Near-infrared spectra of laboratory H$_2$O–CH$_4$ ice mixtures

Max P. Bernstein *, Dale P. Cruikshank, Scott A. Sandford

NASA Ames Research Center, MS 245-6, Moffett Field, CA 94035, USA

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 CH$_4$ and H$_2$O/CH$_4$ = 87, 20, and 3 solid mixtures at temperatures from 15 to 150 K. We compare and contrast the absorptions of CH$_4$ in solid H$_2$O with those of pure CH$_4$. Changes in selected peak positions, profiles, and relative strength with temperature are presented, and absolute strengths for absorptions of CH$_4$ in solid H$_2$O are estimated. Using the two largest ($\nu_3 + \nu_4$) and ($\nu_1 + \nu_4$) near-IR absorptions of CH$_4$ at 2.324 and 2.377 µm (4303 and 4207 cm$^{-1}$), respectively, as examples, we show that peaks of CH$_4$ in solid H$_2$O are at slightly shorter wavelength (higher frequency) and broader than those of pure solid CH$_4$. 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 H$_2$O are irreversible. It is to be hoped that these observations of changes in the positions, profiles, and relative intensities of CH$_4$ absorptions with concentration and temperature will be of use in understanding spectra of icy outer Solar System bodies.

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

1. Introduction

Infrared (IR) spectra have demonstrated that solid CH$_4$ 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 N$_2$ 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 UB$_{313}$ (Trujillo et al., 2005; Brown et al., 2005), and FY9 (Barkume et al., 2005), and CH$_4$ is known to be present in number of comets (Gibb et al., 2003).

Since H$_2$O is nearly ubiquitous in the outer Solar System (Roush, 2001) CH$_4$ on icy planetesimals is likely to come into contact with H$_2$O, potentially changing its spectral properties. Since mathematical addition of spectra of pure materials is not equivalent to the spectra of actual mixtures, fitting CH$_4$ profiles in spectra of outer Solar System bodies will require lab spectra of solid CH$_4$ mixed at a molecular level with H$_2$O at relevant temperatures.

Near-IR spectra of CH$_4$ as a pure solid and mixed in N$_2$ 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 CH$_4$ were published recently (Gerakines et al., 2005), and real and imaginary indices of refraction ($n_s$ and $k_s$) have been determined for both pure methane (Khare et al., 1989; Pearl et al., 1991) and pure H$_2$O, 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 CH$_4$ intimately mixed with solid H$_2$O, as it is likely it will be found on some icy bodies in the outer Solar System. Since an interaction with H$_2$O on a molecular level has been shown to cause significant changes in the position and profile of CH$_4$ absorptions in the mid-IR (e.g., Hudgins et al., 1993), the presence of H$_2$O 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 H$_2$O–CH$_4$ 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 H$_2$O 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 CH$_4$ 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 H$_2$O 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 H$_2$O 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 $\sim 10^{-5}$ 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 H$_2$O/CH$_4$ = 87, 20, and 3 mixtures, and of pure CH$_4$.

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 CH$_4$ (a lower H$_2$O/CH$_4$ 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 H$_2$O/CH$_4$ = 20 gas mixture that was vapor deposited onto the same substrate at 74 K (after a delay as described above) has a composition that is similar but not identical to the gas phase in the bulb. 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 in both the mid- and near-infrared.

The mid-IR spectra (i.e., Fig. 1) were measured on a Bio-

rad Excalibur FTS 3000 spectrometer with ambient DTGS and LN$_2$ 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 $\sim 10$ µm thick. H$_2$O 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 CH$_4$ in H$_2$O, mixed at a molecular level. Pure H$_2$O deposited under these conditions is in its high density amorphous form when deposited at 15 K, and after warming the H$_2$O 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 H$_2$O in these mixtures but our IR spectra of H$_2$O/CH$_4$ mixtures are consistent with previous observations of phases of pure H$_2$O, so the results described below probably include near-IR spectra of CH$_4$ in various amorphous and crystalline phases of H$_2$O 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 peri-or signal to noise spectra for pure ices, there are some cases where the measurement of ices 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 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 2.326 µm (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 cm² 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 cm² 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,

<table>
<thead>
<tr>
<th>Position</th>
<th>FWHM</th>
<th>Area²</th>
<th>Position</th>
<th>FWHM</th>
<th>Area²</th>
<th>Position</th>
<th>FWHM</th>
<th>Area²</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O/CH₄ = 87</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O/CH₄ = 20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O/CH₄ = 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure CH₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1

Peak positions², widths², and areas² for CH₄ in solid H₂O at 15 K.

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

b 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 cm² per molecule. See Section 2.2 for details.
5100, 3250, 2200, 1600, and 750 cm\(^{-1}\)) are typical of those observed previously for pure amorphous solid H\(_2\)O (Hudgins et al., 1993; Gerakines et al., 2005). Solid H\(_2\)O 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 CH\(_4\). The mid-IR absorptions of CH\(_4\) in H\(_2\)O have been published previously (Hudgins et al., 1993) but to our knowledge near-IR spectra of H\(_2\)O–CH\(_4\) mixtures have not. In Table 1 we summarize the CH\(_4\) absorptions we have observed in frosts of vapor deposited pure CH\(_4\), and three mixtures (H\(_2\)O/CH\(_4\) = 87, 20, and 3) at 15 K. In general, the absorptions of CH\(_4\) diluted in H\(_2\)O are broader and appear at slightly shorter wavelength than in the spectrum of pure CH\(_4\). This, and other observations, will be exemplified in subsequent figures using the two strongest near-IR absorptions of CH\(_4\), the (\(\nu_3 + \nu_4\)) and (\(\nu_1 + \nu_4\)) 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 H\(_2\)O/CH\(_4\) ratio. This is demonstrated in Fig. 2, where the 2.3–2.4 µm (4350–4150 cm\(^{-1}\)) IR spectrum of pure CH\(_4\) is plotted with those of the three H\(_2\)O/CH\(_4\) mixtures. The effect is most apparent for the H\(_2\)O/CH\(_4\) = 87 mixture (top trace, Fig. 2), where the central positions of these two peaks fall short of those in pure CH\(_4\) (lower trace, marked by hatched lines). The (\(\nu_1 + \nu_4\)) and (\(\nu_1 + \nu_4\)) absorptions of CH\(_4\) in the H\(_2\)O/CH\(_4\) = 87 mixture are shifted by 1.6 \times 10^{-3} and 2.3 \times 10^{-3} µm (3 and 4 cm\(^{-1}\)), respectively, from those in pure solid CH\(_4\) under identical conditions.

In addition to these small shifts in position, these two absorptions in the H\(_2\)O/CH\(_4\) = 87 mixture are ∼3 and 1.5 times broader than those in pure solid CH\(_4\) at the same temperature. As a result, the shoulders evident on the sides of the (\(\nu_3 + \nu_4\)) and (\(\nu_1 + \nu_4\)) absorptions of pure solid CH\(_4\) are obscured in H\(_2\)O/CH\(_4\) mixtures (compare lower and upper spectra in Fig. 2).

The positions, profiles, and relative intensities of CH\(_4\) absorptions in an H\(_2\)O/CH\(_4\) mixture depend on temperature as well as concentration. The two strong CH\(_4\) 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 CH\(_4\) peaks behave in a similar fashion, e.g., the 2\(\nu_3\) absorption shifts from 1.671 to 1.686 µm (5985 to 5994 cm\(^{-1}\)) and the (\(\nu_2 + \nu_3 + \nu_4\)) 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 CH\(_4\). Spectra have been offset for clarity.

Fig. 3. The 2.3–2.4 µm (4360–4150 cm\(^{-1}\)) IR spectra of an H\(_2\)O/CH\(_4\) = 20 ice mixture at 15 K (top), during warming up to 150 K (middle), and re-cooling back to 30 K (bottom). The temperature-dependent shifts in the position, width, and relative intensity of CH\(_4\) absorptions are reversible on re-cooling (see Figs. 4–6), despite the fact that the phase changes of the water ice are irreversible. The absolute intensity never entirely recovers, presumably due to sublimation of CH\(_4\). 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
position. 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 H₂O/CH₄ = 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 H₂O/CH₄ = 20 ice is warmed to 74 K. Vapor deposition of an H₂O/CH₄ = 20 mixture at 74 K gave a H₂O/CH₄ = 200 ice, ten times more dilute because the CH₄ 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 H₂O/CH₄ = 20 mixture is less than one. The longer wavelength peak has less area at all concentrations at 15 K, even for pure CH₄. The reverse (i.e., a 2.380/2.325 μm peak area ratio greater than one) was reported for pure solid CH₄ 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 H₂O into which the CH₄ is frozen.

4. Discussion

We have seen that the positions, profiles, and relative areas of CH₄ near-IR absorptions in H₂O differ slightly but significantly from those of pure CH₄. That the near-IR absorptions of CH₄ in H₂O differ, but not radically, from those of pure CH₄ is perhaps not surprising given that CH₄ is a simple hydrocarbon that does not hydrogen bond with H₂O. Thus, while CH₄ (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 CO₂ (Bernstein et al., 2005) or molecules that hydrogen bond, such as NH₃ (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 CH₄ is pure or intimately mixed with H₂O on the surfaces of icy bodies, like Quaoar. Based on the high H₂O/CH₄ 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 UB₃₁₃ (Trujillo et al., 2005; Brown et al., 2005) and FY9 (Barkume et al., 2005) were reported to be more consistent with a CH₄-rich H₂O-poor surface.

The differences in positions of these peaks in the spectrum of pure CH₄ vs CH₄ in solid H₂O is reminiscent of what was seen
previously in comparisons of pure CH$_4$ with CH$_4$ in solid N$_2$ (Quirico and Schmitt, 1997). In that case the central positions of the ($\nu_3 + \nu_4$) and ($\nu_1 + \nu_4$) combination modes (at 2.380 and 2.325 $\mu$m) of CH$_4$ in N$_2$ were, like those of CH$_4$ in H$_2$O, shortward of their positions in pure CH$_4$ (Quirico and Schmitt, 1997; Fig. 7 and Table XI). Thus, the central positions of 2.380 and 2.325 $\mu$m peaks of CH$_4$ in N$_2$ are closer that of CH$_4$ in H$_2$O than to that of pure CH$_4$. However, out of these three cases the widths are greatest for CH$_4$ in H$_2$O, so one should be able to distinguish based on peak profiles.

We have observed the 2.380 and 2.325 $\mu$m peaks of CH$_4$ 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 H$_2$O (into which the CH$_4$ is frozen) are irreversible. This is quite different from the irreversible changes in the spectra of CH$_3$OH in H$_2$O (unpublished results), perhaps because CH$_3$OH forms hydrogen bonds with H$_2$O, whereas CH$_4$ does not.

The relative peak areas of the 2.380 and 2.325 $\mu$m peaks of CH$_4$ change with concentration and temperature. For most of our ices the area of the latter absorption (2.325 $\mu$m, 4300 cm$^{-1}$) exceeds the former (2.380 $\mu$m, 4200 cm$^{-1}$)—even for pure CH$_4$—whereas the opposite was observed for pure CH$_4$ 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 (H$_2$O/CH$_4$ = 87), we note that the relative peak areas (and heights) differ significantly from those of pure CH$_4$ (compare top and bottom traces in Fig. 2).

That the broad peaks of CH$_4$ in H$_2$O are still observed at 150 K in the lab reminds us that volatiles such as CH$_4$ will persist in solid H$_2$O 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 H$_2$O to crystallize, and yet CH$_4$ would remain. Subsequent cooling would leave in a surface with signatures of crystalline H$_2$O, but CH$_4$ 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 CH$_4$ from the H$_2$O/CH$_4$ (= 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 CH$_4$. Thus, there must be a reversible decrease in intrinsic per-molecule intensity of these CH$_4$ peaks on warming that could result in an underestimate (of up to a factor of two) in the amount of CH$_4$ present.

Another interesting feature observed in our H$_2$O/CH$_4$ mixtures is the peak at 1.89 $\mu$m ($\sim$5300 cm$^{-1}$) seen in Fig. 1, which may be indicative of amorphous H$_2$O since it diminishes on warming (see Fig. 3 in Schmitt et al., 1998). We conjecture, based on its position, that this peak may be an overtone combination of two H$_2$O absorptions, the $\sim$6.3 $\mu$m ($\sim$1600 cm$^{-1}$) bending mode and the 2.74 $\mu$m (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 H$_2$O/CH$_4$ solid mixtures.
2. The absorptions of CH$_4$ in H$_2$O are broader and shifted to higher frequency compared to those of pure solid CH$_4$ at the same temperature.
3. The absorptions of CH$_4$ in H$_2$O 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 H$_2$O (into which the CH$_4$ 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-02-0SS-01-PGG). The authors thank Dr. L.J. Allamandola for useful comments and guidance, and the expert technical and experimental support of Robert Walker.

References


Grundy, W.M., Schmitt, B., Quirico, E., 2002. The temperature-dependent spectrum of methane ice I between 0.7 and 5 µm and opportunities for near-infrared remote thermometry. Icarus 155, 486–496.


