Using surface science techniques to investigate the interaction of acetonitrile with dust grain analogue surfaces

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Surface science methodologies, such as reflection-absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD), are ideally suited to studying the interaction of molecules with model astrophysical surfaces. Here we describe the use of RAIRS and TPD to investigate the adsorption, interactions and thermal processing of acetonitrile and water containing model ices grown under astrophysical conditions on a graphitic dust grain analogue surface. Experiments show that acetonitrile physisorbs on the graphitic surface at all exposures. At the lowest coverages, repulsions between the molecules lead to a decreasing desorption energy with increasing coverage. Analysis of TPD data gives monolayer desorption energies ranging from 28.8–39.2 kJ mol\(^{-1}\) and an average multilayer desorption energy of 43.8 kJ mol\(^{-1}\). When acetonitrile is adsorbed in the presence of water ice, the desorption energy of monolayer acetonitrile shows evidence of desorption with a wide range of energies. An estimate of the desorption energy of acetonitrile from crystalline ice (CI) shows that it is increased to \(\sim 37 \text{ kJ mol}^{-1}\) at the lowest exposures of acetonitrile. Amorphous water ice also traps acetonitrile on the graphite surface past its natural desorption temperature, leading to volcano and co-desorption. RAIRS data show that the C≡N vibration shifts, indicative of an interaction between the acetonitrile and the water ice surface.

1. Introduction

Dust grains have been found in a number of astrophysical regions including the interstellar medium (ISM, the space between the stars), comets and planetary atmospheres (1, 2). In many of these regions, the grains are covered in multi-component molecular ices. The exact constituents of these ices are region dependent, but the main constituents are usually water and methanol (see for example Pontoppidan et al. (3)). Astrophysical ices also contain smaller amounts of volatile molecules such as carbon monoxide, methane and carbon dioxide and so called complex organic molecules (COMs) (4) (in astronomical terms, COMs are defined as carbon-containing molecules with six or more atoms). Surface processes, such as addition reactions (5, 6) and thermal and energetic processing (see for example (7–13) and references therein) have been shown to be crucial in the formation of many of the molecules found in these ices and in the gas phase (2). Ultrahigh vacuum (UHV) surface science techniques, such as RAIRS and TPD, have been shown to play an important role in understanding the complex chemistry taking place on grain surfaces. Approximately 1% of the total mass of the ISM is attributed to dust grains (1, 14). These grains are primarily carbonaceous and silicaceous in nature (1, 2) and, due to the cold temperatures in the ISM (20–30 K), are covered in molecular ices. Over 200 molecules have been identified in the gas phase in the ISM to date, ranging from small diatomics such as hydrogen (15) and carbon monoxide (16) to larger COMs such as HC\(_{11}\)N (4, 17). Laboratory surface science investigations have shown that model dust grains play a critical role in the formation of many of these species. For example, it is now widely agreed that H\(_2\) forms in
the ISM via the recombination of H atoms on dust grain surfaces (see for example (5) and references therein). Laboratory investigations have also shown that atom and radical addition reactions on grain surfaces are the main formation route for a range of molecules of varying complexity, such as water (18, 19), CO$_2$ (20) and methanol (6, 21). The formation of more complex species, such as hydrocarbons, alcohols and nitriles, has also been demonstrated upon irradiating adsorbed ices with low energy protons, ions and electrons (see for example (9, 22–30) and references therein).

In addition to reactive processes, thermal processing also plays a very important role as it leads to the sublimation of species from ices into the gas phase. Once in the gas phase, molecules are available to react to form other species. Hence it is important to understand the desorption of molecules from the ices. Surface science studies of the sublimation of model ices are therefore crucial for understanding and modelling such processes. A number of laboratory studies have used TPD to investigate the thermal induced sublimation of a large number of molecules from dust grains analogous to those found in the ISM.

For example, desorption has been investigated from metallic surfaces (see (31, 32) for examples), from carbonaceous surfaces (see (33, 34) for examples), from silicate surfaces (see (32, 34) for examples), from forsterite (see (35) for example) and from bulk-like ice surfaces (see (36, 37) for examples). Through analysis of TPD (33, 38–43) and infrared data (44–47), kinetic parameters of molecules have been determined and incorporated into models in order to accurately describe the desorption of molecular ices from dust grains on astrophysically relevant timescales (48–50).

While interstellar ice is comprised of multiple components, laboratory studies often investigate the desorption of pure molecular ices adsorbed on a variety of metallic, graphitic and silicate substrates in order to provide the basis for understanding more complex ice systems (31, 41, 51, 52). Water is the dominant component of interstellar ices, comprising ~60–70%, depending on the region. Water ice exhibits a range of phases determined by its growth conditions (53). At temperatures below 130 K, water exists as amorphous solid water (ASW) (54, 55). Two phases of ASW have been identified: a high-density amorphous phase at temperatures ~10 K and a low-density, less porous, phase between 35 K and 65 K (55). As water ice is heated, a phase change occurs from ASW to CI as the temperature increases from 130 K to 160 K (53, 56, 57). The different water ice phases have been shown to have a significant impact on the adsorption and desorption of other molecular species co-deposited on top of or within water ice (33, 37, 58–61).

To illustrate the use of UHV surface science investigations in understanding the adsorption and surface chemistry of ices on dust grain analogue surfaces, this paper describes the adsorption of acetonitrile (CH$_3$CN) (**Figure 1(a)**) and water-containing ices on a graphitic dust grain analogue surface, highly oriented pyrolytic graphite (HOPG). HOPG is considered to be a suitable analogue of carbonaceous dust grain surfaces and has been used previously in a range of studies of astrophysical relevance (33, 62, 63). Here we study the adsorption and desorption of acetonitrile and water-containing ices of various configurations, shown in **Figure 1(b)**. Acetonitrile–HOPG and acetonitrile–water interactions have been characterised and kinetic parameters for desorption have been determined in order to provide a detailed overview of the desorption behaviour and the effect of water on the acetonitrile. We also show how these data can be used to describe desorption under relevant astrophysical conditions. To the best of our knowledge, the adsorption and desorption of acetonitrile and water has not been described in detail on a graphitic surface previously.

Acetonitrile is the simplest organic nitrile and is significant in astrophysical terms due to the C≡N group, which plays an important role in amino acid formation and hence potentially in the prebiotic chemistry necessary for life (64). It has been detected in a number of astrophysical environments such as protoplanetary disks, Titan’s atmosphere, comets and the ISM (65–79). Previous studies of acetonitrile adsorption on a range of substrates have demonstrated the formation of weakly bound physisorbed monolayer and multilayer ices (31, 80–85). Spectroscopic
investigations have characterised the nature and orientation of acetonitrile on the surface and in the gas and liquid phases (7, 80–82, 84, 86–89). Infrared spectra, recorded as a function of annealing temperature, show a change in band shape and intensity, indicating a phase change of amorphous to crystalline acetonitrile at a temperature between 95–110 K (7, 84, 90–94). TPD and infrared spectroscopy have also been used to study the interactions of acetonitrile with water and heavy water (D₂O) in layered and mixed ice complexes (83, 95–97). Non-thermal processing of acetonitrile ices, using electrons, photons and high energy ions, has also been investigated (7, 84, 98).

2. Methodology

In order to understand the desorption of molecules from model dust grains at the low pressures and temperatures relevant to astrophysical conditions, experiments were carried out using a stainless steel UHV chamber with a base pressure of <2 × 10⁻¹⁰ mbar. The methodologies used here have been described previously (99, 100). Briefly, the HOPG sample was cooled to a base temperature of 29 K. Acetonitrile (Sigma Aldrich, purity 99.9%) and deionised water were purified by a series of freeze-pump-thaw cycles prior to deposition. A range of ice configurations were grown by background dosing, including pure acetonitrile; layered acetonitrile/water ices; and acetonitrile:water mixtures, as shown in Figure 1(b). Two types of layered ices were investigated, consisting of acetonitrile on CI and on ASW. CI and ASW were grown as described previously (99, 100). Exposures are measured in Langmuir (Lm) where 1 Lm = 1 × 10⁻⁶ mbar s.

TPD data were recorded with a linear heating rate of 0.50 ± 0.01 K s⁻¹. A range of mass fragments were monitored for acetonitrile and water. The mass fragments for each species exhibited identical behaviour, therefore only the most intense fragments are shown here: m/z = 41 for acetonitrile and m/z = 18 for water. RAIR spectra consist of the co-addition of 256 scans at a resolution of 4 cm⁻¹. RAIRS annealing experiments were carried out by increasing the temperature of the sample and holding it at the target temperature for 3 min, before cooling and recording a spectrum. For all TPD and RAIRS experiments, multiple data sets are recorded to ensure reproducibility of results.

3. Results and Discussion

3.1 Temperature Programmed Desorption for Pure Acetonitrile on Highly Oriented Pyrolytic Graphite

Although pure acetonitrile is not found in astrophysical environments, studying pure ices is useful in order to determine the detailed physical and chemical behaviour of the ice and to provide a comparison with the behaviour in the presence of water ice. Figure 2 shows TPD data recorded following the adsorption of increasing amounts of acetonitrile on HOPG at 29 K. At the lowest exposures investigated, 0.5–2 Lm (Figure 2(a)), a decreasing peak temperature with increasing exposure is observed. This can be assigned to initially repulsive interactions between acetonitrile molecules on the HOPG surface. This effect has been seen for ultra-thin acetonitrile films adsorbed on SiO₂ (84) and for other molecules such as benzene on HOPG (38, 101). Behaviour of this type could also be explained by a distribution of binding sites with different adsorption energies, however this is unlikely in this case since HOPG is a very uniform surface.

For acetonitrile exposures between 3 Lm and 7 Lm (Figure 2(a)) the TPD data show an
approximately constant peak temperature with increasing exposure, which is characteristic of first-order desorption of molecular acetonitrile, and indicates that monolayer desorption occurs over this range of exposures. The low temperature desorption, at approximately 127 K, and the approximately constant peak temperature indicate that acetonitrile forms a physisorbed monolayer on the HOPG surface at the intermediate exposures shown in Figure 2(a). The spectra seen in Figure 2(a) are in contrast to those seen for thin acetonitrile films adsorbed on SiO\textsubscript{2} (8, 84), where the acetonitrile peak temperature decreases with increasing coverage for all monolayer exposures. This difference is likely a consequence of the more uniform HOPG surface compared to the heterogenous SiO\textsubscript{2} surface studied by Abdulgalil et al. (8, 84).

TPD data for increasing exposures of acetonitrile on HOPG from 7–100 L\textsubscript{m} can be seen in Figure 2(b). The data clearly show a single desorption feature which increases in temperature with increasing exposure. Traces in Figure 2(b) also show shared leading edges. These observations are indicative of the desorption of acetonitrile multilayers following zero-order kinetics. This is in good agreement with previous studies of multilayer acetonitrile adsorbed on a range of surfaces (7, 31, 82–84, 95).

Kinetic analysis of the TPD data shown in Figure 2 was performed using methods described previously (33). TPD data can be described by the Polanyi-Wigner equation (Equation (i)) where \( r_{\text{des}} \) is the rate of desorption, \( \theta \) is the coverage, \( t \) is the time, \( A \) is the pre-exponential factor, \( n \) is the order of desorption, \( E_{\text{des}} \) is the activation energy for desorption, \( R \) is the gas constant and \( T \) is the temperature of the substrate.

\[
    r_{\text{des}} = -\frac{d\theta}{dt} = A\theta^n \exp\left(\frac{-E_{\text{des}}}{RT}\right)
\]

Analysis using the Polanyi-Wigner equation enables us to obtain \( n \), \( E_{\text{des}} \) and \( A \). The order of desorption, \( n \), can be obtained from rearrangement of Equation (i) as shown previously (33). This gives the order of desorption from a plot of \( \ln[I(T)] \) (where \( I(T) \) is the recorded mass spectrometer signal at temperature \( T \)) as a function of \( \ln[\theta_{\text{rel}}] \) (where \( \theta_{\text{rel}} \) is the relative coverage, given by the integrated area under the TPD curves) at a fixed desorption temperature. Figures 3(a) and 3(b)

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Fig. 3. (a) An example of a plot used to determine the order of multilayer desorption at a fixed temperature of 131 K; (b) an example of a plot used to determine the order of desorption for monolayer desorption of acetonitrile, at a fixed temperature of 125 K; (c) a plot used to determine the desorption energy of 100 L\textsubscript{m} of acetonitrile adsorbed on HOPG.
show examples of such plots for acetonitrile at fixed desorption temperatures of 125 K (monolayer order) and 131 K (multilayer order) respectively. Plots such as this are produced for a range of temperatures using data on the leading edge of the TPD curves; so called leading edge analysis (33). Average values for the order of the monolayer and multilayer desorption can then be obtained from these plots.

The order of desorption for monolayer acetonitrile was found to be 0.89 ± 0.05. The order for multilayer acetonitrile desorption was determined to be 0.08 ± 0.07. These values are as expected for monolayer and multilayer desorption of physisorbed species (33). These desorption orders were obtained for exposures of acetonitrile from 3–100 L\textsubscript{m}. The lowest exposures (0.5–2 L\textsubscript{m}) were omitted from the analysis of the order of desorption as they show behaviour associated with repulsive interactions and hence do not give meaningful data for the desorption order.

Once the desorption order has been determined, a plot of ln[I(T)]−ln[θ\textrel{rel}] versus 1/T can be used to determine $E_{\text{des}}$ (33). The gradient of this plot is equal to $-E_{\text{des}}/R$. An example of this plot for a 100 L\textsubscript{m} exposure of acetonitrile is shown in Figure 3(c). Desorption energies can be determined for each exposure of acetonitrile to show the variation in desorption energy as a function of exposure, as seen in Figure 4.

The inset to Figure 4 clearly shows a decreasing desorption energy with increasing exposure for the very lowest exposures of acetonitrile on HOPG. Following this, the desorption energy increases to the multilayer desorption energy value. A decrease in desorption energy with increasing exposure was also seen by Abdulgalil et al. for acetonitrile adsorption on SiO\textsubscript{2} (84). The average value of the desorption energy of multilayer acetonitrile is determined to be 43.8 ± 1.7 kJ mol\textsuperscript{−1}. For exposures less than 5 L\textsubscript{m}, assigned to monolayer desorption, the desorption energy ranges from 28.8–39.2 kJ mol\textsuperscript{−1}. The monolayer energy determined here is somewhat lower than that determined by Abdulgalil et al. (84) (35–50 kJ mol\textsuperscript{−1}) and by Bertin et al. (95) (44.4 ± 2.8 kJ mol\textsuperscript{−1}) for monolayer desorption from SiO\textsubscript{2} and α-quartz respectively. This is most likely due to the different binding energy of acetonitrile with the carbonaceous HOPG surface compared to that on a silicate surface. The multilayer desorption energy determined here in reasonable agreement with that determined by Abdulgalil et al. (84) (38.2 ± 1 kJ mol\textsuperscript{−1}).

Once the desorption order and activation energy for desorption have been determined, it is possible to obtain values for the pre-exponential factor for desorption, $A$ (33). The average pre-exponential factor for the desorption of monolayer acetonitrile from HOPG was determined to be $3.4 \times 10^{15} \pm 0.5$ s\textsuperscript{−1}. This value is as expected for the desorption of a monolayer species from a surface. The value obtained for multilayer desorption of acetonitrile from HOPG is $1.4 \times 10^{32} \pm 0.3$ molecules m\textsuperscript{−2} s\textsuperscript{−1}. This value is in good agreement with that previously obtained for the desorption of acetonitrile from SiO\textsubscript{2} (84).

### 3.2 Reflection-Absorption Infrared Spectroscopy of Pure Acetonitrile on Highly Oriented Pyrolytic Graphite

RAIR spectra for acetonitrile adsorbed on HOPG at 29 K are shown in Figure 5. The top spectrum shows that recorded upon adsorption at base temperature. The spectrum shown is for the adsorption of 80 L\textsubscript{m} of acetonitrile on HOPG. Adsorption from 0.5–80 L\textsubscript{m} is not shown here, but shows that bands increase in intensity with increasing amount of acetonitrile on the surface. No frequency shifts are observed for increasing amounts of acetonitrile. This indicates that physisorption is taking place, as already shown by the TPD spectra in Figure 2. The assignments of the bands shown in Figure 5 are given in Table I and are made by comparison with the literature. Bands in the high wavenumber region are assigned to the symmetric and antisymmetric methyl group
stretching modes at 3001 cm\(^{-1}\) and 2941 cm\(^{-1}\) respectively. The C≡N stretching mode is observed at 2253 cm\(^{-1}\) and is the most intense band observed in the spectrum. In the lower wavenumber region, a band at 1373 cm\(^{-1}\) is assigned to the symmetric methyl group deformation mode, while bands at 1412 cm\(^{-1}\) and 1448 cm\(^{-1}\) are also assigned to methyl group deformation modes. The band at 1045 cm\(^{-1}\) is assigned to the methyl group rocking mode (not shown) and a further mode at 914 cm\(^{-1}\) (also not shown) is assigned to the C–C stretching mode.

**Figure 5** also shows the results of annealing the adlayer of acetonitrile adsorbed on HOPG at 29 K. The acetonitrile was annealed in 10 K increments up to its desorption temperature. No changes were observed in the spectra until 100 K and hence these spectra have been omitted from **Figure 5**. Following annealing to 100 K, there is an increase in intensity of the C≡N stretch and a small decrease

![RAIR spectra for the annealing of 80 L of acetonitrile adsorbed on HOPG at 29 K. The three spectral regions where the main acetonitrile vibrational bands are observed are shown. The scale for the spectra is indicated by the scale bar in the middle panel.](image-url)
in the wavenumber of this band to 2251 cm\(^{-1}\). This change is accompanied by intensity changes and frequency shifts for other bands in the spectrum. For example, the methyl group stretching mode at 2941 cm\(^{-1}\) moves downwards to 2939 cm\(^{-1}\) following annealing to 100 K; the band at 1448 cm\(^{-1}\) sharpens and increases in wavenumber to 1454 cm\(^{-1}\); and the band at 1045 cm\(^{-1}\) decreases in wavenumber to 1038 cm\(^{-1}\). Further annealing to 110 K shows an increase in intensity of all of the bands in the spectrum, along with a splitting of the bands at 1410 cm\(^{-1}\) and 1373 cm\(^{-1}\). No further changes in the spectrum are observed and all modes have disappeared from the spectrum by 130 K. The lack of bands in the spectrum following annealing to 130 K is evidence for desorption of acetonitrile by this temperature. This temperature is slightly lower than that observed in the TPD spectra, seen in Figure 2, due to the different nature of heating in both cases.

The observed changes in the RAIR spectra following annealing to 110 K can be assigned to the crystallisation of acetonitrile that occurs upon annealing. Acetonitrile crystallisation has been studied in detail by Hudson (92) and the spectra shown in Figure 5 are in good agreement with the high temperature crystalline phase described by Hudson. The crystallisation of solid phase organic species has been observed previously for a range of molecules (42, 92, 100, 102). Recording infrared spectra for ices adsorbed on model grain surfaces helps to allow the identification and assignment of spectra recorded in astrophysical environments. For example, the presence of acetonitrile has been observed in Titan’s atmosphere and hence accurate infrared spectra can help with assignment of observational data (7, 67, 92, 93).

### 3.3 Acetonitrile Adsorbed in the Presence of Water Ice

As described in the introduction, astrophysical ices contain large amounts of water ice, with the exact amount and ice phase depending on the region of space. Given that astrophysical ices are primarily composed of water ice, it is necessary to investigate the interaction of astrophysically relevant molecules with various configurations of water ice as shown in Figure 1(b).

Figure 6 shows TPD data resulting from the adsorption of thin films of acetonitrile in the presence of water ice in different configurations. It is clear from Figure 6 that the presence of ASW has a significant effect on the desorption behaviour of acetonitrile compared to pure acetonitrile ices (Figure 2). Even at the lowest exposures, three features are observed in the TPD data.

The highest temperature species at approximately 158 K can be assigned to the co-desorption of acetonitrile with the bulk water ice. This assignment is confirmed by the fact that this peak has the same desorption temperature as the main water desorption. This observation of co-desorption has also been seen for other molecules (100, 102, 103) and occurs as the molecules become trapped in the bulk of the water ice when the ASW-CI phase transition occurs (31, 103).

The sharp acetonitrile desorption feature observed at approximately 146 K is assigned to volcano desorption of acetonitrile that becomes trapped in the pores of the water ice as the ASW to CI phase transition occurs at ~145 K. The observation of the volcano and co-desorption peaks provides evidence that the acetonitrile likely diffuses into the water ice surface, prior to the ASW to CI phase...
transition occurring. Volcano and co-desorption have previously been seen for a number of molecules, both smaller volatiles (31, 33, 53, 104) and larger organic species (32, 50, 99, 100), adsorbed on and in ASW. The lowest temperature acetonitrile desorption peak seen in Figure 6(c) can be assigned to the desorption of acetonitrile directly from the amorphous water ice surface.

Significant desorption is only seen directly from the ASW surface once the pores of the ASW are saturated and hence this lowest temperature peak only becomes significant for the higher exposures of acetonitrile on ASW. Further increasing the amount of acetonitrile on the ASW leads to the formation of multilayer acetonitrile with desorption behaviour following that of the pure acetonitrile shown in Figure 2.

In contrast to the behaviour of acetonitrile on ASW (Figure 6(c)), adsorption on CI shows simpler desorption behaviour (Figure 6(b)). There are no desorption features that can be assigned to volcano or co-desorption, as expected since the water ice in Figure 6(b) is grown in the crystalline phase. Instead, desorption directly from the CI surface is the only desorption peak observed in the spectrum. Figure 7 shows a comparison between the desorption of acetonitrile from the bare HOPG surface (Figure 7(c) and 7(d)) and from the CI surface (Figure 7(a) and 7(b)). There is clearly a difference in the desorption behaviour of acetonitrile bonded to CI compared to acetonitrile bonded to HOPG. In particular, for the lowest exposures, equivalent amounts of acetonitrile desorb at a higher temperature from CI than from HOPG. For example 2 Lₘ of acetonitrile desorbs from HOPG at a temperature of ~126 K compared to a temperature of ~139 K from CI. In addition, the peak profiles for acetonitrile desorbing from CI are considerably broader compared to those seen for desorption directly from HOPG.

The broader peak profile for acetonitrile desorbing from CI suggests that there is a range of desorption energies and a distribution of binding sites for the acetonitrile on the CI surface. These observations are in agreement with previous investigations of acetonitrile on CI by Bertin et al. (95) which have also been assigned to the observation of a range of desorption energies for acetonitrile on the CI surface. As seen in Figure 7(a), as the amount of acetonitrile on the CI surface increases above 3 Lₘ there is evidence for an additional peak growing into the TPD at lower temperature. Figure 7(b) shows that this feature can be assigned to the growth of multilayers of acetonitrile on the CI surface as also seen in Figure 7(d) for acetonitrile adsorbed directly on HOPG.

Leading edge analysis can also be applied to the TPD curves shown in Figures 6(b) and 7(a) to provide an estimate of the desorption energy of acetonitrile from the CI surface. Analysis of the TPD...
curves for 1 $L_m$ and 2 $L_m$ of acetonitrile adsorbed on CI, with an assumed desorption order of one, give desorption energies of $36.8 \pm 0.8$ kJ mol$^{-1}$ and $36.6 \pm 0.7$ kJ mol$^{-1}$ respectively. Note that, as already discussed, the shape of the TPD curves for monolayer acetonitrile desorbing from CI indicates that there are a range of desorption energies dictating the desorption. These desorption energy values hence give an estimate of the increase in the desorption energy from the CI surface, compared to the HOPG surface, and do not give the full range of desorption energies across all binding sites. Analysis of multilayer TPD data for acetonitrile adsorbed on CI give the same desorption energies as already determined for pure acetonitrile, as expected. For exposures ≥3 $L_m$, Figure 7(b) shows that the additional low temperature feature assigned to the growth of multilayers is already growing into the TPD curves. Hence it is not appropriate to use a desorption order of one to obtain desorption energies for these spectra. An attempt was also made to determine desorption energies for acetonitrile monolayers desorbing from the ASW surface. However, the complexity of the data are such that it was not possible to determine reliable energies of desorption for this system. Nonetheless, a comparison can be made with the data for monolayer acetonitrile on CI (Figure 7(a) and 6(c)), which show that the monolayer on both water ice surfaces shows similar features. Hence, it is expected that the monolayer acetonitrile on ASW desorbs with a wide range of energies, and from a broad range of binding sites. As for desorption from CI, the desorption energy from the ASW surface is higher than from HOPG, and is likely to be around $\sim37$ kJ mol$^{-1}$, as determined from leading edge analysis of the data resulting from desorption of acetonitrile from CI.

The desorption energy values for 1 $L_m$ and 2 $L_m$ of acetonitrile on CI are significantly higher when compared to equivalent exposures adsorbed directly on HOPG (shown in Figure 4) and correspond to a stronger binding energy of the acetonitrile on the CI surface. This can be assigned to an interaction between the C≡N of the acetonitrile and the water ice, as confirmed by RAIR spectra (shown later). This observation of a higher binding energy on CI is in agreement with previous observations (95).

Figure 6(a) also shows the desorption of acetonitrile from mixed ices, formed by co-deposition of acetonitrile and ASW. It is clear from Figure 6(a) that the behaviour of the mixtures is very similar to that of acetonitrile adsorbed on ASW (Figure 6(c)). This behaviour of acetonitrile in the presence of water ice is consistent with that observed for other organic molecules that have weaker interactions (when compared with strongly hydrogen-bonding species such as methanol) with water ice such as methyl formate (103) and ethyl formate (99). This behaviour occurs as the molecule forms a weak interaction with the polar water ice surface, as shown by the different desorption energy when compared to that on HOPG.

Figure 6 also shows that the acetonitrile has an effect on the temperature of the ASW-CI phase transition. Figure 6(c) shows the volcano desorption peak decreasing in temperature with increasing acetonitrile exposure on the ASW surface. The same effect is also seen for mixed ices (Figure 6(a)) where the ice containing a higher percentage of acetonitrile shows a lower temperature volcano desorption. This effect has been reported previously for species that strongly hydrogen bond to water such as methanol (105). It has also been seen for more weakly bonded species that do still interact with water, such as ethyl formate adsorbed in the presence of water ice (99), and provides evidence for an interaction between acetonitrile and water.

Further evidence for an interaction between acetonitrile and water ice is shown in Figure 8, which shows the C≡N stretch of acetonitrile in different ice configurations at 29 K. From Figure 8 it is clear that in the presence of ASW, either in a
layered or mixed ice configuration, the C≡N stretch has a different line shape when compared to that observed for pure acetonitrile on HOPG. For the mixed ice, the C≡N stretch shifts to 2266 cm⁻¹, compared to 2253 cm⁻¹ for the pure ice, showing evidence of a direct interaction between the acetonitrile and water ice. In contrast, the C≡N stretch for acetonitrile adsorbed on top of ASW shows features for both the pure acetonitrile (2253 cm⁻¹) and for the acetonitrile bonded to water ice (2266 cm⁻¹). Acetonitrile bonded to CI has the same vibrational frequency as that seen for pure acetonitrile. This is unsurprising since the spectra shown in Figure 8 are for the adsorption of 20 Lₐ of acetonitrile in different ice configurations. At this exposure, TPD spectra shown in Figure 7 also show that acetonitrile on CI and on HOPG exhibit similar behaviour. The sensitivity of our RAIRS experiment is less than that of the TPD experiment and hence it is not possible to record RAIR spectra for the very lowest exposures of acetonitrile on the surface.

Figure 9 shows the results of annealing an acetonitrile adlayer adsorbed on top of ASW (Figure 9(a)) and a mixed acetonitrile water layer (Figure 9(b)), focusing on the C≡N region of the spectrum. This is the only spectral region that shows appreciable differences when compared with spectra that result from annealing a pure acetonitrile ice (Figure 5). For acetonitrile adsorbed on top of ASW, annealing the ice leads to the appearance of a high wavenumber shoulder at 2266 cm⁻¹ (Figure 9(a)), initially becoming more prominent following annealing to 110 K. The main C≡N stretch at 2253 cm⁻¹ also sharpens and shifts down in wavenumber slightly to 2251 cm⁻¹. This effect was also seen for the annealing of pure acetonitrile ice (Figure 5) and can be assigned to the crystallisation of the acetonitrile layer adsorbed on top of the ASW. Subsequent annealing of this system to 130 K leads to a complete change in the RAIR spectrum. The sharp feature at 2251 cm⁻¹ disappears from the spectrum and the only band that remains is a very broad feature centred at 2266 cm⁻¹.

Comparing the spectrum at 130 K in Figure 9(a) with the spectrum at 130 K for the annealing of pure acetonitrile (Figure 5) shows that this peak can be assigned to acetonitrile trapped within water ice. Annealing of pure acetonitrile ice to 130 K (Figure 5) leads to complete desorption and no peaks are observed in the RAIR spectrum. However, TPD data for acetonitrile adsorbed on top of ASW show the presence of volcano and co-desorption peaks due to acetonitrile trapped within the ASW structure. Hence, the infrared band seen at 130 K following the annealing of the layered ice can be assigned to acetonitrile trapped within the water ice structure. This band occurs at the same wavenumber as that seen for acetonitrile in a mixed ice at base temperature (Figure 8), further confirming the assignment of this peak to acetonitrile trapped within, and interacting with, water ice. Further annealing to 140 K leads to complete desorption of the acetonitrile from the surface. Note that TPD data for the desorption of acetonitrile from the layered ice show slightly higher desorption temperatures than 140 K. This is due to the different heating methods used in the infrared and TPD experiments.

Figure 9(b) shows RAIR spectra resulting from the annealing of a mixed ice. For this ice, there is no evidence of crystallisation of acetonitrile. This is unsurprising since the acetonitrile is within the water ice matrix and hence cannot nucleate to form a crystalline structure. As seen in Figure 9(b), no changes are observed in the RAIR spectrum until the ice has been annealed to above 100 K. Following annealing to above 100 K the spectrum gradually changes to give a very broad feature with bands centred around 2266 cm⁻¹ and 2280 cm⁻¹. Whilst the 2266 cm⁻¹ band has already been assigned, it is not clear what the exact origin of the band at 2266 cm⁻¹ is. However, it is likely that
this also occurs due to an interaction between the acetonitrile and the water ice, although the exact assignment of the band requires further investigation. As for the acetonitrile on ASW, there is clear evidence for the presence of acetonitrile trapped within the water ice as bands are observed up to 140 K in the spectrum, which is considerably higher than seen for pure acetonitrile.

4. Simulations of Desorption Under Astrophysical Conditions

Data of the type described here can be used to simulate desorption under ‘real’ astrophysical conditions, that is with appropriate ice thicknesses and relevant heating rates. Heating rates in astrophysical environments are considerably slower when compared to those in the laboratory. A typical heating rate in an astrophysical environment is around 1 K century\(^{-1}\)\(^\text{(106)}\), compared to 0.5 K s\(^{-1}\) used in the experiments described here. The thickness of astrophysical ices depends on the region, however an ice thickness of 0.3 µm is considered to be appropriate for star-forming regions (48).

The desorption energies derived from our TPD data shown in Figure 2 have been used to determine the desorption temperature of acetonitrile ices under astrophysically relevant heating rates. It is the desorption temperature, not the desorption energy, that is generally put into astrophysical models and hence it is necessary to determine the desorption temperature under astrophysically relevant conditions. Our simple model uses the Polanyi-Wigner equation (Equation (i)) to simulate desorption at a range of heating rates for an ice thickness of 3.42 × 10\(^{21}\) molecules m\(^{-2}\) of pure acetonitrile. This surface coverage is that calculated for an ice thickness of 0.3 m, using a density for solid acetonitrile of 0.778 g cm\(^{-3}\) as determined by Hudson (92).

Figure 10 shows desorption profiles for pure acetonitrile at a number of heating rates ranging from 0.5 K s\(^{-1}\) (the laboratory heating rate) down to 0.01 K year\(^{-1}\) (an astronomically relevant heating rate). As can clearly be seen, the peak temperature for the desorption of acetonitrile decreases considerably as the heating rate decreases, with a peak temperature of ~90 K being seen for the slowest heating rate. In addition, as the heating rate decreases the width of the desorption peak (in terms of temperature) decreases, with the slowest heating rates showing a relatively sharp desorption event happening at the peak temperature. Note that these simulations have been performed using a desorption order of zero and incorporating a relevant pumping speed in order to simulate TPD profiles. The pumping speed is scaled in accordance with the scaling of the heating rate to allow the production of TPD peaks at different heating rates.

Determination of the desorption temperature under astrophysically relevant heating rates is essential to allow the incorporation of the results of TPD experiments such as those described here into astronomical models of star and planet formation. For example, data of this sort have been used to describe desorption of ices in star-forming regions (48). It is only with appropriate laboratory experiments that accurate values of desorption energies can be incorporated into astronomical models.

5. Conclusions

This paper has described the adsorption and desorption of acetonitrile from model astrophysical ices adsorbed on a carbonaceous dust grain analogue surface, HOPG. RAIRS and TPD data have shown that acetonitrile physisorbs on the HOPG surface at all exposures. At the lowest exposures, repulsions between the adsorbed acetonitrile molecules are observed, which lead to an initially decreasing desorption energy with increasing exposure. Subsequent adsorption leads first to standard monolayer behaviour, and
then to the formation of multilayers of acetonitrile on the surface. Water ice, either in the form of ASW or CI, has a substantial effect on the adsorption and desorption of acetonitrile, with ASW trapping the acetonitrile beyond its natural desorption temperature. Characterising the trapping and desorption behaviour of molecules in interstellar ices is very important for providing astronomers with accurate information for astrophysical models based on experimental data. For example, previous studies have classified the desorption behaviour of small molecules as carbon monoxide-like, water-like or intermediate (31) and a more recent study has extended these classifications to COMs (103), by predicting the trapping and desorption of molecules based on the way that they interact with water ice. Classification of the desorption behaviour of COMs then allows astronomers to correctly model the sublimation of a wide range of molecules including those for which laboratory data does not currently exist. Based on its behaviour as described here, acetonitrile can be classified as a complex intermediate species (103). This means that acetonitrile traps in ASW and desorbs mainly via volcano desorption as ASW undergoes a phase change. However, there is also an interaction between the molecule and the water ice surface giving rise to desorption directly from the water surface which has different characteristics when compared to desorption directly from the dust grain analogue surface. Furthermore, acetonitrile also has an effect on ASW itself as observed for other similarly classified molecules such as methyl formate (103) and ethyl formate (99).

RAIRS can also be used to provide information about the interactions between the ice components. Data of this type can be used to compare with observational data, and hence help to identify the environment in which a molecule is found in space (107). For example, the data reported here clearly show that the band profile of the C≡N stretch of acetonitrile changes markedly in the presence of ASW in a mixed ice.

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References


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