

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

## Part II. The case of CO

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### Abstract

The aim of this paper is to deepen the investigation of vibrational properties of CO adsorbed on amorphous ice, by using the combination of volumetric and spectroscopic isothermal measurements as presented in part I. CO is found to be one of the more interactive molecules that can be physisorbed on ice, as proved by the sharp increase in the adsorbed amount at the monolayer formation. The analysis of the evolution of the infrared signals as a function of equilibrium pressure, for both ice and CO, allows us to elucidate the origin of the peak at  $2139\text{ cm}^{-1}$  as due to CO–CO interactions and to characterize the evolution of the three ice surface signals. Pre-adsorbing  $\text{CF}_4$  or  $\text{CH}_4$  enables site selectivity to be evidenced, CO being preferentially associated to dangling O–H bonds. © 2002 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

The work of Devlin and co-workers [1,2] has shown that the CO molecule is a sensitive probe of the adsorption on ice for two main reasons. Firstly, two distinct CO vibrational modes (which we have measured at  $2154$  and  $2139\text{ cm}^{-1}$ ) are found when the molecule is deposited onto amorphous ice, leading to the characterization of at least two distinct types of adsorption sites. Secondly, the vibrational signal of the free O–H bonds at the ice surface is strongly red-shifted ( $60\text{ cm}^{-1}$ ), leading to clear information on the occupancy of these

surface sites (referred to as dH sites [3]). Various studies have confirmed these results and have discussed the origin of the two CO signals [4–9]. The comparison of the results obtained for  $\text{CO}\cdots\text{CO}$  dimers,  $\text{CO}\cdots\text{H}_2\text{O}$  complexes [8,10], mixed CO:  $\text{H}_2\text{O}$  ices and solid CO clearly shows that a blue shift for the CO vibration like that observed for the band at  $2154\text{ cm}^{-1}$  indicates the existence of a H bond with a water molecule while the  $2139\text{ cm}^{-1}$  signal, close to the solid CO signal, is caused by CO–CO interactions. This allows the high-frequency band to be attributed to the adsorption on the dH site whereas the origin of the low-frequency band is still puzzling. It has been tentatively assigned to CO molecules interacting with other surface sites [1], or to CO molecules interacting with the dH sites in the reverse orientation [7]. It

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may also be due to direct CO–CO interaction [4] or to the formation of CO aggregates.

Two other adsorption sites have been identified for the ice surface, where an electronic oxygen bond is dangling (referred to as dO sites) and where the water molecule is four-coordinated (referred to as s4 sites) [3]. The adsorption of different gases on these three sites has been analyzed in part I [11], and we will focus here on the case of CO, being one of the more interactive molecules. Our experimental set-up has been developed to perform simultaneously both FT-IR spectrometry and volumetry measurements in order to control the adsorbed amount causing the spectral modification [12]. Thermodynamical and structural data like adsorption energy, specific area, and type of wetting, can be deduced from the volumetric measurements. Furthermore, we are able to plot what we call infrared isotherms, i.e., evolution of the various infrared signals as a function of the equilibrium pressure of the gas above the surface. Typical behaviors caused by a pure surface phenomenon, by a multilayer adsorption, or by some enhanced interaction can be easily identified, leading to direct information about the origin of the infrared bands.

In Section 3, we will detail the evolution of the infrared signals during the adsorption process, from submonolayer to bulk, and in Section 4, we will discuss results obtained in the case of successive adsorption of CF<sub>4</sub> or CH<sub>4</sub> with CO on ice.

## 2. Experimental

We performed both infrared spectroscopy (transmission mode) and adsorption isotherms with a sample of amorphous ice prepared by spraying at 40 K a mixture of H<sub>2</sub>O/Ar (1/30) into a copper cell and by carefully annealing it at 90 K. CO was then introduced step by step, allowing infrared spectra as well as equilibrium pressure  $p$  to be measured. The experimental procedure and the method used for determining the surface coverage  $\theta$  are detailed in part I. We present here results obtained for CO deposited at a temperature of 56 K as deduced by measuring saturation pressure  $p^0$  (5.9 Torr) and by using the Clapeyron's

law. In the case of successive adsorption, the temperatures were 51 K for CO, 73 K for CH<sub>4</sub> and 95 K for CF<sub>4</sub>: they were chosen high enough to enable the gases to reach equilibrium, i.e. to have enough mobility.

The origin of the gases was: for CO, Alpha Gaz (chemical purity of 99.997%), for CH<sub>4</sub>, Air Liquide (99.95%), for CF<sub>4</sub>, Linde Gas (99.8%) and for Ar, Linde Gas (99.9996%) and they were used without further purification while H<sub>2</sub>O was distilled by successive cycles of freezing and pumping.

## 3. CO adsorption

Fig. 1 shows the evolution of the infrared spectra, in the  $\nu_{\text{OH}}$  region for the dH site of the substrate, and in the  $\nu_{\text{CO}}$  region for the adsorbate, as the equilibrium pressure is increasing. The two peaks at 2139 and 2154 cm<sup>-1</sup> are both increasing from the very earliest stages of adsorption while only the first one continues increasing at the last stages (for  $p/p^0 > 0.05$ ). At low pressure, almost all the CO amount introduced in the cell is adsorbed on the substrate and the rotational structure of the gas phase is not observed on the spectrum while it clearly appears at higher pressure. The corresponding variation of the dH mode position is an increase in a red-shifted band at 3636 cm<sup>-1</sup> correlated to the decrease of the bare ice

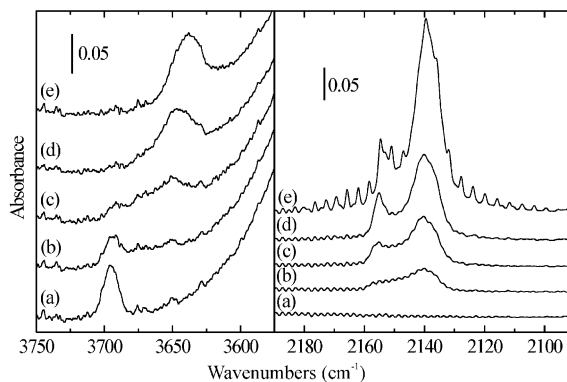


Fig. 1. Infrared spectra of CO adsorbed on ice, left:  $\nu_{\text{dH}}$  region; right:  $\nu_{\text{CO}}$  region, for various relative pressure of CO  $p/p^0$ : (a) bare ice; (b) 0.005; (c) 0.009; (d) 0.031; (e) 1.000. Spectra are offset for clarity.

band at  $3696\text{ cm}^{-1}$ . This variation ends for  $p/p^0$  at roughly 0.05, indicating that pure surface adsorption has ended, at least on the dH sites. It should be noted that both position and intensity of the dH mode are modified by adsorption. In the case of CO, the shift is  $60\text{ cm}^{-1}$  large and the intensity is twice, as measured by the integrated absorbance of the  $\nu_{\text{dH}}$  band, before and at the end of adsorption. These values indicate a strong influence of the adsorbate on the surface vibrational properties of ice. This point has been recently discussed in detail in the work of Manca and Allouche [13] where the modifications in the dangling O–H bond length and vibration frequency have been calculated using an ab initio method for various adsorbates. The authors have clearly shown that they were surprisingly not correlated with the strength of the interaction but that they were rather due to a vibrational Stark effect.

Fig. 2 shows the evolution of the difference between the spectrum of CO adsorbed on ice and that of bare ice, within the  $3720\text{--}3430\text{ cm}^{-1}$  range. The dH signal evolution described above is also evidenced here and, in addition, these difference spectra permit to identify two other surface sig-

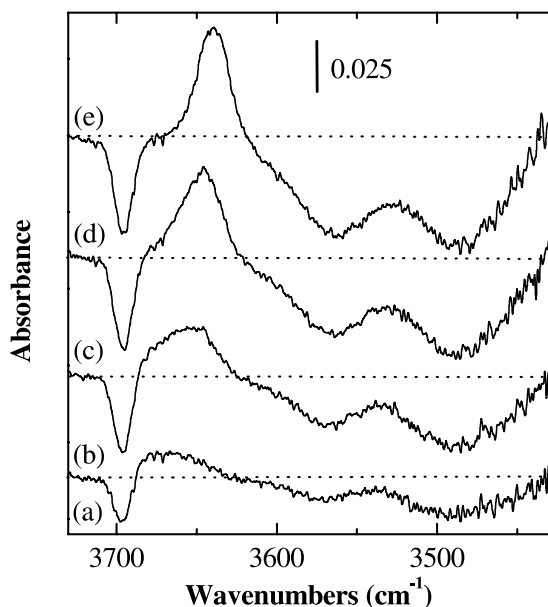


Fig. 2. Same as Fig. 1, in the whole surface  $\nu_{\text{OH}}$  region, the spectrum of bare ice being subtracted.

nals,  $\nu_{\text{dO}}$  at  $3563\text{ cm}^{-1}$  and  $\nu_{\text{s4}}$  at  $3489\text{ cm}^{-1}$ , by their monotonous decrease during adsorption. The widths of these negative signals can be roughly estimated respectively at 55 and  $95\text{ cm}^{-1}$  and are much larger than that of the dH band ( $15\text{ cm}^{-1}$ ). For this reason, contrary to the case of dH, no corresponding positive signal is visible, meaning that the measured signal is the addition of a negative part—due to the disappearance of the bare ice sites—and a positive part—due to the appearance of new O–H interactions caused by CO coverage—of different absorbing cross-section, so that the resulting effect is a decrease. Moreover, at  $p/p^0 = 0.01$ , the initial dH band has totally disappeared while the other signals continue to change, decreasing for the negative bands and both increasing and shifting for the positive dH band. It should also be mentioned that the three  $\nu_{\text{OH}}$  bands are modified roughly simultaneously, indicating limited site selectivity in the adsorption processes. A more detailed analysis can be done for the dH band: decreasing at the earliest stages of adsorption means that dH sites are immediately affected, probably by a close neighboring, while further shifting means that adsorption configuration and interaction strength are continuously changing during the whole formation of the monolayer until the optimum compacity is achieved. This confirms that the dH signal is a very good probe of adsorption, being very sensitive to the local ordering appearing during the monolayer completion.

Fig. 3 shows the complete set of isotherms which can be drawn here, i.e. the standard volumetric isotherm together with arbitrarily normalized infrared isotherms calculated for, on the one hand, the  $\nu_{\text{dH}}$ ,  $\nu_{\text{dO}}$  and  $\nu_{\text{s4}}$  bands of ice and, on the other hand, the  $\nu_{\text{CO}}$  ( $2139\text{ cm}^{-1}$ ) and  $\nu_{\text{CO}}$  ( $2154\text{ cm}^{-1}$ ) bands. Two distinct behaviors are clearly identified:  $\nu_{\text{dH}}$ ,  $\nu_{\text{dO}}$ ,  $\nu_{\text{s4}}$  and  $\nu_{\text{CO}}$  ( $2154\text{ cm}^{-1}$ ) isotherms are type I, i.e. isotherm having a horizontal plateau (for  $p/p^0 > 0.05$ ). This means that they are related to a pure surface phenomenon: the adsorbed amount rapidly increases at  $p/p^0 < 0.05$  as the monolayer is formed and then remains constant, no surface site being free. Conversely,  $\nu_{\text{CO}}$  ( $2139\text{ cm}^{-1}$ ) isotherm is type II, similar to that of the standard volumetric measurements. In this

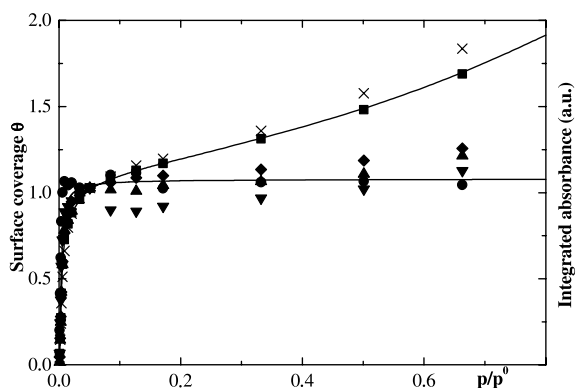


Fig. 3. Isotherms obtained for CO adsorbed on amorphous ice at 56 K. (■) volumetry; (♦)  $\nu_{\text{CO}}$  (2154  $\text{cm}^{-1}$ ); (×)  $\nu_{\text{CO}}$  (2139  $\text{cm}^{-1}$ ); (●)  $\nu_{\text{dH}}$ ; (▲)  $\nu_{\text{dO}}$ ; (▲)  $\nu_{\text{s4}}$ . Surface coverage  $\theta$  is the adsorbed amount divided by that of a monolayer.

case, the adsorbed amount continues to increase for  $p/p^0 > 0.05$  because of multilayer formation. Firstly, these results confirm that the  $\nu_{\text{dH}}$ ,  $\nu_{\text{dO}}$ ,  $\nu_{\text{s4}}$  infrared bands are produced by ice surface only and that the CO peak at 2154  $\text{cm}^{-1}$  is also produced by a sole surface effect. This is in full agreement with its previous attribution, by means of spectroscopy alone, of CO interacting with the dangling H bonds. Secondly, they show that the origin of the CO peak at 2139  $\text{cm}^{-1}$  is multiple: both surface adsorption and multilayer formation contribute to this signal, the latter causing the growth of the band well after that at 2154  $\text{cm}^{-1}$ .

#### 4. Successive adsorptions

We have performed CO adsorption on an icy sample previously coated with a pre-adsorbate:  $\text{CH}_4$  or  $\text{CF}_4$  at  $p/p^0 \approx 0.8$ , i.e. roughly two monolayers. Our aim was to compare the adsorption of CO in the case of a free surface and in the case of such a coated surface.  $\text{CH}_4$  shows a behavior intermediate between that of CO and of  $\text{CF}_4$  (part I) and has been chosen here to make a comparison with  $\text{CF}_4$  as a pre-adsorbate.

Fig. 4A displays the volumetric isotherms obtained by adsorbing CO alone, CO after  $\text{CF}_4$  and CO after  $\text{CH}_4$ , the adsorbed amount being that of CO only. The shape of the CO isotherm is clearly modified by the pre-adsorbate, even more for  $\text{CH}_4$

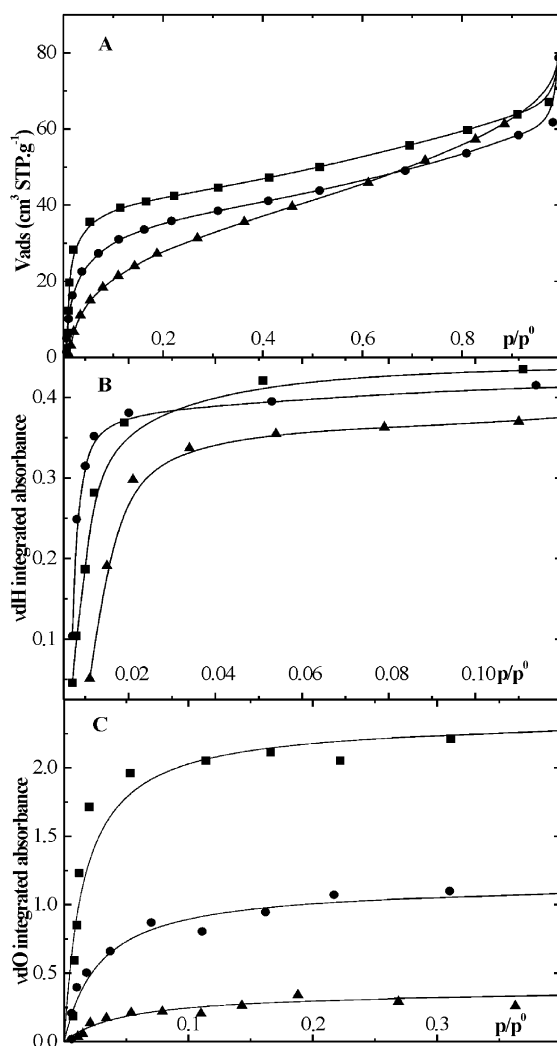


Fig. 4. Isotherms obtained for CO (■) CO/ $\text{CF}_4$  (●) CO/ $\text{CH}_4$  (▲) adsorbed on ice: (A) standard volumetry; (B)  $\nu_{\text{dH}}$ ; (C)  $\nu_{\text{dO}}$ .

than for  $\text{CF}_4$  and, as can be expected, the monolayer capacity is reduced when pre-adsorbing a gas.

Fig. 4B (resp. 4C) displays the dH (resp. dO) infrared isotherms obtained for the same three cases of CO adsorption. dH absorbance increases more sharply at lower pressure in the case of  $\text{CF}_4$  pre-adsorption than in the two other cases, indicating that dH sites are left empty: the hydrophobic nature of  $\text{CF}_4$  has already been invoked for explaining similar observation [1,14]. On the other hand, the filling of the dH sites reaches nearly the

same value for the three cases, as shown by the plateau height. Moreover, we have observed the infrared bands of  $\text{CF}_4$  or  $\text{CH}_4$  decreasing while those of CO were increasing: CO adsorbs on free dH sites and it can also replace a pre-adsorbate molecule. Attraction of CO on dH is more efficient than that of  $\text{CH}_4$  or  $\text{CF}_4$ , in agreement with what is shown by the isotherm shapes in part I, and all the dH sites are filled by CO at the end of adsorption. Conversely, CO clearly adsorbs less on dO sites for  $\text{CF}_4$  pre-adsorption than for sole CO adsorption (Fig. 4C), this effect being even more pronounced for  $\text{CH}_4$  (s4 site behavior has been found analogous). This is consistent with the evolution of the  $\nu_{\text{CO}}$  absorbance which is displayed in Fig. 5 in the case of  $\text{CF}_4$ . Contrary to the case of sole CO (Fig. 1), the peak at  $2154\text{ cm}^{-1}$  is appearing alone at the beginning of adsorption, confirming that only dH sites are being filled by CO. We observe here a site selectivity, CO preferentially interacting with dH sites and inducing a partitioning of the adsorbates: CO on dH sites and  $\text{CF}_4$  or  $\text{CH}_4$  on dO and s4 sites.

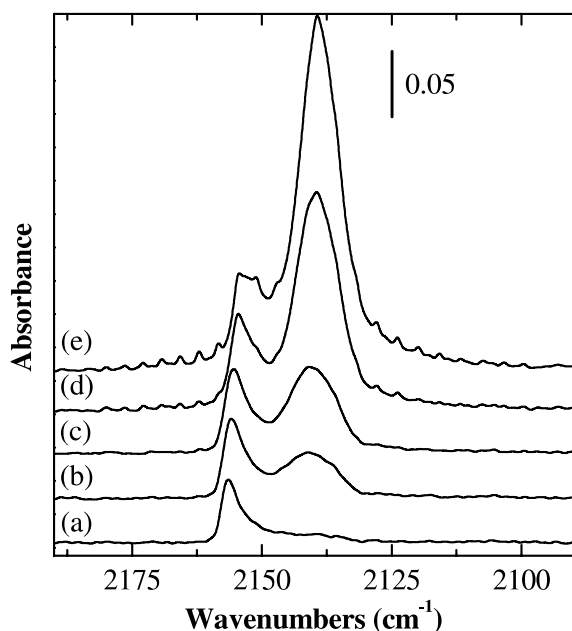


Fig. 5. Infrared spectra in the  $\nu_{\text{CO}}$  region for CO/ $\text{CF}_4$  adsorbed on ice for various CO relative pressure  $p/p^\circ$ : (a) 0.006; (b) 0.018; (c) 0.037; (d) 0.411; (e) 1.000. Spectra are offset for clarity.

## 5. Conclusion

We have performed simultaneously infrared spectroscopy and adsorption isotherm measurements for CO adsorbed on amorphous ice in order to get the modifications in the vibrational properties of both surface and adsorbate, while checking the nature and the quantity of the adsorbed amount.

The analysis of the results obtained has enlightened the attribution of the infrared signal of the CO molecule: the high-frequency peak at  $2154\text{ cm}^{-1}$  is caused by a surface interaction with the dangling H bond only, while the low-frequency peak is caused by both surface and multi-layer effects. The adsorption of CO following a  $\text{CH}_4$  or  $\text{CF}_4$  coating has revealed a site selectivity, CO preferentially adsorbing on dH sites. Our ongoing research program is to compare these experimental observations with ab initio calculations and to simulate the full completion of the monolayer.

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