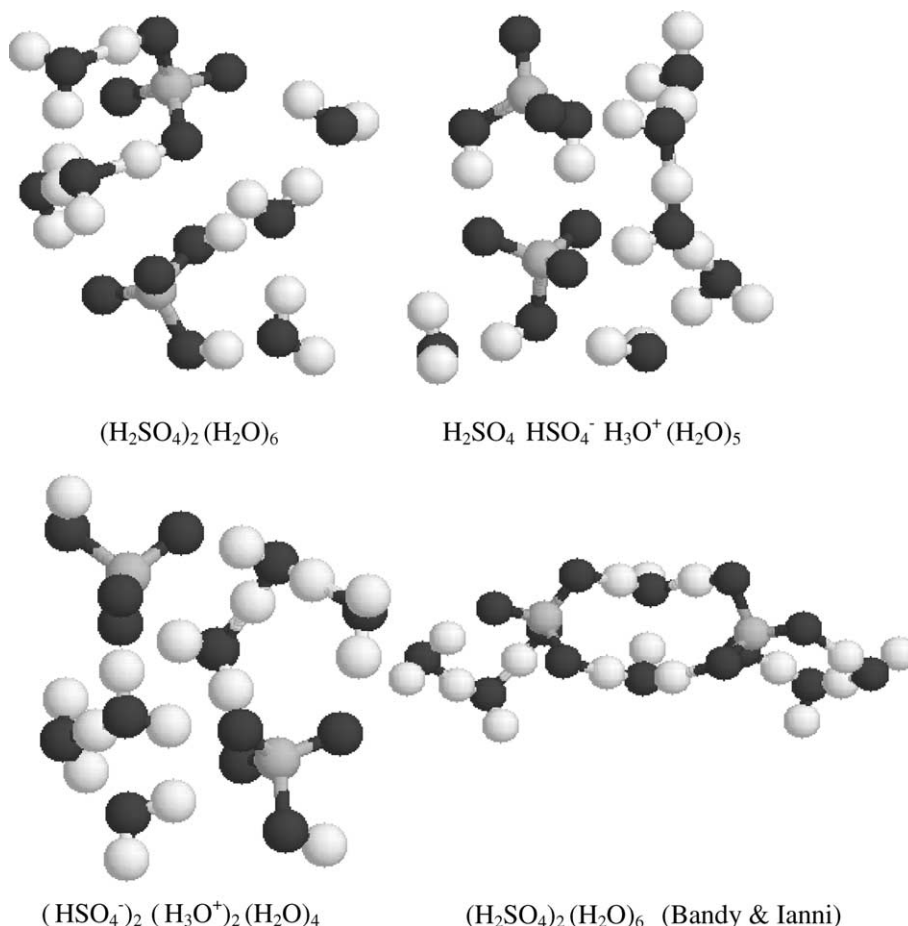


Fig. 8. Energetically favorable structures of $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_6$ for all three kinds of isomers. For comparison, the neutral clusters from Bandy and Ianni [27] are also given.

and Ianni [27]. In this case, our neutral structure is more compact and the number of hydrogen bonds is larger (12) than in the Bandy and Ianni structure (10 bonds) [27]. Our neutral isomer is more stable by 4.6 kcal/mol using the potential developed here and by 4.0 kcal/mol using DMol³. A more detailed ab initio study of two sulfuric acids will be published later [28].

Finally, we carried out long MD simulations of the $(\text{HSO}_4^-)_2(\text{H}_3\text{O}^+)_2(\text{H}_2\text{O})_{48}$ cluster at 250 and 280 K. The computational details are identical with the previous simulation. The duration of the simulation was 6 ns in both temperatures. We report here only the results of the colder cluster. The data of the warmer cluster were very similar. The behavior of the hydroniums were very similar as before, they resided mostly on the surface of the cluster, and the S–O distances varied a lot. The HSO_4^- – H_3O^+ contact pairs had somewhat higher probability than in the case of one sulfuric acid; there existed at least one contact pair during ca. 20% of the simulations, giving a 10% probability per sulfur atom compared with the 7% previously. The new information is the behavior of the sulfuric acids. The S–S distance show that the HSO_4^- – HSO_4^- contact pair is rather common. Using a 5.1-Å cut-off, their probability is ca. 75%. The average S–S distance of the contact pair configurations was 4.6 ± 0.1 Å. The remaining non-contact ion pairs consisted of different solvent separated pairs. The hydroniums were usually far from each other, the average distance being 10.3 ± 0.2 Å.

3.4. Comparisons to some other models

The sulfuric acid–water interactions have been modelled by several groups in the past [9,10,18]. From our point of view, the most relevant are the Kusaka et al. [9] and Kathmann and Hale [10] models. The details of these models can be found in the original papers. The comparison to the Kusaka model is easy and the results are shown in Tables 3 and 4. We see immediately that this parameterization will give ca. 50% higher binding energies than our model or the ab initio calculations. The trend is systematic and starts already with the first water. The main reason to this are the large effective charges of the sulfuric acid used by

Kusaka et al. With the larger clusters (up to 96 waters), the Kusaka model predicts that the ions will form only contact ion pairs. Our model, on the other hand, predicts that the HSO_4^- and H_3O^+ ions are usually rather far from each other. Thus the ions are much stronger bonded in the Kusaka model than in ours.

Another feature of the Kusaka model that differs from our potential is that the *neutral* clusters are more stable than the ionic ones up to clusters with 6 waters ($n = 6$, $E(\text{neutral}) = -89.7$ kcal/mol, $E(\text{ionic}) = -90.8$ kcal/mol, $n = 10$, $E(\text{neutral}) = -141.1$ kcal/mol, $E(\text{ionic}) = -145.4$ kcal/mol). This is in contradiction to the ab initio calculations. We feel that the Kusaka et al. model has too high effective sulfuric acid charges and thus too strong acid–water and acid–acid interactions. When we optimized our parameters we used nine ab initio structures for the neutral isomers and six structures for the ionic ones, while Kusaka et al. used only one neutral and one ionic geometry.

The comparison to the Kathmann and Hale model is problematic. They have constructed a model for $\text{SO}_4^{2\delta}-$ and proton H^δ , where δ is ca. 0.2. This model can be used for neutral clusters but the ionic clusters become strange. The charges of $\text{HSO}_4^{\delta-}$ and $\text{H}_3\text{O}^\delta$ are ca. 0.2 instead of unity. This is in contradiction to the fact that the charges of these ions are close to 1, which is also seen in the calculations of Re et al. [7]. Furthermore, this model does not take into account the OH-bond forming and breaking energies, which are substantial – we used 144 kcal/mol for the $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+$ reaction. We did some calculations with the Kathmann–Hale model, and obtained structures that were entirely different from any of ours. For example, one hydrogen receded between the three oxygens of the HSO_4^- . However, even if the structures were strange, the energies (at 300 K) were close to the ab initio values with $E = -13$ kcal/mol for $n = 1$ and $E = -34$ kcal/mol for $n = 4$.

3.5. Equilibrium structures of $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_n$ at 350 K and ca. 300 K

In order to study the water absorption to sulfuric acid we did MD simulations of H_2SO_4 and

water at two relative humidities (RHs) and at ca. 300 and 350 K. We are interested of how many water molecules are bound to the acid. For comparison to the model presented here we also studied two other water models, namely the SPC/E and MSPC/E [29]. The calculations were done using a cubic box and 100 water molecules. No cut-offs or Ewald method were used for the long range Coulomb interactions. The timestep was 1.2 fs Nose–Hoover thermostat was used to control the temperature of the system. The RH's were ca. 50% and 100% using the computed gas saturation density as reference. The actual RH's and other data are given in Table 6. In this simulations, our main problem was that we did not know the saturation density of our water model. We did some nucleation simulations to estimate this saturation density at 300 K. Our estimation is 2.3×10^{-4} g/cm³. For the other models, the saturation densities are known. The used densities were: 1.48×10^{-5} g/cm³ (SPC/E, 314 K), 9.0×10^{-5} g/cm³ (SPC/E, 350 K), 1.56×10^{-5} g/cm³ (MSPC/E, 300 K), 2.0×10^{-4} g/cm³ (MSPC/E, 350 K) [29].

All models will produce rather small clusters. At 314 K and 50% RH the SPC/E model will basically leave the sulfuric acid unhydrated. The MSPC/E is more realistic, it will produce clusters which on average have 1.2 waters around the sul-

furic acid (50% RH). Our model will produce clusters containing 1.3 waters at 50% RH [0% free acid, 70% monohydrate, 28% dihydrate and 2% trihydrate] and 0.7 waters at 23% RH. These numbers can be compared with experiments. Using the equilibrium constants ($K_1 = 0.13 \pm 0.06$ and $K_2 = 0.016 \pm 0.006$) from Hanson and Eisele [13] at 298 K there would be 1.3 waters around the acid [8% free acid, 51% monohydrate and 41% dihydrate] [30] at 50% RH and 1.0 waters [20%, 59%, 20%] at 23% RH. One should note that Hanson and Eisele did not include the trihydrates to their model due to the large scatter of their data at higher RH's. The trihydrates are rather important to the average cluster size. Using $K_3 = 0.005$ the average number of waters (at 50% RH) will increase to 1.5% and 10% of the clusters are trihydrates. It would be interesting to make a more detailed comparison with distributions but the statistic of the simulations is not very good. The trihydrate is interesting because the proton transfer will happen at this size and the formed double ion cluster should be more attractive for water and this will enhance nucleation.

From the data at ca. 300 K, we can conclude that our sulfuric acid model with the SPC/E water does result too low hydration [31] but when the water is modelled with our model or MSPC/E the

Table 6
Number of water molecules around the sulfuric acid using various water models and temperatures

| <i>T</i> (K) | Appr. RH (%) | This model (RH) | SPC/E (RH) | MSPC/E (RH) | Exp. (<i>T</i> = 298 K) [13] |
|--------------|--------------|-------------------------------|--------------------------------|------------------------------------|-------------------------------|
| 350 | 100 | | 0.74 (99%) sa/w [35,57,8,0] | 4.0 (93%) sa/w [0,0,4,43,21,31] | |
| 350 | 50 | | 0.42 (50%) sa/w [60,38,2,0] | 1.4 (49%) sa/w [5,60,24,10,1] | |
| 314 | 100 | | 1.0 (99%) sa [0,98,1,0] | | |
| 314 | 50 | | 0.1 (50%) w [94,6,0,0] | | |
| 300 | 100 | | | 1.1 (97%) sa [0,90,10,0] | |
| 300 | 50 | 1.3 (50%) sa [0,70,28,2] | | 1.2 (48%) sa [0,79,21,0] | 1.3 (50%) [8,51,41] |
| 300 | 22 | 0.7 (23%) sa/w [30,66,4,0] | | | 1.0 (23%) [20,59,20] |

The reported relative humidities (RHs) based on the actual simulations and calculated water saturation densities. Below in each line is the average cluster size distribution (in %), [free acid, monohydrate, . . . , *n*-hydrate and larger] [30]. The 'w' or 'sa' means the nature of the largest cluster in these simulations. 'w' stands for water, 'sa' means that the sulfuric acid is in the largest cluster and 'w/sa' that the clusters are similar in size. The data with rather poor statistic are marked with italics.

results are in agreement with experiments. The experiments of McGraw and Weber [12] are also in agreement with Hanson and Eisele indicating that the sulfuric acid is solvated but less than the classical theory predicts. Kusaka et al. [9] have also studied the stable clusters. Their model will predict at 39% RH and 300 K that the tetrahydrate would be the dominant species, which result stronger hydration than the classical theory predicts. Thus the Kusaka model will result to too strong hydration.

An other observations that can be made from our simulations is the nature of the largest cluster. It would be natural to assume that the largest cluster will contain the sulfuric acid because the sulfuric acid will help nucleation significantly. The situation in the simulations is not very clear. Some times the acid dominates, some times the waters and often they are of same size.

4. Conclusions

We have constructed a very reliable empirical pair potential model for sulfuric acid and water. This model reproduces well the *ab initio* results of Re et al. Unfortunately there are very few experimental results that can be compared to the calculated values here. Hanson and Eisele [13] have estimated the two first equilibrium constants of sulfuric acid hydration at 298 K. From them one can compute that there will be 1–1.5 waters around the sulfuric acid at RH's 20–50%. This is in good agreement with our model. From these equilibrium constants Hanson and Eisele have calculated the free energies of $n = 1$ and $n = 2$ clusters to be 3.6 ± 1 kcal/mol and 2.3 ± 0.3 kcal/mol, respectively [13]. The theoretical free energies in [7] are 2.4 and 2.0 kcal/mol.

The comparison of our model to the models proposed by Kusaka et al. [9] and Kathmann and Hale [10] indicated very large differences in the energies of the clusters. The Kusaka model also gives qualitatively different results of the acid–water dynamics in the larger clusters compared with our model. The Kathmann–Hale model, on the other hand, is somewhat unconventional from the molecular point of view, and yields structures that should be viewed with caution. This empha-

sizes that the search for a reliable sulfuric acid–water potential is probably not yet over, especially so as very little molecular level experimental data are available for reliable testing of the models.

Our model gives very reasonable results for larger cluster containing one or two sulfuric acids. Our MD simulations of the larger clusters show that the hydronium ion is always on the surface of the cluster and the bisulfate ion inside the cluster. As a result the cluster can have a large dipole moment which is probably important for nucleation. A cluster with large dipole moment will attract water molecules from the gas phase more, thus accelerating the condensation process. Another factor enhancing the nucleation is the larger total binding energy of the ion containing clusters. This will reduce the evaporation coefficient of the clusters significantly. We will address these issues more in a MD study of nucleation we are currently carrying out. Another important general finding is that the second sulfuric acid does not prevent the protonation of the acid molecules. In the presence of one sulfuric acid, three waters seem to be enough to protonate it. With two sulfuric acids, four waters appear to be enough to protonate both of them [28].

In summary, we think that the potential developed here is very suitable for modeling sulfuric acid–water interactions in small clusters. The potential can be used both in molecular dynamics and in Monte–Carlo simulations. We believe that it will prove useful in further studies of cluster structures and in understanding the molecular level mechanisms of sulfuric acid–water nucleation.

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