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Adsorption of Ammonia on Soot at Low Temperatures

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Ammonia is arguably the most important alkaline trace species in the atmosphere. In addition to major ammonia sources on the ground, ammonium has been observed in aircraft exhaust that injects ammonia or ammonium directly into the upper troposphere. If ammonia adsorbs to a soot surface, then reactions in the troposphere between ammonia and other trace gases may be facilitated by soot particles. We examined the uptake of ammonia on *n*-hexane soot using transmission Fourier transform infrared spectroscopy to quantify the uptake of the gas on soot particles between 115 and 173 K and up to 0.1 Pa (10^{-3} Torr) NH_3. At temperatures above 173 K, we see virtually no adsorption of ammonia on soot for NH_3 pressures up to 0.1 Pa (10^{-3} Torr). Between 115 and173 K we find that, upon exposure to the soot, some ammonia sticks rapidly while additional ammonia adsorbs more slowly to the soot. For fast adsorption, the uptake coefficient ranges from $\sim 0.02 \pm 0.01$ at 115 K to $\geq (1.5 \pm 0.8) \times 10^{-4}$ at 153 K. The amount of rapid uptake of NH_3 on soot follows the shape of a Langmuir adsorption isotherm. On the heterogeneous soot surface, this simple uptake behavior implies that ammonia adsorbs to soot onto a group of sites with similar binding characteristics. Between 123 and 153 K the saturation coverage is roughly 0.1 monolayer with a binding energy of 24 ± 1 kJ/mol. At 115 K up to a full monolayer adsorbs with roughly 21 kJ/mol binding energy. Ammonia adsorption on soot is not likely to be significant at temperatures and ammonia partial pressures found in the troposphere.

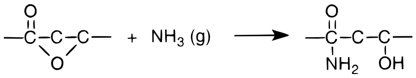
1. Introduction

In recent years, there has been considerable interest in the chemical effect of soot particles in the atmosphere.[1−13] Most atmospheric soot is produced at ground level by fossil fuel and biomass combustion.[14] Aircraft exhaust can inject soot directly into the upper troposphere and sometimes into the lower stratosphere.[14,15] The effect of the soot on the chemical balance and the aerosol distribution of the upper troposphere and lower stratosphere is a matter of great concern.

Much recent interest in gas−soot reactions has focused on nitrogen oxides and nitric acid.[1−11] Longfellow et al.[1] found that HONO was produced from NO_2 and H_2O on methane, propane, hexane, and kerosene soots (at 262, 263, and 296 K). Kalberer et al.[10] found that NO_2 reacted with the surface of suspended soot particles in the presence of water to produce HONO (room temperature, 2−115 ppb of NO_2). Gerecke et al.[2] and Kleffmann et al.[11] observed similar results with NO_2 producing HONO and NO on various soots (room temperature). Rogaski and Williams[4] found that NO_2 is reduced to NO on black carbon (Degussa FW-2, room temperature), while HNO_3 is reduced to NO, NO_2, and H_2O. Chughtai et al.[5,6] found that NO_2 adsorbs irreversibly on *n*-hexane soot while NO physisorbs nonreactively (room temperature, ppm levels of NO_2 and NO in “zero-air”). Choi and Leu[3] found that HNO_3 was reduced to NO, NO_2, and H_2O on graphite and black carbon (Degussa FW-2) but not on hexane or kerosene soot (220 and 295 K).

The reactions of nitrogen oxides and nitric acid on soot are very important, as they may impact the NO_x/NO_y ratio. However, few studies have looked at soot interactions with another important nitrogen species, NH_3. Ammonia is the most important alkaline species in the atmosphere. Though its sources are primarily at the ground level with a relatively short lifetime (≥10 days in the lower atmosphere[16]), the mixing ratios of ammonia near the tropical tropopause are only about 1−2 orders of magnitude lower than those near the tropical boundary layer.[17,18] Furthermore, ammonium associated with aerosol particles exists well above the boundary layer. Talbot et al.[19] report episodes of enhanced aerosol-associated NH_4^+ concentrations (150−250 pptv) above 6 km when crustal and anthropogenic material is transported vertically by storms. Ferry et al.[20] recently reported that 10−30% of aerosols measured near 10 km altitude in a commercial aircraft flight corridor consisted of $(NH_4)_2SO_4$ aerosols. This observation indicates that ammonium is not insignificant in the upper troposphere and suggests that the interaction of ammonia with soot in this region may be interesting. Furthermore, gas/surface interactions are enhanced at the lower temperatures of the upper troposphere. Thus, ammonia in the upper troposphere may interact with soot even if the ammonia partial pressure is rather low.

Chughtai et al.[5] have measured the uptake of ammonia on *n*-hexane soot at room temperature. They find that the uptake of ammonia is nearly independent of ammonia concentration for concentrations between 17 and 68 ppm, yielding a coverage of about 1.2% (about 210 μg of NH_3 per gram of soot) at room temperature. From FTIR studies, they believe that the NH_3 may adsorb via reactions such as



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to produce amide, alcohol, and phenol functionalities. Their EPR studies at room temperature suggest that NH_3 alone does not affect the EPR signal from the soot. Experiments with simul-

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taneous O_2 and NH_3 exposure on soot indicate that these two species adsorb competitively, at least in the ranges 5−25 Torr of O_2 and 12−250 Torr of NH_3.

The present study is motivated by the question of whether significant numbers of soot-surface adsorption sites are available to and are occupied by ammonia below room temperature with ammonia partial pressures close to those found in the atmosphere. We studied the uptake of ammonia on *n*-hexane soot at low temperatures using transmission FTIR spectroscopy to measure the amount of ammonia sticking to the soot as a function of ammonia pressure and soot temperature. At ammonia pressures in the range from 3×10^{-5} to 0.2 Pa (3×10^{-7} to 1×10^{-3} Torr), the ammonia signal was easy to see for soot temperatures between 115 and 153 K. Below 115 K, solid (bulk) ammonia formed at NH_3 pressures above 10^{-3} Pa (7×10^{-6} Torr), while above 173 K, the ammonia signal was too small for reliable measurements. We saw no clear evidence of chemical reactions between NH_3 and soot and between NH_3, trace H_2O, and soot with the infrared spectrometer. Although these temperatures are below those prevalent in the upper troposphere and lower stratosphere, our experiments complement the existing information at room temperature to aid in estimating what may be happening at atmospheric temperatures.

2. Experimental Section

The apparatus and experimental procedures are similar to those used in our previous study of the interaction of sulfur dioxide with soot and are described in detail in the work of Koehler et al.[13] In an adaptation of the method of Akhter et al.,[8] we generate soot by burning 5 mL of *n*-hexane (Aldrich, 99%) with an open flame in a 50-mL beaker. The smoke is directed through an inverted funnel, passes through an aluminum mesh (mosquito screen) that partially quenches the flame, and collects on a germanium wafer. The entire setup is enclosed in a wooden box with small vents to minimize drafts from the room. We allow the *n*-hexane to burn for 105 s and then collect the soot for 50 s. As soot production is a chaotic process, we often have to make several films to get the proper thickness. Our criterion for an acceptable film is an absorbance of 0.27 ± 0.2 at 4000 cm^{-1}. The germanium wafer onto which we collect the soot is 1-in. diameter, 1-mm-thick polycrystalline Ge, and we coat both sides. The Ge is cleaned with acetone and methanol before soot deposition, but the native oxide layer on the germanium is not removed. We examined the cross section of the soot layer with a scanning electron microscope by breaking the soot substrate in half. The SEM images indicate that the soot consists of small particles, roughly 0.1 μm in diameter, forming thin films of 14 ± 4 μm on both sides of the germanium support.[13] Based on studies done in the Smith laboratory,[8,21] the soot consists principally of graphitic sheets with a variety of organic functional groups around the outside. From the mass of our soot film and surface area measurements made by researchers in the Smith laboratory,[8,21] we estimate that our total surface area is 80 times the geometrical area if we include the area inside the pores within each soot particle, but only 35 times the geometric area if one counts only the area on the outside of the spherical particles. Furthermore, as will be described below, we doubt that the ammonia penetrates all the way through the soot layer, and so the effective surface area is even less.

The soot-covered germanium wafer is mounted in the center of a vacuum chamber, base pressure 10^{-5} Pa ($<10^{-7}$ Torr). Ammonia enters the chamber through a variable leak valve and is pumped by a turbomolecular pump. The primary probe is a Nicolet Protégé 460 Fourier transform infrared spectrometer used in transmission mode. We collected 24 scans per spectrum at 8 cm^{-1} resolution, at a rate of 5 scans/min for "series" scans. The soot is nearly transparent in the infrared; thus, the absorption spectrum is sensitive primarily to the amount of NH_3 adsorbed on the soot surface. A Stanford Research System RGA300 monitors the purity of the gases inside the vacuum chamber to ensure that we have little or no background water vapor. The soot is cooled with liquid nitrogen and the temperature controlled by resistive heating, measured by a type-T thermocouple glued to the germanium. Pressure measurements from an ionization gauge, the mass spectrometer, and an MKS pressure transducer ("Baratron") have an estimated absolute uncertainty of 30% but a relative precision of about 10%.

To calibrate the IR signal, we first grew bulk thin films (a few micrometers thick) of ammonia on a flat, clean germanium surface. By monitoring the thin-film interference at a nonabsorbing wavelength (4185 cm^{-1}) and using 1.41 for the index of refraction,[22] we measured the thickness of each film. From the thickness, we determined a calibration factor of 4.0×10^{-8} m per integrated absorbance unit for the 1100 cm^{-1} absorption peak of ammonia. X-ray diffraction studies of ammonia at 77 K show that there are four ammonia molecules per cubic unit cell of 5.084 Å.[23] From this, we can establish a surface density of 9.70×10^{14} molecules/cm^2 and can then convert our IR absorbance measurements into ammonia surface coverages. The interpretation of the surface coverage is detailed in section 3.4 below. The calibration assumes that the optical density is the same for sub-bulk and for bulk ammonia for the 1100 cm^{-1} peak, which is not necessarily true, but likely to be correct to within at least a factor of 2. Ferraro et al.[24] determined that the ν_2 band of ammonia (around 1050−1100 cm^{-1}) changes shape slightly between the liquid, a cold-temperature amorphous phase, an intermediate-temperature metastable phase, and the crystalline phase. However, they report that the integrated peak intensities for these four forms of NH_3 are 100, 128, 146, and 125 cm^{-1}/(mol cm^{-2}), respectively. Thus, the variation in all condensed forms is within 50%, and within the solid forms the integrated intensity varies by less than 20%. Furthermore, for our study, any difference in extinction coefficient between the two films affects our measurement of coverage (which has other, larger uncertainties) but does not affect the determination of the ammonia binding energy (as long as the extinction coefficient is not strongly temperature dependent for the submonolayer soot).

During a typical experiment to measure the submonolayer adsorption of ammonia on soot at various pressures and temperatures, we expose the soot to ammonia for 6 min, evacuate the ammonia and wait 4 min, and then heat the soot briefly to 183 K to evaporate any residual ammonia from the soot. As will be discussed below, we focus our attention primarily on the amount of NH_3 that adsorbs rapidly to the soot, i.e., within the first 5−20 s.

As a blank control experiment, we exposed the clean germanium substrate to ammonia vapor under conditions mimicking those of a typical experiment for ammonia on soot. Unfortunately, we did see a small ammonia adsorption signal in these blank experiments. As a further test of the affinity of germanium to ammonia, we coated a germanium wafer with a thin film of gold (visible by eye but transparent in the infrared, so most likely in the range of tens of nanometers). This gold-coated germanium proved to adsorb even more ammonia than clean germanium. This large adsorption can be explained by ammonia's affinity for the gold surface and by the fact that the gold film has a high surface area because a gold film formed by evaporation consists of columnar structures of gold atoms.[25] We also tried ammonia adsorption on silicon but found that it, too, adsorbs ammonia. Note that both the germanium and silicon wafers have a surface coating of a native oxide. An experiment without a substrate in the chamber showed no ammonia signal in the IR, indicating that ammonia is not adsorbing to the NaCl windows of the vacuum chamber. We did not use NaCl as a substrate for our soot because it is not a good thermal conductor, and we wanted to be able to heat and especially cool the soot fairly quickly to minimize the time for background water to adsorb.

3. Results and Discussion

3.1. Infrared Measurements of Bulk and Submonolayer Ammonia on Soot. When the cold soot film is exposed to ammonia, either bulk, solid ammonia may form or ammonia molecules may adsorb to the soot surface in submonolayer quantities. Bulk condensation occurs for pressures over 5×10^{-4} Pa (4×10^{-6} Torr) with a temperature of 115 K or for pressures above 4×10^{-3} Pa (3×10^{-5} Torr) for 123 K. At higher temperatures and/or lower pressures, smaller amounts of ammonia adsorb to the surface corresponding to less than a full monolayer, with the exact amount dependent on the specific conditions.

We had hoped to measure the uptake of ammonia at temperatures relevant to the troposphere and lower stratosphere. However, with a maximum pressure of ammonia of 0.1 Pa (10^{-3} Torr) for our apparatus, we were not able to detect adsorbed ammonia above 173 K. Therefore, we concentrated our measurements at lower temperatures where enough ammonia adsorbs to produce usable signals. Our aim is thus to contribute lower-temperature measurements to complement other studies of ammonia uptake on soot at room temperature.

The infrared spectrum taken at 8 cm^{-1} resolution of ammonia adsorption on soot is shown in Figure 1a with a clean soot layer used as the background. We see two clear adsorption peaks, one at 1100 cm^{-1} corresponding to the ν_2 mode and another near 3400 cm^{-1}, probably the ν_3 asymmetric stretch or smearing of the ν_1 and ν_3 modes that are not well distinguished for submonolayer adsorption of ammonia on soot. Assignments are based on data for crystalline NH_3 presented by Ferraro et al.[24] and references therein for amorphous NH_3. We do not expect our IR peaks to be as sharp as they would be for bulk crystalline ammonia. Because the ammonia molecules are in contact with the soot surface and the soot surface has a varied chemical structure, the ammonia molecules have a variety of environments leading to inhomogeneous broadening of the ammonia peak. The ν_4 mode should appear around 1600 cm^{-1}, but it is too small to be resolved clearly. The entire baseline slopes very slightly upward toward higher energy due to Mie scattering by the underlying soot layer that is not perfectly canceled by the sloping baseline in the background file of soot without ammonia.

Because the peak near 3400 cm^{-1} experiences slight fluctuations from trace water and is in a region of the spectrum where the baseline is more influenced by Mie scattering, we chose to use the ν_2 peak at 1100 cm^{-1} for quantitative studies of the ammonia uptake. Figure 1b shows a close-up view of the 1100 cm^{-1} peak for both bulk and submonolayer quantities of ammonia on the soot surface. As expected, the absorption band becomes much sharper for the bulk, presumably polycrystalline ammonia. We saw no clear evidence of chemical reactions between NH_3 and soot in the infrared spectra. Occasionally there was some water vapor in the chamber, but even with small amounts of water, we saw no clear signs of chemical reactions between NH_3, H_2O, and soot in the infrared spectra.

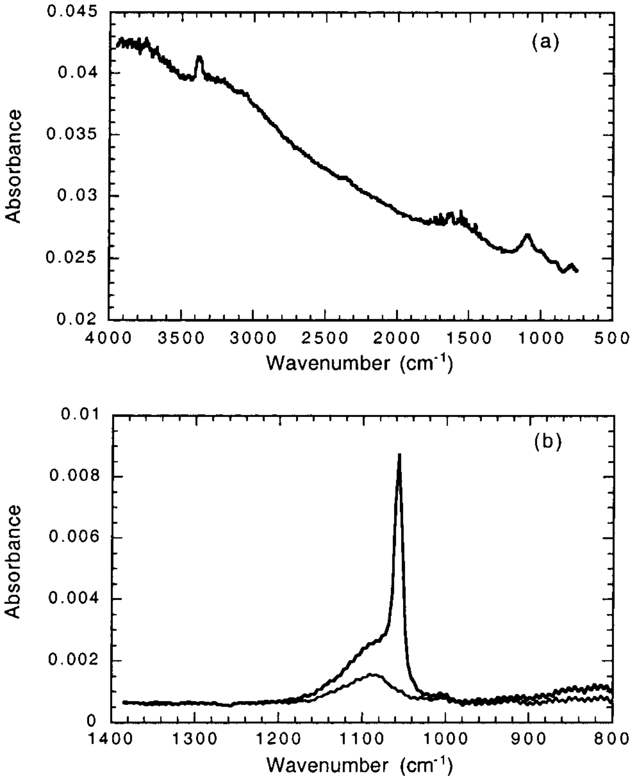

Figure 1. (a) Infrared spectrum of roughly 0.7 ML ammonia adsorbed on soot at 115 K. The broad peak near 3200 cm^{-1} is from trace water adsorption, while the absorptions at 1400−1800 and 3600−4000 cm^{-1} are from trace water vapor outside the vacuum chamber. (b) Close-up of the absorbance peak near 1100 cm^{-1} for both submonolayer (lower trace) and bulk ammonia (upper trace) on soot. The background IR scan for all three spectra is that of a clean soot film.

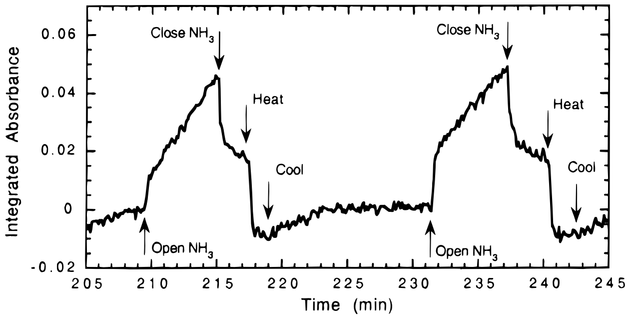

Figure 2. Uptake and desorption of ammonia on soot at 133 K as measured by the integrated absorbance of the 1100 cm^{-1} peak during a typical experiment (using clean soot as the reference). At 209 min, 5×10^{-3} Pa of ammonia is introduced into the chamber for 6 min. At 217 min, the soot surface is heated to 183 K for 2 min to completely remove the residual ammonia and then cooled again to 133 K by 228 min. At 231 min, the ammonia is again introduced into the chamber for a second dose cycle.

3.2. Rapid and Slow Uptake. When we expose the soot to ammonia, we see two modes of adsorption. Initially, ammonia adsorbs rapidly (on the order of seconds). Subsequently, more ammonia adsorbs slowly, with no sign of saturation over 30 min. Figure 2 shows typical time sequences for these experiments. The left vertical axis is the amount of ammonia adsorbed on the soot as measured by the integrated area of the 1100 cm^{-1} IR absorption peak. At 209 min, 5×10^{-3} Pa (4×10^{-5} Torr) ammonia was introduced into the chamber. Ammonia adsorbs rapidly for the first 20 s and then slowly for minutes. We focus mostly on the ammonia rapidly adsorbed at 209−210 min (and at 231−232 min). When we evacuate the ammonia gas after a dose, some of the adsorbed ammonia evaporates rapidly (seconds), some desorbs slowly (minutes), and some remains on the surface (stable for over 30 min) until we heat the soot. For experiments at the coldest temperatures (115 or 123 K), a smaller fraction of the ammonia desorbs rapidly without heating compared to what is observed at warmer soot temperatures. Though our FTIR scan rate does not give us time resolution for the rapid uptake, we can quantify the amount of rapid and slow uptake readily.

The first one or two ammonia doses on a new soot film give roughly 50% more "rapid" ammonia adsorption than subsequent doses. Somehow, these first doses partially passivate the soot surface. After these doses, a very small peak near 1100 cm^{-1} and a tiny peak at 1280 cm^{-1} are observable that do not disappear, even upon raising the reaction temperature to 183 K. These peaks are also observed, together with a peak at 800 cm^{-1}, when ammonia is adsorbed to soot at room temperature.[5] At room temperature overnight, the small peaks fade but the passivation effect largely remains. A study of NO_2 uptake on hydrocarbon soot to form $HONO_{(g)}$ found that at low relative humidity the reactivity was much higher (by a factor of 2−3) on fresh soot compared to that on soot that had been exposed to NO_2.[1]

We performed all of our isothermal uptake experiments on a passivated soot film, in part because we did well over 100 uptake experiments, and each new soot film requires a 1−2-day turnaround to make the soot film and to pump out the system. Using a passivated soot film gave us two advantages. Most importantly, we were able to perform most of the experiments on the same soot film for greatest consistency. Furthermore, since the passivation effect is irreversible even upon raising the temperature to room temperature at 10^{-7} Torr, the chemistry involved in passivation is less likely to be involved in reactions where the soot has the largest impact on the chemical balance of the air. For atmospheric effects, reactions that do not consume reactive sites on the soot surface are more likely to have a significant impact compared to reactions on soot that happen only once at each surface site.

As mentioned in the Experimental Section, we saw an ammonia adsorption signal when we exposed the germanium support, without soot, to ammonia vapor. However, the amount of ammonia adsorbing to the germanium is roughly a factor of 2 or 3 less than the "slow adsorption" on the soot-coated germanium. Furthermore, on germanium we only saw clear signs of "slow adsorption", but not the combination of "rapid" and "slow" adsorption we see on soot-coated germanium. Since ammonia adsorption on the clean germanium surface is not identical to that on the soot-coated germanium surface, we can assert that ammonia is interacting with the soot film on the germanium. The uptake coefficient, discussed in section 3.3 below, for slow adsorption is about 3 times higher for soot-coated germanium compared to clean germanium (using the geometrical surface area for the substrate).

Two possible scenarios for ammonia's interaction with the soot-coated germanium must be considered. First, the ammonia may interact with both the germanium surface and the soot film. While it is difficult to rule out this explanation completely, further experiments point to a second possibility. This second option is that ammonia will adsorb to clean germanium but does not reach the germanium at all when there is a 14 ± 4 μm coating of soot on the germanium. The primary evidence for this second mechanism comes from ammonia uptake experiments on two soot films of different thicknesses. If the ammonia penetrated through the soot to the germanium, we should see more uptake on a soot film that is twice as thick. However, that is not the case, neither for fast nor for slow adsorption. This finding is consistent with the ammonia interacting directly with the soot but not penetrating all the way through the soot film and allows us to discount the germanium blank signal. Our observation parallels that of Longfellow et al.,[1] who found that the uptake of NO_2 by soot was independent of the amount of soot present, suggesting that the NO_2 penetrated only partially into the soot. Furthermore, since the "rapid" ammonia adsorption is not generally observed on a clean germanium surface but is always present on the soot-coated germanium, we feel confident that we can interpret all of the "rapid" adsorption on the soot-coated germanium to be attributable to adsorption on the soot itself. In the isothermal experiments described below, we focus primarily on the amount of ammonia that is rapidly adsorbed to the soot.

The distinction between fast and slow adsorption of a gas on soot is not new. Chughtai et al.[5] saw rapid uptake of SO_2 on *n*-hexane soot followed by slower uptake. We also observed similar behavior with SO_2 on soot but with some significant differences from the NH_3 system as well.[13] In the case of sulfur dioxide, the amount of gas that adsorbed rapidly was always equal to the amount that desorbed rapidly after the gas was removed. Similarly, the slowly adsorbed SO_2 also desorbed slowly without the soot being heated. The transition between fast and slow adsorption was very sharp. We interpret the rapid SO_2 adsorption as SO_2 uptake on the outside of the soot particles including soot particles throughout the 14 ± 4-μm-thick film. (The amount of rapidly adsorbed SO_2 was directly proportional to the thickness of the soot layer for experiments with thicker and thinner soot films.) The slow adsorption and desorption likely correspond to SO_2 diffusing in and out of the pores within the soot particles.

In the case of ammonia adsorption on soot, we also see fast and slow adsorption. Thus, one explanation for rapid and slow adsorption of ammonia on soot is that rapid adsorption corresponds to ammonia adsorption on the outer surface of the soot spheres and that slow adsorption corresponds to diffusion into the pores within the soot particles. Based on the total amount of rapidly adsorbed NH_3, the rapid adsorption must correspond not only to adsorption to the top surface of the soot film, but also to the outer surface of the soot spheres inside the film. If the rapid ammonia adsorption were only onto the outer surfaces of the soot, we would be seeing about 20 monolayers of ammonia outside of the bulk condensation regime.

While the above interpretation is appealing for its simplicity and analogy with other soot studies and may be correct, some evidence points to a slightly more complex mechanism. Unlike the case for SO_2, rapid and slow adsorptions of NH_3 are not quantitatively reversible. At warmer temperatures and higher pressures, more ammonia desorbs rapidly than adsorbs rapidly. (Thus, at least some of the slowly adsorbed ammonia must desorb rapidly.) At colder temperatures and lower pressures, rapid adsorption is larger than rapid desorption. Thus, rapid adsorption and rapid desorption might not correspond to adsorption sites separate from those involved in slow adsorption and slow desorption. One possible explanation is that fast adsorption corresponds to adsorption on acidic functionalities on the surface. In this case, one would expect these sites to be very strongly bonding and perhaps correspond to the slow desorption. However, this simple explanation is not likely since we observed more rapid adsorption if we did not heat the soot between doses, leaving the most tightly bound ammonia on the soot. If the rapidly adsorbed ammonia was adsorbed strongly to acidic functional groups, we would expect these to remain filled if the soot was not cleaned by heating, and so less ammonia should adsorb rapidly when there is no heating between doses.

Another possible explanation for rapid and slow adsorption is that both may occur at the same region, but the surface coverage may affect the uptake characteristics. At higher coverage, the dipole of the ammonia molecule may affect the electron density of a nearby surface site and change that site's affinity for the next ammonia molecule.[26] Thus, rapid adsorption may correspond to unhindered adsorption onto a nearly empty surface and slow adsorption may correspond to ammonia adsorption hindered by the presence of a nearby adsorbed ammonia molecules. The rapid desorption may largely consist of desorption from ammonia that is tightly crowded together and thus weakly bound. Indeed, the amount of ammonia that desorbs rapidly increases as the time for ammonia adsorption (and consequently the coverage) is increased.

The mechanisms suggested above all indicate that fast adsorption is almost certainly adsorption on the surfaces of the soot particles. Further experiments may be needed to assist in determining a satisfactory explanation for the slow adsorption of ammonia on soot. Thus, we focus primarily on fast uptake in this study. In analogy with the behavior of SO_2 on soot, we suspect that all of the rapidly adsorbed ammonia is sticking to the surface of the soot particles, including interstitial spaces, but not diffusing into pores within the soot particles. Unlike the case with SO_2, the amount of rapidly adsorbed ammonia is not doubled when ammonia is adsorbed on a doubly thick soot layer, and so we do not suspect that the ammonia is able to rapidly diffuse throughout the soot layer and does not adsorb on all of the soot particles. Longfellow et al.[1] also report that NO_2 probably samples only a portion of their soot film. As discussed in section 2 above, the total surface area of the outer surfaces of the soot particles is roughly 35 times the geometrical area. If we guess that the ammonia penetrates about halfway through the soot film, then the accessible surface area for ammonia uptake is only about 20 ± 10 times the geometric area. The rapid-adsorption ammonia probably does not penetrate much less than halfway through the soot film, because otherwise our maximum coverages would be more than one monolayer (outside the bulk regime).

3.3. Uptake Coefficient. The fast uptake at most of the temperatures in this study occurred within one or two scans of the infrared spectrometer, too fast for us to measure the rate exactly. Though we did not get detailed data during the fast adsorption, Figure 2 shows that we saw a clear delineation between fast and slow adsorption and can measure the amount of fast adsorption readily. We can use the IR to give an upper limit to the uptake time for fast adsorption, which gives a lower limit to the uptake coefficient.

Using the geometric surface area of the soot, one can calculate the net uptake coefficient simply from the gas pressure, the gas temperature (298 K), and the rate of ammonia adsorbed. We use a net uptake coefficient given by γ_g = (number adsorbed/time)/(number of collisions/time), where the rate of collisions is simply the rate of collisions from the gas phase to a flat surface using $P/(2\pi mkT_{gas})^{1/2}$. This uptake does not take into account the roughness of the surface or multiple internal collisions involved in diffusion into the interstitial spaces. For gas diffusion in the interstitial spaces, the gas temperature is lowered by the cold surface and the uptake coefficient increases, but this correction is less than a factor of 2, and so within the uncertainty.

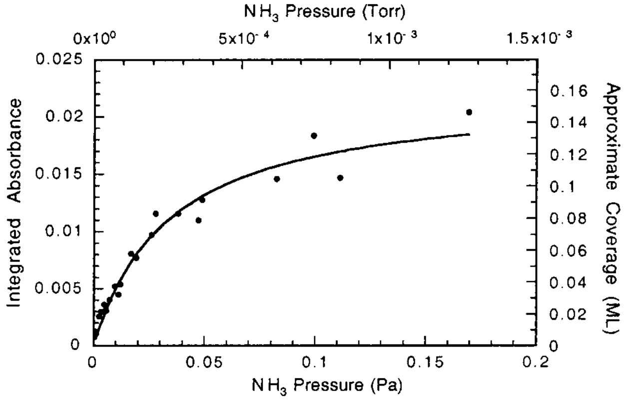

Figure 3. Langmuir isotherm experiment for rapid ammonia adsorption on soot at 153 K. Each data point represents the amount of ammonia that rapidly adsorbs to soot at the indicated pressure. The line is the best fit to the Langmuir isothermal adsorption equation.

Using the geometric surface area of the soot, the uptake coefficient for rapid adsorption ranges from $\gamma_g \geq 0.15 \pm 0.04$ at 123 K to $\geq(3.0 \pm 0.5) \times 10^{-3}$ at 153 K for the lowest pressures. At higher pressures, the measured γ_g decreases by roughly a factor of 10. Even at the lowest pressures, the measured γ_g values are not the *initial* uptake coefficients, but they do represent the lower limit to the initial uptake coefficient. These calculations assume that the geometric surface area is the correct area to use. Since the gas molecules penetrate into the soot, the available surface area is increased by a factor of up to 20 ± 10 by using the outer surface area of the soot spheres and assuming that ammonia penetrates halfway through the film (see discussion in section 3.2 above). Underwood et al.[27] show that γ_g can be corrected by the ratio of the geometric surface area to the BET surface area for very thin films (meaning total accessible surface area) to give the true uptake coefficient. Thus, we estimate that the effect of the total accessible soot surface area is to reduce the uptake coefficient by a factor of 20 ± 10. This estimate gives $\gamma \geq \sim(8 \pm 4) \times 10^{-3}$ at 123 K and $\gamma \geq \sim(1.5 \pm 0.8) \times 10^{-4}$ at 153 K. Because the surface area of a soot film is difficult to quantify, the uptake coefficients in this study have relatively large uncertainties. At 115 K, we see uptake for several scans of the infrared spectrometer and can give a more accurate calculation of $\gamma_g = 0.35 \pm 0.05$ using the geometric surface area at the lowest pressure (2×10^{-5} Pa), and $\gamma \geq \sim 0.02 \pm 0.01$ using the outer surface area of the soot spheres and assuming that ammonia penetrates halfway through the film.

The rate of slow adsorption (averaged over a 6-min period) onto soot is linear with ammonia pressure. There is only a hint of slowing at the highest pressures. From the adsorption rate, one can calculate uptake coefficients of $\gamma_g = 1.5 \times 10^{-3}$ at 123 K and $\gamma_g = 4.0 \times 10^{-5}$ at 153 K using the geometric area of the soot. Because the interpretation of the slow adsorption is not yet clear, we did not attempt to convert these numbers into an uptake coefficient using a corrected surface area. For comparison, the uptake coefficient for slow ammonia adsorption on germanium without soot is about one-third of γ_g for slow adsorption on soot.

3.4. Isothermal Uptake Measurements. Focusing on the rapidly adsorbed ammonia as seen in Figure 2, we measured the amount of ammonia that would rapidly adsorb to soot as a function of ammonia pressure at various temperatures. Figure 3 shows the uptake of ammonia on soot at 153 K. The solid line represents a fit to a simple Langmuir isotherm.[28] Because the soot surface is heterogeneous, one would not expect ammonia uptake to follow a simple Langmuir model. Indeed, our study of SO_2 adsorption on soot[13] showed that SO_2 uptake can be modeled by the sum of three different Langmuir isotherms. Each of the isotherm fits probably represents uptake of SO_2 not on identical sites, but on a group of sites with similar binding characteristics. Likewise, we expect that the uptake of ammonia is not necessarily uptake onto identical sites on the soot, but rather onto a group of sites that have fairly similar binding characteristics and are accessed over the pressure and temperature ranges of our study. It is quite possible, furthermore, that there are other sites that can be filled at higher pressures that would add additional terms to the simple Langmuir isotherm, but these are not observed in our pressure range. At the lowest temperature in our study, 115 K, we see significantly more ammonia adsorption (by a factor of 10) compared to that at the higher temperatures. This coverage clearly indicates the existence of different sites on the soot surface that bind ammonia too weakly to be measurably filled at the warmer temperatures in our pressure range.

While it is unlikely that ammonia adsorption on such a heterogeneous surface is true Langmuir adsorption, the uptake data at each temperature fit the shape of a simple Langmuir isotherm for uptake into sites with similar binding strengths. Thus, we fit the data using a single Langmuir isotherm to obtain a measure of the binding strength and the coverage, as given by

$$\theta = \frac{\beta KP}{1 + KP} \tag{2}$$

Here, θ is the coverage at a given pressure, β represents the number of sites available to be filled at saturation coverage, and P is the pressure of ammonia. K may be viewed as an equilibrium constant derived from the balance between gas uptake (dependent on gas temperature, molecular mass, and accommodation coefficient) and evaporation (dependent on surface temperature, preexponential factor for desorption, and heat of desorption).[13] Both β and K were treated as adjustable parameters in fitting eq 2. θ and β both represent ammonia coverage and may be expressed in a variety of units, such as integrated absorbance of the area of an IR peak, molecules per square centimeter, or monolayer, so long as the same units are used for θ and β. The ratio of θ/β is a measure of the fraction of sites on soot to which ammonia is bound compared to how many sites with similar binding characteristics could accommodate ammonia at saturation.

β is determined in units of integrated absorbance from the raw data. This value can be converted into a coverage in terms of monolayer relative to the actual outer surface area of the soot particles with some assumptions. First, the conversion relies on the calibration between the IR absorbance and the total net coverage in molecules per square centimeter of geometric area as determined by our bulk uptake experiments. Second, the conversion relies on knowing the actual surface area of the soot compared to the geometric area. As mentioned in section 2 above, the total surface area is roughly 80 times the geometrical area,[13] but we do not expect the ammonia to enter the pores within the soot spheres on the time scale of the rapid adsorption. The distinction between the total area of the soot particles and the area of the internal pores within the soot particles decreases the available surface area by a factor of roughly 2.4 based on studies by the Smith group.[21] Moreover, our experiments with ammonia, like those of Longfellow et al.[1] with NO_2, indicate that the gas does not sample the entire thickness of the soot film. We therefore make a guess that the ammonia may penetrate halfway through the soot film during rapid ammonia adsorption. This value is likely to be a reasonable upper limit for the accessible surface area and thus provides a reasonable lower limit to the saturation coverage.

TABLE 1. Parameters Obtained from Fitting the Isothermal Uptake of Ammonia on Soot to the Langmuir Equation

temp (K) (±3)	K from isothermal fit (Pa^{-1})	β from isothermal fit (integrated absorbance)	lower-limit β (ML)[b] (±50%)
173	1.6 ± 1[a]	(0.016)[a]	
153	30 ± 4	0.016 ± 0.001	0.11
143	85 ± 30		
133	500 ± 200	0.018 ± 0.004	0.13
123	2980 ± 550	0.014 ± 0.001	0.10
115	1090 ± 260	0.15 ± 0.02	1.0

[a] Data very scattered and only at low coverage. The value for K was determined by fixing β at 0.016 integrated absorbance to match the β determined at lower temperatures. [b] Lower limit of coverage relative to the total accessible surface area of the soot assuming that ammonia penetrates no more than halfway through the soot film and that ammonia does not penetrate into the pores within each soot particle, as discussed in text.

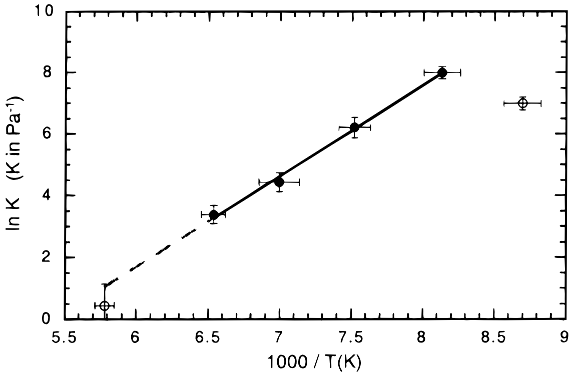

Figure 4. Arrhenius plot of the constant from the fit to the Langmuir isotherm. The solid line represents a fit to the data between 123 and 153 K. The point at 173 K (1000/T = 5.8, open circle discussed in the text) was not used to generate the fit but is connected with the dashed-line extrapolation of the fit. At 155 K (1000/T = 8.7, open circle), much more ammonia adsorbs to soot, indicating that this point represents measurement of adsorption onto sites that are not filled between 123 and 153 K.

Table 1 lists the parameters determined from the isothermal fits for six different temperatures. An Arrhenius plot of the data from 153 to 123 K, Figure 4, gives a clean fit, as shown by the solid line. From the slope, the enthalpy of desorption is 24 ± 1 kJ/mol. This value is reasonable for a weak, physisorption interaction between the ammonia and the soot surface.

At 173 K, the amount of ammonia that adsorbed to the soot was very small, giving signals just barely above the noise, and therefore the data are very scattered. Even at high ammonia pressures, up to 0.2 Pa, we were only able to adsorb 10% as much ammonia as the saturation levels seen at the lower temperatures. Consequently, it was not possible to fit a satisfactory Langmuir isotherm to the data by adjusting both the constant, K, and the saturation coverage, β. However, if we chose to keep the saturation coverage fixed at 0.016 integrated absorbance (the average value observed between 153 and 123 K), we were able to fit the scattered data well enough to determine K to within a factor of 2. This is the open-circle data point at 1000/T = 5.8 in Figure 4. It fits the trend from the other data points surprisingly well. At the coldest end of our temperature range, 115 K, we find adsorption behavior that is not in line with the other data points. Table 1 and Figure 4 show that this K value is lower than one would expect from the temperature trend, and the saturation coverage, β, is nearly 10 times larger.

The value for ΔH_{des} of 24 ± 1 kJ/mol for 123−153 K is in line with weak physisorption of ammonia on the soot. This value is close to a ΔH_{des} of 26 ± 3 kJ/mol measured at 173 K for SO_2 adsorption on soot for most adsorption sites.[13] Some adsorbed SO_2 (about 10%) has a binding energy of 33 ± 3 kJ/mol. A small fraction (<1%) of the soot surface binds SO_2 more strongly, with $\Delta H = 42 \pm 3$ kJ/mol. For the ammonia experiments, we were not able to distinguish between different kinds of adsorption sites at one temperature, even though the surface is heterogeneous and one would expect a variety of binding sites. With our measured saturation coverage of ≥ 0.1 monolayer (ML), only about one-tenth of the surface is participating in ammonia adsorption between 123 and 153 K, probably from a small sampling of relatively similar organic functional groups. In contrast, at the coldest temperature (115 K), we saw uptake to more adsorption sites, in this case with weaker binding. It is likely that these additional weakly binding adsorption sites simply are not stable enough to be observable at the higher temperatures. At 115 K, we are only able to adsorb ammonia to a coverage (θ) that is one-third of the saturation coverage (β) determined from the Langmuir fit because at this temperature submonolayer adsorption is limited to a maximum ammonia pressure of 10^{-3} Pa. At higher pressures, ammonia adsorbs rapidly without bounds in the form of bulk solid ammonia. For the 115 K data, we can estimate $\Delta H_{des} \approx 21$ kJ/mol by assuming an accommodation coefficient of 1 and a lifetime of $\tau = \tau_o\, e^{-\Delta H/RT}$ with $\tau_o = 5 \times 10^{-13}$ s.[13,29] This lower value for the heat of adsorption at 115 K is consistent with weak binding to sites that are not occupied at the warmer temperatures.

In contrast, ammonia adsorbs to Ge(001) and Ge(113) with enthalpies between 80 and 130 kJ/mol.[30] On a water surface, ΔH for ammonia desorption is 41 ± 5 kJ/mol.[31] On gold films, the adsorption energy is estimated to be 56.9 kJ/mol.[25] These three examples all show stronger ammonia−surface interactions, presumably due to the dipole of the ammonia interacting with permanent or induced dipoles at the surface. In contrast, the adsorption sites for ammonia on soot must not have particularly strong dipoles. The model of the soot surface proposed by the Smith group[8,21] indicates that *n*-hexane soot is 87−93% carbon, 1.2−1.6% hydrogen, and 6−11% oxygen. The bulk of the soot consists of graphitic sheets, and roughly 50% of the surface is covered by a variety of carbon−oxygen functionalities and a few C−H or O−H functionalities. Thus, one would expect the surface to have relatively small dipoles, and the interaction of ammonia with soot should be weaker than that with Ge, water, or gold surfaces.

4. Summary and Implications for the Atmosphere

We measured significant uptake of ammonia on soot at low temperatures. Submonolayer ammonia adsorption on soot proceeds in two steps. Initially, ammonia adsorbs rapidly (seconds), while subsequent adsorption proceeds over minutes. The fast uptake probably corresponds to uptake on the outer surfaces of the soot particles. For fast adsorption, the uptake coefficient is ~0.02 ± 0.01 at 115 K and ranges from $\geq 0.008 \pm 0.004$ at 123 K to $\geq (1.5 \pm 0.8) \times 10^{-4}$ at 153 K at the lowest pressures. We focused our study on the rapid adsorption of ammonia. Around 115 K, the saturation coverage is 1.0 ± 0.5 ML. Between 123 and 153 K, the saturation coverage is 0.11 ± 0.05 ML, with a heat of adsorption of 24 ± 1 kJ/mol. Above 173 K, we could not detect ammonia adsorption for pressures up to 1 Pa. At temperatures and ammonia partial pressures typical of the troposphere, ammonia adsorption on soot is not likely to be significant in the absence of acidic coadsorbates on soot.

On the basis of our assessment of the available surface area of our laboratory soot to give coverages, we can extrapolate our surface coverages to atmospheric conditions. Using ammonia mixing ratios of 3.2 ppbv at ground level for the free troposphere,[32] we predict ammonia coverages of about 10^{-7} ML on soot particles from our data on rapid adsorption. Even in heavily polluted air at ground level with 10−100 ppb,[33] the projected ammonia coverage is around 10^{-6} ML. As a comparison, Chughtai et al.[5] measured a coverage of 1.2% at room temperature for 17−68 ppm ammonia. At 3−100 ppb, their data predict coverages of at least 5×10^{-7}−7×10^{-5} ML. Thus, extrapolating our data to room temperature agrees fairly well but gives a value even a little lower than that from the extrapolation of Chughtai et al.'s results to lower pressure.

Two competing effects determine ammonia coverages on soot at higher altitudes. Ammonia concentrations decrease with increasing altitude, which would make ammonia−soot interactions less likely at higher altitudes. Conversely, since atmospheric temperatures decrease with altitude, ammonia−soot interactions are favored at higher altitudes. In the upper troposphere, a model by Dentener and Crutzen[17] gives an ammonia mixing ratio of 8 ppt at 300 hPa (around 9 km, 230 K), which translates into a very low coverage of 10^{-9} ML from our data, despite the colder temperature of the upper troposphere. Hoell et al.[18] measured 0.6−3 ppb ammonia at 10 km, from which we predict ammonia coverages up to 4×10^{-7} ML. Thus, on the basis of our measurements of the "rapid" uptake of ammonia, we conclude that ammonia adsorption on soot is not important in the atmosphere. Depending on the mechanism for slow adsorption, perhaps the slow adsorption could lead to higher ammonia coverages under atmospheric conditions. However, even in this case, slow adsorption is not likely to lead to a more than 1 or 2 orders of magnitude increase in adsorption and so is also not likely to be significant in the troposphere. Ammonia may, however, interact with acidic adsorbates on soot, leading to ammonium coverages higher than the ammonia coverages we predict for ammonia on "clean" soot.

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