

Effect of the Thermal History of Ice Crushed at 77 K on Its Surface Structure As Determined by Adsorption of CH₄ at Low Surface Coverage

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The effect of annealing on the structure of the surface of single crystals of ice crushed at 77.15 K is investigated using methane adsorption at 77.15 and 87.1 K. Methane adsorption isotherms are obtained for surface coverages, θ , between 0.1 and 1.5 monolayers and between 10^{-6} and 10^{-2} monolayer. It is observed that annealing greatly reduces the number of CH₄ molecules adsorbed at low coverage (by a factor of 10 at $P_{\text{CH}_4} = 10^{-4}$ Torr, for annealing at 238 K), but no effect of annealing on adsorption is observed for θ greater than 0.1 monolayer. We propose that these effects are due to the disappearance upon annealing of crystal faces with favorable adsorption sites, which could be faces with high Miller–Bravais indices. From our data, and additional data obtained by other investigators, we conclude that the mode of formation and the thermal history of the ice surface strongly influence its surface structure and adsorption properties. We discuss the possibility that the different modes of formation of ice in the atmosphere will result in different surface and adsorption properties.

Introduction

The structure of the ice surface has been the subject of numerous investigations that used varied techniques.¹ These included NMR, X-rays, ellipsometry, and infrared spectroscopy, which are direct investigations in that they directly investigate the ice surface, and other somewhat indirect techniques such as gas adsorption,^{2–5} which look at the effect of the structure of the ice surface on the adsorption of gases. Despite their indirect character, these adsorption methods have the added interest that their results can be applied to interstellar and atmospheric chemistry.^{5–11}

A question addressed by these adsorption studies is usually: does the mode of formation of the ice, and in particular its thermal history, influence the adsorption of gases on the ice surface? Early studies focused on the adsorption of N₂ on ice for surface coverages, θ , between about 0.1 and 2 monolayers. Adamson et al.² and Ocampo and Klinger³ found that annealing the ice surface resulted in a significant lowering of the BET net heat of adsorption ΔQ_{N_2} (ref 12). Adamson et al.² even measured $\Delta Q_{\text{N}_2} = 0$ for natural snow, from which they concluded that adsorption on snow in the atmosphere was probably a negligible phenomenon. In contrast, Schmitt et al.⁴ found that annealing ice crushed at 77 K had no detectable effect on the adsorption of N₂ or Ar. More recently, Buch et al.¹³ studied by infrared spectroscopy the adsorption of CF₄ on ice nanocrystals formed by vapor condensation in the temperature range 70–90 K and modeled their results assuming several degrees of disorder on their ice surfaces. Although the aim of their work was not the measurement of adsorption isotherms, their results indicate that annealing at 140 K decreases significantly the number of CF₄ molecules adsorbed, when adsorption is in the range of a large fraction of a monolayer which corresponds to CF₄ partial pressures, P_{CF_4} , in the range 0.01–0.06 Torr. Also recently, Chaix et al.⁵ have studied CH₄ adsorption on ice crushed at 77 K, both nonannealed and annealed at 195 K for 15 min, and on natural snow. At

coverages above 0.2 monolayer, no difference in adsorption of CH₄ was observed for the three types of ice. At coverages $\theta = 10^{-6}$ – 10^{-2} monolayer, however, it was found that annealing reduced the number of CH₄ molecules adsorbed on crushed ice, by a factor of 3 for $P_{\text{CH}_4} = 10^{-4}$ Torr. It was also observed unexpectedly that natural snow adsorbed about as much CH₄ as unannealed crushed ice and, therefore, much more than annealed crushed ice.

The present article reports a continuation of the investigations of Chaix et al.⁵ We focus here on the effect of annealing on CH₄ adsorption at low surface coverage. CH₄ was used because its expected weak adsorption should minimize its perturbation of the ice surface. Crushed ice was annealed at 195 K for two different durations and was also annealed at 238 K. Adsorption isotherms were measured at liquid nitrogen (l-N₂) and liquid argon (l-Ar) temperatures (77.15 and 87.1 K) so that the isosteric heat of adsorption (which is in fact the negative of the enthalpy of adsorption: $q^{\text{st}} = -\Delta H_{\text{ads}}$, ref 14) was calculated as a function of surface coverage. Our results are then compared with those of other investigators, in particular with the recent data of Buch et al.¹³ Finally, we briefly discuss the possibility to derive implications of this work for atmospheric chemistry.

Experimental Methods

The ice samples were obtained by crushing ice I_h single crystals made in our laboratory using highly purified water. Crushing was performed under vacuum (10^{-6} Torr) in a stainless steel ball mill held at l-N₂ temperature. The ice samples then remained in the ball mill for the adsorption measurements, so that the ice was never exposed to the atmosphere. Annealing was done by immersing the ball mill containing the ice in a temperature-regulated ethanol bath. Two ice samples were used. The first sample was held at 195 K for two successive times (15 and 30 min) and the second at 238 K for 18 h. The samples were then recooled to l-N₂ temperature and the measurements performed.

The experimental systems used to measure adsorption isotherms of methane on ice has been described in Chaix et al.,⁵ and only the general features will be mentioned here. Two

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TABLE 1: Properties of the Ice Samples

ice crushed at 77.15 K thermal history	weight (g)	surface area (m ²)	ΔQ_{CH_4} (J/mol)	
			$T = 77.15 \text{ K}$	$T = 87.1 \text{ K}$
unannealed	25.40	28.65	1958 \pm 36	1985 \pm 64
annealed at 195 K, 15 min	25.40	24.21	1994 \pm 40	^a
annealed at 195 K, 45 min	25.40	19.76	1957 \pm 38	1966 \pm 42
annealed at 238 K, 18 h	150.01	6.15	1937 \pm 35	2065 \pm 70

^a Not measured.

systems were used. The first one measured the adsorption at high pressure, i.e. corresponding to θ in the range 0.1 to several monolayers, and was of the standard volumetric type. The ice sample, located in the ball mill of volume V_2 , was immersed in a 1-N₂ or 1-Ar bath. Methane was leaked in another container of volume V_1 also immersed in 1-N₂ or 1-Ar, and the pressure in V_1 was measured with a capacitance manometer at room temperature. The valve between V_1 and V_2 was opened, resulting in a pressure drop due to adsorption and to expansion. The pressure was measured again after connection of both volumes. The difference in the number of moles of methane in the gas phase before and after adsorption was calculated with the ideal gas equation, and the amount of methane adsorbed was equated with this difference.¹⁴

The second system measured the adsorption isotherms at low pressures, down to about 10^{-6} Torr, i.e. corresponding to surface coverages in the range 10^{-6} – 10^{-2} monolayer. The main difference with the first system is that a mass spectrometer was used for the pressure measurements, which were then destructive. Because of that, an extra container of volume $V'_1 \approx V_1$ was added to the system and was used to measure the pressure after adsorption, while V_1 was used to measure the pressure before adsorption. Both V_1 and V'_1 were at room temperature. Thermomolecular corrections for thermal transpiration were performed at these low pressures. The surface areas of the samples were determined with the usual BET method^{12,14} using CH₄ or N₂ adsorption at 77 K. By comparing N₂ and CH₄ isotherms and using the usual surface area of an N₂ molecule adsorbed on ice (16.2 \AA^2), we derived the area of a methane molecule adsorbed on ice: 19.18 \AA^2 .

Results

Annealing did not affect the high-pressure adsorption isotherms, which correspond to coverages above 0.1 monolayer. The BET ΔQ_{CH_4} values were the same for all the isotherms, within experimental error, as shown in Table 1. Isothermic heats of adsorption q^{st} were determined using the Clausius–Clapeyron equation, applied to the data obtained at 77.15 and 87.1 K. At high surface coverage, they were found to decrease slightly with increasing coverage: from 11 550 J/mol at $\theta = 0.1$ to 10 200 J/mol at $\theta = 1$ monolayer. The mean value of q^{st} between $\theta = 0.1$ and $\theta = 1$ monolayer was 10 925 J/mol, close to $\Delta Q_{\text{CH}_4} + L = 10 982 \text{ J/mol}$, where $L = 9002 \text{ J/mol}$ is the heat of sublimation of methane, calculated from the Clausius–Clapeyron equation using the saturation vapor pressures of CH₄ at 77.15 and 87.1 K. The q^{st} vs θ plots were independent of the ice thermal history above 0.1 monolayer.

Low-pressure adsorption isotherms at 77.15 and 87.1 K are shown in Figure 1. Even though, for clarity, only one set of adsorption isotherms for unannealed ice is shown in Figure 1, isotherms were measured on both ice samples used here and were found to be identical. It is clear that at low θ , annealing significantly lowers the number of CH₄ molecules adsorbed at a given P_{CH_4} , at both 77.15 and 87.1 K. At 77.15 K for $P_{\text{CH}_4} = 10^{-4}$ Torr, the number of adsorbed molecules decreases by

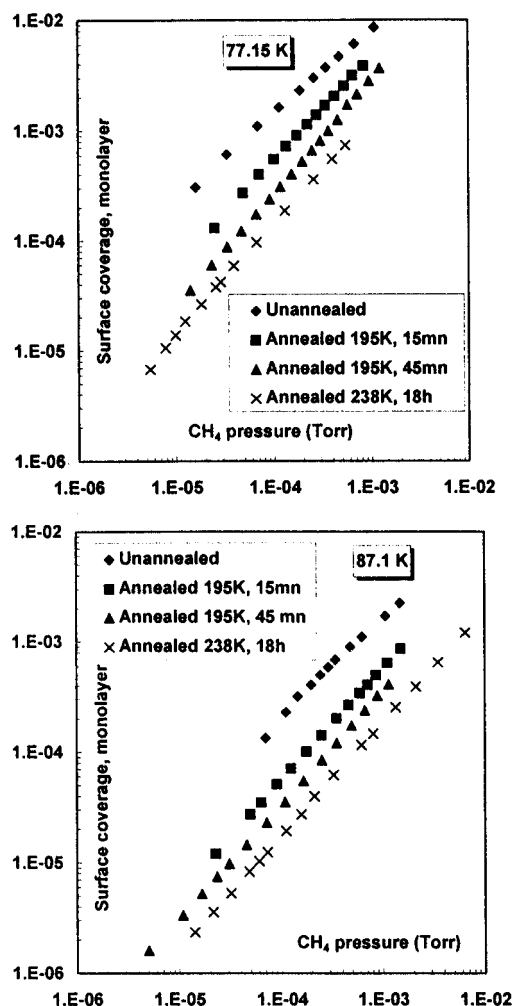


Figure 1. Adsorption isotherms of CH₄ on ice at 77.15 and 87.1 K, for unannealed crushed ice and crushed ice annealed at 195 K for 15 min, 195 K for 45 min, and 238 K for 18 h.

a factor of 3 after annealing for 15 min at 195 K and by a factor of 10 after annealing at 238 K for 18 h. Values of q^{st} were derived from these isotherms and are shown in Figure 2. These values are observed to decrease with θ and to decrease with annealing, especially at very low coverages.

Discussion

Chaix et al.⁵ have already discussed the variation of the adsorption isotherms of CH₄ on crushed ice at 77.15 K, when this ice was annealed at 195 K for 15 min. We will briefly sum up our previous conclusions and detail some of them with the additional data reported here.

The information deduced from the similarity of the adsorption isotherms at high coverage is the following. The surfaces of crushed ice being caused by fracture, a random distribution of crystal faces is expected.¹⁵ During annealing, ice metamorphism takes place, and basal and prism faces will become predominant. Chaix et al.⁵ also observed that the adsorption of CH₄ on natural snow, with a predominance of the (0001) basal planes, was similar to that on crushed ice. We then conclude that adsorption of CH₄ on ice is similar on most crystal faces, and in particular on basal and prism faces. The possibility that faces present in a very low proportion will adsorb CH₄ differently still exists, however, as a low enough proportion would not be detectable at high coverages.

The difference observed at low coverage is attributed to surface defects that disappear upon annealing or to an increasing

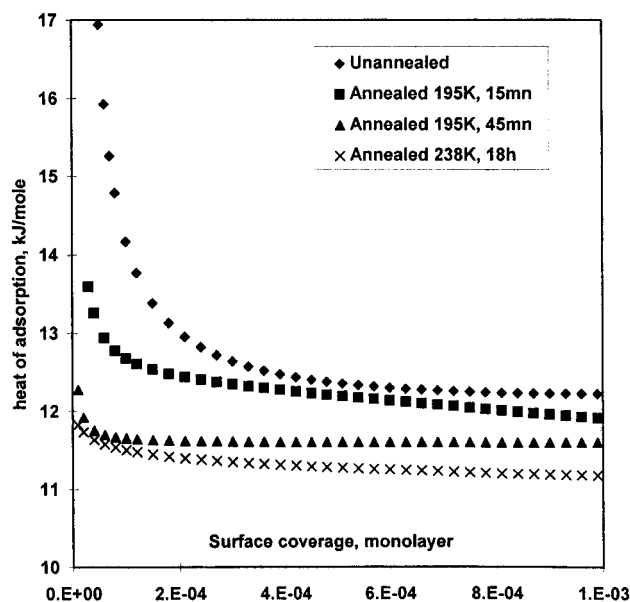


Figure 2. Isosteric heat of adsorption, q^{st} , of methane on ice, from the data of Figure 1. Curves are shown for unannealed crushed ice and crushed ice annealed at 195 K for 15 min, 195 K for 45 min, and 238 K for 18 h.

degree of surface reconstruction during annealing. The surface defects are unlikely to be emerging dislocations, as the number required to explain adsorption differences at $\theta = 10^{-2}$ monolayer is between 10^{11} and 10^{12} cm^{-2} , which is much too high.^{16,17} The surface defects are also unlikely to be dangling OH bonds.¹⁸ Although such bonds could be in a sufficient number on crushed ice to explain the observations, it appears unlikely that, according to Figure 2, the energetics of the interactions between dangling OH bonds and CH_4 could reach several kJ/mol, as CH_4 has neither a dipole nor a quadrupole moment. Surface reconstruction is possible, but our data indicate that such reconstruction would involve only a small fraction of the surface. We then propose that the decrease in adsorption with annealing is due to surface modifications of certain types of crystallographic faces where CH_4 adsorption is more energetic, or more likely to the disappearance of these faces. Such faces could be planes with high Miller–Bravais indices, which would have a large number of steps with favorable adsorption sites. They could also be faces where crushing produced an amorphous character,¹⁹ but this is not our favored interpretation because the crushing was mild.

Steps are not the only potentially favorable adsorption sites. Buch et al.¹³ have performed infrared spectroscopic measurements of CF_4 adsorbed on ice nanocrystals formed by the condensation of water vapor at 70–90 K. They also reported measurement on those crystals annealed at 140 K and modeled their results assuming several surface structures for ice. Their results suggest that the surface of ice has six-coordinated adsorption sites or even larger grooves that could accommodate one or several adsorbed molecules. Buch et al. suggest that the number of such sites will change with annealing, resulting in changes in the energetics of adsorption. It is possible that the conclusions of Buch et al.¹³ apply to our data and that six-coordinated sites or larger grooves were present on our samples. However, major differences exist between the experimental conditions of Buch et al. and ours.

Buch et al. observed experimentally that the intensity of adsorbed CF_4 bands is greater on unannealed ice than on annealed ice, indicating that at high coverage unannealed ice adsorbs significantly more CF_4 than annealed ice. To explain modifications at high coverage, Buch et al. suggest that in their

case surface modifications are extensive and involve most of the ice surface. They propose that the surface of their unannealed ice nanocrystals have a pronounced amorphous character, which partially or mostly disappears upon annealing at 140 K. On the contrary, we observe no detectable changes at high coverage, and our data indicate that only a few percent at the most of the surface is affected by structural changes upon annealing at 238 K.

Our results and those of Buch et al. are not incompatible, however. The crystals that Buch et al. used had dimensions of several nanometers. Before annealing, their surface had an amorphous character, and a lateral disorder remained after annealing at 140 K. Our ice particles were different. They had dimensions of several micrometers. Because they were formed by crushing single crystals, it appears unlikely that their surfaces had a large degree of disorder. Severe mechanical treatment can produce an amorphous surface,¹⁹ but a few minutes in a ball mill is probably insufficient and our data indicate that an amorphous character, if present, was limited to a small fraction of the surface. We then believe that the differences in the effect of annealing observed by Buch et al.¹³ and by us can be explained by the different modes of formation of the ice. Among the parameters that differ in both studies, temperature probably had an important effect, as the lower temperatures of formation used by Buch et al. were certainly responsible for the lower initial surface order.

Adamson et al.² and Ocampo and Klinger³ observed that, at high coverage, the adsorption of N_2 was lower on annealed ice than on nonannealed ice, in contradiction with our results. Adamson et al. used ice made by water vapor condensation, while Ocampo and Klinger used crushed ice similar to ours. We believe that their results are experimental artifacts. Indeed, they used pressure measurement technology of lower quality than what is available nowadays. Moreover, they performed adsorption isotherms with very few data points, and the error on their data was far greater than on ours. We tested this hypothesis by lowering the signal to noise ratio of our data. This was done by measuring high-coverage adsorption isotherms with smaller and smaller amounts of ice of a given sample. Eventually, our ΔQ_{CH_4} values started to decrease, in a manner similar to what those previous investigators observed. When the removed ice was added again, the ΔQ_{CH_4} increased again, and we then suggest that the decrease in ΔQ_{CH_4} observed was due to the decrease in surface area of the ice samples that accompanies annealing. Strengthening our proposition, Schmitt et al.⁴ have performed careful measurements of the effect of annealing of the adsorption of N_2 on crushed ice at high coverages and have obtained results similar to ours.

Conclusion and Atmospheric Applications

The data presented here indicate that annealing ice crushed at 77 K changes its behavior toward CH_4 adsorption at low coverage, at 77.15 and 87.1 K. We propose that these changes are due to the disappearance of crystal faces that adsorb CH_4 more energetically than prism and basal faces. We suggest that these faces have a greater degree of surface disorder than most other faces and that they could be faces with high Miller–Bravais indices, resulting in the presence of steps or of other surface features that favor adsorption. A small proportion of faces with an amorphous character could also explain our observations, but the crushing appears too mild to produce an amorphous surface. The proportion of these faces on the surface of unannealed crushed ice is of a few percent at the most, as their effect is not detected by adsorption measurements at high coverage.

Buch et al.,¹³ who observed the effect of annealing on the surface of ice nanocrystals formed by water vapor condensation in the range 70–90 K, reach a conclusion qualitatively similar to ours: annealing reduces surface disorder. The changes they observe during annealing are much more extensive than what we see, however, as they affect most or all of their ice surface. This is probably because they start with ice samples whose surfaces are much more disordered than ours.

Our data, together with those of Buch et al.,¹³ indicate that both the mode of formation and the thermal history of the ice influence its surface properties and the manner in which gases will adsorb on its surface. An interesting question is then: since adsorption of gases is an important process in atmospheric chemistry, and since ice in the atmosphere can be formed by different mechanisms (freezing of supercooled droplets, water vapor condensation with different growth and cooling rates, etc.), will the mode of formation of atmospheric ice affect its surface properties?

Tropospheric and stratospheric temperatures can be as low as about 185 K. At those temperatures, the ice surface is very dynamic, with rapid evaporation and condensation taking place,²⁰ and it is tempting to suggest that this will result in the loss of any memory effect of the mode of formation. However, Beaglehole and co-workers²¹ have shown using ellipsometry that even at 270 K, optical methods could detect structural differences between prism and basal faces of ice. Because different modes of formation can result in different proportions of crystal faces,²² which, as suggested by the present paper, can have different behaviors toward adsorption, we believe that the adsorption of trace gases may be different on different samples of atmospheric ice. Besides different proportions of crystal faces, other factors could contribute to this effect. These include different concentrations of impurities, which could be dissolved trace gases or aerosols, and the presence of defects having their origin in the ice volume, such as dislocations, small angle boundaries, and grain boundaries. These defects will not be removed by the dynamic character of the ice surface. For example, rimed ice will have numerous grain boundaries, while vapor-grown ice will have very few of them, if any, and it may be interesting to perform adsorption studies at atmospheric temperatures to attempt to detect differences between both types of ice.

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