Ammonia in water-dominated ice mixtures explains the non-detection of the 2152 cm$^{-1}$ band

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ABSTRACT

CO is one of the most abundant ice components on interstellar dust grains. When it is mixed with amorphous solid water (ASW) or located on its surface, an absorption band at 2152 cm$^{-1}$ is always present in laboratory measurements. This spectral feature is attributed to the interaction of CO with dangling-OH bonds (dOH) in ASW. However, this band is absent in observational spectra of interstellar ices. This raises the question whether CO forms a relatively pure layer on top of ASW or is in close contact with ASW, but not via dangling bonds. We performed laboratory experiments to simulate the layered structure of the ice mantle, i.e., we grew CO ice on top of: 1) Pure ASW; 2) NH$_3$:H$_2$O=10:100 mixed ice; and 3) CO$_2$:H$_2$O=20:100 mixed ice. We found that annealing the ice reduces the 2152 cm$^{-1}$ band, and that NH$_3$ blocks the dOH on ASW surface and therefore reduces the 2152 cm$^{-1}$ band more effectively than CO$_2$. We suggest that this difference between NH$_3$ and CO$_2$ can be ascribed to the polarity of the guest molecule (NH$_3$ is a polar species, whereas CO$_2$ is apolar). The polarity implies that the formation of an H-bond between the N atom of ammonia and the dOH is a barrier-less reaction. We also determined the pore surface area of the ice mixtures as a function of the annealing temperature, and found that the non-detection of 2152 cm$^{-1}$ band does not necessarily exclude the possibility of a porous ice mantle.

1. INTRODUCTION

The non-detection of the 2152 cm$^{-1}$ (4.647 μm) band in astronomical observations of interstellar ices is one of the long-standing puzzles of astrochemistry. This feature has been identified in laboratory CO:H$_2$O ice mixtures, whereas it appears to be absent in observational spectra of interstellar ices. The 2152 cm$^{-1}$ band is the result of the interaction between absorbed CO and “dangling-OH” bonds (dOH) on amorphous water-ice surfaces (Devlin 1992; Collings et al. 2003a; Al-Halabi et al. 2004; He et al. 2019). The question then is why CO molecules apparently do not bind to the dangling-OH site in pre- and proto-stellar environments, resulting in spectra lacking the 2152 cm$^{-1}$ band.

At first, the non-detection was attributed to the low signal-to-noise ratio of observations in the 4-μm region, and thus, to the difficulties in resolving this band if the abundance of the responsible interstellar molecules is too low (e.g., Sandford et al. 1988; Ehrenfreund et al. 1997). A second explanation ascribed the non-detection to the low spectral resolution of the observations because of the overlap of several bands in the 4-μm region, such as gas-phase CO rovibrational transitions, the H$_2$ Pfund-β emission line at ∼2149 cm$^{-1}$ (Pontoppidan et al. 2002) and the C–N stretching mode at 2165 cm$^{-1}$ (Schmitt et al. 1989; Schutte & Greenberg 1997; Pendleton et al. 1999; Novozamsky et al. 2001).

With the advent of higher resolution ground-based infrared instrumentation, it has been possible to disentangle the spectral features in the 4-μm region. In particular, the CO ice band was successfully resolved towards a sample of 39 low- to high-mass young stellar objects (YSOs) using the Very Large Telescope Infrared Spectrometer And Array Camera (VLT-ISAAC; Pontoppidan et al. 2003). In the VLT-ISAAC 3–5 μm survey the 2152 cm$^{-1}$ feature was not detected towards any

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source and only stringent upper limits were provided (Pontoppidan et al. 2003). The large sample size, high signal-to-noise ratio and spectral resolution of this set of observations suggested that the non-detection of the 2152 cm\(^{-1}\) band is not linked to the capabilities of existing infrared facilities, but plausibly to the structure and composition of interstellar ices. It is well established that water-based ices in the ISM are amorphous, and a good analog of them is amorphous solid water (ASW). ASW grown by vapor deposition at low temperatures in the laboratory is highly porous with a very large surface area (Stevenson et al. 1999; Kimmel et al. 2001; He et al. 2019). In the blue wing of the broad OH-stretching absorption peak, there are two weak dOH absorption features at 3696 and 3720 cm\(^{-1}\) (Palumbo 2005; Raut et al. 2007a; Bu et al. 2015; He et al. 2019), which are attributed to 3- and 2-coordinated water sites on the pore surface, respectively. It has been demonstrated that the 3720 cm\(^{-1}\) feature is unstable and diminishes when the ASW is slightly annealed (He et al. 2019), while the 3696 cm\(^{-1}\) feature persists even if the ASW is annealed to as high as 130 K. The more stable 3696 cm\(^{-1}\) feature was searched for in the ISM, but was not found (Keane et al. 2001). It is known that the 2152 cm\(^{-1}\) feature is linked to the interaction of CO with dOH, and that there is an anti-correlation between the 2152 cm\(^{-1}\) and 3696 cm\(^{-1}\) bands (He et al. 2019). Therefore, a theory that explains the non-detection of 2152 cm\(^{-1}\) feature when CO is present in the ice should also explain the non-detection of 3696 cm\(^{-1}\) when CO is absent.

The answer to the non-detection of the 2152 cm\(^{-1}\) band was explored with laboratory experiments and theoretical studies. Fraser et al. (2004) carried out experiments of layered CO:CH\(_3\)O ices with different CO coverage. The authors inferred that layered CO:CH\(_3\)O ices, with significant CO, are good interstellar ice analogs over mixed ices because the 2152 cm\(^{-1}\) feature is not evident in their spectra. This is explained by the fact that CO can only react with a minor fraction of dangling-OH bonds - the ones at the layer interface - resulting in a 2152 cm\(^{-1}\) band under the detection limit. In this case, the ASW on dust grains would have a relatively compact structure with only a small surface area, and CO would easily form a “pure” layer on top of the water-dominated layer. However, it is unclear whether the water-dominated layer is fully compact. The absence of 2152 cm\(^{-1}\) peak is unlikely to be explained by a compact ASW structure alone. For example, He et al. (2019) showed (see Fig. 9 in that paper) that CO on an ASW that was annealed to 140 K and cooled down to 20 K still has the 2152 cm\(^{-1}\) peak. For CO on pure ASW, the 2152 cm\(^{-1}\) peak is proportional to the surface area of the ASW (He et al. 2019). Even if we assume that all the interstellar water ice is fully compact, the surface area could still be significant, considering that dust grains could be fluffy. As an alternative explanation, Fraser et al. (2004) further speculated that some species other than CO, in particular CO\(_2\), NH\(_3\), CH\(_4\), and CH\(_3\)OH, could adsorb at dangling-OH binding sites, thus removing the 2152 cm\(^{-1}\) feature in observational spectra. In this scenario, the ASW is still allowed to have a large surface area. However, Fraser et al. (2004) did not provide experimental confirmation of which interstellar ice components can act as effective dOH blocker.

Cuppen et al. (2011) tested this hypothesis by performing a spectroscopic study of CO:CH\(_3\)O:CO\(_2\) and CH\(_3\)OH:CO mixtures. They found that a CH\(_3\)OH:CO 1:1 mixture is sufficient to reproduce the observed width and peak position of the red component of the CO band, as well as the non-detection of the 2152 cm\(^{-1}\) band. In this regard, CH\(_3\)OH:CO mixtures provided a better fit of one low-mass and one high-mass protostars over a H\(_2\)O:CO mixture (Penteado et al. 2015). This finding suggested that CO might reside in H\(_2\)O-poor/CH\(_3\)OH-rich environments in interstellar ices - a concept supported by laboratory experiments and model simulations of CH\(_3\)OH formation from CO ice (Watanabe & Kouchi 2002; Fuchs et al. 2009; Cuppen et al. 2009).

Although convincing, a mixing ratio of CH\(_3\)OH:CO 1:1 does not reflect the average composition of interstellar ices (Boogert et al. 2015). In fact, the CH\(_3\)OH:CO ratio in high-mass YSOs is subjected to large variations (0.2–3; Dartois et al. 1999; Boogert et al. 2002, 2008; Pontoppidan et al. 2003, 2008). In addition, for fewer than a handful of low-mass YSOs the CH\(_3\)OH:CO ratio is ≥ 0.7 (Pontoppidan et al. 2004; Perotti et al. 2020, 2021) and it is only 0.2–0.3 for starless and pre-stellar cores (Boogert et al. 2011; Chu et al. 2020; Goto et al. 2021).

Additionally, although it is plausible that a fraction of CO settles in CH\(_3\)OH-rich ices, a significant amount of it inevitably migrates and interacts with the H\(_2\)O matrix (Collings et al. 2003b; He et al. 2018b; Zamirri et al. 2018), contributing to the 2152 cm\(^{-1}\) band. This consideration is not taken into account in Cuppen et al. (2011) due to the selection of a CH\(_3\)OH:CO mixture which does not contain H\(_2\)O. In summary, although large quantities of CH\(_3\)OH can act as a dangling-OH bond blocker, other more abundant species present in the ices, such as NH\(_3\) and CO\(_2\), might also play a role in the suppression of the 2152 cm\(^{-1}\) band.

According to mid-IR observations, the abundance of NH\(_3\) ice in low- and high-mass star-forming regions is ∼ 5–7% relative to H\(_2\)O (Dartois et al. 2002; Bottinelli...
et al. 2010; Öberg et al. 2011). However, laboratory constraints on optical constants and band strengths have shown that its abundance has been underestimated by up to 30% (Kerkhof et al. 1999; Zanchet et al. 2013). NH$_3$ is believed to form on the ice surface by the H-addition to N atoms (Hiraoaka et al. 1995) while competing with the H-addition to O atoms. This suggests that NH$_3$ is formed simultaneously with water and intimately mixed with water. This might also result in newly formed NH$_3$ molecules reacting with dOH. Similarly, the abundance of CO$_2$ ice in the ISM has been estimated between 10 − 34% compared to H$_2$O (D’Hendecourt & Jourdain de Muizon 1989; de Graauw et al. 1996; Gibb et al. 2004; Pontoppidan et al. 2008; Noble et al. 2013).

The most efficient formation pathways of CO$_2$ are proposed to be the reaction between CO and OH radicals (Noble et al. 2011; Oba et al. 2011; Ioppolo et al. 2011) or between CO and oxygen atoms (Roser et al. 2001). Since water is formed from O and OH as well, it follows that CO$_2$ should also be intimately mixed with water. It is possible that CO is binding to the dOH sites before forming CO$_2$, and therefore blocking the dOH sites (Fraser et al. 2004).

A related question that must be addressed is the quantification of the surface area of ices in the ISM. They play an important role in chemical reactions in the ISM because they provide a surface to adsorb and retain small reactive species, and because they stabilize reaction products by taking away the energy released in chemical reactions. The rate of reactions depends on whether reactions occur in bulk ice or on the ice surface. The rate of diffusion, which largely determines the rate of chemical reactions, is usually much faster on the surface than in bulk. When modeling the chemistry in the ISM, it is necessary to distinguish surface reactions from reactions in bulk ice. For this reason, laboratory measurement of the surface area of astrophysically-relevant ices provides key information for accurate modeling of grain-surface reactions. As demonstrated by He et al. (2019), the pore surface area of ASW decreases with increasing annealing temperature, and the area seems to be proportional to the band area of the 3696 cm$^{-1}$ dOH feature. It is therefore important to examine the pore surface area together with the dOH feature at 3696 cm$^{-1}$ or with the 2152 cm$^{-1}$ feature.

In the present paper, we test whether the absence of the 2152 cm$^{-1}$ feature is due to how CO interacts with water ice and whether molecules such as NH$_3$ and CO$_2$ could block the dOH signatures of ASW. We performed a systematic study of different H$_2$O:NH$_3$ and H$_2$O:CO$_2$ ice mixtures, using porous amorphous solid water (ASW) as the main ice analog component. CO is deposited on top of both mixtures. NH$_3$ and CO$_2$ are selected because they are ubiquitous species in astrophysical environments. In particular, they have been detected in the gas reservoirs of inner and outer regions of protoplanetary disks and in protostellar cores (Gürtler et al. 2002; Gibb et al. 2004; Öberg et al. 2010; Mandell et al. 2012; Salinas et al. 2016; Bosman et al. 2017; Pontoppidan et al. 2019; Najita et al. 2021), and on comets and planets (Mumma & Charnley 2011; Altwegg et al. 2020; Swain et al. 2008; Millan et al. 2021). This work focuses on the 2152 cm$^{-1}$ feature; we do not attempt to tackle the red component at ~2136 cm$^{-1}$. We also do not compare the measured spectra with observations, since our measured spectra are in reflection mode, which should not be compared directly with observations.

This paper is structured as follows. We begin in Section 2 with describing the experimental setup used to record the laboratory spectra. In Section 3 we test the effectiveness of CO$_2$ and NH$_3$ as dangling-OH bond blockers and present the key experimental results. Section 4 discusses the results, and explains them by comparing the chemical behaviors of CO$_2$ and NH$_3$ embedded in H$_2$O. Additionally, it supplies a list of additional dOH-blocker candidates. We summarize our conclusions in Section 5.

2. EXPERIMENTAL SETUP

Experiments were performed using an ultra-high vacuum (UHV) chamber that has been described previously (He et al. 2018a,b, 2019). The main UHV chamber was pumped to a base pressure of 4 × 10$^{-10}$ Torr when the cryostat is off. A gold-coated copper disk was used as the substrate onto which ice samples were grown. The temperature of the substrate can be controlled between 5 and 400 K by using a closed-cycle helium cryostat and a cartridge heater installed right underneath the substrate. The temperature was measured using a calibrated silicon diode sensor to an accuracy of 0.05 K. Gas or vapor were deposited through one of the two UHV variable leak valves, which were controlled by stepper motors interfaced to a computer. A LabVIEW program automates the gas/vapor deposition and calculates the thickness in real time. A more detailed description of the gas deposition is in the Appendix of He et al. (2018a). Although the UHV system is equipped with two highly collimated molecular beam lines for gas deposition, we only used the leak valves because the background deposition from leak valves is a better simulation of the omnidirectional deposition of gases in interstellar space. Water vapor was evaporated from distilled water, which underwent at least three “freeze-pump-thaw” cycles to remove dissolved air. Ice samples were an-
alyzed by a Nicolet 6700 Fourier Transform InfraRed (FTIR) Spectrometer in the Reflection Absorption InfraRed Spectroscopy (RAIRS) configuration. Infrared spectra were obtained by averaging 8 scans every 10 seconds in the range 650–4000 cm$^{-1}$. The infrared beam is at 78°incidence angle relative to the surface normal. In such a reflection mode, the infrared band profile may differ from the transmission mode, such as that in Cuppen et al. (2011). Particularly, the longitudinal optical (LO) mode of CO at 2143 cm$^{-1}$, which appears when the coverage of CO on the surface is relatively high, is only present in reflection mode. In this study, we mostly focus on the relatively weak dOH features at low coverage of CO. Here the difference between reflection and transmission geometry is not important.

3. EXPERIMENTAL RESULTS AND ANALYSIS

3.1. CO deposition on water-dominated ice mixtures

Two sets of experiments were performed in the current study; they are described in this Subsection and in Subsection 3.2. The first set is an extension to the experiments reported in He et al. (2019). With the gold surface at 10 K, 200 monolayers (ML, defined as $10^{15}$ molecule-cm$^{-2}$) of water were grown by vapor condensation on the surface. At this temperature, the water ice is amorphous and highly porous. Afterwards, the water ice was warmed up to an annealing temperature $T_{\text{ann}}$ and remained at this temperature for 30 minutes to stabilize the ice structure. The following annealing temperatures were chosen: $T_{\text{ann}} = 20, 40, 60, 80, 100, \text{ and } 120$ K. After annealing, the ice was cooled down to 20 K before depositing CO gas on top of the water ice, and RAIRS spectra were collected during the CO deposition. We chose to make a layered ice rather than a uniformly mixed one, in order to better represent the layered ice mantle on dust grains (Pontoppidan et al. 2008; Boogert et al. 2015). This is different from other studies in which gases were premixed and then deposited (e.g., Ehrenfreund et al. 1997; Cuppen et al. 2011). In addition to the experiments in He et al. (2019), in this study, we replaced pure water with: (1) Mixed ice of 200 ML H$_2$O and 20 ML NH$_3$; or (2) Mixed ice of 200 ML H$_2$O and 40 ML CO$_2$. Other than the difference in ice composition, the experiments follow the same procedure as that in He et al. (2019). The deposition of H$_2$O:CO$_2$ and H$_2$O:NH$_3$ ice mixtures were accomplished by co-deposition of the two gas/vapor components within 20 minutes and 25 minutes, respectively. Figure 1 demonstrates the procedure of the experiments. RAIRS spectra were measured during CO deposition on ices, a selection of which are shown in Figure 2.

The diffusion rate for CO molecules in porous ASW is very efficient at 20 K (Mispelaer et al. 2013; Karssemeijer & Cuppen 2014; Lauck et al. 2015; He et al. 2018b), and CO molecules are able to penetrate into the porous ice and reach all the surface area in the pores (He et al. 2019). We assume that the same is true in the H$_2$O:CO$_2$ and H$_2$O:NH$_3$ mixtures. At the beginning of the CO deposition, the coverage of CO on the pore surface is small, and all the CO molecules are interacting with the water surface, evidenced by the two peaks centered at $\sim$2139 and $\sim$2152 cm$^{-1}$. As CO gas deposition proceeds, the pore surface area is gradually covered by CO, and eventually builds up as “pure” CO ice; at this stage, CO primarily interacts with other CO molecules rather than with the water surface. This is indicated by the emergence of a 2143 cm$^{-1}$ absorption peak due to the LO mode of CO. Similar to He et al. (2019), we take the CO deposition amount at which the 2143 cm$^{-1}$ peak emerges as the pore surface area of the ASW. Figure 3 shows the pore surface area, in units of monolayers (ML), of the three ices at different annealing temperatures. The error bar accounts for the uncertainty in determining the emergence of the LO peak. One can see that the introduction of 20% CO$_2$ into water ice lowers the pore surface area by almost half, while 10% of NH$_3$ has only a very small impact on the surface area. One possible reason why CO$_2$ more effectively blocks the pore surface area is that CO$_2$ form clusters on the surface of ASW (He et al. 2017), which prevents CO from reaching some pores.
Figure 2. Selected RAIRS spectra of CO deposited on water-dominated ice after the ice was annealed to temperature $T_{\text{ann}}$ and then cooled to 20 K. $T_{\text{ann}}$ is 20, 40, 60, 80, 100, and 120 K from top to bottom. The three columns are for: (1) 200 ML of pure H$_2$O ices; (2) Mixed ices of 200 ML H$_2$O and 20 ML NH$_3$; and (3) Mixed ices of 200 ML H$_2$O and 40 ML CO$_2$. 
The band area of the 2152 cm$^{-1}$ peak in Figure 2 can also be analyzed. By visual inspection, we can see that the peak area decreases at higher annealing temperatures for all three ices. When annealed at 120 K, the 2152 cm$^{-1}$ peak becomes insignificant. In H$_2$O:NH$_3$ mixtures, the decrease in 2152 cm$^{-1}$ peak area is more pronounced. Even if the annealing temperature is only 60 K, the 2152 cm$^{-1}$ peak appears to be the tail of the 2143 cm$^{-1}$ peak rather than a separate peak. When the H$_2$O:NH$_3$ mixture is annealed to 100 K, the 2152 cm$^{-1}$ peak disappears completely. Because the 2152 cm$^{-1}$ peak is directly correlated to the dOH bonds (He et al. 2019), it is evident that 10% of NH$_3$ blocks the dOH bonds more effectively than 20% of CO$_2$, provided that the ice is annealed to higher than 80 K. As discussed above, 20% of CO$_2$ reduces the surface area of ASW by half, which should also reduce the dOH sites proportionally. The fact that the 2152 cm$^{-1}$ peak in the CO$_2$:H$_2$O mixture is not reduced to half further strengthens the argument that CO$_2$ is a less efficient dOH blocker.

To quantify it, we calculated the 2152 cm$^{-1}$ peak area by using the sum of two Gaussian functions to fit the spectra in Figure 2. Because the 2143 cm$^{-1}$ peak only emerges after the surface is saturated by CO, i.e., the 2152 cm$^{-1}$ peak is saturated before the emergence of the 2143 cm$^{-1}$ peak, we only focus on the spectra before the emergence of the 2143 cm$^{-1}$ peak. The advantage is that we only need two components for the fitting. Figure 4 shows examples of the fitting. With a small amount of CO on the surface, the fitting by the sum of two Gaussian functions is excellent. However, after CO fully covers the surface, the fitting becomes worse, as illustrated by the top trace in the left panel. This is also demonstrated in the right panel. As the surface is fully covered by CO, the error bar of the 2152 cm$^{-1}$ band area becomes very large. From the right panel, we can determine the saturation 2152 cm$^{-1}$ peak areas. This analysis procedure is repeated for the ices with different annealing temperatures, and the results are shown in Figure 5. Here we can see clearly that 10% of NH$_3$ effectively blocks the dangling OH bonds as long as the ice mixture is annealed to 100 K. We note that the fitting only calculates the area of the 2152 cm$^{-1}$ peak, but does not consider the shape of it. For H$_2$O:NH$_3$ mixtures annealed to 60 K and above, the 2152 cm$^{-1}$ component looks as if it is the tail of the 2140/2143 cm$^{-1}$ peak rather than a separate peak, making it more difficult to discern than for H$_2$O:CO$_2$ mixtures in astronomical observations.
3.2. Dangling-OH bonds in H$_2$O:NH$_3$ ice mixtures

The results of the first set of experiments presented above suggest that introducing NH$_3$ into water-dominated ice can effectively decrease the 2152 cm$^{-1}$ peak, and that NH$_3$ is an effective dOH bond blocker. In the second set of experiments, we further explore how the concentration of NH$_3$ and temperature of the ice affect the dOH bonds. We fix the amount of water to be 100 ML, and deposited NH$_3$:H$_2$O ice mixtures with mixing ratios ranging from 0:100 to 30:100. After the deposition of the mixture at 10 K, the ice was warmed up at a ramp rate of 6 K/minute, and RAIRS spectra were collected.

The spectra of ice with mixing ratio of NH$_3$:H$_2$O=0:100, 10:100, and 20:100 during warm-up are shown in Figure 6. In pure water ice, both the dangling-OH bands at 3696 and 3720 cm$^{-1}$ are present at the lowest temperature. The 3720 cm$^{-1}$ band disappears by about 60 K, and the 3696 cm$^{-1}$ band persists until above 120 K. For a more detailed discussion of the dOH bands of pure ASW, see He et al. (2019). When 10% or 20% of NH$_3$ is added to the mixture, the 3720 cm$^{-1}$ peak is indiscernible even at the lowest temperatures, and the 3696 cm$^{-1}$ peak is much lower than that for pure ASW, particularly when the ice mixture is warmed up.

Following a similar method as in He et al. (2019), we calculate the area for the 3696 cm$^{-1}$ peak. A broad Gaussian function is used to fit the blue wing of the OH-stretch peak, and two narrow Gaussian functions are used to fit the peaks at 3696 and 3720 cm$^{-1}$. The band area of the 3696 cm$^{-1}$ peak is obtained from the fitting. The results are shown in Figure 7. With a NH$_3$:H$_2$O mixing ratio between 0 and 15%, the dOH band area decreases with increasing NH$_3$ concentration at all temperatures. At higher mixing ratios, the dOH band area becomes less dependent on the concentration. When the mixing ratio is higher than 10%, the dOH band is almost negligible when annealed to 100 K or above. This agrees with the results of the 2152 cm$^{-1}$ peak in Section 3.1. This is not surprising, since it is known that the 2152 cm$^{-1}$ peak is correlated with the dOH band at 3696 cm$^{-1}$ (He et al. 2019).

3.3. H$_2$O:CO$_2$ ice mixtures

One could also perform similar experiments as in Section 3.2 for CO$_2$:H$_2$O mixtures and monitor the dOH region in the infrared. Such experiments have already been performed and presented in Figure 3 of He et al. (2018a). The dOH bonds of water are shadowed by the $\nu_1 + \nu_3$ combination mode, and therefore it is challenging to do an analysis of the dOH at 3696 cm$^{-1}$ similar to that in Section 3.2. Previously Cuppen et al. (2011) measured the infrared spectra of H$_2$O:CO:CO$_2$ mixtures, and found that it takes a large amount of CO$_2$ to suppress the 2152 cm$^{-1}$ band at low temperatures. Even with a mixture of H$_2$O:CO:CO$_2$=2.75:1:10, i.e., 3–4 times more CO$_2$ than H$_2$O, there is still a non-negligible 2152 cm$^{-1}$ peak. It is clear from both Cuppen et al. (2011) and this study that CO$_2$ is a less effective dOH blocker.

4. DISCUSSION

4.1. On the surface area and the non-detection of dOH bands

The porosity of the ice mantle covering dust grains in the ISM is still debated. A porous water ice provides a large catalytic surface area for grain surface reactions to take place, while reactions in a compact ice are challenged by high-diffusion energy barriers for most particles inside bulk compact water ice. The detection of a large variety of complex organic molecules seems to favor the argument that the water-rich ice is somewhat porous and provides a large surface area. However, similarly to the 2152 cm$^{-1}$ band, also the 3696 cm$^{-1}$ dOH band, which is usually present in vapor deposited ASW, has never been detected in interstellar ices (Keane et al. 2001). This raises the questions of why the dOH bands disappear, and whether there is a dOH blocker in the ice. Closely related is the non-detection of the 2152 cm$^{-1}$ peak for CO ice on water surface.

In this study we try to find out whether the ice mantle covering dust grains can have an insignificant 2152 cm$^{-1}$ peak (or equivalently, insignificant 3696 cm$^{-1}$ dOH band), but still has a significant surface area. From Figure 3, 5 and 7, we can see that this is possible if 10% of NH$_3$ is mixed with water, and the ice is annealed to 100 K. In the ISM, ices are not condensed from gas and are formed by chemical reactions on the surface. The energy released from chemical reactions can be absorbed by the ice and create some localized “annealing”, therefore making the ice less porous (Oba et al. 2009; Accolla et al. 2011). The bombardment of cosmic rays can also induce some local heating of ice and therefore change the ice structure (Palumbo 2006; Raut et al. 2007b). Eventually, the state of the ice might be similar to the ice that is condensed from gas and then annealed to a certain temperature. We can define a parameter “equivalent annealing temperature” to describe the state of the ice. If the equivalent annealing temperature of the ice mantle on dust grains is close to 100 K, then the 3696 cm$^{-1}$ dOH band or the 2152 cm$^{-1}$ peak become negligible.
We speculate that this may explain the non-detection of these two features.

4.2. On the effect of polarity on the non-detection of the dOH bands

One important question arises after analyzing the different responses of H$_2$O:NH$_3$ and H$_2$O:CO$_2$ ice mixtures: what makes NH$_3$ a more effective dOH blocker compared to CO$_2$? The answer to this question can be found by comparing the chemical characteristics and behaviors of NH$_3$, CO$_2$ and H$_2$O.

NH$_3$ and H$_2$O are structural analogs and isoelectronic species, as they possess the same number of electrons. Both species are nucleophiles: the O atom in H$_2$O and the N atom in NH$_3$ have two unpaired electrons, which can be “donated” to form hydrogen bonds. Most importantly, since they are characterized by an unequal sharing of valence electrons (i.e., a difference in electronegativity amongst the bonded atoms), NH$_3$ and H$_2$O are defined as polar. They have permanent dipole moments. In contrast, CO$_2$ is a linear molecule with an equal sharing of valence electrons, hence apolar. The fact that NH$_3$ is polar, whereas CO$_2$ is apolar, implies that NH$_3$ can bind more tightly to H$_2$O molecules compared to CO$_2$. This is confirmed by laboratory measurements using temperature programmed desorption (TPD) technique by He et al. (2016), which found that low coverage of NH$_3$ desorbs from water ice at $\sim$140 K, much higher than CO$_2$ which desorbs at $\sim$80 K. Binding energy on water ice was also studied using quantum chemistry calculations. Ferrero et al. (2020) modelled an interstellar ice surface by simulating both crystalline and amorphous water ices with DFT (B3LYP-D3 and M06-2X). The authors of this work determined binding energies for 21 astrochemically-relevant species. On ASW ices, they found that NH$_3$ has a binding energy ranges from 4314 to 7549 K, which is several times higher than CO$_2$ which desorbs at $\sim$80 K. Binding energy on water ice and found in experiments. This strong binding makes NH$_3$ a more effective dangling-OH band blocker over CO$_2$ (Fig. 8).

Henkelman & Feibelman (2016) performed density functional theory (DFT) calculations of the interaction of NH$_3$ with the dangling-OH of water ice and showed that the bond between ammonia and the dOH is promoted by the attraction of the lone pair of the N atom to the dOH of H$_2$O. This is a zero-energy barrier reac-
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Figure 8. Schematic illustration of the interactions between: A) dOH and ammonia (NH$_3$) and B) dOH and carbon dioxide (CO$_2$). NH$_3$ is a polar molecule, it tightly binds to the dOH via H-bonding between the N atom and the dOH. CO$_2$ is an apolar species, with a binding energy three times lower than that of NH$_3$. This implies that NH$_3$ is a more effective dangling-OH band blocker over CO$_2$. The reported binding energies are from Ferrero et al. (2020). The simplified geometries are adaptation of real geometries obtained with quantum chemical calculations in Ferrero et al. (2020).

This is not the case for apolar molecules such as CO or N$_2$, which are not capable to bind as strongly as NH$_3$ to the dangling-OH bonds. Consequently, since their attraction to dOH is weaker, their H-bonding with H$_2$O proceeds with non-zero energy barriers. The highest barrier — and thus weakest binding to water — is found for N$_2$ followed by CO, respectively (Henkelman & Feibelman 2016). This implies lower probabilities for the adsorption of N$_2$ and CO at the dOH sites over NH$_3$, and therefore less effective dOH blocking capabilities at the low temperatures of the interstellar medium (ISM). This result agrees with the inefficient dOH blocking behaviors of CO (Fraser et al. 2004) and CO$_2$ (this work and Cuppen et al. 2011).

Previous laboratory studies on the non-detection of the 2152 cm$^{-1}$ band have proposed that good dOH blockers are those species that form from CO molecules at the dOH sites (e.g., CO$_2$ and CH$_3$OH; Fraser et al. 2004; Cuppen et al. 2011 - see Section 4.3). By working with NH$_3$ and CO$_2$, we have discovered that an important requirement to be a good dOH-bond blocker is the polarity of a molecule, its ability to form H-bonds and reside tightly at the dOH site, therefore impeding CO molecules to react with the dOH. As a general rule we can state that polar molecules, especially NH$_3$ and CH$_3$OH are efficient dOH blockers, whereas apolar species (e.g., CO$_2$) are not good dOH blockers, unless significantly more abundant than polar species, in agreement with the findings of Cuppen et al. (2011). Based on the evidence that ammonia is one of the most abundant polar species of interstellar ices after H$_2$O (its abundance is approximately a factor of 3 higher than that of CH$_3$OH; Zanchet et al. 2013; Boogert et al. 2015), we propose that ammonia is one of the main contributors - although plausibly not the sole - in the suppression of the 2152 cm$^{-1}$ band, and more generally of all the dOH bands.

4.3. Other dangling-OH-blocker candidates

The subsequent hydrogenation of N atoms leading to NH$_3$ at the onset of interstellar ice surfaces is not the unique reaction competing with the hydrogenation
of O atoms, producing dangling-OH binding sites (Hiraoka et al. 1995; Herbst & van Dishoeck 2009). For instance, the C+H reactions forming CH$_4$ occur concurrently with the O+H reactions (Qasim et al. 2020). This implies that CH$_4$ could be a good candidate for the removal/blockage of the 2152 cm$^{-1}$ band binding sites. However, compared to NH$_3$ and CO$_2$, CH$_4$ is more volatile, with similar desorption characteristics as CO (Collings et al. 2004). Laboratory studies have shown that CH$_4$ molecules can easily diffuse on the pore surface and do not bind to the ASW surface — hence to the dangling-OH sites — tighter than CO (He et al. 2018b). We further strengthen this argument on the basis of the apolarity of CH$_4$, which in turn does not make it an efficient dangling-OH blocker. Other species could act as suppressors of the 2152 cm$^{-1}$ band. Potential candidates are those molecules that form onto the ices prior to the CO condensation stage, and that steadily bind to the dangling-OH sites because of their polarity. Examples of this class are: OCN and OCS. Finally, one last category of species that could block the dangling-OH sites are polar molecules that are produced by the interaction of CO at the dangling-OH sites with other species present on the ice surfaces. This includes species such as H$_2$CO, HCOOH and CH$_3$OH or even more complex organic species.

At the current stage it is not clear whether one species contributes to the removal of the 2152 cm$^{-1}$ band more than others or whether this is the result of multiple contributions. Further systematic laboratory experiments of ternary and quaternary mixtures are needed to constrain the composition and structure of ice mantles. In addition, quantum chemical modelling of proper mixed ices, representatives of real astronomical ices (i.e., which include at least CO, CO$_2$, NH$_3$, CH$_4$, and CH$_3$OH) may also help to elucidate the structure and spectroscopic features of the CO band, accounting for the interaction of multiple species in different H$_2$O–ice structural environments. Finally, high-sensitivity near and mid-infrared observations of the dOH bands with the James Webb Space Telescope will provide higher signal-to-noise spectra to compare with model predictions and experimental data.

5. CONCLUSIONS

In this paper, we investigated one of the conundrums of astrochemistry: the absence of the 2152 cm$^{-1}$ band in observational spectra of pre-stellar and proto-stellar environments. By making composite ices in the laboratory that resemble the icy mantles on dust grains, we examine the impact of NH$_3$ and CO$_2$ on the 2152 cm$^{-1}$ band and the pore surface area of the mixed ice. We found that introducing 10% of NH$_3$ in ASW effectively blocks the dOH bonds as long as the ice is annealed to 100 K. At the same time, introducing NH$_3$ exerts only a small impact on the pore surface area of ASW. In comparison, introducing 20% of CO$_2$ in ASW reduces the pore surface area by half, but does block all the dOH bonds regardless of the annealing temperature. We discussed from a chemistry point of view why polar molecules such as NH$_3$ are likely more efficient dOH blockers over apolar molecules. We propose that NH$_3$ is one of the most important dOH blockers which explains the non-detection of the 2152 cm$^{-1}$ band, and the water-dominated layer of the ice mantle can be slightly porous while the 2152 cm$^{-1}$ peak is insignificant.

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REFERENCES

Accolla, M., Congiu, E., Dulieu, F., et al. 2011, Physical Chemistry Chemical Physics, 13, 8037, doi: 10.1039/C0CP01462A

Al-Halabi, A., Fraser, H. J., Kroes, G. J., & van Dishoeck, E. F. 2004, A&A, 422, 777, doi: 10.1051/0004-6361:20035939

Altwegg, K., Balsiger, H., Hänni, N., et al. 2020, Nature Astronomy, 4, 533, doi: 10.1038/s41550-019-0991-9

Boogert, A. A., Gerakines, P. A., & Whittet, D. C. 2015, Annu. Rev. Astron. Astrophys., 53, 541, doi: 10.1146/annurev-astro-082214-122348

Boogert, A. C. A., Hogerheijde, M. R., Ceccarelli, C., et al. 2002, ApJ, 570, 708, doi: 10.1086/339627

Boogert, A. C. A., Pontoppidan, K. M., Knez, C., et al. 2008, ApJ, 678, 985, doi: 10.1086/533425

Boogert, A. C. A., Huard, T. L., Cook, A. M., et al. 2011, ApJ, 729, 92, doi: 10.1088/0004-637X/729/2/92
He et al.

Noble, J. A., Fraser, H. J., Aikawa, Y., Pontoppidan, K. M., & Sakon, I. 2013, ApJ, 775, 85, doi: 10.1088/0004-637X/775/2/85

Novozamsky, J. H., Schutte, W. A., & Keane, J. V. 2001, A&A, 379, 588, doi: 10.1051/0004-6361:20011332

Oba, Y., Miyachi, N., Hidaka, H., et al. 2009, ApJ, 701, 464, doi: 10.1088/0004-637X/701/1/464

Oba, Y., Watanabe, N., Kouchi, A., Hama, T., & Pirroello, V. 2011, Physical Chemistry Chemical Physics (Incorporating Faraday Transactions), 13, 15792, doi: 10.1039/C1CP20596J

¨Oberg, K. I., Boogert, A. C. A., Pontoppidan, K. M., et al. 2011, ApJ, 740, 109, doi: 10.1088/0004-637X/740/2/109

¨Oberg, K. I., Qi, C., Fogel, J. K. J., et al. 2010, ApJ, 720, 480, doi: 10.1088/0004-637X/720/1/480

Palumbo, M. E. 2005, in Journal of Physics Conference Series, Vol. 6, Journal of Physics Conference Series, 211–216, doi: 10.1088/1742-6596/6/1/025

Palumbo, M. E. 2006, A&A, 453, 903, doi: 10.1051/0004-6361:20042382

Pendleton, Y. J., Tielens, A. G. G. M., Tokunaga, A. T., & Bernstein, M. P. 1999, ApJ, 513, 294, doi: 10.1086/306827

Penteado, E. M., Boogert, A. C. A., Pontoppidan, K. M., et al. 2015, MNRAS, 454, 531, doi: 10.1093/mnras/stv1987

Perotti, G., Jørgensen, J. K., Fraser, H. J., et al. 2021, A&A, 650, A168, doi: 10.1051/0004-6361/202039669

Perotti, G., Rocha, W. R. M., Jørgensen, J. K., et al. 2020, A&A, 643, A48, doi: 10.1051/0004-6361/202038102

Pontoppidan, K. M., Salyk, C., Banzatti, A., et al. 2019, ApJ, 874, 92, doi: 10.3847/1538-4357/ab05d8

Pontoppidan, K. M., Schöier, F. L., van Dishoeck, E. F., & Dartois, E. 2002, A&A, 393, 585, doi: 10.1051/0004-6361:20021056

Pontoppidan, K. M., van Dishoeck, E. F., & Dartois, E. 2004, A&A, 426, 925, doi: 10.1051/0004-6361:20041276

Pontoppidan, K. M., Fraser, H. J., Dartois, E., et al. 2003, A&A, 408, 981, doi: 10.1051/0004-6361:20031030

Pontoppidan, K. M., Boogert, A. C. A., Fraser, H. J., et al. 2008, ApJ, 678, 1005, doi: 10.1086/533431

Qasim, D., Fedoseev, G., Chuang, K. J., et al. 2020, Nature Astronomy, 4, 781, doi: 10.1038/s41550-020-1054-y

Raut, U., Famá, M., Teolis, B. D., & Baragiola, R. A. 2007a, JChPh, 127, 204713, doi: 10.1063/1.2796166

Raut, U., Teolis, B. D., Loeffler, M. J., et al. 2007b, JChPh, 126, 244511, doi: 10.1063/1.2746858

Roser, J. E., Vidali, G., Manicò, G., & Pirroello, V. 2001, ApJL, 555, L61, doi: 10.1086/321732

Salinas, V. N., Hogerheijde, M. R., Bergin, E. A., et al. 2016, A&A, 591, A122, doi: 10.1051/0004-6361/201628172

Sandford, S. A., Allamandola, L. J., Tielens, A. G. G. M., & Valero, G. J. 1988, ApJ, 329, 498, doi: 10.1086/166395

Schmitt, B., Greenberg, J. M., & Grim, R. J. A. 1989, ApJL, 340, L33, doi: 10.1086/185432

Schutte, W. A., & Greenberg, J. M. 1997, A&A, 317, L43

Stevenson, K. P., Kimmel, G. A., Dohnalek, Z., Smith, R. S., & Kay, B. D. 1999, Science, 283, 1505, doi: 10.1126/science.283.5407.1505

Swain, M. R., Vasisht, G., Tinetti, G., et al. 2008, arXiv e-prints, arXiv:0812.1844.

Watanabe, N., & Kouchi, A. 2002, ApJL, 571, L173, doi: 10.1086/341412

Zamirri, L., Casassa, S., Rimola, A., et al. 2018, MNRAS, 480, 1427, doi: 10.1093/mnras/sty1927

Zanchet, A., Rodríguez-Lazcano, Y., Gálvez, Ó., et al. 2013, ApJ, 777, 26, doi: 10.1088/0004-637X/777/1/26