ISO–SWS observations of interstellar solid and gaseous CH$_4$

**ABSTRACT.** We present spectra in the 7.35–7.85 μm wavelength range toward the high mass protostellar objects W 33A and NGC 7538 : IRS9, obtained with the Short Wavelength Spectrometer on board of the Infrared Space Observatory (ISO–SWS). In both lines of sight, we detect a prominent absorption band at 7.67 μm together with a series of weak, unresolved absorption lines. Comparison with laboratory spectra shows that the 7.67 μm band can be identified with the ν4 ('deformation') mode of solid state CH$_4$ intimately mixed with polar molecules (i.e., H$_2$O and/or CH$_3$OH) in icy grain mantles. The solid CH$_4$ column density is ~1% relative to solid H$_2$O, and thus CH$_4$ is a minor component of interstellar ice mantles. The detected narrow lines can be unambiguously attributed to the ro-vibrational absorption spectrum of gaseous CH$_4$. Using a rotation diagram and synthetic spectra we show that the CH$_4$ gas is relatively warm ($T \sim 90$ K), and that the gas-to-solid state abundance ratio of interstellar CH$_4$ is low (~0.5). We discuss models for the formation of interstellar CH$_4$. The observations impose strong limitations on time dependent gas phase models, e.g. a low initial CO/C ratio would be required, the CH$_4$ must have been formed and subsequently condensed on the grains within a narrow time window of ~ 10$^7$ yr, and an additional mechanism would be necessary to form polar ice mantles. More likely, interstellar CH$_4$ is formed through grain surface reactions at a high CO/C ratio, which explains the low observed CH$_4$ abundance ($N$(CH$_4$)/$N$(H$_2$) ~ 10$^{-6}$), the presence of CH$_4$ in a polar ice, the low gas-to-solid ratio, and the absence of a strong cold CH$_4$ gas component. The observed warm CH$_4$ gas probably has sublimated from the grains in the ‘hot core’ region surrounding the protostar.
3.1 Introduction

Models of chemistry in interstellar clouds indicate that molecules are formed efficiently in the gas phase through ion-molecule reactions (e.g., CO; Millar & Nejad 1985), on grain surfaces through heterogeneous catalysis (e.g., H₂O; Tielens & Hagen 1982), or by ultraviolet (UV) processing of ice mantles (e.g., ‘XCN’; Lacy et al. 1984). Observations of both the solid and gas phase are essential to test and further constrain these models.

One of the simplest organic species, the CH₄ molecule, can, due to its extreme symmetry, only be observed by its ro-vibrational transitions in the infrared, i.e., the ν₃ ‘stretching’ mode at 3.32 µm and the ν₄ ‘deformation’ mode at 7.46 µm. For solid CH₄, 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 (Chap. 2). Unfortunately, observations of both fundamental modes of interstellar CH₄ 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) tentatively detect solid CH₄ toward W 33A, NGC 7539: IRS9, and NGC 7539: IRS1. Furthermore, the R(0) or R(2) lines of gaseous CH₄ were detected toward these sources and OMC-1: IRc2. The detection of solid CH₄ toward W 33A was recently confirmed by KAO observations (Chap. 2). 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 CH₄ at high grating resolution (R ~ 1700), unhindered by the earth atmosphere. In this Chapter, we present ISO-SWS spectra in the 7.35–7.85 µm spectral region of the deeply embedded protostars W 33A and NGC 7538: IRS9. Dartois et al. (1998) report ISO-SWS observations of gaseous and solid phase CH₄ toward the embedded protostar GL 7009S. For the first time we are able to compare absorption by interstellar solid CH₄ in detail with laboratory studies of ices. The identification of the molecular environment of CH₄ in grain mantles, its column density, the gas temperature as well as the gas-to-solid state ratio, will provide important clues to the chemical and physical history of the CH₄ molecule and its importance for the chemical network in molecular clouds.

In Sect. 3.2 we discuss the reduction and quality of the ISO-SWS observations. The observed solid state and gas phase absorption features in the 7.35–7.85 µm spectral region are identified in Sect. 3.3.1. The detected 7.67 µm feature is fitted with laboratory ices in Sect. 3.3.2. Models of the ν₂/ν₄ dyad of gaseous CH₄ are described in Sect. 3.3.3, and compared to the interstellar spectra. Rotational diagrams are constructed to derive the temperature and column density of interstellar gaseous CH₄. In Sect. 3.4 we discuss the observational constraints that can be put on existing chemical models for the formation of interstellar CH₄. The conclusions are given in Sect. 3.5.
3.2 Observations

The 7.35-7.85 \( \mu m \) spectra of the protostellar objects W 33A and NGC 7538 : IRS9 were observed with ISO–SWS in the full resolution grating mode in revolutions 125 and 98 respectively (‘AOT 6’; Table 3.1). Due to a scanner problem in the region short-ward of 7.45 \( \mu m \), the spectrum of W 33A was re-observed in revolution 332. The old and new spectra agree very well, although the individual detector up and down scans of the new observation overlap better. Perhaps the cosmic ray flux was lower in revolution 332. Nevertheless, some of the weak lines reported here, can be recognized in both spectra. The spectra were reduced with the SWS standard reduction software and calibration files available on June 24 1997 at SRON Groningen (de Graauw et al. 1996; Schaeidt et al. 1996). The standard wavelength calibration was applied (Valentijn et al. 1996) and corrections for spacecraft and source velocities were made, using \( v_{LSR} = +33 \) and \( -60 \) \( \text{km s}^{-1} \) for W 33A and NGC 7538 : IRS9 respectively (Mitchell et al. 1990). Each of the 24 detector up and down scans of both spectra was inspected on detector jumps and excessive noise levels. Within the wavelength range considered here (7.35–7.85 \( \mu m \)) no deviating scans were found. Differences in the flux scale and slope between the scans exist to at most 20% for NGC 7538 : IRS9 and 10% for W 33A. These systematic differences are most likely caused by dark current variations due to detector memory effects in this wavelength range, and cosmic ray hits on the dark current and photometric check observations. We corrected for these effects by fitting low order polynomials to each scan and using these fits to shift the data points per scan to the mean of all data points per scan direction (‘flat-fielding’). Thereafter, data points deviating more than 2.7 sigma from the mean per resolution element were removed. These points are mainly caused by (minor) cosmic ray hits, that were not recognized in the SWS pipeline. Finally, the up and down scans were separately convolved with a Gaussian to \( R = 850 \), and rebinned to two points per resolution element. Although both sources are much smaller (Willner et al. 1982) than the ISO–SWS beam at 7.7 \( \mu m \) (14\( \arcsec \) \( \times \) 20\( \arcsec \)), and therefore the spectral resolution of our observations is comparable to the instrumental resolution for point sources at this wavelength, i.e. \( R \approx 1700 \), we found that smoothing to \( R = 850 \) removes the high frequency fringes seen in many spectra. The frequency of these fringes is the same as the fringes in the detector responsivity, although the amplitude is a factor \( \approx 3 \) larger in the interstellar spectra. This is a result of the low resolution and under-sampling of the current SWS responsivity tables. In order to check our reduction method, we have reduced a spectrum of the standard star \( \alpha \) Lyrae in exactly the same way. We find that none of the absorption features reported in this paper correlates with features in this standard spectrum (Fig. 3.1). The final spectra, i.e. the average of the up and

<table>
<thead>
<tr>
<th>Object</th>
<th>RA (2000.0)</th>
<th>Dec (2000.0)</th>
<th>( \Delta \lambda )</th>
<th>ISO Revolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>W 33A</td>
<td>18( ^{h} ) 14( ^{m} ) 39( ^{s} )</td>
<td>-17( ^{\circ} ) 52( ^{\prime} ) 02( ^{\prime\prime} )</td>
<td>1700</td>
<td>125+332</td>
</tr>
<tr>
<td>NGC 7538 : IRS9</td>
<td>23( ^{h} ) 14( ^{m} ) 01( ^{s} ) 06</td>
<td>+61( ^{\circ} ) 27( ^{\prime} ) 20( ^{\prime\prime} )</td>
<td>1700</td>
<td>98</td>
</tr>
</tbody>
</table>
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3.3 Results

3.3.1 The observed features

The 7.35–7.85 $\mu$m spectrum of W 33A shows a wealth of broad and narrow absorption features (Fig. 3.1). The spectrum short-ward of 7.44 $\mu$m drops because of an absorption band at 7.39 $\mu$m. It has been detected before in ground based observations (Lacy et al. 1991; see also Fig. 2.5). The SWS spectrum is discussed in detail...
### 3.3 Results

<table>
<thead>
<tr>
<th>Object</th>
<th>$\lambda$ (\mu m)</th>
<th>FWHM (\mu m)</th>
<th>$\tau$ (0.005)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NGC 7538 : IRS9</td>
<td>7.674 (0.003)</td>
<td>0.063 (0.005)</td>
<td>0.092 (0.005)</td>
</tr>
<tr>
<td>W 33A</td>
<td>7.676 (0.005)</td>
<td>0.061 (0.007)</td>
<td>0.120 (0.005)</td>
</tr>
<tr>
<td></td>
<td>7.64 (0.015)</td>
<td>0.161 (0.010)</td>
<td>0.082 (0.005)</td>
</tr>
</tbody>
</table>

The 7.39 $\mu$m feature is assigned to absorption by solid CH$_3$HCO or HCOO$^-$ in Schutte et al. (1999), where the 7.5–7.75 $\mu$m band is assigned to absorption by solid SO$_2$ and CH$_4$ (Lacy et al. 1991; Chapt. 2). The ISO–SWS observations are of much better quality, and we further investigate their origin in Sect. 3.3.2. Furthermore, a number of narrow lines, with peak depths of 1-4% of the continuum, can be discerned in the spectrum of W 33A as well. The line at 7.66 $\mu$m coincides with the wavelength of the Q-branch of gaseous CH$_4$ (all gas phase CH$_4$ wavelengths cited in this paper were taken from the HITRAN database; Rothman et al. 1992). It is blended with the CH$_4$ ice band at 7.67 $\mu$m and we used a laboratory ice spectrum to define the continuum for the Q-branch (H$_2$O : CH$_3$OH : CO : CH$_4 = 70 : 40 : 1 : 1$; Sect. 3.3.2). For the other narrow absorption lines, local continuum points were determined by hand and interpolated with a cubic spline. A deep line is present at 7.537 $\mu$m, which corresponds to the wavelength of the R(3) line of gaseous CH$_4$ (Table 3.3). Weaker lines at 7.452, 7.478, 7.505, 7.568, 7.621, 7.729, 7.762, and 7.793 $\mu$m coincide with the wavelengths of the R(5), R(6), R(4), R(2), R(1), R(0), P(2), P(3), and P(4) lines respectively, taken into account that our wavelength resolution is 0.009 $\mu$m (Table 3.3). A tentative detection of the R(0) line was made by Lacy et al. (1991), with an equivalent width of (3.7 ± 1) $10^{-2}$ cm$^{-1}$. At the resolution of our observation, this corresponds to a central depth of 2.4 ± 0.6%. This is a factor 2 larger than the line detected in our ISO–SWS observation (Fig. 3.1; Table 3.3). We note that the line detected toward W 33A by Lacy et al. (1991) is heavily blended with telluric CH$_4$ lines.

Toward NGC 7538 : IRS9, the 7.67 $\mu$m absorption band dominates the spectrum (Fig. 3.1). The spectrum was converted to optical depth scale by adopting a local, straight line continuum. The peak position, width (FWHM) and central optical depth were determined by fitting a Gaussian (Table 3.2). We find that the narrow component of W 33A has the same peak position (7.675 $\mu$m) and FWHM (0.062 $\mu$m) as NGC 7538 : IRS9 within the fitting uncertainties. There is also a hint for the presence of a 7.39 $\mu$m band toward this source (Schutte et al. 1999). Contrary to W 33A, the broad 7.60 $\mu$m band is absent or very weak toward NGC 7538 : IRS9. At 1–2% of the continuum, and 2–7 $\sigma$ significance, we identify the Q-branch, R(3), R(2), R(1), P(2), and P(3) lines (Table 3.3). Weak evidence is found for the P(4)
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Table 3.3— Equivalent widths of observed gaseous CH₄ P and R branch lines. The standard deviation σ is given in parentheses.

<table>
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<tr>
<th>Line</th>
<th>λ [μm]</th>
<th>W [cm⁻¹]</th>
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<tbody>
<tr>
<td>R(0)</td>
<td>7.625</td>
<td>12(11)</td>
</tr>
<tr>
<td>R(2)</td>
<td>7.690</td>
<td>≤6</td>
</tr>
<tr>
<td>R(3)</td>
<td>7.725</td>
<td>12(5)</td>
</tr>
<tr>
<td>P(1)</td>
<td>7.762</td>
<td>28(8)</td>
</tr>
<tr>
<td>P(2)</td>
<td>7.795</td>
<td>12(6)</td>
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A from Lacy et al. (1991)

3.3.2 Laboratory ice fitting

An extensive laboratory study of solid CH₄ in different ices and at different temperatures was presented in Chapter 2. A summary of these results is given Figure 3.2, 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 CH₄ 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 allow to determine the relative abundance of CH₄ 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 (Chapt. 2).

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 CH₄, embedded in polar molecules (Fig. 3.2). Especially H₂O:CH₄ mixtures fit well. Figure 3.2 shows that the laboratory profile broadens and shifts to longer wavelength with decreasing H₂O/CH₄ abundance ratio. With this trend, the best fitting ice has an H₂O/CH₄ abundance ratio in the range 2–16. However, the observed width and peak position can also be obtained by adding CH₃OH to mixtures with a larger H₂O/CH₄ abundance ratio. Thus, the ‘strong interstellar mixture’ (H₂O:CH₃OH:CO:CH₄=70:40:1:1) also fits the observations (Fig. 3.3). Furthermore, the mixture CH₃OH:CH₄=30:1 provides a good fit, when warmed–up to
3.3 Results

Figure 3.2—Laboratory spectroscopy of the deformation mode of interstellar CH$_4$ compared to the observed peak position and FWHM (cross with error bars). Solid dots indicate CH$_4$ in a non-polar matrix, open dots 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. 3.3.2; Chapt. 2). 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 Chapt. 2.

At 30 K. We conclude that solid CH$_4$ is embedded in a matrix of polar molecules, but no clear distinction between H$_2$O– and CH$_3$OH–rich ices and the mixing ratio of these molecules can be made.

It can readily be seen from Fig. 3.2, and the Gaussian peak position and width (Table 3.2), that the broad 7.6 $\mu$m component toward W 33A cannot be explained by a solid state CH$_4$ mixture. This feature was previously detected in a KAO HIFOGS spectrum at low signal-to-noise, and was tentatively identified with absorption due to solid SO$_2$ in a CH$_3$OH-rich ice (Chapt. 2). However, the present high quality ISO-SWS spectrum shows clear evidence for an extent of this broad band up to 7.76 $\mu$m. This is inconsistent with absorption due to SO$_2$ (Fig. 3.3), and the origin of this feature remains unclear.
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Figure 3.3—Comparison of the ISO–SWS spectrum of NGC 7538 : IRS9 with the deformation mode of solid CH$_4$ in (a) the mixture H$_2$O:CH$_4$=16:1 at $T=50$ K and (b) CO:CH$_4$=3:1 at $T=10$ K. This demonstrates that only mixtures of CH$_4$ with polar molecules provide good fits to the observed 7.67 $\mu$m feature. The spectrum of W 33A (divided by 2), is compared to (c) the mixture H$_2$O:CH$_3$OH:CH$_4$:CO=70:40:1:1 with a Gaussian added to correct for the underlying 7.60 $\mu$m feature, and (d) to the best fitting combination of CH$_4$ and SO$_2$ ices to the complete feature: CH$_3$OH:SO$_2$=11:1 at $T=50$ K and CH$_3$OH:CH$_4$=27:1 at $T=20$ K. This shows that the 7.60 $\mu$m feature in W 33A can not be satisfactorily fitted with a combination of CH$_4$ and SO$_2$ ices.

3.3.3 Gas phase CH$_4$ modeling

Models of the ro-vibrational spectrum of the $\nu_2/\nu_4$ dyad of gaseous CH$_4$ are described in detail elsewhere (Helmich 1996; Chapt. 2). An essential parameter in these models is the line broadening due to thermal and turbulent motions. The depth of unresolved, optically thick lines increases at larger $b$ values (the Doppler parameter $b = \text{FWHM}/2\sqrt{\ln 2}$). For $b \geq 3$ km s$^{-1}$, this effect is important at $N$(CH$_4$) $\geq$ 3 $10^{16}$ cm$^{-2}$ for $T=20$ K and at $N$(CH$_4$) $\geq 2$ $10^{17}$ cm$^{-2}$ for $T=120$ K. The high resolution infrared absorption line study of Mitchell et al. (1988; 1990) reveals optically thin $^{13}$CO ro-vibrational lines with $b \sim 5$ km s$^{-1}$ toward W 33A and NGC 7538 : IRS9. This is probably an upper limit, since it is comparable to the instrumental broadening. Rotational emission lines at (sub-)millimeter wavelengths have widths around $b = 3$ km s$^{-1}$, with wings ranging up to 18 km s$^{-1}$ (Goldsmith & Mao 1983; Hasegawa & Mitchell 1995; van Dishoeck, priv. comm.). Here, we will adopt a conservative $b = 3$ km s$^{-1}$ at any gas temperature for both sources, thus avoiding underestimation of the derived CH$_4$ column densities due to optical depth effects.

The CH$_4$ gas temperature can be constrained by the observed depth, and upper limits, of the ro-vibrational lines in the P and R branches, provided these lines
are not too optically thick. For W 33A, the detection of lines up to R(6) indicates that the absorbing gas is warm, since this line originates from an energy level of \( T = 317 \) K above the ground rotational state. The relatively large depth of the R(3) and P(3) lines indicates an excitation temperature of \( T \sim 100 \) K (Fig. 3.4). If the ro-vibrational energy levels are populated according to thermodynamic equilibrium, and the lines are optically thin, the rotational temperature \( (T_{\text{rot}}) \) and total CH\(_4\) gas column density \( (N_{\text{tot}}) \) can be determined unambiguously from a rotation diagram (see e.g. Mitchell et al. 1990 for CO). For CH\(_4\), the construction of such a diagram is complicated by the cluster splitting of each \( J \) transition. Each ro-vibrational line consists of a number of lines from the \( E \), \( F \), and \( A \)-type multiplets (Helmich 1996), with slightly different lower energy levels. The population \( N_{ij} \) of the lower energy level \( E_{ij} \) of cluster line \( i \) with rotational quantum number \( J \) is given by the Boltzmann equation:

\[
\frac{N_{ij}}{g_i} = \frac{N_{\text{tot}}}{Q(T_{\text{rot}})} e^{-E_{ij}/kT_{\text{rot}}} \tag{3.1}
\]

with \( g_i = 2J + 1 \) the statistical weight of level \( J \), \( g_i = 2,3, \) or 5 the statistical weight for the \( E \), \( F \), or \( A \)-type multiplets respectively, and \( Q(T_{\text{rot}}) \) the partition function at rotational temperature \( T_{\text{rot}} \). The equivalent width \( w_{ij} \) of the cluster line originating from level \( E_{ij} \) is then given by (e.g. Spitzer 1978):

\[
w_{ij} = 8.85 \times 10^{-13} N_{ij} f_{ij} \text{ cm}^{-1} \tag{3.2}
\]

with \( f_{ij} \) the oscillator strength of the transition. Now, at the resolution of our observations \( R = 850 \), we do not resolve the individual cluster lines, and we effectively observe the equivalent width of the sum of all the cluster lines: \( w_J = \sum_i w_{ij} \). Then the Boltzmann equation becomes:

\[
\frac{w_J}{8.85 \times 10^{-13} \sum_i g_i f_{ij}(2J + 1)} = \frac{N_{\text{tot}}}{Q(T_{\text{rot}})} e^{-E_{ij}/kT_{\text{rot}}} \tag{3.3}
\]
where we took $E_i J_i \simeq E_j J_j$, which is a very good approximation. We constructed a rotation diagram of CH$_4$, by plotting equation 3.3 logarithmically (Fig. 3.5), using the observed equivalent widths given in Table 3.3. In this plot, a straight line can be fitted to the data, with gradient $-1/T_{\text{rot}}$ and abscissa $\ln(N_{\text{tot}}/Q(T_{\text{rot}}))$. Unfortunately, both abscissa and gradient depend rather strongly on $T_{\text{rot}}$, and the relation to be fitted is non-linear as a function of $T_{\text{rot}}$. For this reason, we took an expansion formula for $Q(T_{\text{rot}})$ from the HITRAN database selection program (Rothman et al. 1992; accurate to 10% for 40 $\lesssim T_{\text{rot}} \lesssim$ 700 K) and fitted the following non-linear equation to the points in Fig. 3.5, using a gradient expansion algorithm (the ‘Marquardt’ method; Bevington & Robinson 1992):

$$y = \ln(N_{\text{rot}}) - \ln(-17.48 + 0.95T_{\text{rot}} + 0.0040T_{\text{rot}}^2) - \frac{x}{T_{\text{rot}}}$$  \hspace{1cm} (3.4)

with $x$ and $y$ representing the axes of Fig. 3.5. With this method we find $T_{\text{rot}} = 110 \pm 15$ K, and $N_{\text{rot}} = (9 \pm 2) \times 10^{16}$ cm$^{-2}$ for the CH$_4$ gas toward W 33A.

CO absorption observations have shown that, besides warm gas, there is a significant cold gas component toward W 33A ($T \approx 25$ K; $N_{\text{cold}} \approx N_{\text{rot}}$; Mitchell et al. 1988). For CH$_4$, the column density of such a cold component is constrained by the depth of the lower rotational lines. It would be visible in the rotation diagram as a steepening of the curve at low energies, provided the lines are optically thin. In Fig. 3.5 there is no evidence for a pronounced cold component. If we assume that all observed lines are optically thin (i.e. $b$ is large enough), the ratio $N_{\text{rot}}/N_{\text{cold}}$ can be limited, using the rotation diagram. We constructed a 2 temperature curve, with a minimum possible $N_{\text{rot}} = 7 \times 10^{16}$ cm$^{-2}$ at maximum $T_{\text{rot}} = 200$ K to fit the higher rotational lines, and $T_{\text{cold}} = 25$ K. Thus, we find that $N_{\text{cold}} \leq 3.5 \times 10^{16}$ cm$^{-2}$, and $N_{\text{rot}}/N_{\text{cold}} \geq 2$ (Fig. 3.5). At these column densities, and $b \geq 3$ km s$^{-1}$, the assumption of low optical depth is still valid. For lower $b$ values, optical depth effects need to be taken into account. Any amount of cold CH$_4$ gas can be hidden in the data,
provided \( b \) is small enough. For example, at \( b = 1.5 \text{ km s}^{-1} \) the spectrum is consistent with \( N_{\text{cold}} \leq 5 \times 10^{16} \text{ cm}^{-2} \), and at \( b = 1.0 \text{ km s}^{-1} \) this is a factor 5 higher. We note that no such narrow components have yet been found in emission line studies of W 33A, and thus a high \( N_{\text{cold}} \) remains to be proven.

For the \( \text{CH}_4 \) lines detected toward NGC 7538 : IRS9 we also constructed a rotation diagram (Fig. 3.5). Although, the uncertainties in the equivalent widths are large for each of the detected lines (Table 3.3), the combination of all lines constrains the gas temperature and column density reasonably well. In the fits to the rotation diagram we included the detection of the R(0) line by Lacy et al. (1991). With the method described above, we find a best fit of \( T_{\text{rot}} = 70 \pm 15 \text{ K} \), and \( N_{\text{tot}} = (4 \pm 2) \times 10^{16} \text{ cm}^{-2} \) for NGC 7538 : IRS9. Again, for this source the rotation diagram does not show evidence for a significant cold gas component. When we assume a minimal \( N_{\text{hot}} = 4 \times 10^{16} \text{ cm}^{-2} \), and maximal \( T_{\text{hot}} = 200 \text{ K} \) (from CO; Mitchell et al. 1990), we derive that \( N_{\text{hot}}/N_{\text{cold}} \geq 2 \) for \( T_{\text{cold}} = 25 \text{ K} \). This anti-correlates with CO, for which \( N_{\text{hot}}/N_{\text{cold}} \) is 2 orders of magnitude lower (Mitchell et al. 1990). Similar to W 33A, a much larger \( N_{\text{cold}} \) can be hidden in the data if \( b \leq 1 \text{ km s}^{-1} \), but at present there is no observational evidence for such small velocity dispersions. A summary of the column densities is given in Table 3.4.

### 3.3.4 \( \text{CH}_4 \) column density and abundance

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 \( A = 7.3 \times 10^{-18} \text{ cm molecule}^{-1} \) for the deformation mode of solid \( \text{CH}_4 \) (Chapt. 2). Using this band strength and the Gaussian depths and widths (Table 3.2), we derive column densities for solid \( \text{CH}_4 \) of \( 1.3 \times 10^{17} \text{ cm}^{-2} \) for NGC 7538 : IRS9 and W 33A respectively. The gas phase \( \text{CH}_4 \) column densities are somewhat smaller (Sect. 3.3.3), yielding gas-to-solid state ratios of 0.7 (W 33A) and 0.3 (NGC 7538 : IRS9; Table 3.5).

The abundance of interstellar \( \text{CH}_4 \) is low: \( X(\text{gas} + \text{ice} \text{CH}_4) \sim 10^{-6} \) (Table 3.4). This value is determined with respect to the integrated hydrogen column density derived from the depth of the silicate bands (Table 3.4; Chapt. 2). However, it is an average along the line of sight, and strong abundance variations may occur locally. Notably, the rather high temperature (\( T \sim 70 \text{ K} \)) of the gas phase \( \text{CH}_4 \) toward NGC 7538 : IRS9 indicates that it is not associated with the large amount of cold CO gas along this line of sight (Mitchell et al. 1990). Contrary, the kinetic temperature of the warm CO component toward NGC 7538 : IRS9 then must reside in a separate volume. However, if we assume a two temperature model for the \( \text{CH}_4 \) gas, at least 70\% of the \( \text{CH}_4 \) could have a temperature of 200 K (Sect. 3.3.3). Then, assuming the warm \( \text{CH}_4 \) and CO gas are in the same volume, we find that \( X(\text{gas} \text{CH}_4) \sim 1.3 \times 10^{-5} \), which is an order of magnitude larger than the average along the line of sight (using a conversion factor \( N(\text{H}_2)/N(\text{CO}) = 5000 \); Lacy et al. 1994).

The temperature of the warm CO component toward W 33A (\( T = 120 \pm 12 \text{ K} \);
### Table 3.4— Solid and gas phase column densities

<table>
<thead>
<tr>
<th>species</th>
<th>W 33A</th>
<th></th>
<th>NGC 7538 : IRS9</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N$</td>
<td>$N/N_{H}^{A,C}$</td>
<td>$N/N(H_{2}O)$</td>
<td>$N$</td>
</tr>
<tr>
<td></td>
<td>$10^{17}$ cm$^{-2}$</td>
<td>$10^{-6}$</td>
<td>$\times100$%</td>
<td>$10^{17}$ cm$^{-2}$</td>
</tr>
<tr>
<td>H$_2$O–ice</td>
<td>430</td>
<td>280</td>
<td>100</td>
<td>68</td>
</tr>
<tr>
<td>H$_2$O–gas</td>
<td>8.6</td>
<td>200</td>
<td>2.0</td>
<td>$&lt;7.5$</td>
</tr>
<tr>
<td>CO–‘polar’ ice</td>
<td>2.8</td>
<td>1.4</td>
<td>0.7</td>
<td>3.2</td>
</tr>
<tr>
<td>CO–‘apolar’ ice</td>
<td>1.1</td>
<td>0.55</td>
<td>0.3</td>
<td>6.4</td>
</tr>
<tr>
<td>CO–gas</td>
<td>400</td>
<td>5</td>
<td>93</td>
<td>140</td>
</tr>
<tr>
<td>CH$_3$OH–ice</td>
<td>39</td>
<td>20</td>
<td>9.1</td>
<td>9.1</td>
</tr>
<tr>
<td>CH$_4$–ice</td>
<td>1.7 (0.2)</td>
<td>0.85 (0.10)</td>
<td>0.4 (0.1)</td>
<td>1.3 (0.1)</td>
</tr>
<tr>
<td>CH$_4$–gas</td>
<td>1.1 (0.2)</td>
<td>0.56 (0.12)</td>
<td>0.3 (0.1)</td>
<td>0.4 (0.16)</td>
</tr>
</tbody>
</table>

$^{A}$ $N_{H} = 2.0 \times 10^{23}$ cm$^{-2}$ (W 33A); $^B$ $N_{H} = 1.6 \times 10^{23}$ cm$^{-2}$ (NGC 7538 : IRS9); $^C$ Tielens et al. (1991);

$^D$ NGC 7538 : IRS9–van Dishoeck & Helmich (1996), W 33A–van Dishoeck (priv. comm. 1997);

$^E$ Mitchell et al. (1990); $^F$ Allamandola et al. (1992); $^G$ This work
3.4 Discussion: physical and chemical history of interstellar CH₄

<table>
<thead>
<tr>
<th>Species</th>
<th>N(gas)/N(solid)</th>
<th>W 33A</th>
<th>NGC 7538 : IRS9</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>100</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>0.7 (0.1)</td>
<td>0.3 (0.1)</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>0.02</td>
<td>&lt;0.11</td>
<td></td>
</tr>
</tbody>
</table>

Mitchell et al. 1990) is comparable to the CH₄ gas temperature, and these molecules may be present in the same volume. In this line of sight, the warm and cold CO gas components are equally abundant, and the local gas phase CH₄ abundance probably does not vary significantly from the average along the line of sight (Table 3.4).

3.3.5 The CH₄ stretching mode

An independent check on the identification of the observed 7.67 μm absorption feature as the deformation mode of interstellar solid CH₄ 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 ~50% larger than the deformation mode. For CH₄ embedded in a polar matrix, the width of the stretching mode is also ~50% larger (Hudgins et al. 1993; Chapt. 2). 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 ~0.13 at 3.32 μm (Whittet et al. 1996). This is larger than the expected optical depth (Table 3.2) of the stretching mode of solid CH₄, and thus the assignment of the 7.67 μm feature to interstellar CH₄ cannot be directly confirmed or rejected with the currently available data. Note that observations of the CH₄ stretching mode require very high signal-to-noise, due to the weakness of protostars at these wavelengths and blending with the broad, deep solid H₂O absorption at 3.0 μm.

3.4 Discussion: physical and chemical history of interstellar CH₄

Our laboratory fits to the ISO–SWS spectra of W 33A and NGC 7538 : IRS9 show that interstellar CH₄ ice is embedded in a matrix of polar molecules. Further evidence for this is obtained by comparing the solid CO and CH₄ column densities (Table 3.4). 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 CH₄ 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 CH₄ associated with this non–polar environment toward
NGC 7538 : IRS9. This is consistent with the best fitting laboratory mixtures. Furthermore, our observations show that the detected CH₄ gas is warm, $T_{\text{rot}} \sim 90$ K. The combined CH₄ gas and ice abundance is $X(\text{CH}_4) \sim 10^{-6}$. The CH₄ gas-to-solid state abundance ratio ($\sim 0.5$) is very low compared to CO, but higher than for H₂O (Table 3.5). There are various ways to form CH₄ 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.

CH₄ may have been formed through grain surface reactions involving accreted atomic C and H, similar to the reaction that converts atomic O into H₂O ice (e.g. Brown et al. 1988). This reaction is very efficient. When starting from an atomic gas, the abundance will be $X(\text{CH}_4) \sim 10^{-4}$, which is two orders of magnitude larger than the observed abundance (Table 3.4). Hence, if the observed CH₄ was formed on grain surfaces, the initial atomic C abundance must have been low. This would locate the formation of CH₄ 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). At the same time, most of the atomic C is locked up in CO, which will, at sufficiently low temperatures, stick to the grains as well. However, CH₄ is absent in non-polar ices. This could imply that during CH₄ formation, the atomic H abundance is still sufficiently high to efficiently hydrogenate accreted CO to CH₃OH. Using the model calculations on CH₃OH formation by Charnley et al. (1997), we find that this conclusion is supported by the low CO/CH₃OH ratio in the polar solid phase ($\sim 0.4$ toward NGC 7538 : IRS9; Allamandola et al. 1992; Tielens et al. 1991).

The low observed gas-to-solid state ratio for CH₄, contrary to CO, is a natural consequence of surface chemistry models. At low temperatures, no CH₄ is expected in the gas phase. The high derived temperature for gaseous CH₄ for both W 33A and NGC 7538 : IRS9 supports the location of the CH₄ in a hot core region near the protostar. Although pure CH₄ ice sublimes at $\sim 20$ K at low interstellar pressures, it sublimates at temperatures up to 90 K in polar ices, depending on the relative amount of CH₄ in the ice (see Sandford & Allamandola (1988) for a discussion on sublimation of H₂O:CO ices). The width and peak position of the interstellar CH₄ ice band indicate that the ratio of CH₄ ice with respect to polar molecules in the ice (H₂O and CH₃OH) is at most 10% (Sect. 3.3.2). Thus the CH₄ sublimation temperature is probably close to 90 K. The observed CH₄ excitation temperature is 70 and 110 K for NGC 7538 : IRS9 and W 33A respectively, and is expected to be close to the gas kinetic temperature. At the high densities in the hot core, the gas and dust temperatures are closely coupled (Ceccarelli et al. 1996), and therefore the observed warm gas phase CH₄ may indeed result from out-gassing of H₂O-rich ices. The somewhat higher gas-to-solid CH₄ ratio toward W 33A could then be related to the larger abundance of warm CO gas in this line of sight. Note that the CH₄ gas-to-solid ratio is significantly higher than the H₂O gas-to-solid ratio (Table 3.5), perhaps indicating that the CH₄ molecules diffuse out off the H₂O ice matrix at temperatures less than 90 K, well before the H₂O ice itself sublimates. We conclude that the presence of CH₄ in a polar ice and the low gas-to-solid ratio are naturally explained in the grain surface models of CH₄. These models are re-
stricled to have a high initial CO/C ratio, and an efficient CH$_3$OH formation at a high atomic H abundance.

Rather than grain surface chemistry, an origin of solid CH$_4$ in UV photolysis of CH$_3$OH containing ices has sometimes been suggested as well (Allamandola et al. 1988; Gerakines et al. 1996). The observed solid CH$_4$/CH$_3$OH ratios of 5\% (W 33A) and 15\% (NGC 7538 : IRS9; Table 3.4) have been reproduced in laboratory experiments (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$_3$OH ices also display a narrow feature near 5.82 $\mu$m, attributed to formaldehyde (H$_2$CO) and higher aldehydes. For irradiation doses consistent with the observed CH$_4$/CH$_3$OH ratio, this band should be $\sim$50\% deeper than the observed CH$_4$ feature, but it is not apparent in the spectrum of NGC 7538 : IRS9 (Schutte et al. 1996). Furthermore, judging from the strength of the 4.62 $\mu$m XCN feature, which is often ascribed to FUV photolysis of interstellar ices (Tegler et al. 1995, and references therein), FUV photolysis has been much more important towards W 33A than towards NGC 7538 : IRS9. Yet, the abundances of solid CH$_4$ are very similar and the solid state CH$_4$/H$_2$O and CH$_4$/CH$_3$OH ratios are much less toward W 33A than toward NGC 7538 : IRS9. Therefore, at present it seems unlikely that photo-processing of CH$_3$OH-rich ices is an important production mechanism of interstellar CH$_4$.

Alternatively, CH$_4$ may have been formed by low temperature gas phase chemistry (e.g. Millar & Nejad 1985; Helmich 1996) and preserved through accretion in ice mantles. In these models, the observed average abundance along the line of sight $X$(CH$_4$) $\sim$ 10$^{-6}$ is produced in a narrow time interval early in the collapsing phase. The high local abundance of $X$(CH$_4$) $\sim$ 10$^{-5}$ toward NGC 7538 : IRS9, if it were located in the same volume as the warm CO gas (Sect. 3.3.1), can never be reproduced by gas phase models. The length of the interval with large CH$_4$ abundances depends strongly on the assumed initial atomic C abundance, i.e. $t$ = (1 – 5) $\times$ 10$^5$ yr when starting from an atomic gas, and $t$ = (0.4 – 2) $\times$ 10$^5$ yr when starting from CO/C=10 (translucent clouds; Helmich 1996). The models with large initial CO/C ratios, and thus a lower CH$_4$ production, are probably more realistic. This is because the free fall time to form molecular clouds from diffuse, atomic clouds ($\sim$ 10$^7$ yr; e.g. Elmegreen 1987) is much larger than the time assumed in gas phase models to form hot cores (10$^5$ – 10$^6$ yr). Thus, at the start of the collapse, the gas is no longer atomic. After this short peak in the gas phase CH$_4$ abundance, the CH$_4$ 'burns' to CO, and consequently the observed CH$_4$ ice must originate from accretion during a very narrow time interval at $t$ $\sim$ 10$^5$ yr. Furthermore, at this (or any) stage of the collapse, little H$_2$O is present ($X$(H$_2$O) = 4 $\times$ 10$^{-7}$), and pure gas phase models cannot explain the formation of polar ice mantles. Grain surface formation of H$_2$O is needed to explain the presence of interstellar CH$_4$ in a polar ice mantle. Other molecules that, in this model, would be formed in the gas phase (CO, CH$_4$) will then co-condense with the atomic O and H and are trapped in the H$_2$O–rich ice. However, inevitably any accreted atomic C will react rapidly to CH$_4$ on the grain surface as well. Thus, if the observed CH$_4$ ice originates primarily from the gas, the CO/C ratio must have been very high during accretion. This
contradicts the low CO/C ratio required to explain the observed CH$_4$ abundance. Finally, at later times ($t > 5 \times 10^5$ yr) these gas phase models predict the absence of (cold) gas phase CH$_4$, since it is easily converted to CO (e.g., Helmich 1996). Since star formation has occurred in the cores of NGC 7538: IRS9 and W 33A, they are probably older than 0.5 million years, and indeed no cold CH$_4$ gas was detected toward these sources. The observed hot CH$_4$ gas is most likely located in a hot core near the protostar, where the gas phase composition reflects evaporated ice mantles. The species released from the grains in the hot core survive on a time scale of $\sim 10^4$ yr (Brown et al. 1988).

Concluding, the observations impose strict conditions on models of gas phase formation of CH$_4$. Contrary to the grain surface models, a low, perhaps unrealistic, initial CO/C abundance is required to explain the observed CH$_4$ abundance, and the time window for CH$_4$ production and accretion on the grains is narrow in any case. Additionally, the presence of CH$_4$ in a polar ice cannot be explained by pure gas phase models. Additional grain surface formation of H$_2$O and CH$_3$OH is required. We conclude that formation of CH$_4$ on grain surfaces is a more likely explanation.

### 3.5 Conclusions

We have obtained 7.35–7.85 $\mu$m spectra of the highly obscured massive 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 $\mu$m. We compare these spectra to laboratory simulations of interstellar solid CH$_4$. We conclude that the observed 7.67 $\mu$m absorption feature toward both sources can be attributed to absorption by the deformation mode of solid CH$_4$ in a polar matrix. Both H$_2$O–, and CH$_3$OH–rich ices can explain the observations. The solid CH$_4$ column density is $\sim 1\%$ of solid H$_2$O.

In addition, we report the detection of ro-vibrational lines of gaseous CH$_4$ in absorption toward both W 33A and NGC 7538: IRS9. From the rotational diagrams we conclude that the absorbing gas is warm toward both sources ($T = 110$ and 70 K respectively). The gas-to-solid CH$_4$ ratio is low, 0.7 and 0.3, and no cold gas has been detected, all in strong contrast with CO. Using velocity broadenings from rotational emission lines, we find that $N_{\text{hot}}/N_{\text{cold}} \geq 2$. A significant amount of cold CH$_4$ gas could be hidden in the data if the velocity broadening $b$ is much less than 2 km s$^{-1}$. High resolution (Fabry-Perot) infrared observations are needed to settle this issue.

We discuss models for the formation of interstellar CH$_4$. Gas phase models can explain the observed abundance ($X(\text{CH}_4) = 10^{-4}$), and the low CH$_4$ gas-to-solid ratio, but the observations impose strong restrictions. First, the presence of CH$_4$ in a polar ice is unexplained by these models, unless an alternative way (i.e., grain surface chemistry) of H$_2$O formation is invoked. Second, to inhibit at the same time grain surface formation of CH$_4$ the CO/C ratio must have been high during accretion. On the other hand, a low initial CO/C is required to produce
the observed abundance of interstellar CH$_4$ in the gas phase. Finally, the formation of CH$_4$ and subsequent accretion on the grains is limited to a narrow time interval ($t = (1 - 5) \times 10^5$ yr), which decreases for (probably more realistic) lower initial CO/C ratios. A more likely explanation is the formation of CH$_4$ from atomic C through grain surface reactions, similar to H$_2$O formation from atomic O. The presence of CH$_4$ in a polar ice mantle and the low gas-to-solid ratio are natural consequences of this model. Since this reaction is very efficient, a high CO/C ratio would be needed to explain the low observed CH$_4$ abundance, i.e. interstellar CH$_4$ is formed at the high densities deep inside the molecular cloud. To inhibit the inclusion of CH$_4$ in a non-polar ice, the accreted CO must have reacted on the grain surface with abundantly present atomic H to form CH$_3$OH, which is in agreement with the low CO/CH$_3$OH ratio in the polar solid phase. The detected warm CH$_4$ gas probably has sublimated from the grains at the high temperatures in the vicinity of the protostar. The gas-to-solid ratio of CH$_4$ is high compared with H$_2$O and may indicate a grain temperature $< 90$ K, when the CH$_4$ molecules diffuse out of the H$_2$O ice matrix, before the H$_2$O itself sublimates. That would be consistent with the derived CH$_4$ rotation temperature for NGC 7538 : IRS9, but seems unlikely at the higher derived temperature toward W 33A. Further laboratory work on the outgassing behaviour of CH$_4$ containing ices is needed, as well as a systematic determination of gas-to-solid ratios in lines of sight tracing different physical conditions.

3.6 Acknowledgements

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