The desorption of H$_2$CO from interstellar grains analogues

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ABSTRACT

Context. Much of the formaldehyde (H$_2$CO) is formed from the hydrogenation of CO on interstellar dust grains, and is released in the gas phase in hot core regions. Radio-astronomical observations in these regions are directly related to its desorption from grains.

Aims. We study experimentally the thermal desorption of H$_2$CO from bare silicate surfaces, from water ice surfaces and from bulk water ice in order to model its desorption from interstellar grains.

Methods. Temperature-programmed desorption experiments, monitored by mass spectrometry, and Fourier transform infrared spectroscopy are performed in the laboratory to determine the thermal desorption energies in: (i.) the multilayer regime where H$_2$CO is bound to other H$_2$CO molecules; (ii.) the submonolayer regime where H$_2$CO is bound on top of a water ice surface; (iii.) the mixed submonolayer regime where H$_2$CO is bound to a silicate surface; and (iv.) the multilayer regime in water ice, where H$_2$CO is embedded within a H$_2$O matrix.

Results. In the submonolayer regime, we find the zeroth-order desorption kinetic parameters $v_0 = 10^{28}$ mol cm$^{-2}$ s$^{-1}$ and $E = 31.0 \pm 0.9$ kJ mol$^{-1}$ for desorption from an olivine surface. The zeroth-order desorption kinetic parameters are $v_0 = 10^{28}$ mol cm$^{-2}$ s$^{-1}$ and $E = 27.1 \pm 0.5$ kJ mol$^{-1}$ for desorption from a water ice surface in the submonolayer regime. In a H$_2$CO:H$_2$O mixture, the desorption is in competition with the H$_2$CO + H$_2$O reaction, which produces polyoxymethylene, the polymer of H$_2$CO. This polymerization reaction prevents the volcano desorption and co-desorption from happening.

Conclusions. H$_2$CO is only desorbed from interstellar ices via a dominant sub-monolayer desorption process ($E = 27.1 \pm 0.5$ kJ mol$^{-1}$). The H$_2$CO which has not desorbed during this sub-monolayer desorption polymerises upon reaction with H$_2$O, and does not desorb as H$_2$CO at higher temperature.

Key words. astrochemistry – molecular processes – ISM: molecules – molecular data

1. Introduction

Formaldehyde (H$_2$CO) is one of the most abundant molecules in the icy mantle covering interstellar grains. Its abundance with respect to water ice varies from 1% to 6% in high- (Keane et al. 2001; Dartois 2005) or low- (Boogert et al. 2008) mass protostars, or hot corinos (Cronin & Pizzarello 1983). These refractory molecules constrain the initial abundances of this water-free chemistry that may lead to precursors of biomolecules.

Comprehensive studies of the desorption of small molecules have been made, enabling the identification of four distinct stages during the process of the desorption of molecules from interstellar grains (Collings et al. 2004, 2003a,b; Burke & Brown 2010; Noble et al. 2012): (a.) the monolayer desorption, that corresponds to the desorption of less than one layer of molecules from a surface; (b.) the multilayer desorption, corresponding to the desorption of several layers of molecules from a surface; (c.) the “molecular volcano” event (Smith et al. 1997), that corresponds to the phase transition between amorphous and crystalline ice, in the course of which molecules of other molecular species are expelled from the water ice; (d.) the co-desorption, corresponding to the dominant water desorption, when the trapped species desorb along with the ice mantle (Collings et al. 2004). Each process has its own desorption energy, and the desorption of interstellar-relevant molecules needs to be modelled taking into account their desorption characteristics,
as determined from laboratory experiments (Viti et al. 2004). According to Collings et al. (2004), molecular species can be ranked into three categories: (i.) water-like species, which co-desorb with water; (ii.) CO-like species, which show a multilayer desorption, a monolayer desorption, a volcano desorption and a co-desorption; and (iii.) intermediate species, which show the volcano desorption, the co-desorption and sometimes the monolayer desorption.

The study of a molecule’s desorption characteristics is coupled with the chemical nature and the structure of the substrate itself. The adsorbate can desorb from either a bare grain surface, composed of amorphous silicate or carbonaceous material (Draine 2003), or from its icy mantle. Ice analogues grown from water vapour deposition onto a surface at 15 K are believed to be microporous (Mayer & Pletzer 1986), as evidenced by the presence of a vibrational band attributed to OH dangling bonds on the pore surfaces at 2.73 microns (3360 cm⁻¹) (Rowland et al. 1991). However, the porosity of the ice mantle on grains in cold molecular interstellar clouds is still a matter of controversy. No dangling bond absorptions have been detected in the infrared spectra of interstellar ices (Keane et al. 2001), which means that the ice is non-porous. Laboratory studies suggest that the porosity of ice mantles could be reduced by cosmic rays impacts (Palumbo 2006; Raut et al. 2008), by UV photon irradiation (Palumbo et al. 2010) or by hydrogen atom bombardment (Accolla et al. 2011), as the grains are constantly processed in the interstellar medium. These laboratory studies suggest that under interstellar conditions, the ice mantle is amorphous and non-porous. Thermally induced segregation can also occur within the ice mantle (Oberg et al. 2009), which can change the energy with which the adsorbate is bound to the substrate.

The aim of this paper is to address how to model the thermal desorption of the formaldehyde molecule H₂CO in a robust and reliable way, complementing the work of Collings et al. (2004), taking into account the complexity of the thermal desorption processes indicated by laboratory data. We study the thermal desorption processes of formaldehyde (H₂CO) from a modeller’s point of view. H₂CO is an interesting benchmark molecule since there is a wealth of radio-observations available in different interstellar environments, and especially in hot cores regions (Wootten et al. 1996). Since H₂CO originates from grain surface chemistry, its observed abundances are directly related to its desorption processes and they offer an indirect way to test H₂CO grain chemistry. The desorption processes can be thermal or non thermal, such as the photodesorption process which has recently been demonstrated in the Horsehead photon-dominated region (Guzmán et al. 2011). The Raman spectral characteristics of H₂CO hydrates (H₂CO within cages of clathrates) in ASW have been previously studied by Chazallon et al. (2008). This study establishes the link between the adsorbate and the substrate, as well as the formation of two crystalline H₂CO-H₂O hydrate phases and the desorption of H₂CO during the crystallisation of ice.

We study the H₂CO thermal desorption processes in different experimental environments: (i.) the multilayer regime, where H₂CO is bound to other H₂CO molecules; (ii.) the submonolayer regime where H₂CO is bound to a water ice surface; (iii.) the submonolayer regime where H₂CO is bound to a silicate surface; and (iv.) the mixed multilayer regime in water ice where H₂CO is embedded within a H₂O matrix. For each environment, we qualitatively observe the relative proportions of H₂CO desorbing via the different desorption processes, and we discuss how, based upon such experimental data, it is possible to retrieve desorption parameters – such as desorption energies and desorption rate pre-exponential factors – that can be easily integrated into existing gas-grain models. The last environment; (iv.), demonstrates the competition between the desorption process and the reaction of H₂CO in the presence of H₂O. At a slow temperature ramp, as exhibited in the interstellar medium, the reaction H₂CO+H₂O is dominant and all the H₂CO is transformed into polyoxymethylene (POM or polyformaldehyde), the polymer of H₂CO, which is more refractory than H₂O. Polyoxymethylene could provide an extended source of H₂CO at the higher temperature observed in comets, and a H₂CO reservoir for prebiotic chemistry (Milam et al. 2006).

2. Experiments

The desorption experiments of H₂CO in a multilayer regime (Sect. 3.1), and of H₂CO mixed with H₂O (Sect. 3.3), were performed in Marseille on the RING experimental set-up (Theule et al. 2011). Briefly, a gold plated copper surface is maintained at low temperature using a closed-cycle helium cryostat (ARS Cryo, model DE-204 SB, 4 K cryogenator) within a high-vacuum chamber at a few 10⁻⁹ mbar. H₂O is outgassed into a vacuum line using standard manometric techniques. H₂CO is obtained by gently warming paraformaldehyde. Molecular solids samples are formed by spraying the room-temperature gas onto the gold surface. Porous, amorphous ice analogues are grown by depositing water vapour onto the gold surface held at 15 K. Amorphous, non-porous (or compact) ice analogues are grown by depositing water vapour onto the surface between 90 K and 130 K. Such a compact ASW ice has no or little porosity, which prevents the trapping of molecules in pores.

The infrared spectra are recorded by means of Fourier-transform reflection absorption infrared Spectroscopy (FT-RAIRS) using a Vertex 70 spectrometer with either a DTGS detector or a liquid N₂ cooled MCT detector. A typical spectrum has a 1 cm⁻¹ resolution and is averaged over a few hundred interferograms. The sample temperature is measured with a DTGS 670 Silicon diode with a 0.1 K uncertainty. The temperature is controlled using a Lakeshore Model 336 temperature controller and a heating resistance. A Hiden HAL VII RGA quadrupole mass spectrometer (QMS) measures desorbing gas-phase species. In a typical temperature-programmed desorption experiment (TPD), the mass spectra are recorded with the QMS as the products are being desorbed from the surface, heated by a 4 K/min temperature ramp. The concentration ratio of the deposited molecular solids is derived from their IR spectra right after deposition. For each molecule, the characteristic bands are integrated, and then divided by their corresponding band strengths to estimate their column densities (molecules cm⁻²). For H₂O, we use the values of 3.1×10⁻¹⁷ cm molecule⁻¹ for the band strength of the libration mode at 760 cm⁻¹ and 1.2×10⁻¹⁷ cm molecule⁻¹ for the band strength of the OH bending mode at 1670 cm⁻¹ (Gerakines et al. 1995). For H₂CO we use the CO stretching mode band at 1721 cm⁻¹, which has a band strength of 9.6×10⁻¹⁸ cm molecule⁻¹ (Schutte et al. 1996). A 30% uncertainty on the band strengths, and therefore on calculated column densities, is probably conservative enough.

The H₂CO desorption experiments in the sub-monolayer regime (Sect. 3.2) were performed in Cergy-Pontoise using the FORMOLISM experimental set-up (Amaud et al. 2006). Briefly, the apparatus consists of an ultra-high vacuum stainless steel chamber, with base pressure in the low 10⁻¹⁰ mbar range, containing an amorphous silicate-coated gold surface (5–400 K)
3. Results

3.1. Desorption of pure H$_2$CO in the multilayer regime

These experiments were performed on the RING experimental set-up. Pure H$_2$CO is deposited at 15 K on the gold surface to obtain a multilayer sample of H$_2$CO. Using the column density derived from the IR band at 1721 cm$^{-1}$, we can estimate that the sample thickness is approximately 50 monolayers. The solid H$_2$CO sample is submitted to a 4 K/min temperature ramp. The TPD curve of H$_2$CO given by the QMS signal exhibits a zeroth-order thermal desorption pattern, characteristic of bulk desorption. The temperature is measured with a calibrated silicon diode clamped on the sample holder and controlled by computer to ±0.2 K with an accuracy of ±1 K in the 8–400 K range.

Reactants are introduced into the vacuum chamber via two separate triply differentially pumped beam lines aimed at the cold surface. The first beam line is used to deposit CO with a flux that was previously calibrated using temperature-programmed desorption by determining the CO exposure time required to saturate the CO monolayer on compact ice (Kimmel et al. 2001). The second beam line is used to introduce H atoms. Desorption of molecules from the surface is monitored using a quadrupole mass spectrometer positioned directly in front of the surface.

The measured QMS signal is proportional to the instantaneous desorption rate; the coefficient of proportionality is related to both the collection efficiency and the ionisation yield of the QMS spectrometer. The desorption rate $\varphi$ is normalised to a one monolayer coverage ($10^{15}$ molec cm$^{-2}$) and to a 1 cm$^2$ surface by dividing by the integral of the QMS curve and multiplying by $10^{15}$ molec cm$^{-2}$ × 1 cm$^2$. We fit the rising edge of the normalised desorption rate $\varphi$ curve with a zeroth-order Polanyi-Wigner equation, as a function of temperature $T$ (Redhead 1962; Carter 1962):

$$\varphi(T) = \frac{dN}{dT} = \frac{v_0}{\beta} \exp \left( -\frac{E}{R \times T} \right),$$

where $N$ is the surface coverage (molecules cm$^{-2}$), $v_0$ is the zeroth-order pre-exponential factor of the rate constant, $E$ is the desorption energy, $R$ is the ideal gas constant, and $\beta$ the temperature ramp rate ($\beta = 1/15$ K s$^{-1}$ in our case). Since $v_0$ and $E$ are correlated, we can obtain a non physically relevant $E$ by adjusting both $v_0$ and $E$ on the TPD curve. Instead, we choose to fix $v_0$ to a physically relevant value, in order to compare the desorption energies of different molecules. So we fix $v_0$ to $10^{28}$ molec cm$^{-2}$ s$^{-1}$ using a typical $10^{15}$ molec cm$^{-2}$ surface density of sites and a typical $10^{13}$ s$^{-1}$ adsorbate-surface oscillation frequency. Both values can change by a factor of a few, according to the nature of the adsorbed molecule and of the surface. The surface coverage is related to the average distance between two adsorption sites, and the oscillation frequency to the nature of the interaction between the surface and the adsorbate. The uncertainty in $v_0$ is directly correlated to the derived value of $E$.

Fitting the rising edge of the TPD curve with only $E$ as a free parameter and fixing $v_0 = 10^{28} \pm 0$ molec cm$^{-2}$ s$^{-1}$, we obtain $E = 31.3 \pm 0.5$ kJ mol$^{-1}$ for the multilayer desorption of pure H$_2$CO. The ±0.5 kJ mol$^{-1}$ uncertainty on $E$ is the dispersion of $E$ from different TPD experiments. The uncertainty on the fit itself or on choosing different portion of the rising edge of the TPD curve gives an approximate 0.03 kJ mol$^{-1}$ uncertainty on $E$. With both $v_0$ and $E$ as free parameters, we obtain $v_0 = (2.3 \pm 0.1) \times 10^{27}$ molec cm$^{-2}$ s$^{-1}$ and $E = 30.0 \pm 0.4$ kJ mol$^{-1}$.

Varying the oscillation frequency from 10$^{12}$ s$^{-1}$ to 10$^{14}$ s$^{-1}$ gives a ±2 kJ mol$^{-1}$ spread on $E$. So we choose to use the coupled solution $v_0 = 10^{28} \pm 0$ molec cm$^{-2}$ s$^{-1}$, $E = 31.3 \pm 0.5$ kJ mol$^{-1}$ to express the zeroth-order desorption rate of multilayer H$_2$CO.

The value of the pre-exponential factor is an important parameter to take desorption into account. Its value must be specified alongside the desorption energy in astrochemical models, and not arbitrarily fixed or independently calculated, only taking the experimentally measured desorption energy as input.

3.2. Desorption of H$_2$CO in the sub-monolayer regime

The submonolayer experiments were performed on the FORMOLISM set-up. Temperature programmed desorption experiments are performed with H$_2$CO in the sub-monolayer regime, i.e. H$_2$CO ≤ 10$^{15}$ mol cm$^{-2}$. H$_2$CO is produced by the hydrogenation of one layer of $^{13}$CO deposited on top of either a compact amorphous ice or a silicate surface. In both cases, two experiments are performed, bombarding the $^{13}$CO surface with H atoms for 30 min and 45 min respectively, which corresponds to a fluence of 1.8 × 10$^{16}$ and 2.4 × 10$^{16}$ H atoms cm$^{-2}$ respectively. In our conditions, TPD spectra show that CH$_3$OH is formed at a level less than 1% (Fuchs et al. 2009; Watanabe & Kouchi 2002). Then, the remaining $^{13}$CO and the H$_2$CO irradiation product are submitted to a 0.04 K s$^{-1}$ temperature ramp and they desorb. Figure 2 shows the m/z 31 TPD curve for the desorption of the H$_2$CO sub-monolayer on a compact amorphous ice surface and of a silicate surface.

3.2.1. Desorption of H$_2$CO in the sub-monolayer regime on an ASW surface

H$_2$CO desorption in the sub-monolayer regime on a compact non-porous amorphous ice surface (deposited at 110 K and cooled down to 10 K) can be fitted by first-order desorption kinetics, which is typical of sub-monolayer desorption. The
instantaneous desorption rate $\varphi(T)$ as a function of temperature $T$ for first-order kinetics is given by (Redhead 1962):

$$\varphi(T) = \frac{\mathrm{d}N}{\mathrm{d}T} = \frac{v_1}{\beta} \times N \times \exp\left(\frac{-E}{R \times T}\right),$$  

(2)

where $N$ is the surface coverage (molecules cm$^{-2}$), $v_1$ is the first-order pre-exponential factor of the rate constant, $E$ is the desorption energy, and $R$ is the ideal gas constant.

At temperature $T_p$, the desorption rate $\varphi(T)$ is at its maximum, and Eq. (2) can be derived:

$$\frac{E}{R \times T_p^2} = \frac{v_1}{\beta} \times \exp\left(\frac{-E}{R \times T_p}\right).$$  

(3)

We fit the experimental TPD curves in three different ways. The different uncertainties are determined from the spread by taking m/z 30 and m/z 31 for the two different experiments, with 30 min and 45 min H bombardment respectively.

First, following Redhead (1962), we can obtain from Eq. (2) the equation describing the shape of the first-order desorption rate curve:

$$\ln\left(\frac{N_p}{N}\right) = \frac{E}{R \times T_p} \left(\frac{1}{T} - \frac{1}{T_p}\right) + \left(\frac{T}{T_p}\right)^2 \exp\left(\frac{-E}{R \times T_p}\right) - 1,$$  

(4)

where $N_p$ is the surface coverage at the temperature where the desorption rate is at its maximum ($T_p$).

The experimental TPD curves are fitted with Eq. (4), which gives $T_p$ and the desorption energy $E = 15.0 \pm/\pm 1.5$ kJ mol$^{-1}$. With these values for $T_p$ and $E$, Eq. (3) gives $v_1 = 2 \times 10^{5} \pm/\pm 1$ s$^{-1}$. Once again, the correlation between $E$ and $v_1$ prevents us from deriving accurate values for these two parameters.

An alternative method is to fix $v_1 = 10^{13}$ s$^{-1}$ and to take the maximum desorption rate temperature $T_p$ determined from the fit of the TPD curve with Eq. (4). This determination of $T_p$ is slightly more accurate than simply taking the maximum of the TPD curve. We then solve Eq. (3) with these values for $v_1$ and $T_p$ to find $E = 25.0 \pm/\pm 0.1$ kJ mol$^{-1}$, $v_1 = 10^{13}$ s$^{-1}$ and $E = 25.0 \pm/\pm 0.1$ kJ mol$^{-1}$ are physically more realistic values (lying between the values of 14.5 kJ mol$^{-1}$ for CO (Burke & Brown 2010) and 46.6 kJ mol$^{-1}$ for H$_2$O (Fraser et al. 2001)), and the pair of parameters well reproduces the overall desorption rate.

Finally, we can also fit the TPD curve using a zeroth-order Polanyi-Wigner equation, as expressed in Eq. (1), fixing $v_0 = 10^{13}$ s$^{-1} \times 10^{16}$ mol cm$^{-2}$ = 10$^{25}$ mol cm$^{-2}$ s$^{-1}$. We find $E = 27.1 \pm/\pm 0.5$ kJ mol$^{-1}$. So, we see that the values of the desorption energies derived upon assuming zeroth- or first-order desorption kinetics differ by approximately 4%. However, using Eq. (1) or Eq. (2), with either $v_0 = 10^{28}$ mol cm$^{-2}$ s$^{-1}$ or $v_1 = 2 \times 10^{5} \pm/\pm 1$ s$^{-1}$, makes a significant difference when applied within gas-grain models. Thus, it is important to take the correct couple of solution ($\nu$, $E$) when inputting experimental data in models.

3.2.2. Desorption of a H$_2$CO in the sub-monolayer regime on a silicate surface

We follow the same procedures to extract the desorption parameters from the TPD curves of the H$_2$CO desorption in the sub-monolayer regime on a silicate surface. Silicate surfaces are representative of grain bare surfaces during the transition from diffuse to molecular clouds. We find $v_1 = 10^{13} \pm/\pm 0.5$ kJ mol$^{-1}$ and $E = 29.2 \pm/\pm 0.9$ kJ mol$^{-1}$ assuming first-order desorption kinetics and $v_0 = 10^{28}$ mol cm$^{-2}$ s$^{-1}$, and $E = 31.0 \pm/\pm 0.9$ kJ mol$^{-1}$ assuming zeroth-order desorption kinetics. As for the ASW surface, on the silicate surface, the derived desorption energies differ by only few percent. As expected, H$_2$CO is more tightly bound on a silicate surface than on a water ice surface.

3.3. Interaction of H$_2$CO with ASW

We now want to further investigate how a water ice environment affects the desorption of a simple hydrogen-bound molecule such as H$_2$CO. To do this we perform three types of experiments. In the first type, several layers of H$_2$CO are deposited on top of a thick water ice film to investigate how the ASW substrate affects the H$_2$CO multilayer desorption seen in Sect. 3.1. In the second, several layers of H$_2$O are deposited on top of a solid H$_2$CO film. In the third, H$_2$CO is mixed in the gas phase with H$_2$O and deposited as an homogeneous film. This latter scenario is probably the closest to the interstellar ice morphology, if one assumes that CO is hydrogenated into H$_2$CO during the mantle build-up, which is therefore homogeneously mixed with H$_2$O in the inner polar component of the interstellar ice.

Figure 3 shows the IR spectra of the three types of H$_2$CO ice mixtures immediately after deposition at 15 K. We can see from this spectrum that, upon deposition, the $\nu_{CO}$ band of H$_2$CO is located at 1720 cm$^{-1}$, which is characteristic of a solid-state H$_2$CO:H$_2$O mixture (Schutte et al. 1993). For each mixture, the H$_2$CO:H$_2$O concentration ratio is obtained from the integration of their IR absorption bands as described in Sect. 2. The H$_2$CO:H$_2$O ice mixtures are deposited either on a 15 K or a 90 K gold surface to obtain either a porous or a non-porous compact ice, in order to understand how the ice morphology may affect our results. The H$_2$CO:H$_2$O ice mixture TPD curves exhibit several desorption features that we label M (multilayer desorption from the surface of water ice), V (volcano) and C (co-desorption with H$_2$O) following the designation in Collings et al. (2004).

3.3.1. Desorption of H$_2$CO on top of ASW

We deposit a film of H$_2$CO on top of a porous ASW film at 15 K with an abundance ratio of 1/14 between the H$_2$CO/H$_2$O layers. The ASW film is deposited first, and then the H$_2$CO film is deposited at the same temperature on top of it. A temperature-programmed desorption experiment is performed on the H$_2$CO/H$_2$O layered system, which exhibits M and V desorption features, as seen in Fig. 4.
tributed to dangling OH, integration of its characteristic IR bands. Mixture
concentration ratio of each species in the mixture is determined from the
where H₂CO is on top of H₂O, mixture
is porous.

tio). Two features, labelled M and C on the TPD curve, correspond to
respectively. The weak C feature corresponds to the co-desorption
corresponds to the physisorption of H₂CO to surrounding

As expected, the M feature corresponds to the multi-
layer regime desorption, as described in Sect. 3.1, of the
H₂CO bounded to other H₂CO molecules by van der Waals in-
teractions. The weak C feature corresponds to the co-desorption of
H₂CO molecules trapped within the H₂O network. This corresponds to the physisorption of H₂CO to surrounding
H₂O molecules, and to a trapping of H₂CO molecules in
the form of hydrates (Chazallon et al. 2008). The presence of
H₂CO molecules trapped within the ice indicates that the
H₂CO molecules have penetrated from the surface into the first
monolayers of ASW. This is evidence that H₂CO can diffuse
downwards in ASW and that an appreciable quantity of it can
be trapped within the ice as hydrates, which co-desorb with the
bulk of the ice mantle. This co-desorption phenomenon is dif-
ferent to the desorption of adsorbed H₂CO on an ASW surface
as studied in Sect. 3.2.1, and has a desorption energy similar to
that of H₂O, which has a 48 kJ mol⁻¹ desorption energy (Fraser
et al. 2001) and is expected to desorb in this temperature range,
as shown in Fig. 5d.

3.3.2. H₂CO below ASW
To illustrate the diffusion of H₂CO within ASW, and its rela-
tionship with desorption, we deposit an ASW film on top of a
H₂CO film in order to form a H₂O/H₂CO layered system
where H₂CO has to diffuse to reach the surface and desorb. First
the H₂CO film is deposited at 15 K, and then H₂O is deposited at
the same temperature on top of the H₂CO film. The TPD curves
of three layered systems with different H₂O/H₂CO abundance
ratios are displayed in Fig. 5.

During the TPD experiments, H₂CO must diffuse through
the bulk of ASW in order to reach the ASW surface, and then
to desorb to be detected by the QMS. When the ASW film is
thin, as in layered system (a), the TPD curve is similar to the
pure formaldehyde desorption TPD curve (Fig. 1). No V and
C features are observed for H₂CO under a thin ASW film. As
the ASW film thickness increases, the monolayer desorption M fea-
ture broadens and shifts to higher temperature, as seen in Fig. 5
for layered systems (b) and (c). The broadening of the M feature
is due to the time delay necessary for the H₂CO molecules to dif-
fuse in the ASW film, and this delay increases with ASW thick-
ness. The V feature is visible in layered systems (b) and (c), but
not in layered system (a). As expected, the thicker the ASW film,
the more H₂CO is trapped. The C feature is visible for the thick-
est ASW film, layered system (c). These three experiments il-
ustrate that the diffusion of H₂CO through an ASW film, firstly,
slowly down the desorption and, secondly, allows the trapping of
H₂CO molecules within the ASW ice; the thicker the ice film, the
more pronounced the slowing and trapping effects. We can ob-
serve that in a TPD experiment, the trapping within closed pores
during pore collapse (the V feature, Smith et al. 1997), occurs at
a lower dilution than the trapping by the formation of hydrates
(the C feature), as seen by comparison of the (b) and (c) layered
systems. The molecular volcano desorption and co-desorption
must be taken into account in gas-grain models, as done in Viti
et al. (2004), although it is difficult to account quantitatively of
the relative proportion of each desorption process. Interstellar
grains are thinner than our laboratory ice analogues, and H₂CO
is formed from homogeneously mixed CO, so we need to study
more realistic ice analogues.

3.3.3. Diffusion and reactivity of H₂CO within ASW
To better understand the relationship between H₂CO and H₂O
in an ice analogue closer to an interstellar ice, we performed
experiments on thinner, homogeneously mixed, and diluted
H₂CO:H₂O ice mixtures, with a typically 1–2% concentration
During the interruption period at 135 K in experiment (b), infrared spectra were taken at 30 min intervals. Study of the evolution of the IR spectra with time at the fixed 135 K temperature shows that, during the interruption, the H$_2$CO CO stretching mode absorption band at 1735 cm$^{-1}$ disappears, while several IR bands appear in the spectra. Figure 7, left panel, shows the time evolution of the difference spectra of the 1735 cm$^{-1}$ H$_2$CO CO stretching mode absorption over 15 h. On the right panel, the area under the $\nu$$_{CO}$ H$_2$CO absorption band has been plotted as a function of time held at 135 K. It is evident from this figure that the abundance of H$_2$CO in the ice mixture has decreased during the time that the surface is held at 135 K. After 15 h at 135 K, it has not fully disappeared 100%. It is interesting to note that the $\nu$$_{CO}$ band can be deconvolved into two separate components: a small component at 1720 cm$^{-1}$ corresponding to H$_2$CO in ASW and a dominant component at 1735 cm$^{-1}$. The position of the $\nu$$_{CO}$ band at 1735 cm$^{-1}$ indicates the presence of H$_2$CO hydrates (Chazallon et al. 2008). This confirms that, when in ASW, H$_2$CO molecules are trapped in clathrates.

The bands which appear in the infrared spectrum of the H$_2$CO:H$_2$O mixture during the interruption can be assigned to polyoxymethylene (POM) (Schutte et al. 1993). Figure 8 compares the IR spectra of the interrupted experiment at 215 K, when all the H$_2$CO has desorbed via the desorption regimes detailed above, with a reference spectrum for the POM. The reference spectrum was obtained from a H$_2$CO:H$_2$O:NH$_3$ ice mixture (an excess of H$_2$CO with respect to NH$_3$ in a H$_2$O dominant ice) following the methodology of Schutte et al. (1993). The agreement between the two spectra shows that we have formed POM. Compared to the POM reference spectrum (Fig. 8d), an excess in the OH band, between 3300 and 3500 cm$^{-1}$, is evident in our experimental spectrum at 215 K (Fig. 8c). This excess indicates the production of short CH$_2$-O$_n$ chains, which results in an enhanced proportion of OH to CH groups located in the polymer chains.

This IR study shows that the H$_2$CO trapped in the ASW ice has polymerised to form short chain polymers of the type -CH$_2$-O$_n$-, called polyoxymethylene. Because we are working in a dilute H$_2$CO:H$_2$O ice mixture, with 1–2% H$_2$CO, this means that H$_2$CO monomers have diffused within the ASW ice, become trapped, and then concatenated to form POM. Such a polymerisation reaction is not observed in a pure H$_2$CO solid. This confirms experiments carried out in Sect. 3.3.2 on the ability of H$_2$CO to diffuse within ASW. However, one may imagine that, as in the experiments in Sect. 3.3.2, H$_2$CO would diffuse, reach the surface, and then desorb, rather than becoming trapped and polymerising. To evaluate the proportion of initial

Fig. 6. TPD spectra (m/z = 30) for the H$_2$CO:H$_2$O mixtures, a) 1:14 deposited at 15 K, heated at 2 K min$^{-1}$ 90–210 K, b) 1:8 deposited at 15 K, heated at 2 K min$^{-1}$ 90–135 K, held at 135 K for 14.5 h, heated at 2 K min$^{-1}$ 135–210 K, c) 1:6 deposited at 90 K, heated at 2 K min$^{-1}$ 90–210 K, d) 1:9 deposited at 90 K, heated at 2 K min$^{-1}$ 90–135 K, held at 135 K for 18 h, heated at 2 K min$^{-1}$ 135–210 K. The arrows indicate that an isothermal break of several hours was made in the TPD experiment. M, V, and C correspond to the multilayer, the volcano and co-desorption desorptions, respectively. The asterisk indicates a double peaked structure, observed as a result of desorption of H$_2$CO from the radiation shield.

Fig. 7. Left hand panel: difference spectra of the H$_2$CO stretching mode absorption at 1735 cm$^{-1}$ while the surface is held at 135 K. These data correspond to trace b in Fig. 6. Black corresponds to time =0, light grey corresponds to time =14.5 h. Right hand panel: these data are the calculated area under the peak for the same absorption band, plotted as a function of time held at 135 K.
H$_2$CO that reacts and the proportion of H$_2$CO that escapes in the gas phase, we compare the kinetics of the reaction of H$_2$CO and production of POM in Fig. 9. As H$_2$CO is highly diluted into ASW, we can fit these curves with first-order reaction kinetics, and we obtain approximately $3.5 \times 10^{17}$ molecules of H$_2$CO (initial concentration) and $4 \times 10^{17}$ molecules of POM (final concentration), taking the band strength from Schutte et al. (1993). Therefore, we can conclude that the initial H$_2$CO present in the ice mixture mainly reacts to form the POM, and that little, if any, H$_2$CO escapes in the gas phase. Furthermore, the QMS signal measured during the isothermal period of experiments (b) and (d) does not indicate any H$_2$CO desorption, which confirms, within the observational limits of our experiments, that most of H$_2$CO reacts and does not desorb. POM is refractory, since it desorbs around 280 K in our experimental conditions. The solid-state H$_2$CO reactivity must be taken into account into gas-grain models as it lowers gas-phase quantity calculated in present models.

4. Discussion

We have illustrated in this work how the desorption of H$_2$CO is intrinsically linked to the ASW ice substrate. Figure 10 summarises the different desorption experiments performed on H$_2$CO. In the multilayer regime, bulk H$_2$CO ice desorbs following zeroth-order kinetics, which can be modelled using a Polanyi-Wigner equation with the parameters $v_0 = 10^{27} \pm 0$ molec cm$^{-2}$ s$^{-1}$ and $E = 31.3 \pm 0.5$ kJ mol$^{-1}$. In the submonolayer regime, H$_2$CO desorbs following first-order desorption kinetics. It is however simpler, and as accurate, to model this desorption as a zeroth-order desorption, employing the Polanyi-Wigner equation with the parameters $v_0 = 10^{27}$ molec cm$^{-2}$ s$^{-1}$ and $E = 27.1 \pm 0.5$ kJ mol$^{-1}$ for the desorption from an ASW surface and with the parameters $v_0 = 10^{28}$ molec cm$^{-2}$ s$^{-1}$ and $E = 31.0 \pm 0.5$ kJ mol$^{-1}$ for a silicate surface. These parameters have been obtained by fixing the pre-exponential factor, $v_0$, as the physically relevant value of $10^{15}$ molec cm$^{-2}$ s$^{-1}$ for the desorption energy as a single parameter instead of invoking the coupled parameters, pre-exponential factor and desorption energy. Using this simple scale it is easy to determine whether one type of molecule desorbs faster or slower than another, and especially to compare its desorption with that of H$_2$O, i.e. to determine whether a molecule is volatile or refractory. Implementing this comparison using the values we derived in this work, we see that a H$_2$CO molecule which is bound by van der Waals interactions to other H$_2$CO molecules desorbs in the multilayer regime with an energy (31.3 ± 0.5 kJ mol$^{-1}$) greater than the desorption energy (27.1 ± 0.5 kJ mol$^{-1}$) of H$_2$CO bound by hydrogen bonds to H$_2$O molecules on an ASW surface. The 31.0 ± 0.9 kJ/mol value for H$_2$CO for a silicate surface is close to the H$_2$CO on H$_2$CO value. This tells us that, either the H$_2$CO monomers aggregate to form clusters whose desorption value is close to that in the multilayer regime, or that silicate-H$_2$CO van der Waals interactions are similar in energy to H$_2$CO-H$_2$CO interactions, or that H$_2$CO is hydrogen bounded to a SiOH silanol group if the silicate surface is hydrated. Due to the low hydrogenation yield of H$_2$CO produced from CO, the latter explanation is probably more plausible.
The H$_2$CO desorption influenced by interaction with the ASW network is the most interesting from an astrochemical perspective, as this environment is the closest to real interstellar ice. It is also a case to study illustrating how conducting standard laboratory experiments can result in false conclusions being drawn. A standard TPD experiment of a H$_2$CO:H$_2$O mixture (of the type performed in Sect. 3.3.3, experiments (a) and (c)) may lead us to conclude that H$_2$CO has a multilayer regime desorption, similar to that of pure H$_2$CO desorption, and that, like many other molecules (CO$_2$, NH$_3$, ...), a fraction of the H$_2$CO is trapped within the closed pore network of ASW. It is eventually released both during the volcano desorption (i.e. the pore collapse associated with the phase transition from amorphous ice to crystalline ice) and the co-desorption (when the H$_2$O mantle desorbs), as seen in traces (a) and (c) of Fig. 6. However, interrupting the TPD experiments at a temperature between the monolayer desorption and the volcano desorption allows the simulation of the extremely slow heating rates encountered in star formation regions (Viti & Williams 1999). Curves (b) and (d) of Fig. 6 lead to a totally different conclusion. Indeed, H$_2$CO molecules are trapped in the ice – either within pores or as hydrates (Chazzillon et al. 2008) – and can diffuse and react with themselves in a H$_2$O environment (which both initiates the polymerisation reaction and lowers the reaction barrier) to form the POM polymer. In our experimental conditions, the polymerisation reaction is faster than diffusion to the surface and thus dominates the H$_2$CO chemistry before H$_2$O desorption, as well as preventing volcano desorption or co-desorption. Moreover, diffusion within the ice and trapping within the pores offer an efficient way to concentrate diluted molecules, enhancing the possibility of a rich ice chemistry. Furthermore, POM is acting as a reservoir of H$_2$CO, which could then be released at higher temperature in the interstellar medium, i.e. at temperatures where neither H$_2$CO nor H$_2$O would be expected to be present in the solid-phase. Other competitive reactions with low-reaction barriers, such as the reaction H$_2$CO + NH$_3$ that forms aminomethanol NH$_2$CH$_2$OH (Bossa et al. 2009), or the reaction H$_2$CO + NH$_3$ that forms hydroxycetonitril HOCH$_2$CN (Danger et al., in prep.), can also occur, preventing the desorption of H$_2$CO.

Crucially, this work illustrates the importance of taking the diffusion process into account. There are three competitive processes: the diffusion of the H$_2$CO molecule – which probably leads to the formation of hydrates – within the ASW mantle; the desorption of the H$_2$CO molecule from the top layer of ASW (the surface); and the reactivity between H$_2$CO monomers. Diffusion is needed both because molecules need to reach the surface in order to desorb and because molecules need to meet for a reaction to occur. Which of the three processes is dominant depends on the interstellar grain morphology and initial abundances. In the extreme case where the grain has a radius much greater than the thickness of the ASW mantle and there is a very low initial abundance of H$_2$CO with respect to H$_2$O, the number of steps required to reach the surface in the radial direction is much smaller than the number of steps required to diffuse in the circular direction and encounter diluted potential reactants. So most of the molecules will diffuse towards the surface to desorb. At the opposite extreme, where the grain radius is small and the ice is very thick, circular diffusion will favour reactivity, which will dominate over radial diffusion and desorption processes. H$_2$CO is present in interstellar ices at abundances on the order of a few percent with respect to water, and the ice mantle has a typical thickness of few tens of monolayers, so radial diffusion, which is related to desorption, and circular diffusion, which is related to reactivity, are likely to be around the same order of magnitude. Within this grain-mantle system, we see that diffusion is central to correctly modelling both desorption and reactivity, as well as their competition. However, very few data exist on the diffusion of simple molecules in ice at low temperature (Livingston et al. 2002), so diffusion is currently a major issue for modelling desorption on interstellar grains.

The interstellar grain shape adopted in models is also of importance. A central conclusion drawn from this study is that there is no easy answer to the question of how to correctly model the desorption of H$_2$CO from ice mantles. If using a multilayer grain chemistry model, one can consider that the value of $E = 27.1 \pm 0.5$ kJ/mol for the H$_2$CO desorption from an ASW surface should be adopted. If using a simpler model, which does not take into account the actual multilayer nature of the mantle, the diffusion between the different layers towards the surface must be accounted for. We could measure the desorption energy as a function of the ice thickness and select the energy corresponding to an average ice mantle thickness. This effective desorption energy that encompasses the diffusion can be directly implemented in such a simple model. We hypothesise that this effective value should be close to 31 kJ mol$^{-1}$ as shown in Fig. 5 where we can see that the diffusion process retards the desorption of H$_2$CO. It is evident that the coupling between diffusion and desorption must be better understood. We have illustrated the extent to which studying diffusion within ASW is a necessary step towards that goal.

5. Conclusion

In this work we studied the desorption of H$_2$CO from different surfaces and demonstrated how its desorption is intrinsically linked to ASW in interstellar ices through trapping and reactivity. In the multilayer regime, bulk H$_2$CO ice desorbs following zeroth-order kinetics, which can be modelled using a Polanyi-Wigner equation with the parameters $v_0 = 10^{28} \pm 0$ molec cm$^{-2}$ s$^{-1}$ (fixed), $E = 31.3 \pm 0.5$ kJ mol$^{-1}$. In the submonolayer regime, H$_2$CO desorbs following first-order desorption kinetics. It is however simpler, and as accurate, to model this desorption as a zeroth-order desorption, employing the Polanyi-Wigner equation with the parameters $v_0 = 10^{28}$ molec cm$^{-2}$ s$^{-1}$ and $E = 27.1 \pm 0.5$ kJ/mol for the desorption from an ASW surface and with the parameters $v_0 = 10^{28}$ molec cm$^{-2}$ s$^{-1}$ (fixed) and $E = 31.0 \pm 0.9$ kJ/mol for a silicate surface.

The interaction of H$_2$CO with the ASW mantle is complex, as the desorption of H$_2$CO is linked with its diffusion in ASW, with its trapping inside the closed pore network of ASW (volcano desorption) and as hydrates (co-desorption with H$_2$O), and with the reactivity of H$_2$CO with H$_2$O. For slow temperature increases, as encountered in the interstellar medium, the reaction of H$_2$CO with H$_2$O is faster than its desorption, resulting in the production of the polymer polyoxymethylen. This study also highlights the importance of the diffusion process as it delays desorption and enables trapped molecules to encounter other molecules in the ice, increasing the probability of reactions occurring. Diffusion studies of small molecules within ASW must be undertaken in order to quantitatively account for the relationship between diffusion and desorption, and diffusion and reactivity.

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