Uptake of acetone, ethanol and benzene to snow and ice: effects of surface area and temperature

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Abstract
The interactions of gas-phase acetone, ethanol and benzene with smooth ice films and artificial snow have been studied. In one technique, the snow is packed into a cylindrical column and inserted into a low-pressure flow reactor coupled to a chemical-ionization mass spectrometer for gas-phase analysis. At 214 and 228 K, it is found for acetone and ethanol that the adsorbed amounts per surface area match those for adsorption to thin films of ice formed by freezing liquid water, when the specific surface area of the snow (as determined from Kr adsorption at 77 K) and the geometric surface area of the ice films are used. This indicates that freezing thin films of water leads to surfaces that are smooth at the molecular level. Experiments performed to test the effect of film growth on ethanol uptake indicate that uptake is independent of ice growth rate, up to $2.4 \, \mu \text{m} \, \text{min}^{-1}$. In addition, traditional Brunauer–Emmett–Teller (BET) experiments were performed with these gases on artificial snow from 238 to 266.5 K. A transition from a BET type I isotherm indicative of monolayer formation to a BET type II isotherm indicative of multilayer uptake is observed for acetone at $T \geq 263$ K and ethanol at $T \geq 255$ K, arising from solution formation on the ice. When multilayer formation does not occur, as was the case for benzene at $T \leq 263$ K and for acetone at $T \leq 255$ K, the saturated surface coverage increased with increasing temperature, consistent with the quasi-liquid layer affecting adsorption prior to full dissolution/multilayer formation.

Keywords: snow, ice, atmospheric chemistry, BET, surface area

1. Introduction
The uptake of trace gases to ice is of considerable environmental importance (Abbatt 2003, Huthwelker et al. 2006). In the middle atmosphere, chemicals adsorb to ice crystals leading to gas-phase scavenging and reactions on the ice surface. Cloud scavenging is also a lower atmospheric phenomenon, where it has been modeled that ice clouds affect levels of toxic species (Lei and Wania 2004). Finally, small volatile organic compounds are observed in the interstitial air in the Arctic snow pack (Sumner and Shepson 1999). Chemically, uptake to ice is of interest because the ice surface is not a rigid solid (Girardet and Toubin 2002). Water molecules at the surface become increasingly mobile as the temperature approaches the melting point, creating a quasi-liquid layer.

Outstanding issues remain that preclude a full understanding of how gases interact with ice and snow surfaces. First, many studies have been conducted at low temperatures characteristic of the middle atmosphere, primarily with ice-coated-wall flow tube and Knudsen cell techniques. Early work was with vapor-deposited ice but most studies now freeze thin films of liquid water to form ice that is frequently assumed to be smooth at the molecular level. The justification behind this assumption is that trace gas adsorption isotherms of nitric acid and small oxygenated organics indicate a saturated surface coverage close to that of a full monolayer, i.e. 2 to

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3 \times 10^{14} \text{ molecules cm}^{-2}, when the uptakes are referenced to the geometric surface area (Sokolov and Abbatt 2002, Winkler et al 2002, Kerbrat et al 2007a). That is, if the film is smooth at the molecular level, then the saturated uptakes are consistent with a substantial fraction of a monolayer coverage. Validation that the films are smooth using traditional BET adsorption techniques with an inert gas, CH\textsubscript{2} or N\textsubscript{2} are intractable in our laboratory because of limitations associated with our current BET apparatus.

A second uncertainty is how the quasi-liquid layer affects gas uptake. Below about 245 K, experiments from our group suggest that the effects are not sufficient to significantly alter the magnitude of the uptake. In particular, in ice-coated-wall flow tubes, the uptake of small organics is fully reversible and well described by Langmuir isotherms that extrapolate to the same saturated surface coverage from 198 to 245 K (Sokolov and Abbatt 2002, Winkler et al 2002, Kerbrat et al 2007a). The gas-to-surface equilibrium constants are consistent with simple adsorption, being similar to the values for adsorption to liquid water (Donaldson and Anderson 1999) and increasing with decreasing temperature. On the other hand, experiments performed by McNeill et al (2006) indicate that the quasi-liquid layer induced by HCl adsorption has a very strong enhancement effect on the uptake of acetic acid.

To address these uncertainties in this letter, we take advantage of the development of a large-scale artificial snow source at the University of Toronto (Meyer et al 2006) by performing two sets of experiments that are impossible with thin films of ice formed by freezing liquid water. In particular, with so much available surface area, the specific surface area of the snow can be measured with BET methods. Then, by measuring the uptakes of volatile organic compounds (VOCs) to the snow at low temperatures in a co-axial cold trap, we can compare the uptakes per unit surface area to those measured on thin ice films by the same technique. If the two agree, then this validates the assumption in the community that the thin ice films are indeed smooth at the molecular level. Second, with the high surface area of the snow, we can initiate BET adsorption measurements of trace VOCs, such as acetone, ethanol and benzene, allowing for these gas–ice interactions to be studied at high temperatures for the first time.

2. Experimental details

2.1. Formation and characterization of the artificial snow

The artificial snow is formed by rapid expansion of liquid water through a nozzle into a cold room at 253 K. This permits the formation of large quantities of high surface area snow that can be formed with reproducible specific surface area, density and grain size. The snow has a density (0.16 g cm\textsuperscript{-3}) similar to that of recently deposited snow and consists of snow grains about 0.1 mm in diameter. The snow was stored at temperatures of at least 256 K. Refer to Meyer et al (2006) for more detail on the snow formation and characterization.

The specific surface area of snow was measured by BET Kr adsorption, as described in Aubin and Abbatt (2003) for the measurement of the surface areas of soot films. The technique is similar to that of Legagneux et al (2002) used for measuring the surface area of snow. Briefly, 10 to 20 g of snow was added to a cold 22 cm-long, 3.0 cm-i.d. adsorption cell made of stainless steel and fitted with copper gasket seals. The entire cell was placed in a liquid nitrogen dewar and evacuated with a rotary pump. Kr was then delivered to the evacuated cell from a gas line of known volume and pressure (measured with MKS Capacitance Manometers, models 122 (100 Torr full scale) and 220 (10 Torr full scale)). The difference in pressures after exposing the snow cell to Kr, as well as knowledge of the respective volumes, allows for the uptake of Kr to be measured. Control experiments at 77 K without snow indicated that minor Kr uptake occurs onto the walls of the chamber. The volume of the filled sample holder was measured by expanding He into the holder.

2.2. Uptake to snow and ice in the flow tube at \( T \lesssim 228 \text{ K} \)

Uptakes to thin films of ice were performed using a technique described earlier (Abbatt 1997, Ullerstam et al 2005). In particular, a 2.0 cm-i.d. pyrex tube was fully wetted on the inside with distilled water. It was then inserted into a cold, low-pressure flow tube coupled to a chemical-ionization mass spectrometer (CIMS). The temperature of the tube dropped below the freezing point of water within a few minutes, forming a transparent ice film. Uptake measurements were performed by establishing a trace gas flow through a movable injector initially positioned with its tip downstream of the ice film. An uptake was initiated by rapidly withdrawing the injector so as to expose the gas to the film. The CIMS monitored the change in trace gas signal. Trace gases were delivered from dilute bulb mixtures in N\textsubscript{2}. Total pressure in the flow tube was about 2 Torr, with a total flow of 800 sccm.

For the snow experiments, between 5 and 15 g of artificial snow were packed into a chilled pyrex tube in a low temperature freezer. A small plug of glass wool was placed at one end of the tube to keep the snow in place. Because an injector could not be used to add the trace gas, we employed a three-way valve whereby the trace gas was initially routed directly to the downstream end of the flow tube, so bypassing the snow. The flow was then directed to the back of the flow tube to initiate an uptake, and then re-routed to the downstream end to terminate the exposure. In the absence of snow, controls were conducted to ensure that the trace gas CIMS signal remained constant during this flow switching and that the uptake of trace gas onto the cold glass wool was negligible relative to the uptake to snow.

For most of the ice and snow experiments, the carrier gas flow was conditioned with water vapor to match the vapor pressure over ice at the temperature of the experiments. In a few additional experiments designed to measure the uptake of ethanol with growing ice films, the entering carrier gas flow was supersaturated with water vapor as described in Ullerstam and Abbatt (2005).

CIMS detection employed proton-transfer from H\textsubscript{3}O\textsuperscript{+} and its water clusters, as formed by passing a trace flow of water vapor through a Po-210 source (see Thornberry and Abbatt (2004) for more details). Benzene, ethanol and acetone were
detected at m/zs of 79, 47 and 59, respectively. Note that flow tube experiments with snow samples at temperatures above 245 K are not possible because the evaporation and growth rates of the snow are very fast. If there is a small imbalance between the partial pressure of water vapor in the incoming flow and the vapor pressure of the snow in the flow tube, either considerable evaporation or growth of the snow results. This would make the uptakes unreliable because the total surface area present is not accurately known.

2.3. Uptake to snow in a static cell at T $\geq 238$ K

To measure uptakes to snow at high temperatures, the same approach and apparatus used to measure Kr adsorption to snow was employed. Because the experiment is performed in a static mode, the problems with snow evaporation/growth are avoided. Although the partial pressure range accessible to these experiments is much higher than in the flow tube experiments, the advantage of working at high pressure is that the nature of the adsorption isotherm close to surface saturation can be explored.

3. Results and discussion

3.1. Characterization of the artificial snow

The adsorption of Kr to the snow followed a classic type II isotherm, with very large uptake occurring close to the saturated vapor pressure at 77 K (Adamson 1990). By taking the area of the Kr atom to be 0.202 nm$^2$ (Rouquerol 1999), the specific surface area of the artificial snow was measured to be between 580 and 680 cm$^2$ g$^{-1}$, where the variation arose from different batches of snow preparation. The precision from a single batch was $\pm 10\%$ (1-sigma), from about 10 measurements on different samples. This specific surface area is similar to that of natural snow (Dominé et al. 2007). Also, the surface area remained stable over periods of weeks in the freezer, probably because no measurements were made in the first few days after it was formed when it may have been annealing and its surface area stabilizing.
surface saturation on these ice films occurs at uptakes of about $2 \times 3 \times 10^{14}$ molecules cm$^{-2}$ when using the geometric surface area as a reference (Sokolov and Abbatt 2002, Winkler et al 2002, Kerbrat et al 2007a). Thus, surface saturation occurs when a large fraction of a monolayer is present.

We should note that good agreement between adsorbed quantities of acetone to different ice/snow surfaces has been observed by others (e.g. Bartels-Rausch et al 2004), indicating that the preparation mode of the snow appears to not affect the uptake so long as the specific surface area is known. Also, a recent comparison of two different methods to measure the specific surface area of natural snow concluded that natural snow is smooth up to the 30 μm size (Kerbrat et al 2007b).

Also plotted in figure 2 are ethanol uptakes to ice films measured when the film was growing at an average rate of between 0.7 and 2.4 μm min$^{-1}$; experiments with benzene and acetone were not attempted. See Ullerstam and Abbatt (2005) for a detailed description of this experimental technique. Contrary to nitric acid uptake where growing ice conditions led to enhanced uptake, this effect was not observed with ethanol. We interpreted enhanced uptake for nitric acid as due to the formation of a metastable solution of nitric acid in the newly formed ice. Given that the solubility of ethanol in ice will be lower than that of nitric acid, the results are reasonable. They indicate that the dynamic nature of ice growth exhibited in the environment may not significantly affect the total degree to which ethanol, and other similar molecules, is sequestered by ice. It may only be extremely soluble molecules that show this effect.

### 3.3. Uptake to snow in a static cell at $T \geq 238$ K

Given the high surface area of the snow, initial experiments were performed to evaluate VOC uptakes with a static BET approach. In particular, by measuring the uptake onto snow with a known total surface area, we generated uptake data of the type shown in figures 3 and 4 for acetone and benzene. Ethanol experiments were also performed but are not shown due to space limitations; see below. In each plot, data from individual uptake experiments at one temperature on one snow sample were generated, and then fitted to a BET adsorption isotherm. The apparent saturated surface coverages derived from the BET fits are given in table 1, as averages of roughly 4 replicate measurements. For the flow tube experiments, the uncertainty reflects the 1-σ uncertainty from the Langmuir fits.

![Figure 3](image1.png)  
**Figure 3.** Uptakes of benzene as measured in the BET apparatus ($P_e$ (263 K) = 14.4 Torr, $P_e$ (255 K) = 8.51 Torr, $P_e$ (246 K) = 4.49 Torr).

![Figure 4](image2.png)  
**Figure 4.** Uptakes of acetone as measured in the BET apparatus ($P_e$ (266.5 K) = 49.6 Torr, $P_e$ (263 K) = 40.8 Torr, $P_e$ (255 K) = 25.5 Torr, $P_e$ (246 K) = 14.4 Torr, $P_e$ (238 K) = 8.3 Torr).

| Gas   | Experimental technique | Temperature (K) | Apparent saturated uptake amount (cm$^2$) |
|-------|------------------------|-----------------|------------------------------------------|
| Acetone | BET  | 255 | $(5.7 \pm 0.9) \times 10^{14}$ |
| Acetone | BET  | 246 | $(4.8 \pm 0.08) \times 10^{14}$ |
| Acetone | BET  | 238 | $(3.5 \pm 0.08) \times 10^{14}$ |
| Acetone | Flow tube | 214 | $(2.1 \pm 0.2) \times 10^{14}$ |
| Benzene | BET  | 263 | $(1.7 \pm 0.2) \times 10^{15}$ |
| Benzene | BET  | 255 | $(9.3 \pm 0.4) \times 10^{14}$ |
| Benzene | BET  | 246 | $(3.5 \pm 1.2) \times 10^{14}$ |
| Benzene | Flow tube | 218 | $(5.1 \pm 0.6) \times 10^{13}$ |

![Table 1](image3.png)  
**Table 1.** Saturated surface coverages from adsorption isotherm fits for experiments on snow. For the BET experiments, the uncertainty reflects the 1-σ uncertainty precision of roughly 4 replicate measurements. For the flow tube experiments, the uncertainty reflects the 1-σ uncertainty from the Langmuir fits.
II isomers (see figure 4, for the highest two temperatures for acetone). However, care should be taken in interpreting these observations. Benzene uptakes (figure 3) show no indication of multilayer adsorption for the range of $P/P_0$ explored (where $P_0$ is the pure liquid vapor pressure at that temperature), whereas those for acetone and ethanol exhibited conditions where apparent multilayer growth occurred at low values of $P/P_0$. In particular, for the ethanol work (not shown), the curves exhibited type II isotherms from 266.5 to 255 K for $P/P_0$ from 0.01 to roughly 0.2. We believe this effect arises from formation on the surface of a thermodynamically stable solution of these gases dissolved in water. From earlier studies of HCl uptake to ice, it was shown that such solutions form if the partial pressure of the adsorbing gas matches that of a solution in equilibrium with ice at the temperature of the experiment (Abbatt et al. 1992). Indeed, from the melting point of acetone/water binary mixtures (Flick 1998), and from the vapor pressures of such solutions (Washburn 2003), the transition to unlimited acetone uptake observed at 266.5 and 263 K are at $P/P_0$ values consistent with such behavior. From a qualitative sense, we believe this general melting effect arises for ethanol and acetone because the solubility of these species is so much higher than that of benzene.

For the uptakes of acetone at lower temperatures where this surface dissolution does not occur, the saturated surface coverage matches well with that measured using the flow tube at 214 K on snow. Also, Winkler et al. (2002) reported a saturated surface coverage of $2.7 \times 10^{14}$ molecules cm$^{-2}$ from a coated-wall flow tube experiment. Note that the saturated surface coverage increases with increasing temperature, as was observed with benzene. This is suggestive that the quasi-liquid layer plays a role in affecting the uptake, or that some level of surface pre-melting is occurring. Indeed, enhanced surface uptake may be a prelude to full dissolution of the ice surface. These results now stand alongside those of McNeill et al. (2006) which showed that the uptake of acetic acid could be increased by the formation of the quasi-liquid layer induced by HCl adsorption.

4. Conclusions

The agreement between the adsorption uptakes of acetone and ethanol to snow and ice is consistent with the surfaces of ice formed by liquid water being smooth at the molecular level. It also suggests that the extent of gas-to-surface partitioning is not affected by how the substrate is formed. At low temperature, it was found that the uptake of ethanol is not affected by whether the ice substrate is growing at an average rate of a few microns/minute, in contrast to the behavior of a more soluble material, such as nitric acid. At high temperature there is enhanced uptake in the saturated limit as the quasi-liquid layer grows, for both benzene and acetone. It is possible that such uptake is a prelude to full dissolution of the ice surface, which occurs when the partial pressure of soluble species such as acetone and ethanol is sufficiently high.

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