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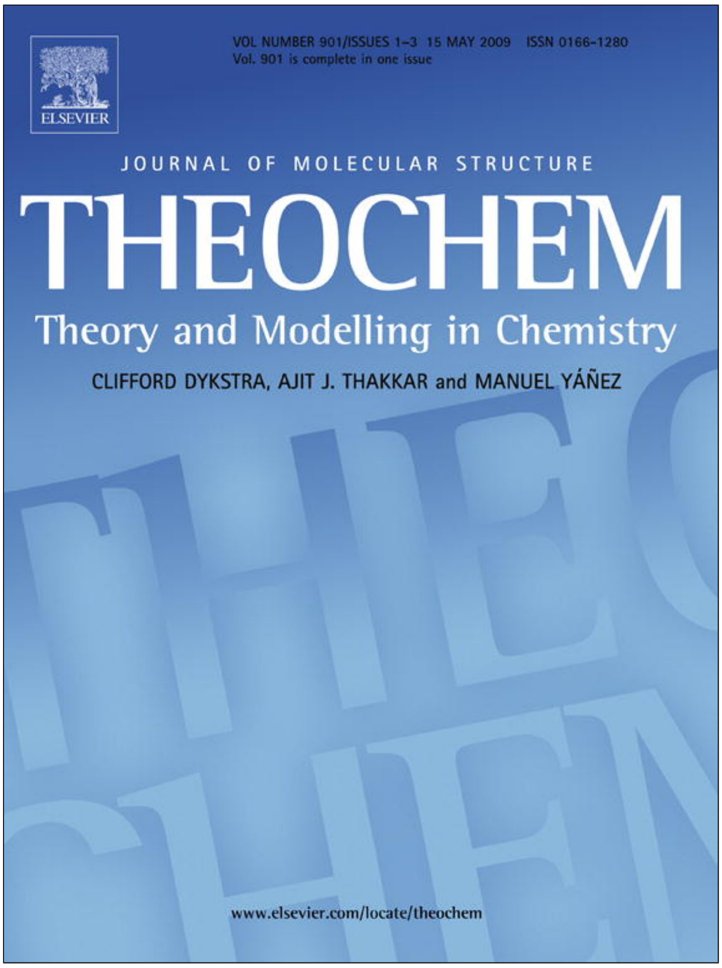
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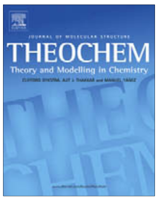

The sign preference in sulfuric acid nucleation

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ABSTRACT

The binding of sulfuric acid to a series of anions and cations of varying chemical complexity is studied using quantum chemical methods. Sulfuric acid is bound much more strongly to anions than cations, as expected from structural and general chemical considerations, and previous computational studies on charged sulfuric acid–water clusters. The results are likely to explain the sign effect observed in atmospheric nucleation phenomena, and indicate that the first steps of ion-induced nucleation are controlled by the specific chemical interactions between the core ion and the condensing molecules rather than by general physical (*e.g.* electrostatic) effects.

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1. Introduction

Sulfuric acid is thought to be one of the most important molecules participating in new-particle formation through nucleation in the troposphere and lower stratosphere [1]. While the majority of atmospheric new-particle formation is likely to occur via neutral pathways especially in the lower troposphere [2], ion-induced nucleation always contributes some fraction, and its importance is likely to increase with altitude [3]. In several experimental studies [4–10], the ion-induced component of atmospheric nucleation has been observed to be related predominantly to negative clusters. While this so-called sign effect is puzzling if treated from a purely macroscopic physical point of view, it can easily be rationalized in chemical terms, especially if sulfuric acid is assumed to be the molecule responsible for the first steps of nucleation. In this paper we give a qualitative chemical justification for the negative sign preference of sulfuric acid nucleation, and demonstrate the effect quantitatively using quantum chemical calculations.

Sign preference in ion-induced nucleation has recently been the focus of several investigations [11–16]. Nadykto et al. [14] demonstrated that the sign effect for any given vapor–ion combination can relatively easily be predicted based on the quantum chemically calculated, or experimentally measured, binding energies or complexation free energies of a small set of cluster structures corresponding to the first few vapor molecules clustering around the core ion. In a very recent study, Nadykto et al. [17] compared the binding of sulfuric acid and water to clusters containing HSO_4^- and H_3O^+ core ions, and found that sulfuric acid is significantly more strongly bound to the HSO_4^- clusters, indicating a negative sign preference. In this study, we extend their analysis to encompass a series of other core ions of varying degrees of chemical complexity.

2. General reasoning

While accurate energy models (in practice, quantum chemistry methods) are required to give quantitative predictions for sign preference in ion-induced nucleation, qualitative predictions or explanations can, at least for some systems, be made based on relatively simple chemical concepts such as partial charges, hydrogen bonding and acidity or basicity. For example, the alleged preference of water molecules to negative ions rather than positive ones [5,6,11,15] could be explained by the simple fact that water contains two hydrogen atoms with partial positive charges ($+\delta$) but only one oxygen atom with a partial negative charge (-2δ). Since unlike charges attract, a single water molecule could thus, in principle, form two bonds to a negatively charged ion, but only one bond to a positively charged ion. (The term "bond" here refers loosely to any interaction involving orbital overlap.) If the $H^{+\delta}\cdots X^-$ and $O^{-2\delta}\cdots Y^+$ bond lengths were equal and the interaction were purely electrostatic, the difference would not matter, as the magnitude of the negative partial charge of the water oxygen atom is exactly twice that of the positive partial charge on the hydrogen atoms. (Or, to put it another way, the strength of an electrostatic charge–dipole attraction depends only on the magnitudes, not the signs, of the charge and dipole.) However, due to the small size of the hydrogen atom, the $H^{+\delta}\cdots X^-$ bond lengths could, in general, be expected [11] to be somewhat shorter than the $O^{-2\delta}\cdots Y^+$ bond lengths, leading to a stronger net bonding for the anion–water

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clusters. Also, the energy of real chemical bonds will, in addition to electrostatic contributions, contain contributions from *e.g.* exchange-repulsion, polarization, charge transfer or dispersion interactions, which are not directly proportional to the strength of the electrostatic interaction.

Unfortunately, the issue is complicated by geometrical factors. If the X^- ion is small (*e.g.* a monatomic ion such as Cl^-), the formation of two $H^{+\delta}\cdots X^-$ bonds from the same water molecule will not be energetically favorable because the O–H–X angles for such a cluster would be far too small for efficient orbital overlap. (Alternatively, the $H^{+\delta}\cdots X^-$ bond lengths corresponding to favorable O–H–X angles would be far too large.) Thus, the minimum-energy geometry for *e.g.* $H_2O\cdot Cl^-$ contains only one H···Cl bond, not two [18], and water molecules are, on average, more attracted to monatomic positive ions than monatomic negative ions [14]. For larger, polyatomic ions, even more geometrical factors need to be considered. For charged but chemically inert clusters that are large enough to form two bonds to a single water molecule without the O–H-cluster bond angles being excessively bent (such as the >10 nm SiO_2 particles studied by Chen and Cheng [15]), a slight negative sign preference might be predicted on the basis of the above discussion. Anionic molecular ions with multiple binding sites, such as $NO_3{}^-$, could also be expected to be particularly efficient at binding water molecules. On the other hand, in the ion-induced nucleation of pure water, a positive sign preference could be expected (and has been observed in molecular dynamics studies [19]), as the H_3O^+ ion can form bonds to the oxygen atoms of three water molecules (one for each hydrogen), while the OH^- ion will only form one bond to the hydrogen atom of one water molecule (plus possibly a quite weak $OH^-\cdots OH_2$ bond).

For ions and/or condensing molecules with strong acid or basic characteristics, proton transfer reactions may also affect the binding. If the condensing molecule is an acid and the core ion is an anion able to act as a base (X^-), then reactions of the type

$$HA + X^- \Rightarrow A^- \cdot HX$$

may occur. (Here, HA indicates any acid molecule and A^- the corresponding conjugate base.) Even if proton transfer does not occur for the isolated $HA\cdots X^-$ pair, the acid nature of HA is likely to significantly strengthen the $H\cdots X^-$ bonding. Also, proton transfer may be catalyzed by the condensation of further molecules onto the $HA\cdot X^-$ dimer cluster. Similarly, acidic cations of the type XH^+ may be expected to bond strongly and/or donate protons to condensing molecules capable of acting as bases (*e.g.* H_2O, NH_3 and various amines). The confusion surrounding sign preference in nucleation mechanisms involving water may well be related to the fact that water is capable of acting as both an acid and a base, and its binding to ions will thus depend very strongly on, not only the ion sign, but on the chemical identity (and specifically, the acid–base nature) of the core ion.

From a simple "bond-counting" point-of-view, the negative sign preference in atmospheric nucleation (assumed here to be dominated by sulfuric acid) may be slightly surprising, as the H_2SO_4 molecule can form two bonds via its positively partially charged S—O—H hydrogen atoms and two bonds via its negatively partially charged S=O oxygen atoms. (Since bonding to the S—O—H oxygen atoms is also possible we might indeed expect sulfuric acid to show a slight positive sign effect.) On the other hand, in terms of acid–base chemistry, the observations are hardly surprising, as sulfuric acid is a strong acid, and thus likely to bond strongly to any negative ion with even the slightest basic characteristics. Furthermore, it should be noted that the three-member S—O—H groups are much more flexible than the two-member S=O groups. Thus, the sulfuric acid molecule can "grab" negative ions with its S—O—H "claws", while no such flexibility is possible for bonding to positive ions. Therefore, both chemical and geometric considerations indicate that sulfuric acid nucleation is likely to display a strong negative sign preference, as demonstrated recently for the specific case of charged sulfuric acid–water clusters [17].

It should be noted that although the sign preference phenomenon is related to orbital overlap and is thus "quantum–mechanical" in the same sense as all chemical interactions, it does not involve any specific quantum–mechanical behavior of atomic nuclei, such as tunneling. In any case, it appears clear that, regardless of terminological issues, quantum chemical models are, at present, the only simulation methods capable of accurately describing and predicting sign preference.

3. Computational results

To demonstrate the role of chemical interactions in sulfuric acid ion-induced nucleation, we have computed the binding energies and Gibbs free energies of complexation for sulfuric acid with six simple inorganic ions: OH^-, H_3O^+, Li^+, F^-, Na^+ and Cl^- at a moderately high level of theory. To assess whether or not the conclusions drawn from these simple species can be applied to more chemically complicated ions present in the atmosphere, qualitatively reliable data for dimer clusters of sulfuric acid with the cations ammonium ($NH_4{}^+$) and dimethylammonium ($(CH_3)_2NH_2{}^+$), and the anions formed by the deprotonation of limonic acid ($C_9O_4H_{14}$) and limononic acid ($C_{10}O_3H_{16}$) to form their conjugate bases ($C_9O_4H_{13}{}^-$ and $C_{10}O_3H_{15}{}^-$, respectively) have also been computed. These anions and cations were selected based on experimental studies indicating that amines or amine salts [20] on one hand, and oxidation products of limonene [21] on the other hand, may be involved in atmospheric nucleation. Data for various neutral dimers are given for comparison in order to qualitatively compare the interaction energies of "typical" neutral and ionic clusters.

For the simple inorganic ions, the geometries and vibrational frequencies have been computed at the MP2(full)/6-311++G(3df,3pd) level [22,23] using the Gaussian 03 program suite [24] with default convergence criteria (3×10^{-4}, 4.5×10^{-4} and 1×10^{-6} atomic units with respect to the root mean square force, maximum force and electronic energy, respectively). For the more complicated ions, the multistep methodology described by Ortega et al. [25], employing BLYP/DZP geometries and vibrational frequencies with RI-MP2 or RI-CC2 energy corrections with the Spartan [26], SIESTA [27] and Turbomol [28] programs, has been used. Due to the large size of the organic ions, the final electronic energies have, in these cases, been computed at the RI-MP2(frozen-core)/aug-cc-pV(T+d)Z level instead of the more demanding (but only slightly more accurate) RI-CC2/aug-cc-pV(T+d)Z level. In all cases, qualitative estimates of the complexation Gibbs free energies (at 298 K and 1 atm reference pressure) have been computed using the rigid rotor and harmonic oscillator approximations. The formation energies for $H_2SO_4\cdot NH_3$ and $H_2SO_4\cdot NH_4{}^+$ clusters have been computed at both levels of theory employed in this study in order to assess the possible differences between the methods.

The computed binding energies and Gibbs free energies of complexation for clusters of sulfuric acid with H_2O, OH^-, H_3O^+, Li^+, F^-, Na^+ and Cl^- are presented in Table 1. The corresponding cluster structures are shown in Fig. 1. All structures are drawn using the MOLEKEL 4.3 visualization package [29]. The binding energy data for $H_2SO_4\cdot H_2O$ are in good agreement with the higher-level data previously reported by Kurtén et al. [30], indicating that the neglect of higher-order correlation in this study is likely to cause only minor errors. Accurate free energies would require the inclusion of anharmonic vibrational effects [16], but as the focus here is a semi-quantitative comparison of binding energetics this would not be cost-effective; the errors caused by anharmonicity on the complexation free energies of hydrogen-bonded dimers are likely to be only on the order of 1–2 kcal/mol [30].

Table 1
Electronic energies and standard Gibbs free energies (at 298 K and 1 atm reference pressure) for dimer-forming reactions involving sulfuric acid and various simple molecules or ions, at the MP2(full)/6-311++G(3df,3pd) level.

Reaction	ΔE_{elec} (kcal/mol)	$\Delta G°$ (kcal/mol)
$H_2SO_4 + H_2O \Rightarrow H_2SO_4{\cdot}H_2O$	−13.5	−3.0
$H_2SO_4 + H_3O^+ \Rightarrow H_2SO_4{\cdot}H_3O^+$	−34.8	−28.0
$H_2SO_4 + OH^- \Rightarrow HSO_4^-{\cdot}H_2O$[a]	−95.6	−84.6
$H_2SO_4 + Li^+ \Rightarrow H_2SO_4{\cdot}Li^+$	−37.7	−31.5
$H_2SO_4 + Na^+ \Rightarrow H_2SO_4{\cdot}Na^+$	−27.2	−20.2
$H_2SO_4 + F^- \Rightarrow \Rightarrow HSO_4^-{\cdot}HF$[b]	−81.2	−74.4
$H_2SO_4 + Cl^- \Rightarrow H_2SO_4{\cdot}Cl^-$	−46.8	−39.9

[a] No metastable $H_2SO_4{\cdot}OH^-$ was found; proton transfer is likely barrier less.
[b] A $H_2SO_4{\cdot}F^-$ transition state with ΔE_{elec} of −76.3 kcal/mol was also found.

For each stoichiometry, several input configurations were generated, and in some cases more than one minimum-energy geometry were found in the subsequent geometry optimizations. Only the results for the most stable structures are reported here. Cartesian co-ordinates and energetics of all identified minima are reported in the Supplementary information. In the geometry optimization, the $H_2SO_4{\cdot}OH^-$ cluster immediately rearranged to give $HSO_4^-{\cdot}H_2O$, which is not surprising given that H_2SO_4 is a much stronger acid than H_2O. We were unable to find any metastable structures corresponding to $H_2SO_4{\cdot}OH^-$. A similar phenomena occurred also for the $H_2SO_4{\cdot}F^-$ cluster, where the initial structure found in the geometry optimization corresponded to a transition state (*i.e.* one of the vibrational frequencies were imaginary), and a subsequent optimization (with second derivatives calculated at each step) showed the global minimum to be $HSO_4^-{\cdot}HF$. This is consistent with gas-phase deprotonation reaction energies [31], which indicate that H_2SO_4 is a significantly stronger acid than HF in the gas-phase. Based on chemical intuition, the $H_2SO_4{\cdot}H_3O^+$ cluster might be expected to contain two H-bonds from H_3O^+ hydrogen atoms to S=O oxygen atoms. (This pattern is indeed seen for $H_2SO_4{\cdot}NH_4^+$, as described below.) However, the global minimum structure (to which all input geometries with two hydrogen bonds rapidly reverted) corresponds to a cluster with single, abnormally short, H-bond. Closer inspection reveals that the hydrogen in question is almost equally shared between the H_3O^+ and H_2SO_4 molecules, as the $H{\cdots}OH_2$ distance (1.135 Å) is only slightly shorter than the $H{\cdots}O{=}S$ distance. It is possible that this prediction of a shared proton may be an artifact of the method used. However, MP2 with a large basis set should give quite reliable structures for hydrogen-bonded clusters. In any case, the level of theory required to obtain significantly more reliable results (*e.g.* CCSD(T) and a quadruple-zeta basis set) would be computationally far too demanding for geometry optimizations on this cluster. An optimization at the PW91/6-311++G(3df,3pd) level (the method used by Nadykto et al. [14,17]) yielded a similar structure as the MP2 calculation. The ions in the minimum-energy structures for $H_2SO_4{\cdot}Na^+$ and $H_2SO_4{\cdot}Cl^-$ clusters are all bonded to two atoms of the sulfuric acid molecule (S=O oxygens for the cation and S—O—H hydrogens for the anion), while the minimum-energy structure for $H_2SO_4{\cdot}Li^+$ contains only one ion-molecule bond. No other minima were found for the $H_2SO_4{\cdot}Cl^-$ cluster, while alternate isomers for $H_2SO_4{\cdot}Na^+$ and $H_2SO_4{\cdot}Li^+$ with one and two bonds, respectively, were identified (see the Supplementary information for energetics and coordinates). Due to its larger flexibility and thus higher entropy, the single-bonded $H_2SO_4{\cdot}Na^+$ isomer was actually slightly lower (by 1.2 kcal/mol) in free energy than the double-bonded one, though the latter was more stable with respect to the electronic energy. The different structure of the minimum-energy geometries for the $H_2SO_4{\cdot}Na^+$ and $H_2SO_4{\cdot}Li^+$ clusters is likely due to the difference in bond lengths: as the lithium ion is much smaller, the optimal $Li^+{\cdots}O{=}S$ bond length is much shorter, and a double-bonded structure would therefore require much smaller (and thus more strained) bond angles.

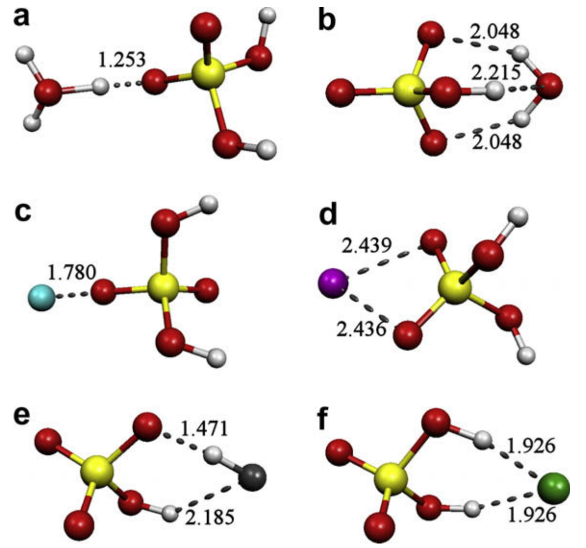

Fig. 1. The minimum-energy structures (at the MP2(full)/6-311++G(3df,3dp) level) of dimer clusters containing H2SO4 together with various simple ions: (a) $H_2SO_4{\cdot}H_3O^+$, (b)$HSO_4^-{\cdot}H_2O$, (c) $H_2SO_4{\cdot}Li^+$, (d) $H_2SO_4{\cdot}Na^+$, (e) $HSO_4^-{\cdot}HF$, (f)$H_2SO_4{\cdot}Cl^-$. Ion–molecule interactions are indicated by dashed lines, with distances given in Ångström. Color coding: yellow = sulfur, red = oxygen, white = hydrogen, light blue = lithium, violet = sodium, grey = fluorine and green = chlorine. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

It can be seen from Table 1 that sulfuric acid is significantly more strongly bound to the negative ions than the positive ions. For the special case of water and its two ionic forms, the difference in binding energies between negative and positive clusters is actually more than three times the difference in binding energies between the neutral and positive cluster. (The data by Nadykto et al. [17] indicates that the same trend persists for the addition of further sulfuric acid molecules to the clusters.) Thus, at least in this special case, the specific chemical interactions related to the ion sign are, in fact, much more important than the general physical electrostatic effects related to the presence of an electric charge. For the monatomic ions, the difference in binding energies between anionic and cationic clusters is somewhat smaller, but still considerable. For the ion pairs in the same row of the periodic table the differences are 19.6 kcal/mol and 43.6 kcal/mol for Na^+/Cl^- and Li^+/F^-, respectively. The stronger binding to sulfuric acid of Li^+ and F^- compared to Na^+ and Cl^-, respectively, is probably explained mainly by electrostatics: the lighter ions are smaller, but still carry the same charge, hence the bond lengths are shorter (by around 0.4–0.5 Å as seen from Fig. 1) and the bonds stronger. The binding energy of $H_2SO_4{\cdot}Cl^-$ is roughly similar to that of $H_2SO_4{\cdot}HSO_4^-$, which was computed by Ortega et al. [25] to be around 50 kcal/mol at the RI-CC2/aug-cc-pV(T+d)Z//BLYP/DZP level. The differences between binding energies obtained using different correlated *ab initio* methods are likely to be quite small compared to the differences in binding energies between *e.g.* the anionic and cationic clusters compared here.

In the two clusters in which proton transfer occurs, it should be noted that the reaction energies given in Table 1 are not really representative of the stability of the clusters with respect to dissociation. The electronic energy changes for the dissociation of $HSO_4^-{\cdot}H_2O$ into $HSO_4^- + H_2O$ and $HSO_4^-{\cdot}HF$ into $HSO_4^- + HF$ are only about +17 and +22 kcal/mol, respectively, at the MP2(full)/6-311++G(3df,3pd) level. (For comparison, the $HSO_4^- \cdot H_2O \Rightarrow HSO_4^- + H_2O$ dissociation energy was computed to be +15 kcal/mol in Ref. [30], using a high-level combination method including MP4 correlation.) The binding of sulfuric acid to anions which are conjugate bases of weaker acids should thus be seen primarily as formation route for the effectively nucleating [17] ion HSO_4^-, rather than as direct sources of extremely stable clusters.

In atmospheric conditions, the ions investigated in this study are not likely to be found in their free form, but in hydrated clusters together with one or more water molecules. Similarly, also sulfuric acid molecules are expected to be hydrated by one or two water molecules in most conditions [30]. The energetics for sulfuric acid–ion cluster formation will therefore be affected by the presence of water molecules in the clusters, and will in general depend on the relative humidity. Modeling the hydration of clusters is a computationally demanding task, as discussed *e.g.* by Kurtén et al. [32]. If the full effects of hydration were to be included, the ion clusters in Table 1 would have to be treated at a significantly lower level of theory. Since the sulfuric acid–ion binding energies are much higher than the acid–water binding energies, and (at least for the anionic clusters) also higher than typical ion–water binding energies, it is very unlikely that hydration would change the qualitative patterns described here. For example, the difference of 60 kcal/mol between the binding energies of sulfuric acid to OH^- and H_3O^+ is certainly much larger than any possible effect of hydration on the binding energetics. In their study on HSO_4^-–H_2SO_4–H_2O and H_3O^+–H_2SO_4–H_2O clusters, Nadykto et al. [17] found that the cationic clusters are more strongly hydrated than the anionic clusters. Especially the $HSO_4^- \cdot H_2SO_4$ cluster was predicted to remain unhydrated in atmospheric conditions, which may seem surprising given that both free HSO_4^- and free H_2SO_4 are strongly hydrated [30]. However, the observation is likely explained simply by the extremely strong binding between HSO_4^- and H_2SO_4: the binding of water is unfavourable simply because it disrupts the acid–ion bonding pattern. Due to this difference in the water affinities, hydration was found [17] to slightly decrease the differences in the binding of sulfuric acid to the clusters, but this did not change the qualitative conclusion that sulfuric acid prefers anions. The same is very likely to apply also to the clusters studied here.

Though the basis set used is rather large, we have also computed the basis-set superposition error for the clusters of sulfuric acid with monatomic ions using the counterpoise (CP) method [33]. This was done to check if there is a systematic difference in the basis-set superposition between anionic and cationic clusters related to, for example, the greater diffuseness of anionic orbitals [34]. (For the cluster containing the fluoride ion, the $H_2SO_4 \cdot F^-$ transition state was used in the calculation instead of the $HSO_4^- \cdot HF$ minimum geometry to keep the results comparable, and to avoid problems in defining the fragments for the CP calculation.) The results, presented in Table 2, indicate that while the BSSE values are rather high even for this large basis set, and the anions have somewhat larger absolute BSSE values than the cations, there is no systematic trend in the relative values – the largest and smallest BSSE as a percentage of the total binding energies occur for the cationic clusters, with the anionic clusters lying in between. Also, all the absolute BSSE values fall within 4 kcal/mol of each other; an order of magnitude less than the differences in binding energies. It should be noted that for large basis sets including diffuse functions, the counterpoise correction may somewhat exaggerate the real basis-set error for MP2 calculations [30,35]. In any case, it is clear that the inclusion of BSSE corrections does not change the qualitative ordering of the cluster stabilities and the central conclusions of this study.

Table 2
Basis-set superposition errors (BSSE) for selected clusters, computed using the Counterpoise method, at the MP2(full)/6-311++G(3df,3pd) level.

Cluster	BSSE energy (kcal/mol)
$H_2SO_4 \cdot Li^+$	1.8
$H_2SO_4 \cdot Na^+$	2.6
$H_2SO_4 \cdot F^-$ [a]	5.7
$H_2SO_4 \cdot Cl^-$	4.1

[a] Computed for the $H_2SO_4 \cdot F^-$ transition state, not the $HSO_4^- \cdot HF$ minimum.

Table 3
Electronic energies and standard Gibbs free energies (at 298 K and 1 atm reference pressure) for dimer-forming reactions involving sulfuric acid and various chemically complicated molecules or ions, at the RI-MP2(frozen-core)/aug-cc-pV(T+d)Z//BLYP/DZP level. (Values in brackets computed at the MP2(full)/6-311++G(3df,3pd) level.)

Reaction	ΔE_{elec} (kcal/mol)	ΔG (kcal/mol)
Neutrals		
$H_2SO_4 + NH_3 \Rightarrow H_2SO_4 \cdot NH_3$	−16.49 (−17.6)	−4.91 (−7.9)
$H_2SO_4 + (CH_3)_2NH \Rightarrow H_2SO_4 \cdot (CH_3)_2NH$	−23.85	−7.28
$H_2SO_4 + C_9O_4H_{14} \Rightarrow H_2SO_4 \cdot C_9O_4H_{14}$ [a]	−20.00	−6.54
$H_2SO_4 + C_{10}O_3H_{16} \Rightarrow H_2SO_4 \cdot C_{10}O_3H_{16}$ [b]	−21.93	−7.97
Anions		
$H_2SO_4 + C_9O_4H_{13}^- \Rightarrow H_2SO_4 \cdot C_9O_4H_{13}^-$ [a]	−45.31	−28.00
$H_2SO_4 + C_{10}O_3H_{15}^- \Rightarrow H_2SO_4 \cdot C_{10}O_3H_{15}^-$ [b]	−56.20	−48.23
Cations		
$H_2SO_4 + NH_4^+ \Rightarrow H_2SO_4 \cdot NH_4^+$	−20.26 (−22.7)	−9.93 (−14.7)
$H_2SO_4 + (CH_3)_2NH_2^+ \Rightarrow H_2SO_4 \cdot (CH_3)_2NH_2^+$	−18.50	−7.07

[a] Neutral or deprotonated form of limonic acid.

[b] Neutral or deprotonated form of limononic acid.

Table 3 lists the computed binding energies and Gibbs free energies of complexation for clusters of sulfuric acid with the neutral and cationic forms of ammonia/ammonium and dimethylamine/dimethylammonium, and the neutral and anionic (i.e. deprotonated) forms of limonic acid and limononic acid. The corresponding cluster structures are shown in Fig. 2. The data in Table 3 follow the same general pattern as that in Table 1: sulfuric acid is bound much more strongly to anions than to cations. For the specific cations and anions presented here, the acid–cation binding energies are close to the corresponding acid–neutral molecule binding energies, while the acid–anion binding energies are over twice as large. For the strong base/weak acid pair dimethylamine/dimethylammonium, the binding energy of the neutral complex is actually larger than that of the cationic complex. Again, the chemical sign effect related to structural issues and acid–base affinities is evidently stronger, and much more important, than the electrostatic effect related to the charge–dipole interaction.

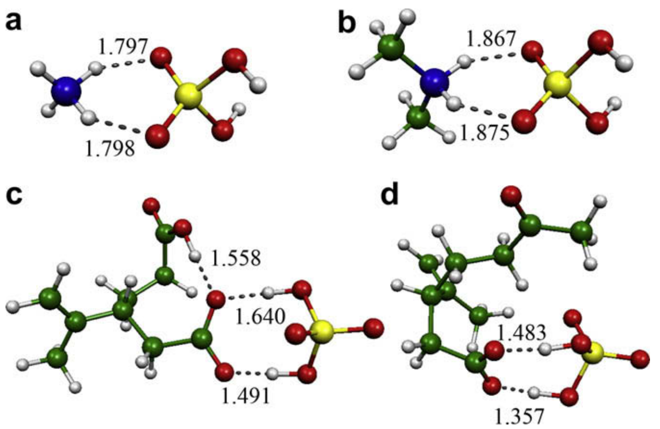

Fig. 2. The minimum-energy structures (at the RI-MP2(frozen-core)/aug-ccpV(T+d)Z//BLYP/DZP level) of dimer clusters containing H2SO4 together with various chemically complex ions: (a) $H_2SO_4 \cdot NH_4^+$, (b) $H_2SO_4 \cdot (CH_3)_2NH_2^+$, (c) $H_2SO_4 \cdot C_9O_4H_{13}^-$ (limonic acid), (d) $H_2SO_4 \cdot C_{10}O_3H_{15}^-$ (limononic acid). Ion–molecule interactions are indicated by dashed lines, with distances given in Ångström. Color coding: yellow = sulfur, red = oxygen, white = hydrogen, blue = nitrogen and green = carbon. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

The acid-ammonium and acid-ammonia binding predicted at the RI-MP2/aug-cc-pV(T+d)Z//BLYP/DZP level is somewhat weaker than at the MP2(full)/6-311++G(3df,3pd) level, especially with respect to the complexation free energies. This is probably partially due to the larger anharmonicity of MP2 vibrational frequencies compared to DFT ones. The difference between the methods is, in any case, small compared to the anion–cation differences.

The dimer containing the ion formed from limononic acid is significantly more strongly bound than that containing the ion formed from limonic acid, despite the fact that the latter contains more strongly polar functional groups that could be expected to participate in the bonding. The reason for this anomaly is probably that the limonic acid monomer (in both its neutral and deprotonated forms) is able to form strong internal hydrogen bonds, leading to relatively weaker complexation energies.

The binding energies of sulfuric acid to Cl^- and the two organic anions presented here are all in the range 45–55 kcal/mol, which is roughly similar to the 50 kcal/mol binding energy of $H_2SO_4{\cdot}HSO_4^-$ [25]. This is probably representative of the typical range of sulfuric acid–anion binding energies in the atmosphere.

4. Conclusions

Based on chemical considerations, and supported by quantum chemical results, sulfuric acid is shown to bind much more strongly to anions than to cations of varying chemical complexity. This is likely to be the reason behind the sign effect observed in atmospheric nucleation events. The effect of ion sign is shown to be much more important than the overall effect of charge. For strongly basic molecules such as amines, the neutral molecule–sulfuric acid binding energies may actually be larger than the corresponding cation–sulfuric acid binding energies. Sulfuric acid–anion binding energies are predicted to lie in the 45–55 kcal/mol range for a variety of different types of anions that might be found in the atmosphere. Our analysis demonstrates that sign preference, at least in the specific case of sulfuric acid nucleation, can be predicted qualitatively based on general chemical considerations, though quantum chemical calculations are needed to obtain quantitative values.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2009.01.024.

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