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Using laboratory studies of CO–H₂O ices to understand the non-detection of a 2152 cm⁻¹ (4.647 μm) band in the spectra of interstellar ices

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ABSTRACT
We present results from laboratory experiments on layered CO–H₂O-ice systems, carried out from sub-monolayer to multilayer CO coverages, and review recent experimental data, as published by the authors. Under certain specific laboratory conditions the 2152 cm⁻¹ feature, associated with CO molecules adsorbed at dangling-OH bonds at the ice surface, is ‘missing’. A detailed analysis is used to understand why the same feature is not detected in spectra of interstellar ices. We conclude that the dangling-OH sites do exist in interstellar ices but that the sites are blocked by another species. The astronomical implications of this deduction are discussed.

Key words: astrochemistry – line: identification – molecular data – methods: laboratory – ISM: lines and bands – infrared: ISM.

1 INTRODUCTION
A feature is clearly seen at 2152 cm⁻¹ (4.647 μm) in laboratory spectra of mixed CO–H₂O solids that has never been detected in observations of interstellar ices in the 4 μm (K-band) region. Historically, the non-detection of the ‘2152 cm⁻¹ absorption band’ (2152-band) in astronomical spectra was always assumed to be because published observations did not have high enough resolution or signal-to-noise ratios so as fully to decipher the spectrum in this wavelength region (Ehrenfreund et al. 1997a; Sandford et al. 1988), or because the 2152 cm⁻¹ feature was hidden by other spectral features, such as the CN stretching vibration at 2165 cm⁻¹, interference from gas-phase CO lines, or the H₂ Pfund-β emission line at around 2152 cm⁻¹ (Schmitt, Greenberg & Grim 1989). However, recent detections of a solid-CO feature on over 30 lines of sight towards low-, medium- and high-mass young stellar objects (YSOs), in observations made with the VLT-ISAAC by Pontoppidan et al. (2003), did have sufficient resolution and signal-to-noise to decipher fully the solid-CO spectrum, and decouple it from other spectral features in this wavelength region (see Section 2). No absorption feature was detected at 2152 cm⁻¹, even when the overall solid-CO feature had an optical depth of greater than 4, so stringent upper limits have been placed on the optical depth of the 2152-band, ranging from 0.01 to 0.15 (see Table 1). It seems likely therefore that the non-detection of the 2152-band is related to the morphology and chemistry of interstellar ices rather than the abilities of telescopes or observational instruments.

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Table 1. Ratios between the optical depths of the 2136 cm$^{-1}$ (2139 cm$^{-1}$) components in the solid-CO stretching region and at 2152 cm$^{-1}$, obtained for sources observed with the VLT-ISAAC by Pontoppidan et al. (2003).

<table>
<thead>
<tr>
<th>Source</th>
<th>2152 cm$^{-1}$ band upper limit (from obs. spectrum)</th>
<th>2136-COH component fitted optical depth</th>
<th>Ratio 2136-COH component fitted 2152</th>
<th>2139-CO$_{vdW}$ component fitted optical depth</th>
<th>Ratio 2139-CO$_{vdW}$ component fitted 2152</th>
</tr>
</thead>
<tbody>
<tr>
<td>IRS42</td>
<td>0.02</td>
<td>0.07</td>
<td>3.5$^*$</td>
<td>0.53</td>
<td>26.5</td>
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<td>1.75</td>
<td>43.75</td>
</tr>
<tr>
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<td>0.08</td>
<td>1.6$^*$</td>
<td>0.34</td>
<td>6.8</td>
</tr>
<tr>
<td>IRS51</td>
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<td>0.42</td>
<td>14</td>
<td>4.54</td>
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</tr>
<tr>
<td>IRS63</td>
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<td>0.28</td>
<td>9.33</td>
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<tr>
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<td>WL12</td>
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<td>EC90B</td>
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<td>0.19</td>
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<td>SVS4-9</td>
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<td>6.6</td>
<td>0.93</td>
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</tbody>
</table>

*In some cases, the error on the optical depth of the fitted 2139-CO$_{vdW}$ or 2136-COH component of the band is essentially as large as the measurement itself (i.e. no clear band is present) so the ratio no longer has any physical significance and is shown in italics.

Whittet et al. (1998), and towards the galactic centre (e.g. Moneti, Cernicharo & Pardo 2001). Its relative abundance (to solid H$_2$O) is 1 to 20 per cent, but abundances of up to 50 per cent have been reported (Chiar et al. 1994).

When analysing these solid-CO spectra, a ‘mix-and-match’ method has been employed, using the co-addition of multiple, weighted, laboratory spectra to reproduce the observational line-profile, and to decipher the attributes of the interstellar ice. The term ‘polar’ is used to denote environments where the bonding between molecules in the ‘apolar’ layer depends upon weaker van der Waals interactions. We refer henceforth to these phases as the ‘hydrogen bonding’ (2139-CO$_{vdW}$) and ‘van der Waals bonding’ (2139-CO$_{vdW}$) components, respectively.

No exact fit has ever been made with the ‘mix-and-match’ method, and a degeneracy exists between the laboratory spectra, recorded under different experimental conditions, which may be employed to obtain a reasonable fit. As an alternative, Pontoppidan et al. (2003) used phenomenological fits to decompose over 30 detections of solid CO towards different high-, medium- and low-mass YSOs, observed using the VLT-ISAAC. With the advantage of being freed from the (limited) existing laboratory parameter space, the fits were significantly better than the laboratory profile matches, and the fitted components were easily associated with either the 2139-CO$_{vdW}$ or 2136-COH environments. In their data set, the 2139-CO$_{vdW}$ was never observed without the 2136-COH also being present, although the reverse was not true. Their work demonstrated that up to 90 per cent of the solid CO along any line of sight was present in a pure CO layer above other ice components, up to 16 per cent of which migrates into the underlying H$_2$O-ice layer as the grain is warmed, giving rise to the 2136-COH component (Pontoppidan et al. 2003).

Table 1 shows the optical depths of the fitted components corresponding to the 2139-CO$_{vdW}$ and 2136-COH environments in all of the sources observed by Pontoppidan et al. (2003). It also gives stringent upper limits for the optical depth of each spectrum at 2152 cm$^{-1}$, ranging from 0.01 to 0.15. Even when the optical depth of the 2136-COH component exceeds 1, as in SVS4-9, the upper limit on the optical depth of a 2152-band is 0.1. In the spectrum with the deepest 2139-CO$_{vdW}$ component (in IRS51 = 4.54), the 2152-band has an optical depth upper limit of 0.03. A 2152 cm$^{-1}$ absorption feature is simply not detected in spectra of interstellar ices.

2.2 Relevant laboratory studies of mixed CO–H$_2$O ices

Previously, laboratory astrochemistry studies have focused on obtaining transmission spectra of ice mixtures, at 1 or 2 cm$^{-1}$ resolution, deposited at or below 15 K under high vacuum (HV) conditions. In the case of pure CO ices and CO–H$_2$O ice mixtures, laboratory spectra have been obtained over a range of component concentrations, temperatures, spectral resolutions and ice
thickness, sometimes including additional species in the ices (e.g. Ehrenfreund et al. 1996; Givan, Loewenschuss & Nielsen 1998; Palumbo 1997; Sandford et al. 1988). In some cases, the ices were further processed by annealing, UV exposure or electron/ion bombardment (e.g. Ehrenfreund et al. 1997a, 1998; Gerakines et al. 1995; Hudson & Moore 1999; Satorre, Palumbo & Strazzulla 2000; Schmitt et al. 1989). The spectra of the mixed CO–H2O ices can be summarized as follows: below around 80 K, the published laboratory spectra have two distinct features, one around 2139 cm\(^{-1}\) and one around 2152 cm\(^{-1}\) with relative intensities of about 2:1: when heated above 80 K the 2152 cm\(^{-1}\) band disappears and the 2139 cm\(^{-1}\) band narrows and shifts towards 2136 cm\(^{-1}\). This feature disappears by about 200 K, where H\(_2\)O desorbs (under these conditions). For further details see, for example, an earlier publication on mixed H\(_2\)O–CO ices by Sandford et al. (1988). The 2136 cm\(^{-1}\) band is related to the 2136-CO\(_{\text{III}}\) component in observational spectra. At a similar resolution under HV conditions, pure CO ices show a single feature around 2139 cm\(^{-1}\), which disappears completely by around 35 K, when the CO has fully desorbed. This feature is related to the 2139-CO\(_{\text{vdW}}\) component in observational spectra.

It is spectra from databases of this genre of laboratory work that are used in ‘mix-and-match’ fitting of observational spectra. Typically, the observed 2136-CO\(_{\text{III}}\) component is fitted with a laboratory spectrum of CO diluted in a H\(_2\)O-rich ice. Even when grain shape effects are taken into account (Tielens et al. 1991), the laboratory spectra are always narrower than the interstellar spectra, so an exact fit to the red wing of the solid-CO band in the observed spectrum is not possible. Furthermore, below \(\approx 80\) K, laboratory spectra always have a 2152 cm\(^{-1}\) component that is significantly more intense than the optical depth of the observational spectrum at the same wavelength, and clearly does not fit the blue wing of the solid-CO band in the observation. Thus the problem of the ‘missing’ 2152-band arises: why do we detect a 2152-band in the laboratory but not in observations?

### 3 EXPERIMENTAL RESULTS FROM LAYERED CO–H\(_2\)O ICES

A series UHV experiments was recently conducted by this group on solid H\(_2\)O–CO systems, and are the subject of previous publications, and described in detail therein (Collings et al. 2002, 2003a,b). In particular, the reader should note that three major differences exist between these studies and previous work on interstellar ice analogues (described in Section 2.2):

(i) under UHV conditions the ice system cannot be contaminated by additional accretion of H\(_2\)O over the lifetime of the experiment (Fraser & van Dishoeck 2004);

(ii) this work studied sequentially deposited layers of H\(_2\)O and CO ice for the first time, in addition to mixed H\(_2\)O–CO ices;

(iii) in comparison with transmission spectroscopy, reflection absorption (RAIRS) spectroscopy is at least 50 times more sensitive.

Fig. 1 gives an overview of the pertinent results from the RAIRS experiments. It shows in 1(a)–(c) previously unpublished spectra of the CO stretching region from sequentially deposited CO–H\(_2\)O layers, and, for comparison, 1(d) shows previously published spectra (Collings et al. 2003a) of a mixture of 5 per cent CO in H\(_2\)O (mixing ratio 1:20). Equal amounts of H\(_2\)O (57 \(\mu\)g cm\(^{-2}\)) were deposited on the surface in each layer experiment at (a) 8 K, to form porous amorphous solid water (porous ASW), (b) 83 K, to form compact ASW, and (c) annealed at 140 K for 2 hours in a dynamic background pressure of 1 \(\times\) 10\(^{-8}\) mbar H\(_2\)O, to form cubic crystalline water ice (I\(_\text{h}\)) (Fraser et al. 2001). The H\(_2\)O-ice was then quenched to 8 K before depositing the CO layer. The layered spectra are divided into (i) a sub-monolayer exposure of CO (0.07 \(\mu\)g cm\(^{-2}\)) at 8 K (as deposited) and (ii) multilayer exposures of CO (0.35 \(\mu\)g cm\(^{-2}\)) at 8 K (as deposited) and after annealing at 30 and 80 K. In (ii), the initial CO exposure (at 8 K) is equivalent to the same exposure that would be required to form \(~7.5\) monolayers (ML) of CO on a flat surface, such that the integrated area under the each of the spectra at 8 K is constant. In many of the spectra shown in Fig. 1 two broad bands are evident, at around 2136–2139 cm\(^{-1}\) and 2152 cm\(^{-1}\), but under certain conditions the 2152-band is not observed.

### 3.1 Assignment of the spectroscopic features

From an analysis of the spectra shown in Figs 1(a)–(d), three distinct vibrational frequencies for CO on and in H\(_2\)O environments can be identified: one at 2152 cm\(^{-1}\), one at 2139 cm\(^{-1}\) and (at higher temperatures) one at 2136 cm\(^{-1}\). In combination with the results of previous experimental and theoretical work (Al-Halabi, van Dishoeck & Kroes 2004; Al-Halabi et al. 2003, 2004; Collings et al. 2002, 2003a,b; Devlin 1992; Manca, Roubin & Martin 2000; Manca & Allouche 2001; Manca et al. 2001), these features have been associated with various binding sites for CO on and in H\(_2\)O environments, as summarized in Fig. 2.

The 2152-band is associated with CO molecules that are bound to dangling-OH at ice–vacuum or ice–ice interfaces, i.e. CO interacting with OH bonds from H\(_2\)O molecules protruding from these interfaces and not participating in the hydrogen bonding network. Theoretical studies identify this binding site as the most strongly bound configuration for CO on any H\(_2\)O-ice surface (Manca et al. 2001; Al-Halabi et al. 2003; Al-Halabi et al. 2003, 2004), and involve CO interacting with many water molecules at the H\(_2\)O–vacuum interface (Al-Halabi et al. 2004).

A second binding site for CO at H\(_2\)O-ice interfaces, associated with the spectroscopic feature at 2139 cm\(^{-1}\), has been identified from theoretical (Al-Halabi, van Dishoeck & Kroes 2004; Al-Halabi et al. 2003, 2004; Manca et al. 2001) and experimental studies (Collings et al. 2002, 2003a,b; Manca & Allouche 2001; Manca, Martin & Roubin 2002). The precise molecular configuration of this binding site on amorphous H\(_2\)O-ice surfaces has not yet been determined, although it is most probably related to CO molecules interacting with those H\(_2\)O molecules at the ice surface fully participating in the hydrogen-bonding network. Al-Halabi et al. (2004) describe this configuration as CO–bonded OH; Collings et al. (2003b) describe it as a parallel H\(_2\)O–CO complex. On I\(_\text{h}\), the binding sites associated with the 2139 cm\(^{-1}\) band are identified as CO interacting with the lone pairs of electrons on the oxygen of the H\(_2\)O molecule, in a variety of configurations (Manca et al. 2001).

It is important to appreciate that pure CO ices also exhibit an infrared absorption feature at around 2139 cm\(^{-1}\) (Ewing & Pimentel 1961), attributed to solid-CO stretching vibrations. Consequently, if multilayers of CO are present on the H\(_2\)O-ice surface, then the observed CO spectrum will be dominated by a feature at 2139 cm\(^{-1}\), arising from solid-CO stretching vibrations in the multilayer (see Fig. 2). This implies that in interstellar spectra of solid CO, the 2139-CO\(_{\text{vdW}}\) component is also dominated by solid-CO vibrations from the pure CO ‘overlay’, but may include a (non-detectable) contribution from CO–H\(_2\)O interactions at the CO–H\(_2\)O-ice interface (Pontoppidan et al. 2003; Fraser et al. 2004). If multilayers of crystalline CO are present, RAIRS spectra can exhibit LO–TO...
Figure 1. RAIR spectra of the CO-stretching region of thermally processed CO–H2O films. (a)–(c) Sequentially deposited layers of CO deposited at 8 K on to a H2O film (57 μg cm−2) (a) adsorbed at 8 K (porous ASW), (b) adsorbed at 83 K (compact ASW), (c) adsorbed at 8 K and annealed at 140 K for 2 hours in a dynamic background pressure of 1 × 10−8 mbar of H2O to form Ic. (i) Submonolayer coverage of CO (0.07 μg cm−2), (ii) multilayer coverage of CO (0.35 μg cm−2), from top to bottom as deposited at 8 K, and heated to 30 and 80 K. (d) A co-deposited mixture of ~5 per cent CO in H2O (57 μg cm−2) adsorbed at 8 K.

splitting, associated with the longitudinal and transverse optical modes of the solid (Chang, Richardson & Ewing 1988; Collings et al. 2003a). Such splitting is clearly present in the 8 K multilayer exposure spectra in Figs 1(a)–(c), suggesting that when CO is deposited on H2O-ice surfaces at around 8 K, a crystalline and not an amorphous solid-CO layer is formed. A more detailed discussion of the spectroscopy and behaviour of the CO over-layer can be found in Collings et al. (2003a,b). In transmission spectroscopy, the same splitting can only be observed if at least some of the light from the background source is polarized: such features, at around 2139 and 2143 cm−1, have been identified on lines of sight towards low-mass YSOs (Pontoppidan et al. 2003).

A third infrared feature, at 2136 cm−1, emerges as the ice system is warmed above ≈80 K. Previously, it has been suggested that this is associated with CO molecules isolated within the H2O matrix in substitutional or interstitial sites (Sandford et al. 1988). However, theoretical studies of CO–H2O systems clearly show that substituting or intercalating CO within H2O ice is highly unstable: in fact the energy barrier for CO migration into the bulk is at least double the desorption energy barrier (Al-Halabi et al. 2003, 2004). Such findings are entirely consistent with experimental evidence – the 2136 cm−1 feature is never observed experimentally when H2O–CO ices are deposited, only when they are heated. The precise molecular configuration of this ‘bulk’ 2136 cm−1 feature remains an open question, but it is clear that it is closely related to the trapping of CO molecules in the ‘ice’ as a result of the H2O matrix collapsing around the CO molecule before it can desorb (Collings et al. 2002, 2003a,b).

Other spectroscopic features can be identified in Fig. 1, but are not relevant to this paper and therefore not discussed here. For more information the reader is directed elsewhere (Collings et al. 2002, 2003a,b). For the remainder of this paper, it is necessary only to recall that two binding sites exist for CO at H2O interfaces, associated with the 2152 and 2139 cm−1 spectral features, one binding site exists for CO in CO multilayers, also associated with the 2139 cm−1 spectral feature, and one binding site exists for CO trapped in the H2O-ice matrix, associated with the 2136 cm−1 spectral feature (see Fig. 2). These bulk 2139 and 2136 cm−1 bands are directly related to the 2139-COvdW and 2136-COvH observational features, respectively.

4 EXPLAINING THE MISSING 2152-BAND
The experimental evidence summarized in Section 3 and illustrated in Fig. 1 shows that it is relatively simple to construct a
CO–H₂O-ice system in the laboratory where the 2152-band is not evident, particularly if layered rather than mixed ice analogues are used. It is important to note that in all the laboratory spectra presented here the signal-to-noise ratio is better than in the astronomical data, so if the 2152-band exists, it will be detected. The evidence implies that the 2152 cm⁻¹ feature is absent from all the existing interstellar spectra either because the binding sites associated with this band are absent from interstellar ices (i.e. no dangling-OH are present on interstellar ice), or, if the sites do exist, the CO does not, or is somehow prevented from, ever adsorbing there. The following sections explore which of these scenarios is most likely in the interstellar case.

4.1 Experimental evidence on the existence of dangling-OH binding sites in H₂O-ices

4.1.1 The evolution of the 2152-band in mixed CO–H₂O ices

The 2136-CO H component of the interstellar solid-CO band is thought to arise from the evolution of a layered-ice into a mixed-ice system (see Section 2.1). In fact, the laboratory spectra of layered CO–porous ASW systems and mixed CO–H₂O systems are almost indistinguishable from one another above 80 K (compare Fig. 1(a) (ii) 80 K and Fig. 1(d) (ii) 80 K), so some additional understanding is to be gained by analysing the mixed-ice spectra on the basis of the spectral assignments made from the layered-ice systems (see Section 3.1).

As a consequence of the deposition techniques used to grow ‘mixed’ ices in the laboratory (i.e. deposition of an H₂O–CO gas mix or co-deposition of CO and H₂O), all the CO molecules are deposited at interfaces. Below about 20 K, as H₂O and CO molecules land at the substrate they are ballistically deposited, i.e. they stick where they land, so each new molecule colliding with the ice is actually deposited at the ‘current’ ice–vacuum interface. As further molecules are deposited, the interface becomes buried, so the structure finally acquired is a porous ‘mixed’ ice, where all the CO molecules reside in binding sites indistinguishable from those at the ice–vacuum interface (see Fig. 2). Consequently, two bands, a 2152 cm⁻¹ band and a 2139 cm⁻¹ band, are observed, suggesting that all the CO molecules reside in interfacial binding sites. The occupation ratio of these sites is about 1:2. As the mixed ice is warmed two phenomena occur: the CO becomes mobile, and the H₂O ice re-structures, collapsing around the CO. A competition exists: if the surrounding H₂O matrix collapses on the CO before it can reach...
an ice–vacuum interface, the CO is trapped in the matrix, otherwise it desorbs. Experimentally this is observed as a loss of the interfacial binding sites, i.e. the 2152 cm$^{-1}$ band disappears completely in mixed ices heated above $\approx 80$ K, and the 2139 cm$^{-1}$ band evolves into the 2136 cm$^{-1}$ band. The transition from one state to the other means that, at temperatures up to about 80 K, the overall peak position may lie somewhere between 2139 and 2136 cm$^{-1}$, but the laboratory line profile of CO can be decomposed into contributions from these two components (Fraser et al. 2004).

The 2139 cm$^{-1}$ band can be observed in the laboratory without a separately resolved 2136 cm$^{-1}$ feature being present – in observations, as mentioned in Section 2.1, this is never the case. In the laboratory when the 2139 cm$^{-1}$ band is present, the 2152-band is present. However, if only the 2136 cm$^{-1}$ feature exists, no 2152-band is seen. This compares with the astronomical case, where on certain lines of sight the spectrum is dominated by the 2136-COH band.

4.1.2 Evolution of the 2152-band in layered CO–H$_2$O ices at sub-monolayer CO coverage

At sub-monolayer coverages, CO molecules probe only the external ice–vacuum interface (Figs 1(a)–(c) (i) and Fig. 2), and two features are observed in the RAIR spectra, corresponding to the two interfacial binding sites, at 2152 and 2139 cm$^{-1}$. On porous ASW, compact ASW and I$_1$, the ratio between the occupation of these sites remains roughly constant, between 1:2 and 1:3 (2139 cm$^{-1}$ sites are always more heavily populated than 2152 cm$^{-1}$ sites).

This result does not help us directly in explaining the missing 2152-band, but can be inverted, to place stringent limitations on the coverage of CO on interstellar ices. If the interstellar 2139-CO$_{\text{int}}$ signal arises from sub-monolayer coverages of CO on icy interstellar grains, then one would expect to detect a 2152-band of around half the intensity of the 2139-CO$_{\text{int}}$ component. As the 2152-band is not detected, CO coverages must be much greater, probably multilayers thick.

4.1.3 Evolution of the 2152-band in layered CO–porous ASW

With increasing CO exposures, it is expected that adsorption will continue at interfacial H$_2$O sites, until the ice surface is covered by a single layer (monolayer) of CO. Thereafter, CO multilayers will build-up, evinced by a significant increase in the intensity of the 2139 cm$^{-1}$ feature, attributable to solid-CO stretching vibrations. However, below about 15 K, as CO molecules land at the substrate they are deposited ballistically. This suggests that not all the interfacial 2152 cm$^{-1}$ binding sites are populated when CO is deposited at 8 K, because at such low temperatures CO simply ‘sticks and stops’ at the initial collision site, rather than diffusing to the energetically more favourable, strongest binding site. Such low-temperature behaviour has been well documented in other gas–surface systems, where the lack of adsorbate mobility means that adsorbrates sample a statistical distribution of all possible binding sites at the surface rather than diffusing to the energetically-favoured strongest binding sites (Brown et al. 1995; Brown, Gardner & King 1995; Rutten et al. 1997). Consequently, as the CO exposure at the H$_2$O ice is increased, the 2152-band appears to saturate, and the 2139 cm$^{-1}$ feature increases in intensity, commensurate with the growth of CO multilayers at the ice–vacuum interface, before all the surface binding sites on the H$_2$O are actually occupied (compare Fig. 1(a) (i) and (ii) 8 K). This laboratory process is entirely comparable with the interstellar case, where CO condensed on to interstellar grains will have insufficient energy to diffuse across the ice surface, leading to the build-up of ‘pure’ CO layers, consistent with observations (Pontoppidan et al. 2003).

It may then be suggested that we have found the solution to the ‘missing’ 2152-band problem. CO accretion in space (which will also be ballistic) would lead to a spectrum dominated by a 2139 cm$^{-1}$ band associated with solid-CO stretching vibrations from a CO multilayer, so one would never expect to detect the tiny 2152-band associated with the small fraction of CO molecules residing at the H$_2$O-ice CO-ice interface: even in the laboratory spectra the 2152-band is hardly visible (Figs 1(a)–(c) (ii) 8 K). This is not the case, however, because for CO adsorbed on porous ASW (Fig. 1(a)) the 2152-band increases in intensity as the ice is heated, accompanied by a decrease in the intensity of the 2139 cm$^{-1}$ feature (compare Fig. 1(a) (ii) 8 K and 30 K). Even if a 2152-band were not observed on lines of sight probing cold dust ($\approx 10$ K), those probing just slightly warmer dust ($\approx 15$ K) would be expected to exhibit 2152-bands.

The reason for the increase in the 2152-band intensity with temperature is related to the physical chemistry and morphology of the ice system. As the ices are heated, the system essentially restructures: complimentary desorption studies (not shown here) confirm that below $\approx 20$–25 K no CO desorption occurs (Collings et al. 2002, 2003a,b). CO molecules diffuse from the CO multilayer to the surfaces of pores within the porous ASW, i.e. those interfaces in the H$_2$O-ice structure that are not facing the external vacuum interface (see Fig. 2). Porous ASW is a metastable amorphous solid with long porous channels connected to the external vacuum interface (Kimmel et al. 2001a,b), and a total surface area many orders of magnitude greater than the geometric surface area of the substrate on which it is grown (Dohnalek et al. 2003). Consequently, all the CO that was accumulated in the CO multilayers is able to ‘find’ a binding site somewhere on the H$_2$O-ice surface. This results in an increase in the intensity of the 2152-band, as occupancy of these interfacial binding sites increases, but a decrease in the intensity of the 2139 cm$^{-1}$ feature, as the solid-CO layer is lost (compare Fig. 1(a) (ii) 8 K and 30 K). However, as stated earlier, two binding sites contribute to the total intensity of the 2139 cm$^{-1}$ band, and whilst the solid-CO population is decreasing, the CO–H$_2$O interfacial binding site population is increasing. In Fig. 1(a) (ii) 30 K, the ratio between the 2152 and 2139 cm$^{-1}$ bands is about 1:2 (very similar to the sub-monolayer coverage (Fig. 1(a) (i)), i.e. by 30 K the two features observed in the RAIR spectra again correspond to CO occupying only the two interfacial binding sites, at 2152 and 2139 cm$^{-1}$.

Between $\approx 25$ and 80 K, CO desorption from the porous ASW surface competes with trapping, as the porous ASW structure collapses. Surface desorption dominates: in fact both the 2152 and the 2139 cm$^{-1}$ bands reduce significantly in intensity until, by 80 K, both the 2152 and 2139 cm$^{-1}$ bands have completely disappeared (Fig. 1(a) (ii) 80 K). The remaining CO signal arises from CO molecules trapped in the H$_2$O-matrix, i.e. the 2136 cm$^{-1}$ feature. Although some dangling-OH binding sites must remain at the ice surface, they can no longer be occupied by CO as its sticking probability on such a ‘warm’ surface is essentially zero (Al-Halabi et al. 2004).

4.1.4 Evolution of the 2152-band in layered CO–compact ASW and CO–I$_1$ ices

The 2152-band has negligible intensity relative to the 2139 cm$^{-1}$ band following multilayer CO exposures at 8 K on compact ASW...
(Fig. 1(b) (ii) 8 K) and Ic (Fig. 1(c) (ii) 8 K). Both spectra are dominated by solid-CO contributions to the 2139 cm$^{-1}$ band from the CO multilayer. Unlike porous ASW, the accessible surface area on Ic is smooth and flat, so the total surface area is almost equal to the geometric surface area the ice is deposited over (Kimmel et al. 2001a). As the CO–Ic system is heated, CO simply desorbs from the CO multilayer and by 25 K almost no CO remains on the Ic surface (Fig. 1(c) (ii) 30 K). The 2152-band and 2139 cm$^{-1}$ feature disappear. Conversely, the surface of compact ASW is roughened, with deep ‘hills and valleys’ (see Fig. 2), and although its total surface area is greater than that of Ic, it is significantly less than that of porous ASW (Kimmel et al. 2001a). As the CO–compact ASW system is heated from 8 to 30 K, the absolute intensity of the 2152-band changes by a factor of about 3–4 (see Fig. 1(b) (ii) 8 K and 30 K). Some of the CO desorbs directly from the CO multilayer, but the remainder clearly probes those ‘hills and valleys’ of the external H$_2$O-ice surface that were not covered by CO during the ballistic deposition (see Fig. 2). The remaining CO occupies the 2152 and 2139 cm$^{-1}$ interfacial binding sites in a ratio of about 1:5 (Fig. 1(b) (ii) 30 K). Since compact ASW has no large-scale internal porous structure it is not able to trap volatile species (like CO). Consequently, as the ice system is heated to 80 K, both the 2152 and 2139 cm$^{-1}$ bands decrease in intensity, until by 80 K all the CO has desorbed (Fig. 1(b) (ii) 80 K).

Could interstellar H$_2$O-ice be non-porous? Clearly, of all the ices investigated here, CO adsorbed on Ic gives the weakest 2152-band, which could have been detectable in interstellar spectra because the associated binding sites (i.e. dangling-OH) do not exist on interstellar H$_2$O ice. What if the sites do exist, but CO is somehow prevented from ever adsorbing to them?

4.2 Experimental evidence on the blocking / removal of the 2152-band binding sites

Previous infrared experiments have shown that when an alternative molecule, which binds more strongly to H$_2$O-ice interfaces than CO, is pre-adsorbed at the H$_2$O-ice surface prior to CO exposure, some of the available adsorption sites can be selectively ‘blocked’, preventing CO adsorbing there (Devlin 1992; Martin, Manca & Roubin 2002). For example: when CO is adsorbed on an I$_2$ surface that has been previously exposed to CF$_4$, the 2152-band appears first, and at low CO exposures its intensity is greater than that of the 2139 cm$^{-1}$ CO–H$_2$O surface feature. This is because CF$_4$ preferentially adsorbs at the centre of the hexagonal rings in the surface structure, blocking the water shafts and leaving only the dangling-OH binding sites accessible (Buch et al. 1996). However, at multilayer CO exposures the spectrum is once again dominated by the 2139-CO$_{2\mu}$ feature, primarily attributable to solid-CO vibrations in the CO multilayers. Conversely, if ethylene oxide (C$_2$H$_4$O) is pre-adsorbed to the surface, it forms a hydrogen bond with the dangling ‘OH’, therefore blocking the 2152 cm$^{-1}$ binding sites. When the surface is exposed to CO, the 2152-band is not seen (Devlin 1992). Clearly, neither CF$_4$ nor C$_2$H$_4$O are particularly abundant interstellar solid phase species, but these experiments do illustrate the feasibility of the 2152 cm$^{-1}$ binding sites being blocked.

In the interstellar case, species that might block the 2152 cm$^{-1}$ binding sites fall into one of three categories:

(1) less volatile species formed in the gas phase, or atoms, ions, or radicals which freeze out at the H$_2$O surface before CO condenses there, and that bind more tightly to the dangling-OH sites, e.g. O$_2$, OCS, C$_2$H$_2$;

(2) molecules that bind effectively to the dangling-OH sites after being formed at the surface, possibly even displacing more weakly bound CO molecules at those sites, or involving CO at dangling-OH sites in the reaction, e.g. CO$_2$, CH$_3$OH, HCOOH;

(3) molecules that form at the ice surface as the ice itself is re-actively formed, e.g. where N + H or C + H may be competing with H + O at a grain surface, the dangling-OH sites may become blocked by, for example, NH$_3$ or CH$_4$.

Could all of the dangling bond sites on the ice surface be occupied in this way before CO adsorption occurs? Some of the most likely species to be found blocking the 2152 cm$^{-1}$ binding sites are themselves manufactured at the surface, and usually include CO as a reagent, e.g. CH$_3$OH, CO$_2$ (the latter being a particularly good candidate as it is ubiquitous in interstellar ices). This is a dichotomy for solid-state astrochemistry. Of course, there is a chance that CO does adsorb at dangling-OH sites, but that the CO–dangling-OH is a short-lived intermediate state in a reaction pathway generating one of the blocking species mentioned previously. If the rate of reaction producing the ‘blocking species’ is high, relative to the rate of formation of the CO–dangling-OH (either by adsorption or diffusion...
of CO), then the 2152 cm$^{-1}$ site would never be sufficiently highly populated by CO molecules to be readily detected. Not enough experimental data currently exist on surface reaction mechanisms or kinetics to confirm or refute this hypothesis, although with the number of groups now working with UHV experiments, such issues will be addressed by the authors and others in the near future.

5 DISCUSSION

5.1 The 2136-COH/2152 or the 2139-CO$_{vdW}$/2152 optical depth ratio

The ratio of the ‘optical depth of observational spectra at 2136 cm$^{-1}$’ to the ‘optical depth at 2152 cm$^{-1}$’ is widely used in the astronomy literature to place an upper limit on the optical depth of the 2152-band and give some indication of ice properties, e.g. temperature or degree of processing, by comparing the ratio with that obtained experimentally from mixed H$_2$O–CO ices. In fact, as Fig. 3 illustrates, this is a non-sensical exercise, not least because the 2152-band is not detected in astronomical spectra.

For the laboratory spectra, the ratio ('main'/2152) means the ‘integrated intensity of the most intense solid-CO adsorption peak in the laboratory spectrum’ divided by the ‘integrated intensity of the 2152 cm$^{-1}$ feature (if it exists). As indicated by the dashed dividing line at 80 K in Fig. 3(a), 'main'/2152 ratios below 80 K can be read as 2139 cm$^{-1}$/2152 cm$^{-1}$ intensity ratios, and above 80 K as 2136 cm$^{-1}$/2152 cm$^{-1}$ intensity ratios. In Fig. 3 this ratio is plotted against ice temperature for a variety of CO–H$_2$O systems. Of course, once the 2152-band disappears, the ratio fails to have any physical significance. In addition to the ices discussed in Section 4.1, data is included from three previous studies of mixed H$_2$O–CO ices (Sandford et al. 1988; Schmitt et al. 1989; Fraser et al. 2004). Fig. 3(b), an enlargement of Fig. 3(a) in the 10–70 K range, shows very good agreement is obtained between these (mixed-ice) results and those from previous (mixed-ice) studies.

In the mixed ices, the trend is for the initial ratio to be small, around 2 or 3, and increase non-linearly as the ice is warmed. The ratios in the layered ice systems all start relatively high (over 20), because at 8 K the ‘main’ peak in the spectrum is dominated by the solid-CO multilayer peak (at 2139 cm$^{-1}$), as described in Section 4.1. As the ice layers are heated from 8–20 K, the ‘main’/2152 cm$^{-1}$ ratio decreases, reflecting the change in occupation of the solid-CO and H$_2$O-ice interfacial binding sites, as described in Section 4.1. At higher temperatures, the ratio increases rapidly, reflecting the desorption of CO from the interfacial binding sites, and (for porous ASW) trapping of the remaining CO within the H$_2$O matrix.

The maximum lower limits on the ‘main’/2152 ratio, as constrained by the ‘upper limits’ on the (non-detected) optical depth of the 2152-band from the observational data (detailed Table 1), are indicated by the cross-hatched area for 2136-COH/2152, plus the right-hatched area for 2136-COH$_{vdW}$/2152. In the literature it is then argued that laboratory ices with ‘main’/2152 ratios above this limit are suitable candidates for determining the interstellar ice structure and temperature, i.e. from this comparison we could suggest that interstellar ices are compact ASW, layered ices, heated above 40–50 K, or mixed ices above 80 K. Of course, we have previously ruled both these ice configurations out (see Section 4.1). The comparison simply does not work in the case of the 2136-COH/2152 ratio because the 2136-COH feature actually probes ices where CO is trapped within the H$_2$O matrix, whereas the 2152-band arises from ices where CO resides in the H$_2$O-ice interfaces; these are two separate CO populations.

No useful constraints can be placed on interstellar ice temperature or morphology based on the 2139-CO$_{vdW}$/2152 ratio either, since the 2139 cm$^{-1}$ feature is a combination of solid-CO and interfacial CO–H$_2$O interactions, dominated by the former at very low temperatures, then by the latter at intermediate temperatures; again, these are two separate CO populations. Assuming CO was never able to diffuse into the porous H$_2$O ice below, the 2139-CO$_{vdW}$/2152 ratio would give some idea of the CO multilayer thickness in interstellar ice, by constraining the solid (2139-CO$_{vdW}$)-to-surface (2152 cm$^{-1}$) ratio. Provided that the ice-surface binding sites were not blocked by another species, this may have been a true measure of the grain surface area available for chemistry on interstellar grains, rather than invoking such a number from H$_2$ formation rates. However, Pontoppidan et al. (2003) showed that up to 16 per cent of the CO
multilayer does migrate into the H$_2$O ice, and it is clear from the arguments in Sections 4.1 and 4.2 that the 2152 cm$^{-1}$ binding sites are blocked to CO adsorption in interstellar regions. The important message provided from Fig. 3 is that 2136-CO$_{\text{H}}$/2152 and 2139-CO$_{\text{OH}}$/2152 ratios do not place any constraints on interstellar ice properties and have no physical significance.

5.2 Implications for the morphology and growth of interstellar ice mantles

In reaching the conclusions in Sections 4.1, 4.2 and 5.1, it is possible to make other observations associated with the nature of interstellar ices due to the non-detection of a 2152-band in interstellar spectra:

1) nothing can be inferred about the underlying phase or temperature of the interstellar H$_2$O ice from the non-detection of the 2152-band;

2) the non-detection of a 2152-band is a strong indication of significant CO coverages on interstellar ices (in the multilayer rather than sub-monolayer regime), corroborating observational evidence (Pontoppidan et al. 2003);

3) layered CO–porous ASW ice systems are good laboratory analogues for interstellar CO–H$_2$O containing ices when compared with intimately mixed H$_2$O–CO ices, because if the latter were a good analogue of interstellar ices, a strong 2152-band could have been detected.

If CO was accreted onto interstellar grains as H$_2$O ice was forming, a mixed ice, at low temperature, would result. Spectra of this ice would have the 2152-band. As the 2152-band is missing along all lines of sight, it is clear that this cannot be the accretion mechanism. Furthermore, heating or annealing of mixed H$_2$O–CO ices would result in significant CO trapping in the H$_2$O matrix (Collings et al. 2003a,b), which is not observed in regions where the majority of the CO is in the gas phase, and H$_2$O-ice spectra appear to be ‘warm’ (>30 K), e.g. AFGL 2591, S140 IRS 1 and Mon R2 IRS 3 (Gibb et al. 2004). This is corroborated by the fact that gas-phase CO depletion is only observed in the densest interstellar regions (Bacmann et al. 2002; Jørgensen, Schönber & van Dishoeck 2004).

Together this suggests interstellar CO-layeres are accreted over other ice layers subsequent to H$_2$O-ice formation, and would mean we could find lines of sight where cold H$_2$O and other ices were observed but solid CO was not.

Finally, observations have demonstrated that on all lines of sight some CO resides in a H$_2$O dominated environment, evinced by the 2136-CO$_{\text{H}}$ feature, attributable to some of the CO migrating from the 2139-CO$_{\text{OH}}$ onto H$_2$O-interfaces in the H$_2$O-layer below, where it becomes trapped as the grain is heated and the H$_2$O-structure collapses (Collings et al. 2003a,b; Pontoppidan et al. 2003). Any localized energy input to the ice mantle (via thermal heating, electron bombardment or absorption of photons or exothermic surface reactions) would give sufficient energy to some of the CO molecules in the vicinity for them to migrate on to the internal interfaces of the H$_2$O-rich ice. Further energy inputs would lead to competition between CO desorption (from the uppermost CO layer) and trapping of the CO on the internal interfaces of the H$_2$O-rich ice, as the ice structure collapsed. The fact that the 2139-CO$_{\text{OH}}$ feature is never observed in isolation suggests that the initial ice processing is fast on an astronomical time-scale, so grains will exist where both 2139-CO$_{\text{OH}}$ and 2136-COH features can be observed, or where only 2136-COH features are detected.

6 SUMMARY

The main outcome of this work has been to ascertain that the 2152-band is not detected in interstellar spectra because the binding sites associated with this CO–H$_2$O absorption feature are already occupied by a species other than CO, as opposed to the sites not existing in interstellar H$_2$O ice. Of course, in the vastness of interstellar space it would be impossible to say that not one CO molecule could not be adsorbed at a dangling-OH site, but clearly no telescope in the near future will be able to detect one such molecule–ice interaction (it cannot yet be done in the laboratory!) This has significant implications for our conceptual picture of how interstellar ices are accreted onto, and then evolve on, interstellar grains.

It remains an issue for the laboratory, observational, and theoretical astrochemists to determine unequivocally why it is that the CO cannot bind to the 2152 cm$^{-1}$ binding site in interstellar and protostellar environments. Further systematic and careful UHV experiments are required, in particular to determine the nature of reactively formed H$_2$O ice, and to understand the reaction mechanisms of solid-state processes involving CO, particularly solid-state HCO and CO$_2$ formation. In addition, high-resolution, ground-based mapping of solid CO towards YSO regions, coupled with high-resolution observations in the range 2–10 μm with a single space-based instrument, should be made, so that a consistent picture can be built of solid-state and gas-phase H$_2$O and CO infrared bands. Finally, it is very clear from this work, and previous observations by Pontoppidan et al. (2003), that CO–H$_2$O containing interstellar ices are best represented by the evolution of a layered ice model, rather than a mixed ice. If we adopt the layered scenario per se, then astrochemical models and laboratory experiments must also be adapted to reflect such a change.

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