METHANE ABUNDANCE VARIATIONS TOWARD THE MASSIVE PROTOSTAR NGC 7538 IRS 9^{1,2}

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Received 2004 March 4; accepted 2004 July 8

ABSTRACT

Absorption and emission lines originating from the ν_3 C–H stretching manifold of gas-phase CH_4 were discovered in the high-resolution ($R = 25,000$) infrared L -band spectrum along the line of sight toward NGC 7538 IRS 9. These observations provide a diagnostic of the complex dynamics and chemistry in a massive star-forming region. The line shapes resemble P Cygni profiles with the absorption and emission components shifted by $\sim 7 \text{ km s}^{-1}$ with respect to the systemic velocity. Similar velocity components were observed in CO at $4.7 \mu\text{m}$, but in contrast to CH_4 , the CO shows deep absorption due to a high-velocity outflow as well as absorption at the systemic velocity due to the cold outer envelope. It is concluded that the gas-phase CH_4 abundance varies by an order of magnitude in this line of sight: it is low in the envelope and the outflow ($X[\text{CH}_4] < 0.4 \times 10^{-6}$) and at least a factor of 10 larger in the central core. The discovery of solid CH_4 in independent ground- and space-based data sets shows that methane is nearly entirely frozen onto grains in the envelope. It thus appears that CH_4 is formed by grain surface reactions, evaporates into the gas phase in the warm inner regions of protostellar cores, and is efficiently destroyed in shocks related to outflows.

Subject headings: astrochemistry — infrared: ISM — ISM: abundances — ISM: molecules — stars: formation — stars: individual (NGC 7538 IRS 9)

1. INTRODUCTION

Among the suite of molecules observed in interstellar and circumprotostellar media,⁶ methane is relatively poorly studied. CH_4 has no permanent dipole moment and therefore cannot be observed by pure rotational transitions at radio wavelengths. Its strongest fundamental ($v = 1 - 0$) rovibrational transitions, i.e., the ν_3 C–H stretching and the ν_4 C–H bending modes, occur at 3.32 and $7.67 \mu\text{m}$, respectively. Strong telluric absorption at these wavelengths hinders interstellar CH_4 studies. Gas- and solid-phase CH_4 have been positively identified at $7.67 \mu\text{m}$ in three sight lines: the massive protostars NGC 7388 IRS 9, W33A, and GL 7009 S (Lacy et al. 1991; Boogert et al. 1996, 1997, 1998; Dartois et al. 1998). CH_4 was detected only in the solid state in low-resolution *Infrared Space Observatory* (ISO) observations at $7.67 \mu\text{m}$ toward ~ 30 low-mass protostars (White et al. 2000; Gürtler et al. 2002; Alexander et al. 2003), the Galactic center (Chiar et al. 2000), and an external galactic nucleus (Spoon et al. 2001). A recent low-resolution *Spitzer Space Telescope* spectrum shows absorption by solid CH_4 toward the young, low-mass protostar IRAS 08242+5100 (Noriega-Crespo et al. 2004; Boogert et al. 2004).

Observations of CH_4 provide insight into the basic principles of astrochemical networks. In the presence of atomic C and H, CH_4 is rapidly formed on cold grains, just as H_2O is formed

from atomic O and H (e.g., Brown et al. 1988). Perhaps surprisingly, the observed gas- and solid-state CH_4 abundances are low, not more than a few percent with respect to CO and H_2O (Lacy et al. 1991; Boogert et al. 1998). This points to relatively low atomic C abundances at the time of CH_4 formation, when most C is already locked up in CO. In this same scenario the high CH_3OH abundances in several lines of sight may be explained by hydrogenation of abundantly present CO (Dartois et al. 1999; Pontoppidan et al. 2003), and large CO_2 abundances may be explained by oxidation of CO. The dominance of a CO- and O-based, rather than C-based, chemistry is stressed by the profiles of solid CO_2 absorption bands, which show an intimate mixture of CO_2 , CH_3OH , and H_2O in the ices (Gerakines et al. 1999; Boogert et al. 2000). Nevertheless, even at relatively low abundances methane is proposed to be the starting point of a rich chemistry leading to the complex organic molecules observed in dense clouds like the TMC-1 ridge (Markwick et al. 2000). To further test the role of CH_4 in interstellar chemistry, basic diagnostics, such as gas-phase abundances, gas-phase/solid-phase abundance ratios, gas-phase temperatures, and abundance gradients need to be measured in more lines of sight.

In this work we report the discovery of absorption and emission features arising from the $3.32 \mu\text{m}$ C–H stretching mode of gas- and solid-phase CH_4 . A previous attempt to detect CH_4 at this wavelength was unsuccessful and indicated an abundance of less than 10^{-6} with respect to H in the Orion BN object (Knacke et al. 1985). We study the line of sight toward the massive protostar NGC 7538 IRS 9, because its high radial velocity of $V_{\text{lsr}} = -57 \text{ km s}^{-1}$ (e.g., van der Tak et al. 2000) facilitates the separation of telluric and interstellar lines. NGC 7538 IRS 9 is a well-studied massive protostar, known for its large ice and gas columns (Whittet et al. 1996; Mitchell et al. 1990) and a prominent molecular outflow (Mitchell et al. 1991). The $R(0)$ and $R(2)$ lines of the bending mode of gas-phase CH_4 and solid-state CH_4 were detected in this source by Lacy et al. (1991). Unambiguous confirmations of these detections were obtained with space-based observations (Boogert et al. 1996, 1998). Here we independently confirm the presence of CH_4 by detecting many lines from the $3.32 \mu\text{m}$ stretching mode as well

¹ Some of the data presented herein were obtained at the W. M. Keck Observatory, which is operated as a scientific partnership among the California Institute of Technology, the University of California, and the National Aeronautics and Space Administration. The Observatory was made possible by the generous financial support of the W. M. Keck Foundation.

² Based on observations with ISO, an ESA project with instruments funded by ESA Member States (especially the PI countries: France, Germany, the Netherlands, and the United Kingdom), and with the participation of ISAS and NASA.

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⁶ See the compilation at <http://www.cv.nrao.edu/~awootten/allmols.html>.

as the ice band. The high spectral resolution of these observations permits a line profile analysis in which we determine gas-phase conditions in the various environments along the line of sight, such as the envelope, the hot core, and the outflow. This in turn elucidates the formation and destruction pathways of CH_4 in these different environments.

The Keck/NIRSPEC and *ISO* SWS observations are discussed in § 2 and presented in § 3.1. A profile analysis of the gas-phase absorption and emission CH_4 lines, in conjunction with previously reported high-resolution CO observations, is presented in §§ 3.2.1 and 3.2.2. The ice band profile is discussed and compared with the C–H bending mode in § 3.3. The implications of these results on the formation and evolution history of the CH_4 molecule in protostellar environments are discussed in § 4.1. The origin of the low-velocity, warm gas, responsible for the P Cygni-like line profiles, is further constrained in § 4.2. We conclude with future prospects in § 5.

2. OBSERVATIONS

2.1. Keck/NIRSPEC $R = 25,000$ Spectroscopy

The high-resolution *L*-band spectrum of the massive protostar NGC 7538 IRS 9 was obtained with the NIRSPEC spectrometer (McLean et al. 1998) at the Keck II telescope atop Mauna Kea. Observations were made on five different nights with clear and dry weather conditions: UT 2002 December 17 and 18, 2003 July 10 and 11, and 2003 November 2. NIRSPEC was used in the echelle mode with the $0''.43 \times 24''$ slit, providing a resolving power of $R = \lambda/\Delta\lambda = 25,000$ ($\sim 12 \text{ km s}^{-1}$). The $2.9\text{--}4.1 \mu\text{m}$ region was almost fully covered in five echelle settings, each covering five Nyquist-sampled wavelength orders of $\sim 0.05 \mu\text{m}$ on the 1024^2 pixel array. Two small regions centered on 2.97 and $3.12 \mu\text{m}$ were not covered. The on-source integration time per setting was 20 minutes. Several CH_4 rovibrational lines, as well as the solid CH_4 band at $3.32 \mu\text{m}$, were observed multiple times to verify their reality. At $V_{\text{lsr}} = -57 \text{ km s}^{-1}$ for NGC 7538 IRS 9, the Doppler velocity with respect to Earth was -53.5 , -82.4 , and -64.0 km s^{-1} for the three observing runs. This proved to be sufficient to separate interstellar and telluric CH_4 lines and guarantees their reality. The spectra presented in this paper are an average of all the data. The data were reduced in a standard way, using IDL routines (Boogert et al. 2002). Atmospheric absorption features were divided out using the standard star HR 8585 (A1 V), which is bright ($V = 3.78$) and reasonably close to NGC 7538 IRS 9 (an air mass of $1.20\text{--}1.30$ vs. 1.34 for NGC 7538 IRS 9). The spectral shape and hydrogen absorption features in the standard star were divided out with a Kurucz model atmosphere. The hydrogen absorption profiles in the Kurucz model are accurate to 1%–2%, and residuals can be seen near strong lines. This does not affect the region of main interest for this paper ($3.15\text{--}3.65 \mu\text{m}$), except perhaps near $3.297 \mu\text{m}$, because of the $\text{H I Pf}\delta$ line. Overall, a good telluric correction was achieved, resulting in signal-to-noise ratio (S/N) values of ~ 110 in the region of CH_4 at $3.32 \mu\text{m}$, ~ 40 at the bottom of the H_2O ice band at $3.0 \mu\text{m}$, and ~ 200 at wavelengths greater than $3.5 \mu\text{m}$. Strong atmospheric lines, i.e., with less than 50% of the maximum transmission in each setting, leave residuals and were removed from the final spectrum. The spectra were wavelength-calibrated on the atmospheric emission lines, using an atmospheric model spectrum (P. van der Valk & P. Roelfsema 1995, private communication). All orders were subsequently combined by applying relative multiplication factors. For the analysis of the emission lines (§ 3.2.1), the spectrum is flux-calibrated by scaling to the

continuum brightness of the data presented in Whittet et al. (1996). Finally, in conjunction with the CH_4 features, we analyze Keck/NIRSPEC *M*-band CO lines in NGC 7538 IRS 9, previously published in Boogert et al. (2002).

2.2. ISO SWS $R = 1500$ Spectroscopy

The $3.26\text{--}3.38 \mu\text{m}$ spectral region of NGC 7538 IRS 9 was observed multiple times in the high-resolution $R = 1500$ AOT06 mode of the Short Wavelength Spectrometer (SWS) on board *ISO* (Kessler et al. 1996; de Graauw et al. 1996). From the *ISO* archive we have selected the longest integrations in this wavelength range, corresponding to TDT numbers 39002336 (UT 1996 December 11), 75101049 (UT 1997 December 5), and 85200455 (UT 1998 March 16). All observations were part of the ICE_BAND/DWHITTET guaranteed time program and have not been previously published. The combined on-target integration time in the $3.26\text{--}3.38 \mu\text{m}$ region amounts to 5219 s. The individual data sets were processed with SWS Interactive Analysis and calibration files, version 10.1, in 2003 April at SRON/Groningen. The three AAR products were combined, and the detector scans were aligned to the mean using second-order polynomials. Then, in this highly oversampled spectrum, data points deviating more than 3σ from the mean per resolution element were removed. Finally, the data points were averaged and re-sampled to an $R = 1500$ Nyquist-sampled grid. The resulting S/N is 100 but significantly poorer at the outer $0.015 \mu\text{m}$ edges.

3. RESULTS

3.1. Features in the $3.1\text{--}3.6 \mu\text{m}$ Spectral Region

The *L*-band spectrum of NGC 7538 IRS 9 is dominated by the deep absorption band of the O–H stretching mode of H_2O ice (Willner et al. 1982; Whittet et al. 1996). Its peak optical depth at $3.0 \mu\text{m}$ is ~ 4.5 . The most prominent substructure in the long-wavelength wing of H_2O is the well-known, yet unidentified, $3.47 \mu\text{m}$ absorption band (Allamandola et al. 1992; Brooke et al. 1996; Dartois et al. 2002). We applied a smooth spline continuum to extract this band on an optical depth scale (Fig. 1). The results were verified by applying low-order polynomials to continuum regions described in previous studies (e.g., Brooke et al. 1999). The absorption shape is in good agreement with the low-resolution spectrum of Allamandola et al. (1992), as is the presence of a subband at $3.53 \mu\text{m}$, attributed to the C–H stretching mode of solid CH_3OH . A previously undetected absorption band is apparent by a downturn in the continuum slope at $3.32 \mu\text{m}$. Although it is in a spectral region badly affected by the telluric CH_4 *Q*-branch, its presence is confirmed in Keck/NIRSPEC observations on different dates. In addition, a feature at the same wavelength is found in the space-based *ISO* SWS spectrum (Fig. 1). We thus conclude that this feature is real and is due to the stretching mode of solid CH_4 (§ 3.3). Not immediately obvious in Figure 1 but clearly detected on close inspection (Fig. 2) are *P*-, *Q*-, and *R*-branch lines of gas-phase CH_4 . This is the first time that the $3.32 \mu\text{m}$ ice and gas features have been detected in a circumprotostellar environment.

A number of additional features, not further discussed in this paper, are visible in the high-resolution Keck/NIRSPEC spectrum. Although they are reproduced in observations at different dates, they are entirely new and need to be confirmed in a larger sample of sources or, as for solid CH_4 , in independent data. A weak feature at $3.36 \mu\text{m}$ coincides with the C–H stretch modes of ethanol (Allamandola et al. 1992) and ethane (Boudin et al. 1998). Interestingly, another band of ethane at $3.47 \mu\text{m}$ seen in laboratory ices appears to be present in NGC 7538 IRS 9 as

FIG. 1.—The $R = 25,000$ Keck/NIRSPEC L -band spectrum of NGC 7538 IRS 9 on an optical depth scale, after correction for H_2O ice absorption. The broad, deep absorption is the well-known, yet unidentified, “ $3.47 \mu\text{m}$ ” absorption band. The presence of absorption by the C—H stretching mode of solid CH_4 is confirmed in the $R = 1500$ ISO SWS spectrum. P -, Q -, and R -branch wavelengths of gas-phase CH_4 are indicated at the top, where the numbers refer to the lower rotational J values. The gas-phase lines are further highlighted in Fig. 2. Additional solid-state absorption features are superposed on the $3.47 \mu\text{m}$ band. The most secure identification is that of methanol (Allamandola et al. 1992). Other possible identifications are indicated by arrows, but these are not further discussed in this paper: ethanol (Allamandola et al. 1992), ethane (Boudin et al. 1998), formaldehyde (Schutte et al. 1996), and diffuse medium aliphatic C—H stretching modes (Sandford et al. 1991). The weak, broad inflection near $3.25 \mu\text{m}$ is possibly due to absorption by aromatic hydrocarbons (Brooke et al. 1999).

FIG. 2.—Magnification of the Keck/NIRSPEC spectrum of NGC 7538 IRS 9 in spectral regions surrounding gas-phase CH_4 rovibrational lines ($\Delta\lambda = 0.006 \mu\text{m}$ or $\Delta v = 530 \text{ km s}^{-1}$). This is the same data as shown in Fig. 1, but on a flux/continuum scale. The gaps in the spectra are regions with less than 50% atmospheric transmission that were removed from the data. The thick gray line superposed on each observed spectrum depicts a two-component LTE model, composed of a 6 km s^{-1} blueshifted absorption component ($T = 55 \text{ K}$, $N = 2.5 \times 10^{16} \text{ cm}^{-2}$) and an 8 km s^{-1} redshifted emission component ($T = 600 \text{ K}$, $N = 5.8 \times 10^{16} \text{ cm}^{-2}$; Table 4). The rovibrational transition, the lower rotational energy level (in K), and the center wavelength (in μm) are indicated in the bottom left and right corners of each panel, respectively. Note that CH_4 emission is detected up to the highest excitation levels, i.e., up to $R(15)$ and $P(14)$.

well. Finally, weak absorptions at 3.47 and 3.41 μm are also close to the C—H stretch mode of single-bonded carbon in CH and CH₂ groups in aliphatic hydrocarbons, normally seen in diffuse lines of sight only (e.g., Pendleton et al. 1994).

3.2. Gas-Phase Line Profiles at $R = 25,000$

3.2.1. Gas-Phase CH₄

Rovibrational absorption and emission lines of gaseous CH₄ are clearly detected toward NGC 7538 IRS 9 (Fig. 2). Although the telluric CH₄ lines are deep, the large blueshift of NGC 7538 IRS 9 with respect to the Earth (§ 2.1) separates many interstellar lines well. The lines appear mostly in absorption up to lower energy levels with $J = 3$, and entirely in emission above $J = 6$. Intermediate J levels have P Cygni–like line profiles, i.e., redshifted emission and blueshifted absorption. Such line profiles are usually associated with expanding envelopes (see § 4.2, however). Note that for $J > 4$ multiple emission and absorption peaks appear for each J level. These line splittings are intrinsic to the CH₄ molecule and result from rotation-vibration interactions with the spin manifolds of the four equivalent H nuclei. Thus E-, F-, and A-type multiplets occur with spin statistical weights of $g_s = 2, 3$, and 5, respectively.

The observed lines are analyzed using the 2001 update of the HITRAN 2000 database (Rothman et al. 2003; Brown et al. 2003). All HITRAN transitions contributing to each observed interstellar line are identified, and the number of transitions responsible for at least 90% of the line strength is indicated in column (3) of Tables 1 and 2. For example, at the resolution of our observations, the $P(11)$ transition is split into four separate emission lines, which are composed of some nine strong transitions. The contribution of each observed line to the total emission or absorption per J level is indicated in column (4) of Tables 1 and 2 and is calculated in the optically thin limit as

$$\frac{F'_J}{F_J} = \frac{\sum_i g_{i,J} A_{i,J}}{\sum_n g_{n,J} A_{n,J}} \times 100\%, \quad (1)$$

where $g_{i,J}$ is the product of the rotation ($2J+1$) and nuclear spin (g_s) statistical weights and $A_{i,J}$ is the corresponding Einstein coefficient for transition i at rotational level J . The summation over i is for all transitions in the wavelength range of an observed emission line (col. [2] in Tables 1 and 2), while the summation over n is for all transitions at rotational level J . For several J levels only part of the emission or absorption is observed as some components lie in poor atmospheric regions. For example, only half of the $R(8)$ line flux is seen, and for the Q -branch the clearly detected absorption component represents only a few percent of the total Q -branch absorption. Finally, the observed emission-line fluxes F'_J listed in Table 1 are corrected for the underlying H₂O absorption using a wide-coverage ISO SWS spectrum (Whittet et al. 1996). The resulting continuum flux of 1.5 Jy is corrected for foreground extinction using the Galactic extinction law (Draine 2003) and the A_V derived in § 4.2. Thus, the observed line fluxes are scaled to an unextincted continuum flux of 23.7 Jy.

In order to derive basic physical parameters, we construct a rotation diagram for the CH₄ emission lines. The Boltzmann equation of a single transition i at upper rotational level J is

$$\frac{N_{i,J}}{g_{i,J}} = \frac{N_{\text{tot}}}{Q(T_{\text{rot}})} e^{-E_{i,J}/kT_{\text{rot}}}, \quad (2)$$

TABLE 1
CH₄ EMISSION-LINE STRENGTHS TOWARD NGC 7538 IRS 9

$\Delta v(J)$ (1)	λ^a (μm) (2)	Lines ^b (3)	F'_J/F_J^c (%) (4)	F'_J^d ($10^{-21} \text{ W cm}^{-2}$) (5)
$R(15)$	3.15812–3.15864	11	84	5.2 (1.1)
	3.15767–3.15792	3	13	<3.3
$R(14)$	3.16677–3.16720	13	73	3.8 (0.7)
	3.16626–3.16665	5	26	1.5 (0.4)
$R(13)$	3.17545–3.17595	13	81	9.0 (0.8)
	3.17498–3.17534	4	16	4.3 (0.8)
$R(12)$	3.18435–3.18485	14	74	13.6 (3.0)
	3.18390–3.18428	4	26	4.8 (0.5)
$R(11)$	3.19295–3.19325	2	21	3.8 (1.5)
$R(10)$	3.20211–3.20253	3	34	3.5 (1.0)
$R(9)$	3.21178–3.21229	6	78	10.7 (3.0)
	3.21146–3.21179	2	22	3.0 (0.8)
$R(8)$	3.22087–3.22118	3	47	4.8 (0.8)
$R(6)$	3.24014–3.24080	6	100	25.1 (1.5)
$R(5)$	3.25019–3.25064	4	100	12.5 (1.4)
$R(4)$	3.26017–3.26054	4	100	7.5 (1.0)
$R(3)$	3.27035–3.27063	3	100	6.6 (0.5)
$R(1)$	3.29105–3.29127	1	100	1.5 (0.5)
$R(0)$	3.30165–3.30187	1	100	1.5 (0.6)
$P(2)$	3.33435–3.33463	2	100	1.8 (0.4)
$P(3)$	3.34573–3.34600	3	45	2.1 (0.5)
$P(4)$	3.35708–3.35736	1	23	1.9 (0.6)
	3.35679–3.35703	3	77	1.9 (0.9)
$P(5)$	3.36860–3.36901	2	45	≥ 4.8
	3.36814–3.36860	2	55	4.5 (0.6)
$P(6)$	3.37967–3.38022	3	48	7.8 (0.8)
$P(7)$	3.39182–3.39230	2	42	>5
	3.39138–3.39176	2	32	3.5 (0.4)
$P(8)$	3.40379–3.40411	1	14	≥ 1.6
	3.40318–3.40370	3	48	6.8 (0.4)
$P(9)$	3.41577–3.41613	2	18	>2.7
	3.41509–3.41560	2	22	4.1 (0.4)
$P(10)$	3.42719–3.42772	3	35	4.2 (0.7)
$P(11)$	3.44128–3.44172	3	30	3.2 (0.4)
	3.44072–3.44109	1	11	1.6 (0.2)
	3.44009–3.44057	3	37	3.9 (0.2)
	3.43944–3.43982	2	22	2.0 (0.2)
$P(12)$	3.45380–3.45441	4	43	4.7 (0.3)
	3.45313–3.45347	2	13	1.4 (0.3)
	3.45252–3.45296	2	16	1.1 (0.4)
	3.45175–3.45208	3	27	1.9 (0.3)
$P(13)$	3.46664–3.46711	3	23	1.1 (0.4)
	3.46566–3.46629	3	31	0.8 (0.3)
	3.46501–3.46548	3	28	1.8 (0.3)
	3.46406–3.46457	2	17	0.8 (0.3)
$P(14)$	3.47952–3.48004	3	22	1.9 (0.4)
	3.47814–3.47899	4	35	0.6 (0.3)
	3.47757–3.47796	2	16	<0.8
	3.47659–3.47707	3	27	1.7 (0.4)

^a Integration region after correction for 8 km s^{−1} redshift.

^b Number of blended lines in integration interval.

^c Percentage of emission with respect to total emission for this upper J level.

^d 1 σ errors in parentheses.

where $N_{i,J}$ and $E_{i,J}$ are the column density and the energy of the upper level of a single multiplet component, respectively. Assuming that collisional excitation is applicable, $E_{i,J}$ includes a vibrational $v = 1$ excitation energy of 4348 K (Lide 1994); N_{tot} and T_{rot} are the total CH₄ column density and rotational temperature. Throughout this paper we take the rovibrational partition function, $Q(T_{\text{rot}})$, from the HITRAN database, which

TABLE 2
CH₄ ABSORPTION-LINE STRENGTHS TOWARD NGC 7538 IRS 9

$\Delta\nu(J)$ (1)	λ^a (μm) (2)	Lines ^b (3)	F'_J/F_J^c (%) (4)	Equivalent Width ^d (10^{-3} cm^{-1}) (5)
$R(4)$	3.26003–3.26031	3	77	10.0 (1.4)
$R(3)$	3.27019–3.27051	3	100	12 (1)
$R(1)$	3.29092–3.29121	1	100	12.7 (0.4)
$R(0)$	3.30151–3.30179	1	100	17.6 (1.0)
Q	3.31234–3.31296	4	2	35 (6)
$P(2)$	3.33423–3.33453	2	100	6.5 (0.8)
$P(3)$	3.34530–3.34584	3	100	12.3 (0.7)
$P(4)$	3.35660–3.35694	3	61	5.9 (0.8)

^a Integration region after correction for 6 km s⁻¹ blueshift.

^b Number of blended lines in integration interval.

^c Percentage of absorption with respect to total absorption for this lower J level.

^d 1 σ errors in parenthesis.

is applicable at $T_{\text{rot}} = 70\text{--}3000$ K (Fischer et al. 2003). At lower temperatures we calculate $Q(T_{\text{rot}})$ from lines in the HITRAN database. In the optically thin limit, the flux F'_J of a partial J transition is obtained by summation over all multiplet lines,

$$F'_J = \sum_i F_{iJ}, \quad (3)$$

and thus the observed F'_J relates to equation (2) as

$$\frac{4\pi F'_J}{hc\nu_J \Omega \sum_i g_{iJ} A_{iJ}} = \frac{N_{\text{tot}}}{Q(T_{\text{rot}})} e^{-E_J/kT_{\text{rot}}}. \quad (4)$$

Here we make use of the fact that the upper energy level E_J and transition frequency ν_J are nearly the same for all multiplet lines (to within 0.1%); Ω is the size of the emitting region, for which we assume the value of 4.3×10^{-14} sr derived from CO emission lines, 2 orders of magnitude smaller than the solid angle corresponding to the $0''.42$ wide slit (§ 4.2). The rotation diagram constructed from the observed CH₄ emission lines indicates a rotational temperature of 600 ± 100 K (Fig. 3). Although T_{rot} is well constrained, the derived column density of $5.8^{+1.6}_{-3} \times 10^{16} \text{ cm}^{-2}$ is accurate to within a factor of ~ 3 only (3 σ errors).

To further illustrate the goodness of fit, to investigate possible optical depth effects, and to model the complex blend of CH₄ absorption and emission lines, we have also constructed single-temperature LTE models. The level populations are calculated according to equation (2). Emission-line fluxes and absorption equivalent widths at any optical depth are calculated following Genzel (1992) and Spitzer (1978), respectively, applying the Voigt function for the line profiles. The observed line profiles are fitted by adding a single-temperature redshifted emission model to a single-temperature, blueshifted absorption model. We find that a blueshift of 6 km s⁻¹ and a redshift of 8 km s⁻¹ are needed, and that both components are unresolved at the spectral resolution of 12 km s⁻¹. The validity of the temperature and column density derived from the emission-line rotation diagram is confirmed by the relatively low model line optical depth; for example, at a Doppler parameter of $b_D = 1$ km s⁻¹, $N_{\text{tot}} = 5.8 \times 10^{16} \text{ cm}^{-2}$, and $T = 600$ K, the peak optical depth is 0.33 [in the $R(8)$ line]. The absorption column is well constrained to $N(\text{CH}_4) = 3 \pm 1 \times 10^{16} \text{ cm}^{-2}$ at $T_{\text{ex}} = 55 \pm 15$ K for intrinsic

FIG. 3.—Rotation diagram of CH₄ emission lines toward NGC 7538 IRS 9. P-branch lines are shown by filled circles, and R-branch lines are shown by open circles. The solid line represents a least-squares best fit to the data corresponding to a rotational temperature of 600 K at a column density of $5.8 \times 10^{16} \text{ cm}^{-2}$ in a solid angle of 4.3×10^{-14} sr. The dashed lines represent extreme (3 σ) physical parameters that still fit the data: $T_{\text{rot}} = 500$ K and $N(\text{CH}_4) = 20 \times 10^{16} \text{ cm}^{-2}$, and $T_{\text{rot}} = 700$ K and $N(\text{CH}_4) = 2.6 \times 10^{16} \text{ cm}^{-2}$.

line widths of $b_D = 0.5\text{--}3$ km s⁻¹ (Table 4). The narrowest lines are optically thick ($\tau = 5$ at $b_D = 0.5$ km s⁻¹), while they are optically thin for $b_D > 1$ km s⁻¹. We take $b_D = 3$ km s⁻¹ as a preferred value throughout this paper, because the larger line widths are usually preferred toward NGC 7538 IRS 9 (Mitchell et al. 1990; Boonman & van Dishoeck 2003), but values of $b_D > 3$ km s⁻¹ are inconsistent with the unresolved CH₄ lines observed. The physical parameters derived from the CH₄ stretching mode are in good agreement with the parameters from the bending mode at $7.67 \mu\text{m}$ in lower resolution spectra (Lacy et al. 1991; Boogert et al. 1998).

Finally, absorption or emission lines of the ¹³CH₄ and CH₃D isotopes have not been detected. Study of the ¹³CH₄ lines is complicated, because the isotope wavelength shift is comparable to the separation of J levels, and thus the ¹³CH₄ and ¹²CH₄ lines are blended. The column density upper limits are a factor of 3–7 smaller compared to the CH₄ column density. At ¹²C/¹³C and H/D isotope ratios of at least 50 in dense clouds (Wilson & Rood 1994; Ceccarelli et al. 2001), these upper limits are not significant.

3.2.2. Gas-Phase CO

At first glance, the line profiles of the fundamental rovibrational CO transitions at $4.7 \mu\text{m}$, as published in Mitchell et al. (1990) and Boogert et al. (2002), look similar to those of CH₄. They show P Cygni profiles as well, in ¹²CO, ¹³CO, and perhaps even the C¹⁸O isotope, with the strength of emission versus absorption increasing for higher J levels. On closer inspection, however, the absorption profiles of CO and CH₄ differ. The low- J isotopic CO lines peak at 0 km s⁻¹, compared to -6 km s⁻¹ for CH₄ (Fig. 4a). Higher J CO lines ($E_{\text{low}} \geq 100$ K), on the other hand, are dominated by absorption at blueshifted velocities ≥ 16 km s⁻¹, which is absent in CH₄ (Fig. 4b). This provides clues to the formation and evolution history of CH₄ (§ 4.1), and in this context it is relevant to quantify the physical conditions of the absorbing and emitting CO gas as well (Table 4).

FIG. 4.—Line profiles of CH₄ and CO isotopologues on a velocity scale corrected for the earth and heliocentric velocity. Lines of similar lower energy level are plotted: (a) 0 K and (b) ~100 K. For reference, we have indicated the systemic velocity with a vertical dashed line. Note the very different profile of CH₄ compared to CO lines. The -16 km s⁻¹ outflow is absent in CH₄, and the R(0) CH₄ line does not peak at the systemic velocity, indicating that CO and CH₄ have a different chemical origin and evolution (§ 4.1). (c) Emission-dominated CH₄ and CO line profiles. The high-*J* CO line profile toward NGC 7538 IRS 9 is an average over the individual lines *P*(27), *P*(28), *P*(30), and *P*(34). The emission lines clearly peak at +8 km s⁻¹, opposite what is expected for P Cygni line profiles (§ 4.2).

We analyzed the $R = 25,000$ Keck/NIRSPEC spectrum of Boogert et al. (2002) and arrive at different conclusions compared to Mitchell et al. (1990, 1991). First, and most importantly, in the Keck/NIRSPEC data blueshifted absorption at 16 km s⁻¹ is seen up to J levels as high as 20, but only up to $J = 3$ in Mitchell et al. (1991). In the rotation diagram constructed from the integrated ¹³CO absorption equivalent widths, this high-velocity gas is responsible for the linear part above energies of 100 K (Fig. 5; Table 3). From this a column density of $N(^{12}\text{CO}) = 3.5 \pm 1.0 \times 10^{18} \text{ cm}^{-2}$ at a temperature of $T_{\text{rot}} = 270 \pm 100 \text{ K}$ (3σ) is derived. The column density is comparable to that found by Mitchell et al. (1991), but T_{rot} is a factor of 10 higher in the Keck/NIRSPEC data. A second difference is that C¹⁸O lines are detected in the high S/N Keck/NIRSPEC data. The ¹³CO/C¹⁸O absorption-line ratios of corresponding J levels are equal to the interstellar isotope ratio of 6.9 at large Galactocentric radii (Wilson & Rood 1994) within a 20% error margin (see the C¹⁸O data points in the ¹³CO rotation diagram; Fig. 5). An important consequence is that reliable CO column densities can be derived, and thus reliable CH₄ abundances in the various velocity ranges (§ 4.1). The steep part of the ¹³CO rotation diagram, corresponding to gas at velocities of -8 to +11 km s⁻¹, indicates $T_{\text{rot}} = 20 \pm 7 \text{ K}$ and a column density of $N(^{12}\text{CO}) = 3.5 \pm 1.0 \times 10^{18} \text{ cm}^{-2}$, which is a factor of 4 less compared to that found by Mitchell et al. (1990). This is due to our factor of 2 smaller measured equivalent widths and presumably lower assumed line opacity.

For the emission lines, the observed ¹²CO/¹³CO peak strength ratio is 6 ± 2 at intermediate upper J levels of 7–15. Using the standard radiative transfer equation, the peak optical depth of the ¹²CO emission lines, τ_{12} can be derived from

$$\frac{F(^{12}\text{CO})}{F(^{13}\text{CO})} = \frac{1 - e^{-\tau_{12}}}{1 - e^{-\tau_{12}/80}}. \quad (5)$$

At a ¹²CO/¹³CO isotope ratio of 80 (Boogert et al. 2002), it follows that $\tau_{12} = 13 \pm 4$. Such an optical depth corresponds

to a column density of $N(^{12}\text{CO}) = 3.2 \pm 1.0 \times 10^{18} \text{ cm}^{-2}$ at an intrinsic line width of $b_D = 3 \text{ km s}^{-1}$. We further discuss the origin of the emitting gas in § 4.2.

3.3. The Solid CH₄ Absorption Bands

Solid CH₄ has been detected by its C–H bending mode at 7.67 μm in ISO SWS observations of NGC 7538 IRS 9

FIG. 5.—Rotation diagram of ¹³CO (filled circles) and C¹⁸O (open circles) absorption lines toward NGC 7538 IRS 9. The C¹⁸O column densities have been scaled up by a factor of 6.9 to match the abundance of interstellar ¹³CO (Wilson & Rood 1994). The good agreement of these isotopes in this plot implies that the ¹³CO absorption lines are optically thin. The solid line represents a two-component gas with rotational temperatures of 20 and 270 K both at a ¹³CO column density of $4.65 \times 10^{16} \text{ cm}^{-2}$. Note that the 20 K gas absorbs at the systemic velocity, while the warm component absorbs at much higher velocity (Fig. 4).

TABLE 3
GAS-PHASE CO ABSORPTION TOWARD NGC 7538 IRS 9

$\Delta v(J)^a$	EQUIVALENT WIDTH ^b (10^{-3} cm^{-1})	
	^{13}CO	C^{18}O
$R(18)$	2 (1)	...
$R(17)$	5 (2)	...
$R(16)$	3 (1.1)	...
$R(15)$	6.5 (2)	...
$R(13)$	10 (2)	...
$R(12)$	16 (3)	...
$R(11)$	12 (4)	<4.5
$R(10)$	16 (3)	<4.5
$R(9)$	18 (5)	5 (1)
$R(7)$	30 (8)	2.2 (1.0)
$R(6)$	30 (2)	3.9 (1.2)
$R(5)$	41 (3)	4.7 (1.2)
$R(4)$	71 (4)	5.6 (1.0)
$R(3)$	71 (4)	5.2 (0.8)
$R(2)$	...	13.7 (1)
$R(0)$	55 (3)	10 (2)
$P(1)$	55 (2)	6.4 (1.5)
$P(2)$	56 (3)	...
$P(3)$	74 (2)	...
$P(4)$	27 (2)	...
$P(18)$	<15	...
$P(19)$	3.4 (0.4)	...
$P(21)$	2.5 (0.8)	...
$P(22)$	<6	...

^a Transitions not listed have not been observed, are in a poor atmospheric region, or are blended with a brighter isotope.

^b 1 σ errors in parentheses.

(Boogert et al. 1996). The peak position and width of the interstellar band are well fitted with an amorphous, low-temperature (10 K) laboratory ice in which CH_4 is diluted in an H_2O matrix. This same laboratory ice gives an excellent fit to the new $3.32 \mu\text{m}$ absorption feature detected in the Keck/NIRSPEC and ISO SWS spectra, not only in peak position and width, but also to the peak optical depth of 0.1. We thus attribute this interstellar band in its entirety to the C—H stretching mode of solid CH_4 in an H_2O -rich ice (Fig. 6). A mismatch with the observed ISO SWS spectrum on the low-wavelength wing is attributed to emission by the strong Q -branch of gaseous CH_4 (Fig. 6). Indeed, a better match is obtained after subtracting the model constructed from the observed P - and R -branch lines from the ISO SWS spectrum (§ 3.2.1). In contrast, contamination of gas-phase emission to the $7.67 \mu\text{m}$ ice band is small because the continuum emission at this wavelength is more than an order of magnitude brighter compared to the continuum at $3.32 \mu\text{m}$ (Whittet et al. 1996). Indeed, a weak inflection at $7.66 \mu\text{m}$ is due to Q -branch absorption. Simultaneous fits of the C—H stretch and bend modes highlight the good fit of $\text{CH}_4:\text{H}_2\text{O}$ ices (Fig. 6). Pure CH_4 ices and mixtures with CO, otherwise highly abundant in this line of sight (Tielens et al. 1991; Boogert et al. 2002), can be excluded at a high confidence level. Note that the C—H stretching mode of CH_4 better discriminates between polar and apolar ices than does the bending mode. Mixtures with other high-dipole molecules, such as NH_3 and CH_3OH , do not provide equally good fits compared to H_2O , but at present we cannot exclude combinations of these polar species.

4. DISCUSSION

4.1. Astrochemical Implications

The detections of both the $3.32 \mu\text{m}$ stretch and the $7.67 \mu\text{m}$ bend modes firmly establish the presence of both gaseous and solid CH_4 in the interstellar medium. The gas-state+solid-state abundance averaged along the line of sight of the massive

FIG. 6.—(a) Stretching mode of solid CH_4 observed with ISO SWS (thick histogram) and KECK/NIRSPEC (thin histogram), compared to a number of laboratory ice simulations (smooth gray line). At the very top the effect of removing the Q -branch emission of gas-phase CH_4 is shown. (b) The CH_4 bending mode is fitted with the same laboratory ice, without scaling the peak optical depth. Best fits are obtained with H_2O -rich ices. Note the poor fit of CO-rich ices to the CH_4 stretching mode.

TABLE 4
CH₄ AND CO PHYSICAL PARAMETERS TOWARD NGC 7538 IRS 9

Species	Location ^a	Phase ^b	V^c (km s ⁻¹)	T_{ex}^d (K)	N^d (10 ¹⁷ cm ⁻²)	$N/N_{\text{H}}^{d,e}$ (10 ⁻⁶)	Notes
CH ₄	Outflow	Gas/absorption	-16	270	<0.1	<0.4	Assumed T
CH ₄	Core	Gas/absorption	-6	55 ± 15	0.3 ± 0.1	≥3	$b_D = 0.5-3$ km s ⁻¹
CH ₄	Envelope	Gas/absorption	0	20	<0.1	<0.3	Assumed T
CH ₄	Core	Gas/emission	+8	600 ± 100	0.58 ^{+1.6} _{-0.3}	1.9 ^{+7.2} _{-0.9}	4.3 × 10 ⁻¹⁴ sr ^f
CH ₄ ^g	Envelope	Ice/absorption	...	...	1.3 ± 0.1	2.1 ± 0.7 ^h	
CO.....	Outflow	Gas/absorption	-16	270 ± 100	35 ± 10	100	Optically thin ¹³ CO
CO.....	Core	Gas/absorption	-6	55	<10	100	Assumed T
CO.....	Envelope	Gas/absorption	0	20 ± 7	35 ± 10	100	Optically thin ¹³ CO
CO.....	Core	Gas/emission	+8	500 ± 150	30 ± 10 ⁱ	100	4.3 × 10 ⁻¹⁴ sr ^f
CO ^j	Envelope	Ice/absorption	...	...	18 ± 2	36 ± 10 ^h	

^a Assumed location from velocity; see also §§ 4.1 and 4.2.

^b In gas or ices, in emission or absorption.

^c Velocity with respect to systemic $V_{\text{lsr}} = 57$ km s⁻¹.

^d Errors are 3 σ .

^e Assuming $N_{\text{H}}/\text{CO} = 1 \times 10^4$ from Lacy et al. (1994).

^f Solid angle derived from CO emission.

^g Boogert et al. (1998).

^h Ice abundance with respect to CO gas+ice abundance in envelope.

ⁱ Uncertainty in column dominated by uncertainty in line opacity.

^j Boogert et al. (2002).

protostar NGC 7538 IRS 9 is $X[\text{CH}_4] = 2 \times 10^{-6}$, and the absorption gas-state/solid-state abundance ratio is 0.23. A combined high-resolution CO/CH₄ line profile analysis shows that the abundance, as well as the gas-state/solid-state abundance ratio of CH₄, varies *locally* by an order of magnitude, however (Table 4). An ice+gas abundance of a few $\times 10^{-6}$ is found in the outer envelope (systemic velocity), the inner envelope (-6 km s⁻¹), and the compact emission component (+8 km s⁻¹). In the outer envelope, at 20 K, the coldest component along the line of sight, at least 90% of the CH₄ is frozen on grains. Within the envelope a segregation is present as well; CH₄ is intimately mixed with H₂O and CH₃OH rather than with CO. In the warm, low-velocity inner regions of NGC 7538 IRS 9, CH₄ is mostly present in the gas phase. These enhanced abundances strongly contrast with the absence of CH₄ in the massive, high-velocity -16 km s⁻¹, warm ($T \simeq 270$ K) outflow seen in CO ($X[\text{CH}_4] < 0.4 \times 10^{-6}$).

These new results provide clues to the formation and evolutionary history of CH₄, refining previous scenarios (Lacy et al. 1991; Boogert et al. 1998). In time-dependent pure gas-phase models, such as the “standard” dense cloud model of Lee et al. (1996) and the UMIST model of Millar et al. (1997), gas-phase CH₄ abundances of a few $\times 10^{-6}$ are achieved after 10⁵ yr. Although this is comparable to the observed abundances, there are strong arguments against a gas-phase origin: the low gas-state/solid-state ratio, and the intimate mixture between CH₄ and H₂O in the ices in the envelope. For comparison, CO, a typical gas-phase product, has an order-of-magnitude larger gas/solid phase ratio compared to CH₄, even in the cold gas phase. H₂O, on the other hand, is formed by hydrogenation of oxygen on the grains at low temperatures (e.g., Jones & Williams 1984), and a low gas/solid-state ratio is observed (Boonman & van Dishoeck 2003). It is thus likely that CH₄ was formed on grain surfaces by hydrogenation of atomic C, at the same time that H₂O was formed from atomic O. The low observed CH₄ abundance points to a formation time when most of the C was already locked up in CO (Boogert et al. 1998).

The gas-phase CH₄ abundance in the -6 and +8 km s⁻¹ components is comparable to the solid-state abundance in the

envelope. The CH₄ may thus have been released from the grains in the inner regions near the protostar. Because CH₄ is diluted in an H₂O-rich ice (Fig. 6), its sublimation temperature is close to that of H₂O: 90 K (Tielens & Whittet 1996; Hiraoka et al. 1998). The temperature of the +8 km s⁻¹ emission component is indeed well above 90 K. The gas at -6 km s⁻¹, however, has a temperature of 55 ± 15 K only. While in one massive protostar, W33A, CH₄ gas at $T = 110$ K was detected (Boogert et al. 1998), a lower temperature of 50 K was also measured in another line of sight, GL 7009S (Dartois et al. 1998). We speculate that the icy mantles did not thermally evaporate as a result of protostellar radiative heating, but by a mild shock that has briefly heated the grains above 90 K. Subsequently, the gas has cooled radiatively or adiabatically as the inner NGC 7538 IRS 9 core expands outward with a (current) velocity of 6 km s⁻¹.

Shocks may have had a profound impact on the higher velocity gas. CH₄ is absent at velocities of 16 km s⁻¹ and above, where warm CO ($T = 280$ K) is very abundant. After release from the grains, CH₄ must have efficiently chemically reacted. The observed CO velocities up to 35 km s⁻¹ point to the presence of nondestructive C-type shocks. These shocks have been well studied in the context of molecular chemistry. At initial densities of 10⁵ cm⁻³, shocks with velocities of 15–35 km s⁻¹ have peak temperatures of 500–2500 K (Bergin et al. 1998). At such high temperatures, and at the low expected shock pressures,⁷ CH₄ is rapidly driven into CO (Prinn & Fegley 1989). The occurrence of a C shock therefore explains the absence of CH₄ in the outflow of NGC 7538 IRS 9. The importance of shock chemistry in high-mass cores was deduced from low gas/solid CO₂ abundance ratios as well (Charnley & Kaufman 2000), and by the abundance ratios of S-bearing species (Hatchell & Viti 2002). One distinct characteristic of shock chemistry is the formation of H₂O at temperatures above 250 K (e.g., Bergin et al. 1998). H₂O columns comparable to CO are expected, i.e., 2.8×10^{18} cm⁻²

⁷ $\log_{10}(P) = -13$ bar, assuming a factor of 2 density enhancement at a maximum temperature of 2500 K for a 35 km s⁻¹ shock (Kaufman & Neufeld 1996; Bergin et al. 1998).

for the NGC 7538 IRS 9 outflow (Table 4). This is a factor of 3.5 larger than the upper limit to the gas-phase H_2O abundance derived from *ISO* SWS $6\ \mu\text{m}$ spectra (Boonman & van Dishoeck 2003). High-resolution $6\ \mu\text{m}$ spectra are required to further investigate the presence of H_2O in the line of sight of NGC 7538 IRS 9, the effect of blended emission and absorption components, and the relation to shocks and outflows.

4.2. Nature of the Low-Velocity Warm Gas

The elevated temperature of the low-velocity, $6\text{--}8\ \text{km s}^{-1}$, absorption and emission components seen both in CO and CH_4 locates this gas in the inner regions of the protostellar core. The present observations further constrain the origin of this material.

The area of the radiating physical body can be calculated by matching the ^{12}CO column density derived from the isotope ratio (§ 3.2.2) to the emission-line fluxes. The measured ^{12}CO line fluxes need to be corrected for continuum absorption by foreground material. We derive a $4.7\ \mu\text{m}$ continuum extinction magnitude of $A_{4.7} = 1.8 \pm 0.6$ using the interstellar extinction law of Draine (2003) and an optical extinction A_V of 60 ± 20 . The latter is derived from the A_V/N_{H} relation of Bohlin et al. (1978), and the average line-of-sight hydrogen column density from this work (Table 4) and that from the silicate absorption band (Tielens et al. 1991). The extinction-corrected line fluxes are thus matched at a solid angle of 4.3×10^{-14} sr. At the distance to NGC 7538 IRS 9 of 2.8 kpc (Crampton et al. 1978) this corresponds to a radius of 70 AU. The similarity of CO and CH_4 velocities and emission-line widths (Fig. 4c) indicates that both molecules are present in this same volume.

The CO and CH_4 gas detected on these scales may well be related to the dense material that was inferred on scales of $\leq 300\text{--}600$ AU from unresolved 3 mm continuum interferometer images (van der Tak et al. 2000). This intense emission is unrelated to the envelope and instead may originate from a dense shell or circumstellar disk. The P Cygni-like line profiles in both CO and CH_4 may suggest that an expanding envelope is the preferred geometry. In these line profiles the absorption component is redshifted by the shell expansion velocity, and the emission component is centered at the systemic velocity and is broadened by twice the expansion velocity. Mitchell et al. (1991) argue that the CO emission component is blueshifted because of the effect of deep absorption by foreground material at the systemic velocity. This hypothesis can be tested by the profiles of the highest J transitions, which should not have foreground contributions. We find that even the lines from the highest rotational levels of CO are blueshifted by $+8\ \text{km s}^{-1}$ (Fig. 4c). Furthermore, the CH_4 emission lines peak at this same velocity and are also unresolved. Perhaps the NGC 7538 IRS 9 core moves within its envelope by $8\ \text{km s}^{-1}$ and the observed peak of the emission line is the center of the P Cygni profile. In this scenario the shell expansion velocity is $14\ \text{km s}^{-1}$, and an emission-line width of $28\ \text{km s}^{-1}$ is expected. Such broad lines are inconsistent with the observations as well. We conclude that the line profiles are not true P Cygni type profiles and thus are inconsistent with a spherically symmetric expanding envelope.

It is unclear what the relation is between the 55 K absorbing gas seen at $-6\ \text{km s}^{-1}$ and the 500 K emitting gas at $+8\ \text{km s}^{-1}$. More detailed dynamical models of circumstellar disks, accretion flows, and outflows are required. The possibility of photon excitation needs to be considered as well. As noted in Mitchell et al. (1991) the similarity of CO absorption- and emission-line profiles between a number of massive protostars suggests that these lines trace a fundamental property of their inner cores. This is strengthened by the similarity of the CH_4 line profiles.

5. CONCLUSIONS AND FUTURE WORK

Using high-resolution L - and M -band spectroscopy, we have shown that the gas-phase CH_4 abundance varies considerably in the line of sight of the massive protostar NGC 7538 IRS 9. This is a result of specific molecule formation and destruction processes: CH_4 is formed on grain surfaces and subsequently evaporated from the grains in the inner regions of the protostar. Both evaporation by photon heating and by shocks likely have played roles. CH_4 efficiently “burns” to CO in the highest velocity shocked regions. The gas-phase CH_4/CO abundance ratio is thus a sensitive tracer of shock chemistry. High spectral resolution observations of other species, in particular H_2O at $6\ \mu\text{m}$, are required to further test the importance and nature of shock chemistry in high-mass star-forming regions. The Stratospheric Observatory For Infrared Astronomy (SOFIA) will offer this opportunity in the near future (Lacy et al. 2002). Observations of the $3.32\ \mu\text{m}$ CH_4 stretch mode in more lines of sight require high radial velocities ($>30\ \text{km s}^{-1}$) or temperatures that populate the highest J levels to avoid saturated telluric lines. In this respect, the $7.67\ \mu\text{m}$ bending mode may be more suited. Future observations of CH_4 toward low-mass protostars are particularly exciting, as the CH_4/CO ratio is a sensitive tracer of protoplanets. In the relatively low pressure solar nebula low CH_4/CO abundances occur. The higher pressure in protoplanetary subnebulae, however, favors higher CH_4/CO ratios (Prinn & Fegley 1989). Variations of the CH_4 abundance between solar system comets possibly trace such physical condition gradients in the early protoplanetary disk (Gibb et al. 2003).

The research of A. C. A. B. and G. A. B. is supported by the *Spitzer* Legacy Science program and by the Owens Valley Radio Observatory through NSF grant AST 02-28955. The authors wish to recognize and acknowledge the very significant cultural role and reverence that the summit of Mauna Kea has always had within the indigenous Hawaiian community. We are most fortunate to have the opportunity to conduct observations from this mountain. We thank Jan Cami for providing a copy of *ISO* SWS IA, Fred Lahuis for an independent reduction, Tim Brooke for suggesting the possible ethane identification, and Yuk Yung for help with the wavelength calibration. Suggestions by an anonymous referee have led to an improved presentation of the data.

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