SPECTROSCOPIC EFFECTS IN CH₄/H₂O ICES

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ABSTRACT

Recent observations of CH₄ in different astrophysical objects encourage laboratory research on methane/water ice mixtures. An IR spectroscopy laboratory investigation is presented on these systems. Co-deposited samples are formed by vapor deposition of CH₄ and H₂O on a cold substrate, in a wide range of stoichiometries, from very diluted mixtures to CH₄/H₂O = 2.5 values. Samples are prepared at 14 K and at 40 K, and their temperature behavior is studied when they are warmed up to 60 K. The spectroscopic analysis is centered on the methane features, and also on the water dangling bonds (DBs) that appear in the spectra of the mixtures. The IR forbidden ν_1 band shows up in the spectrum (3.44 μm), indicating some form of distorted methane. The combination bands $\nu_3 + \nu_4$ and $\nu_1 + \nu_4$ are seen at 2.32 and 2.38 μm , and the $\nu_2 + \nu_3$ band weakly at 2.21 μm . Whereas ν_3 is not shifted in spectra of mixed samples, the wavenumber peak of ν_4 and its combination bands vary in a 6 cm^{-1} range, providing a possible estimation for the relative methane concentration in the sample. Bands in the spectra of mixtures are always broader than their counterparts in pure CH₄ ice. The intensity of ν_4 appears to increase in mixed samples with respect to the pure solid. Raising the temperature of the ices up to 60 K liberates part of the methane, but a fraction is retained with a maximum value of $\sim 7\% \pm 2\%$. This limit may provide information on the temperature properties of astrophysical objects. The different spectral characteristics of water DBs with increasing methane proportion in mixed samples can also furnish information to estimate the stoichiometry of the mixture.

Key words: infrared: general – ISM: lines and bands – Kuiper Belt – methods: laboratory – molecular data

Online-only material: color figure

1. INTRODUCTION

Methane (CH₄) is one of the key species in astrophysical media, where it plays an important role in processes leading to the formation of complex organic molecules (Dartois et al. 2005). Methane ice has been detected mostly toward high-mass sources (Boogert et al. 1996), but new evidence from the *Spitzer Space Telescope* has revealed the presence of CH₄ ice in low-mass star-forming regions and young stellar objects (YSOs; Öberg et al. 2008). CH₄ ices have also been identified in different outer solar system objects (i.e., Licandro et al. 2006; Schaller & Brown 2007) and in comets (i.e., Gibb et al. 2003). Gaseous methane is present in the atmospheres of several planets and satellites (Jupiter, Titan, Saturn, Uranus), as well as in Mars (Formisano et al. 2004), where the presence of clathrate hydrate deposits at the polar caps and in some areas of the planetary subsurface (Chastain & Chevrier 2007) has been suggested. Methane ice bands are an important feature in the spectra of outer solar system objects (Cruikshank et al. 1976; Brown et al. 2005; Licandro et al. 2006), where they have been considered a diagnostic tool for the physical and chemical properties of ice dwarf planets (Abernathy et al. 2009). These last authors have recently reported a blue shift in some of these bands in the near-IR spectra of the dwarf planet Eris, probably in correlation with increasing methane dilution in nitrogen, a more volatile species than CH₄, but whose presence in Eris has not been confirmed yet. The detection of methane on the Kuiper Belt Object (KBO; 50000) Quaoar (Schaller & Brown 2007), where water ice is dominant, is yet another example of the relevance of this system. These authors measured pure CH₄ bands at 2.32 and 2.38 μm , plus another feature at 2.2 μm , whose assignment to ammonia or methane may be under debate.

The procedure of formation of CH₄ on cool grains is not positively established. Hydrogenation of atomic C is most likely, in a similar process to the formation of H₂O or CH₃OH from O or CO precursors respectively, but direct freezing of gas phase molecules or photochemical reactions of CH₃OH (Gerakines et al. 1996) cannot be discarded. In most cases, methane ice has been detected in concurrence with water ice, which is always the largest abundance species. Depending on the line of sight, CH₄/H₂O concentrations range between 0.5% and 5%, reaching in a few particular cases values as high as 13% (Öberg et al. 2008). The structure, morphology, and thermal and photochemical processing of mixed methane/water ices constitute a very interesting and current concern topic.

Laboratory investigations have contributed to this field. Hudgins et al. (1993) measured optical constants and absorption intensities on mid-infrared spectra of pure CH₄ and a CH₄/H₂O = 0.05 mixture at different temperatures. Absolute absorption intensities (*A* values) for near-IR absorptions of these systems were reported. The *A* values of two different mixtures with CH₄/H₂O = 0.04 and 0.97 were also determined by Kerkhof et al. (1999). The evolution of the IR spectra of CH₄/H₂O ices under electron irradiation has confirmed the formation of methanol (Wada et al. 2006) and other species like C₂H₆ (Hodyss et al. 2009). Also, irradiation of pure CH₄ ice with an electron gun has revealed the formation of many species as, e.g., acetylene or ethane (Bennett et al. 2006). Boogert et al. (1997) measured the ν_4 peak position and width variations with mixture ratios and temperature. Bernstein et al. (2006) have measured changes in peak positions, profiles, and relative strength of IR bands with temperature and methane concentration in near-infrared spectra of laboratory CH₄/H₂O ice samples. These authors stress the importance of laboratory investigations to fully understand the effects on observed spectra of concentration and temperature of mixed samples. Horimoto et al. (2002) and Raut et al. (2007)

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have also studied CH₄/H₂O ice mixtures generated by CH₄ adsorption on water ice, aiming to obtain information about the morphology of some water ices.

We have undertaken a comprehensive study of all the IR bands of methane between 2 and 20 μm in CH₄/H₂O ice mixtures. This investigation was partly motivated by recent observations of methane ice toward a water ice-rich KBO as Quaoar (Schaller & Brown 2007) via its 2.21 μm IR band, or toward low-mass star-forming regions by the Spitzer IRS (Öberg et al. 2008) via the broadband at 7.7 μm . Possible modifications of methane bands due to the presence of water and its application to astrophysical observations were another encouragement to commence this work. This study may also help to interpret future IR observations, for example, those made by the infrared-optimized *James Webb Space Telescope*. Moreover, our results could be helpful in the discernment of the thermal processing or molecular environment of objects that contain CH₄/H₂O ice mixtures.

Using IR spectroscopy, we study samples of different concentrations in the 14 K–60 K temperature range. We have followed the variations with CH₄ concentration in band peaks and band-widths for the main IR bands of methane, and have detected the appearance of the IR-forbidden ν_1 band, with a small but not negligible intensity, which could be taken as an indication of a distorted CH₄ configuration inside the ice mixture. In addition, our spectra exhibit changes in the dangling bond (DB) bands of water. By thermal treating of the samples we arrive at interesting conclusions regarding the amount of CH₄ that can remain embedded above the sublimation temperature of methane, and discuss possible astrophysical consequences of our findings.

2. EXPERIMENTAL SECTION

The experimental set-up was described in detail before (Carrasco et al. 2002; Gálvez et al. 2008) and only a brief description will be given here, indicating the main changes introduced in the system. Solid samples of H₂O, CH₄, and of mixtures of the two species were deposited from the vapor phase on a cold substrate located in a high vacuum cylindrical chamber, evacuated by a turbomolecular pump. The liquid-N₂-based cooling system used in previous works has been replaced by a closed cycle helium cryostat. The substrate is mounted now on a cold finger with a heating foil for temperature control. The temperature of the substrate is measured with Si diodes and can be controlled, with 1 K accuracy, between 14 K and 300 K by means of a Lakeshore temperature control module. The background pressure in the chamber when the substrate is cold is around 10^{-8} mbar. The chamber is coupled to a Fourier transform infrared (FTIR) spectrometer Bruker Vertex70 through a purged pathway, with KBr windows for the incident and transmitted radiation, which is focused on exit onto a liquid-N₂ refrigerated MCT detector. In the transmission configuration used in this work a 1 mm thick Si wafer was used as a substrate. Spectra were recorded with a nominal resolution of 2 cm^{-1} (corresponding to ca. 0.5 cm mirror displacement in the interferometer), co-adding 500 scans for each spectrum. Controlled flows of H₂O (distilled water, three times freeze-pump-thawed) and CH₄ (99.95%, Air Liquide) were admitted through independent needle valves to backfill the chamber. The main chamber is coupled, by means of a regulation valve, to a differentially pumped chamber containing an Inficon, Transpector 2 quadrupole mass spectrometer (QMS). With this configuration the pressure in the QMS chamber can be maintained below 2×10^{-6} mbar for all the experimental

conditions of the present work. The absolute deposition pressure was determined from the growth rate of solid films of the pure species on the substrate (Maté et al. 2003). Film thickness values, needed for the calculation of the growth rate, were derived by simulating our transmission spectra with optical constants from the literature. This procedure is expected to be more accurate than the derivation based on the density and the integrated band strength. In any case the differences found between the two methods are not too large, ranging from 5% to 20% with most values between 10% and 15%. The larger discrepancies are found for the thinnest films. For water ice grown at 14 K, the spectra were reproduced with the data of Hudgins et al. (1993) at 10 K. A sticking coefficient of one and a density of 1.1 g cm^{-3} (Narten et al. 1976) were assumed at this temperature. For CH₄ at 14 K, a sticking coefficient of 1 (Sandford & Allamandola 1990) and a density of 0.47 g cm^{-3} (Satorre et al. 2008) were used. A mean value of the optical constants given by Hudgins et al. (1993) for pure CH₄ at 10 K and 20 K was used to simulate the IR spectra, because the CH₄ spectrum undergoes considerable changes in this temperature interval. The calibration of the QMS remained stable in the course of the present experiments as verified by periodic checks. The estimated error in the absolute pressure values is $\sim 10\%$. Deposition pressures ranged between approximately 2×10^{-7} and 5×10^{-5} mbar.

Films of mixed CH₄/H₂O ices were prepared by co-deposition: water and CH₄ were introduced into the chamber simultaneously, at the appropriate ratio, and deposited on the substrate at 14 K or 40 K. To monitor the temperature dependence the ices were subjected to a gradual warm-up (10 K min^{-1}), after deposition at 14 K, and spectra were recorded at 30 K and 60 K.

Column densities of water and CH₄ in the ice mixtures were calculated via the Lambert–Beer relation, using the integrated values of the infrared absorption bands and the corresponding integrated absorption coefficients, A . The bands chosen for this purpose were the ν_1 band of water around 3.1 μm (3200 cm^{-1}) and the ν_4 band of CH₄ at $\sim 7.7 \mu\text{m}$ (1300 cm^{-1}). Reference values were taken from Hudgins et al. (1993). For our samples at low temperatures we used $A = 8.085 \times 10^{-18} \text{ cm/molecule}$ for pure CH₄ ice (corrected assuming a CH₄ density of 0.47 g cm^{-3}), and $A = 1.7 \times 10^{-16} \text{ cm/molecule}$ for water. A small temperature correction (Hudgins et al. 1993) was applied in mixtures at 40 K and 60 K yielding $8.17 \times 10^{-18} \text{ cm/molecule}$ for CH₄, and $1.77 \times 10^{-16} \text{ cm/molecule}$ for water.

3. RESULTS AND DISCUSSION

Figure 1 shows the overall mid-IR spectrum ($5000\text{--}500 \text{ cm}^{-1}$, $2\text{--}20 \mu\text{m}$) of a 0.3:1 CH₄:H₂O ice mixture at 14 K. Spectra of pure H₂O and CH₄ at the same temperature have been included for comparison. Broad absorptions are due to water and sharp features are caused by CH₄. The insets show a magnified view of specific regions where interesting but weak changes over the spectra of pure compounds are observed. The top left spectra show the magnification of the DB bands of water at $\sim 3670 \text{ cm}^{-1}$. These bands are discussed below. On the top right window, the ν_1 band of CH₄, forbidden by symmetry in pure methane ice, emerges in the spectrum of the mixture at 2903 cm^{-1} , the same wavenumber where it is observed in Raman spectra. This interesting feature has recently been reported by Hodyss et al. (2009).

The temperature evolution of the IR spectra of a mixture generated at 14 K is presented in Figure 2. No significant

Figure 1. IR spectrum of (a) pure CH₄ ice, (b) pure H₂O ice, and (c) CH₄/H₂O = 0.3 co-deposited ice mixture, all at 14 K. Spectra (b) and (c) are offset for clarity. Absorbance values in all figures are given in absorbance units ($-\log_{10} I_{\text{sample}}/I_{\text{substrate}}$).

changes are observed in peak positions or widths of the diluted methane bands when the sample is heated to 30 K. However, when the temperature is raised to 60 K, most of the methane evaporates causing important spectral variations. Methane absorptions drastically diminish although the strongest bands are still detectable. The ν_3 band appears at 3011 cm^{-1} and ν_4 at 1302 cm^{-1} , i.e., with slight blueshifts from the pure methane spectrum (2 and 1 cm^{-1} , respectively). Amorphous water ice transforms from the high-density phase (HDA) to the low-density form (LDA) in the temperature range of 38–80 K (Jenniskens et al. 1995), causing a gradual intensity increase of all water bands. We have observed this growth when the temperature of the mixtures is raised to 60 K for all bands except for the DB band that vanishes instead. We will comment on the O–H DB bands below. In the rest of this work we are not concerned with the modifications in the main water bands due to the presence of methane.

3.1. Peak Positions, Widths, and Areas

In Figure 3, we represent our measured values (solid circles) for the peak maximum and band width (full width at half-maximum, FWHM) of the main CH₄ absorptions versus methane proportion in the mixture, for ices at 14 K. To elaborate this figure, broadbands due to water absorptions were subtracted using appropriate baselines. Typical 2σ uncertainties in peak wavenumber and FWHM were 1 cm^{-1} and about 2 cm^{-1} , respectively, related to the signal-to-noise ratio and the spectral resolution of our measurements. Table 1 collects a number of data interpolated from the graphs plotted in Figure 3 for five significant ratios, together with results for pure methane, and data of a mixture generated at 40 K. We summarize also in Table 1 the relative areas of the methane bands with respect to that of the ν_4 band. A 10% error is estimated for these magnitudes.

As can be appreciated in Figure 3, the stretching fundamentals of CH₄, ν_3 , and ν_1 do not suffer any appreciable frequency shifts with varying mixture concentration, whereas the bending mode ν_4 , and combination bands where this mode is involved, ($\nu_3 + \nu_4$, $\nu_1 + \nu_4$, and $\nu_2 + \nu_4$), can span a wavenumber region of up to 6 cm^{-1} . Interestingly, a blueshift from pure methane values, indicated by dotted lines, is produced in dilute mixtures,

Figure 2. Temperature evolution of the IR spectrum of a CH₄/H₂O = 0.3 co-deposited ice mixture generated at 14 K (a) and heated to 30 K (b) and 60 K (c). Spectra (b) and (c) are offset for clarity.

followed by a redshift when the concentration is raised. Due to its low intensity we detect the $\nu_2 + \nu_3$ band only in samples with 10^{17} molecules cm^{-2} of methane or more (see Figure 4). When observed, it is about 100 times weaker than the ν_4 band and it does not appreciably shift in frequency with varying mixture proportion. All bands in the composite samples are broader than in the pure methane spectrum.

The overall agreement with previous literature results is reasonable, better in peak positions than in width data. We have included in Figure 3 the results by Hudgins et al. (1993) on the ν_4 and ν_3 wavenumbers of a mixture generated at 10 K (open squares), those by Boogert et al. (1997) for the peak position and FWHM of ν_4 for samples of three different CH₄/H₂O proportions at 10 K (down-pointing triangles), data by Bernstein et al. (2006), who studied in detail the mid-IR region (up-pointing triangles), and the recent peak values by Hodyss et al. (2009; open circles). Note that in some cases there are appreciable discrepancies with previous literature works, especially in the FWHM values at low methane proportions. Most previous measurements correspond to samples with low methane proportion, while our results extend the range of values up to a CH₄/H₂O ratio of 2.5.

There are fairly large variations in the values of the relative intensities of the observed bands. Our results are listed in the last column of Table 1, taking ν_4 as reference. Hudgins et al. (1993) measured 1.5 for the ν_3/ν_4 band intensity ratio in pure CH₄, a value which substantially drops to 0.76 for a CH₄/H₂O = 0.05 sample, that could be a consequence of the large increase in the intensity of ν_4 that they register in the mixture, with $A(\text{mixture})/A(\text{pure}) = 1.237$ for this band. Inaccuracies in the determination of the integrated intensity of the ν_3 band of CH₄ due to local baseline problems associated with the proximity of the $3\text{ }\mu\text{m}$ band of water may also affect the ratio. The result of Hudgins contradicts that of Kerkhof et al. (1999), who measured an almost unchanged ν_4 intensity in their samples, with $A(\text{mixture})/A(\text{pure}) = 1.05$, for CH₄/H₂O = 0.042. Our values do not help solving this discrepancy. We obtain a ν_3/ν_4 intensity ratio of 1.39 for pure methane ice, close to Hudgins et al. (1.5), and on the other hand, a 1.1 ratio for our sample with CH₄/H₂O = 0.05, which implies a modest change in the intensity of ν_4 , more in agreement with the results of Kerkhof

Figure 3. Peak positions and FWHM of methane bands in 14 K co-deposited mixtures as a function of methane proportion in the solid. Dotted lines represent pure methane ice values. Solid circles: measurements of the present work; down-pointing triangles: data at 10 K from Boogert et al. (1997); up-pointing triangles: data at 15 K from Bernstein et al. (2006); open squares: data from Hudgins et al. (1993); open circles: data from Hodyss et al. (2009) at 20 K. Solid lines are curves fitted to the experimental data.

(A color version of this figure is available in the online journal.)

et al., and far from the value of Hudgins et al. (1993; 0.76). Bernstein et al. (2006) used yet another magnitude to study the intensity characteristics. They quoted an intensity ratio $v_3/(v_3 + v_4)$ of 18 for pure CH_4 , with no significant variation in mixtures. On the other hand, we measure 20 for this quantity in pure methane, a value that decreases with increasing CH_4 dilution, reaching 14 for $\text{CH}_4/\text{H}_2\text{O} = 0.02$ samples.

No intensity changes with mixture composition were appreciated between the three combination bands presented in Figure 4. We estimated the values of 0.14 and 0.61 for the $(v_2 + v_3)/(v_3 + v_4)$ and $(v_1 + v_4)/(v_3 + v_4)$ intensity ratios, respectively. Bernstein et al. (2006) measured for pure methane ice values of 0.12 and 0.56, respectively and Grundy et al. (2002) 0.15 and 1.93, respectively. Those combination bands were used by Schaller & Brown (2007) to prove the presence of methane on the KBO (50000) Quaoar (see Figure 2(A) on that paper). To simulate the reflectance spectrum in that region they took the data from Grundy et al. (2002). It is worth mentioning that the $2.21 \mu\text{m}$ band is very weak in all laboratory IR absorption spectra, and it appears enhanced in the modeled reflectance spectra

Figure 4. IR spectrum of (a) pure CH_4 ice; (b) a $\text{CH}_4/\text{H}_2\text{O} = 2.6$ co-deposited ice mixture, all at 14 K. Spectrum (b) is offset for clarity.

Table 1
Spectral Peak Positions, Widths, and Band Areas for CH₄/H₂O
Mixtures at 14 K

Peak Position		FWHM (cm ⁻¹)	Mode	Relative Area ^a
(cm ⁻¹)	(μm)			
Pure CH ₄				
4528.3	2.2083	8.4	ν ₂ +ν ₃	0.010
4300.8	2.3251	5.5	ν ₃ +ν ₄	0.069
4202.9	2.3793	8.7	ν ₁ +ν ₄	0.042
3009	3.3234	4.5	ν ₃	1.392
2815.5	3.5518	7.3	ν ₂ +ν ₄	0.035
1301.1	7.6858	7.1	ν ₄	1
CH ₄ /H ₂ O = 0.02				
4302.5	2.3242	16.7	ν ₃ +ν ₄	0.073
4205.2	2.3780	15.7	ν ₁ +ν ₄	0.039
3008.9	3.3235	14.3	ν ₃	1.05
2903.1	3.4446	9.9	ν ₁	0.03
2818.3	3.5482	11.7	ν ₂ +ν ₄	0.078
1303.5	7.6717	11.6	ν ₄	1
CH ₄ /H ₂ O = 0.1				
4301.9	2.3246	16.3	ν ₃ +ν ₄	0.073
4204.7	2.3783	15.6	ν ₁ +ν ₄	0.039
3008.9	3.3235	14.1	ν ₃	1.1
2903.1	3.4446	9.6	ν ₁	0.032
2817.2	3.5496	11.6	ν ₂ +ν ₄	0.051
1302	7.6805	11.6	ν ₄	1
CH ₄ /H ₂ O = 0.25				
4301.1	2.3250	15.4	ν ₃ +ν ₄	0.073
4204	2.3787	15.3	ν ₁ +ν ₄	0.04
3008.9	3.3235	13.8	ν ₃	1.18
2903.1	3.4446	9.2	ν ₁	0.034
2816.1	3.5510	11.3	ν ₂ +ν ₄	0.043
1300.4	7.6899	11.5	ν ₄	1
CH ₄ /H ₂ O = 1				
4529.5	2.2077	14.7	ν ₂ +ν ₃	0.010
4299.4	2.3259	13	ν ₃ +ν ₄	0.07
4202.1	2.3798	14.1	ν ₁ +ν ₄	0.041
3008.9	3.3235	12.7	ν ₃	1.3
2903.2	3.4445	8	ν ₁	0.025
2814.5	3.5530	10.6	ν ₂ +ν ₄	0.039
1298.3	7.7024	11	ν ₄	1
CH ₄ /H ₂ O = 2.5				
4528.4	2.2083	14.3	ν ₂ +ν ₃	0.009
4298.8	2.3262	11.9	ν ₃ +ν ₄	0.06
4201.3	2.3802	12.8	ν ₁ +ν ₄	0.039
3008.9	3.3235	11.7	ν ₃	1.2
2903.4	3.4442	7.3	ν ₁	0.018
2813.7	3.5540	10	ν ₂ +ν ₄	0.037
1298	7.7042	10.2	ν ₄	1
T = 40 K				
CH ₄ /H ₂ O = 0.25				
4300.7	2.3252	17.6	ν ₃ +ν ₄	0.071
4203.5	2.3790	14.8	ν ₁ +ν ₄	0.041
3009.1	3.3233	14.7	ν ₃	1.204
2903.2	3.4445	8.2	ν ₁	0.03
2816.2	3.5509	13.5	ν ₂ +ν ₄	0.032
1299.9	7.6929	9.5	ν ₄	1

Notes.

^a Relative areas, normalized to the ν₄ band of CH₄. Estimated uncertainty of 10% for these values.

(compare Figure 4 of the present work with Figure 2(A) of Schaller & Brown 2007).

It can be concluded that the use of relative intensities to infer ice characteristics in astrophysical measurements cannot be encouraged until the discrepancies discussed in the previous paragraphs are explained.

Figure 5. Dangling bond double peak as a function of methane proportion. Spectra for increasing CH₄ ratio are offset for clarity.

Finally, our results indicate that the integrated areas of these IR bands do not depend strongly on the temperature, as we have found no variations upon heating the samples from 14 to 30 K, or even when the mixtures are generated at 40 K, as collected in the bottom section of Table 1.

3.2. Water Dangling Bond Spectra

Two spectral features are usually attributed to DBs in amorphous water ice (ASW) and ice mixtures with other compounds, at 3720 cm⁻¹ (DB1) and 3696 cm⁻¹ (DB2). In our experiments these bands are very weak for ASW either at 14 or 40 K, but grow in intensity and suffer some alterations in mixed water–methane samples. We present in Figure 5 a study of this spectral region for mixtures with increasing CH₄ ratio, prepared at 14 K. For the lowest CH₄ proportion the DB1 and DB2 bands only become slightly stronger than in ASW. Note the factor of 3 for the corresponding intensities in the lower graphs of the figure. However, for a CH₄/H₂O ratio of 0.08, which could be attained in some astrophysical objects, new features appear at 3669 and 3661 cm⁻¹ (called DB1' and DB2', respectively), still weak but observable. For increasing CH₄ relative concentrations, these two peaks grow in intensity and tend to merge into one stronger, single band at ~ 3680 cm⁻¹. A similar behavior is observed for samples prepared at 40 K (not shown here).

The redshift of the DB double peak observed in CH₄/H₂O ice mixtures with respect to pure water ice has been observed before by Raut et al. (2007) in water ices generated at 40 K and subsequently exposed to methane. It has been interpreted as a result of an interaction of the free water molecules in the porous structure with methane. A similar behavior with DB low-frequency shifts and almost no intensity change with respect to pure water ice were observed for ASW exposed to H₂ (Hixson et al. 1992) or CO₂ (Kumi et al. 2006). However, in co-deposited samples as those studied in this work, the morphology of the mixture generated could be very different, allowing for a higher proportion of methane which may stay trapped inside the ASW. As far as we know there are no other literature works where the strength of the DB bands is studied in co-deposited samples of water and other species. We currently analyze the behavior of the DB bands in both sequential and co-deposited CH₄/H₂O ice mixtures, and the results will be discussed in a future publication.

Figure 6. CH₄/H₂O number of molecules ratio in co-deposited ice mixtures vs. partial pressure ratio of the gas admitted in the chamber. Solid circles: samples deposited at 14 K; open circles: deposition at 40 K. A dashed line of unity slope has also been drawn for reference.

Table 2

DB Peak Positions and Relative Area for CH₄/H₂O Mixtures at 14 K

CH ₄ /H ₂ O	Peak Position		Peak Position		10 ³ Area ^a
	(cm ⁻¹)	(μm)	(cm ⁻¹)	(μm)	
0.02	3721.5	2.6871	3697.0	2.7049	0.02
0.08	3696.1	2.7056	3664.4	2.7290	0.04
0.27	3684.2	2.7143	3664.6	2.7288	0.4
0.82	3683.8	2.7146	3672.0	2.7233	1.3
1.69	3682.9	2.7153	3675.0	2.7211	2.2
2.61	3682.7	2.7154	3675.5	2.7207	26.9

Note.

^a Integrated area of the DB bands relative to the ν₁ band of pure water.

Table 2 collects the numerical values of the spectral data represented in Figure 5. Although the DB bands are weak in general, if methane is the major species present in the ice mixture, such values could provide a rough quantification of the CH₄/H₂O ratio.

3.3. Temperature Dependence of Methane Proportion in Ice

The composition of the co-deposited ice mixtures depends not only on the relative ratio of the gases admitted into the chamber, but also strongly on the deposition temperature. We have conducted experiments where the substrate was kept at 14 K and at 40 K. In Figure 6, the CH₄/H₂O number of molecules ratio in the ice is represented versus the partial pressure ratio of the incoming gases, for these two temperatures. The $n_{\text{CH}_4}/n_{\text{H}_2\text{O}}$ ratio is calculated as indicated in Section 2, i.e., based on measurements of spectral band intensities *A* and comparison to accepted reference values of the pure species. Ices vapor deposited at 14 K present a ratio closer to the one in the gas phase, as expected for a temperature where both species have a sticking factor of 1. However, a deviation of up to 30% from a linear slope is observed for high methane concentrations. If a sticking coefficient of 1 for both molecules is assumed, this 30% deviation must be related to changes in *A* with the stoichiometry of the mixture. A disparity of ~15% in the

Table 3

CH₄/H₂O Number of Molecules Ratio in the Ice after Warming at 60 K for Samples Deposited at 14 K and 40 K

$n_{\text{CH}_4}/n_{\text{H}_2\text{O}}$		$n_{\text{CH}_4}/n_{\text{H}_2\text{O}}$	
<i>T</i> = 14 K	<i>T</i> = 60 K	<i>T</i> = 40 K	<i>T</i> = 60 K
0.020	0.015	0.001	0.001
0.030	0.023	0.138	0.047
0.082	0.048	0.238	0.054
0.273	0.086	0.247	0.054
0.631	0.091	0.291	0.070
0.768	0.074	0.375	0.070
0.820	0.063	0.368	0.068
1.690	0.064		
2.608	0.060		

composition between estimations from gas partial pressures and spectroscopic measurements was found by Boogert et al. (1997) for dilute mixtures with CH₄/H₂O < 0.5. Kerkhof et al. (1999) confirmed the change in *A* through the direct measurement of the band intensity variation of ν₄ in a CH₄/H₂O = 0.97 mixture. A ratio, $A(\text{mixture})/A(\text{pure}) = 1.21$, was obtained by these authors.

In samples co-deposited at 40 K, the CH₄/H₂O ratio in the solid is around five times lower than the partial pressure ratio in the vapor used for its generation (see 40 K graph in Figure 6). This fact can be ascribed to the low sticking coefficient of methane at 40 K.

Thermal processing of the samples can provide interesting evidence for, e.g., ices in cometary nuclei. In our experiments, ices generated at 14 K and 40 K have been warmed at 10 K minute⁻¹ up to 60 K. We have found that, although this temperature is higher than the methane sublimation point, the samples retain a certain amount of CH₄. By using the same procedure as above, we have measured the CH₄/H₂O ratio in the ice sample warmed at 60 K, with the results shown in Table 3, where the initial composition of the gas phase at either 14 K or 40 K is also indicated. Interestingly, for initial mixtures with CH₄/H₂O > ~0.25 the amount of CH₄ in the solid at 60 K seems to reach a maximum value of ~7% (±2%) independently of the composition and deposition temperature of the gas phase. According to this, the methane concentration measured in an astrophysical object can provide in some cases direct information on its temperature: CH₄/H₂O ratios above 0.07 would indicate that the temperature of the system has never reached a value of 60 K or higher. On the other hand, observed ratios below this threshold of 0.07 do not convey information on the temperature of the object. The way that other constituents in the sample, or other effects such as, e.g., irradiation of the ices, could affect the methane concentration, is beyond the scope of this work.

Notesco et al. (1997) generated a CH₄:H₂O:C₂H₆ mixture at 50 K with a CH₄/H₂O ratio of 0.42 at 50 K that transforms to 0.039 at 60 K. The low-mass YSOs studied by Öberg et al. (2008) present an average methane abundance relative to solid H₂O of 5.8%. These results fall within the threshold value of our experiments. The closeness of the average value of methane on those YSOs to our 0.07 saturation value may be a coincidence, but it could also be interpreted as an indication of the history of those objects, which might have been formed at lower temperatures, containing a higher amount of methane, being warmed later at a temperature near 60 K, thereby retaining about the maximum amount of methane that water ice admits.

4. CONCLUSIONS

This paper presents an investigation on the spectroscopic properties of low-temperature ices formed by mixtures of CH₄ and H₂O. The study reports data on band peaks and band widths of the spectral features of the CH₄ spectrum in the mid-IR region, and their variation with the relative concentration of both species. The study deals also with the spectral signatures of water DBs. The analysis of the spectra reveals different composition of the ices and the gas mixtures from which they are generated. The main conclusions are the following:

1. Besides the asymmetric stretching and bending fundamentals ν_3 and ν_4 respectively, and the combination bands $\nu_3 + \nu_4$, $\nu_1 + \nu_4$, $\nu_2 + \nu_4$ and $\nu_2 + \nu_3$ normally observed in this frequency range, the dipole-forbidden ν_1 band appears with appreciable intensity at 2903 cm⁻¹ (3.44 μ m), indicating a distorted form of methane in the solid. This band reaches a relative intensity of 2%–3% with respect to ν_4 , probably in the present detection limit for spectra of astrophysical objects. The 2.21 μ m feature observed on the KBO (50000) Quaoar (Schaller & Brown 2007) is weak in our IR absorption spectra, but it appears to be enhanced in the reflectance model used by Schaller & Brown (2007).
2. The ν_3 fundamental is not shifted in the spectra of mixtures of different CH₄/H₂O ratios from its wavenumber value in for pure methane. However, the ν_4 band and all of its combination bands are altered from their values in pure methane ice, spanning a frequency range of several wavenumbers. The tendency is to decrease in frequency with increasing CH₄ concentration in the mixtures. Thus, the observed wavenumber for ν_4 could give information to estimate the methane fraction in the sample. The weak combination bands mentioned above convey the same information, and could be useful in cases where the spectral region around ν_4 is obscured by other spectral particularities.
3. All observed CH₄ bands are broadened in the spectra of the mixed samples, and the width decreases with rising CH₄ relative concentration. In dilute mixtures, the FWHM of the ν_3 and ν_4 bands is ~ 14 cm⁻¹ (~ 0.015 μ m and ~ 0.07 μ m, respectively), as compared to ~ 6 cm⁻¹ in pure methane. Our value agrees well with the ν_4 width measured by Boogert et al. (1996) in their spectra from deeply embedded protostars (0.063 μ m). Good accord is also found with the ν_3 width measured by Boogert et al. (2004) from a massive protostar (0.06 μ m). However, those values are considerably smaller than the ν_4 width reported by Öberg et al. (2008) from their spectra of low-mass YSOs (0.16 μ m). This discrepancy is most probably due to the much lower spectral resolution of the latter measurements and the possible blending of contributions from other species (SO₂) to the feature considered.
4. The relative ν_3/ν_4 band intensity measured from our spectra varies from 1.39 in pure methane to 1.1 in a CH₄/H₂O = 0.02 mixture at 14 K. At this temperature, the intensity of the ν_4 band may change up to 30% in mixed samples with high methane concentration with respect to its value in pure CH₄ ice. Our measurements, covering a broad range of mixing ratios, complement previous results of Boogert et al. (1997) and Kerkhof et al. (1999), 15% and 21% for stoichiometries of 0.5 and 1, respectively.
5. From our study of the temperature evolution of CH₄/H₂O ice mixtures generated at 14 K and 40 K and warmed up to

60 K, we conclude that in all cases, even for samples with a high initial methane proportion, the amount of methane retained in the ice at 60 K is never higher than a saturation value of $\sim 7\% \pm 2\%$. This limit may provide information on the temperature properties of astrophysical objects.

6. The dangling bond bands of water in ice mixtures evolve with increasing CH₄/H₂O ratios, from very weak and split features to a single stronger band. Again, this band, in spite of its weakness, can furnish information on the characteristics of the mixed sample.

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