Volumetric and infrared co-measurements of CH₄ and CO isotherms on microporous ice

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Abstract

CH_4 and CO adsorption isotherms on microporous ice surfaces have been performed simultaneously by pressure measurements and infrared spectrometry in the 50–80 K temperature range in order to compare the two techniques: volumetric isotherms allow evaluation of the surface area of the ice and the net heat of adsorption by the BET model, while infrared spectrometry gives complementary information on the nature of the chemical or physical bonding interaction. Our results show that the two methods are well correlated and that their comparison provides valuable information on the different adsorption sites. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The reactivity and the structure of amorphous ice have been extensively studied over many years because of its importance in the interstellar dust. A lot of experiments have been performed in order to characterize the ice surface, particularly by adsorption isotherms [1–5]. An important result has been obtained by Mayer and Pletzer [2,3] who have shown that amorphous ice is a microporous solid. This microporosity is nevertheless associated with a large external surface: type II isotherms are observed containing contributions both from the micropores (type I) and from the external surface. Micropores whose dimensions do not exceed 20 Å lead to specific confined adsorption – their contribution is dominant for the first stages of adsorption while, for higher coverages, the external surface allows the development of multilayer adsorption. On the other hand, infrared spectroscopy has been widely used to characterize the surface structure of amorphous ice, especially by the Devlin group [6–8]. They have established that free OH groups exist at ice cluster surfaces and within pores of amorphous ice. These free OH groups, called dangling OH, can be used as a probe for adsorption on ice provided that they present a measurable band in infrared spectra. The band centered at 3696 cm⁻¹ is assigned to the free OH group of a three-coordinated surface water molecule.

This Letter is aimed at presenting the first results of simultaneous measurements of isotherms by volumetry and by infrared spectroscopy, and shows a possible correlation between these two techniques.

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For such experiments, it is interesting to use an adsorbate which exhibits infrared active modes in order to compare the modification of the corresponding absorbance with that of the dangling OH of the ice surface. The probe molecules chosen here are methane (CH_4) and carbon monoxide (CO) for the following reasons:

- they are frequently used as a probe of solid surfaces,
- they do not significantly perturb the surface because of their poor affinity with water,
- they are components of the interstellar dust.

The case of carbon monoxide as a test of our experimental set-up was particularly interesting because its adsorption on ice surface has already been widely studied by infrared spectroscopy [9–11]. Moreover, previous work in our laboratory [12] presented the first CO isotherms on amorphous ice obtained by this last technique.

2. Experimental section and methods

Isotherm experiments were measured in a stainless steel cell with two sapphire windows enabling infrared spectra to be taken in the range 4000–1600 cm^{-1} in the transmission mode. This cell was connected to a stainless steel volume with two pressure gauges in the 10^{-1}–10^5 Pa pressure range. Then, it was included in a closed-cycle helium cryostat with KBr windows maintained continuously under a vacuum better than 10^{-4} Pa. The cell temperature could be adjusted between 40 and 300 K with a precision of 0.1 K.

Infrared spectra were collected using a Nicolet 7199 FTIR spectrometer. The resolution was 1 cm^{-1} and 200 scans were collected per spectrum.

The CH_4 and CO physical properties are reported in Table 1. We will present the results concerning only one isotherm for each gas. The

Table 1
Physical properties for CH_4 and CO [20]: triple point (τ), critical temperature (T_c) and critical pressure (P_c)

Gas	τ (K, kPa)	T_c (K)	P_c (Pa)
CH_4	90.7, 11.8	190.5	4655.7
CO	68.1, 15.4	132.9	3498.7

temperature of the cell was determined by measuring the saturation pressure (p^0) and using Clapeyron's law [1] (for CH_4, $T = 71.9$ K; for CO, $T = 52.6$ K). For the two gases, the working temperature is less than the triple point temperature (τ).

Due to our experimental set-up, icy samples were prepared as follows: a gas mixture H_2O/Ar (1/30) was pulsed once into the cell maintained at 40 K and pumped under a vacuum better than 10^{-4} Pa. At this temperature, both water and argon are trapped. The sample was then slowly annealed to 80 K while the cell was continuously pumped for about 5 h so that argon could desorb. The quantity of ice formed was about 2 mg.

Volumetric isotherms were obtained point by point and for each adsorption step – i.e., for each value of the equilibrium pressure – the infrared spectrum was recorded.

In the Brunnauer, Emmet and Teller (BET) model [15], adsorption occurs by the formation of stacks of molecules on each surface adsorption site. The adsorption of a molecule on a vacant (resp. already occupied) site is characterized by the energy ϵ (resp. ϵ'). The difference between these two adsorption energies is called the net heat of adsorption ΔQ. The surface coverage θ is given by the relation:

$$\theta = \frac{v_{ads}}{v_m} = \frac{Cp/p^0}{(1 - p/p^0)(1 + (C - 1)p/p^0)}, \qquad (1)$$

where v_{ads} is the volume (in cm^3 STP) occupied by molecules adsorbed on the surface and v_m is the monolayer volume. C is called the BET constant. This model is well suited for type II isotherms. The determination of the two parameters v_m and C by fitting the experimental isotherm allows us to evaluate [15,16] the specific surface area of ice, a and the net heat of adsorption, ΔQ. We can estimate the heat of adsorption ($\Delta_{ads}h$) by adding to ΔQ the enthalpy of condensation ($\Delta_{cond}h$). The corresponding values of $\Delta_{cond}h$ are: 4.2 kj/mol for CH_4 and 8.3 kj/mol for CO.

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[1] For CH_4 [13] (resp. CO [14]), the coefficients are: $A = 510.9$ (resp. $A = 433.7$) and $B = 7576$ (resp. $B = 1062$).

3. Results

3.1. Adsorption of methane

Fig. 1 displays infrared spectra of CH_4 adsorbed on amorphous ice in the CH stretching region and in the dangling OH region varying with respect to CH_4 equilibrium pressure for some steps of the adsorption isotherm at the temperature of 71.9 K. In these two regions, the baseline was not horizontal because the bands are on each side of the intense v_3 band of ice at 3240 cm^{-1}. As the CH_4 pressure increases, we observe a decrease in the absorbance of the dangling OH band (v_{dbOH}) at 3696 cm^{-1} while a new one centered at 3674 cm^{-1} is appearing. This weak red shift (22 cm^{-1}) demonstrates the existence of a weak interaction between methane and dangling OH groups of ice surface.

Concerning the stretching mode of methane, we can identify spectra corresponding to the gas phase with its well-known rotational structure and an additional broad band centered at 3010 cm^{-1} probably due to the sorbed molecules. In the following, the v_{CH} absorbance will correspond to the absorbance of this broad band, the rotational and ice contributions both being subtracted.

Fig. 2a shows the corresponding volumetric isotherm (square) of the adsorption of CH_4 as a function of p/p^0. It is a type II isotherm and this confirms that the amorphous ice we prepared is a porous material with both micropores and an external surface. Fig. 2b shows the same isotherm in
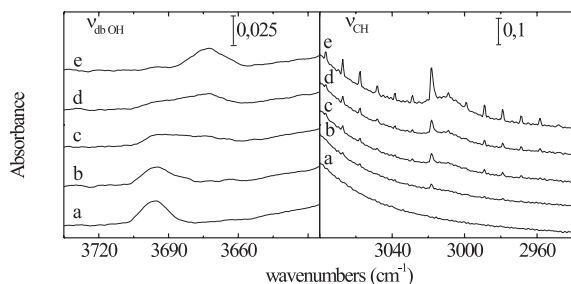

Fig. 2. (a) Isotherms of CH_4 adsorbed on ice at 71.9 K: (□) volumetry, (○) v_{CH} infrared band, and (△) shifted v_{dbOH} infrared band; (b) fit with the BET model (–) of the volumetric values (□).

an extended scale in order to detail the BET fit (deduced from (1)) of the first part of the curve, where the isotherm rises and reaches a plateau. The BET parameters used in Fig. 2b are: $v_m = 25.4 \pm 0.3$ cm^3 STP g^{-1} and $C = 14.7 \pm 0.1$. They lead to a specific surface area equal to 121 ± 1 m^2 g^{-1} using CH_4 as adsorbate with a cross-section of 17.6 Å^2 for our sample of amorphous ice; the net heat of adsorption is equal to 1.6 ± 0.3 kJ mol^{-1} for CH_4 on ice. So, we obtain a heat of adsorption of about 5.8 ± 0.3 kJ mol^{-1}.

Our value of specific surface area of amorphous ice is in the range of those found by Mayer and Pletzer [2,3], whereas our method for preparing the

Fig. 1. CH_4 adsorbed on ice at $T = 71.9$ K: infrared spectra of the dangling OH of the ice and the CH stretching mode of methane for different pressures of CH_4: (a–e) 0, 15.0, 56.7, 115.1 and 405.9 Pa.
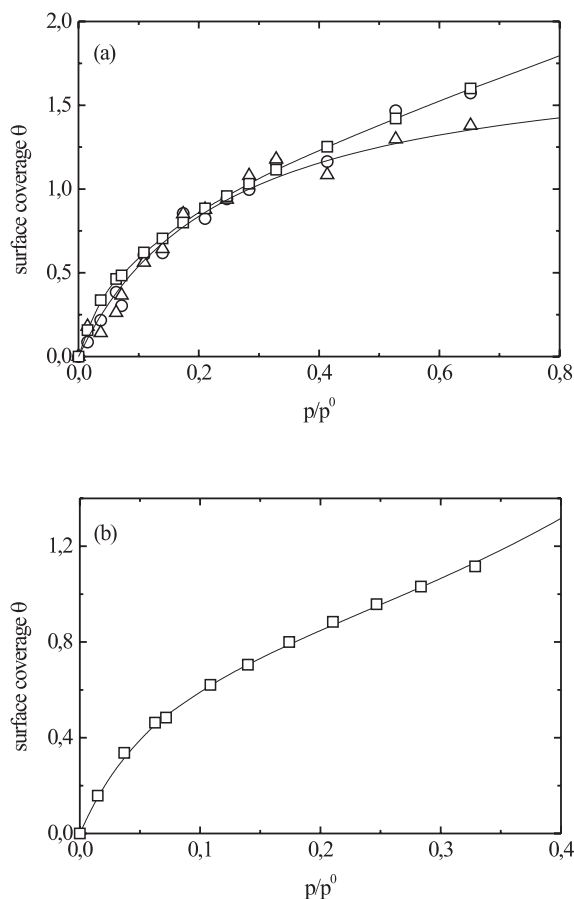
samples is different. Concerning the net heat of adsorption, Chaix et al. [17,18] have found a value of about 1.9 kJ mol^{-1} on three other kinds of ice surface (natural snow, nonannealed and annealed crushed ice) and this compares quite well with our results. In the case of methane on ice, the adsorbate–adsorbant interaction is indeed weak and we do not expect that the net heat of adsorption will depend on the detail of the ice structure.

We have also deduced the isotherm curve from infrared absorbance measurements. We have first checked that the v_{CH} absorbance was proportional to v_{ads} in a large range of p/p^0 ($0 < p/p^0 < 0.8$). Then, we have normalized the absorbance in order to get the surface coverage. We have normalized in the same manner the shifted v_{dbOH} absorbance by using the factor corresponding to the domain of its linear dependence with v_{ads} ($0 < p/p^0 < 0.3$). So, we can compare from Fig. 2a the volumetric isotherm and the infrared ones. The isotherm deduced from v_{CH} clearly follows the volumetric measurements and this validates the use of the integrated absorbance as a quantitative method to obtain an isotherm. On the other hand, the isotherm deduced from v_{dbOH} looks like a type I isotherm which represents a pure surface phenomenon and this confirms that the dangling OH behaviour is a probe of monolayer completion within the porous structure. These experimental evidences lead us to conclude that the v_{CH} infrared signal corresponds to CH$_4$ adsorbed not only on the dangling OH groups. Actually, it also represents multilayer adsorption on the external surface.

3.2. Adsorption of carbon monoxide

Fig. 3 displays the spectral evolution of the dangling OH band (v_{dbOH}) and of the fundamental band of CO adsorbed (v_{CO}) on ice depending on the CO equilibrium pressure for some steps of the adsorption isotherm at $T = 52.6$ K. As for methane, we observe a monotonous decrease of the initial v_{dbOH} band at 3696 cm^{-1} and a correlated increase in a red shifted band at 3642 cm^{-1}. This shift (54 cm^{-1}) has already been observed (Sadlej [19] found a frequency shift of 60 cm^{-1} at 30 K and Devlin [9], 44 cm^{-1} on D$_2$O ices at temperatures
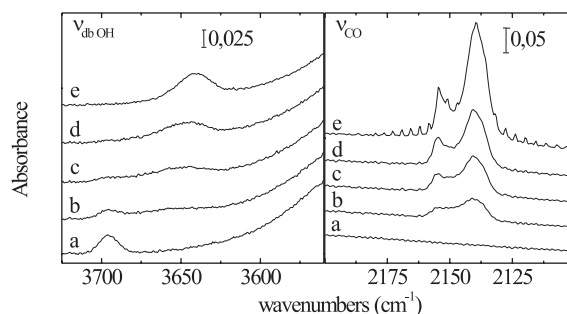

Fig. 3. CO adsorbed on ice at $T = 52.6$ K: infrared spectra of the dangling OH of the ice and the CO stretching mode of carbon monoxide for different pressures of CO: (a–e) 0, 3.1, 6.1, 13.4, 53.3, and 234.6 Pa.

above 28 K) and is larger than the one measured for CH$_4$ (22 cm^{-1}). This clearly suggests that the interaction with the dangling OH groups is stronger for CO than for CH$_4$. In the v_{CO} region, the signal due to adsorbed CO is intense and appears as a doublet: the minor component centered at 2154 cm^{-1} and the strongest peak at 2139 cm^{-1} have already been characterized ([9–11]) and correspond to two adsorption sites. Using CO as adsorbate is thus a tool to study and differentiate at least two kinds of sites on the ice surface. As for CH$_4$, we have normalized the infrared bands v_{CO} and v_{dbOH} in order to plot the corresponding isotherms.

Fig. 4a shows the four isotherms corresponding to volumetric and spectrometric (v_{dbOH}, v_{CO} at 2139 and at 2154 cm^{-1}) measurements. We can notice that the knee of the isotherm is clearly better defined and located at lower relative pressure than for CH$_4$. This confirms that interaction between CO and ice is stronger than between CH$_4$ and ice. In Fig. 4b, we have plotted the isotherm model (obtained with (1)) in an extended range with the following parameters: $v_m = 47 \pm 1$ cm^3 g^{-1} STP and $C = 116 \pm 5$, so that the net heat of adsorption of this molecule is equal to 2.1 ± 0.2 kJ mol^{-1}. This latter value compares well with the one previously measured by Allouche [12]: 2.3 kJ mol^{-1}. It leads to a heat of adsorption equal to 10.4 ± 0.2 kJ mol^{-1}.

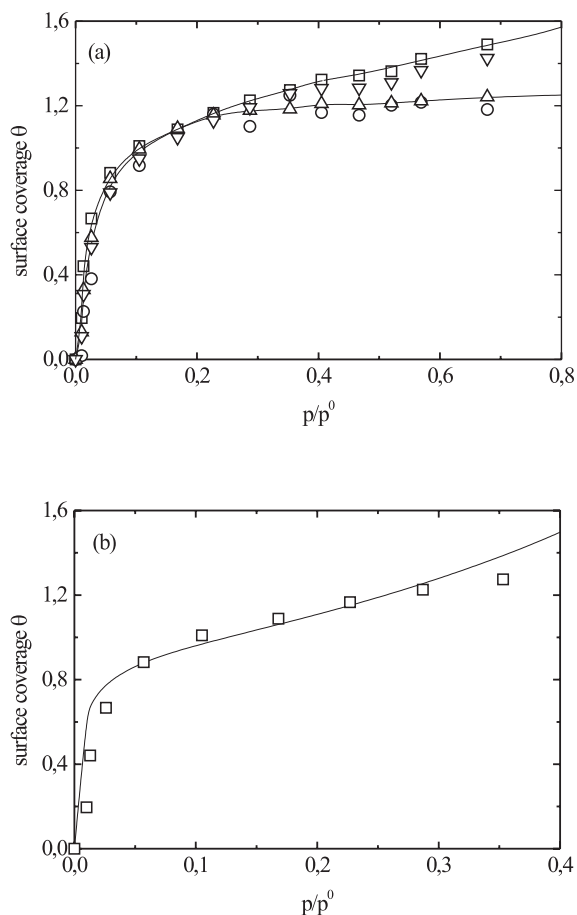As for CH$_4$, the volumetric measurements give type II isotherms whereas infrared absorbance of

Fig. 4. (a) Isotherms of CO adsorbed on ice at 52.6 K: (□) volumetry, (▽) v_{CO} infrared band at 2139 cm^{-1}, (△) v_{CO} infrared band at 2154 cm^{-1}, and (○) shifted v_{dbOH} infrared band; (b) fit with the BET model (–) of the volumetric values (□).

shifted v_{dbOH} suggests a type I isotherm. The v_{CO} absorbance at 2154 cm^{-1} has the same behaviour as the shifted v_{dbOH} absorbance and this strongly indicates that this signal is due only to CO adsorbed on dangling OH of ice surface. This confirms what has already been found, for example by Devlin [9] using CF$_4$ and ethylene oxide in order to select adsorption sites on ice surface and also by Palumbo [10] using co-deposition and diffusion in ice. On the contrary, the isotherm followed by the second v_{CO} band at 2139 cm^{-1} exhibits the same behaviour as the manometric one, even in the range $0.3 < p/p^0 < 1$. It shows that the corresponding adsorption site is not the dangling OH

since it is a type II rather than a type I isotherm. This eliminates the hypothesis of another orientation of the adsorbate on the dangling OH as described by Allouche [12]. Note that this v_{CO} band has been assigned in a previous work to CO molecules interacting with the oxygen atoms of the pore-surface water molecules [9].

4. Summary

This Letter presents the first results obtained for volumetric and infrared co-measurements of CH$_4$ and CO isotherms on amorphous ice. These standard volumetric isotherms allowed us to evaluate the heat of adsorption of two adsorbates: for CO, the values are in good agreement with the ones already measured; for CH$_4$, we get a value close to the one determined on other kinds of ices.

One of the main results is the characterization of the isotherm deduced from v_{dbOH} absorbance as a type I isotherm, while the volumetric measurements lead to a type II isotherm. This allows us to quantify by a new method how much the dangling OH mode characterizes a surface phenomenon.

The correlation between the two measurements and the consistency of the results obtained, in particular, in the case of CO (type I isotherm for the signal at 2154 cm^{-1}; type II for the one at 2139 cm^{-1}), prove the potentialities of the method. They also show that this experimental set-up could be used to differentiate and eventually characterize adsorption sites on the ice surface.

New descriptions are under calculation for the second v_{CO} at 2139 cm^{-1} in order to model this site on the ice surface. We also consider studying the adsorption on amorphous ice of other molecules containing a CO group by the same method.

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