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Laboratory studies of ice formation pathways from ammonium sulfate particles

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Abstract

Cirrus clouds are composed of ice particles and their formation pathways have been studied extensively in the laboratory. The ability of ammonium sulfate particles to act as nuclei for cirrus clouds has been of particular importance because of their ubiquitous presence in the upper troposphere. The results of past laboratory experiments of homogeneous ice nucleation from ammonium sulfate particles show a wide range of freezing conditions. In the present study, a flow tube apparatus equipped with Fourier transform infrared spectroscopy was used to resolve these discrepancies. It was found that when ammonium sulfate particles were preconditioned at 100% relative humidity (RH) prior to experimentation, the particles froze at conditions predicted by the homogeneous ice nucleation model developed by Koop et al. (2000). If the particles were not preconditioned at 100% RH, they froze at warmer temperatures and lower ice saturation ratios than predicted by Koop et al. (2000). In order to determine if a population of effloresced particles affected freezing conditions for particles that were not preconditioned at 100% RH, a series of depositional ice nucleation experiments were carried out on dry ammonium sulfate particles. For freezing temperatures between 215 and 231 K, ice nucleated on the particles at ice saturation ratios (S_{ice}) between 1 and 1.05. These conditions are much lower than predicted by Koop et al. (2000) and explain the differences in freezing conditions among preconditioning methods. In similar experiments, Abbatt et al. (2006) hypothesized that a small fraction of effloresced ammonium sulfate particles induced ice nucleation at S_{ice} values lower than expected. The current study confirms the Abbatt et al. (2006) hypothesis and, to our knowledge, is the first study to directly observe ice nucleating onto freely flowing dry ammonium sulfate particles at S_{ice} values approaching unity.

1 Introduction

Cirrus cloud formation is largely controlled by the nucleation potential of the aerosol particles available in the upper troposphere. The ability of individual particles to nucleate ice depends directly on their microphysical and chemical properties. Because sulfate particles are ubiquitous in the upper troposphere (Murphy et al., 1998), their ability to nucleate ice has been extensively studied.

As discussed by Abbatt et al. (2006) many experiments have been performed to determine the conditions at which ice homogeneously nucleates from ammonium sulfate particles. The results of these experiments show a wide range of freezing conditions and do not agree with the homogeneous ice nucleation model developed by Koop et al. (2000). The experimental techniques used to investigate homogeneous ice nucleation in ammonium sulfate particles can be divided into two general categories. Those studies performed with freely floating deliquesced ammonium sulfate particles (i.e. Chen et al., 2000; Chelf and Martin, 2001; Cziczo and Abbatt, 1999; Hung et al., 2002; Prenni et al., 2001; Wise et al., 2004) generally found warmer freezing temperatures and lower ice supersaturation S_{ice} values than those found by studies using solid substrates or emulsions (i.e. Bertram et al., 2000; Koop et al., 1999)

Because accurate climate modeling requires a complete understanding of cirrus cloud formation mechanisms, these discrepancies have to be resolved. It has been hypothesized that factors such as methods used to determine solution concentration, particle size, particle size distributions, residence times, and fraction of particles frozen contribute to differences in the ammonium sulfate freezing temperatures observed. Hung and Martin (2002) suggested that the major discrepancies can be resolved by considering the number of freezing events occurring. However, Hung and Martin (2001) also found that no volume nucleation rate function exists that can reconcile all experimental results.

Abbatt et al. (2006) showed that laboratory measurements support an ice nucleation pathway by depositional ice nucleation onto solid ammonium sulfate aerosol particles.

Using a cloud chamber, they found that solid ammonium sulfate particles (formed at less than 10% RH) were efficient ice nucleators (onset S_{ice}=1.20 at 221 K). In this experiment, Abbatt et al. (2006) inferred the presence of solid ammonium sulfate particles because of the conditions under which they were produced. A similar ice nucleation experiment using a cloud chamber was conducted by Mangold et al. (2005). They found that the onset of ice nucleation occurred for ammonium sulfate particles in the range of $1.2<S_{ice}<1.27$ (temperatures between 197 and 221 K). Although FTIR spectroscopy showed that the majority of the ammonium sulfate particles were supercooled solutions at these conditions, the presence of a small fraction of effloresced particles could not be ruled out. Therefore, it was thought that a small fraction of effloresced particles acted as heterogeneous ice nuclei at low S_{ice} values.

In addition to the cloud chamber studies, Abbatt et al. (2006) directly studied the ice nucleating ability of effloresced ammonium sulfate particles deposited on a hydrophobic support. These experiments showed that, depending on the preparation method, solid ammonium sulfate acted as efficient ice nuclei. In agreement with Abbatt et al. (2006), Shilling et al. (2006) showed that 1 in 1×10^5 solid ammonium sulfate particles deposited on a plate acted as ice nuclei at S_{ice}values lower than that predicted for homogeneous nucleation.

The present manuscript provides data that resolves discrepancies between ice nucleation experiments performed using freely flowing ammonium sulfate particles and particles supported by substrates. It is shown that the existence of solid ammonium sulfate particles causes warmer freezing temperatures and lower S_{ice} values due to depositional nucleation. Thus, the experiments performed confirm the Abbatt et al. (2006) hypothesis that the conditions at which homogeneous ice nucleation occur (using a flow tube system) are skewed due to the presence of a small number of effloresced ammonium sulfate particles. Lastly, by properly preconditioning the particles, the undesired solid ammonium sulfate particles were eliminated and the freezing conditions agree with the Koop et al. (2000) water activity based homogeneous nucleation theory.

2 Experimental

2.1 Flow tube system

The flow tube system used to measure homogeneous ice nucleation in deliquesced ammonium sulfate particles was similar to that used in Wise et al. (2004) and in Prenni et al. (2001). The same system was also used to study depositional ice nucleation onto effloresced ammonium sulfate particles. However, the experimental procedure was slightly modified in this study. Therefore, a description of the flow tube system (Fig. 1) and experimental procedure are given here.

Ammonium sulfate particles were generated by feeding a 10 wt% ammonium sulfate solution at 0.2 ml/min into an atomizer (TSI 3076) using a Harvard apparatus syringe pump. After atomization, the deliquesced particles were passed over conditioning baths with a variety of different compositions depending on the type of experiment conducted. For homogeneous ice nucleation experiments, the particles were passed over conditioning baths such as pure water and sulfuric acid solutions. In addition to these baths, other solutions such as a saturated ammonium nitrate solution (~60% RH, Martin, 2000) and an ammonium nitrate/sodium chloride solution at the eutonic composition (~40% RH, Martin, 2000) were used to precondition the aerosol particles (see section 2.2 below). For depositional ice nucleation experiments, two 98 wt% sulfuric acid baths (<10% RH) were used to ensure the atomized ammonium sulfate particles were effloresced prior to entering the flow tube system.

Following the preconditioning baths, the particles passed through a series of jacketed flow tubes at ~3.5 L/min. The flow tubes were cooled using recirculating flows of methanol from two Neslab refrigerators. The first series of flow tubes will be referred to as the conditioning region and were cooled to temperatures ranging from −5°C to −40°C. Each day, distilled water was added to the conditioning region thus coating the bottom of the tube walls with ice. The amount of water vapor in the conditioning region was set by the temperature of the region and was determined using ice vapor pressure measurements from Marti and Mauersberger (1993). In addition, the water vapor in the conditioning region was directly measured using a CR-1A chilled mirror hygrometer (Buck Research Instruments, L.L.C., sample flow rate ∼3.5 L/min).

The conditioning region served different purposes depending on the type of experiment carried out. During homogeneous ice nucleation experiments, the conditioning region was used to set the composition of the deliquesced ammonium sulfate particles entering it. If the particles in the conditioning region were in equilibrium with the water vapor at that temperature, the particles had a well-defined composition and water activity. During depositional ice nucleation experiments, the water vapor pressure created by the ice in the conditioning region was not used to set particle composition because the particles entering it were effloresced and the RH was held below the deliquescence RH of ammonium sulfate (80%). Rather, the water vapor created by the ice was used to produce a supersaturation of water vapor in the colder observation region (cooled in a range from −35°C to −60°C).

Ice nucleation during both homogeneous and depositional nucleation experiments occurred in the observation region and was detected using FTIR transmission spectroscopy. The junction between the conditioning tube and the observation tube is termed the transition region, and was cooled (by separate Neslab refrigerators) on one end at the observation temperature and on the other end at the conditioning temperature. Because the temperature drop from the conditioning to the observation region occurred in this transition region, the aerosol particles had time to reach the observation temperature before being monitored using FTIR spectroscopy. During homogeneous ice nucleation experiments, when the temperature was dropped in the observation region and no ice formed, particle composition remained the same. As the temperature was dropped in the observation region during depositional ice nucleation experiments, the particles remained effloresced.

Temperature was measured using thermistors placed at the cold end of the conditioning region and the middle of the observation region. Specifically, the thermisor placed in the conditioning region was frozen into the ice coating the bottom of the flow tube and the thermistor placed in the observation region was placed in the aerosol particle flow. Each thermistor was calibrated against a reference temperature measurement to ±0.20 K over the temperature range studied.

2.2 Determination of aqueous particle composition and water activity

During homogeneous ice nucleation experiments, the aqueous composition of pure ammonium sulfate particles was determined using two separate methods. When the aerosol particles were in equilibrium with the temperature and water vapor in the ice coated conditioning region, particle composition was calculated using the Aerosol Inorganics Model (AIM method (Clegg et al., 1998a, b, 2000); available at http://www.aim.env.uea.ac.uk/aim/aim.php). Particle composition was also determined directly from collected infrared spectra (IR method) using the composition calibration curve constructed by Chelf and Martin (2001). Using the IR method, the particles did not need to be in equilibrium with the temperature and water vapor in the ice coated conditioning region. Particle composition calculated using the IR method was also used to determine particle water activity. Specifically, particle composition prior to the formation of ice was used in conjunction with the AIM model (at the observation region temperature) to calculate water activity.

Wise et al. (2004) used a similar flow tube apparatus to study homogeneous ice nucleation from aqueous ammonium sulfate and mixed ammonium sulfate/dicarboxylic acid particles. The temperature at which homogeneous ice nucleation occurred was dependant on the composition of the aerosol particles. Therefore, Wise et al. (2004) took great care to match the ammonium sulfate composition determined using the AIM method with the composition determined using the IR method. Because the conditioning region of the flow tube apparatus had a finite length, gas phase water had to be removed from the atomized particles in order for the particles to attain equilibrium with water vapor in the conditioning region. Wise et al. (2004) removed gas phase water by passing the aerosol particles over sulfuric acid baths.

In the present study, gas phase water was also removed from the particles using various types of conditioning baths. However, the conditioning baths were arranged in two different configurations. In the first configuration, a water bath (100% RH) was used to precondition the aerosol particles exiting the atomizer. This ensured that all the particles were liquid. Following the water bath the particles were passed over a secondary bath. The secondary bath was either a saturated ammonium nitrate solution (~60% RH), an ammonium nitrate/sodium chloride solution at the eutonic composition (~40% RH), or a 48 wt% sulfuric acid bath (~40% RH). The secondary baths were used to reduce gas phase water, but did not remove enough water vapor to effloresce the particles. It was found that the secondary baths did not remove enough gas phase water to allow the particles to attain equilibrium with the water vapor in the conditioning region. Therefore, the composition determined using the IR method and the AIM method were not the same prior to ice nucleation. In this case, the IR method was used to determine particle composition and water activity. In the second configuration, sulfuric acid baths ranging in composition from 35% to 98% (50% to <10% RH) were used to precondition the aerosol particles exiting the atomizer. Using these sulfuric acid baths, the composition of the ammonium sulfate particles determined using the IR method and the AIM method were approximately the same prior to ice nucleation.

2.3 Determination of homogeneous ice nucleation

At the beginning of a homogeneous ice nucleation experiment, an infrared spectrum was taken at a temperature well above the freezing temperature to ensure that no ice was present in the particles. At this temperature, particle composition was determined using the IR method and recorded. The temperature of the observation region was then incrementally cooled while keeping the conditioning region at a constant temperature. Because the conditioning region was maintained at a constant temperature, the water vapor pressure the particles experienced in the conditioning region remained the same. Therefore, prior to the onset of freezing, the particle composition remained approximately the same. In order to confirm that particle composition remained the same as the observation tube temperature was lowered, the composition of the aerosol particles was monitored using FTIR spectroscopy at each temperature.

At the freezing point, several changes occurred in the infrared spectrum of the particles. The OH-stretching region, which has a maximum at ~3300 cm^{-1} for liquid solutions. (Hung et al., 2002) shifted to lower frequencies and the H_2O stretch centered at ~800 cm^{-1} shifted to higher frequencies. At the onset of homogeneous ice nucleation, the changes in the IR spectra were visually subtle. However, the onset of freezing was apparent when the peak area ratio of the sulfate band (1180 cm^{-1} to 1025 cm^{-1}) to the integrated water band (1751 cm^{-1} to 1549 cm^{-1}) was monitored. When the particles began to freeze, the area of the integrated water band decreased. Thus, the peak area ratio increased substantially. When the peak area ratio changed by a substantial amount the particles had begun to freeze. If the temperature in the observation region was dropped 1°C past the onset temperature, ice features in IR spectrum were visibly apparent.

2.4 Determination of ice formation in depositional nucleation

At the beginning of a depositional ice nucleation experiment, an infrared spectrum was taken under conditions at which it was not possible for the particles entering the conditioning region to deliquesce. Furthermore, the conditions were such that it was impossible to nucleate ice on the solid ammonium sulfate particles. For example, when the conditioning region was held at a colder temperature than observation region, water vapor was not supersaturated in the observation region. Therefore, no ice could condense on the solid particles.

After a spectrum of dry ammonium sulfate particles was recorded, the temperature of the conditioning region was incrementally warmed while keeping the observation region at a constant temperature. As the temperature of the conditioning region was warmed, the water vapor pressure the particles experienced in the conditioning region increased. Using this method, it was possible to attain water vapor supersaturation in the observation tube while maintaining the RH in the conditioning region below the deliquescence RH of ammonium sulfate. At the onset of depositional ice nucleation, the changes in the IR spectra were again visually subtle. However, any change in the

IR spectra (i.e., small shoulder at ~3300 cm^{-1}) was interpreted to be ice condensing on the dry ammonium sulfate particles. When the water vapor supersaturation was further increased in the observation region, changes in the IR spectra due to ice became apparent.

2.5 Determination of critical ice saturation ratios(S_{ice})

A parameter widely used in cloud microphysical models is the temperature dependent critical ice saturation ratio, S_{ice}, which is defined as:

$$S_{ice} = VP_{H_2O}/VP\ (T, ice) \quad (1)$$

where VP_{H_2O} is the water partial pressure at the freezing temperature and VP (T, ice) is the vapor pressure of water over ice at the same temperature. Prior to the onset of homogeneous nucleation, particle composition (determined using the IR method) was used to calculate particle water activity (determined using the AIM model). Particle water activity in turn set VP_{H_2O}. Using the temperature of the observation region, VP (T, ice) was calculated using measurements from Marti and Mauersberger (1993). S_{ice} was then calculated.

At the onset of depositional ice nucleation, the production of ammonium sulfate particles was stopped and particle-free dry nitrogen was flowed into the conditioning and observation regions. VP_{H_2O} was measured at the exit of the observation region using the chilled mirror hygrometer (sample flow rate ~3.5 L/min). S_{ice} was then calculated using the method outlined above.

In order to measure VP_{H_2O} in the observation region using the chilled mirror hygrometer, a particle-free gas stream was necessary. If particles were present in the gas stream, the hygrometer erroneously measured water vapor pressure. As explained in the previous paragraph, the chilled mirror hygrometer was used to experimentally determine VP_{H_2O} in the observation region for depositional ice nucleation experiments. This is possible because prior to depositional ice nucleation water did not condense on the particles. Thus it was possible to measure VP_{H_2O} without ammonium sulfate particles in the dry nitrogen flow. Conversely, in homogeneous ice nucleation experiments, water vapor can condense on the particles. Therefore, water vapor pressure must be measured with the particles in the gas stream. Because this is not possible with the hygrometer, VP_{H_2O} was determined using the AIM model.

3 Results and discussion

3.1 Ice nucleation in aqueous ammonium sulfate particles

Figure 2 presents IR spectra recorded during a homogeneous ice nucleation experiment. In this type of experiment the aerosol particles were preconditioned using a distilled water bath followed by an ammonium nitrate/sodium chloride solution at the eutonic composition. In this figure spectral data are shown when the aqueous ammonium sulfate particles were cooled from 222 K (spectrum 1) to 219 K (spectrum 4) in the observation region while holding the conditioning region at a constant 243 K.

Prior to flowing particles into the experimental apparatus, the water vapor pressure in the conditioning region was measured with the chilled mirror hygrometer. It was found that there was good agreement in the water vapor pressure measured with the hygrometer and the water vapor pressure determined using ice vapor pressure measurements from Marti and Mauersberger (1993) at 243 K. Once this check was completed, the homogeneous ice nucleation experiment was started.

At 222 K no ice was observed in the infrared spectrum and the ammonium sulfate concentration was calculated to be ~28 wt% using the IR method. In addition to monitoring the concentration of the particles, the peak area ratio of the sulfate band to the integrated water band was recorded. At 222 K the ratio was found to be ~2.7. When the temperature in the observation region was dropped to 220 K, the peak area ratio was similar to the ratio obtained at 222 K. At 219 K a large increase in the peak area ratio was observed.

In order to illustrate the determination of the onset of freezing, a plot of the ratio of the sulfate band to the integrated water band is shown in Fig. 3. The data points correspond to the data points in Fig. 2, with the addition of several peak area ratios at warmer observation region temperatures than 222 K. Between 232 K and 220 K, the peak ratios fluctuated between 2.3 and 3.3. A significant increase in the peak area ratio was not observed until the observation tube temperature reached 219 K. At this temperature a population of the particles froze.

Figure 4 is an example of the IR spectra obtained during the second type of homogeneous ice nucleation experiment. In this particular experiment, a 98 wt% sulfuric acid bath followed by a 45 wt% sulfuric acid bath (RH∼46%) were used to precondition the aerosol particles after they were generated with the atomizer. These conditions mirror those used in Wise et al. (2004) and were chosen to test for consistency over the intervening years. Spectral data were obtained when the aqueous ammonium sulfate particles were cooled from 229 K (spectrum 1) to 220 K (spectrum 4) in the observation region while holding the conditioning region at a constant 261 K.

At 229 K no ice was observed in the infrared spectrum and the ammonium sulfate concentration in the particle was calculated to be ∼29 wt% using the IR method. The concentration of ammonium sulfate (assuming that the particles were in equilibrium with the water vapor in the conditioning region) calculated using the AIM method was ∼31 wt%. Therefore, the particles in this experiment had approximately the same composition as the previous experiment. In addition, the assumption that the sulfuric acid baths removed enough gas phase water to allow the particles to attain equilibrium with the water vapor in the conditioning region was valid. Similar to the previous experiment, the peak ratio of the sulfate band to the integrated water band was monitored. At 229 K the ratio was found to be ∼2.9. The spectrum obtained when the observation region was cooled to 225 K shows a peak area ratio substantially greater than at previous temperatures. Therefore, a population of particles froze at 225 K. As the temperature in the observation region was dropped to 220 K, the IR spectrum of ice was apparent.

The only difference in the experimental setup for the freezing data recorded in Fig. 2

and 4 were the configurations of the preconditioning baths. Namely, the aerosol particles shown in Fig. 2 were preconditioned at 100% RH while the particles shown in Fig. 4 were not. It is apparent that the onset of freezing occurred at a warmer temperature for the particles that were not preconditioned with the water bath prior to entering the flow tube apparatus. In order to determine if this difference was systematic, multiple ice nucleation experiments were performed using each preconditioning bath configuration. The results of these experiments are shown in Fig. 5.

Figure 5 is a plot of temperatures at which the onset of freezing occurred versus water activity for aqueous ammonium sulfate particles. The filled circles represent temperatures at which ice nucleated in particles that were preconditioned at RH values equal to 100%. The open circles represent temperatures at which ice nucleated in particles that were preconditioned at RH values <100%. As the particles became more concentrated in ammonium sulfate (lower water activity), they froze at progressively lower temperatures. Over the range of water activities studied, the particles preconditioned at 100% RH froze at systematically lower temperatures than particles preconditioned at RH values <100%.

The particles preconditioned at RH values <100% appear to freeze at substantially warmer temperatures than what would be predicted using the water activity based nucleation theory developed by Koop et al. (2000) (represented with a solid line in Fig. 5). This result is consistent with other groups employing a flow tube apparatus to study homogeneous ice nucleation in ammonium sulfate particles (i.e. Cziczo and Abbatt, 1999 and Wise et al., 2004). The particles preconditioned at 100% RH also appear to supercool somewhat less than what would be predicted using the water activity based nucleation theory. However, the freezing data with which Koop et al. (2000) used to construct the line shown in Fig. 5 does have substantial spread. The shaded area in Fig. 5 represents an estimation of the range in freezing data presented by Koop et al. (2000). The freezing conditions for particles preconditioned at 100% RH are close to the Koop et al. (2000) freezing data within error. In addition, many of the data points in Koop et al. (2000) represent median freezing temperatures rather than the onset of freezing reported here. Therefore, the temperatures at which ice formed from ammonium sulfate particles preconditioned at 100% RH agree with the Koop et al. (2000) water activity based nucleation theory.

Prior to freezing, the ammonium sulfate particles for all experiments presented in Figure 5 appear to be deliquesced using the IR spectra. Therefore, the water activity of the particles should constrain the freezing temperature according to the Koop et al. (2000) homogeneous ice nucleation model. Obviously, the ammonium sulfate particles preconditioned at RH values less than 100% do not agree well with the Koop et al. (2000) model while the particles preconditioned at 100% RH do agree. This phenomenon can be explained by comparing the results shown in Fig. 5 to the results obtained by Abbatt et al. (2006).

Using a cloud chamber, Abbatt et al. (2006) (supplemental materials) performed ice nucleation experiments in which the average RH in the cloud chamber was not low enough to effloresce the particles. In these experiments, two distinct modes of ice nucleation were observed. The first mode of ice nucleation was observed at an S_{ice} value of 1.15 (at 223 K) and the second mode was observed at an S_{ice} value of 1.55. It was hypothesized that portions of the air in the cloud chamber were dryer than that of the average value. It was concluded that some of the particles effloresced and nucleated ice at the low S_{ice} value of 1.15 while the remainder of the particles (deliquesced) nucleated ice at the higher S_{ice} value of 1.55 (in agreement with that predicted by Koop et al., 2000).

In the freezing experiments presented here, it is possible that a fraction of the particles effloresced after being generated using the atomizer. Furthermore, it is possible that a fraction of the particles effloresced after being exposed to RH values less than 35% in certain sulfuric acid conditioning baths. Therefore, if the particles were not passed over the 100% RH bath, the effloresced particles nucleated ice at temperatures warmer than predicted using the Koop et al. (2000) model. This hypothesis explains the discrepancy in freezing temperatures between particles preconditioned at RH values <100% and RH values equal to 100%.

Wise et al. (2004) had concerns that solid ammonium sulfate particles were present in the flow tube system. However, they found that when the atomized ammonium sulfate particles were cooled below the para- to ferroelectric phase transition (223 K) no distinct changes in the infrared spectrum occurred. Furthermore, they found that the asymmetric 1420 cm^{-1} ammonium peak, which indicates the presence of solid ammonium sulfate, was not present in the IR spectra. Therefore Wise et al. (2004) concluded that solid ammonium sulfate particles were not affecting their experimental results. This conclusion appears to be at odds with the hypothesis presented above for the differences in freezing temperatures. However, it is possible that not enough particles effloresce when exiting the atomizer to allow the signatures of solid ammonium sulfate to appear in the IR spectra prior to ice nucleation.

3.2 Depositional ice nucleation onto solid ammonium sulfate particles

It is not possible to measure the concentrations of effloresced and deliquesced particles for the ice nucleation experiments presented in Fig. 5. However, it is possible to test the hypothesis that ice heterogeneously nucleated onto a population of effloresced particles. Using the flow tube apparatus, ice nucleation experiments were carried out in which effloresced ammonium sulfate particles were injected into the system. IR spectra for a typical heterogeneous ice nucleation experiment are shown in Fig. 6. Spectral data were obtained when the effloresced ammonium sulfate particles were warmed from 235 K (spectrum 1) to 247 K (spectrum 4) in the conditioning region while the observation region was held at a constant ∼215 K.

At a conditioning tube temperature (T_{cond}) of 235 K, the IR spectrum shows effloresced ammonium sulfate particles. The existence of effloresced ammonium sulfate particles is confirmed by the absence of the peak corresponding to the OH-stretching region (maximum of ∼3300 cm^{-1}) of water. Furthermore, there is no evidence of ice formation. Therefore, the RH in the conditioning region was low enough keep the particles effloresced and it was also low enough to not prevent ice condensation on the particles in the observation region (S_{ice} was too low). The water vapor pressure the particles experienced was increased by warming the conditioning region to 236 K (spectrum 2). Under these conditions, the particles remained effloresced and no ice condensed onto them. When T_{cond} was warmed to 238 K, subtle changes in the IR spectrum were observed. A small shoulder appeared at ~3350 to 3500 cm^{-1} and broad peak centered at ~835 cm^{-1} appeared. These small changes in the IR spectrum were due to the condensation of a small amount of ice onto the effloresced ammonium sulfate particles. As the temperature in the conditioning region was warmed to 247 K, the IR absorption due by ice was apparent.

In the preceding experiment, it was found that ice condensed on the surface of dry ammonium sulfate particles when the conditioning region was held at 238 K while holding the observation region at 215 K. Because the system was not in equilibrium, S_{ice} was measured by determining the vapor pressure of water in the observation region using the chilled mirror hygrometer. The water vapor pressure measured from the observation tube for the experiments shown in Figure 6 was ~0.0112 torr. Using the measured water vapor pressure and the theoretical water vapor pressure of ice in the observation region at 215 K (~0.0106 torr), S_{ice} is calculated to be ~1.05. S_{ice} could not simply be calculated using the temperature of the two cells because water vapor was lost to the walls of the observation region. This is because the observation tube walls were much colder than the conditioning region. Thus water vapor pressure must be measured directly using the hygrometer.

A summary of the heterogeneous ice nucleation data obtained in this study is shown in Figure 7. It can be seen that over the temperature range studied (215–232 K), S_{ice} is between 1 and 1.05. The S_{ice} values determined for heterogeneous ice nucleation are not dependant on temperature and are significantly lower than that predicted using the homogeneous ice nucleation model developed by Koop et al. (2000) (thick solid line in Fig. 7).

3.3 Comparison of freezing conditions with previous studies

A variety of experimental procedures have been used to determine S_{ice} as a function of freezing temperature for different modes of ice nucleation from ammonium sulfate particles. The results of the studies presented in Abbatt et al. (2006) (Fig. 1B), in addition to the results of the depositional ice nucleation experiments presented in this manuscript, are plotted in Fig. 8. The solid symbols in Fig. 8 signify freezing conditions for homogeneous ice nucleation and the open symbols correspond to freezing conditions for depositional ice nucleation. The thick solid line in Figure 8 represents the homogeneous ice nucleation model developed by Koop et al. (2000) and the thin solid line is an S_{ice} of 1.

Literature values of S_{ice} for the homogeneous nucleation of ice in ammonium sulfate particles range from ∼1.2 to 1.6 at freezing temperatures from 205 to 235 K. In addition to the wide spread in experimental conditions in which ice nucleated from the particles, the experimental results are at odds with the homogeneous ice nucleation model developed by Koop et al. (2000). Abbatt et al. (2006) provided a detailed discussion for the discrepancies in freezing conditions for ammonium sulfate particles. The main conclusion from the Abbatt et al. (2006) manuscript was that a small fraction of effloresced ammonium sulfate particles were present in the homogeneous ice nucleation studies. The small fraction of effloresced particles then induced ice formation at lower S_{ice} values than predicted with the Koop et al. (2000) homogeneous ice nucleation model.

In order to lend credence to this theory, Abbatt et al. (2006) used a cloud chamber to depositionally nucleate ice onto solid ammonium sulfate particles. The presence of solid ammonium sulfate particles in their experiment was inferred from the generation conditions. They found that at 221 K the onset of ice formation occurred at an S_{ice}=1.20 (open square in Fig. 8). Furthermore, Abbatt et al. (2006) studied the ice nucleating ability of effloresced ammonium sulfate particles deposited on a hydrophobic support (open circle). These experiments also showed that solid ammonium sulfate could act as efficient ice nuclei. As final evidence that effloresced ammonium sulfate particles were efficient ice nucleators, Abbatt et al. (2006) presented data from Shilling et al. (2006). The Shilling et al. (2006) experiments showed that 1 in 1×10^5 solid ammonium sulfate particles deposited on a plate acted as ice nuclei at S_{ice} values lower than that predicted for homogeneous nucleation (open triangles).

Many groups used a flow tube apparatus similar to the one used in this study to determine the conditions at which ice nucleates from ammonium sulfate particles. Of the experiments presented in Fig. 8, Cziczo et al. (1999) and Wise et al. (2004) used a flow tube system. The results of these two studies were no different than the results of other studies that used different experimental apparatus to study homogeneous ice nucleation. Namely, the conditions in which ice nucleated from ammonium sulfate particles were variable and disagreed with the Koop et al. (2000) homogeneous ice nucleation model. It was shown in Fig. 2 that when the ammonium sulfate particles were preconditioned at 100% RH prior to entering the flow tube system, freezing temperatures agreed with the Koop et al. (2000) homogeneous ice nucleation model. Using the AIM model, S_{ice} was calculated for the ammonium sulfate particles preconditioned at 100% RH (vertical bowties in Fig. 8) and the values do agree well with Koop et al. (2000). Similarly, the AIM model was used to calculate S_{ice} for ammonium sulfate particles preconditioned at RH values <100% RH (horizontal bowties in Fig. 8) and the values do not agree well with Koop et al. (2000). This finding supports the hypothesis of Abbatt et al. (2006) that a small fraction of effloresced ammonium sulfate particles were present in the flow tube although it was not detected in the IR spectra.

Finally, our S_{ice} values for depositional ice nucleation onto solid ammonium sulfate particles compare well with the few other data points available. For example, the data agrees well with that of Abbatt et al. (2006) and Shilling et al. (2006). Therefore, this study agrees with previous studies in that solid ammonium sulfate is an efficient ice nucleus.

4 Conclusions

Three different types of ice nucleation experiments were performed using ammonium sulfate particles in the flow tube apparatus. In the first type of experiment, a water bath (100% RH) was first used to precondition the aerosol particles exiting the atomizer. Following the water bath the particles were passed over a secondary bath which reduced gas phase water, but did not remove enough water vapor to effloresce the particles. Thus all particles entering the flow tube system were deliquesced. In the second type of experiment, sulfuric acid baths ranging in composition from 35% to 98% (50% to <10% RH) were used to precondition the aerosol particles exiting the atomizer. Although effloresced particles were not detected in the IR spectra, it was inferred that the preconditioning baths in this configuration did effloresce some particles. In the third type of experiment, two 98 wt% sulfuric acid baths (<10% RH) were used to ensure the atomized ammonium sulfate particles were effloresced prior to entering the flow tube system.

Different freezing conditions were realized depending on the type of ice nucleation experiment performed. It was found that when a small fraction of effloresced particles were allowed in the flow tube system, ice nucleated at warmer temperatures and lower S_{ice} values than predicted using the Koop et al. (2000) homogeneous ice nucleation model. Conversely, when the particles were fully deliquesced, ice nucleated at temperatures and S_{ice} values in agreement with the Koop et al. (2000) model. Finally, when all the particles were effloresced, ice depositionally nucleated on the particles at conditions similar to those seen by in agreement with measurements performed by Abbatt et al. (2006) and Shilling et al. (2006).

The experiments performed here using the flow tube apparatus show that effloresced ammonium sulfate particles affect freezing conditions. The experimental results confirm the Abbatt et al. (2006) hypothesis that a small fraction of effloresced ammonium sulfate particles induce ice nucleation at temperatures warmer than expected . Therefore, the major discrepancies in ammonium sulfate freezing temperatures reported in the literature can be explained by including depositional nucleation as a pathway ice formation which was previously thought to be solely homogeneous nucleation.

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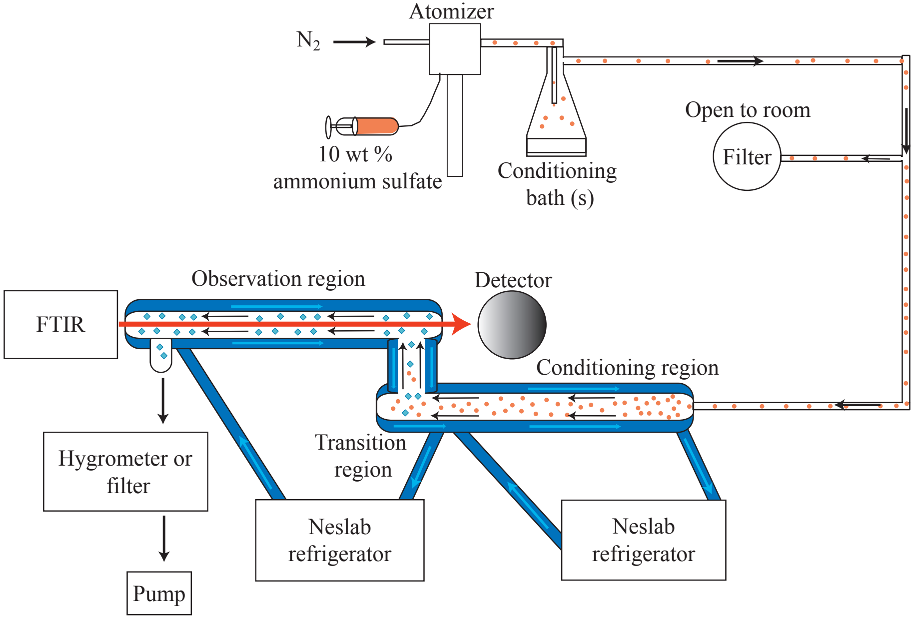

Fig. 1. Experimental setup used for measuring ice nucleation. Ammonium sulfate particles were generated using a TSI atomizer, were passed over conditioning baths, and entered a series of temperature controlled flow tubes. The first set of flow tubes were covered with ice. The water vapor pressure created by the ice was used to set aerosol composition for the homogeneous nucleation experiments and was used to create a supersaturation of water vapor for the depositional nucleation experiments. Ice nucleation was measured using Fourier transform infrared spectroscopy (FTIR) in the observation region. At the onset of depositional ice nucleation, the particle flow was stopped and water vapor pressure was measured using a chilled mirror hygrometer. For all other experiments a filter was used to remove particles prior to entering the pump.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀▮
▶▮
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

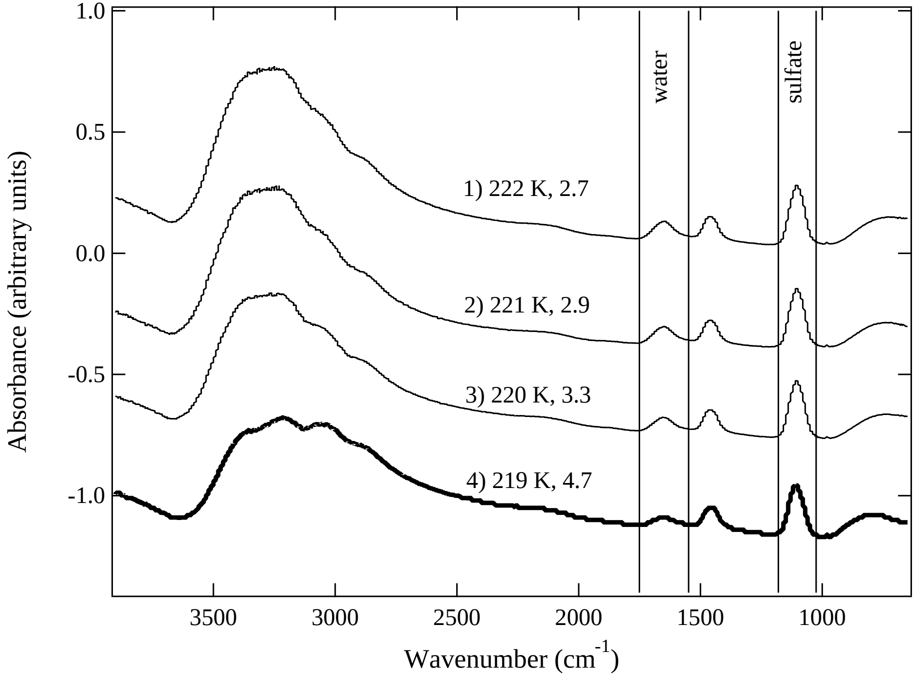

Fig. 2. IR spectra of aqueous ammonium sulfate particles (preconditioned using a distilled water bath) as the temperature was dropped in the observation region from 222 K to 219 K. The onset of ice nucleation occurred at 219 K and caused a substantial increase in the sulfate to water peak area ratio (4.7, peaks highlighted with vertical lines). The spectrum in which ice is present is denoted with a thicker line and all spectra are offset for clarity.

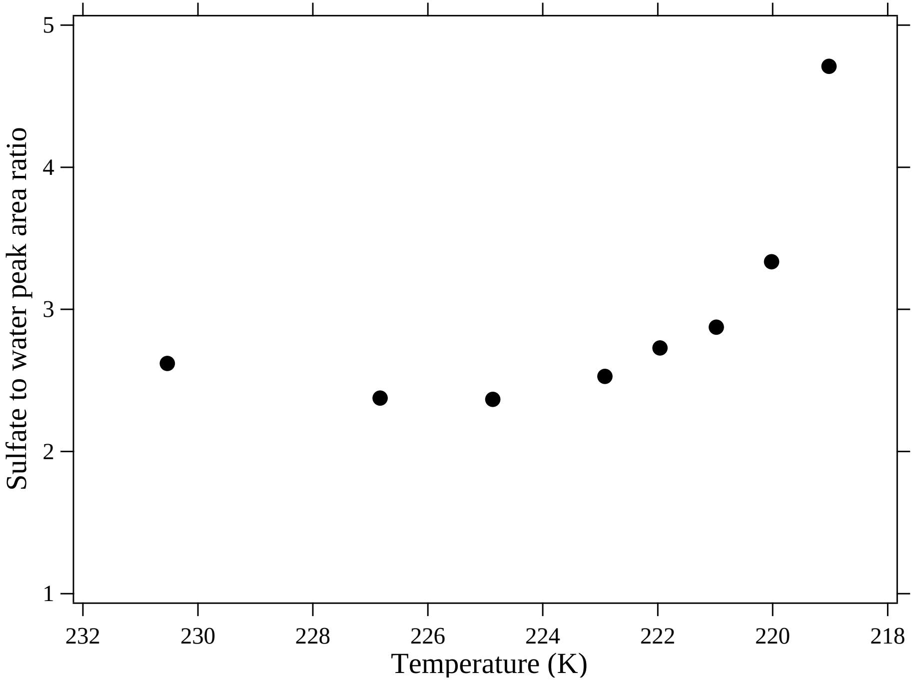

Fig. 3. Sulfate to water peak area ratio versus temperature for the homogeneous ice nucleation experiment described in Fig. 2. At 219 K, a significant increase in the peak area ratio occurred which signaled the onset of ice formation.

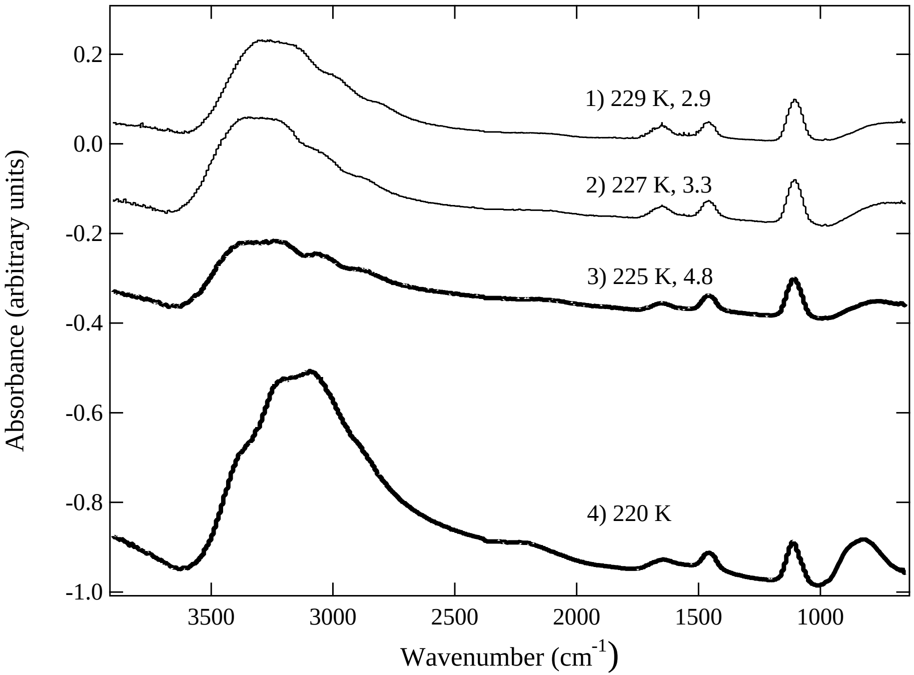

Fig. 4. IR spectra of aqueous ammonium sulfate particles (preconditioned using 98 and 45 wt% sulfuric acid baths) as the temperature was dropped in the observation region from 229 K to 220 K. The onset of ice nucleation occurred at 225 K and caused a substantial increase in the sulfate to water peak area ratio (4.8). As the temperature of the observation region was dropped to 220 K, ice features became more prominent. The spectra in which ice is present are highlighted with thicker lines and all spectra are offset for clarity.

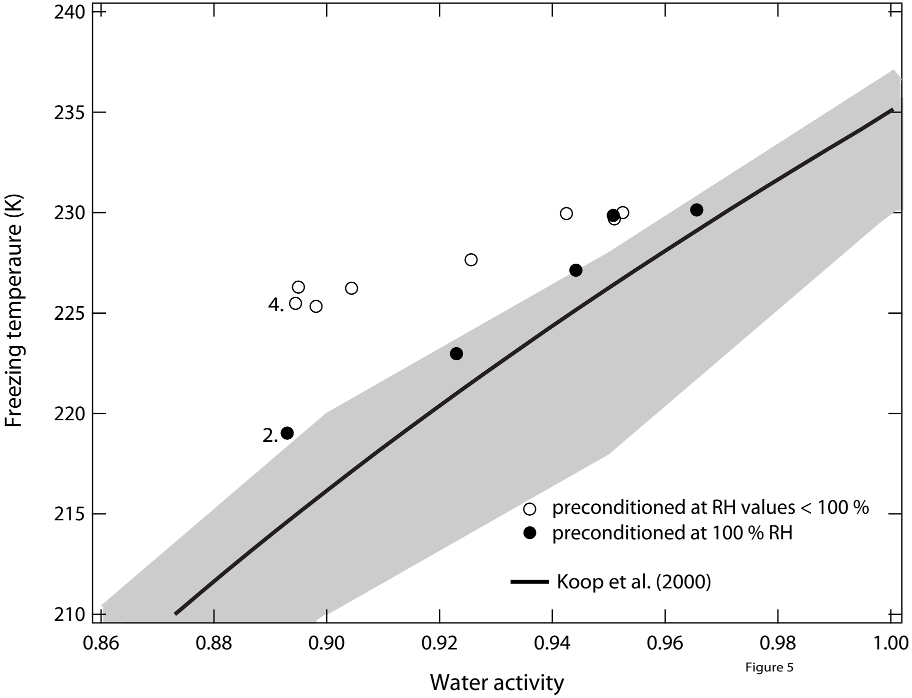

Fig. 5. Freezing temperature versus water activity for ammonium sulfate particles preconditioned at RH values <100% (open circles) and preconditioned at 100% RH (filled circles). For comparison, freezing temperatures predicted using the water activity based nucleation theory developed by Koop et al. (2000) are shown as a solid line. The spread in the data points used to construct the solid line is represented by the shaded area. The IR spectra shown in Fig. 2 were used to produce the point highlighted with the "2" and the IR spectra shown in Fig. 4 were used to produce the point highlighted with the "4".

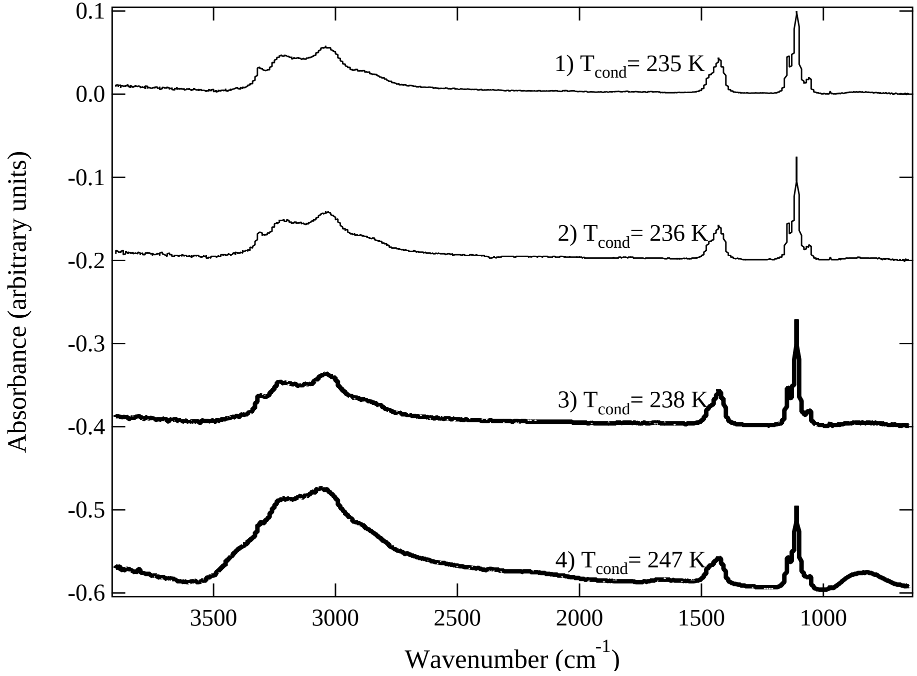

Fig. 6. IR spectra of effloresced ammonium sulfate particles (preconditioned using two 98 wt% sulfuric acid baths) as the temperature was raised in the conditioning region from 235 K to 247 K. The observation region was held at a constant 215 K. The onset of ice nucleation occurred when the conditioning region temperature reached 238 K. The spectra in which ice is present are highlighted with thicker lines and all spectra are offset for clarity.

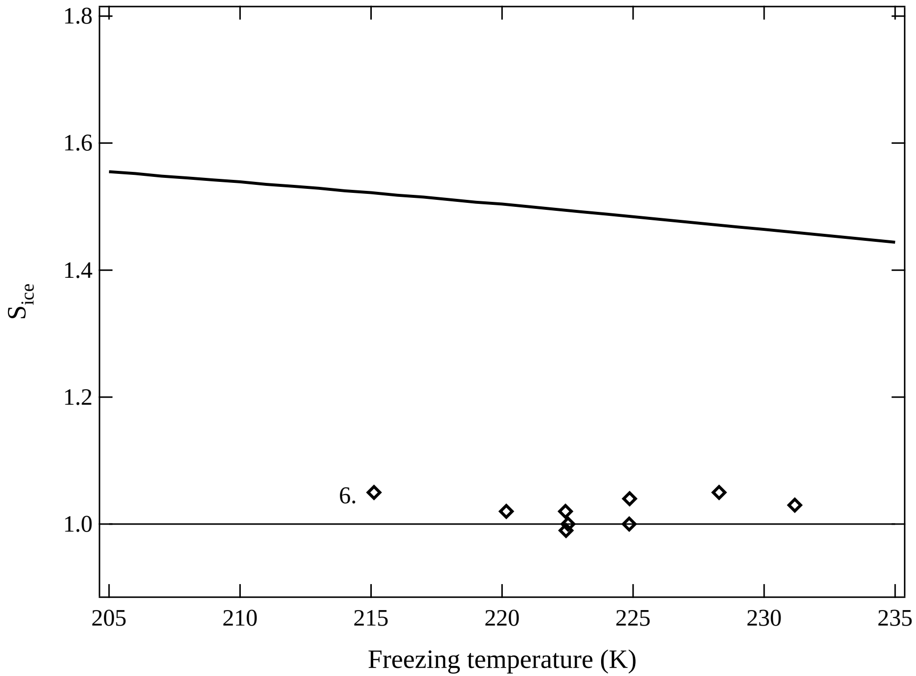

Fig. 7. Ice saturation ratio S_{ice} as a function of freezing temperature for heterogeneous ice nucleation onto solid ammonium sulfate particles in this study (open diamonds). The thick solid line represents the homogeneous ice nucleation model developed by Koop et al. (2000) and the thin solid line is an S_{ice} of 1. The IR spectra shown in Figure 6 were used to produce the point highlighted with the “6”.

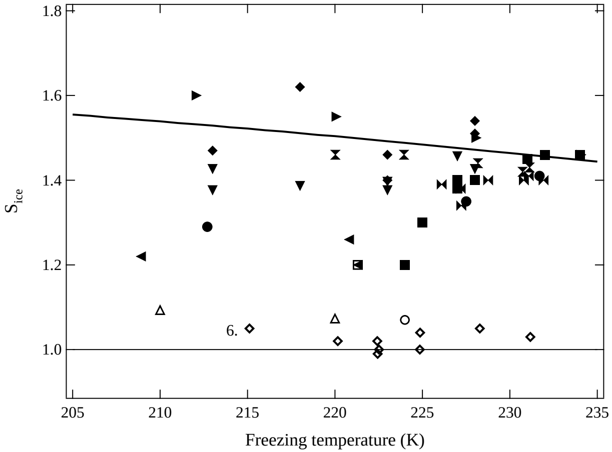

Fig. 8. Ice saturation ratio S_{ice} as a function of freezing temperature for ammonium sulfate particles (adapted from Abbatt et al., 2006). The solid symbols represent conditions for homogeneous ice nucleation: Cziczo and Abbatt (1999) (squares); Wise et al. (2004) (circles); Bertram et al. (2000) (right pointing triangles); Chen et al. (2000) (0.1% freezing, down pointing triangles); Chen et al. (2000) (1% freezing, diamonds); Mangold et al. (2005) (left pointing triangles). The bowties represent conditions for the ice nucleation experiments presented in Fig. 5 of this study: preconditioned at 100% RH (vertical bowties); preconditioned at <100% (horizontal bowties). Open symbols represent conditions for depositional nucleation: Abbatt et al. (2006) (hydrophobic support, circles); Abbatt et al. (2006) (particles formed at less than 10% RH in a cloud chamber, square); Shilling et al. (2006) (hydrophobic support, triangles); this study (freely floating particles, diamonds). The thick solid line represents the homogeneous ice nucleation model developed by Koop et al. (2000) and the thin solid line is an S_{ice} of 1. The IR spectra shown in Fig. 6 were used to produce the point highlighted with the “6”.