Desorption of N₂, CO, CH₄, and CO₂ from interstellar carbonaceous dust analogues

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ABSTRACT

The interaction of volatile species with carbonaceous interstellar dust analogues is of relevance in the chemistry and physics of dense clouds in the interstellar medium. Two deposits of hydrogenated amorphous carbon (HAC), with different morphologies and aromatic versus aliphatic ratio in their structure, have been grown to model interstellar dust. The interaction of N₂, CO, CH₄, and CO₂ with these two surfaces has been investigated using thermal programmed desorption (TPD). Desorption energy distributions were obtained by analysing TPD spectra for one monolayer coverage with the Polanyi–Wigner equation. The desorption energies found in this work for N₂, CO, and CH₄ are larger by 10–20 per cent than those reported in the literature for siliceous or amorphous solid water surfaces. Moreover, the experiments suggest that the interaction of the volatiles with the aromatic substructure of HAC is stronger than that with the aliphatic part. Desorption of CO₂ from the HAC surfaces follows zero-order kinetics, reflecting the predominance of CO₂–CO₂ interactions. A model simulation of the heating of cold cloud cores shows that the volatiles considered in this work would desorb sequentially from carbonaceous dust surfaces with desorption times ranging from hundreds to tens of thousands of years, depending on the molecule and on the mass of the core.

Key words: astrochemistry – molecular data – methods: laboratory: molecular – methods: laboratory: solid state – ISM: evolution – ISM: molecules.

1 INTRODUCTION

The adsorption of molecules on the surface of dust grains is crucial for the physics and chemistry of interstellar (IS) clouds. Binding, diffusion, and reaction of these molecules are determinant for the chemical inventory in many astronomical environments, including comets, trans-neptunian objects, and icy moons in the Solar system (Van Dishoeck 2014). IS dust is formed in the envelopes of asymptotic giant branch stars and in supernova explosions. It consists mostly of silicates and carbonaceous materials with a small amount of metal oxides, carbides, and sulphides. It is estimated that nearly 100 per cent of Si, Fe, and Mg, 30 per cent of O, and 50–60 per cent of C in the diffuse interstellar medium (ISM) may be locked in the grains (Nieva & Przybilla 2012; Williams & Ceccci-Pestellini 2016). In the cold interior of dense cores, atoms and molecules freeze out on grain surfaces, forming ice mantels (Öberg et al. 2011; Boogert, Gerakines & Whittet 2015). Infrared (IR) observations show that in these ice layers, H₂O is always the predominant molecule, followed by CO and CO₂. Methanol, NH₃, and CH₄ are also found in appreciable amounts. N₂ and O₂ are also expected to be in the ices of the coldest cores, but their pure

forms are not easily detectable with IR spectroscopy, although some weak feature could be detectable in ice mixtures or surfaces, due to symmetry breaking. Heating of the grains in the course of the cloud collapse that leads to star formation activates both chemistry and desorption, which in turn determine the gas-phase composition of hot cores (Viti & Williams 1999; Viti et al. 2004; Aikawa et al. 2008; Garrod & Widicus Weaver 2013; Theulé et al. 2013). In the outer regions of a forming star, volatile species can be retained on the grains and then incorporated to larger bodies like asteroids, comets, planets, and moons (Cruikshank 2005; Brown 2012).

The desorption kinetics of small volatile molecules from analogues of IS dust surfaces has been studied at different laboratories. A review of work till 2010 can be found in Burke & Brown (2010). Various groups have investigated the low-temperature desorption of molecules from silica and silicates (Noble et al. 2012; Smith et al. 2014; Collings et al. 2015; Suhasaria, Thrower & Zacharias 2017), carbonaceous matter (Vidali et al. 1991; Bolina, Wolff & Brown 2005; Ulbricht et al. 2006; Edridge et al. 2013; Smith, May & Kay 2016; Takeuchi et al. 2017; Smith & Kay 2019), and water ice (Collings et al. 2004; Gálvez et al. 2007; Raut et al. 2007; Herrero et al. 2010; Noble et al. 2012; Fayolle et al. 2016; He, Acharyya & Vidali 2016; Smith et al. 2016). Most studies on silicate analogues and water ice have been performed with amorphous samples, since they are prevalent in the ISM, but data for the desorption from

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crystalline water ice (Gálvez et al. 2007; Noble et al. 2012) and crystalline silicates (Smith et al. 2014; Suhasaria et al. 2017), which are of relevance in more energetic environments, are also available. As for carbonaceous solids, the published studies have centred on graphite and graphene. However, observations show that most of the IS carbon is probably locked in some kind of hydrogenated amorphous carbon (HAC) with a significant aliphatic component (Dartois et al. 2007; Jones et al. 2013; Molpeceres et al. 2017; Günay et al. 2018).

The presence of IS carbonaceous dust is usually related with the intense absorption band at $3.4\ \mu\text{m}$ observed in the diffuse ISM. Since the first observations, HAC (or a-C:H) was considered a likely carrier for this band (Duley & Williams 1983), which is assumed to be essentially due to CH_x stretching vibrations of aliphatic groups. Laboratory work with different candidates corroborated the adequacy of HAC as a probable carrier of this feature (Pendleton & Allamandola 2002). Further observations from space-based observatories revealed the presence of additional absorption bands at $6\text{--}6.4\ \mu\text{m}$ ($C=C$ aromatic stretching vibrations) and at 6.8 and $7.2\ \mu\text{m}$ ($CH_{2,3}$ bending vibrations), which were also well accounted for by HAC (Dartois et al. 2005, 2007). Two competing models have been proposed for the IS grains. One model assumes a structure formed by small aromatic islands linked by aliphatic chains, with possible olefinic contributions (Dartois et al. 2005, 2007; Kwok & Zhang 2013). The other model proposes a larger fraction of aromatic content, with a mostly graphitic structure and small aliphatic contributions (Chiar et al. 2013; Steglich et al. 2013). Although the actual nature of HAC in dust grains is not known, recent experiments and models emphasize the relevance of the aliphatic component (Molpeceres et al. 2017; Günay et al. 2018). In principle, the characteristics of the grains do not have to be the same everywhere. A variety of sizes and compositions ranging from small ($0.3\text{--}10\ \text{nm}$) H-poor aromatic-rich particles to large ($>100\ \text{nm}$) H-rich aliphatic-rich grains has been proposed in a recent dust model by Jones and co-workers (Jones et al. 2013, 2014). The distinct grain populations could possibly account not just for the IR absorptions mentioned above, but also for the $220\ \text{nm}$ bump observed in the UV extinction curve and for the aromatic infrared bands (AIBs) seen in emission and usually associated with polycyclic aromatic hydrocarbons (PAHs).

In this work, we have studied the desorption of N_2 , CO , CH_4 , and CO_2 from the surfaces of two HAC samples with different composition and morphology. Desorption energy distributions for one monolayer (ML) coverage were derived from thermal-programmed desorption (TPD) measurements. The desorption energies obtained for the HAC surfaces are compared to literature data for desorption from other astrophysically relevant surfaces like silicate analogues, water ice, or graphite, and the astrophysical implications are discussed.

2 EXPERIMENTS

2.1 Dust generation – plasma reactors

HAC films (HAC1) and dust deposits (HAC2), taken as IS carbonaceous dust analogues, were produced in radiofrequency (rf) discharges, using CH_4 or C_2H_2 as fuel gases. Both, film and dust deposits, were made to completely cover the $25 \times 25\ \text{mm}^2$ surface of $5\ \text{mm}$ thick Al plates used as substrates for spectroscopy and desorption measurements.

The HAC1 films were generated in an inductively coupled rf discharge of CH_4/He . The experimental set-up was described in

detail in Maté et al. (2014) and Peláez et al. (2018). Briefly, the reactor consists of a horizontal Pyrex tube ($30\ \text{cm}$ length, $4\ \text{cm}$ diameter), with an external 10 turns Cu coil wrapped around its central part, and connected to a $13.56\ \text{MHz}$ rf generator with its matching unit. The tube can be evacuated to a background pressure of $10^{-5}\ \text{mbar}$ with a turbomolecular pump backed by a dry pump. Under operation, the turbomolecular pump connection is closed and the reactor is evacuated with a rotary pump connected to the end of the tube through a coarse regulating valve. The Al substrate was placed some $3\ \text{cm}$ beyond the coil in the direction of gas flow. Mixtures of CH_4 ($5\ \text{sccm}$) and He ($10\ \text{sccm}$) were introduced into the reactor through gas flow controllers, up to a pressure of $0.27\ \text{mbar}$. A $40\ \text{W}$ discharge was applied for eight minutes for the deposition of each sample. Film growth was monitored by observing the interference signal produced by a He–Ne laser beam reflected on the centre of the sample and detected by a photodiode. A detailed characterization of HAC1 films with scanning electron microscopy (SEM), IR spectroscopy, and UV-visible reflectivity measurements was presented in Peláez et al. (2018). The analyses showed that the deposited films were homogeneous, with flat surfaces and with a high proportion of hydrogen in their composition.

The HAC2 dust deposits were produced by gas-phase polymerization in a capacitively coupled rf discharge of C_2H_2/Ar . The plasma reactor employed for the generation of these samples is a newly developed set-up that has been described in detail in Jiménez-Redondo et al. (2019). Briefly, it consists of a stainless steel chamber, $40\ \text{cm}$ diameter, $30\ \text{cm}$ height, with several ports for vacuum pumps, gas inlets, pressure measurement, and diagnostics. A residual pressure $<10^{-7}\ \text{mbar}$ is achieved by means of a turbomolecular pump and a dry pump. During discharge operation, the chamber is evacuated by a rotary pump with a rough regulating valve. The plasma is produced between two stainless steel parallel electrodes, each of them $1\ \text{cm}$ thick and $20\ \text{cm}$ diameter, with a gap of $3\ \text{cm}$ between them. The electrodes are located in the middle of the reactor. The lower electrode and the chamber are grounded; the upper one is connected to a $13.56\ \text{MHz}$ rf generator with its matching unit. The Al substrates were placed directly on the lower electrode. Mixtures of C_2H_2 ($2\ \text{sccm}$) and Ar ($5\ \text{sccm}$) were introduced through gas flow controllers into the reactor, up to a pressure of $0.31\ \text{mbar}$, and a $15\ \text{W}$ discharge was applied for $80\ \text{min}$. The discharge was pulsed with on/off cycles of $14\ \text{s}/6\ \text{s}$. During the ‘on’ part of the cycle, particles were formed and grew between the electrodes. Each time the discharge was interrupted, at the beginning of the ‘off’ part of the cycle the particles fell on the substrate. Dust production in the gas phase was evinced by the Mie scattering of a $532\ \text{nm}$ laser beam, vertically expanded by a cylindrical lens. The scattered light was recorded with a CCD camera through a narrow-band pass $532\ \text{nm}$ optical filter placed perpendicularly to the laser beam. Light scattering could also be easily observed with the naked eye. SEM images of HAC2 samples showed a rough surface made by the irregular accumulation of particles with a diameter of $\approx 130\ \text{nm}$.

Once an HAC sample was generated, it was removed from the reactor and a low-angle ($4\ \text{deg}$) reflection–absorption IR spectrum was recorded *ex situ* under ambient conditions with a Fourier Transform Infrared (FTIR) spectrometer. Subsequently, the deposit was introduced in an ultra-high vacuum (UHV) chamber for desorption experiments. To test possible degradation of the carbonaceous material, IR spectra taken just after removing the deposit from the UHV chamber, and several weeks after, were compared. No changes were appreciated in the IR features.

The thickness of the two HAC deposits used in this work was ≈ 500 nm. It was estimated from the baseline interference pattern observed in the IR spectra, assuming the real part of the refractive index of both HAC samples to be 1.7 (Jacob 1998).

2.2 Desorption of volatiles – UHV chamber

The adsorption of volatile molecules on carbonaceous surfaces has been performed in a UHV chamber recently built at the IEM laboratory. It consists of a cylindrical 250 mm diameter stainless steel body, pumped by a 700 l s^{-1} turbomolecular pump, with a closed cycle He cryostat mounted in a rotatable flange at the top. After proper baking of the walls, the system can reach $\approx 10^{-10}$ mbar. The chamber is provided with a quadrupole mass spectrometer (QMS) and is coupled to an FTIR spectrometer through 63CF ZnSe windows to record grazing-angle reflection–absorption IR spectra or transmission spectra. Two independent gas inlets are located in a plane perpendicular to the axis of the cylindrical chamber at the same height as the sample holder at the cryostat. One of the inlets is for condensable species and the other one for gases. Both lines have UHV precision leak valves, with adjustable leaks down to $1 \times 10^{-10} \text{ Torr sec}^{-1}$, connected to microchannel array plates for direct vapour deposition on a cold surface. The line employed in this work to introduce volatile species has a microchannel plate with 10 microns $\times$ 1 mm capillaries, which is mounted in a funnel-shaped piece connected to the precision leak valve. The 20 mm diameter open surface of the array is placed at 40 mm from the cold sample surface. The Al substrates with the HAC1 or HAC2 samples were placed in the cold head of the cryostat embedded in a Cu sample holder that provides good thermal contact. Indium foil is used to further ensure the good contact. The temperature is monitored, to an accuracy of 0.5 K, with two silicon diodes at the bottom and top of the sample holder. A Lakeshore temperature controller is employed to program temperature ramps at the desired velocity. The position of the two temperature sensors allows the observation of possible temperature gradients at the sample surface during the TPD experiments.

To control the amount of gas introduced in the UHV chamber, a pre-chamber has also been built. It has different inlet ports for gases or condensable species, a vacuum gauge of the Pirani–Pening type and a capacitance manometer for pressure measurement. It is pumped by a 400 l s^{-1} turbomolecular pump and/or a rotatory pump. To control the gas dose introduced in the chamber, the UHV leak valve position was fixed and the pre-chamber gas pressure and deposition time varied. Pre-chamber gas pressures between 0.5 and 12 mbar, and deposition times between 5 s and 2 min, were employed.

The QMS has been mounted in a flange at a 45 deg angle with respect to the plane of the sample. A translation manipulator allows approaching the QMS end to a distance of 10 mm from the sample surface. The QMS is moved close to the sample to perform TPD experiments and it is subsequently moved away to allow the rotation of the cryostat. No evidence of desorption induced by electrons from the QMS source is appreciated in the IR spectra of the ices, after a five-minute QMS recording at 10 mm from the substrate. If any contribution of electron-induced desorption is present, it is negligible in comparison with the large thermal desorption induced in the fast TPD experiments performed in this work.

To investigate the interaction of the volatile species with the carbonaceous surfaces, N_2 (Alphagaz 1), CO (Alphagaz, N47), CH_4 (Alphagaz, N35), and CO_2 (Alphagaz, N38) were introduced in the UHV chamber. Deposition temperatures were 17 K for N_2 and CO,

Figure 1. Scheme of the geometry of the TPD experiments.

25 K for CH_4 , and 60 K for CO_2 , all chosen to guarantee a sticking probability close to one for the molecules on the surfaces. The cryostat was then rotated by 180 deg in order to place the sample facing the QMS (see Fig. 1). A linear heating rate of 20 K min^{-1} was programmed for all the TPD experiments presented in this work.

For the analysis of the TPD curves, it is necessary to establish the one ML dose. In this work it was determined by inspecting the TPD spectra, as described by other authors (Noble et al. 2012; Smith et al. 2016). The onset of multilayer desorption, which is revealed by the appearance of a small peak or a shoulder in the low-temperature edge of the TPD curves (see Fig. 3), marks the ML coverage and defines the ML dose. Lower coverages are then determined by the ratio between the integrated TPD areas, compared with the 1 ML area. The estimation of the ML dose by the onset of multilayer desorption could be done for N_2 , CO, and CH_4 . However, CO_2 behaves differently, as will be discussed later, and the transition from ML to multilayer desorption is not manifest in the shape of the TPD curves. For CO_2 , it has been assumed that the same deposition conditions (leak valve position, pre-chamber pressure, and deposition time) that lead to the formation of one ML of CH_4 will lead to the formation of 1 ML of CO_2 .

The main source of error in the TPD experiments is the possible inaccuracy in the temperature measurements. The silicon diodes employed in this work have an accuracy of ± 0.1 K in the temperature readings. As indicated above, two temperature sensors, one near the heating tape at the top (T_B) and the other at bottom of the sample holder (T_A), have been used. In spite of the fast temperature ramp programmed, 20 K min^{-1} , just small differences were observed between the T_A and T_B readings. At the end of the N_2 , CO, and CH_4 heating ramps, a maximum difference of 1 K appears in the readings of the two sensors, which increases to 2 K in CO_2 ramps. However, the temperature gradients must be lower in the sample, since sensor B is located near the heating element, and relatively far from the sample position (see Fig. 1). Sensor A is closer to the sample, and therefore the reading of this sensor was taken as the actual sample temperature. An error of ± 0.5 K was estimated for the temperature of the sample during the heating process.

3 RESULTS

3.1 Infrared spectra of HAC

IR spectra of the two HAC samples generated for this work are presented in Fig. 2 in the spectral intervals relevant for astronomical

Figure 2. IR spectra of HAC1 (lower panel) and HAC2 (upper panel), compared with the IR spectra observed towards the IR Galaxy IRAS 0 8572+3915 (middle panel), taken from (Dartois et al. 2007).

observations. In the same figure, they are compared with the IR absorption spectrum towards the IR galaxy IRAS 0 8572+3915 as reported in Dartois et al. (2007). The assignment of the bands is also given. As can be seen, the HAC1 film is essentially aliphatic, with bands that correspond to sp^3 CH_3 and CH_2 antisymmetric and symmetric stretches ($\approx 3.4 \mu m$) and bends (6.9 and $7.28 \mu m$). The spectrum does not show appreciable features at 3.3 or $6.2 \mu m$, assigned to sp^2 $C-H$ and $C=C$ stretches, respectively. On the other hand, the HAC2 dust sample has both aliphatic and aromatic bands. Specific techniques for surface analysis such as X-ray photoelectron spectroscopy (XPS), which would provide a better characterization of the superficial sp^2/sp^3 ratio, are not available in our laboratory, but we plan to use it in the future in collaboration with other groups. The profile of the $3.4 \mu m$ band in HAC1 is in somewhat better agreement with that of astronomical observations but, overall, the accordance is better between observations and HAC2. In particular, the broad absorption around $6.2 \mu m$, which is assigned to $C=C$ stretching of aromatic or olefinic groups, is found in the astronomical spectrum and is also seen in HAC2 but not in HAC1. The relative intensity of the $6.2 \mu m$ band in HAC2 is higher than that measured towards IRAS 0 8572+3915, but part of the intensity of this band in the laboratory sample, especially for wavelengths smaller than $6 \mu m$, might be due to contamination by CO groups, which is frequently observed in HAC produced in acetylene plasmas. As indicated in the introduction, different HAC compositions and grain sizes are likely present in the ISM, and the two samples studied here may be representative of this diversity.

3.2 Desorption from hydrogenated amorphous carbon

Fig. 3 shows the TPD spectra for N_2 , CO , CH_4 , and CO_2 films deposited on HAC1 (film, bottom panels) and HAC2 (dust, top panels) heated at $20 K min^{-1}$. In all cases, the 1 ML coverage is represented with a black curve thicker than the rest. The dotted vertical lines mark features of the curves that are discussed below. For the three lighter gases, the displayed desorption spectra correspond to 1 ML coverages and below. In the case of CO_2 , both sub-monolayer and multilayer TPDs are represented. The TPD spectra of N_2 , CO , and CH_4 have comparatively similar shapes, whereas those of CO_2 are different from the rest. We will consider the three lighter molecules first.

Clear differences are visible in the desorption of N_2 , CO , and CH_4 from the two HAC materials. As an overall tendency, TPD curves extend to higher temperatures in the desorption from HAC2, indicating a stronger interaction of the molecules with the dusty surface. The HAC2 spectra present two broad unresolved maxima, in contrast with the single broad peak observed for HAC1. Both, in HAC1 and HAC2, the TPD curves point to a distribution of adsorption energies with a tail decaying gradually towards the high-energy end, but in the case of HAC2, the two-peak profile suggests the presence of two distinct groups of desorption sites. A close inspection of the spectra shows that, for each molecule, the onset of multilayer desorption, indicated by the small peaks or shoulders in the rising edges of the 1 ML curve, is found at the same temperature for HAC1 and HAC2, as expected, since multilayer desorption is governed by interactions between the molecules of the

Figure 3. Thermal programmed desorption spectra from HAC2 (top panels) and HAC1 (bottom panels) of N_2 , CO, CH_4 , and CO_2 performed at 20 K min^{-1} . The deposition temperatures were 17, 17, 25, and 60 K for N_2 , CO, CH_4 , and CO_2 , respectively.

volatile species. For a given molecule, the position of the first broad maximum is also similar (within $\approx 1\text{--}2 \text{ K}$) in HAC1 and HAC2. This indicates the presence of a distribution of sites with similar adsorption energies in the two carbonaceous surfaces. Since both materials contain similar molecular groups, as evidenced by their IR spectra, the observation is not surprising. It is also interesting to look at the evolution of the TPDs with coverage. For N_2 , CO, and CH_4 , the peak maxima shift to lower temperatures with increasing coverage and no alignment of the TPD curves to the high- or low-temperature edge is appreciated. As convincingly shown in He & Vidali (2014), this behaviour is typical for situations in which barriers for diffusion are relatively high. Upon heating, the molecules desorb from the surface rather than diffusing to the most favourable adsorption sites. A prevalence of diffusion over desorption would translate in an alignment of the coverage-dependent curves at the high-energy falling edge, which is not observed in our experiments.

A major factor affecting the shape of the TPD curves, and their evolution with coverage, is the strength of the attractive or repulsive interactions between the adsorbate molecules (Nieskens et al. 2003). Attraction between CO_2 molecules determines the TPD

spectra for this species. The interaction between CO_2 molecules is stronger than that between CO_2 molecules and the investigated HAC surfaces. Consequently, the CO_2 molecules do not form a homogeneous ML on top of the surface, but segregate forming islands, even for sub-monolayer coverages, that desorb following zero-order kinetics at temperatures of multilayer desorption. For this reason it is not possible from the TPD shapes to determine the coverage corresponding to a single ML, as mentioned in the experimental section. This is also the reason why the TPD curves from HAC1 and HAC2 do not differ much at first sight. A slight change (1 K) in the peak temperature for the 1 ML curves, and some differences in the desorption spectra for very low coverages are found. A similar behaviour was observed in previous studies on the desorption of CO_2 from other surfaces (Noble et al. 2012; Edridge et al. 2013; Smith et al. 2016; He, Emtiaz & Vidali 2017; Suhasaria et al. 2017).

In this work only the 1 ML TPD experiments will be used to extract information about desorption energies from the two types of carbonaceous surfaces investigated. The approximations chosen will be described in the following section.

3.3 TPD analysis: desorption energies

Desorption of gases from solid surfaces is usually described by the Polanyi–Wigner rate equation (Polanyi & Wigner 1928), which is an Arrhenius-type equation with an activation energy and a pre-exponential factor that can be derived from the analysis of TPD spectra. However, the interpretation of the data is not always straightforward, since most surfaces present a distribution of energy sites with different desorption energies and, as mentioned above, other processes like surface diffusion (He et al. 2017) or the interaction between neighbouring adsorbate molecules (Nieskens et al. 2003; Jansen 2004) can also influence the measured TPD profiles. As a result of all these effects, desorption kinetics can be complex (King 1975) and the kinetic parameters (desorption energies and pre-exponential factors) become coverage dependent. Theoretical simulations using the dynamic Monte Carlo method have proven useful for the estimation of the effects of lateral interactions on the coverage-dependent kinetic parameters (Nieskens et al. 2003; Jansen 2004). Given the complexity of a thorough desorption analysis, in most cases, kinetic parameters and specifically desorption energies are derived from desorption curves using various approximations (King 1975; Nieskens et al. 2003). In this work we have followed the inversion analysis method as in Tait et al. (2005) and Zubkov et al. (2007).

The TPD spectra are described by the Polanyi–Wigner equation, which can be conveniently expressed as:

$$\frac{d\theta}{dT} = -\nu \theta^n \beta^{-1} \exp\left(-\frac{E_d(\theta)}{k_B T}\right), \quad (1)$$

where θ is the coverage ($\theta = 1$ for 1 ML), n the desorption order, ν the pre-exponential factor (which is assumed to be coverage independent), β the heating ramp (in our case 20 K min^{-1}), and E_d the desorption energy. The equation can be rearranged to give the coverage-dependent desorption energy:

$$E_d(\theta) = -k_B T \ln\left(\frac{(-\frac{d\theta}{dT})}{\nu \theta^n \beta^{-1}}\right). \quad (2)$$

This equation has been solved using the experimental TPD spectra corresponding to 1 ML coverage (presented in Fig. 3), assuming first-order desorption ($n = 1$) for N_2 , CO , and CH_4 and zero-order desorption ($n = 0$) for CO_2 , and a constant pre-exponential factor for all gases, of $\nu = 10^{13} \text{ s}^{-1}$. Note that when desorption is expressed in terms of dimensionless coverage units, the pre-exponential factor has units of frequency irrespective of the reaction order.

The choice of an adequate pre-exponential factor is debated in the literature. In transition state theory, this frequency factor is given by the quotient between the partition functions of the adsorbate in the transition state and in the adsorbed state. It is usually interpreted as the frequency of the ‘attempt’ vibration of an adsorbate molecule trying to escape from the surface, but it is not easy to determine from first principles. Various approaches are used by different authors. Some groups use empirical fits to the data, which is common in the analysis of zero-order multilayer desorption (Martín-Doménech et al. 2014; Suhasaria et al. 2017; Luna et al. 2018). Smith et al. (2014, 2016) use an iterative procedure to fit the best pre-exponential factor from a set of desorption curves from sub-monolayer coverages. Ulbricht et al. (2006) compute the ν factors using a model based on vapour pressure data. Other authors, such as He & Vidalí (2014), He et al. (2016, 2017), or Noble et al. (2012) just assume a value, usually in the 10^{12} – 10^{14} s^{-1} range, which corresponds to the typical vibration frequencies of small molecules. The weak (logarithmic)

Figure 4. N_2 , CO , CH_4 , and CO_2 desorption energies from HAC1 (black solid lines) and HAC2 (red dashed lines) surfaces, obtained from equation (2) with a pre-exponential factor $\nu = 10^{13} \text{ s}^{-1}$.

dependence of the desorption energy on the pre-exponential factor warrants this procedure, but care must be taken when comparing results from different sources, since variations of several orders of magnitude in the pre-exponential factor are sometimes found, and such variations have an appreciable influence in the estimated desorption energies.

The desorption energies obtained in this work using equation (2) are represented in Fig. 4. From the $E_d(\theta)$ curves, it is possible to calculate the distribution of binding-site energies, which is given by the expression: $P(E) = -d\theta/dE$. Fig. 5 displays the normalized site probability obtained for the two surfaces investigated. The maxima in the energy distributions are indicated with the vertical lines in Fig. 5 and their positions are listed in Table 1. For the HAC2 sample, there are two columns, under the labels HAC2_A and HAC2_B, that correspond, respectively, to the low- and high-energy maxima.

4 DISCUSSION

The desorption energies of N_2 , CO , CH_4 , and CO_2 from the surfaces of the HAC solids grown in this work can be compared with previous literature data on the desorption of these gases from other astrophysically relevant surfaces. Previously investigated IS dust analogues include graphite (Piper & Morrison 1984; Vidalí et al. 1991; Ulbricht et al. 2006; Edridge et al. 2013), graphene (Smith et al. 2016; Takeuchi et al. 2017; Smith & Kay 2019), amorphous silica (Noble et al. 2012; Collings et al. 2015), and crystalline silicates

Figure 5. N_2 , CO , CH_4 , and CO_2 distribution of adsorption sites calculated with: $P(E) = -\frac{dP}{dE}$, from the data in Fig. 4.

Table 1. Desorption energy maxima (kJ mol^{-1}) obtained for 1 ML coverage TPD curves, derived from the inversion analysis (maxima of the energy site probability distributions). A pre-exponential factor $\nu = 10^{13} \text{ s}^{-1}$ has been used in all cases. The errors correspond to the estimated uncertainties in the measured sample temperatures.

Gas	HAC1	HAC2 _A	HAC2 _B
N_2	8.5 ± 0.2	8.6 ± 0.2	10.9 ± 0.2
CO	9.6 ± 0.2	9.0 ± 0.2	13.2 ± 0.2
CH_4	11.2 ± 0.2	10.8 ± 0.2	14.7 ± 0.2
CO_2	21.8 ± 0.2	22.1 ± 0.2	

(Smith et al. 2014; Suhasaria et al. 2017). More extensive is the literature on the interaction of those volatiles with amorphous or crystalline solid water (Gálvez et al. 2007; Raut et al. 2007; Herrero et al. 2010; Noble et al. 2012; Fayolle et al. 2016; Smith et al. 2016).

Averaged values of the energies for desorption, E_d , from HAC1 and HAC2, have been calculated by integration of the site probability distributions given in Fig. 5. They are listed in Table 2, together with literature values for desorption energies from other surfaces. Many of the E_d values in this table were derived using the Polanyi–Wigner rate equation, and the corresponding pre-exponential factors are also given. Desorption energies from HAC1

Table 2. Average desorption energies, E_d , from HAC obtained in this work by integration of the site probability distributions presented in Fig. 5, compared with literature values for desorption of the same molecules from other surfaces of astrophysical relevance. Most of the listed values were derived through a kinetic analysis of TPD spectra. The associated pre-exponential factors are also included. Unless otherwise stated, they correspond to 1 ML coverages. HOPG is highly ordered pyrolytic graphite. ASW_p and ASW_{np} stand for porous and non-porous amorphous solid water.

Molecule	Surface	E_d (kJ mol^{-1})	Reference
N_2	HAC1	9.3 ± 0.2 (10^{13} s^{-1})	this work
	HAC2	10.0 ± 0.2 (10^{13} s^{-1})	this work
	graphene	11.6 ($1.7 \times 10^{13} \text{ s}^{-1}$)	Smith et al. (2016)
	HOPG	13 ± 1 ($5 \times 10^{10} \text{ s}^{-1}$)	Ulbricht et al. (2006)
	graphite	10 ± 1	Vidali et al. (1991)
	SiO_x	6.9 ± 0.3 (10^{12} s^{-1})	Collings et al. (2015)
	ASW _{np}	9.6 ($4.1 \times 10^{15} \text{ s}^{-1}$)	Smith et al. (2016)
	ASW _{np}	7.6 (10^{12} s^{-1})	He et al. (2016) ^a
	ASW _{np}	8.7 ($6.5 \times 10^{11} \text{ s}^{-1}$)	Fayolle et al. (2016) ^b
	ASW _p	7.9 (10^{12} s^{-1})	He et al. (2016) ^a
CO	HAC1	10.3 ± 0.2 (10^{13} s^{-1})	this work
	HAC2	10.6 ± 0.2 (10^{13} s^{-1})	this work
	graphene	12.5 ($1.9 \times 10^{13} \text{ s}^{-1}$)	Smith et al. (2016)
	HOPG	13 ± 1 ($6 \times 10^{14} \text{ s}^{-1}$)	Ulbricht et al. (2006)
	graphite	11	Vidali et al. (1991)
	SiO_x	7.2 (10^{12} s^{-1})	Noble et al. (2012)
	SiO_x	7.3 ± 0.2 (10^{12} s^{-1})	Collings et al. (2015)
	Mg_2SiO_x	9.3 ± 0.1 (10^{12} s^{-1})	Suhasaria et al. (2017)
	ASW _{cryst}	7.2 (10^{12} s^{-1})	Noble et al. (2012)
	ASW _{np}	8.4 (10^{12} s^{-1})	Noble et al. (2012)
	ASW _{np}	11.8 ($3.5 \times 10^{16} \text{ s}^{-1}$)	Smith et al. (2016)
	ASW _{np}	8.1 (10^{12} s^{-1})	He et al. (2016) ^a
	ASW _{np}	9.7 ($7.1 \times 10^{11} \text{ s}^{-1}$)	Fayolle et al. (2016) ^c
	ASW _p	8.6 (10^{12} s^{-1})	He et al. (2016) ^a
CH_4	HAC1	12.2 ± 0.2 (10^{13} s^{-1})	this work
	HAC2	12.5 ± 0.2 (10^{13} s^{-1})	this work
	graphene	14.9 ($2.1 \times 10^{13} \text{ s}^{-1}$)	Smith et al. (2016)
	HOPG	17 ± 2 ($4 \times 10^{15} \text{ s}^{-1}$)	Ulbricht et al. (2006)
	graphite	13.7 ± 0.1	Piper & Morrison (1984)
	Mg_2SiO_x	11 ± 0.1 (10^{12} s^{-1})	Suhasaria et al. (2017)
	ASW _{np}	11.4 ($9.8 \times 10^{14} \text{ s}^{-1}$)	Smith et al. (2016)
	ASW _{np}	9.3 (10^{12} s^{-1})	He et al. (2016) ^a
	ASW _p	7.4 – 8.0	Raut et al. (2007)
	ASW _p	7.1 – 9.1	Herrero et al. (2010)
CO_2	HAC1	22.5 ± 0.2 (10^{13} s^{-1})	this work
	HAC2	23.4 ± 0.2 (10^{13} s^{-1})	this work
	graphene	26.4 ± 1.5 ($6.2 \times 10^{14} \text{ s}^{-1}$)	Takeuchi et al. (2017) ^d
	graphene	26.1 ± 2 ($5 \times 10^{15} \text{ s}^{-1}$)	Smith & Kay (2019)
	HOPG	24 ± 2 ($2 \times 10^{14} \text{ s}^{-1}$)	Ulbricht et al. (2006)
	graphite	20	Vidali et al. (1991)
	HOPG	20.2 ± 2.3 (9.9×10^{14})	Edridge et al. (2013)
	SiO_x	18.8 (10^{12} s^{-1})	Noble et al. (2012)
	Mg_2SiO_4 (10–15 per cent Fe^{2+})	33 (10^{19} s^{-1})	Smith et al. (2014)
	Mg_2SiO_x	20.9 ± 0.3 (10^{13} s^{-1})	Suhasaria et al. (2017)
	ASW _{cryst}	19.7 (10^{12} s^{-1})	Noble et al. (2012)
	ASW _{cryst}	18.8 ± 2	Gálvez et al. (2007)
	ASW _{np}	20.7 ± 2	Gálvez et al. (2007)
	ASW _{np}	17.5 ± 7.5 ($2.7 \times 10^7 \text{ s}^{-1}$)	Edridge et al. (2013)
	ASW _{np}	19.6 (10^{12} s^{-1})	Noble et al. (2012)

^a Values calculated from equation 3 of He et al. (2016) for 1 ML coverage.

^b Average of the values given in table 1 of Fayolle et al. (2016) for 1.4 and 0.7 ML.

^c Average of the values given in table 1 of Fayolle et al. (2016) for 1.3 and 0.8 ML.

^d For a coverage of 0.6 ML.

Table 3. Comparison of energies of desorption maxima (kJ mol^{-1}) from HAC1, HAC2 (this work, taken from Table 1) with those from graphite and graphene surfaces taken from the literature for a common pre-exponential factor $\nu = 10^{13} \text{ s}^{-1}$.

	HAC1 (this work)	HAC2 _A (this work)	HAC2 _B (this work)	Graphite (Ulbricht et al. 2006) ^a	Graphene (Smith et al. 2016; Smith & Kay 2019)
N_2	8.5 ± 0.2	8.6 ± 0.2	10.9 ± 0.2	11.0	11.6^b
CO	9.6 ± 0.2	9.0 ± 0.2	13.2 ± 0.2	12.1	12.5^b
CH_4	11.2 ± 0.2	10.8 ± 0.2	14.7 ± 0.2	14.4	14.9^b
CO_2	21.8 ± 0.2	22.1 ± 0.2		21.4	21.6^c

^aFor consistency in the comparison, these values are calculated with the Redhead (Redhead 1962) formula using the T_p and β values given in table 3 of Ulbricht et al. (2006) and the same pre-exponential factor ($\nu = 10^{13} \text{ s}^{-1}$) as in this work.

^bThe pre-exponential factors used by Smith et al. (2016) are in the 10^{13} s^{-1} range, and are thus comparable with those of this work.

^cCalculated with the Redhead formula using the $T_p = 84.5 \text{ K}$ and $\beta = 1 \text{ K s}^{-1}$ of Smith & Kay (2019).

and HAC2 surfaces are close, though slightly lower than those given in the literature for graphite and graphene surfaces. They are larger than those reported for silicate analogues. On average, N_2 and CO desorption energies from HAC1 and HAC2 are found to be $\sim 3\text{--}4 \text{ kJ mol}^{-1}$ larger than those from amorphous siliceous surfaces. Desorption energies from solid water surfaces have a large disparity, but always remain below the values determined for desorption from HAC. These results indicate that carbonaceous surfaces, irrespective of their structure and composition, will retain volatile molecules at higher temperatures than siliceous surfaces or water ice, and this could have important astrophysical implications.

It is interesting to take a closer look at the diverse TPD profiles for HAC1 and HAC2 presented in Fig. 3. The differences in these profiles must be a consequence of differences either in the morphology or in the structure of their respective surfaces. The morphologies of the two solids are indeed dissimilar, however they are not deemed to be the main cause of their different TPD profiles. HAC1 is a film and HAC2 a deposit of dust particles, but both are uniform throughout the whole exposed surfaces. The higher irregularity of HAC2 could be manifest in a broadening of the desorption energy distribution with respect to that of HAC1, but maintaining a smooth profile. The appearance of secondary maxima or shoulders points to the existence of two distinct categories of adsorption sites for N_2 , CO , and CH_4 , more likely related with the different chemical structures of the two solids.

Table 3 presents the desorption energies found in this work using the inversion analysis (the same as in Table 1) and those taken from previous experiments for graphite and graphene surfaces. As shown in Table 2 in the original publication of Ulbricht et al. (2006) on desorption from graphite, very different pre-exponential factors, varying by four orders of magnitude between N_2 and CO_2 , were used for the four molecules under consideration. For consistency in the comparison, desorption energies have been re-calculated with the same method (Redhead equation, Redhead 1962), employing the original data on desorption maxima and heating ramps (Ulbricht et al. 2006), but with the pre-exponential factor used in this work ($\nu = 10^{13} \text{ s}^{-1}$). The same correction has been applied to the data of Smith & Kay (2019) on the desorption of CO_2 from graphene. It can be seen that the desorption energies obtained from the high temperature shoulder (HAC2_B) in the HAC2 TPD spectra are close to those corresponding to graphite or graphene surfaces (see last three columns in Table 3). As mentioned above, the two peaks

in the HAC2 TPD curves indicate the presence of two groups of energy sites in the surface and, although some effects of the different solid morphologies cannot be completely excluded, the E_d values of Table 3 strongly suggest that the second maxima in the TPD spectra of HAC2 correspond to desorption from the aromatic part of the carbonaceous structure that was evinced in the IR spectra of this sample (see Fig. 2). The other group of adsorption sites (HAC2_A) is observed also in the HAC1 analogue and is likely related with the aliphatic part of the solid structure. This interpretation suggests that the volatile molecules have a stronger interaction with the delocalized cloud of π electrons in the aromatic rings. Theoretical calculations have been undertaken in our group to help interpret these observations and will be reported in a future work.

The desorption energy distributions of CO_2 from HAC1 and HAC2 (lower panel of Fig. 5) are very narrow, with widths below one degree, and they do not display the two maxima profile of the other three molecules for HAC2. The seeming structure of the peaks is just numerical noise of the inversion procedure. As commented on in the discussion of the TPD spectra, CO_2 does not wet the HAC surfaces but rather forms droplets on top, and desorbs following zero-order kinetics, revealing a stronger interaction between CO_2 molecules than between CO_2 and the adsorbates. The dispersion of interaction energies within the CO_2 droplets is very small. In this respect, the extremely narrow peak of the HAC2 distribution is noteworthy. Consequently, the E_d from HAC1 and HAC2 are alike. Under these circumstances, the E_d values could be expected to be similar to the sublimation enthalpy of CO_2 , but they are in fact lower since the most recent sublimation enthalpies reported for CO_2 lie in the $27\text{--}29 \text{ kJ mol}^{-1}$ range (Bryson, Cazcarra & Levenson 1974; Shakeel, Wei & Pomeroy 2018). Note that a better agreement between E_d and sublimation enthalpy is obtained with a higher value of the pre-exponential factor (Takeuchi et al. 2017; Smith & Kay 2019). A similar behaviour is observed in the desorption of CO_2 from most of the surfaces relevant for astrophysical dust (see references in Table 2). An average desorption energy of $21 \pm 4 \text{ kJ mol}^{-1}$ is observed for the surfaces listed in Table 2. The large desorption energy (33 kJ mol^{-1}) given by Smith et al. (2014) for a silicate surface is mostly due to the large pre-exponential factor employed by these authors (10^{19} s^{-1}). With a lower value, similar to those employed by most authors ($10^{12}\text{--}10^{14} \text{ s}^{-1}$), an analysis of the same data would lead to a desorption energy in the $20\text{--}23 \text{ kJ mol}^{-1}$ interval.

Figure 6. N_2 and CO TPD curves of 1 ML coverage desorption from HAC2. Surfaces with indication of the location of the two maxima (HAC2_A and HAC2_B).

The ratio between N_2 and CO desorption energies from solid particles is important for the interpretation of the gas-phase CO and N_2 abundances in different astronomical environments. Comparative studies on the desorption of these two molecules from water ice were reported in Öberg et al. (2005) and Fayolle et al. (2016). Both, multilayer and sub-monolayer coverages, as well as compact and porous water ice, were investigated by these authors and in all cases, they found N_2/CO_2 desorption energy ratios of ≈ 0.9 . A similar value (0.94) was found by Collings et al. (2015) for the N_2/CO_2 desorption energy ratio from amorphous silica in the ML and multilayer regimes. The N_2/CO_2 E_d ratios obtained for the carbonaceous surfaces of this work are 0.9 for HAC1 and 0.94 for HAC2 (see Table 2). A similar ratio (0.93) is obtained for desorption energies from graphene (Smith et al. 2016). The same energy ($E_d = 13 \pm 1 \text{ kJ mol}^{-1}$) was reported by Ulbricht et al. (2006) for the desorption of both N_2 and CO from graphite, but, as indicated above, very different pre-exponential factors were used for the two molecules in that work. Using the values corrected for a pre-exponential factor of $\nu = 10^{13} \text{ s}^{-1}$ given in Table 3, the N_2/CO_2 E_d ratio is 0.91. In summary, similar N_2/CO_2 desorption energy ratios are found for all the IS dust surface analogues studied thus far in the laboratory.

Considering just the second peak (HAC2_B) in the desorption of HAC2, a N_2/CO_2 E_d ratio of 0.83 is derived from Table 3, somewhat lower than the ratios discussed thus far. Fig. 6 presents a comparison of the N_2 and CO, 1 ML, TPD desorption spectra from HAC2 surfaces and shows that the assumed aromatic sites, corresponding to the HAC2_B maxima (see discussion above), are appreciably more stable for CO than for N_2 . The difference between the E_d ratio for the HAC2_B, and those of other aromatic surfaces discussed in the previous paragraph, might be due to a different structure of the aromatic component of HAC2, which could be made of small aromatic islands, as compared with the large aromatic sheets of graphite and graphene. But no conclusion can be drawn on this point with the present data.

5 ASTROPHYSICAL IMPLICATIONS

The higher binding energies found in this work for N_2 , CO, and CH_4 on carbonaceous materials than on water ice or amorphous silica implies that these molecules will have a larger lifetime on the surface of the carbonaceous dust surfaces. Therefore, the probability for these species to take part in surface chemistry will increase. The lifetime of a volatile species, assuming no chemical destruction or photo-desorption, can be estimated via the expression:

$$t_{1/2} = -\frac{1}{\nu} \ln \left(\frac{1}{2} \right) e^{E_d/k_B T_{\text{gr}}}, \quad (3)$$

where T_{gr} represents the grain temperature. For example, at $T_{\text{gr}} = 20 \text{ K}$, an increase of 1 kJ mol^{-1} in the binding energy translates in a growth of three orders of magnitude in the lifetime. For this temperature, estimates of $t_{1/2}$ with the E_d values of this work indicate that N_2 would evaporate from the grains in $\approx 10^5 \text{ yr}$, a time shorter than the $\approx 10^7 \text{ yr}$ lifetime of a dense cloud. The lifetime of CO, $5 \times 10^6 \text{ yr}$, would already approach this limit, and both CH_4 and CO_2 would remain on the carbonaceous grains till the beginning of cloud collapse.

A very simple model of accretion and desorption, following the work of (Acharyya et al. 2007), is used to simulate the desorption of the volatiles during the heating of a cold cloud core, employing the binding-site energy distributions obtained in this work. We will consider the simple case of desorption of N_2 , CO, CH_4 , and CO_2 , without gas-phase or solid-state chemistry, from bare carbonaceous (HAC) surfaces during the heating of cold cores.

The time evolution of the density of molecules trapped in the dust grains of a given species X, $n_s(X)$, depends on the rates of accretion (R_{acc}) and desorption (R_{des}):

$$\frac{dn_s(X)}{dt} = R_{\text{acc}} - R_{\text{des}}. \quad (4)$$

The accretion rate is given by the simple formula:

$$R_{\text{acc}} = \sigma \gamma_s \nu n_g(X) n_{\text{gr}}, \quad (5)$$

where $\sigma = \pi r_{\text{gr}}^2$ is the grain cross-section and r_{gr} is the grain radius, γ_s is the sticking coefficient, ν is the thermal velocity of the gas-phase molecules of species X, and $n_g(X)$ and n_{gr} are the densities of gas-phase X molecules and grains, respectively. The rate of desorption is obtained from the Polanyi–Wigner equation (equation 1), which now depends on the grain temperature.

The surface coverage θ can be related to the solid density $n_s(X)$ through the following expression:

$$\theta = \frac{n_s(X)}{n_{\text{gr}} N_{\text{gr}}}, \quad (6)$$

where N_{gr} represents the number of surface sites in a grain, which can be related to its size and the surface density of sites, S_{gr} :

$$N_{\text{gr}} = 4\pi r_{\text{gr}}^2 S_{\text{gr}}. \quad (7)$$

The desorption rate can then be written as

$$R_{\text{des}} = \nu n_s(X)^n (n_{\text{gr}} N_{\text{gr}})^{1-n} \exp \left(-\frac{E_d(n_s(X))}{k_B T_{\text{gr}}} \right). \quad (8)$$

At the start of the simulation, the whole density of X molecules, $n_T(X) = n_s(X) + n_g(X)$, is assumed to be in the solid state. At each time-step, $n_s(X)$ is calculated by numerical integration of equation (4) and $n_g(X)$ is obtained by subtraction.

In order to perform the calculations, adequate values for some of these parameters need to be chosen. Surface grains are assumed to have a radius of $r_{\text{gr}} = 0.1 \mu\text{m}$, a surface site density of

$S_{gr} = 10^{15} \text{ cm}^{-2}$, and a fractional abundance of $n_{gr}/n(H_2) = 10^{-12}$. The fractional abundances of the different molecular species are 10^{-6} for N_2 (Womack, Ziurys & Wyckoff 1992), 10^{-4} for CO (Acharyya et al. 2007), 10^{-7} for CH_4 (Boogert et al. 1998), and 10^{-7} for CO_2 (Charnley, Rodgers & Ehrenfreund 2001). A specific issue arises for CO , since its abundance is so high that, in the initial conditions of our model, the surface coverage is much larger than one, which does not occur for the other species. Each grain would be expected to contain close to 100 MLs of CO . Two different modelling approaches have been taken in this case. First, the desorption was simulated assuming that while the surface coverage is larger than one, the desorption energy is equal to 7.1 kJ mol^{-1} (Acharyya et al. 2007), corresponding to multilayer desorption of CO ice. For sub-monolayer coverages, the experimental site probability distribution was used. The second approach entails an increase in the grain size. For $r_{gr} = 1 \mu\text{m}$, all the CO molecules can be frozen out on the grains without surpassing the ML coverage, and the simulation proceeds as usual. Grains of this size could be present in significant concentrations in the ISM (Jones et al. 2013).

The temperature increase is chosen to mimic the heating rate during core warm-up. A linear dependence with time is assumed: $T_{gr} = T_{gr}^0 + \beta t$, and the initial temperature is chosen to be $T_{gr}^0 = 10 \text{ K}$. The value of β is taken from the work of Viti & Williams (1999). The usual choice of $1/100 \text{ K yr}^{-1}$ (Noble et al. 2012; Suhasaria et al. 2017) corresponds to a $60 M_{\odot}$ star, while a slower heating is expected for less-massive stars. Thus, we have chosen to use two different β values, $1/100 \text{ K yr}^{-1}$ and $1/1000 \text{ K yr}^{-1}$, in our calculations. For representation purposes, the heating rate is given through t_c , defined as the time needed for the temperature to increase by 1 K .

The removal of the accretion rate from the model results in a negligible change in the time evolution of the densities, and is found to be only relevant for very large time-scales (i.e. low heating rates) such as the $t_c = 10^6 \text{ yr}$ used in the work of Acharyya et al. (2007) to simulate a cold core at near constant temperature.

Inspection of Fig. 7 shows that, for a given adsorbate and surface, desorption takes place at slightly lower temperatures for the lower heating rate (dashed lines), as expected. Desorption from HAC2 is slower or takes place at higher temperatures than in HAC1 in accordance with the energy distributions of the molecules on the two surfaces (see Figs 4 and 5). For the two most volatile species, N_2 and CO , desorption is practically over for temperatures of 32–35 K. The desorption curves are parallel, shifted by about 2 K towards lower T values for N_2 . This is associated with desorption times of about $2 \times 10^3 \text{ yr}$ for the fast heating rate and about $(2.2\text{--}2.4) \times 10^4 \text{ yr}$ for the slow heating rate. The desorption processes just commented on correspond to ML or sub-monolayer coverages. This is adequate for N_2 on standard $0.1 \mu\text{m}$ grains and for CO on large grains (e.g. $1 \mu\text{m}$), which can also be present in significant concentrations (Jones et al. 2013). However, due to its high abundance, most CO molecules in cold cores are adsorbed in multilayers on the $0.1 \mu\text{m}$ grains, and desorb more suddenly at an appreciably lower temperature (16–17 K), corresponding to shorter core evolution times. Methane molecules desorb at temperatures between 31 and 41 K from the HAC surfaces. Desorption should be virtually complete by $3.2 \times 10^3 \text{ yr}$ for the fast heating rate and by $3 \times 10^4 \text{ yr}$ for the slow heating rate. Finally, CO_2 , with narrow E_d distributions (see Fig. 5), desorbs more suddenly at temperatures of 50–57 K. These desorption temperatures corresponds to core evolution times of $(4.7\text{--}5) \times 10^3 \text{ yr}$ (fast heating rate) and $(4.7\text{--}5) \times 10^4 \text{ yr}$ (slow heating rate) for complete desorption.

Figure 7. Gas density fractions during core warm-up obtained from the model for N_2 , CO , CH_4 , and CO_2 using the site probability distributions obtained for each substrate, HAC1 and HAC2, and for two different heating rates. For CO , multilayer desorption occurs for the smaller dust radius considered ($0.1 \mu\text{m}$), and the curves for HAC1 and HAC2 overlap in that case.

Fig. 8 compares the ML desorption of CO from different grain surfaces during the evolution of a massive cold core with an assumed heating rate of $1/100 \text{ K yr}^{-1}$. Desorption from HAC1 and HAC2 was simulated with the E_d distributions derived in this work, and that from ASW_{np} and SiO_x with the E_d distributions from Noble et al. (2012). For consistency with the data of this reference, a pre-exponential factor $\nu = 10^{12} \text{ s}^{-1}$ has also been used for the simulations of HAC1 and HAC2, instead of the $\nu = 10^{13} \text{ s}^{-1}$ factor employed throughout this work. Given the weak dependence of the desorption energy on the pre-exponential factor, this change has no significant influence in the simulated desorption curves as can be seen by comparing Figs 7 and 8 (see also discussion in He et al. 2016).

Overall, desorption takes place at higher temperatures from the HAC surfaces than from those of ASW and SiO_x , as expected from the respective average desorption energies (see Table 2), but the distinct shapes of the desorption curves reflect also interesting details of the corresponding energy distributions. The slower rate

Figure 8. Simulated evolution of the relative density of CO molecules in the gas phase during the warm-up of a massive cold core ($1/100 \text{ K yr}^{-1}$). The grain surfaces corresponding to each curve are indicated in the figure. The desorption parameters for HAC1 and HAC2 are derived in this work, those for non-porous amorphous ice and amorphous silica were taken from Noble et al. (2012).

of desorption from HAC2, as compared with HAC1 at the higher temperatures, is largely due to the second maximum of the HAC2 E_d distribution, which is absent in HAC1 (Fig. 5). The energy distributions for desorption for CO_2 on ASW_{np} and SiO_x are parametrized in Noble et al. (2012). The E_d distribution for ASW_{np} has roughly the same threshold as those for the carbonaceous surfaces, but is narrower, which results in a steeper rise. The corresponding distribution for desorption from SiO_x has a lower threshold, but is broader, with a long decaying tail extending to higher energies. As a consequence, desorption from SiO_x starts at a lower temperature but ends approximately at the same temperature than that from HAC1.

6 SUMMARY AND CONCLUSIONS

(1) Two deposits of HAC, taken as analogues of IS carbonaceous grain surfaces, were grown in rf discharges of hydrocarbon precursors and characterized by IR spectroscopy. The first deposit (HAC1), produced in a CH_4/He inductive discharge, is a flat film dominated by aliphatic chains. The second one (HAC2), generated in a capacitive $\text{C}_2\text{H}_2/\text{Ar}$ plasma, consists of an accumulation of dust particles, with average size of 130 nm, and contains a mixture of aliphatic and aromatic structures.

(2) The sub-monolayer and ML desorption of N_2 , CO , CH_4 , and CO_2 from the two HAC surfaces was investigated by measuring TPD spectra at cryogenic temperatures under ultra-high vacuum. The Polanyi-Wigner equation was inverted to derive the 1 ML desorption energies. In all cases a pre-exponential factor of 10^{13} s^{-1} was assumed.

(3) For all the gases considered, the interaction with HAC2 is found to be somewhat stronger than that with HAC1. For N_2 , CO , and CH_4 , the HAC2 TPD spectra show a secondary maximum at higher temperatures indicating the presence on the surface of two kinds of adsorption sites. The TPD spectra of CO_2 reflect zero-order kinetics with a single peak for the two HAC surfaces.

(4) For N_2 , CO , and CH_4 , a comparison of literature values of desorption energies from graphene and graphite with the energies corresponding to the secondary high-energy maxima in the HAC2 TPD spectra, strongly suggests that these maxima are due to desorption from the aromatic component of HAC2.

(5) On average, the 1 ML energies for desorption from the two HAC samples investigated in this work are higher than those reported in the literature for siliceous surfaces, and are close to the literature values for graphite or graphene. They are also higher than most of the values reported for amorphous water ice, although in this case there is a big data dispersion due to the very variable ice morphologies. Typically, the desorption energies for carbonaceous surfaces are higher by $\approx 10\text{--}20$ per cent than those from water ice and silicate analogues.

(6) The desorption of N_2 , CO , CH_4 , and CO_2 from the carbonaceous dust analogues produced in this work during the heating of cold stellar cores has been simulated with a simple model. The simulations have been carried out for two different heating rates ($1/100$ and $1/1000 \text{ K yr}^{-1}$), representative of cores of different mass. For the higher heating rate, differences of hundreds to thousands of years are found in the desorption, and thus in the availability for gas-phase or surface chemistry of the various gases. For the slower heating rate these differences grow to tens of thousands of years.

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