Infrared Observations of the Response of NaCl, $MgCl_2$, NH_4HSO_4, and NH_4NO_3 Aerosols to Changes in Relative Humidity from 298 to 238 K

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Infrared extinction spectroscopy has been used to monitor liquid-to-solid and solid-to-liquid phase transitions of a variety of model tropospheric aerosols over a temperature range from 298 to 238 K. Uptake and loss of water were induced by controlling the relative humidity (RH) as submicron-sized aerosols passed through a low-temperature, atmospheric pressure flow tube on a time scale of tens of seconds. Observation of the absorption features of condensed-phase liquid water showed that NaCl aerosols deliquesced at a RH within ±2% of the thermodynamic value from 298 to 253 K, whereas efflorescence did not occur until 40 ± 5% RH. No hydrate formation was observed. By contrast, aerosols composed of species with considerably lower deliquescence points, including $MgCl_2$, NH_4HSO_4, and NH_4NO_3, exhibited a strong inhibition to efflorescence down to 2% RH. As aerosols, the only one of these three which began to effloresce was $MgCl_2$, and only at relative humidities below 2%. $MgCl_2{\cdot}6H_2O$ is the likely product. NH_4HSO_4 aerosols were induced to effloresce when sprayed onto an infrared window and subjected to relative humidities of less than 1% for periods of hours. These findings strongly suggest that, in the absence of heterogeneous nuclei, a wide variety of inorganic aerosols will exist as liquid solutions in the atmosphere regardless of relative humidity and temperature conditions.

Introduction

The roles that aerosols play in a number of tropospherically relevant issues depend on their phase. In particular, kinetics studies have shown that atmospherically important heterogeneous processes occur at significantly different rates on solid versus liquid substrates. The rate of the N_2O_5 hydrolysis reaction, for example, is strongly inhibited when liquid ammonium sulfate aerosols crystallize.[1,2] Similarly, the retention of condensed-phase liquid water by sea salt aerosols at low relative humidity (RH) has been shown to control the kinetics of a variety of reactions, including processes which give rise to HCl and photochemically active chlorinated species. For example, the reaction of HNO_3 with NaCl proceeds considerably faster on aqueous particles than on solids.[3] Also, the reaction of NO_2 with synthetic sea salt has been shown to proceed via the $MgCl_2{\cdot}6H_2O$ hydrate, implying that anhydrous NaCl is not a fully representative model of atmospheric marine aerosols.[4] Beyond chemical processes, the phase of tropospheric aerosols is also directly related to global climate, through the ability of aerosols to scatter and absorb radiation and to promote cloud nucleation.

Solid salts take up water to form an aqueous solution at the deliquescence relative humidity specific to that material. From a thermodynamic perspective, the reverse process of water loss to form a crystalline solid from a solution—efflorescence—should occur at the same relative humidity. Numerous experimental studies on small particles have shown that there is no kinetic hindrance to the uptake of water and that deliquescence occurs at the thermodynamic value (for example, see refs 5−21). However, since the early work of Orr et al.,[5] it has been known that small particles readily form supersaturated solution droplets before the precipitation of the anhydrous salt occurs. The determination of the efflorescence relative humidity of a variety of aerosol particles has been studied at room temperature,[5−16] but the temperature dependence of this process has been investigated for only a few systems.[17−21]

The focus of this work is upon low-temperature studies of deliquescence and efflorescence, with specific goals motivated by a number of previous studies. In particular, it has been shown that deliquescence of ammonium sulfate occurs at the thermodynamic value at temperatures down to the eutectic and that the efflorescence RH has little temperature dependence.[19,20] By investigating other chemical systems we intend to see if this is general behavior. In room-temperature studies, submicron-sized NH_4HSO_4 aerosols have been shown to not effloresce, even at relative humidities as low as 2%.[8] By working at lower temperatures and with other chemical systems, we can investiage whether this kinetic inhibition to crystallization is common. Finally, we are interested in whether hydrates form from salt solutions under conditions of low relativity humidity and temperature. This interest is prompted by the thermodynamic stability of hydrates of both NaCl and $MgCl_2$ under these conditions.

Four atmospherically relevant chemical species were chosen for these studies. In particular, particles composed of NaCl and $MgCl_2$ have been investigated to better understand the behavior of particles of marine origin. We are particularly interested to see whether hydrates form in the $MgCl_2$ system, due to the impact that these may have on the heterogeneous reactivity of sea salt aerosols at low relative humidity. We have also attempted to crystallize the anhydrous phase from NH_4HSO_4 and NH_4NO_3 solution droplets at a variety of temperatures. NH_4HSO_4 is present in continental regions where sulfate aerosols are partially neutralized by ammonia, whereas NH_4NO_3

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may form in regions with high concentrations of ammonia and nitric acid, but little sulfate.[22]

Experimental Section

The infrared aerosol spectroscopy technique and apparatus used in these studies have been described in detail previously.[8,19] Briefly, aerosol particles were produced from aqueous solutions using a commercial atomizer that produces a log-normal aerosol size distribution with number mean radius of 0.18 μm and geometric standard deviation of 1.8. Although no sizing experiments were done in this work, Mie theory was used previously to fit spectra of $(NH_4)_2SO_4$ aerosol particles formed with this apparatus.[19] The fits confirmed that the atomizer produced a distribution of particle sizes as specified. Per specifications, the number density of particles was about 10^6 particles/cm^3 for the flow of 3000 sccm of N_2 formed at 35 psi inlet pressure. Solutions of NaCl, $MgCl_2$, and NH_4NO_3 were prepared directly from reagent-grade material, whereas NH_4HSO_4 solutions were produced from equimolar amounts of $(NH_4)_2SO_4$ and H_2SO_4. The salt solutions used in the atomizer were close to saturation to maximize the dry particle size.

The aerosol flow was split in two after exiting the atomizer, with a fraction discarded and the remainder, from 200 to 3500 sccm, kept for observation. This flow subsequently passed through a variable-length diffusion dryer containing silica gel which removed some of the water from the aerosols. The path length and residence times in the dryer were varied by adjusting the length of a glass injector tube. With the injector passing entirely through the dryer, the aerosol flow was not exposed to the silica gel and no water was lost. Complete withdrawal of the injector resulted in extended exposure and reduction in relative humidity to $\leq$10% at the lowest flow rates. In a few experiments, the aerosol lines and dryer were wrapped in heating tape in order to facilitate further water removal. In these cases, the relative humidity could be dropped to <5%.

For experiments below 298 K, a single-jacketed precooler (a 40 cm long, 3.10 cm i.d. glass tube) was used to reduce the temperature of the aerosol flow to just above that at which observations were made. A refrigerated bath circulated heat-transfer fluid through the jacket of the precooler. The relative humidity of the aerosol flow could be adjusted by addition of two N_2 flows, one of which was dry and one completely saturated with water by passing it through a bubbler at 298 K. These flows were combined prior to addition to the precooler in order to ensure that they were well mixed. Variation of the ratio of the flows and the variable drying in the dryer allowed control of the relative humidity.

After the precooler, the flow passed into an infrared absorption cell consisting of a single-jacketed glass tube (84 cm long, 6.35 cm i.d.). The infrared beam produced by a Fourier transform infrared spectrometer was redirected and collimated so that it passed along the centerline of the absorption cell. Two 1.25 cm radius, 0.2 cm thick AgCl windows were mounted on glass tubes supported at the ends of the absorption cell by threaded O-ring compression joints. Only aerosols within the central portion, or observation region, were monitored by using the glass tubes and windows to optically isolate this area from the remainder of the cell. This was done to ensure that the aerosol particles equilibrated with gas-phase water and that the flow attained a constant temperature prior to reaching the observation region. Thermocouples were located within this region to ensure that the flow was isothermal both radially and axially. After the absorption cell, the beam was focused onto a MCT detector.

For a *deliquescence-mode* experiment, aerosols at low RH were prepared by passing them through the dryer and adding dry N_2. A gradual increase in wet N_2 and decrease in dry N_2, such that the total flow remained constant, was used to raise the relative humidity until the deliquescence point was reached and the dry particles were spectroscopically observed to take up condensed-phase water. *Efflorescence-mode* experiments were performed by passing aqueous aerosols at high relative humidity from the precooler into the absorption cell. The aerosol flow was then diluted by dry gas such that an increase in the flow of dry gas resulted in progressively lower relative humidities until concentrated liquid aerosols crystallized to form solid particles. Again, the total flow was kept constant. For experiments performed at a typical flow rate of 2000 sccm, the residence time in the observation region was ~30 s. A third experiment was performed in *static mode* to extend the observation time. In this mode, a flowing experiment was performed until all flows were shut off and the outlet sealed. Spectra were taken for up to 30 min, at which point gravitational settling led to insufficient signal.

The spectral range from 4000 to 500 cm^{-1} was utilized for two reasons. First, lines of gas-phase water are present from 3900 to 3450 cm^{-1} and from 2000 to 1300 cm^{-1}. As described in refs 8 and 19, the lines were used to monitor in situ the relative humidity of the flow with uncertainties of 1%, 2%, 4%, and 6% at 298, 273, 253, and 238 K, respectively. Second, condensed-phase features associated with water and constituent ions lie in this spectral range. Specifically, the OH stretch, HOH bend, and H-bond of liquid water are centered at 3450, 1640, and 650 cm^{-1}, respectively. The presence of these features was used to determine the phase of particles. While neither NaCl nor $MgCl_2$ contain ions which absorb in this range, both NH_4HSO_4 and NH_4NO_3 are infrared active. Specifically, the NH stretch and ammonium deformation modes are observed at 3300−2800 and 1450−1420 cm^{-1}, respectively. Two sulfate modes are seen at 1115 and 620 cm^{-1} and three bisulfate modes at 1200−1300, 1053, and 877 cm^{-1}. The NO_3^- ion exhibits an intense asymmetric stretch at 1376 cm^{-1}, a symmetric stretch at 1046 cm^{-1}, and a deformation at 828 cm^{-1}. All of these absorption features have been identified previously.[12,23,24]

Results and Discussion

1. NaCl. The deliquescence relative humidity of sodium chloride was determined by preparing dry particles by passing the aerosol flow through the entire length of the diffusion dryer. 2000 sccm of dry gas was initially added, resulting in an aerosol sample with a low relative humidity at the observation temperature. For example, for an experiment at 273 K, a spectrum observed at 10% RH is shown as the upper curve in Figure 1. The gradual increase in extinction at higher wavenumbers is due to greater light scattering in this regime. While there are no absorption features due to the constituent ions of NaCl, there is a small, but finite, absorption feature due to the OH stretch. The increased noise from 3900 to 3450 cm^{-1} and from 2000 to 1300 cm^{-1} results from imperfect subtraction of gas-phase water lines. These features are larger in the upper three traces because these spectra have been scaled compared to the lower one, to emphasize the condensed phase OH stretch. It should also be said that features at 2350 cm^{-1}, attributed to a CO_2 gas-phase impurity arising from a small amount of air in the diffusion dryer, have been subtracted from the spectra. This CO_2 could be reduced to undetectable values if the diffusion dryer were flushed with dry N_2 for very long times. We assume its presence does not affect our results.

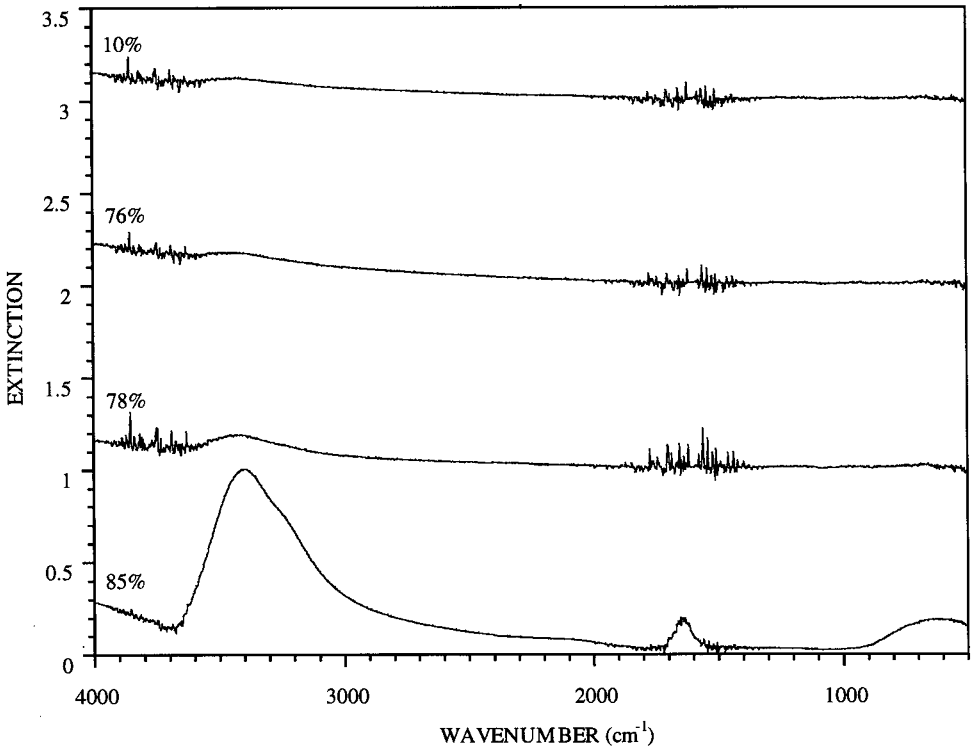

Figure 1. Infrared spectra of NaCl aerosol prepared in a deliquescence-mode experiment at 273 K. Spectra have been scaled and vertically offset for clarity. Relative humidity with respect to water is indicated for each spectrum. Notice the small absorption due to the OH stretch feature which occurs even at low relative humidity.

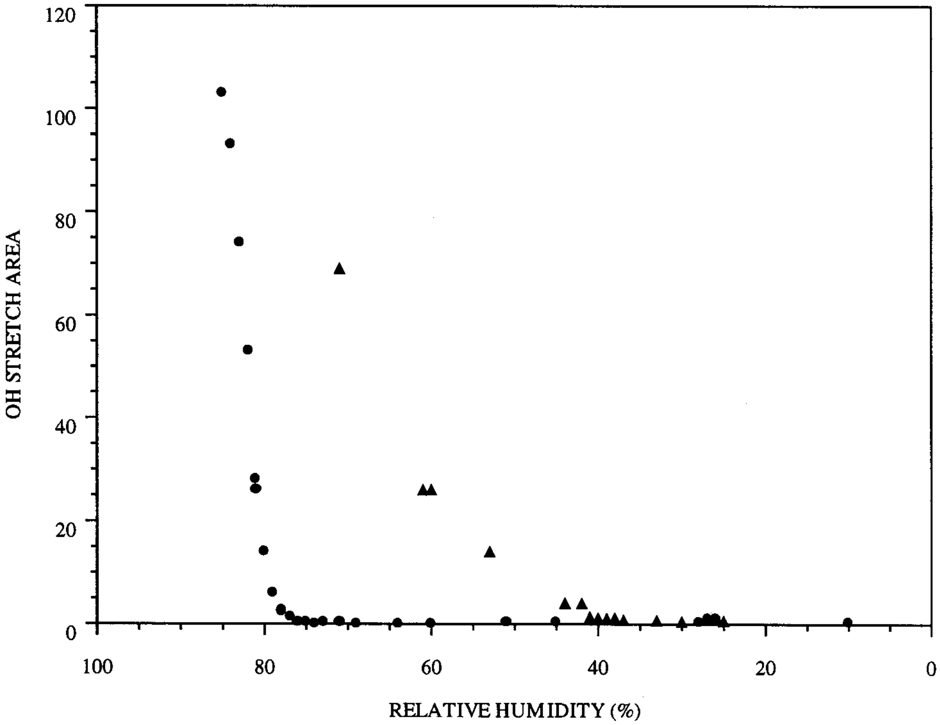

Figure 2. Residual area of the OH stretch mode (2600−3700 cm^{-1}) after subtraction of low relative humidity features, for NaCl deliquescence-mode (circles) and efflorescence-mode (triangles) experiments at 273 K.

The relative humidity of the aerosol flow was incrementally raised by addition of wet N_2 and the simultaneous reduction of dry N_2 such that the combination remained at 2000 sccm. Some of the spectra which were continuously recorded as the relative humidity was increased are shown as the lower curves in Figure 1. No changes were observed in the spectra until the deliquescence point was reached (78% RH), where absorption of the OH stretch became more intense.

Accurate determination of the deliquescence point was accomplished by subtraction of the initial spectrum from subsequent, higher relative humidity, spectra. The results are presented as the solid squares in Figure 2 for a deliquescence experiment at 273 K. Deliquescence is marked by a rapid increase in the area of this feature, the onset of which was observed at 75 ± 2%, 78 ± 2%, 77 ± 3%, and 80 ± 4% RH for experiments at 283, 273, 263, and 253 K, respectively. In

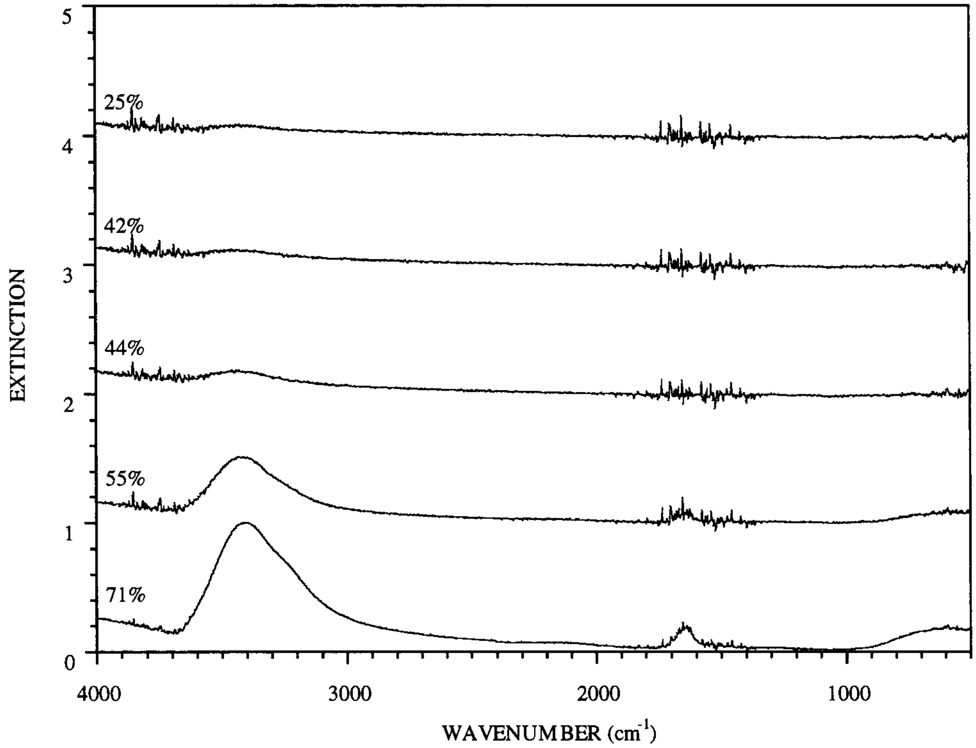

Figure 3. Infrared spectra of NaCl aerosol prepared in an efflorescence-mode experiment at 273 K. Relative humidity with respect to water is indicated for each spectrum.

previous work we measured 75 ± 1 at 298 K.[8] The estimated uncertainties in these points are related to both the determination of the RH and the scatter of the data points.

Efflorescence-mode experiments were performed by addition of approximately 2000 sccm of wet N_2 to NaCl aqueous aerosols, resulting in an aerosol sample at high relative humidity. The relative humidity was then lowered by incrementally decreasing the humid flow and increasing the dry N_2 flow. A set of successive spectra, recorded as the relative humidity was lowered, is shown in Figure 3. Condensed phase water features are clearly visible below the deliquescence point. The strength of the OH stretch after subtraction of the final, lowest RH spectrum recorded is plotted as triangles in Figure 2 for an experiment at 273 K. Water features are strong past the deliquescence point, gradually decreasing as relative humidity is lowered, until a steady value is reached at a much lower gas-phase water content. The points at which the area of the OH stretch is observed to reach a steady value are 43 ± 2, 45 ± 3, 38 ± 3, 41 ± 4, and 35 ± 4 for experiments performed at 298, 283, 273, 263, and 253 K, respectively, where the 298 K point was measured previously.[8] These are the temperature-dependent efflorescence points.

The small absorption due to the OH stretch at low relative humidities was present at all temperatures. Efflorescence points are reported as the relative humidity at which the OH stretch decreases to this steady, but nonzero value. This low RH feature was previously examined at room temperature by Cziczo et al.[8] Specifically, aerosol particles at RHs below the efflorescence point were exposed to gas-phase D_2O. The condensed-phase DO stretch was not observed to form and it was argued that the water was most likely physically trapped in subsurface pockets unable to exchange with the environment. Recently, Weis and Ewing have performed a quantitative infrared study of this phenomenon.[25] They conclude that the amount of water retained is too great to be due to adsorption and is most likely due to water physically trapped in the aerosol particle.

Although there are a number of room-temperature studies of NaCl deliquescence and efflorescence,[5,9,13] there is only one set of low-temperature studies, performed using optical microscopy of particles mounted on a slide.[21] Our results, both in this work and in our earlier room-temperature study, are in good agreement with all previous studies. The deliquescence points lie within ±2% RH of the theoretical relative humidity for all temperatures.[26] Weis and Ewing observed considerable water loss below 50% and infer crystallization at ~44% RH in a flow tube system similar to the one used here.[25] These workers also observed comparable absorption in the OH stretch feature present below the efflorescence point.

Two additional results are noteworthy. First, static experiments were conducted at each temperature at a few percent RH above the efflorescence points. None resulted in crystallization over 30 min time periods. Second, whereas the dihydrate of NaCl is stable from 273 K to the eutectic temperature (252 K),[26] no indication of its formation was observed. Observation of a hydrate of $MgCl_2$, as described below, indicates that the formation of $NaCl{\cdot}2H_2O$ should have been evident had it occurred.

2. $MgCl_2$. One motivation for studying the temperature dependence of the $MgCl_2$ system was to better understand the deliquescence and efflorescence behavior of sea salt aerosols. After Na^+ and Cl^-, Mg^{2+} is the most common ion found in seawater, in a molar amount about 10% as great as the primary constituents.[27] The presence of $MgCl_2$ in seawater is of particular interest because it is known to readily form a hexahydrate above 270 K, with a deliquescence point considerably lower (33% RH at 298 K) than that of NaCl (75%).[26,27] It is not known how readily this hydrate forms, nor whether the hydrate easily exchanges water with its surroundings or instead behaves like a crystalline salt particle.

Experiments were initially performed as for the NaCl system, from 273 to 238 K. Considerably more condensed-phase water was observed at low relative humidity than for NaCl, with all

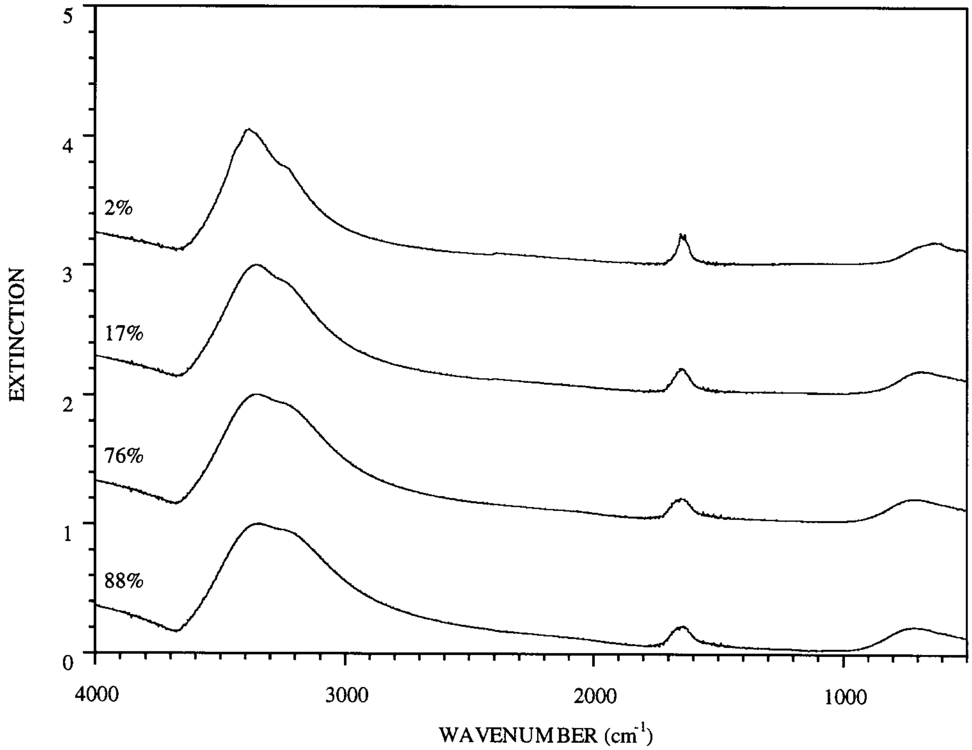

Figure 4. Infrared spectra of $MgCl_2$ aerosol prepared in a deliquescence-mode experiment at 273 K. Relative humidity with respect to water is indicated for each spectrum. Notice the substantial absorption of the condensed water modes which occur at low relative humidity.

three infrared features distinct. As the dry N_2 flow was reduced and small amounts of wet N_2 were added, all three condensed-phase water modes became more intense, implying water uptake and the existence of aqueous particles. In this mode, experimentation normally began at ~10% RH. To maximize sample drying, additional experiments were performed by using low aerosol flow rates to maximize particle residence time in the dryer. This, combined with dry N_2 flows in excess of 2000 sccm and use of heating tape around the dryer and injector, facilitated greater water removal. Using this configuration, initial relative humidities on the order of 1–2% were possible at the higher temperatures. A typical spectrum at 273 K is shown as the upper curve in Figure 4 where it is seen that the water features have significant character at very low relative humidity. The OH stretch is narrow with pronounced shoulders, there are two distinct peaks in the HOH bend, and the H-bond shifts to lower frequency. As described below, we believe the changes are due to efflorescence and formation of a hydrate. Although a low relative humidity was attained, subsequent addition of gas-phase water continued to result in immediate uptake, as shown in Figure 5 for an experiment at 273 K. This is in agreement with behavior we observed for $MgCl_2$ at room temperature.[8]

To attain the lowest relative humidities possible, an experiment was performed at 273 K by passing a very small (~500 sccm) aerosol flow through the dryer, which was wrapped in heating tape to facilitate water removal. The resulting spectrum, shown in Figure 6, was recorded at less than 1% RH. The differences between this spectrum and that of liquid water are accentuated. Given its character—sharp modes arising from condensed phase water—it is quite likely that this is a spectrum of a hydrate, most likely $MgCl_2{\cdot}6H_2O$. However, we believe that the sample is not entirely solid because, when small amounts of saturated N_2 were added, there was considerable uptake of water and the spectra became indistinguishable from those in Figure 4. Had the particles fully effloresced to form the hexahydrate, they should not have deliquesced until much higher relative humidities (33%).[27] As in the case of the NaCl system, static-mode experiments were performed on $MgCl_2$ aerosols for each observation temperature at <10% RH. No spectral changes were observed under these conditions. The only previous low RH data available on this system are those of Winkler and Junge, who studied small samples suspended on a microbalance.[10] These workers reported incomplete loss of H_2O at ~30% RH at 298 K.

Two other hydrates of $MgCl_2$ are thermodynamically stable over a portion of the temperature and relative humidity range investigated. Specifically, $MgCl_2{\cdot}8H_2O$ is stable from 256 to 270 K and $MgCl_2{\cdot}12H_2O$ from the eutectic temperature (240 K) to 256 K.[26] Regardless of temperature, the low relative humidity spectra did not differ from that in Figure 4, implying that either all the hydrates are spectroscopically similar or only one hydrate—presumably $MgCl_2{\cdot}6H_2O$—formed in our experiment.

3. NH_4HSO_4 and NH_4NO_3. Both NH_4HSO_4 and NH_4NO_3 aerosols responded to deliquescence-mode experiments in a manner similar to $MgCl_2$ particles. Specifically, as observed previously for NH_4HSO_4 at 298 K,[8] no combination of relative humidity and temperature, from 273 to 238 K, was observed to crystallize the anhydrous phase for either system. Low particle flow rates were used in combination with dry flows in excess of 2500 sccm such that initial relative humidities of 2% were attained. A spectrum of NH_4HSO_4 aerosols taken under these conditions at 273 K is shown in Figure 7. Although very low relative humidity was possible, this method did not result in the large changes in the spectrum which would indicate formation of dry ammonium bisulfate. Addition of wet N_2 to samples at 2% relative humidity resulted in water uptake, as shown by the increased intensity of the condensed-phase water modes in higher relative humidity spectra in Figure 7. A plot of the OH stretch area after subtraction of the lowest relative humidity spectrum is shown in Figure 8 for a deliquescence-

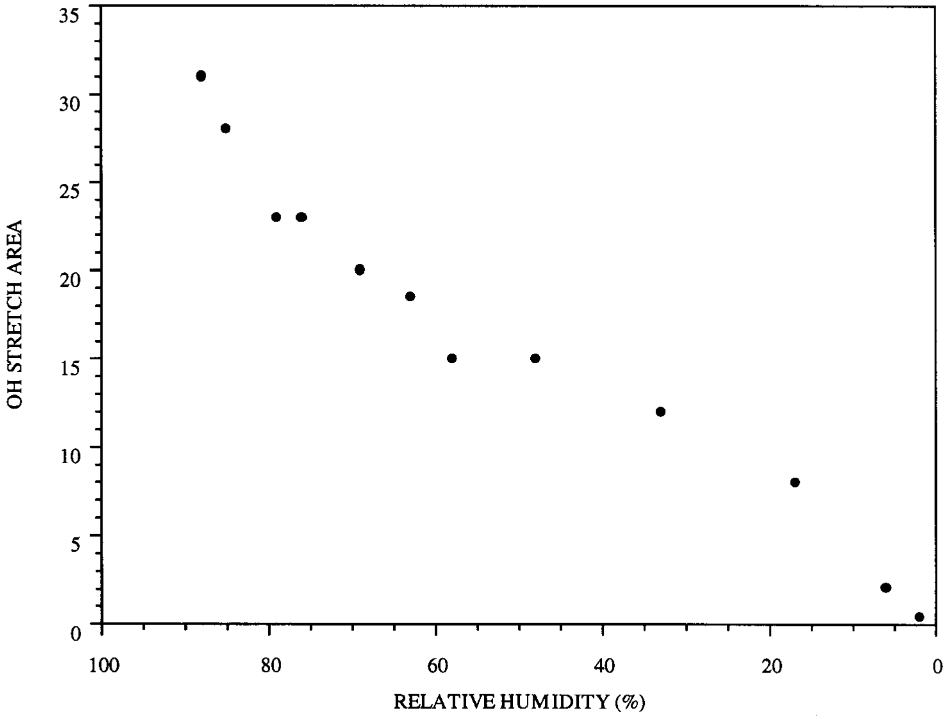

Figure 5. Residual area of the OH stretch mode (2500−3675 cm^{-1}) after subtraction of low relative humidity features, for $MgCl_2$ aerosols in a deliquescence-mode experiment at 273 K.

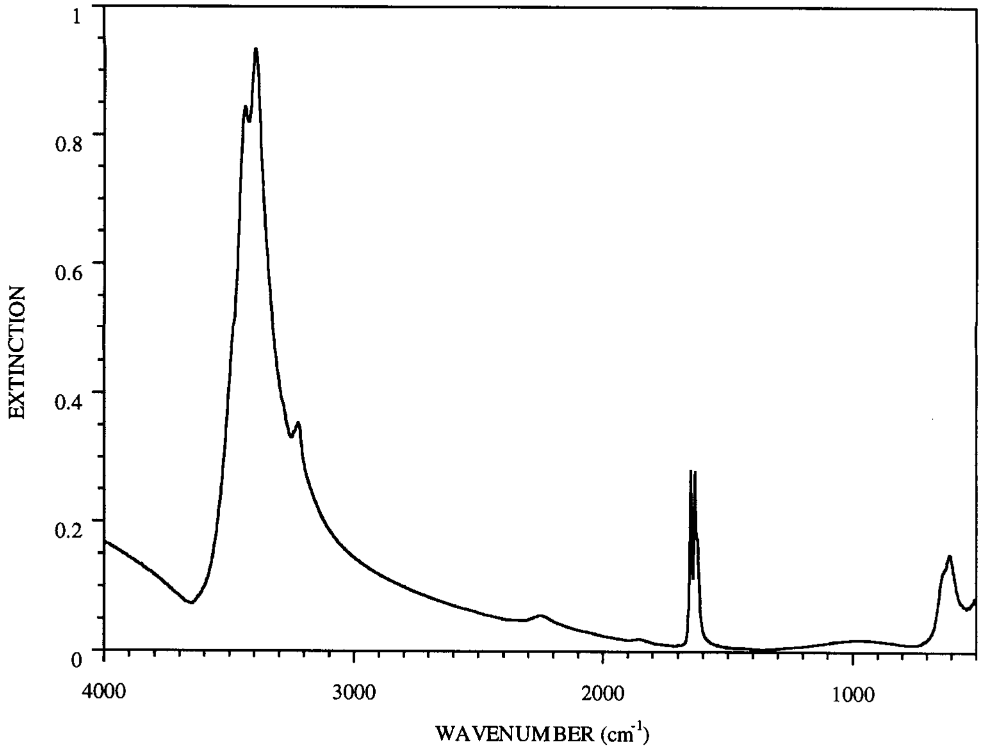

Figure 6. Infrared spectrum of $MgCl_2$ aerosol at <1% relative humidity at 273 K. Notice the sharp absorption features in the condensed-phase water bands.

mode experiment performed at 273 K. Particles take up gas-phase H_2O beginning at very low relative humidity.

Further support for the contention that solid ammonium bisulfate was not formed in these experiments comes from two sources. First, the lowest RH spectra recorded at each observation temperature are distinctly different from a literature spectrum for dry ammonium bisulfate, which contains more infrared features, including the formation of doublets from the sulfate and bisulfate modes in the 1500−500 cm^{-1} range.[24] Second, an experiment was performed where a thin film of ammonium bisulfate aerosols was sprayed onto one of the AgCl windows in the absorption cell. 3000 sccm of dry N_2 was passed through the system for long periods, during which time the relative humidity in the flow tube was always less than 1%. After approximately 6 h, the spectrum of the thin film began to exhibit sharp features and doublets in the 1500−500 cm^{-1} range. A spectrum recorded under these conditions is presented in Figure 9. In addition to the sharpened sulfate, bisulfate, and

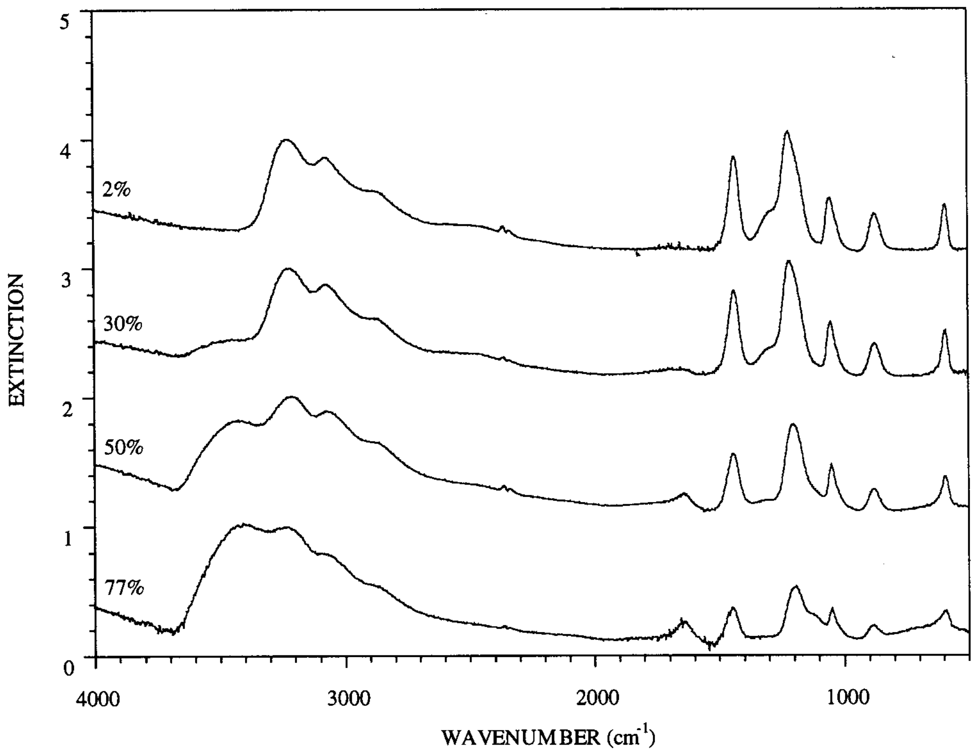

Figure 7. Infrared spectra of NH_4HSO_4 aerosol prepared in a deliquescence-mode experiment at 273 K. Relative humidity with respect to water is indicated for each spectrum. The small feature at 2350 cm^{-1} arises from trace amounts of CO_2 in the flow.

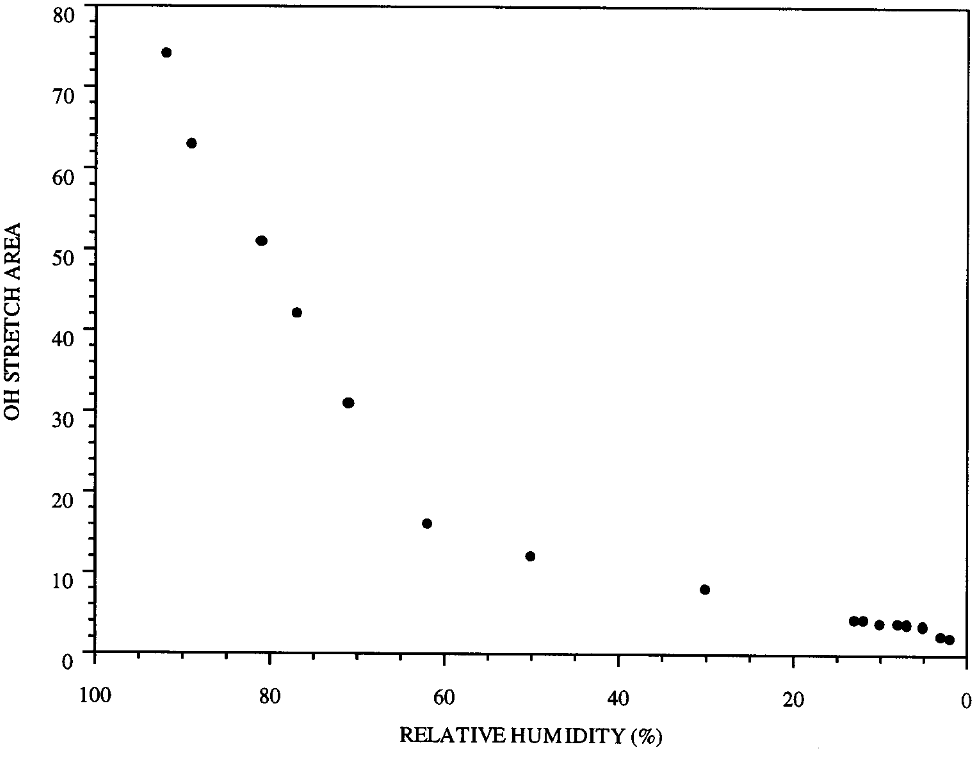

Figure 8. Residual area of the OH stretch mode (3000−3700 cm^{-1}) after subtraction of low relative humidity NH_4HSO_4 features for a deliquescence-mode experiment at 273 K.

ammonium modes, a broad peak became apparent at ~2450 cm^{-1}. These features resemble modes found in the literature spectrum of dry ammonium bisulfate solid.[24] A flow of N_2 saturated with water was added to the system to raise the relative humidity above the thin film. Condensed-phase water features became apparent at a relative humidity of 40% at 298 K, in agreement with the theoretical deliquescence point of ammonium bisulfate and with one previous experimental measurement of the deliquescence point.[14,26] At higher relative humidities, condensed-phase water modes became apparent, and the sharp features and doublets transformed into the peaks found in the low relative humidity spectra observed in deliquescence-mode studies. After water uptake, the flow of saturated gas was terminated so that the relative humidity in the system returned to <1%. The solid ammonium bisulfate features did not reappear immediately. Instead, approximately 6 h were again required.

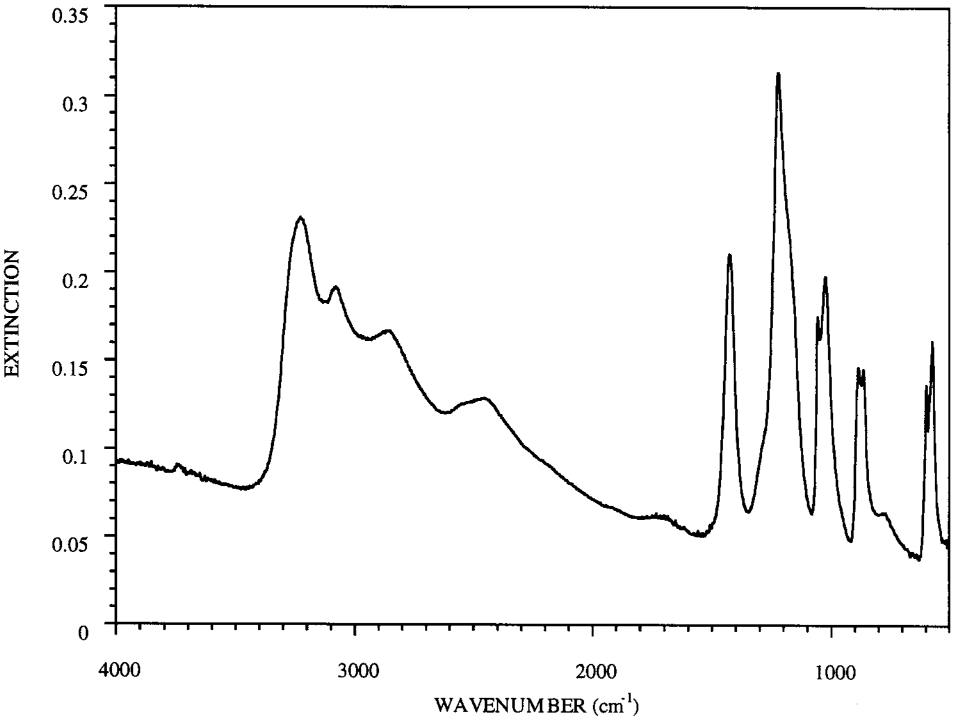

Figure 9. Room-temperature infrared spectrum of a thin film of NH_4HSO_4 aerosols on a AgCl window after prolonged exposure to relative humidities less than 1%. Note the sharp peaks and doublets in the region from 1500 to 500 cm^{-1} which are not present in low relative humidity spectra recorded in deliquescence-mode (refer to Figure 7).

Any gas-phase water added to the system before this time was immediately taken up by the material on the windows, indicating that crystallization of the anhydrous phase had not yet occurred. We believe this experiment substantiates our claim that dry NH_4HSO_4 aerosols were not formed during normal deliquescence-mode experiments and that aqueous particles composed of this salt are extremely difficult to crystallize.

With particles suspended for long time periods in an electrodynamic balance, Tang and Munkelwitz found that ammonium bisulfate solution droplets often remained liquid at pressures as low as 10^{-6} Torr.[15] Both Whitby, and Mozurkewich and Calvert observed immediate growth of ammonium bisulfate particles exposed to water vapor when using a DMA even after extensive exposure to a diffusion dryer.[2,9] Neither group observed crystallization below 10% relative humidity. Two studies have formed fully dry ammonium bisulfate particles. Tang and Munkelwitz observed deliquescence, which implies that efflorescence had taken place, in submicrometer radius ammonium bisulfate particles in a flow system, but this was only after the aerosols had undergone an intensive cooling−heating−cooling cycle.[14] Recently, Imre et al. reported temperature-dependent efflorescence points for ∼2.5−5 μm radius ammonium bisulfate particles suspended in an electrodynamic balance.[17] It is clear from most of these studies that efflorescence does not take place easily in this chemical system. The disagreement between our work and that of Imre et al. is difficult to reconcile.

As in the case of NH_4HSO_4, NH_4NO_3 was not observed to crystallize at any temperature from 298 to 238 K. Figure 10 illustrates a typical experiment for which the initial relative humidity was 1% at 273 K. Reduction of the flow of dry N_2 and addition of wet N_2 resulted in immediate water uptake, as shown in Figure 10, and by the dependence of the strength of the OH stretch upon relative humidity in Figure 11. A previous study on the NH_4NO_3/H_2O system was conducted at room temperature by Tang.[16] In agreement with our results, it was reported that particles in a continuous flow system did not crystallize and exhibited significant water uptake at 30% RH, well below the theoretical deliquescence point of 62% at 298 K.[26] Static-mode experiments performed on both ammonium bisulfate and nitrate at <10% relative humidity did not result in pronounced spectral changes at all temperatures.

Conclusions and Atmospheric Implications

The major result from this work is the demonstration that submicrometer-sized aqueous aerosols composed of NaCl, $MgCl_2$, NH_4HSO_4, and NH_4NO_3 supersaturate readily under low-temperature conditions commonly encountered in the troposphere. Although these systems have been examined at room temperature, there have been almost no low-temperature studies performed previously.

For the specific case of NaCl this work extends to low-temperature measurements which indicate that deliquescence is not a kinetically hindered process on our time scales and that efflorescence occurs at approximately 40% RH. The temperature-independent nature of the efflorescence point is similar to that demonstrated by ammonium sulfate aerosols.[19,20] The dihydrate of NaCl, a thermodynamically favorable crystalline solid at low temperature, was not observed on our experimental time scales, whereas a small amount of physically trapped water was observed in effloresced particles at all temperatures.

Changes in the infrared spectra of aerosols derived from a solution of $MgCl_2$ suggest that a hydrate of this salt forms but only after extensive sample drying at extremely low relative humidity. Addition of gas-phase water vapor to particles subjected to intense drying resulted in immediate uptake, indicating incomplete crystallization. These results suggest that if the RH is lowered in the atmosphere, although NaCl may precipitate from sea salt aerosols, $MgCl_2$ will continue to coexist in a concentrated liquid state under all conditions commonly encountered. Recently, field measurements have observed particles which support this model. In particular, in studies of

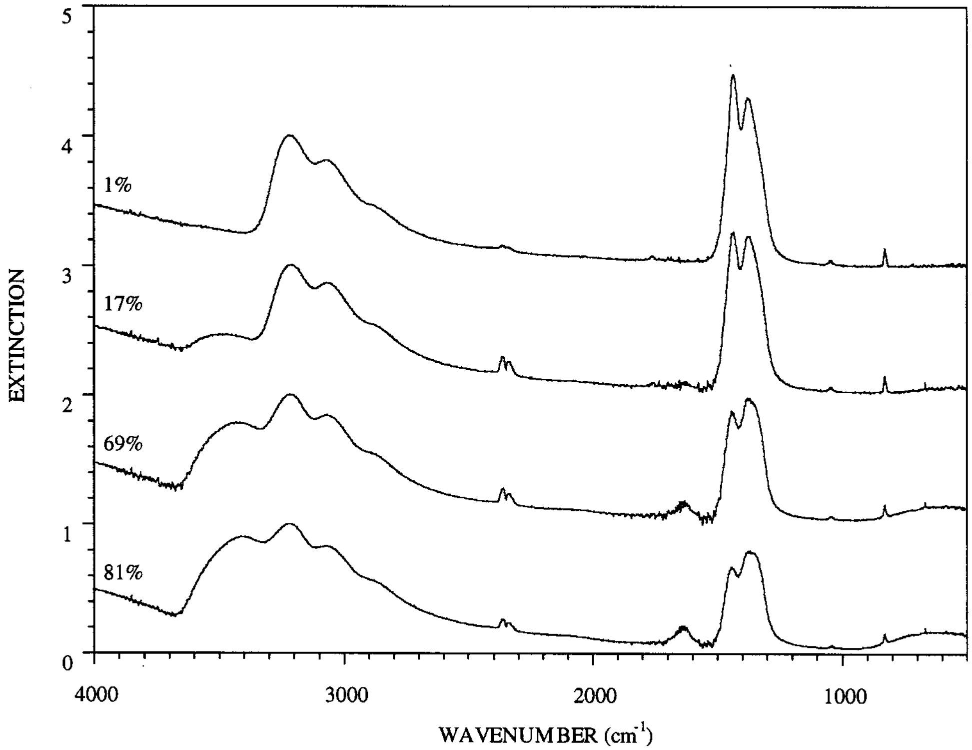

Figure 10. Infrared spectra of NH_4NO_3 aerosol prepared in a deliquescence-mode experiment at 273 K. Relative humidity with respect to water is indicated for each spectrum. The small features at 2350 and 670 cm^{-1} arise from trace amounts of CO_2 in the flow.

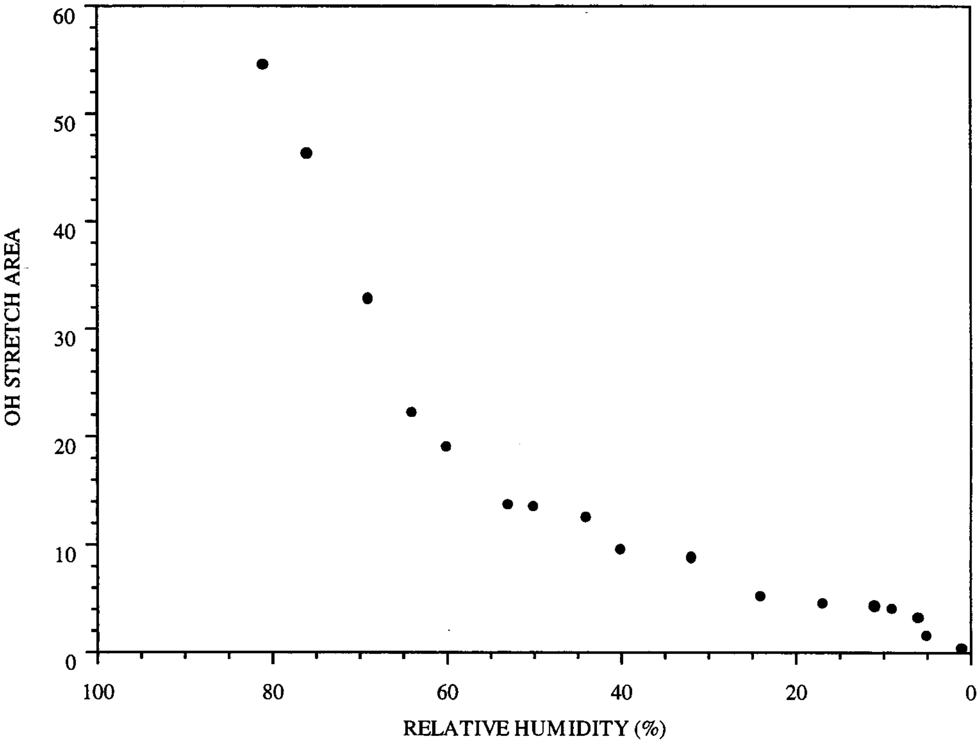

Figure 11. Residual area of the OH stretch mode (3000−3700 cm^{-1}) after subtraction of low relative humidity NH_4NO_3 features for a deliquescence-mode experiment at 273 K.

individual marine particles using laser ionization mass spectrometry, Murphy et al. observe homogeneous particles at 80% RH, whereas the mass spectra of aerosols below 40% RH have much less consistent ratios of NaCl to other salts.[28] In the low RH regime, the authors suggest that the mass spectra most likely result from partial ionization of a particle composed of a crystalline solid (NaCl) and a residual brine containing $MgCl_2$.

In the case of NH_4HSO_4 and NH_4NO_3, this work shows that the formation of an anhydrous solid is kinetically inhibited under temperatures and relative humidities commonly encountered in the troposphere. This is in contrast to the behavior of species with considerably higher deliquescence points, such as NaCl and $(NH_4)_2SO_4$, which readily effloresce. Apparently, the extent to which these systems are below their deliquescence point, i.e., how metastable they are, affects whether efflorescence is observed on our experimental time scale of up to 30 min.

Although we cannot work with longer time scales, we believe that the results are indicative of general aerosol behavior in the atmosphere because the dependence of the rates of nucleation phenomena of this type upon temperature and relative humidity are so strong.[29] As an illustration of the extent to which these efflorescence processes are kinetically hindered, an experiment was performed on a thin film of particles. This showed that many hours of drying were required at relative humidities below 1% before solid ammonium bisulfate salt crystallized. It seems unlikely that either of these ammonium salts will effloresce under typical atmospheric conditions unless solid nuclei that promote crystallization are components of the particles.[30]

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