ABSTRACT

The desorption characteristics of molecules on interstellar dust grains are important for modelling the behaviour of molecules in icy mantles and, critically, in describing the solid–gas interface. In this study, a series of laboratory experiments exploring the desorption of three small molecules from three astrophysically relevant surfaces is presented. The desorption of CO, O$_2$ and CO$_2$ at both submonolayer and multilayer coverages was investigated from non-porous water, crystalline water and silicate surfaces. Experimental data were modelled using the Polanyi–Wigner equation to produce a mathematical description of the desorption of each molecular species from each type of surface, uniquely describing both the monolayer and multilayer desorption in a single combined model. The implications of desorption behaviour over astrophysically relevant time-scales are discussed.

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

1 INTRODUCTION

The interaction of molecular species with surfaces is of critical importance in astrophysical environments. Much interstellar chemistry occurs on or in the icy layers which cover dust grains in molecular clouds, the birthplace of stars and planets (Fraser, McCoustra & Williams 2002). These dust grains are believed to be composed of silicates and carbonaceous material (Draine 2003). The silicate is at least $\sim$95 per cent amorphous, as determined from the breadth of the 9.7-$\mu$m band (Li & Draine 2002), and although its composition has not been determined precisely, it is well approximated by amorphous olivine (MgFeSiO$_3$) (Sofia & Meyer 2001; Draine 2003). The silicates are believed to be ‘fluffy’ in nature, with a large surface area upon which reactions can occur (Mathis 1998).

At the low temperatures in molecular clouds ($T < 20\,\text{K}$), atoms and molecules freeze out on to these silicate surfaces, forming the icy mantles. Amorphous solid water (ASW) is by far the largest component of this ice, with abundances of $\sim 1 \times 10^{-4}$ with respect to the total H column density (Williams & Herbst 2002), equivalent to coverages of up to 100 monolayers (ML). Given that the extinction threshold for H$_2$O mantles is $A_V \sim 3.3$ mag (Whittet et al. 1988), it is reasonable to assume that between the dense pre-stellar cores (where dust grains are completely coated by this ice mantle) and the cloud edges (where competition between ice formation and photodesorption of H$_2$O yields a population of bare silicate grains; Smith, Sellgren & Brooke 1993), there must be a region where icy surfaces and bare silicates co-exist.

As interstellar regions evolve, the icy grains are further processed, either by gentle heating or by cyclic desorption–deposition events (Visser et al. 2009), producing crystalline H$_2$O. This has been detected in various stellar and pre-planetary environments, including, for example, M giant stars (Onsont et al. 1990), Quaoar in the Kuiper Belt (Jewitt & Luu 2004), Trans Neptune Objects (Merlin et al. 2007), comets (Lisse et al. 2006) and in the outer discs around T Tauri stars (Schegerer & Wolf 2010).

As gas–grain modelling of interstellar environments becomes more sophisticated (Wakelam et al. 2010; Acharyya, Hassel & Herbst 2011; Cuppen & Garrod 2011), key questions impeding the full implementation of surface chemistry include: what effect does the underlying grain surface have on the desorption characteristics of key molecules and to what extent is this desorption affected as we move from the multilayer to submonolayer coverage regime? A third issue is how to realize the transition between the multilayer and monolayer regimes in a gas–grain model without overloading the model with many more layers of complexity.

CO, O$_2$ and CO$_2$ are all interstellar molecules that potentially could populate bare interstellar grains at submonolayer coverages. On ice, only one previous study focused on submonolayer coverages of CO, highlighting the spectroscopic rather than desorption characteristics of the porous ASW:CO system (Collings, Dever & McCoustra 2005). To date, no desorption studies of CO, O$_2$ or
CO$_2$ have been made on a silicate surface, at either multilayer or submonolayer coverages.

CO is the second most abundant interstellar molecule (Tielens 2005) and is known to form in the gas phase, then freeze-out on to H$_2$O-covered grains to form overlayers of pure CO ice, the layer thickness critically depending on gas density rather than on grain temperature (Pontoppidan et al. 2003). Consequently, extensive temperature programmed desorption (TPD) studies have been made of multilayer CO coverages on various surfaces, including Au (Collings et al. 2004; Bisschop et al. 2006; Fuchs et al. 2006; Acharyya et al. 2007), H$_2$O (Collings et al. 2003a,b), a meteorite sample (Mautner et al. 2006) and highly oriented pyrolytic graphite (HOPG; Ulbricht et al. 2006).

It is widely accepted that both CO$_2$ and H$_2$O form on dust grains in molecular clouds, and recent studies suggest that at least some of the CO$_2$ and H$_2$O is formed concurrently (Goumans, Uppal & Brown 2008; Ioppolo et al. 2011; Noble et al. 2011). Since CO is the key precursor to CO$_2$ formation, such mechanisms would require CO freeze-out on to bare grain surfaces long before CO ice or even large quantities of H$_2$O ice are detected. Although tenuous, spectroscopic observational and experimental evidence exists for such a freeze-out process (Fraser et al. 2005), but an investigation of the desorption behaviour of CO at submonolayer coverages on ice and silicate surfaces is vital if we want to be certain that it can reside at an interstellar grain surface long enough to form more complex species.

Similarly, O$_2$ is a potential precursor in H$_2$O formation (Ioppolo et al. 2008; Oba et al. 2009) and is also a species likely to form in the gas phase and then freeze-out on to grain surfaces, rather than forming on the grain itself. However, as a homonuclear diatomic O$_2$ is infrared inactive, its detection in interstellar ice, though occasionally claimed via a forbidden transition (Elsila, Allamandola & Sandford 1997), remains elusive. It is not clear whether this is related to the weak transition probability, lack of a significant O$_2$ population in the ice, or that the O$_2$ has rapidly reacted (upon adsorption) to exclusively form H$_2$O. Nevertheless, the multilayer desorption behaviour of O$_2$ has been studied previously alongside CO and N$_2$ (Fuchs et al. 2006; Acharyya et al. 2007), as well as on Au, porous ASW (Collings et al. 2004) and TiO$_2$ (Dolnalek et al. 2006). These studies show that the multilayer desorption characteristics of O$_2$ are very similar to CO, so it is interesting from both a chemical and astrophysical viewpoint to also investigate the desorption behaviour of O$_2$ at submonolayer coverages on ice and silicate surfaces.

The desorption characteristics of CO$_2$ have not been extensively studied on any surface, despite it being one of the most abundant solid phase molecular species in the interstellar medium (ISM). Recently, the desorption characteristics of multilayer CO$_2$ were reported from porous ASW, and have been previously studied on HOPG (Ulbricht et al. 2006), porous ASW and Au (Collings et al. 2004). However, given that the observational (Pontoppidan 2006) and experimental (Noble et al. 2011) evidence shows that a fraction of CO$_2$ ice must form concurrently with the water ice layer, some CO$_2$ molecules must populate both the bare silicate grains and the ice layers at submonolayer coverages.

Here we present an experimental study of the desorption of CO, O$_2$ and CO$_2$ from three different surfaces: non-porous ASW, crystalline ice and amorphous olivine-type silicate. As these are, for the first time, all undertaken in the same experimental set-up – FORmation of MOLeCules in the InterStellar Medium (FORMOLISM; Amiaud et al. 2006) – we are able to investigate both the individual effect of each surface on the desorption charac-

teristics, as well as determining whether the molecular composition or morphology of the surface is most relevant in determining the desorption behaviour of molecules. For each of the nine combinations of CO, O$_2$ and CO$_2$ on each surface, our study has encompassed both the multilayer and submonolayer regimes. These data are modelled to determine a simple analytical expression which accurately calculates both the submonolayer and the multilayer desorption energies. By changing the model to incorporate interstellar, rather than experimental, heating rates, we are able to address the key questions above, namely what effect does the underlying surface have on the desorption characteristics of the molecules adsorbed there, and how is this desorption modified in the submonolayer coverage regime.

2 EXPERIMENTAL

The experiments were conducted using the FORMOLISM set-up, described in detail elsewhere (Amiaud et al. 2006; Lattelais et al. 2011). Briefly, the set-up consists of an ultrahigh vacuum chamber (base pressure $\sim 10^{-10}$ mbar), containing a silicate-coated copper sample surface, operating at temperatures between 18 and 400 K. The system is equipped with a quadrupole mass spectrometer (QMS), which is used for the TPD experiments. A sample of either O$_2$, CO or CO$_2$ was deposited on to the surface at 18 K via the triply differentially pumped beam line; a linear temperature ramp was then applied to the surface, and the QMS used to measure the desorption of each species into the gas phase, as a function of temperature.

Three surfaces were investigated in this study: non-porous ASW (H$_2$O(np), crystalline ice (H$_2$O(c)) and amorphous silicate (SiO$_x$). The SiO$_x$ surface was recently installed in the FORMOLISM experiment (Lemaire et al. 2010), and mimics bare dust grains in molecular clouds. The silicate is amorphous in nature, as evidenced by infrared spectroscopic studies, while TPD experiments, including those presented in this study, reveal the surface to be non-porous on the molecular scale.

The silicate surface is capable of reaching base temperatures of 18 K, which is how the molecular deposition temperature on all the surfaces was pre-determined. For the ice surfaces, 50 ML films were grown on top of the silicate surface by spraying water vapour from a microchannel array doser located 2 cm in front of the surface. The water vapour was obtained from deionized water which had been purified by several freeze–pump–thaw cycles, carried out under vacuum. H$_2$O(np) mimics the ASW which comprises the bulk of interstellar ice, and H$_2$O(c) mimics the crystalline ice seen in some star-forming regions. To produce H$_2$O(np), water was dosed while the surface was held at a constant temperature of 120 K. To form H$_2$O(c), the surface was held at 120 K during the deposition, then flash heated at 50 K min$^{-1}$ to 140 K, and finally at 10 K min$^{-1}$ to 142.5 K. For each type of ice surface, the temperature was then held constant until the background pressure in the chamber stabilized, before cooling it back down to 18 K, at which temperature adsorbates were dosed on to the respective surfaces.

For each of the nine combinations of molecule and surface, a series of depositions were made, varying the adsorbate surface coverage, from submonolayer to multilayer, as outlined in Table 1. After the first adsorbate exposure, the surface was then heated at a rate of 10 K min$^{-1}$ until the adsorbate was fully desorbed from the surface (below 100 K on the ice surfaces and 130 K on the silicate surface). The original surface therefore remained intact, and by purposefully keeping the temperature of the ice below 100 K no further thermal annealing of the ice occurred during an experimental sequence. Subsequently, the surface was then recooled to 18 K, and a
new coverage of the same adsorbate added. In this way we could be
certain the same surface was used for a single series of adsorbate
exposures, allowing real comparison of the coverage effect for the
first time. In the multilayer, the underlying surface is generally not
important to the desorption, as adsorbate–adsorbate interactions
between molecules determine the kinetics. In the submonolayer, the
interaction between the adsorbate and the substrate is fundamental
in determining the desorption characteristics. Thus, by including
both regimes, we hoped to probe the differences between these two
coverages for different molecules and different surfaces.
A porous ASW surface was not included in this study for two
reasons. First, the presence of pores in the ice surface can produce
very complex desorption profiles, due to the competing kinetics
which arise after entrapment of adsorbates in the pores (e.g. Collings
et al. 2003a). Worse still, pore collapse starts at only 10–15 K, so
the experimental approach used here, of exposing a single ice surface
to a variety of adsorbate coverages, is simply not possible with the
porous ASW. A new ASW sample would have been required for
each experiment; each time we form a porous ice in the laboratory
its structure will be slightly different, resulting in a massive change
in surface area and non-reproducible adsorbate exposures being
required to obtain monolayer coverages. Furthermore, one aim of
this experiment is to compare surface characteristics using a single
model for the whole data set, and such an approach would not
have been possible when including both porous and non-porous
ices, again because the monolayer surface area is difficult to define.
Secondly, it has recently been shown experimentally that it is very
likely that all water ice in interstellar regions will be non-porous
ASW (Accolla et al. 2011), even though observations previously
suggested that invoking a porous ASW was the only way to explain
observed quantities of mixed H$_2$O and CO ices (Pontoppidan et al.
2003).

3 RESULTS AND DISCUSSION

3.1 Experimental data
All the TPD results are shown in Fig. 1. The results are ordered top
to bottom by surface type, H$_2$O$_{(np)}$, H$_2$O$_{(c)}$ and SiO$_2$, and left to right
by adsorbate molecule, O$_2$, CO and CO$_2$. For each molecule–surface
combination, the main window shows the series of submonolayer
exposure TPD spectra, derived from the lowest molecular coverage,
up to 1 ML (as per the values given in Table 1). The inset shows the
equivalent data for coverages of 1 ML and above.

The spectrum which represents 1 ML is chosen by visual inspection
of all TPD spectra in the series, and is defined in this study as the
highest coverage spectrum which includes only (sub)monolayer
desorption characteristics, and has no multilayer component. For a
fully wetting molecule, such as CO or O$_2$, this coverage is assumed
to contain 10$^{15}$ molecules cm$^{-2}$, the generally accepted definition
of a monolayer (Amitai et al. 2006). In the case of CO$_2$, however, a
lower exposure of the species was required before intermediate and
multilayer desorption characteristics were observed, i.e. the 1 ML
coverage contains fewer than 10$^{15}$ molecules. Thus, in this study, we
have defined the coverage as $\theta = \text{exposure}/N_{\text{mono}}$, where exposure
is the number of molecules deposited on the surface and $N_{\text{mono}}$ is
the number of molecules in the designated 1 ML deposition. This
definition is necessary to allow modelling of the CO$_2$ data in the
same fashion as the CO and O$_2$ data, as discussed in Section 3.2.

By inspection of Fig. 1, it is immediately apparent that, for all
cases, the TPD line profile differs between the submonolayer and
the multilayer regime, as expected. In some cases (shown in grey in
Fig. 1), an intermediate region is visible in those TPD spectra which
trace coverages between 1 ML and the multilayer, for example in
CO or CO$_2$ on H$_2$O$_{(np)}$. It is clear that structural reorganizations
must occur at these intermediate coverages, as desorption spectra
with double and triple peaked profiles are observed. Describing
such processes is beyond the scope of this paper and for this reason
these particular data have been omitted from the later modelling,
only being shown here for completeness.

For both O$_2$ and CO$_2$, it is also apparent from Fig. 1 that the TPD
line profiles are similar in the submonolayer regime, independent
of the underlying surface. For CO, this is clearly not the case,
although the multilayer data are more consistent across all surfaces.
Likewise, in both the submonolayer and multilayer regimes,
the TPD spectra for different adsorbates on the SiO$_2$ surface strongly
resemble each other; the same cannot be said for the ice surfaces.
For all the adsorbates, it is evident that multilayer desorption from
the crystalline ice surface starts at a slightly higher temperatures
than from either the amorphous ice or amorphous SiO$_2$ surface,
suggesting a trend dependent on the morphology of the underlying
surface. Specifically, for O$_2$, the peak temperature occurs between
30.9 and 32.6 K, but starts around 24–25 K on amorphous surfaces
(H$_2$O$_{(np)}$ and SiO$_2$), compared to 25–26 K from H$_2$O$_{(c)}$. For CO, the
peak temperatures are in the range 28.1–28.9 K, desorption starts
at 22–23 K from the amorphous substrates and 23–24 K from H$_2$O$_{(c)}$.
For CO$_2$, the peak desorption range is wider (79.3–83.0 K) and
desorption begins at 63–65 K from SiO$_2$, 64–65 K from H$_2$O$_{(np)}$ and
66–67 K from H$_2$O$_{(c)}$.

To compare the sticking efficiency of each molecule on each
surface, the area under the TPD peak, corrected for QMS sensi-
tivity (Matar et al. 2010), was plotted against deposition time for
each molecule on each surface (see Fig. 2). Data can be divided
into adsorbates – circle (CO), triangle (O$_2$) and square (CO$_2$) – and
surfaces – H$_2$O$_{(np)}$ in black, H$_2$O$_{(c)}$ in light grey and SiO$_2$ in dark
grey. Such a direct comparison is possible because the experimental
method employs the same surface for a series of adsorbate expo-
sures. Furthermore, the dosing rates of all three molecules, and
the effective beam pressures employed, are always approximately
equal. Straight lines of the form $y = mx + c$ were fitted to each
molecule–surface combination and overlaid on the experimen-
tal data in Fig. 2. Within experimental uncertainty (shown as error
bars in Fig. 2), these straight line fits all pass through zero, as ex-
pected, indicating that the sticking probability is constant (within

Table 1. Description of experimental exposures.

| Molecule | Surface | Depositions$^a$ (ML) |
|----------|---------|---------------------|
| O$_2$    | H$_2$O$_{(np)}$ | 0.25, 0.50, 0.75, 1, 1.25, 1.38, 1.75, 2.25, 2.75 |
| O$_2$    | H$_2$O$_{(c)}$  | 0.08, 0.17, 0.50, 0.67, 1, 1.33 |
| SiO$_2$  |         | 0.20, 0.60, 1, 1.20, 1.60, 1.67 |
| CO       | H$_2$O$_{(np)}$ | 0.25, 0.50, 0.75, 0.88, 1, 1.06, 1.13, 1.25, 1.75, 2.50 |
| CO       | H$_2$O$_{(c)}$  | 0.10, 0.20, 0.60, 0.80, 1, 1.20, 1.60 |
| SiO$_2$  |         | 0.50, 1, 1.25, 1.75, 2.25 |
| CO$_2$   | H$_2$O$_{(np)}$ | 1.2, 4, 6, 10, 20 |
| CO$_2$   | H$_2$O$_{(c)}$  | 1.2, 3, 5, 10 |
| SiO$_2$  |         | 0.5, 1, 2, 3, 5, 10 |

$^a$Defined as exposure/$N_{\text{mono}}$, where $N_{\text{mono}}$ is defined in Section 3.1.
$^b$Modelled, but omitted from Fig. 3 for clarity.
$^c$Omitted from model (shown in grey in Fig. 1).
Desorption from \( H_2O_{(np)} \), \( H_2O_{(c)} \) and SiO
g

Figure 1. TPD spectra of \( O_2 \), CO and CO\(_2\) from \( H_2O_{(np)} \), \( H_2O_{(c)} \) and SiO
g

<10 per cent) across the dynamic range of each experiment. This
means that no discernible change in sticking probability occurs for
any molecule on any surface between the submonolayer and mul-
tilayer regimes. Adsorbate coverage is always linear as a function
of exposure time. Crucially, for all three adsorbate molecules,
the sticking efficiency on \( H_2O_{(np)} \) (black lines in Fig. 2) is slightly lower
when compared with the other two surfaces. This is likely due to
the fact that the average adsorption energy on \( H_2O_{(np)} \) peaks at a
lower energy than for the other substrates.

One final point to emphasize is the distinction between the time
at which a surface will have been exposed to an equivalent dose of
10\(^{15}\) molecules (generally defined as the number of molecules in
one monolayer for a wetting molecule) and the coverage (exposure
time) at which the TPD data show a deviation from submonolayer
to multilayer behaviour, defined above as \( N_{\text{mono}} \). For CO and \( O_2 \),
\( N_{\text{mono}} \) is reached on all surfaces between around 250 and 300 s
exposure; for CO\(_2\), the switch from monolayer to multilayer occurs
at much lower surface coverages (exposure times \( \sim \)30 per cent
for CO and \( O_2 \)). We postulate that this difference is related to the
wetting behaviour of the molecules, and come back to this issue in
Section 3.3.

3.2 Modelling

To obtain a more quantitative understanding of the interactions
between the molecules and the surfaces, the TPD spectra were
reproduced from an empirical kinetic model. To do this, the results
were divided into sets of TPD spectra associated with submonolayer
and multilayer behaviour and the kinetic parameters in each regime
determined independently, before being recombined to reproduce
the experimental TPD data. A simple model was therefore derived

\[
\frac{dN}{dt} = AN^a e^{-E_{ads}/kT},
\]

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where \( A \) is the pre-exponential factor, \( N \) is the number of adsorbed molecules on the surface (cm\(^{-2}\)), \( n \) is the order of the reaction, \( E_{\text{ads}} \) is the energy of adsorption of a molecule to the surface (eV), \( k \) is the Boltzmann constant (eV molecule\(^{-1}\) K\(^{-1}\)), and \( T \) is the temperature of the surface (K). The units of \( A \) depend on \( n \): molecule\(^{-1}\) cm\(^{2}\) s\(^{-1}\). Reformulating equation (1) to reflect the measured experimental TPD signal gives

\[
r = -\frac{dN}{dt} = \frac{A}{\beta} N^n e^{-E_{\text{ads}}/kT},
\]

where \( \beta \) is the rate of heating, in this case \( dT/dt = 10 \text{ K min}^{-1} \).

When the rate of desorption is independent of surface coverage, as is the case in multilayer desorption, \( n = 0 \) and the TPD desorption profiles share a common leading edge as is readily apparent from the insets in Fig. 1.

For each molecule–surface combination, the leading edge of the highest multilayer exposure TPD spectrum was used to determine \( E_{\text{ads}} \) (in K). Although some multilayer desorption TPD data show that the order of reaction can deviate slightly from zero (e.g. Brown & Bolina 2007), it is a reasonable approximation, so henceforth we assume \( n = 0 \). As applied previously by Acharyya et al. (2007), the pre-exponential factor in equation (2) was assumed to be a function of \( E_{\text{ads}} \), approximated by

\[
A = N_{\text{ML}} v = N_{\text{ML}} \sqrt{\frac{2N_{\text{ML}} E_{\text{ads}}}{\pi^3 M}},
\]

where \( M \) is the mass of the adsorbate molecule, and \( N_{\text{ML}} \sim 10^{15} \text{ cm}^{-2} \). The key advantage of this method is that the multilayer fitting requires only one variable, \( E_{\text{ads}} \), removing the interdependency of fitting both the pre-exponential factor and \( E_{\text{ads}} \) concurrently. The results of fitting \( E_{\text{ads}} \) are presented in Table 2.

In the submonolayer regime, the rate of desorption is dependent on surface coverage, \( \theta = N/N_{\text{mono}} \leq 1 \), where \( N_{\text{mono}} \) (as defined in Section 3.1) is the maximum number of molecules on the surface prior to the onset of intermediate or multilayer desorption behaviour.

### Table 2. Multilayer desorption parameters calculated using equation (2), compared to previous literature values in italics.

| Molecule | Surface | Calculated values\(^a\) \( \nu \) \( (10^{26} \text{ molecule cm}^{-2} \text{s}^{-1}) \) | \( E_{\text{ads}} \) (K) |
|----------|---------|--------------------------------------------------------------------------------|-------------------|
| \( \text{O}_2 \) | \( \text{H}_2\text{O}(\text{np}) \) | 6.9 | 898(30) |
| \( \text{H}_2\text{O}(\text{c}) \) | 7.0 | 936(40) |
| SiO\(_2\) | 6.9 | 895(36) |
| Au | 6.9 | 912(15)\(^b\) | 925(25) |
| CO | \( \text{H}_2\text{O}(\text{np}) \) | 7.1 | 828(28) |
| \( \text{H}_2\text{O}(\text{c}) \) | 7.1 | 849(55) |
| SiO\(_2\) | 7.1 | 831(40) |
| Au | 7.2 | 858(15)\(^b\) | 826(24)\(^b\) | 855(25)\(^b\) |
| CO\(_2\) | \( \text{H}_2\text{O}(\text{np}) \) | 9.3 | 2267(71) |
| \( \text{H}_2\text{O}(\text{c}) \) | 9.5 | 2356(83) |
| SiO\(_2\) | 9.3 | 2269(80) |
| \( \text{Porous ASW} \) | – | 2690(50)\(^f\) |
| \( \text{HOPG} \) | – | 2982\(^\circ\) |

\(^a\)For values calculated in this work, the values in parentheses are the total calculated error, including the 3\( \sigma \) statistical errors on \( E_{\text{ads}} \) calculated during the fit of the equation (2) and the experimental uncertainties. In all other cases, the error is as quoted in the relevant literature.

\(^b\)Acharyya et al. (2007), using an identical multilayer modelling method.

\(^c\)Fuchs et al. (2006), calculated assuming a fixed-pre-exponential factor.

\(^d\)Collings et al. (2003b), calculated assuming a fixed pre-exponential factor.

\(^e\)Oberg et al. (2005), Fuchs et al. (2006) and Bisschop et al. (2006), calculated assuming a fixed-pre-exponential factor.

\(^f\)Sandford & Allamandola (1990), calculated using spectroscopic data, assuming a zeroth-order desorption profile.

\(^g\)Burke & Brown (2010), calculated empirically with a non-integer reaction order.

Previous publications have shown that the reaction order can deviate slightly from 1 (e.g. Brown & Bolina 2007), but for the purposes of this work we assume \( n = 1 \). In general, in the case of first-order desorption, the peaks of the TPD data appear at a single temperature value, provided that the desorption energy is independent of coverage (Fraser et al. 2001). However, as is evident from the main panels in Fig. 1, in this instance it is the trailing edge of the TPD curves that are common in each molecule–surface system. Such behaviour is known to arise when the adsorbate is occupying multiple sites on the surface, such that the adsorption energy is a continuous function of the number of molecules on the surface (e.g. Dohmala et al. 2001; Amiaud et al. 2006). By inverting equation (2), a TPD spectrum can be converted to a function, \( E(N) \), given by

\[
E(N) = -kT \ln \left(\frac{r \beta}{AN}\right).
\]

To fit \( E(N) \) for each molecule–surface system, we first select the TPD spectrum equating to the surface exposure just prior to the appearance of multilayer peaks, or (in the case of CO\(_2\)) more complex desorption characteristics, and define this as the monolayer coverage, i.e. \( \theta = N/N_{\text{mono}} = 1 \), ensuring the maximum range of adsorption sites and energies at the surface are included. This is a very reasonable approach, given that it is well known that \( E(N) \) is independent of reaction order at exactly \( N = N_{\text{mono}} \) (Ulbricht et al. 2006). This monolayer TPD is then fitted using an analytical expression of \( E(N) \), redefined in terms of surface coverage, \( E(\theta) \), as:

\[
E(\theta) = -kT \ln \left(\frac{r \beta}{AN}\right).
\]

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**Figure 2.** Area under TPD peak, corrected for QMS sensitivity, plotted against deposition time. Experimental data are plotted as points, with H\(_2\)O on black, H\(_2\)O\(_2\) in light grey and SiO\(_2\) in dark grey; CO as circles, CO\(_2\) as squares and O\(_2\) as triangles. Overplotted are the straight line fits to the data, as described in the text. Colours are as above for the three surfaces, with CO solid, CO\(_2\) dashed and O\(_2\) dot–dashed lines. As expected, for each molecule–surface combination, the area increases with deposition time, and the straight line fit goes through zero, within experimental errors. For each molecular species, sticking occurs approximately equivalently on all three surfaces, with an error of <10 per cent, although sticking is slightly lower on H\(_2\)O\(_{\text{np}}\) for all molecules.
desorption from multilayers, rather than the crystalline surface causing unusual desorption, is taken from Table 2, errors on the model, as illustrated by the overplotted dot–dashed surface when compared with the amorphous H

\[ E(\theta) = \alpha_0 + \alpha_1 \theta + \alpha_2 \theta^2 + \alpha_3 e^{\alpha_4 \theta} + \alpha_5 e^{\alpha_6 \theta} + \alpha_7 e^{\alpha_8 \theta} + \alpha_9 e^{\alpha_{10} \theta}. \]

(5)

The resulting coefficients \(\alpha_0-\alpha_{10}\) are listed in Table 3 and can then be used to calculate \(E(\theta)\) from equation (5), which can then be substituted into equation (4), along with an appropriate value for \(A\), to reproduce all TPD data for a specific molecule–surface system.

As the choice of \(A\) has a large effect on the value of \(E(\theta)\) calculated from the model, we first attempted to reproduce the submonolayer coverages by concurrently optimizing \(A\) (Stirniman et al. 1996). During the calculation of \(E(N, A)\), \(A\) was set at a fixed range of values from \(10^5\) to \(10^{15}\) s\(^{-1}\). The optimal value of \(A\) is the one which minimizes the difference between the functions \(E(N)\) for each submonolayer coverage in terms of least squares. This method was not always successful for all molecule–surface combinations, as there was not always a minimum in the least-squares calculation. In those cases where a minimum was calculated, the corresponding \(A\) value was found to be significantly lower than the expected value (typically around \(10^6\) s\(^{-1}\), whereas the actual \(A\) expected was \(10^{15}\)). This optimization method for \(A\) assumes that there is no difference in the occupation of the high energy binding sites (i.e. the tail of the TPD spectra) with increasing coverage. Thus, all \(E(N)\) calculated for a given \(A\) value should coincide at low coverage; in our experiments, there were some minor differences in the tails of the TPD spectra, and consequently this method was rejected. To reproduce the TPD spectra at submonolayer coverages, \(A\) was fixed at \(10^3\) s\(^{-1}\).

To successfully reproduce all the TPD data, from submonolayer to multilayer regimes, the results from the two coverage models are then combined, such that (a) when \(\theta \leq 1\), in equation (2), \(E_{\text{sh}}\) is replaced by \(E(N)\) (derived from equation 5), \(n = 1\) and \(N \leq N_{\text{mono}}\); and (b) when \(\theta > 1\), the TPD is the sum of the monolayer trace generated in (a), plus equation (2), where \(E_{\text{sh}}\) is taken from Table 2, \(A\) defined by equation (3), \(n = 0\) and \(N\) is redefined as \(N - N_{\text{mono}}\).

### 3.3 Discussion

From Fig. 3, it is clear that the combined model can very accurately reproduce the desorption profiles of all molecular species on all surfaces (O\(_2\), CO and CO\(_2\) on H\(_2\)O\(_{\text{np}}\), H\(_2\)O\(_c\) and SiO\(_x\)). In particular, the model faithfully reproduces the submonolayer coverage TPD spectra. Although in a few cases the model data do not perfectly describe the empirical line profiles, the two clearly coincide within the 3σ errors on the model, as illustrated by the overplotted dot–dashed lines on the submonolayer coverage of CO\(_2\) on H\(_2\)O\(_c\). These errors are omitted from all the other plots for clarity. The errors result from the assumption that all the TPD spectra are concurrent in the highest energy binding sites, i.e. their tails overlap, which is a necessary assumption when applying this model.

The multilayer TPD spectra, and their associated fits, are shown in the insets of Fig. 3. Most importantly, as noted previously from the experimental data, the model data also show that multilayer desorption begins at the same temperature for each molecule–surface combination (the leading edges of the TPDs are identical), although the onset of this desorption occurs at a higher temperatures on the H\(_2\)O\(_{\text{np}}\) surface when compared with the amorphous H\(_2\)O\(_{\text{np}}\) and SiO\(_x\) surfaces. From Table 2, it is clear that \(E_{\text{sh}}\) is consistently marginally greater on the crystalline surface, as compared to the amorphous surfaces, resulting in slightly lower desorption rates from crystalline surfaces and the later onset (in time or temperature) of the desorption process. This trend is even consistent with previously reported results (see Table 2). Given that species such as CO, CO\(_2\) and O\(_2\) could be present on interstellar ices or grains at multilayer coverages of up to a few ML, this result indicates that a similar effect from underlying surface crystallinity could be relevant in interstellar regions.

It should be noted that the desorption energies of species from H\(_2\)O\(_{\text{np}}\) are consistently higher than for the same species desorbing from either of the amorphous surfaces, H\(_2\)O\(_{\text{np}}\) and SiO\(_x\). One possible explanation for this trend is that the ordered structure of the crystalline water surface induces larger scale interactions among the desorbed molecules. The study of Dohnalek et al. (1999) revealed that amorphous water deposited on top of crystalline water displayed a degree of crystalline nature in its first layer due to interaction with the ordered surface of the underlying crystalline substrate. It is possible that O\(_2\), CO and CO\(_2\) experience similar interactions with the crystalline water surface, although these bonds would likely be of lower energy than for a water–water system. Another possibility is that rather than the crystalline surface causing unusual desorption energies, it is in fact the values from amorphous surfaces that are altered due to the presence of defects in the crystalline structure which prevent normal monolayer and multilayer regimes to build up on these surfaces.

Surprisingly, given its ubiquity in interstellar ices, the multilayer desorption energy of pure CO\(_2\) ice is not widely reported in the literature. One value has been measured previously from multilayers of CO\(_2\) on HOPG (Burke & Brown 2010), where analysis proved that the reaction order is zero, and estimated the magnitude of the pre-exponential factor at around \(10^{20}\). However, consistent with the rather complex TPD spectra shown in grey in the insets in Fig. 1, it was very difficult to undertake a detailed analysis of multilayer CO\(_2\) desorption from the HOPG surface. Consequently, the value of
Figure 3. Modelled TPD spectra. Experimental data, as in Fig. 1, are plotted in black diamonds; coverages up to and including 1 ML are shown in the main window, with coverages of 1 ML and greater inset. Model data are overplotted as coloured/grey lines. Typical 3σ errors on the model are overplotted as dot–dashed lines on the plot of CO₂ on H₂O(c) only, for clarity. Some of the original TPD data are omitted for clarity (see Table 1). See text for full discussion.

E_{ads} quoted by Burke & Brown (2010) is not only somewhat higher than the value calculated here, but also has a quoted error greater than the value of E_{ads} itself (±19 484 K, which is omitted in Table 2 for clarity). Three other multilayer CO₂ desorption measurements are claimed in the literature, as indicated in Table 2; unfortunately, all three were determined from transmission infrared data, assuming the desorption kinetics were first, and not zeroth, order. Consequently, although included for completeness, as the values are often quoted in models, the numbers are not comparable to the results quoted here.

For multilayer coverages of CO and O₂, the E_{ads} calculated from this model can be compared directly to previous (multilayer) results in the literature (see Table 2). Within the errors, our results for CO and O₂ on H₂O(c) – a crystalline surface – are identical to those obtained previously by Acharyya et al. (2007) for O₂ and CO on a polycrystalline Au substrate, using the same fitting method. This last point is particularly relevant when comparing the results, as both here and in Acharyya et al. (2007) the parametrization of the fit is reduced to one by expressing the pre-exponential factor in terms of E_{ads}. Consequently, our pre-exponential factor also correlates well with that reported by Acharyya et al. (2007) previously. Even though the calculated E_{ads} for the amorphous surfaces are slightly lower than the result from the H₂O(c) surface, they also are consistent within the calculated error, with the values from Acharyya et al. (2007). The other values of E_{ads} listed in Table 2 for CO and O₂ on polycrystalline Au (Collings et al. 2003b; Öberg et al. 2005; Bisschop et al. 2006; Fuchs et al. 2006) were calculated assuming a fixed pre-exponential factor (A) of magnitude around 10^{30}. As A and E_{ads} are not mutually exclusive, it is not possible to make a direct comparison between these data and our results; however, it is interesting to note that despite a difference of over four orders of magnitude in the value of the pre-exponential factor, the reported values of E_{ads} are all remarkably consistent. The question is only the extent to which these subtle differences in the value of E_{ads} affect the desorption of ice multilayers in interstellar space and how to account for such subtleties in gas–grain models (see Section 4).

In modelling the submonolayer desorption of key interstellar molecules from different surfaces, the aim was to provide the chemical modelling community with a useful equation (equation 5 and Table 3) for mathematically describing the desorption characteristics of the surfaces, as well as an indication of the coverage at which a particular adsorbate’s behaviour switches from the submonolayer...
to the multilayer regimes (a measure of $N_{\text{mono}}$). The excellent agreement between experimental data and the model is also validation of our method, described in Section 3.2. The only limitation of this method is the certainty with which we have empirically selected the TPD curve used to model submonolayer desorption characteristics. This curve represents the highest coverage at which only monolayer desorption characteristics are seen, rather than, necessarily, a coverage of $10^{15}$ molecule cm$^{-2}$ (the generally accepted definition of one monolayer). However, it is possible that an exposure time of a few seconds more or less could have been a slightly better model system to represent (sub)monolayer desorption. This is the limitation introduced by our chosen method of deposition calibration.

Of all the data fitted here, only the CO–ice systems show minute deviations at the highest submonolayer coverages, and such effects could be due to CO, as the smallest molecule studied, somehow being able to probe defects and cracks in the ice surface, prior to forming a multilayer, as described previously in studies of CO on ASW (Collings et al. 2003a,b), an effect omitted from this model. This may also explain why in these systems it is difficult to reproduce a perfect match in the transition regime between the monolayer and multilayer coverages. Likewise, although the fits shown here to the CO–ice systems are excellent, a number of ‘intermediate’ TPD spectra, shown in grey in Fig. 1, with double and triple TPD peaks, had to be omitted from the modelling process. These spectra are indicative of 2D island growth on a surface, as seen in the formation of N$_2$ ices, and indicate that the growth mechanism of CO$_2$ on any ice surface is different from that of CO or O$_2$ (Oberg et al. 2005; Fayolle et al. 2011). Whilst each island is entirely independent of another on the surface and there is no diffusion between them or bridges linking them, we can consider that we are in the submonolayer coverage regime. Once the islands have fully merged and overlayers of CO$_2$ ice form, then we can be certain we are in a multilayer regime. This is what we assume here; again a more full description of the ‘intermediate’ stages is beyond the scope of this paper. Nevertheless, such effects should not detract from the broad applicability of the submonolayer model. Furthermore, as a general rule the outcome of our monolayer TPD choice suggests that for CO and O$_2$, it is reasonable to assume $N_{\text{mono}} = 10^{15}$, whereas for CO$_2$ it is around $N_{\text{mono}} = 3 \times 10^{14}$. This result is consistent with the exposures discussed previously in Fig. 2 and reflects the CO$_2$ island growth.

As can be seen from the main panels in Fig. 3, at very low coverages (<0.5 ML) there is sometimes a small deviation in the leading edge of the modelled desorption compared to the experimental results, most evident on the SiO$_2$ surface. Although this lies within the error range of the fitting, there are two potential explanations for why such discrepancies could arise, both related to the assumption made in the model that all desorptions from a given surface share the same TPD trailing edge profile. As the sites in the tail of the TPD are the most energetically favourable, it follows that any adsorbate able to diffuse across the surface will bind most readily to these sites, occupying them first on adsorption and last on desorption. Such an effect has clearly been seen previously with H$_2$ and D$_2$ on ice surfaces (Amiaud et al. 2006). Even under ultrahigh vacuum conditions, molecules such as H$_2$, CO and H$_2$O are still present in the experimental chamber, all be it at exceptionally low concentrations (partial pressures around $10^{-13}$–$10^{-14}$). Consequently, over the very long time-scales required to complete the experiments described here (14–16 h per single molecule–surface combination), it is potentially possible that some of the surface sites could be dynamically occupied for a short period by a ‘pollutant’ adsorbate, thus blocking the adsorbate molecule of interest from occupying a highest energy binding site. Such an effect would then lead to higher occupation of the lower energy binding sites and a mismatch between the experimental and model data, the latter appearing at slightly higher temperatures. Such an effect would not have been evident in the work of Amiaud et al. (2006) because they were only cyclically heating their ice surfaces between 10 and 30 K, and consequently could complete the experiment on a much shorter time-scale than was possible here. As H$_2$ and CO are reasonably volatile pollutants, the build-up of H$_2$O would be most likely to have an effect on the nature of the surface, and such an effect would be most evident on the non-ice surface, i.e. SiO$_2$. However, as the experimental sequence was always run from low to high coverage, if this were the key reason for any discrepancy, it should be more pronounced as we get towards the monolayer coverage data. Evidently, this is not the case.

It is also important to consider mass effects; in comparison to the H$_2$–ice system studied previously (Amiaud et al. 2006), CO, O$_2$ and CO$_2$ are more massive molecules, and therefore likely to diffuse more slowly on the surfaces. Therefore, unlike the H$_2$ when deposited on the surface at relatively low concentrations, CO, O$_2$ and CO$_2$ may not sample all the binding sites before adsorbing, just ballistically depositing in a ‘stick and stop’ process. Subsequently, during the TPD warming, all the molecules will diffuse, but again the heavier molecules may not fully sample the surface before desorbing. Then, at very low coverages, not all the highest energy binding sites will be occupied, and the TPD tails may not be quite coincident. As a result, the model would slightly underestimate the leading edge of such TPD curves. From this explanation, it is also possible to rationalize why the discrepancy between the model and empirical data would be greatest on the SiO$_2$ surface: the breadth of the submonolayer TPD peaks from the molecule–silicate systems in comparison to the molecule–ice systems clearly indicates a broader range of binding sites on the SiO$_2$ surface. By contrast, the water surfaces have a narrow and energetically similar range of binding sites, which may also intimate that the ice surfaces do not have many dangling bonds or much proton disorder in them (Fraser et al. 2004). This is contrary to what we might expect, as it is often assumed that amorphous water ice potentially has a very broad range of binding sites at its surface. However, without spectroscopic data we cannot comment further on this here. Consequently, the probability of sampling the highest energy binding sites is even lower at low coverages on SiO$_2$ than the ice surfaces, provided the diffusion rates on all three surfaces are approximately equal. Nevertheless, these tiny differences should not detract from the excellence of the fits, nor that the model can be executed whilst ignoring the pumping speed in the chamber; this is because in FORMALISM the pumping is so effective that as soon as a molecule desorbs from the surface, it is effectively removed from the chamber – in experiments, without such efficient pumping the experiments described here would simply be impossible to undertake, as the TPD tails may never overlap.

To compare the $E(\theta)$ calculated here with previous adsorption energy values of CO, O$_2$ and CO$_2$ as reported in the literature, we have produced Table 4. This shows the specific values of $E(\theta)$ for each molecule on each surface at coverages ranging from $\theta = 0.1$ to 1.0. The errors on each energy value are determined by the error on the fit to the experimental data and are around ±25 K in all cases. The comparison is rather complicated by the fact that no one else has ever considered fitting coverage-dependent adsorption energies for these particular molecules at submonolayer coverages on surfaces of astrophysical relevance. In general, the effective adsorption energy is higher at lower coverage, reflecting that the highest energy binding sites are occupied first, and tends towards the
Table 4. Calculated values of $E(\theta)$ at a range of submonolayer surface coverage values, calculated using equation (5) and the coefficients from Table 3.

| Molecule | Surface  | $E(\theta)/K$ |
|----------|----------|---------------|
|          |          | $E(0.1)$ | $E(0.2)$ | $E(0.5)$ | $E(0.9)$ | $E(1.0)$ |
| O$_2$    | H$_2$O(np) | 1161   | 1082   | 972    | 928    | 914    |
|          | H$_2$O(c)  | 1149   | 1092   | 1017   | 975    | 969    |
|          | SiO$_2$    | 1255   | 1146   | 1019   | 945    | 930    |
| CO       | H$_2$O(np) | 1307   | 1247   | 1135   | 956    | 863    |
|          | H$_2$O(c)  | 1330   | 1288   | 1199   | 1086   | 1009   |
|          | SiO$_2$    | 1418   | 1257   | 1045   | 896    | 867    |
| CO$_2$   | H$_2$O(np) | 2346   | 2258   | 2197   | 2197   | 2236   |
|          | H$_2$O(c)  | 2514   | 2451   | 2364   | 2341   | 2361   |
|          | SiO$_2$    | 3008   | 2798   | 2487   | 2317   | 2271   |

calculated multilayer value for the same molecule–surface system as the coverage rises towards that of a monolayer. Although, by the monolayer coverages, the trend again emerges that the binding energy on the crystalline surface is consistently higher than on the amorphous surfaces, the same is not true at lower coverages.

Previous studies using different methods have reported the monolayer energy of CO as 1564 $\pm$ 120 K on HOPG (Ulbricht et al. 2006), 1624 $\pm$ 360 K on meteorite (Mautner et al. 2006) and 1179 $\pm$ 24 K on a highly porous ASW (Collings et al. 2003b). Certainly, our values for CO on the ice surfaces cover a range of values including the result of Collings et al. (2003b), and at the lowest coverages our value on the SiO$_2$ surface is closer to that reported for HOPG. It is pertinent to compare the lowest coverage since the HOPG data were measured in a molecular beam scattering experiment, indicating that only a low concentration, dynamic coverage was resident on the HOPG surface for a relatively short time, and therefore must have been occupying the highest energy binding sites. The meteorite sample would no doubt encompass a much wider variety of binding sites than even the amorphous silicate used here, so again it is not surprising that the desorption energy is even higher on this surface. This excellent agreement between our results and previous results is further justification that our model is viable and effectively reproduces the effects of submonolayer desorption from a variety of interstellar-relevant surfaces.

For O$_2$, previous calculated submonolayer energies are 1082 $\pm$ 120 K on HOPG (Ulbricht et al. 2006) and 1203 K on graphite (Bojan & Steele 1987). Again our values at the lowest coverages on SiO$_2$ compare favourably with previously reported values from carbon-based surfaces. The desorption energy of the CO$_2$ monolayer has been calculated as 2766 $\pm$ 241 K on HOPG (Ulbricht et al. 2006), 3079 $\pm$ 20 K on graphite (Terlain & Larher 1983), 2553 $\pm$ 232 K on H$_2$O(c) (Andersson et al. 2004), 2490 $\pm$ 240 K on H$_2$O(np) and 2393 $\pm$ 240 K on H$_2$O(g) (Gálvez et al. 2007). Certainly, the range of our data compares favourably with these values; in particular, at the lowest coverages, the value of $E(\theta)$ for CO$_2$ on SiO$_2$ is consistent with the molecular beam scattering result from HOPG, and the value of $E(\theta)$ for CO$_2$ on H$_2$O(g) is identical within the quoted errors to that measured by Andersson et al. (2004), who also used a molecular beam scattering experiment and therefore probed the highest energy binding sites for CO$_2$ on the crystalline ice surface. Interestingly, the value calculated by Gálvez et al. (2007) for desorption from H$_2$O(np) is higher than that from H$_2$O(g), a result in contrast to the data presented here. However, within the stated experimental errors of the study, these values are consistent with our results. Such excellent overlap between the results also verifies our earlier assumptions in terms of choosing the appropriate TPD spectrum to define as the monolayer coverage for CO$_2$ on the ice surfaces and indeed our calculation of $N_{\text{mono}}$.

The adsorption behaviour of the molecule–surface combinations can be divided into roughly three categories related to the difference between the multilayer energy (or adsorbate–adsorbate interactions) and the energy distribution of the surface adsorption sites. These behaviours can be explained with reference to Fig. 4, a plot of the modelled energy as a function of coverage, $E(\theta)$. Where the energy of the multilayer is significantly higher than the energy distribution at coverages below 1 ML, as is the case for CO on H$_2$O(c), molecules will preferentially adsorb on to the substrate at low coverages, rather than starting to form a multilayer or island. In this ‘full wetting’ regime, the multilayer appears only after all of the sites on the surface are filled. All the CO lines (solid) in Fig. 4 follow this regime.

Where the multilayer energy is lower than the monolayer energy, such as for CO on H$_2$O(np), molecules preferentially form clusters (or islands) on the surface at very low coverages, well before 1 ML. In this ‘non-wetting’ regime, these islands, which are multilayers thick, do not cover the whole substrate but eventually build long towers which may join and overlap, until eventually multilayer zeroth-order desorption is observed. All the CO$_2$ submonolayer coverages on any H$_2$O ice surface follow this regime (see Fig. 4).

These two ‘wetting’ and ‘non-wetting’ regimes can be further contrasted by considering the TPD spectra of CO on H$_2$O(c) versus those of CO$_2$ on H$_2$O(np). In Fig. 1, CO$_2$ rapidly forms a double-peaked multilayer desorption profile, while CO shows a gradual filling of the surface sites before a multilayer feature forms.

Intermediate between these two regimes, molecules first fill the lowest energy surface sites, before starting to form multilayer islands on top of the existing monolayer, before the monolayer coverage is fully complete. This occurs where the energy of the final binding sites in the monolayer is equal to or greater than that of the multilayer binding sites, and usually is only seen at exposures close to $N_{\text{mono}}$. These three states are relatively easy to observe in Fig. 4, although the exact boundaries between the regimes are

![Figure 4](https://academic.oup.com/mnras/article-abstract/421/1/768/990656)
mg

Table 5. Adsorption behaviour of each molecule–surface combination, estimated from the modelled energies in Tables 2 and 3 and the desorption characteristics in Fig. 1.

| Molecule | Surface   | Behaviour                  |
|----------|-----------|----------------------------|
| O₂       | H₂O\(_{\text{np}}\) | Full wetting/intermediate |
|          | H₂O\(_{\text{c}}\)   | Full wetting/intermediate  |
|          | SiO\(_{\text{x}}\)   | Full wetting               |
| CO       | H₂O\(_{\text{np}}\) | Full wetting               |
|          | H₂O\(_{\text{c}}\)   | Full wetting               |
|          | SiO\(_{\text{x}}\)   | Full wetting               |
| CO₂      | H₂O\(_{\text{np}}\) | Non-wetting                |
|          | H₂O\(_{\text{c}}\)   | Non-wetting                |
|          | SiO\(_{\text{x}}\)   | Non-wetting/intermediate   |

*Full wetting* behaviour is seen for molecules which fill all the lowest energy sites on the surface before forming a multilayer. ‘Intermediate’ behaviour is when the molecules start to fill the surface, but form islands before it is full. ‘Non-wetting’ behaviour is when islands are almost immediately formed by molecules on the surface.

difficult to define, as island growth is difficult to reproduce and analyse experimentally. Nevertheless, the regimes associated with each molecule–surface combination are summarized in Table 5.

4 ASTROPHYSICAL IMPLICATIONS

Under astrophysical conditions, the heating rate is likely to be of the order of 1 K century\(^{-1}\) (hot core heating rate; Viti & Williams 1999), many orders of magnitude slower than the laboratory value of 10 K min\(^{-1}\) employed here. By simulating the desorption profiles of the molecule–surface combinations here, it is possible to investigate whether surface type and coverage is likely to affect desorption characteristics on astrophysically relevant time-scales.

Fig. 5 presents the results of such a simulation for all molecule–surface combinations, assuming a 2 ML coverage of each species on each grain (i.e. one multilayer and one monolayer). This seems reasonable as none of these species (except possibly CO) forms large pure ice overlayers in the ISM. In Fig. 5, the dot–dashed line shows the modelled desorption characteristics of 2 ML of CO from H₂O\(_{\text{np}}\) if only multilayer desorption is considered. It is evident that without including the submonolayer component of the model, the desorption time is vastly underestimated (by over a few times 10\(^4\) years or 10–15 K), particularly for CO and CO₂. This is a comparable error to that introduced when gas–grain models treat multilayer desorption as first order, as suggested previously (Fraser et al. 2001), and illustrates that submonolayer desorption characteristics are fundamental to describing the overall desorption profile of species on astrophysical time-scales.

Fig. 5 shows that for O₂, there is the least difference between the time (or temperature) at which desorption would be completed in the multilayer-only model versus the combined multilayer–monolayer model. However, monolayers of both CO and CO₂ are able to reside directly at the surface for thousands of years, or at equivalent temperatures 10–15 K higher, than those predicted by multilayer desorption alone, particularly on the amorphous silicate surface. In quiescent regions of the ISM or at the edges of molecular clouds, where grains are warmer, this would suggest that small molecules, like CO and CO₂, could easily be present on the grain surfaces, potentially undergoing chemistry to generate larger chemical species, long before detectable ice layers really form. Such processes have been postulated previously (Fraser et al. 2005), and it remains an interesting follow-on from this work to see which chemical species will form in astrochemical models when these submonolayer desorption data are considered.

What is also clear from Fig. 5 is that, while the molecules desorb at different times (and temperatures), there is a clear pattern to the order of desorption from the various substrates. The onset of desorption from the amorphous surfaces, H₂O\(_{\text{np}}\) and SiO\(_{\text{x}}\), occurs almost concurrently for all species, while desorption from H₂O\(_{\text{c}}\) occurs later, at a higher temperature. This delay in desorption from crystalline surfaces indicates that in regions where crystalline water is predicted to dominate, for example on processed ices inside discos around young stellar objects (YSOs; Visser et al. 2009) or even cometary surfaces (Roush 2001), volatile species will not start desorbing from grain surfaces for a few thousand years longer (or over temperature ranges of a few kelvin higher) than anticipated from zeroth-order desorption kinetics models. Such differences are subtle, but when one considers that these molecules will be highly mobile at such temperatures, the potential for complex chemistry to occur on the grain surfaces is increased. Furthermore, it is exactly these inner disc regions, where crystalline water ice is predicted to be found, from which hot core and hot corino gases are populated by desorbing molecules (e.g. Viti & Williams 1999; van der Tak, van Dishoeck & Caselli 2000; Cazaux et al. 2003; Semenov et al. 2010; Favre et al. 2011).

Similarly, the simulation results in Fig. 5 show the residence time of molecules on a H₂O\(_{\text{c}}\) surface is significantly higher than on the amorphous surfaces. Starting from a 2 ML coverage, the time taken for 50 per cent of the O₂ on SiO\(_{\text{x}}\) or H₂O\(_{\text{np}}\) to desorb is 8000 years, while on H₂O\(_{\text{c}}\) this value is 8700 years, an increase of 8.75 per cent. Similarly, the difference between desorption of 50 per cent of the molecules from H₂O\(_{\text{np}}\) and from H₂O\(_{\text{c}}\) is 8.82 per cent for CO and 6.97 per cent for CO₂.

5 CONCLUSIONS

A key aim of this work was to address what effect the underlying dust grain surface could have on the desorption characteristics of molecules adsorbed there, and how this desorption is modified in the submonolayer coverage regime compared to the multilayer regime.

This work used TPD to measure the desorption characteristics of O₂, CO and CO₂ from H₂O\(_{\text{np}}\), H₂O\(_{\text{c}}\) and SiO\(_{\text{x}}\) over
submonolayer to multilayer coverages. The experimental data were modelled using the Polanyi–Wigner equation, combining different approaches to reproduce the submonolayer and multilayer TPD traces, in particular by varying $E_{\text{ads}}$ as a function of coverage in the submonolayer regime. The desorption can be categorized as ‘full wetting’, ‘intermediate’ or ‘non-wetting’ behaviour, and the switching point is well described by $N_{\text{mono}}$, an empirical measure of the coverage at which pure monolayer desorption stops. On both a laboratory and an astrophysically relevant time-scale, the desorption characteristics of molecules from the amorphous substrates H$_2$O$_{\text{(np)}}$ and SiO$_2$ were found to be very similar, while on the crystalline surface H$_2$O$_{\text{(c)}}$, molecules desorbed at higher temperatures and on a longer time-scale.

It would be relatively trivial to implement the data presented here into astrochemical models; it would require only a subroutine to describe the submonolayer, coverage-dependent $E_{\text{ads}}$, which can be calculated using the parameters presented in this paper and the coverage $N_{\text{mono}}$, at which the true monolayer desorption ends and beyond which a fixed $E_{\text{ads}}$ and zeroth-order desorption can be implemented.

Previously, Green et al. (2009) concluded that surface type is relatively unimportant and rather it is the heating rate and grain size that dominate desorption kinetics; we do not disagree that both these factors are important, but by not considering the submonolayer case, this previous work overlooks certain intricacies. First, the results presented here suggest that the surface type is the dominant factor controlling desorption under submonolayer coverage conditions. This definition of surface type must include both the surface material and the degree of crystallinity, and not simply the material alone. From the data presented here, it is clear that the desorption characteristics of molecular species from H$_2$O$_{\text{(np)}}$ and SiO$_2$, two amorphous surfaces, are much more similar than those from H$_2$O$_{\text{(np)}}$ and H$_2$O$_{\text{(c)}}$, which are composed of the same underlying material. Secondly, while the size of the grain is critical to desorption characteristics, it is both the surface area and the surface–adsorbate interaction which must be considered. Without including information on whether the surface–adsorbate interaction is wetting or non-wetting, it is not possible to know the coverage at which behaviour switches from submonolayer (to intermediate) to the multilayer regime, i.e. the value of $N_{\text{mono}}$. As it is notoriously difficult to calculate physisorption surface–adsorbate energies theoretically, this is necessarily an empirically determined value, highlighting the importance of experiments such as those presented here.

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