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On the stability and dynamics of (sulfuric acid)(ammonia) and (sulfuric acid)(dimethylamine) clusters: A first-principles molecular dynamics investigation

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ABSTRACT

The main pathway of new-particle formation in the atmosphere is likely to begin from small sulfuric acid clusters stabilized by other compounds, such as ammonia or amines. Here, we present the results of first-principles molecular dynamics simulations probing the stability and dynamics of (sulfuric acid)(ammonia/dimethylamine) clusters with two, three and four sulfuric acid molecules and a varying number of the bases. In each of the eight simulated clusters, an energetic equilibrium was reached and 35 ps of equilibrium data was collected in the $NVT(T = 300\ \mathrm{K})$ ensemble. The clusters exhibited pronounced thermal motion including rotations of the molecules within the clusters. Regardless of the continuous movement, the clusters stayed bound together. The calculated electric dipole moments were found to be sensitive to the thermal motion and consequently, large fluctuations were observed. In addition, the vibrational spectra for all the clusters were determined, indicating that the thermal motion differs from purely harmonic motion.

1. Motivation

Currently, one of the most pressing research problems the scientific community faces is the formation and growth of atmospheric aerosol particles. For example, some of these tiny particles take part in the processes deteriorating the quality of air, directly affecting the daily lives of millions of people [1]. On a grander scale, aerosol particles are intimately tied to the climate and climate change via different radiative processes [2]. The numerous and interconnected feedback mechanisms, ranging over several orders of magnitude in space and time, make aerosol particle formation and its consequences very elusive to study, both experimentally and theoretically [3]. Here, we adapt bottom-up approach to tackle the phenomenon: we present results from first-principles molecular dynamics simulations of atmospheric sulfuric acid clusters – thus concentrating on the smallest space and time regimes of sub-nanometer and -nanosecond.

The main driving agent of new-particle formation in the atmosphere is sulfuric acid [4,5]. However, the measured ambient concentrations of sulfuric acid are several orders of magnitude too small for it to alone explain the observed new-particle formation events and the acid alone does not account for most of the further aerosol particle growth either [6,7]. Traditionally, the explanation for the observations has been sought from some combination of sulfuric acid, water and ammonia "nucleating particles" [8]. The role of ions has also been extensively discussed [9,10]. However, state-of-the-art laboratory measurements concluded that sulfuric acid particle formation enhanced by ammonia and ions cannot explain the boundary-layer formation events [11]. Recently, the participation of various amines in the process has drawn a lot of attention. Theoretical studies, motivated by filter sample findings [12], first suggested that amines, such as dimethylamine, stabilize the smallest sulfuric acid clusters much more strongly than the standard candidate ammonia, and thus possibly enhance the particle formation more effectively [13,14]. The suggestion was later strengthened by various experiments, and further experimental and theoretical work has studied the clusters of sulfuric acid and amines [15–22]. The current paper continues this line of research: we focus on the dynamics and stability of sulfuric acid–ammonia and sulfuric acid–dimethylamine clusters.

The bulk of the previous theoretical studies have been static structure optimization calculations [23]. In such calculations, one typically tries to find the global minimum energy cluster as a function of the molecular coordinates, that is, to find the arrangement of the molecules in the cluster which minimizes the electronic

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ground state energy. Once such a cluster is found, all the molecular vibrations are often assumed to be harmonic. In addition, the clusters are most often assumed to rotate rigidly and the translational degrees of freedom are taken to be those of an isolated ideal gas particle. The partition function is then constructed under these assumptions, yielding various thermodynamical quantities via the machinery of statistical mechanics. This scheme includes the temperature and entropy into the electronic structure calculations, thus effectively interpolating the results from $T = 0$ K to, say, $T = 300$ K. The main shortcoming of the scheme is the lack of detailed and non-ideal descriptions of the kinetic energy contributions. To address this issue and to obtain insight on how the small clusters behave when the temperature and the kinetic energy are explicitly taken into account, we performed first-principles molecular dynamics (FPMD) simulations. One prior attempt has been performed to use FPMD on atmospheric (sulfuric acid)(base) clusters [24]. In that investigation, the threshold of proton transfer in hydrated sulfuric acid clusters (up to two acid molecules with six water molecules) with various bases was studied. The results differed partly from standard quantum chemical results [14], possibly due to the dynamical effects, demonstrating that dynamics of atmospheric sulfuric acid clusters should be studied in more detail.

Here, we extend the body of atmospherically relevant FPMD simulations in both size and simulation time: the largest cluster studied here contains four sulfuric acid and four dimethylamine molecules, and equilibrium data was collected for all the clusters for 35 ps (the simulation details are given in Section 2). To achieve this, one compromise had to be made: the exclusion of water. Although in the atmosphere there are several orders of magnitude more water than sulfuric acid, ammonia or dimethylamine, not much is currently known about the hydration state of the clusters formed by the latter molecules. Agreeably, FPMD would be a good method to investigate the role of water in the clusters, especially as water is often lost from small clusters during detection in the experiments. However, the inclusion of water molecules would increase the computational cost and complexity significantly, and thus it is left for future studies. Furthermore, as the main goal of the present paper is to study the dynamics and stability of sulfuric acid clusters, the exclusion of water might be a good first order approximation as the binding of sulfuric acid with water is considerably weaker than with ammonia or dimethylamine.

2. Simulations

We performed Born–Oppenheimer based first-principles molecular dynamics simulations, where the atomic nuclei evolve in time according to the classical equations of motion. However, the forces driving the dynamics are calculated from electronic structure theory [25,26]. All the simulations were performed using the CP2K program package (www.cp2k.org) and the forces were calculated within Kohn–Sham density functional theory as implemented in the Quickstep [25] module of CP2K. We used the PBE functional [27], which has been previously shown to work well for polar hydrogen-bonding liquids [28,29] and recently in the context of atmospheric clusters [30,31]. The density functional was used with a dual basis set method [26]: a doubly polarized triple-ζ Gaussian-type basis set in real-space and a plane-wave basis set with a cut-off of 600 Ry in the momentum-space. Norm-conserving GTH pseudo-potentials were used for the core electrons [32]. The convergence criteria for the wavefunction was 10^{-7} Hartrees. The size of the simulation box was $20 \times 20 \times 20$ Å^3 in all of the simulations.

Once the forces were obtained, the system was propagated in time with a timestep of 0.5 fs in the canonical *NVT* ensemble. The temperature was set to the ambient $T = 300$ K where every degree of freedom was controlled by individual Nosé–Hoover chain thermostats [33] with a coupling constant of 2000 cm^{-1}. The canonical ensemble was chosen as we wanted to observe how the small clusters behave under constant temperature. Especially, we were interested to see how the presumably stable clusters responded when the system possessed kinetic energy at $T \neq 0$ K conditions. Guided by a recent quantum chemical study [18], which extensively searched for the most stable molecular clusters, we chose six (sulfuric acid)$_m$(base)$_n$ clusters (with $m = 2, 3, 4$) separately with the two base molecules, ammonia and dimethylamine (henceforth, sulfuric acid will be abbreviated as SA, ammonia as Amm and dimethylamine as DMA). In this size range, the (SA)$_m$(Amm)$_n$ clusters with $n = m - 1$, and the clusters of (SA)$_m$(DMA)$_n$ with $n = m$ were found to be the most stable ones [18]. In addition to these six clusters, we included the clusters of (SA)$_3$(Amm)$_3$ and (SA)$_2$(DMA)$_1$ into this study, as the stability of these clusters was very close to the most stable ones [18], and further, it extended our data set in a way that we were able to directly compare the roles of the base molecules in the clusters of (SA)$_2$(base)$_1$ and (SA)$_3$(base)$_3$.

We took the initial geometries from the literature [18] and optimized the clusters with the level of theory used in the simulations. While it is true in general that the minima found with different methods are not necessarily the same, here this matter is of secondary importance: the optimized initial clusters were only used as starting points for the equilibration simulations. To be able to draw meaningful physical conclusions based on the simulations, the clusters need to be first equilibrated. Thus, only after the clusters had successfully reached an energetic equilibrium, 35 ps production run simulations were performed. All the analysis is based on the production runs. The results of the simulations are presented in the following section: first, we discuss the energetic and structural properties observed in the simulations, after which we focus on the electric dipole moments and on the vibrational–rotational spectra.

3. Results and discussion

3.1. Energetics and structural considerations

One of the motivating questions behind this investigation was to find out how the presumably stable atmospheric small clusters behave if the temperature is taken into account explicitly. One fundamental way to answer this question is to look at the energetics of the clusters. In Figs. 1 and 2 one can see the potential energy as a function of time over the whole trajectory for all the studied ammonia- and amine-containing clusters, respectively. There are at least two interesting features to notice.

First, an energetic equilibrium is reached in all of the clusters. Typically, this happened within a few picoseconds. The only cluster not to equilibrate within ten picoseconds, was the cluster of (SA)$_4$(Amm)$_3$. Curiously, even 45 ps was not enough to relax the structure. Intrigued by this, the simulation was continued. The cluster finally reached an equilibrium after ~55 ps. To ascertain this, and to collect equilibrium data for the cluster, the simulation was continued for another 35 ps.

In general, the bonding patterns in the studied clusters are largely dictated by proton transfers from sulfuric acid molecules to the base molecules. The proton transfers create ion pairs within the electrically neutral clusters and the resulting hydrogen bonds are relatively strong. In all of the initial starting structures, the base molecules had accepted one proton from the acids. In other words, all the ammonia molecules NH_3 were in the form of NH_4^+ and all the dimethylamine molecules $(CH_3)_2NH$ were in the form of $(CH_3)_2NH_2^+$, that is, as ammonium and dimethylaminium ions,