Deliquescence, efflorescence, and supercooling of ammonium sulfate aerosols at low temperature: Implications for cirrus cloud formation and aerosol phase in the atmosphere

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Abstract. Motivated by the roles which tropospheric aerosols play in cloud formation processes and heterogeneous chemistry, low-temperature phase transitions of submicron sized (NH₄)₂SO₄ aerosols have been directly observed using Fourier transform infrared extinction spectroscopy. In particular, deliquescent relative humidities have been measured down to 254 K and efflorescence points to 238 K. In agreement with previous studies, it was observed that solid particles deliquesced at the thermodynamic value, whereas efflorescence of aqueous aerosols did not occur until a substantially lower relative humidity was reached. By observing the formation of spectral features due to ice, the same apparatus was used to monitor freezing of supercooled, micron-sized aerosol particles over a composition range from 0 to 49 weight percent (wt%) (NH₄)₂SO₄. The freezing of pure water aerosols occurred at 39 deg of supercooling, i.e., at a temperature of 234 K, in good agreement with the literature value. Ammonium sulfate aerosols exhibited significantly less than 39 deg of supercooling when referenced to the equilibrium freezing line. These results indicate that ammonium sulfate aerosols will promote cirrus cloud formation in the upper troposphere at higher temperatures and lower relative humidities than previously believed.

1. Introduction

In order to accurately evaluate the importance of ammonium sulfate aerosols to a variety of tropospheric phenomena, it is important to know the physical state in which these particles exist for the range of relative humidity and temperature conditions encountered in the troposphere. Although the physical state of an inorganic aerosol can be accurately predicted if the aerosol is at thermodynamic equilibrium with the ambient conditions, aerosols are known to frequently exist in a thermodynamically metastable state, either strongly supercooled or supersaturated. In such situations, calculations of nucleation rates can provide rough estimates of the kinetic stability of the metastable state, but experimental studies are necessary if an accurate determination is required.

The impact that aerosol phase may have upon tropospheric chemistry and cloud physics can be considerable. For example, from a reactive chemistry perspective, it has been shown in two independent studies that the reactivity of NO₂ on ammonium sulfate varies dramatically between liquid and solid aerosols, with the liquid substrates promoting the NO₂ hydrolysis reaction much more favorably than the solids [Mozurkiewich and Calvert, 1988; Hu and Abbatt, 1997]. This issue is of importance to the conversion rates of NO to NO₂ in both the boundary layer and free troposphere, where relative humidities are frequently sufficiently low that solid ammonium sulfate salt can be thermodynamically stable.

The phase of aerosols is also of considerable importance to a number of climate-related phenomena. For example, one set of potential mechanisms for the formation of high-altitude cirrus clouds involves ice formation via processes involving sulfate aerosols [Sassen and Dodd, 1988; Heymsfield and Sabbin, 1989; Jensen et al., 1994; DeMott et al., 1994]. The sulfate aerosols, which are believed to contain ammonium ions to some extent, may promote nucleation by two distinct mechanisms within regions of the atmosphere supersaturated with respect to the formation of ice. Taking fully-ammoniated sulfate aerosols as an example, a solid ammonium sulfate particle may act as a deposition nucleus, with ice crystals forming via gas-to-solid heterogeneous nucleation. Alternatively, the rate-determining step for cloud formation may be the liquid-to-solid phase transition undergone when a supercooled ammonium sulfate aqueous particle freezes to form ice. To date we are unable to determine which of these mechanisms is of more importance because low temperature studies are lacking for both the conditions under which ammonium sulfate aerosols exist as solids and liquids in the atmosphere, and the ability of solid ammonium sulfate to heterogeneously nucleate ice.

Given that the real refractive index of a solid ammonium sulfate particle is significantly higher than that of a supersaturated ammonium sulfate aqueous particle, it is also important to note that the phase of sulfate aerosols will have a significant effect upon the ability of tropospheric aerosols to scatter incoming solar radiation. This effect is most likely to be important in the continental boundary layer, where sulfate aerosol loadings are highest and the aerosols are principally composed of ammonium sulfate [Warneck, 1988]. Only now are state-of-the-art radiative transfer models taking into consideration the importance which the metastability of aerosols may have on the transmission of ultraviolet and visible light through the troposphere [Ferlick and Frederick, 1998].

Beyond measurements of the equilibrium freezing temperatures as a function of composition, the majority of experimental studies of phase transitions within the (NH₄)₂SO₄/H₂O binary system have been performed at room temperature. This is especially true for studies involving the phenomena of deliquescence and efflorescence of aerosols. In particular, experiments using optical particle scattering techniques [Tang and Munkelwitz, 1977], particle mobility [Ott et al., 1958], and infrared spectroscopy
[Weis and Ewing, 1996; Cziczo et al., 1997] have been used to study the uptake and loss of water by (NH₄)₂SO₄ aerosols as a function of relative humidity at room temperature. From this work, there is a general consensus that solid aerosols 10 μm or less in size readily take up water and liquefy close to the theoretical deliquescence point of 80% RH, and that liquid particles readily supersaturate as the relative humidity is lowered, until they finally crystallize at 33 to 37% RH, with the precise efflorescence point being somewhat dependent upon the size of the aerosols. To date there have only been a handful of measurements of deliquescence and efflorescence points below room temperature [Tang and Munkelwitz, 1993; Xu et al., 1998; Onasch et al., 1998].

Most deliquescence and efflorescence phenomena occur at relative humidities which are subsaturated with respect to the formation of ice. However, atmospheric aerosols may also exist within high relative humidity regions which are supersaturated with respect to the formation of ice. Such aerosols become dilute as they adjust their composition to keep their water vapor pressure in equilibrium with the ambient conditions. In order to determine the rates of cirrus cloud formation in such regimes, the crucial parameter to be determined is the extent to which aerosols supercool as a function of their composition. That is, for a fixed relative humidity and aerosol composition, there is a temperature below which the nucleation rate of a supercooled aerosol is sufficiently fast that freezing occurs on a timescale shorter than the residence time of the aerosol under those conditions. Although there have been a number of studies of the amount of supercooling displayed by the nitric- and sulfuric-acid/water binary systems [Anthony et al., 1995; Bertram et al., 1996; Clapp et al., 1997; Martin et al., 1997; Bertram and Sloan, 1998], there have been no experimental measurements of the extent of supercooling exhibited by dilute ammonium sulfate aerosols. Indeed, any models of the extent of supercooling which are exhibited by ammonium sulfate aerosols, or any other salt aerosols for that matter, are dependent upon a small suite of laboratory measurements performed for the most part with relatively large droplet sizes [e.g., Pruppacher and Neiburger, 1961; Reischel and Voller, 1975; Rasmussen, 1982]. The need for improved measurements of the amount of supercooling exhibited by salt aerosols is clear, given that global climate models require a parameterization which allows them to initiate high-altitude cirrus clouds under a specific set of relative humidity and temperature conditions.

We have recently performed the first studies of the deliquescence and efflorescence points of salt aerosols using infrared spectroscopy to determine aerosol phase [Cziczo et al., 1997]. The advantages of this technique are that condensed phase spectral features can be readily identified via infrared spectroscopy as being associated with either solid or liquid particles, and that submicron sized aerosols, i.e., similar in size to those found in the atmosphere, can be used. The disadvantage is that the observation time within the flow tube is relatively short. Experimental techniques used elsewhere offer complementary advantages and disadvantages. In particular, electrodynamic balance experiments [e.g., Xu et al., 1998, and references therein] can be operated over long times but only relatively large aerosols have been studied, and experiments performed with aerosols mounted on solid substrates [e.g., Martin et al., 1997] can also be performed slowly, but they may be subject to heterogeneous effects. In this paper we extend our flow tube technique to the study of the low-temperature deliquescence, efflorescence, and supercooling tendencies of ammonium sulfate aerosols.

2. Experimental Procedure

A schematic representation of the apparatus used to monitor the infrared spectra of (NH₄)₂SO₄ aerosols at variable temperature and composition is shown in Figure 1. Aerosol particles were produced by passing approximately 3000 cm³ min⁻¹ STP (flow 1) of dry N₂ through a commercial atomizer (TSI Model 3076). The salt solutions in the atomizer used in this work were all prepared from reagent grade material and doubly distilled, deionized water. According to instrument specifications, this flow contained a lognormal distribution (mean number diameter ~35 μm, σ ~1.8) of particles with a number density of ~2 × 10⁶ cm⁻³. After exiting the atomizer the flow was split into two, with one fraction discarded through a check valve (flow 1a) and the other kept for observation. Rotation of the valve from completely open to completely closed varied the flow of retained aerosols (flow 1b) from approximately 300 cm³ min⁻¹ STP to the atomizer's total output of ~3000 cm³ min⁻¹ STP. The retained aerosol flow subsequently passed through a variable-length diffusion dryer. The path length and residence time in the commercial dryer was varied by adjusting the length of a 0.64-cm-OD glass injector tube.

To reduce the temperature of the aerosol flow to just above that at which observations were made, a single-jacketed 'precooler' (a 40-cm long, 3.10 cm ID glass tube) was used. A refrigerated bath circulated cold heat-transfer fluid through the jacket of the precooler. The relative humidity could be adjusted by addition of two N₂ flows, one of which was dry (flow 2) and one which was completely saturated (flow 3) at 298 K by passing it though a water bubbler. Flows 2 and 3 were combined prior to addition to the precooler in order to ensure that they were well mixed. Variation of the ratio of flow 2 to flow 3 and the variable drying of the aerosol flow enabled us to 'set' the relative humidity and composition of the aerosol particles that we wished to observe.

After the precooler, the flow passed into a single-jacketed, insulated glass tube (84 cm-long, 6.35 cm-ID) which served as an absorption cell. Copper/constantan thermocouples accurate to ±0.5 degree were located within the absorption cell to measure temperature. The aerosol flow, upon exiting the precooler, was further reduced in temperature by a few K within the first 32 cm of the absorption cell. The temperature of the next 32 cm of the absorption cell was constant, both radially and axially, within the accuracy of the thermocouples. It is also the region where the lowest temperatures were attained in the experiment. All observations of the aerosol particles were performed in this space, where the residence time varied from ~30 s for the lowest total flow rate of 2000 cm³ min⁻¹ STP, to ~12 s for the highest total flow rate of 5000 cm³ min⁻¹.
The flow pattern of the coolant was such that, upon leaving the low-temperature bath, it first circulated through the absorption cell and then passed to the precocooler before reentering the bath at a somewhat higher (~2 K) temperature. In this way, the aerosol flow was gradually cooled until it reached its lowest temperature in the observation region of the absorption cell.

The aerosol particles were observed with a Nicolet Magna 550 Series II Fourier Transform Infrared Spectrometer. The spectral range from 500 to 5000 cm\(^{-1}\) was scanned at 4 cm\(^{-1}\) resolution for 100 scans over an observation time of 62 s. As shown in Figure 1, the infrared beam from the spectrometer was collimated by two mirrors before it passed along the centerline of the absorption cell. Two 2.5-cm-diameter, 0.2-cm-thick AgCl windows were mounted on glass tubes of the same OD which in turn were supported by threaded O-ring compression joints at the ends of the absorption cell. Thus, although the IR beam passed down the entire length of the absorption cell, only aerosols within the central, constant-temperature portion of the cell were monitored. After the absorption cell, two more mirrors were used to focus the beam onto a MCT detector. All optics, the detector, and the interior of the glass tubes were insulated to avoid condensation and thus to maintain a uniform temperature.

We performed an efflorescence-mode experiment by passing aqueous aerosols at high relative humidity from the precocooler to the absorption cell. First, the aerosols reached the observation temperature, they were diluted by dry gas from flow 4, which was also at the observation temperature. Increasing the rate of flow 4 resulted in progressively lower relative humidities until concentrated liquid aerosols crystallized to form solid (NH\(_4\))\(_2\)SO\(_4\) particles. The complete loss of condensed phase water from the aerosols at relative humidities below the efflorescence point (see Results and Discussion) is an indication that complete mixing between flow 4 and the main aerosol flow occurred. Note that flow 4 was used to lower the relative humidity because efflorescence would occur in a region of the apparatus slightly warmer than the observation region if flow 2 had been used. A constant mixing ratio of water vapor corresponds to increasingly lower relative humidities at higher temperatures, e.g., ~8% RH change per degree at 273 K. Thus, if the aerosol crystallized in the precocooler, which was 2 K warmer than the observation region, then an efflorescence relative humidity 16% higher than the true value would have been measured.

We initiated a freezing-mode experiment by preparing aqueous aerosol particles at room temperature and then introducing them to the precocooler. By varying the initial solution concentration in the atomizer from pure water to saturated ammonium sulfate, as well as the rates of flows 1b, 2, and 3, we could set the composition of the particles for the experiment. The flows were combined in the precocooler, which cooled the aerosol flow to a few degrees above 233 K, i.e., the temperature at which we observed freezing in pure water. The absorption cell was slightly cooler, by about 2 K, than the precocooler. This insured that the initial aerosol sample would consist of supercooled liquid particles and not ones containing ice. The infrared spectra of the aerosols were monitored as the observation temperature and precocooler temperature were gradually lowered together, always maintaining at least a 2 K difference between the two. This was to ensure that the lowest temperature was encountered just as the particles reached the observation region. As the particles were increasingly cooled they also experienced increasing relative humidity, until freezing occurred. Typically, aerosol flow rates (flow 1b) in excess of 2500 cm\(^3\) min\(^{-1}\) STP were used in combination with a carrier gas flow (flows 2 and 3) in excess of 1000 cm\(^3\) min\(^{-1}\) STP. As discussed in more detail later, the motivation for this large total flow was to maintain supersaturated conditions with respect to ice throughout the observation region.

Finally, experiments could also be performed in static-mode. Unlike the previous three experiment types, a static experiment was one in which observations were made of a non-flowing aerosol sample. Aerosols were passed through the system until a steady state was reached. At this point all flows were shut off and the exhaust port was blocked. Spectra could then be taken of the same aerosol parcel for up to 30 min, at which point gravitational settling of the aerosols led to insufficient extinction signal. One experiment performed in this mode involved preparation of liquid aerosols at 235 K and a subsequent lowering of the absorption cell temperature after the flows had been shut off. Via gas-phase diffusion, the aerosols quickly attained equilibrium with ice by interaction with the flow tube walls. Thus the freezing point which was measured in this experiment was for aerosols in equilibrium with the vapor pressure of ice.

The concentration of ammonium sulfate in an aqueous aerosol is determined by the relative humidity of the air with which the aerosol is at equilibrium. Thus, in order to relate aerosol composition to relative humidity we have used output from the model described by Clegg et al. [1998]. This model is expected to be reasonably accurate close to room temperature, where there is sufficient experimental data to constrain the parameterizations, but the lack of low-temperature thermodynamic data may make the model less accurate in those regimes. We should note that we use the term “relative humidity” in this paper as referenced to the saturation vapor pressure of liquid water. Also, as we assume throughout that the aerosol compositions are in equilibrium with the ambient water vapor. It is easily shown that for the lowest temperatures used, the time to saturate an aerosol with water vapor is no more than a few tenths of a second, i.e., much shorter than typical residence times in the flow tube [Schwarz, 1986].

In order to monitor relative humidity in the observation region, gas-phase water absorption lines present in the extinction spectra (see Figure 2) were integrated following the approach described by Cziczo et al. [1997]. In order to calibrate the strength of the water lines at a specific observation temperature, we prepared a known relative humidity in the observation region by adding a known ratio of flow 2 to flow 3, without aerosol present. Integration of the gas-phase H\(_2\)O absorption due to water vapor in the observation region was then used to estimate the relative humidity of the aerosol from the measurement of the integrated absorption due to water vapor in flow 3.

![Figure 2](image-url)
lines in the spectral region from 1764 to 1778 cm\(^{-1}\) from 0 to 100% RH at each observation temperature produced calibration curves which were then fit with a fourth-order polynomial. We validated this method of determining relative humidity in two ways. First, we checked our calibration of 100% RH by producing flows of liquid water aerosols at each temperature. Second, when performing static experiments at various temperatures where the walls of the flow tube were coated with ice, we checked that the relative humidity monitored spectroscopically was that corresponding to saturation with respect to ice. On the basis of these tests and the accuracy with which we know our flow rates, we report relative humidities accurate to ±1.2, 4 and 6% at 298, 273, 253, and 238 K, respectively. The increase in uncertainty at lower temperatures arises from weaker absorption signals due to lower concentrations of water vapor in the flow tube.

Another method was used to determine aerosol composition below 238 K. In particular, based upon the approach of Anthony et al. [1995] in their study of \(\text{H}_2\text{SO}_4/\text{H}_2\text{O}\) aerosol freezing, we have produced a calibration curve for the dependence of the composition of aqueous \((\text{NH}_4)_2\text{SO}_4\) aerosols on the area ratio of the \(\text{H}_2\text{SO}_4\) band from 1684 to 1600 cm\(^{-1}\) and a sulfate band from 1150 to 1050 cm\(^{-1}\) (see Figure 3). This calibration was performed from 298 to 253 K using gas-phase water absorption lines to determine the relative humidity and thus the aerosol composition [Clegg et al., 1998]. It is apparent that the ratio of the \(\text{H}_2\text{O}\) to \(\text{SO}_4^{2-}\) feature becomes smaller as the \((\text{NH}_4)_2\text{SO}_4\) aerosols become increasingly concentrated. Given the lack of temperature dependence observed at high temperatures, we believe this calibration is also valid for temperatures below 238 K.

3. Results and Discussion

3.1. Deliquescence

In order to determine the relative humidity at which the uptake of water by solid particles occurs, we prepared dry ammonium sulfate aerosols by passing them through the entire length of the dryer. Dry gas from flow 2 was also added, producing an aerosol sample at the observation temperature with a low relative humidity. As an example, the initial spectrum, at 23% RH, of a deliquescence experiment performed at 273 K is shown as the upper curve in Figure 3. Infrared spectra of \((\text{NH}_4)_2\text{SO}_4\) aerosol prepared in a deliquescence-mode experiment at 273 K. Spectra have been scaled and vertically offset for clarity. Relative humidity with respect to water is indicated for each spectrum. Features at 2350 and 670 cm\(^{-1}\) arise from small levels of gas-phase \(\text{CO}_2\) present after background subtraction.

Figure 3. Ratio of the area of the \(\text{HOH}\) bend at 1640 cm\(^{-1}\) to that of the \(\text{SO}_4^{2-}\) mode at 1115 cm\(^{-1}\) versus wt% \((\text{NH}_4)_2\text{SO}_4\). Data are for 298 K (circles), 273 K (triangles), and 253 K (squares) (see text for explanation).

Figure 4. The scattering and absorption features associated with the spectrum have previously been identified [Socrates, 1994; Wets and Engin, 1996]. In particular, aerosol scattering is visible as the increasing extinction with wavenumber above ~3400 cm\(^{-1}\). Four distinct absorption features are associated with the constituent ions of \((\text{NH}_4)_2\text{SO}_4\) (see Figure 2). The modes due to condensed phase water molecules, namely the \(\text{OH}\) stretch, \(\text{HOH}\) bend, and \(\text{H}\) bond at 3450, 1640, and 650 cm\(^{-1}\), respectively, are absent from the spectrum, as expected for dry \((\text{NH}_4)_2\text{SO}_4\) particles.

The relative humidity of the aerosol flow was incrementally raised by adding \(\text{N}_2\) saturated with \(\text{H}_2\text{O}\) vapor from flow 3, and the spectra were recorded as a function of RH (see Figure 4). No changes were seen to occur in the condensed-phase spectra as relative humidity was raised below the deliquescence point. At the deliquescence point, condensed phase water features become apparent, in particular the strong \(\text{OH}\) stretch. Within a few percent relative humidity above the

Figure 5. Residual area of the \(\text{OH}\) stretch mode after subtraction of dry \((\text{NH}_4)_2\text{SO}_4\) features, for deliquescence-mode experiments. Data are presented as a function of relative humidity and temperature, as marked in kelvin for each panel.
deliquescence point, all the water modes are strong, the ionic modes broaden to some extent, and the NH₄⁺ mode at ~1450 cm⁻¹ shifts ~30 cm⁻¹ to higher frequencies.

In order to accurately determine the deliquescence point, difference spectra were generated by subtracting successive aerosol spectra, one from another. As the relative humidity was raised, no residual infrared features were observed until condensed-phase water features appeared, marking the onset of deliquescence. To illustrate this effect, we have subtracted a low RH spectrum from all other spectra within a deliquescence-mode experiment, and plotted the residual areas of the OH stretch mode as a function of relative humidity (see Figure 5). The relative humidity marking the onset of H₂O uptake offers a more accurate determination of deliquescence than does simple visual inspection of spectra. In this manner, the deliquescence relative humidities at 283, 273, 263, and 254 K were measured to be 81±2, 82±2, 82±3, and 83±4% RH, respectively. Previously, we measured the value at 298 K to be 79±1% [Cziczo et al., 1997]. These values are within ±1% of the theoretical deliquescence relative humidity [Linke, 1965; Clegg et al., 1998], as shown in Figure 6, and they are very similar to the recent results of Xu et al. [1998]. These data indicate that deliquescence is not a kinetically inhibited process at temperatures significantly below room temperature, in agreement with the observations of Tang and Munkelwitz [1993].

Previous workers [e.g., Martin, 1998] have suggested that dry salt particles will liquify at temperatures lower than that of the eutectic (254 K). In order to examine aerosol behavior under these conditions, we exposed solid aerosols to large flows of saturated gas (flow 3) at low temperatures. Regardless of the amount of saturated gas added, we did not measure relative humidities in excess of that for ice; i.e., we were not able to create supersaturated conditions with only gas-phase water vapor as a source. No deliquescence or ice nucleation was observed under these conditions.

3.2. Efflorescence

For efflorescence-mode experiments, aqueous aerosols were initially prepared at high relative humidity (~85%) at room temperature, where it is certain they are liquids. Unlike a deliquescence experiment, these liquid aerosols continued to exhibit the OH stretch, HOH bend, and hydrogen bonding modes associated with condensed phase water when they were exposed to relative humidities below the deliquescence point (see Figure 7). As the relative humidity was increasingly lowered, the liquid water features continuously decreased in strength until a point was reached at which the spectra ceased to contain H₂O modes and the spectra became indistinguishable from one another. This is the efflorescence point.

To determine this relative humidity precisely, we again obtained difference spectra by subtracting the driest spectrum from those at higher relative humidities. The residual areas of the OH stretch, shown in Figure 8 as a function of relative humidity, clearly illustrate the retention of liquid water well below the deliquescence relative humidity. The gradual decrease in the OH stretch intensity as a function of relative humidity, as compared to the rapid rise in Figure 5, indicates that there is a continuous and steady loss of liquid water as the aerosol becomes more concentrated, until efflorescence occurs. From our previous studies, crystallization did not occur until 33±2% RH at 298 K [Cziczo et al., 1997]. Experiments at lower temperatures

![Figure 6](image1.png)

**Figure 6.** Deliquescence relative humidity of (NH₄)₂SO₄ as a function of temperature. Theoretical curve derived from Clegg et al. [1998] and Linke [1965] is shown as a solid line. Experimental deliquescence points are also shown: Tang and Munkelwitz [1992] (circles) and this work (squares).

![Figure 7](image2.png)

**Figure 7.** Infrared spectra of (NH₄)₂SO₄ aerosol prepared in an efflorescence-mode experiment at 273 K. Relative humidity with respect to water is indicated for each spectrum. Spectra have been scaled and vertically offset for clarity.

![Figure 8](image3.png)

**Figure 8.** Residual area of the OH stretch mode after subtraction of dry (NH₄)₂SO₄ features, for efflorescence-mode experiments. Data are presented as a function of relative humidity and temperature, as marked in kelvin for each panel.
indicated that crystallization occurred at 37±3, 42±4, and 41±6% RH for 273, 253, and 238 K, respectively. The increased uncertainty in efflorescence at lower temperatures arises from the increased uncertainty in the relative humidity and the increased scatter shown in Figure 8.

Because the efflorescence point of (NH₄)₂SO₄ aerosols may also vary with the volume of the particles, it is useful to know the aerosol size distribution which was used in our work. According to specifications, the atomizer produces a lognormal size distribution of aqueous aerosols with a number mean diameter of 0.35 μm. For the saturated ammonium sulfate solutions used in the atomizer, it is calculated that the diameter of the aerosols should decrease to 0.26 μm when they crystallize. Thus we believe that aerosols just slightly larger than this lower size limit are efflorescing. As confirmation, spectra of dry (NH₄)₂SO₄ particles were fit using standard Mic theory [Bohren and Huffman, 1983] and room-temperature refractive constant data from Toon et al. [1976]. For all spectra from 298 to 238 K, least squares fits indicated a mean diameter 0.28 μm with a standard deviation of 1.4, assuming a lognormal size distribution.

When comparing our results to those of other studies, we have pointed out previously [Cziczo et al., 1997] that the efflorescence relative humidity we measure at room temperature is somewhat lower than that reported by Tang et al. [1993] for 15-μm-diameter particles levitated in an electrodynamical balance. While the difference between these two values may be due to experimental uncertainty, it may also be related to the volume dependence of the likelihood of germ formation within the aerosol. That is, the probability of homogeneously nucleating a germ within a submicron aerosol is significantly smaller than in one of order 10 μm, leading to a greater excursion from equilibrium before crystallization occurs. At lower temperatures, the efflorescence points we measure show much less dependence on temperature than do those of Xu et al. [1998], whereas they are relatively similar to the values of Onasch et al. [1998] which were measured with a similar technique to our own. It should be noted that since efflorescence point measurements involve determining the final point at which a small amount of water is no longer present in an aerosol, there is a tendency for efflorescence point measurements to err to too high relative humidities, as was the case in an initial interpretation of our data.

3.3. Supercooling

For freezing experiments where ice is formed, the water vapor content in the flow tube is invariably supersaturated with respect to the formation of ice prior to the nucleation event. To prepare such conditions in the flow tube required that a total flow rate of greater than 3000 cm² min⁻¹ STP be used. In that regime, the supersaturation with respect to ice which we measure when we flow supercooled aerosols through the flow tube is independent of the total flow to the ±2% RH level. If a much smaller flow rate is used, say 250 cm² min⁻¹ STP, the timescale for diffusion to the flow tube walls is significant relative to the transit time of aerosols through the observation region. Since the walls are invariably coated with ice, we observe that the relative humidity in the flow tube is saturated with respect to ice in this case. Thus we have performed the freezing experiments with a total flow rate of greater than 3500 cm² min⁻¹ STP, i.e. in a regime where the timescale for diffusion of water vapor to the walls is minimized.

Figure 9 illustrates the changes which occur in the spectrum of liquid water when freezing occurs. Specifically, very few changes occurred in the spectra of supercooled water aerosols from 273 to 235 K. At lower temperatures, the OH stretch broadened and shifted to lower frequencies, the HOH bend becomes considerably broader and weaker in intensity at its peak, and the H-bonding mode narrowed and shifted to higher frequencies. All of these spectral features have been previously observed as indicators of ice formation in pure water [Clapp et al., 1996] and H₂SO₄/H₂O solutions [Anthony et al., 1995; Bertram et al., 1996]. As illustrated in Figure 9, the transition from liquid water to ice occurred over a temperature range of roughly 2 deg., from 235 to 233 K. At 233 K and lower, the ice spectra are all indistinguishable from each other. At the intermediate temperature of 234 K, we believe the spectrum is indicative of a partially frozen aerosol sample; i.e., some of the particles are frozen and some are not. The range of temperatures over which complete freezing of an aerosol sample is seen to occur, similar to that previously observed by Bertram et al. in their study of ice formation from sulfuric acid aerosols, may arise from the polycrystalline nature of our aerosol flow. The freezing temperature of 234 K which we infer as the onset of spectral changes from Figure 9 is in very good agreement with previous experimental studies for 1 μm aerosols [e.g., Anderson et al., 1980; Pruppacher and Klett, 1980]. It should be noted that the relatively large scattering feature at high frequencies in Figure 9 indicates that the aerosols were considerably larger than those which exit the room temperature atomizer. This is to be expected because as the aerosol flow cools the large amounts of water vapor present at room temperature will be both scavenged by the aerosols, and lost to the walls of the flow tube to some extent. To confirm that the gas-phase water vapor does not homogeneously nucleate to form new aerosols as the temperature is lowered, we performed a control experiment where a room temperature nitrogen flow saturated with water vapor was cooled to 206 K, and no aerosols were observed to form in the infrared spectra.

For the freezing of (NH₄)₂SO₄ aerosols, all experiments were started at a temperature where the aerosols were known to exist as liquids. The observation temperature was then incrementally lowered until freezing occurred and spectra ceased to change as a function of temperature. Spectroscopically, the indicators of ice formation that were observed in pure water also appeared in the (NH₄)₂SO₄ particles (see Figure 10). Interestingly, however, the modes associated with ammonium sulfate did not narrow as observed when solid ammonium sulfate forms. In particular, from the deliquescent and efflorescence experiments it is known that the ammonium mode at ~1430 cm⁻¹ systematically shifts by 30 cm⁻¹ when crystallization into solid salt occurs. The fact that such a shift does not occur in our freezing experiments, indicates that solid ammonium sulfate does not simultaneously nucleate with ice. Whether the salt ions remain in liquid solution in coexistence with ice, or whether an amorphous solid forms, is difficult to determine from the spectra alone.
Figure 10. Spectra of dilute (NH₄)₂SO₄ aerosols as a function of temperature (as marked in kelvin for each spectrum). The upper two spectra are of liquid particles and the lower two of particles containing ice. The intermediate spectrum, at 231 K, is partially frozen. The composition of the liquid aerosol at 232 K, as determined using the calibration in Figure 3, is 15 wt%. Spectra are scaled and vertically offset for clarity.

As in the water experiments, there is a range of temperatures over which the entire aerosol sample freezes. For example, for the data in Figure 10 the entire aerosol sample is liquid at 232 K and it is entirely frozen, e.g., where spectral changes cease, by 230 K. Using the calibration curve in Figure 3, the aerosols present just before freezing started to occur (i.e., at 232 K) have a composition of 15±2 wt%, where the uncertainty in the composition is set by the scatter of points in the calibration curve. Similarly, freezing was observed at 234, 232, 231, 228, 227, 225, 224 K for 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, and 120 wt% (NH₄)₂SO₄ particles, respectively. The corresponding relative humidities of each point are 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, and 0%. [Clegg et al., 1998].

In order to examine the possibility that aerosol freezing was caused by heterogeneous nucleation of ice on contaminants in the (NH₄)₂SO₄ salt from which the atomizer solution was prepared, three experiments were performed using a solution filtered to remove all particulate matter above 0.02 μm diameter. The results of these experiments are the freezing points reported above for 28, 32, and 41 wt%. These points do not significantly differ from unfiltered solution data points, and it is therefore our belief that homogeneous nucleation is responsible for aerosol freezing.

As with the aerosols in the efflorescence and deliquescent experiments, we used Mie theory to determine the size of the ice aerosols formed in the water freezing experiments. Noting that some inaccuracy may result from using refractive index data for ice [Clapp et al., 1995] measured at somewhat lower temperatures than the temperatures of our experiments, the least squares fit to our ice spectra gave a mean radius of 1.05±0.02 μm and a standard deviation of 0.4±0.1. Unfortunately, the low-temperature refractive index data for ammonium sulfate solutions are not available to allow size determination of the aerosols before they freeze.

With no previous measurements of the freezing points of micron sized droplets of ammonium sulfate solutions, we compare our results to expressions which are thought to describe the amount of supercooling exhibited by salt solutions, and to calculations from classical homogeneous nucleation theory. First, to specify the freezing temperatures of ice from (NH₄)₂SO₄ solutions the following relation has been used in cirrus-cloud formation models:

\[
\Delta T_{\text{f}}(\text{wt}%) = \Delta T_{\text{th}} + \lambda \Delta T(\text{wt}%) \quad (1)
\]

where \(\Delta T_{\text{f}}\) is the predicted supercooling of an ammonium sulfate aerosol, \(\Delta T_{\text{th}}\) is the supercooling of a pure water droplet (39 K), \(\lambda\) is the equilibrium melting-point depression for the specific concentration of salt in the aerosol, and \(\lambda\) is a sensitivity parameter [Sassen and Dodd, 1988; DeMott et al., 1994]. These models use a value of \(\lambda=1.7\) (refer to curve A in Figure 11), chosen by reference to the work of Rasmussen [1982] on the supercooling exhibited by aqueous droplets of substances such as NH₄F, NH₄Cl, NaCl and NaF (but not (NH₄)₂SO₄) when they exist as eutaxons in a paraffinic carrier fluid. A constant suppression of the freezing line of 39 K (i.e., \(\lambda=1\)) has also been proposed for use in cirrus-cloud formation models [Martin, 1998]. Compared to our freezing points, both of these values of \(\lambda\) overestimate the supercooling, with increasing error at higher composition. It should be pointed out that the \(\lambda=1\) curve (B in Figure 11) is based on experimental measurements performed by Pruppacher and Neiburger [1963] using concentrations of salts in 2-mm-sized droplets of up to 1 M. For concentrations up to 1 M (NH₄)₂SO₄, which corresponds to 13 wt%, the comparison between our data and the \(\lambda=1\) line is reasonable.

The freezing points of solution droplets can also be predicted by classical homogeneous nucleation theory, as has been done by Jensen et al. [1991, 1994], for example. In particular, we have calculated the temperature at which the rate of critical germ formation in a 1-μm drop is 1 s⁻¹, using the expression for the nucleation rate within solution drops given by Pruppacher and Klett [1980, equation 7-52]. Although a variety of input is required for these calculations, the two most important are the energy required for the diffusion of water molecules across the water/ice boundary (ΔPₚ) and the free energy of formation of a critical ice germ (ΔFₚ). For the former, ΔPₚ we use the expression given by Jensen et al. [1994], which was derived from observations of the freezing rate of pure water. We assume that this value is appropriate for nucleation calculations involving solutions. For the second term, ΔFₚ we estimate that the surface tension which exists between ice and the ammonium sulfate solution to be that between ice and supercooled water [Pruppacher and Klett, 1980, Equation 5.48].

From Figure 11 it is apparent that the experimental freezing points are significantly higher than have been suggested to be the case in

![Figure 11](image-url)
previous cirrus-cloud modeling studies (curves A and B). Although the nucleation calculations (curve C) predict freezing temperatures which are somewhat closer to the experimental data, the lack of lower-temperature thermodynamic data required to perform these calculations makes them highly uncertain. Indeed, we attempted to estimate the surface tension which would exist between ice and supercooled solutions of ammonium sulfate but given the lack of input data our best estimates gave highly unrealistic predictions that freezing temperatures would begin to increase as a function of aerosol composition past approximately 30 wt%.

Thus, at this point we can offer no explanation for why concentrated solution droplets exhibit less supercooling than more dilute droplets. Although the results are surprising, we have not been able to identify a systematic error which invalidates them. In particular, filtered solutions give comparable supercoolings to unfiltered solutions, and the errors in aerosol composition which could arise from the uncertainty in the RH gradient mentioned above (±2%) are minor for the highest compositions, i.e., those which deviate most strongly from previous freezing models. However, since the particles undergo rapidly changing environmental conditions as they pass from the atomizer to the observation region and because the model which connects aerosol composition and relative humidity could be better constrained [Clegg et al., 1998], additional studies with a different experimental approach are clearly warranted.

3.4. Static-Mode

One additional freezing experiment was performed, by operating in static-mode. In particular, aerosols were produced at 235 K as for a freezing experiment. Then, all flows were shut off, the exhaust port sealed and the temperature bath was set to provide a continuous reduction in temperature as a function of time. By taking spectra frequently, it was observed that the aerosol particles quickly (< 2 min) equilibrated to the vapor pressure of ice at the temperature of the observation region. Since the vapor pressure of ice decreases as the temperature is lowered, the particles continuously released condensed phase water as they remained in equilibrium with ice. At 219 K the spectrum of the aerosols changed dramatically, as shown in Figure 12. Clearly visible are a number of very sharp absorption features as part of the NH$_4^+$ and SO$_4^{2-}$ bands which were not observed with dry

![Figure 12. Spectrum, at 215 K, of aerosol particles which have begun to freeze when at equilibrium with the vapor pressure of ice (see text for discussion). Gas-phase CO$_2$ features arising from a slow leak of air into the absorption cell during the static-mode experiment have been subtracted, giving rise to the gaps in the spectrum near 2350 and 670 cm$^{-1}$.](image)

![Figure 13. Temperature composition phase diagram of (NH$_4$)$_2$SO$_4$/H$_2$O. Contours of constant relative humidity above aqueous (NH$_4$)$_2$SO$_4$ solutions are shown as dotted lines with the relative humidity indicated in %].](image)

Figure 13. Temperature composition phase diagram of (NH$_4$)$_2$SO$_4$/H$_2$O. Contours of constant relative humidity above aqueous (NH$_4$)$_2$SO$_4$ solutions are shown as dotted lines with the relative humidity indicated in %. The two liquid-solid coexistence curves are marked as I and D for ice and deliquescence, respectively. Experimental deliquescence curves (squares), efflorescence curves (triangles) and freezing data points are shown (circles), as is the static point (diamond) along the ice line I. A sample trajectory, to illustrate aerosol composition dependence on changing temperature, at a constant gas-phase partial pressure (0.108 mbar) is shown as a thick solid line marked T.

4. Atmospheric Implications

We can use the results of this study to make predictions of the phase in which ammonium sulfate aerosols exist throughout the atmosphere. Starting in the warm boundary layer, it is expected that a liquid ammonium sulfate particle formed at high relative humidities will only solidify if the relative humidity is taken to quite low values, of less than 33% at room temperature and to somewhat higher values at lower temperatures. If such low relative humidities are encountered, then the particle will solidify and will not deliquesce until it encounters a relative humidity of approximately 80%, the exact value being dependent upon the temperature.

One manner by which such a high relative humidity could arise is via the rising and cooling of an air mass associated with synoptically driven air motions. This example is important because it has been proposed that high-altitude cirrus clouds may form via the low-temperature freezing of deliquescent sulfate aerosols [Sassen and Dodd, 1988; Heymsfield and Sabin, 1988; Jensen et al., 1994; DeMott et al., 1994; Martin, 1998; Tabazadeh and Toon, 1998].
particular, if the air mass rises and cools sufficiently, the relative humidity may become supersaturated with respect to the formation of ice. The phase changes that result are most clearly illustrated using a temperature/composition solid-liquid phase diagram for ammonium sulfate aerosols. As shown in Figure 13, where all the experimental data measured in this work are indicated, along with lines of constant relative humidity. Also shown in Figure 13 are the two solid-liquid coexistence curves, labeled as D and I, for the deliquescent and ice lines, respectively. Note that at temperatures below the eutectic these curves are extrapolations of higher temperature data.

As the temperature is lowered, consider particles traveling along a trajectory of constant gas-phase water-vapor partial pressure which is denoted in Figure 13 by a solid line marked T. Two scenarios can be envisaged. In the first, if the particle has not experienced sufficiently low relative humidities for it to crystallize (roughly 40-50% RH), then it will cross the ice line as a liquid which becomes increasingly dilute as the temperature is lowered. Although the particle exists within an environment which is supersaturated with respect to the formation of ice when it passes to the left of the ice line, it will not freeze until the trajectory crosses the freezing line, as determined experimentally in this work. For the trajectory shown, that point occurs at 228 K and 20 wt% ammonium sulfate, i.e., at a relative humidity greater than 90%. The liquid-to-solid phase transition occurring within the aerosol would then be the trigger for cirrus cloud formation.

The second scenario arises if the particle has experienced sufficiently low relative humidities at high temperature that it has solidified to solid ammonium sulfate. In this case, the ability of the solid particle to promote ice nucleation heterogeneously, via vapor deposition, needs to be examined. If this process occurs very readily, then ice could form just as the particle crosses the ice line, and the environment becomes supersaturated with respect to the formation of ice. If that process is not facile, then two possibilities arise when the temperature is lowered further and the trajectory meets the extrapolated deliquescence line. Either the particle will deliquesce, become a liquid, and then freeze at 228 K as in the first scenario or it will not deliquesce and it will remain a solid to low temperatures and very high relative humidities, and perhaps heterogeneously nucleate ice under these conditions. Without experiments, we do not yet know whether solid ammonium sulfate will deliquesce at temperatures below the eutectic, i.e., to form a supercooled liquid. Similarly, without knowing its properties as a deposition nucleus for ice formation, we can not yet assess the atmospheric importance of ammonium sulfate tetrahydrate, which will likely form under ice saturation conditions at temperatures below about 220 K.

As mentioned in the Results and Discussion section, the most significant result from our experiments is the temperature of the freezing line shown in Figure 13. Freezing is observed to occur at a significantly higher temperature than thought previously. Thus a significant conclusion from our work is that the regime over which supercooled ammonium sulfate aerosols are kinetically stable is considerably smaller than previously thought. Correspondingly, cirrus cloud formation occurring via the scenario delineated above will occur at higher temperatures and lower relative humidities than was previously believed to be the case.

As further observations are made of the aerosol composition of the upper troposphere and of the conditions under which high altitude cirrus form, it will be possible to evaluate the importance of the freezing temperatures measured in this work. Given that aerosol compositions are not limited to ammonium sulfates, we are currently extending these measurements to other chemical systems which may be present in the atmospheric aerosol. We are also hoping to measure the ability of solid ammonium sulfate to heterogeneously nucleate ice, so that we can fully assess the role of ammonium sulfate aerosols in cirrus cloud formation processes. These studies are of considerable importance given that the stability region of liquid solutions of ammonium sulfate is somewhat smaller than previously believed.

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