

## INFRARED SPECTRA AND OPTICAL CONSTANTS OF ELUSIVE AMORPHOUS METHANE

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### ABSTRACT

New and accurate laboratory results are reported for amorphous methane ( $\text{CH}_4$ ) ice near 10 K for the study of the interstellar medium (ISM) and the outer solar system. Near- and mid-infrared (IR) data, including spectra, band strengths, absorption coefficients, and optical constants, are presented for the first time for this seldom-studied amorphous solid. The apparent IR band strength near  $1300\text{ cm}^{-1}$  ( $7.69\ \mu\text{m}$ ) for amorphous  $\text{CH}_4$  is found to be about 33% higher than the value long used by IR astronomers to convert spectral observations of interstellar  $\text{CH}_4$  into  $\text{CH}_4$  abundances. Although  $\text{CH}_4$  is most likely to be found in an amorphous phase in the ISM, a comparison of results from various laboratory groups shows that the earlier  $\text{CH}_4$  band strength at  $1300\text{ cm}^{-1}$  ( $7.69\ \mu\text{m}$ ) was derived from IR spectra of ices that were either partially or entirely crystalline  $\text{CH}_4$ . Applications of the new amorphous- $\text{CH}_4$  results are discussed, and all optical constants are made available in electronic form.

*Key words:* astrochemistry – ISM: abundances – ISM: molecules

### 1. INTRODUCTION

At present we are engaged in an extensive program to record infrared (IR) reference spectra of solids at low temperatures with which to determine complex indices of refraction ( $n - ik$ ). Such results are needed for studies of both interstellar and planetary chemistry, mainly for determinations of abundances of ices in the outer solar system and the interstellar medium (ISM). To date we have examined the simplest members of the alkyne and alkene classes of hydrocarbons, acetylene and ethylene, and have found significant and unexpected problems with the literature on both molecules to the extent that our new work replaces much of the old (Hudson et al. 2014a, 2014b). Recently we have turned our attention to  $\text{CH}_4$ , methane, the simplest alkane, but here too we have encountered problems with the literature results and these have motivated this Letter.

Methane is one of the few molecules that form ices of interest to both interstellar and planetary astrochemists. It can, in principle, exist in three phases under vacuum or near-vacuum conditions. The high-temperature phase is a plastically crystalline solid with a degree of rotational disorder lacking in the low-temperature, more-ordered crystalline form, the reversible transition between the two being at 20.4 K (Clusius 1929). The third  $\text{CH}_4$  phase is an amorphous one formed by the slow condensation of methane from the gas phase at temperatures on the order of 20 K and lower. Although limited sets of optical constants for the two crystalline phases have been published (Pearl et al. 1991; Hudgins et al. 1993), we have not found optical constants for  $\text{CH}_4$  ices that are unequivocally amorphous. Further, we have discovered significant questions about the amorphous character of essentially all  $\text{CH}_4$ -ice samples whose spectra appear in the literature.

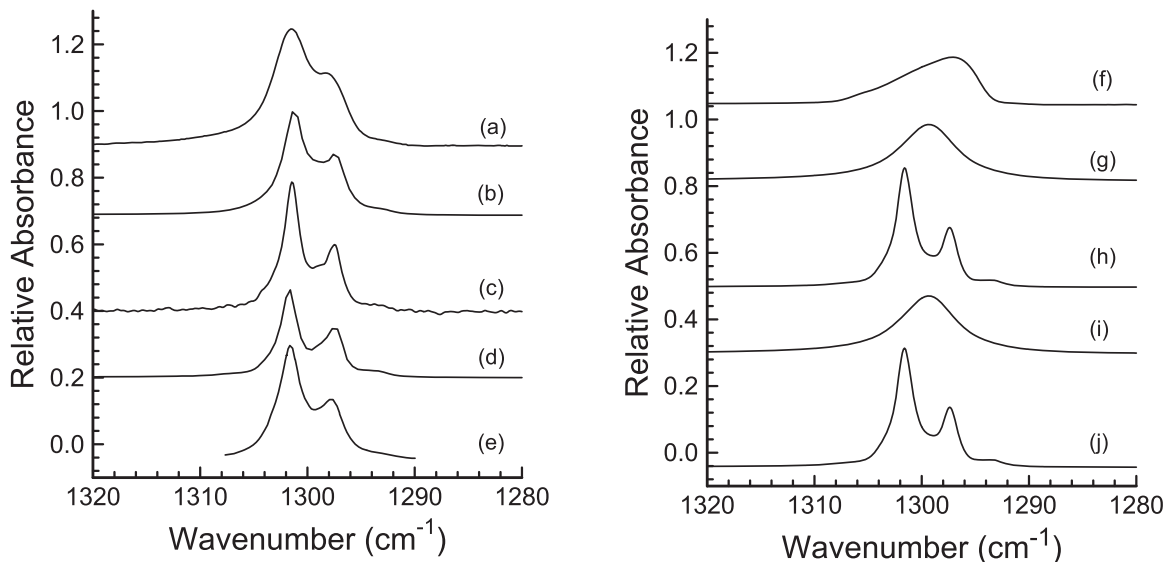
As an example of these difficulties, Figures 1(a)–(e) show the  $1300\text{ cm}^{-1}$  ( $\nu_4$ ) IR feature of  $\text{CH}_4$  deposited at  $\sim 15\text{ K}$  as published over about 20 years by five independent sets of researchers. The degree of reproducibility is reassuring as in each case the  $\nu_4$  absorption is seen to have two distinct components with about the same relative intensities. However, we have found (vide infra) that warming a  $\text{CH}_4$ -ice sample that possesses these same spectral characteristics causes the two

peaks to coalesce, and that recooling such ices to  $\sim 15\text{ K}$  then regenerates the original spectra of Figures 1(a)–(e), an unusual reversible behavior for amorphous organic compounds, but one in agreement with the behavior of methane’s two crystalline phases (Savitsky & Hornig 1962). We conclude that despite the reported temperatures of  $\text{CH}_4$  condensation, the spectra of Figures 1(a)–(e) are not for an amorphous ice, but for a crystalline  $\text{CH}_4$  sample formed on deposition.

Knowing the phase of a laboratory sample is important as many ices in the ISM and the outer solar system are expected to be amorphous, and so efforts to quantitatively analyze them for  $\text{CH}_4$  will be severely hindered without an appropriate laboratory reference spectrum and band strengths. Moreover, a proper, well-characterized set of IR features is critical for any accurate calculation of optical constants. This Letter addresses such problems by presenting IR spectra of amorphous  $\text{CH}_4$  along with associated band strengths, absorption coefficients, and optical constants, apparently the first for amorphous  $\text{CH}_4$  in the literature.

### 2. EXPERIMENTAL METHODS

Descriptions of our experimental setup, ice preparation method, and spectral measurements have been published, so only a summary is needed here. See, for example, Hudson & Moore (2004) and Moore et al. (2010). Briefly,  $\text{CH}_4$  (Matheson Research Grade) in a vacuum line was flowed through a controlled leak valve onto a pre-cooled (8–30 K) KBr substrate inside a stainless steel high-vacuum chamber ( $\sim 10^{-7}$  Torr). The sample gas was condensed at  $\sim 1.5 \times 10^{17}$  molecules  $\text{min}^{-1}$  to an ice thickness of 0.5–5  $\mu\text{m}$  as determined by a laser (670 nm) interference fringe-counting system. After deposition, transmission spectra ( $0.5\text{ cm}^{-1}$  resolution, 100 co-added scans) of the ice were recorded in situ with a Perkin-Elmer Spectrum GX Fourier-transform IR spectrometer equipped with a room-temperature DTGS detector. After the initial spectrum was recorded, the sample was warmed or cooled in increments of a few degrees with temperatures being measured (precision  $\sim 0.2\text{ K}$ ) with a silicon diode inserted into the metal frame holding the KBr substrate. Spectra were recorded to document any changes in band position, intensity,



**Figure 1.** Infrared spectra of the  $\nu_4$  band of  $\text{CH}_4$ . Left column:  $\text{CH}_4$  deposited at (a) 12.5 K, Mulas et al. (1998), (b) 10 K, Gerakines et al. (1996), (c) 15 K, Alsindi et al. (2003), (d) 10 K, Hudgins et al. (1993), and (e) 15 K, de Barros et al. (2011). Right column:  $\text{CH}_4$  deposited in the present work at (f)  $\sim 10$  K, (g) then warmed to 30 K and held there about 8 hr, (h) recooled to 10 K, (i) rewarmed to 30 K, and (j) recooled to 10 K.

and shape. Methane ices were studied at 8–40 K, and all samples rapidly sublimed at higher temperatures. The great majority of measurements were made in the 8–12 K range, and for simplicity we refer to these simply as at 10 K. As an extra check on our temperature calibration, we recorded IR spectra of crystalline  $\text{CD}_4$  at 10–30 K, and observed phase changes to occur at 22 and 27 K, as expected (Clusius et al. 1937; Kansal & Trikha 1994). Residual  $\text{H}_2\text{O}$  in the vacuum line and the  $\text{CH}_4$  source was the only contaminant detected, and could be seen in trace amounts ( $\leq 0.01$  absorbance units) in the 3700–3500 and 1600  $\text{cm}^{-1}$  regions of our spectra, far from the IR peaks of interest.

Methane’s IR spectra were recorded from 5000 to 400  $\text{cm}^{-1}$  (2.0–25  $\mu\text{m}$ ), with special attention being given to the molecule’s  $\nu_4$  region (1300  $\text{cm}^{-1}$ , 7.69  $\mu\text{m}$ ) and the near-IR features at 4600–4100  $\text{cm}^{-1}$  (2.17–2.44  $\mu\text{m}$ ). Apparent band strengths ( $A'$ ) and apparent absorption coefficients ( $\alpha'$ ) were determined from appropriate Beer’s law plots as described in Hudson et al. (2014a) and references therein.

In calculating ice thicknesses, absorption coefficients, and band strengths of amorphous  $\text{CH}_4$ , values of the ice density ( $\rho$ ) and a reference value of the refractive index ( $n$ ) were needed, both near 10 K. For the density we adopted  $\rho = 0.47 \text{ g cm}^{-3}$  (Satorre et al. 2008), which gives a number density of  $\rho_N = 1.77 \times 10^{22} \text{ molecules cm}^{-3}$ . Using the two-laser method of our previous work with hydrocarbons (Hudson et al. 2014a, 2014b) we measured  $n$  of amorphous  $\text{CH}_4$  five times at  $\sim 10$  K and got an average value of  $n = 1.28$  with a standard error of  $\pm 0.008$ . Our  $n$  is essentially identical to the average of the two values of Satorre et al. (2008, Figure 3) for a similar temperature and wavelength.

### 3. RESULTS

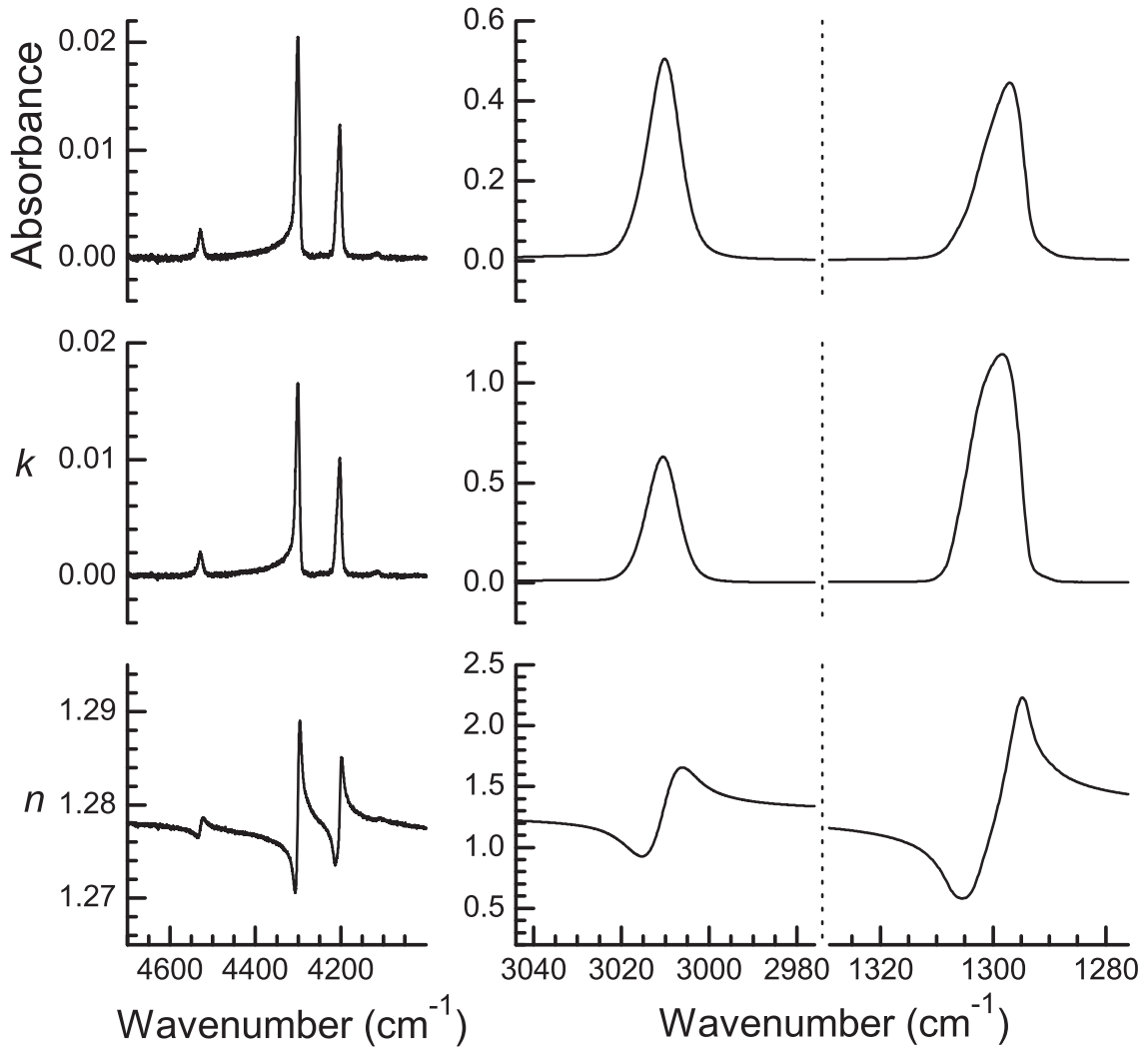
There are many similarities among the  $\text{CH}_4$  spectra in (a)–(e) of Figure 1, but in our hands a different result was obtained. Figure 1(f) is the IR spectrum of  $\text{CH}_4$  ice made in our laboratory near 10 K. On either warming such samples to  $\sim 30$  K or on depositing  $\text{CH}_4$  directly at  $\sim 30$  K, a sharp

symmetric peak as in Figure 1(g) was observed, which subsequent recoiling to 10 K changed into two well-resolved features of Figure 1(h) that matched those shown in Figures 1(a)–(e). The conversion between the single sharp feature near 30 K and the doublet near 10 K was completely reversible, as shown in Figures 1(g)–(j). Additional work showed that either depositing  $\text{CH}_4$  above  $\sim 20$  K and then cooling or depositing about 10 times faster at 10 K also produced the double-peaked absorption. Very slow coolings revealed that the transition to the double-peaked pattern consistently occurred at 20–21 K. Two confirmations of our results came through independent spectral measurements of  $\text{CH}_4$  deposited at 8.8 K on an aluminum substrate and in methane work by one of us on a similar experimental set-up in a different laboratory (Gerakines et al. 2005). We emphasize that the conversion from the spectrum of Figure 1(f) to that of Figure 1(g) was irreversible, as expected for an amorphous-to-crystalline phase change. Combining all of these results, we assign the spectrum of Figure 1(f) to amorphous  $\text{CH}_4$ . The spectra in Figures 1(g) and (i) are of phase-I crystalline  $\text{CH}_4$ , and traces in Figures 1(h) and (j) are for phase-II crystalline  $\text{CH}_4$ .

Figure 2(a) shows enlargements of three regions of the spectrum of amorphous  $\text{CH}_4$ , for a deposition at  $\sim 10$  K. We combined such spectra with a Kramers–Kronig routine to calculate the optical constants  $n$  and  $k$  of amorphous  $\text{CH}_4$ , which also are shown in Figure 2. Spectra and optical constants are available in electronic form on our group’s website (<http://science.gsfc.nasa.gov/691/cosmicice/constants.html>) for the 5000–400  $\text{cm}^{-1}$  range studied.

### 4. DISCUSSION

The interpretation of our results is straightforward. On slowly depositing methane gas near 10 K, amorphous  $\text{CH}_4$  ice was formed, which then crystallized irreversibly into methane’s high-temperature solid phase (phase I) on warming to 30 K. Recooling generated the low-temperature crystalline phase (phase II) of  $\text{CH}_4$ , with a transition near 20.4 K (Clusius 1929;



**Figure 2.** Enlargements of selected sections of the near- and mid-infrared spectrum and associated optical constants  $n$  and  $k$  of amorphous  $\text{CH}_4$  at  $\sim 10$  K. The  $\text{CH}_4$  sample whose spectrum is shown had a thickness of  $0.5 \mu\text{m}$ .

Savitsky & Hornig 1962). The reversible cycling between spectral band shapes shown in Figures 1(g)–(j) can be taken as the sine qua non for crystalline  $\text{CH}_4$ , but we are unaware of a similar figure in the astrochemical literature that shows this high degree of reversibility. The pronounced asymmetry of the  $1300 \text{ cm}^{-1}$  feature is similar to that of other intense small-wavenumber (long-wavelength) absorptions in amorphous hydrocarbons, such as acetylene (Hudson et al. 2014a) and ethane (Hudson et al. 2014b). See Keefe et al. (2012) for a more general discussion of such shapes.

#### 4.1. Optical Constants and Band Strengths

To the best of our knowledge Figure 2 is the first publication of the IR features of amorphous  $\text{CH}_4$ . Similarly, the optical constants of Figure 2 are the first of their kind. These spectra and optical constants can be valuable in studies of low-temperature  $\text{CH}_4$  ices in astronomical environments, but even more so if combined with measures of band strengths. As in our recent papers on  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$ , we distinguish between apparent and absolute measures of intensity (Hudson et al. 2014a, 2014b). Apparent intensities, either absorption coefficients ( $\alpha'$ ) of spectral peaks or integrated intensities ( $A'$ ) of IR bands, are found by graphing either a peak height or band area

as a function of ice thickness and evaluating the slope of the resulting line, similar to work with standard Beer's law plots (further details in Hudson et al. 2014a). For the ices used in nearly all laboratory studies of this type,  $\alpha'$  and  $A'$  include the effects of reflections and optical interference in ways that are difficult to predict. In contrast, absolute absorption coefficients ( $\alpha$ ) of spectral peaks and absolute integrated intensities ( $A$ ) of IR bands are found from optical constant  $k$  as follows:

$$\alpha(\tilde{\nu}) = 4\pi\tilde{\nu}k(\tilde{\nu}) \quad (1)$$

$$A = \frac{1}{\rho_N} \int_{\text{band}} \alpha(\tilde{\nu}) d\tilde{\nu}, \quad (2)$$

where  $\tilde{\nu}$  is wavenumber, almost always in units of  $\text{cm}^{-1}$ , and  $\rho_N$  is the number density of molecules in the ice, here in units of molecules  $\text{cm}^{-3}$ . This designation between apparent and absolute measures of intensity has long been made in the molecular spectroscopy literature (e.g., Maeda & Schatz 1961; Wexler 1967; Scrocco et al. 1972), but has not always been recognized in astrochemical papers.

Table 1 lists  $\alpha'$ ,  $\alpha$ ,  $A$ , and  $A'$  for several regions of the IR spectrum of amorphous  $\text{CH}_4$ . All published values we have found for  $\text{CH}_4$  ices at 10–20 K are for samples that are either

**Table 1**  
Peak Positions, Absorption Coefficients, and Band Strengths for Amorphous CH<sub>4</sub> at 8 K

Peak Position <sup>a</sup> cm <sup>-1</sup> (μm)	α' cm <sup>-1</sup>	Peak Position <sup>b</sup> cm <sup>-1</sup> (μm)	α cm <sup>-1</sup>	Integration Range cm <sup>-1</sup>	A' cm molecule <sup>-1</sup>	A cm molecule <sup>-1</sup>
4529 (2.208)	107	4529 (2.208)	114	4559–4496	$8.76 \times 10^{-20}$	$9.37 \times 10^{-20}$
4301 (2.325)	879	4301 (2.325)	893	4428–4246	$8.15 \times 10^{-19}$	$8.55 \times 10^{-19}$
4203 (2.379)	514	4202 (2.380)	528	4240–4167	$3.89 \times 10^{-19}$	$3.97 \times 10^{-19}$
4115 (2.430)	14	4115 (2.43)	16	4144–4094	$1.29 \times 10^{-20}$	$1.75 \times 10^{-20}$
3846 (2.600)	86	3846 (2.600)	95	3853–3836	$3.24 \times 10^{-20}$	$4.16 \times 10^{-20}$
3010 (3.322)	21,860	3011 (3.321)	23,810	3160–2930	$1.40 \times 10^{-17}$	$1.41 \times 10^{-17}$
2814 (3.554)	467	2814 (3.554)	510	2865–2785	$3.95 \times 10^{-19}$	$4.04 \times 10^{-19}$
1297 (7.710)	16,980	1299 (7.698)	18,630	1345–1255	$9.71 \times 10^{-18}$	$1.04 \times 10^{-17}$

<sup>a</sup> Determined from peaks in the absorbance spectrum.

<sup>b</sup> Determined from the calculated  $k$  values.

partially or wholly crystalline, and so it is not surprising that they differ somewhat from our numbers in Table 1. (Note also that most of the quantities designated by  $A$  in the astrochemical literature on ices are, in fact,  $A'$ .) A full analysis of the uncertainties for all of the band strengths and absorption coefficients in Table 1 is in progress and results will be given in a follow-on paper. However, at present we can report that for both  $\nu_3$  and  $\nu_4$ , the features of most interest to interstellar astronomers, we find  $A \approx A'$  with a relative uncertainty of about 1% for  $A(\nu_3)$ ,  $A'(\nu_3)$ ,  $A(\nu_4)$ , and  $A'(\nu_4)$ .

#### 4.2. Implications for Laboratory Measurements on CH<sub>4</sub> Ice

Part of the value of our new results is that they can help evaluate the phase of frozen CH<sub>4</sub> when such information is otherwise not available. For the CH<sub>4</sub> feature of Figure 1 each of the spectral traces in (a)–(e) is now seen to be either that of phase-II crystalline CH<sub>4</sub> ice or perhaps the crystalline material contaminated with some amount of amorphous solid, despite the fact that all five samples were reported as being made at 10–20 K. Key to this assessment is our mid-IR result for amorphous CH<sub>4</sub> and knowledge of the double-peaked feature at 1300 cm<sup>-1</sup> for phase-II crystalline CH<sub>4</sub>. Turning to the near-IR region, the paper of Bernstein et al. (2006) on H<sub>2</sub>O + CH<sub>4</sub> mixtures included a near-IR spectrum of pure CH<sub>4</sub> deposited at 15 K. A distinct feature at 4314 cm<sup>-1</sup> in their Figure 2 shows that their sample was at least partially crystalline, as no such absorption is present in amorphous CH<sub>4</sub>, but it is present in phase-II crystalline CH<sub>4</sub> (Baciocco et al. 1987; Khanna & Ngoh 1990). The same peak in Figure 4 of Gálvez et al. (2009) also betrays some crystallinity for their CH<sub>4</sub>-ice sample, which was deposited at 14 K.

In some of these cases the results derived from such spectra will hardly depend on the initial CH<sub>4</sub> phase, such as if product identification is the goal in a photo- or radiation chemistry experiment. However, in other cases the failure to accurately recognize the phase of methane ice can lead to severe difficulties, such as in kinetic studies where a correct initial abundance may be needed to work out a mass balance, but an inappropriate band strength is adopted, or in trying to establish trends and draw conclusions from widths and positions of methane spectral bands.

An important point here is that neither the temperature at which methane is condensed nor the temperature at which a spectrum is recorded is a universal and reliable indicator of the phase of a CH<sub>4</sub>-ice sample. Our experiments showed that either rapid deposition of CH<sub>4</sub> at ~10 K or deposition above ~20 K,

followed by cooling, produced the double-peaked 1300 cm<sup>-1</sup> features of phase-II crystalline CH<sub>4</sub>. This suggests that the reason the published spectra of Figures 1(a)–(e) are not of pure amorphous CH<sub>4</sub> is because of (a) too high a deposition rate, leading to excessive energy release on gas condensation, (b) too poor a thermal conductivity for the substrate used, (c) too low of a cryostat cooling efficiency, (d) the location of the temperature sensor, or (e) some combination of these factors. We assume that these same spectra faithfully represent what was measured in each laboratory, but they should not be taken a priori as the spectra of amorphous CH<sub>4</sub> in the ISM or the outer solar system.

Many other interesting and relevant papers can be found in the CH<sub>4</sub>-ice literature. Older work by Pipes et al. (1978) is still valuable, but the intense  $\nu_3$  and  $\nu_4$  fundamental bands of their methane spectra appear saturated, prohibiting an assessment of the phase of their samples. Also, their use of a 20 K deposition temperature is of concern, being close to the 20.4 K phase-transition temperature. An early paper by d’Hendecourt & Allamandola (1986) was influential in describing the calculations needed and spectra expected for laboratory work on astronomical ices. Their 10 K methane ice appears to have been crystalline, not amorphous, from the positions of the two components reported near 1300 cm<sup>-1</sup>.

Among the more recent papers, that of Mejía et al. (2013) is interesting for many reasons, not least of which is that the lower spectrum in their Figure 1 may well be that of amorphous CH<sub>4</sub>. However, the small size shown for key spectral features hinders an independent evaluation and the figure’s lack of a vertical numerical scale prohibits the extraction of quantitative information, such as  $\alpha'$  values, which could help determine the ice’s phase. It also is curious that certain features of the spectrum after ion irradiation of the sample are said to be consistent with those of phase-II crystalline CH<sub>4</sub>, whereas irradiation typically amorphizes ices rapidly at 15 K. Similarly, it is difficult to know what is meant when a methane spectrum is described as having “some amorphous features” (de Barros et al. 2011) when the present paper is the first to present the spectrum of amorphous CH<sub>4</sub>.

In many cases, published IR transmission spectra are on too small a scale to permit independent verification, examination, and reproduction of the authors’ work, and similar comments apply to IR spectra of CH<sub>4</sub> recorded with reflectance-absorbance methods (e.g., Moore & Hudson 2003; Bennett et al. 2006). This is not the case with the long paper of Hudgins et al. (1993). We initially were surprised that the CH<sub>4</sub> spectra

shown there were said to be for an ice with a thickness of  $0.03 \mu\text{m}$ , but the authors' inclusion of useful enlargements of key spectral regions, and detailed descriptions of experiments, revealed that the sample's actual thickness was  $0.3 \mu\text{m}$ .

#### 4.3. Implications for Astronomical Observations of $\text{CH}_4$ Ice

An immediate implication of our work is the need to reassess the  $\text{CH}_4$  band strengths and optical constants used by astronomical observers. The strength of the methane band at  $1300 \text{ cm}^{-1}$  ( $7.69 \mu\text{m}$ ), as reported by Hudgins et al. (1993) and later modified by Boogert et al. (1997), is  $7.3 \times 10^{-18} \text{ cm molecule}^{-1}$ . This value and scaled versions for various ice densities have been used in analyzing both ISO (Gibb et al. 2004) and *Spitzer* (Öberg et al. 2008) IR observations. The spectrum on which this band strength is based is shown in Figure 1(d), taken from Hudgins et al. (1993). Our conclusion is that until now all of the methane IR spectra, band strengths, and optical constants available for interstellar studies in this spectral region are for crystalline  $\text{CH}_4$ , presumably the low-temperature phase (phase II) of the solid. In contrast, our Table 1 shows that the intensity of the corresponding IR band of amorphous  $\text{CH}_4$  is  $A'(1300 \text{ cm}^{-1}) = 9.71 \times 10^{-18} \text{ cm molecule}^{-1}$ , which is about 33% higher than the crystalline- $\text{CH}_4$  value.

Although our measurements were made with pure  $\text{CH}_4$ , they have a significant bearing on the derived abundances of interstellar  $\text{CH}_4$  mixed with  $\text{H}_2\text{O}$  ice. The methane absolute intensities often used by IR astronomers are based on those of pure  $\text{CH}_4$  but scaled to the IR band area of a laboratory sample of  $\text{CH}_4$  in a mixed molecular ice of known composition (e.g., Kerkhof et al. 1999). Moreover, the reference  $\text{CH}_4$  band intensity for this scaling typically is taken from data on crystalline  $\text{CH}_4$  (d'Hendecourt & Allamandola 1986; Hudgins et al. 1993), as opposed to the amorphous  $\text{CH}_4$  results presented here. A similar scaling for the intensity of the methane feature near  $1300 \text{ cm}^{-1}$  ( $7.69 \mu\text{m}$ ), using the results for amorphous  $\text{CH}_4$  in our Table 1, would give a larger band strength for  $\text{CH}_4$  in  $\text{H}_2\text{O}$ -ice. Our band strengths can, of course, be re-scaled using appropriate densities to estimate  $A'$  for amorphous  $\text{CH}_4$  in mixtures dominated by other solids (e.g.,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ). See Boogert et al. (1997) for examples.

Another implication of our results is that the spectral models of cold planetary bodies, primarily Kuiper belt objects, that rely on the optical constants of  $\text{CH}_4$  in the near-IR might need re-evaluation. Our optical constants should be helpful in determining the physical state of cold objects on the edge of the solar system and unraveling their hydrocarbon chemistry (Brown et al. 2007; Cruikshank et al. 2015). The main spectral data available until now for  $\text{CH}_4$  at these wavelengths are the absorption coefficients of Quirico & Schmitt (1997), which are for crystalline  $\text{CH}_4$ . Whether, for example, methane mixes with nitrogen to form an amorphous solid at  $\sim 30 \text{ K}$  or whether the two materials segregate to form crystalline solids or whether another scenario applies is unknown, partly due to the lack of near-IR optical constants for amorphous  $\text{CH}_4$  with which to interpret and synthesize spectra. Our results fill this gap.

## 5. CONCLUSION

We have presented for the first time details of the near- and mid-IR spectra of surprisingly elusive amorphous  $\text{CH}_4$  ice

along with IR optical constants, absorption coefficients, and band strengths. Both apparent and absolute versions of  $\alpha$  and  $A$  have been tabulated and all results made available online. The apparent band strength near  $10 \text{ K}$  of the amorphous- $\text{CH}_4$  fundamental near  $1300 \text{ cm}^{-1}$  ( $7.69 \mu\text{m}$ ) has been found to be about 33% larger than the value for crystalline  $\text{CH}_4$ . With IR data on both the amorphous and crystalline phases of solid  $\text{CH}_4$  finally available, it should now be possible to compute accurate  $\text{CH}_4$  abundances from astronomical spectra and to better correlate them with temperature, the presence of other molecules, and so forth. Additional work is in progress.

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