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Solid methane toward deeply embedded protostars*

A.C.A. Boogert[1], W.A. Schutte[2], A.G.G.M. Tielens[3], D.C.B. Whittet[4], F.P. Helmich[2], P. Ehrenfreund[2], P.R. Wesselius[1,5], Th. de Graauw[1,5], and T. Prusti[6]

[1] Kapteyn Astronomical Institute, P.O. Box 800, 9700 AV Groningen, The Netherlands
[2] Leiden Observatory, P. O. Box 9513, 2300 RA Leiden, The Netherlands
[3] MS 245-3, NASA Ames Research Center, Moffet Field, CA 94035, USA
[4] Department of Physics, Applied Physics & Astronomy, Rensselaer Polytechnic Institute, Troy, NY 12180, USA
[5] SRON, P.O. Box 800, 9700 AV Groningen, the Netherlands
[6] ISO Science Operations Centre, Astrophysics Division, ESA, Villafranca del Castillo, P.O. Box 50727, E-28080 Madrid, Spain

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Abstract. We report on the detection of an absorption feature near 7.67 μm toward the deeply embedded protostellar objects W 33A and NGC 7538 : IRS9. Comparison with laboratory spectra shows that this feature can be identified as the ν_4 ('deformation') mode of solid state CH_4 embedded in polar molecules (i.e., H_2O and/or CH_3OH) in icy grain mantles. The solid CH_4 column density relative to solid H_2O is 0.4–1.9%. Unlike solid CO, solid CH_4 does not seem to be subjected to out–gassing toward the warm source W 33A. The low gas–to–solid ratio for CH_4 argues that CH_4 is formed on grains either by hydrogenation of accreted C or by ultraviolet processing of CH_3OH–rich ices.

Key words: ISM: dust, extinction – ISM: molecules – ISM: abundances – infrared: ISM: lines and bands – stars: individual: NGC 7538: IRS9 – stars: individual: W 33A

1. Introduction

Theoretical models predict that molecular clouds may contain considerable quantities of methane (CH_4) in the gas (e.g., Millar & Nejad 1985; Herbst & Leung 1986) or solid phase (e.g., Tielens & Hagen 1982). The extremely symmetric CH_4 molecule can only be observed by its ro-vibrational transitions in the infrared, i.e. the ν_3 'stretching' mode at 3.32 μm and the ν_4 'deformation' mode at 7.66 μm. For solid CH_4 these ro–vibrational lines merge into single broad bands, but somewhat shifted in wavelength due to interaction of the molecules in the matrix and particle shape effects (Boogert et al. 1997, henceforth B97). Observations of both fundamental modes of interstellar CH_4 are severely hindered by telluric absorption. Ground based and airborne (KAO) observations of the 7.66 μm band have been done toward some bright protostellar sources. Lacy et al. (1991) detected solid and gaseous CH_4, and their detection toward W 33A was recently confirmed by KAO observations (B97). Both studies have to deal with rather poor signal-to-noise ratios due to telluric absorption or technical limitations.

With the Short Wavelength Spectrometer on board of the Infrared Space Observatory (ISO–SWS; Kessler et al. 1996; de Graauw et al. 1996) it is possible to observe solid and gaseous CH_4 at high grating resolution (R$\simeq$1800), unhindered by the earth atmosphere. In this letter we present ISO–SWS spectra in the 7.4–8.0 μm range of the deeply embedded protostars W 33A and NGC 7538 : IRS9. For the first time we are able to compare absorption by interstellar solid CH_4 in detail with laboratory studies of ices. The identification of the molecular environment of CH_4 in grain mantles, its column density, as well as the gas–to–solid state ratio, will provide important clues to the formation history of the CH_4 molecule and its importance for the chemical network in molecular clouds.

2. Observations

The protostellar objects W 33A and NGC 7538 : IRS9 were observed with ISO–SWS in full grating mode ('AOT 6'). Both sources are much smaller than the ISO–SWS beam at 7.7 μm ($14'' \times 20''$; Willner et al. 1982). Therefore, the resolution of the observations is comparable to the instrumental resolution for point sources at this wavelength, i.e. R$\simeq$1800. The latest version of the standard ISO–SWS reduction procedure and calibration files was applied (OLP version 5.0 at 2/9/96; de Graauw et al. 1996; Schaeidt et al. 1996). The individual up and down detector scans of the ISO–SWS spectra show some systematic

Send offprint requests to: A.C.A. Boogert (boog@astro.rug.nl)

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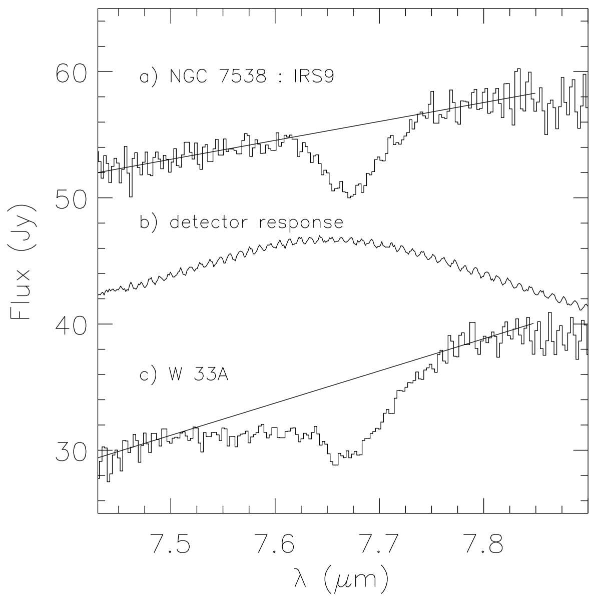

Fig. 1. ISO–SWS spectra of the deeply embedded protostars NGC 7538 : IRS9 (**a**) and W 33A (**c**). The straight lines indicate the adopted continua. For comparison the detector response, scaled to the brightness of these sources, is shown (**b**).

differences in the flux level, as well as the spectral slope. This is probably caused by inaccuracies in the flux calibration, and the dark current subtraction (de Graauw et al. 1996). To minimize these systematic contributions to the noise, the detector scans were aligned by fitting straight lines and subsequently multiplying each scan to the mean level. This resulted in 10% lower RMS noise for W 33A and 70% for NGC 7538 : IRS9. Then the spectrum was resampled to the instrumental resolution with two points per resolution element. Figure 1 shows the final spectra. To check the reliability of the observed spectra, we have also plotted the detector response curve. No obvious residuals of the detector responsivity are apparent in the interstellar spectra.

3. Results

The spectrum of NGC 7538 : IRS9 shows a single, Gaussian shaped absorption feature near 7.67 μm. The spectrum was converted to optical depth scale by adopting a local, straight line continuum, as indicated in Figure 1a. Then, the peak position, width (FWHM) and central optical depth were determined by fitting a Gaussian (Table 1). The spectrum of W 33A reveals a broad absorption between 7.5–7.75 μm, that clearly is composed of two components (Fig. 1c). These distinct components were satisfactorily fitted by two Gaussians on optical depth scale (Table 1), using the continuum indicated in Figure 1c. We find that the narrow component of W 33A has the same peak position (7.675 μm) and FWHM (0.062 μm) as NGC 7538 : IRS9 within the fitting uncertainties. The broad feature in W 33A is centered on 7.631 μm, and is evidently very weak or absent toward NGC 7538 : IRS9.

4. Identification of the observed features

An extensive laboratory study of interstellar solid CH_4 in different ices and at different temperatures was made in B97. Their results are summarized in Figure 2, complemented with some laboratory data of Hudgins et al. (1993) for non–polar mixtures. It shows the peak position and width of the deformation mode of solid CH_4 in a sample of ices after deposition at T=10 K. The width and peak position are good discriminators between polar and non–polar matrices and the relative abundance of CH_4 in the matrix. Upon warm–up to 30 and 50 K the separation of polar and non–polar ices in this diagram decreases, but is still present (B97).

A comparison of the ISO–SWS observations with the laboratory simulations shows that the observed 7.67 μm feature is likely due to absorption by interstellar solid CH_4, embedded in polar molecules (Fig. 2). Especially H_2O:CH_4 mixtures fit well. The solid line in Figure 2 shows that the laboratory profile broadens and shifts to larger wavelength with decreasing H_2O/CH_4 abundance ratio. With this trend, the best fitting ice has an H_2O/CH_4 abundance ratio in the range 2–16. However, the observed width and peak position can also be obtained by adding CH_3OH to mixtures with a larger H_2O/CH_4 abundance ratio (Fig. 2). Thus, the 'strong interstellar mixture' (H_2O:CH_3OH:CO:CH_4=70:40:1:1) also fits the observations (Fig. 3). Furthermore, the mixture CH_3OH:CH_4=30:1 provides a good fit, when warmed–up to 30 K. We conclude that solid CH_4 is embedded in a matrix of polar molecules, but no clear distinction between H_2O– and CH_3OH–rich ices and the mixing ratio of these molecules can be made.

A reliable check on the identification of the observed 7.67 μm absorption feature as the deformation mode of interstellar solid CH_4 can be made by observing the 3.32 μm stretching mode as well. In laboratory experiments, the integrated optical depth of the stretching mode is $\sim$50% larger than the deformation mode. For polar molecules the width of the stretching mode is also $\sim$50% larger (Hudgins et al. 1993; B97). Therefore, the peak optical depth of the stretching and deformation modes are expected to be similar. The grating scan of NGC 7538 : IRS9 has an RMS noise on optical depth scale of $\sim$0.13 at 3.32 μm (Whittet et al. 1996). This is larger than the expected optical depth (Table 1) of the stretching mode of solid CH_4, and thus the assignment of the 7.67 μm feature to interstellar CH_4 can not be directly confirmed or rejected with the currently available data. Note that observations of the CH_4 stretching mode require very high signal-to-noise, due to the weakness of protostars at these wavelengths and blending with the broad, deep solid H_2O absorption at 3.0 μm. Nevertheless, it is very important to observe this mode as an independent check on the presence and molecular environment of CH_4 in ice mantles.

It can readily be seen from Fig. 2 that the broad component toward W 33A can not be explained by a solid state CH_4 mixture. Ro–vibrational absorption spectra of gaseous CH_4 show a distinct Q–branch at 7.66 μm and sharp, but weaker lines in the P– and R–branches, for the physical conditions toward W 33A

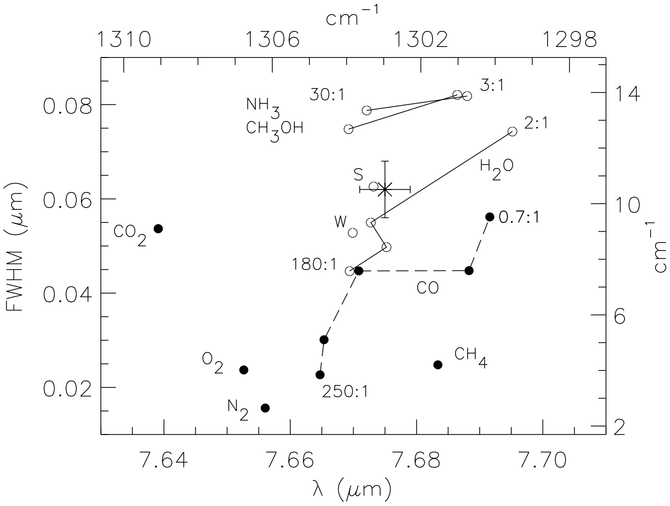

Fig. 2. Laboratory spectroscopy of the deformation mode of interstellar CH_4 compared to the observed peak position and FWHM (cross with error bars). Bullets indicate CH_4 in a non–polar matrix, circles a polar matrix. The mixing ratio of N_2, O_2, and CO_2 with CH_4 is 20:1. The 'S' indicates the 'strong interstellar mixture', and 'W' its weak equivalent (Sect. 4; B97). For the other mixtures, a line is drawn between points with an increasing CH_4 abundance. For each series the highest and lowest abundances relative to CH_4 are indicated. The temperature for all mixtures is 10 K. Further details can be found in B97.

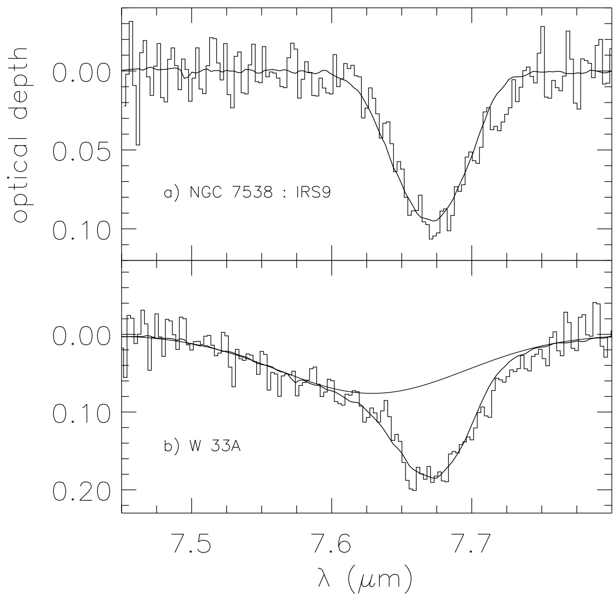

Fig. 3. Comparison of the ISO–SWS spectra with the deformation mode of solid CH_4 in the 'strong interstellar mixture' (Sect. 4). **a**: NGC 7538 : IRS9. **b**: W 33A, the laboratory spectrum is added to a Gaussian fit of the underlying broad component, which can not be ascribed to absorption by solid CH_4.

and at the resolution of our observations (Helmich 1996; B97). The spectrum of W 33A does not show these narrow lines, and therefore we conclude that the broad 7.63 μm absorption feature is not due to gaseous CH_4. Instead, this feature may be due to solid SO_2 (B97).

5. Solid CH_4 column densities and chemistry

The column density of ice species can be derived by dividing the integrated optical depth by the molecular band strength A. We adopt a matrix independent A= 7.3 10^{-18} cm molecule^{-1} for the deformation mode of solid CH_4 (B97). Using this band strength and the Gaussian depths and widths (Table 1), we derive column densities of $N(CH_4)$ = 1.3 and 1.7 10^{17} cm^{-2} for NGC 7538 : IRS9 and W 33A respectively.

The column density of solid CH_4 is compared to other ices in Table 1. There are two independent solid CO components toward these sources: CO in a polar and in a non–polar environment (Tielens et al. 1991). The solid CH_4 column density is ∼50% of solid CO in a polar environment for both sources. In contrast, while toward the warm source W 33A most of the non-polar CO (sublimation temperature ∼20 K) has evaporated from the grains, the cold source NGC 7538 : IRS9 has an abundant non–polar CO component. Apparently, there is very little solid CH_4 associated with this non–polar environment toward NGC 7538 : IRS9. This is consistent with the best fitting laboratory mixtures (Fig. 2). Note that non–polar molecules can be stored in an H_2O matrix up to the H_2O sublimation temperature.

There are various ways to form CH_4 both in the gas phase and on grain surfaces. Each of these processes has its own characteristics which may be 'traced' back in the observations. Our obser-vations , as well as the observations by Lacy et al. (1991) indicate a low gas phase CH_4 column density (N(gas)/N(solid)$<$ 1). This may indicate that the formation of CH_4 molecules is closely related to interstellar grains.

We can distinguish two classes of models for the formation of interstellar CH_4 on grains. First, CH_4 can be formed by hydrogenation of atomic C on grain surfaces. Since solid H_2O is formed in a similar way from accreted oxygen, the predominance of solid CH_4 in a polar environment is a natural consequence of this model (Tielens & Hagen 1982). The observed low solid CH_4/H_2O ratio might locate the formation of CH_4 then deep inside molecular clouds, where most of the elemental carbon is locked up in CO and gaseous C is only a trace species (Keene 1990).

Second, solid CH_4 can be formed efficiently by UV photolysis of ice mixtures containing CH_3OH, resulting in solid CH_4/CH_3OH ratios of $\simeq$0.1 (Allamandola et al. 1988). The observed solid CH_4/CH_3OH ratio is in good agreement with the laboratory experiments (Table 1; Gerakines et al. 1996). In this model, solid CH_4 would also be preferentially confined to polar environments. However, the laboratory spectra of photolysed CH_3OH ices also display a narrow feature near 5.82 μm, attributed to formaldehyde (H_2CO) and higher aldehydes. For irradiation doses consistent with the observed CH_4/CH_3OH ratio, this band should be ∼50% deeper than the observed CH_4 feature, but it is not apparent in the spectrum of NGC 7538 : IRS9

Table 1. Gaussian parameters of the observed absorption features. The solid CH_4 column density is given as a percentage of solid H_2O, solid CO in a polar environment (CO–p), solid CO in a non–polar environment (CO–np) and CH_3OH ice.

Object	λ	FWHM	τ	N(CH_4)				
	μm	μm		10^{17} cm^{-2}	%H_2O	%CO − p	%CO − np	%CH_3OH
NGC 7538 : IRS9	7.674±0.003	0.063±0.005	0.092±0.005	1.3±0.1	1.9[a]	41[d]	20[d]	14[c]
W 33A	7.676±0.005	0.061±0.007	0.120±0.005	1.7±0.2	0.4[b]	61[d]	155[d]	4.4[c]
	7.631±0.007	0.161±0.010	0.082±0.005	...	...	...	...	...

[a] 3.0 μm band [b] 6.0 μm band [c] 3.54 μm band (Allamandola et al. 1992; Schutte et al. 1996) [d] Tielens et al. (1991)

(Schutte et al. 1996). Furthermore, the solid CH_4/CH_3OH ratio is lower toward W 33A compared to NGC 7538 : IRS9. This anti–correlates with the 4.62 μm absorption band, generally ascribed to energetic processing of ice mantles (Tegler et al. 1995, and references therein). Additional laboratory work is necessary to address these problems and to assess the importance of UV photolysis for the formation of interstellar solid CH_4.

6. Conclusions

We have obtained 7.4–8.0 μm spectra of the highly obscured protostars W 33A and NGC 7538 : IRS9, using the SWS spectrometer on board of the ISO satellite. Both sources exhibit a narrow absorption feature near 7.67 μm. We compare these spectra to laboratory simulations of interstellar solid CH_4 and calculations of gas phase CH_4. We conclude that the observed 7.67 μm absorption feature toward both sources can be ascribed to absorption by the deformation mode of solid CH_4 in a polar matrix. Both H_2O–, and CH_3OH–rich ices can explain the observations. The solid CH_4 column density is 0.4–1.9% of solid H_2O. No gas phase CH_4 was observed, and therefore we conclude that the formation of CH_4 is closely related to interstellar dust grains. Thus, interstellar CH_4 is likely formed on grain surfaces by hydrogenation of atomic C or by UV photolysis of CH_3OH in ice mantles. Both models can explain the observed CH_4 abundance and the polarity of the ice in which CH_4 is embedded.

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