Fundamental data on the desorption of pure interstellar ices

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ABSTRACT
The desorption of molecular ices from grain surfaces is important in a number of astrophysical environments including dense molecular clouds, cometary nuclei and the surfaces and atmospheres of some planets. With this in mind, we have performed a detailed investigation of the desorption of pure water, pure methanol and pure ammonia ices from a model dust-grain surface. We have used these results to determine the desorption energy, order of desorption and the pre-exponential factor for the desorption of these molecular ices from our model surface. We find good agreement between our desorption energies and those determined previously; however, our values for the desorption orders, and hence also the pre-exponential factors, are different to those reported previously. The kinetic parameters derived from our data have been used to model desorption on time-scales relevant to astrophysical processes and to calculate molecular residence times, given in terms of population half-life as a function of temperature. These results show the importance of laboratory data for the understanding of astronomical situations whereby icy mantles are warmed by nearby stars and by other dynamical events.

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

1 INTRODUCTION
Recent work (e.g. Collings et al. 2004; Viti et al. 2004) has shown the importance of using experimentally determined kinetic parameters to describe the desorption of icy mantles from grain surfaces. Desorption processes have been found to be particularly important in hot-core regions (Williams 1998; Viti et al. 2004). Hot cores are small, dense, relatively warm, optically thick and transient objects detected in the vicinity of newly formed massive stars. Hot cores exhibit a range of molecular species due to the evaporation of processed ice, formed during the star formation process. As well as giving an understanding of the chemistry of hot cores (Viti et al. 2004; Brown et al. 2006), data of this type can also be used to determine molecular residence times of ices on grain surfaces as a function of temperature. These residence times are useful as they provide a measure of the ice stability with respect to sublimation. Understanding ice sublimation is important in a number of astrophysical environments including dense molecular clouds, cometary nuclei and the surfaces and atmospheres of planets. With this in mind, we have undertaken a detailed study of the adsorption and desorption of pure water (Bolina, Wolff & Brown 2005a), pure methanol (Bolina, Wolff & Brown 2005b) and pure ammonia (Bolina & Brown 2005) ices from a model dust-grain surface and the results of these experiments, and resulting astrophysical simulations, are described here.

Water (H₂O) is the most abundant species in molecular ices in dense interstellar regions (Whittet 1993, 2003; Ehrenfreund & Schutte 2000) and hence it plays a significant role in the chemistry of the interstellar medium (ISM). A clear understanding of the adsorption and desorption of H₂O is therefore crucial in understanding gas–grain interactions and, in turn, the chemistry of the ISM. H₂O exists in a number of different forms on grain surfaces, including high- and low-density amorphous ice and crystalline ice (Jenniskens & Blake 1994, 1996; Fraser et al. 2001), and the physical properties of the ice are dictated by its structure. Furthermore, it has been shown that for mixed ices that contain H₂O, the desorption of all species in the ice is controlled by the behaviour of the H₂O (Collings et al. 2004).

Methanol (CH₃OH) is also found in the ISM, frozen out on the surface of dust grains (Gibb et al. 2004) and is one of the more commonly detected species in molecular ices. It has been found to have an abundance of between 5 and 50 per cent of that of H₂O (Sandford & Allamandola 1993; Pontoppidan et al. 2003; Pontoppidan, van Dishoeck & Dartois 2004). CH₃OH influences both the chemical and physical properties of interstellar ices and hence affects their sublimation. As for H₂O, it is therefore important to have accurate kinetic parameters that describe the desorption of CH₃OH from grain surfaces.

Ammonia (NH₃) is also an important molecule in the ISM. Dust grains can provide an opportunity for freeze-out of NH₃ at low temperatures and are also implicated in its formation by the surface catalysed hydrogenation of N atoms. The importance of NH₃ in the ISM has been demonstrated by the observation of NH₃ in interstellar ices (Whittet 1993), where it has been found to have an abundance of around 5–30 per cent relative to water ice (Whittet et al. 1996; Lacy et al. 1998; Chiar et al. 2000; Dartois & d’Hendecourt 2001; Gibb,
NH₃ is also an important carrier of nitrogen in the ISM and is involved in many reactions involving nitrogen chemistry (Tielens & Hagen 1982; Nejad, Williams & Charnley 1990). Hence a complete understanding of the interaction of NH₃ with dust-grain surfaces, and its sublimation from those surfaces, is required to accurately model the chemistry of the ISM.

Previous studies of the desorption of H₂O ice from a CsI surface determined surface binding energies from spectroscopic data (Sandford & Allamandola 1988). The studies found that the binding energy of H₂O on H₂O ice was 4815 ± 5007 ± 50 K for unannealed and annealed ice samples, respectively. These studies assumed that the H₂O desorption obeyed first-order kinetics. A more recent study (Fraser et al. 2001) used a direct experimental method to show that H₂O ice desorption from a Au surface obeys zero-order kinetics. This study found that the H₂O had a surface binding energy of 5773 ± 60 K and a pre-exponential factor of 10^{14±2} molecules m⁻² s⁻¹. The discrepancy between these previous studies has important implications for our understanding of the desorption of H₂O ice from grain surfaces and hence further studies are essential.

There has been only one previous reported investigation of the binding energies of CH₃OH and NH₃ in model interstellar ices (Sandford & Allamandola 1993). Spectroscopic data were used to give a binding energy for CH₃OH on CH₃OH ice of 4235 ± 15 K and for NH₃ on NH₃ ice of 3075 ± 25 K. Both CH₃OH and NH₃ were assumed to obey first-order desorption kinetics. A recent study (Fraser et al. 2001) used a direct experimental method to show that CH₃OH ice desorption from a Au surface obeys zero-order kinetics. This study found that the CH₃OH had a surface binding energy of 3535 ± 2 K and a pre-exponential factor of 10^{14±2} molecules m⁻² s⁻¹. The discrepancy between these previous studies has important implications for our understanding of the desorption of CH₃OH and NH₃ from grain surfaces under astrophysical conditions and to determine the molecular residence times of the pure ices on the grain surfaces as a function of temperature.

### 3 RESULTS AND DISCUSSION

#### 3.1 Experimental results

Fig. 1 shows example TPD spectra recorded for the desorption of increasing thicknesses of pure H₂O ice from an HOPG surface (Bolina et al. 2005a). As already discussed, exposure is measured in L_m, which is the molecular area of a monolayer of H₂O used in the experiments to model a dust grain is highly oriented pyrolytic graphite (HOPG). HOPG, and other carbon-based surfaces, can be considered suitable analogues of dust grains and have previously been used in investigations of H₂ formation on dust-grain surfaces (Katz et al. 1999; Pirronello et al. 1999; Perry et al. 2002; Perry & Price 2003). This study is the first to perform simulations using kinetic parameters derived directly from experimental data on grain-like surfaces and comparisons with previous data allow us to determine whether the nature of the surface is important in determining desorption from dust grains. Note that the nature of the surface is likely to be more important for thin ices than for thick ices and also more important for strongly bound molecular species than for weakly bound species.
of monolayer CH$_3$OH from the HOPG surface is observed. With increasing exposure, the desorption of CH$_3$OH multilayers is seen and at very high exposures a phase transition, that occurs as a result of the TPD heating process, leads to the observation of a high-temperature shoulder on the TPD spectra. This shoulder is observed due to the formation of crystalline CH$_3$OH (Bolina et al. 2005b).

The desorption of pure NH$_3$ ice from the HOPG surface has also been investigated using TPD (fig. 3, Bolina & Brown 2005). Two desorption features are seen in the spectra as a function of increasing exposure. An initial, low-temperature, peak observed following low doses of NH$_3$ on to the HOPG surface is assigned to the desorption of monolayers of NH$_3$. A larger, high-temperature, peak which increases in temperature with increasing NH$_3$ coverage is assigned to the formation of crystalline CH$_3$OH (Bolina et al. 2005b).

TPD spectra are described by the Polanyi–Wigner equation (de Jong & Niemantsverdriet 1990):

$$r_{\text{des}} = \frac{d\theta}{dt} = v_{\text{a}}\theta^n \exp \left( -\frac{E_{\text{des}}}{RT} \right),$$

(1)

where $r_{\text{des}}$ is the rate of desorption, $v_{\text{a}}$ is the pre-exponential factor for the desorption process of order $n$, $\theta$ is the surface coverage, $E_{\text{des}}$ is the desorption energy, $R$ is the gas constant and $T$ is the surface temperature. The kinetic parameters, $v_{\text{a}}$, $E_{\text{des}}$ and $n$, uniquely describe the desorption of a particular species from a surface and can be extracted from experimental TPD spectra using the methods described previously (Bolina et al. 2005a,b; Bolina & Brown 2005). Kinetic parameters obtained for the desorption of pure ices from HOPG are presented in Table 1 (Bolina et al. 2005a,b; Bolina & Brown 2005). To allow a direct comparison with previous data (Sandford & Allamandola 1988, 1993; Fraser et al. 2001), desorption energies are given in temperature units (K). Note that, due to the conversion of the H$_2$O ice from the amorphous to the crystalline phase during the TPD heating process, the kinetic parameters for H$_2$O given in Table 1 are for the desorption of crystalline H$_2$O. To give an indication of the accuracy of these kinetic parameters, Fig. 2 shows a comparison of the experimental data recorded for NH$_3$ desorption and the simulated TPD spectra for NH$_3$ that result from inserting the kinetic parameters in Table 1 into the Polanyi–Wigner equation. It can clearly be seen that there is good agreement between the desorption energies obtained here and those determined previously. For H$_2$O we report a desorption energy of 4799 ± 96 K for crystalline H$_2$O (peak B in Fig. 1), while Fraser et al. (2001) obtained a desorption energy of 5773 ± 60 K and Sandford & Allamandola (1988) reported a binding energy for H$_2$O on annealed H$_2$O ice of 5070 ± 50 K. For CH$_3$OH, our desorption

Table 1. Table showing the kinetic parameters previously derived for the desorption of pure H$_2$O, pure CH$_3$OH and pure NH$_3$ ices from an HOPG surface (Bolina et al. 2005a,b; Bolina & Brown 2005). These parameters have been used to simulate the desorption of pure molecular ices under astrophysical conditions.

<table>
<thead>
<tr>
<th></th>
<th>Desorption order $n$</th>
<th>Desorption energy (K)</th>
<th>Pre-exponential factor$^a$ (molec m$^{-2}$ s$^{-1}$)</th>
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<tr>
<td>H$_2$O</td>
<td>0.26 ± 0.02</td>
<td>4799 ± 96</td>
<td>1 × 10$^{7.5 \pm 1}$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.25 ± 0.05</td>
<td>2790 ± 144</td>
<td>8 ± 3 × 10$^{25}$</td>
</tr>
<tr>
<td>CH$_3$OH multilayer</td>
<td>0.35 ± 0.21</td>
<td>4931 ± 98</td>
<td>6 × 10$^{25 \pm 1}$</td>
</tr>
<tr>
<td>CH$_3$OH monolayer</td>
<td>1.23 ± 0.14</td>
<td>5773 ± 95</td>
<td>9 × 10$^{2.3} \pm 1$</td>
</tr>
</tbody>
</table>

$^a$The units given for the pre-exponential factors for H$_2$O, NH$_3$ and CH$_3$OH multilayers are those for zero-order desorption, despite the fractional desorption order obtained from the data; $^b$the units given for the pre-exponential factor for monolayer CH$_3$OH are those for first-order desorption (s$^{-1}$) despite the fractional desorption order obtained from the data.

Figure 1. TPD spectra recorded following increasing exposures of H$_2$O on an HOPG surface initially at 90 K. Panel (i) shows spectra recorded following doses of 0.04, 0.06, 0.1, 0.2, 0.3, 0.4, 1 and 2 L$_{\text{H}_2\text{O}}$ of H$_2$O; panel (ii) shows spectra recorded following doses of 2, 3, 7, 10 and 15 L$_{\text{H}_2\text{O}}$ of H$_2$O and panel (iii) shows spectra recorded following doses of 15, 20, 50, 100 and 275 L$_{\text{H}_2\text{O}}$ of H$_2$O. The rate of desorption in each graph is given in arbitrary units. Adapted with permission from J. Phys. Chem. B, 2005, 109, 16836. Copyright 2005 American Chemical Society.
energy of 4931 ± 98 K is slightly higher than that of 4235 ± 25 K obtained by Sandford & Allamandola (1993). Finally, for NH3 our desorption energy of 2790 ± 144 K is slightly lower than that of 3075 ± 25 K reported previously (Sandford & Allamandola 1993).

It is likely that the small difference in the desorption energies derived in the different experiments is due to the values of desorption order determined for the systems by the three groups, as discussed below.

Whilst the desorption energies obtained in our study and the previous studies are similar, the orders of desorption are rather different. Sandford & Allamandola (1988, 1993) assumed first-order desorption for H2O, CH3OH and NH3, while Fraser et al. (2001) found that H2O showed zero-order desorption kinetics. Our results, shown in Table 1, are closer to those of Fraser et al. (2001) and reveal a fractional desorption order. It is useful at this point to discuss the physical significance of the desorption order. H2O, CH3OH and NH3 are all bound weakly to the surface and form physisorbed multilayers of molecular ices. Confirmation of this comes from the low values of desorption energy obtained for these species, here and in previous investigations, which is characteristic of physisorption. A feature of multilayer formation is that the adsorption of one molecule does not affect the adsorption or desorption of other molecules on the surface – that is the rate of desorption is independent of the amount (coverage) of species on the surface. Hence, as shown in equation (1), the species shows zero-order desorption. The previous assumption of Sandford & Allamandola (1988, 1993) that H2O, CH3OH and NH3 obey first-order desorption kinetics is therefore incorrect. It is also clear from looking at the TPD spectra in Fig. 1 (Bolina et al. 2005a) that H2O desorption does not show perfect zero-order desorption kinetics. A feature of zero-order desorption is that the TPD spectra share leading edges, which the spectra in Fig. 1 do not. TPD spectra recorded for CH3OH and NH3 desorption from HOPG also do not share leading edges and therefore again do not show zero-order desorption (Bolina & Brown 2005; Bolina et al. 2005b). Instead, as seen in Table 1, fractional desorption orders were obtained for H2O, CH3OH and NH3 desorption from the HOPG surface. This fractional desorption order can be attributed to the hydrogen bonding that exists in the molecular ices which ensures that the desorption of one molecule is not independent of the desorption of other molecules. Hydrogen-bonded systems have previously been shown to exhibit fractional-order desorption kinetics (Wu, Truong & Goodman 1993; Nishimura, Gibbons & Tro 1998) and infrared data recorded for H2O, CH3OH and NH3 adsorbed on HOPG (Bolina et al. 2005a,b; Bolina & Brown 2005) also provide evidence for the existence of hydrogen bonding in these pure ice systems. Due to the differences in desorption order between our data and previous data (Sandford & Allamandola 1988, 1993; Fraser et al. 2001), the pre-exponential factors given in Table 1 are also different to those reported previously.

### 3.2 Desorption under astrophysical conditions

The desorption temperatures for pure H2O, CH3OH and NH3 ices recorded in our experiments (Bolina et al. 2005a,b; Bolina & Brown 2005), and shown for H2O in Fig. 1, cannot be used directly in astrochemical models. This is because desorption is a non-equilibrium process and hence the temperature at which it occurs is influenced by both the rate of heating of the ice and, for non-first-order processes such as multilayer desorption, by the thickness of the ice. During star formation, the rate at which the temperature rises is dependent on the mass of the star (Viti et al. 2004). Hence, high-mass stars will have a faster heating rate than low-mass stars. It has been shown that a dust grain in a hot core is typically heated at a rate of the order of 1 K century$^{-1}$ (Viti & Williams 1999; Viti et al. 2004), clearly impractical in laboratory studies.

To determine the extent to which desorption temperatures vary between laboratory and astrophysical conditions we have simulated the desorption of pure H2O, CH3OH and NH3 ices from an HOPG surface at a range of different heating rates. The simulations use a method developed by Collings et al. (2004) and involve calculating the rate of change of gas phase concentration of the desorbing species as a function of temperature. In this way, the simulations produce traces which resemble typical TPD ‘peaks’. Constructing the simulation is a two-step process involving the rate of desorption from the surface and the rate of pumping of the gas phase species out of the system. This can be expressed as

$$\frac{d\text{[ice]}}{dt} = k_d \theta^n - k_p \text{[ice]},$$

(2)

where $\text{[ice]}$ is the gas phase concentration of the desorbing molecular ice, $\theta$ is the surface coverage, $n$ is the order of the desorption, $k_p$ is the rate of pumping of the gas phase species and $k_d$ is the rate constant for desorption, described in equation (3).

$$k_d = v_\theta \exp \left(-\frac{E_{des}}{RT}\right),$$

(3)

The pumping rate used in each simulated spectrum is scaled in proportion to the heating rate, with a heating rate of 10 K s$^{-1}$ having a pumping rate of 300 s$^{-1}$ (the experimentally measured pumping...
The results shown in Fig. 3 can be directly compared to a previous simulation of H_2O desorption from a Au substrate by Collings et al. (2004). Both studies show good agreement in the desorption temperature of H_2O ice at astrophysically relevant heating rates, despite the fact that they were performed on different surfaces. At a heating rate of 1 K century^{-1}, desorption temperatures of 103 and 105 K are evaluated by this study and by Collings et al. (2004), respectively. This suggests that the desorption temperature of H_2O ice at astrophysically relevant heating rates is independent of the substrate used to model the grain surface. This is not surprising since H_2O is physisorbed on both the Au and the HOPG surface, and hence the surface itself does not play a large role in the adsorption. This is important since the exact nature of dust grains in the ISM is still the subject of some debate. It is not possible to compare the results shown in Fig. 3 for CH_3OH and NH_3 desorption with other work as there are no previous simulations of this type for the desorption of pure CH_3OH or pure NH_3 ices under astrophysical conditions.

The simulations presented in Fig. 3 can also be adjusted to more astrophysically relevant environments. In the ISM, there are no pumping effects and so the simulations shown in Fig. 3 have also been run ignoring the effect of pumping. In this case, the gas phase concentration of a species is simply equal to the total number of molecules desorbed from the grain surface. As there is no pumping mechanism in this model, the gas phase concentration of each species saturates when all of the molecules have desorbed from the surface. Fig. 4 shows the gas phase concentration of NH_3, H_2O and CH_3OH multilayers desorbing from a model grain surface as a function of heating rate and temperature. The simulations use the parameters shown in Table 1 and heating rates from 1 K century^{-1} to 10 K s^{-1}. The simulations were run for an initial surface coverage of 9.5 \times 10^{21} \text{ molec m}^{-2}, hence the cumulative gas phase desorption saturates at this value. Note that, for each desorption spectrum shown in Fig. 3, the temperature of the desorption peak is identical to the temperature at which desorption to the gas phase is complete for the corresponding heating rate, as seen in Fig. 4.

The data shown in Fig. 4 can be compared with similar simulations, produced using the desorption parameters determined by other groups. Fig. 5(a) shows a comparison of the gas phase concentration of NH_3 as a function of temperature using both our kinetic parameters and those previously determined by Sandford & Allamandola (1993). Both simulations were run using an initial surface coverage of 9.5 \times 10^{21} \text{ molec m}^{-2} and a heating rate of 1 K century^{-1}. It is clear from Fig. 5(a) that there is a small difference between the two sets of data, with the simulations based on the kinetic parameters derived by Sandford & Allamandola (1993) showing greater rates of desorption at a given temperature than simulations based on our data. Although the difference in desorption rates is small for a heating rate of 1 K century^{-1}, it will be larger for faster heating rates. Whether or not this small difference will be significant for astrochemical models will depend on the accuracy of the models themselves.

The data shown in Fig. 4 for H_2O desorption can also be directly compared with previous simulations of H_2O desorption performed by Collings et al. (2004). Collings et al. (2004) simulated multilayer water desorption from a Au substrate as a perfect zero-order process. A feature of zero-order desorption is that, for a given heating rate, desorption profiles for varying coverages can be laid on top of each other (Collings et al. 2004). Hence simulations, such as those shown in Fig. 4, can be extrapolated for ice layers of any thickness. However, the simulations presented here for H_2O (and also for NH_3 and CH_3OH) multilayers show fractional, not zero-order desorption. The observation of a fractional desorption order means that it
An important consequence of gas–grain interactions in the ISM is that molecules are depleted from the gas phase when they are adsorbed on the surface of dust grains. The rate of depletion from the gas phase is an important consideration in modelling the true column density of molecules present in dark clouds such as H₂O, CH₃OH and NH₃ (Sandford & Allamandola 1993). The residence time of a molecule on a dust grain, and hence the rate of depletion, can be calculated as a function of grain temperature using the kinetic parameters shown in Table 1. The residence time is equal to the half-life of the surface population. The half-life can be calculated as a function of grain temperature using the kinetic parameters shown in Table 1. The half-life is defined in equation (3). As clearly shown in previous studies (Fraser et al. 2001), this concentration is equivalent to ~100
layers of ice, which is the number of molecules expected to accrete on a dust grain during the lifetime of a dark cloud (Hasegawa & Herbst 1993).

The half-life of H$_2$O molecules within H$_2$O multilayers, as a function of temperature, is shown in Table 2. Table 2 also lists the half-life of H$_2$O molecules on H$_2$O ice surfaces determined using the kinetic parameters evaluated by Fraser et al. (2001) and Sandford & Allamandola (1988). In both of the previous studies, H$_2$O desorption from the multilayer (or the desorption of H$_2$O from H$_2$O ice) was modelled for the desorption of crystalline and amorphous ice. The simulations presented here relate only to the desorption of crystalline ice, as already noted, as the kinetic parameters in Table 1 were evaluated for crystalline H$_2$O ice only (Bolina et al. 2005a).

Table 2 shows that H$_2$O would remain on the surface for an appreciable time (defined as a time longer than 10$^2$ yr) up to a temperature of 90–100 K, while Fraser et al. (2001) noted a temperature of 110–120 K and Sandford & Allamandola (1993) noted a temperature of 100–110 K. This difference can be explained by the different kinetic parameters used in the different simulations, in particular the order of desorption and pre-exponential factors. This study modelled desorption as a fractional-order process, while the study by Fraser et al. (2001) modelled H$_2$O desorption as a zero-order process and Sandford & Allamandola (1993) modelled the desorption as a first-order process.

Similar analysis has been carried out to calculate the half-life of multilayers of NH$_3$ adsorbed on the surface of model dust grains. Table 3 lists the half-life of NH$_3$ calculated in this study and in a previous study by Sandford & Allamandola (1993). Table 3 shows that there is generally good agreement between this study and the previous work, with both studies showing that NH$_3$ can remain on the surface of dust grains up to a temperature of ~60 K. This agreement is encouraging, although rather surprising, since the two studies employ completely different kinetic parameters.

Table 4 shows a similar analysis carried out to determine the half-life of CH$_3$OH molecules on CH$_3$OH ice. In contrast to the NH$_3$, there is a small difference between the calculated half-life of CH$_3$OH in this study and that obtained by Sandford & Allamandola (1993). This study shows that CH$_3$OH can remain on the surface of dust grains at temperatures up to ~90 K, while Sandford & Allamandola (1993) calculated a temperature of ~80 K. This discrepancy most probably arises from the differences in the kinetic parameters used in the two calculations, and shows the importance of using correct desorption orders to determine kinetic parameters for CH$_3$OH desorption.

4 ASTROPHYSICAL IMPLICATIONS

The new results reported here need to be taken into account in astrophysical situations in which ice-coated dust grains are warmed from...
and for pure NH₃ ice sublimation occurs at ∼55 K. Thus, as warming occurs, the chemical composition of the layered ices and of the gas phase will vary in a predictable way which can be incorporated into appropriate astrochemical models. It is only with the incorporation of this new data into astrochemical models that it will become clear whether or not the data presented here are significant for star-forming regions. Preliminary studies of the effect that the new data for H₂O have on astrochemical models (Brown et al. 2006) suggest that differences are observed for low-mass stars. However, further work is necessary to determine the effects of this data under a range of different conditions.

## 5 CONCLUSIONS

This paper reports the results of new experiments on the desorption of pure molecular ices from a model grain surface. The experimental data have been used to determine the desorption temperatures of these ices under interstellar conditions, and the results obtained for the desorption of H₂O ice are in good agreement with previous results (Collings et al. 2004). The half-lives of these ices against thermal desorption are also presented as a function of temperature. For H₂O ice, there is some variation between the half-lives calculated here and those determined previously (Sandford & Allamandola 1993; Fraser et al. 2001); however, for NH₃ ices the agreement between our data and previous studies (Sandford & Allamandola 1993) is good. For the sublimation of pure CH₃OH ices, there is only a small difference between our data and previous data (Sandford & Allamandola 1993). These results show the importance of laboratory data for the understanding of astronomical situations in which dust grains coated with icy mantles are warmed by nearby stars or dynamical events.

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**Table 4.** Table showing the half-life of CH₃OH molecules on an HOPG model grain surface as a function of temperature. The data from this study are shown in bold. For comparison, the table also shows previous results obtained by Sandford & Allamandola (1993).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>This study</th>
<th>Half-life (t½ yr) Sandford &amp; Allamandola (1993)</th>
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<tr>
<td>10</td>
<td>4.2 × 10⁻⁷</td>
<td>8.4 × 10⁶³</td>
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<tr>
<td>20</td>
<td>2.3 × 10⁻⁷</td>
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<td>30</td>
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<td>5.6 × 10⁻⁷</td>
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