Near-infrared laboratory spectra of solid H_2O/CO_2 and CH_3OH/CO_2 ice mixtures

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Abstract

We present near-IR spectra of solid CO_2 in H_2O and CH_3OH, and find they are significantly different from that of pure solid CO_2. Peaks not present in either pure H_2O or pure CO_2 spectra become evident when the two are mixed. First, the putative theoretically forbidden CO_2 (2ν_3) overtone near 2.134 μm (4685 cm\(^{-1}\)), that is absent from our spectrum of pure solid CO_2, is prominent in the spectra of H_2O/CO_2 = 5 and 25 mixtures. Second, a 2.74-μm (3650 cm\(^{-1}\)) dangling OH feature of H_2O (and a potentially related peak at 1.89 μm) appear in the spectra of CO_2–H_2O ice mixtures, but are probably not diagnostic of the presence of CO_2. Other CO_2 peaks display shifts in position and increased width because of intermolecular interactions with H_2O. Warming causes some peak positions and profiles in the spectrum of a H_2O/CO_2 = 5 mixture to take on the appearance of pure CO_2. Absolute strengths for absorptions of CO_2 in solid H_2O are estimated. Similar results are observed for CO_2 in solid CH_3OH. Since the CO_2 (2ν_3) overtone near 2.134 μm (4685 cm\(^{-1}\)) is not present in pure CO_2 but prominent in mixtures, it may be a good observational (spectral) indicator of whether solid CO_2 is a pure material or intimately mixed with other molecules. These observations may be applicable to Mars polar caps as well as outer Solar System bodies.

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1. Introduction

Near-infrared (IR) reflection spectra of outer Solar System objects show that CO_2 occurs on the solid surfaces of several bodies in the Solar System. In addition to the seasonal deposits of solid CO_2 on Mars, carbon dioxide in the coma of some comets is presumed to evaporate from solid CO_2 in their nuclei; comets also contain CH_3OH (Mumma et al., 1993). Grundy et al. (2003) found three bands of solid CO_2 in the 2-μm region in the spectrum of the uranian satellite Ariel. Carbon dioxide is also seen in the reflectance spectra of Jupiter’s satellites Europa, Ganymede, and Callisto (McCord et al., 1997, 1998; Hibbits et al., 2000, 2003) and Saturn’s satellites Phoebe (Clark et al., 2005) and Iapetus (Buratti et al., 2005). In all of these cases, the CO_2 stretching fundamental band usually at 4.27 μm is shifted slightly to shorter wavelength (4.26 μm) and is presumed to originate from CO_2 that is complexed in some way with other surface materials. The occurrence of CO_2 in the form of fluid or gaseous inclusions in minerals has been suggested by the authors of the papers cited above.

On Triton, an environment that is dominated by N_2 (Cruikshank et al., 1993; Stansberry, 2004), CO_2 might have been frozen into an inert matrix of solid N_2, but lab experiments have shown that the IR absorptions (especially the 4ν_2 + ν_3 band) are more consistent with pure CO_2 (Quirico et al., 1999) than CO_2 in N_2 (Quirico and Schmitt, 1997). Even if they were originally mixed, presumably seasonal temperature cycling and surface–atmosphere exchange has caused the ice components to separate on Triton and Pluto (e.g., Grundy and Buie, 2001) and on Mars (Bibring et al., 2004). The IR spectrum of pure solid CO_2 has been
well studied (Hansen, 1997; Quirico and Schmitt, 1997; Gerakines et al., 2005) and modeled (Bini et al., 1991), so it is well understood.

Solid H₂O is ubiquitous in the outer Solar System (Roush, 2001), and it is inevitable that CO₂ will come into intimate contact with H₂O at various temperatures and in varied proportions. For example, reflectance spectra of icy Galilean and saturnian satellites show strong near-IR absorptions of H₂O and CO₂. Although good near-IR spectra of pure CO₂ and CO₂ in N₂ have been published (Hansen, 1997; Quirico and Schmitt, 1997; Gerakines et al., 2005), to our knowledge no near-IR spectra of CO₂ in H₂O are available. The interaction between CO₂ and H₂O (and CH₃OH) on a molecular level has been shown to cause significant changes in the position and profile of CO₂ peaks in the mid-IR (Sandford and Allamandola, 1990; Dartois et al., 1999; Ehrenfreund et al., 1999; Palumbo and Baratta, 2000), so it seems reasonable that the presence of H₂O could change near-IR CO₂ peaks as well. Indeed, in this paper we show that this is the case, especially for the classically ‘forbidden’ 2ν₃ overtone near 2.134 μm.

The coincidence of CO₂ and CH₃OH in spectra of comets shows that these molecules coexist in the ices of the nucleus, but it is unknown if they occur as a molecular mix or in some other configuration. Both CH₃OH and H₂O ices have been found on the Centaur object 5145 Pholus (Cruikshank et al., 1998), thought to be a former Kuiper belt object and therefore a large ‘proto-comet,’ but CO₂ has not yet been detected.

In this paper we display near-IR spectra of H₂O–CO₂ and CH₃OH–CO₂ ice mixtures at temperatures from 15 to 150 K. Among other things we highlight the enhancement of the probable 2ν₃ overtone of CO₂ near 2.134 μm (4685 cm⁻¹), and its potential as an observational (spectral) indicator of whether solid CO₂ is a pure material or intimately mixed with other molecules. We present these results in Section 3, and briefly discuss the results and potential implications for Solar System studies in Section 4.

### 2. Materials and methods

The basic techniques and equipment employed for this study have been described previously as part of our mid-IR studies of various compounds in H₂O at low temperature (Hudgins et al., 1994). Details associated with the materials and methods used that are unique to this particular study are provided below.

The H₂O (purified via a Millipore Milli-Q water system to 18.2 MΩ) and the CH₃OH (99.93% HPLC grade, Aldrich) were freeze-pump thawed at least three times to remove dissolved gases prior to use. CO₂ (bone dry, Matheson) was used without further purification. Samples were mixed at room temperature in volume-calibrated, greaseless glass bulbs and allowed to equilibrate for at least 24 h before use. The background pressure in the gas-handling system was ≈10⁻⁵ mbar, compared to total pressures in the sample bulbs of tens of millibars, so the contaminant levels in the bulbs associated with the mixing process were negligible. Bulbs containing H₂O/CO₂ = 5 and 25, and CH₃OH/CO₂ = 5 mixtures were used to prepare the samples.

Once prepared, glass sample bulbs were transferred to the stainless steel vacuum manifold where the sample mixture was vapor-deposited onto a CsI window cooled to 15 K by an Air Products Displex CSW 202 closed-cycle helium refrigerator. Gas mixtures were deposited first for 10 min against a cold shield before depositing onto the sample window so as to minimize the bias in the ice towards the more volatile component early in the deposit. We find that this procedure gives a solid sample more representative of the gas phase mixing ratio in the bulb, but presumably also depends on the components and the substrate temperature.

Typical samples were deposited at a rate sufficient to produce samples ~0.1 μm thick after a few minutes. The spectra that include the mid-IR (Figs. 1 and 7) are only tenths of micrometers thick, whereas the others are ~10 μm thick. Under these conditions the samples are composed of an intimate mixture of the CO₂ in H₂O or CH₃OH. Pure H₂O deposed under these conditions is in its high density amorphous form when deposited at 15 K and after warming, the H₂O goes through several phase transitions (Jenniskens and Blake, 1994; Jenniskens et al., 1995). Clearly, the situation for mixtures is more complex. We do not know the phase of the H₂O in these mixtures but our IR spectra of H₂O/CO₂ mixtures are broadly consistent with previous observations of phases of pure H₂O.

In Table 1, we report relative areas for the absorptions of CO₂ in H₂O and CH₃OH because we have no accurate absolute scale against which to compare the peak areas. However, we can give an estimate of the intrinsic (absolute) absorptivities for these absorptions of CO₂ in solid H₂O given certain assumptions. If we assume that the intrinsic strength of the 4.270 μm (2342 cm⁻¹) ν₂, fundamental asymmetric stretch of CO₂ in the spectrum of the H₂O/CO₂ = 25 ice is the same as that of an H₂O/CO₂ = 20 mixture, then it should be ≈2 × 10⁻¹⁶ cm/molec according to Sandford and Allamandola (1990). Since the numbers on Table 1 are normalized to the ν₃ band, the relative numbers in Table 1 (at least for the H₂O/CO₂ = 25 ice) can be converted to intrinsic per-molecule absorptivities (A values) by multiplying by ≈2 × 10⁻¹⁶ cm/molec.

The intensity of the 2.135 μm (4700 cm⁻¹) ‘forbidden’ 2ν₃ overtone of CO₂ in H₂O or CH₃OH is sensitive to conditions (i.e., concentration, temperature); we have observed it to vary in strength by as much as a factor of two in CO₂–CH₃OH mixtures. As a result, the areas reported for the 2.135 μm (4700 cm⁻¹) absorptions should be regarded as more uncertain than those of the other CO₂ absorptions.
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Table 1

Peak areas for solid CO2 in H2O and CH3OH at 15 K

<table>
<thead>
<tr>
<th>Modea</th>
<th>H2O/CO2 = 25</th>
<th>H2O/CO2 = 5</th>
<th>CH3OH/CO2 = 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position (cm−1)</td>
<td>FWHM (cm−1)</td>
<td>Areab</td>
</tr>
<tr>
<td>2ν1 + ν3</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ν1 + 2ν2 + ν3</td>
<td>4960</td>
<td>&gt;10</td>
<td>~6 × 10−4</td>
</tr>
<tr>
<td>4ν2 + ν3</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2ν3</td>
<td>4685</td>
<td>27</td>
<td>0.012</td>
</tr>
<tr>
<td>ν1 + ν3</td>
<td>3700</td>
<td>12</td>
<td>0.013</td>
</tr>
<tr>
<td>3650c</td>
<td>20</td>
<td>6.4 × 10−3</td>
<td>3653d</td>
</tr>
<tr>
<td>2ν2 + ν3</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ν3</td>
<td>2342</td>
<td>11</td>
<td>1.0</td>
</tr>
<tr>
<td>13C–ν3</td>
<td>2278</td>
<td>8</td>
<td>0.010</td>
</tr>
<tr>
<td>ν2</td>
<td>653</td>
<td>21</td>
<td>0.15</td>
</tr>
</tbody>
</table>

a Mode assignments from Quirico and Schmitt (1997) and Sandford and Allamandola (1990).

b Peak areas are normalized to the CO2 peak near 2340 cm−1 (4.274 µm). The relative numbers can be converted to absolute values by multiplying by ~2 × 10−16 cm/molec (see Section 2).

c These are not CO2 peaks, they are probably caused by H2O (or CH3OH).

d This area probably represents a lower limit, this peak is difficult to integrate accurately because of its proximity to the 3 µm OH band of H2O.

3. Results

Fig. 1 displays a full (1.75–22 µm; 5700–450 cm−1) IR spectrum of an H2O/CO2 = 5 mixture at 15 K. The broad strong absorptions at ~2.0, 3.1, 6.3, and 13.3 µm (5090, 3250, 1600, and 750 cm−1) are typical of those observed previously for pure amorphous solid H2O (Hudgins et al., 1994; Gerakines et al., 2005). Solid H2O is also responsible for the sharper, weaker, features near 1.89 µm (5300 cm−1) and 2.74 µm (3650 cm−1), see discussion for details. The sharp mid-IR peaks of CO2 in solid H2O appear at 15.3 µm (654 cm−1), 4.39 µm (2278 cm−1), and 4.270 µm (2342 cm−1), and these have been well studied (Sandford and Allamandola, 1990; Dartois et al., 1999). The shorter wavelength, less intense, (near) IR absorptions of CO2 in solid H2O are at 2.701, 2.784, 2.135, 2.072, 2.015, and 1.967 µm (4684 cm−1) and 4827 cm−1, and 5083 cm−1. Table 1 lists the peak positions, full widths at half maximum height (FWHM) and relative areas of all observed absorptions of CO2.

The CO2 absorption at 4.270 µm (2342 cm−1) that dominates the mid-IR and Fig. 1 corresponds to ν3, the asymmetric stretch of CO2. We believe that the peak at 2.135 µm (4684 cm−1) is 2ν3, the theoretically ‘forbidden’ first overtone of the asymmetric stretch of CO2 (see inset in Fig. 1). Because we have not performed isotopic studies, this assignment is based merely on the fact that it appears at twice the frequency of ν3 and behaves in a manner consistent with it being a ‘forbidden’ feature, i.e., this peak is absent from or very much weaker in spectra of pure solid CO2 (see below).

Below we present a series of figures highlighting spectral regions of particular interest. The figures in this paper show primarily spectra of H2O/CO2 = 5 mixtures because these display the CO2 absorptions with better signal-to-noise, but the positions and widths are representative of what is seen for H2O/CO2 = 25 (see table for details).

Fig. 2 shows 2.667–2.817 µm (3750–3550 cm−1) IR spectrum of pure CO2 (top trace) compared with that of an H2O/CO2 = 5 ice mixture at 15 K. The two peaks at 2.701 and 2.784 µm (3702 and 3592 cm−1) can be attributed to the ν1 + ν3 and 2ν2 + ν3 combination modes of CO2, respectively (Sandford and Allamandola, 1990; Quirico and Schmitt, 1997).

These absorptions of CO2 in solid H2O are 4–5 times broader and shifted by 0.005 and 0.006 µm (−7 and −8 cm−1), respectively, relative to pure solid CO2 under the same conditions. The central broad absorption near 2.74 µm
Fig. 2. The 2.667–2.817 µm (3750–3550 cm\(^{-1}\)) IR spectrum of pure CO\(_2\) (above) compared with that of an H\(_2\)O/CO\(_2\) = 5 ice mixture at 15 K (below). The ∼2.70 and 2.78 µm (3702 and 3592 cm\(^{-1}\)) absorptions of CO\(_2\) in H\(_2\)O are significantly broader and shifted to longer wavelength than those of pure CO\(_2\). The central broad feature near 2.74 µm (3650 cm\(^{-1}\)) is an absorption of H\(_2\)O, not CO\(_2\), so it does not appear in the upper spectrum. The lower spectrum drops off to the right because of the large 3 µm H\(_2\)O band (see Fig. 1).

(3650 cm\(^{-1}\)) is very similar to that assigned by Rowland et al. (1991) to the ‘dangling’ OH of H\(_2\)O and discussed in an astrophysical context by Ehrenfreund et al. (1996). This feature is observed when any molecule mixed into solid H\(_2\)O breaks up its hydrogen bonding network. Thus, it is not specific to CO\(_2\).

Fig. 3 highlights the 2\(\nu_3\) ‘forbidden’ overtone of CO\(_2\) at 2.135 µm (4684 cm\(^{-1}\)) previously seen in the inset in Fig. 1. In this figure the 2.08–2.27 µm (4800–4400 cm\(^{-1}\)) IR spectra of H\(_2\)O/CO\(_2\) = 5 and = 25, CH\(_3\)OH/CO\(_2\) = 5, and H\(_2\)O:CH\(_3\)OH:CO\(_2\) = 100:2.5:1 mixtures are compared to those of pure CO\(_2\) and pure H\(_2\)O under the same conditions. The 2\(\nu_3\) overtone of the asymmetric stretch of CO\(_2\) near 2.135 µm (4684 cm\(^{-1}\)) is present in all of the ice mixtures, but it is too weak to be observed in the spectrum of pure CO\(_2\) (above), although there are at least 100 times more CO\(_2\) molecules in the sample that produced the upper trace than in the lower ones.

There are three sharp peaks in the spectrum of pure CO\(_2\) at 2.072, 2.015, and 1.967 µm (4827, 4962, and 5083 cm\(^{-1}\)) (Hansen, 1997; Quirico and Schmitt, 1997; Gerakines et al., 2005), as can be seen in the upper trace in Fig. 4. Compared to pure CO\(_2\) these absorptions from the mixture are 3–5 times broader and shifted to longer wavelength by 0.002, 0.004, and 0.003 µm (6, 10, and 5 cm\(^{-1}\)), respectively. This is comparable to the broadening and shifting of the 2.70 and 2.78 µm (3702 and 3593 cm\(^{-1}\)) CO\(_2\) peaks in Fig. 2. This entire region of the spectrum is spanned by a broad H\(_2\)O band (see also Fig. 1), and this causes a broad dip in the spectra of H\(_2\)O–CO\(_2\) mixtures that somewhat obscures these CO\(_2\) peaks.

Fig. 5 shows the temperature dependence of the 2.70 and 2.78 µm (3702 and 3593 cm\(^{-1}\)) absorptions of a H\(_2\)O/CO\(_2\) = 5 ice mixture between 15 and 100 K. Sharp peaks con-
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Fig. 5. Temperature dependence of the 2.67–2.82 µm (3750–3550 cm$^{-1}$) IR spectrum of an H$_2$O/CO$_2$ = 5 ice mixture. The broad features at ∼2.70 and 2.79 µm (3700 and 3590 cm$^{-1}$) of CO$_2$ in H$_2$O are visible over the entire temperature range. The sharper peaks superimposed upon them that appear, broaden, and then diminish with warming are similar to those produced by pure CO$_2$.

Fig. 6. The 2.0–22 µm (5000–450 cm$^{-1}$) IR spectrum of an CH$_3$OH/CO$_2$ = 5 ice mixture. As in Figs. 1 and 3, the 2ν$_3$ overtone of CO$_2$ is clearly visible at ∼2.14 µm (4682 cm$^{-1}$), and the pair of CO$_2$ peaks at ∼2.70 and 2.79 µm are also present. The other absorptions between 2 and 3 µm are caused by methanol.

4. Discussion

We have shown that near-IR spectra of CO$_2$ in H$_2$O or CH$_3$OH at low temperature look very different than those pure CO$_2$ under the same conditions. First, absorptions of
CO₂ in H₂O or CH₃OH are 3–5 times broader and are shifted to longer wavelength by 0.002–0.006 µm (−5 and −10 cm⁻¹) than those of pure CO₂ under the same conditions. Second, and perhaps most significantly, CO₂ in H₂O (or CH₃OH) produces new absorptions that are simply not present (or greatly diminished) in the spectra of the pure materials.

In particular, our near-IR spectra of 1 and 10 µm thick H₂O/CO₂ = 5 and 25 ices show a fairly strong (∼10⁻¹⁸ cm/molecule) peak near 2.135 µm (4684 cm⁻¹) interpreted to be the 2ν₃ overtone of CO₂ that is very much weaker in near-IR spectra of our pure CO₂ frost (see Fig. 3) and absent from spectra of a thick CO₂ monocrystal grown in a closed cell (E. Quirico, private communication). A very weak peak near ∼2.128 µm (4700 cm⁻¹) was observed in the published spectrum of a thick sample of pure CO₂ (Quirico and Schmitt, 1997) and both they and we think this is the same feature. They observed that small feature to be >7000 times weaker than the 2.70 µm (3700 cm⁻¹) CO₂ peak, whereas these two are of comparable intensity in our spectra of H₂O–CO₂ mixtures (see Table 1). This indicates that the CO₂ 2ν₃ absorption is enhanced by a factor of ∼10⁴ in our H₂O–CO₂ mixtures, over that of pure CO₂. This formally ‘forbidden’ absorption has also been reported as a weak feature in the spectra of CO₂ isolated in Ar (Sandford et al., 1991) and N₂ matrices (Quirico and Schmitt, 1997), where we estimate it at least 1000 times less intense than in H₂O or CH₃OH. The fact that this forbidden transition is observed so strongly suggests that the symmetry of the CO₂ is broken by interactions with neighboring molecules—literally being bent by the water ‘matrix’ for example. However, were this the case then one might expect that the ν₁ mode near 7.5 µm (1340 cm⁻¹) might also be visible, but in our spectra it is not. We do not have a good explanation for why this is the case, but the behavior of the ν₁ mode is complicated by its near coincidence with 2ν₂ (2 × 667 cm⁻¹ = 1334 cm⁻¹) and the concomitant Fermi resonance (Drago, 1992). It is to be hoped that theoretical modeling will be amenable to solving this problem.

The intensification of the 2ν₃ peak may be a general feature of CO₂ interactions with molecules that can hydrogen bond, since it was also observed in H₂S–SO₂–CO₂ ice mixtures (Sandford et al., 1991). Formally ‘forbidden’ transitions in N₂ (Bernstein and Sandford, 1999) and O₂ (Ehrenfreund et al., 1992) have been observed in H₂O and at least that of N₂ is sensitive to the molecular environment. Similarly, we observe the relative intensity of the 2.135 µm (4684 cm⁻¹) peak to change depending on the conditions (i.e., concentration, temperature, etc.), consistent with it being the CO₂ 2ν₃ overtone.

Spectra of frosts vapor deposited at low temperature (such as we have shown here) can differ from those of thick ices made by the cooling of higher temperature materials in a closed cell. It may be that thin films have crystallographic defects that locally break the crystal symmetry making the 2ν₃ feature more intense in vapor deposited frosts than it would be in thicker samples annealed in a closed cell. In any case, the intensity of the band is clearly controlled by the abundance of band activator (here H₂O), so, it is a powerful indicator of an H₂O–CO₂ interaction (the relative intensity of the 2ν₃ peak to change depending on the conditions (i.e., concentration, temperature, etc.), consistent with it being the CO₂ 2ν₃ overtone.

Other features enhanced in spectra of H₂O–CO₂ mixtures relative to those of either pure material include the 2.74 µm (3650 cm⁻¹) and 1.89 µm (∼5300 cm⁻¹) absorptions of H₂O. The 2.74 µm (3650 cm⁻¹) feature is certainly not specific to CO₂, it is known to be caused by other guest molecules in H₂O (Rowland et al., 1991). The 1.89 µm (∼5300 cm⁻¹) peak has appeared previously in published spectra of low temperature amorphous H₂O (Schmitt et al., 1998), and we think it an overtone combination of the aforementioned non-specific 2.74 µm (3650 cm⁻¹) feature with the strong 6.3 µm (∼1600 cm⁻¹) bending mode of H₂O. This 1.89 µm peak may be a useful measure of the phase of
the ice, since it diminishes on warming (see Fig. 3 in Schmitt et al., 1998).

During warming of H₂O/CO₂ = 5 ices we observe at ∼2.70 and ∼2.79 µm (3700 and 3590 cm⁻¹) the broad, shifted, peaks of CO₂ in H₂O and also sharper peaks that resemble those of pure CO₂ (see Fig. 5). The results for CH₃OH/CO₂ = 5 ices are very similar (see Fig. 7). Although the absorptions seen in Fig. 7 between 2.67 and 2.82 µm (3750–3550 cm⁻¹) look like pure CO₂, they cannot be, both because the temperature is above that at which pure CO₂ would sublime, and also because the corresponding 2.135 µm (4684 cm⁻¹) peak is observed although it is absent from spectra of pure CO₂. Thus, if this CO₂ is ‘pure’ it is still in small domains, i.e., not a layer of pure CO₂ on top of a layer of pure H₂O. These observations are consistent with previous studies of the temperature dependence of the 4.27 µm (2340 cm⁻¹) CO₂ peak, TEM micrographs (Blake et al., 1991) and the ∼15 µm (∼650 cm⁻¹) CO₂ peak (Ehrenfreund et al., 1998) in ternary CO₂–H₂O–CH₃OH mixtures. This is reminder that CO₂ can be trapped in H₂O ice at temperatures well above that at which it would normally sublime, so small amounts of solid CO₂ may be observed as long as H₂O ice is present, in our vacuum system up to almost 200 K.

The case of CO₂ in H₂O and CH₃OH exemplifies what is probably a general rule: intermolecular interactions with H₂O will cause significant changes in IR absorptions, so combining spectra of pure materials will not be adequate to reproduce spectra of mixtures. The results reported here have obvious implications for the interpretation of IR spectra of ices in environments where CO₂ might come into contact with H₂O, such as Mars polar caps and outer Solar System objects. Even in environments where one might expect CO₂ to be separate from H₂O because it is more volatile, CO₂ could be formed trapped in solid H₂O by the oxidation of carbon compounds. Since the CO₂ (2ν₁) overtone near 2.134 µm (4685 cm⁻¹) is essentially not present in pure CO₂ but is prominent in mixtures with H₂O, near-IR spectra could be used to determine if, in a Mars polar cap or on the surface of an icy body in the outer Solar System, CO₂ is mixed intimately with another molecule or separate. Since the absorptions of CO₂ in H₂O are broad and thus have lower spectral contrast, they may have been overlooked or assigned to other causes in the past. For example, there is a peak near 2.13 µm on the short wavelength shoulder of the N₂ absorption in the spectrum of Triton presented in Fig. 2 from Quirico et al. (1999) that could be the (2ν₁) overtone of CO₂ in H₂O. The three shorter wavelength CO₂ absorptions (seen in Fig. 4) would be even smaller and thus lost in the noise. However, there is also a nearby shoulder in the lab spectrum of pure N₂ so the presence of this shoulder is merely consistent with some CO₂ in H₂O. It is to be hoped that future observations of Triton, Mars, and other objects where solid H₂O and CO₂ are present will allow for the accurate determination of whether there may be some CO₂ intimately mixed with H₂O.

5. Conclusions

1. We have presented the first near-IR spectra of H₂O/CO₂ and CH₃OH/CO₂ mixtures vapor deposited at 15 K and warmed to 150 K.
2. The spectrum of CO₂ in H₂O is not the same as the sum of the spectra of the pure components. In particular, the 2.135 µm (4684 cm⁻¹) absorption of CO₂ is thousands of times stronger in the mixtures than in pure CO₂.
3. The presence of this absorption in the spectra of Solar System objects will be a good indicator of whether the CO₂ is intimately mixed with H₂O.

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