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The growth mechanism of sulfuric acid clusters: Implication for the formation of cloud condensation nuclei

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ABSTRACT

The investigation on the growth mechanism of sulfuric acid clusters is helpful for the understanding about the formation of cloud condensation nuclei. The sulfuric acid may aggregate in linear, bent, or orbicular modes with two types of hydrogen bonds, viz. OH…OH and OH…O=S. The length of the linear mode polymers increases linearly along with the degree of polymerization (DP). The bent conformation distorts into the linear configuration when the DP is over 6. The diameter of the central ring generated by OH…OH hydrogen bonds in orbicular conformation increases distinctly from 3.441 Å in tetramer to 7.543 Å in nonamer. The IR spectra exhibit distinct variations along with both the DP and the coupling modes. As can be employed to infer the detailed geometrical structures of sulfuric acid polymers. The linear structure is more stable as compared to the bent and the orbicular conformations. The variation of the Gibbs free energy indicates that the sulfuric acid can aggregate with a larger DP in linear mode. The temperature effect on the stability of the sulfuric acid polymer is more significant as compared with that of the pressure. The complex with high DP tends to be more stable at higher temperature, while the complex with low DP prefers low temperature. The findings are helpful for further study on atmospheric aerosol growth and the formation of cloud nucleation.

1. Introduction

The gas-to-particle conversion process of new particle formation generates the atmospheric aerosols (AA) and influences the concentration of ambient particulate matter. Atmospheric nucleation is the dominant source of aerosol particles in the global atmosphere and an important player in aerosol climatic effects. The AA degrade visibility, negatively affect human health, directly or indirectly influence climate by absorbing and reflecting solar radiation and modifying cloud formation, as well as impact the air quality. Furthermore, the AA scatters and absorbs solar and terrestrial radiation, as well as influences the formation and properties of clouds. The impacts of aerosol particles on clouds are the largest individual source of uncertainty in estimates of the Earth's energy balance (Tang, Cziczo, & Grassian, 2016). The structures and reactivities of the molecular clusters have attracted extensive attentions experimentally and theoretically. AA is the basis for the formation of cloud condensation nuclei (CCN). Some useful information for particle formation has been afforded, although the underlying chemical mechanisms of AA and CCN have not been elucidated. The lack of complete understanding of the role of AA and CCN on the climate system forms a bottleneck for reliable and accurate projections of climate change.

It has been observed that the atmospheric aerosol formation is essentially a two-step process, as proposed based on theoretical

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arguments (Kulmala, Kerminen, Anttila, Laaksonen, & O'Dowd, 2004; Kulmala, Pirjola, & Mäkelä, 2000) and laboratory experiments (Kulmala et al., 2013; Wagner and Strey, 2001). The disagreement between the ambient data and the experiments, which is related to experimental design and sulfuric acid nucleation in ultraclean laboratory conditions, can explain the atmospheric nucleation rates (Sipila et al., 2010). To reveal the role of sulfuric acid in the AA formation and the following formation of CCN, extensive efforts have been devoted. Johnston discovered that the sulfuric acid uptake onto the investigated clusters had a small activation free-energy barrier (Bzdek, Depalma, Ridge, Laskin, & Johnston, 2013; Depalma, Bzdek, Ridge, & Johnston, 2014). The formation and growth of molecular cluster containing sulfuric acid, water, ammonia, and dimethylamine were explored using a combination of Monte Carlo configuration sampling, semiempirical calculations, and density functional theory calculations (DePalma, Doren, & Johnson, 2014). Compared the interactions of sulfuric acid with trimethylamine and water, it is observed that the binding energies decrease with the increasing of water molecules (Xu and Fan, 2015) Stimulated by a series of studies concerned with the formation of sulfuric acid, the gaseous formic sulfuric anhydride was observed and characterized by microwave spectroscopy (Mackenzie, Dewberry, & Leopold, 2015). The characteristics involving the growth mechanism, the hydrate distributions, the influences of humidity and temperature, as well as the Rayleigh scattering properties were determined using a basin-hopping algorithm with the density functional theory (DFT) (Lv et al., 2015). The molecular interaction of pinic acid with sulfuric acid was studied by exploring the thermodynamic landscape of cluster growth, the favorable interactions between pinic acid and sulfuric acid imply that pinic acid could contribute to the subsequent growth of an existing nucleus by condensation (Elm, Kurtén, Bilde, & Mikkelsen, 2014). A computational study was executed on structures, hydration, and electrical mobilities of bisulfate ion-sulfuric acid-ammonia/dimethylamine clusters (Tsona, Henschel, Bork, Loukonen, & Vehkamäki, 2015). The protonation dynamics and hydrogen bonding in aqueous sulfuric acid were implemented combining simulations and experiments (Niskanen et al., 2015).

It has been demonstrated that the sulfuric acid is the key atmospheric nucleation precursor owing mainly to its low vapor pressure and the propensity to form strong hydrogen bonds (Herb, Nadykto, & Yu, 2011; Kuang, McMurry, McCormick, & Eisele, 2008; Kumar, Sinha, & Francisco, 2016; Petaja et al., 2009; Weber et al., 1996; Zhang, Khalizov, Wang, Hu, & Xu, 2012). The atmospheric nucleation rates depends on the sulfuric acid concentration, corresponding to a critical nucleus of four to nine sulfuric acid molecules, as agrees with predictions under classical nucleation theory (Berndt et al., 2005; McGraw & Zhang, 2008; Young et al., 2008; Zhang et al., 2004) Strongly bound dimer of sulfuric acid has been measured by means of chemical ionization mass spectrometry (Petäjä et al., 2011). It is imperative to precisely quantify the chemical makeup of the critical nucleus to improve models used to assess the environmental and climate impacts of aerosols (Zhang, 2010).

In this paper, the changes of structural characteristics, infrared spectra, as well as binding energies along with the growth of sulfuric acid molecules are explored employing the Becke's three-parameter Lee-Yang-Parr (B3LYP) exchange correlation functional within the DFT framework. The number of sulfuric acid in the cluster ranges from 2 to 9. The diameters of the orbicular clusters composed by more than 8 sulfuric acid molecules are larger than 1.0 nm. These sulfuric acid molecules interact through the hydrogen bonds, which play an important role in the formation of small atmospheric clusters. As can grow to form a critical nucleus and eventually an aerosol particle, that impacts climate (Kanakidoum et al., 2005). The emphasis is put on the variation of chemistry and physical properties along the degree of polymerization (DP) of sulfuric acid cluster to present some useful information on nucleation and aerosol growth.

2. Computational methods

The classical molecular dynamics (MD) simulations were conducted using the Forcite program of Materials Studio 6.0, (Accelrys Inc) with the COMPASS force field adopted. Sun (1998) The amorphous orthorhombic box containing 100 H_2SO_4 molecules (with a density of 1.84 g/cm^3) was first geometrically optimized through the energy minimization. The lattice parameters of the box are 20.683 Å in lengths and 90.0° in angles. MD simulations were then performed in the NPT ensemble for 200 ps, in which the Nose thermostat (Nose, 1984) and the Berendsen barostat (Berendsen, Postma, van Gunsteren, DiNola, & Haak, 1984) were used to maintain the temperature at 298 K and the pressure at 0.1 MPa, respectively. The particle motion was integrated by the velocity Verlet algorithm with a time step of 1 fs, and the trajectory frame was outputted every 20 fs. The long-range electronic interactions were calculated by the Ewald summation method. All atoms of H_2SO_4 molecules were allowed to move freely during the MD simulations.

The hybrid DFT methods have been proven generally effective and inexpensive in describing large free radicals and intermolecular complexes. The B3LYP functional donates results whose accuracy matches that of the best ab initio results. Especially, the reliability of the B3LYP/6–311 + + G (d, p) level has been established (Yan, Bu, Cao, & Li, 2004; Yan & Bu, 2005; Yan, Bu, & Li, 2005). The optimizations of sulfuric acid monomer and dimer are carried out employing several DFT functionals and MP2 method at 6–311 + + G (d, p) basis set. The results (Table S1) indicate the reliability of B3LYP functional. Therefore, the geometries of sulfuric acid clusters, $(H_2SO_4)_n$, where $2 \leq n \leq 9$, were optimized with the B3LYP (Becke, 1988, 1993; Lee, Yang, & Parr, 1988) DFT method in Gaussian09 (Frisch et al., 2010) at the 6–311 + + G(d, p) basis set. Accurate information about gas-phase molecular, electronic structure, and the stretching mode can be obtained from IR spectral analysis. In turn, it provides an important touchstone for computational studies. In addition, the absence of imaginary frequency in the IR vibrational spectra ensured that the optimized structures were local minina on the potential energy surfaces. The binding energy (E_b) is derived by subtracting the energies of monomers from that of the polymer. The zero-point vibrational energy (ZPE) is included in the calculation of E_b.