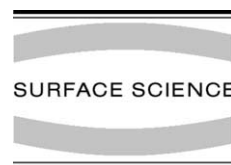




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Adsorption of small molecules on amorphous ice: volumetric and FT-IR isotherm co-measurements

Part I. Different probe molecules

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Abstract

Ar, Kr, CH₄, N₂, CO and CF₄ adsorption on amorphous ice has been studied by using a combination of volumetric isotherm measurements and FT-IR spectroscopy. We have been able to characterize the modifications in the three vibrational surface modes of ice throughout the adlayer formation and to observe different types of wetting. For these gases, we have measured the net heat of adsorption within a range of 1–2.6 kJ mol^{−1}, showing the weakness of surface interaction and conversely, we have measured the shift of the dangling OH bond within a range of 7–60 cm^{−1}, showing its high sensitivity to the adsorption process. We have succeeded in correlating both techniques by measuring the evolution of vibrational surface modes as a function of the relative pressure, from submonolayer to bulk. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption isotherms; Infrared absorption spectroscopy; Physical adsorption; Vibrations of adsorbed molecules; Water; Amorphous surfaces

1. Introduction

Amorphous ice is known to be involved in the processes occurring during the formation of molecules in the interstellar medium and studying gas–ice interactions is therefore of fundamental interest. Infrared absorption spectroscopy has widely proved to be a powerful tool to understand this interaction: a main reason is that the ice surface modes are infrared active and are sensitive probes of adsorption [1–3]. In this paper, we present an investigation of several probe molecules, adsorbed on amorphous ice, using adsorption isotherm volu-

metry and infrared spectroscopy simultaneously. This method allows us to control the surface coverage and to measure the modification in the infrared active bands of surface and of adsorbate—if any—during adsorption. We will give some experimental details and a brief description of the co-measurement protocol in Section 2, and we will present results obtained for Ar, Kr, CH₄, N₂, CO and CF₄ adsorbed on ice for temperatures between 53 and 95 K in Section 3.

2. Experimental section

The combination of the two techniques (volumetry and infrared spectroscopy) was possible with a sample in a copper cell with two sapphire

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windows connected to a classical volumetric apparatus [4]. The cell temperature was maintained constant using a cryocooler CTI Cryogenics model 22 and a temperature controller Lake Shore Cryotonic Inc. For each adsorbate introduction into the cell, equilibrium pressure p and the infrared spectrum were measured. Infrared spectra were recorded in transmission mode using a Nicolet 7199 FT-IR spectrometer. The resolution was 1 cm^{-1} and 200 scans were collected per spectrum. We were able to measure simultaneously classical adsorption isotherms, i.e. evolution of the adsorbed amount versus relative pressure p/p^0 (p^0 being the saturation pressure), and infrared adsorption isotherms, i.e. evolution in the integrated absorbance of the different vibrational modes versus p/p^0 .

Our ice sample was formed by spraying a gaseous mixture $\text{H}_2\text{O}:\text{Ar}$ (1:30) into the cell held at 40 K and was slowly annealed (0.2 K min^{-1}) up to 90 K in order to sublime argon. Then, the amorphous ice ($\approx 2\text{ mg}$) was cooled down to the chosen temperature. For such samples, we measured a specific surface area of more than $100\text{ m}^2\text{ g}^{-1}$ by the standard volumetric method, using methane as probe molecule [4]. We thus obtained a stable ice within the temperature range 40–100 K with a very good reproducibility.

We used the following probe molecules: methane (Air Liquide, 99.95%), nitrogen (Alpha Gaz, 99.9990%), carbon monoxide (Alpha Gaz, 99.997%), argon (Linde Gaz, 99.9996%), krypton (Linde Gaz, 99.990%) and tetrafluoromethane (Linde Gaz, 99.8%). They are widely used for studies of two-dimensional physisorbed films [5] and are expected not to significantly alter the ice surface. Adsorption temperatures T were chosen to be $T = 0.4T_c$ (T_c being the critical temperature) in order to achieve analogous thermodynamical properties for each gas. The temperatures mentioned in Table 1 were determined by measuring the saturation pressure and by using the Clapeyron's law.

At the end of the experiment, the gas was totally desorbed allowing another probe molecule to be adsorbed on the same ice sample. After such an adsorption–desorption cycle, we checked that the ice surface had not been modified by recovering

Table 1

Adsorbate properties

	T	p^0	v_m	ΔQ	R
CH_4	73	4.19	25	1.8	4.25
N_2	56	18.13	33	2.5	3–4.1
CO	56	7.53	33	2.6	—
Ar	53	0.69	22	1.2	3.84
Kr	78	2.06	13	1.2	3.96
CF_4	95	2.23	—	—	5.28

Monolayer capacity v_m ($\text{cm}^3\text{ STP g}^{-1}$) and net heat of adsorption ΔQ (kJ mol^{-1}) deduced from BET model; adsorption temperature T (K); relative pressure p^0 (Torr); size R (Å).

the same infrared spectrum and the same surface specific area.

3. Results and discussion

The adsorption isotherms measured for different probe molecules are shown in Fig. 1: the adsorbed amount per ice mass v_{ads} ($\text{cm}^3\text{ STP g}^{-1}$) is plotted versus p/p^0 . According to the IUPAC classification [6] Ar, Kr, CH_4 , N_2 and CO adsorption isotherms are type II, which indicates the formation of the adsorbed layer within two stages. Firstly, the adsorbed amount rises more or less sharply at low relative pressure ($p/p^0 < 0.2$)

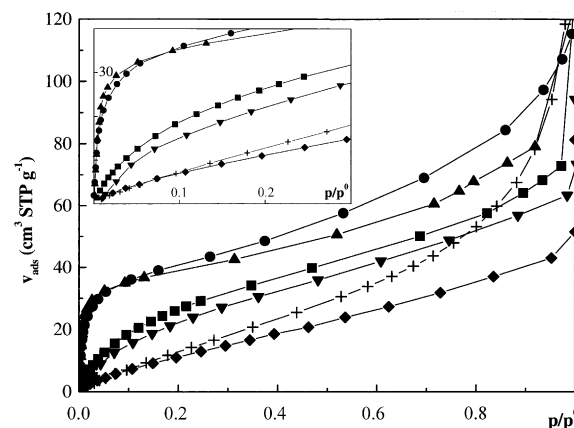


Fig. 1. Adsorption isotherms of different adsorbates on amorphous ice: (■) CH_4 at 73 K, (●) N_2 at 56 K, (▲) CO at 56 K, (▼) Ar at 53 K, (◆) Kr at 78 K and (+) CF_4 at 95 K. The inset shows the first stages of adsorption on an expanded scale. Solid lines are guides for eyes.

because of monolayer formation and secondly, the increase is almost linear indicating multilayer formation. When the equilibrium pressure is reached, there is condensation and the layer becomes a liquid or solid bulk. At the earliest stages, N_2 and CO isotherms clearly rise more sharply than those of Ar, CH_4 and Kr (this behavior has already been pointed out in the cases of N_2 , CO and Ar [7]) due to a stronger molecule–ice surface interaction. In fact, only N_2 and CO possess a quadrupole moment, probably leading to specific interaction with ice surface.

A type III isotherm is measured for CF_4 , not presenting any knee at low p/p^0 . This feature is indicative of very weak adsorbent–adsorbate interactions and shows that CF_4 does not wet the ice surface, in agreement with its hydrophobic character. The layer growth is probably achieved by three-dimensional clustering on ice surface.

To summarize, we have measured three different isotherm shapes giving evidence for three types of wetting: monolayer and multilayer for N_2 and CO, very weakly bonded monolayer and multilayer for Ar, CH_4 and Kr, and no wetting for CF_4 .

We used the BET model [5,8], well suited to describe type II isotherms, to estimate the monolayer capacity v_m and the net heat of adsorption ΔQ , which is the difference between the enthalpy of adsorption and the enthalpy of condensation (Table 1). It is worth noting that v_m and ΔQ are not determined for CF_4 , due to the meaningless results of the BET method in this case. It should also be mentioned that the v_m values are not correlated to the size of the molecule: for example the CH_4 value of v_m is twice that of Kr despite the equality of their radii. This indicates a higher density of the adsorbed phase for CH_4 than for Kr. The low ΔQ values confirm that, in all cases, the adsorbed monolayer weakly interacts with the ice surface. The value obtained for methane ($\Delta Q = 1.8 \text{ kJ mol}^{-1}$) is in the same range than those obtained for adsorption on slightly attractive surfaces like MCM-41 ($\Delta Q = 1 \text{ kJ mol}^{-1}$) [9] and graphite (0001) ($\Delta Q = 5 \text{ kJ mol}^{-1}$) [10], whereas it is rather different to that obtained on microporous adsorbent-like MFI-type zeolite ($\Delta Q = 9 \text{ kJ mol}^{-1}$) [11] where interactions are expected to be enhanced by a confinement effect.

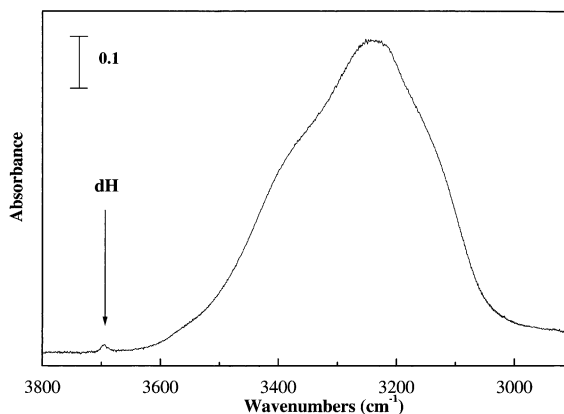


Fig. 2. Infrared spectrum of bare amorphous ice at 50 K.

The infrared spectrum of bare ice shown in Fig. 2 is that of an amorphous ice sample, the amorphous nature of the ice being unambiguously characterized by the shape of the broad band centered roughly at 3250 cm^{-1} due to the in-bulk modes [12]. The weak peak at 3696 cm^{-1} is due to the three-coordinated surface molecules presenting a dangling OH bond, referred to as dH molecules [13]. Two other vibrational surface modes at 3563 and 3489 cm^{-1} are evidenced in Fig. 3, where the difference spectra between the gas/ice spectrum measured at $v_{\text{ads}} = v_m$ and the bare ice spectrum are displayed. They have been assigned to the three-coordinated surface molecules presenting a free electron pair on the oxygen atom (referred to as dO molecules) and to four-coordinated surface molecules (referred to as s4 molecules), respectively [1]. For each probe molecule, all the surface vibrational modes are modified during adsorption: whatever the configuration of the adsorbed phase is, the molecules are in interaction with all surface sites. It should be noted that CF_4 shows the weakest alteration in the dH, dO and s4 modes, in agreement with its very limited wetting of the surface. Though all the surface modes are expected to be shifted by adsorption, a red-shift is observed for the dH mode only: dO and s4 peaks are probably too broad to enable the red-shifted positions to be observed. This width is due to a strong coupling with the bulk modes through the hydrogen bond network. We can now distinguish

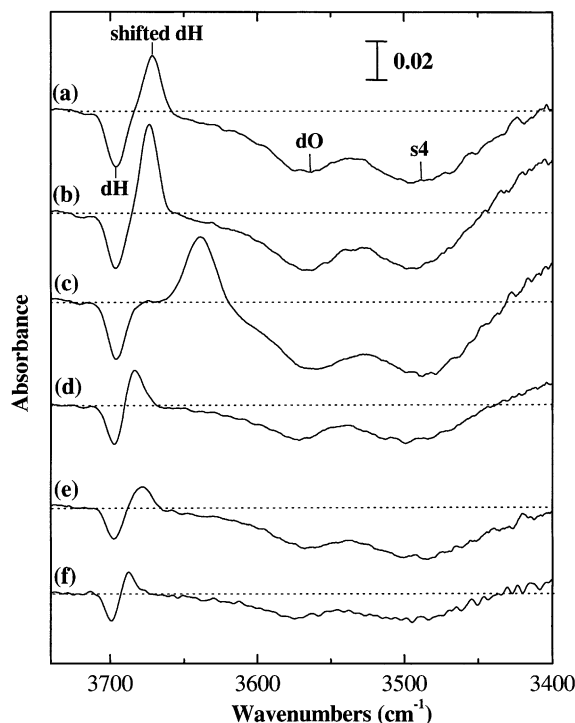


Fig. 3. Infrared difference spectra (gas/ice spectrum measured at $v_{\text{ads}} = v_{\text{m}}$, adsorption temperature T , minus bare ice spectrum measured at the same temperature): (a) CH_4 , $T = 73$ K and $p/p^0 = 0.17$, (b) N_2 , $T = 56$ K and $p/p^0 = 0.05$, (c) CO , $T = 56$ K and $p/p^0 = 0.05$, (d) Ar , $T = 53$ K and $p/p^0 = 0.23$, (e) Kr , $T = 78$ K and $p/p^0 = 0.25$, (f) CF_4 , $T = 95$ K and $p/p^0 = 0.20$. Spectra are offset and smoothed (12 cm^{-1}) for clarity. Dotted lines represent the origin for each difference spectrum.

two groups of spectra: firstly, Ar , Kr and CF_4 spectra showing weak alteration and secondly, CH_4 , N_2 and CO spectra showing higher alteration for the same coverage. This is consistent with the higher net heat of adsorption and the higher density exhibited by the latter molecules.

For each gas, we have drawn the infrared absorbance evolution of both surface and adsorbate—when an infrared signature is available—vibrations as a function of p/p^0 . Such infrared isotherms are presented in Fig. 4 in the case of CH_4 . The CH stretching mode of methane observed at 3010 cm^{-1} leads to type II isotherm similar to that of volumetric measurements, showing the good correlation existing between the two techniques. The three surface O–H modes (v_{dH} , v_{dO}

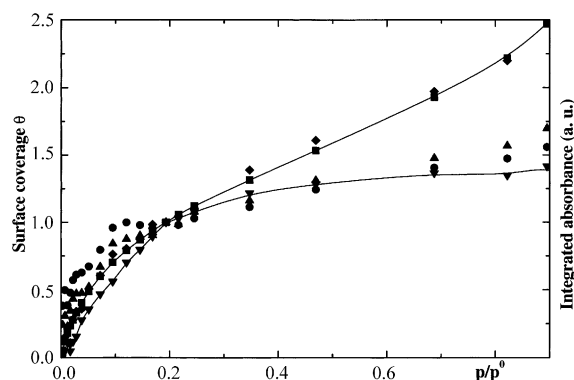


Fig. 4. Infrared and volumetric isotherms of CH_4 on amorphous ice at $T = 73$ K: (■) volumetric measurement, (◆) v_{CH} , (●) v_{s4} , (▲) v_{dO} , (▼) v_{dH} . Solid lines are guides for eyes.

and v_{s4}) lead to type I isotherms, confirming that they are sensitive only to the monolayer formation occurring at low p/p^0 . Our results give no evidence for site selectivity: as shown for methane in Fig. 4, the alteration of the different surface signals occurs at roughly the same p/p^0 for all the gases.

We now focus on the dH mode shifted by the different adsorbates. Fig. 3 and Table 2 clearly show that both its position and its intensity are in all cases modified. We have measured a red-shift within a range of $7\text{--}60 \text{ cm}^{-1}$, in agreement with previous results [1]. This shift strongly depends on the nature of the adsorbate and is clearly not directly linked to the net heat of adsorption. For example, a 22 cm^{-1} red-shift is obtained with a net heat of adsorption of 2.5 kJ mol^{-1} in the case of

Table 2

Infrared data of the dH mode for different adsorbates on amorphous ice

	T	v_{dH}	Δv_{dH}	A_{dH}/A_0
Bare ice	50–100	3696	–	–
CH_4	73	3672	–24	1.1
N_2	56	3674	–22	1.7
CO	56	3636	–60	2.1
Ar	53	3684	–12	1.0
Kr	78	3681	–17	1.0
CF_4	95	3691	–7	1.0

Adsorption temperature T (K); position of the dH mode v_{dH} (cm^{-1}); shift of the dH mode Δv_{dH} (cm^{-1}); ratio between integrated absorbance of the shifted dH mode A_{dH} and integrated absorbance of bare ice dH mode A_0 .

nitrogen, whereas a three times larger red-shift (60 cm^{-1}) is obtained with a comparable value of net heat of adsorption (2.6 kJ mol^{-1}) in the case of carbon monoxide. A recent study has shown that the frequency shift more likely depends on the electric field variation at the OH bond of ice [14]. Table 2 shows that CO and N_2 present the larger intensity enhancement which is probably correlated to their specific quadrupolar interaction already mentioned: in fact, it is well known that the infrared intensity is strongly dependent on binding and for example, increases as the strength of H-bonding increases.

4. Conclusion

CH_4 , N_2 , CO, Ar, Kr and CF_4 adsorption isotherms at temperatures between 50 and 100 K provide evidence for different types of wetting. We have measured low values of the heat of adsorption showing that the ice is weakly attractive for these gases, the highest values being obtained for CO and N_2 . Our results have also clearly shown modifications induced by the adsorption in the three surface vibrations which are consistent with the type of wetting. For the monolayer capacity, both the position and the intensity of the dangling OH mode strongly depend on the nature of the adsorbate, and potentially give fruitful informa-

tion on the nature of the interaction. Finally, by comparing the volumetric and spectroscopic isotherms in all studied cases, the whole surface sites seem to be simultaneously affected by the adsorption process.

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