Laboratory H$_2$O:CO$_2$ ice desorption data: entrapment dependencies and its parameterization with an extended three-phase model

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ABSTRACT

Context. Ice desorption affects the evolution of the gas-phase chemistry during the protostellar stage, and also determines the chemical composition of comets forming in circumstellar disks. From observations, most volatile species are found in H$_2$O-dominated ices.

Aims. The aim of this study is first to experimentally determine how entrapment of volatiles in H$_2$O ice depends on ice thickness, mixture ratio and heating rate, and second, to introduce an extended three-phase model (gas, ice surface and ice mantle) to describe ice mixture desorption with a minimum number of free parameters.

Methods. Thermal H$_2$O:CO$_2$ ice desorption is investigated in temperature programmed desorption experiments of thin (10–40 ML) ice mixtures under ultra-high vacuum conditions. Desorption is simultaneously monitored by mass spectrometry and reflection-absorption infrared spectroscopy. The H$_2$O:CO$_2$ experiments are complemented with selected H$_2$O:CO, and H$_2$O:CO$_2$:CO experiments. The results are modeled with rate equations that connect the gas, ice surface and ice mantle phases through surface desorption and mantle-surface diffusion.

Results. The fraction of trapped CO$_2$ increases with ice thickness (10–32 ML) and H$_2$O:CO$_2$ mixing ratio (5:1–10:1), but not with one order of magnitude different heating rates. The fraction of trapped CO$_2$ is 44–84% with respect to the initial CO$_2$ content for the investigated experimental conditions. This is reproduced quantitatively by the extended three-phase model that is introduced here. The H$_2$O:CO and H$_2$O:CO$_2$:CO experiments are consistent with the H$_2$O:CO$_2$ desorption trends, suggesting that the model can be used for other ice species found in the interstellar medium to significantly improve the parameterization of ice desorption.

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

1. Introduction

In pre-stellar cores, cold outer protostellar envelopes and protoplanetary disk midplanes, most molecules, except for H$_2$, are frozen out on dust grains, forming ice mantles. The main ice component in most lines of sight is H$_2$O, followed by CO and CO$_2$, with a typical abundance of (0.5–1.5) × 10$^{-4}$ for H$_2$O ice with respect to H$_2$ around solar-type protostars (van Dishoeck 2006). Infrared observations of pre-stellar cores show that most CO$_2$ ice and some of the CO ice is mixed with H$_2$O (Knez et al. 2005). The remaining CO and CO$_2$ are found in separate ice layers. Based on these observations, H$_2$O and CO$_2$ are thought to form simultaneously on the grain surface during the early stage of cloud formation. When the cloud becomes denser, gas phase CO freezes out on top of the water-rich ice, resulting in a bilayered ice mantle, as described in Pontoppidan et al. (2008).

Once the pre-stellar core starts collapsing into a protostar, it heats its environment, including the icy grains. This results in the desorption of the CO-rich layer into the gas phase, in structural changes in the water-rich ice layer, and eventually in the desorption of the water-rich layer (Pontoppidan et al. 2008). Such an ice desorption scheme provides most of the gas phase reactants for the chemistry taking place at later stages in these warm regions (Doty et al. 2004). It is therefore crucial to understand ice mixture desorption and to effectively implement it in astrochemical networks. The aim of this study is to provide a laboratory basis for this process and to demonstrate how it can be modeled both in the laboratory and in space.

Laboratory experiments have provided most of the current knowledge about ice thermal desorption, including desorption energies for most pure simple ices (Sandford & Allamandola 1988, 1990; Fraser et al. 2001; Collings et al. 2004; Öberg et al. 2005; Brown & Bolina 2007; Burke & Brown 2010). Desorption from ice mixtures differs from pure ice desorption because of different binding energies between the mixture components (e.g., the CO binding energy increases from 830 K in pure ice to 1180 K in H$_2$O-dominated ice mixtures Collings et al. 2003) and because of trapping of volatile species in the H$_2$O hydrogen-bonding ices (Collings et al. 2004). Volatile components therefore desorb from H$_2$O-rich ice mixtures at a minimum of two different temperatures, corresponding to the desorption of the species from the surface of the H$_2$O ice and from molecules trapped inside the bulk of the H$_2$O ice, which only start desorbing at the onset of H$_2$O desorption. Additional desorption is sometimes observed at the temperature for pure volatile ice desorption and during ice re-structuring, e.g., at the H$_2$O phase.
change from amorphous to crystalline (Viti et al. 2004). This H$_2$O restructuring occurs at $\sim$140 K in the laboratory (for astrophysical timescales the re-structuring temperature and desorption temperature decrease), which is close to the onset of H$_2$O desorption (Collings et al. 2004).

Of the different ice mixture desorption features, the entrapment of volatile species in H$_2$O ice is astrochemically the most important to quantify. The trapping of CO in a water ice results in a factor of five increase in the effective desorption temperature. In a recent cloud core collapse model, this corresponds to trapped CO desorbing at 30 AU from the protostar compared to pure CO ice desorbing at 3000 AU. The case is less dramatic, but still significant, for CO$_2$, which desorbs at $\sim$300 AU when pure, and at 30 AU if trapped in H$_2$O ice (Aikawa et al. 2008; Visser et al. 2009). Efficient ice trapping may therefore allow some volatiles to stay frozen on the dust grains during accretion of envelope material onto the forming protoplanetary disk (Visser et al. 2009).

There are only a few models that have incorporated the effects of ice mixture desorption. Collings et al. (2004) investigated the desorption of 16 astrophysically relevant species from H$_2$O:X 20:1 ice mixtures. Viti et al. (2004) and Visser et al. (2009) used the results of Collings et al. (2004) to split up the abundance of volatiles in up to four different flavors, with different desorption temperatures. These correspond to the fraction of each ice desorbing at the pure ice desorption temperature, from a H$_2$O surface, during H$_2$O ice restructuring and with H$_2$O, respectively. This approach has provided information on the potential importance of ice trapping for the chemical evolution during star formation. However, this model does not take into account specific ice characteristics such as ice thickness, volatile concentration and heating rate, on which the amount of trapped volatiles in the water ice may also depend (Sandford & Allamandola 1988). These characteristics need to be determined experimentally to correctly parameterize step models, where such are sufficient to model ice desorption. Strong dependencies on e.g. ice thickness or concentration would however warrant the development of a more continuous parameterization of ice desorption than the assignment of flavors.

These dependencies are naturally included in a few ice mixture desorption models of specific binary ices (Collings et al. 2003; Bisschop et al. 2006). The molecular specificity of these models, together with a large number of fitting parameters has, however, prevented their incorporation into larger astrochemical models. Therefore, in most gas-grain networks, desorption is still treated as if ices were pure, disregarding volatile entrapment in the water matrix (e.g. Aikawa et al. 2008).

Another problem with current gas-grain codes is that evaporation is often incorporated as a first-order process, while it is experimentally found to be a zeroth-order process with respect to the total ice abundance for ices thicker than one monolayer. Desorption models from the last decades have shown the necessity of using a zeroth order kinetics (Fraser et al. 2001; Collings et al. 2003). Incorporating ice desorption as a first-order process with respect to the total ice abundance effectively means that molecules throughout the whole ice are allowed to desorb at the same time, which is non-physical (Fraser et al. 2001; Bisschop et al. 2006). This can be solved by treating the bulk and surface of the ice as separate phases as it has been done by Pontoppidan et al. (2003) and Pontoppidan et al. (2008) for CO ice desorption and by Collings et al. (2005) for H$_2$O desorption and crystallization. Its successful use in astrochemical models makes this approach an attractive option to parameterize laboratory ice desorption, since the results can then be easily transferred into an astrophysical context. In this family of models, molecules are only allowed to desorb from the surface, which is continuously replenished by molecules coming from the mantle, and therefore the desorption kinetics are automatically treated correctly. This model results in a zeroth-order desorption behavior, in agreement with the experiments, since the number of molecules available for desorption remains constant in time. The model also results in trapping of volatiles in the bulk of the ice since the mantle molecules cannot desorb into the gas phase. The three-phase model we build on was first introduced by Hasegawa & Herbst (1993), but despite its advantages in treating different ice processes, it has not been generally used for ice mixture desorption, nor has it been further developed, presumably because it did not correctly reproduce the experimentally observed amount of volatiles trapped in the water ice.

The goals of the present study are first to experimentally characterize how the trapping efficiency of CO$_2$ in H$_2$O ice depends on different ice characteristics (e.g. atomic ratios and mixing proportions of different species) and second to use these experiments as a guide to improve our understanding of the trapping process within the three-phase model framework. The description of the extended three-phase model is explained in Sect. 2.1. The experiments used to get information on the volatile entrapment and to calibrate the model are described in Sect. 3. Laboratory results on H$_2$O:CO$_2$ ices, complemented by H$_2$O:CO and H$_2$O:CO$_2$:CO ice desorption results, are presented in Sect. 4. Section 5 presents the model fitting parameters and model results. Finally, the consequences of treating ice mixture desorption with the extended three-phase model under astrophysical conditions are discussed in Sect. 6.

2. Desorption model

This study addresses the desorption of volatiles mixed with water and how to predict the fractions of volatiles in the ice and gas phase during a warm-up of the ice. The model is a system of rate equations based on the Hasegawa & Herbst (1993) model, but with the addition of diffusion. It aims at providing a solution for the amount of volatiles trapped in water with respect to the ice characteristics that can be directly included into astrochemical models, as used by Viti et al. (2004) and Visser et al. (2009). The model applies to species in the water-rich ice layer; the interface with an upper CO-rich ice layer is not treated here.

2.1. Basic three-phase model

The model used here to predict the trapping of volatile species in a water dominated ice is based on the three-phase model by Hasegawa & Herbst (1993). In this model, gas-grain interactions are addressed by considering three phases: the gas phase,
the surface of the ice and the bulk/mantle of the ice (Fig. 1). The original model includes reactions between species in both gas and solid phase, as well as accretion from the gas to the ice and thermal and non-thermal desorption. Thermal desorption alone is presented here. The model is based on the principle that molecules can only desorb from the surface into the gas phase and that the mantle molecules can only migrate to the surface following the desorption of a surface molecule. The time-dependent gas abundance of species \( i \) is given by

\[
\frac{dn_i}{dt} = R_{\text{evap}}
\]

where,

\[
R_{\text{evap}} = \left( v e^{-E_i/T} \right) n_i^s
\]

with \( n_i^s \) and \( n_i^t \) the gas phase and surface abundance of species \( i \), respectively, \( E_i \) its binding energy in K, and \( v \) a pre-exponential factor taken equal to \( 10^{12} \text{ s}^{-1} \), which is a standard value for physisorbed species (Biham et al. 2001). The surface abundance of species \( i \) can be written as:

\[
\frac{dn_i^s}{dt} = -R_{\text{evap}} + R_{\text{repl}}
\]

where,

\[
R_{\text{repl}} = \alpha \left[ \sum_j \left( v e^{-E_j/T} \right) n_j^m \right] \sum_{m} n_j^m
\]

where \( n_j^m \) is the mantle abundance of species \( j \), \( \sum_j n_j^m \) the total number of molecules in the mantle and \( \alpha \) is the ice coverage on the surface, which is set to 2 ML to account for surface roughness. The first term in Eq. (3) represents the loss of molecules \( i \) from the surface by thermal desorption. The second term is related to the replenishment of the surface sites by mantle molecules: the empty sites created by the desorption of any type of species from the surface, \( \sum_j \left( v e^{-E_j/T} \right) n_j^s \), are statistically filled by molecules coming from the mantle. The probability for these molecules to be species of type \( i \) is equal to its mantle fraction, \( \sum_j n_j^m \). The mantle abundance, \( n_j^m \), of species \( i \) changes according to

\[
\frac{dn_j^m}{dt} = -R_{\text{repl}}
\]

Because of the term \( \frac{n_j^m}{\sum_j n_j^m} \), the replenishment of the surface phase by the mantle molecules during ice mixture desorption depends only on the mixing ratio of each species in this model, e.g., for a \( \text{H}_2\text{O}:\text{CO}_2 \) 1:1 ice mixture, a molecule that desorbs into the gas phase has a 50% chance to be replaced by a water molecule and a 50% chance to be replaced by a \( \text{CO}_2 \) molecule. This results in desorption of some volatile species around the pure ice desorption temperature and the rest remains trapped in the water ice since water molecules quickly saturate the surface phase.

The ice abundances \( n_i^t \) and \( n_i^m \) are all in \( \text{cm}^{-3} \), a unit directly related to the gas phase abundance. The abundance of species \( i \) on the surface is defined via the relation

\[
n_i = N_i^s n^d
\]

where \( N_i^s \) is the average number of molecules \( i \) on the grain surface, and \( n^d \) is the dust abundance. The same relation applies for the mantle abundance.

### 2.2. Extended three-phase model

The original three-phase model does not account for the preferred replenishment of the surface phase by volatile mantle species or that volatile species may diffuse more easily in the ice compared to water. Öberg et al. (2009b) showed that this diffusion can result in segregation of the ice components, which is important for temperatures well below the desorption energy of most volatile species in an ice mixture. This demixing mechanism changes the surface replenishment probabilities proposed in the original three-phase model by Hasegawa & Herbst (1993). Our proposed extension of the three-phase model accounts for this by introducing a mantle-surface diffusion term. Trapping of volatiles still occurs, but the surface-mantle diffusion of volatiles is enhanced compared to the original model, resulting in that more than 50% of the empty sites are filled by volatiles species. Quantitatively, this changes the surface and mantle abundances \( n_i^t \) and \( n_i^m \) as follows:

\[
\frac{dn_i^t}{dt} = -R_{\text{evap}} + R_{\text{repl}} + R_{\text{diff}},
\]

and

\[
\frac{dn_i^m}{dt} = -R_{\text{repl}} - R_{\text{diff}}
\]

with

\[
R_{\text{diff}} = f_i v \left[ n_{\text{H}_2\text{O}}^m \sum_j n_j^m e^{-E_{\text{H}_2\text{O}}/T} - n_i^m \sum_j n_j^m e^{-E_{\text{H}_2\text{O}}/T} \right]
\]

and

\[
E_{\text{diff}} = \epsilon_{\text{H}_2\text{O}} \left( \frac{E_{\text{H}_2\text{O}} - E_i}{2} \right)
\]

for \( i \neq \text{H}_2\text{O} \), and where \( \epsilon_{\text{H}_2\text{O}} \) is the energy barrier for a volatile molecule \( i \) and a water molecule to swap (i.e. change position) within the ice and \( f_i \) a fraction between 0 and 1 that is described below. The expression for the gas phase abundance remains unchanged (see Eq. (1)). The diffusion term \( R_{\text{diff}} \) is added to the surface abundance (subtracted from the mantle abundance) to enhance the mantle to surface circulation for a volatile species \( i \) at the expense of the water, thus, \( R_{\text{diff}} \) is expressed differently for volatile and water molecules. The volatile ice diffusion rate depends on the balance of the probability of volatile molecules to move from the mantle to the surface at the expense of a water molecule and on the probability of the reverse process. This swapping process probability depends on the energy barrier \( \epsilon_{\text{H}_2\text{O}} \) of the process and on the energy difference before and after the swap, equal to \( E_{\text{H}_2\text{O}} - E_i \). The diffusion rate for the water molecules is the negative sum of the diffusion rates for the volatiles, \( R_{\text{diff}} = -\sum_i R_{\text{diff}} \), since the total abundance of molecules in the mantle and in the surface is not affected by the diffusion process. A similar formalism was used to describe \( \text{H}_2\text{O}:\text{CO}_2 \) segregation in Öberg et al. (2009b); an exchange of a surface \( \text{H}_2\text{O} \) molecule and a mantle volatile is generally energetically favorable because \( \text{H}_2\text{O} \) forms stronger bonds than volatile species and a mantle \( \text{H}_2\text{O} \) molecule can form more bonds compared to a surface \( \text{H}_2\text{O} \) molecule.

From segregation studies of binary ices, it has become clear that only a limited fraction of the mantle participates in the mantle-surface circulation and that this fraction depends on the
The experiments in this study are chosen to simultaneously provide data directly relevant to ice desorption in different astrophysical environments (with different ices) and to construct a proof-of-concept model for ice mixture desorption. The focus is on CO2 desorption from H2O ice mixtures, one of the most important ice systems around protostars, with supporting experiments on CO desorption. While interstellar ices are expected to be complex mixtures, it is still useful to investigate desorption from binary H2O:volatile ice mixtures since the H2O:volatile interactions are expected to dominate the desorption process in space, both because H2O is the major ice constituent and because H2O generally forms stronger bonds with itself and with volatiles than volatiles do. This hypothesis has been further tested by performing TPD experiments of two tertiary H2O:CO2:CO ice mixtures.

The ice thickness and structure in the experiments are chosen to be as similar as possible to the existing observational constraints on interstellar ices. Interstellar ices are estimated to be less than 100 monolayers (ML) thick from the maximum amount of oxygen available for ice formation. The experimentally grown ices are between 10 and 40 ML, since it is only possible to quantify ice thicknesses up to a certain limit (40 ML in our case) using reflection-absorption infrared spectroscopy (Teolis et al. 2007). Information on ice structure in space is limited, but the lack of a water dangling vibration at 3700 cm−1 suggests a less porous ice than typically produced in the laboratory. We minimized the porosity of ice analogues by injecting gas perpendicularly to the cold surface when growing the ices (Stevenson et al. 1999; Kimmel et al. 2001).

3.2. Experimental procedures

All desorption experiments are performed with CRYOPAD. This set-up has been described in detail elsewhere (Fuchs et al. 2006). The set-up consists of an ultra high vacuum (UHV) chamber with a base pressure of ~10−10 mbar at room temperature. Ices are grown on a gold-coated substrate situated at the center of the chamber that can be cooled down to 16 K by a close cycle He cryostat. The relative sample temperature is controlled with a precision of 0.1 K using a resistive heating element and a temperature control unit. The absolute sample temperature is given with a 2 K uncertainty. The system temperature is monitored with two thermocouples, one mounted on the substrate face, the other on the heater element.

A fourier transform spectrometer is used for reflection-absorption infrared spectroscopy (FT-RAlRS) to record vibrational absorption signatures of molecules condensed on the gold surface. The spectrometer covers 700–4000 cm−1 with a typical resolution of 1 cm−1 and an averaged spectrum consists of a total of 256 scans. Ice evaporation is induced by linear heating of the substrate (and ice) in TPD experiments. RAIR spectra are acquired simultaneously to monitor the ice composition during the TPD. A quadrupole mass spectrometer (QMS) is positioned at 4 cm, facing the ice sample to continuously analyze the gas-phase composition mass-selectively and to obtain desorption curves of evaporating molecules during the TPD experiments.

Mixtures and pure gas samples are prepared from 13CO2 (Indugas, min 99% of 13CO2), CO2 (Praxair, 99% purity), 13CO (Cambridge Isotope Laboratories, 98% purity) and from gaseous water at the saturation pressure of a de-ionized liquid sample at room temperature. The de-ionized water is purified by three freeze-pump-thaw cycles. The samples are prepared separately, then injected in the chamber via an inlet pipe directed along the normal of the gold surface. In all gas samples, an isotopologue of CO was used to separate the QMS signal from background CO and N2. Similarly, an isotopologue of CO2 was used to minimize the overlap in RAIR spectra between CO2 ice and atmospheric CO2 gas outside the UHV chamber.
H$_2$O and CO$_2$ ice amounts are determined directly using the RAIRS band strengths provided by Öberg et al. (2009c,a) for CRYOPAD. From these measurements the absolute ice thicknesses are known within 50%. The relative ice abundance uncertainties are smaller, ~20%, and due to small band strength variations with ice composition and temperature.

Table 1 lists the set of TPD experiments performed to calibrate and test the desorption model presented in Sect. 2.1. The TPD experiments begin with the deposition of pure or mixed ice samples on the gold substrate cooled to 16–19 K, and continue with a slow heating of the ices at a constant specified rate until the desorption of the molecules from the surface is complete. The evaporated gas phase molecules are continuously monitored by the QMS. RAIR spectra of the ices are acquired before heating to determine ice thicknesses and mixture ratios as described above. Spectra are also recorded during the warm-up as a second independent way to determine the ice composition and to monitor eventual structure modifications.

The infrared data are reduced by subtracting a local baseline around the molecular features. Mass spectrometric data are reduced by subtracting the ion current from species present in the background for each mass channel. Absolute yields cannot be directly obtained by the QMS since it is situated away from the background for each mass channel. The trapped percentage of volatiles in each event and the desorption of trapped volatiles. The implications of this ice desorption process is discussed below, but it is important to note that this is not incorporated into the model framework and this may be a limitation to step-wise desorption models, whether using our parameterization or any of the previously published ones. Quantifying this process would require an additional set of experiments where the mass spectrometer is mounted closer to the substrate to allow for the detection of very low desorption rates.

4. Experimental analysis

4.1. Complementarity of RAIRS and QMS

Figure 2 illustrates the agreement between desorption curves derived from QMS and RAIRS data for CO$_2$ in a 5:1 water-dominated H$_2$O:CO$_2$ ice, 18 ML thick and heated at 1 K.min$^{-1}$ rate (Exp. 11). The upper left panel in Fig. 2 shows the CO$_2$ stretching band recorded at different temperatures during warm-up: after ice deposition at 22 K, at 62 K where segregation is known to be efficient (Öberg et al. 2009b), during the first ice desorption peak around 79 K, in the temperature interval between pure CO$_2$ desorption and H$_2$O desorption, and during desorption of the trapped CO$_2$. The right panel shows the desorption rate of CO$_2$ derived from the same experiment by mass spectrometry. The bottom panel presents the cumulative ice loss versus temperature for this experiment, obtained both by integrating the CO$_2$ mass signal with respect to the temperature, and by integrating the CO$_2$ infrared signal recorded at specific temperatures. The uncertainties the fractional ice loss curves derived by infrared and by mass spectrometry agree well; there seems to be only a small systematic offset for the 80–130 K range. This implies that the first RAIR spectrum of the ice after deposition can be used to derive quantitative results from the TPD experiments.

Figure 2 also shows that there is evidence for some ice loss between the two main desorption peaks. The cumulative QMS and infrared spectroscopy signals match each other at these intermediate temperatures, which points to that the measurements trace actual ice desorption in between the pure ice desorption event and the desorption of trapped volatiles. The implications of this ice desorption process is discussed below, but it is important to note that this is not incorporated into the model framework and this may be a limitation to step-wise desorption models, whether using our parameterization or any of the previously published ones. Quantifying this process would require an additional set of experiments where the mass spectrometer is mounted closer to the substrate to allow for the detection of very low desorption rates.

4.2. Desorption trends

Figure 3 shows the desorption of CO$_2$ from H$_2$O:CO$_2$ ice mixtures of different thicknesses (a), with different CO$_2$ concentrations (b), and heated at different rates (d). In addition there are two CO TPD curves from H$_2$O:CO mixtures with different CO concentrations (c). For reference, Fig. 3e) presents the TPD curves of pure CO, CO$_2$, and H$_2$O ice heated at 1 K min$^{-1}$. The fraction of trapped volatile is obtained by integrating the QMS signal for temperatures above 110 K and dividing it by the QMS signal integrated over the entire 20–160 K range. The chosen temperature of 110 K is well below the onset of the second desorption peak and the volatiles that desorbed during the first CO$_2$ or CO desorption peak are (almost) entirely pumped, though as discussed above there seems to be a low-level type of desorption occurring between the main desorption peaks. Whether due to finite pumping or actual desorption this results in a 10–20% uncertainty in the determination of the trapped fraction, i.e., the choice of temperature integration limits affects the estimated amount of trapped ice by <20%. The trapped percentage of volatiles in each experiment, defined with respect to the initial volatile ice content, is reported in the second last column of Table 1. The last column of Table 1 presents the trapped abundance of volatiles...
Table 1. Overview of the desorption experiments.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Sample</th>
<th>Ratio</th>
<th>Thick. (ML)</th>
<th>Heat. rate (K.min(^{-1}))</th>
<th>Trapped CO(_2)/CO ice % wrt. CO(_2)/CO</th>
<th>Trapped CO(_2)/CO ice % wrt. H(_2)O</th>
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<td>1</td>
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<td>(^{13})CO(_2)</td>
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<td>1</td>
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</tr>
<tr>
<td>3</td>
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<td>13</td>
<td>1</td>
<td>9</td>
<td>4.5</td>
</tr>
<tr>
<td>17</td>
<td>H(_2)O:CO</td>
<td>1:1</td>
<td>17</td>
<td>1</td>
<td>4</td>
<td>4.0</td>
</tr>
<tr>
<td>18</td>
<td>H(_2)O:CO(_2):(^{13})CO</td>
<td>11:4:1</td>
<td>16</td>
<td>1</td>
<td>32/19</td>
<td>12/2</td>
</tr>
<tr>
<td>19</td>
<td>H(_2)O:CO(_2):(^{13})CO</td>
<td>20:1:1</td>
<td>30</td>
<td>1</td>
<td>92/96</td>
<td>5/5</td>
</tr>
</tbody>
</table>

4.2.1. Thickness dependency

Figure 3a presents the desorption of a H\(_2\)O:CO\(_2\) 10:1 ice mixture for different initial ice thicknesses and shows that the amount of trapped CO\(_2\) (desorption around 140 K) increases with ice thickness. In contrast the amount of CO\(_2\) desorbing around 70 K is independent of ice thickness in the experimentally investigated range. This implies that only CO\(_2\) molecules from the top part of the ice are available for desorption at the CO\(_2\) desorption temperature. This can be explained by either a highly porous ice that allows CO\(_2\) to “freely” desorb from the top layers or by diffusion from the top layers of the mantle phase to the surface. In both cases the surface is eventually totally saturated by water molecules, trapping the rest of the volatiles in the ice mantle.

4.2.2. Mixing ratio dependency

The dependence of the volatile trapping with the mixture ratio is presented in Fig. 3b) for H\(_2\)O:CO\(_2\) and in Fig. 3c) for H\(_2\)O:CO ice mixtures. In both cases the trapped fraction decreases as the volatile to H\(_2\)O ratio increases. In other words, the amount of pores exposed to the surface or the diffusion length scale of volatiles in the ice must increase with increasing volatile concentration. A similar dependency was noted in Öberg et al. (2009b) when measuring segregation in ices. Increased diffusion may either be due to a gradually looser binding environment in the volatile-rich ices or a break-down of H\(_2\)O ice structure in the presence of higher concentrations of volatiles. The thick H\(_2\)O:CO ice experiments (Exps. 14, 15 and 17) with initial mixture ratios of 10:1, 5:1 and 1:1 show a continuous decline of the trapping fraction, which suggests that either the ice becomes continuously more porous or that the diffusion path length increases gradually with volatile concentration.
4.2.3. Molecular dependency

Similarly to Sandford & Allamandola (1990) and Collings et al. (2004) we find that the trapping efficiencies of the investigated CO$_2$ and CO in H$_2$O ice are radically different. When comparing Figs. 3b) and c), it appears that CO is much more mobile than CO$_2$ in the H$_2$O ice as demonstrated by the higher trapping fraction of CO$_2$ compared to CO in similar H$_2$O ice mixtures. Sandford & Allamandola (1990) explained this difference from a combination of different binding energies of CO and CO$_2$ in H$_2$O ice due to molecular size, shape and electronic differences. These binding energies may equally affect the probability of escaping through an ice pore or diffusing through the bulk of the ice.

4.2.4. Heating rate dependency

In Fig. 3d, the heating rate of the ice is varied for a H$_2$O:CO$_2$ 5:1 ice of 10–12 ML between 0.5, 1 and 5 K.min$^{-1}$. This does not appreciably affect the trapping efficiency of CO$_2$ in the H$_2$O ice and implies that the process responsible for exchanges between the surface and the mantle is fast compared to the experimental warm-up time. If this was not the case, a lower heating rate would have resulted in a smaller amount of trapped CO$_2$, since a slower heating means more time for the migration of mantle molecules to the surface.

The lack of a heating rate dependency on the trapped amount of volatiles (same trapped percentage in Exp. 10, 11 and 12) also implies that there is a rather sharp boundary between the molecules in the upper layers that can diffuse to the surface (whether through pores or bulk diffusion) and molecules deeper in the ice that cannot. Even if the volatiles deep in the ice can diffuse within the ice mantle, diffusion “upwards” must quickly become slow as the surface layers saturate with H$_2$O molecules or alternatively all accessible pores have been emptied. This explains that the amount of desorbing CO$_2$ molecules at low temperatures is thickness independent (the H$_2$O “ice cap” will become impenetrable after a certain amount of CO$_2$ molecules have desorbed) and that entrapment efficiencies are unaffected by lower heating rates.

4.3. Tertiary mixtures

The desorption rates for the tertiary mixtures (Exps. 18 and 19) are presented in Fig. 4a). Similarly to the binary experiments, the trapping of volatiles is more efficient for a lower volatile to H$_2$O ratio. The desorption curves for CO$_2$ are not affected by the presence of CO. Thus the CO-CO$_2$ interaction does not have a significant impact on the amount of CO$_2$ trapped within the water matrix. Overall the TPD curves resemble the addition of desorption curves from two separate binary mixtures, except for a small fraction of CO that desorbs with CO$_2$ in the H$_2$O:CO$_2$:CO 11:4:1 mixture (lower panel in Fig. 4). It is unclear whether this desorption is due to a co-desorption of CO with CO$_2$ or to a release of CO that has been trapped under a barrier of CO$_2$ surface molecules. The observed similarity supports the use of binary ice mixtures as templates to study diffusion and desorption even though they are not directly representative of interstellar ice mixtures.

When comparing the desorption of CO from a tertiary and a binary ice mixture with the same H$_2$O:CO ratio and ice thickness, it appears that less CO is trapped in the tertiary mixture. This may be due to ice structure changes, as discussed above, or to shielding of CO from the sticky water molecules by CO$_2$ molecules (the CO-CO$_2$ bond is weaker than the H$_2$O-CO one), lowering the CO diffusion barrier. The CO$_2$ and CO desorption curves from the dilute tertiary mixture both contain a small additional peak around 150 K, only seen elsewhere in the thickest H$_2$O:CO$_2$ 10:1 ice experiment. A similar double peak was noted in the 20:1 desorption experiments of Collings et al. (2004).

4.4. Ice diffusion mechanisms: pore versus bulk diffusion

The main mechanism behind diffusion in the ice mantle is not known and may differ between different ices. Most previous studies have focused on diffusion in cracks and pores and pore collapse has been introduced to explain ice trapping. The observation that both CO and CO$_2$ become trapped even though they partly desorb at their, very different, pure ice desorption temperatures is difficult to reconcile with pore collapse as the main trapping mechanism, however. That is, it would imply efficient H$_2$O pore collapse both at ~30 K and ~70 K.

Even if pore collapse does not provide a complete explanation of why ices become trapped, some kind of internal surface hopping may explain why molecules can diffuse out of the ice. In this scenario, the CO$_2$ desorption ice thickness dependency is due to that the pores and cracks that are open to the surface only go down to a certain depth, in this case a few ML for H$_2$O:CO$_2$ 5:1. The different CO and CO$_2$ trapping efficiencies may then be either due to different ice structures or to CO desorbing easier through pores compared to CO$_2$. Pore diffusion may thus be consistent with these particular experimental results, but ice diffusion is present also in other ices that are known to be quite compact, e.g. CO ice (Bisschop et al. 2006). While it is possible that diffusion occurs through completely different mechanisms in different ices, the concept of ice bulk diffusion has the prospect of approximating mixing and de-mixing processes in all kinds of ices, regardless of structure.

In the bulk diffusion scenario, an amorphous ice is viewed like a very viscous liquid, whose viscosity decreases with the volatility of the ice molecules. In Öberg et al. (2009b) this was modeled as molecules swapping places with a barrier significantly higher than surface hopping. Volatile molecules will tend to swap their way towards the surface because it is energetically favorable to have the molecules that form weaker bonds in the
surface layer (where fewer bonds can be made due to the ice-vacuum interface). Trapping is explained by that when volatile molecules diffuse from the top mantle layers to the surface and desorb, the top mantle layers become saturated with H₂O and therefore viscous enough to be impenetrable. The low desorption rate of volatiles between the volatile and H₂O ice desorption peaks would however suggest that under some experimental conditions, small amounts of volatiles can escape through this H₂O barrier. More experiments are required to test under which conditions this is a reasonable approximation. The model presented below is an attempt to include the most important features of this concept while still keeping the number of parameters low.

5. Model parametrization and performance

5.1. Parametrization

The pure ice desorption energies are derived from fitting the three-phase model to the experimental pure ice desorption curves with the results: \( E_{\text{H}_2\text{O}} = 4400 \text{ K} \), \( E_{\text{CO}_2} = 2440 \text{ K} \) and \( E_{\text{CO}} = 1010 \text{ K} \). The H₂O value is lower than the one found in Fraser et al. (2001). This discrepancy is probably due to a combination of that we use a single experiment, do not include the pumping speed and fix the pre-exponential factor to \( \nu = 10^{12} \text{ s}^{-1} \) for every species here. The value in Fraser et al. (2001) should still be used when modeling the absolute desorption temperature. For the purpose of parametrizing the desorption fractions we prefer our value for the sake of consistency. The remaining model parameters \( \epsilon_{\text{H}_2\text{O}} \) and \( c_i \) are obtained separately for CO₂ and CO. This is done through a \( \chi^2 \) analysis, where trapping fractions from the model are compared to those from the binary experiments for a grid of \( \epsilon_{\text{H}_2\text{O}} \) and \( c_i \) values. The minimum \( \chi^2 \) value for CO₂ is obtained for \( \epsilon_{\text{H}_2\text{O}} = 2500 \text{ K} \), \( c_{\text{CO}_2} = 20.5 \text{ ML} \), but the swapping energy for \( \text{H}_2\text{O}:\text{CO}_2 \), which is linked to the ability of CO₂ to swap with H₂O within the solid phase, is not well-constrained between 1600–3200 K (Fig. 5). In contrast, the parameter \( c_{\text{CO}} \), related to available amount of CO₂ from the ice mantle that can migrate to the surface, is well constrained which suggests that even at laboratory time scales mixture desorption is mainly governed by how large a part of the mantle is eligible for swapping with the surface, rather than the swapping barriers.

The CO experiments can be fitted with \( \epsilon_{\text{CO}_{2-\text{H}_2\text{O}}} = 960 \text{ K} \) and \( c_{\text{CO}} = 80 \text{ ML} \), but these are based on only a few experiments and the inequalities \( \epsilon_{\text{H}_2\text{O}-\text{CO}}(\epsilon_{\text{H}_2\text{O}-\text{CO}_2} \text{and } c_{\text{CO}})\text{CO}_2 \) are alone well constrained.

5.2. Model performance

5.2.1. Desorption trends modeling

Figure 6 shows the simulations of the binary mixture desorption using the optimized model parameters from the previous section. Generally the qualitative agreement is good and the model captures the trends that were observed experimentally. The exact shapes of the modeled and experimental desorption curves differ for several reasons. First, the model does not take into account the range of environments from which the molecules desorb, e.g., the H₂O/volatile fraction changes during the desorption process and even a pure ice has a range of different binding sites. This affects both the position and the width of the peak. Second, the model does not consider the different water ice structures present at different temperatures; water ice crystallizes around 140 K (see the desorption peaks for water in Fig. 3e), which may affect the shape and position of the second desorption peak of the volatiles. Finally, the model does not include finite
The increase of the trapped amount of volatiles with ice thickness and the experimental observation that the same amount of molecules desorbs around the volatile pure desorption temperature, regardless of the ice thickness, are reproduced in the model because diffusion between the mantle and surface is only allowed from a fraction of the mantle, \( f_i \), which depends on the kind of volatile and mixing ratio with water. This fraction is independent of the ice thickness. Thus the same amount of volatile molecules migrates to the surface regardless of ice thickness, followed by saturation of the surface phase by water molecules. The rest of the volatiles is trapped in the mantle until \( \text{H}_2\text{O} \) desorption, thus the trapped fraction depends on the ice thickness.

The observed concentration effect on the trapping efficiency is reproduced by the model because the fraction of volatiles migrating to the surface depends on the mixing ratio of the volatile with respect to water, \( x_{\text{mix}} \). The lower the concentration of volatiles in the ice is, the smaller the fraction of volatile molecules make it to the surface and the more become trapped. The higher mobility of \( \text{CO} \) compared to \( \text{CO}_2 \) is also reproduced by the model as the molecular parameter \( c_{\text{CO}} \) is lower than \( c_{\text{CO}_2} \). Thus more volatiles are able to diffuse to the surface in the case of \( \text{H}_2\text{O}:\text{CO} \) mixtures.

Experimentally, a low desorption rate is sometimes observed between the volatile and \( \text{H}_2\text{O} \) desorption temperature. In the model, the diffusion barrier energy is low enough that the diffusion process is complete before desorption of the volatile takes place and therefore there is no desorption between the pure and \( \text{H}_2\text{O} \) desorption peaks. Such a low diffusion energy barrier is needed to reproduce that the trapping efficiency is insensitive to the heating rate (within the explored heating rate range). There is probably a second diffusion process at play at these intermediate temperatures, which cannot be reproduced by the current, simple parameterization.

### 5.2.2. Quantitative agreement

Figure 7 compares the volatile trapping fractions obtained by the optimized \( \text{H}_2\text{O}:\text{CO}_2 \) model to those found experimentally. The error bars include the uncertainties due to the choice of the temperature from which we integrate the second QMS peak and are between 10–20% for the different experimental data points. The error bars on the model results originate from the uncertainties in the input ice thicknesses, mixing ratios and binding energies and these were obtained by varying the model input values within the experimental uncertainty ranges and then comparing the model results. In general, the uncertainty in the mixing ratio has the largest effect, resulting in model prediction uncertainties of \( \sim 15\% \). We conclude that \( \text{CO}_2 \) desorption from binary mixtures is quantitatively described by the model.

### 5.2.3. Predictive power

Figure 4b shows the output of the model for the \( \text{H}_2\text{O}:\text{CO}_2:\text{CO} \) tertiary ice mixture experiments (Exp. 18 and 19). These experiments were not used to constrain the model and are as a test of its predictive power. The concentration dependency in these experiments is reproduced by the model; an increase in the concentration of volatiles leads to a decrease in the trapping fraction.

For the higher concentration mixture, \( \text{H}_2\text{O}:\text{CO}_2:\text{CO} = 11:4:1 \), the model gives a \( \text{CO} \) desorption peak around 70 K (corresponding to the pure \( \text{CO}_2 \) desorption temperature), peak that was also experimentally observed (Fig. 4a, bottom panel). In the model, this peak results from the formation of free desorption sites on the surface due to desorption of \( \text{CO}_2 \). \( \text{CO} \) molecules that are mixed with water migrate to and desorb from the surface easily since the swapping and binding energies are very low compared to the \( \text{CO}_2 \) values.

In addition to reproducing these qualitative trends for tertiary mixtures, the three-phase model also treats correctly the desorption order of both \( \text{CO}_2 \) desorption peaks. Finally Fig. 7 shows that the model provides a reasonable quantitative agreement between the predicted and experimentally determined amounts of \( \text{CO}_2 \) trapped in the tertiary ice mixtures (black diamonds). This is very promising for extending this proof-of-concept model to more species and more complex mixtures.

### 6. Astrophysical implications

Trapping of volatiles in \( \text{H}_2\text{O} \) ice is a crucial parameter when predicting the chemical evolution during star and planet formation (Viti et al. 2004). The modified three-phase desorption model is used here to test the effect of different initial ice compositions and ice thicknesses on ice mixture desorption. Ultimately the three-phase model should, however, be integrated in a protostellar collapse model to simulate the ice desorption accurately during star formation. The prime advantage of the three-phase model, as initially introduced by Hasegawa & Herbst (1993) and extended here, is that it can treat surface and ice chemistry correctly, since it differentiates between surface molecules that can react with gas phase molecules, and mantle molecules that are protected from further processing.

Figure 8 shows the amount of \( \text{CO}_2 \) ice with respect to the original \( \text{H}_2\text{O} \) ice abundance as a function of temperature for different ice thicknesses and mixing ratios heated at 1 K per 100 years, typical for infall of material during protostar formation (Jørgensen et al. 2005).
7. Conclusions

Desorption from H$_2$O-rich ice mixtures is complex in that the amount of trapped ice depends not only on the species involved, but also on the mixture ratio and the ice thickness; there is no constant fraction of volatile species trapped in a H$_2$O ice. This complex behavior can be reproduced by extending the three-phase model introduced by Hasegawa & Herbst (1993).

Using the H$_2$O:CO$_2$ ice system as a case study, we showed that a three-phase model that includes mantle-surface diffusion can reproduce the amount of trapped ice quantitatively in a range of binary ice mixtures. The appropriate input parameters for the H$_2$O:CO$_2$ system are a swapping energy $\epsilon_{\text{H}_2\text{O}-\text{CO}_2} = 2250$ K and a molecular parameter $c_{\text{CO}_2} = 20.5$ ML, which describes from which ice depth diffusion to the surface can occur.

In the model, the different CO$_2$ and CO behavior can only be reproduced if $\epsilon_{\text{MoO}-\text{CO}} < \epsilon_{\text{MoO}-\text{CO}_2}$ and $c_{\text{CO}} > c_{\text{CO}_2}$. This suggests that diffusion/molecule swapping in H$_2$O-rich ices depends equally on the breaking of the H$_2$O-volatile bond (parametrized here by the swapping barrier height) and on the mass/volume of the diffusing volatile (parametrized here by the ice thickness that the molecule can diffuse through). The experimental trends found for H$_2$O:CO and H$_2$O:CO$_2$:CO ice mixture desorption are consistent with the H$_2$O:CO$_2$ trends, which suggests that the three-phase model is generally appropriate to model ice mixture desorption.

However the ice desorption process is implemented in astrochemical models, this study demonstrates that it is vital to understand how ice mixture desorption depends on the ice characteristics. The extended three-phase model naturally treats ice
desorption with the right kinetic order and reproduces volatile entrapment. Its use in astrochemical networks for grain-gas interactions should improve the predictions of gas-phase and grain-surface species abundances in astrophysical environments.

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