QUANTUM CHEMICAL STUDIES OF ATMOSPHERICALLY RELEVANT MOLECULAR CLUSTERS AND THEIR ROLE IN PARTICLE FORMATION

by

Joseph William DePalma, Jr.

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry and Biochemistry

Summer 2014

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ABSTRACT

The goal of this dissertation is to gain a more complete understanding of the chemical mechanisms governing new particle formation (NPF), a key process that influences the concentration of atmospheric particulate matter. NPF is a gas-to-particle process, first beginning with the nucleation of ambient vapors into small molecular clusters which then grow rapidly by condensation of additional trace vapors to larger, climatically relevant sizes. The climatically relevant size is greater than approximately 50 nm in diameter, where the newly formed particle may act as a cloud condensation nucleus (CCN), i.e. the seed for cloud droplet formation. CCN have important implications for Earth's radiation balance and it has been suggested that nearly 50% of all CCN arise from NPF. Despite the prevalence of this process, the early stages of NPF and how many of the newly formed particles go on to have climatic effects is not well understood, hindering climate modeling efforts. Further developing a fundamental, chemical understanding of exactly how NPF occurs will ultimately reduce the uncertainties in climate modeling.

In this dissertation, the tools of computational chemistry are used to explore various chemical aspects of NPF. The key species in NPF is sulfuric acid, but since sulfuric acid alone cannot explain observed nucleation and growth rates, other chemical species must be involved in the process most notably water, ammonia, amines and various types of carbon-containing molecules. NPF is often studied using mass spectrometric and optical spectroscopic techniques, but both have significant limitations. Mass spectrometry provides excellent information on the composition of

both molecular clusters and new particles but cannot provide explicit structural information and is limited to the detection of charged species. Optical spectroscopic techniques provide direct structural and energetic information but are limited in cluster size and composition that can be studied due to the need for ultracold trapping techniques. Computational chemistry is not limited by composition or charge and has a wide array of methods to span the structure space from the smallest cluster to the largest particle. As such, it is an ideal tool for studying NPF.

Cluster formation is a complex process that involves contributions from a variety of trace species in the atmosphere. In this work, a large variety of clusters of varying compositions and charges are examined, with the intent to compare studies on charged clusters to experimental information then extend to experimentally inaccessible uncharged clusters. Both inorganic-based and organic-based clusters are investigated. For the inorganic clusters, each polarity of cluster studied has a slightly different composition and are modeled as follows:

- 1. Positively charged clusters: $[(BH^+)_x(HSO_4^-)_{x-1}(H_2SO_4)_y]^+$ with $B = NH_3$, DMA; $2 \le x \le 11$; y = 0,1
- 2. Negatively charged clusters: $[(BH^+)_x(HSO_4^-)_{x+1}(H_2SO_4)_y]^-$ with $B = NH_3$, DMA; $1 \le x \le 4$; $0 \le y \le 3$
- 3. Uncharged clusters: $[(BH^+)_x(HSO_4^-)_x(H_2O)_y]$ with $B = NH_3$, DMA; $2 \le x \le 8$; $1 \le y \le 10$ (only for x = 4,5,6)

All inorganic clusters, independent of cluster composition or charge, have the maximum number of hydrogen bonds due to proton transfers between sulfuric acid and bases (whether ammonia or amines) in the cluster. The true driving force for cluster formation is electrostatic forces between the ions and molecules of the cluster;

an extensive network of hydrogen bonds is also important in cluster energetics. Total charge plays a significant role in cluster structure. Positively charged clusters contain only cation-anion hydrogen bonding interactions (except for those with a neutral sulfuric acid). Negatively charged and uncharged clusters contain cation-anion, anion-anion and ion-molecule interactions. For the uncharged clusters studied, water also plays a minor role in cluster structure, showing a bonding preference for more hydrophilic species such as sulfuric acid and ammonia over amines while inserting itself between ion-ion hydrogen bonds. This has the effect of offering mild cluster stabilization compared to anhydrous clusters.

The work in this dissertation explores different mechanisms for the formation of atmospherically relevant organic and inorganic molecular clusters, and indicates there are several energetically favorably pathways which clusters could grow. Amines such as dimethylamine are found to displace ammonia in ammonium bisulfate clusters across an array of cluster compositions. Amine substitution has both a size and charge dependence, occurring more favorably in smaller, positively charged clusters than in negatively charged or uncharged clusters. In addition, amine substitution is driven by the competition between the stronger binding of cluster-bound ammonium ions versus the stronger gas phase basicity of dimethylamine. The dependence on size and charge suggests amine clusters are likely important contributors to the sub-1nm ambient cluster pool. The addition of sulfuric acid to positively charged clusters of the form $[(NH_4^+)_x(HSO_4^-)_{x-1}]^+$ proceeds wth a small activation barrier, consistent with observations that the uptake of sulfuric acid into molecular clusters proceeds at or near the collision limit. The addition of ammonia to $[(NH_4^+)_x(HSO_4^-)_{x-1}(H_2SO_4)]^+$ clusters, however, has to overcome a substantial activation barrier. Therefore, since these

clusters are observed in ambient ion studies, cluster growth cannot proceed via the traditionally accepted simple neutralization mechanism and likely includes contributions from a variety of pathways.

The role of low volatility organic molecules in NPF is hotly debated but it is clear that they contribute to particle growth. In order to study how organic molecules impact NPF, the structures and thermochemistry of molecular clusters composed of the dimers of the oxidation products of α -pinene, such as *cis*-pinic acid, terpenylic acid and *cis*-pinonic acid were calculated. The non-covalent dimers form from ring-type hydrogen bonding between carboxylic acid groups; the covalent dimers form from classical organic reactions such as hydroperoxide formation. Gas and condensed phase modeling of dimer formation from these and other relevant α -pinene oxidation products indicate the hydrogen bound dimers, dehydrated aldols and hydroperoxides all have favorable dimerization free energies, and thus can form in sufficient concentrations to contribute to particle nucleation and growth as well as influencing fundamental chemical properties such as volatility.

From a broader perspective, the work in this dissertation shows that trace atmospheric gases such as sulfuric acid, ammonia, amines and oxidized organics are key players in the formation of new particles and ultimately are drivers of global climate. The formation of these clusters is a delicate balance between ambient concentration, thermodynamics and kinetics. Nitrogenic species such as amines are important contributors to the nucleation of new particles whereas highly oxidized low volatility carbonaceous species contribute to the continued growth of freshly nucleated particles.

Chapter 1

INTRODUCTION AND METHODS

1.1 Aerosols and their Effect on Climate

1.1.1 Aerosol Background

Aerosols are suspensions of solid particles or liquid droplets in a gas; for environmental relevance, the gas is the Earth's atmosphere. Aerosols have been a topic of considerable interest in the scientific community for nearly a century due to their persistent occurrence in everyday life. From a scientific perspective, aerosols have been linked to adverse effects on human health as well as being able to impact climate via a variety of mechanisms. Therefore, developing a complete understanding of the mechanisms of aerosol formation and their properties is essential.

Aerosols are typically classified for regulatory purposes by their size and mass. The US Environmental Protection Agency (EPA) has established two broad classes which classify particulate matter based on mass.¹ The first of these classes is PM_{10} which is defined as the aggregate mass of all particles with an aerodynamic diameter of 10 microns (micrometers (10^{-6} m)) and less. Particles which fall in this class are known as coarse particles, and often originate from sources such as sea spray, mechanical grinding, or high voltage electrical discharges.^{2,3} The second of these particle mass classes is $PM_{2.5}$ and is defined as the aggregate mass of all particles. The EPA has

considered extending their regulatory efforts by adding a new particle class, $PM_{0.1}$. Like the other PM classes, $PM_{0.1}$ is the aggregate mass of all particles with an aerodynamic diameter of 0.1 microns, or 100 nanometers (1 nanometer = 10^{-9} m), and less. Particles which fall in this subset of the other particle classes are known as ultrafine particles. Figure 1.1 shows aerosol number concentration, surface area concentration and volume concentration as a function of particle diameter for typical urban aerosols.



Figure 1.1: Particle number, surface area, and volume distributions as a function of particle diameter.

From Figure 1.1, the largest sized particles, PM₁₀, represents the vast majority of the observed particle mass since particle mass varies with the cube of particle diameter assuming spherical particles. Coarse particles represent the smallest number concentration but often the greatest volume and mass concentration of all observed particles. Fine particles contain most of the surface area and an appreciable potion of the number and volume/mass concentrations. Ultrafine particles represent the greatest number of particles observed, but very little surface area or volume/mass. Ultrafine and fine particles have the greatest impact on environmental processes and health effects that are based on particle number concentrations. Coarse and fine particles which are based on total particle mass concentrations.

1.1.2 Climatic Effects of Aerosols

It is generally accepted that aerosols have an impact on global climate, and their role in climate processes serves as motivation for developing a more complete understanding of their composition and formation mechanisms. According to the 2007 Intergovernmental Panel on Climate Change⁴, aerosols contribute to a net negative radiative forcing on the Earth. Table 1.1 summarizes climate data from the IPCC and shows the climatic effects of aerosols relative to that of other natural and anthropogenic climate processes.

Table 1.1: Data from the 2007 Intergovernmental Panel on Climate Char	nge ⁴ indicating
how radiative forcing is impacted by certain climatically re-	elevant species
and their level of scientific understanding. RF stands for ra	diative forcing
and LOSU stands for Level of Scientific Understanding.	

Туре	RF Source	Specific Type	RF Values (W/m ²)	Spatial Scale	LOSU
Anthropogenic	Long-lived Greenhouse Gases	CO ₂	1.66 (1.49 to 1.83)		High
		CH ₄	0.48 (0.43 to 0.53)	Global	
		N ₂ O	0.16 (0.14 to 0.18)		
		Halocarbons	0.34 (0.31 to 0.37)		
	Ozone	Stratosphere	-0.05 (-0.15 to 0.05)	Continental to Global	Medium
		Troposphere	0.35 (0.25 to 0.65)		
	Stratospheric H ₂ O vapor from CH ₄	H ₂ O	0.07 (0.02 to 0.12)	Global	Low
	Surface albedo	Land use	-0.2 (-0.4 to 0)	Local to continental	Med- Low
		Black carbon on snow	0.1 (0.0 to 0.2)		
	Total Aerosol	Aerosol direct effect	-0.5 (-0.9 to -0.1)	Continental to Global	Low
		Cloud albedo effect	-0.7 (-1.8 to -0.3)		
	Linear contrails		0.01 (0.003 to 0.03)	Continental	Low
Natural	Solar Irradiance		0.12 (0.06 to 0.30)	Global	Low
Total Net Anthropogenic			1.6 (0.6 to 2.4) W/m ²		

Table 1.1 shows a variety of mechanisms which contribute to positive radiative forcing on the Earth, nearly all of which are anthropogenic (i.e. caused by human

activities). The number in the radiative forcing (RF value) column indicates the magnitude of the contribution to the total radiative forcing (given in the last line of Table 1.1) each specific species contributes with the numbers in parentheses are the error associated with the specific measurement, a qualitative measure of the level of scientific understanding associated with the specific mechanism. The error values for the positive radiative forcing mechanisms, such as greenhouse gases, are small relative to magnitude of the radiative forcing effect. This indicates that the scientific community at large has developed a near-complete understanding of the mechanism of how the species contributes to radiative forcing. Aerosols have the opposite effect on climate; this implies that aerosols will reduce the temperature of the Earth by not allowing incoming solar radiation to pass through the atmosphere where it can become trapped and contribute to the rising temperature of the Earth. Aerosols achieve this negative radiative forcing via two distinct mechanisms. The first is the direct effect, where aerosols themselves scatter and reflect incoming solar radiation back to the solar system. The second effect is a more complicated effect known as the cloud albedo effect. Aerosol particles can serve as cloud condensation nuclei $(CCN)^{5,6}$, which are the hygroscopic seeds for droplet formation within clouds. The aerosol particles serving as CCN increase the reflectivity of the cloud, and thus incoming solar radiation is scattered and reflected back to the solar system; these radiative forcing magnitude of these processes are shown in Table 1.1. Both of these albedo processes have the net effect of cooling the Earth. Despite the importance of these processes, the magnitudes of the error associated for each mechanism in Table 1.1 are very large relative to those of other processes, and indicates a low level of scientific

understanding as to the exact mechanism behind these processes. The negative radiative forcing effects of aerosols are shown in Figure 1.2.



Figure 1.2: The processes governing the formation, growth and climate impact of atmospheric aerosols.

1.1.3 Aerosol Formation Processes

Aerosols can either be formed from primary processes or secondary processes. Primary particles are emitted directly into the atmosphere; sources include mechanical actions such as grinding metal, combustion, biomass burning and volcanic activity. Aerosols can also be formed from secondary formation processes, of which the most prevalent is new particle formation.^{7,8} New particle formation (NPF) is a gas-toparticle conversion consisting of two distinct steps: nucleation and growth.⁹ The energetic landscape of the new particle formation process is diagrammed in Figure 1.3. Nucleation is the process where gas phase precursor molecules come together to form small molecular clusters, which are the energetic saddle point in the NPF free energy landscape. The cluster structure at the saddle point is called the critical cluster, and the nucleation rate J is a function of the formation free energy of the critical cluster¹⁰:

$$J = \operatorname{Cexp}(\frac{-\Delta G_{cc}}{kT}) \tag{1}$$

where C is the critical cluster concentration, ΔG_{cc} is the formation free energy of the critical cluster, k is Boltzmann's constant, and T is the system temperature. Once at the critical cluster, cluster growth via the condensation of other gas phase species or coagulation with other molecular clusters is an energetically favorable process. Partitioning between the gas and condensed phase is driven by molecular weight and volatility¹⁰, and those molecules which are sufficiently oxidized or have low enough volatility will partition to the condensed phase and form aerosol. The true chemical nature and the mechanisms of NPF will be discussed throughout this dissertation; in short, the main chemical components of the NPF process are sulfuric acid¹¹⁻¹³, water, bases (such as ammonia¹⁴⁻¹⁶ and amines¹⁷⁻¹⁹) and oxidized carbonaceous compounds.²⁰⁻²² With respect to this dissertation, new particles formed from both the molecular clustering and oxidation processes are explored in order to elucidate the explicit chemical mechanisms which drive the NPF process.

There exists a clear rationale for continuing to study and explore the formation and composition of ambient ultrafine particulate matter due its important role in global climate and human health. Continued research efforts will increase the level of scientific understanding about the broader impacts of aerosols on the environment and ultimately lead to improved global climate models and a more complete picture of how anthropogenic activities have impacted the world we live in.



Figure 1.3: Free energy versus cluster size (r) for the new particle formation process.

1.2 Introduction to Quantum Chemical Methods Used To Study Aerosols

1.2.1 Fundamentals of Quantum Chemistry

The use of quantum chemical methods to study molecular systems has been steadily increasing over the last few decades due to both the development of methods designed for large-scale systems as well as increases in the power of supercomputers. Quantum chemical calculations have becomes accessible to all areas of science, and the use of calculations provides an avenue with which to better interpret experimental measurements as well as explore systems which are experimentally inaccessible.

The central purpose of all quantum chemical methods is to find the selfconsistent solutions of the Schrödinger Equation²³, famously represented as:

$$\hat{H}\Psi = E\Psi \tag{2}$$

where \hat{H} is the Hamiltonian of the system, Ψ is the wavefunction of the system and E is the total energy of the system. The Hamiltonian of any quantum system is the operator used to describe the potential energy and kinetic energy of the system; \hat{H} is often given as T + V, where T is the kinetic energy operator and V is the potential energy operator. For the purposes of this dissertation, \hat{H} has the functional form:

$$\hat{H} = -\sum_{i=1}^{N} -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) - \sum_{i=1}^{N} \frac{Ze^2}{r_i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{e^2}{r_{ij}}$$
(3)

where the first sum is the kinetic energy operators for the *N* electrons in the molecule, the second sum is the potential energy for the attractive interactions between the electrons and the nuclei of the atoms in the molecule, the third sum is the potential energy of electron-electron repulsive interactions, \hbar is Planck's constant divided by 2π *Z* is the atomic number of each atomic nucleus in the molecule, e is the elementary charge and m is the mass of the atom in the molecule. The kinetic energy is defined as $p^2/2m$, and from the deBroglie equation ($p = -i\hbar\frac{\partial}{\partial x}$) it can be seen that the kinetic energy (in 3-dimensions) has the functional form given in Eq. 3.

The Ψ in Eq. 2 is the wavefunction, which describes all of the measurable information about the system, including its quantum state, momentum, etc. The solutions to the deceptively simple equation given in Eq. 2 are what all quantum chemical methods are looking to calculate as accurately as possible.

Quantum chemistry comes in many different flavors, all with varying degrees of precision as to how they calculate the total ground state energy of the system under investigation.²⁴ Some of the most commonly used methods for molecular quantum chemical calculations include Hartree-Fock (HF) theory, semi-empirical methods, density functional theory (DFT), and *ab initio* post-SCF methods such as Møller-Plesset second order perturbation theory, known as MP2. Since there is no exact solution to quantum chemical problems containing more than a single electron, each method has approximations for the interactions of an electron with the other electrons in a multi-electron system, and each can be used with a variety of basis function sets to describe the atomic and molecular orbitals. The work described in this dissertation made use of semi-empirical methods and density functional theory with modest-sized basis sets, so the generalities of each as well as the details of the specific method used will be described in separate sections.

1.2.2 Semi-empirical Quantum Chemistry and the AM1 Method

Semi-empirical quantum chemical methods are often the first choice for studying the electronic structure of very large molecular systems containing hundreds of atoms. Semi-empirical theory makes use of varying degrees of the Neglect of Diatomic Differential Overlap (NDDO) approximation²⁵, in which the matrices (and thus the integrals) describing the overlap of the molecular orbitals on two adjacent atoms within the molecule are replaced by the unit matrix (an N x N square matrix where the diagonals are 1). This greatly reduces the number of computations involved, often by several orders of magnitude. An additional feature of the NDDO approximation for semi-empirical theory is the use of experimental atomic data for the molecular geometry, enthalpies of formation and dipole moments to parameterize the

method, which facilitates approximate solutions for the required one-center and twocentered two-electron integrals while being able to neglect the three- and four-centered two-electron integrals. These approximations are valid provided the semi-empirical method has parameters for the elements in the molecule the method will be applied to. Because the semi-empirical methods contain their own functions, no additional basis set is necessary. In short, semi-empirical methods reduce the solutions of the Schrödinger Equation to that of the valence electronic energy while treating that of core electrons simply as bulk nuclear charge.²⁴

The semi-empirical method used throughout the work in this dissertation is the Austin Model 1²⁶, commonly known as the AM1 method; AM1 is one of the earliest and more robust semi-empirical methods to make use of the NDDO approximation. AM1 was first published in 1985 by the research group of Michael J.S. Dewar at the University of Texas-Austin²⁶, and was designed to replace the older Modified Neglect of Diatomic Overlap (MNDO) method, which failed to capture the nature of hydrogen bonding with sufficient accuracy as well as poorly calculating transition state structures. The AM1 method improved upon the older methods by improving the Gaussian-type function describing the electronic repulsion of atoms at very short interatomic distances, which greatly increased the accuracy of located structures and molecular properties such as ionization potentials and electron affinities. From the perspective of this dissertation, AM1 was used since it was parameterized with many of the atoms and molecules studied in this dissertation, including water, ammonia, dimethylamine, and sulfuric acid (parameters for the S atom and sulfur-containing molecules came in 1993²⁷). Therefore, with its speed and reasonable accuracy, AM1

was used to generate initial structures for the computational work shown in this dissertation.

1.2.3 Density Functional Theory and the PW91 Method

The implementation of density functional theory (DFT) into modern quantum chemical computing has been a revolution for electronic structure calculations, bringing much of accuracy of *ab initio* methods in line with the speed of simpler Hartree-Fock and semi-empirical methods. DFT calculation methods have made reasonably accurate calculations possible for nearly every molecular system, and have been instrumental in developing new experimental approaches across a wide variety of scientific disciplines. It is within this context that DFT was used for the bulk of the computations described in this dissertation.

The fundamentals of modern DFT were rigorously proved by Nobel Laureate Walter Kohn in the 1960's, first with Pierre Hohenberg in 1964²⁸, then with Lu Jeu Sham in 1965.²⁹ The Hohenberg-Kohn Theorem²⁹ proved that for molecules with a ground sate which has non-degenerate energy, all of the relevant molecular properties, including the total energy, wavefunction and vibrational frequencies could be determined from the ground state electron probability density. The exact functional which describes the electron probability density was, and remains today, unknown. Kohn and Sham took this one step further, and proved that if the ground state electron density was known, then it was possible to calculate all molecular properties *without* having to calculate the molecular wavefunction.²⁹ This was achieved by their calculating the exact ground state probability density of a reference system of non-interacting electrons with their own orbitals, which when coupled to the Hohenberg-Kohn Theorem as described above, allows for computing the true ground state

electron probability density. However, what holds back the Kohn-Sham method, analogous to using the Hohenberg-Kohn theorem directly, is the exact functional used to calculate the energy from the electron density is unknown; all functionals used for this purpose are approximations in some way. The different density functional methods all have their own functionals which attempt to address this and calculate as accurately as possible the true ground state electron density and its energy.

There are many, many different types of DFT methods, but all follow the same basic relationship to calculate the ground state electronic energy from the electron probability density. This fundamental equation is as follows²⁴:

$$E_{o} = -\sum_{\alpha} Z_{\alpha} \int \frac{\rho(r_{1})}{r_{1\alpha}} dr_{1} - \frac{1}{2} \sum_{i=1}^{n} \left\langle \theta_{i}^{KS}(1) \nabla_{1}^{2} \theta_{i}^{KS}(1) \right\rangle \\ + \frac{1}{2} \int \int \frac{\rho(r_{1})\rho(r_{2})}{r_{12}} dr_{1} dr_{2} + E_{xc}[\rho]$$
(5)

with Z_{α} being the atomic number of nucleus α , θ_i^{KS} are the Kohn-Sham orbitals of the non-interfacing reference system, $\rho(\mathbf{r})$ is the electron density and $E_{xc}[\rho]$ is a functional used to describe the kinetic and potential energies of the electron-electron interactions. This functional in also known as the exchange-correlation functional, and the different versions of this functional are what separate the different DFT methods. The first and third term of Eq. 5 are expressions from classical mechanics and are solved accordingly. The second term containing the non-interacting orbitals is solved the same way it is solved in other quantum chemical methods, typically via changing the orbitals to minimize the overall system energy.

The exchange and correlation functionals most often used in the atmospheric chemistry field are those from the research group of John P. Perdew and co-workers at Tulane University published in 1992³⁰ and subsequently updated in 1996³¹; these are

known as the PW91 series of functionals and this functional pair was used for all the DFT work in this dissertation. The PW91 exchange-correlation functional pair has shown to provide some of the best cost-accuracy balance among the many DFT methods used in atmospheric chemistry and has been used the most, making a large quantity of information available for comparison to both higher level quantum chemical methods and the limited experimental data which exists for atmospherically relevant molecular clusters.³²⁻³⁶

PW91 is part of a series of functionals which are known as gradient-corrected, subject to the generalized gradient approximation (GGA).²⁴ What the gradient correction takes into account is that the electron density may not be uniform (i.e. the electron density varies quickly with respect to nuclear position). This implies a non-zero first derivative of the density with respect to position and thus not including density gradients (as well as accounting for the different spins of the electrons with separate gradients for up and down) into the formalism does not reflect the true nature of the system's electron density. While PW91 lacks the more advanced features of modern DFT methods, such as parameters for long range interactions and electron dispersion, it has proven to be a cost-effective, robust and reliable method for computing the structures and thermochemistry of weakly bound molecular systems and has provided excellent comparisons to experimental methods used in atmospheric chemistry.³²⁻³⁶

1.2.4 Monte Carlo Conformational Searching

In any system composed of weak interactions among its components, there exists the likelihood that at any given time t, the system could exist in many different local minimum geometries. Simply calculating the ground state electronic energy of a
single local minimum geometry may not lead to an accurate result for the molecular properties of interest. Weakly bound molecular systems necessitate the need for a thorough conformational sampling to ensure the best minimum geometries on the potential energy surface are located.

There are many different methods used for conformational searching. A common example is molecular dynamics simulation³⁷, which integrate Newton's equations of motion subject to chemical information input as a force field, to build a series of trajectories of molecular motion which allows for the calculation of molecular properties as the system evolves in time. A second approach commonly used for conformational searching are the Monte Carlo methods. Monte Carlo simulations are a way to sample atomic and molecular configurations from a Boltzmann-weighted distribution in a statistical ensemble (such as the NVT or canonical ensemble),³⁷ but can also be used to thermally anneal a system at high temperature to get over any potential energy barriers. The weighting factor for the Boltzmann distribution is the famous expression exp(-E/kT), where E is the energy of the configuration, k is Boltzmann's constant and T is the temperature. The Boltzmann probability distribution is then given by:

$$P(E) = \frac{e^{-E_{/kT}}}{\int_0^\infty e^{-E_{/kT}}}$$
(6)

This distribution equation implies that configurations which are lower in energy should be more populated at a given T. Performing this distribution on a large number of molecular configurations should produce a distribution of populated cluster geometries within a small energy window provided enough individual geometries are sampled. Ideally, this should represent the likely cluster configurations they system will be in as it moves along its potential energy surface. There are various algorithms for choosing geometries according to the Boltzmann distribution given in Eq. 6. The most common is the Metropolis Monte Carlo method.³³ The Metropolis method picks a trial configuration of the system of interest via random atomic motion and calculates the probability ratio that this trial configuration will fall within the Boltzmann distribution without having to compute the complete partition function for the ensemble the system is in. This method was first published by Metropolis and co-workers in 1953³⁸ and has found consistent use throughout all areas of chemistry and physics.

For the configuration searching used for the work in this dissertation, the Metropolis Monte Carlo method was used as follows. Each system of interest was first optimized with semi-empirical quantum mechanics to a reasonable minimum state X_i (although starting at an optimized structure is not a requirement of Monte Carlo methods). Then, trial configurations were made by moving the atoms of the molecule in a random direction subject to the boundary condition that the atoms are only allowed to move a small, user-defined distance from their initial equilibrium positions. This constraint has the effect of allowing bond lengths, bond and dihedral angles to vary and proton transfers to occur naturally within the system. This new configuration, called Xt has its total electronic energy calculated with the same semiempirical method used to generate the initial configuration X_i. If the X_t configuration has a lower energy than the initial configuration, the trial configuration is accepted as a new configuration and its energy becomes part of running average energy of the system. If the X_t configuration has a higher energy than the initial configuration (a positive energy change), the Boltzmann probability ratio of the configuration trial configuration relative to the initial configuration is calculated, and if the ratio is much

less than 1, the move is rejected and the energy of the initial configuration is added to the running average energy. This implies that configurations with large, unfavorable changes in energy are not accepted and the configuration search in producing good minimum geometries. This process is repeated until a large number of accepted geometries is produced, often several thousand; this allows for the best structures to be used as input for for geometry optimizations and vibrational frequency-based thermochemistry calculations using more rigorous quantum chemical methods.

Monte Carlo simulations for molecular configuration searching require the user to define the size of the random motion used to generate new trial configurations as well as the temperature of the system, as it controls how strong the interactions are between atoms. For the work described in this dissertation, the value of maximum atomic motion was 0.5 to 1.5 Å, which approximately corresponds to 1-3 times the most probable distance between the single electron and proton of the hydrogen atom (known as the bohr) and allows for a very broad range of geometries to be sampled. The other consideration which needs to be taken into account is the trial configuration While there is no rule regarding appropriate values for the acceptance ratio. acceptance ratio, values of 0.3 to 0.7 (30 to 70 percent) are generally considered suitable³², with smaller values being a result of long Monte Carlo runs. The atomic step size and acceptance ratio go hand-in-hand; smaller step sizes sample less of the configuration space and often lead to a higher number of accepted configurations and vice versa. For the work described here, the trial configuration acceptance ratio typically varied between 0.35 to 0.55, due to the larger atomic displacements used and the long run times.

1.3 Quantum Chemical Modeling using the *Gaussian* Software Package

Easily accessible, graphical user interface (GUI) based molecular modeling packages have been available for quite some time. Undoubtedly, the single most commonly used and one of the most powerful software packages in the *Gaussian* suite of programs, first developed by Nobel Laureate John Pople and co-workers in 1984 at Carnegie Mellon University. The *Gaussian* software has undergone numerous revisions in its 30 years; the current version in *Gaussian09* revision D.01.³⁹ *Gaussian09* is an all-in-one package; it can perform nearly all of the most commonly used quantum chemical calculation types and includes a large variety of built-in basis sets. In addition, additional input can be specified into an input or parameter file that allows for the use of in-house methods/basis sets or methods not published in the commercial version of the software. *Gaussian09* was used for much of the quantum chemical calculations for the work in this dissertation.

1.3.1 The Gaussian09 Input File

Figure 1.4 shows a picture of standard *Gaussian09* input file; the specific input file is for the geometry optimization and frequency calculation of a neutral sulfuric acid molecule. The input file is where all the hardware information, molecule specifications(s) and type of calculation is stored for reading in by the software.

```
%nprocshared=2
%mem=2000MB
%chk=Sulfuric_Acid_PW91.chk
# opt=tight freq pw91pw91/6-31++G(d,p) Int=(grid=ultrafine,acc2e=11) geom=connectivity
SA
0 1
                                                   -0.00600000
S
                     0.00560000 0.16650000
                     -0.45840000 1.42050000 0.23230000
1.28170000 -0.22520000 -0.25710000
0
                     -0.45840000
0
                     -0.56830000 -0.76380000
0
                                                   1.19200000
0
                    -0.90600000 -0.48090000 -1.18070000
                     -1.36850000 -0.52830000
-0.62960000 -1.27270000
Н
                                                   1.65640000
Н
                                                   -1.63690000
1 2 2.0 3 2.0 4 1.0 5 1.0
2
3
4 6 1.0
5 7 1.0
 6
```

Figure 1.4: Image of a basic *Gaussian09* input file indicting the hardware specifications, job type(s) and the molecule being studied.

The first section of the input file contains the hardware specifications attached to the job being run. The first two lines in this section specify the number of computer processors (also known as cores) for the job's load to be distributed across and the maximum amount of computer memory to be devoted to running the job. *Gaussian09* is designed to run using parallel processors with maximum efficiency for geometry optimizations and analytic frequencies obtained by using a 1:1 of processor to memory ratio and higher. The parameters shown in Figure 1.4 are set based on the physical specifications of the computer which this job was run on. The third line in the input file specifies the name of the checkpoint file. Checkpoint files are the heart of running calculations using *Gaussian09*; they are where important information, such as geometries, integrals, gradients, force constants, energies, etc. are stored as the calculation proceeds; a checkpoint file must be specified before a job will run. Since

checkpoint files store necessary data, they can be used as an input data source for future jobs which require old data as input via "read" commands in the input file. Additionally, checkpoint files can be re-formatted in various ways to give useful information, such as atomic or molecular orbitals, electrostatic potentials and atomic charges.

The next section of the input file is known as the run card, and it is where the job related information is specified. Specifically, the input file in Figure 1.4 contains the following job related items:

- 1. Opt this command requests that the geometry specified in the file be optimized to a minimum
- 2. Freq this command requests that after the optimization of the geometry has finished, the vibrational (IR) frequencies of the molecules be calculated and used to calculate thermochemistry
- 3. Method/Basis set this command specifies the specific method and basis set be used to perform the requested computational tasks
- 4. Integration criteria *Gaussian09* uses numerical integration over a grid of points³⁵, and the number of points in the grid can be changed to larger values for more accurate calculations. Additionally, the accuracy with which the 2 electron integrals are calculated is set to the maximum value (Acc2E=11)
- 5. Connectivity options Chemical bonds are an abstraction designed for visual appearance and are not a quantity which is calculated in quantum chemical methods. This option ensures that the resulting output has the appropriate chemical bonds drawn on the structure for visualization purposes.

The input file also allows for a wide array of other input to be added to the file,

such as different temperatures and pressures (for the thermochemistry calculations), vibrational frequency or thermochemical scaling factors and solvent fields to perform calculations mimicking the effects of solvating the system (the default is *in vacuo*).

The last section of the input file shown in Figure 1.4 is the molecule specification. The molecule specification includes the atomic symbol of each atom in the molecule and the Cartesian coordinates of each atom in 3-dimensional space. The charge and spin multiplicity of the molecule is specified directly above the coordinates. The use of Cartesian coordinates to represent atoms in a molecule is by far the most common method used in the quantum chemistry literature, as it allows for simple transfer between software packages. Cartesian coordinates do not specify any chemical connectivity information about the system; they simply give atomic positions. This is the purpose of the last section of the input file in Figure 1.4; this small section gives the connectivity data to be used in the calculation. In the example, Atom 1 (the S) is connected to Atom 2 (the first O) by a single bond of 2.0 Å and so on for the entire molecule. Gaussian09 can use other coordinate systems, such as the more traditional internal (also known as Z-matrix) coordinates, which specifies connectivity via values for atomic distances (R), bond angles (A), and dihedral angles (D). The output of a Gaussian09 file contains the final geometry in both coordinate systems and they can be used interchangeably. Gaussian, Inc. has published a comprehensive users' guide to their software⁴⁰ which gives more details about the program, its capabilities as well as its limitations.

1.3.2 Special Calculation Types Used For the Work in This Dissertation

Much of the work contained in this dissertation was performed using standard quantum chemical calculations including geometry optimizations and the calculation of thermochemistry via vibrational frequencies. However, certain aspects of the work required calculations beyond these basic calculations. Chapter 4 required the calculation of transition state structures and intrinsic reaction coordinates and Chapter 5 necessitated the use of solvation modeling. Each type of calculation will be summarized in a separate section below.

1.3.2.1 The Optimization of Transition State Structures

The calculation of transition state structures has proven to be a quantum chemical challenge, and specific methods have been developed over the years to tackle this issue. A transition state (TS) of a chemical reaction is a structure intermediate of the reactants and products in the direction of the reaction; the TS of a reaction is an energetic maximum in one direction and a minimum in all others, and is considered mathematically a first order saddle point. Transition states are extremely difficult to experimentally characterize which makes theoretical tools indispensible in studying complex chemical reactions.

The *Gaussian09* software has several protocols which can be used to find TS structures. The most robust of these is the Synchronous Transit Quasi Newton method, first published by H.B. Schlegel and co-workers in 1993.^{41,42} The method uses as input the reactants and products of a reaction, and has an option to use an empirical guess for a TS structure to improve convergence. The method, specified in the Gaussian09 software as QST2 or QST3, is a hybrid method consisting of two different structure optimization schemes. The general path to calculating a TS structure is given in Figure 1.5. In relation to the input file example in Figure 1.4, TS optimizations using the QST3 method are specified by the run card keyword "opt=qst3" instead of simply "opt".



Figure 1.5: Potential energy surface indicating the basic calculation scheme of calculating a transition structure using the STQN method.

The QST3 method, which was the method of choice for the work in this dissertation, begins with an estimation of a curved path up the potential energy surface connecting the reactants and products using the guess for the TS as a guide. The ascent up this curved path is guided by the calculation of a vector (heavy black arrow in Figure 1.5) tangent to the estimated curved path. Note that while the potential energy surface (PES) in Figure 1.5 only shows the ascent vector on one side of the TS structure, this occurs simultaneously starting from each end of the curved path. Once a reasonable maximum energy "hilltop" is reached on the PES (the orange dot in Figure 1.5), the optimization algorithm is changed to the eigenvector following

method to arrive at the final TS structure. The eigenvector following method proceeds from the structure near the top of the PES. This structure has its Hessian matrix (which is the matrix of the force constants, the second derivatives of the potential energy with respect to nuclear position) calculated; the eigenvectors of the diagonalized Hessian matrix are used to choose which molecular coordinate represents the maximum of the PES. This maximum eigenvector is followed uphill perpendicular to the estimated curved path until the maximum point parallel to the initial path is reached. Transition states are characterized in *Gaussian09* by having one and only one negative frequency in the output. Vibrational frequencies are calculated from the square roots of the eigenvalues of the diagonalized mass-weighted Hessian matrix; an imaginary frequency implies the eigenvalue associated with that second derivative has a complex (i) factor. From a physical perspective, this corresponds to a negative curvature of the corresponding normal mode, and consequently the TS structure on which this second derivative is derived from is passing through an energy maximum on the PES. All TS structures considered in this work have one and only one imaginary vibrational frequency although the TS structure may be lower in total energy than either the reactants or products due the complexities of gas phase ion-molecule reactions and their long range ion-dipole interactions.43

1.3.2.2 Calculating the Intrinsic Reaction Coordinate of a Reaction

In order for TS structures to make physical sense for the reactions they are calculated for, the reaction path connecting the TS to both the reactants and products must be verified. *Gaussian09* has a protocol for this called the Intrinsic Reaction Coordinate, or IRC calculation. The IRC calculation was developed in 1981 by Nobel

Laureate Kenichi Fukui as a method to energetically connect reactants and products to a hypothesized TS structure.⁴⁴

The IRC of a chemical reaction is the lowest potential energy pathway between reactants and products where the kinetic energy is zero. The IRC starts at the hypothesized TS structure and the pathways are followed in both directions down the potential energy surface, with subsequent geometry optimizations at each point on the path. This is achieved by mass-weighting the coordinates of the TS structure and following the path of steepest descent down each side towards the reactants and products. Briefly, steepest descent follows the negative of the gradient (the first derivative of the potential energy with respect to nuclear position), with the step size for each step chosen by the user until a minimum geometry with zero gradient is reached. If the structures (and corresponding electronic energies) at the end of the IRC calculation match those of the reactants and products, the TS connect them together and the reaction path is complete.

From a *Gaussian09* calculation perspective, the IRC calculation is specified by the run card keyword "IRC". The only input specification needed for an IRC calculation is the TS structure and its force constants, which is where checkpoint files show their true value. Additional input needed for an IRC calculation is the number of points to calculate on each side of the TS; more points enhance convergence to the reactants and products but will take longer to do so. All TS structures in this work were found to be connected by a single reaction path between it and the reactants and products.

1.3.2.3 Modeling the Effects of Solvent

Solvation alters both the structures and thermochemistry of molecular systems. The general effect of solvation is a release of energy as a gas phase molecule is brought into the condensed phase. The typical energetic cycle for a solvating a gas phase molecule and computing the free energy of a solvated reaction is given in Figure 1.6. The type of solvation modeled by the cycle in Figure 1.6 is called implicit solvation. Implicit solvation techniques model the solvation of a system without the use of direct (explicit) solvent molecules interacting with the system of interest.

Figure 1.6: Complete solvation cycle of gas phase molecules into the solvated phase.

There are two common types of implicit solvation models used to model reactions like the series given in Figure 1.6: the conductor-like screening model (COSMO) and the polarizable continuum model. Both types of model surround the molecules (via a molecule-shaped cavity) with a continuous dielectric which becomes polarized via the polarity of the molecule in the cavity. COSMO is not available in *Gaussian09* and will not be discussed further. Both models seek to calculate the free energy of solvation, which is the energy released when a gas phase molecule is

solvated and is composed of electrostatic, non-electrostatic, and cavity formation energetic terms.

The polarizable continuum model⁴⁵⁻⁴⁷ (PCM) computes the electrostatic contributions to the solvation free energy by self-consistently solving the nonhomogeneous Poisson equation. The non-electrostatic contribution is the energy needed to create the molecular solute cavity within the continuous dielectric, and is dependent on the system of atomic radii chosen to represent the spheres which constitute the atoms of the molecule in the cavity. The version of the PCM used for the work in this dissertation is called the SMD model of Marenich et al.⁴⁸ This version of the PCM has been proven to be an excellent choice for the computation of solvation free energies, which is the difference between the optimized solvated and gas phase total electronic energies. The general scheme of a polarizable continuum calculation is given in Figure 1.7. For use in Gaussian09, SMD-based polarizable continuum model calculations are specified by the following keywords: "SCRF=(solvent=solvent, smd)" where *solvent* is any of the numerous solvents (i.e. dielectric constants) available within the Gaussian09 software. SCRF, which stands for self-consistent reaction field, can be specified as an option to be used with all of the standard calculation types such as single point energies, geometry/transition state optimizations and vibrational frequency calculations.



Figure 1.7: Basic scheme of the method of action behind the polarizable continuum model indicating the molecular cavity and the polarizable solvent used to calculate the electrostatic contributions to the electronic energy.

1.4 Goals of Dissertation

The primary goal of this dissertation is to explore the direct chemical mechanisms of atmospheric new particle formation (NPF) in order to develop a more complete understanding of what governs this process. New particle formation is a critical yet poorly understood process governing the concentrations of ambient particulate matter. Much of the lack of understanding arises from available experimental methods not being able to explore the molecular-level first steps of NPF. NPF begins with clusters in the sub-nm size range, and currently available analytical techniques for chemically characterizing systems this small have significant limitations. For example, the most commonly used tool to study NPF is mass spectrometry. Mass spectrometry analyzes charged species with high precision; however, the vast majority of NPF proceeds through uncharged species which means that mass spectrometry is not directly applicable. The work in this dissertation uses

the toolbox of quantum chemistry to explore the formation and growth of the molecular clusters which are the beginning of NPF. Quantum chemistry is ideally suited to exploring these clusters; it is not limited as experimental measurements are by composition or charge, and approximations exist to study systems much larger than newly formed molecular clusters. For experimentally accessible systems, quantum chemistry provides fundamental information such as molecular structures, energies and electronic/vibrational spectra which aid in interpreting experimental measurements. For these reasons, quantum chemistry is an indispensible tool and is absolutely necessary in order to explore both experimentally accessible and experimentally inaccessible systems.

Chapter 2 of this dissertation describes the structures of positively and negatively charged clusters of sulfuric acid with ammonia and/or dimethylamine $((CH_3)_2NH \text{ or DMA})$ across a range of sizes and compositions relevant to mass spectral data collected in our laboratory. Ion-induced nucleation, which involves charged clusters, is a small but important portion of NPF because the initial steps of changed cluster formation can be studied experimentally. Cluster structural features will be discussed in the context of which features are unique to clusters of a certain composition as well as charge. Cluster formation energetics, including binding and amine substitution, are discussed to explore differences in basicity and how structure ties into the electrostatic processes.

Chapter 3 of this dissertation describes the use of quantum chemical methods to probe the fundamental chemical process which govern molecular cluster formation from atmospherically relevant precursors. Cluster formation in the atmosphere is dominated by uncharged molecular clusters; approximately 90% of all atmospheric NPF occurs through the formation of uncharged clusters. Hydration also likely plays a role on cluster stabilization due to the high concentration of water vapor in the atmosphere. Cluster structural features will be discussed in the context of which features are unique to anhydrous clusters and hydrated clusters. Cluster energetics, including formation, binding, hydration and amine substitution, are discussed to explore the role of hydration of cluster formation and growth as well as provide insight into the fundamental chemistry driving the process.

Chapter 4 of this dissertation explores the growth mechanism of sulfuric acidammonia clusters via the calculation of transition state structures and reaction paths for the sequential addition of sulfuric acid and ammonia molecules to pre-existing charged clusters. The structures of the transition states reveal the potential energy surface for the growth of sulfuric acid-ammonia clusters is very complex, having several activation barriers along the path. The significant structural differences between the transition states of ammonia and sulfuric acid addition are discussed in the context of the mechanism of how each molecule adds to a cluster. In turn, the calculated activation barriers are used to predict the uptake coefficient for each molecule which describes cluster growth. The presence of an activation barrier alters the final observed cluster distribution and governs which clutters can go on to have an impact on the environment. The results of the work in this chapter highlight the complexities of cluster formation and the likelihood that numerous cluster growth pathways exist.

Chapter 5 of this dissertation details use of quantum chemical methods to investigate the formation of oligomeric species relevant to the chemistry of secondary organic aerosol (SOA). The oxidation of hydrocarbon species, especially high

emission terpenes from coniferous vegetation, is a large contributor to the total aerosol budget. The chemistry of terpene oxidation is very complex, often encompassing thousands of individual products, with the molecular mass and volatility of these products determining which partition to the particle phase. The results of this chapter describe the dimerization free energies of relevant dimers formed from the oxidation products of α -pinene, and these free energies are used to calculate equilibrium constants which in turn are used to explore dimerization in the gas and condensed phases. The results of this work shed light on the role of dimers in SOA chemistry and highlight their complexity.

Chapter 6 summarizes the atmospheric relevance of the work shown throughout this dissertation and puts into context how each chapter addressed the main goal of the dissertation. This chapter also provides some future directions for the continued use of quantum chemical methods for studying new and exciting systems of atmospheric relevance. Future topics of interest where computational chemistry can have a significant impact is the role of water on atmospherically relevant cluster structures and how water impacts ion mobility. A second topic which can benefit from computational quantum chemistry is further investigating larger molecular clusters which are well beyond the hypothesized nucleation barrier and will likely contain both inorganic and organic components. The continued use of computational chemistry is essential for furthering the fundamental understanding of the molecular mechanisms of new particle formation and its impact on climate change.

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Chapter 2

THE STRUCTURES AND REACTIVITY OF CHARGED MOLECULAR CLUSTERS CONTAINING SULFURIC ACID, AMMONIA, AND DIMETHYLAMINE

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2.1 Introduction

The role of atmospheric particles in global climate change has been established, but is not well understood. New particle formation (NPF) is a key process governing atmospheric particle concentrations.^{1,2} Particles arising from NPF can grow large enough (~100 nm) to act as cloud condensation nuclei (CCN)¹⁻⁷ and may ultimately affect global climate by scattering solar radiation (albedo effect) as well as by influencing precipitation patterns.⁸ Uncertainties in modeling aerosol effects on climate can be reduced through an improved molecular-level understanding of the mechanisms underlying NPF.

Two of the most important species implicated in NPF are sulfuric acid and ammonia.⁹⁻¹⁴ Ternary homogenous nucleation (THN) studies of sulfuric acid-water-ammonia systems have shown that ammonia decreases the thermodynamic barrier to nucleation, thereby increasing the nucleation rate.¹⁵⁻¹⁷ However, recent work has

shown that organic species can contribute significantly to nanoparticle growth during NPF.¹⁸⁻²¹ In fact, amines and organic aminium salts appear to be particularly promising candidates for enhancing NPF rates, either by reducing the barrier to nucleation^{22,23} or by contributing to particle growth.^{19,20,24-26} Nonetheless, the exact nature and role of organic species in NPF is poorly understood, as direct observation of the chemical composition of ambient particles and clusters <10 nm diameter is a challenging analytical problem.²⁷ Therefore, computational studies are needed to augment experimental measurements.

The role of ion-induced nucleation in NPF also has received much attention, and may represent as much as 10% of all nucleation in the atmosphere.²⁸ More importantly, recent advances in measurement technology have allowed ambient ions to be chemically characterized, which facilitates study of the chemical mechanisms associated with charged cluster formation and growth.²⁹ Initial ambient measurements suggest that negatively charged clusters containing sulfuric acid and ammonia are important in NPF,³⁰ but the role of organic species remains unclear.

Computational studies of neutral and charged clusters containing sulfuric acid, ammonia, amines, and/or water have been undertaken to characterize both structure and energetics.³¹⁻⁵² These studies have focused on the formation energetics and reaction thermochemistry of small clusters by attaining chemical accuracy (within 1 kcal/mol of experiment) using a variety of *ab initio* and density functional (DFT) methods. From a structural standpoint, the geometries of small clusters containing ammonia and sulfuric acid (as well as water) have been largely consistent with one another, with small differences in bond lengths and angles but with the relevant atomic interactions intact. Intermolecular proton transfer from a sulfuric acid molecule to a

base molecule is the dominant binding mechanism within a cluster. The cluster formation energetics calculated with *ab initio* methods^{31,34,39-41,45,46,48,50} have been shown to be more reliable than those calculated with DFT methods,^{38,43-45,47,49} which is important when considering particle formation mechanisms under ambient conditions. However, the general observation that both ammonia and organic molecules lower the nucleation barrier remains true independent of the calculation type.

Recent work in our laboratory has focused on the reaction of charged ammonium salt clusters with amines.⁵³⁻⁵⁶ These measurements show that incorporation mechanisms of amine into a cluster is dependent on both the size and charge of the cluster. To better understand these dependencies, we have performed molecular electronic structure calculations of positively and negatively charged clusters containing sulfuric acid, ammonia and dimethylamine (DMA) using an approach that combines Monte Carlo configuration sampling, semi-empirical methods, and DFT. The results provide significant insight into how cluster structure and energetics are influenced by size and charge.

2.2 Computational Methods

Initial positively charged cluster geometries with the general formula $[(NH_4^+)_x(HSO_4^-)_y]^+$, where x = y+1 and $1 \le y \le 10$, were constructed from individual optimized monomers of ammonia, sulfuric acid, and DMA, then optimized to a minimum at the AM1⁵⁷ level of theory using the HyperChem 8.0.8 GUI-based molecular modeling package.⁵⁸ Each successive cluster (increasing in size) was constructed from the cluster preceding it in size by adding a sulfuric acid molecule and an ammonia molecule to the structure. There are many possible minima for molecular

clusters and the configuration space must be sampled adequately in order to ensure a minimum close to the global minimum. Monte Carlo conformational searches using the Metropolis algorithm were performed in the NVT ensemble using HyperChem 8.0.8 to generate a test set of configurations for further optimizations. The search parameters were as follows: 0.50 Å trial (maximum) atomic coordinate displacement, 298.15 K simulation temperature, and 4000 coordinate displacement steps, with energy calculated at every point with the AM1 self-consistent field (SCF) method. Of the 4000 structures generated for every cluster studied, the ten most energetically favorable structures were selected for full optimization with AM1. In general, optimization led to greater displacements of hydrogen and oxygen atoms than nitrogen and sulfur atoms, which tended to strengthen hydrogen bonds. Typically, four or five of these structures would be within 8 kJ/mol of the most stable structure.

The most stable structures (one structure per cluster size) from the AM1/Monte Carlo method defined above were further optimized with the PW91 functional of Perdew and Wang^{59,60} using the 6-31++G(d,p) basis set as implemented in *Gaussian09* (version A.02)⁶¹ and NWChem.⁶² The default optimization convergence criteria and integration grids were used. To show that the default optimization and grid densities were sufficient for the desired level of accuracy, the binding energy (defined the energy released when gas phase ions come together to form a cluster) was calculated for the "2-1" positively charged cluster. The results are given in Table A1 of Appendix A, where the calculation using default criteria is compared to those using tight optimization cutoffs and/or ultrafine integration grids. A reduction of 0.6 kJ/mol in the binding energy is found between the default criteria and tighter

optimization/finer grid densities, confirming that the default criteria are sufficient for this study.

PW91 was used since it has been shown to give good results for the geometries of complexes with hydrogen bonds^{33,63-66} and has a relatively low computational cost. The DFT calculations predicted the same dominant interactions as AM1 (e.g., both predict that hydrogen 1 on the first ammonium ion has a hydrogen bond to oxygen 1 on the bisulfate ion), but the hydrogen bond lengths were overestimated by ~0.5 Å using AM1. A cluster containing the dimethylammonium ion ([(CH₃)₂NH₂]⁺ or DMAH⁺) in the form [(DMAH⁺)_x(HSO₄⁻)_y]⁺ was constructed using the same approach.

The vibrational frequencies for each cluster were calculated at the PW91 level to check for the presence of minima (or saddle points) and to estimate the thermochemistry. The thermochemistry was estimated using the standard harmonic oscillator and rigid rotor approximations. The results from the vibrational analysis indicated no imaginary frequencies for any of the clusters. In order to account for errors in the harmonic oscillator/rigid rotor approximation and anharmonicity, the frequencies were scaled by 0.982. This scaling factor was calculated in accordance with the NIST Computational Chemistry Comparison Benchmark Database method⁶⁷ and is done for the specific combination of DFT method/basis set. Briefly, the NIST method is:

$$c = \frac{\sum (\nu_i \cdot \omega_i)}{\sum (\omega_i^2)}$$

where c is scaling factor for the molecule, v_i is the experimental frequency (from the database), and ω_i is the calculated frequency at PW91/6-31++G(d,p). This was done for a test set of 50 molecules covering a wide range of functional groups as well as water, ammonia and sulfuric acid. The final scaling factor was determined by

averaging over the individual scaling factors for the test set molecules. The scale factor calculated indicates the very good performance of the PW91 functional in reproducing frequency and thermochemical data.

The negatively charged clusters containing DMA were constructed somewhat differently than the positively charged clusters. The initial negatively charged cluster, $[(H_2SO_4)_3(NH_4^+)(HSO_4^-)_2]^-$, was constructed in the same manner as the positively charged clusters by bringing together optimized monomers of sulfuric acid, ammonium and bisulfate ions. To create the next cluster, $[(H_2SO_4)_3(DMAH^+)(HSO_4^-)_2]^-$, the ammonium ion was replaced with a previously optimized dimethylammonium cation and the structure was optimized. The other three negatively charged clusters, $[(H_2SO_4)_2(DMAH^+)_2(HSO_4^-)_3]^-$, $[(H_2SO_4)(DMAH^+)_3(HSO_4^-)_4]^-$ and $[(DMAH^+)_4(HSO_4^-)_5]^-$, were constructed by successive addition of DMA, taking a proton from an available sulfuric acid molecule, thereby forming bisulfate. The specific sulfuric acid molecule that was selected for neutralization did not significantly affect the optimized cluster structure. The resulting clusters were then subjected to the same Monte Carlo search procedure and DFT optimizations as the positively charged clusters.

2.3 Results and Discussion

2.3.1 Structure Optimization and Visualization

Figures 2.1 through 2.4 present the lowest energy structures calculated for the specific series of clusters in this study. Due to thermal fluctuations, it is likely that the presented structures lie within a range of populated structures near the minimum on the potential energy surface. This is illustrated in Table A2 of Appendix A, where the Gibbs free energies for the five lowest energy structures of the "2-1" cluster

(nomenclature discussed later) are compared at both the AM1 and PW91 levels of theory. Also given is the location of each structure in the Monte Carlo conformation search described in the experimental section. The AM1 free energies of the four higher energy structures are within 4 kJ/mol of the lowest energy structure. Optimizing the five structures at the PW91 level gives nearly identical geometries that differ by less than 0.1 kJ/mol.

The presented structures in Figures 2.1-2.4 include dashed lines to show hydrogen bonding between relevant atoms on different species (ions and/or neutral molecules). Hydrogen bonds indicate the species that most closely interact with each other and are used in this discussion to describe and visualize the three-dimensional structure from a two-dimensional image. However as discussed later, hydrogen bonds represent only a small contribution to the cluster binding energy, which is mostly determined by electrostatic interactions.

2.3.2 Positively Charged Clusters of Ammonia and Sulfuric Acid

Figures 2.1 and 2.2 present the most stable optimized structures for a series of clusters of the form $[(NH_4^+)_x(HSO_4^-)_y]^+$ where x = y+1. In these structures, hydrogen bonding is evident between the hydrogen atoms of the ammonium ions and the oxygen atoms of the bisulfate ions. The structures indicate that ammonium is the only hydrogen bond donor. In the discussion below, the nomenclature X-Y refers to the number of ammonium/dimethylammonium and bisulfate ions, respectively, in the cluster.

The 2-1 cluster (Figure 2.1a) exhibits a structure with the two ammonium ions flanking the central bisulfate ion. Structures for the 3-2 and 4-3 clusters (Figures

2.1b,c) show successive "layers" of ammonium and bisulfate ions. Hydrogen bonding occurs across layers of opposite polarity but not within layers. The medium size clusters, 5-4 through 7-6 clusters, are shown in Figure 2.1d-f. These structures also exhibit hydrogen bonding between ammonium and bisulfate ions but no bisulfate-bisulfate interactions.



Figure 2.1: Optimized structures of small positively charged ammonium bisulfate clusters in the form [(NH₄⁺)_x(HSO₄⁻)_y]⁺. a) 2-1; b) 3-2;c) 4-3; d) 5-4; e) 6-5; f) 7-6. Nitrogen atoms are blue, hydrogen atoms are white, oxygen atoms are red and sulfur atoms are yellow Hydrogen bonds indicated by dashed lines.

The largest clusters, 8-7 through 11-10, are shown in Figure 2.2. These structures show an additional feature: encapsulation of a central ammonium ion. Encapsulation is defined as an ammonium ion that participates in four hydrogen bonds to surrounding bisulfate ions, and the arrangement of surrounding ions is such that a gas phase molecule would be sterically hindered from interacting with the ammonium ion. In this regard, the encapsulated ion can be thought of as residing in the cluster "core" while other ammonium ions reside on the cluster surface. In the 8-7 cluster (Figure 2.2a), a partially closed "pocket" is formed around the central ammonium ion (shown in green). Encapsulation becomes more evident as the cluster size increases, as illustrated by the space filling structures (scaled to van der Waals radii) in Figure 2.2.



Figure 2.2: Optimized structures of large positively charged ammonium bisulfate clusters in the form $[(NH_4^+)_x(HSO_4^-)_y]^+$. a,e) 8-7; b,f) 9-8; c,g) 10-9; d,h) 11-10. Ball and stick models are on the left, space filling models are on the right. Color scheme is same as in Figure 2.1, except the encapsulated ammonium is circled/highlighted in green.

2.3.3 Positively Charged Clusters of Dimethylamine and Sulfuric Acid

Figure 2.3a shows the structure of the fully substituted 5-4 dimethylammonium bisulfate cluster. The hydrogen bonding network of this cluster is similar in character to that for the 5-4 ammonium bisulfate cluster in Figure 2.1d; that is nitrogenic protons on the cations interact with oxygen atoms on the anions, while protons on the bisulfate groups are non-interacting. However, there are important differences as well. The ammonium cluster has 14 hydrogen bonds whereas the DMAH⁺ cluster has only 10 hydrogen bonds. This difference arises because each dimethylammonium ion can engage in only two hydrogen bonds, while some ammonium ions engage in three hydrogen bonds. Second, the DMAH⁺ cluster is physically larger than the ammonium cluster, about 10% by volume, meaning that ions are further apart and electrostatic interaction is decreased.



Figure 2.3: Optimized structures of dimethylammonium bisulfate clusters a) $[(DMAH^+)_5(HSO_4^-)_4]^+$ and b) $[(DMAH^+)_4(HSO_4^-)_5]^-$. Color scheme is same as in Figure 2.1. Hydrogen bonds indicated by dashed lines.

2.3.4 Negatively Charged Clusters of Ammonia and Sulfuric Acid

Previous computational modeling of negatively charged clusters has focused mainly on small clusters containing a few ammonia and sulfuric acid molecules. Ortega et al.⁴⁵ examined the stability of negatively charged clusters containing up to four sulfuric acids and concluded that incorporation of ammonia would not be favored in clusters of this size. However, their results also indicate that ammonia incorporation might become more favorable in larger clusters. Indeed, ambient ion measurements have observed the presence of ammonia in clusters containing four or more sulfuric acids.^{28,29} Recent laboratory work in our group has shown ammonia incorporation in this size range as well.⁵⁵ For these reasons, this study is focused on clusters having five sulfuric acid molecules plus varying numbers of ammonia or DMA molecules. In the nomenclature below, the number of sulfuric acid itself or the bisulfate ion.

Figure 2.4a shows the structure of the $[(H_2SO_4)_3(NH_4^+)(HSO_4^-)_2]^-$ cluster. There are three sulfuric acid molecules in the center flanked by two bisulfate ions (bisulfate ions are indicated with green dots). The ammonium ion is in close proximity to a bisulfate ion. The sulfuric acid molecules are hydrogen bonded to the two bisulfate ions, but not to each other. One bisulfate ion has four hydrogen bonds, all to sulfuric acid molecules. The other has five hydrogen bonds: one to the ammonium ion and four to sulfuric acid molecules. Three protons on the ammonium ion engage in hydrogen bonding: two to sulfuric acid molecules and one to a bisulfate ion. The structure in Figure 2.4a is similar to those computed by Ortega et al.,⁴⁵ who examined smaller clusters of ammonia and sulfuric acid ([(H₂SO₄)_x(NH₄⁺)_y(HSO₄⁻)],
with $1 \le x \le 3$ and $0 \le y \le 1$). The Ortega structures show hydrogen bonding between bisulfate and sulfuric acid, but not among multiple sulfuric acid molecules.

Figure 2.4b shows the structure of the $[(H_2SO_4)_2(NH_4^+)_2(HSO_4^-)_3]^-$ cluster. As described in the Computational Methods section, this cluster was assembled by adding an ammonia molecule to the structure in Figure 2.4a. To ensure unbiased results, ammonia addition was performed three separate times, once at each sulfuric acid molecule. The resulting structures (not shown) have hydrogen bond lengths that vary by approximately 0.1-0.2 Å, but the dominant interactions and structural motifs are unchanged. The three bisulfate ions in the cluster are all hydrogen bonded together. The sulfuric acid molecules are hydrogen bonded to two of the bisulfate ions and also to each other. While one ammonium ion hydrogen bonds to a sulfuric acid molecule, all other hydrogen bonds of the ammonium ions are to bisulfate ions.

2.3.5 Negatively Charged Clusters of Dimethylamine and Sulfuric Acid

Figures 2.4c and 2.4d show the structures of the negatively charged clusters $[(H_2SO_4)_3(DMAH^+)(HSO_4^-)_2]^-$ and $[(H_2SO_4)_2(DMAH^+)_2(HSO_4^-)_3]^-$. These clusters contain some features that are similar to the corresponding ammonium clusters and other features that are dissimilar. In the $[(H_2SO_4)_3(DMAH^+)(HSO_4^-)_2]^-$ cluster (Figure 2.4c), the three sulfuric acid molecules hydrogen bond to each other in a similar arrangement to the neutral sulfuric acid trimer.⁴⁵ The central sulfuric acid molecule is hydrogen bonded to a dimethylammonium cation. One of the bisulfate ions is hydrogen bonded to the dimethylammonium cation, and the two bisulfate ions are hydrogen bonded to each other.

Figure 2.4d presents the structure of $[(H_2SO_4)_2(DMAH^+)_2(HSO_4^-)_3]^-$, which has a trimer of bisulfate ions hydrogen bonded to each other with the dimethylammonium ions on opposite sides of the trimer. The two sulfuric acid molecules are hydrogen bonded together, with one hydrogen bonded to the bisulfate trimer and the other to a dimethylammonium cation. The sulfuric acid bonding pattern is very similar to $[(H_2SO_4)_2(NH_4^+)_2(HSO_4^-)_3]^-$.

The negatively charged dimethylammonium bisulfate cluster $[(DMAH^+)_4(HSO_4^-)_5]^-$ is shown in Figure 2.3b. All five bisulfate ions are hydrogen bonding together: the three bisulfate ions in the center of the cluster are similar to the trimer in Figure 2.4d, while the other two bisulfate ions are hydrogen bonded to opposite ends of this trimer. Surrounding the central bisulfate ions are four dimethylammonium ions, two on each side of the trimer, and these are bound to the outer bisulfate ions. Not surprisingly, the $[(DMAH^+)_4(HSO_4^-)_5]^-$ cluster is about 35% larger by volume than the $[(H_2SO_4)_3(DMAH^+)(HSO_4)_2]^-$ cluster. The hydrogen bonding network in the $[(DMAH^+)_4(HSO_4^-)_5]^-$ cluster is quite different from that of the 5-4 positively charged cluster in Figure 2.3a. Although the two clusters are similar in size, shape and composition, no hydrogen bonds exist among bisulfate ions in the positively charged cluster whereas several such interactions exist in the negatively charged cluster.

For several clusters, both positively and negatively charged, the hydrogen bonding network can be counterintuitive. For example, one O atom on a bisulfate ion may engage in two hydrogen bonds while other O atoms on the same ion do not appear to engage in hydrogen bonding at all. In some negatively charged clusters, an ammonium ion appears to hydrogen bond with a sulfuric acid molecule, while a bisulfate ions in the same cluster does not hydrogen bond to an ammonium ion.



Figure 2.4: Optimized structures of negatively charged clusters of sulfuric acid and ammonia or DMA. a) $[(H_2SO_4)_3(NH_4^+)(HSO_4^-)_2]^-;$ b) $[(H_2SO_4)_2(NH_4^+)_2(HSO_4^-)_3]^-;$ c) $[(H_2SO_4)_3(DMAH^+)(HSO_4^-)_2]^-;$ d) $[(H_2SO_4)_2(DMAH^+)_2(HSO_4^-)_3]^-.$ Color scheme is same as in Figure 2.1. Bisulfate ions are indicated by green dots.

2.3.6 Cluster Binding Energies

Table 2.1 gives the electronic energies, enthalpies and Gibbs free energies for some of the clusters determined in this work, along with the charged and neutral building blocks of these clusters. Values for the remaining clusters are given in Table A3 of Appendix A. Table 2.1 allows important aspects of cluster binding to be explored. We define the cluster binding energy as the free energy change that occurs when the building blocks, i.e. gas phase ions and (for acidic negatively charged clusters) sulfuric acid molecules, come together to form a cluster. Chemical reactions and binding energies for several clusters are given in Table 2.2. Note that our definition of binding energy describes how tightly the building blocks are held together. The binding energy is not a measure of the favorability of cluster formation in the atmosphere since that process begins with neutral molecules, not ions.

	E (kJ/mol)	H (kJ/mol)	G (kJ/mol)
Positively Charged Clusters			
$[(NH_4^+)_5(HSO_4^-)_4]^+$	-8095978	-8095873	-8096177
$[(DMAH^{+})_{5}(HSO_{4})_{4}]^{+}$	-9126829	-9126682	-9127091
Negatively Charged Clusters			
$[(H_2SO_4)_2(NH_4^+)_2(HSO_4^-)_3]^-$	-9486752	-9486659	-9486933
$[(H_2SO_4)_3(NH_4^+)(HSO_4^-)_2]^-$	-9338291	-9338207	-9338461
$[(\mathrm{H}_{2}\mathrm{SO}_{4})_{3}(\mathrm{DMAH}^{+})(\mathrm{HSO}_{4}^{-})_{2}]^{-}$	-9544445	-9544351	-9544634
$[(H_2SO_4)_2(DMAH^+)_2(HSO_4)_3]^-$	-9899070	-9898962	-9899271
$[(DMAH^+)_4(HSO_4^-)_5]^-$	-10608243	-10608105	-10608485
Neutral Molecules			
NH ₃	-148353	-148343	-148404
(CH ₃) ₂ NH	-354497	-354483	-354564
H ₂ SO ₄	-1838133	-1838116	-1838208
Molecular Ions			
$\mathrm{NH_4}^+$	-149203	-149193	-149255
$(CH_3)_2NH_2^+$	-355416	-355401	-355481
HSO ₄	-1836845	-1836829	-1836922

Table 2.1: Electronic energies (including ZPE), enthalpies and Gibbs free energies of selected clusters, molecules and molecular ions. Calculated with PW91/6-31++G(d,p) at gas phase standard states of 1 atm and 298 K.

Reaction	ΔΕ	ΔH	ΔG
	(kJ/mol)	(kJ/mol)	(kJ/mol)
1. 5 $\mathrm{NH_4^+}$ + 4 $\mathrm{HSO_4^-} \rightarrow [(\mathrm{NH_4^+})_5(\mathrm{HSO_4^-})_4]^+$	-2584	-2594	-2217
2. 5 DMAH ⁺ + 4 HSO ₄ ⁻ \rightarrow [(DMAH ⁺) ₅ (HSO ₄ ⁻) ₄] ⁺	-2373	-2363	-1997
$3.4 \text{ DMAH}^+ + 5 \text{ HSO}_4^- \rightarrow [(\text{DMAH}^+)_4(\text{HSO}_4^-)_5]^-$	-2357	-2358	-1950
4. 3 $H_2SO_4 + NH_4^+ + 2 HSO_4^- \rightarrow [(H_2SO_4)_3(NH_4^+)(HSO_4^-)_2]^-$	-997	-1006	-739
5. 3 $H_2SO_4 + DMAH^+ + 2 HSO_4^- \rightarrow [(H_2SO_4)_3(DMAH^+)(HSO_4^-)_2]^-$	-938	-942	-685
$6. 2 H_2 SO_4 + 2 NH_4^+ + 3 HSO_4^- \rightarrow [(H_2 SO_4)_2 (NH_4^+)_2 (HSO_4^-)_3]^-$	-1548	-1559	-1243
7. 2 H ₂ SO ₄ + 2 DMAH ⁺ + 3 HSO ₄ ⁻ \rightarrow [(H ₂ SO ₄) ₂ (DMAH ⁺) ₂ (HSO ₄ ⁻) ₃] ⁻	-1439	-1443	-1128

Table 2.2: Binding energies for selected clusters. All values are calculated with PW91/6-31++G(d,p) at gas phase standard states of
1 atm and 298 K.

The relative binding strength of NH_4^+ vs. $DMAH^+$ in positively charged clusters can be assessed by comparing the binding energies determined from the following reactions:

$$5 \text{ NH}_4^+ + 4 \text{ HSO}_4^- \rightarrow [(\text{NH}_4^+)_5(\text{HSO}_4^-)_4]^+$$
 (1)

$$5 \text{ DMAH}^+ + 4 \text{ HSO}_4^- \rightarrow \left[(\text{DMAH}^+)_5(\text{HSO}_4^-)_4\right]^+$$
(2)

As shown in Table 2.2, the free energy change is more negative for Rxn. 1 than Rxn. 2. In other words, ions in the 5-4 ammonium bisulfate cluster are more tightly bound than in the 5-4 dimethylammonium bisulfate cluster. The stronger binding of NH_4^+ relative to DMAH⁺ can be rationalized by a combination of both hydrogen bonding interactions as well as electrostatic interactions between the ions in the cluster. NH_4^+ can potentially engage in four hydrogen bonds while DMAH⁺ can engage in only one or two. The 5-4 ammonium bisulfate cluster has 14 hydrogen bonds, whereas the 5-4 dimethylammonium bisulfate cluster has only 10 hydrogen bonds. Because a hydrogen bond of this type $(N-H\cdots O)$ has an approximate strength of 8 kJ/mol⁶⁸ in a neutral cluster, the difference in binding energy due to hydrogen bonding (approximately 32 kJ/mol in favor of the ammonium bisulfate cluster based on four additional hydrogen bonds) is almost an order of magnitude smaller than the total difference in binding energy (220 kJ/mol in favor of the ammonium bisulfate cluster). Therefore, electrostatic interactions must dominate cluster binding. The DMAH⁺ ion is larger than the ammonium ion, which increases the inter-ion distance and decreases the electrostatic attraction between oppositely charged ions. Together, the larger number of hydrogen bonds and more compact structure of the ammonium cluster cause binding to be stronger than in the DMAH⁺ cluster.

The binding of $DMAH^+$ and HSO_4^- in positively vs. negatively charged clusters can be assessed by comparing the free energy changes for Rxn. 2 (the 5-4 cluster) and Rxn. 3 (the 4-5 cluster):

$$4 \text{ DMAH}^+ + 5 \text{ HSO}_4^- \rightarrow [(\text{DMAH}^+)_4(\text{HSO}_4^-)_5]^-$$
(3)

The 5-4 and 4-5 clusters contain the same total number of ions, but the relative numbers of each type are different. As shown in Table 2.2, the free energy change is 47 kJ/mol more negative for Rxn. 2 than Rxn. 3. This difference can be rationalized on the basis of the types of interactions in each cluster. In the 5-4 cluster, there are 10 hydrogen bonds and all are between a DMAH⁺ proton and a HSO₄⁻ oxygen. In the 4-5 cluster, there are 13 total hydrogen bonds with 8 between a DMAH⁺ proton and a HSO₄⁻ oxygen, and 5 between a HSO₄⁻ proton and HSO₄⁻ oxygen. Even though there are more total hydrogen bonds in the 4-5 (negatively charged) cluster, the closer spacing of negative ions to each other causes binding to be weaker than in the (positively charged) 5-4 cluster.

Finally, the relative binding strength of $DMAH^+$ and NH_4^+ with HSO_4^- in negatively charged clusters can be assessed by comparing the binding energies obtained from Rxns. 4 and 5:

$$3 H_2SO_4 + NH_4^+ + 2 HSO_4^- \rightarrow [(H_2SO_4)_3(NH_4^+)(HSO_4^-)_2]^-$$
 (4)

$$3 H_2SO_4 + DMAH^+ + 2 HSO_4^- \rightarrow [(H_2SO_4)_3(DMAH^+)(HSO_4^-)_2]^-$$
 (5)

As with the positively charged clusters, the free energy change is more negative for formation of a cluster containing NH_4^+ (Rxn. 4) than DMAH⁺ (Rxn. 5) i.e. NH_4^{++} is more tightly bound than DMAH⁺. From Table 2.2, the free energy

difference between these two reactions is 54 kJ/mol, which is similar in magnitude to the difference in binding per cation between the positively charged 5-4 clusters in Rxns. 1 and 2 (44 kJ/mol per cation). A similar conclusion is reached when comparing the binding energies obtained from Rxns. 6 and 7:

$$2 H_2 SO_4 + 2 NH_4^+ + 3 HSO_4^- \rightarrow [(H_2 SO_4)_2 (NH_4^+)_2 (HSO_4^-)_3]^-$$
(6)

$$2 \operatorname{H}_2 \operatorname{SO}_4 + 2 \operatorname{DMAH}^+ + 3 \operatorname{HSO}_4^- \rightarrow [(\operatorname{H}_2 \operatorname{SO}_4)_2(\operatorname{DMAH}^+)_2(\operatorname{HSO}_4^-)_3]^-$$
(7)

From Table 2.2, the free energy difference is 115 kJ/mol which corresponds to 58 kJ/mol per cation.

The difference between DFT and correlated wavefunction methods such as MP2 or coupled cluster theory to calculate free energies are well established, and when possible correlated wavefunction methods are preferred because they are more accurate. In particular, PW91 has been extensively compared to wavefunction methods.^{48,49} To explore possible inaccuracies of the PW91 results reported here, the formation free energies of several small negatively charged clusters containing a bisulfate ion and an amine molecule were calculated with PW91 and compared to the values reported by Kurtén et al.³⁸ obtained with MP2. The results are shown in Table A4 of Appendix A. The PW91 values are less favorable than the MP2 values, ranging from a fraction of a kJ/mol for [(NH₃)(HSO₄⁻)]⁻ to 6 kJ/mol for [((CH₃)₂NH)(HSO₄)]⁻ and 13 kJ/mol for [((CH₃)₃N)(HSO₄⁻)]⁻. These differences are small relative to the magnitudes of the cluster binding energies in Table 2.2, suggesting that conclusions drawn from the PW91 method used in this work are valid.

Table 2.3: Free energy changes for DMA substitution. All values are calculated with PW91/6-31++G(d,p) at gas phase
standard states of 1 atm and 298 K.

Reaction	ΔE (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)
8. $[(NH_4^+)_5(HSO_4^-)_4]^+ + 5 DMA \rightarrow [(DMAH^+)_5(HSO_4^-)_4]^+ + 5 NH_3$	-133	-112	-112
9. $[(H_2SO_4)_3(NH_4^+)(HSO_4^-)_2]^- + DMA \rightarrow [(H_2SO_4)_3(DMAH^+)(HSO_4^-)_2]^- + NH_3$	-10	-5	-13
$ 10. [(H_2SO_4)_2(NH_4^+)_2(HSO_4^-)_3]^- + 2 DMA \rightarrow \\ [(H_2SO_4)_2(DMAH^+)_2(HSO_4^-)_3]^- + 2 NH_3 $	-31	-24	-19

60

2.3.7 Thermodynamics of Amine Substitution

As outlined in the Introduction section, recent work has also shown that organic amines efficiently substitute for ammonia in ammonium bisulfate clusters. The thermodynamics of DMA substitution is explored in Table 2.3, where ΔE , ΔH , and ΔG^o for two substitution reactions are given. For DMA substitution into the positively charged 5-4 cluster,

$$[(NH_4^+)_5(HSO_4^-)_4]^+ + 5 DMA \rightarrow [(DMAH^+)_5(HSO_4^-)_4]^+ + 5 NH_3$$
(8)

 ΔG° = -112 kJ/mol, which corresponds to an average free energy change of -22 kJ/mol per cation (five substitution steps total). Upper limits for ΔG° measured by Bzdek et al. for DMA substitution into small (2-1 to 4-3) ammonium bisulfate clusters range from <-16 kJ/mol to <-25 kJ/mol per step depending on the specific cluster and substitution step.^{56,57} These limits are consistent with ΔG° for Rxn.8.

The favorability of DMA substitution for ammonia in these clusters can be thought of as a tradeoff between binding and gas phase basicity:

$$\Delta G_{substitution} = \Delta G_{binding} + \Delta G_{basicity}$$

where $\Delta G_{substitution}$ is the free energy change for substitution as given by Rxn. 8, $\Delta G_{binding}$ is the difference in binding energy as given by the difference between Rxns. 1 and 2, and $\Delta G_{basicity}$ is the difference in gas phase basicity between DMA and ammonia. The difference in binding energy between the ammonium and DMAH⁺ 5-4 clusters favors formation of the ammonium cluster by 220 kJ/mol, or 44 kJ/mol per cation. On the basis of binding alone, one would not expect DMA to substitute for ammonia. However, DMA is a stronger base than ammonia and this drives Rxn. 8 in the direction written. The calculated gas phase basicities for DMA and NH₃ using PW91 are 891 kJ/mol and 825 kJ/mol, respectively making formation of DMAH⁺ about 66 kJ/mol more favorable than the ammonium ion. (The experimentally measured gas phase basicities for DMA and ammonia and are 897 and 819 kJ/mol, respectively.⁶⁹) The greater gas phase basicity of DMA relative to ammonia (66 kJ/mol) more than compensates for the weaker binding of DMAH⁺ relative to ammonium (44 kJ/mol), making DMA substitution for ammonia favorable.

DMA substitution is also thermodynamically favorable in negatively charged clusters. As shown in Table 2.3, $\Delta G^{\circ} = -13$ kJ/mol and -19 kJ/mol, respectively for the two reactions below:

$$[(H_{2}SO_{4})_{3}(NH_{4}^{+})(HSO_{4}^{-})_{2}]^{-} + DMA \rightarrow$$

$$[(H_{2}SO_{4})_{3}(DMAH^{+})(HSO_{4}^{-})_{2}]^{-} + NH_{3} \qquad (9)$$

$$[(H_{2}SO_{4})_{2}(NH_{4}^{+})_{2}(HSO_{4}^{-})_{3}]^{-} + 2 DMA \rightarrow$$

$$[(H_{2}SO_{4})_{2}(DMAH^{+})_{2}(HSO_{4}^{-})_{3}]^{-} + 2 NH_{3} \qquad (10)$$

The calculated structures and resulting energies for these negative clusters are consistent with experimental data⁵⁶ for substitution. Bzdek et al. found that while amine substitution into negatively charged ammonia clusters was efficient, the uptake coefficients were much smaller than positively charged clusters of similar size⁵⁴. Although no ΔG° values were reported for the negatively charged clusters, the smaller uptake coefficients for negatively charged clusters can be interpreted as a less favorable ΔG° for substitution as indicated by the values in Table 2.3. As with the positively charged clusters, the greater gas-phase basicity of DMA relative to ammonia compensates for the weaker binding of DMAH⁺ relative to NH₄⁺ in the negatively charged clusters, making DMA substitution for ammonia favorable.

2.3.8 Kinetics of Dimethylamine Substitution for Ammonia

The cluster structures and energies determined in this work provide insight into size and charge dependence of amine substitution kinetics. For small positively charged ammonium bisulfate clusters exposed to incoming DMA molecules, the substitution of DMA for ammonia occurs with near unit reaction probability for all ammonium ions in the original cluster.^{50,51} Efficient substitution of DMA for ammonia is also observed for negatively charged clusters.⁵² This is consistent with the calculations reported here, which show that substitution is thermodynamically favorable. Furthermore, the structures in Figures 2.1a to 2.1f and Figures 2.4a and 2.4b are consistent with a fast substitution rate. All ammonium ions in these clusters reside on the surface, meaning that they are freely accessible to interact with an incoming DMA molecule with no apparent steric impediment to proton transfer from NH_4^+ to DMA and subsequent expulsion of NH₃.

Figures 2.2a to 2.2d show that an ammonium ion becomes encapsulated in the center of the cluster as the cluster size increases. As for the smaller clusters, the surface ammonium ions are freely accessible to an incoming DMA molecule. However, encapsulation of the central ammonium ion could sterically hinder DMA substitution. Bzdek et al.⁵⁴ have measured the substitution rates and determined reaction probabilities for DMA substitution into the 8-7 through 11-10 clusters. They found that DMA substitutes for the first several ammonium ions in these clusters with a reaction probability near 1. However, DMA substitution for the last ammonium ion (i.e. the 8th substitution in the 8-7 cluster, the 9th substitution in the 9-8 cluster, etc.) becomes less probable with increasing cluster size. For the 8-7 cluster, the probability of the final DMA substitution is 0.51 ± 0.15 per collision. For the 9-8 cluster, the probability of the final DMA substitution is 0.08 ± 0.02 per collision. For the 10-9

and 11-10 clusters, substitution of the final ammonium ion is not observed at all, meaning that the reaction probabilities are less than 10^{-3} per collision. Figures 2a-2d suggest an explanation for the decrease in observed reaction probability, which coincides with the onset of an encapsulated ammonium ion in the calculated cluster structure. As the cluster size increases, the pocket around the central ion closes and steric hindrance becomes more severe. It should be noted that in addition a kinetic barrier, there may be a thermodynamic barrier although this possibility was not explored.

2.4 Conclusions

Calculations of molecular structure and energetics were performed for positively and negatively charged molecular clusters containing sulfuric acid, ammonia, and DMA using classical sampling, with energetics calculated by semiempirical quantum mechanics followed by optimization with DFT. Computed structures and associated energies were used to determine the binding energies and thermochemistry of these clusters and their reactions with DMA. The structures indicate an extensive hydrogen bond network for both positively charged and negatively charged clusters. However, cluster binding is determined mostly by electrostatic interactions rather than hydrogen bonding. The thermodynamics of amine substitution for ammonia is governed by two competing effects: 1) the binding energy which favors formation of ammonium clusters, and 2) the gas-phase basicity of the incoming base which favors formation of DMAH⁺ clusters. Because DMA is a substantially stronger base than ammonia, it can overcome the stronger binding of the ammonium ion, resulting in a thermodynamically favorable substitution. Substitution clusters, where all ammonium ions are on the surface of the cluster. However, with increasing cluster size an ammonium ion can become encapsulated in the core of the cluster, rendering slower the kinetics of the final substitution step due to steric hindrance. These findings are consistent with experimental data on amine-ammonia chemistry in charged molecular clusters. The results of this work enhance our structural and electronic understanding of atmospherically significant clusters and chemical processes.

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Chapter 3

THE FORMATION AND GROWTH OF MOLECULAR CLUSTERS CONTAINING SULFURIC ACID, WATER, AMMONIA AND DIMETHYLAMINE

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3.1 Introduction

Ambient nanoparticle concentrations are determined in large part by secondary processes where gas phase molecules come together to nucleate and grow new particles.¹ Many of these particles grow large enough to serve as cloud condensation nuclei (CCN),² which may influence climate by altering Earth's radiation balance.³ Key molecules involved in the formation and early growth of nanoparticles include sulfuric acid⁴, water and bases (ammonia⁵, amines⁶). Numerous computational studies⁷⁻²⁶ have focused on the formation of small clusters containing these molecules since the energetics of cluster formation largely determine ambient nucleation rates. An important conclusion of both computational and experimental work is amines can substantially increase nucleation rates, owing to favorable cluster formation energetics relative to ammonia.²⁷⁻³⁰ In contrast, relatively little work has

been directed toward understanding the subsequent growth and reactivity of these newly formed clusters, especially with respect to the role of amines vs. ammonia.

Experimental measurements of reaction rates and energetics of clusters containing up to 11 sulfuric acid molecules with either ammonia or amines have shown that amines substitute readily for ammonia.³¹⁻³⁴ Most experiments have been performed with dimethylamine (DMA) though methyl- and trimethylamine were also studied. Since these experiments were based on the use of mass spectrometry, they were necessarily constrained to anhydrous clusters which were positively or negatively charged. Subsequent computational studies of these anhydrous, charged clusters have provided insight into the roles of structure and energetics on reactivity.³⁵ Proton transfer from an acid molecule to a base molecule in the cluster produces ions that are strongly bound by electrostatic forces. The relative stability of a cluster containing amine vs. ammonia is determined by two opposing processes. Proton transfer to an amine molecule is more favorable than to an ammonia molecule as reflected by the higher gas-phase basicities of amines. However, ammonium ions bind more tightly with bisulfate ions than do aminium ions. The net effect is that clusters with amines are more favorably formed than clusters with ammonia, and the substitution of amine for ammonia occurs with high probability, at least on the surface of the cluster.³²

Since most atmospheric nucleation proceeds through neutral (uncharged) clusters that are likely to be hydrated,^{10,36-38} additional computational work is needed to fully understand cluster growth and reactivity under atmospherically relevant conditions. Of particular interest is whether or not the free energy advantage of forming small amine clusters relative to small ammonia clusters is replicated in larger

clusters. In the work described here, uncharged clusters containing equal numbers of acid and base molecules plus a varying number of water molecules are investigated. The structures and energies of these clusters provide insight into cluster growth and reactivity.

3.2 Computational Methods

Initial cluster geometries with the general formula $[(BH^+)_n(HSO_4)_n]$, where $2 \le n \le 8$ and $B = NH_3$ or $(CH_3)_2NH$ (DMA) were constructed from individual optimized molecules of ammonia, sulfuric acid, and dimethylamine using a previously described multi-step configuration searching method³⁵ with modifications to improve the reliability of the searching and quality of the generated structures. Briefly, the initial clusters were optimized with AM1 semi-empirical theory,³⁹ configuration sampled with a Monte Carlo conformational search using the HyperChem 8.0.8 GUI-based modeling package,⁴⁰ then optimized with the PW91^{41,42} DFT method as implemented in *Gaussian09* (rev. C.03).⁴³ All calculations and Monte Carlo simulations were performed at standard state conditions (298 K and 1 atmosphere pressure).

Structures and energies were also obtained for the following hydrated clusters: $[(BH^+)_n(HSO_4^-)_n(H_2O)_y]$ with $4 \le n \le 6$ and $1 \le y \le 10$. The hydrated clusters were constructed starting from the optimized structures of the anhydrous clusters, making use of the periodic box solvation feature of HyperChem 8.0.8. Cluster geometries were placed in a periodic box to define where water molecules were allowed to be. The water molecules used in the box solvation method employed here were first optimized at the AM1 level. Ten water molecules were placed at random inside the box around the cluster, and the system was minimized using AM1 to get an initial structure. In order to create the other hydrated clusters, a single water molecule was removed from the structure and the new system minimized. To reduce the bias of choosing which water molecule to remove, all water molecules in the cluster were numbered, and each removed separately and the system minimized. This was done for the nine possible $[(BH^+)_n(HSO_4^-)_n(H_2O)_9]$ clusters and so on for every hydrated cluster investigated. From this, we conclude the specific water molecule removed did not affect the overall electronic energy and the lowest energy isomer was used for the Monte Carlo search. Pure water cluster minimum geometries ((H₂O)₂ through (H₂O)₁₀) from Temelso et al.⁴⁴ were re-optimized using PW91/6-31++G(d,p). 36 total pure clusters were optimized; only the most favorable per water cluster size were used to compute the final thermodynamic quantities (total of 9 final pure water clusters).

In order to increase the reliability of the resulting cluster structures and energies, the Monte Carlo conformational search was extended to 10,000 points while increasing the maximum atomic displacement to 1.5 Å to sample a wider variety of configurations with a trial configuration acceptance ratio of ~50%. At a given temperature, there will be multiple minima populated near the most stable energy, usually within 3 kcal/mol of an identified most stable minimum. Thus, the cluster will likely exist in all these configurations at some time. The stable geometries within 3 kcal/mol of the identified most stable minimum (approximately 8-12 structures per cluster size) from the Monte Carlo conformational search were kept for the DFT optimizations. For this study, tight optimization criteria, ultrafine integration grids, and the maximum two-electron integral accuracy available in *Gaussian09* were used to better characterize low frequency vibrational modes as well as take into account the doubly diffuse character and more modest size of the chosen basis set. In addition, the

resulting energies were scaled using the scaling factor derived in our previous work using the NIST method (0.982).³⁵

To further explore the validity and utility of the PW91/6-31++(d,p) method, we have computed the cluster formation free energy of the anhydrous uncharged clusters using different DFT methods and larger basis sets. Specifically, we used PW91/6-311++G(3df,3pd), the dispersion corrected method ω-B97X-D/6-311++G(3df,3pd) of Chai and Head-Gordon⁴⁵ and M06-2X/6-311++G(3df,3pd) of Zhao and Truhlar⁴⁶ with the D3 damping function for dispersion corrections of Grimme et al.⁴⁷; we re-optimized all geometries and calculated new thermochemistry (with the same optimization parameters and two-electron integral accuracy) using each method. The results (available as Figure B1 in Appendix B) indicate using PW91/6-31++G(d,p) tends to over-estimate free energies, with values ~25-35 kJ/mol more favorable than using the dispersion-corrected methods. Although PW91/6-311++G(3df,3pd) is a significant improvement due to the larger basis set, it too overestimated cluster formation relative to the dispersion corrected methods. However, the difference between PW91/6-31++(d,p) and the dispersion corrected methods is consistent throughout all cluster sizes, so the trends in cluster formation energy and thus reactivity are captured by this simpler method.

Thermodynamic properties for each cluster were averaged over the 8-12 low energy structures (after DFT optimization) using the Boltzmann distribution:

$$< X > = \frac{\sum_{i=1}^{N} X_i e^{-E_i / k_B T}}{\sum_{i=1}^{N} e^{-E_i / k_B T}}$$

where X_i is the value of the property for configuration *i*, E_i is the energy of configuration *i*, N is the number of configurations, k_B is Boltzmann's constant, and T is the system temperature. Values for free molecules and molecular ions were taken as those for the lowest energy structure.

Cartesian coordinates and complete thermochemical data for the specific clusters, free molecules, and molecular ions considered in this study are provided in Appendix B.

3.3 **Results and Discussion**

3.3.1 Structural Features of Uncharged Clusters

The clusters studied are of the form $[(BH^+)_n(HSO_4^-)_n(H_2O)_y]$ where n = 2-8, B = NH₃ or DMA, and y = 0-10. Cluster formulas are written based on the computed structures, which uniformly show proton transfer from each sulfuric acid molecule to a base molecule, while the water molecules remain unionized. Figure 3.1 shows representative structures, each containing five sulfuric acid and five base molecules plus either zero or five water molecules. Proton transfer between acid and base molecules is readily apparent. For the anhydrous clusters in Fig. 3.1a (ammonia) and 3.1c (DMA), most hydrogen bonds are between a base cation and a bisulfate anion, though a few hydrogen bonds are observed between two bisulfate anions. In this regard, the uncharged structures studied here are similar to negatively charged clusters studied previously³⁵ in that both cation-anion and anion-anion interactions are observed. In contrast, previously studied positively charged clusters exhibit only cation-anion interactions. Similar to our previous study of charged clusters,³⁵ the

greater size of DMA causes its clusters with sulfuric acid to be larger than those with ammonia.



Figure 3.1: Selected uncharged bisulfate clusters containing ammonia, DMA, and water. (a) [(NH4⁺)5(HSO4⁻)5]; (b) [(NH4⁺)5(HSO4⁻)5(H2O)5]; (c) [(DMAH⁺)5(HSO4⁻)5]; (d) [(DMAH⁺)5(HSO4⁻)5(H2O)5]. Nitrogen atoms are blue, hydrogen atoms are white, oxygen atoms are red, sulfur atoms are yellow and carbon atoms are gray. Hydrogen bonds indicated with dashed lines. Water molecules are colored purple and have been reduced in size for clarity

The hydrated clusters in Fig. 3.1b and 3.1d exhibit similar structural features to the anhydrous clusters. All acid and base molecules are ionized via proton transfer. While water molecules remain neutral, they form hydrogen bonds with cations, anions and other water molecules. For the hydrated ammonia cluster in Fig. 3.1b, there are more hydrogen bonds of water molecules with bisulfate ions (nine) than with ammonium ions (four), and the presence of water reduces the number of bisulfate-bisulfate hydrogen bonds relative to the anhydrous cluster in Fig 3.1a. The reduction of bisulfate-bisulfate hydrogen bonds upon hydration is observed for clusters containing both bases, but is more pronounced for ammonia clusters, with a complete removal when ten waters are reached for clusters containing 5 ammonia molecules and 5 sulfuric acid molecules. For the hydrated DMA cluster in Fig. 3.1d, water is less likely to hydrogen bond with the protonated DMA ion (one such hydrogen bond) than the bisulfate (eight such hydrogen bonds).

The structures in Figure 3.1 are representative of clusters having a broad range of acid, base and water molecules. Acid and base molecules are uniformly ionized. Water is more likely to hydrogen bond with the ammonium ion than protonated DMA. As the number of water molecules in the cluster increases, water-water hydrogen bonding becomes more prevalent and the effect is more pronounced in the DMA clusters than ammonia clusters. The calculated structures reported here are consistent with recent spectroscopic studies of similar clusters.^{7,17,48-53} Spectral shifts for the N-H stretch and the appearance of N-H···O-S vibrational modes indicate complete proton transfer from sulfuric acid to the base.⁴⁸⁻⁵³ In addition, water is uniformly observed to hydrogen bond to amines, sulfuric acid and their ions without itself becoming ionized.

3.3.2 The Energetics of Cluster Formation

The free energy of cluster formation ($\Delta G_{cluster}$) is defined here as the free energy change when neutral molecules combine to give a cluster. Table 3.1 contains complete thermochemical data for the clusters to ne discussed below. For the anhydrous clusters in Figure 3.1a,c using data from Table 3.1:

$$5 \text{ NH}_3 + 5 \text{ H}_2\text{SO}_4 \rightarrow [(\text{NH}_4^+)_5(\text{HSO}_4^-)_5]; \Delta \text{G}^\circ_{\text{cluster}} = -420 \text{ kJ/mol}$$
(1)

$$5 \text{ DMA} + 5 \text{ H}_2\text{SO}_4 \rightarrow [(\text{DMAH}^+)_5(\text{HSO}_4^-)_5]; \Delta G^{\circ}_{\text{cluster}} = -470 \text{ kJ/mol}$$
(2)

Formation of both clusters is highly favorable, though the free energy change is greater for the DMA cluster than the ammonia cluster by about 10 kJ/mol per base molecule. This difference is not surprising since the gas phase basicity of DMA is greater than ammonia by 77 kJ/mol, indicating that its cation is more easily formed by proton transfer.

The relative values of $\Delta G_{cluster}^{\circ}$ for ammonia and DMA clusters can be understood in the context of the cluster binding energy (ΔG_{bind}°), which is defined as the free energy change when the respective ions are brought together to form the cluster. For the clusters in Eq. 1-2 from data in Table 3.1:

 $5 \text{ NH}_4^+ + 5 \text{ HSO}_4^- \rightarrow [(\text{NH}_4^+)_5(\text{HSO}_4^-)_5]; \quad \Delta G_{\text{bind}}^\circ = -2595 \text{ kJ/mol}$ (3)

 $5 \text{ DMAH}^+ + 5 \text{ HSO}_4^- \rightarrow [(\text{DMAH}^+)_5(\text{HSO}_4^-)_5]; \Delta \mathring{G}_{\text{bind}}^\circ = -2312 \text{ kJ/mol}$ (4)

While the binding energy is not directly relevant to cluster formation in the atmosphere, it provides insight into the interaction between cations and anions in a cluster. The binding energies in Eq. 3-4 are much larger than can be explained by the number of hydrogen bonds observed in Fig. 3.1a and 3.1c. This indicates, not surprisingly, that electrostatic interaction is the main contributor to binding. In this regard, Eq. 3-4 indicate that binding in the ammonia cluster is more favorable than in the DMA cluster by about 57 kJ/mol per base. Nonetheless, formation of a DMA

cluster is more favorable than an ammonia cluster (Eq. 1-2) because of the more favorable gas-phase basicity of DMA overcomes its less favorable binding.

	E (kJ/mol)	H (kJ/mol)	G (kJ/mol)
Anhydrous Clusters	, , , , , , , , , , , , , , , , , , , ,		,,
[(NH ₄ ⁺) ₅ (HSO ₄ ⁻) ₅]	-9933262	-9933143	-9933477
$[(DMAH^+)_5(HSO_4)_5]$	-10964045	-10963883	-10964329
Hydrated Clusters			
$[(NH_4^+)_5(HSO_4^-)_5(H_2O)_5]$	-10936252	-10936099	-10936509
$[(DMAH^{+})_{5}(HSO_{4}^{-})_{5}(H_{2}O)_{5}]$	-11967034	-11966839	-11967350
Neutral Molecules			
NH ₃	-148353	-148343	-148404
$(CH_3)_2NH$	-354497	-354483	-354564
H_2SO_4	-1838133	-1838116	-1838208
H ₂ O	-200550	-200542	-200596
Molecular Ions			
NH4 ⁺	-149203	-149193	-149255
$(CH_3)_2 NH_2^+$	-355416	-355401	-355481

Table 3.1: Electronic energies (including ZPE), enthalpies and Gibbs free energies of selected clusters, molecules and molecular ions. Calculated with PW91/6-31++G(d,p) at gas phase standard states of 1 atm and 298 K.

3.3.3 Hydrated Cluster Formation

To study the effect of water on cluster formation, the free energies of cluster formation were determined for hydrated clusters. For the clusters in Fig. 3.1b and 3.1d from data in Table 3.1:

$$5 \text{ NH}_3 + 5 \text{ H}_2\text{SO}_4 + 5 \text{ H}_2\text{O} \rightarrow$$

[(NH₄⁺)₅(HSO₄⁻)₅(H₂O)₅]; ΔG[°]_{cluster} = -470 kJ/mol (5)

 $5 \text{ DMA} + \text{H}_2\text{SO}_4 + 5 \text{ H}_2\text{O} \rightarrow$

$$[(DMAH^{+})_{5}(HSO_{4}^{-})_{5}(H_{2}O)_{5}]; \Delta G^{\circ}_{cluster} = -510 \text{ kJ/mol}$$
(6)

Comparison of Eq. 5-6 with Eq. 1-2 shows that the addition of five water molecules to these clusters only has a minor influence, lowering the free energy of cluster formation by about 40-50 kJ/mol, or approximately 10%. The difference in formation free energy between the anhydrous and hydrated clusters appears to be relatively small; this can be rationalized by examining in more detail the three broad effects which drive the formation of these clusters. The first of these competing effects is hydrogen bonding. The water molecules added to the clusters increases the number of hydrogen bonds in the cluster; this is clearly illustrated by the clusters given in Figure 3.1. For example, the hydrated ammonia cluster in Fig. 3.1b has 25 hydrogen bonds while the anhydrous ammonia cluster in Fig. 3.1a has only 14 hydrogen bonds. The increase in hydrogen bonding has the net effect of making the interaction energy more negative for the hydrated clusters. The second of these competing effects are the subtle changes in the electrostatic forces within the cluster due to hydration. The hydrogen bonds have some polarization, which increases their strength. However, the ions in the cluster are farther apart due to the water molecules between them, which serves to reduce the strength of the interactions. The overall effect of this interplay is that the hydrated clusters have more favorable interaction energies than the anhydrous clusters. As an example, consider the difference in ΔE_0 between Eqs. 1 and 5; this difference is ~240 kJ/mol more negative for the hydrated cluster (the using the data in Tables B1 and B2 in Appendix B). The third and final of these competing effects is the loss of entropy due to the addition of water molecules to the anhydrous cluster, which serves to counteract the more negative interaction energy upon hydration. To explore the magnitude of this contribution to the free energy, the formation entropies for the clusters given in Eqs. 1,2, 5 and 6 were computed using the data contained in Tables B1-B3 of Appendix B. Respectively, $\Delta S_{form} = -1.43$ kJ/mol·K for Eq. 1, -1.41 kJ/mol·K for Eq. 2, -2.10 kJ/mol·K for Eq. 5 and -2.12 kJ/mol·K for Eq. 6. For example, for the ammonia clusters in Eq. 1 and Eq. 5, $\Delta(\Delta S_{form}) = -0.67$ kJ/mol·K, which at 298 K corresponds to a ~+200 kJ/mol contribution to the difference in the free energy of cluster formation and approximately ~40 kJ/mol per water molecule. The net effect is that all of these factors combine to result in a formation free energy difference between the clusters in Eqs. 1 and 5 of approximately -50 kJ/mol. These three broad effects are all comparable in magnitude and the competition among them will depend on cluster size (n), degree of hydration (y) and cluster formation temperature and serves to highlight the complex interactions which compose molecular clusters.

The size dependence of the free energy of cluster formation is shown in Figures 3.2a and 3.2b for both ammonia and DMA clusters. Included in this plot is the effect of adding 1-10 water molecules for clusters containing 4, 5 and 6 acid and base molecules. The black trace in each plot shows the size dependence of the anhydrous clusters. As illustrated by Eq. 1-2, cluster formation is highly favorable, and the free energies decrease monotonically with increasing cluster size. The free energies of cluster formation for the ten hydrates of clusters containing 4-6 acid and base molecules are summarized by the boxes and whiskers which give the full range of values, average and median values, and 25%-75% values. These plots confirm the conclusion of Eq. 5-6 that water has a relatively small effect on cluster formation. For both the ammonia and DMA clusters, the boxes and whiskers for the hydrated clusters

uniformly lie below the formation free energies of the corresponding anhydrous clusters, but the magnitude of the free energy change is less than $\sim 25\%$ of the corresponding anhydrous cluster, even for the most hydrated clusters of a given size.

Although the formation free energies of anhydrous DMA clusters are more negative than those of the corresponding ammonia clusters, the formation free energies for hydrated clusters of the two bases become similar in magnitude as the number of water and base molecules in the cluster increase. This trend is illustrated in Figure 3.3, where the formation free energies of the anhydrous and hydrated ammonia vs. DMA clusters are directly compared. The addition of water molecules does not alter the formation free energy difference between clusters containing 4 ammonia molecules and those containing 4 DMA molecules. For clusters containing 5 base molecules, however, the formation free energy difference becomes smaller as the number of water molecules increase. For clusters containing 6 base molecules, formation of the ammonium cluster actually becomes more favorable than the DMA cluster when the number of water molecules in the cluster is large.

The free energies of formation for hydrated clusters also were determined by replacing the free water molecules in Eq. 5-6 with water molecular clusters having the geometries reported by Temelso et al.⁴⁴ (which were re-optimized at PW91/6-31++G(d,p)). Starting with a pre-existing water molecular cluster, which already has its own set of hydrogen bonds and electrostatic interactions, gives a much smaller change in the formation free energy between hydrated and anhydrous clusters. While the boxes and whiskers become much smaller than those in Figure 3.2, the overall trend remains the same. Water has a minor, stabilizing effect on cluster formation.

The cluster distribution formalism of Paasonen et al.³⁶ was used to calculate the relative populations of hydrated clusters at 298 K and 50% RH from the formation free energies. Table 3.2 gives the number of water molecules for the most populated hydrated cluster for each type of base and number of base molecules. The full distributions are given in Appendix B. Table 3.2 shows that under atmospherically relevant conditions, ammonia clusters contain more water molecules than DMA clusters, and the number of water molecules increases with increasing number of base molecules in the cluster.



Figure 3.2: Formation free energy versus n (number of acid and base molecules) for ammonium bisulfate and dimethylammonium bisulfate clusters. Boxes and whiskers summarize the values for the 10 hydrates (y=1 to 10) of the n=4,5,6 clusters. (a) [(NH₄⁺)_n(HSO₄⁻)_n(H₂O)_y]; (b) [(DMAH⁺)_n(HSO₄⁻)_n(H₂O)_y].



Figure 3.3: Cluster formation free energy versus number of water molecules in the cluster for ammonium bisulfate and dimethylammonium bisulfate clusters.

Table 3.2:Most probable number of water molecules in the most populated hydrated
cluster and the percentage of all clusters the most probable cluster
represents for each cluster composition. Hydrated cluster populations are
given in Appendix B.

Cluster	# water molecules	% of total clusters
$[(NH_4^+)_4(HSO_4^-)_4]$	2	99.9
$[(NH_4^+)_5(HSO_4^-)_5]$	7	97.2
$[(NH_4^+)_6(HSO_4^-)_6]$	7	77.2
$[(DMAH^+)_4(HSO_4^-)_4]$	1	99.6
$[(DMAH^+)_5(HSO_4^-)_5]$	1	94.5
$[(DMAH^+)_6(HSO_4^-)_6]$	2	94.5
3.3.4 Energetics of Cluster Growth

Figure 3.4 shows the change in free energy for cluster growth (ΔG_{growth}) as defined by the following equations where one acid molecule and one base molecule are added to a preexisting cluster:

$$[(BH^{+})_{n}(HSO_{4}^{-})_{n}] + H_{2}SO_{4} + B \rightarrow [(BH^{+})_{n+1}(HSO_{4}^{-})_{n+1}]$$
(10)

$$[(BH^{+})_{n}(HSO_{4})_{n}(H_{2}O)_{y}] + H_{2}SO_{4} + B \rightarrow [(BH^{+})_{n+1}(HSO_{4})_{n+1}(H_{2}O)_{y}]$$
(11)

The box and whisker plots show the range of growth free energies for the hydrated clusters. Cluster growth is an exothermic process for both ammonia and DMA clusters, with or without water. The growth free energies for anhydrous ammonia clusters in Fig 3.4a can be compared to the bulk value for formation of anhydrous ammonium bisulfate solid from ammonia and sulfuric acid gases:

$$\Delta G^{o}_{growth} = \Delta G^{o}_{f}(NH_{4}HSO_{4}(s)) - [\Delta G^{o}_{f}(NH_{3}(g)) + \Delta G^{o}_{f}(H_{2}SO_{4}(g))]$$
(12)

Using tabulated values for the standard formation free energies of ammonia⁴⁸ and ammonium bisulfate⁴⁹ (in addition to calculating a gas phase value for sulfuric acid using PW91), the resulting ΔG^{o}_{growth} is -41 kJ/mol. This value is significantly less favorable than the range of growth free energies in Fig.3.4a, which fall in the -50 to -127 kJ/mol range, and shows that nanometer size molecular clusters grow more favorably than the bulk solid.

Water has a very different effect on the growth of clusters containing ammonia and DMA. The box and whisker plots for hydrated ammonia clusters in Fig. 4a are generally below the values for the anhydrous clusters, whereas the box and whisker plots for hydrated DMA clusters in Fig. 3.4b are generally above the values for the anhydrous clusters. While water enhances growth of ammonia clusters, it inhibits growth of DMA clusters. However, in either case, growth is still favorable by 50 kJ/mol or more for each step.



Figure 3.4: Formation free energy versus n (number of acid and base molecules) for ammonium bisulfate and dimethylammonium bisulfate clusters. Boxes and whiskers summarize the values for the 10 hydrates (y=1 to 10) of the n=4,5,6 clusters. (a) [(NH₄⁺)_n(HSO₄⁻)_n(H₂O)_y]; (b) [(DMAH+)_n(HSO₄⁻)_n(H₂O)_y].

3.3.5 Energetics of Base Substitution

For uncharged clusters, DMA substitution for ammonia in a bisulfate cluster is given by the following equation:

$$[(\mathrm{NH}_4^+)_n(\mathrm{HSO}_4^-)_n] + n \,\mathrm{DMA} \rightarrow [(\mathrm{DMAH}^+)_n(\mathrm{HSO}_4^-)_n] + n \,\mathrm{NH}_3 \tag{13}$$

Figure 3.5 shows free energies of substitution, ΔG^{o}_{sub} , tabulated on a per molecule basis by dividing the free energy change in Eqn. 13 by n, the total number of base molecules undergoing substitution. For the anhydrous clusters, amine substitution for ammonia is most favorable in the smallest clusters and becomes less favorable as the cluster size increases. This trend is enhanced for the hydrated clusters. While most hydrates of the cluster containing 4 ammonia and 4 sulfuric acid molecules have more favorable substitution free energies than the anhydrous cluster, most hydrates of clusters containing 5 or 6 ammonia and sulfuric acid molecules have less favorable substitution free energies than the corresponding anhydrous cluster.



Figure 3.4: Substitution free energy (on a per molecule basis) versus number of acid and base molecules for all clusters. The line connects anhydrous clusters. Boxes and whiskers summarize the values for the 10 hydrates (y = 1 to 10) of the n= 4,5,6 clusters.

3.4 Conclusions

Molecular electronic structure and energy calculations were performed on clusters composed of sulfuric acid, ammonia, DMA, and water to determine the impact of water on cluster formation, growth and reactivity. All clusters, independent of hydration, exhibit proton transfer such that all acid and base molecules are ionized while the water molecules remain unionized. While an extensive hydrogen bonding network is observed, the driving force for cluster formation is electrostatic attraction of ions produced by proton transfer from acid molecules to base molecules. Water enhances the growth of clusters containing ammonia, but can inhibit both the substitution of DMA for ammonia and the growth of clusters containing DMA. While DMA and other amines can significantly impact nucleation i.e. formation of clusters containing one or a few sulfuric acid molecules,^{6,56,57} this work shows that the free energy advantage of forming amine clusters relative to ammonia clusters becomes less pronounced at larger sizes, especially when the clusters are hydrated.

This study focused on conditions (STP) that are relevant to boundary layer nucleation. One might expect somewhat different behavior under conditions relevant to the free troposphere. For this reason, a few calculations were performed at 255 K and 0.5 atm for anhydrous ammonium bisulfate clusters. The results are provided in Table B4 of Appendix B. Cluster formation free energies were found to be ~15-20% more favorable (more negative) than those computed at STP, while the free energy for cluster growth was ~15% less favorable. The relatively small difference between these two sets of conditions suggests that the general conclusions of this study may be relevant throughout the troposphere.

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Chapter 4

ACTIVATION BARRIERS IN THE GROWTH OF MOLECULAR CLUSTERS CONTAINING SULFURIC ACID AND AMMONIA

4.1 Introduction

Atmospheric new particle formation (NPF) is a gas-to-particle conversion process which influences the concentration of ambient particulate matter.¹ While the chemical mechanisms of NPF have not been fully elucidated, important species include sulfuric acid²⁻⁴, water, bases⁵⁻⁸ (such as ammonia and amines) and carbonaceous matter.⁹⁻¹² The structures and reactivities of the molecular clusters driving NPF have been the focus of experimental and theoretical investigations¹³⁻²⁸, and both approaches have provided valuable insight into the chemical mechanisms underlying particle formation. In order to effectively model both the correct formation pathway as well as the rate of particle formation, energetic barriers must be considered. In the few modeling studies of cluster growth energetics,^{28,29} the barriers explored have been only thermodynamic barriers, i.e. the Gibbs free energy difference between a product cluster and the reactant species. To our knowledge, the direct transition states between reactant and product clusters have not been explored. If an activation barrier must be traversed when going from reactant to product, it will impact both the pathways and rates of cluster growth.

Our research group has studied the formation and reactivity of clusters between sulfuric acid and a base (ammonia or amine) using a combination of experimental and computational approaches.³⁰⁻³⁶ In recent experimental work, we explored the kinetics

and energetics of the fragmentation of charged ammonium bisulfate clusters using Fourier transform ion cyclotron resonance mass spectrometry in order to elucidate possible cluster growth mechanisms.³¹ Based on the assumption that cluster growth is the reverse of cluster fragmentation, activation barriers were found to exist for the addition of ammonia to charged clusters but not for the addition of sulfuric acid (i.e. proceeds at or near a collision-limited rate). The computational work reported here complements the experimental work by exploring the structure and energetics of the transition state between reactant and product clusters previously studied experimentally and assessing their implications for cluster growth.

4.2 Computational Methods

Geometries of clusters with the general formula $[(BH^+)_n(HSO_4)_{n-1}(H_2SO_4)_m]^+$, where $2 \le n \le 4$ and m=0,1 were adapted from our previous work.^{31,32} Briefly, the initial clusters were optimized with AM1³⁷ semi-empirical theory, configuration sampled with a Monte Carlo conformational search using the HyperChem 8.0.8³⁸ GUI-based modeling package, then optimized with the PW91^{39,40} DFT method in *Gaussian09* (rev. C.03)⁴¹ with the 6-31++G(d,p) basis set. Clusters were originally optimized using default optimization criteria, but in order to improve structure reliability, better characterize low vibrational frequencies and account for the smaller size of the chosen basis set, the structures of all reactant, product, and transition state clusters were re-optimized with tight optimization convergence criteria (SCF convergence = 10^{-8} a.u. versus default SCF convergence = 10^{-6} a.u.) and ultrafine numerical integration grids [(95,590) grid, with 95 radial function shells and 509 angular points per radial shell versus the default (75,302) grid, with 75 radial function shells and 302 angular points per radial shell]. These are options available within the *Gaussian09* software as Int=(grid=ultrafine,acc2e=11) and Opt=tight. Since these modifications have proven successful in our previous work,^{9,30} no additional benchmarking work was performed for this study.

Structures and energies of transition states were found for both the addition of ammonia and sulfuric acid to a pre-existing positively charged cluster. The same pathways were studied in our previous experimental work on cluster fragmentation energetics.³¹ Transition state structures were located for each reaction pathway using QST3 method⁴² in *Gaussian09*, which requires as input guess structures for the reactants, products and transition state. Reactant clusters needed for the first step of the QST3 method were constructed by optimizing a previously optimized starting cluster with either NH_3 or H_2SO_4 placed near but separated from the likely reaction coordinate depending on the step being investigated and optimized to a minimum using the PW91/6-31++G(d,p) method. Transition state structural guesses were constructed by modifying the reactant cluster's coordinates using the "Opt=ModRedundant" keyword in Gaussian09 to isolate the portion of the cluster near the empirically guessed reaction coordinate in addition to varying bond lengths and angles of the incoming H₂SO₄ or NH₃ molecule. The product cluster was one of the re-optimized clusters from our previous work on charged clusters.³⁰

All transition states were found to have one and only one imaginary frequency, corresponding to a negative eigenvalue in the normal mode analysis. In order to confirm that the optimized transition state structures connect the reactant and product clusters, each transition state (TS) structure was used as input for an Intrinsic Reaction Coordinate (IRC) calculation. Activation barriers were then computed as the difference in Gibbs free energy between the reactant cluster and the optimized TS

structure. Free energies for the reactions given in Eqs. 1-4 were calculated as the Gibbs free energy difference between the final product cluster and the sum of the free energies of the precursor product cluster and the free molecules of either NH_3 or H_2SO_4 depending on the reaction.

Cartesian coordinates for all reactant, product and transition state clusters as well as the free molecules of ammonia and sulfuric acid are provided in Appendix C.

4.3 **Results and Discussion**

4.3.1 Transition State Structural Features

Reactant and product clusters are of the form $[(BH^+)_n(HSO_4^-)_{n-1}(H_2SO_4)_m]^+$, where $2 \le n \le 4$ and m=0, 1. The structural features of these clusters have been described in detail elsewhere.^{30,31} Briefly, wherever possible within the clusters proton transfer occurs between ammonia and sulfuric acid molecules to produce ammonium and bisulfate ions. While these clusters feature a substantial hydrogen bonding network between cations and anions as well as hydrogen bonds between sulfuric acid and bisulfate, cluster formation is driven primarily by strong electrostatic attraction between the ammonium and bisulfate ions.^{30,32} The only uncharged species observed in any of the clusters studied are the extra sulfuric acid molecules in clusters having m=1.

Transition states were calculated for the following reaction pathways:

$$[(NH_4^+)_2(HSO_4^-)]^+ + H_2SO_4 \rightarrow [(NH_4^+)_2(HSO_4^-)(H_2SO_4)]^+$$
(1)

$$[(NH_4^+)_2(HSO_4^-)(H_2SO_4)]^+ + NH_3 \rightarrow [(NH_4^+)_3(HSO_4^-)_2]^+$$
(2)

$$[(NH_4^+)_3(HSO_4^-)_2]^+ + H_2SO_4 \rightarrow [(NH_4^+)_3(HSO_4^-)_2(H_2SO_4)]^+$$
(3)

$$[(NH_4^+)_3(HSO_4^-)_2(H_2SO_4)]^+ + NH_3 \rightarrow [(NH_4^+)_4(HSO_4^-)_3]^+$$
(4)

A single transition state (TS) structure was found to connect the reactants and products for each of the pathways shown in Equations 1-4. Figures 4.1 and 4.3 show pathways and TS structures for sulfuric acid addition (Eqs. 1 and 3). Figures 4.2 and 4.4 show pathways and TS structures for ammonia addition (Eqs. 2 and 4).

Figure 4.1 illustrates the reaction pathway for addition of H_2SO_4 to the $[(NH_4^+)_2(HSO_4^-)]^+$ cluster (Eq. 1). As the H_2SO_4 molecule approaches the cluster, one of its protons begins to interact with an oxygen atom on the bisulfate ion. At the same time, the two ammonium ions in the cluster begin to move toward the H_2SO_4 molecule so that their protons can interact with the incoming oxygen atoms. In the TS, two hydrogen bonds have been formed with the incoming H_2SO_4 molecule, one with the "top" ammonium ion in the figure and one with the bisulfate ion. Analysis of the imaginary frequency for the TS (using the GaussView visualization package) reveals that this frequency corresponds to an internal rotation of the "bottom" NH_4^+ ion so that it too can begin to hydrogen bond to the H_2SO_4 molecule. In the product cluster structure, the H_2SO_4 molecule hydrogen bonds to all three ions, and the total number of hydrogen bonds has increased from four in the reactant cluster to six in the product cluster.



Figure 4.1: Cluster of H_2SO_4 to the $[(NH_4^+)_2(HSO_4^-)]^+$ cluster showing the structure of the transition state and the presence of a small activation free energy barrier. The sulfur atom of the incoming H_2SO_4 molecule is marked with a green dot.

The reaction pathway for Eq. 3, shown in Figure 4.3, is analogous to that for Eq. 1. As the incoming H_2SO_4 molecule approaches the reactant cluster, it begins to interact with a bisulfate ion and two of the three ammonium ions in the cluster. In the TS, three hydrogen bonds have been formed with the incoming H_2SO_4 molecule, two to ammonium ions and one to a bisulfate ion. Analysis of the negative eigenvalue associated with this structure indicates that the imaginary frequency corresponds to the internal rotation of the third ammonium (*not* interacting with the incoming H_2SO_4 molecule) so that hydrogen bonding to the bisulfate ion can occur. In the product cluster structure, the H_2SO_4 molecule still engages in the three hydrogen bonds, and a

new hydrogen bond has been formed between the third ammonium ion and the bisulfate ion interacting with the H_2SO_4 molecule, increasing the hydrogen bond count from six in the reactant cluster to nine in the productcluster.

The transition state structures for Eqs. 1 and 3 represent constrained structures resulting from the shifting of internal reactant cluster hydrogen bonds to the incoming reactant sulfuric acid molecule. Analysis of the reaction coordinate for each structure indicate that the calculated TS structures are in fact energetic maxima along the potential energy surface resulting from the internal rotation of an ammonium ion, which has a small energetic barrier.

Figure 4.2 illustrates the reaction pathway for Eq. 2, addition of NH₃ to the $[(NH_4^+)_2(HSO_4^-)(H_2SO_4)]^+$ cluster. As the NH₃ molecule approaches the cluster, the nitrogen atom begins to interact with the cluster bound H₂SO₄ molecule. This interaction causes ionic and molecular species in the cluster to move apart. In the TS, the hydrogen bond between the sulfuric acid molecule and bisulfate ion has been broken and the incoming NH₃ molecule has formed a new hydrogen bond to the previously hydrogen-bound OH group of the sulfuric acid molecule. Analysis of the imaginary frequency for the TS indicates this frequency corresponds to a lengthening of the O-H bond in the H₂SO₄ molecule coupled to a decrease of the distance between the incoming NH₃ molecule and OH group. These motions represent the beginning of a proton transfer, although it has not occurred in the TS. In the product cluster, proton transfer has been completed to form a new ammonium ion and a new bisulfate ion, along with some additional hydrogen bonding.

The reaction pathway for Eq. 4, addition of NH_3 to the $[(NH_4^+)_3(HSO_4^-)_2(H_2SO_4)]^+$ cluster, is shown in Figure 4.4 and exhibits analogous

features to that for Eq. 2. The NH₃ molecule approaches the cluster and begins to interact with the cluster-bound sulfuric acid molecule. This interaction causes ionic and molecular species in the cluster to move apart. The TS structure shows formation of a hydrogen bond between sulfuric acid and the incoming NH₃ molecule and a breaking of the hydrogen bond between sulfuric acid and bisulfate. Analysis of the imaginary frequency for the TS indicates this frequency corresponds to several coupled motions: lengthening of the O-H bond in the H₂SO₄, a decrease of the distance between the OH group and the nitrogen atom of the incoming NH₃ molecule, and a decrease of the distance between a proton of the incoming NH₃ molecule and the oxygen atom on the bisulfate ion that was previously hydrogen bonded with the sulfuric acid molecule. These motions represent the beginning of a proton transfer between ammonia and sulfuric acid, although as in the TS for Eq. 2 it has not yet occurred. The product cluster has a completed proton transfer to form a new ammonium ion and a new bisulfate ion, as well as additional hydrogen bonds between the new bisulfate ion and two other cluster-bound ammonium ions.

Optical spectroscopic studies of ammonium bisulfate and amine-bisulfate positively charged clusters indicate that they are only composed of hydrogen bonding and proton transfer interactions between acid and base ions, as evidenced from the presence of coupled vibrational modes. For example, both Johnson and Johnson⁴³ and Rozenberg et al.^{27,44} report that in charged clusters containing one extra ammonium/aminium ion, there is no evidence for hydrogen bonding interactions between acid moieties (bisulfate) in the cluster; all interactions occur between acid and base ions. The only clusters where acid-acid hydrogen bonds are observed (via the presence of an O-H…O coupled vibration mode) are in clusters containing equal

numbers of acid and base molecules. These features are consistent with the reactant, product and TS structures reported here. Product clusters from Eqs. 1 and 3 have equal numbers of acid and base ions with a clear H_2SO_4 -bisulfate hydrogen bonding interaction. Product clusters from Eqs. 2 and 4 are only composed of acid-base interactions. This, coupled to the lack of unifying reaction coordinate calculations for alternate TS structures, suggest that the TS structures, reactions paths and activation barriers for the reactions given in Eqs. 1-4 and Figs. 4.1-4.4 represent likely cluster formation pathways.



Figure 4.2: Cluster of NH_3 to the $[(NH_4^+)_2(HSO_4^-)(H_2SO_4)]^+$ cluster showing the structure of the transition state and the height of the activation free energy barrier. The nitrogen atom of the incoming NH_3 molecule is marked with a green dot.



Figure 4.3: Cluster growth pathway for the addition of H_2SO_4 to the $[(NH_4^+)_3(HSO_4^-)_2]^+$ cluster showing the structure of the transition state and the presence of a small activation free energy barrier. The sulfur atom of the incoming H_2SO_4 molecule is marked with a green dot.



Figure 4.4: Cluster growth pathway for the addition of NH_3 to the $[(NH_4^+)_3(HSO_4^-)_2(H_2SO_4)]^+$ cluster showing the structure of the transition state and the height of the activation free energy barrier. The nitrogen atom of the incoming NH_3 molecule is marked with a green dot.



Figure 4.5: Complete PES for the entire studied cluster growth pathway including energies. Pathways for H_2SO_4 addition have red lines and pathways for NH₃ addition have blue lines. Stable product clusters have black lines. $[C1]^+$ is $[(NH_4^+)_2(HSO_4^-)]^+$, $[C2]^+$ is $[(NH_4^+)_2(HSO_4^-)(H_2SO_4)]^+$, $[C3]^+$ is $[(NH_4^+)_3(HSO_4^-)_2]^+$, $[C4]^+$ is $[(NH_4^+)_3(HSO_4^-)_2(H_2SO_4)]^+$, $[C5]^+$ is $[(NH_4^+)_4(HSO_4^-)_3]^+$.

4.3.2 Alternative TS Structures and Reaction Mechanisms

The TS structures described above are the lowest energy structures found that directly connect via the intrinsic reaction coordinate (IRC) to the reactant and product cluster structures. Intuitively, one might expect the incoming ammonia molecule to interact with a dangling (non-hydrogen bonded) proton on either a sulfuric acid molecule or bisulfate anion in the cluster. However, none of these interactions give reasonable TS structures. When the incoming ammonia molecule interacts with the dangling proton on the sulfuric acid molecule (Eqs. 2 and 4), the TS structures do not connect to the products. The imaginary frequencies of these TS are small (\sim -50 cm⁻¹) and correspond to an internal ammonia rotation unrelated to the beginning of proton transfer. Even though these types of cluster TS structures are lower in total energy than the pre-proton transfer TS structures given in Figs. 4.2 and 4.4, they do not lead the stable low energy observed products.

When the ammonia molecule interacts with the dangling proton on a bisulfate ion that itself is interacting with the sulfuric acid molecule (Eqs. 2 and 4), the TS structures do not connect to the products and the free energy barriers are much higher than those shown in Figs. 4.2 and 4.4. A high energy barrier is not surprising, since proton transfer by this process would produce an energetically prohibitive sulfate anion, which then requires substantial rearrangement and a second proton transfer, this time from the sulfuric acid molecule, to generate the product cluster.

When the ammonia molecule interacts with the dangling proton on the bisulfate ion that is not interacting with the sulfuric acid molecule (Eq. 4), the TS structures do not connect to the product. The imaginary frequencies are small (\sim -70 cm⁻¹) and correspond to an internal ammonia rotation unrelated to the beginning of a proton transfer.

4.3.3 Activation Barriers in Cluster Growth

Figure 4.5 depicts the entire potential energy surface for cluster growth by sequential addition of sulfuric acid and ammonia as given in Eqs. 1-4. This reaction sequence represents the expected growth pathway for positively charged clusters as determined from a kinetic model based on the thermodynamics of the equations, i.e. just the starting and end points of Figures 1-4.²⁸ However, Figure 4.5 shows that

thermodynamic analysis gives an incomplete picture of cluster growth since activation free energy barriers exist for both the H₂SO₄ and NH₃ addition steps.

For the positively-charged clusters investigated in this work, addition of a sulfuric acid molecule is fundamentally different from addition of an ammonia molecule. For the sulfuric acid additions in Eqs. 1 and 3, there is a small activation free energy barrier caused by the internal rotation of the ammonia molecule to accommodate the incoming molecule as well as maximize the hydrogen bonding in the newly formed product cluster. The sulfuric acid molecule simply hydrogen bonds to the cluster with little structural change, i.e. there is no proton transfer or other covalent bond breaking with only hydrogen bonds being both broken and remade. The TS energies are 8-12 kJ/mol higher than the reactants, while the products are 30-40 kJ/mol lower in energy than the reactants.

For the ammonia additions in Eqs. 2 and 4, the TS activation free energies are 30-50 kJ/mol higher than the reactants, even though the products are about 65-100 kJ/mol lower in energy than the reactants. The activation free energy barriers for ammonia addition come from the significant structural change that occurs as the system approaches the TS. The incoming ammonia molecule initiates what proves to be an energetically costly charge separation process among ions in the cluster plus breaking of a hydrogen bond between the cluster-bound sulfuric acid molecule and bisulfate ion. This restructuring of the cluster is the source of the activation free energy barrier observed for these reactions.

The heights of the activation free energy barriers calculated and shown in Fig. 4.5 are consistent with the values determined experimentally by fragmenting the "product" clusters in Eqs. 1-4 to produce the corresponding "reactant" clusters.³¹ In

the cluster fragmentation study, the reverse activation barrier for molecular loss was computed as the difference between the threshold energy for fragmentation (E_0) obtained from the experiment and the zero-point corrected electronic energy obtained from DFT-based computations. For H₂SO₄ loss, the results showed little or no reverse activation barrier. The values reported here for TS structures with an activation free energy barrier in the low kJ/mol range are consistent with the lack of a significant experimentally determined activation barrier. For ammonia loss, the cluster fragmentation study gave reverse activation barriers in the 60-70 kJ/mol range, which are similar in magnitude to the 30-50 kJ/mol activation free energy barriers for the computational work reported here. Note that the barriers determined from the fragmentation study were subject to substantial uncertainty. Table 4.1: Electronic energies (including ZPE), enthalpies, and Gibbs free energies of selected reactant/product clusters, transition state clusters and molecules. Energies are calculated at the PW91/6-31++G(d.p) level at gas phase standard states of 1 atm and 298 K.

	E (kJ/mol)	H (kJ/mol)	G (kJ/mol)
Reactant Clusters			
$[(NH_4^+)_2(HSO_4^-)]^+ + H_2SO_4$	-3974107	-3974084	-3974256
$[(NH_4^+)_2(HSO_4^-)(H_2SO_4)]^+ + NH_3$	-4122574	-4122517	-4122710
$[(NH_4^+)_3(HSO_4^-)_2]^+ + H_2SO_4$	-5960839	-5960765	-5960998
$[(NH_4^+)_3(HSO_4^-)_2(H_2SO_4)]^+ + NH_3$	-6109265	-6109183	-6109437
Product Clusters			
$[(NH_4^+)_2(HSO_4^-)]^+$	-2135919	-2135885	-2136020
$[(NH_4^+)_2(HSO_4^-)(H_2SO_4)]^+$	-3974133	-3974084	-3974257
$[(NH_4^+)_3(HSO_4^-)_2]^+$	-4122633	-4122576	-4122765
$[(NH_4^+)_3(HSO_4^-)_2(H_2SO_4)]^+$	-5960853	-5960779	-5961011
$[(NH_4^+)_4(HSO_4^-)_3]^+$	-6109316	-6109235	-6109480
Transition State Clusters			
$[(NH_4^+)_2(HSO_4^-)\cdots(H_2SO_4)]^+$	-3974126	-3974078	-3974248
$[(NH_4^+)_2(HSO_4^-)(H_2SO_4)\cdots(NH_3)]^+$	-4122522	-4122468	-4122656
$[(NH_4^+)_3(HSO_4^-)_2\cdots(H_2SO_4)]^+$	-5960827	-5960753	-5960985
$[(NH_4^+)_3(HSO_4^-)_2(H_2SO_4)\cdots(NH_3)]^+$	-6109238	-6109156	-6109407
Free Molecules			
H ₂ SO ₄	-1838133	-1838116	-1838208
NH ₃	-148380	-148370	-148404

4.3.4 Implications of Activation Barriers for Cluster Growth

The presence of an activation barrier on the potential energy surface for cluster growth has profound implications on the currently accepted mechanisms of new particle formation. Molecular uptake determines both cluster composition and rate of growth. An estimate of the uptake coefficient (γ), defined as the probability that a collision between an incoming molecule and reactant cluster results in cluster growth, can be determined from the activation barrier:

$$\gamma = e^{-\Delta G^{\ddagger}/kT} \tag{6}$$

where ΔG^{\ddagger} is the activation free energy barrier (in kJ/mol), k is Boltzmann's constant (in kJ/mol*K) and T is the system temperature (K). Sulfuric acid uptake in Eqs. 1 and 3 has a small activation free energy barrier; the activation free energy barrier is +8 kJ/mol for Eq. 1 and +12 kJ/mol for Eq. 3. Using Eq. 6, these values correspond to an uptake coefficient of approximately 4% and 1% for Eqs. 1 and 3, respectively. Note that the calculations have an uncertainty on the order of 4 kJ/mol, so it is possible that the uptake coefficients are higher. Fast uptake of sulfuric acid is consistent with fragmentation energetics of the product clusters (i.e. the reverse of Eqs. 1 and 3) and with previous experimental studies indicating sulfuric acid drives cluster growth.^{3,4,45}

Ammonia uptake is fundamentally different from sulfuric acid uptake. Activation barriers for the ammonia addition steps in Eqs. 2 and 4 are +53 kJ/mol and +29 kJ/mol respectively, corresponding to uptake coefficients of $\sim 10^{-10}$ and 10^{-5} respectively using Eq. 6. As noted before, these activation barriers are consistent with fragmentation energetics of the product clusters (reverse of Eqs. 2 and 4). While the rates of Eqs. 2 and 4 have not been explicitly studied in the forward direction, ammonia uptake into other types of acidic clusters have been reported.^{33,34} Ammonia uptake into positively charged ammonium methansulfonate clusters and negatively charged ammonium bisulfate clusters is often too slow to be measured, and when it is measurable the uptake coefficients are in the 10^{-4} to 10^{-3} range. These same studies show that uptake of dimethylamine into the analogous dimethylammonium

methanesulfonate and bisulfate clusters is also slow, though somewhat faster than ammonia uptake.

The calculated uptake coefficients for ammonia are too low for charged clusters to grow sequentially by Eqs. 1-4 under atmospherically relevant conditions, vet all of these clusters are observed in nucleation experiments.^{15,16,45} How, then, does cluster growth occur? This work focused exclusively on one-step mechanisms for ammonia addition. It is possible that the reaction mechanisms for Eqs. 2 and 4 involve multiple intermediates and TS structures, rather than just a single TS that directly connects to the reactants and product. One such possibility is formation of a preassociation complex between the ammonia molecule and reactant cluster. It is known that long-range ion-dipole and ion-induced dipole forces can result in the formation of long-lived orbiting complexes.^{46,47} A simple steady state kinetic treatment suggests the association rate increases with the lifetime of the complex, as given by the strength of the interaction. While the magnitude of long-range ion-dipole and ion-induced dipole attractions are not readily available from the calculations reported here, they can be estimated to be in the 5-15 kJ/mol range for an ion-molecule separation of 6-10 Å. This interaction energy is sufficient to give a long-lived complex that could subsequently react to form the product cluster.

A second possibility is that charged clusters are formed by a set of reactions different from Eqs. 1-4. For example, charge migration could cause a charged cluster to become neutralized, with NH₃ addition subsequently proceeding through the neutral (uncharged) cluster. After addition has occurred, charge could migrate back to the product cluster. Almedia et al.¹⁵ discuss that while ion-induced nucleation can be important under certain atmospheric conditions, ion-ion recombination and other

similar ion conversion/neutralization processes usually occur on much faster time scales than ion-induced nucleation. Olenius et al.²⁸ studied the growth of ammonia-sulfuric acid clusters using a kinetic model based on thermodynamic barriers alone. Even without consideration of activation barriers, they found that growth proceeds mostly through neutral rather than charged clusters owing to fast charge migration.

Another example of an alternative growth pathway would be ammonia addition into a highly acidic cluster where additional proton transfer sites exist such as a cluster containing two additional sulfuric acid molecules (m = 2). Highly acidic charged clusters have been observed in ambient ion studies⁴⁸, so it is plausible that growth could occur through these species. Since ammonia uptake into neutral or highly acidic species such as these has not been studied experimentally or theoretically, it is unclear whether or not activation barriers exist and what the magnitudes of these barriers might be.

4.4 Conclusions

Molecular electronic structure and energy calculations were performed to determine the transition state structures and activation free energy barriers in the growth of positively charged molecular clusters containing sulfuric acid and ammonia. Transition state structures for the addition of sulfuric acid indicate that the sulfuric acid molecule simply sticks to the reactant cluster via hydrogen bonding, whereas ammonia addition requires significant structural rearrangement of the cluster prior to proton transfer. The addition of sulfuric acid has low activation free energy barrier and the calculated uptake coefficient is relatively high. Ammonia addition has a significant activation barrier that precludes growth under atmospherically relevant conditions. However, there are other ways that charged clusters can grow, for example through formation of a pre-association complex between ammonia molecule and reactant cluster prior to reaching the transition state, or by a completely different pathway such as charge neutralization prior to ammonia uptake. Additional experimental and computational work is needed to fully explore the impact of activation barriers on the mechanisms, pathways and growth rates of various composition charged and neutral clusters.

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Chapter 5

THE OLIGOMERIZATION OF HIGHLY OXIDIZED ORGANIC MOLECULES AND ITS IMPLICATIONS FOR SECONDARY ORGANIC AEROSOL FORMATION AND REACTIVITY

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5.1 Introduction

Atmospheric aerosol influences human health and global climate. Organic matter comprises much of the global aerosol budget,¹ yet a detailed molecular level understanding of its formation and reactivity remains elusive.² A significant fraction of organic aerosol is secondary in nature (secondary organic aerosol, or SOA),³ whereby volatile organic compounds (VOC) emitted from biogenic (e.g. α -pinene) and/or anthropogenic (e.g. toluene) sources⁴ react with an atmospheric oxidant (OH, O₃, NO₃)⁵ to produce a variety of products, which may subsequently undergo further oxidation. Oxidation products having very low vapor pressures may induce nucleation of new particles in the atmosphere.⁵ Oxidation products having somewhat higher vapor pressures can partition from the gas phase onto pre-existing particles.⁶ In either case, the total aerosol mass loading increases, owing to the formation of SOA. While much is known about these processes, global aerosol models can underestimate SOA

mass loadings by up to two orders of magnitude, which highlights the need for an improved molecular level understanding of SOA formation.^{7,8}

Laboratory reactors, where the experimental conditions can be tightly controlled, are typically used for detailed mechanistic studies of biogenically-derived SOA.⁹⁻²⁷ Oligomers, defined here as large molecules formed by the coupling of two or more "monomer" oxidation products, may constitute over one half of the aerosol mass formed in these experiments.²⁴ Because of the large number of monomers and ways they can be coupled together, the distribution of oligomeric molecules is complex, often encompassing more than a thousand distinct molecular formulas even when produced from a single VOC precursor.¹⁹ This complexity, along with the inherent difficulties of experimentally characterizing these molecules^{14,26} makes studying the impact of oligomers on SOA formation and reactivity a challenging problem. For this reason, theoretical investigations are needed to augment experimental studies and probe the detailed fundamental chemistry of oligomer formation and its impact on particle formation and growth.

The formation of oxidation products of monoterpenes and the oligomerization of these products has been explored theoretically with a variety of methods.²⁸⁻⁵⁰ Oxidation products formed through the Criegee intermediate during ozonolysis of mono- and sesquiterpenes, and the subsequent partitioning of these products between the gas and condensed phases has been extensively studied by Pankow,^{28-30,40,44,45,49} culminating in widely used equations,⁶ in which the fraction of an organic species in the condensed phase can be predicted based on its molecular mass and vapor pressure. Other SOA formation models, such as the multi-step combinatorial aerosol yield models of Couvidat and Seigneur⁴¹ and Capouet et al.³⁹ take Pankow's equations
further by incorporating kinetics and explicit chemical equations into the phasespecific partitioning. Oligomers of various monomer oxidation products have also been studied using classical thermodynamics and quantum mechanics. Most notably, the series of papers by Barsanti and Pankow²⁸⁻³⁰ have studied oligomers resulting from the accretion reactions of a wide variety of monomers using the methods of equilibrium thermodynamics. Others have used mass transfer modeling coupled to the yield function³⁸ to predict the evolution of the total aerosol mass incorporating dimers. Quantum chemical studies have suggested the existence of favorable pathways for oligomer formation; however, due to the size and complexity of most SOA systems, have been limited to small molecular systems such as carbonyl oxides,³² smaller aldehydes,³⁵ glyoxal/methylglyoxal,^{34,37} and the oxidation products of isoprene and cis-pinic acid/norpinic acid.³⁶

In this work, quantum chemical structure optimizations coupled to continuum solvation modeling are used to probe the formation of specific dimer compounds in both the gas and condensed phases in order to explore more generally how oligomers can influence the formation of SOA.

5.2 Oligomer Formation Pathways Examined In This Study

This study focuses on oligomers produced by α -pinene ozonolysis, a reaction that has been extensively studied both experimentally and theoretically in the past.^{10,12-17,19,22-31,33,36,38-42,44,45,48} Monomer products of this reaction contain functional groups such as alcohols, aldehydes, ketones, carboxylic acids, and peroxides, all of which can serve as reactive sites for oligomerization. Some of the postulated dimerization mechanisms include aldol addition, acid-catalyzed esterification, and anhydride formation; this list is not exhaustive, but gives the scope of the type of chemical reactions which could potentially drive oligomer formation. Recently, MS and MS/MS measurements with high accuracy and precision have been used to confirm the formation of oligomers from specific monomer products and formation mechanisms.^{20,25} It is that experimental work which guides the computational work reported here. In order to cover as much of the potential structure space as possible while keeping the task computationally feasible, specific monomers were chosen for this study that cover the range of functional groups known to exist in biogenic SOA such as carboxylic mono- and di- acids, alcohols, aldehydes and ketones. Dimers, rather than higher order oligomers, were studied as they have been characterized experimentally, and are in the appropriate size range for the level of quantum theory being employed. Table 5.1 shows the monomers and dimers studied here.

5.3 Computational Methods

Initial structures of the monomer and dimer molecules given in Table 5.1a,b were optimized to a minimum energy at the AM1 level of theory⁵¹ using the HyperChem 8.0.8 GUI-based molecular modeling package.⁵² Once the AM1 optimization was complete, the conformations of all structures were sampled using Monte Carlo conformational sampling in the NVT ensemble using HyperChem 8.0.8; the AM1 self-consistent field energy was sampled at every point in the conformational search. The Monte Carlo sampling was run for 4000 individual points per structure. From the conformational search, the most stable structure of each monomer and dimer were further optimized with the PW91 functional of Perdew and Wang^{53,54} using the 6-31++G(d,p) basis set as implemented in *Gaussian09* (version C.01).⁵⁵ Tight optimization criteria, ultrafine integration grids, and maximum two electron integral accuracy were used to increase the reliability of the structure calculations by taking

into account the diffusivity of the chosen basis set while characterizing as best as possible low frequency vibrational modes. PW91 was used since it has been shown to give good results for thermochemistry at a relatively low computational cost.^{56,57} To validate the use of PW91/6-31++G(d,p) and not a larger basis set, Tables D1 and D2 in Appendix D show benchmarked values for ΔG_d° in both the gas phase and condensed phase (with water) using PW91 calculated with the 6-311++G(2d,2p) and 6-311++G(3df,3pd) basis sets making use of the geometries calculated at PW91/6-31++G(d,p). The values for ΔG_d° in both the gas phase and condensed phase using the different basis sets in Tables D1 and D2 change little when compared to values obtained with PW91/6-31++G(d,p) given in Tables 5.2 and 5.3 and do not alter our conclusions about dimerization significantly in either phase.

The vibrational frequencies for each monomer and dimer were calculated at the PW91/6-31++G(d,p) level to check for the presence of minima (or saddle points) and to estimate the thermochemistry using the standard rigid rotor and harmonic oscillator (RRHO) approximations. The results from the frequency calculations indicated no imaginary frequencies for any of the monomers and dimers considered in this work. In order to account for errors in the RRHO approximation as well as basis set incompleteness, the thermodynamic correction to the electronic energy (known as the internal thermal energy correction or E_{Total} in *Gaussian09* terminology) was scaled by 0.982, computed using the NIST Computational Chemistry Comparison Benchmark Database method.⁵⁸ This scaling factor was computed using a test set of 50 small organic molecules covering a wide range of common functional groups found in SOA chemistry as well as water, ammonia and sulfuric acid. No other inorganic molecules were used to derive the basis set scaling factor. The test set of molecules for the

scaling factor calculation included functional groups consistent with highly oxidized monoterpene products including carboxylic acids, aldehydes, ketones, alkenes, and alcohols. Specific example molecules from the test set include methanol, acetonitrile, ethanol, formic acid, acetaldehyde, and acetone. The final scaling factor was determined by averaging over the individual scaling factors for the test set molecules. Complete thermochemical information for all systems are contained in Tables D3 through D8 in Appendix D; additionally, ball-and-stick structures for selected molecules, and Cartesian coordinates for all molecules studied are also in Appendix D.

Both gas and condensed phase dimer formation reactions were studied. For the condensed phase, the effects of solvation on the pathways listed in Table 5.1 were modeled using the SMD universal continuum model⁵⁹ as implemented in Gaussian09 (version C.01) with water, methanol, and acetonitrile being used as continuum solvent environments. The solvation model calculates the free energy of solvation ($\Delta G_{\rm s}^{\circ}$), which is the energy released when taking a molecule from the gas phase to the solvated phase. The SMD model is a modern variant of the standard polarizable continuum model, where the solute molecule is immersed in a cavity surrounded by a continuous dielectric to represent the solvent. There are no explicit chemical or functional group interactions between the solvent continuum and the solute within the Specifically, the dielectric constants are 78.4, 32.6, and 35.7 for water, cavity. methanol, and acetonitrile respectively. The electrostatic contributions to the solvation free energy are the solutions to the non-homogeneous Poisson equation, and the non-electrostatic contribution is the energy needed to create the molecular solute cavity within the continuous dielectric. As the molecular structure of each molecule is likely to change during solvation, each structure was re-optimized using the solvent model with the PW91 functional, 6-31++G(d,p) basis set, and identical optimization criteria and scaling factor. The free energy of solvation was then computed as the difference in ground state total electronic energies between the optimized solvated geometry and optimized gas phase geometry.

Туре	Monomer 1	Monomer 2	Dimer		
Terpenylic acid (TA) dimer	O OH	ОН	он о		
<i>cis</i> -pinic acid (cPA) Dimer	но-Сосон	но-Состорон	но оно о он		
TA-cPA non- covalent dimer (alkyl carboxylate)	ОНОН	но-Состорн	о он о он он		
TA - cPA non-covalent dimer (carboxylate)	ОН	но-Состорон	о он о он он		

Table 5.1a: List of monomers and non-covalent dimers in this work.

Туре	Monomer 1	Monomer 2	Dimer
Peroxy- hemiacetal	о	о	
Aldol Addition		о о он	O OH OH
Hemi-acetal	но-Сон	0=	HO-CO-OH
Esterification	о о о о	о о он	о о о о
Anhydride	но-0-С-Он	о о он	но
Di(a- hydroxy) ether	о он	ОСОН	о о о о о о о о о о о о о о о о о о о

Table 5.1b: List of monomers and covalent dimers in this work.

5.4 **Results and Discussion**

5.4.1 Considerations of Thermodynamic Standard States

Tables 5.2-5.5 give the thermochemical results for formation of the dimers shown in Table 5.1a,b. Table 5.2 gives the results for the gas phase dimer formation and Tables 5.3-5.5 for the three condensed phases. Calculations were performed using

the standard states of 298 K and either 1 atmosphere for the gas phase and 1 M for the condensed phase, and also at 373 K.

The free energy of dimerization, $\Delta G_d^{\circ}(g)$, is defined here as the free energy change that occurs when two monomer molecules combine to give a dimer molecule. In this calculation, the free energy of each reactant and product molecule is obtained from the total electronic energy plus a correction term:

$$\Delta G_d^{\circ}(g) = \left(\sum_{dimer} (E_{SCF} + G_{corr})_i\right) - \left(\sum_{mono} n_i (E_{SCF} + G_{corr})_i\right) \tag{1}$$

where E_{SCF} is the total electronic energy of the optimized structure, G_{corr} is the aforementioned correction term for the free energy (described in detail below), and n_i is the number of species *i*. G_{corr} is defined as $H_{corr} - TS_{Total}$, with $H_{corr} = E_{Total} + k_B T$. E_{Total} is the internal thermal energy, and is the sum of all energetic contributions (translational, rotational, vibrational, electronic and zero point energy). Note the electronic contribution to the internal thermal energy is 0 as it is independent of the system temperature. The scaling factor determined from the NIST method is applied only to certain terms in the E_{Total} expression, so it is not simply a vibrational frequency multiplicative scale factor applied wholesale to every correction term calculated in *Gaussian09*. G_{corr} is then calculated from the scaled E_{Total} as described above (thus is considered scaled) and the sum of it and the total electronic energy (E_{SCF}) is the Gibbs free energy for a specific molecule.

Equation 1 gives the free energy of dimerization in the gas phase. In order to calculate the free energy of dimerization in solution, the gas phase free energies of dimerization have to be modified in order to include the effects of the continuum solvent surrounding each monomer and dimer. This implies representing the gas

phase dimerization energies in the thermodynamic standard state of the condensed phase (1 M solution concentrations) as follows:

$$\Delta G_{d}^{\circ}(g, 1M) = \Delta G_{d}^{\circ}(g) + RT \ln \frac{Q^{\circ'}(g, 1M)}{Q^{\circ}(g)} = \Delta G_{d}^{\circ}(g) - RT \ln 24.5$$
(2)

where $\Delta G_d^{\circ}(g)$ is the gas phase dimerization free energy of the dimer pathway (eq. 1), and the $Q^{\circ'}$ and Q° are the reaction quotients derived from standard state conversions. A detailed description of the reaction quotients and standard state conversion factors is given by Cramer.⁶⁰ We note that the 24.5 term in Equation (2) is only for 298 K; at 373 K, it has a value of 30.6.

To find $\Delta G_a^{\circ}(aq \text{ or solv})$, the last step is to include the ΔG_s° computed from using the SMD solvent model:

$$\Delta G_{d}^{\circ}(aq \ or \ solv) = \Delta G_{d}^{\circ}(g, 1M) + \sum_{i} n_{i} \Delta G_{s,i}^{\circ}$$
(3)

where $\Delta G_d^{\circ}(g, 1M)$ is the gas phase dimerization free energy represented in the solution standard state (Equation 2), and the sum is the free energy of solvation for the dimer formation pathway, taken as the appropriate sum and difference of the individual solvation free energies of the monomers and dimers.

As a first pass at interpreting these data, the plausibility of dimer formation via a specific pathway in a given phase is given by:

If $\Delta G_d^{\circ}(g) < 0$, then the pathway could efficiently occur in the gas phase.

If $\Delta G_d^{\circ}(aq \text{ or solv}) < 0$, then the pathway could efficiently occur in the condensed phase.

If $\Delta G_d^{\circ}(g)$, and $\Delta G_d^{\circ}(aq \text{ or solv}) > 0$, then the pathway is likely to not occur in either phase.

Using these initial criteria, the pathways can be grouped into three distinct subsets: pathways likely to form oligomers in the gas phase, pathways likely to form oligomers in the condensed phase, and pathways which are unlikely to form oligomers in either phase.

5.4.2 Pathways Likely to Form Oligomers

As shown in Table 5.2, the non-covalent dimers (all three combinations of *cis*pinic acid and terpenylic acid) and the covalently bound peroxyhemiacetal dimer have $\Delta G_d^{\circ}(g) < 0$, suggesting that gas phase dimer formation is likely in each case.

Qualitatively, the non-covalent dimer results in Table 5.2 are consistent with previous experimental studies that have detected similar species in the gas phase, such as the acetic acid dimer⁶¹ and the benzoic acid dimer,⁶² and previous computational work on the *cis*-pinonic acid dimer.³² Quantitatively, the non-covalent dimer results in Table 5.2 are consistent with earlier computational work that has reported interaction energy, i.e. $\Delta E_d^{\circ}(g)$, rather than $\Delta G_d^{\circ}(g)$. Sloth et al.³⁶ studied non-covalent homo- and heterodimers dimers of *cis*-pinic acid and norpinic acid across a wide array of conformations, reporting values for $\Delta E_d^{\circ}(g)$ ranging from -35.7 kJ/mol to -89.2 kJ/mol using HF/6-31G(d), B3LYP/6-311G(d,p) and PW91/6-311G(d,p). Additionally, Claeys et al.⁶³ report a very favorable theoretical gas phase interaction energy of -72 kJ/mol for the terpenylic acid non-covalent dimer using B3LYP/6-311+G(d). For comparison, the results in Table 5.2 correspond to $\Delta E_d^{\circ}(g)$ for dimers of *cis*-pinic acid and terpenylic acid of -32.1 kJ/mol and -81.6 kJ/mol, respectively calculated at the PW91/6-31++G(d,p) level of theory.

Dimer	$\frac{\Delta G_d^{\circ}(g) \text{ (kJ/mol)}}{@ 298 \text{ K}}$	$\frac{\Delta G_d^{\circ}(g) \text{ (kJ/mol)}}{@ 373 \text{ K}}$	
Terpenylic acid dimer	-33.3	-21.3	
cis-pinic acid dimer	-27.0	26.1	
Terpenylic Acid - cis-pinic acid non-covalent dimer (alkyl carboxylate)	-30.4	-18.6	
Terpenylic Acid - cis-pinic acid non-covalent dimer (carboxylate)	-29.1	-17.0	
Peroxyhemiacetal	-14.5	52.2	
Aldol Addition	9.76	23.8	
Hemi-acetal	32.9	46.7	
Esterification	27.2	52.2	
Anhydride	72.5	52.3	
Di(α-hydroxy) ether	81.8	110.2	

Table 5.2:Gas phase dimerization free energies or all dimerization pathways studied.All values calculated using the gas phase standard state of 1 atm.

The results for condensed phase dimerization in Tables 5.3-5.5 indicate most of the dimers which are favorable in the gas phase can also be formed favorably in the condensed phase across a broad range of solvent properties at 298 K. Specifically, the non-covalent *cis*-pinic acid and terpenylic acid homodimers and the peroxyhemiacetal dimer have negative ΔG_d° values in all three solvent environments. The heterodimers of *cis*-pinic acid and terpenylic acid, interestingly, are not favorable in either water or methanol, but are favorable in acetonitrile, which is intermediate in polarity between the other two solvents. Among the covalently-bound dimers, the peroxyhemiacetal has a favorable dimerization free energy in all three solvents as well as the gas phase. The hydrated aldol has a favorable dimerization free energy in water, but not in the organic solvents or gas phase. As will be discussed later, no dimers form at 373 K, as indicated by the positive values for all free energies of dimerization.

The condensed phase results in Tables 5.3-5.5 are consistent with previous experimental studies. Shipman et al.⁶⁴ have shown that dimers of formic and trifluoroacetic acids persist in solution even at low concentrations and only break apart upon heating. Gadermann and co-workers⁶⁵ have concluded that acetic acid and formic acid aerosols exist as long chains of non-covalently linked molecules as evidenced by shifts in IR spectra. Hall and Johnston²⁴ used high performance mass spectrometry to identify many dimer products in SOA produced by α -pinene ozonolysis, including a hydrated aldol from the reaction of pinonaldehyde with *cis*-pinonic acid and a peroxyhemiacetal formed from hydroperoxide monomers that were structurally similar to those in Table 5.1. Several groups have reported the presence of peroxyhemiacetals and acylhydroperoxides in similar types of SOA samples.^{22,66,67} Theoretical work by Barsanti and Pankow²⁸ and Tong et al.³⁵ predict formation of aldol-type oligomers in the condensed phase but not the gas phase.

5.4.3 Pathways Unlikely to Form Oligomers

In addition to determining which pathways could form oligomers in the gas phase and/or condensed phases, the computational results in Tables 5.2 and 5.3 also predict four pathways which will likely not occur in either phase. These are the hemiacetal, ester, anhydride, and the di(α -hydroxy) ether paths, all of which have $\Delta G_d^{\circ} > 0$ in both phases. These results are consistent with the experimental work of Hall and Johnston²⁴ who could find no conclusive evidence for formation of hemi-acetals, esters, anhydrides, and di(α -hydroxy) ethers in SOA derived from α -pinene ozonolysis.

Table 5.3: Free energy of solvation and dimerization free energies for all pathways studied using water (ϵ =78.4) as the solvent continuum at 298 K and select pathways at 373 K. All values calculated in standard states for solvated pathways at a concentration of 1 M.

Dimer	$\frac{\sum n_i \Delta G_{s,i}^{\circ}}{\text{(kJ/mol)} (a)}$ 298 K	ΔG [°] _d (aq) (kJ/mol) @ 298 K	$\frac{\sum n_i \Delta G_{s,i}^{\circ}}{\text{(kJ/mol)} (a)}$ 373 K	ΔG [°] _d (aq) (kJ/mol) @ 373 K
Terpenylic acid dimer	32.2	-9.09	32.0	10.7
<i>cis</i> -pinic acid dimer	-2.36	-37.5	-1.88	24.3
Terpenylic acid - <i>cis</i> -pinic acid non-covalent dimer (alkyl carboxylate)	56.7	18.4	33.1	25.2
Terpenylic Acid - <i>cis</i> -pinic acid non-covalent dimer (carboxylate)	55.4	18.4	31.8	6.85
Peroxy- hemiacetal	17.9	-4.54	19.4	71.6
Aldol Addition	-5.75	-4.07	-5.14	18.4
Hemi-acetal	7.36	34.2	N/A	N/A
Esterification	-11.3	15.9	N/A	N/A
Anhydride	9.44	61.0	N/A	N/A
Di(a-hydroxy) ether	19.5	93.5	N/A	N/A

Table 5.4: Free energy of solvation and dimerization free energies for select pathways using methanol (ε=32.6) as the solvent continuum at 298 K and select pathways at 373 K. All values calculated in standard states for solvated pathways at a concentration of 1 M.

Dimer	$\frac{\sum n_i \Delta G_{s,i}^{\circ}}{\text{(kJ/mol)} (a)}$ 298 K	$\begin{array}{c} \Delta G_d^{\circ}(MeOH) \\ \text{(kJ/mol)} (a) 298 \\ \text{K} \end{array}$	$\frac{\sum n_i \Delta G_{s,i}^{\circ}}{\text{(kJ/mol)} (a)}$ 373 K	ΔG [°] _d (MeOH) (kJ/mol) @ 373 K	
Terpenylic acid dimer	34.3	-6.91	34.3	5.04	
<i>cis</i> -pinic acid dimer	3.29	-31.8	3.28	21.4	
Terpenylic Acid - <i>cis</i> - pinic acid non-covalent dimer (alkyl carboxylate)	34.8	26.9	34.8	26.9	
Terpenylic Acid - <i>cis</i> - pinic acid non- covalent dimer (carboxylate)	33.3	-3.68	33.3	8.37	
Peroxy- hemiacetal	21.4	-1.03	23.0	67.3	
Aldol Addition	-1.08	0.59	-1.08	14.8	

Table 5.5: Free energy of solvation and dimerization free energies for select pathways pathways using acetonitrile (ϵ =35.7) as the solvent continuum at 298 K and select pathways at 373 K. All values calculated in standard states for solvated pathways at a concentration of 1 M.

Dimer	$\frac{\sum n_i \Delta G_{s,i}^{\circ}}{\text{(kJ/mol)} @ 298}$ K	ΔG [°] _d (ACN) (kJ/mol) @ 298 K	$\frac{\sum n_i \Delta G_{s,i}^{\circ}}{\text{(kJ/mol)} @}$ 373 K	ΔG [°] _d (ACN) (kJ/mol) @ 373 K
Terpenylic acid dimer	23.9	-17.4	23.9	-5.38
<i>cis -</i> pinic acid dimer	-4.95	-40.1	-4.95	13.3
Terpenylic Acid - <i>cis</i> - pinic acid non-covalent dimer (alkyl carboxylate)	36.8	-1.47	36.8	-2.69
Terpenylic Acid - <i>cis</i> - pinic acid non-covalent dimer (carboxylate)	35.8	-1.18	35.8	-2.14
Peroxy- hemiacetal	22.2	-0.24	22.2	68.3
Aldol Addition	11.0	12.7	11.0	26.9

5.4.4 Gas Phase Dimers as Particle Formation Agents

New particle formation occurs when gas phase species come together to form stable molecular clusters that subsequently grow to the size of several tens of nanometers.⁶⁸ For ambient new particle formation in a boreal forest environment, Riipinen et al.⁶⁹ have suggested that gas phase concentrations of non-volatile organic molecules on the order 10^6 to 10^7 molecules/cm³ are needed. For laboratory experiments where SOA is generated by the oxidation of α -pinene, it has been argued that particle formation proceeds by the formation of non-covalent dimers of carboxylic acids.^{33,70} It is within this context that the dimerization free energies in Table 5.2 are assessed with respect to new particle formation. This assessment requires knowledge of relevant gas phase concentrations of the monomer precursors.

Ambient levels of α -pinene vary significantly based on location, time-of-day and time-of-year, with values ranging from about 0.05 to 4 ppbv.⁷¹⁻⁷¹ Laboratory experiments use significantly higher concentrations, typically on the order of 5 to 500 ppb, owing to the need to generate sufficient aerosol for chemical analysis.⁷⁴⁻⁷⁶ Reported ambient concentrations of monomer oxidation products, measured by extraction of filter samples, include 7 ng/m³ for *cis*-pinic acid, ⁷¹ 0.6-46.5 ng/m³ for *cis*-pinonic acid ^{71,72} and 8.5 to 15 ng/m³ for terpenylic acid.⁷¹ These measurements suggest that ambient oxidation product concentrations are about 10% or less of the α pinene concentration.

Figure 5.1 shows plots of equilibrium dimer concentration vs. starting organic vapor concentration assuming that all molecules exist initially as monomers. For hetero-dimers, the starting concentration is split evenly between the two monomers. For a starting concentration of several hundred pptv, which represents the approximate upper limit in ambient air, the only dimer able to contribute to nucleation as defined by Riipinen et al.⁶⁹ (>10⁶ cm⁻³) is the terpenylic acid non-covalent dimer. A reasonable estimate of the uncertainty for the DFT-calculated free energy of dimerization is approximately +/- 4 kJ/mol. The dashed lines bracketing the solid line for the terpenylic acid dimer in Figure 5.1 show the effect of this uncertainty. The

upper dashed line (more favorable free energy) predicts a starting concentration of about 100 pptv is sufficient to generate the needed dimer concentration, while the lower dashed line (less favorable free energy) predicts a somewhat larger starting concentration, around 500 pptv.

As the starting concentration increases into the range used for laboratory studies, more dimers are able to contribute to nucleation. For example, a starting concentration of 10 ppbv gives a dimer concentration above 10^6 cm⁻³ for all three non-covalent dimers and the peroxyhemiacetal. The results in Figure 5.1 confirm the hypothesis that terpenylic acid represents a key nucleating agent in ambient air,⁶³ while a variety of particle formation pathways exist in most laboratory experiments.

The above discussion is focused on nucleation by organic acids alone and comparing the computational results to experimental measurements. However, other nucleation pathways exist, most notably those involving sulfuric acid in combination with organics. Recent chamber and theoretical studies⁷⁷⁻⁷⁹ involving this combination suggest that sulfuric acid nucleation is enhanced by the addition of highly functionalized organic acids. In addition, it has been suggested that nucleation by organic molecules alone may not occur, as organic molecules are often hydrophobic and sulfuric acid is needed to assist growth.⁸⁰ Clusters of sulfuric acid with organic molecules is beyond the scope of the work presented here.



Figure 5.1: Plot of the fraction of dimer formed versus the total starting concentration of the starting monomer for select gas phase dimers at 298 K. (cPA)₂ is cis-pinic acid dimer, PH is peroxyhemiacetal dimer, (TA)₂ is terpenylic acid dimer, and TA-cPA is terpenylic-acid-cis-pinic acid alkyl carboxylate dimer. Dashed lines indicate bracket concentration range for the terpenylic acid dimer.

5.4.5 Condensed Phase Dimers in SOA

Oligomer formation in the condensed phase changes the effective molecular weight, which in turn affects a number of important properties (e.g. vapor pressure and solubility) and processes (e.g. gas-particle partitioning and water uptake).² In the condensed phase, any individual molecular component constitutes a minor fraction of the total mass. Assuming a liquid-like phase, the remaining matter can be regarded as "solvent", either aqueous or organic in character. In a study of laboratory SOA

generated from α -pinene ozonolysis, major products such as *cis*-pinic acid and *cis*-pinonic acid were found to constitute 15% and 7%, respectively, of the SOA mass.²⁴ Since on the order of 1000 unique molecular formulas can be assigned among the products of α -pinene SOA,^{17,19,50} a more typical mass fraction of a single compound might be on the order of 10⁻³. It is within this context that condensed phase dimer formation is studied based on the dimerization free energies in Tables 5.3-5.5.

Depending on whether the product is a homo- or hetero- dimer, the equilibrium expression can be written as:

$$K_{eq} = \frac{[Dimer]}{[Monomer]^2} \quad or = \frac{[Dimer]}{[Monomer\ 1][Monomer\ 2]} \tag{4}$$

where the total concentration is given by:

$$[Total] = [Monomer] + 2[Dimer] or$$
$$= [Monomer 1] + [Monomer 2] + 2[Dimer]$$
(5)

from which the fraction existing as dimers can be determined:

$$f_{dimer} = \frac{[Dimer]}{[Total]} \tag{6}$$

Figures 5.2 and 5.3 show plots of f_{dimer} vs. total concentration for two different scenarios, an aqueous-like medium (Figure 5.2) and a methanol-like medium (Figure 5.3). In each case, the total concentration is expressed as the mass fraction (sum of monomer and dimer masses divided by total SOA mass) assuming a density of 1.2 g/cm³ and for heterodimers, the monomer concentration is split evenly between the two reactants. In both media, almost all of the *cis*-pinic acid exists as a non-covalent dimer, even for a mass fraction of 10^{-4} . The terpenylic acid dimer and

peroxyhemiacetal are also quite favorably formed, reaching dimer fractions well above 0.1 for a total mass fraction of 0.01. The hydrated aldol is less favorable, but still reaches a dimer fraction of 0.1 for a mass fraction above 0.1. Figure 5.3 also shows dimer fractions for the non-covalent heterodimer of *cis*-pinic acid and terpenylic acid via the β -carbon terminus of *cis*-pinic acid, which had a favorable $\Delta G_d^{\circ}(solv)$ in methanol. Together, these calculations show specific dimerization reactions can be very efficient, which is consistent with experimental measurements showing oligomers can represent half of the total mass of laboratory SOA.^{13,24,63}

This work used an implicit solvation technique, the polarizable continuum model, to represent the interaction of the monomers and dimers with water. Another possible approach is explicit hydration, where hydrogen bonding between individual water molecules and organic monomers/dimers is considered. Water has been shown to promote hydrogen bonding in clusters of carboxylic acids and sulfuric acid, thereby making the free energy of cluster formation more favorable.^{81,82}



Figure 5.2: Plot of the fraction of dimer formed versus mass fraction of the starting monomer in total SOA for each favorable condensed phase dimer in the water continuum at 298 K. Squares represent cis-pinic acid dimer, circles represent terpenylic acid dimer, triangles for the peroxyhemiacetal dimer, and diamonds for the aldol addition dimer.



Figure 5.3: Plot of the fraction of dimer formed versus mass fraction of the starting monomer in total SOA for each favorable condensed phase dimer in the methanol continuum at 298 K. Squares represent cis-pinic acid dimer, circles represent terpenylic acid dimer, triangles for the peroxyhemiacetal dimer, diamonds for the aldol addition dimer, and hexagons for the terpenylic acid-cis-pinic acid carboxylate dimer.

5.4.6 Thermal Stability in the Condensed Phase

As mentioned previously, gas-particle partitioning of semi-volatile organic molecules can strongly influence the total amount of SOA that is formed. Pankow's equations⁶ are often used to predict the fraction of organic matter existing in the particle phase, but can underestimate this fraction if oligomerization is not taken into account. Oligomer formation increases the molecular weight and decreases the vapor

pressure, both of which would be expected to enhance partitioning to the particle phase. This process could explain in part why atmospheric models tend to underpredict ambient SOA levels.¹⁷ Experimentally, gas-particle partitioning is often assessed in thermal denuder experiments where the aerosol is heated to a temperature of about 100°C to evaporate semi-volatile materials and thereby assess volatility.^{20,21} Implicit in this experiment is the assumption that molecular compounds simply evaporate at the higher temperature rather than decompose to smaller (and more volatile) products.

In order to explore oligomer thermal stability, the same dimer formation pathways studied at 298 K were also studied at 373 K in both water-like and methanol-like media, and the data are presented in Tables 5.3-5.5. As seen in these tables, the free energies of formation for every dimerization reaction in both solvation media are considerably less favorable (more positive $\Delta G_d^{\circ}(aq \text{ or solv})$) at 373 K vs. 298 K. Table 5.6 gives the calculated dimer fractions at 373 K relative to 298 K for water and methanol. In each case, the ratio is much less one, independent of the solvent medium. These results are consistent with recent experimental work²⁶ showing that oligomers decompose when α -pinene SOA is heated in a thermal denuder to 100°C. Table 5.6. Ratios of dimer fractions $[(f_{dimer,373})/(f_{dimer,298})]$ of select condensed phase dimers in water and methanol derived using the predicted standard state ΔG_d° for each pathway. Values for the remaining dimers given in Table D9 of Appendix D.

	cis-Pinic	cis-Pinic	Terpenylic	Terpenylic	Aldol	Aldol
	Acid Dimer	Acid Dimer	Acid Dimer	Acid Dimer	Addition	Addition
Mass Fraction						
of Monomer in	Water	Methanol	Water	Methanol	Water	Methanol
total SOA mass						
0.001	5.21E-06	1.28E-05	6.45E-04	1.71E-02	6.45E-04	1.08E-02
0.01	5.23E-05	1.28E-04	2.83E-03	5.05E-02	7.63E-04	1.13E-02
0.1	5.75E-04	1.40E-03	2.25E-02	2.40E-01	2.13E-03	1.65E-02

5.5 Conclusions

Quantum mechanical calculations of the molecular structure and thermochemistry were performed for monomers and dimers relevant to the formation of SOA from the oxidation of α -pinene. These calculations were performed in the gas phase and condensed phase using water, methanol, and acetonitrile solvent continua in a multi-step method consisting of classical sampling, optimization and energy calculations using semi-empirical and density functional quantum methods at both 298 K and 373 K.

The quantum chemical modeling results were used to calculate equilibrium constants, with the aim of estimating the concentration of dimers existing in each phase at a particular concentration level of total organic material. Using these estimated concentrations, the role of gas phase dimers as nucleating agents was explored, as well as the number of condensed phase dimers which are formed as a function of total SOA mass and the role of temperature in dimer stability. Gas phase dimers of terpenylic acid have the highest concentrations at relevant ambient concentrations, implicating them as a potential nucleating species. In the condensed phase, the dimer to monomer ratio often exceeds 10% under relevant conditions, which is sufficient to influence chemical properties and processes. The fraction of dimers at 373 K vs. 298 K is very small, indicating dimers decompose when heated. The computational findings presented here are consistent with recent experimental observations showing an important role for oligomers in SOA chemistry.

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Chapter 6

CONCLUSIONS AND FUTURE DIRECTIONS

6.1 Atmospheric Relevance of Dissertation Work

In this dissertation, the tools of computational chemistry were used to gain an improved understanding of fundamental chemical process governing the formation of new particles in the atmosphere. New particle formation (NPF) begins with the formation of molecular clusters smaller than 1 nm that are a difficult system to characterize experimentally, highlighting the need for computations. Investigating the structure and energetics of molecular clusters across a broad range of compositions, sizes and polarities gives information on the role of specific chemical species. Cluster computations were performed using a combination of quantum chemical techniques, including the semi-empirical AM1^{1,2} method and density functional (DFT) method PW91.^{3,4} Configuration sampling, an important aspect of calculating accurate geometries of weakly-bound molecular systems, was done making use of a hybrid searching method combining Monte Carlo⁵ motion searching with the AM1^{1,2} method for energy computations. DFT offers the best cost-accuracy balance among the standard quantum chemical methods while allowing for the computation of accurate structures without reaching the limits of computational power. DFT, specifically the oft-used PW91 method, was used to calculate the final geometries and thermochemistry of the systems studied in this dissertation. Developing a more accurate picture of the early steps of molecular cluster and nanoparticle growth is critical for determining the impact of new particle formation on global climate.

6.1.1 The Structures of Molecular Clusters Formed in New Particle Formation

Because the dominant species contributing to NPF are acids, bases and water, it has been suggested that the nucleation of new particles must proceed via the formation of hydrogen bound molecular clusters.^{6,7} Experimentally determining the structures of these types of clusters is an analytical challenge. Commonly used mass spectrometric methods with high resolving power, such as FTICR-MS provide accurate cluster compositions but cannot provide direct information about the specific molecular orientations critical to assessing cluster reactivity.⁸⁻¹¹ Spectroscopic methods, such as cryogenic pulsed ion¹² infrared spectroscopy or ultracold argon matrix infrared spectroscopy¹³⁻¹⁵, are starting to come online and provide incredibly useful information about the weakly bound nature of molecular clusters, but their use is limited to very small clusters since larger clusters are too vibrationally "hot" and simply fall apart. For these reasons, computations are invaluable at probing structural details.

Chapters 2-4 explored the structures of both charged and uncharged molecular clusters containing sulfuric acid, ammonia and dimethylamine (and their corresponding ions) and water. Because these clusters are composed of the same molecules, it is expected that their molecular structures would be composed of similar types of interactions. Independent of cluster composition or charge, the structures of these clusters are composed of a large network of short-distance hydrogen bonds derived from the proton transfer from sulfuric acid to a base, which suggests that the true driving force for cluster formation is the electrostatic interactions between the species which compose the cluster bonding network. The proton transfers occurring in these types of clusters are extensive, with nearly all cluster constituents being ions. In

only molecules remaining uncharged being excess acid molecules (for example, in acidic negatively charged clusters) or water. While this is a general feature of these clusters, there are specific features unique to both the different compositions and different cluster polarities. Positively charged clusters consist only of hydrogen bonds between the acidic bisulfate ions and the basic ammonium or dimethylammonium These types of interactions are often very short in length and are the most ions. energetically favored; as a consequence, these clusters are the most compact in terms of diameter. In addition, positively charged clusters have the single remaining proton on the bisulfate ion pointing into free space. Negatively charged clusters share similar structural features as their positively charged counterparts, but also have anion-anion interactions as well as anion-molecule hydrogen bonds. These interactions less energetically favored than protonated base-bisulfate interactions and as a result these clusters are larger than the positively charged clusters of similar composition. The uncharged clusters have structures which are intermediate between those of their charged analogs. The anhydrous uncharged clusters contain both cation-anion and anion-anion interactions, but because they do not contain any neutral sulfuric acid molecules like the negatively charged clusters, there are no bisulfate-sulfuric acid interactions. These structural features impart distinct reactivity that depends on cluster charge.

Chapter 5 describes the structures of clusters composed purely of oxidized organic molecules. The clusters in Chapter 5 are the dimers which result from the reactions of the oxidation products of α -pinene. The dimers in Chapter 5 fall into two sets: non-covalent dimers and covalent dimers. The non-covalent dimers are formed via hydrogen bonding between the carboxylic acid termini of the monomer oxidation

products. These hydrogen bonds form the well-known two hydrogen bond ring system typical of carboxylic acids. The covalent dimers are formed from classical organic reactions such as aldol addition and peroxide formation. These reactions occur in both phases, and each phase exhibits specific reactions which occur in it; consequently, dimers have an impact on both the nucleation and growth of new particles.

The structural results of Chapters 2-4 agree with recent results gathered from ultracold infrared spectroscopic studies of sulfuric acid molecular clusters.¹²⁻¹⁵ First, these studies concluded that these types of clusters, independent of composition, contain a significant hydrogen bond network as evidence from coupled IR spectral modes. Hydrogen bonding in positively charged clusters occurs only between sulfuric acid ions and base ions, whereas hydrogen bonds between bisulfate ions are observed in charged clusters. Other studies including water in the clusters have indicated that water molecules stabilize the formation of acid-base hydrogen bonds via interacting with both acid and base ions within cluster structures. Experimental observations such as these offer strong support for the computational structural results presented in Chapters 2-4, which describe molecular clusters with structural features consistent with those observed in the experiments. Cluster structure imparts reactivity and it is of critical importance to understand how the unique structural features impact the energetics and ultimately which clusters populate the final distribution.

6.1.2 Energetic Features Governing Cluster Growth

Assessing cluster energetics and reactivity is a complex and challenging task. The molecular picture of cluster formation is difficult to pin down because the potential energy surfaces are often shallow, broad and contain features resulting from many different energetic processes. As with the structural features described above, modern analytical tools such as mass spectrometry¹⁶ and pulsed cluster IR spectroscopy¹² have been able to provide some information about bond energies and related energetic features but cannot resolve the level of detail of specific molecular interactions. Computations are thus necessary in order to explore in great detail the specific energy landscapes of cluster formation.

Chapters 2-4 focused specifically on cluster formation energetics for acid-base clusters. These clusters are composed of an extensive network of hydrogen bonds which indicate exactly how the cluster structure is arranged. However, the true driving force for cluster formation is the electrostatic interactions between the clusters constituents. These clusters, independent of size, composition or polarity, all have very strong electrostatic forces, and the role of electrostatic forces can be examined in a few different contexts. The first of these is the cluster binding energy, which is the free energy of forming each cluster from its constituent ions. This quantity is not directly relevant to atmospheric processes, but serves to highlight complex interactions driving cluster formation. The binding energies for all the clusters studied in this dissertation are large and negative, indicative of the strong forces holding these clusters together. Within charged clusters, positively charged clusters have more favorable binding energies than negatively charged clusters. This is due to the types of interactions within the cluster: the anion-anion and ion-molecular interactions are longer in length and less electrostatically favorable, which serves to drive the free energy to less negative values. Positively charged clusters have only cation-anion interactions, which are shorter and more electrostatically favored. Binding is a composition dependent process. Ammonia clusters bind more favorably than amine clusters due to the ammonium ion's smaller radius and increased hydrogen bonding capacity.

The cluster formation free energy is the free energy change of forming a cluster from its constituent molecules, and is an atmospherically relevant process. Formation free energies are both polarity and composition dependent. Like binding energies, formation free energies are more favorable for charged clusters than uncharged clusters because of the extra ion within the cluster. For all clusters, the formation free energies of amine containing clusters are more favorable even though ammonia binds better in clusters. This is due to the much stronger gas phase basicity of amines driving the proton transfer reactions critical to cluster formation.

The energetic effects of hydration on cluster formation were explored in Chapter 3 of this dissertation. Hydration is a ubiquitous process in the atmosphere due to the high concentration of water vapor. Sulfuric acid, ammonia and amines all interact very strongly with water molecules. Water has a small stabilizing effect that enhances formation of clusters containing both ammonia and amines, but with a greater enhancement for ammonia containing clusters. There is also a clear size dependence to hydration: larger clusters tend to hav more water in their structure than smaller clusters, independent of composition. Water also appears to enhance cluster growth (via the addition of an acid-base pair to a pre-existing cluster) for ammonia clusters but inhibits that of amine clusters. These energetic features are the result of three main competing processes: hydrogen bonding with water molecules, electrostatic force changes upon hydration and the loss of entropy. All of these effects are
energetically similar in magnitude but strongly depend on local cluster size and composition.

6.1.3 Chemical Mechanisms of Cluster Formation

The energy landscape of molecular cluster formation has contributions from a variety of different processes and all are in a delicate balance with one another. Base incorporation into growing molecular clusters as a growth mechanism has been extensively studied in our laboratory and has been shown to be a key process for cluster growth. Chapters 2 and 3 focus on this process in extensive detail. Amine substitution for ammonia in both charged and uncharged clusters was found to be an energetically favorable process, with the computational results for the free energy of substitution matching nicely with experimental results derived from observed rate Amine substitution is a charge dependent process, occurring more constants. favorably in positively charged clusters than in either negatively charged or uncharged clusters. This process is also size dependent, occurring more favorably in smaller clusters than in larger clusters. The mechanism of amine substitution is driven by two competing energetic factors: acid base binding energies competing with amine basicity. Amines are substantially stronger bases than ammonia and this drives the substitution process in the forward direction. However, ammonia binds better in clusters, so there is an energetic penalty paid in order for the amine to displace the ammonia. The size dependence of amine substitution occurs due to steric hindrance. As clusters grow, base molecules eventually can become surrounded by other molecules in the cluster, eventually driving some molecules to the "core" of the This "core" base ion is then rendered inaccessible to incoming amine cluster molecules and cannot be substituted for. This effect would only be exacerbated as the

"surface" ammonium ions in a cluster are already substituted. The cluster hydration studied in Chapter 3 also has an effect on amine substitution. Hydration appears to enhance substitution for smaller clusters but inhibit it for larger clusters. These effects all combine to suggest that amines and amine chemistry is of critical importance for the initial steps of cluster formation but would have less of an effect on the continued growth of these clusters into new particles.

Chapter 4 described the detailed potential energy surface of charged ammonium bisulfate cluster growth. Recent experiments performed in our laboratoy studied the fragmentation energetics of charged ammonium bisulfate clusters as a way to infer the cluster growth mechanisms.¹⁷ Cluster growth was hypothesized to occur via sequential addition of acid followed by base. Calculations of this explicit growth pathway via examining the transition states and reaction paths of each addition step do not fully support this model. Sulfuric acid addition has small activation free energy barriers in the +8-12 kJ/mol range; this is consistent with experimental and field observations that sulfuric acid uptake is reasonably fast. The addition of ammonia, however, had an activation barrier ranging from ~+29-53 kJ/mol. Thus, the uptake coefficients derived from these activation free energy barriers are far too small for clusters to grow via this mechanism and therefore ammonium bisulfate clusters must grow via another mechanism. Nonetheless, the formation of ammonia-sulfuric acid clusters is an important feature of the NPF process.

Chapter 5 focused on the role of oxidized organics as a mechanism for cluster growth as organics make up a significant portion of the global aerosol budget. Chapter 5 detailed a study aimed to understand experimental measurement of organiconly particle formation in both the gas phase and condensed phase. Low volatility organics form in both phases and can contribute to the formation of molecular clusters by being able to partition to the condensed phase or condense onto pre-existing particles. Gas phase hydrogen bond dimers and peroxides were formed favorably and many exist in large enough abundance to nucleate and form clusters. Condensed phase hydrogen bond dimers as well as peroxides and aldols exist in sufficient concentrations to influence both chemical properties and aerosol partitioning.

The results described in Chapters 2-4 correlate well with broad spectrum measurements made in the CLOUD (Cosmics Leaving OUtdoor Droplets) chamber at the European Organization for Nuclear Research (known as CERN) on both inorganicbased and organic-based nucleation.¹⁸⁻²⁰ The CLOUD chamber, which is a very large environmental chamber used to simulate the atmosphere, represents an extremely clean and controllable environment with which to perform experiments on the nucleation of new particles from trace gas precursors with the outlets of the chamber being attached to an extensive suite of both aerosol and chemical instrumentation. Sulfuric acid-base nucleation has been studied extensively in the chamber, with ammonia based nucleation by Kirkby et al.¹⁸ and amine based nucleation being reported by Almeida et al.¹⁹ The studies of ammonia nucleation revealed that surprisingly, amine substitution was a key factor in the results. This was due to amines being a trace contaminant in the chamber, even though the chamber was designed to be extremely clean before experiments begin. Amine clusters were observed with high intensity, implicating amines as key players in the formation of the smallest clusters and further implicating amines as a critical species in NPF. An additional result of the Kirkby et al.¹⁸ study was the observed clusters formed in the sulfuric acid-ammonia system did not grow at the collision-limited rate they were expected to follow. This is consistent with the presence of an activation barrier to cluster growth akin to the barrier to ammonia addition described in Chapter 4 of this dissertation. Additionaly, the presence of an activation barrier is consistent with the results obtained from a modeling study which calculated cluster distributions using quantum chemical/kinetic methods and compared those to the observed cluster distributions from the CLOUD chamber.^{20,21} Such a barrier would alter the final distribution of clusters, which cluster compositions grow out of the cluster pool, and ultimately which clusters could potentially impact climate. CLOUD work continued with the Almeida et al.¹⁹ study of sulfuric acid-amine nucleation which showed that amine clusters essentially outcompete ammonia clusters and enhance particle formation rates by proceeding at the collision limited rate independent of cluster polarity.

Organic-assisted nucleation and growth has been studied in laboratory and field measurements²²⁻²⁴, and the results of the work presented in Chapter 5 is consistent with these observations. The combined modeling and field study by Paasonen et al.²³ is the most complete work to date on the direct correlation of organic vapors condensing onto sulfuric acid-based particles. Organic vapors had a direct impact on observed and modeled nucleation rates via the presence of a substantial enhancement in the rates when low volatility organics were included as part of the framework. This suggests that organic vapors must have strong intermolecular interactions with each other in order to form stable clusters.

The resolved features of the cluster formation energy landscape presented in this dissertation is key to enhancing the accuracy of global climate models and their predicative ability to model the effects of aerosols on climate. Of particular note is the potential inclusion of aerosol kinetic mechanisms, such as the presence of the activation barriers presented in Chapter 4 and the formation of multiphase organic dimers presented in Chapter 5. What these results serve to show is how the reactions of very low abundance gases in the atmosphere can have a substantial impact on fundamental aerosol formation processes and need to be incorporated into climate models.

6.2 Future Directions for Studying Molecular Clusters and New Particle Formation

The work in this dissertation provided both a framework for modeling molecular clusters as well as insight into the direct chemical mechanisms governing new particle formation. The results of this work have answered important questions about cluster formation mechanisms but have also asked new questions that remain unanswered. Two novel areas of study and potential ways to address them are provided below.

6.2.1 Molecular Structure, Electrical Mobility Shifts and Collisional Cross Sections of Hydrated Amine Clusters

In order to gain a complete understanding of the fundamental chemistry behind aerosol reactions, information about the kinetics of reactions is necessary. Aerosol reactions occur via the collisions of molecules with pre-existing particles or molecular clusters; this implies understanding the probability of these collisions occuring. This probability is known as the collisional cross section, and it is the area around a particle where an incident particle needs to approach in order for a reaction to occur. Calculating the collisional cross sections is a modeling challenge due to a number of factors, one example being the inelastic versus elastic collision energy transfer.²⁵ One of the emerging methods used to tackle this problem has been to study the cross sections with a combination of ion mobility spectrometry and mass spectrometry to ascertain both electrical mobility and chemical composition followed by using the determined cluster compositions as input for collisional cross section modeling.²⁶⁻²⁹ This approach has been successfully applied to large biomolecules²⁹ and inorganic nanoparticles²⁷ with relatively fixed compositions but has not provided clear information for atmospherically relevant clusters.

Atmospherically relevant molecular clusters, particularly those composed of sulfuric acid and bases such as dimethylamine, have constantly changing compositions as molecules condense into and evaporate out of the cluster. One of the key questions is how the uptake of water drives these changes in composition, which in turn alters the electrical mobility and ultimately the collisional cross sections and chemical reactivity. Hydration, as shown in Chapter 3 of this dissertation, can have very different effects on formation and growth depending on cluster size and composition. This suggests that the local molecular structure of a hydrated dimethylamine bisulfate cluster strongly influences both the measured ion mobility as well as the collisional cross section. Therefore, quantum chemistry provides a way to survey a broad array of accurate cluster structures which can be used to calculate observed electrical mobility shifts and collisional cross sections.

6.2.2 Understanding the Formation of Larger Clusters with both Organic and Inorganic Components

Because of the large variety of oxidized organic molecules in the atmosphere and their very complex chemistry, their reactions and role in new particle formation is a very challenging analytical problem to tackle. Recent laboratory and field measurements have indicated that sulfuric acid nucleation can occur with oxidized organic molecules and that organic species are the key to furthering particle growth via condensation into freshly formed particles.^{6,22-24,33,34} However, these laboratory and field measurements were not able to identify exact molecular structures contributing to their observations due to limited resolution of the utilized mass spectrometers. This is an area where quantum chemistry is not limited in scope.

Quantum chemical methods have been used for quite some time as survey tools for both large molecular systems and small systems with many molecular structures. The classic example of this is the use of molecular mechanics and quantum chemistry to screen the activity of potential therapeutic targets (commonly known as small molecules) against the active site of an enzyme or protein, with structures often being found in a library of molecules. When considering the system of sulfuric acid clusters and highly oxidized organic molecules, the idea would be identical: create a library of small molecules (the oxidized organics) and the larger target molecule (a sulfuric acid-base cluster) and let them interact in varying numbers using lower levels of theory, such as semi empirical quantum chemical methods or well-parameterized molecular mechanics force fields, to see which molecules interact most favorably with the cluster. This can be followed by further energetic refinement with density functional methods where size permits using hybrid techniques like mixed theory QM/MM modeling. One can envision building large libraries of oxidized molecules derived from the ozonolysis of important precursor molecules: biogenic sources such as isoprene, α -/ β -pinene and limonene as well as anthropogenic organic emissions such as toluene or alkyl cyclic siloxanes. Screened interactions like these can be directly compared to measurements of cluster composition using high resolution mass spectral approaches to develop a better understanding of how organic molecules interact with sulfuric acid-base clusters. Building libraries of interactions provides a unique way to survey the broad and complex energy landscape driving new particle formation.

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Appendix A

COMPLETE THERMOCHEMICAL DATA, OPTIMIZATION INFORMATION AND MOLECULAR COORDINATES FOR CHARGED MOLECULAR CLUSTERS

A.1 Additional Thermochemical Tables and Optimization Information

Table A1: Comparison of optimization criteria and integration grid density on cluster binding energy. All calculations performed on 2-1 ammonium bisulfate cluster; values in hartrees.

Cluster or Ion	G, Default Criteria	G, Tight Optimization with default grids	G, Default optimization with ultrafine grids	G, Tight optimization with ultrafine grids
NH_4^+	-56.848074	-56.848074	-56.848073	-56.848073
HSO ₄ ⁻	-699.646488	-699.646488	-699.646711	-699.646707
2-1 Cluster	-813.566833	-813.566838	-813.566825	-813.566820
ΔG _{bind}	-0.224197	-0.224202	-0.223968	-0.223967
ΔG _{bind} (kJ/mol)	-588.629224	-588.642351	-588.027984	-588.025389

Criteria Parameters:

- 1. <u>Default Optimization</u>: RMS Force = $3*10^{-4}$ a.u; RMS Displacement = $1.2*10^{-3}$ a.u; SCF convergence = 10^{-6} a.u.
- 2. <u>Tight Optimization:</u> RMS Force = 10^{-5} a.u; RMS Displacement = $4*10^{-5}$ a.u; SCF convergence = 10^{-8} a.u.
- 3. <u>Default (Fine) Integration Grid:</u> pruned (75,302) grid, with 75 radial function shells and 302 angular points per radial shell
- 4. <u>Ultrafine Integration Grid:</u> pruned (95,590) grid, with 95 radial function shells and 509 angular points per radial shell

Table A2: Comparison of low energy isomer stabilities from Monte Carlo conformational search. Lowest five isomers (all within 4 kJ/mol of most stable) shown for 2-1 ammonium bisulfate cluster. Values presented in order of stability and given in kJ/mol (calculated at gas phase standard conditions)

Cluster	Monte Carlo Step #	AM1 G (kJ/mol)	PW91 G (kJ/mol)
$[(NH_4^+)_2(HSO_4^-)_1]^+$	122	-107.48	-2136019.757
$[(NH_4^+)_2(HSO_4^-)_1]^+$	92	-106.87	-2136019.733
$[(NH_4^+)_2(HSO_4^-)_1]^+$	54	-106.59	-2136019.728
$[(NH_4^+)_2(HSO_4^-)_1]^+$	447	-105.04	-2136019.725
$[(NH_4^+)_2(HSO_4^-)_1]^+$	845	-104.12	-2136019.723

Table A3: Comparison of PW91 cluster formation free energies with published values calculated using correlated wavefunction methods for series of small negative clusters.¹ Values given in kJ/mol (values from reference converted from kcal/mol).

Cluster	ΔG (PW91)	$\Delta G (RI-MP2-TZ)^{1}$
$[(NH_3)(HSO_4)]$	7.97	7.32
$[(CH_3)NH_2(HSO_4)]^-$	3.54	5.02
$[(CH_3)_2NH(HSO_4)]^-$	2.83	-3.18
$[(CH_3)_3N(HSO_4)]^{-1}$	15.0	2.10

<u>Note:</u> RI-MP2-TZ = RI-MP2/aug-cc-pV(T+d)Z

1. Kurtén, T.; Loukonen, V.; Vehkamäki, H.; Kulmala, M. *Atmos. Chem. Phys.* **2008**, *8*, 4095-4103.

	E	Н	G
Positively Charged Clusters			
$[(NH_4^+)_2(HSO_4^-)_1]^+$	-2135919	-2135885	-2136020
$[(NH_4^+)_3(HSO_4^-)_2]^+$	-4122597	-4122541	-4122729
$[(NH_4^+)_4(HSO_4^-)_3]^+$	-6109296	-6109207	-6109454
$[(NH_4^+)_4(HSO_4^-)_3]^+$	-8095978	-8095873	-8096177
$[(NH_4^+)_6(HSO_4^-)_5]^+$	-10082654	-10082527	-10082878
$[(NH_4^+)_7(HSO_4^-)_6]^+$	-12069370	-12069216	-12069635
$[(NH_4^+)_8(HSO_4^-)_7]^+$	-14056065	-14055891	-14056349
$[(NH_4^+)_9(HSO_4^-)_8]^+$	-16042748	-16042552	-16043050
$[(NH_4^+)_{10}(HSO_4^-)_9]^+$	-18029469	-18029253	-18029793
$[(NH_4^+)_{11}(HSO_4^-)_{10}]^+$	-20016140	-20015894	-20016501
$[(DMAH^{+})_{5}(HSO_{4})_{4}]^{+}$	-9126829	-9126682	-9127091
Negatively Charged Clusters			
$[(H_2SO_4)_2(NH_4^+)_2(HSO_4^-)_3]^-$	-9486752	-9486659	-9486933
$[(H_2SO_4)_3(NH_4^+)(HSO_4^-)_2]^-$	-9338291	-9338207	-9338461
$[(H_2SO_4)_3(DMAH^+)(HSO_4)_2]^-$	-9544445	-9544351	-9544634
$[(H_2SO_4)_2(DMAH^+)_2(HSO_4^-)_3]$	-9899070	-9898962	-9899271
$[(H_2SO_4)(DMAH^+)_3(HSO_4)_4]$	-10253587	-10253458	-10253828
$[(DMAH^{+})_{4}(HSO_{4})_{5}]^{-}$	-10608243	-10608105	-10608485

Table A4:Thermochemical parameters for all clusters discussed in Chapter 2 and
not discussed. All values are in kJ/mol and calculated at gas phase
standard state of 1 atm and 298 K.

A.2 Cartesian coordinates for optimized free molecules, molecular ions, and cluster geometries given in Chapter 2.

Sulfuric Acid (H ₂ SO ₄)				
S	-0.041051	0.116907	-0.005283	
0	-0.503645	1.481157	0.236644	
0	1.344855	-0.266772	-0.261704	
0	-0.521366	-0.844237	1.247885	
0	-0.989918	-0.439758	-1.236017	
Н	-1.358702	-0.472479	1.601060	
Н	-0.573672	-1.258718	-1.582586	

Ammonia (NH₃)

Н	0.119902	0.104506	0.322174
Ν	-0.287899	0.858690	0.878649
Н	0.442767	1.556541	1.033208
Н	-1.017870	1.297662	0.313669

Dimethylamine ((CH₃)₂NH)

Ν	-0.565534	-0.340881	-0.058111
С	-0.657498	1.115761	-0.010334
С	0.809827	-0.825464	0.020039
Н	-1.116774	-0.745655	0.702103
Η	-1.714398	1.421753	-0.014380
Н	-0.161324	1.576172	0.874312
Н	-0.184386	1.538848	-0.911944
Н	0.815795	-1.925612	0.037994
Н	1.359489	-0.503649	-0.879987
Η	1.374801	-0.456073	0.906109

Bisulfate Ion (HSO₄⁻)

S	0.160971	-0.021465	-0.000028
0	0.314224	-0.826342	-1.257267
0	-1.521151	0.433242	-0.000088
0	0.314096	-0.826363	1.257218
0	0.819501	1.315510	0.000020
Н	-1.984109	-0.427556	0.000147
11	-1.70+107	-0.427550	0.000147

Ammonium Ion (NH₄⁺)

Η	0.072229	-0.435680	0.707763
Ν	0.059382	0.596598	0.725020
Н	1.027427	0.953550	0.685815
Η	-0.470182	0.947852	-0.088765
Η	-0.391956	0.920679	1.595267

Dimethylammonium Ion ((CH₃)₂NH₂⁺)

Ν	-0.204318	0.323327	0.139523
С	-0.339687	1.813538	-0.059209
С	1.212335	-0.191107	0.055861
Η	-1.398668	2.087560	0.019187
Η	0.244457	2.321452	0.717199

Н	0.047711	2.067522	-1.052901
Η	1.205860	-1.276539	0.212291
Η	1.610452	0.049031	-0.937036
Η	1.807198	0.302961	0.833064
Η	-0.602967	0.067324	1.056503
Η	-0.782872	-0.164870	-0.562082

2-1 Ammonium Bisulfate [(NH₄⁺)₂(HSO₄⁻)]⁺

S	0.0926330	0.0291690	0.0436470
0	-0.9441440	-1.0574120	0.1080650
0	0.8853420	0.2423840	1.2849000
0	-0.9229480	1.3493990	-0.1617640
0	0.9636210	-0.0372320	-1.1880160
Н	-0.3888750	2.1705310	-0.2065500
Н	-3.9393520	-0.5285770	0.8304630
Ν	-3.4218920	-0.3172620	-0.0310800
Η	-3.3680910	0.7020090	-0.1594500
Н	-2.3810960	-0.6828090	0.0365080
Н	-3.9057380	-0.7401190	-0.8321560
Н	2.9339180	-0.0973480	0.8885490
Ν	3.3401170	-0.2874400	-0.0470150
Н	2.4795260	-0.2093360	-0.7035660
Η	4.0611810	0.4058940	-0.2770550
Н	3.7438540	-1.2311510	-0.0739080

3-2 Ammonium Bisulfate [(NH₄⁺)₃(HSO₄⁻)₂]⁺

S	-2.4826990	0.0739780	0.0176770
0	-1.7496580	-1.0566230	0.7458420
0	-3.9447670	-0.0068130	0.0044940
0	-1.9598740	-0.1947820	-1.5765980
0	-1.8627400	1.3908430	0.4037110
Н	-2.7634130	-0.1179730	-2.1351870
Н	-0.7290200	2.2213250	-0.4600420
Ν	0.1820730	2.6416940	-0.8172740
Н	0.3228590	2.3880940	-1.8017000
Н	0.1862260	3.6619460	-0.7123530
Н	0.9479000	2.1842100	-0.2447070
S	2.4826480	-0.0739490	0.0175860
0	3.9447270	0.0065860	0.0039220
0	1.8625460	-1.3906600	0.4039340
0	1.9593930	0.1946570	-1.5765880
0	1.7500320	1.0568450	0.7458670

Η	2.7628130	0.1179010	-2.1353560
Η	-0.7289310	-0.4468360	1.9530310
Ν	0.0003230	-0.0002560	2.5847650
Η	-0.4457610	0.7093860	3.1768280
Η	0.4468150	-0.7106310	3.1756410
Η	0.7292190	0.4469980	1.9531190
Η	-0.1863120	-3.6617860	-0.7128630
Ν	-0.1820230	-2.6415110	-0.8175390
Η	-0.9477830	-2.1840460	-0.2448630
Η	0.7291000	-2.2213250	-0.4602080
Н	-0.3227900	-2.3876480	-1.8019010

4-3 Ammonium Bisulfate [(NH₄⁺)₄(HSO₄⁻)₃]⁺

S	-3.3548230	-1.3176200	0.0846780
0	-2.5948060	-0.5656220	-1.0168330
0	-4.3460770	-2.2946580	-0.3785280
0	-4.2133970	-0.0027340	0.7325280
0	-2.4220490	-1.7738890	1.1630240
Н	-4.9943010	-0.3805020	1.1903240
Н	0.6728830	-1.3423610	1.4068180
Ν	-0.0103660	-0.8953680	2.0766740
Н	0.0971910	0.1355080	2.0355480
Н	-0.9879100	-1.1657960	1.7717830
Н	0.1670830	-1.2324920	3.0284380
S	0.3091740	2.4747550	0.0124680
0	-0.8947420	3.3130770	-0.2878570
0	0.3450920	1.1391400	-0.6390540
0	0.1271940	2.0080890	1.6448780
0	1.5888530	3.2513850	-0.0298740
Н	0.0846170	2.8183570	2.1956490
Η	0.5053070	-1.7209370	-1.1911320
Ν	-0.1096730	-1.2855910	-1.9354230
Н	-0.1182640	-1.8630740	-2.7819620
Н	-1.0930580	-1.1333640	-1.5701960
Н	0.2906430	-0.3552560	-2.1238050
Н	-3.9193110	2.1172490	-0.2769980
Ν	-3.2194230	2.0830820	-1.0290770
Н	-3.6086430	2.4920160	-1.8848210
Н	-2.3362690	2.5971730	-0.7373400
Н	-2.9898240	1.0523080	-1.1606000
Н	4.6540180	2.3339010	0.4933880
Ν	3.9360180	1.8593340	-0.0646170

Η	3.7285350	0.8882950	0.3384810
Н	3.0349920	2.4256760	-0.0625530
Н	4.2717660	1.7521270	-1.0279880
S	2.9931080	-1.7082720	0.0483410
0	3.2418890	-0.5234700	0.9428870
0	3.9472300	-2.8212980	0.1064500
0	3.1326160	-1.0434950	-1.5148090
0	1.5200930	-2.0978090	0.1128580
Н	3.7501090	-1.6405560	-1.9890970

5-4 Ammonium Bisulfate [(NH₄⁺)₅(HSO₄⁻)₄]⁺

S	2.5363800	2.9880820	0.0537040
0	3.1837120	2.4136410	1.2769330
0	3.4220130	3.3499260	-1.0629470
0	1.7182960	4.3585570	0.5715310
0	1.3145710	2.1571420	-0.3702810
Н	2.3874170	5.0274720	0.8306780
Н	-1.0913670	3.7468180	1.0024900
Ν	-1.0552900	2.7528950	0.7546780
Н	-1.2394360	2.1447450	1.5826040
Н	-1.7766970	2.5060680	0.0443610
Н	-0.0902850	2.5325540	0.3528420
S	-1.4178330	-0.6594530	2.4836180
0	-0.0256840	-0.8515680	1.9943350
0	-1.9351650	0.7409600	2.5228970
0	-1.4741260	-1.0895610	4.0717480
0	-2.3918290	-1.5919890	1.7587710
Η	-1.1391510	-2.0083510	4.1592220
Η	1.4040590	1.1969090	-1.7838470
Ν	1.3124330	0.3802230	-2.4477140
Н	1.7278400	0.5999500	-3.3583680
Н	1.8092680	-0.4339750	-1.9880460
Н	0.2990460	0.1654540	-2.5408420
Н	2.9778880	0.7563830	1.6238140
Ν	2.7774040	-0.2770020	1.7104160
Н	3.4578990	-0.7393370	2.3215930
Н	1.8163600	-0.4261010	2.0704610
Н	2.8135640	-0.7191720	0.7531460
Н	-5.3118690	-0.3991110	0.6556130
Ν	-4.4755320	0.0411100	1.0535510
Η	-4.7319020	0.6307980	1.8532030
Н	-3.7709390	-0.6873110	1.3801740

Н	-3.9881090	0.6240240	0.3110190
S	-2.7124960	0.6301370	-2.0998500
0	-2.9853840	1.3881770	-0.8104430
0	-2.8382370	1.3997450	-3.3445050
0	-3.9610480	-0.5087800	-2.0603170
0	-1.4662110	-0.2170910	-1.9703650
Н	-4.3784850	-0.4925970	-2.9480020
S	2.3565790	-2.9071470	-0.6140830
0	1.0886370	-3.3914190	-1.2701230
0	2.5666960	-1.4119090	-0.8198910
0	3.5863340	-3.5116170	-1.5338720
0	2.5441330	-3.3224160	0.7935980
Η	3.5733920	-4.4896760	-1.4522280
Η	-1.5566090	-1.8634610	-1.2575070
Ν	-1.4244410	-2.7269160	-0.6807990
Н	-0.4036700	-3.0323710	-0.7830650
Н	-1.6646570	-2.4787420	0.3048250
Η	-2.0413520	-3.4734410	-1.0158310

6-5 Ammonium Bisulfate [(NH₄⁺)₆(HSO₄⁻)₅]⁺

S	-3.7779657	-0.1927335	-2.6099879
0	-3.8345137	1.2479515	-2.2015539
0	-4.4478737	-0.5449685	-3.8684249
0	-4.5445357	-1.0640385	-1.3764459
0	-2.3599557	-0.7448905	-2.4356219
Н	-5.4786367	-1.1691685	-1.6560759
Н	-2.6421307	-3.6008495	-0.9096909
Ν	-2.0549277	-2.7895175	-0.6933489
Н	-2.3324277	-2.3860735	0.2288561
Н	-1.0519667	-3.0673795	-0.6192489
Н	-2.1908827	-2.0451795	-1.4437379
S	-2.0719687	-0.6354495	2.7735211
0	-2.6814577	0.6471705	2.3429831
0	-2.3008087	-1.8478445	1.9345101
0	-2.8172117	-1.0676465	4.1875961
0	-0.5883157	-0.5060775	3.1290751
Н	-2.9721297	-0.2510655	4.7087891
Н	-1.0314000	0.2093460	-2.4108860
Ν	-0.1182660	0.6676480	-2.1530350
Н	0.1949510	1.3091670	-2.8875150
Н	-0.2451360	1.2016130	-1.2393960
Н	0.5789100	-0.0870060	-1.9933490

Н	-3.6325497	1.9461905	-0.6991709
Ν	-3.4733677	2.4660395	0.2099681
Н	-4.3520827	2.8898325	0.5242041
Н	-3.1277097	1.8017655	0.9310021
Н	-2.7473277	3.2140435	0.0552121
Н	-0.2485350	-3.7851240	3.2221350
Ν	0.4213120	-3.1269300	2.8088670
Н	0.0660870	-2.1311480	2.9588510
Н	1.3409620	-3.2475180	3.2460420
Н	0.5101890	-3.2989830	1.7654880
S	1.7986953	-2.4673465	-0.4523419
0	0.6559813	-3.3074115	0.0841111
0	3.0224843	-3.2763595	-0.7875769
0	2.1685153	-1.5694345	0.8684831
0	1.3977283	-1.5558295	-1.5642559
S	-0.1819987	3.4768835	0.3089421
0	0.3414993	3.8755215	1.6600031
Ο	-0.4175577	1.9720085	0.2543341
Ο	1.0078403	3.7708355	-0.7923619
Ο	-1.3426187	4.2599875	-0.1929039
Н	1.8561890	1.2312630	1.7732980
Ν	1.2743400	1.4574290	2.6036600
Н	0.8512680	2.4169260	2.3857090
Н	0.5142050	0.7488890	2.7223070
Н	1.8594580	1.5020720	3.4435300
S	4.1105220	1.1044580	-0.2589590
Ο	5.2741320	1.9895530	-0.1192460
Ο	4.2682150	-0.3108820	0.2532070
Ο	3.9894830	0.7793300	-1.9534500
Ο	2.7676070	1.6685310	0.1141100
Н	4.4106410	1.5401480	-2.4077340
Н	5.7063070	-1.9440710	-1.4178930
Ν	4.8974950	-1.9648810	-2.0505530
Н	4.5628720	-0.9800470	-2.1666290
Н	5.1678690	-2.3698210	-2.9533830
Н	4.1172810	-2.5513640	-1.5883880
Н	1.2531199	4.7386065	-0.7361720
Н	2.7265822	-2.0976119	1.4911317

7-6 Ammonium Bisulfate [(NH₄⁺)₇(HSO₄⁻)₆]⁺

S	1.5651310	-2.1466120	-2.8104890
0	3.0079580	-2.4142390	-2.5612490

0	0.8800710	-3.2430470	-3.5842080
0	1.5296540	-0.7935440	-3.8623190
0	0.7661590	-1.6387070	-1.6650820
Н	2.0523530	-1.0193330	-4.6611550
Н	-1.7788660	0.0567200	-1.5666130
Ν	-0.9991100	0.3952470	-0.9638260
Н	-0.9775110	1.4363420	-0.9399480
Н	-1.1695770	0.0659000	0.0131650
Н	-0.1061020	-0.0207330	-1.2879170
S	2.6016100	2.0641980	-1.7285980
0	3.9261200	1.5241440	-2.1650780
0	2.0052600	1.2742550	-0.5929510
0	1.5481030	1.8748670	-3.0002350
0	2.5738480	3.5498510	-1.5281630
Н	1.6004060	0.9291400	-3.3148690
Н	0.6896600	-3.9145930	3.4801220
Ν	0.9941100	-3.0017270	3.8321350
Н	1.6449460	-2.5208100	3.1245390
Н	0.1472970	-2.3684710	3.9551060
Н	1.4953050	-3.1201820	4.7188120
Н	5.6945860	-1.0666840	-1.2581900
Ν	4.7389680	-0.8254430	-0.9768980
Н	4.0730290	-1.5118640	-1.3973020
Н	4.6808240	-0.8150380	0.0739080
Н	4.4859580	0.1241220	-1.3649200
Н	0.1143710	4.8442360	-3.1207250
Ν	0.3369040	4.8496250	-2.1203740
Н	1.2978240	4.3985870	-1.9505100
Н	0.3040080	5.8106800	-1.7633830
Н	-0.3562590	4.2587980	-1.5784390
S	-2.0423300	3.9311590	0.4253470
0	-1.1410640	3.1768820	-0.5407860
0	-2.1462290	5.3723240	0.1175260
0	-1.1062010	3.8106070	1.8425330
0	-3.3171670	3.2160840	0.7172240
Н	-1.4686010	4.4664010	2.4751890
S	3.6030620	-0.7986030	2.6825820
0	3.1212540	0.4905640	3.2716360
0	2.5168030	-1.6644570	2.1012190
Ο	4.0736380	-1.7365460	3.9898360
Ο	4.7952130	-0.6634410	1.7927350
Н	4.7529350	-1.2357130	4.4896580
Η	0.1819670	0.9676820	2.0024740

Ν	0.9678250	1.6530680	1.9359370
Н	0.5870400	2.5844250	2.1553490
Н	1.7464460	1.3541590	2.5712250
Н	1.3484620	1.6504990	0.9558000
S	-1.8852180	-1.0657690	2.7311540
0	-1.0494400	-1.2496020	3.9546860
0	-3.3377910	-0.8368690	3.0000960
0	-1.7266020	-2.5177540	1.9750040
0	-1.3252420	-0.0245610	1.7750390
Η	-2.2162080	-2.5033320	1.1003270
Η	-4.1750320	0.3052460	2.1211050
Ν	-4.7038560	0.8876910	1.4081730
Η	-4.1304760	1.7170080	1.1244180
Η	-4.8796520	0.2534750	0.5981170
Η	-5.5953140	1.2078740	1.7996840
S	-3.8196180	-1.7653260	-1.2902040
0	-3.2714320	-0.7445920	-2.2347590
0	-2.7251410	-2.5467140	-0.5845590
0	-4.4592260	-2.9859860	-2.2371230
0	-4.9098110	-1.2801220	-0.4006150
Η	-5.2604270	-2.6340660	-2.6814490
Η	-1.3763370	-5.0250930	-2.2962520
Ν	-1.4816020	-4.0478520	-2.5895730
Η	-0.5491110	-3.6880880	-2.9892790
Η	-2.2230500	-3.9951600	-3.2988870
Н	-1.7996130	-3.4663370	-1.7681010
8-7 Ammonium Bisulfate [(NH4 ⁺)8(HSO4 ⁻)7] ⁺			

S	-5.1354220	0.3976140	1.1192150
0	-5.6080200	1.4336060	2.1028770
0	-5.4450450	0.7603870	-0.3020870
0	-6.0011730	-0.9772010	1.4830980
0	-3.7319750	-0.0767750	1.3312110
Н	-6.9566160	-0.7575730	1.4530340
Н	-3.3545640	-1.7058390	1.6492270
Ν	-2.9611180	-2.6783640	1.7550930
Η	-3.4379190	-3.1736680	2.5139600
Н	-3.0737710	-3.1896860	0.8483060
Н	-1.9263780	-2.5974750	1.9415130
S	3.4985160	1.5215280	2.2555470
0	3.9517190	2.9303370	2.0563820
0	2.0086370	1.3661680	2.2335240

0	3.9562230	1.1191760	3.8544240
0	4.2493460	0.4640890	1.5119850
Η	3.6016860	1.8080770	4.4545660
Н	0.0033660	-0.6797450	0.7522090
Ν	0.4835260	0.0797450	0.2284320
Н	-0.1836310	0.7674680	-0.1714800
Н	1.1166110	0.5741360	0.8961500
Н	1.0479330	-0.3643850	-0.5309830
Н	1.8598080	4.7035650	0.0141880
Ν	1.8518780	4.5769850	1.0660010
Н	0.9307150	4.1315110	1.2725070
Н	2.6398000	3.9578530	1.3748790
Н	1.9156570	5.4861550	1.5340690
Н	4.4858390	-2.2813510	4.0608730
Ν	3.7518160	-1.7006100	3.6434880
Н	3.7924530	-0.7298680	4.0195500
Н	3.8947430	-1.6279330	2.6230440
Н	2.7894370	-2.1482010	3.7790310
S	0.8818330	-3.1031900	2.2448190
0	1.3085900	-2.8541400	3.6601490
0	0.6134060	-4.5431300	1.9231950
0	2.2200464	-2.6423714	1.4196918
0	-0.2633360	-2.2070940	1.8066900
S	2.1567860	3.2299327	-2.6021352
0	3.1067191	3.5408289	-3.6708752
0	2.6765722	2.3402652	-1.4858150
0	0.9218710	2.4296434	-3.3131626
0	1.5013688	4.4554839	-1.9231083
Η	3.7353090	1.5163220	-1.4625130
Ν	4.3358330	0.6375980	-1.3886140
Η	3.6938380	-0.1620110	-1.6180570
Η	5.1372750	0.6616060	-2.0257380
Η	4.6308150	0.5511820	-0.3979600
S	2.5525760	-2.5342820	-2.1358420
0	3.8782490	-2.6491550	-2.7539720
0	2.2891950	-3.5180900	-0.9761980
0	1.4814790	-2.9489630	-3.2823250
0	2.2188210	-1.1298030	-1.6628140
Η	1.4517120	-5.0711320	-0.9620800
Ν	0.5845580	-5.5658380	-0.6367400
Η	-0.1902330	-5.1564400	-1.2069410
Η	0.6454340	-6.5822260	-0.7439640
Η	0.4718270	-5.2828420	0.3740190

S	-2.0896080	-3.0744300	-1.7836920	
0	-2.8668080	-3.8754920	-0.7861740	
0	-1.7988180	-1.6626480	-1.3991630	
0	-3.0647460	-2.8579050	-3.1086810	
0	-0.8749750	-3.8363960	-2.2702390	
Н	-3.3699040	-3.7367870	-3.4205360	
Н	-4.1086270	0.7255740	-1.3873600	
Ν	-3.2623600	0.6435900	-2.0133690	
Н	-3.5325530	0.7752960	-2.9931000	
Н	-2.5457210	1.3565450	-1.7359270	
Н	-2.8270140	-0.3004310	-1.8849560	
S	-1.7196840	3.4617072	-0.4347556	
0	-1.0043770	3.5820962	0.8737414	
0	-1.2733760	2.2040672	-1.2098366	
0	-1.3705690	4.7187492	-1.3647336	
0	-3.2159520	3.4797742	-0.3305386	
Н	-5.3574310	4.6057180	1.6386680	
Ν	-4.6320780	3.9214700	1.8770980	
Н	-5.0655410	2.9482860	1.9962250	
Н	-3.9170330	3.8531750	1.0823420	
Н	-4.1665570	4.2069590	2.7445640	
Н	-2.1352822	4.8739947	-2.0563518	
Н	1.3046012	1.8383580	-4.0280416	
Н	1.2888379	-2.0876695	-3.8429873	
Н	3.0233769	-3.2216602	1.7404247	
9-8 Ammonium Bisulfate [(NH ₄ ⁺) ₉ (HSO ₄ ⁻) ₈] ⁺				

S	-0.7867000	-2.7328000	2.6643000
0	-1.2564000	-1.6048000	1.7968000
0	-2.1828000	-3.0657000	3.5149000
0	0.2338000	-2.3053000	3.6866000
0	-0.4111000	-3.9964000	1.9617000
Н	-2.0024000	-3.8143000	4.1224000
S	-5.1280000	0.1229000	-1.9905000
0	-6.3865000	0.1252000	-2.7372000
0	-4.9312000	1.2143000	-0.9727000
0	-3.8556000	-0.0213000	-2.8395000
0	-5.1152000	-1.2681000	-1.0395000
Н	-5.9951000	-1.4400000	-0.8751000
Ν	0.0010000	0.9559000	2.5365000
Н	-0.6574000	1.3882000	3.2121000
Н	0.9174000	0.7664000	2.9702000

Н	0.1306000	1.6304000	1.7329000
Н	-0.4341000	0.0660000	2.2089000
0	-2.3360000	2.0853000	3.7838000
Н	-2.7669000	2.4826000	4.5689000
S	-3.5294000	1.7628000	2.6134000
0	-4.4330000	0.7454000	3.2382000
0	-2.6720000	1.2155000	1.5182000
0	-4.1798000	3.0812000	2.3556000
Н	2.0636000	-2.6752000	-2.7084000
Ν	1.5861000	-1.9346000	-3.2606000
Н	1.5560000	-2.1942000	-4.2515000
Н	2.0714000	-1.0119000	-3.1398000
Н	0.5962000	-1.8300000	-2.8780000
Н	-3.1661000	-1.5510000	1.5161000
Ν	-4.1990000	-1.4688000	1.6098000
Н	-4.5675000	-2.3499000	1.9813000
Н	-4.3940000	-0.6776000	2.2812000
Н	-4.6282000	-1.2677000	0.6712000
Н	-4.9156000	4.5552000	-0.5955000
Ν	-4.3219000	3.7742000	-0.3018000
Н	-4.3833000	3.6172000	0.7394000
Н	-4.6225000	2.8761000	-0.7653000
Н	-3.3193000	3.9714000	-0.4988000
S	-0.2078000	4.5739000	-1.0610000
0	0.7208000	5.3757000	-0.2252000
0	0.2845000	3.2073000	-1.4431000
0	-0.2784000	5.4772000	-2.4581000
0	-1.6313000	4.5241000	-0.5535000
Н	-0.8687000	5.0054000	-3.1326000
0	-2.9271000	-2.7073000	-1.2716000
S	-1.9177000	-2.6531000	-2.3833000
0	-0.8449000	-1.6006000	-2.0994000
0	-2.6771000	-2.2141000	-3.7381000
0	-1.2851000	-3.9698000	-2.7129000
Н	-2.3359000	-2.7189000	-4.4173000
Ν	-1.7515000	0.9072000	-1.2959000
Н	-1.2665000	-0.0170000	-1.3330000
Н	-2.5778000	0.7861000	-1.9360000
Н	-1.1158000	1.6611000	-1.6286000
Н	-2.0915000	1.1250000	-0.3410000
S	3.5650000	1.7945000	-2.9394000
0	2.4695000	0.8287000	-3.0696000
0	3.2078000	3.1320000	-2.3050000

0	4.8865000	1.3027000	-2.4300000
0	3.8736000	2.2637000	-4.5587000
Н	4.7843000	2.6825000	-4.5771000
S	3.8263000	1.1139000	2.0257000
0	3.0583000	0.4591000	3.1331000
0	3.4995000	0.5176000	0.6759000
0	5.4256000	0.5760000	2.1774000
0	3.8754000	2.5939000	2.0571000
Н	5.8366000	1.0653000	2.9227000
Η	3.3890000	-2.9060000	4.1690000
Ν	2.9181000	-2.4435000	3.3850000
Η	3.1439000	-1.4273000	3.3792000
Η	3.2289000	-2.8787000	2.4711000
Η	1.8639000	-2.5269000	3.4894000
Η	-0.2317000	-4.6128000	0.3158000
Ν	0.0964000	-5.0205000	-0.5905000
Н	0.0702000	-6.0436000	-0.5397000
Н	1.0775000	-4.6886000	-0.7568000
Н	-0.5100000	-4.6767000	-1.3918000
Н	5.5600000	-1.1204000	-0.8043000
Н	6.2925000	0.0273000	0.2253000
Ν	6.1859000	-0.2553000	-0.7614000
Н	5.6727000	0.5132000	-1.2740000
Н	7.1000000	-0.4414000	-1.1860000
Н	4.5250000	-5.4238000	-1.1250000
S	4.0020000	-3.3812000	-0.5023000
0	2.8222000	-3.4640000	-1.4293000
0	4.8257000	-2.1554000	-0.7871000
0	5.0435000	-4.5904000	-0.9181000
0	3.6597000	-3.5812000	0.9429000
Н	2.2476000	4.8783000	-0.0938000
Н	3.2799000	4.0051000	-1.0887000
Ν	3.2578000	4.5314000	-0.1788000
Н	3.4745000	3.8886000	0.6048000
Н	3.9205000	5.3122000	-0.1955000
10-9 A	mmonium Bis	ulfate [(NH4 ⁺)	10(HSO ₄ ⁻)9] ⁺
S	-0.4343000	0.5099000	3.2323000
0	0.3757000	-0.7270000	3.3680000
0	-0.1880000	1.5986000	4.2206000
0	-2.0109000	0.0617000	3.4953000

O -0.4603000 1.0263000 1.8008000

Н	-2.3036000	0.1074000	4.4286000
Н	-4.7313000	-1.6177000	1.7017000
Ν	-4.0034000	-1.7483000	0.9931000
Н	-4.3857000	-2.2576000	0.1575000
Н	-3.6420000	-0.8175000	0.6543000
Н	-3.2108000	-2.3231000	1.3826000
S	-1.6813000	-3.6090000	3.1885000
0	-2.2687000	-2.5015000	4.0130000
0	-1.8904000	-3.3687000	1.7066000
0	-2.6551000	-4.9259000	3.4300000
0	-0.3030000	-4.0338000	3.5563000
Н	-2.4972000	-5.2551000	4.3413000
Н	0.4123000	0.1817000	0.5206000
Ν	1.0680000	0.0204000	-0.2762000
Н	1.9737000	0.4763000	-0.0345000
Н	1.2001000	-0.9974000	-0.4766000
Н	0.6878000	0.4667000	-1.1369000
Н	2.0138000	-1.8041000	3.1124000
Ν	2.1719000	-2.8215000	3.0073000
Н	2.9201000	-3.1256000	3.6383000
Н	1.2706000	-3.3009000	3.2435000
Н	2.4430000	-3.0231000	2.0063000
Н	-1.4891000	-4.3179000	0.2513000
Ν	-1.2499000	-4.6853000	-0.6995000
Н	-1.7233000	-5.5817000	-0.8522000
Н	-1.5716000	-3.9953000	-1.4161000
Н	-0.1953000	-4.8171000	-0.7428000
S	-3.8310000	-2.5671000	-2.5657000
0	-4.5878000	-3.0685000	-1.3729000
Ο	-4.2826000	-1.1733000	-2.9773000
0	-4.2239000	-3.5602000	-3.8236000
0	-2.3482000	-2.7019000	-2.4957000
Н	-5.2027000	-3.6009000	-3.8876000
S	2.1477000	-3.6462000	-0.7873000
0	1.4628000	-4.9558000	-0.5619000
0	1.1443000	-2.6052000	-1.2974000
0	3.1822000	-3.9207000	-1.9936000
0	2.9252000	-3.1168000	0.3833000
Н	2.8705000	-4.6495000	-2.5043000
Н	1.4364000	-1.9289000	-2.8864000
Ν	1.8147000	-1.1799000	-3.5244000
Н	2.0517000	-1.5484000	-4.4499000
Н	1.1325000	-0.3947000	-3.5735000

Н	2.6727000	-0.8165000	-3.0074000
S	0.4674000	2.4503000	-3.3259000
0	1.9265000	2.7205000	-3.2469000
0	-0.2218000	2.7427000	-4.5977000
0	-0.2994000	3.4661000	-2.2561000
0	0.1320000	1.0294000	-2.8073000
Н	0.0233000	4.3028000	-2.0782000
Н	-1.5439000	0.7446000	-3.3608000
Ν	-2.5239000	0.8377000	-3.7270000
Н	-3.0256000	1.5268000	-3.1087000
Н	-2.4765000	1.1846000	-4.6907000
Н	-3.0547000	-0.0624000	-3.6523000
S	-4.2283000	1.4898000	-0.6482000
0	-3.1041000	0.5649000	-0.2659000
0	-4.8243000	2.2556000	0.4849000
0	-5.4513000	0.5439000	-1.1752000
0	-3.8366000	2.3835000	-1.8169000
Н	-6.3253000	0.7554000	-0.7656000
Н	-4.1218000	2.8741000	3.6441000
Ν	-3.4877000	2.5203000	2.9203000
Н	-3.0772000	1.6141000	3.2259000
Н	-4.0129000	2.3896000	2.0164000
Н	-2.7053000	3.2250000	2.7653000
S	4.1216000	1.1600000	1.6717000
0	3.8733000	1.6799000	3.0428000
0	3.1755000	1.7575000	0.6365000
0	3.6685000	-0.4409000	1.7834000
0	5.5425000	1.1800000	1.2032000
Н	4.1233000	-0.7622000	2.4426000
Н	2.6711000	2.8495000	3.4176000
Ν	1.8562000	3.4370000	3.7358000
Н	1.0795000	2.7847000	4.0085000
Н	2.1308000	4.0127000	4.5375000
Н	1.5080000	4.0501000	2.9536000
Н	-3.2650000	4.0450000	-1.6708000
Ν	-2.6706000	4.9050000	-1.7779000
Н	-1.8608000	4.6347000	-2.3661000
Н	-3.2003000	5.6713000	-2.2042000
Н	-2.2596000	5.2046000	-0.8400000
S	-0.6705000	4.6402000	1.3417000
0	-1.3135000	5.6329000	0.4268000
0	0.7668000	4.9156000	1.6310000
0	-0.7210000	3.2347000	0.4075000

0	-1.4627000	4.2976000	2.5725000
Η	-0.6269000	2.4341000	1.0247000
S	5.0588000	-0.8288000	-1.8057000
0	5.1349000	-2.1944000	-2.4033000
0	5.9593000	0.2196000	-2.3688000
0	5.5265000	-1.0691000	-0.2356000
0	3.6201000	-0.3302000	-1.7297000
Н	6.4296000	-1.1760000	-0.3339000
Н	4.8504000	3.4389000	-1.7273000
Ν	4.3612000	2.5387000	-1.7582000
Н	3.5349000	2.6005000	-2.3878000
Η	5.0121000	1.7806000	-2.0805000
Н	3.9995000	2.2838000	-0.7975000

11-10 Ammonium Bisulfate [(NH₄⁺)₁₁(HSO₄⁻)₁₀]⁺

S	2.7217000	-0.5161000	3.4919000
0	1.6631000	-1.4285000	4.0208000
0	4.0213000	-1.2530000	3.2576000
0	3.0485000	0.6133000	4.6797000
0	2.3051000	0.3684000	2.3626000
Η	3.2605000	0.1287000	5.5060000
Н	3.4069000	3.4983000	2.5796000
Ν	2.4934000	3.1644000	2.2557000
Η	1.7367000	3.4730000	2.8924000
Η	2.3055000	3.5588000	1.3011000
Η	2.5026000	2.1157000	2.2314000
S	-1.2116000	2.7085000	2.7367000
0	-1.2637000	1.4612000	3.5382000
0	-0.5076000	2.6046000	1.4072000
0	-0.1137000	3.7216000	3.5495000
0	-2.4811000	3.4966000	2.6602000
Н	-0.4378000	3.8404000	4.4677000
Н	1.5661000	0.9151000	-0.3787000
Ν	0.6534000	0.4307000	-0.1880000
Н	0.8339000	-0.5183000	0.2009000
Н	0.1376000	1.0259000	0.4879000
Н	0.1089000	0.3318000	-1.0703000
Н	-0.1335000	-1.4918000	3.5794000
Ν	-1.0793000	-1.3453000	3.1672000
Н	-1.8506000	-1.7869000	3.6949000
Н	-1.2675000	-0.3217000	3.1219000
Η	-1.1344000	-1.7549000	2.2139000

Н	-2.2475000	5.2636000	0.5388000
Ν	-1.5656000	4.8297000	-0.0945000
Н	-2.0914000	4.3464000	-0.8700000
Н	-0.9167000	5.5260000	-0.4969000
Н	-1.0296000	4.0948000	0.4242000
S	1.5609000	4.5858000	-1.3568000
0	1.8057000	4.7845000	0.1054000
0	2.7774000	4.5906000	-2.2210000
0	0.6725000	5.9594000	-1.8118000
0	0.5402000	3.5291000	-1.6560000
Н	1.2809000	6.7293000	-1.7996000
S	-4.3225000	-0.9825000	2.2669000
0	-5.0814000	-0.0189000	3.1343000
0	-3.2443000	-0.2466000	1.4722000
0	-5.3995000	-1.4453000	1.1257000
0	-3.8040000	-2.1933000	2.9645000
Н	-6.3881000	-1.4020000	1.4330000
Ν	-3.4788000	-0.5792000	-1.2110000
Η	-2.5986000	-0.4691000	-1.7534000
Η	-3.8795000	-1.5237000	-1.3860000
Η	-4.1415000	0.1805000	-1.4476000
Η	-3.2984000	-0.4919000	-0.1637000
S	-0.1598000	-0.9110000	-3.6487000
0	-1.0378000	-1.9702000	-4.2226000
0	0.5674000	-0.0415000	-4.5991000
Ο	1.0449000	-1.6562000	-2.7997000
0	-0.9144000	-0.0723000	-2.5904000
Н	-0.9605000	1.5248000	-3.3689000
Ν	-0.9953000	2.5334000	-3.6626000
Н	-0.8261000	2.6081000	-4.6701000
Н	-1.9215000	2.9151000	-3.3778000
Н	-0.2595000	3.0391000	-3.1052000
S	4.3535000	1.7606000	-0.7304000
0	2.8949000	2.0022000	-0.4514000
0	5.2166000	1.9200000	0.4856000
0	4.8053000	2.8779000	-1.8062000
0	4.6054000	0.4356000	-1.4264000
Н	5.6810000	2.8972000	-2.1419000
Н	7.1240000	-0.1793000	2.2358000
Ν	6.2794000	-0.3605000	1.6847000
Н	5.5008000	-0.6677000	2.3095000
Н	5.9737000	0.5201000	1.1936000
Η	6.4783000	-1.1204000	0.9588000

S	0.1095000	-3.4498000	0.1657000
0	1.0454000	-2.3444000	0.5878000
0	0.0190000	-3.5431000	-1.3554000
0	-1.3415000	-2.8340000	0.6576000
0	0.3331000	-4.7478000	0.8306000
Н	-1.6592000	-3.5866000	1.1794000
Н	2.4572000	-3.2006000	1.3710000
Ν	3.2203000	-3.6872000	1.8934000
Н	3.6074000	-3.0009000	2.5709000
Н	2.8280000	-4.5046000	2.3711000
Η	3.9714000	-3.9699000	1.1941000
Н	4.0674000	-0.3426000	-2.9881000
Ν	3.8346000	-1.2104000	-3.5220000
Η	2.8253000	-1.4238000	-3.3864000
Н	4.0377000	-1.0890000	-4.5189000
Н	4.4351000	-1.9881000	-3.0988000
S	5.4366000	-2.9131000	-0.7291000
0	5.3732000	-3.0120000	-2.2249000
0	5.0835000	-4.1797000	-0.0151000
0	4.1806000	-1.9128000	-0.2634000
0	6.6844000	-2.2389000	-0.2284000
Η	4.3484000	-0.9898000	-0.6346000
S	-4.5464000	-4.4609000	-0.6531000
0	-5.5506000	-3.9573000	0.3244000
0	-4.8242000	-5.7429000	-1.3158000
0	-3.1084000	-4.7382000	0.2913000
0	-3.9806000	-3.3881000	-1.5700000
Η	-3.3304000	-5.3574000	1.0190000
Η	-1.6495000	-3.5766000	-3.7451000
Ν	-1.9534000	-4.3657000	-3.1309000
Η	-2.1029000	-5.2330000	-3.6552000
Η	-1.2043000	-4.4681000	-2.4136000
Н	-2.8355000	-4.0719000	-2.6204000
S	-4.4286000	3.3419000	-1.4633000
0	-4.6957000	4.4040000	-0.4576000
0	-2.9993000	3.3578000	-1.9671000
0	-5.2417000	3.6858000	-2.8618000
0	-4.8872000	1.9782000	-1.0144000
Н	-6.2037000	3.6723000	-2.6677000
Η	-5.0534000	2.2076000	0.9124000
Ν	-5.0463000	2.3687000	1.9407000
Η	-4.1391000	2.8052000	2.2077000
Н	-5.8162000	2.9989000	2.1851000

Н	-5.1334000	1.4259000	2.4529000

5-4 Dimethylammonium Bisulfate [((CH₃)₂NH₂)⁺)₅(HSO₄⁻)₄]⁺

S	4.2234680	0.8451930	1.3981130
0	4.8759380	0.5775100	0.0601750
0	3.2752850	2.0179290	1.3318160
0	5.4369010	1.3166370	2.4302680
0	3.6897650	-0.3691300	2.0628340
Η	5.8213980	2.1488490	2.0832410
S	-3.1472920	-1.9537800	1.4362320
0	-2.1290340	-2.9046460	0.9224980
0	-2.6365290	-0.8195930	2.2734370
0	-4.1047950	-2.7569890	2.5281050
0	-4.0904000	-1.4545100	0.3463120
Н	-4.3554340	-3.6179470	2.1312610
S	-2.0214550	2.3526980	-0.9870560
0	-2.2156720	2.5298930	0.5040030
0	-0.6907820	2.8524490	-1.4581230
0	-3.1391930	3.3783930	-1.7131360
0	-2.4690710	1.0257490	-1.4788450
Н	-2.7866020	4.2893370	-1.6359580
S	1.1726850	-1.3193690	-1.5147670
0	0.9821430	-0.1614160	-0.5877240
0	1.9119300	-2.4696220	-0.9021990
0	2.2344280	-0.6908990	-2.6783850
0	-0.0254500	-1.7193930	-2.3188110
Η	1.8952700	-1.0172850	-3.5377750
Ν	4.6520800	-2.1081610	-0.5003270
С	5.1631650	-2.9287940	0.6353110
С	5.3039630	-2.3983620	-1.8076090
Η	3.6123240	-2.2517380	-0.5983230
Η	4.7749760	-1.0779610	-0.2711870
Н	4.6673020	-2.5865340	1.5513870
Н	4.9449870	-3.9876310	0.4449920
Η	6.2470580	-2.7805260	0.7264860
Η	4.8479690	-1.7576290	-2.5719130
Η	6.3780870	-2.1860970	-1.7308680
Н	5.1495250	-3.4541070	-2.0657410
Ν	-2.7642410	-1.9695130	-2.1582670
С	-3.3468610	-1.2883210	-3.3517390
С	-2.8230800	-3.4602910	-2.2227810

Н	-1.7560370	-1.6915870	-2.0641720
Н	-3.2518900	-1.6504400	-1.2868320
Н	-3.2266510	-0.2067640	-3.2192340
Η	-2.8099270	-1.6253940	-4.2475330
Η	-4.4086450	-1.5549950	-3.4339380
Η	-2.3930790	-3.8584510	-1.2963460
Η	-3.8703460	-3.7736450	-2.3226180
Н	-2.2431020	-3.8001440	-3.0896190
Ν	1.9893990	2.9504440	-0.8905070
С	2.0057260	4.3970810	-0.5301060
С	2.7219460	2.6403890	-2.1522710
Η	2.4290030	2.4149310	-0.0921110
Н	0.9878790	2.6549630	-0.9947230
Н	1.4499330	4.5347640	0.4051600
Н	3.0449420	4.7211990	-0.3927840
Н	1.5292400	4.9732320	-1.3329540
Н	2.6331600	1.5660570	-2.3521340
Н	2.2747720	3.2165220	-2.9728020
Н	3.7775750	2.9130360	-2.0272710
Ν	0.0890510	-0.2986320	2.1118140
С	0.2826300	1.0597430	2.7050650
С	0.7447760	-1.4037440	2.8761290
Н	-0.9416230	-0.4965430	2.0685470
Н	0.4485660	-0.2991330	1.1274370
Н	-0.3232600	1.7728460	2.1295110
Н	-0.0600830	1.0385960	3.7477440
Н	1.3458100	1.3265920	2.6544330
Н	0.5399170	-2.3480860	2.3562090
Н	1.8229180	-1.2086430	2.9163130
Н	0.3126510	-1.4351360	3.8844660
Ν	-4.6285660	1.2525750	1.0450110
С	-5.6268860	1.8317950	0.1004640
С	-5.0312100	1.3373370	2.4785450
Н	-4.4542170	0.2476190	0.7882750
Н	-3.6961650	1.7404930	0.9052410
Н	-5.2303420	1.7568070	-0.9187140
Н	-6.5704520	1.2778440	0.1886580
Н	-5.7882750	2.8881590	0.3493040
Н	-4.2637050	0.8364170	3.0799780
Н	-5.1202850	2.3932760	2.7644180
Н	-5.9964200	0.8321360	2.6142340

4-5 Dimethylammonium Bisulfate [((CH₃)₂NH₂)⁺)₄(HSO₄⁻)₅]⁻

S	1.5470390	1.3191020	-0.5515760
0	0.0908810	1.9249330	-0.9175780
0	1.3179570	0.0013970	0.1509010
0	2.1112020	2.3867520	0.3612040
Н	-0.5420560	1.2086850	-1.2894520
0	2.3406310	1.1550040	-1.8137840
S	-0.4369130	-1.7564760	2.7441580
0	0.6999960	-2.6324410	2.2897270
0	-0.0526740	-0.6988160	3.7224300
0	-0.8302130	-0.8408040	1.3024930
0	-1.7167860	-2.4576440	2.9974050
Н	0.0349020	-0.4723540	0.8978400
S	-1.8818860	-1.1344450	-2.0337790
0	-0.5866940	-1.6190640	-2.5510290
0	-2.2510310	-1.9274560	-0.6379190
0	-1.8425280	0.3544170	-1.6420660
0	-3.0950540	-1.4387810	-2.8702700
Н	-1.6716250	-1.5752960	0.1213720
Н	-3.3038200	1.2246120	-1.6246130
S	-4.7593120	1.9850140	-0.1382750
0	-6.0823880	2.6018690	-0.3630270
0	-4.2160010	1.6585320	-1.6646530
0	-3.7287760	2.8674870	0.5265850
0	-4.7975190	0.6225930	0.5570080
Ν	2.7343180	-2.5414140	0.4293500
С	2.1955300	-2.8591120	-0.9265460
С	3.6310310	-3.5977370	0.9702030
Н	3.2933850	-1.6468350	0.3871200
Н	1.9377600	-2.3999600	1.1026220
Η	1.5133420	-2.0593460	-1.2365460
Η	1.6473610	-3.8093770	-0.8751970
Н	3.0413620	-2.9296220	-1.6223820
Н	3.0682680	-4.5365400	1.0577180
Η	4.4833480	-3.7130390	0.2882030
Η	3.9844710	-3.2843110	1.9603170
Ν	4.7440080	2.7056060	-0.0424130
С	4.9423960	4.0172700	-0.7048720
С	5.5218140	2.5094400	1.2099630
Η	3.6965380	2.5720610	0.1584980
Η	4.9744420	1.9294360	-0.7303740

Н	4.3166220	4.0502420	-1.6058980
Н	5.9993390	4.1353250	-0.9804760
Н	4.6413620	4.8223470	-0.0206790
Н	6.5944030	2.5970220	0.9918250
Н	5.2149790	3.2649470	1.9466280
Н	5.3091770	1.4968420	1.5755130
Ν	-2.0788060	1.5243510	2.2063460
С	-2.9343350	1.1207420	3.3578070
С	-0.9234620	2.3883470	2.5786010
Н	-1.7006980	0.6497270	1.7642490
Н	-2.6896160	2.0236880	1.4886740
Н	-3.7753530	0.5383060	2.9617910
Н	-3.3109960	2.0269430	3.8516070
Н	-2.3327020	0.5161750	4.0488460
Н	-1.3054220	3.3096310	3.0391490
Н	-0.2846500	1.8349610	3.2793500
Н	-0.3573500	2.6314920	1.6701880
S	5.5681480	-0.6455670	-0.7926310
0	4.6512250	-0.5304850	0.4152800
0	6.9547960	-0.1837920	-0.5400200
0	5.3820190	-1.9196270	-1.5395320
0	4.9957460	0.6092030	-1.8170250
Н	3.9970060	0.5467000	-1.8998510
Ν	-5.2701070	-1.3426430	-1.2024870
С	-6.4582400	-0.9190360	-1.9862790
С	-5.4201020	-2.6393970	-0.4961280
Н	-4.4282560	-1.3897150	-1.8513930
Н	-5.0521580	-0.5717900	-0.4829400
Н	-6.2329130	0.0509960	-2.4471690
Н	-7.3196050	-0.8111690	-1.3131880
Н	-6.6734300	-1.6683930	-2.7608520
Н	-6.2346580	-2.5620410	0.2372960
Н	-5.6455700	-3.4309310	-1.2245350
Н	-4.4723920	-2.8620790	0.0092850

$[(H_2SO_4)_3(NH_4^+)(HSO_4^-)_2]^-$

S	2.4664000	2.3634400	0.2659030
Õ	2.2927700	1.9397550	-1.1731180
0	1.1174650	3.1297280	0.7375100
0	2.5234070	1.0733030	1.1540940
0	3.5644250	3.2889820	0.5480200
Η	0.2811180	2.6698670	0.4222500
Η	3.0229540	-0.2837850	0.5165980
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S	-0.1005270	-0.7960860	2.1669210
0	0.5215480	-2.0522640	2.6692630
0	0.6753860	0.4631800	2.6916550
0	0.1850720	-0.7825210	0.5885710
0	-1.5441330	-0.6108740	2.4712200
Η	1.4840210	0.7538970	2.0297920
Н	-0.6374130	-0.6716610	-0.0421070
S	-2.8634840	-1.7399570	-0.5979340
0	-2.2779600	-2.9810590	0.0010350
0	-3.5023360	-0.8633820	0.6859140
0	-1.7229020	-0.8225210	-1.0991710
0	-3.9740300	-1.8698170	-1.5442530
Н	-2.8019040	-0.8424380	1.4169810
Н	-2.0706190	0.5891600	-1.8178040
Ν	0.4437650	-3.6486790	0.3173590
Н	0.6139770	-3.1831660	1.2409330
Н	1.1523970	-3.2856410	-0.3864830
Н	-0.5382910	-3.4063460	0.0363230
Н	0.5368200	-4.6639600	0.4091340
S	3.0028180	-1.4998320	-1.3543910
0	3.2462950	-1.2439450	0.2217930
0	4.2400300	-1.2688950	-2.1083950
0	2.3907290	-2.8580910	-1.4372940
0	1.8452890	-0.4839980	-1.7705090
Н	2.0735970	0.5150670	-1.5524740
S	-2.4267380	2.3724460	-0.6734390
0	-2.6865180	3.7685570	-1.0015740
0	-2.3178550	1.5511630	-2.0558350
Ο	-1.2758830	1.9879170	0.1901270
0	-3.7771170	1.7997550	0.0206150
Η	-3.6679810	0.8298040	0.2750300

$[(H_2SO_4)_2(NH_4^+)_2(HSO_4^-)_3]^-$

S	-3.8686410	-0.0212640	0.7744230
0	-3.6385020	1.3970260	1.1863380
0	-3.2098980	-0.1474010	-0.7113190
0	-3.0001740	-1.0192810	1.6610480
0	-5.2427940	-0.5111830	0.7590510
Н	-2.5105780	-0.9506350	-0.8148300
Η	-0.2361400	-0.6648450	-0.4762930
S	0.6161210	-0.4409370	1.5456710

0	1.7252170	0.4651850	1.9931770
0	-0.6727950	-0.1874220	2.2765520
0	0.4231160	-0.0144060	-0.0125300
0	1.0015440	-1.9097270	1.5363280
Н	-2.0465610	-0.6585470	1.8755570
S	4.7570530	0.5476070	-0.0868330
0	3.5748710	0.3042400	-1.0592660
0	4.3289920	-0.3468910	1.2586940
0	6.0133880	-0.0853340	-0.5265600
0	4.7862750	1.9844870	0.3204980
Η	3.4606690	0.0009140	1.6057300
Ν	2.0215150	2.4101810	-0.1730970
Η	1.7164660	1.9923130	0.7265470
Η	2.8411490	3.0065150	0.0050570
Н	1.2285170	2.9104780	-0.6302940
Η	2.3931910	1.6023890	-0.7401400
Η	-2.3499230	1.1899960	-1.4440030
Η	-2.3303800	2.2452120	0.8615290
S	-1.5737820	3.1912000	-0.9687200
0	-1.4782380	2.7345940	0.5744380
0	-2.7850050	3.9800070	-1.2172750
0	-0.2447570	3.7586170	-1.2830460
0	-1.6259080	1.7939820	-1.7950550
S	-0.9388860	-3.1454490	-1.1771590
0	-2.0405760	-3.9198310	-1.7530520
0	0.4088920	-3.2663840	-1.8199450
0	-1.2731960	-1.6199620	-1.0493310
0	-0.8020720	-3.6565730	0.3753180
Η	-0.1639270	-3.0508140	0.8603650
Η	1.9325200	-2.5774040	-1.2962120
Ν	2.7303160	-2.2279270	-0.7099250
Н	2.3631790	-2.1871590	0.2649870
Н	3.5295010	-2.8657710	-0.7560980
Н	3.0526410	-1.2368790	-0.9713750

$[(H_2SO_4)_3((CH_3)_2NH_2^+)(HSO_4^-)_2]^-$

S	3.7144930	-1.1274620	-1.1842440
0	3.4462350	-1.0373020	0.2852410
0	2.3065820	-1.2478250	-1.9634660
0	4.3383630	0.2634760	-1.6771030
0	4.5827050	-2.1950600	-1.6660650
Н	1.6748980	-0.5130410	-1.6572130

S	1.3589640	2.3326430	-0.9968340
0	1.4453980	2.6074850	0.4756670
0	2.6930790	2.2502010	-1.6746430
0	0.7899380	0.7659420	-1.1468710
0	0.3703210	3.2007900	-1.7136980
Н	3.6720510	1.0477440	-1.5809660
Н	-0.1214210	0.7227430	-0.6780290
S	-2.6424620	1.6968560	-0.5556340
0	-1.4235250	1.1044110	0.1306090
0	-2.1307740	2.3180450	-1.9689850
0	-3.5991900	0.6048780	-1.0299520
0	-3.3086400	2.7364910	0.2604080
Η	-1.2035490	2.7164890	-1.8452140
Н	-3.8014690	-0.8147590	-0.1154150
S	-2.7423340	-2.4023230	-1.0839450
0	-3.0657090	-3.8005800	-1.3436990
0	-3.8211200	-1.8247790	-0.0184840
0	-1.3705150	-2.0423680	-0.6219290
0	-3.0457120	-1.5387420	-2.4121480
Н	-3.1483460	-0.5685080	-2.1084990
Н	-0.5803800	-2.4993530	0.6807070
Н	2.1073960	-0.9542000	1.0891660
S	0.4873770	-1.7424430	2.4592170
0	1.2585860	-0.6367740	1.5667250
0	1.3874860	-2.4080300	3.4049400
0	-0.6761380	-0.9701670	2.9668730
0	0.0274750	-2.8675970	1.4154460
Ν	-0.1060480	1.8520010	2.5948520
С	-1.2298940	2.7788960	2.9063170
С	0.9901680	1.8730860	3.6031680
Η	-0.4636270	0.8741780	2.5136960
Η	0.3154370	2.0958030	1.6561550
Н	-1.9753060	2.7228160	2.1020030
Н	-0.8330820	3.8005300	2.9743890
Η	-1.6771610	2.4862240	3.8659210
Н	1.3970190	2.8908060	3.6607010
Н	0.5917550	1.5628550	4.5778570
Н	1.7711080	1.1774520	3.2759780

$[(H_2SO_4)_2((CH_3)_2NH_2^+)_2(HSO_4^-)_3]^-$

S	5.4602410	0.0209770	0.2325360
0	4.4855490	0.8248490	-0.5556590

0	4.8221710	-0.2990260	1.6842030
0	5.5418570	-1.4380700	-0.4665820
0	6.8179710	0.5139320	0.4243440
Н	4.0246930	-0.9064090	1.5039300
Н	4.6159290	-1.8340220	-0.3819570
S	1.7322520	-1.7618400	0.1914380
0	1.6168640	-1.0627210	-1.1357630
0	3.1826580	-2.0220120	0.5840900
0	1.2053790	-0.7180670	1.3461960
0	0.9006920	-2.9821270	0.3265650
Н	1.0937190	0.2049580	0.9537210
S	-2.5967560	-2.8454740	-0.8018470
0	-2.1598970	-1.4092340	-0.3946330
0	-1.2157100	-3.5287230	-1.3693090
0	-3.0382380	-3.5856110	0.4134040
0	-3.5028150	-2.8316630	-1.9745700
Н	-0.4736770	-3.3281970	-0.7289310
Н	-1.0050580	2.0770710	1.2642700
S	-3.1514700	2.6475740	0.9744320
0	-3.4007060	3.8942310	1.7240550
0	-4.1993290	1.5828650	1.0700290
0	-2.6286150	2.8473660	-0.4340440
0	-1.8287120	1.8715010	1.7711010
S	1.3469900	2.4398110	-0.7697580
0	1.4699240	1.3549050	-1.9432120
0	0.6785630	3.6276900	-1.2778120
0	0.7619050	1.7483110	0.4318190
0	2.8619160	2.8632890	-0.4368830
Н	3.4842070	2.0631640	-0.3866090
Н	1.5690240	0.3944770	-1.5626330
Ν	-2.9263660	0.6385500	-1.9684890
С	-4.3836350	0.4751850	-2.2223540
С	-2.0877250	0.6572030	-3.1943770
Н	-2.7752370	1.5273030	-1.3942700
Н	-2.6100870	-0.1746500	-1.3540950
Н	-4.9040550	0.5954350	-1.2634270
Н	-4.5636690	-0.5285920	-2.6300590
Н	-4.7190610	1.2524070	-2.9230820
Н	-2.2050760	-0.2977870	-3.7240350
Н	-2.4005340	1.4909170	-3.8380280
Н	-1.0376260	0.7941130	-2.9061170
Ν	-2.5439600	-0.8744270	2.2018210
С	-3.9579030	-1.1360530	2.5877540

С	-1.5504740	-1.6187620	3.0222840
Η	-2.4099420	-1.1476690	1.1727310
Η	-2.3409370	0.1529900	2.2118280
Η	-4.5958860	-0.4601600	2.0068970
Η	-4.1843730	-2.1864080	2.3626260
Η	-4.0839850	-0.9302570	3.6600090
Η	-0.5424660	-1.3790270	2.6622660
Η	-1.6603800	-1.3307500	4.0771810
Η	-1.7363420	-2.6934450	2.8971020

[(H₂SO₄)((CH₃)₂NH₂⁺)₃(HSO₄⁻)₄]⁻

S	0.8764130	-1.9690680	-0.5980150
0	-0.2826910	-2.0100320	-1.7987600
0	1.4213690	-0.5795750	-0.6934440
0	1.9025280	-3.0052620	-0.9738330
Н	-0.9398120	-2.7050500	-1.5281130
0	0.1499330	-2.2835270	0.6797600
S	-2.1815040	3.7550630	-1.2310730
0	-0.8181480	3.9384950	-0.6074810
0	-2.1711000	2.5822360	-2.2070440
0	-3.1748690	3.2553600	0.0139170
0	-2.8209530	4.9795600	-1.7416730
Н	-2.7239260	2.4725670	0.4521340
S	-2.2105960	0.6066170	2.4450210
0	-2.1125150	0.9668220	0.9764790
0	-3.5607910	1.4298790	3.0102680
0	-2.6431670	-0.8265400	2.6325860
0	-1.0654610	1.0532330	3.2658730
Η	-3.2672630	2.3470920	3.1932420
Η	-1.1861750	-3.2285760	0.4387990
S	-3.4278280	-3.3918120	0.2807650
0	-3.6747480	-4.0956360	1.5457650
0	-1.8694140	-3.6606840	-0.1841620
0	-4.2175750	-3.6747870	-0.9262600
0	-3.4749160	-1.8037810	0.5015810
Η	-3.1216380	-1.4673330	1.4572650
Ν	1.1163120	2.1506960	-0.0607650
С	1.4994690	2.4122420	1.3596390
С	2.1155300	2.6633410	-1.0447180
Н	1.0008340	1.1234680	-0.2060930
Η	0.2018720	2.6497480	-0.2644780
Η	0.7647460	1.9304150	2.0182730

Η	1.4900180	3.4980700	1.5216520
Η	2.5117320	2.0219140	1.5292650
Η	2.1386470	3.7580840	-0.9708730
Η	3.1038850	2.2464840	-0.8078970
Η	1.7865200	2.3763370	-2.0514950
Ν	4.3688710	-1.8228930	-1.1914480
С	5.4991650	-2.7832270	-1.2939360
С	4.3083280	-0.8435430	-2.3131260
Η	3.4436200	-2.3346330	-1.1314590
Η	4.4814290	-1.3108650	-0.2709850
Η	5.4512050	-3.4732780	-0.4421760
Н	6.4378210	-2.2153460	-1.2562350
Η	5.4161620	-3.3448680	-2.2343600
Η	5.2082690	-0.2169000	-2.2731080
Η	4.2415660	-1.3941700	-3.2618370
Н	3.4074060	-0.2342840	-2.1749610
Ν	-3.4318460	0.3465010	-1.5591360
С	-4.8641640	0.6404680	-1.2769960
С	-3.2250840	-0.6495450	-2.6452160
Н	-2.9240000	1.2677640	-1.8120910
Н	-2.9919870	0.0074320	-0.6820610
Н	-4.9096490	1.4301750	-0.5171490
Н	-5.3550100	-0.2737690	-0.9199640
Н	-5.3366900	0.9977120	-2.2014910
Н	-3.7149640	-1.5948170	-2.3729390
Η	-3.6554740	-0.2477010	-3.5721810
Н	-2.1463830	-0.8064600	-2.7715050
S	5.8862530	0.7422230	0.8509420
0	4.7792240	1.7258140	0.6235340
0	6.5647130	0.2492260	-0.3851160
0	6.7444260	0.9997110	2.0301060
0	4.9965870	-0.7430420	1.2581610
Н	4.3511320	-0.5058660	1.9540810

Appendix B

COMPLETE THERMOCHEMICAL DATA, HYDRATION DISTRIBUTIONS AND CARTESIAN COORDINATES FOR UNCHARGED MOLECULAR CLUSTERS

B.1 Complete thermochemical information and hydrated cluster distributions for the uncharged clusters studied in Chapter 3.

Table B1: Extended thermochemical parameters for all dry uncharged clusters and free molecules/molecular ions discussed in article and not discussed. All values are in hartrees and calculated at gas phase standard state of 1 atm and 298 K. Note: all values are Boltzmann averages.

	<e></e>	<h></h>	<g></g>
Dry Uncharged Clusters			
$[(NH_4^+)_2(HSO_4^-)_2]$	-1513.321021	-1513.30328	-1513.370598
$[(NH_4^+)_3(HSO_4^-)_3]$	-2269.999824	-2269.972533	-2270.049988
$[(NH_4^+)_4(HSO_4^-)_4]$	-3026.687437	-3026.641085	-3026.752707
$[(NH_4^+)_5(HSO_4^-)_5]$	-3783.379330	-3783.333885	-3793.461213
$[(NH_4^+)_6(HSO_4^-)_6]$	-4540.062730	-4540.007486	-4540.158302
$[(NH_4^+)_7(HSO_4^-)_7]$	-5296.760010	-5296.697260	-5296.861354
$[(NH_4^+)_8(HSO_4^-)_8]$	-6050.036811	-6050.383678	-6050.546442
$[(DMAH^{+})_{2}(HSO_{4}^{-})_{2}]$	-1670.375494	-1670.350893	-1670.431691
$[(DMAH^+)_3(HSO_4^-)_3]$	-2505.537629	-2505.510814	-2505.638712
$[(DMAH^+)_4(HSO_4^-)_4]$	-3340.773411	-3340.724375	-3340.862120
$[(DMAH^{+})_{5}(HSO_{4}^{-})_{5}]$	-4175.983791	-4175.921969	-4176.091625
$[(DMAH^+)_6(HSO_4^-)_6]$	-5011.196733	-5011.124287	-5011.312798
$[(DMAH^{+})_{7}(HSO_{4})_{7}]$	-5846.403251	-5846.318328	-5846.539624
$[(DMAH^{+})_{8}(HSO_{4})_{8}]$	-6681.600335	-6681.502593	-6681.753671

Table B2: Extended thermochemical parameters for all ammonium bisulfate hydrated clusters discussed in article and not discussed. All values are in hartrees and calculated at gas phase standard state of 1 atm and 298 K. Note: all values are Boltzmann averages; see manuscript.

	<e></e>	<h></h>	<g></g>
Cluster			
$[(NH_4^+)_4(HSO_4^-)_4(H_2O)]$	-3103.078128	-3103.038156	-3103.156600
$[(NH_4^+)_4(HSO_4^-)_4(H_2O)_2]$	-3179.503624	-3179.462634	-3179.579808
$[(NH_4^+)_4(HSO_4^-)_4(H_2O)_3]$	-3255.892994	-3255.848909	-3255.975846
$[(NH_4^+)_4(HSO_4^-)_4(H_2O)_4]$	-3332.297846	-3332.25032	-3332.384
$[(NH_4^+)_4(HSO_4^-)_4(H_2O)_5]$	-3408.694757	-3408.645944	-3408.780498
$[(NH_4^+)_4(HSO_4^-)_4(H_2O)_6]$	-3485.096201	-3485.045067	-3485.184257
$[(NH_4^+)_4(HSO_4^-)_4(H_2O)_7]$	-3561.508409	-3561.455171	-3561.598763
$[(NH_4^+)_4(HSO_4^-)_4(H_2O)_8]$	-3637.908857	-3637.853253	-3638.002362
$[(NH_4^+)_4(HSO_4^-)_4(H_2O)_9]$	-3714.3065	-3714.246917	-3714.405732
$[(NH_4^+)_4(HSO_4^-)_4(H_2O)_{10}]$	-3790.723098	-3790.662805	-3790.824705
$[(NH_4^+)_5(HSO_4^-)_5(H_2O)]$	-3859.77923	-3859.73102	-3859.86513
$[(NH_4^+)_5(HSO_4^-)_5(H_2O)_2]$	-3936.195316	-3936.145287	-3936.28106
$[(NH_4^+)_5(HSO_4^-)_5(H_2O)_3]$	-4012.587092	-4012.533644	-4012.678441
$[(NH_4^+)_5(HSO_4^-)_5(H_2O)_4]$	-4088.998091	-4088.943155	-4089.090872
$[(NH_4^+)_5(HSO_4^-)_5(H_2O)_5]$	-4165.397807	-4165.339617	-4165.495604
$[(NH_4^+)_5(HSO_4^-)_5(H_2O)_6]$	-4241.807472	-4241.747715	-4241.903578
$[(NH_4^+)_5(HSO_4^-)_5(H_2O)_7]$	-4318.217446	-4318.15472	-4318.319544
$[(NH_4^+)_5(HSO_4^-)_5(H_2O)_8]$	-4394.61531	-4394.550055	-4394.720169
$[(NH_4^+)_5(HSO_4^-)_5(H_2O)_9]$	-4471.020182	-4470.952475	-4471.128448
$[(NH_4^+)_5(HSO_4^-)_5(H_2O)_{10}]$	-4547.431923	-4547.362461	-4547.521559
$[(NH_4^+)_6(HSO_4^-)_6(H_2O)]$	-4616.469483	-4616.413563	-4616.563044
$[(NH_4^+)_6(HSO_4^-)_6(H_2O)_2]$	-4692.882795	-4692.824773	-4692.976158
$[(NH_4^+)_6(HSO_4^-)_6(H_2O)_3]$	-4769.281423	-4769.220316	-4769.380202
$[(NH_4^+)_6(HSO_4^-)_6(H_2O)_4]$	-4845.686001	-4845.621674	-4845.789027
$[(NH_4^+)_6(HSO_4^-)_6(H_2O)_5]$	-4922.094425	-4922.027868	-4922.199125
$[(NH_4^+)_6(HSO_4^-)_6(H_2O)_6]$	-4998.502637	-4998.432457	-4998.613322
$[(NH_4^+)_6(HSO_4^-)_6(H_2^-)_7]$	-5074.907867	-5074.835927	-5075.019794
$[(NH_4^+)_6(HSO_4^-)_6(H_2^-)_8]$	-5151.31228	-5151.238711	-5151.42534
$[(NH_4^+)_6(HSO_4^-)_6(H_2O)_9]$	-5227.715163	-5227.639218	-5227.831278
$[(NH_4^+)_6(HSO_4^-)_6(H_2O)_{10}]$	-5304.098682	-5304.01945	-5304.21783

	<e></e>	<h></h>	<g></g>
Cluster			
$[(DMAH^{+})_4(HSO_4^{-})_4(H_2O)]$	-3417.190792	-3417.140129	-3417.28142
$[(DMAH^{+})_4(HSO_4^{-})_4(H_2O)_2]$	-3493.585517	-3493.531543	-3493.680718
$[(DMAH^{+})_4(HSO_4^{-})_4(H_2O)_3]$	-3569.981455	-3569.924081	-3570.08006
$[(DMAH^{+})_4(HSO_4^{-})_4(H_2O)_4]$	-3646.391454	-3646.331963	-3646.493245
$[(DMAH^{+})_4(HSO_4^{-})_4(H_2O)_5]$	-3722.798822	-3722.737053	-3722.903805
$[(DMAH^{+})_4(HSO_4^{-})_4(H_2O)_6]$	-3799.206875	-3799.143113	-3799.311703
$[(DMAH^{+})_4(HSO_4^{-})_4(H_2O)_7]$	-3875.604115	-3875.536092	-3875.716432
$[(DMAH)_4(HSO_4)_4(H_2O)_8]$	-3952.003365	-3951.934207	-3952.1165
$[(DMAH^{+})_4(HSO_4^{-})_4(H_2O)_9]$	-4028.411961	-4028.340317	-4028.526744
$[(DMAH^{+})_4(HSO_4^{-})_4(H_2O)_{10}]$	-4104.820868	-4104.749364	-4104.936899
$[(DMAH^+)_5(HSO_4^-)_5(H_2O)]$	-4252.401906	-4252.339089	-4252.508307
$[(DMAH^+)_5(HSO_4^-)_5(H_2O)_2]$	-4328.801398	-4328.735246	-4328.912409
$[(DMAH^+)_5(HSO_4^-)_5(H_2O)_3]$	-4405.202945	-4405.134339	-4405.316306
$[(DMAH^+)_5(HSO_4^-)_5(H_2O)_4]$	-4481.65351	-4481.535388	-4481.71768
$[(DMAH^{+})_{5}(HSO_{4}^{-})_{5}(H_{2}O)_{5}]$	-4558.00201	-4557.927626	-4558.122445
$[(DMAH^{+})_{5}(HSO_{4}^{-})_{5}(H_{2}O)_{6}]$	-4634.41449	-4634.33922	-4634.535919
$[(DMAH^{+})_{5}(HSO_{4}^{-})_{5}(H_{2}O)_{7}]$	-4710.802638	-4710.722865	-4710.945699
$[(DMAH^{+})_{5}(HSO_{4}^{-})_{5}(H_{2}O)_{8}]$	-4787.211649	-4787.129956	-4787.34232
$[(DMAH^{+})_{5}(HSO_{4}^{-})_{5}(H_{2}O)_{9}]$	-4863.614189	-4863.530383	-4863.74548
$[(DMAH^{+})_{5}(HSO_{4})_{5}(H_{2}O)_{10}]$	-4940.006046	-4939.919416	-4940.141655
$[(DMAH^{+})_{6}(HSO_{4})_{6}(H_{2}O)]$	-5087.891297	-5087.516304	-5087.711636
$[(DMAH^{+})_{6}(HSO_{4}^{-})_{6}(H_{2}O)_{2}]$	-5164.006294	-5163.928318	-5164.130264
$[(DMAH^{+})_{6}(HSO_{4}^{-})_{6}(H_{2}O)_{3}]$	-5240.402593	-5240.321517	-5240.531615
$[(DMAH^{+})_{6}(HSO_{4}^{-})_{6}(H_{2}O)_{4}]$	-5316.802851	-5316.720041	-5316.932831
$[(DMAH^{+})_{6}(HSO_{4}^{-})_{6}(H_{2}O)_{5}]$	-5393.215784	-5393.13061	-5393.348454
$[(DMAH^{+})_{6}(HSO_{4})_{6}(H_{2}O)_{6}]$	-5469.611583	-5469.523004	-5469.747775
$[(DMAH^{+})_{6}(HSO_{4}^{-})_{6}(H_{2}O)_{7}]$	-5546.02162	-5545.933041	-5546.157812
$[(DMAH^{+})_{6}(HSO_{4}^{-})_{6}(H_{2}O)_{8}]$	-5622.40951	-5622.316493	-5622.553228
$[(\overline{DMAH}^+)_6(\overline{HSO_4})_6(\overline{H_2O})_9]$	-5698.810757	-5698.715	-5698.956216
$[(DMAH^+)_6(HSO_4^-)_6(H_2O)_{10}]$	-5775.220794	-5775.123092	-5775.369878

Table B3: Extended thermochemical parameters for all ammonium bisulfate hydrated clusters discussed in article and not discussed. All values are in hartrees and calculated at gas phase standard state of 1 atm and 298 K. Note: all values are Boltzmann averages; see manuscript.

Table B4: Thermochemical data for select clusters using data computed at 255 K and 0.5 atm with the PW91/6-31++G(d,p) method. All data in hartrees and 1 hartree = 2625.5 kJ/mol.

	\mathbf{E}	Н	G
Dry Uncharged Clusters			
$[(NH_4^+)_4(HSO_4^-)_4]$	-3026.693974	-3026.664616	-3026.754020
$[(NH_4^+)_5(HSO_4^-)_5]$	-3783.380526	-3783.345270	-3793.445758
Free Molecules/Ions			
H_2SO_4	-700.107741	-700.101270	-700.131355
NH ₃	-56.504837	-56.501588	-56.521215

Using the data above:

- 1. 4 NH₃ + 4 H₂SO₄ → [(NH₄⁺)₄(HSO₄⁻)₄]; Δ G°(255 K, 0.5 atm) = -0.14374 hartree = -377.4 kJ/mol
- 2. 5 NH₃ + 5 H₂SO₄ → [(NH₄⁺)₅(HSO₄⁻)₅]; Δ G°(255 K, 0.5 atm) = -0.182908 hartree = -480.2 kJ/mol
- 3. $[(NH_4^+)_4(HSO_4^-)_4] + NH_3 + H_2SO_4 \rightarrow [(NH_4^+)_5(HSO_4^-)_5]; \Delta G^{\circ}(255 \text{ K}, 0.5 \text{ atm})$ = -0.039168 hartree = -102.8 kJ/mol



Figure B1: Comparison of the cluster formation free energy computed using different density functional methods, basis sets, and dispersion corrections for a series of ammonia containing molecular clusters of the form [(NH4)x(HSO4)x], where x is the number of base and acid ions and the cluster and corresponds to the x-axis in the plot.



Figure B2: Hydrated clusters population relative to the zero water cluster as a function of number of water molecules in the hydrated cluster for the 4-4 ammonium bisulfate cluster. Distributions were calculated using the formalism of Paasonen et al. at 298 K and at 50% RH.



Figure B3: Hydrated clusters population relative to the zero water cluster as a function of number of water molecules in the hydrated cluster for the 5-5 ammonium bisulfate cluster. Distributions were calculated using the formalism of Paasonen et al. at 298 K and at 50% RH



Figure B4: Hydrated clusters population relative to the zero water cluster as a function of number of water molecules in the hydrated cluster for the 6-6 ammonium bisulfate cluster. Distributions were calculated using the formalism of Paasonen et al. at 298 K and at 50% RH.



Figure B5: Hydrated clusters population relative to the zero water cluster as a function of number of water molecules in the hydrated cluster for the 4-4 dimethylammonium bisulfate cluster. Distributions were calculated using the formalism of Paasonen et al. at 298 K and at 50% RH.



Figure B6: Hydrated clusters population relative to the zero water cluster as a function of number of water molecules in the hydrated cluster for the 5-5 dimethylammonium bisulfate cluster. Distributions were calculated using the formalism of Paasonen et al. at 298 K and at 50% RH.



Figure B7: Hydrated clusters population relative to the zero water cluster as a function of number of water molecules in the hydrated cluster for the 6-6 dimethylammonium bisulfate cluster. Distributions were calculated using the formalism of Paasonen et al. at 298 K and at 50% RH.

B.2 Cartesian coordinates for optimized free molecules, molecular ions, and cluster geometries discussed in Chapter 3.

Sulfuric Acid (H₂SO₄)

~	0 0 1 1 0 5 1	0 11 (000	0 00 50 00
S	-0.041051	0.116907	-0.005283
0	-0.503645	1.481157	0.236644
0	1.344855	-0.266772	-0.261704
0	-0.521366	-0.844237	1.247885
0	-0.989918	-0.439758	-1.236017
Н	-1.358702	-0.472479	1.601060
Н	-0.573672	-1.258718	-1.582586

Ammonia (NH₃)

Η	0.119902	0.104506	0.322174
Ν	-0.287899	0.858690	0.878649
Н	0.442767	1.556541	1.033208
Н	-1.017870	1.297662	0.313669

Dimethylamine ((CH₃)₂NH)

Ν	-0.565534	-0.340881	-0.058111
С	-0.657498	1.115761	-0.010334
С	0.809827	-0.825464	0.020039
Η	-1.116774	-0.745655	0.702103
Η	-1.714398	1.421753	-0.014380
Η	-0.161324	1.576172	0.874312
Н	-0.184386	1.538848	-0.911944
Η	0.815795	-1.925612	0.037994
Н	1.359489	-0.503649	-0.879987
Н	1.374801	-0.456073	0.906109

Bisulfate Ion (HSO₄⁻)

S	0.160971	-0.021465	-0.000028
0	0.314224	-0.826342	-1.257267
0	-1.521151	0.433242	-0.000088
0	0.314096	-0.826363	1.257218
0	0.819501	1.315510	0.000020
Н	-1.984109	-0.427556	0.000147

Ammonium Ion (NH₄⁺)

0.072229	-0.435680	0.707763
0.059382	0.596598	0.725020
1.027427	0.953550	0.685815
-0.470182	0.947852	-0.088765
-0.391956	0.920679	1.595267
	0.072229 0.059382 1.027427 -0.470182 -0.391956	0.072229 -0.435680 0.059382 0.596598 1.027427 0.953550 -0.470182 0.947852 -0.391956 0.920679

Dimethylammonium Ion ((CH₃)₂NH₂⁺ or DMAH⁺)

Ν	-0.204318	0.323327	0.139523
С	-0.339687	1.813538	-0.059209
С	1.212335	-0.191107	0.055861
Н	-1.398668	2.087560	0.019187
Н	0.244457	2.321452	0.717199
Н	0.047711	2.067522	-1.052901
Н	1.205860	-1.276539	0.212291
Н	1.610452	0.049031	-0.937036
Н	1.807198	0.302961	0.833064
Н	-0.602967	0.067324	1.056503
Н	-0.782872	-0.164870	-0.562082

5-5 Ammonium Bisulfate [(NH₄)₅(HSO₄)₅]

S	3.8249770	-0.2611740	-2.2549600
0	3.5514900	-1.6800410	-1.8614630
0	4.5875800	-0.0733320	-3.5029410
Ο	4.7827370	0.3982570	-1.0133060
Ο	2.5881930	0.6129340	-2.0983190
Н	5.7087410	0.2772860	-1.3090950
Н	3.3864830	3.4494680	-0.7097020
Ν	2.6686270	2.7831030	-0.4108120
Η	2.8522460	2.4881680	0.5684340
Η	1.7109980	3.2414960	-0.4545850
Н	2.6951810	1.9409980	-1.0514770
S	1.7722180	0.6165500	2.6204170
Ο	2.7234600	-0.5013670	2.3565700
Ο	0.7731470	0.8404610	1.4996460
Ο	2.7074520	2.0373420	2.4040280
Ο	1.2007720	0.6848310	3.9806500
Н	3.3625690	2.0681610	3.1315390
Н	0.9278260	-0.0518180	-2.0736190
Ν	-0.0562890	-0.2589780	-1.7879610

Н	-0.6045410	-0.6549530	-2.5569870
Η	-0.0428490	-0.9559980	-0.9906940
Н	-0.5116180	0.6305170	-1.4666460
Н	2.7403820	-1.9123160	1.2725500
Ν	2.9504300	-2.7186490	0.6400430
Н	3.7879080	-3.2027200	0.9764480
Н	2.1269280	-3.3797010	0.6377490
Η	3.1314110	-2.3372650	-0.3242900
S	-1.0739460	3.2996070	-0.1746570
0	0.2252710	3.9839820	-0.4795360
0	-2.2631390	4.2191040	-0.1833130
0	-1.0180820	2.8062340	1.3906220
0	-1.3285470	2.0716910	-1.0116070
Η	-0.2638990	2.1419150	1.4913280
S	-0.4298330	-3.3084440	0.6200760
0	-1.4120690	-3.2498640	1.7587340
0	0.1276390	-1.9228390	0.3339390
0	-1.2463400	-3.7829330	-0.7144400
0	0.6579860	-4.3216640	0.7560240
Η	-1.9654170	-3.1061130	-0.8827440
Η	-0.8244180	-0.1757590	1.8333060
Ν	-1.7344960	-0.5705810	2.1511200
Н	-1.6531390	-1.6332590	2.1259240
Η	-1.9332880	-0.2335740	3.0980840
Η	-2.4964840	-0.2833980	1.4915140
S	-4.0462550	-0.9932000	-0.8012390
0	-5.1651540	-1.9313690	-0.6042240
0	-3.8225950	0.0190160	0.3130040
0	-4.5332920	0.0720700	-2.0429870
0	-2.7550980	-1.5831920	-1.2855040
Н	-5.0285200	-0.4778760	-2.6845450
Н	-4.1350910	1.6560930	-0.1022240
Ν	-4.3415580	2.5773800	-0.5779290
Н	-4.4041380	2.3440680	-1.5765990
Н	-5.2386650	2.9503610	-0.2543690
Н	-3.5414620	3.2822880	-0.4093570

5-5 Dimethylammonium Bisulfate [((CH₃)₂NH₂)₅(HSO₄)₅]

S	3.4672850	0.2199970	-2.3621480
0	4.2617840	-0.0378970	-1.1146160
0	3.2898360	-0.9667010	-3.2385570
0	4.3509560	1.3716160	-3.2126480

0	2.1942200	1.0009520	-2.1261590
Н	5.2421360	0.9898160	-3.3543060
S	2.1276380	0.8228570	2.8449100
0	3.2354830	-0.1679460	2.8907910
0	1.7556440	1.3026840	1.4710920
0	2.7477370	2.2437540	3.4992370
0	0.9482730	0.4722890	3.7102050
Η	3.1276660	2.0011390	4.3687900
S	-1.2758710	2.9189760	0.4134140
0	-0.2060950	3.9799720	0.3544310
0	-2.0061390	2.8413120	1.7057000
0	-0.5011210	1.4809470	0.1623670
0	-2.1984880	2.9616320	-0.7927570
Η	0.2881980	1.3860950	0.7965900
S	0.0834830	-3.1258500	0.4424650
0	-0.3998490	-3.4696510	1.8271560
0	0.0482350	-1.6388510	0.1948350
0	-0.9324390	-3.8251910	-0.6278450
0	1.4045980	-3.7585560	0.1030540
Η	-1.7483020	-3.2398780	-0.7357250
S	-4.2511720	-1.7647260	-0.9687440
0	-5.1366610	-2.9442000	-0.8699760
0	-4.4115470	-0.7178790	0.0984650
0	-4.7736950	-0.9040890	-2.3522830
0	-2.8049220	-2.0597610	-1.2723960
Η	-5.1668100	-1.5823870	-2.9386170
Ν	3.8193250	-2.5691170	0.0383130
С	4.4244440	-2.7337870	1.3910730
С	4.4523250	-3.4063260	-1.0202200
Н	3.9325150	-2.0340200	2.0791980
Н	4.2765910	-3.7711850	1.7182520
Н	5.4970220	-2.5043010	1.3339620
Η	3.9976910	-3.1493220	-1.9850640
Η	5.5289070	-3.1930470	-1.0529470
Η	4.2801530	-4.4645230	-0.7861930
Η	2.7947680	-2.8521310	0.0909830
Η	3.8819530	-1.5649490	-0.2622090
Ν	-1.1045510	-1.2639350	3.2648640
С	-1.4689090	-1.7038860	4.6362370
С	-2.1955960	-0.5540700	2.5383420
Η	-0.6052150	-2.2075250	5.0882520
Η	-1.7416010	-0.8273570	5.2386940
Н	-2.3162430	-2.3999760	4.5805480

Η	-1.8376320	-0.3226100	1.5292840
Η	-3.0773150	-1.2040350	2.4738180
Η	-2.4325430	0.3798430	3.0642000
Η	-0.2659500	-0.6246930	3.3304260
Η	-0.8093350	-2.1108480	2.6942870
Ν	-4.6566880	1.9760140	-0.2762740
С	-5.5290460	2.2323330	-1.4527340
С	-5.1708210	2.5553720	0.9953590
Η	-5.1171900	1.6994610	-2.3178640
Η	-6.5391250	1.8532130	-1.2475840
Н	-5.5644340	3.3124270	-1.6478200
Η	-4.4007870	2.4279420	1.7657750
Η	-5.3558000	3.6284640	0.8523070
Н	-6.1022430	2.0460440	1.2767970
Н	-4.5392740	0.9291240	-0.1604470
Н	-3.6772900	2.3709270	-0.4661130
Ν	2.1978080	3.4440370	-0.7482100
С	2.1697590	4.2562230	-1.9958120
С	3.3413950	3.7556710	0.1543060
Н	1.2767540	3.9821050	-2.5704420
Н	2.1227530	5.3202100	-1.7302360
Н	3.0697220	4.0444160	-2.5873940
Η	3.2632630	3.1142580	1.0393570
Н	4.2821790	3.5595090	-0.3770030
Н	3.2838670	4.8124890	0.4464760
Н	1.2731540	3.5944220	-0.2361500
Н	2.2301540	2.4351840	-1.0314700
Ν	-0.2281460	-0.4809610	-2.3203270
С	-1.3114170	0.4042400	-2.8347670
С	0.0130630	-1.6779270	-3.1783820
Н	-1.4293970	1.2574000	-2.1549280
Н	-1.0281080	0.7515710	-3.8381080
Н	-2.2420760	-0.1749640	-2.8780230
Н	0.8063890	-2.2840650	-2.7278340
Н	-0.9155440	-2.2583600	-3.2325060
Н	0.3288880	-1.3441390	-4.1747020
Н	0.6606390	0.0681540	-2.2377840
Н	-0.4268210	-0.8147630	-1 3446140

[(NH₄)₅(HSO₄)₅(H₂O)₅] Cluster

S	-3.9571920	1.4213780	-1.9181670
0	-3.6569930	2.8782890	-1.9340640

0	-4.6935590	0.8932820	-3.1031790
0	-5.0362510	1.1598590	-0.6106130
0	-2.7938690	0.5814450	-1.4554670
Н	-5.9210970	1.4450270	-0.9223840
Н	-4.1625560	-2.2429910	-1.4355290
Ν	-3.4028360	-2.1026290	-0.7254370
Н	-3.7289360	-2.2343860	0.2453980
Н	-2.5878170	-2.7416840	-0.8958180
Н	-3.0904780	-1.1125590	-0.8382400
S	-2.2415440	-1.1524320	2.7596610
0	-2.8902890	0.1004300	3.2274450
0	-1.5017120	-1.0219150	1.4487250
0	-3.5107570	-2.1738930	2.2531920
0	-1.5103890	-1.9119310	3.8124610
Н	-4.0183410	-2.4355300	3.0491110
Н	-0.9232410	0.8157330	-1.9253230
Ν	0.0535660	0.6279340	-1.6410410
Н	0.7476750	0.6600620	-2.4307060
Н	0.3149080	1.2776420	-0.8581100
Н	0.1031800	-0.3610310	-1.3139190
Н	-2.8307060	3.0358100	1.1530410
Ν	-2.0789410	3.4238320	0.4918330
Н	-1.7449500	4.3615190	0.7477890
Н	-1.2272410	2.8122020	0.5285440
Н	-2.4843760	3.4223510	-0.4644360
S	0.2228020	-3.3113650	-0.7075460
0	-1.1611070	-3.7591830	-1.0432150
0	1.2503080	-4.4109230	-0.7608230
0	0.2341770	-2.9001100	0.8905160
0	0.6685210	-2.0788320	-1.4522270
Н	-0.4852370	-2.1966820	1.0771970
S	1.3646690	3.4025010	0.7220320
0	2.4264830	3.2135000	1.7630280
0	0.4418220	2.1463860	0.6561250
0	2.0921290	3.3690990	-0.7287050
0	0.5406300	4.6314990	0.8185230
Н	3.1201190	3.4842160	-0.5817630
Н	1.3116940	0.8352730	1.5664540
Ν	2.0814640	0.3332630	2.0736880
Н	2.5362960	1.0586350	2.6432400
Н	1.7224720	-0.4849650	2.6538460
Н	2.7693370	-0.0203480	1.3739870
S	4.9006290	-0.1693650	-0.6939940

0	5.5287180	0.9752180	0.0186500
0	3.8163540	-0.8656900	0.1132220
0	6.0399330	-1.4159900	-0.7120280
0	4.5411630	0.0732840	-2.1173000
Н	6.8106410	-1.0880950	-1.2215630
Н	3.7130840	-2.5024540	-0.2015610
Ν	3.7231550	-3.5467480	-0.4043700
Н	4.3036530	-3.6989130	-1.2357030
Н	4.1531380	-4.0356810	0.3871090
Η	2.7112510	-3.9102000	-0.5682450
0	1.2665540	-1.9431970	3.3761030
Η	0.3517780	-1.9141320	3.7507880
Н	1.1747710	-2.5794130	2.6352780
0	2.0118250	-0.1857690	-3.3904200
Η	2.9139010	-0.0262240	-3.0274630
Η	1.7998910	-1.1024340	-3.1243280
0	4.5769560	3.5986220	-0.1250520
Н	4.3850350	3.7215600	0.8278730
Н	5.0063520	2.7092140	-0.1780110
0	-5.2941580	-1.8210160	-2.7532320
Η	-5.1333110	-0.8753820	-3.0057960
Η	-5.3937990	-2.3133690	-3.5847200
0	-4.0460630	2.2146970	1.8716400
Η	-4.5263740	1.8015880	1.1203280
Н	-3.6787980	1.4573260	2.3927040

$[((CH_3)_2NH_2)_5(HSO_4)_5(H_2O)_5]$ cluster

-3.5881260	1.5819400	-1.2340730
-3.9886320	0.8910450	0.0706370
-4.0921660	2.9772120	-1.3016670
-4.3192290	0.7382190	-2.4165390
-2.1058160	1.4342000	-1.4879870
-3.6324130	0.0785240	-2.7904770
-0.8178490	-2.6871530	2.5960940
-1.8767990	-1.6957490	2.9521140
-0.7510870	-3.0375120	1.1405520
-1.3160870	-4.1551550	3.2286250
0.5206990	-2.4141470	3.2265280
-1.4972500	-4.0074000	4.1804190
0.4791090	-2.5609380	-2.1072360
-0.5785720	-3.6163720	-2.1781480
1.6577130	-2.7934760	-2.9977040
	-3.5881260 -3.9886320 -4.0921660 -4.3192290 -2.1058160 -3.6324130 -0.8178490 -1.8767990 -0.7510870 -1.3160870 0.5206990 -1.4972500 0.4791090 -0.5785720 1.6577130	-3.58812601.5819400-3.98863200.8910450-4.09216602.9772120-4.31922900.7382190-2.10581601.4342000-3.63241300.0785240-0.8178490-2.6871530-1.8767990-1.6957490-0.7510870-3.0375120-1.3160870-4.15515500.5206990-2.4141470-1.4972500-4.00740000.4791090-2.5609380-0.5785720-3.61637201.6577130-2.7934760

0	1.1532510	-2.6170570	-0.6086160
0	-0.1164100	-1.1674230	-2.2425460
Н	0.4131860	-2.6525220	0.0844490
S	0.5563540	2.4737240	1.9537330
0	1.0198330	2.3537110	3.3946690
0	0.3273780	1.1540280	1.3051780
0	1.8356840	3.2038760	1.2429180
0	-0.6126050	3.4278050	1.8124820
Н	1.8313500	3.0192070	0.2459390
S	2.4425470	1.7538130	-2.1542300
0	3.3728850	2.1527530	-3.2270690
0	2.9831930	0.7223730	-1.1789390
0	1.1689620	1.0648000	-2.9210290
0	1.8534250	2.9370730	-1.3895360
Н	0.7826280	0.2598490	-2.4446440
Ν	-3.0641720	2.3140880	2.2165200
С	-2.9635940	1.4704190	3.4394340
С	-4.0098390	3.4570210	2.3346920
Н	-2.2758810	0.6378290	3.2430020
Н	-2.5827380	2.0821170	4.2681810
Н	-3.9574990	1.0745550	3.6884630
Н	-4.0730700	3.9568330	1.3597720
Н	-5.0032270	3.0784760	2.6097690
Н	-3.6448840	4.1534970	3.1010860
Н	-2.0949530	2.6956410	1.9938640
Н	-3.3711910	1.7183220	1.3915620
Ν	2.2502540	-0.1805220	3.4023150
С	2.8830870	-0.4363270	4.7279470
С	3.2204920	-0.1919230	2.2635220
Н	2.0977430	-0.4627240	5.4941180
Н	3.4027450	-1.4027400	4.6954500
Н	3.5839090	0.3830540	4.9346160
Н	2.6742710	0.0638850	1.3474030
Н	3.9939330	0.5592820	2.4645020
Н	3.6502800	-1.1988020	2.1799030
Н	1.5107960	-0.8971360	3.2301980
Н	1.7644070	0.7562380	3.4273100
Ν	4.0240490	-1.6369710	-2.1802870
С	4.8532450	-1.2860000	-3.3675850
С	4.7561190	-2.4084790	-1.1343780
Н	4.2449810	-0.6882870	-4.0577930
Н	5.7125290	-0.6938270	-3.0284580
Н	5.1888700	-2.2085260	-3.8592900

Н	4.0734390	-2.6137250	-0.3005810
Н	5.1092060	-3.3534910	-1.5681700
Н	5.5978730	-1.7986000	-0.7820160
Н	3.6525860	-0.7397940	-1.7659870
Н	3.1608180	-2.1604730	-2.4901670
Ν	-3.0642900	-3.7077790	-0.8920580
С	-4.0583300	-3.7079530	-2.0007750
С	-3.0817780	-4.9521350	-0.0745550
Η	-3.9159400	-2.7959960	-2.5945980
Н	-3.8951730	-4.5901400	-2.6347750
Н	-5.0696250	-3.7342280	-1.5737290
Н	-2.3236570	-4.8619040	0.7120480
Н	-4.0772250	-5.0699440	0.3739570
Н	-2.8561330	-5.8128880	-0.7184420
Н	-2.1040300	-3.5816260	-1.2985040
Н	-3.2666660	-2.8670730	-0.2453200
Ν	-0.7233110	3.6585550	-2.0740220
С	-0.8743550	3.8615550	-3.5393060
С	-1.1602640	4.8159580	-1.2444000
Н	-0.5016720	2.9654930	-4.0508710
Н	-1.9365010	4.0161470	-3.7706870
Н	-0.2886420	4.7370120	-3.8506140
Н	-0.9595290	4.5803290	-0.1898520
Н	-0.5966870	5.7101440	-1.5440870
Η	-2.2368700	4.9685360	-1.3963640
Η	-1.2866870	2.7933080	-1.7986020
Н	0.2793500	3.4205270	-1.8553680
0	2.7837950	-3.6245020	1.7350200
Η	2.0350440	-3.3982690	2.3273110
Η	2.3572600	-3.7193510	0.8620540
0	3.6602060	2.6711860	4.2258370
Η	2.7390790	2.8149650	3.9012770
Н	4.1917420	3.3427780	3.7676040
0	-2.6108170	-1.0206870	-3.3638640
Η	-1.7195020	-1.0104140	-2.9096560
Η	-2.4136830	-0.9330150	-4.3120750
0	5.6951850	0.6150430	-0.4814990
Н	4.7693040	0.9112780	-0.6461260
Η	6.2388760	1.4142860	-0.5790040
0	-3.7830490	-1.7385130	0.7847820
Н	-3.1561510	-1.6762680	1.5433130
Η	-3.8652190	-0.8113710	0.4316240

Appendix C

CARTESIAN COORDINATES FOR THE REACTANT, PRODUCT AND TRANSITION STATES OF CHARGED AMMONIM BISULFATE CLUSTERS

C.1 Cartesian coordinates for all optimized reactant, product and transition state clusters as well as free molecules

Sulfuric Acid (H₂SO₄)

S	-0.041051	0.116907	-0.005283
0	-0.503645	1.481157	0.236644
0	1.344855	-0.266772	-0.261704
0	-0.521366	-0.844237	1.247885
0	-0.989918	-0.439758	-1.236017
Н	-1.358702	-0.472479	1.601060
Н	-0.573672	-1.258718	-1.582586

Ammonia (NH₃)

Η	0.119902	0.104506	0.322174
Ν	-0.287899	0.858690	0.878649
Η	0.442767	1.556541	1.033208
Η	-1.017870	1.297662	0.313669

[(NH4⁺)₂(HSO₄⁻)]⁺ Product Cluster

S	0.0926330	0.0291690	0.0436470
0	-0.9441440	-1.0574120	0.1080650
0	0.8853420	0.2423840	1.2849000
0	-0.9229480	1.3493990	-0.1617640
0	0.9636210	-0.0372320	-1.1880160
Н	-0.3888750	2.1705310	-0.2065500
Н	-3.9393520	-0.5285770	0.8304630
Ν	-3.4218920	-0.3172620	-0.0310800
Н	-3.3680910	0.7020090	-0.1594500
Н	-2.3810960	-0.6828090	0.0365080
Н	-3.9057380	-0.7401190	-0.8321560
Н	2.9339180	-0.0973480	0.8885490

Ν	3.3401170	-0.2874400	-0.0470150
Н	2.4795260	-0.2093360	-0.7035660
Η	4.0611810	0.4058940	-0.2770550
Η	3.7438540	-1.2311510	-0.0739080

[(NH4⁺)2(HSO4⁻)(H2SO4)]⁺ Product Cluster

S	1.9887350	-0.0085370	-0.2811940
0	0.9503220	1.0224360	-0.7502830
0	1.9066080	-0.1996400	1.2119110
0	3.3539480	0.8324900	-0.6082200
0	1.9642280	-1.2718200	-1.0543970
Н	4.1320470	0.2499510	-0.4652780
Н	0.5772280	2.6146740	2.0294490
Ν	0.0989230	2.7464890	1.1301470
Н	0.0644570	3.7451420	0.8948610
Н	0.5991650	2.1817890	0.3705220
Н	-0.8632200	2.3414290	1.1686430
Н	1.2268110	-1.8387920	1.4360940
Ν	0.6875410	-2.6855700	1.1079360
Н	0.7164570	-3.4602070	1.7799070
Н	-0.2907620	-2.3658080	0.9367940
Η	1.1110320	-2.9519070	0.2050690
S	-2.1530590	-0.0775350	-0.0812220
0	-1.7074940	-1.2605520	0.6751620
0	-2.2096720	1.2238000	0.6297680
0	-1.3599630	0.0832160	-1.4560870
0	-3.6116430	-0.4692480	-0.6356410
Н	-0.4044770	0.4366460	-1.2646050
Н	-4.0354620	0.3123430	-1.0570850

[(NH4⁺)₃(HSO₄⁻)₂]⁺ Product Cluster

S	2.2028840	0.0034100	0.0125310
0	1.6110070	1.3568450	0.2717740
0	1.8602920	-0.9994880	1.0827540
0	3.8098520	0.3164900	0.1104440
0	1.9416200	-0.5305640	-1.3725490
Η	4.3085140	-0.5115880	-0.0610480
Η	0.7583140	-0.4109590	2.2021750
Η	-0.7583040	0.4117640	2.2020100
Ν	-0.0000070	0.0005040	2.8259610
Η	-0.4033050	-0.7336810	3.4184010

Η	0.4032640	0.7348800	3.4181820
Н	0.8670550	-1.7904000	-1.4966890
Ν	0.0703810	-2.4989970	-1.4941820
Η	0.4050330	-3.4038250	-1.1455440
Η	-0.6822180	-2.1126570	-0.8432420
Н	-0.3073450	-2.6168560	-2.4405720
S	-2.2028780	-0.0033980	0.0125320
0	-1.6110060	-1.3567370	0.2722840
0	-1.8602470	0.9999080	1.0823610
0	-1.9416420	0.5300430	-1.3727590
0	-3.8098470	-0.3164240	0.1106010
Н	-4.3085050	0.5115850	-0.0612370
Н	-0.8670730	1.7898180	-1.4973590
Н	0.6821870	2.1123110	-0.8439920
Ν	-0.0704040	2.4984210	-1.4950820
Н	-0.4050700	3.4033660	-1.1467620
Н	0.3073420	2.6159580	-2.4415040

$[(NH_4^+)_3(HSO_4^-)_2(H_2SO_4)]^+$ Product Cluster

S	-2.5677490	-1.5360690	0.0243480
0	-2.2581100	-0.8207310	-1.2593560
0	-1.3910950	-2.1983480	0.6802120
0	-3.5557860	-2.7433870	-0.4907690
0	-3.3551040	-0.6697100	0.9742400
Η	-3.7327140	-3.3482430	0.2620990
Η	0.0445240	0.1354700	2.1980270
Ν	0.2060370	-0.8670600	2.4460070
Η	1.1870310	-1.1025850	2.1839810
Η	0.0495400	-1.0254070	3.4464640
Η	-0.4616800	-1.4455460	1.8594840
S	-0.0254600	2.3120390	0.0512910
0	0.9488880	1.5288540	-0.8346740
0	-1.2327890	2.7043060	-0.7400550
0	0.7684470	3.6821020	0.4772980
0	-0.2964370	1.6660640	1.3600510
Η	0.8780440	4.2444250	-0.3207340
Η	0.3610050	0.3613390	-2.1367630
Ν	0.1320670	-0.5966430	-2.4849460
Η	0.8845400	-1.2155510	-2.1279040
Η	-0.8073430	-0.8586680	-2.0609850
Н	0.0966430	-0.6257830	-3.5089760
Н	-4.2104740	2.4153290	0.6427480

Ν	-3.7489570	1.7961680	-0.0326740
Н	-4.3202460	1.7367490	-0.8830430
Н	-2.7945790	2.1779360	-0.2791650
Н	-3.6329020	0.8121390	0.3827100
S	3.1900880	-0.9123090	-0.0147470
0	2.8267350	-1.1766950	1.3984850
0	2.4245670	-1.5852670	-1.0773690
0	3.2893680	0.6577480	-0.2746780
0	4.7299730	-1.3374970	-0.2468430
Н	2.3440760	1.0639640	-0.4243060
Н	5.2511820	-1.1309200	0.5610480

[(NH4⁺)4(HSO4⁻)3]⁺ Product Cluster

S	-2.8566260	-1.4434300	0.0942600
0	-2.2697290	-1.1692790	-1.2692760
0	-1.8727420	-2.0607490	1.0487770
0	-3.9644160	-2.6146410	-0.2542820
0	-3.5948280	-0.2708280	0.6668710
Η	-4.4158060	-2.8732020	0.5785340
Η	0.8272800	-0.9715490	2.0402190
Ν	-0.0252550	-0.4384990	2.3386780
Η	-0.0480240	0.4436590	1.7698730
Η	-0.8538210	-1.0187790	2.0553320
Η	-0.0220880	-0.2409120	3.3434580
S	-0.0593470	2.8714090	0.0813490
0	1.1825830	3.4438030	-0.5389630
0	-1.3091940	3.3590220	-0.5903090
0	-0.1105720	3.4291750	1.6449830
0	-0.0083110	1.3903320	0.2935820
Η	-0.1676150	4.4087160	1.6245850
Η	0.1218580	-2.9509520	-0.3951250
Ν	0.0632280	-2.6415060	-1.3775710
Η	0.0118530	-3.4559280	-1.9983210
Η	-0.8122240	-2.0505310	-1.4662630
Η	0.9449720	-2.0843250	-1.5589500
Η	-3.5562070	1.0564990	-0.4307310
Ν	-3.2850920	1.6442150	-1.2659870
Η	-4.0937510	2.1441660	-1.6491250
Η	-2.5132070	2.3284050	-0.9927390
Н	-2.9209370	0.9694720	-1.9538710
S	2.9007170	-1.4173220	0.0644730
0	3.6078200	-0.1917470	0.5717300

0	1.8093820	-1.9459300	0.9428610
0	2.4621060	-1.2600100	-1.3743340
0	3.9883900	-2.6530220	0.1235820
Н	2.4545830	2.5004610	-0.8762590
Н	4.8342700	-2.3469850	-0.2678930
Η	3.1325880	1.4533380	-2.0483780
Ν	3.3008320	1.9008540	-1.1399050
Н	3.4416230	1.1243990	-0.4244270
Η	4.1388380	2.4890790	-1.1995220

[(NH₄⁺)₂(HSO₄⁻)]⁺ + H₂SO₄ Reactant Cluster

S	-1.9541540	0.2455550	0.2044840
0	-0.7230260	0.9316110	0.7812780
0	-1.6662230	-0.4289980	-1.1175370
0	-2.8437090	1.5939320	-0.1418760
0	-2.6801380	-0.6278550	1.1552590
Н	-3.7217040	1.3209480	-0.4865330
Н	0.0121371	3.5329451	-1.3913722
Ν	-0.6116940	3.5018245	-0.5723466
Н	-1.6038912	3.5326614	-0.8388021
Η	-0.3909274	2.5931601	-0.0417714
Н	-0.3790892	4.3057232	0.0234823
Η	-1.8246914	-2.3118512	-0.9268368
Ν	-2.2096001	-3.0051595	-0.1868566
Н	-2.9515832	-3.5971694	-0.5786720
Н	-1.4536680	-3.5961425	0.1815495
Η	-2.5872131	-2.4052657	0.5659517
S	2.7990637	-1.1482163	0.1728513
0	2.4190437	-2.0911423	-0.8740247
0	2.8312207	0.3086967	-0.1094657
0	1.9421137	-1.3864133	1.5361213
0	4.2453417	-1.6441453	0.7086993
Н	1.0867717	-0.8514433	1.4665463
Н	4.5852927	-1.0152643	1.3831383

$[(NH_4^+)_2(HSO_4^-)(H_2SO_4)]^+ + NH_3$ Reactant Cluster

S	1.9195390	0.6734350	-0.1805010
0	0.6214010	1.3185530	-0.7152340
0	1.7961570	0.3346610	1.2723240
0	2.8938690	1.9977690	-0.2944490
0	2.4312420	-0.4002770	-1.0569550

3.8021950	1.7391930	-0.0251010
-1.5993800	2.5594000	0.7323550
-0.7247110	3.1321790	0.7024020
-0.3760140	3.3058490	1.6521300
-0.0277570	2.5275600	0.1499190
-0.8941910	4.0260590	0.2271640
1.2564010	-1.3824670	1.7160020
0.7926880	-2.3160080	1.6564220
-0.2161110	-2.1374310	1.5145870
1.2202500	-2.8530550	0.7595700
0.9351660	-2.8447780	2.5226450
-2.2972050	-0.2406730	-0.0698420
-1.8148020	-1.1462730	0.9814170
-2.6570920	1.1518450	0.3037900
-1.3244050	-0.2258980	-1.3359870
-3.5830610	-0.9799830	-0.7070710
-0.4955460	0.3792980	-1.1381620
-4.0369940	-0.3776060	-1.3381570
1.8608440	-3.3747010	-0.5862250
1.2042370	-3.8288430	-1.2285600
2.2040860	-2.5212510	-1.0486080
2.6580990	-4.0095850	-0.4811780
	3.8021950 -1.5993800 -0.7247110 -0.3760140 -0.0277570 -0.8941910 1.2564010 0.7926880 -0.2161110 1.2202500 0.9351660 -2.2972050 -1.8148020 -2.6570920 -1.3244050 -3.5830610 -0.4955460 -4.0369940 1.8608440 1.2042370 2.2040860 2.6580990	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

$[(NH_4^+)_3(HSO_4^-)_2]^+ + H_2SO_4$ Reactant Cluster

S	-3.1203850	-1.3828190	-0.0439020
0	-2.5417760	-0.3209320	-0.9933170
0	-4.2408870	-2.1668520	-0.5701290
0	-3.7423160	-0.3439660	1.1405530
0	-2.0092460	-2.1486280	0.6093280
Η	-4.4848680	-0.8240520	1.5667500
Η	-0.7738680	-1.5985570	1.5684990
Ν	0.1351080	-1.2580590	2.0000090
Н	0.2087260	-1.5296710	2.9855440
Н	0.9162140	-1.6594570	1.4490170
Н	0.1822240	-0.2184530	1.8920410
S	0.4580430	2.2722540	0.1448630
0	1.1836140	1.4641600	-0.9373760
0	-0.6449300	3.0784620	-0.4640740
0	1.5747920	3.3163590	0.7315210
0	0.0840050	1.4646550	1.3336250
Н	1.7249820	4.0229590	0.0652590
Н	-1.0940040	-0.6830520	-1.7715530

-0.1090140	-0.6821120	-2.1734780
-0.1258340	-0.8312480	-3.1880630
0.3277530	0.2397320	-1.9259760
0.4737270	-1.4029790	-1.7108660
-3.8731140	2.7650680	-0.9552990
-3.2437920	2.2237770	-0.3529240
-3.1114280	1.2327170	-0.7155500
-2.2849680	2.6686190	-0.3156600
-3.6416640	2.1481910	0.5910610
3.2688860	-1.2254790	-0.1756830
1.8526520	-1.6839290	-0.2735930
4.3777430	-2.0567790	-0.6160320
3.4116520	0.2078990	-0.8502230
3.3832560	-0.9199040	1.4437600
2.5352320	0.7578250	-0.7706450
4.3316140	-0.8205420	1.6833940
	-0.1090140 -0.1258340 0.3277530 0.4737270 -3.8731140 -3.2437920 -3.1114280 -2.2849680 -3.6416640 3.2688860 1.8526520 4.3777430 3.4116520 3.3832560 2.5352320 4.3316140	-0.1090140-0.6821120-0.1258340-0.83124800.32775300.23973200.4737270-1.4029790-3.87311402.7650680-3.24379202.2237770-3.11142801.2327170-2.28496802.6686190-3.64166402.14819103.2688860-1.22547901.8526520-1.68392904.3777430-2.05677903.41165200.20789903.3832560-0.91990402.53523200.75782504.3316140-0.8205420

$[(NH_4^+)_3(HSO_4^-)_2(H_2SO_4)]^+ + NH_3$ Reactant Cluster

S	-2.8227140	-1.2086090	0.3071850
0	-2.0072420	-0.9928670	-0.9295360
0	-2.0761220	-1.7554610	1.4877020
0	-3.8508340	-2.4162420	-0.1605260
0	-3.6751550	-0.0136500	0.6555830
Н	-4.3690120	-2.6983180	0.6241130
Н	0.1951690	0.2986700	2.5351590
Ν	0.1130100	-0.7125250	2.7289060
Н	0.8697790	-1.1901890	2.1786840
Н	0.2061650	-0.9024700	3.7314240
Н	-0.8145660	-1.0529450	2.3483150
S	0.1284720	2.4721430	-0.0977940
0	0.9703020	1.8291660	-1.2579210
0	-1.0231160	3.1550290	-0.7380480
0	1.0938900	3.6154130	0.5544040
0	-0.1237490	1.5334100	1.0048760
Н	1.2018770	4.3486840	-0.0913270
Н	0.8346350	-2.2337860	-2.2835150
Ν	0.2668460	-2.5827290	-1.4114450
Н	0.8565230	-2.3996090	-0.5684860
Н	-0.6289510	-2.0478190	-1.2987700
Н	0.0617560	-3.5841110	-1.4839540
Н	-4.2719080	2.7097510	-0.8231870
Ν	-3.5517230	2.0133150	-1.0443880

Η	-3.6848250	1.6826090	-2.0064080
Η	-2.5990790	2.4475480	-0.9529830
Н	-3.6245580	1.1714670	-0.3637880
S	2.8743820	-0.6218990	0.5258250
0	3.0694930	0.3232300	1.6407220
0	1.8591570	-1.7112610	0.7871840
0	2.6236920	0.0527500	-0.8269570
0	4.2440950	-1.4971410	0.2786500
Н	1.6980430	1.0835480	-0.9449460
Н	5.0093020	-0.8828040	0.3195340
Η	2.5133620	-2.2017060	-3.8737000
Ν	1.8772980	-1.5578010	-3.3942870
Η	2.4508650	-0.9342410	-2.8112260
Н	1.4398670	-0.9812440	-4.1189290

$[(NH_4^+)_2(HSO_4^-)]^+ + H_2SO_4^- TS$

S	1.9552840	-0.0484910	-0.2800930
0	0.9315450	0.9978360	-0.7493790
0	1.8668560	-0.2399570	1.2112010
0	3.3355450	0.7740880	-0.6018040
0	1.9164120	-1.3066580	-1.0601240
Н	4.1027770	0.1726190	-0.4803260
Н	-0.0412070	2.2594270	1.9108220
Ν	0.2671430	2.8028320	1.0944850
Н	1.0273080	3.4416680	1.3567530
Н	0.5896640	2.1016020	0.3330450
Η	-0.5416980	3.3308880	0.7439560
Η	1.1624220	-1.8888080	1.4352260
Ν	0.5989350	-2.7120880	1.0950580
Η	0.5963910	-3.4930030	1.7602870
Н	-0.3685970	-2.3553990	0.9201390
Η	1.0182850	-2.9858500	0.1927770
S	-2.1357060	-0.0461120	-0.0678700
0	-1.7638060	-1.2797660	0.6495040
0	-2.0169760	1.2438510	0.6432400
0	-1.4026070	0.0501610	-1.4907130
0	-3.6487750	-0.3147340	-0.5534830
Η	-0.4535650	0.4065060	-1.3339720
Η	-4.0131170	0.4902160	-0.9856400

S	-2.3014040	0.1364010	-0.0011360
0	-0.8815410	0.6371610	0.2330070
0	-2.4314830	-0.5332400	-1.3414400
0	-3.0985250	1.5885610	-0.1144810
0	-2.8564170	-0.6277780	1.1389520
Н	-4.0621120	1.4141700	-0.1841150
Н	0.9436970	2.8861050	0.0823130
Ν	-0.0701210	3.1032230	0.1227680
Н	-0.3620730	3.6178460	-0.7155040
Н	-0.5618040	2.1293000	0.1684640
Н	-0.2845260	3.6597720	0.9576160
Н	-1.2065860	-1.6040810	-1.5910010
Ν	-0.3409070	-2.2275470	-1.4995840
Н	0.4984520	-1.6829140	-1.7662370
Н	-0.2499290	-2.4578810	-0.4749610
Н	-0.4232830	-3.0753610	-2.0703750
S	2.4287450	0.1467590	-0.0940040
0	1.9261860	-0.4528100	-1.3370360
0	2.3695220	1.6077030	0.1139040
0	1.7944630	-0.6090600	1.1866110
0	3.9704200	-0.3167800	0.0553740
Н	0.8949810	-0.9947820	0.9762920
Н	4.4647730	0.3569000	0.5737900
Ν	-0.4564470	-2.4862530	1.4729090
Н	0.0962660	-2.4113600	2.3352660
Н	-1.3332910	-1.9660550	1.6412920
Н	-0.7206840	-3.4782280	1.4376110

$[(NH_4^+)_3(HSO_4^-)_2]^+ + H_2SO_4^- TS$

S	-2.6713000	-1.2624700	0.1255840
0	-1.9645330	-0.8842360	-1.1441090
0	-1.8245270	-1.9501370	1.1506950
0	-3.7449720	-2.3941470	-0.4072120
0	-3.4773300	-0.1199140	0.6923960
Η	-4.1899720	-2.7913330	0.3728690
Н	0.4768870	-0.0346650	2.3896330
Ν	0.3978160	-1.0591170	2.4998680
Η	1.1335570	-1.4947870	1.8830600
Η	0.5141070	-1.3378250	3.4790160
Н	-0.5389500	-1.3538300	2.1161700

S	0.2586650	2.3783540	0.0135260
0	1.0512810	1.9499050	-1.2837960
0	-0.8975990	3.1779030	-0.4397650
0	1.2858880	3.3464910	0.8339080
0	0.0312500	1.2431320	0.9244830
Η	1.4256650	4.1746720	0.3231190
Η	1.0697370	-1.3398780	-1.9181200
Ν	0.3444670	-2.1052810	-1.9082230
Η	0.6573750	-2.7518290	-1.1682810
Η	-0.5987330	-1.6922160	-1.6366290
Η	0.2903470	-2.5875710	-2.8112770
Η	-4.4318540	2.3890340	-0.9727010
Ν	-3.5018130	2.1681420	-0.6000120
Н	-2.8043420	2.1449350	-1.3561180
Η	-3.1870790	2.9023980	0.0475920
Η	-3.5064590	1.2029220	-0.0898070
S	2.9088810	-0.8523300	-0.0154730
0	3.3101920	0.1556230	0.9798170
0	2.0290560	-1.9752680	0.4627500
0	2.2907010	-0.2217530	-1.2885520
0	4.2224900	-1.6672810	-0.5638400
Η	1.8178761	0.7007404	-1.2046324
Η	4.9397350	-1.0198460	-0.7407600

$[(NH_4^+)_3(HSO_4^-)_2(H_2SO_4)]^+ + NH_3 TS$

S	2.8362750	-1.4491580	-0.0138220
0	2.1411940	-0.9446330	1.2196090
0	1.9179390	-2.1274830	-0.9931590
0	3.7997620	-2.6363620	0.6017930
0	3.7368870	-0.4276230	-0.6436030
Н	4.2952970	-3.0469490	-0.1395280
Н	0.3203450	0.2824060	-2.1719300
Ν	0.1445950	-0.7107710	-2.5106330
Н	-0.7764230	-1.0195720	-2.1525620
Н	0.1787140	-0.7712230	-3.5326230
Н	0.8911920	-1.3103850	-2.0606340
S	0.1162160	2.1708190	-0.1507430
0	-0.8667680	1.2365400	0.4790700
0	1.0669830	2.7813980	0.8477240
0	-0.7402320	3.4140730	-0.8250480
0	0.8318240	1.6194680	-1.3504660
Н	-1.2164500	3.8909970	-0.1125940
Н	-0.8588620	-0.9957830	2.2630110
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Ν	-0.3676560	-1.7407590	1.7097260
Н	-0.8662000	-1.8452100	0.8049270
Н	0.6494050	-1.4495890	1.5192490
Н	-0.3899440	-2.6315690	2.2175020
Н	3.8287340	2.7455230	-0.7509040
Ν	3.6106540	2.1916000	0.0846170
Н	4.2969880	2.3997760	0.8176580
Н	2.6264070	2.4419710	0.4170750
Н	3.6503190	1.1569480	-0.1651930
S	-3.2500860	-0.7291590	-0.4290330
0	-3.5412260	0.4894020	-1.1796270
0	-2.0158500	-1.5093250	-0.7119470
0	-3.3658990	-0.5179840	1.1747760
0	-4.4485660	-1.8105580	-0.5816000
Н	-2.6046590	0.0127730	1.5565350
Н	-5.3032280	-1.3327460	-0.6743270
Ν	-1.5962230	0.5936280	3.1690750
Н	-2.4754470	0.9687110	3.5421810
Н	-1.1306240	1.3509830	2.6524010
Н	-1.0220410	0.4016860	3.9976630

Appendix D

GEOMETRY COMPARISONS, BENCHAMARK INFIORMATION, COMPLETE THEMOCHEMICAL INFORMATION AND DIMER FRACTION RATIOS FOR α-PINENE OLIGOMERS

D.1 Geometry comparisons, benchmark information and complete thermochemical information for α-pinene oligomers studied in Chapter 5.



Figure D1: Comparison of the gas phase (a and c) and water solvated (b and d) geometries for the cis-pinic acid non-covalent dimerization pathway at 298 K. Carbon atoms are gray, oxygen atoms are red and hydrogen atoms are white. Hydrogen bonds indicated with dashed lines.



Figure D2: Comparison of the gas phase (a and c) and water solvated (b and d) geometries for the peroxyhemiacetal covalent dimerization pathway at 298 K. Carbon atoms are gray, oxygen atoms are red and hydrogen atoms are white.

Table D1: Benchmark information for gas phase dimerization free energies calculated using PW91 with the 6-311++G(2d,2p) and 6-311++G(3df,3pd) basis sets at 298 K. Calculated as single point energies using the appropriate geometry and thermal correction to the free energy from PW91/6-31+G(d,p) basis set. Values are in atomic units (hartrees) except delta values which are in kJ/mol.

Basis Set	6-311++G(2d,2p)			6-311++G(3df,3pd)		
Molecule	E _{SCF}	G _{corr}	ΔG	E _{SCF}	G _{corr}	ΔG
<i>cis</i> -pinic acid	-652.2864481	0.178181	24.6	-652.3099267	0.178181	26.6
<i>c</i> -PA dimer	-1304.585471	0.359552	-24.0	-1304.633156	0.359552	-20.0
terpenylic acid	-612.999466	0.153695	-29.1	-613.0220257	0.153695	-30.1
TA dimer	-1226.029609	0.326981	1	-1226.075086	0.326981	

Table D2: Benchmark information for condensed phase (water based) dimerization free energies calculated using PW91 with the 6-311++G(2d,2p) and 6-311++G(3df,3pd) basis sets at 298 K. Calculated as single point energies using the appropriate geometry and thermal correction to the free energy from PW91/6-31+G(d,p) basis set and using the guidelines for solvent modeling given in the Computational Methods section Chapter 5. Values are in atomic units (hartrees) except delta values which are in kJ/mol.

Basis Set	6-311++G(2d,2p)			6-311++	G(3df,3pd)	
Molecule	E _{SCF}	G _{corr}	ΔG	E _{SCF}	G _{corr}	ΔG
<i>cis</i> -pinic acid	-652.2864481	0.177234	20.2	-652.3099267	0.177234	20.2
<i>c</i> -PA dimer	-1304.585471	0.376003	-29.2	-1304.633156	0.376003	-30.3
terpenylic acid	-612.9994663	0.15242	-4.29	-613.0220257	0.15242	-5.39
TA dimer	-1226.029609	0.326693		-1226.075086	0.326693	

Table D3: Extended thermochemical information for all gas phase monomers and dimers studied at 298 K. All data given in atomic units (hartrees) and calculated at 1 atm standard pressure. E0 is the total electronic energy plus the calculated zero-point energy.

	Eelectronic	E ₀	Н	G
Monomers and Dimers				
Aldehyde/Ester, Monomer 1	-613.9886324	-613.774962	-613.760717	-613.81498
Norpinic Acid	-612.8163022	-612.625122	-612.611481	-612.664714
Water	-76.40614442	-76.385374	-76.381594	-76.403047
cis-Pinic Acid	-652.1170908	-651.897756	-651.882923	-651.939023
Pinonaldehyde	-540.9333194	-540.69855	-540.683672	-540.739374
cis-Pinonic Acid	-616.1829323	-615.942516	-615.926797	-615.985277
Hemi-acetal, Monomer 1	-691.3748758	-691.129607	-691.113146	-691.172996
Hydroperoxide Monomer	-616.5539273	-616.265256	-616.246954	-616.311105
2,2-dimethyl-3- formyl-cyclobutyl- methanoic acid	-614.001715	-613.788042	-613.773866	-613.827351
Terpenylic Acid	-612.8391131	-612.646997	-612.633867	-612.685447
Anhydride Dimer	-1150.378773	-1149.998549	-1149.97223	-1150.05702
<i>cis</i> -Pinic Acid Dimer	-1304.246025	-1303.807751	-1303.777582	-1303.888326
Ester Dimer	-1150.388493	-1150.007643	-1149.981583	-1150.066283
Aldol Addition	-1157.124428	-1156.644819	-1156.614859	-1156.705867
Hemi-acetal Dimer	-1232.320842	-1232.319765	-1231.804217	-1231.898657
Peroxyhemiacetal Dimer	-1233.065018	-1232.539042	-1232.503656	-1232.627733
Di(α-hydroxy) Ether Dimer	-1230.180364	-1229.721777	-1229.692819	-1229.781454
Terpenylic Acid Dimer	-1225.710232	-1225.325059	-1225.298599	-1225.383575
TA-cPA non- covalent Dimer (alkyl carboxylate)	-1264.987068	-1264.574749	-1264.546601	-1264.636033
TA-cPA non- covalent Dimer (carboxylate)	-1264.986692	-1264.574331	-1264.5462	-1264.63554

Table D4: Extended thermochemical information for all gas phase monomers and dimers studied at 373 K. All data given in atomic units (hartrees) and calculated at 1 atm standard pressure

	Eelectronic	E ₀	\mathbf{H}	G
Monomer and Dimers				
Aldehyde/Ester, Monomer 1	-613.988632	-613.774962	-613.753931	-613.829364
Norpinic Acid	-612.816302	-612.625122	-612.604996	-612.678807
Water	-76.406144	-76.385374	-76.380633	-76.408544
cis-Pinic Acid	-652.1170907	-651.897756	-651.875806	-651.953905
Pinonaldehyde	-540.9333193	-540.698518	-540.676636	-540.754148
cis-Pinonic Acid	-616.1829323	-615.942516	-615.919322	-616.000797
Hemi-acetal, Monomer 1	-691.374876	-691.129607	-691.105248	-691.188907
Hydroperoxide Monomer	-617.256129	-616.995445	-616.970569	-617.055599
Terpenylic Acid	-612.8391131	-612.646997	-612.627515	-612.69911
Anhydride Dimer	-1150.378773	-1149.998549	-1149.95954	-1150.079731
<i>cis</i> -Pinic Acid Dimer	-1304.246025	-1303.807751	-1303.763095	-1303.897857
Ester Dimer	-1150.379399	-1149.998549	-1149.95954	-1150.079731
Aldol Addition Dimer	-1157.138285	-1156.658676	-1156.61372	-1156.745885
Hemi-acetal Dimer	-1232.320842	-1231.835882	-1231.790319	-1231.925249
Peroxyhemiacet al Dimer	1233.065018	-1233.999574	-1233.950727	-1234.091316
Terpenylic Acid Dimer	-1225.71023	-1225.325059	-1225.285752	-1225.40635
TA-cPA non- covalent Dimer (alkyl carboxylate)	-1264.987068	-1264.574759	-1264.532996	-1264.660087
TA-cPA non- covalent Dimer (carboxylate)	-1264.986692	-1264.574331	-1264.532592	-1264.659496

Table D5: Extended thermochemical information for all monomers and dimers studied in the water solvent continuum at 298 K. All data given in atomic units (hartrees) and calculated at 1 M standard concentration.

	Eelectronic	Eo	Η	G
Monomers and Dimers				
Aldehyde/Ester, Monomer 1	-614.008066	-613.794961	-613.780848	-613.834314
Norpinic Acid	-612.841869	-612.651522	-612.638034	-612.690262
Water	-76.419787	-76.399267	-76.395487	-76.416952
cis-Pinic Acid	-652.136101	-651.917986	-651.903213	-651.958867
Pinonaldehyde	-540.947935	-540.71382	-540.698992	-540.75408
cis-Pinonic Acid	-616.200257	-615.960121	-615.944816	-616.001221
Hemi-acetal, Monomer 1	-691.402217	-691.157485	-691.141122	-691.200122
Hydroperoxide Monomer	-656.572585	-656.283898	-656.266071	-656.328372
2,2-dimethyl-3- formyl-cyclobutyl- methanoic acid	-614.023523	-613.811463	-613.797016	-613.8511
Terpenylic Acid	-612.8622	-612.671196	-612.658	-612.70978
Anhydride Dimer	-1150.40658	-1150.027329	-1150.001246	-1150.083976
<i>cis</i> -Pinic Acid Dimer	-1304.284761	-1303.847501	-1303.817789	-1303.908758
Ester Dimer	-1150.424067	-1150.044457	-1150.018682	-1150.100762
Aldol Addition Dimer	-1157.156374	-1156.693331	-1156.663888	-1156.752049
Hemi-acetal Dimer	-1232.360469	-1231.875708	-1231.845495	-1231.937455
Peroxyhemiacetal Dimer	-1313.151544	-1312.571296	-1312.536062	-1312.63972
Di(α-hydroxy) Ether Dimer	-1230.212123	-1229.75576	-1229.726795	-1229.814345
Terpenylic Acid Dimer	-1225.744199	-1225.360902	-1225.334572	-1225.417506
TA-cPA non- covalent Dimer (alkyl carboxylate)	-1265.01657	-1264.607566	-1264.57919	-1264.668765
TA-cPA non- covalent Dimer (carboxylate)	-1265.016683	-1264.606983	-1264.578894	-1264.667498

Table D6:Extended thermochemical information for all monomers and dimers
studied in the water solvent continuum at 373 K. All data given in
atomic units (hartrees) and calculated at 1 M standard concentration

	Eelectronic	E ₀	Н	G
Monomers and				
Dimers				
cis-Pinic Acid	-652.1361011	-651.917986	-651.896055	-651.973642
Pinonaldehyde	-540.9479353	-540.71382	-540.691939	-540.769236
cis-Pinonic Acid	-616.2002563	-615.960121	-615.937355	-616.016218
Hydroperoxide Monomer	-657.2744961	-657.013693	-656.989347	-657.071996
Terpenylic Acid	-612.8622006	-612.671196	-612.651613	-612.723497
<i>cis</i> -Pinic Acid Dimer	-1304.284761	-1303.847501	-1303.803283	-1303.933224
Aldol Addition Dimer	-1157.170235	-1156.693308	-1156.649135	-1156.775843
Peroxyhemiaceta l Dimer	-1314.554902	-1314.02897	-1313.980846	-1314.117865
Terpenylic Acid Dimer	-1225.744198	-1225.360902	-1225.321676	-1225.439775
TA-cPA non- covalent Dimer (alkyl carboxylate)	-1265.01657	-1264.607565	-1264.565452	-1264.692795
TA-cPA non- covalent Dimer (carboxylate)	-1265.016683	-1264.606983	-1264.578894	-1264.667498

Table D7: Extended thermochemical information for all monomers and dimers studied in the methanol solvent continuum at 298 K. All data given in atomic units (hartrees) and calculated at 1 M standard concentration.

	Eelectronic	Eo	Н	G
Monomers and Dimers				
cis-Pinic Acid	-652.1404442	-651.922103	-651.907344	-651.963116
Pinonaldehyde	-540.9539212	-540.719476	-540.704825	-540.759436
<i>cis</i> -Pinonic Acid	-616.205946	-615.965748	-615.950406	-616.00693
Hydroperoxide Monomer	-656.5812004	-656.292482	-656.274668	-656.336694
Terpenylic Acid	-612.8650724	-612.673862	-612.660693	-612.712241
<i>cis</i> -Pinic Acid Dimer	-1304.29148	-1303.853688	-1303.824107	-1303.914686
Aldol Addition Dimer	-1157.16564	-1156.703411	-1156.673819	-1156.764175
Peroxy- hemiacetal Dimer	-1313.167383	-1312.587192	-1312.550221	-1312.654901
Terpenylic Acid Dimer	-1225.749083	-1225.365376	-1225.337193	-1225.440668
TA-cPA non- covalent Dimer (alkyl carboxylate)	-1265.023118	-1264.613931	-1264.585562	-1264.675609
TA-cPA non- covalent Dimer (carboxylate)	-1265.02332	-1264.612867	-1264.584872	-1264.672615

	Eelectronic	Eo	Η	G
Monomers				
and Dimers				
cis-Pinic Acid	-652.1404442	-651.922103	-651.9002	-651.977919
Pinonaldehyde	-540.9539212	-540.719476	-540.697789	-540.773935
<i>cis</i> -Pinonic Acid	-616.205946	-615.965748	-615.942954	-616.021956
Hydroperoxide Monomer	-657.2821483	-657.021265	-656.996991	-657.079177
Terpenylic Acid	-612.8650724	-612.673862	-612.654319	-612.725897
<i>cis</i> -Pinic Acid Dimer	-1304.291483	-1303.853688	-813.809641	-1303.939049
Aldol Addition Dimer	-1157.179497	-1156.703411	-1156.659066	-1156.788513
Peroxy hemiacetal Dimer	-1314.56882	-1314.043616	-1313.995238	-1314.132915
Terpenylic Acid Dimer	-1225.749083	-1225.365376	-1225.322667	-1225.490123
TA-cPA non- covalent Dimer (alkyl carboxylate)	-1265.023118	-1264.613931	-1264.571844	-1264.699755
TA-cPA non- covalent Dimer (carboxylate)	-1265.02332	-1264.612867	-1264.571214	-1264.696175

Table D8: Extended thermochemical information for all monomers and dimers studied in the methanol solvent continuum at 373 K. All data given in atomic units (hartrees) and calculated at 1 M standard concentration.

	cPA-TA non covalent dimer (alkyl carboxylate)	cPA-TA non- covalent dimer (alkyl carboxylate)	cPA-TA non- covalent dimer (carboxylate)	cPA-TA non- covalent dimer (carboxylate)	Peroxy- hemiacetal	Peroxy- hemiacetal
Mass Fraction of Monomer in total SOA	Water	Methanol	Water	Methanol	Water	Methanol
0.0001	5.09F-01	2 94F-01	1 86E+02	1 53E-02	1 20F-02	5 17F-02
0.0005	2.02E-01	1.16E-01	7.43E+01	6.18E-03	2.28E-03	1.68E-03
0.001	5.07E-01	2.88E-01	1.86E+02	1.57E-02	4.45E-04	2.21E-04
0.005	2.02E-01	1.15E-01	7.40E+01	6.95E-03	8.75E-07	2.59E-06
0.0075	3.37E-01	1.92E-01	1.23E+02	1.23E-02	2.81E-06	7.51E-06
0.01	5.07E-01	2.88E-01	1.85E+02	1.95E-02	4.16E-06	2.38E-06
0.025	3.01E-01	1.71E-01	1.96E+02	1.50E-02	2.28E-06	1.69E-06
0.05	1.96E-01	1.12E-01	7.10E+01	1.34E-02	1.29E-07	2.09E-07
0.075	3.29E-01	1.87E-01	1.16E+02	2.81E-02	1.23E-06	3.49E-07
0.1	5.07E-01	2.88E-01	1.72E+02	5.12E-02	7.05E-07	3.46E-07

Table D9: Ratios of dimer fractions $[(f_{dimer,373})/(f_{dimer,298})]$ of remaining favorable condensed phase dimers in water and methanol derived using the predicted standard state ΔG_d° (aq or solv) for each pathway.