Near-infrared spectra of laboratory H₂O–CH₄ ice mixtures

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Received 13 July 2005; revised 17 October 2005
Available online 13 December 2005

Abstract

We present 1.25–19 µm infrared spectra of pure solid CH₄ and H₂O/CH₄ = 87, 20, and 3 solid mixtures at temperatures from 15 to 150 K. We compare and contrast the absorptions of CH₄ in solid H₂O with those of pure CH₄. Changes in selected peak positions, profiles, and relative strength with temperature are presented, and absolute strengths for absorptions of CH₄ in solid H₂O are estimated. Using the two largest \( (\nu_3 + \nu_4) \) and \( (\nu_1 + \nu_4) \) near-IR absorptions of CH₄ at 2.324 and 2.377 µm (4303 and 4207 cm⁻¹), respectively, as examples, we show that peaks of CH₄ in solid H₂O are at slightly shorter wavelength (higher frequency) and broader than those of pure solid CH₄. With increasing temperature, these peaks shift to higher frequency and become increasingly broad, but this trend is reversible on re-cooling, even though the phase transitions of H₂O are irreversible. It is to be hoped that these observations of changes in the positions, profiles, and relative intensities of CH₄ absorptions with concentration and temperature will be of use in understanding spectra of icy outer Solar System bodies.

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Keywords: Ices; Infrared observations; Spectroscopy; Surfaces, planets; Surfaces, satellites

1. Introduction

Infrared (IR) spectra have demonstrated that solid CH₄ is present on a number of outer Solar System objects, including Triton (Cruikshank et al., 1982) and Pluto (Cruikshank et al., 1976), where it is thought to be frozen into N₂ ice (Quirico et al., 1999; Grundy and Buie, 2001), the Kuiper Belt Objects (KBOs) Quaoar (Brown, 2003, and personal communication), 90377 Sedna (Barucci et al., 2005), 2003 UB₃₁₃ (Trujillo et al., 2005; Brown et al., 2005), and FY9 (Barkume et al., 2005), and CH₄ is known to be present in number of comets (Gibb et al., 2003).

Since H₂O is nearly ubiquitous in the outer Solar System (Roush, 2001) CH₄ on icy planetesimals is likely to come into contact with H₂O, potentially changing its spectral properties. Since mathematical addition of spectra of pure materials is not equivalent to the spectra of actual mixtures, fitting CH₄ profiles in spectra of outer Solar System bodies will require lab spectra of solid CH₄ mixed at a molecular level with H₂O at relevant temperatures.

Near-IR spectra of CH₄ as a pure solid and mixed in N₂ have been measured in the lab at various temperatures and concentrations (Quirico and Schmitt, 1997; Grundy et al., 2002). Absolute absorption intensities (A values) for near-IR absorptions of pure solid CH₄ were published recently (Gerakines et al., 2005), and real and imaginary indices of refraction (ns and ks) have been determined for both pure methane (Khare et al., 1989; Pearl et al., 1991) and pure H₂O, albeit for just the hexagonal phase (Grundy and Schmitt, 1998). Despite this wealth of beautiful data, there is a lack of near-IR spectra of CH₄ intimately mixed with solid H₂O, as it is likely it will be found on some icy bodies in the outer Solar System.

Since an interaction with H₂O on a molecular level has been shown to cause significant changes in the position and profile of CH₄ absorptions in the mid-IR (e.g., Hudgins et al., 1993), the presence of H₂O could change peaks in the near-IR as well. This would complicate the interpretation of reflection spectra of outer Solar System bodies. In this paper we present near-IR spectra of H₂O–CH₄ ice mixtures at various concentrations and temperatures from 15 to 150 K, and document how peaks shift and broaden, both as a result of interactions with H₂O and as a result of changes in temperature. It is to be hoped that this data will be used, in conjunction with observations, to constrain
the state of solid CH₄ on the surface of outer Solar System bodies.

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., 1993). Details associated with the materials and methods used that are unique to this particular study are provided below. Supplementary and related electronic materials (including additional spectra) are available at our web site, http://www.astrochem.org.

2.1. Experimental procedure

The H₂O was purified via a Millipore Milli-Q water system to 18.2 MΩ and freeze-pump thawed at least three times to remove dissolved gases prior to use. Methane (Matheson UHP = 99.97%) was used without further purification. Samples were pre-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 millibar, so the contaminant levels in the bulbs associated with the mixing process were negligible. Bulbs were made of H₂O/CH₄ = 87, 20, and 3 mixtures, and of pure CH₄.

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. If this is not done then the first ice that condenses has a higher proportion of CH₄ (a lower H₂O/CH₄ ratio) than in the gas phase in the bulb. We find that this procedure gives a solid sample more representative of the gas-phase mixing ratio in the bulb, but also certainly depends on the substrate temperature. While samples vapor deposited at 15 K (after a delay as described above) have compositions that match the gas-phase mixing ratio in the sample bulb, a H₂O/CH₄ = 20 gas mixture that was vapor deposited onto the same substrate at 74 K produced an ice that was less likely to condense at higher temperature. Warming to 74 K an ice that was vapor deposited at 15 K does not cause such a dramatic loss of methane (see Fig. 2). IR spectra were measured on a Bio-rad Excalibur FTS 3000 spectrometer with ambient DTGS and LN₂ cooled MCT detectors and salt and quartz beam splitters that permit measurements in both the mid- and near-infrared.

The mid-IR spectra (i.e. Fig. 1) were measured for ices only tenths of micrometer thick, whereas the others are ~10 µm thick. H₂O mixtures were deposited at a rate sufficient to produce samples a few tenths of a micrometer thick after a few minutes. Under these conditions the samples are composed of CH₄ in H₂O, mixed at a molecular level. Pure H₂O deposited 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/CH₄ mixtures are consistent with previous observations of phases of pure H₂O, so the results described below probably include near-IR spectra of CH₄ in various amorphous and crystalline phases of H₂O ice depending on the temperature. The pure methane film (Fig. 2) was
deposited faster, at a rate that produced a 2-µm thick ice after ~7 min of deposit.

We note as a caveat that spectra of frosts vapor deposited at low temperature (such as we shall present here) can differ from those of thick ices made by the cooling of higher temperature materials in a closed cell (Quirico and Schmitt, 1997; Section 2). While the closed cell technique provides vastly superior signal to noise spectra for pure ices, there are some cases where it is not applicable. For example, when working with perior signal to noise spectra for pure ices, there are some cases where the components with very different volatilities (such as is the case where it is not applicable. For example, when working with perior signal to noise spectra for pure ices, there are some cases where the components with very different volatilities (such as is the case here with CH₄ and H₂O) the measurement of ices where the components are mixed as a molecular level would presumably be precluded by preferential condensation of the less volatile component before the more volatile one. In addition, water ice condensed in such a closed cell would presumably form and remain in whatever crystalline phase formed during cool-down, whereas our warm-up and cool down procedure allows us to explore both amorphous and crystalline phases that may be relevant to outer Solar System environments where the H₂O ice is present (Roush, 2001; Hansen and McCord, 2004).

2.2. Peak areas and uncertainties

The areas we report in Table 1 for the near-IR absorptions of CH₄ in H₂O are all normalized relative to the peak near 4300 cm⁻¹, because we have no absolute scale against which to directly measure true intensities of the peaks. However, we can estimate intrinsic (absolute) absorptivities (A values) of our near-IR absorptions if we accept the A values of mid-IR absorptions of CH₄ in H₂O/CH₄ = 20 reported by Hudgins et al. (1993) and ratio the areas of our near-IR CH₄ absorptions to the mid-IR peaks for which A values are known. Given that for an H₂O/CH₄ = 20 ice the intrinsic strength of the 3.323 μm (3009 cm⁻¹) C–H stretch of CH₄ is 3.6 × 10⁻¹⁸ cm per molecule, and that of the 7.675 μm (1303 cm⁻¹) C–H wag is 4.7 × 10⁻¹⁸ (Hudgins et al., 1993) then the A values for the two largest near-IR methane peaks at 2.326 and 2.379 μm (4300 and 4203 cm⁻¹) are 2.4(±0.4) × 10⁻¹⁹, and 1.4(±0.3) × 10⁻¹⁹, respectively. Thus, the normalized band areas in Table 1 can be converted to absolute A values (at least for the H₂O/CH₄ = 20 ice) by multiplying by ~2 × 10⁻¹⁹ cm per molecule.

The error reported above (~20%) is only the scatter from five measurements, and thus reflects the uncertainty in the precision, not the full uncertainty in the accuracy. Since our A values are based on those of Hudgins et al. (1993), who claim an accuracy of no better than a factor of two, we can claim no better.

3. Experimental results

Fig. 1 shows the overall near- and mid-IR spectrum (1.25–19.2 μm; 8000–520 cm⁻¹) of an H₂O/CH₄ = 20 solid mixture at 15 K. The inset shows a (70×)-magnified view of absorptions too weak to be seen in the upper trace. The broad strong absorptions at approximately 1.5, 2.0, 3.0, 4.5, 6.0, and 13 μm (6700, 3848, 3716, 3532, 3309, and 7167 cm⁻¹) are intrinsic, not the full uncertainty in the accuracy. Since our A values are based on those of Hudgins et al. (1993), who claim an accuracy of no better than a factor of two, we can claim no better.

### Table 1

Peak positions⁴, widths⁵, and areas⁶ for CH₄ in solid H₂O at 15 K

<table>
<thead>
<tr>
<th>H₂O/CH₄ = 87</th>
<th>H₂O/CH₄ = 20</th>
<th>H₂O/CH₄ = 3</th>
<th>Pure CH₄</th>
</tr>
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<tbody>
<tr>
<td>Position</td>
<td>FWHM</td>
<td>Area</td>
<td>Position</td>
</tr>
<tr>
<td>7485</td>
<td>~30</td>
<td>2.4 × 10⁻²</td>
<td>7487</td>
</tr>
<tr>
<td>7450–7025</td>
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<td>0.29</td>
<td>7360–7260</td>
</tr>
<tr>
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<td>~50</td>
<td>See above</td>
<td>7128</td>
</tr>
<tr>
<td>sh 6040</td>
<td></td>
<td></td>
<td>7083</td>
</tr>
<tr>
<td>5985</td>
<td>18</td>
<td>0.10</td>
<td>sh 7062</td>
</tr>
<tr>
<td>5984</td>
<td>13</td>
<td>5.2 × 10⁻²</td>
<td>sh 6000</td>
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<td>5798</td>
<td>15</td>
<td>3.1 × 10⁻²</td>
<td>5978</td>
</tr>
<tr>
<td>sh 5602</td>
<td></td>
<td></td>
<td>5919</td>
</tr>
<tr>
<td>5564</td>
<td>15</td>
<td>4.0 × 10⁻²</td>
<td>5800</td>
</tr>
<tr>
<td>4532</td>
<td>0.1</td>
<td>0.15</td>
<td>5574</td>
</tr>
<tr>
<td>4304</td>
<td>20</td>
<td>1.0</td>
<td>5595</td>
</tr>
<tr>
<td>4206</td>
<td>0.73</td>
<td>0.53</td>
<td>sh 5574</td>
</tr>
<tr>
<td>4301</td>
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<td>16</td>
<td>0.54</td>
<td>4119</td>
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<td>3848</td>
</tr>
<tr>
<td>3009</td>
<td>10</td>
<td>18</td>
<td>3009</td>
</tr>
</tbody>
</table>

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⁴ All positions and peaks widths (FWHM) are given in wavenumbers.

⁵ Peak areas are relative, having been normalized to the CH₄ peak near 4300 cm⁻¹ (2.326 μm). The relative numbers can be converted to approximate absolute values (at least for the H₂O/CH₄ = 20 ice) by multiplying by ~2 × 10⁻¹⁹ cm per molecule. See Section 2.2 for details.
NIR spectra of H₂O/CH₄ ices

5100, 3250, 2200, 1600, and 750 cm⁻¹) are typical of those observed previously for pure amorphous solid H₂O (Hudgins et al., 1993; Gerakines et al., 2005). Solid H₂O is also responsible for the sharper, weaker, feature near 1.89 µm (5300 cm⁻¹), see discussion for details.

The other, sharp features at 1.671, 1.725, 1.797, 2.208, 2.325, 2.379, 3.323, and 7.68 µm (5984, 5798, 5564, 4529, 4301, 4204, 3009, and 1302 cm⁻¹) are caused by CH₄. The mid-IR absorptions of CH₄ in H₂O have been published previously (Hudgins et al., 1993) but to our knowledge near-IR spectra of H₂O–CH₄ mixtures have not. In Table 1 we summarize the CH₄ absorptions we have observed in frosts of vapor deposited pure CH₄, and three mixtures (H₂O/CH₄ = 87, 20, and 3) at 15 K. In general, the absorptions of CH₄ diluted in H₂O are broader and appear at slightly shorter wavelength than in the spectrum of pure CH₄. This, and other observations, will be exemplified in subsequent figures using the two strongest near-IR absorptions of CH₄, the (ν₃ + ν₄) and (ν₁ + ν₄) combination modes near 2.326 and 2.381 µm (4300 and 4200 cm⁻¹), respectively, as examples.

Peak width and central peak frequency increase with H₂O/CH₄ ratio. This is demonstrated in Fig. 2, where the 2.3–2.4 µm (4350–4150 cm⁻¹) IR spectrum of pure CH₄ is plotted with those of the three H₂O/CH₄ mixtures. The effect is most apparent for the H₂O/CH₄ = 87 mixture (top trace, Fig. 2), where the central positions of these two peaks fall short of those in pure CH₄ (lower trace, marked by hatched lines). The (ν₁ + ν₄) and (ν₁ + ν₄) absorptions of CH₄ in the H₂O/CH₄ = 87 mixture are shifted by 1.6 × 10⁻³ and 2.3 × 10⁻³ µm (3 and 4 cm⁻¹), respectively, from those in pure solid CH₄ under identical conditions.

In addition to these small shifts in position, these two absorptions in the H₂O/CH₄ = 87 mixture are ~3 and 1.5 times broader than those in pure solid CH₄ at the same temperature. As a result, the shoulders evident on the sides of the (ν₁ + ν₄) and (ν₁ + ν₄) absorptions of pure solid CH₄ are obscured in H₂O/CH₄ mixtures (compare lower and upper spectra in Fig. 2).

The positions, profiles, and relative intensities of CH₄ absorptions in an H₂O/CH₄ mixture depend on temperature as well as concentration. The two strong CH₄ absorptions near 2.325 and 2.380 µm at 15 K are seen in Fig. 3 to (blue) shift and broaden with increasing temperature from 15 to 150 K. The other CH₄ peaks behave in a similar fashion, e.g., the 2ν₁ absorption shifts from 1.671 to 1.668 µm (5985 to 5994 cm⁻¹) and the (ν₂ + ν₃ + ν₄) from 1.724 to 1.722 µm (5800 to 5807 cm⁻¹) over the range of 15–150 K (not shown). These temperature-dependent changes are, to a great extent, reversible on re-cooling, despite the fact the phase changes of the water ice are irreversible. The absolute intensity never entirely recovers, presumably due to sublimation of CH₄. Spectra have been offset for clarity.

symbols in Fig. 4) yielded peak positions that were, within uncertainties, consistent with those observed for the ice vapor deposited at 15 K and then warmed. This suggests that peak position depends more on the temperature at the time of observation than at the time of initial deposit.

As can be seen from Fig. 5, the pattern for changes in the peak width vs temperature are very similar to those for peak
Fig. 5. Peak widths vs temperature for the 2.32 and 2.38 µm (4300 and 4200 cm$^{-1}$; ▲ and ●, respectively) methane absorptions of an H$_2$O/CH$_4$ = 20 ice. From left to right vapor deposited at 15 K, warmed to 150 K, and then re-cooled to 30 K. The peak widths increase with increasing temperature, but return to essentially the original values on re-cooling. The empty symbols represent the widths of the same peaks vapor deposited at 74 K.

Fig. 6. The ratio of the 2.38/2.32 µm (4200/4300 cm$^{-1}$) methane absorptions vs temperature for an H$_2$O/CH$_4$ = 20 ice vapor deposited at 15 K, warmed to 150 K, and then re-cooled to 30 K. Like the position and width, the ratio of areas seems to be reversible with respect to temperature.

As before, the effect is reversible, the same pattern for both peaks, and an ice deposited at ~74 K displays peak widths equivalent to those in the spectra of ices deposited at low temperature and then warmed to 74 K.

The changes in the $(\nu_1 + \nu_4)/(\nu_3 + \nu_4)$ (i.e., 2.380/2.325 µm) peak area ratio on warming of ices vapor deposited at 15 K seen in Fig. 6 is similar to those seen above for peak position and width. The relative areas of the two main peaks vary reversibly with temperature. However, vapor deposition of an H$_2$O/CH$_4$ = 20 gas mixture onto a substrate at 74 K produced an ice with a 2.380/2.325 µm peak area ratio very close to one, very much higher than what is observed when an H$_2$O/CH$_4$ = 20 ice is warmed to 74 K. Vapor deposition of an H$_2$O/CH$_4$ = 20 mixture at 74 K gave a H$_2$O/CH$_4$ = 200 ice, ten times more dilute because the CH$_4$ is less likely to condense at higher temperatures. The 2.380/2.325 µm peak area ratio close to one is expected for a more dilute mixture (see Fig. 2). Thus, the fact that the peak ratio after warming to 74 K differs from that deposited at 15 K and warmed to 74 K is a result of a concentration effect.

At all temperatures the 2.380/2.325 µm peak area ratio for an H$_2$O/CH$_4$ = 20 mixture is less than one. The longer wavelength peak has less area at all concentrations at 15 K, even for pure CH$_4$. The reverse (i.e., a 2.380/2.325 µm peak area ratio greater than one) was reported for pure solid CH$_4$ at 21 K (Quirico and Schmitt, 1997; Table III). However, this is not necessarily inconsistent, since our samples were vapor deposited as a frost at 15 K, whereas theirs were prepared by cool-down of a sample in a closed cell. These very different modes of sample preparation are known to sometimes display spectral differences (see Section 2).

Overall, the peak positions, widths, and relative areas are all temperature sensitive but reversible, despite the fact that these same parameters change irreversibly for the H$_2$O into which the CH$_4$ is frozen.

### 4. Discussion

We have seen that the positions, profiles, and relative areas of CH$_4$ near-IR absorptions in H$_2$O differ slightly but significantly from those of pure CH$_4$. That the near-IR absorptions of CH$_4$ in H$_2$O differ, but not radically, from those of pure CH$_4$ is perhaps not surprising given that CH$_4$ is a simple hydrocarbon that does not hydrogen bond with H$_2$O. Thus, while CH$_4$ (and thus its spectrum) could not but be affected somewhat by the ‘matrix’ into which it is frozen, there are no dramatic changes of the type that one sees for CO$_2$ (Bernstein et al., 2005) or molecules that hydrogen bond, such as NH$_3$ (Schmitt et al., 1998). Nevertheless, it is to be hoped that the combined systematic changes of positions, widths, and relative peak heights recorded here will help observers ascertain whether CH$_4$ is pure or intimately mixed with H$_2$O on the surfaces of icy bodies, like Quaoar. Based on the high H$_2$O/CH$_4$ ratios in comets (Gibb et al., 2003) one might naively predict the highest dilution mixture to be representative of what would be observed on an outer Solar System object. However, the recently acquired spectra of Kuiper Belt Objects 2003 UB$_{313}$ (Trujillo et al., 2005; Brown et al., 2005) and FY9 (Barkume et al., 2005) were reported to be more consistent with a CH$_4$-rich H$_2$O-poor surface.

The differences in positions of these peaks in the spectrum of pure CH$_4$ vs CH$_4$ in solid H$_2$O are reminiscent of what was seen...
previously in comparisons of pure CH₄ with CH₄ in solid N₂ (Quirico and Schmitt, 1997). In that case the central positions of the (ν₃ + ν₄) and (ν₁ + ν₄) combination modes (at 2.380 and 2.325 µm) of CH₄ in N₂ were, like those of CH₄ in H₂O, shortward of their positions in pure CH₄ (Quirico and Schmitt, 1997; Fig. 7 and Table XI). Thus, the central positions of 2.380 and 2.325 µm peaks of CH₄ in N₂ are closer that of CH₄ in H₂O, shortward of to that of pure CH₄. However, out of these three cases the widths are greatest for CH₄ in H₂O, so one should be able to distinguish based on peak profiles.

We have observed the 2.380 and 2.325 µm peaks of CH₄ to shift to higher frequency and increasing width with increasing temperature. These are the same trends that were observed for pure methane (Grundy et al., 2002). We have also noted that ices vapor deposited at 74 K have peak positions and widths equivalent to those deposited at 15 K and then subsequently warmed. These changes with temperature are reversible, despite the fact the phase changes of the H₂O (into which the CH₄ is frozen) are irreversible. This is quite different from the irreversible changes in the spectra of CH₃OH in H₂O (unpublished results), perhaps because CH₃OH forms hydrogen bonds with H₂O, whereas CH₄ does not.

The relative peak areas of the 2.380 and 2.325 µm peaks of CH₄ change with concentration and temperature. For most of our ices the area of the latter absorption (2.325 µm, 4300 cm⁻¹) exceeds the former (2.380 µm, 4200 cm⁻¹)—even for pure CH₄—whereas the opposite was observed for pure CH₄ by Quirico and Schmitt (1997). Since their ices were formed at elevated temperature by cooling down a closed cell, and ours were vapor deposited at 15 K, we think that the peak ratio differences between experiments is caused by our very different experimental methods (see Section 2.1). In our most dilute ice deposited at 15 K (H₂O/CH₄ = 87), we note that the relative peak areas (and heights) differ significantly from those of pure CH₄ (compare top and bottom traces in Fig. 2).

That the broad peaks of CH₄ in H₂O are still observed at 150 K in the lab reminds us that volatiles such as CH₄ will persist in solid H₂O to much higher temperatures than they would as pure solids. Thus it is possible that an object dominated by water ice might experience a transient heating event that would cause the H₂O to crystallize, and yet CH₄ would remain. Subsequent cooling would leave in a surface with signatures of crystalline H₂O, but CH₄ absorptions with positions, profiles and relative proportions indicative of the final lower temperature (see Figs. 3–6).

The areas of the methane peaks are observed to diminish with increasing temperature. Some of this loss of intensity on warming must be the result of sublimation of CH₄ from the H₂O/CH₄ (≈ 20) mixture because the features never entirely recover the original intensity they possessed before heating (see Fig. 2). However, sublimation can account for only part of the effect, because after re-cooling the peaks recover some of the lost area, but the experimental design does not allow re-condensation of CH₄. Thus, there must be a reversible decrease in intrinsic per-molecule intensity of these CH₄ peaks on warming that could result in an underestimate (of up to a factor of two) in the amount of CH₄ present.

Another interesting feature observed in our H₂O/CH₄ mixtures is the peak at 1.89 µm (∼5300 cm⁻¹) seen in Fig. 1, which may be indicative of amorphous H₂O since it diminishes on warming (see Fig. 3 in Schmitt et al., 1998). We conjecture, based on its position, that this peak may be an overtone combination of two H₂O absorptions, the ∼6.3 µm (∼1600 cm⁻¹) bending mode and the 2.74 µm (3650 cm⁻¹) dangling OH feature, the latter of which is not visible in the figures in this paper, but has been presented elsewhere (Rowland et al., 1991; Bernstein et al., 2005).

5. Summary

1. We have presented the first near-IR spectra of H₂O/CH₄ solid mixtures.
2. The absorptions of CH₄ in H₂O are broader and shifted to higher frequency compared to those of pure solid CH₄ at the same temperature.
3. The absorptions of CH₄ in H₂O become broader, shift to higher frequency, and display changes in relative and absolute intensity with increasing temperature from 15 to 150 K. These changes are reversible on re-cooling, despite the fact the phase changes of the H₂O (into which the CH₄ is frozen) are irreversible.
4. The positions and profiles of peaks vapor deposited at 74 K are equivalent to those deposited at 15 K and then subsequently warmed, but the relative intensities are significantly different because of concentration effects.

Acknowledgments

This work was supported by NASA’s Planetary Geology and Geophysics program (NRA-02-OSS-01-PGG). The authors thank Dr. L.J. Allamandola for useful comments and guidance, and the expert technical and experimental support of Robert Walker.

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