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Laboratory investigations of the interaction between benzene and bare silicate grain surfaces

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ABSTRACT
Experimental results on the thermal desorption of benzene (C6H6) from amorphous silica (SiO2) are presented. The amorphous SiO2 substrate was imaged using atomic force microscopy, revealing a surface morphology reminiscent of that of interplanetary dust particles (IDPs). Temperature-programmed desorption (TPD) experiments were conducted for a wide range of C6H6 exposures, yielding information on both C6H6–SiO2 interactions and the C6H6–C6H6 interactions present in the bulk C6H6 ice. The low-coverage experiments reveal complicated desorption behaviour that results from both porosity and roughness in the SiO2 substrate, and repulsive interactions between C6H6 molecules. Kinetic parameters were obtained through a combination of direct analysis of the TPD traces and kinetic modelling, demonstrating the coverage dependence of both desorption energy and pre-exponential factor. Experiments were also performed whereby the pores were blocked by pre-exposure of the SiO2 to water vapour. C6H6 was observed to be adsorbed preferentially on the SiO2 film not covered by H2O at the temperature at which these experiments were performed. This observation means that intermolecular repulsion likely becomes important at smaller C6H6 exposures on grains with a H2O mantle. Kinetic modelling of C6H6 multilayer desorption yields kinetic parameters in good agreement with previous studies, with the SiO2 having little impact on the desorption beyond the first few layers.

Key words: molecular data – molecular processes – methods: laboratory – ISM: molecules.

1 INTRODUCTION
Carbon is thought to exist in many forms throughout the interstellar medium (ISM). In particular, polycyclic aromatic hydrocarbons (PAHs) are generally considered to be one of the most important classes of carbon-bearing molecule (Ehrenfreund & Sephton 2006). PAHs have been proposed as carriers of both the diffuse interstellar bands (DIBs) (Duley 2006 and references therein) and the unidentified infrared bands (UIRs) (Allamandola, Hudgins & Sandford 1999). Absorption features corresponding to the UIRs have been observed towards several protostellar objects and towards the Galactic Centre (Bregman & Temi 2001 and references therein). PAH emission features have been observed in a wide range of environments (see e.g. Kaneda, Onaka & Sakon 2005; Lagadec et al. 2006; Flagey et al. 2006; Kassis et al. 2006; Smith et al. 2007), demonstrating their ubiquitous nature. As with many gas-phase molecules, it is likely that PAHs are also present mixed in the water (H2O) ice dominated mantles surrounding grains in the dense ISM under suitably cold conditions. Laboratory spectra of PAHs in appropriate ice matrices are essential in aiding the interpretation of observational spectra. To this end, there have been several experimental studies of the infrared absorption spectra of PAH/H2O ice mixtures (Sandford, Bernstein & Allamandola 2004; Bernstein, Sandford & Allamandola 2005; Bernstein et al. 2007).

We are currently undertaking work to investigate the irradiation of PAHs with both photons and electrons. As a first step for understanding the relevant processes, we are focusing on benzene (C6H6), primarily for reasons of experimental convenience, before considering simple PAH species and their heterocyclic analogues, including pyridine (C5H4N). As ultraviolet (UV) absorption characteristics of small PAHs and C6H6 are similar, any knowledge obtained from studies of this simpler system will contribute positively to our understanding of processes involving PAH larger species. Furthermore, to aid in interpreting the results of irradiation experiments, it is necessary to understand the nature of the pre-irradiated ice. For example, in our recently reported experimental measurements of the photodesorption of C6H6 from H2O ice (Thrower et al. 2008), the desorption of both C6H6 and H2O was found to depend strongly on the morphology of the ices. It is clear that a more detailed understanding of the interactions between both C6H6 and H2O and the underlying substrate is required. As far as we are aware, there

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have been no experimental studies of the interaction between C₆H₆ and suitable grain mimics. We have chosen a grain mimic based on a thin film of amorphous silica in order to represent the silicate grain population. Compared to our previous study of the desorption of CO from meteorite nanoparticles (Mautner et al. 2006), such a substrate is likely to be more reproducible in the laboratory. The surface will also be chemically much less complex, allowing a more fundamental approach to the study of adsorption on the grain mimic surface to be adopted.

Evidence suggests that C₆H₆ is readily destroyed in diffuse regions by interaction with protons and UV photons (Ruiterkamp et al. 2005). However, in denser regions and circumstellar envelopes where molecules are more shielded from the interstellar radiation field, the C₆H₆ lifetime is expected to be much longer. Evidence for this has come from the Infrared Space Observatory mission with the observation of C₆H₆ in the carbon-rich protoplanetary nebula (PPN) CRL 618, accompanied by C₄H₂ and C₆H₂ (Cernicharo et al. 2001). These observations have suggested that a significant amount of organic chemistry occurs in C-rich PPNs. Various mechanisms have been put forward for the synthesis of C₆H₆ in environments exhibiting different physical and chemical conditions. In the dense ISM, the formation of hydrocarbon species, including C₆H₆, via a gas-phase ion neutral scheme involving atomic hydrogen has been proposed (McEwan et al. 1999). A mechanism initiated by reaction of a range of ions with acetylene (C₂H₂) has been shown to account for the significantly higher C₆H₆ abundance observed in CRL 618 (Woods, Miller & Zijlstra 2002). A series of reactions based on soot formation involving C₂H₂ has also been proposed as a likely route for the synthesis of C₆H₆ and PAHs in circumstellar envelopes (Frenklach & Feigelson 1989; Cherchneff, Berker & Tielens 1992). It has been suggested that organometallic catalysis in these environments may lead to an increased C₆H₆, and therefore PAH, production rate (Ristorcelli & Klotz 1997). In protostellar discs, a different mechanism has been proposed (Woods & Willacy 2007), whereby C₆H₆ is formed via c-C₆H₂⁺ (where c- denotes a cyclic species). Following adsorption of this protonated species on a grain surface, proton transfer and charge neutralization yield adsorbed C₆H₆ and H. The efficiency of this proton transfer mechanism on returning C₆H₆ to the gas phase will depend on how strongly the adsorbed C₆H₆ is bound to the grain surface. In this work, it was noted that values in the existing literature for the desorption energy of a C₆H₆ molecule from a bare grain surface can range from 4700 K to as much as 7500 K (Arnett, Hutchinson & Healy 1988; Hasegawa & Herbst 1993; Lozovik, Popov & Letokhov 1995; Garrod & Herbst 2006). In only one of these studies (Arnett et al. 1988) is a value derived experimentally, with gas–solid chromatography being used to obtain the desorption energy from graphite, yielding a value of 39 ± 3 kJ mol⁻¹ (4750 ± 360 K). This is clearly not the most appropriate experiment on which to base an understanding of adsorption to interstellar grains. There have been many experimental studies of the adsorption of C₆H₆ on both single crystal and polycrystalline metal surfaces (See e.g. Jakob & Menzel 1989; Haq & King 1996; Rockey, Yang & Dai 2006). On many substrates, C₆H₆ has been found to adsorb plane parallel to the substrate, bonding via the π electrons. Amorphous silica is widely used as a support for catalysts and has been studied extensively. It is well known that exposure of silica surfaces to H₂O results in reaction to form surface hydroxyl (OH) groups known as silanols. The resulting hydrophilic surface has been studied recently by ab initio methods (Tielens et al. 2008). H₂O was shown to interact with three binding sites with adsorption energies of 44, 46 and 50 kJ mol⁻¹, characteristic of hydrogen bonding interactions. C₆H₆ has been shown to form weak hydrogen bonds to water via the aromatic ring (Suzuki et al. 1992), indicating that such bonds may also be important in the adsorption of C₆H₆ on a hydroxylated SiO₂ surface.

2 EXPERIMENTAL METHODS

The experiments described here were conducted in a stainless steel ultrahigh vacuum (UHV) chamber that has been described in detail elsewhere (Oakes 1994). The chamber is pumped by a combination of liquid-nitrogen-trapped diffusion pumps and a titanium sublimation pump. Following bakeout to remove water adsorbed on internal surfaces, a base pressure of 2 × 10⁻¹⁰ torr is routinely obtainable. The substrate was a 10 mm diameter, polished stainless steel disc that was attached to molybdenum support posts on an oxygen-free high-conductivity copper mount by tantalum wires. Experiments were conducted on both the polished stainless steel surface and a thin film of SiO₂ deposited on this surface in order to gain some insight into the effect of the SiO₂ on adsorption. The SiO₂ films were deposited in a separate chamber by electron beam evaporation of bulk material. The substrate was maintained at room temperature during the evaporation, and ~200 nm of SiO₂ were deposited as measured by a quartz crystal microbalance situated close to the substrate. The film thickness of 200 nm was chosen in order to provide a film thick enough that pathways to the stainless steel substrate are limited without introducing interference effects into any future infrared studies. The substrate was cleaned by heating to 500 K for 15 min before cooling, prior to conducting experiments.

The substrate was cooled to a base temperature of around 115 K by a liquid nitrogen reservoir in thermal contact with the sample mount. This temperature is significantly higher than that of dust grains in dense clouds (10–20 K), however, preliminary experiments on a system with a substrate base temperature of 10 K (not shown) have demonstrated that C₆H₆ does not desorb below 120 K. Similarly, previous experiments (Fraser et al. 2001; Bolina, Wolff & Brown 2005) have also shown that H₂O does not desorb below the base temperature used in the experiments described here. The substrate could be heated resistively by passing current through the support wires. A K-type (Chromel-Alumel) thermocouple, spotwelded to the edge of the substrate, was used for temperature monitoring. A programmable controller (Eurotherm) was used to provide a linear heating ramp (β) of 0.1 ± 0.02 K s⁻¹ during temperature-programmed desorption (TPD) experiments.

UV-spectroscopy grade C₆H₆ (Fluka) and deionized H₂O were further purified by repeated freeze-pump-thaw cycles on a dedicated stainless steel preparation line pumped by a diffusion pump. To avoid cross-contamination, the C₆H₆ and H₂O were purified on independent manifolds, each with a fine leak valve for dosing into the main UHV chamber. Layers of C₆H₆ and H₂O were deposited on to the substrate by backfilling the chamber to a pressure as measured by an uncalibrated ion gauge. Exposures are reported in Langmuir (1 L = 1 × 10⁻⁶ torr s). Though it is not possible to accurately determine coverages with our experimental arrangement, the surface concentration of adsorbed molecules was estimated by using a simple collision theory, assuming a sticking probability of unity and an ion gauge sensitivity correction factor of 6 for C₆H₆ (Waddill & Kesmodel 1985).

The desorption of H₂O and C₆H₆ molecules during TPD experiments was monitored using a quadrupole mass spectrometer (QMS) (modified VG Micromass PC300D) with a cross-beam ion source and channel electron multiplier detector that was operated in analogue (current) mode. The QMS was housed in a
3 RESULTS AND DISCUSSION

In order to assess the nature of the amorphous silica substrate used in these experiments, the surface morphology of the film was investigated using an atomic force microscopy (AFM) prior to mounting in the UHV chamber. AFM images were obtained with a silicon nitride tip operated in constant force contact mode. At present, there is no detailed understanding of the morphology of interstellar grains. A reasonable approximation can be made by considering that of interplanetary dust particles (IDPs). Whilst it is important to recognize that IDPs are likely to have been processed during the formation of the Solar system, we consider only the overall structure of the surface, neglecting any chemical modifications which are not represented in our grain mimic. Fig. 1 shows a 20 × 20 μm region of the amorphous silica surface along with a scanning electron microscope (SEM) image of an IDP. For clarity, the AFM image has been exaggerated in the vertical direction. The amorphous silica surface appears to reproduce the morphology of the IDP well on a similar length-scale. The likely presence of pores on grain surfaces, which are not present with the polycrystalline Au substrate used in our earlier studies, may have important consequences for the morphology of adsorbates.

Fig. 2 shows TPD traces for the desorption of C$_6$H$_6$ from the bare amorphous silica surface for low, intermediate and large exposures of C$_6$H$_6$. In all cases, the C$_6$H$_6$ was deposited whilst the substrate was at its base temperature of 115 K, and the TPD traces were obtained with a heating rate, β, of 0.1 K s$^{-1}$ to a temperature of 210 K, above which no further C$_6$H$_6$ desorption was detected. At the smallest exposure, a single desorption feature (Peak A) is present at around 180–190 K. As the exposure is increased, this peak moves to lower temperature whilst retaining the same high-temperature tail. Peak A appears to saturate between 0.5 and 1 L with further exposure leading to the appearance of a much sharper peak (Peak B) centred around 140 K. This peak continues to shift to lower temperature, though to a lesser extent than that observed for Peak A. As will be discussed, we attribute Peak A to a combination of C$_6$H$_6$ desorption from the surface of the SiO$_2$ and from within pores in the film. Peak B can be attributed to desorption of C$_6$H$_6$ from a more crowded layer formed on the surface of the SiO$_2$ film when filling of the pores is complete. At around 3 L, Peak B saturates and Peak C begins to grow at around 140 K. This peak is contributed to desorption from the first few multilayers of the solid C$_6$H$_6$ ice. It is clear that the leading edges of this peak are not coincident as would be exhibited by zero-order desorption. This can be interpreted in terms of a fractional-order desorption process. This may arise either when islands of C$_6$H$_6$ form upon the first layer or as a consequence of the inherent roughness of the underlying SiO$_2$ film. It is also interesting to note that as this peak grows, Peak B is reduced indicating that desorption of the C$_6$H$_6$ monolayer cannot occur until multilayer desorption begins. Beyond around 10 L, a single desorption peak (Peak D) dominates the TPD traces with no monolayer peak being resolved. This peak displays coincident leading edges for all exposures up to the maximum investigated (500 L), and can be attributed to zero-order desorption from bulk C$_6$H$_6$ ice.

The desorption from the lowest exposures of C$_6$H$_6$ reflects the nature of the surface/adsorbate interaction. Typically, desorption from a submonolayer coverage on a flat, well-ordered surface will yield a narrow, slightly asymmetric peak, characteristic of first-order desorption kinetics. Here, the desorption shows a broad tail extending to high temperature which reflects the rather more complicated nature of the SiO$_2$ surface. This tail can be interpreted in two ways. If the surface, rather than having one type of binding site with a characteristic desorption energy, has a distribution of binding sites, a molecule will preferentially adsorb in the sites with higher binding energies. As the coverage is increased, binding sites with progressively lower binding energies will be occupied. Desorption will occur from those sites with the lowest binding energy first, with the desorption profile reflecting the distribution of binding energies. However, whilst a small distribution of binding energies on this surface might be expected, it is unlikely that this would lead to C$_6$H$_6$ desorption over such a broad range of temperatures. An alternative explanation is that the observed tail is due

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to the presence of pores in the SiO$_2$. This behaviour, where the peak gradually shifts to lower temperature with increasing coverage, has previously been observed in the desorption of CO from a highly porous H$_2$O film deposited at 10 K (Collings et al. 2003). This was interpreted as being due to molecules bound within pores desorbing and then re-adsorbing elsewhere on the pore surface. It may then take several of these desorption, re-adsorption steps until the C$_6$H$_6$ desorbs from the SiO$_2$ substrate into the UHV chamber itself, resulting in a much broader desorption profile. In order to investigate this further, experiments were performed where the surface was first exposed to a small amount of H$_2$O. C$_6$H$_6$ was then deposited to an exposure of 0.5 L. Fig. 3 shows TPD traces for the desorption of 0.5 L of C$_6$H$_6$ from bare SiO$_2$ and SiO$_2$ that had been pre-exposed to small exposures of H$_2$O. If the broad tail of Peak A were due to a wide distribution of binding energies, then at low-coverages H$_2$O would be expected to bind preferentially at those sites with the highest binding energy. The C$_6$H$_6$ would then be adsorbed in sites with lower binding energies resulting in a narrowed desorption tail, i.e. the one that is reduced in intensity at higher desorption temperatures. However, in these experiments the tail is reduced at lower desorption temperatures with the development of a two peak profile. This indicates that Peak A is not due to a significant distribution of binding energies. As the amount of H$_2$O to which the SiO$_2$ surface is pre-exposed is increased, Peak A is reduced to progressively higher desorption temperatures. As Peak A is reduced, the C$_6$H$_6$ desorption comes to be dominated by a peak similar to Peak B in Fig. 2. These observations can be explained by considering the relative mobilities of C$_6$H$_6$ and H$_2$O. At the substrate temperature used in these experiments, C$_6$H$_6$ will be more mobile than H$_2$O upon adsorption, and will adsorb throughout the pore network when H$_2$O is not present. On the other hand, H$_2$O, upon adsorption, will be relatively immobile as a consequence of strong hydrogen bonding to SiO$_2$ surface OH groups, and will not penetrate as deeply into the pore network as C$_6$H$_6$. C$_6$H$_6$ dosed after small amounts of H$_2$O will therefore still be able to adsorb deep within the pores, with the desorption profile displaying the high-temperature tail. The stronger interaction between H$_2$O and the SiO$_2$ surface means that pre-deposited H$_2$O cannot be displaced by C$_6$H$_6$. The total number of sites available for C$_6$H$_6$ adsorption

![Figure 2. TPD traces for C$_6$H$_6$ desorption from amorphous SiO$_2$. C$_6$H$_6$ exposures displayed are (a) 0.1, 0.2, 0.5, 0.7, 0.8 and 1 L, (b) 2, 3, 4 and 5 L and (c) 10, 20 and 50 L.](image)

![Figure 3. TPD traces resulting from the desorption of 0.5 L C$_6$H$_6$ from (i) bare amorphous SiO$_2$ and SiO$_2$ that had been exposed to, (ii) 0.5 L, (iii) 3 L and (iv) 5 L H$_2$O.](image)
within the pore network will therefore be reduced, particularly near
the surface, resulting in the observed reduction in the desorption
profile from lower temperatures. Exposure to larger amounts of
H\textsubscript{2}O will block the pathways to the pore network resulting in C\textsubscript{6}H\textsubscript{6}
adsorbing preferentially on the parts of the SiO\textsubscript{2} film that remain
exposed, rather than on the surface of the pre-adsorbed H\textsubscript{2}O. This
gives rise to the appearance, at higher water pre-exposures, of Peak
B which was previously attributed to the desorption of C\textsubscript{6}H\textsubscript{6} from
the surface of the SiO\textsubscript{2} film. The non-wetting behaviour of C\textsubscript{6}H\textsubscript{6}
on H\textsubscript{2}O has also been observed in experiments where C\textsubscript{6}H\textsubscript{6} was
adsorbed on a thick layer of H\textsubscript{2}O sufficient to completely cover
the polished stainless steel disc prior to the deposition of the SiO\textsubscript{2}
from a comparison with initial TPD experiments performed with
the impact of surface roughness and the presence of pores comes
within the pore network prior to desorption. Further evidence for
the coefficient, which can be expressed as

\[ \text{r}_{\text{des}} = -\frac{\text{d}N}{\text{d}t} = k_{\text{des}}N^n, \]

where \( N \) is the surface concentration of the adsorbed species
in molecules cm\textsuperscript{-2}, \( n \) is the desorption order and \( k_{\text{des}} \) is the rate
coefficient, which can be expressed as

\[ k_{\text{des}} = \nu \exp\left(-\frac{E_{\text{des}}}{k_BT}\right), \]

where \( \nu \) is the pre-exponential factor, \( E_{\text{des}} \) is the desorption energy
in Joules and \( T \) is the surface temperature in kelvin. The units of
\( \nu \) depend on the order, being molecules cm\textsuperscript{-2} s\textsuperscript{-1} and s\textsuperscript{-1} for \( n \) =
0 and 1, respectively. If the temperature ramp is linear, as was
the case in these TPD experiments, the rate equation can be expressed as
(Attard & Barnes 1998)

\[ \frac{\text{d}N}{\text{d}T} = \left(N^n/\nu/\beta\right) \exp\left(-E_{\text{des}}/k_BT\right). \]

where \( \beta \) is the heating rate in K s\textsuperscript{-1}. If the pumping speed is
sufficiently high, as expected in our UHV system, the signal from
the QMS is directly proportional to \( \text{d}N/\text{d}T \).

It is clear that in order to obtain the kinetic parameters for
a particular TPD trace, the surface concentration of adsorbed
molecules is required. We are able to obtain approximate sur-
face concentrations by the application of a simple collision theory
(Atkins & de Paula 2002), in which the collision frequency, \( Z \) in
molecules m\textsuperscript{-2} s\textsuperscript{-1}, for molecules striking a surface can be expressed as

\[ Z = \frac{P}{(2\pi mk_BT)^{1/2}}, \]

where \( P \) is the partial pressure of the species being deposited, \( m \) is
the molecular mass in kg and \( T \) is the gas temperature (i.e. 298 K).
Multiplication by the dosing time yields the surface concentration
assuming a sticking coefficient of unity. The pressure reading from
the ion gauge must be scaled by the appropriate sensitivity factor,
6 in the case of benzene (Waddil & Kesmodel 1985). Small vari-
ations in the dosing conditions can impact on the resulting surface
concentration. For this reason, the highest dose of 500 L was taken
to be exactly 500 L. The TPD trace for 500 L was integrated to ob-
tain the TPD yield. Actual values were then obtained for the other
doses by comparison of TPD yield with that obtained for 500 L.
Fig. 4 shows how the TPD yield varies with increasing dose. It is
clear that there are significant variations at the lowest dose, with
actual doses being significantly smaller than expected. Comparison
with the highest dose, expected to be the most accurate, is therefore
required.

Kinetic modelling was performed using the Chemical Kinetics
Simulator (CKS) package\textsuperscript{2} (Houle & Hinsberg 1995) to stochasti-
cally integrate the differential equations describing the desorption
process. We have used this approach previously in the analysis of
the desorption of pure water ice (Fraser et al. 2001) and of CO from
a water ice matrix (Collings et al. 2003). A simple mechanism for
the desorption process was constructed:

\[ \text{C}_6\text{H}_6(\text{ads}) \rightarrow \text{C}_6\text{H}_6(\text{g}), \]

(5)

\[ \text{C}_6\text{H}_6(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{pumped}), \]

(6)

where the concentration of C\textsubscript{6}H\textsubscript{6} (ads) is equivalent to \( N \), the
surface concentration of adsorbed molecules. Equation (5) describes
the desorption step and equation (6) describes the removal of ben-
zene from the UHV chamber by the pumping system, which is
proportional to the concentration of C\textsubscript{6}H\textsubscript{6} (g). With the knowledge of
the C\textsubscript{6}H\textsubscript{6} surface concentration, the three variables that remain

\textsuperscript{2} Chemical Kinetics Simulator (cks), version 1.0, IBM Almaden Research
Center, 650 Harry Road, Mailstop ZWX1D1, San Jose, CA, USA. Further
information may be obtained from the cks web site at http://www.almaden.
ibm.com/st/msim/cksindex.html.
unknown are the pre-exponential factor for the desorption step, the desorption energy and the pre-exponential factor for the pumping step, hereafter referred to as the pumping speed. Using this model, TPD spectra were simulated for the case of multilayer desorption for raw exposures of 10, 20, 50, 100, 200 and 500 L. Zero-order desorption kinetics (i.e. n = 0) were assumed given the good coincidence of the leading edges. \( \nu \), \( E_{\text{des}} \) and the pumping speed were systematically varied and resulting simulated traces were compared with the experimental results through the use of an appropriate scaling factor. Fig. 5 shows a comparison between the experimental and simulated TPD traces for large exposures of C\(_6\)H\(_6\). The experimental data are best simulated with a \( \nu \) value of \( 10^{2.7\pm1.0} \) molecules cm\(^{-2}\) s\(^{-1}\) and an \( E_{\text{des}}/k_B \) value of 5600 ± 100 K (46.6 ± 0.8 kJ mol\(^{-1}\)). It is clear that these kinetic parameters describe the experimental TPD traces well over a large exposure range. There is some small deviation from the experimental data for the lowest exposure simulations, which likely results from the desorption order becoming slightly non-zero. This is consistent with the clearly fractional-order desorption kinetics observed at exposures of around 10 L, evidenced by non-coincident leading edges. With our approach, it is not possible to obtain reliable results from simulations of fractional-order desorption due to the introduction of another unknown variable. The value for \( E_{\text{des}} \) is in good agreement with reported values for the sublimation energy of condensed C\(_6\)H\(_6\), which generally lie in the range of 44–47 kJ mol\(^{-1}\) (Chickos & Acree 2002) and with previously reported values for the desorption of multilayers of C\(_6\)H\(_6\) from metal surfaces (see, e.g., Jakob & Menzel 1989).

It is clear that the desorption of C\(_6\)H\(_6\) is complicated by the presence of pores, which has a large impact on the desorption profile. A combination of further experimental work and more detailed analysis will be required to fully understand the effect that this porosity has on the desorption process. This is discussed in more detail in the Conclusions section of this paper. However, it is possible to obtain a general insight by modelling the desorption using first-order desorption kinetics. In this approximation, the steps involved in escaping from the pores are combined into one simple desorption step. Whilst this clearly oversimplifies the desorption process, it is useful in providing an indication of kinetic parameters. Two approaches were used to observe the trends in the desorption energy, \( E_{\text{des}} \), and the pre-exponential factor, \( \nu \), as a function of C\(_6\)H\(_6\) exposure. In the first instance, the TPD traces were analysed by assuming a pre-exponential factor of \( 10^{13} \) s\(^{-1}\), as in the frequently invoked Redhead method (Attard & Barnes 1998). Rather than using the Redhead expression directly, the TPD traces were simulated using the kinetic modelling procedure described above to obtain the desorption energy. Our approach was to fit the leading edge of the desorption trace, corresponding to simple first-order desorption. The presence of the tail due to desorption from pores makes the determination of the surface concentration minus the tail component difficult. However, by using the pumping speed and the scaling factor obtained during the multilayer analysis, the only unknown variables were \( E_{\text{des}} \) and the surface concentration. These were then systematically varied to obtain the best values. This analysis reveals a wide range of values for \( E_{\text{des}}/k_B \), decreasing from 6250 K (52 kJ mol\(^{-1}\)) at the lowest exposure to 4800 K (39.5 kJ mol\(^{-1}\)) at exposures of around 1 L. The obtained \( E_{\text{des}}/k_B \) values are shown in Table 1.

Given the complicated nature of the surface, it is highly probable that the assumption that \( \nu \) does not vary with coverage will not hold. For this reason, an independent method was used to obtain values for \( E_{\text{des}} \). This method has been described previously (Bolina et al. 2005), and is derived by considering that the QMS signal, \( I(T) \), is directly proportional to the desorption rate:

\[
I(T) \propto N^\nu \exp(-E_{\text{des}}/k_BT),
\]

which can be rearranged to yield

\[
\ln[I(T)] \propto n \ln[\nu] + n \ln[N] - E_{\text{des}}/k_BT.
\]

Thus for a given TPD experiment, a plot of \( \ln[I(T)] - n \ln[N] \) versus \( 1/T \) for the leading edge will have a gradient of \(-E_{\text{des}}/k_B\), from which the desorption energy can be obtained. The value for \( E_{\text{des}}/k_B \) resulting from this analysis is 5300 ± 200 K (44 ± 2 kJ mol\(^{-1}\)). In this analysis, this value is independent of coverage in the submonolayer regime. The uncertainty on this value is larger than that obtained for multilayer desorption because of the significantly lower signal-to-noise ratio in the low-coverage regime. This value was then used to obtain corresponding \( \nu \) values using appropriate kinetic modelling to reproduce the leading edge of the desorption traces. The values of \( \nu \) that were obtained ranged from \( 4 \times 10^{10} \) s\(^{-1}\) at the lowest exposure to \( 7 \times 10^{14} \) s\(^{-1}\) at exposures of around 1 L. The obtained \( \nu \) values are shown in Table 1. Fig. 6 shows a comparison between (a) the experimental TPD traces and

![Figure 5](http://mnras.oxfordjournals.org/)

**Figure 5.** (a) TPD traces for C\(_6\)H\(_6\) multilayer desorption. Exposures are 10, 20, 50, 100, 200 and 500 L. (b) Shows the simulated TPD traces that result from a zero-order kinetic model with \( E_{\text{des}}/k_B = 5600 \) K and \( \nu = 5 \times 10^{20} \) molecules cm\(^{-2}\) s\(^{-1}\).
Table 1. Kinetic parameters obtained for the desorption of C₆H₆ from the SiO₂ surface. The surface concentrations are those that best reproduce the experimental data based on the pumping speed and scaling factor obtained from the multilayer analysis. Both $E_{\text{des}}$ values for a fixed value of $v = 10^{13}$ s⁻¹ (the Redhead model) and $v$ values obtained for a fixed $E_{\text{des}}/k_B$ value of 5300 K (obtained from the leading edge analysis) are shown.

<table>
<thead>
<tr>
<th>C₆H₆ exposure/L</th>
<th>C₆H₆ surface concentration/molecules cm⁻² (excluding pore contribution)</th>
<th>$\nu$ des $k_B^{-1}$/K ($v = 1 \times 10^{13}$ s⁻¹)</th>
<th>$\nu$/s⁻¹ ($E_{\text{des}}/k_B = 5300$ K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>$(1.0 \pm 0.5) \times 10^{12}$</td>
<td>6250</td>
<td>$4.0 \times 10^{10}$</td>
</tr>
<tr>
<td>0.2</td>
<td>$(2.0 \pm 0.5) \times 10^{12}$</td>
<td>5890</td>
<td>$3.0 \times 10^{11}$</td>
</tr>
<tr>
<td>0.5</td>
<td>$(4.0 \pm 0.5) \times 10^{12}$</td>
<td>5290</td>
<td>$1.1 \times 10^{13}$</td>
</tr>
<tr>
<td>0.7</td>
<td>$(7.0 \pm 0.5) \times 10^{12}$</td>
<td>4990</td>
<td>$1.0 \times 10^{14}$</td>
</tr>
<tr>
<td>0.8</td>
<td>$(9.5 \pm 0.5) \times 10^{12}$</td>
<td>4930</td>
<td>$1.5 \times 10^{14}$</td>
</tr>
<tr>
<td>1</td>
<td>$(1.9 \pm 0.5) \times 10^{13}$</td>
<td>4750</td>
<td>$7.0 \times 10^{14}$</td>
</tr>
</tbody>
</table>

Figure 6. (a) TPD traces for the desorption of C₆H₆ from amorphous SiO₂. Exposures are 0.1, 0.2, 0.5, 0.7, 0.8 and 1 L. (b) Shows the simulated TPD traces first-order kinetic modelling. The fixed value of $E_{\text{des}}/k_B = 5300$ K was obtained from leading edge analysis of the experimental traces.

(b) those obtained from kinetic modelling. The small values of $\nu$ at low coverages are unphysical, and demonstrate the limitations of modelling pore escape as a one-step process. At larger coverages, $\nu$ increases to values that would be expected for simple first-order desorption. The large increase in $\nu$ in going from 0.8 to 1 L is likely related to the restructuring of the monolayer observed as Peak B in Fig. 2. Such restructuring, which occurs as a result of repulsive interactions between C₆H₆ molecules as the monolayer becomes more crowded, has been observed previously in studies of C₆H₆ adsorption on single crystal surfaces. Waddill & Kesmodel (1985) observed the appearance of a TPD peak at lower temperature as the C₆H₆ coverage on both Pd(111) and Pd(100) was increased towards monolayer saturation and attributed this to repulsive interactions. Repulsive interactions can have a significant effect on the observed desorption energy of a molecule, in the case of C₆H₆ on Pd(111). Monte Carlo simulations (Tysoe et al. 1993) have shown the repulsion energy to be 6.5 kJ mol⁻¹ (780 K). Whilst in these experiments the C₆H₆ was chemisorbed on the substrate resulting in significantly higher desorption energies than observed in our experiment, where the C₆H₆ is more weakly bound, there is no reason to assume that the repulsive interaction would be significantly different. In some cases, for example on polycrystalline Ag (Bahr & Kempter 2007), the increase in intermolecular repulsion has been shown to result in the formation of a second layer where the C₆H₆ molecules are adsorbed with their plane tilted with respect to the substrate. This reduces the overlap between the C₆H₆ $\pi$ orbitals and substrate orbitals, resulting in a decrease in desorption energy.

On SiO₂, C₆H₆ is likely to form weak hydrogen bonds with OH groups on the hydroxylated surface as has been observed in gas-phase C₆H₆–H₂O clusters (Suzuki et al. 1992). However, we have no specific evidence from these experiments to support this. The roughness of the surface means that C₆H₆ will not be bound in one particular orientation, rather it will adopt a distribution of orientations that optimizes the binding energy. As the coverage is increased, repulsive interactions increase, resulting in some restructuring of the monolayer. This leads to a decreased desorption energy and an increasing pre-exponential factor.

4 ASTROPHYSICAL IMPLICATIONS

The experiments outlined here demonstrate the complexity of the interaction between molecules and dust grain surfaces. Surface roughness and the presence of pores have a large impact on the desorption of C₆H₆ from such surfaces, particularly at low coverages. The desorption kinetics are affected by interactions between adjacent C₆H₆ molecules, the heterogeneous nature of the SiO₂ surface and the presence of pores within the film. These results indicate that the nature of C₆H₆ adsorption is likely to be sensitive to the astrophysical environment in which the grain is situated.

We first consider grains in the dense ISM where C₆H₆ abundance is expected to be relatively low due to destruction by interaction with UV photons. The distribution of adsorbed C₆H₆ will depend on the C₆H₆ mobility, and therefore the grain temperature. As grains in the ISM tend to be at the lowest temperatures, C₆H₆ mobility will be reduced making it unlikely that C₆H₆ molecules will penetrate as far into the pore network as they would at high temperatures when mobility is much higher. The TPD experiments described here probe the high-mobility regime as molecules will become mobile...
during warm-up. This same migration due to increased mobility will also occur as grains warm, though the extent to which molecules penetrate the pore network will depend on the presence of any other species that may block access to the pores. The relative mobilities of these species will also be important as observed through the experiments where the surface was first exposed to H$_2$O. Such a situation would occur in the dense ISM where significant amounts of H$_2$O ice tend to be adsorbed on to grain surfaces. Under these circumstances, mobile C$_6$H$_6$ is unable to penetrate the pore network if the H$_2$O has previously been sufficiently mobile to penetrate, or there is sufficient H$_2$O to block access to the pores. The resulting desorption would then be dominated by the kinetics observed at exposures of around 1 L in these experiments, where intermolecular repulsion plays an important role.

This behaviour will also have important consequences for the return of C$_6$H$_6$ to the gas phase following formation in protostellar discs. The efficiency of this process will depend on the residence time of C$_6$H$_6$ on the grain surface which will in turn depend on the grain temperature and the C$_6$H$_6$–grain interaction. However, whilst we expect the binding energy between C$_6$H$_6$ and a silicate grain surface to be fairly uniform across the surface, this will be modified by the presence of any pre-adsorbed species. If the grain temperature is sufficiently low to allow formation of a monolayer of C$_6$H$_6$, or significant H$_2$O ice is present then intermolecular repulsion will lead to a more efficient return of C$_6$H$_6$ to the gas phase than would be expected from a simple consideration of grain temperature and binding energy alone. It is also important to note that carbonaceous grains are likely to dominate in such an environment. The interaction between C$_6$H$_6$ and, for example, a graphitic surface will be significantly different, though the arguments presented here relating to intermolecular repulsion and the presence of adsorbed H$_2$O would be expected to hold.

Whilst absorption in pores has a strong effect on the experimental desorption profiles obtained with a heating rate of 0.1 K s$^{-1}$, it is likely that this is not the case at astronomical heating rates. We are currently developing a simple kinetic model to describe the desorption from pores in terms of the mechanism described previously. This model will be based on our previous model for the desorption of H$_2$O multilayers from adsorbed bulk C$_6$H$_6$ ice, which displays simple zero-order kinetics with a desorption energy of 5600 ± 100 K and a pre-exponential factor of 10$^{29.7±1.0}$ molecules cm$^{-2}$ s$^{-1}$, in good agreement with previous studies. However, the desorption of small amounts of C$_6$H$_6$ from the SiO$_2$ surface demonstrates the effect the underlying surface can have on the desorption process. The presence of pores within the SiO$_2$ and a rough surface, along with the effect of repulsive interactions between C$_6$H$_6$ molecules, leads to complicated desorption kinetics within the first few C$_6$H$_6$ layers. At low coverages, the desorption of C$_6$H$_6$ molecules from within pores has an important influence on the desorption profile. C$_6$H$_6$ molecules bound within pores are likely to be re-adsorbed several times before desorbing from the surface. This leads to a high-temperature tail being superimposed on the peak related to desorption from the SiO$_2$ surface. Increasing C$_6$H$_6$ coverage towards monolayer saturation leads to an increased repulsion between C$_6$H$_6$ molecules, resulting in a decreased surface binding energy and an increased pre-exponential factor. It is clear that in order to gain a better understanding of the adsorption on grain surfaces, the coverage dependencies of the kinetic parameters need to be isolated. In particular, our kinetic model needs to be modified to specifically include a description of the desorption from pores. Such a model would include both re-adsorption and gas-phase diffusion steps in order to isolate the kinetic parameters for the desorption process. Further insights into the desorption process will be aided by experiments performed on a flat, crystalline SiO$_2$ surface with no pores, which will help to identify the morphological effects of the grain surface on desorption kinetics. This work has demonstrated the sensitivity of the desorption process to both physical and chemical conditions in the local environment.

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