Segregation effect and N$_2$ binding energy reduction in CO-N$_2$ systems adsorbed on water ice substrates

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ABSTRACT

Context. CO and N$_2$ are two abundant species in molecular clouds. CO molecules are heavily depleted from the gas phase towards the centre of pre-stellar cores, whereas N$_2$ maintains a high gas phase abundance. For example, in the molecular cloud L183, CO is depleted by a factor of $\approx 400$ in its centre with respect to the outer regions of the cloud, whereas N$_2$ is only depleted by a factor of $\approx 20$. The reason for this difference is not yet clear, since CO and N$_2$ have identical masses, similar sticking properties, and a relatively close energy of adsorption.

Aims. We present a study of the CO-N$_2$ system in sub-monolayer regimes, with the aim to measure, analyse and elucidate how the adsorption energy of the two species varies with coverage, with much attention to the case where CO is more abundant than N$_2$.

Methods. Experiments were carried out using the ultra-high vacuum (UHV) set-up called VENUS. Sub-monolayers of either pure $^{13}$CO or pure N$_2$ and $^{13}$CO-N$_2$ mixtures were deposited on compact amorphous solid water ice, and crystalline water ice. Temperature-programmed desorption experiments, monitored by mass spectrometry, are used to analyse the distributions of binding energies of $^{13}$CO and $^{15}$N$_2$ when adsorbed together in different proportions.

Results. The distribution of binding energies of pure species varies from 990 K to 1630 K for $^{13}$CO, and from 890 K to 1430 K for $^{15}$N$_2$. When a CO-N$_2$ mixture is deposited, the $^{15}$N$_2$ binding energy distribution is strongly affected by the presence of $^{13}$CO, whereas the adsorption energy of CO is unaltered.

Conclusions. Whatever types of water ice substrate we used, the N$_2$ effective binding energy was significantly lowered by the presence of CO molecules. We discuss the possible impact of this finding in the context of pre-stellar cores.

Key words. astrochemistry – methods: laboratory: molecular – ISM: molecules

1. Introduction

CO and N$_2$ are two of the most abundant species in molecular clouds and they affect the abundances of many other molecules. CO is the second most abundant molecule after H$_2$ in the gas phase and is highly abundant in the solid phase. CO ice absorption features are seen superposed on the spectra of background sources or embedded protostars (e.g. Chiar et al. 1995; Pontoppidan et al. 2003). The solid CO abundance varies strongly from source to source, but can be as high as 10$^{-4}$ with respect to H$_2$ in the coldest cores (Pontoppidan et al. 2005).

The amount of N$_2$ in the gas and in the solid state is uncertain, since N$_2$ cannot be detected directly as it lacks a permanent dipole moment. The abundance of gas phase N$_2$ is usually inferred from the presence of its daughter species N$_2$H$^+$ mainly formed via the reaction N$_2$ + H$^+_3$ $\rightarrow$ N$_2$H$^+$ + H$_2$. Similarly, HCO$^+$ is formed from CO following a similar reaction scheme CO + H$^+_3$ $\rightarrow$ HCO$^+$ + H$_2$. But CO is also one of the main destroyers of N$_2$H$^+$ in the gas phase via the reaction CO + N$_2$H$^+$ $\rightarrow$ N$_2$ + HCO$^+$. When CO freezes out on to dust grains, N$_2$H$^+$ abundance is enhanced, as confirmed by the anti-correlation of the abundances of N$_2$H$^+$ with CO and HCO$^+$ in the pre- and proto-stellar regions (Bergin et al. 2001; Tafalla et al. 2002; Di Francesco et al. 2004; Pagani et al. 2005; Jorgensen 2004). This anti-correlation was sometimes quantitatively explained by assuming that a ratio of 0.65 exists between the binding energies of N$_2$ and CO, allowing N$_2$ to stay in the gas phase while CO can freeze out on to H$_2$O-covered grains (Bergin & Langer 1997). However, for pure species in thin layers or mixed species thick layers, such a high difference in binding energy between N$_2$ and CO has never been reported (Öberg et al. 2005; Bisschop et al. 2006; Fayolle et al. 2016).

Freeze-outs of CO and N$_2$ are difficult to quantify in dark clouds. N$_2$ is not directly detectable as explained above, and emission of the depleted CO in the central parts of the clouds is so weak that it is completely masked by the strong, unattenuated emission of the envelope. Since H$^+_3$ reacts with both species, the products of the reactions (DCO$^+$, N$_2$H$^+$, and N$_2$D$^+$) can be used to trace their abundance as shown in Pagani et al. (2012). By using this method, Pagani et al. (2012) reported a steeper depletion profile of CO with respect to N$_2$ towards the centre of the L183 pre-stellar core. The origin of this selective depletion remains unknown.

There are many possible explanations, although none of them is fully convincing. It can be due to the imperfection of the gas phase chemical network, which was recently improved (Le Gal et al. 2014). If the microphysics at the surface of grains plays a role, we can basically think of two possibilities. The first possible explanation is of chemical origin, namely can be a differentiation in the chemical properties once CO and
N₂ are both present on the surface of grains. It is known that CO can be hydrogenated into methanol (Hirao et al. 1994; Watanabe & Kouchi 2002; Minissale et al. 2016), whereas N₂ does not react with H atoms (Ioppolo et al. 2015; Fedoseev et al. 2015). Moreover, N-atom diffusion is faster than that of O atoms (Minissale et al. 2015), and N₂ is also very stable when compared to O₂ or CO. However, there are not quantitative studies about the [N+H] or [N₂+H] reactive networks to be able to make a clear prediction about the impact of the surface chemistry. The second possible explanation is of physical origin, since there exist reasons to think that some physical processes can play an important role, and especially a surface segregation effect of certain species. Previously, we found that H₂ isotopologues as well as molecular hydrogen of different spin states desorb at different temperatures (Dulieu et al. 2005; Amiaud et al. 2008, 2015), which can lead to appreciable changes in the abundance of H₂ isotopologues adsorbed on dust grains (Kristensen et al. 2011). Later, we have demonstrated that this segregation mechanism can also apply to molecules whose binding energy distributions are close, like O₂ and CO (Noble et al. 2015). We have shown that a small average difference of 85 K between the centres of two binding energy distributions can fully explain the observed kick-out mechanism of O₂ by CO during the desorption phase. We used the Fermi-Dirac statistics in order to calculate the adsorption site population distribution, and we managed to reproduce all the features of the CO and O₂ desorption traces.

In the present article, we propose a study of the desorption of N₂ and CO mixtures from different water ice substrates in the sub-monolayer regime. As for multi-layer regimes see Bisschop et al. (2006). Since the desorption mechanism takes place in the very outer layer, our study focuses on thin layers to mimic the action of the underlying icy template as in Fayolle et al. (2016). Here, we study CO:N₂ mixtures relevant to polar ices (water-dominated) covering dust grains, with CO being always the most abundant species (Taquet et al. 2012; Pagani et al. 2012). We use ¹³CO molecules and ¹⁵N₂ molecules in order to be able to distinguish the two species by mass spectrometry. The water ice substrates used in this study are compact and porous amorphous solid water, and poly-crystalline water ice. Experimental studies have shown that interstellar porous ice analogues can be compacted quite efficiently by UV irradiation, cosmic ion bombardment, and H-atom recombination at their surface (Palumbo et al. 2010; Palumbo 2006; Raut et al. 2008; Accolla et al. 2011), which suggests that water ice in space is almost certainly amorphous and non-porous (compact). We have however carried out a series of experiments also on poly-crystalline ice as it provides a more ordered surface, and because studying water ice templates other than a compact amorphous substrate alone can be of interest for specific interstellar environments where ices may have undergone energetic processing, for example protostellar objects (Dartois et al. 2002).

This paper is organized as follows: Sect. 2 focuses on the experimental methods. In Sect. 3 we present the experimental results. In Sect. 4 we will derive the desorption energy distributions and apply a model that is able to reproduce the desorption behaviour of CO:N₂ mixtures using a simple Fermi-Dirac statistical approach. Finally, we will address the astrophysical implications of these findings.

### 2. Experimental protocol

All experiments were performed using the UHV set-up named VENUS (VÊrs de NoUvelles Synthèses) based in the LERMA laboratory at the University of Cergy Pontoise. VENUS is a new apparatus that will be described in detail in a forthcoming paper so the set-up and the experimental techniques are only summarized here. The experiments take place under ultrahigh vacuum (UHV) conditions (base pressure $8 \times 10^{-11}$ mbar) in a stainless steel chamber. The sample holder is made of a circular copper mirror coated with gold, and mounted onto the cold head of a closed-cycle He cryostat. The sample temperature can be controlled in the 7–350 K range by using a regulated resistive heater clamped on the back of the sample holder.

The first step of each experimental run is the deposition of a water ice substrate. To grow the water ice substrate we use the so-called background deposition as follows: water vapour is injected into the main chamber until a pressure of $1.2 \times 10^{-8}$ mbar is reached, and is kept constant during the deposition process until the desired ice thickness is attained. The purity of the water vapour, meaning the absence of air contamination or H₂ release from the walls of the chamber, is monitored via a quadrupole mass spectrometer (QMS). The water ice thickness deposited on the gold surface is monitored via a Fourier Transform InfraRed Spectrometer (FTIR), used in a grazing-angle reflection absorption configuration. The calibration of the water ice thickness via FTIR and QMS was carried out in a separate set of experiments when the amount of water ice deposited was measured as a function of time using the H₂O partial pressure in the chamber, since a given pressure corresponds to – within the accuracy of the pressure gauge – a precise flux of molecules impinging on the walls of the chamber. Subsequently, the comparison between the number of deposited water layers and the infrared/mass spectra allows definition of the one-monolayer standard expressed in IR-band area units or TPD peak area units, with an accuracy of ±0.2 monolayers. Typically, a substrate of 15 layers of compact amorphous solid water ice (c-ASW) is grown by keeping the surface temperature at 110 K during water deposition. Once the deposition phase is finished, we wait until the partial pressure of water vapour in the main chamber has reached its pre-dosing value ($<10^{-10}$ mbar), and only then the sample temperature is cooled further or increased. To obtain a poly-crystalline ice (PCI) substrate, the sample holder is held at 110 K during the deposition, then flash heated to 145 K, and simultaneously the water ice film phase transition, from amorphous to crystalline, is monitored via both QMS and FTIRS. When the phase transition is complete, we cool the surface to 10 K before commencing the experiments. During the crystallisation phase, we estimated a loss of about 3 out of 15 initial layers of water ice, although we determined – by analysis of the desorption profiles of CO and N₂ – that the icy substrate remains thick enough that the adsorbed molecules interact with the crystalline template only. Finally, the porous amorphous solid water (p-ASW) ice substrate is formed by growing 5 monolayers of ice at a surface temperature of 40 K on top of the c-ASW substrate, then it is annealed to 55 K to stabilize the film morphology before the subsequent heating-cooling experiments between 10 and 55 K. Although the degree of porosity of the p-ASW substrate is less pronounced than that of an ice film grown at 10 K and not annealed, the p-ASW ice substrate we use maintains the same overall properties as far as the physisorption binding energies are concerned (Fillion et al. 2009).

Once the desired water ice substrate is formed, the surface temperature is cooled to 10 K. CO and N₂, isotopically labelled ($^{12}$CO and $^{15}$N₂), can be dosed onto the surface via one triple-differentially-pumped molecular beam. The composition of the beam is monitored through a second QMS located in the
second stage of the beam-line. The surface is held at 10 K during every CO/N$_2$ deposition. In case of deposition with CO-N$_2$ mixtures, the gas is previously prepared in a dedicated reservoir to be connected to the beam source. The injected flow of gas is set to 0.3 standard cubic centimetre per minute (sccm$^1$), which gives a pressure of around 2 x $10^{-4}$ mbar in the first stage of the beamline. After going through 3 stages of differential pumping and two diaphragms, the molecular beam is well collimated (2-mm diameter) and reaches the main chamber causing here an increase in pressure less than 1 x $10^{-11}$ mbar.

The temperature-programmed desorption (TPD) technique is a powerful method for determining the binding energies of the molecules adsorbed on surfaces. It consists in increasing the surface temperature linearly with time and simultaneously recording the desorbing molecules using mass spectrometry. VENUS is equipped with a QMS placed 5 mm in front of the sample. The heating ramp is constant, $\beta = 0.2$ K s$^{-1}$, for all experiments, and starts from a temperature of 10 K, which is the CO/N$_2$ deposition temperature. TPD analysis is used to derive multi-layer desorption energies of species deposited as thick films, and it also allows us to derive the distribution of adsorption energies on a given surface in the case of sub-monolayer regimes. The adsorption energy is in fact dependent on the amount of molecules deposited, that is the coverage. Therefore, we have to keep in mind that there are three important experimental parameters to take into account: the type of species, the type of surface, and the coverage (Kimmel et al. 2001; Fillion et al. 2009; Noble et al. 2012).

The coverage is given in monolayer (ML) units, with the typical approximation that 1 ML = 1 x $10^{15}$ molecules cm$^{-2}$, which corresponds to the number of adsorption sites per cm$^2$ on compact amorphous solid water. It is a unit of surface density: when the coverage equals 1 ML, it means that all the adsorption sites of the ice surface are occupied in the case of a fully wetting molecule, such as CO or N$_2$. Should another molecule come to the surface it will adsorb onto an already adsorbed molecule so as to begin a second-monolayer layer. With respect to first-layer particles, molecules that belong to the second layer exhibit weaker interactions with the substrate, and their desorption properties are, in general, dominated by molecule-molecule interactions. The first-monolayer layer is complete and the surface coverage is equal to 1 ML only for substrates that have a planar geometry, namely c-ASW and PCI substrates. In the case of porous substrates, the number of binding sites per cm$^2$ increases with water ice film thickness. In fact, porous water ice possesses a 3D structure and the number of adsorption sites is proportional to the geometrical area of the porous ice 3D network.

3. Experimental results

3.1. Pure species

Figure 1 shows three typical sets of TPD curves: $^{15}$N$_2$ desorbing from c-ASW (top panel), $^{13}$CO desorbing from c-ASW (middle panel), and $^{13}$CO desorbing from p-ASW (bottom panel). Figure 2 shows TPD spectra of $^{13}$CO (top panel) and $^{15}$N$_2$ (bottom panel) desorbing from PCI. Each curve corresponds to a given dose, that is the initial coverage at 10 K. For each species deposited on a specific water ice substrate, a family of TPDs exhibits the so-called “filling behaviour”, described by Kimmel et al. (2001). Each type of substrate shows a distribution of adsorption sites with various energy depths, which is why desorption from a full first-monolayer layer occurs over a wide window of temperature, from around 25 K to 55 K. When only a small fraction of a monolayer (e.g. <0.25 ML) is initially present, the desorption only occurs at temperatures in the high end of the TPD peaks, which corresponds to desorption of molecules from sites with the highest binding energies. As the dose is increased, because the best (high-depth) sites are already occupied, molecules are forced to occupy lower energy sites, so desorption occurs earlier and the TPD peak shifts towards lower temperatures. In fact, available sites are progressively filled beginning from high-depth sites towards low-energy ones. The TPD profiles have a leading edge appearing at lower temperature with increasing coverage as is apparent from Figs. 1 and 2, while TPD spectra of a given molecule-substrate system all share a common tail. When the deposited amount reaches 1 ML, a second-monolayer is begun by molecules that form physisorption bounds with molecules of the first-monolayer layer. The presence of molecule-molecule bindings produces a new low-temperature feature (a bump or a real peak) in the TPD profiles corresponding to coverages >1 ML. If the exposure is increased further, the low-temperature peak maximum shifts towards higher temperatures, although the leading edge of all the high-coverage exposures remains unchanged. This is the

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$^1$ 1 sccm = 592 m$^3$ Pa s$^{-1}$ in SI units.
signature of the second-monolayer or multi-layer desorption, which follows a so-called zeroth order desorption. It should be noted that the multi-layer peaks of N$_2$ and CO, desorbing from c-ASW or PCI, appear for the same dose, which indicates that the number of adsorption sites is the same for the two molecule-substrate systems. On the contrary, the multi-layer peak of CO appears after an exposure of 1.5 ML when the substrate is p-ASW ice, which means that the porous substrate exhibits 1.5 more adsorption sites with respect to c-ASW and PCI, due to its 3D structure.

From the analysis of the TPD profiles it is possible to estimate the distribution of binding energies. The desorption rate can be described in terms of an Arrhenius law:

$$r(N, E_b, T) = -\frac{dN}{dt} = A N^n e^{-(E_b/k_B T)},$$  \hspace{1cm} (1)$$

where $r$ is the desorbing flux in ML s$^{-1}$, $E_b$ is the binding energy in J, $A$ is the pre-exponential factor in s$^{-1}$, $N$ is the total number of molecules adsorbed on the surface expressed in ML, $n$ is the order of the desorption kinetics, $k_B = 1.38 \times 10^{-23}$ J K$^{-1}$ is the Boltzmann constant, and $T$ is the temperature of the surface in K. The order $n$ corresponds to the number of reactants necessary to activate the desorption. It corresponds to a stoichiometric coefficient in the desorption equation. The zeroth order represents a desorption kinetics that is independent of the amount of available adsorbate. This is the case of thick films consisting of multi-layers, whose number of molecules at their surface remains constant during desorption, as one molecule that comes off the surface is replaced by another one lying just underneath. The first-order desorption corresponds to the desorption of an adsorbate whose coverage is lower or equal to one monolayer, which is the case of the present study. First-order kinetics implies that the desorption rate is proportional to the number of molecules present on the surface, provided that each molecule has no strong interaction with its neighbours, which means that no reaction is at play. Therefore, for CO and N$_2$ physisorbed on water ice we assume that $n = 1$. The pre-exponential factor can be specifically determined, but it turns out to be coupled with the binding energy $E_b$. However, for the purposes of this work, and to obtain results that can be easily compared to previous publications, we adopt the generally accepted value $A = 10^{13}$ s$^{-1}$, corresponding to the typical vibrational frequency of CO and N$_2$ physisorbed on the surface.

By inverting Eq. (1), the desorption energy $E_b$ can be calculated as a function of coverage $N$. We use the inverted Polanyi-Wigner equation following Dohnalék et al. (2001), also called the classical inversion method, which is now commonly used in laboratory astrophysics (Noble et al. 2012; Collings et al. 2015; He et al. 2016). The first step consists in calculating the number of molecules that have desorbed at a given temperature $T$. To perform this step, the TPD spectrum is integrated between $T_0$ (deposition temperature) and $T$, then divided by the area of the TPD peak $A_{1ML} = \int_{T_0}^{T} \frac{dN}{dT}$ corresponding to 1 ML exposure:

$$N'(T) = \frac{\int_{T_0}^{T} \frac{dN}{dT}}{A_{1ML}}.$$  \hspace{1cm} (2)$$

$N'(T)$ is thus the fraction of molecules (expressed in ML units) that has already desorbed at temperature $T$. The coverage as a function of $T$ can be expressed as the amount of deposited molecules, the initial coverage $N_0$, minus the fraction of molecules desorbed at temperature $T$:

$$N(T) = N_0 - N'(T).$$  \hspace{1cm} (3)$$

Knowing $N(T)$, it is now possible to invert Eq. (1):

$$E_b = k_B T \times \ln \left[ \frac{A N(T)}{r(T)} \right].$$  \hspace{1cm} (4)$$

$E_b$ is the desorption barrier and will be expressed in kelvins ($J/k_B$) henceforth.

Figure 3 shows the distributions of binding energies for $^{13}$CO and $^{15}$N$_2$ on c-ASW. At zero coverage the binding energy of CO is close to 1600 K and that of N$_2$ is around 1400 K. Each curve corresponds to a given TPD shown in Fig. 1. The longer the curve the greater the deposited dose, until a maximum value is reached. CO and N$_2$ have no strong interaction with their neighbours, which means that the maximum of the binding energy has a slight tendency to increase with the dose, which may indicate that at higher coverages a larger fraction of deepest sites is occupied so the desorption process is slowed down. In
fact, the more molecules on the surface, the more molecules are pushed to diffuse and occupy all the available sites. Also, at full coverage on c-ASW ice, the binding energy of the least bound molecules is close to the multi-layer barrier value.

On the other hand, an exposure of 1 ML on porous ASW ice does not correspond to complete occupation of the available sites, because porous ASW has a larger effective area as we explained above. An exposure of about 1.5 ML is necessary before build-up of the second layer on porous water ice (see Fig. 1, bottom panel). We can also notice that the maximum binding energy found on p-ASW is close to the maximum value obtained for c-ASW (1600 K, corresponding to molecules desorbing up to 55 K). This result seems to be not consistent with experiments carried out using H\textsubscript{2} (Fillion et al. 2009), or with the elegant demonstration by Kimmel et al. (2001) who used N\textsubscript{2}. In fact, TPD tails from p-ASW tend to extend to higher temperatures with respect to more ordered substrates, which indicates the presence of deeper adsorption sites associated to larger topological disorder. In this work this does not seem to be the case. The reason for this is that the deposition temperature of water molecules (40 K) and the subsequent thermal annealing until 55 K smoothen the deepest adsorption sites, located on less stable configurations of water clusters showing a reduced number water molecules coordinations. Moreover, the ice thickness that was used in this study is so low that there cannot be a geometrical pore effect (Dohnálek et al. 2003). Yet, if the two binding energy upper values are similar for p- and c-ASW, the shape and a greater number of binding sites on porous water ice results in a global shift towards the high-energy (-temperature) half of the TPD peak.

3.2. Mixed species
We have performed different TPD experiments of mixed species varying the total doses as well as the relative ratios. Figure 6 shows the change in TPD shape obtained by increasing the CO dose (from 0.45 to 1.27 ML) and keeping relatively constant and small the N\textsubscript{2} dose (from 0.065 to 0.11 ML). The gas mixture is
prepared in a reservoir before injection into the beam source. We cannot control precisely the partial pressure of each species, which implies that we have fluctuations of the N\textsubscript{2} dose. For this reason, we do not have a very good control a priori of the individual amounts deposited, although we can finely control the total deposited amount of the mixed species. Finally, we can precisely measure the mixture composition a posteriori, by integrating the TPD curves. Figure 6 shows that the CO desorption profiles seem to be una.

We have previously shown that mixed species or isotopologues physisorbed in sub-monolayer regimes compete for occupying the adsorption sites. Because each site can harbor only one molecule, the repartition of each species among sites of various depth can be calculated using the Fermi-Dirac statistics (Dulieu et al. 2005; Amiaud et al. 2006, 2015; Kristensen et al. 2011). Here, for both CO and N\textsubscript{2}, the binding sites are described by a binding energy distribution, approximated as a Gaussian function. We assume that the molecules are spread over the binding sites following the Fermi-Dirac statistical equilibrium. For one species, we have

$$p(E, T, \mu) = g(E) \times \left[ 1 + \exp \left( \frac{E - \mu}{k_BT} \right) \right]^{-1},$$

where \(p(E, T, \mu)\) is the population distribution given in the Fermi-Dirac formalism, the function \(g(E)\) represents the number of sites between the binding energy \(E\) and \(E + dE\), and \(\mu\) is the Fermi energy or chemical potential, which in turn is linked to the total number of molecules, \(N\), given by

$$N = \int_0^\infty p(E, T, \mu) dE.$$

The rate of desorption, obtained by integrating the desorption probability over the full binding energy distribution and weighted by the probability of occupying the given sites, is

$$\phi = \int_0^\infty p(E, T, \mu) \times \mathcal{A} \, e^{-E/k_BT} dE.$$

The Fermi-Dirac statistical method describes the distribution of one adsorbate over the binding site distribution for experiments of pure molecules. Nevertheless, it is not hard to implement in the case of a mixtures of species. Eq. (5) can be rewritten for CO, assuming that the number of sites available, \(g(E)\), is reduced by the presence of the other adsorbate \(p_{\text{CO}}(E)\):

$$p_{\text{CO}}(E, T, \mu_{\text{CO}}, \mu_{\text{N}}) = (g_{\text{CO}}(E) - p_{\text{CO}}(E)) \times \left[ 1 + \exp \left( \frac{E_{\text{CO}} - \mu_{\text{CO}}}{k_BT} \right) \right]^{-1}.$$

There is a similar equation for N\textsubscript{2} and there are two relationships required to calculate the two chemical potentials \(\mu_{\text{CO}}\) and \(\mu_{\text{N}}\). The coupled desorption of both adsorbates is calculated for each species, using Eq. (7), at each step of the simulation. The probability that an adsorption site is vacant decreases with binding energy, namely, the deepest sites are more likely to be populated. Moreover, if two species have different adsorption

### Table 2. CO:N\textsubscript{2} mixtures: energy ranges for N\textsubscript{2} and CO obtained as a function coverage and [CO]/[N\textsubscript{2}] ratio on c-ASW and PCI.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Dose (ML)</th>
<th>[CO]/[N\textsubscript{2}] ratio</th>
<th>(E_{\text{b,M}}^{15}\text{N}_2) (K)</th>
<th>(E_{\text{b,M}}^{13}\text{CO}) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-ASW</td>
<td>0.75</td>
<td>2.3</td>
<td>1030–1220</td>
<td>1220–1620</td>
</tr>
<tr>
<td>PCI</td>
<td>0.5</td>
<td>7</td>
<td>950–1100</td>
<td>1160–1600</td>
</tr>
<tr>
<td>PCI</td>
<td>0.75</td>
<td>11.4</td>
<td>920–1100</td>
<td>1050–1610</td>
</tr>
</tbody>
</table>
energies, molecules with higher absorption barriers have a higher probability of occupying a binding site. Taking into account this simple statistics, we have shown that it is fair to assume that there can be binding energy distributions having identical shapes for two (or more) different species, provided that the centres of each energy distribution are spaced by a constant value. Even for molecules such as O$_2$ and CO, which exhibit larger differences of desorption profiles with respect to CO and N$_2$ used in this study, we were able to successfully fit the experimental TPD curves (Noble et al. 2015).

Here we have tested our Fermi-Dirac model for the simpler case of N$_2$ and CO mixtures. It is a simpler case because pure N$_2$ desorption peaks seem to be only slightly shifted towards lower temperatures when compared with pure CO profiles. Figure 3 shows that CO and N$_2$ distributions of binding energies are separated only by a value of $\approx$200 K, at least for a coverage in the range 0–0.5 ML. In the case of CO and O$_2$ it was not so obvious, because the multi-layer peak of O$_2$ appears at higher temperatures than the multi-layer peak of CO, which indicates that the multi-layer energy of O$_2$ is higher than that of CO. Therefore, the assumptions made above were certainly not warranted for a coverage close to 1 ML. In the present study concerning N$_2$ and CO mixtures deposited on c-ASW and PCI, we can see that the experimental profiles shown in the top panel of Fig. 7 (c-ASW substrate, [CO]/[N$_2$] ratio between 1.9 and 2.3) are well fitted. The CO profiles are well reproduced. Looking at the TPD tails, it should be noted that the difference between simulations and experiments is of the same order of uncertainty that exists from one experimental curve to another, as can be easily seen in Fig. 1. In Fig. 7 (bottom panel), we show the fitted TPD profiles of CO and N$_2$ mixtures from PCI ([CO]/[N$_2$] ratio between 7 and 11.4). The good quality of the fits in Fig. 7 is the verification of our hypothesis that the competition for adsorption sites is the main physical source of the differentiated desorption of CO and N$_2$. Hence, by adding a constant energy shift of 100 K between the energy distributions of CO and N$_2$, it is possible for us to simulate the desorption behaviour of the CO-N$_2$ system in a sub-monolayer regime, independently of their relative abundance and of the type of water ice substrate. As far as N$_2$ traces are concerned, we could have increased the quality of the fit if we had fitted the N$_2$ energy distribution separately, but we believe that it is not necessary. Our main goal is to develop a model based on simple assumptions, that will be easily applicable to grains in astrophysical conditions, where the exact composition of the surfaces is not well known and so neither are the exact binding energy distributions.

From our experiments and analysis, it is evident that the small difference in binding energies of N$_2$ and CO has a dramatic effect on the desorption temperature of N$_2$ whenever the two species are both present on the surface. This is apparent from Fig. 7 by looking at the locations of the arrows and of the vertical dashed lines. The position of the arrows (corresponding to highest temperature desorption in CO-N$_2$ experiments) and the position of the vertical dashed lines (highest temperature desorption in pure ices desorption) were calculated using Eq. (12) of Luna et al. (2017), which allows us to express the high-energy desorption values displayed in Tables 1 and 2 as temperatures in kelvins. It is evident that blue arrows (N$_2$ in CO-N$_2$ system) exhibit a considerable shift towards lower temperatures with respect to the blue dashed lines (pure N$_2$ experiments). Conversely, red arrows (CO in CO-N$_2$ system) show no or very little shift with respect to the pure ice case, which confirms that CO molecules always tend to populate the most energetically favourable adsorption sites in CO:N$_2$-mixture ratios $\geq$2.

The shift in temperature between red arrows and red dashed lines can be used to estimate the errors on each energy value and is around $\pm$30 K in all cases. The Fermi-Dirac analysis of the desorption of mixed species is a powerful tool to simulate TPD spectra, as well as other fine effects measurable in the laboratory, such as the difference in binding energy of the ortho- and para-state of D$_2$ molecules (Amiaud et al. 2008). However, it is not used in astrophysical models because it is highly demanding in terms of computing time. Therefore, it would be good to know if we can describe the competition mechanism between different molecules in a simpler way and, in particular, by adopting the commonly used approach based on the classical Arrhenius-type model.

Figure 8 displays the distribution of binding energies on c-ASW (top panel) and on PCI (bottom panel) obtained from the classical inversion method. On compact amorphous water ice, the case of pure CO (dotted blue curve) and pure N$_2$ (dashed red curve) monolayer exposures are the same as those shown in Fig. 3. We can clearly see that these curves are nearly parallel, except for the very high coverage region (>0.8 ML) where they tend to converge. The other three solid lines presented in Fig. 8 concern a TPD experiment where a 1 ML-dose CO:N$_2$ mixture (0.65 ML of CO + 0.35 ML of N$_2$) was deposited on compact water ice. As expected, the CO trace (solid blue line) is unchanged with respect to the pure case (dashed blue curve), it goes from 0 ML coverage to 0.65 ML (point C, corresponding to the onset of desorption). On the contrary, the N$_2$ binding energy profile (solid red curve) is strongly shifted towards lower energies by about 200 K. Actually, the desorption of the deposited mixture begins with the desorption of N$_2$ (point A), which continues and terminates at point B. Only then, CO desorption starts (point C), and finishes when zero coverage is reached (point D), as expected. The most striking feature of the energy profiles described above is that points B and C have exactly the same value of binding energy (=1200 K). It is like the desorption process is continuously evolving from point A to point D, except that CO desorption takes over only when there is no more N$_2$ on the surface. To demonstrate this extreme simplification, in Fig. 8 we also plotted the sum of CO and N$_2$ energy traces, considering them as a single desorbing population. The sum of the two is shown in black, and we can see that it is very similar to the energy distribution of the pure CO case. The same competition effect is even more prominent on the PCI substrate, which confirms that CO occupies the highest energy binding sites, pushing N$_2$ to less favourable surface adsorption sites. This case is represented in Fig. 8 (bottom panel), where we show the energy distribution of a CO:N$_2$ = 10:1 mixture (0.91 ML of CO + 0.09 ML of N$_2$). The onset of the desorption corresponds to the desorption of N$_2$ (point A) and the desorption process is complete at point D (end of the desorption of CO), corresponding to zero coverage.

It should also be noted that when the surface coverage is nearly full and a second layer is beginning to be built, the binding energy distribution of the CO-N$_2$ system tends the N$_2$-multi-layer binding energy, though it never reaches this lower limit value, indicating that the CO-N$_2$ interaction is slightly stronger than the N$_2$-N$_2$ interaction.

From this analysis, a very simple and straightforward conclusion that we can draw is that the effective binding energy of N$_2$, in presence of CO molecules, depends on the total coverage (CO+N$_2$), and not on the partial coverage of N$_2$ alone. On the contrary, the binding energy of CO is due only to the coverage of CO molecules, and is unaffected by the presence of N$_2$. 

T. Nguyen et al.: N$_2$ desorption modified by CO presence
As opposed to what experiments have shown before (Fuchs et al. 2006; Fayolle et al. 2016), there could actually be a relatively high difference between the effective binding energy of CO and N$_2$ on cold interstellar dust grains. One simple model that could explain this hypothesis is that the effective binding energy of N$_2$ is reduced from 1400 K (pure N$_2$, at very low coverage) to 900 K (CO+N$_2$ mixture, at monolayer coverage almost complete), corresponding to a reduction by a factor of $\approx 1 - 900/1400 = 0.35$. This is consistent with the scenario proposed from the analysis of binding energies vs. coverage of Fig. 8. However, this is also a rather simplistic approach, because as the CO:N$_2$ mixture is deposited and the surface gets filled the CO binding energy decreases too.

A more consistent view is to consider that N$_2$ is always desorbing prior to CO whenever N$_2$ and CO are both present on the surface of icy grains. Of course, the two different behaviours will be apparent only if the temperature is high enough that desorption or accretion is under way. Therefore, in the case of very cold dust ($T_{\text{dust}} < 13$ K), thermal desorption will be too weak and both N$_2$ and CO will keep accreting on dust grains.
In pre-stellar cores, the inner part of the cloud meets this condition (Bergin & Tafalla 2007). However, even in these dark and cold media, dust grains can experience temperature fluctuations (e.g. Bron et al. 2014) induced by cosmic rays (or secondary UV photons). This concept has been largely used in models since the work of Hasegawa & Herbst (1993). In fact, Hasegawa & Herbst (1993) consider that the binding energy is a key parameter that determines the abundance of a certain species in the gas phase, via the Arrhenius-like desorption rate. Therefore, if we imagine a distribution of temperature jumps, also in case of small spikes (>35 K), N2 is likely to desorb, but not all CO, as confirmed by our experiments. We can even consider that, as to nano-sized grains, temperature variations can also be induced by release of chemical energy, see for example calculations by Navarro-Ruiz et al. (2014). Nonetheless, the presence of nano-sized grains in pre-stellar core is unlikely because of the coagulation that leads to the coreshine (Pagani et al. 2010), grain sized distribution under coagulation processes (Ormel et al. 2009), and because the observational signature of very small grains at 60 μm (Laureijs et al. 1991; Stepnik et al. 2003) vanishes on the edge of the cloud.

It is also striking to note that the values of desorption energy used in previous models, as in Caselli (2002), are 1210 K and 787 K, for CO and N2 respectively, are quite consistent with the range of energy values that can be extrapolated from the present work. The former energy barrier coincides with CO binding energy on compact water ice at a relatively low coverage of 0.2 ML, or may also coincide with CO binding energy on porous ice at moderate coverage. The N2 energy barrier can be considered a typical value of binding energy of pure molecular nitrogen multilayers.

The complex modelling of pre-stellar cores, that should include dynamics of clouds as well as an accurate rate of accretion on grains and chemical reactions, is beyond the scope of this paper. In fact, none of the pre-stellar core models currently in use apply Fermi-Dirac statistics or a binding site distribution when simulating the solid-gas exchange. Although we cannot determine a single effective value for the binding energy of N2 and CO on grains, we can however provide a distribution of all ranges of binding energy of the CO-N2 systems investigated, that can be used to simulate the surface segregation/competition of the adsorbates in specific, astrophysically relevant situations. The values are reported in Table 2.

Our results imply that CO and N2 mixtures deposited on water-dominated icy mantles present different ranges of thermal desorption temperatures in different interstellar and circumstellar environments. In particular, in pre-stellar cores different CO and N2 binding energies may explain the later freeze-out, or early sublimation, of N2. On the other hand, in circumstellar disks, where radial temperature profiles greatly affect freeze-out of different volatiles, the segregation effect could explain why the observed N2H+ emission is such a robust tracer of the CO condensation front (Qi et al. 2013, 2015).

Previously, we already proposed an analytical expression to fit TPD profiles of pure CO in Noble et al. (2012), and other authors extended this subject to cover different conditions and regimes (He et al. 2016; Collings et al. 2004). The present case, where two species are present on the surface at the same time, makes very difficult to derive the absorption energy as a function of several variables. To know the effective binding energy, as long as both N2 and CO are on the surface, one has to know the relative coverage, which depends on the cloud conditions and history, then has to assume that CO will not desorb and that the lowest energy binding sites are occupied by N2. Assuming that CO and N2 sub-monolayer mixtures are adsorbed on a water ice template, only when N2 is completely gone, CO can start to leave the surface.

5. Conclusions

In this work, we studied sub-monolayer mixtures of N2 and CO deposited on two types of water ice substrates. N2 and CO co-adsorbed on an amorphous surface show very different desorption behaviour when mixed than when adsorbed separately. We derived the distribution of binding energies and put in evidence that a segregation mechanism is at play. N2 and CO have close binding energies, with N2 adsorption barrier being slightly lower. If taken as pure species, the shape of their binding energy distribution as a function of coverage is similar. When mixed, CO molecules push-out N2 molecules of the highest energy adsorption sites, thus nitrogen is forced to almost completely leave the surface before CO begins to desorb. We conducted TPD experiments of CO:N2 mixtures from compact amorphous ice and poly-crystalline ice, and obtained similar results in the two cases. Experiments clearly show that the presence of CO reduces the effective binding energy of N2 in CO:N2 mixture ratios of ~2:1 and ~10:1, whereas we determined that the opposite effect does not occur within the same N2:CO-mixture ratios. In dark clouds,
or in other environments where CO and N$_2$ can meet on the surface of water-dominated icy mantles, a selective desorption may be the most probable scenario. It is yet to be confirmed that this is one of the main reasons explaining the lower depletion of N$_2$ towards the centre of pre-stellar cores with respect to CO, although it is certainly a possibility that modellers have to take into consideration.

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