Using laboratory studies of CO–H$_2$O 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–H$_2$O-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–H$_2$O 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 H$_2$ 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.

In this article we address the reasons why the 2152-band is never observed on lines-of-sight towards YSOs, drawing on new evidence from ultrahigh vacuum (UHV) laboratory experiments on the H$_2$O and H$_2$O–CO solid systems, shown here for the first time, and recent work by the authors (Collings et al. 2002, 2003a,b; Fraser et al. 2001) (see Sections 3 and 4). These studies have shown that, under certain laboratory conditions, particularly in *layered* solid systems, the 2152-band is missing from laboratory CO–H$_2$O spectra (see Section 3). In fact, the 2152-band is associated with CO adsorbed on 'dangling-OH' bonds at H$_2$O-ice interfaces (see Section 3.1). We therefore conclude that the non-detection of the 2152-band in *K*-band observations indicates that in interstellar ices the dangling-OH binding sites are either inaccessible to CO molecules or do not exist. The astrophysical implications of these arguments are discussed in Section 5.

2 BACKGROUND

2.1 Solid CO in interstellar ices, inferences from observations

The presence of solid CO in interstellar regions is generally inferred from a broad absorption feature at 2139 cm^{-1} (4.675 μm), attributed to the stretching vibration of the ^{12}CO bond. Following the first reported detections by Soifer et al. (1979) and Lacy et al. (1984), many observations have been made on lines of sight towards high- and low-mass YSOs (e.g. Boogert et al. 2001; Boogert, Blake & Tielens 2002b; Boogert, Hogerhijde & Blake 2002a; Ehrenfreund et al. 1997b; Kerr, Adamson & Whittet 1991; Pontoppidan et al. 2003; Shuping et al. 2000; Teixeira, Emerson & Palumbo 1998; Teixeira & Emerson 1999; Tielens et al. 1991; Thi et al. 2002; van den Ancker, Tielens & Wesselius 2000), towards background sources that probe the dense interstellar medium (e.g. Chiar et al. 1994, 1995, 1998;

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

Source	$2152\,\text{cm}^{-1}$ band upper limit (from obs. spectrum)	2136-CO_H component fitted optical depth	Ratio $\dfrac{2136\text{-}CO_H}{2152}$	2139-CO_{vdW} component fitted optical depth	Ratio $\dfrac{2139\text{-}CO_{vdW}}{2152}$
IRS42	0.02	0.07	*3.5**	0.53	26.5
IRS43	0.04	0.15	3.75	1.75	43.75
IRS44	0.05	0.08	*1.6**	0.34	6.8
IRS51	0.03	0.42	14	4.54	151.3
IRS63	0.03	0.28	9.33	1.69	56.3
WL6	0.04	0.12	*3**	2.04	51
WL12	0.04	0.11	*2.75**	0.79	19.75
CRBR2422	0.06	0.47	7.83	4.38	73
Elias32	0.02	0.39	19.5	0.14	7
RNO91	0.06	0.43	7.17	0.25	4.17
EC90A	0.02	0.24	12	2.09	104.5
EC90B	0.03	0.19	6.33	1.11	37
SVS4-9	0.10	1.07	10.7	1.63	16.3
SVS4-5	0.08	0.59	7.38	3.32	41.5
Cha INa2	0.10	0.27	*2.7**	0.03	*0.3**
Cha IRS6A	0.15	0.55	3.67	3.22	21.47
HH100	0.03	0.25	8.33	1.32	44
RCRAIRS5A	0.04	0.42	10.5	3.33	83.25
RCRAIRS5B	0.10	0.33	*3.3**	2.34	23.4
RCRAIRS7A	0.06	0.39	6.5	1.41	23.5
RCRAIRS7B	0.08	0.77	9.63	1.74	21.75
Reipurth 50	0.03	0.41	13.66	0.51	17
TPSC78	0.02	0.21	10.5	0.12	6
L1489	0.02	0.36	18	0.58	29
LLN20	0.05	0.29	5.8	0.38	7.6
LLN33	0.05	0.33	6.6	0.93	18.6

*In some cases, the error on the optical depth of the fitted 2139-CO_{vdW} or 2136-CO_H 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_2O) 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 (Ehrenfreund et al. 1996, 1997a,b; Gerakines et al. 1995; Palumbo 1997; Sandford et al. 1988; Schmitt et al. 1989). At least two laboratory spectra, recorded at different temperatures from different ice mixtures, one H_2O-ice rich, dubbed 'polar' ice, and one CO-ice rich, dubbed 'apolar' ice, are required to produce a reasonable fit to the observational data (Tielens et al. 1991). The terms 'polar' and 'apolar' are however chemically misleading descriptions; the 'polar' phases are really dominated by hydrogen bonding networks, whereas 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' (2136-CO_H) 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-CO_H environments. In their data set, the 2139-CO_{vdW} was never observed without the 2136-CO_H 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_2O-ice layer as the grain is warmed, giving rise to the 2136-CO_H component (Pontoppidan et al. 2003).

Table 1 shows the optical depths of the fitted components corresponding to the 2139-CO_{vdW} and 2136-CO_H 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-CO_H 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 $2152\,\text{cm}^{-1}$ absorption feature is simply not detected in spectra of interstellar ices.

2.2 Relevant laboratory studies of mixed CO–H_2O ices

Previously, laboratory astrochemistry studies have focused on obtaining transmission spectra of ice mixtures, at 1 or $2\,\text{cm}^{-1}$ resolution, deposited at or below 15 K under high vacuum (HV) conditions. In the case of pure CO ices and CO–H_2O 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–H$_2$O 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$_H$ 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$_{vdW}$ 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$_H$ 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 ≈ 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 infrared (RAIR) 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 μg 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 1×10^{-8} mbar H$_2$O, to form cubic crystalline water ice (I$_c$) (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 μg cm^{-2}) at 8 K (as deposited) and (ii) multilayer exposures of CO (0.35 μg 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 be 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-ice–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$_c$, 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$_{vdW}$ component is also dominated by solid-CO vibrations from the pure CO 'overlayer', 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, RAIR spectra can exhibit LO–TO
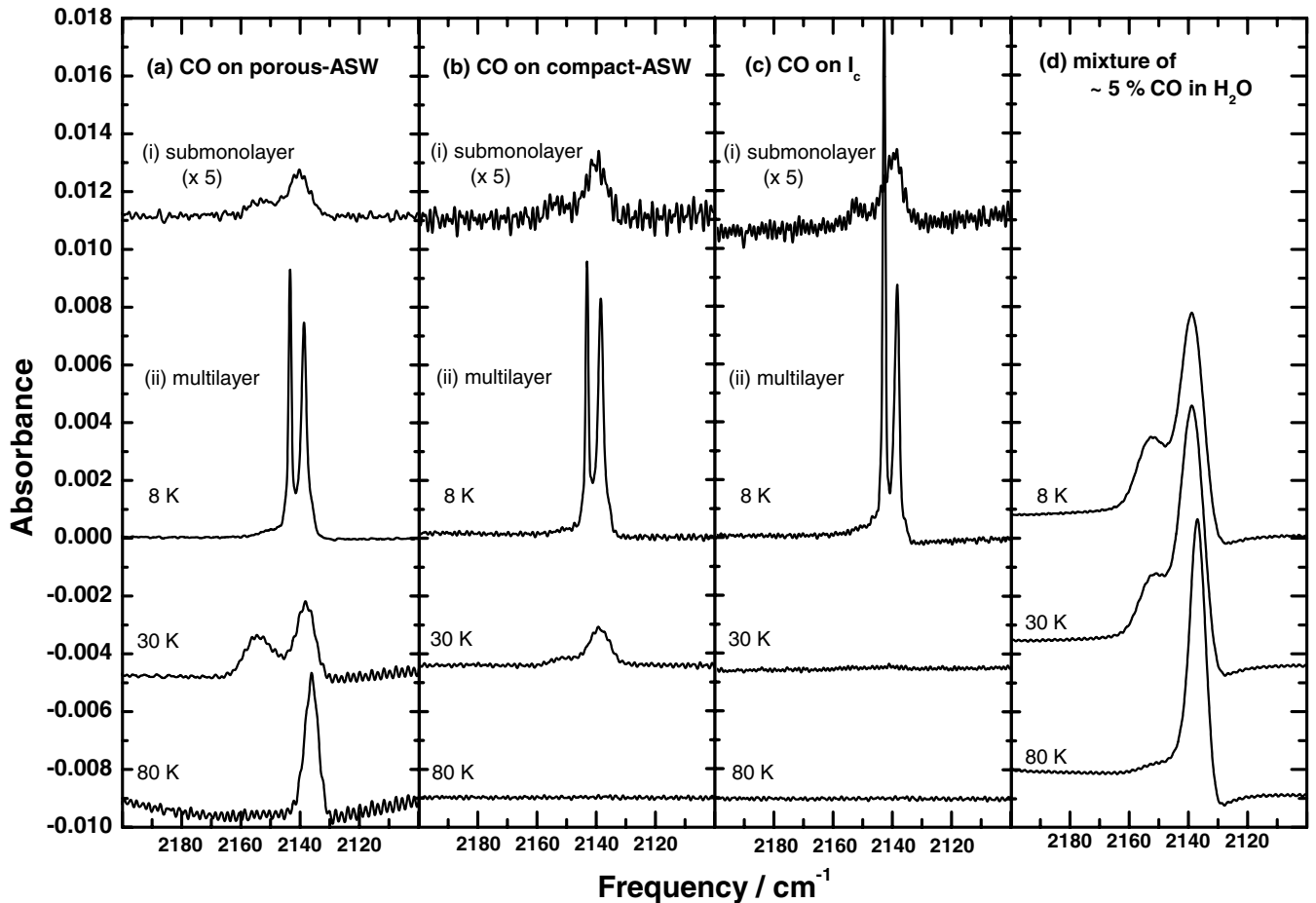
Figure 1. RAIR spectra of the CO-stretching region of thermally processed CO–H$_2$O films. (a)–(c) Sequentially deposited layers of CO deposited at 8 K on to a H$_2$O film (57 µg cm^{-2}) (a) adsorbed at 8 K (porous ASW), (b) adsorbed at 83 K (compact ASW), (c) adsorbed at 8 K and annealed at 140 K for 2 hours in a dynamic background pressure of 1×10^{-8} mbar of H$_2$O to form I$_c$. (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 $\sim$ 5 per cent CO in H$_2$O (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 H$_2$O-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 $\approx$ 80 K. Previously, it has been suggested that this is associated with CO molecules isolated within the H$_2$O matrix in substitutional or interstitial sites (Sandford et al. 1988). However, theoretical studies of CO–H$_2$O systems clearly show that substituting or intercalating CO within H$_2$O 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 H$_2$O–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 H$_2$O 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 H$_2$O 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 H$_2$O-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-CO$_{vdW}$ and 2136-CO$_H$ 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
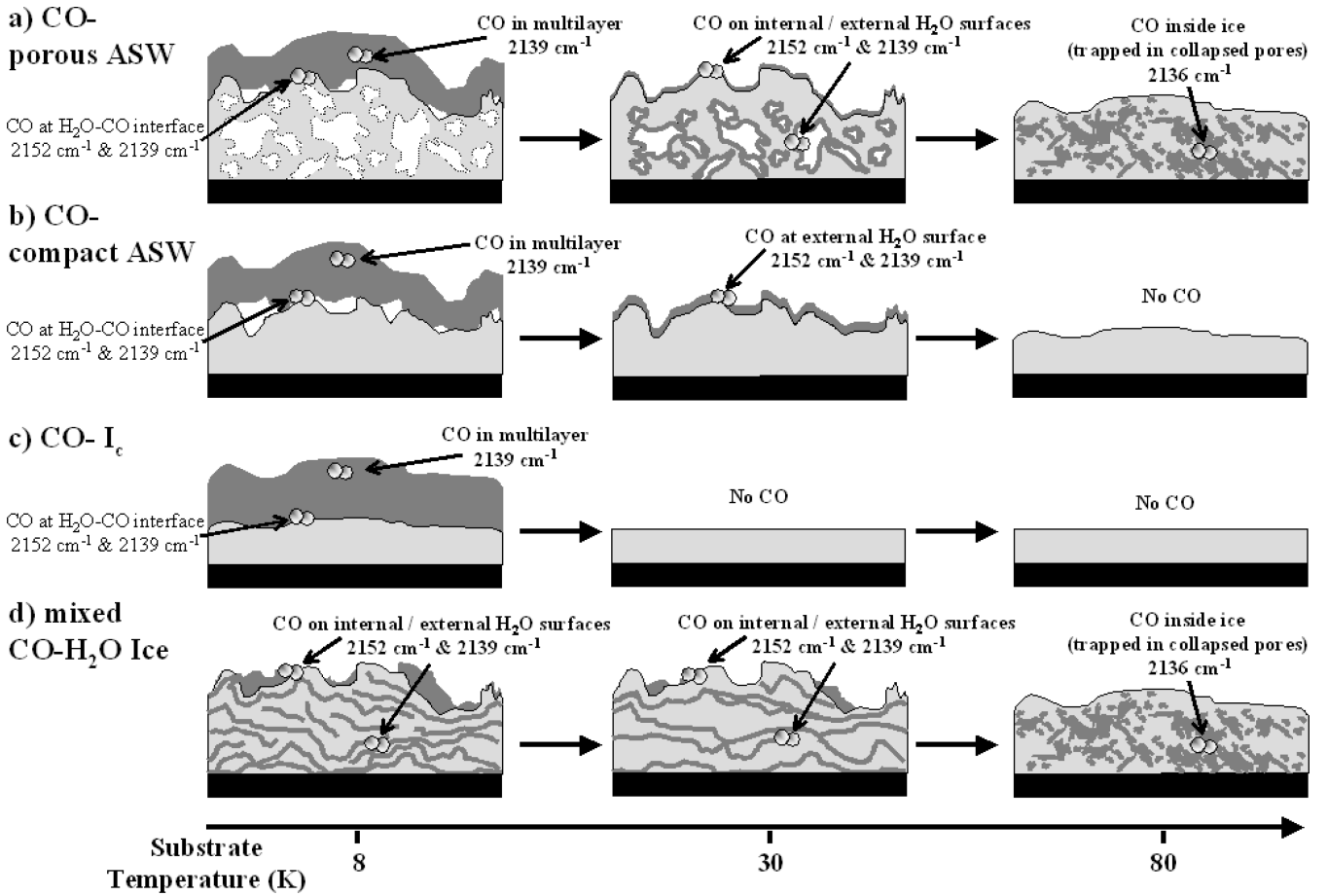
Figure 2. To illustrate the binding sites for CO on and in (a) porous ASW, (b) compact ASW, (c) I_c and (d) CO–H_2O mixed ices. Examples are given at the same three temperatures as the experimental spectra in Figs 1(a)–(c) (ii) and (d), i.e. 8, 30 and 80 K. H_2O ice is represented in light grey, with its external, i.e. ice–vacuum interface, illustrated with a black solid line, and its internal interfaces, i.e. pore surfaces, illustrated by a dotted black line. CO-ice is represented in dark grey. 'Test' CO molecules are shown at specific locations around the ice structure, and labelled with the accompanying characteristic IR vibrational frequency. The dominant IR feature is shown in bold text. The multilayer 2139 cm⁻¹ CO vibrations are related to the 2139-CO_{vdW} interstellar feature: the 2136 cm⁻¹ feature, characteristic of CO trapped within the H_2O matrix, is related to the 2136-CO_H feature.

CO–H_2O-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 H_2O-ices

4.1.1 The evolution of the 2152-band in mixed CO–H_2O 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–H_2O 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 H_2O–CO gas mix or co-deposition of CO and H_2O), all the CO molecules are deposited at interfaces. Below about 20 K, as H_2O 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 are 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 H_2O ice re-structures, collapsing around the CO. A competition exists: if the surrounding H_2O 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 ≈ 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-CO_H component, e.g. Cha Ina2, Elias 32 and TPSC 78 (see Table 1), and no 2152-band is detected.

4.1.2 Evolution of the 2152-band in layered CO–H_2O 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_c, 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_{vdW} 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_{vdW} 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_2O 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 adsorbates 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_2O 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_2O 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_2O-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_2O-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 accommodated in the CO multilayers is able to 'find' a binding site somewhere on the H_2O-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_2O 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 ≈ 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_2O-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_c 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 I_c (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 I_c 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–I_c system is heated, CO simply desorbs from the CO multilayer and by 25 K almost no CO remains on the I_c 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 I_c, 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 I_c gives the weakest 2152-band throughout its thermal history. However, 3 μm interstellar spectra of solid H$_2$O show unequivocally that the water-ice is amorphous and not crystalline (Keane et al. 2001; Gibb et al. 2004, *and references therein*). Spectroscopically it would be very difficult to distinguish between populations of amorphous H$_2$O ices that have been heated and those that have not, simply from the interstellar profile of the 3 μm water band. Perhaps the structure of interstellar H$_2$O more closely resembles compact ASW. This seems an ideal solution, except for two mitigating factors: at H$_2$O–CO ice temperatures between about 15 and 30 K the intensity of the 2152-band is about 10–20 per cent of the intensity of the 2139 cm^{-1} band, not so weak that it should never have been observed: more troublesome is that compact ASW is not able to trap volatile species such as CO, so whatever the thermal history of such an ice, one would never observe the 2136-CO$_H$ feature! Additionally, invoking a scenario for trapping of CO within porous ASW ice matrices explains many other observational traits towards IRAS 16293-2422 (Schöier et al. 2002), assists in modelling the differences between class 0 and class I protostellar objects (Jørgensen, Schöier & van Dishoeck 2002), and provides more realistic gas abundances of many species in astrochemical models comparable with observations (Viti 2003).

Assuming interstellar H$_2$O ice is porous and amorphous (like porous ASW), still leaves us with the problem of explaining the missing 2152-band. No porous ASW ice produced in the laboratory to date has been proven to be devoid of dangling-OH bonds. Consequently, no porous ASW ice, exposed to some amount of CO at some surface temperature, fails to give rise to a significant 2152-band, which could have been detectable in interstellar observations. Some CO always adsorbs at the interfacial H$_2$O–CO binding sites corresponding to the 2152-band. Clearly the solution does not rest only with the morphology of the underlying ice layer. Perhaps, for all its successes in describing trapping of volatiles in interstellar ice, the binary H$_2$O–CO layer system is still an over-simplification of an interstellar ice analogue? Of course, one obvious question mark lies over the ice itself; in the laboratory the H$_2$O-ices are vapour-deposited from the gas phase, yet on interstellar grains H$_2$O ice is

formed via chemical reactions (O'Neil & Williams 1999). Perhaps this ice will be formed without the presence of dangling-OH bonds, yet with a spectroscopy resembling amorphous ice? It is a pertinent open question for laboratory astrochemists to study and understand the formation and structure of H$_2$O ice formed at grain surfaces. However, all these arguments are based around the assumption that the 2152-band is not observed 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_c 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$_{vdW}$ 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 reactively 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 rebuke 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-CO$_H$/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 in Table 1), are indicated by the cross-hatched area for 2136-CO$_H$/2152, plus the right-hatched area for 2139-CO$_{vdW}$/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-CO$_H$/2152 ratio because the 2136-CO$_H$ 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.
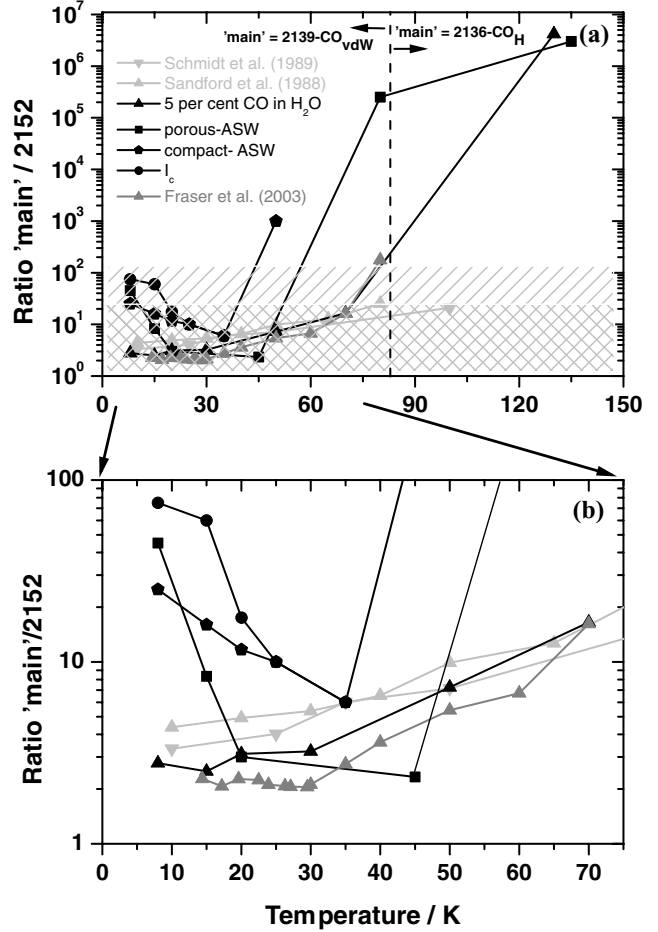

Figure 3. (a) Comparison between the integrated absorption intensities of the 'main' and 2152 cm^{-1} bands in the solid-CO stretching region, obtained in the laboratory for various H$_2$O–CO ice systems. At temperatures below about 80 K, the 'main' spectral feature is at around 2139 cm^{-1} (equivalent to the 2139-CO$_{vdW}$ band identified in astronomical spectra): above 80 K the 'main' spectral feature is at around 2136 cm^{-1} (equivalent to the 2136-CO$_H$ band), as indicated by the dashed line. The cross-hashed region represents the upper limit to the range of 2136/2152 optical depth ratios determined from the observations of Pontoppidan et al. (2003). The cross-hashed region plus the single-hashed region represents the upper limit to the range of 2139/2152 optical depth ratios determined from the observations of Pontoppidan et al. (2003). Data obtained by the authors are shown in black: for comparison previous and new data on mixed ices by other groups are shown in grey. (b) Expansion of (a) in the low temperature–low ratio regime. The legend for each graph is identical, but is only shown in part (a) for clarity.

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_2O 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_H/2152 and 2139-CO_{vdW}/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_2O 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_2O containing ices when compared with intimately mixed H_2O–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_2O 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_2O–CO ices would result in significant CO trapping in the H_2O 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_2O-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, Schöier & van Dishoeck 2004). Together this suggests interstellar CO-ice layers are accreted over other ice layers subsequent to H_2O-ice formation, and would mean we could find lines of sight where cold H_2O 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_2O dominated environment, evinced by the 2136-CO_H feature, attributable to some of the CO migrating from the 2139-CO_{vdW} onto H_2O-interfaces in the H_2O-layer below, where it becomes trapped as the grain is heated and the H_2O-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_2O-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_2O-rich ice, as the ice structure collapsed. The fact that the 2139-CO_{vdW} feature is never observed in isolation suggests that the initial ice processing is fast on an astronomical timescale, so grains will exist where both 2139-CO_{vdW} and 2136-CO_H features can be observed, or where only 2136-CO_H 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_2O absorption feature are already occupied by a species other than CO, as opposed to the sites not existing in interstellar H_2O 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_2O 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_2O and CO infrared bands. Finally, it is very clear from this work, and previous observations by Pontoppidan et al. (2003), that CO–H_2O 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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