Studios of Binary Layered CH$_3$OH/H$_2$O Ices Adsorbed on a Graphite Surface

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Reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) have been used to investigate binary layered ice systems consisting of methanol deposited on top of various thicknesses of water ice, grown on an underlying graphite surface. RAIRS shows that there is no difference between the RAIR spectra recorded for pure ices and that recorded for the layered ices, suggesting that there is no discernible interaction between the layers during adsorption. However, annealing the ice layers leads to intermixing, as evidenced by a 50 cm$^{-1}$ downshift of the O–H stretching frequency of the mixed ice, compared to that expected from a simple combination of the pure water and pure methanol O–H stretching bands. TPD shows several new species when compared with TPD spectra for pure ices, confirming that mixing of the ice layers occurs on heating. A TPD peak that can be assigned to the trapping of methanol within the water ice is observed. TPD peaks for the desorption of monolayer and multilayer methanol are also observed.

Introduction

Methanol (CH$_3$OH) is one of the most abundant molecular species observed in the interstellar medium (ISM) where it is usually found in the form of interstellar ices, frozen out on the surface of dust grains. CH$_3$OH is typically observed within water (H$_2$O) rich ices and, where present, is often the most abundant molecule after H$_2$O.$^{3,4}$ Its abundance in grain mantles is predicted to vary between 0.05 and 0.50 relative to H$_2$O.$^{5,7}$ although it is generally considered that the lower abundance estimates are more accurate.$^7$

Given the close association of CH$_3$OH with H$_2$O in the ISM, a detailed understanding of the adsorption of CH$_3$OH on, and its desorption from, the surface of ice-covered grains is vital to enable accurate modeling of the ISM and to explain the observed gas-phase abundances of CH$_3$OH and H$_2$O.$^8$ The adsorption and desorption of ices is also important in cometary environments and in regions where shocks lead to sudden heating of the grains, and hence to desorption (followed by subsequent readsoption) of the ices.$^9$–$^{11}$ With this in mind, we have used reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD) to investigate the adsorption of CH$_3$OH on H$_2$O layers of various thicknesses adsorbed on a highly oriented pyrolytic graphite (HOPG) substrate held at around 97 K.

Dust grains in the ISM consist mainly of carbonaceous and siliceous material and are often covered in films of ice.$^2$ HOPG can therefore be considered as a suitable dust grain analogue and this surface has previously been used in investigations of H$_2$ formation on dust grains.$^{12}$–$^{15}$ The temperature in the ISM, where these ice-covered grains are found, is around 10–20 K. Although the experiments described here were not performed at this temperature, they still allow an understanding of the interaction of CH$_3$OH with layers of H$_2$O ice to be gained. The temperature of the ices found in comets and in shocked regions is often somewhat higher than that in the ISM, and can be as high as 100 K.

We have previously investigated the adsorption of pure CH$_3$OH$^{16}$ and pure H$_2$O$^{17}$ on the surface of HOPG. However, combining studies of pure ices does not necessarily give reliable results when modeling the behavior of mixed ices. It is for this reason that we have performed detailed investigations of the adsorption and desorption of binary layered ices consisting of CH$_3$OH deposited on top of H$_2$O ice. H$_2$O ice is known to exist in a number of different phases depending on the temperature and deposition conditions.$^{18}$–$^{20}$ Previous studies have shown that H$_2$O ice grows as amorphous solid water (ASW) at deposition temperatures less than 135 K. ASW is therefore the dominant phase of the H$_2$O layers upon which CH$_3$OH is adsorbed in this work.

ASW has aroused much interest as it undergoes a structural transition that alters its porosity and surface area and can result in the trapping of volatile species.$^{21}$–$^{25}$ Collings and co-workers have shown, using TPD, that CO can be trapped within the pores of amorphous ice$^{24}$ and Bar-Nun and co-workers$^{22}$ have highlighted the ability of ASW to trap Ar within a clathrate hydrate complex. Clathrate hydrates are crystalline regions of H$_2$O ice that enclose or encage small amounts of a guest molecule within the structure.$^{26}$ They are generally formed under high-pressure conditions and there is therefore some discussion about whether they will form in the ISM. TPD experiments of Collings and co-workers$^{27}$ have suggested that CH$_3$OH is too large to diffuse into the porous structure of H$_2$O ice, however, Blake and co-workers$^{26,28,29}$ have suggested that CH$_3$OH can form a clathrate structure, albeit a slightly distorted version, described as a type II clathrate hydrate.

There are several previous studies of mixed CH$_3$OH and H$_2$O ices,$^{26,27,30$–$33}$ however there are few previous studies of binary layered ice systems. Souda and co-workers performed a detailed study of CH$_3$OH and D$_2$O layers, in particular focusing on how layered structures of CH$_3$OH and D$_2$O intermix.$^{34,35}$ They observed thermally induced isotope scrambling$^{35}$ and their studies showed that the two layers completely intermix above the glass transition temperature of D$_2$O/H$_2$O$^{34}$ at 136 K.

There have been a number of previous infrared studies of mixed CH$_3$OH and H$_2$O ices,$^{36}$–$^{38}$ sometimes with additional species such as CO and NH$_3$ within the mix.$^{30,31}$ Although these previous studies focused on intimate mixtures, rather than the discrete layered structures described here, the work has em-
phasized the importance of conducting infrared studies of complex H$_2$O dominated ices. In addition, there has been some suggestion in the literature that mixed polar ice mantles may undergo molecular segregation\textsuperscript{39} to form layered structures, hence studying layered ices is of relevance to these systems.

Here we describe RAIRS and TPD investigations of the adsorption of CH$_3$OH on various thicknesses of ASW, grown on an underlying HOPG substrate at \sim 97 K. Three separate adsorbate systems were studied to explore the adsorption and desorption of CH$_3$OH as a function of the underlying H$_2$O multilayer thickness. Our previous studies of pure H$_2$O adsorption on HOPG\textsuperscript{17} showed that three-dimensional islands of H$_2$O began to form on the surface following an exposure of \textasciitilde 1–2 L. Bare patches of HOPG were also present at this exposure. As a result, the adsorption of CH$_3$OH on H$_2$O ice films resulting from exposures of 2, 10, and 50 L, corresponding to thin, medium, and thick multilayers of H$_2$O ice, respectively, were investigated. These will be described as CH$_3$OH/H$_2$O(2 L), CH$_3$OH/H$_2$O(10 L), and CH$_3$OH/H$_2$O(50 L), where the number in parentheses represents the exposure used to create the underlying H$_2$O ice in the layered system.

**Methodology**

Experiments were performed in an ultrahigh vacuum (UHV) chamber that has a base pressure of \textasciitilde 2 \times 10^{-10} \text{ mbar}. The HOPG sample was purchased from Goodfellow Ltd. and was cleaved prior to installation in the UHV chamber, using the “Scotch Tape” method.\textsuperscript{40} The sample was mounted on the end of a liquid nitrogen cooled cold finger and its temperature was monitored with an N-type thermocouple. Temperature control, during dosing and TPD experiments, was achieved via the use of a Eurotherm temperature controller coupled to Itools software. The sample was cleaned before each experiment by annealing at 500 K in UHV for 3 min. Sample cleanliness was confirmed by the absence of any desorption during TPD experiments performed with no dosage. Ices were grown in situ by exposing the cold HOPG surface, held at 97 K, to a stream of gas by back-filling the chamber through a high precision leak valve.

All exposures are reported in Langmuir (L), where 1 L = 10^{-6} \text{ mbar s}, and were recorded during dosing with a mass spectrometer. All spectra were taken with a Hiden Analytical HAL201 quadrupole mass spectrometer before each experiment and during dosing.

RAIR spectra were recorded with a Mattson Instruments RS1 Research Series Fourier transform infrared spectrometer coupled to a liquid nitrogen cooled MCT detector. All spectra were taken at a resolution of 4 cm\textsuperscript{-1} and are the result of the co-addition of 256 scans. In RAIRS experiments where the sample was heated, it was annealed to a predetermined temperature, held at this temperature for 3 min, and then cooled back down to the base temperature before a spectrum was recorded. TPD spectra were recorded with a Hiden Analytical HAL201 quadrupole mass spectrometer. All TPD spectra were recorded at a heating rate of 0.50 \pm 0.01 K s\textsuperscript{-1}.

**Results and Discussion**

**RAIRS Data.** (A) Adsorption. Increasing exposures of CH$_3$OH were dosed onto an existing film of H$_2$O ice, grown on HOPG at 97 K, to form a layered ice structure. The deposition temperature of 97 K is well below the glass transition temperature of H$_2$O (136 K) and hence the H$_2$O ice formed is in the ASW phase. The phase of the H$_2$O ice film was confirmed by comparing the O–H stretching region of the pure H$_2$O RAIR spectrum with previous studies that have documented the crystalline/amorphous infrared fingerprint\textsuperscript{17,42,43} of H$_2$O ice. The RAIR spectra showed that, following an exposure of 50 L of H$_2$O, the main O–H peak produced is centered at 3392 cm\textsuperscript{-1} with a low frequency shoulder at 3324 cm\textsuperscript{-1}. The appearance of the O–H stretching region of the pure H$_2$O ice films was characteristic of the formation of ASW.\textsuperscript{17}

Figure 1 shows RAIR spectra of the CH$_3$OH/H$_2$O(50 L) system following the adsorption of increasing amounts of CH$_3$OH onto the H$_2$O ice film. The initial trace obtained, following the adsorption of 50 L of H$_2$O, shows the features expected for pure H$_2$O adsorbed on HOPG,\textsuperscript{17} namely a broad peak between 3050 and 3600 cm\textsuperscript{-1}, assigned to the O–H stretch. The other traces in Figure 1 show the effect of depositing increasing amounts of CH$_3$OH on top of the H$_2$O ice. With an initial 3 L exposure of CH$_3$OH an additional peak is observed in the spectrum at 1045 cm\textsuperscript{-1}. Increasing the exposure beyond 7 L results in the appearance of additional spectral features at 1134, 1460, 2831, 2950, and 2987 cm\textsuperscript{-1}. Figure 1 also shows that the appearance of the broad O–H feature between 3050 and 3600 cm\textsuperscript{-1} noticeably changes when the CH$_3$OH exposure exceeds 20 L, with the growth of a new band centered on 3280 cm\textsuperscript{-1} being observed. Exactly the same vibrational features are observed regardless of the thickness of the underlying H$_2$O layer. The only observed difference is a change in the shape of the O–H peak, with the CH$_3$OH/H$_2$O(50 L) system showing a broader O–H peak with a more pronounced high-frequency shoulder, corresponding to the greater H$_2$O contribution to the spectrum.
The bands observed in the spectra shown in Figure 1 can all be assigned by comparison with the spectra previously obtained for pure H$_2$O$^{17}$ and pure CH$_3$OH$^{16}$ adsorbed on HOPG. Table 1 summarizes the assignments of the RAIRS bands observed in Figure 1, along with the previously reported vibrational bands observed for pure CH$_3$OH adsorbed on HOPG.$^{16}$ If the complex O–H stretching region, which contains contributions from both the CH$_3$OH and H$_2$O present in the ice, is ignored then Figure 1 and Table 1 show that the CH$_3$OH vibrational bands have the same frequencies as those previously recorded for the formation of physisorbed CH$_3$OH multilayers on HOPG.$^{16}$ This observation, and the fact that none of the vibrational bands seen in Figure 1 saturate as the exposure increases up to 300 L, indicates that physisorbed multilayers of CH$_3$OH are formed on top of the underlying layer of H$_2$O ice, as expected.

Any differences between the adsorption of CH$_3$OH on bare HOPG and that on an underlying H$_2$O ice film will only be observable for the lower CH$_3$OH exposures shown in Figure 1, where the CH$_3$OH is bonding directly to the H$_2$O ice film or to the bare HOPG surface. Once multilayers begin to grow there will be no observed difference between the spectra shown in Figure 1 and those previously recorded for CH$_3$OH adsorbed on a bare HOPG surface.$^{16}$ However, even at low CH$_3$OH exposures, the spectra shown in Figure 1 are identical with those previously recorded for CH$_3$OH adsorption on bare HOPG. In addition, there are no observable differences between the RAIR spectra recorded for the CH$_3$OH/H$_2$O(2 L), CH$_3$OH/H$_2$O(10 L), and CH$_3$OH/H$_2$O(50 L) systems. These observations suggest that CH$_3$OH adsorption on bare HOPG cannot be distinguished from CH$_3$OH adsorption on a H$_2$O ice film. This is surprising, since it might be expected that CH$_3$OH would bond more strongly to H$_2$O than to HOPG. However, this fact is also confirmed by TPD (see later), which shows that it is not possible to distinguish separate desorption peaks for the adsorption of CH$_3$OH on HOPG and on the H$_2$O ice surface. This observation suggests that the intermolecular interactions between adjacent CH$_3$OH molecules are much more important in dictating CH$_3$OH adsorption on HOPG than the interactions between CH$_3$OH and the surface.

Confirmation of the observation that there is no noticeable change in the layered ices compared to the pure ice films comes from a closer inspection of the O–H stretching region between 3600 and 2600 cm$^{-1}$. Figure 2 compares the O–H stretching region for pure CH$_3$OH, pure H$_2$O, and the layered ice consisting of 50 L of CH$_3$OH deposited on top of 50 L of H$_2$O. Pure H$_2$O has a broad peak centered at 3390 cm$^{-1}$, pure CH$_3$OH has a peak at 3260 cm$^{-1}$, and the CH$_3$OH/H$_2$O(50 L) layered system gives a peak centered at 3330 cm$^{-1}$. Figure 2 shows that the RAIR spectrum resulting from the layered ice is well modeled by a simple addition of the pure H$_2$O and pure CH$_3$OH spectra, suggesting that the sequential exposure of CH$_3$OH and H$_2$O onto the HOPG surface has caused little perturbation from the pure systems. Figure 2 implies that either the interactions between CH$_3$OH and H$_2$O are the same as those found in the pure ices or that the two species have remained as layers, without any mixing taking place during adsorption. RAIR spectra that result from the annealing of the sequentially deposited ice layers and TPD spectra for the same ice systems (shown later) do show evidence for mixing of the CH$_3$OH and H$_2$O layers. However, the RAIR spectra presented in Figure 2 show that this mixing only occurs as a result of the heating that occurs in the TPD experiment.

(B) Annealing and Desorption of the Ice Layers. Following adsorption, the desorption and annealing behavior of the three CH$_3$OH/H$_2$O layered ice systems was investigated. The behavior of all three ice systems was similar and hence the CH$_3$OH/H$_2$O-(50 L) system has been chosen to illustrate the desorption behavior. Figure 3A shows RAIR spectra, focusing on the O–H stretching region, resulting from annealing the layered ice that results from depositing 50 L of CH$_3$OH on top of 50 L of H$_2$O ice. Figure 3B shows spectra focusing on the C–O stretching region, following annealing of the same ice. Figure 3A shows that there is little change to the O–H stretching region of the RAIR spectrum until the ice is annealed above 135 K. Annealing to 145 K causes the broad peak centered at 3361 cm$^{-1}$ to increase in amplitude and split into two peaks at 3361 and 3236 cm$^{-1}$. Annealing to 155 K causes the band at 3236 cm$^{-1}$ to increase in intensity and an additional low frequency shoulder at 3150 cm$^{-1}$ appears in the spectrum. This observed change in the O–H stretching region between 135 and 155 K can be assigned to the amorphous to crystalline phase transition of the H$_2$O ice film as previously observed for pure H$_2$O adsorbed on HOPG.$^{15}$ Heating the ice above 155 K leads to a rapid loss in intensity of all of the bands seen in Figure 3A, indicating desorption of both the CH$_3$OH and H$_2$O layers. By 180 K, only a small peak at 3236 cm$^{-1}$ remains in the spectrum.

The peak at 3236 cm$^{-1}$ that remains in the spectrum, even after annealing to 180 K, has not previously been reported for either pure CH$_3$OH or pure H$_2$O ice adsorbed on HOPG. However, further detailed tests investigating the desorption of pure H$_2$O from the HOPG surface show that this peak can be assigned to the presence of pure H$_2$O. Integrating the area under the peaks shown in Figure 3A shows that the bands at 2943.

### Table 1: The Assignment of the Vibrational Bands

<table>
<thead>
<tr>
<th>Band assignment</th>
<th>Layered CH$_3$OH/H$_2$O (50 L)</th>
<th>Multilayer CH$_3$OH (HOPG)$^{16}$</th>
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</thead>
<tbody>
<tr>
<td>$v$(O–H)</td>
<td>3402$^a$</td>
<td>3260</td>
</tr>
<tr>
<td>$v$(CH$_3$)</td>
<td>3280</td>
<td>2983</td>
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<td>$v$(CH$_3$)</td>
<td>2831</td>
<td>2833</td>
</tr>
<tr>
<td>$v$(C–O)</td>
<td>1460</td>
<td>1134</td>
</tr>
<tr>
<td>$v$(C–O)</td>
<td>1134</td>
<td>1132</td>
</tr>
<tr>
<td>$v$(C–O)</td>
<td>1045</td>
<td>1045</td>
</tr>
</tbody>
</table>

$^a$ The 3402 cm$^{-1}$ feature present in the layered system is attributed to the $v$(O–H) stretch of the H$_2$O layer.

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Figure 2. RAIR spectra for 50 L of pure H$_2$O, 50 L of pure CH$_3$OH, and 50 L of CH$_3$OH dosed onto an underlying 50 L H$_2$O layer, all deposited at 97 K. The fit generated by the addition of the pure CH$_3$OH and H$_2$O spectra is shown as a dashed line.
and 2830 cm$^{-1}$, which can be assigned purely to CH$_3$OH, disappear from the spectrum around 170 K. This is higher than the desorption temperature of pure CH$_3$OH adsorbed on HOPG,$^{16}$ which completely disappears from the RAIR spectrum by $\sim$155 K. Interactions between the CH$_3$OH and H$_2$O that occur on heating therefore cause the CH$_3$OH to desorb at a higher temperature than observed for the pure ice system. The integrated area of the O–H stretch and the total integrated spectral area do not fall to zero until the annealing temperature is increased above 180 K, confirming the desorption of the H$_2$O layer at this temperature.

Figure 3 shows the sequential heating of the layered ice formed by depositing 50 L of CH$_3$OH on top of 50 L of H$_2$O ice on top of 50 L of CH$_3$OH adsorbed on HOPG at 97 K. (A) the O–H stretching region between 2600 and 3800 cm$^{-1}$ and (B) the C–O stretching region between 980 and 1150 cm$^{-1}$.

Figure 3. RAIR spectra showing the sequential heating of the layered ice consisting of 50 L of CH$_3$OH deposited on top of 50 L of H$_2$O ice annealed to 155 K, all grown on HOPG at 97 K. The fit generated by the addition of pure CH$_3$OH and pure H$_2$O spectra is shown as a dotted line. The inset shows the fit shifted down by 50 cm$^{-1}$ to show the good overlap with the spectrum recorded for the layered CH$_3$OH/H$_2$O(50 L) ice annealed to 155 K.

Figure 4. RAIR spectra for 50 L of pure H$_2$O annealed to 150 K, 50 L of pure CH$_3$OH annealed to 141 K, and 50 L of CH$_3$OH adsorbed on top of 50 L of H$_2$O ice annealed to 155 K, all grown on HOPG at 97 K. The fit generated by the addition of the pure CH$_3$OH and pure H$_2$O spectra is shown as a dotted line. The inset shows the fit shifted down by 50 cm$^{-1}$ to show the good overlap with the spectrum recorded for the layered CH$_3$OH/H$_2$O(50 L) ice annealed to 155 K.

Note that the infrared spectrum resulting from the annealing of CH$_3$OH compared to that of pure CH$_3$OH,$^{16}$ indicates that the CH$_3$OH and H$_2$O when the ice layers are annealed. This was not observed during adsorption at 97 K (see Figure 2) and therefore occurs as a direct result of the heating process. It is most likely that this interaction is caused by a temperature induced mixing of the H$_2$O and CH$_3$-OH overlayers, as previously observed by Souda.$^{34}$ The downshift in the frequency of the O–H stretching mode suggests that the CH$_3$OH and H$_2$O form a hydrogen-bonded complex when the layers intermix. Strong hydrogen bonds act to weaken the O–H bond and therefore lower the frequency of the stretching vibration. They are also expected to increase the frequency of the O–H librational and bending modes, as these are both inhibited by hydrogen bonding.$^{35}$ However, these modes are not observed in the spectra reported here as they occur below the cutoff frequency of the MCT detector used in these experiments. In previous studies of matrix isolated CH$_3$OH:H$_2$O complexes, Bakkus and co-workers$^{16}$ observed a downshift of 20 cm$^{-1}$ in the O–H stretch when CH$_3$OH hydrogen bonds to O–H and acts as a proton donor. Hence the observed 50 cm$^{-1}$ downshift in the frequency of the O–H band for the layered ices, seen in Figure 4, can be attributed to the formation of a CH$_3$OH:H$_2$O complex.

Figure 3B shows the spectral region between 980 and 1150 cm$^{-1}$ (the C–O stretching region) for the spectra that result from annealing the binary layered ice consisting of 50 L of CH$_3$-OH and 50 L of H$_2$O. Heating results in a decrease in the intensity of the C–O stretch at 1044 cm$^{-1}$ and a small downshift in frequency, with increasing annealing temperature. Immediately after heating, a small shoulder also appears at 1013 cm$^{-1}$. In contrast to the pure CH$_3$OH system,$^{16}$ the C–O stretch at 1044 cm$^{-1}$ does not obviously split on heating, as would be expected for CH$_3$OH crystallization. However, it is likely that the shoulder at 1013 cm$^{-1}$ indicates the beginning of CH$_3$OH crystallization, as indicated by the frequency downshift of the 1044 cm$^{-1}$ C–O stretching mode. Results for the annealing of...
pure CH$_3$OH adsorbed on HOPG$^{16}$ indicate that crystallization is not observed for CH$_3$OH doses of less than 50 L, and therefore it is likely that the 50 L CH$_3$OH exposure in this study is just approaching the threshold coverage required for crystallization. Integration of the areas under the peaks shown in Figure 3B again shows that the bands assigned only to CH$_3$OH remain in the spectrum until ~170 K.

The annealing process was also repeated for each of the three ice systems, with a thicker CH$_3$OH overlayer formed by an exposure of 300 L of CH$_3$OH on top of the underlying H$_2$O layer. Unsurprisingly, the observed behavior is the same as that previously seen for the annealing of 300 L layers of pure CH$_3$OH adsorbed on HOPG.$^{16}$ Both the O–H and C–O stretching bands are observed to split on annealing, providing evidence for crystallization of the CH$_3$OH ice. However, the desorption temperature of the CH$_3$OH is higher in the layered systems, compared to pure CH$_3$OH, as already noted.

**TPD Data.** TPD was also used to investigate the adsorption of various exposures of CH$_3$OH adsorbed on an underlying H$_2$O ice film. During TPD experiments, the desorption traces for masses 31, 32, and 18 were recorded simultaneously. Mass 31 is the major fragment detected by the mass spectrometer for CH$_3$OH and is therefore reported in preference to mass 32 throughout.

**A Water Desorption.** Figure 5 shows H$_2$O TPD spectra that result from the desorption of a binary layered ice system, grown on HOPG at 97 K, consisting of 2, 10, or 50 L of ASW with various thicknesses of CH$_3$OH dosed on top. In each trace (Figure 5A,B,C) the same amount of H$_2$O has been adsorbed, but the thickness of the CH$_3$OH layer is increasing in each case.

For the thinnest sublayer of H$_2$O ice, in the CH$_3$OH/H$_2$O(2 L) system, a single H$_2$O desorption peak is observed at 139 K for all CH$_3$OH exposures ≤50 L (Figure 5A). The integrated area under the H$_2$O TPD peaks seen in Figure 5A for the desorption of the 2 L H$_2$O layer also remains constant with increasing CH$_3$OH exposures ≤50 L. However, as the CH$_3$OH overlayer exposure increases to 100 L the H$_2$O TPD spectrum (Figure 5A) broadens and an additional peak is observed at 150 K. Following a 300 L exposure of the CH$_3$OH overlayer, the H$_2$O TPD spectrum in Figure 5A now shows a very sharp peak at 140 K with a shoulder at 143 K and a smaller peak at ~152 K. The integrated area underneath the H$_2$O TPD trace also increases following the deposition of 100 L or more of CH$_3$OH. The sharp H$_2$O desorption peak observed in Figure 5A coincides with the maximum desorption of CH$_3$OH (see later), also observed at 140 K.

Figure 5B shows H$_2$O desorption traces for the CH$_3$OH/H$_2$O-(10 L) system. Following low exposures of CH$_3$OH onto the H$_2$O ice film, a single peak at 144 K is observed in the TPD spectrum. As the CH$_3$OH exposure increases, the H$_2$O desorption peak shifts up in temperature (see inset to Figure 5B), and, following a 300 L dose of CH$_3$OH, the peak temperature of the H$_2$O desorption is shifted to 155 K. As observed for the desorption of H$_2$O from the CH$_3$OH/H$_2$O(2 L) system, the H$_2$O desorption peak also broadens with increasing thickness of the CH$_3$OH overlayer. Despite this broadening, however, the total integrated area of the 10 L H$_2$O TPD peaks seen in Figure 5B is constant as a function of increasing CH$_3$OH exposure.

H$_2$O TPD spectra for the CH$_3$OH/H$_2$O(50 L) binary layered ice system also behave in a similar manner, as shown in Figure 5C. Again, for low exposures of CH$_3$OH a single H$_2$O desorption peak is recorded, which shifts up in temperature as the CH$_3$OH exposure increases (see inset to Figure 5C). In contrast to the CH$_3$OH/H$_2$O(10 L) system, the shift in peak temperature is fairly small with the peak initially being observed at 154 K and shifting up to 157 K following the adsorption of 300 L of CH$_3$OH. The H$_2$O desorption peak also broadens as the CH$_3$OH exposure increases, although this broadening is not as pronounced as that observed for the CH$_3$OH/H$_2$O(10 L) system. As for the CH$_3$OH/H$_2$O(10 L) system, the integrated area of the H$_2$O TPD peaks in Figure 5C is constant with increasing CH$_3$OH overlayer exposure. For both the 10 (Figure 5B) and 50 L (Figure 5C) H$_2$O traces, the sudden change observed in the H$_2$O desorption rate for the H$_2$O layers covered with thinner CH$_3$OH overlayers (left-hand traces in the figure) is most likely due to the crystallization of the underlying H$_2$O layer. The crystallization is masked at higher CH$_3$OH doses as it takes place before the H$_2$O desorption occurs, due to the increased desorption temperature of the H$_2$O layer with increasing CH$_3$OH overlayer thickness.

For each layered ice system, the H$_2$O exposure remains constant and hence the desorption temperature of the H$_2$O should also remain constant. The observed broadening and shifting of the H$_2$O TPD peaks in the CH$_3$OH/H$_2$O(10 L) and CH$_3$OH/H$_2$O(50 L) layered ices can be understood by comparing the
desorption temperature expected for pure H$_2$O ices, resulting from 10 and 50 L exposures on bare HOPG, with the desorption temperature of the overlying CH$_3$OH layer in each case. Figure 5 clearly shows that H$_2$O desorption is inhibited by the presence of thick overlayers of CH$_3$OH, which act to hold the H$_2$O in place on the surface. This results in a broadening of the H$_2$O desorption peak and an increasing peak temperature with increasing thickness of the CH$_3$OH overlayer. Due to the sequential nature of the dosing, the H$_2$O cannot desorb until the overlaying CH$_3$OH has already desorbed. Hence, in cases where the CH$_3$OH desorption occurs around, or beyond, the pure H$_2$O desorption temperature, a delay will occur in the H$_2$O desorption resulting in a broadening of the TPD spectrum and a higher peak temperature. This is exactly what is observed for the CH$_3$OH/H$_2$O(10 L) system. A 10 L dose of pure H$_2$O desorbs from HOPG with a peak temperature of around 144 K. The desorption peak temperature of CH$_3$OH ice varies from around 130 to 145 K as the dose increases from 10 to 300 L, and hence as the CH$_3$OH dose increases there is a competition between the desorption of the H$_2$O and the CH$_3$OH that leads to a broadening and delay in the H$_2$O desorption. For the CH$_3$OH/H$_2$O(50 L) system, there is a much less pronounced effect on H$_2$O desorption as the CH$_3$OH overlayers thickness increases, since the desorption temperature of 50 L of pure H$_2$O is ~153 K, 10 K higher than the peak temperature of the desorption of a 300 L layer of CH$_3$OH (~144 K). Hence, in the CH$_3$OH/H$_2$O(50 L) system, the desorption of the H$_2$O layer is less affected by the presence of the CH$_3$OH overlayers.

It is clear from Figure 5 that the H$_2$O desorption observed for the CH$_3$OH/H$_2$O(2 L) system behaves somewhat differently compared to the other two layered ice systems. At low exposures of CH$_3$OH the H$_2$O desorption temperature remains approximately constant, but as the CH$_3$OH exposure increases above 100 L, the desorption temperature, peak shape, and integrated area of the 2 L H$_2$O desorption peak changes dramatically. The desorption temperature of a 2 L layer of pure H$_2$O is 139 K. The thicker CH$_3$OH overlayers therefore hold the underlying H$_2$O ice on the HOPG surface well past its expected desorption temperature. Hence by the time that a CH$_3$OH overlayers 300 L has desorbed, with a peak desorption temperature of 144 K, the H$_2$O explodes from the surface at a rate that exceeds the pumping speed of the vacuum chamber, leading to a very sharp TPD peak and large integrated peak area.

**B) Methanol Desorption.** TPD spectra following low exposures of CH$_3$OH adsorbed on 2, 10, and 50 L of H$_2$O ice adsorbed on HOPG at 97 K are shown in Figure 6. Figure 7 shows TPD spectra resulting from high exposures of CH$_3$OH on the same H$_2$O layers. For CH$_3$OH desorbing from the thinnest layer of H$_2$O ice (2 L), shown in Figures 6A and 7A, the TPD spectra are comprised of two peaks. At the lowest CH$_3$OH exposures, a single desorption peak is observed at 134 K. As the CH$_3$OH exposure is increased this peak shifts up in temperature to 136 K and appears to saturate between 7 and 10 L of CH$_3$OH exposure. For CH$_3$OH doses ≥7 L a second lower temperature desorption peak is also observed that shifts up in temperature with increasing CH$_3$OH dose, and grows to dominate the spectrum (Figure 7A). The peak does not saturate following a 300 L exposure of CH$_3$OH indicating, as already shown by RAIRS, that the CH$_3$OH is physisorbed on the underlying H$_2$O surface. Further evidence for the formation of physisorbed CH$_3$OH comes from a plot of the total integrated area of the TPD peaks seen in Figures 6 and 7 as a function of exposure (not shown) that shows a linear increase, that never saturates, with increasing CH$_3$OH dose. The TPD spectra for the CH$_3$OH/H$_2$O(2 L) layered ice are essentially identical with those observed for the desorption of pure CH$_3$OH adsorbed on HOPG.16 The higher temperature peak, observed at low CH$_3$OH exposures, is therefore assigned to the formation of monolayer CH$_3$OH and the lower temperature peak that dominates the TPD spectra at high coverage is assigned to the desorption of multilayer CH$_3$OH.

TPD spectra for the desorption of CH$_3$OH deposited on thicker layers of H$_2$O ice (10 and 50 L) are more complex. Figure 6B shows a series of TPD spectra for increasing exposures of CH$_3$OH on 10 L H$_2$O ice. At very low CH$_3$OH exposures only a single high-temperature peak is observable at 145 K, labeled α. Increasing the exposure of CH$_3$OH does not lead to an increase in the intensity of this peak, suggesting that it has already saturated after only a 3 L CH$_3$OH dose. Instead, increasing the CH$_3$OH exposure leads to the appearance of a second lower temperature peak at 133 K, labeled β. At exposures of 7 L and above a third peak, labeled γ, appears as a low
temperature shoulder on peak $\beta$. Increasing the CH$_3$OH exposure above 15 L (Figure 7B) leads to an increase in peak $\gamma$, which grows to dominate the spectrum. Peak $\gamma$ does not saturate, and by 300 L this peak has reached a desorption temperature of 143 K (Figure 7B). At higher CH$_3$OH exposures ($\geq$50 L) an additional high-temperature shoulder, labeled $\delta$, is also observed at ca. 140–145 K.

Figure 6C shows TPD spectra for increasing doses of CH$_3$OH on an underlying 50 L layer of H$_2$O ice. At CH$_3$OH exposures below 5 L, a broad desorption peak is observed between 124 and 160 K. Within this broad feature there is a single high-temperature peak at 153 K, labeled $\alpha$. Increasing the CH$_3$OH exposure up to 10 L results in a saturation of the intensity of the $\alpha$ peak and an increase in the intensity of the lower temperature part of the broad desorption trace, although there is still no well-defined TPD peak observed. Following a CH$_3$OH exposure of 15 L, three additional peaks can also be observed—a low-temperature peak labeled $\gamma$, a shoulder labeled $\beta$, and an additional peak at 145 K. Increasing the CH$_3$OH exposure beyond 15 L leads to the $\gamma$ peak growing to dominate the spectrum as seen in Figures 6C and 7C. Following a CH$_3$OH dose of 100 L, the $\gamma$ peak splits into two clearly defined peaks. The low-temperature peak at 137 K is thought to be peak $\gamma$ and the higher temperature peak is labeled $\lambda$. By 300 L the $\gamma$ peak dominates the spectrum and the $\lambda$ peak is still visible as a small peak at 146 K.

Assignment of the various TPD peaks seen for CH$_3$OH bonded to the H$_2$O layer can be made from a comparison of the TPD spectra observed in Figures 6 and 7 with those previously recorded for the desorption of CH$_3$OH from the bare HOPG surface. A comparison of low exposure (7 L) TPD spectra for CH$_3$OH adsorbed on a bare HOPG surface (dotted trace) and on various thicknesses of H$_2$O ice at 97 K is shown in Figure 8A. From Figure 8A, it is clear that it is possible to assign peaks $\beta$ and $\gamma$ by comparison with the TPD spectra recorded for CH$_3$OH desorption from bare HOPG. Peak $\beta$ is therefore assigned to the desorption of CH$_3$OH from the monolayer. If the H$_2$O and CH$_3$OH TPD traces are plotted on the same graph (Figure 9) it is clear that the $\beta$ peak shares its leading edge with the H$_2$O desorption, suggesting that it desorbs as the H$_2$O first begins to sublime. This is consistent with the assignment of this peak to the desorption of monolayer CH$_3$OH adsorbed on top of the H$_2$O ice. Further evidence for the assignment of peak $\beta$ to the formation of monolayer CH$_3$OH comes from a plot of the integrated area of each species in the TPD spectrum as a function of dose, as shown in Figure 10. The data in Figure 10 were
produced by using a peak fitting package (SpXZeigR, Igor Pro, Wavemetrics Inc.) to separate out the individual contributions from the $\alpha$, $\beta$, and $\gamma$ peaks. Note that it was only possible to perform peak fits for CH$_3$OH dosed onto 2 and 10 L of H$_2$O ice as fits for the CH$_3$OH/H$_2$O(50 L) data were ambiguous. Figure 10 clearly shows that the area of the $\beta$ peak saturates with increasing exposure—a clear sign that this feature is due to the formation of a CH$_3$OH monolayer.

Surprisingly, it is not possible to distinguish between monolayer formation on the H$_2$O ice surface and monolayer formation on the HOPG surface. This was also the case for the RAIRS data, as discussed earlier. H$_2$O does not wet the HOPG surface, and instead has a tendency to form three-dimensional islands. The result of this is that, following a 2 L exposure of H$_2$O (and maybe even following a 10 L H$_2$O exposure), bare patches of HOPG will be present. Hence CH$_3$OH will initially adsorb on both the bare HOPG and the H$_2$O islands. However, since only one monolayer CH$_3$OH TPD peak is seen in Figure 8A, CH$_3$OH bound to H$_2$O must have a similar desorption energy to CH$_3$OH directly adsorbed on HOPG. It is most likely that this is because the interactions between the CH$_3$OH molecules are more important than the interactions between the molecules and the surface.

Figure 8 shows that peak $\gamma$ is also seen at the same temperature for the pure and layered ices and can therefore be assigned to desorption from within the multilayers of CH$_3$OH. As expected, the behavior of the multilayer TPD peak is identical for the three layered ice systems and for the pure CH$_3$OH ice. The $\delta$ peak, seen in the high-exposure TPD spectra for the CH$_3$OH/H$_2$O(10 L) system (Figure 7B), is thought to be due to the formation of crystalline CH$_3$OH and has been observed previously.$^{16,45}$ RAIRS data, reported earlier, confirm that crystalline CH$_3$OH is formed when CH$_3$OH overlayers resulting from a dose of $\geq$ 50 L are heated above 130 K. The $\lambda$ peak visible in the high exposure spectra of the CH$_3$OH/H$_2$O-(50 L) layered ice system (Figure 7C) is more difficult to assign. However, it is noted that the $\lambda$ peak occurs at the same temperature as the amorphous to crystalline phase transition of H$_2$O (the amorphous to crystalline phase transition for pure H$_2$O adsorbed on HOPG occurs at 145–150 K)$^{17}$ and it is therefore possible that the associated structural rearrangement leads to the release of CH$_3$OH molecules that have become trapped within the bulk of the H$_2$O ice as a result of heat induced mixing of the layers. This is a so-called “molecular volcano” peak and has previously been observed for co-deposited layers of CCl$_4$ and ASW.$^{46}$ A similar peak is also seen for the desorption of CH$_3$OH from co-deposited CH$_3$OH/H$_2$O ice systems.$^{47}$ The

![Figure 9. TPD spectra for 7 L of CH$_3$OH (solid line) deposited on an underlying layer of 10 L of H$_2$O ice on an HOPG surface at 97 K. The H$_2$O TPD trace (dotted line) is also shown for comparison. Note that there is not a considerably larger amount of H$_2$O on the surface compared to CH$_3$OH, as implied by the relative intensities of the CH$_3$OH and H$_2$O TPD peaks seen in this spectrum. The mass spectrometer response to H$_2$O is around 5 times larger than that to an equivalent amount of CH$_3$OH, hence the apparent observation that more H$_2$O is present than CH$_3$OH.](image)

![Figure 10. Curves showing the integrated area of the $\alpha$, $\beta$, and $\gamma$ TPD peaks shown in Figures 6 and 7 for (A) the CH$_3$OH/H$_2$O(2 L) and (B) the CH$_3$OH/H$_2$O(10 L) layered ice systems adsorbed on HOPG at 97 K.](image)
observation of this peak clearly indicates that, as already suggested by the RAIRS data, mixing of the H$_2$O and CH$_3$OH layers occurs on heating.

The final feature observed in the TPD spectra in Figures 6 and 8 that still remains to be assigned is the $\alpha$ peak, observed following the lowest exposure of CH$_3$OH onto the underlying H$_2$O ice films. Figure 9 clearly shows that the $\alpha$ CH$_3$OH peak desorbs at the same time as the bulk of the H$_2$O ice. Peak $\alpha$ is a new peak that has not previously been observed for the desorption of CH$_3$OH from bare HOPG. It shows a desorption that is typical of trapped molecules and may represent CH$_3$OH trapped within the bulk of the H$_2$O ice. Previous work has suggested that CH$_3$OH forms a type II clathrate hydrate with H$_2$O ice; however, this seems unlikely in this case given that clathrate hydrates tend to form under high-pressure conditions. RAIRS data, reported earlier, have shown evidence for a strong hydrogen bonding interaction between the H$_2$O and the CH$_3$OH that occurs on annealing. It is therefore likely that this trapped CH$_3$OH species is hydrogen bonded to the H$_2$O that surrounds it, although the exact nature of the CH$_3$OH:H$_2$O complex that is formed is unknown.

RAIRS data have already shown that no interaction occurs between the H$_2$O and CH$_3$OH when adsorption occurs. Hence this trapping must occur as a result of the heating of the layered ice. Since the H$_2$O is deposited in the form of ASW, it will have a very porous and open structure. Any CH$_3$OH deposited onto this H$_2$O ice will therefore cover the surface and may also fill any holes within the ice structure. Previous work has shown that the pores of ASW, grown at 100 K, are too small for CHBr$_3$ to diffuse into and therefore it is also likely that CH$_3$OH is too large to enter the pores of ASW, as previously indicated by Collings. Heating of the ice will first lead to the desorption of monolayer CH$_3$OH, once the appropriate desorption temperature is reached. Heating the layered ice also leads to the conversion of ASW to crystalline ice, as evidenced by the O$-$H stretching region of the RAIR spectra. When this crystallization process takes place, some CH$_3$OH becomes trapped within the bulk of the H$_2$O ice, most likely at grain boundaries between the amorphous and crystalline ice which lead to holes being present in the annealed ice structure. This CH$_3$OH can only desorb when the bulk of the H$_2$O ice desorbs, as seen in Figure 9. The observed trapping leads to CH$_3$OH being retained on the surface for longer than expected when compared to CH$_3$OH adsorption on bare HOPG, as already noted in the RAIR spectra.

It is clear from Figure 8A that the three different layered ices show differences in the desorption temperature and the intensity of the saturated $\alpha$ peak. In fact, the percentage contribution of the $\alpha$ peak to the individual TPD curves increases with increasing thickness of the underlying H$_2$O layer. These differences can be understood by considering the differences in the structure of the H$_2$O ice film for the three layered ice systems. A 2 L exposure of H$_2$O ice will result in some three-dimensional structure to the ice layer, as H$_2$O tends to grow by island formation. However, bare patches of HOPG are also present and hence not much H$_2$O ice is available to trap the CH$_3$OH. Following a 10 L exposure of H$_2$O, the ice film has a greater volume, and so many more grain boundaries are formed on heating and hence more CH$_3$OH is trapped when crystallization occurs. Following a 50 L exposure of H$_2$O ice, considerable multilayer formation occurs, and the larger volume of the H$_2$O ice film leads to an increased amount of the trapped CH$_3$OH species that gives rise to peak $\alpha$. Figure 8A shows that the peak temperature of the $\alpha$ feature apparently increases as the thickness of the underlying H$_2$O layer increases. However, since the trapped CH$_3$OH desorbs only when the bulk H$_2$O ice desorbs then this temperature increase is most likely a function of the increasing desorption temperature of the underlying H$_2$O layer.

To confirm the assignment of peak $\alpha$, a series of TPD experiments were performed for CH$_3$OH deposited on a sublayer of crystalline, rather than amorphous, H$_2$O ice (Figure 8B). The crystalline ice layer was formed by adsorbing H$_2$O on an HOPG surface held at an elevated temperature of 145 K. The surface was then cooled back to 97 K before dosing CH$_3$OH. The phase of the H$_2$O ice was confirmed by using RAIRS. Adsorption of CH$_3$OH on crystalline H$_2$O ice results in a less intense desorption feature, peak $\alpha$, and monolayer feature, peak $\beta$. As seen in Figure 8B, on the crystalline H$_2$O ice surface the multilayer feature, peak $\gamma$, is observed following a lower CH$_3$OH dose. These observations can be explained by considering the structure of the crystalline H$_2$O ice surface. Crystallization of the ice leads to a much denser structure, therefore reducing the surface area available for monolayer adsorption and reducing the entrapment of the CH$_3$OH. Hence the monolayer CH$_3$OH peak now saturates at a lower dose and multilayer growth is noted at lower coverages. A small $\alpha$ peak is still observed for CH$_3$OH adsorption on crystalline H$_2$O and can be explained by incomplete crystallization, as previously seen for H$_2$O adsorbed on bare HOPG. Notesco and Bar-Nun have also reported that a small amount of trapping can still take place within the crystalline phase of H$_2$O ice.

Previous work has observed similar trapping behavior for mixed CH$_3$OH/H$_2$O ices and the formation of type II clathrate hydrates has been proposed to explain the tendency of CH$_3$OH to remain on the surface until the H$_2$O has sublimed. Blake and co-workers suggested the formation of the clathrate hydrate structure from around 130 K, when intermixing occurs. While we clearly see evidence of a strong interaction between the CH$_3$OH and the H$_2$O ice, we are unable to determine the exact nature of the trapped CH$_3$OH species without further structural investigations.

Conclusions

RAIRS investigations of the adsorption of CH$_3$OH onto an underlying H$_2$O ice film show that both CH$_3$OH and H$_2$O adsorb molecularly in a physisorbed state and that they remain isolated from each other in a layered morphology. RAIRS data also show that CH$_3$OH adsorption on an underlying layer of H$_2$O ice (grown in the form of ASW) cannot be distinguished from CH$_3$OH adsorption on bare HOPG, suggesting that the interactions between the individual CH$_3$OH molecules are more important than the interactions between the CH$_3$OH molecules and the surface. Annealing the layered ice leads to mixing of the CH$_3$OH and H$_2$O layers. TPD also shows evidence of mixing that occurs as a result of heating, with a TPD peak being observed that can be assigned to the trapping of CH$_3$OH within the H$_2$O ice structure. The TPD peak assigned to the trapped species increases in size as the thickness of the underlying H$_2$O layer increases, and is thought to arise due to the entrapment of CH$_3$OH at grain boundaries (or holes) that form in the H$_2$O ice as the amorphous to crystalline phase transition takes place. It is proposed that it is this trapped CH$_3$OH species that gives rise to the observed 50 cm$^{-1}$ shift in the O$-$H band observed in the RAIR spectra. TPD peaks are also seen for the desorption of monolayer and multilayer CH$_3$OH and, as seen with RAIRS, TPD cannot distinguish between monolayer CH$_3$OH desorbing from the H$_2$O surface and monolayer CH$_3$OH desorbing from
the bare HOPG surface. Additional TPD peaks are also observed that can be assigned to the formation, and desorption, of crystalline CH$_3$OH and also to the desorption of CH$_2$OH that occurs as the H$_2$O crystalline to hexagonal ice phase transition occurs.

The data reported here are of relevance to studies of the desorption of interstellar ices in areas such as comets, star-forming regions, and hot cores. Previous work has attempted to categorize the molecules found in interstellar ices according to their desorption characteristics. These categories were then used to model the desorption of interstellar ices in hot core regions. CH$_3$OH was categorized as a “H$_2$O-like” species, meaning that it shows desorption characteristics similar to those of H$_2$O. CH$_3$OH desorbing from a H$_2$O layer was not observed meaning that it shows desorption characteristics similar to those of H$_2$O.

The apparent difference between our results and the previous results could be explained by the different exposure ranges of the two experiments. Our experiments were performed over a wide range of CH$_3$OH exposures; however, the previous results only investigated the desorption of 5 L of CH$_3$OH adsorbed on the underlying H$_2$O ice surface. Hence it is clear that the previous classification of CH$_3$OH was limited by the exposure range used. Indeed, the authors of the previous work pointed out that their study was an attempt at initial categorization of astrochemically relevant molecular species and that more detailed studies were needed to give a full understanding of the relevant adsorption systems. Our data have recently been used in astrochemical models to observe the effect of the different categorization of CH$_3$OH on the chemistry observed in star-forming regions.

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References and Notes